SNAP CODES: **010406**
040201

SOURCE ACTIVITY TITLE: **SOLID FUEL TRANSFORMATION PLANTS**
Coke Oven Furnaces
Coke Oven (Door Leakage and Extinction)

NOSE CODE: **104.12**

NFR CODE: **1 A 1 c**
1 B 1 b

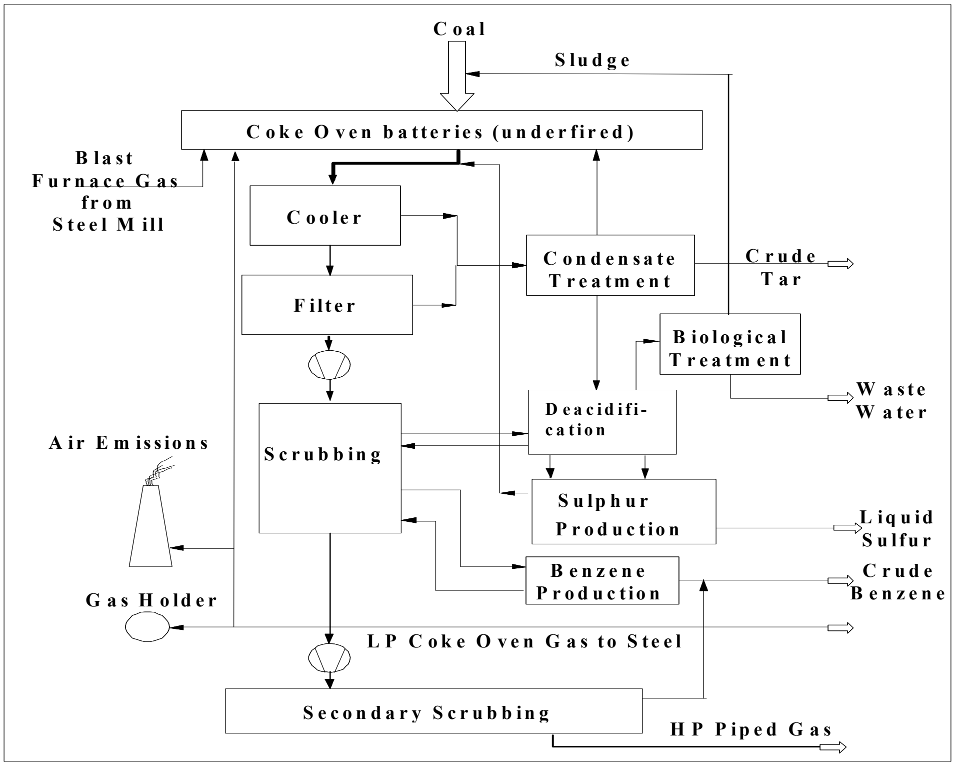
1 ACTIVITIES INCLUDED

Coke-production in general can be divided into the following steps:

Coal handling and storage, coke oven charging, coal coking, extinction of coke, and coke oven gas purification. Combustion in coke oven furnaces (SNAP 010406) is treated in this chapter as well as door leakage and extinction (SNAP 040201).

Figure 1-1 gives a key plan of a coke plant with emission relevant process steps and the by-product recovery section.

Figure 1-1: Key plan of a coke plant (Rentz et al. 1995)



2 CONTRIBUTION TO TOTAL EMISSIONS

Table 2-1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code†**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Coke Oven Furnaces	010406*	0.5	0.3	0	0	0.2	1.0	-	-	-
Coke Oven (Door Leakage and Extinction)	040201	0.1	0.1	0.2	0.1	0.5	0.1	-0.1	0.1-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
† = SNAP90 code 030202
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

Table 2-2: Contribution to total heavy metal emissions of the OSPARCOM-HELCOM-UNECE inventory for 1990 (up to 38 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Coke Oven (Door Leakage and Extinction)	040201	0.3	1.3	1.3	0.2	1.0	0.1	0.1	0.1

The emissions of persistent organics are also relevant. According to this OSPARCOM-HELCOM-UNECE inventory, coke ovens contributed some 3.1 % to total emissions of PAH in 1990.

Coke production is unlikely to be a significant source of sulphurhexafluoride (SF6), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs), (ETC/AEM-CITEPA-RISOE 1997).

3 GENERAL

About 90 % of the coke consumed in the EU is used in pig iron production. The major part is used in blast furnaces, followed by iron foundries, non-ferrous smelters, and the chemical industry.

3.1 Description

Coke and coke by-products (including coke oven gas) are produced by the pyrolysis (heating in the absence of air) of suitable grades of coal. The process also includes the processing of coke oven gas to remove tar, ammonia (usually recovered as ammonium sulphate), phenol, naphthalene, light oil, and sulphur before being used as a fuel for heating the ovens (World Bank Group 1997).

For coke production, hard coal is crushed, mixed and sieved. The coal is transported to the coke oven, which is charged by the mixture. After heating for 14 to 36 hours at 1,150-1,350°C, in the absence of oxygen, the coked mixture is pressed out of the coke chambers into special wagons. Subsequently, the hot coke will be extinguished.

The emissions related to coke production can be attributed to four sub-processes, namely:

- Coal handling and storage: emitting coal dust,
- Coke production and extinction: emitting coal and coke dust and coke oven gas,
- Coke oven gas handling and purification: emitting benzene, toluene, xylene, phenol, PAH, H_2S, HCN and NH_3,
- Combustion of coke oven gas: emitting C_xH_y, SO_2, NO_x, CO, CO_2, HF and soot.

3.2 Definitions

Production of coke:	heating of coal mixtures in absence of oxygen at high temperatures
Extinction of coke:	cooling of the hot coke after removal from the coke-chambers
Coke oven gas:	the gas formed during coking of the coal

3.3 Techniques

In the coke making process, bituminous coal is fed (usually after processing operations, which control the size and the quality of the feed) into a series of ovens. The coke oven itself is a chamber, built of heat resistant bricks, generally 0.4-0.7 m wide, 4-8 m high and 12-18 m long. A chamber has two doors, one at each end, covering almost the full cross-sectional area. In the roof, there are 3-5 charging holes and a gas outlet ("ascension pipe"). Commonly 40 to 70 chambers, alternating with heating walls, form a coke oven battery (Dutch Notes on BAT 1997). Combustion of gases in burners in the flues between the ovens provides heat for the process. In order to improve the energy efficiency, regenerators are located right under the ovens, exchanging heat from flue gases with combustion air or fuel. Coke oven gas from the by-product recovery plant is the common fuel for underfiring the ovens at most plants, but blast furnace gas, and infrequently, natural gas may also be used (US-EPA 1985).

The ovens are sealed and heated at high temperatures. The generation of steam, gases, and organic compounds starts immediately after charging and they are exhausted via ascension pipes into the crude gas collecting system (Dutch Notes on BAT 1997). Volatile compounds are processed to recover combustible gases and other by-products. After coking, the vertical doors on each end of an oven are removed, a long ram pushes the coke from the oven into a rail quench car, which goes to a quench tower. There, large volumes of water are sprayed onto the coke mass to cool it, so that it will not continue to burn after being exposed to air. Alternatively, circulating an inert gas (nitrogen), also known as dry quenching can cool it. Coke is screened and sent to a blast furnace or for storage.

The raw coke oven gas exits at temperatures of about 760 to 870 °C and is shock cooled by spraying recycled flushing liquor in the gooseneck. This spray cools the gas to 80 to 100 C, precipitates tar, condenses various vapours, and serves as the carrying medium for the condensed compounds. These products are separated from the liquor in a decanter and are subsequently processed to yield tar and tar derivatives (US-EPA 1985b, van Osdell et al. 1979).

The gas is then passed either to a final tar extractor or an electrostatic precipitator for additional tar removal. When the gas leaves the tar extractor, it carries 75 % of the ammonia and 95 % of the light oil originally present when leaving the oven. The ammonia is recovered either as an aqueous solution by water absorption or as ammonium sulphate salt. The gas leaving the saturator at about 60°C is taken to final coolers or condensers, where it is typically cooled with water to approximately 24°C. During this cooling, some naphthalene separates and is carried along with the wastewater and recovered. The remaining gas is passed into a light oil or benzene scrubber, over which is circulated a heavy petroleum fraction called wash oil or a coal-tar oil, which serves as the absorbent medium. The oil is sprayed in the top of the packed absorption tower while the gas flows up through the tower. The wash oil absorbs about 2 to 3 % of its weight of light oil, with a removal efficiency of about 95 % of the light oil vapour in the gas. The rich wash oil is passed to a countercurrent steam stripping column. The steam and light oil vapours pass upward from the still through a heat exchanger to a condenser and water separator. The light oil may be sold as crude or processed to recover benzene, toluene, xylene, and solvent naphtha (US-EPA 1985b, van Osdell et al. 1979).

After tar, ammonia, and light oil removal, the gas undergoes final desulphurisation (e. g. by the Claus process) at some coke plants before being used as fuel. The coke oven gas has a rather high heating value, in the order of 20 kJ/m^3 (STP). Typically, 35 to 40 % of the gas is returned to fuel the coke oven combustion system, and the remainder is used for other plant heating needs (US-EPA 1985b, van Osdell et al. 1979).

Although most benzene is obtained from petroleum, some is recovered through distillation of coke oven light oil at coke by-product plants. Light oil is a clear yellow-brown oil which contains coal gas components with boiling points between 0 and 200°C. [30] Most by-product plants recover light oil, but not all plants refine it. About 13-18 l of light oil can be produced from coke ovens producing 1 Mg of furnace coke. Light oil itself contains from 60 to 85 % benzene (US-EPA 1985, Loibl et al. 1993).

3.4 Emissions

The coke oven is a major source of fugitive emissions into the air. The coking process emits sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon dioxide (CO_2), carbon monoxide (CO), ammonia (NH_3), particulate matter, and heavy metals. In general, emissions of nitrous oxide (N_2O) are not relevant. Coke ovens are an important source of PAH emissions (polycyclic aromatic hydrocarbons).

The components of coke oven gas (raw gas) and their concentration can be given as follows.

Table 3.1: Composition of raw coke oven gas (Winnacker 1982)

Components of coke oven gas	Concentration [Vol.-%]
H_2	58 - 65
CH_4	24 - 29
CO	4.6 - 6.8
C_nH_m	2 - 4
CO_2	1.5 - 2.5

Besides these compounds, the following by-products are also components of the coke oven gas produced: tar, phenol, benzene, pyridine, ammonia, H_2S, HCN, CS_2 (carbon bisulphide) (Winnacker 1982). The by-product recovery section of a coking plant (e.g. ammonia processing, tar processing) may release significant amounts of NMVOC, CH_4, NH_3 and particulate matter (covered by SNAP code 040201).

Furthermore, continuous and discontinuous releases of emissions into the air can be distinguished (Dutch Notes on BAT 1997):

Continuous emissions to air:

- Emissions from storage and handling of raw materials and products,
- Oven door and frame seal leakage,
- Ascension pipe leakage,
- Charging holes leakage,
- Coke oven firing,
- Vent systems in gas treatment plant,
- Desulphurisation plant.
-

Discontinuous emissions to air:

- Oven charging,
- Coke pushing,
- Coke cooling.

3.5 Controls

Charging:
Dust particles from coal charging can be evacuated by the use of jumper-pipe system and steam injection into the ascension pipe or controlled by fabric filters (World Bank Group 1997).

Coking:
Emissions decrease with the increase of the size of the ovens. Large ovens increase batch size and reduce the number of chargings and pushings, thereby reducing associated emissions. Emissions are also reduced by constant coking conditions, cleaning, and a low-leakage door construction e. g. with gas sealings (Dutch Notes on BAT 1997).

Pushing:
Emissions from coke pushing can be reduced by maintaining a sufficient coking time thus avoiding the so-called "green push". Fugitive emissions can be controlled by sheds, enclosed

cars or travelling hoods. Captured gases should be treated in fabric filters (World Bank Group 1997).

Quenching:
Dry quenching creates lower emissions compared to wet quenching. Gases released from the dry quenching unit can be extracted and filtered. In the case of wet quenching, measures have to be taken to prevent pollutant transfer from wastewater to the air (Dutch Notes on BAT 1997).

By-product recovery:
In the processing of light oil, tar, naphthalene, phenol, and ammonia vapour recovery systems can be used. Tail gases from desulphurisation (Claus plant) can be returned to the coke oven gas system.

Combustion of coke oven gas:
Flue gases from coke oven firing contain NO_x, SO_2 and particulate matter as main pollutants. SO_2 emissions depend on the degree of desulphurisation of the coke oven gas. NO_x emissions may be reduced by low-NO_x-firing techniques.

4 SIMPLER METHODOLOGY

For the simpler methodology, where limited information is available, default emission factors may be used together with information on coke production in a given country or region without further specification of the type of process technology or efficiency of control equipment. This procedure does not distinguish combustion emissions and emissions from door leakage and extinction. Default emission factors are provided in Section 8.1.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.

5 DETAILED METHODOLOGY

The assessment of emissions with the more detailed methodology requires knowledge of the four sub-processes of coke production. If detailed information about the local situation is available this should prevail over the use of default emission factors. Reference emission factors for comparison with users data are provided in Section 8.2.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

Standard statistics on coke production and fuel consumption (e. g. International Energy Agency, United Nations, Eurostat, International Iron and Steel Institute etc.).

7 POINT SOURCE CRITERIA

Integrated iron and steel plants with production capacities of more than 3 million Mg/a have to be treated as point sources according to the CORINAIR90 methodology. Coke oven furnaces included in these integrated iron and steel plants have to be considered as a part of the point source.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default emission factors for use with simpler methodology (Source: Pacyna et al, 2002)

Pollutant	**Emission factors**	**Units**
Arsenic	0.01	g/t coke
Cadmium	0.01	g/t coke
Chromium	0.15	g/t coke
Copper	0.1	g/t coke
Mercury	0.01	g/t coke
Nickel	0.1	g/t coke
Lead	0.25	g/t coke
Zinc	0.4	g/t coke

8.2 Detailed methodology

In table 8.2a average overall emission factors are presented for coke production. For reference (Emission Registration 1990), emissions due to coke oven gas purification and fuel combustion are included. In the other references from this table it is not clear if fuel combustion is included or not.

Table 8.2a: Overall emission factors for coke production (g/Mg coke produced)

Compound	**Plant type**	**Emission factor**	**Data Quality**	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Country or region**	**Ref.**
Particulates	*All processes*	*500 - 900*	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany*	(Luftreinh. 1989)
Particulates	*All processes*	53	*E*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1990)
Particulates	*All processes*	800 - 5000	*E*	*n. a.*	*n. a.*	*n. a.*	*USA*	*(US-EPA 1990)*
VOC	*All processes*	730 - 2800$^{2)}$	*E*	*n. a.*	*n. a.*	*n. a.*	*Netherlands* *USA*	(E. Registr. 1990), *(US-EPA 1990)*
PAH	*All processes*	29	*E*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1990)
B(a)P	*All processes*	0.16 - 0.6	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands*	(Luftreinh. 1989), (E. Registr. 1990)
Arsenic	*All processes*	0.003 - 0.03, 0.32$^{1)}$	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany,* *USA*	(Luftreinh. 1989), *(US-EPA 1990)*
Cadmium	*All processes*	0.0007 - 0.8	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands*	(Luftreinh. 1989), (E. Registr. 1990)
Chromium	*All processes*	0.17 - 0.34	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands*	(Jockel W. 1991), (E. Registr. 1990)
Copper	*All processes*	0.09 - 0.05	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands*	(Jockel W. 1991), (E. Registr. 1990)
Mercury	*All processes*	0.004 - 0.04	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands*	(Luftreinh. 1989), (E. Registr. 1990)

Table 8.2a (continued): Overall emission factors for coke production (g/Mg coke produced)

Compound	**Plant type**	**Emission factor**	**Data Quality**	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Country or region**	**Ref.**
Nickel	*All processes*	0.065 - 0.19	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands*	(Jockel W. 1991), (E. Registr. 1990)
Lead	*All processes*	0.08 - 0.6, 2.85[1]	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands* *USA*	(Luftreinh. 1989), (E. Registr. 1990), *(US-EPA 1990)*
Zinc	*All processes*	*0.22 - 0.58, 6.49*[1]	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany* *Netherlands* *USA*	(Jockel W. 1991), (E. Registr. 1990), *(US-EPA 1990)*

[1] calculated with EPA coke dust profile *(US-EPA 1990)*
[2] expressed as methane

According to the detailed methodology emissions should be calculated individually for all sub-processes. Emission factors for the process steps listed below are summarised in table 8.2.b

In table 8.2c, emission factors are given for the detailed sub-processes for total particulate, NO_x, SO_2, CO, VOC and NH_3 as reported in the USA (US-EPA 1985).

8.2.1 Coal handling

Coal handling consists of transport, pulverising, screening, and blending of several types of coal and storage. Table 8.2 includes factors for emissions of coal dust from the total process of coal handling.

8.2.2 The coking process (without combustion)

Emissions during coking operations are caused by the charging of the coal into the ovens, the oven/door leakage during the coking period, and by pushing the coke out of the ovens. In table 8.2, overall emission factors for these activities are presented for VOC, NMVOC and PAH.

8.2.3 Coke oven gas purification

The coke oven gas collected from the ovens during the coking process is subjected to various operations for separating ammonia, coke oven gas, tar, phenol, benzene, toluene, xylene, pyridine etc. In table 8.2b, emission factors are given for the purification process of coke oven gas. The numbers are derived from data of a Dutch coke plant (Emission Registration 1992).

8.2.4 Combustion

Heat, necessary for the coking process, is generated by gas combustion in the flues between the ovens. Coke oven gas is the common fuel for underfiring the ovens at most plants but other gases (blast furnace gas, natural gas) may be used as well. The combustion also causes emissions. In table 8.2b, emission factors are given for combustion emissions, related to the thermal energy input.

Table 8.2b: Emission factors for sub-processes of coke production

Compound	Plant type	Emission factor	Data Quality	Abatement type	Abatement efficiency	NAPFUE code	Country or region	Ref.
Coal dust	*Coal handling*	*80 - 2500 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*USA*	*(US-EPA 1985)*
Coal dust	*Coal handling*	*150 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1981)
VOC	*Coking process*	*151 - 590 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1990) (E. Registr. 1992)
VOC	*Coking process*	*2880 g* CH_4*/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*USA 1967*	*(US-EPA 1985)*
VOC	*Coking process*	*1030 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Germany 1975*	*(Schade 1980)*
CH_4	*Coking process*	*122 - 639 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands, Germany*	(E. Registr. 1992), *(Schade 1980)*
NMVOC	*Coking process*	*29 - 400 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands, USA*	(E. Registr. 1992), *(Breidenbach 1982)*
PAH	*Coking process*	*10 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	*(Duiser et al. 1989)*
VOC	*Gas purification*	*213 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1992)
Benzene	*Gas purification*	*157 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1992)
Toluene	*Gas purification*	*27 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1992)
Xylene	*Gas purification*	*26 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1992)
PAH - 16 EPA	*Gas purification*	*47 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1992)
Phenol	*Gas purification*	*3.2 g/Mg coke produced*	*C*	*n. a.*	*n. a.*	*n. a.*	*Netherlands*	(E. Registr. 1992)
SO_2	*C. oven furnaces*	*0.5 g/GJ*	*C*	*n. a.*	*n. a.*	*301*	*Europe*	*CORINAIR90*

Table 8.2b (continued): Emission factors for sub-processes of coke production

SO_2	*C. oven furnaces*	*14 g/GJ*	*C*	*n. a.*	*n. a.*	*303*	*Europe*	*CORINAIR90*
SO_2	*C. oven furnaces*	*500 g/Mg coal; 650 g/Mg coke; 3.3 g/GJ*	*C*	*Desulphurisation*	*n. a.*	*304*	*Europe*	*(CITEPA 1992), CORINAIR90*
SO_2	*C. oven furnaces*	*1500 g/Mg coal; 3300 g/Mg coke; 1355 g/GJ*	*C*	*No desulphurisation*	*n. a.*	*304*	*Europe*	*(CITEPA 1992), CORINAIR90*
NO_x	*C. oven furnaces*	*100 - 250 g/GJ*	*C*	*n. a.*	*n. a.*	*301*	*Europe*	*CORINAIR90*
NO_x	*C. oven furnaces*	*90 g/GJ*	*C*	*n. a.*	*n. a.*	*303*	*Europe*	*CORINAIR90*
NO_x	*C. oven furnaces*	*14 - 250 g/GJ*	*C*	*n. a.*	*n. a.*	*304*	*Europe*	*CORINAIR90*
NO_x	*C. oven furnaces*	*30 - 178 g/GJ*	*C*	*n. a.*	*n. a.*	*305*	*Europe*	*CORINAIR90*
NMVOC	*C. oven furnaces*	*1 - 5 g/GJ*	*C*	*n. a.*	*n. a.*	*301, 303, 305*	*Europe*	*CORINAIR90*
NMVOC	*C. oven furnaces*	*1 - 133 g/GJ*	*C*	*n. a.*	*n. a.*	*304*	*Europe*	*CORINAIR90*
CH_4	*C. oven furnaces*	*0.02 - 2.5 g/GJ*	*C*	*n. a.*	*n. a.*	*301, 304*	*Europe*	*CORINAIR90*
CH_4	*C. oven furnaces*	*3 g/GJ*	*C*	*n. a.*	*n. a.*	*303*	*Europe*	*CORINAIR90*
CH_4	*C. oven furnaces*	*0.02 - 0.3 g/GJ*	*C*	*n. a.*	*n. a.*	*305*	*Europe*	*CORINAIR90*
CO	*C. oven furnaces*	*1 - 300 g/GJ*	*C*	*n. a.*	*n. a.*	*301, 305*	*Europe*	*CORINAIR90*
CO	*C. oven furnaces*	*20 g/GJ*	*C*	*n. a.*	*n. a.*	*303*	*Europe*	*CORINAIR90*
CO	*C. oven furnaces*	*2 - 518 g/GJ*	*C*	*n. a.*	*n. a.*	*304*	*Europe*	*CORINAIR90*
CO_2	*C. oven furnaces*	*42 - 56 kg/GJ*	*C*	*n. a.*	*n. a.*	*301, 303, 304*	*Europe*	*CORINAIR90*
CO_2	*C. oven furnaces*	*105 - 280 kg/GJ*	*C*	*n. a.*	*n. a.*	*305*	*Europe*	*CORINAIR90*
N_2O	*C. oven furnaces*	*1.1 - 3 g/GJ*	*C*	*n. a.*	*n. a.*	*301, 303, 304, 305*	*Europe*	*CORINAIR90*

Table 8.2c: PM emission factors for the coking sub-processes (kg/Mg coal) (US-EPA 2001)

Process	Control	Emission factors, kg/Mg coal					
		TSP	**Rating**	**PM_{10}**	**Rating**	**$PM_{2.5}$**	**Rating**
Charging	Uncontrolled	0.35	E	*0.17*	*E*	*0.085*	*E*
	Scrubber	0.007	E	*0.0053*	*E*	*0.0035*	*E*
	Modern	0.00031	E	*0.00031*	*E*	*0.00031*	*E*
Door leaks	Uncontrolled	0.26	E	*0.13*	*E*	*0.065*	*E*
	Older controlled	0.02	E	*0.015*	*E*	*0.01*	*E*
	Modern controlled	0.0079	E	*0.0079*	*E*	*0.0079*	*E*
Lid leaks	Uncontrolled	0.026	E	*0.013*	*E*	*0.065*	*E*
	Older controlled	0.0036	E	*0.0024*	*E*	*0.0018*	*E*
	Modern controlled	0.000048	E	*0.000036*	*E*	*0.000024*	*E*
Offtake leak	Uncontrolled	0.026	E	*0.013*	*E*	*0.065*	*E*
	Older controlled	0.0033	E	*0.0025*	*E*	*0.0017*	*E*
	Modern controlled	0.00016	E	*0.00016*	*E*	*0.00016*	*E*
Coke oven pushing	Uncontrolled	0.695	D	0.30	E	0.12	E
	Hood + fabric filter	0.19	B	*0.17*	*E*	*0.14*	*E*
	Hood + scrubber	0.19	A	0.17	E	0.14	E
	Shed + FF	0.19	B	*0.17*	*E*	*0.14*	*E*
Coke quenching	Uncontrolled, clean water	0.57	E	0.17	E	0.063	E
	Uncontrolled, dirty water	2.6	E	0.59	E	0.50	E
	Tall tower, Clean water	0.73	D	0.072	E	0.044	E
	Normal tower , clean water, maintained	0.15	D	*0.12*	*E*	*0.08*	*E*
	Tall tower/poorly maintained, dirty water	1.37	D	0.44	E	0.28	E
	Normal tower, dirty water, maintained	0.27	D	*0.20*	*E*	*0.14*	*E*
Combustion stack	Uncontrolled (BFG)	0.1	E	0.1	E	0.1	E
	Uncontrolled (raw COG)	0.2	B	*0.2*	*E*	*0.2*	*E*
	Uncontrolled (deS COG)	0.034	A	*0.034*	*E*	*0.034*	*E*
	Fabric filter (COG)	0.11	C	*0.11*	*E*	*0.11*	*E*
	Fabric filter/ESP (BFG)	0.031	D	*0.031*	*E*	*0.031*	*E*
Coal crushing	Cyclone	0.055	D	*0.041*	*E*	*0.028*	*E*
	Rotoclone	0.027	E	*0.020*	*E*	*0.014*	*E*
Coal mill	Building enclosure	*0.0009*	*E*	0.0009	E	*0.0009*	*E*
Preheater	Uncontrolled	1.8	D	1.8	E	1.1	E
	Scrubber	0.13	D	0.12	E	0.11	E
	ESP	0.006	D	*0.005*	*E*	*0.003*	*E*
Coke handling	Cyclone	0.003	D	*0.002*	*E*	*0.002*	*E*
Coke screening		0.011	E	*0.008*	*E*	*0.006*	*E*
Soaking		0.008	E	*0.006*	*E*	*0.004*	*E*
Combustion stack	Non-recovery oven	0.9	B	*0.9*	*E*	*0.9*	*E*
Charging	Non-recovery oven	0.013	D	0.0065	E	0.004	E

Data are from draft AP-42 update of 2001.

USEPA particle size data were collected primarily in 1970s and applicability to modern plant are unknown.

Information in italics is ‘expert judgement’ and extrapolation from USEPA particle size data.

9 SPECIES PROFILES

Table 9-1 presents profiles for VOC emissions of the coking process.

Table 9.1: VOC profiles for the coking process (% weight)

Compound	(Frohne)	(Fudal. 1992)	(VOC 1980)[1]	(Peter 1992)	(Emis. Registr 1992)	(Emis. Registr 1990)	(Emis. Registr 1990)	proposal
CH_4	72	66	45.3	45.4[4]	80.8	62.1	47.4	60
C2-C10 aliphates						17.8	13.6	16
C2	1.0	7.4	8	0.7[2]	4.2			5
C2=	1.1	18.1	27.7		1.0			1-10
C2=-	0.2	0.4	1.2					
C3	0.5	1.6	0.5	1.3[3]				
C3=	0.3	0.6	1.9					
C4	0.8	1.1		2.6				
C4=	0.1	0.4	0.6					
C4==								
C5	1.0			1.3				
C>5	1.0			14.0				
Benzene	7.7	3.4	14.1	11.5	9.7	5.9	4.5	7
Toluene	1.6	0.9	0.7	1.7	1.9	6.7	5.1	1-5
C8 aromatics	0.9			2.9				
C>8 aromatics	0.3			6.6				
Xylene		0.3		2.1	0.6	7.6	5.8	1-5
Styrene					0.3			
Aromatics + benzene							23.7	
Others	11.5			10.0	1.5			
Total	100	100	100	100	100	100	100	

[1] stack sample; probably only fuel combustion; [2] total c2;
[3] total c3; [4] calculated

In table 9.2, profiles of non-methane volatile organic compounds (NMVOC) emissions are given for the coking process.

Table 9.2: NMVOC profiles for the coking process (% weight)

Compound	(Frohne)	(Fudal. 1992)	(VOC 1980)[1]	(Peter 1992)	(Emis. Registr 1992)	(Emis. Registr 1990)	(Emis. Registr 1990)	(Altieri 1945)
C2-C10 aliphates						46.9	25.8	
C2	3.6	21.7	14.5	1.3[2]	22.1			30.3
C2=	3.9	53.0	50.4		5.2			58.0
C2=-	0.7	1.1	2.2					1.2
C3	1.8	4.8	0.9	2.3[3]				1.9
C3=	1.1	1.7	3.5					8.1
C4	2.9	3.4		4.8				0.5
C4=	0.36	1.1	1.1					
C4==								
C5	3.6			2.5				
C>5	3.6			25.6				
Benzene	27.5	9.9	25.6	21.0	50.7	15.5	8.5	
Toluene	5.7	2.5	1.3	3.8	10.0	17.7	9.7	
C8 aromatics	3.2			5.3				
C>8 aromatics	1.1			12.1				
Xylene		0.8		3.8	3.1	20.0	11.0	
Styrene					1.4			
Aromatics + benzene							45.0	
Others	41.1			18.3	7.5			
Total	100	100	100	100	100	100	100	100

[1] stack sample; probably only fuel combustion; [2] total c2; [3] total c3

Table 9.3: Species profiles for polycyclic aromatic hydrocarbons (PAH) expressed as percentage of total PAH

	(Bjorseth et al. 1978) battery personal top sampling (average)		(Eisenhut et al. 1982) oven doors	(Tonkelaar et al. 1983) near coke plant	(Duiser et al. 1989) proposal
total PAH emission factor (g/Mg)	15		2.5	8	10
fluorene	4.4	0.6			2
phenanthrene	19.8	2.6		45.9	30
anthracene	6.2	1.1		7.6	8
fluoranthene	12.8	11.9	1.5	14.3	14
3,6-dimethylphenanthrene				0.8	
benzo(b)fluorene	1.3	4.1		2.1	
pyrene	9.5	8.4	0.9	6.9	9
benzo(a)phenanthrene	0.8	2.8			2
benzo(a)anthracene	3.4	8.5	4.7	3.1	5
chrysene+trifenylene	4.4	11.0	5.9	3.4	4
total low mol PAH	88	62		84	74
benzo(b)fluoranthene	1.9	4.7	5.7	2.5	5
benzo(j)fluoranthene					
benzo(k)fluoranthene	2.2	7.7	2.1	1.1	
benzo(a)pyrene	1.8	4.3	7.1	2.5	5
benzo(e)pyrene	0.6	1.8	6.2	1.6	4
perylene	1.5	3.6	2.4	0.5	1
indeno(1,2,3,-cd)pyrene	1.3	2.9	6.2	1.8	3
benzo(g,h,i)perylene	0.9	1.7	6.2	4.4	3
anthanthrene	0.7	4.5		0.7	1
coronene					2
dibenzo(a,h)anthracene			4.4		2
dibenzo(a,j)anthracene				0.3	
dibenzo(a,i)pyrene				0.3	
3-methylcholanthene				0.3	
total high mol. PAH	12	38		16	26

10 UNCERTAINTY ESTIMATES

The quality classification of the emission factors is estimated to be B-C.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge on abatement techniques, dust removal efficiencies and operating techniques is limited; measurement data on the composition of dust is poor.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

If treated on an area basis, national emission estimates can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Coke production can be considered as a continuous process.

14 ADDITIONAL COMMENTS

No additional comments are given

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency
Compilation of Air Pollutant Emission Factors AP 42

PARCOM-ATMOS Emission Factors Manual

16 VERIFICATION PROCESSES

Verification of the emissions can be done by measurements.

17 REFERENCES

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18 BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP 42 or the PARCOM-ATMOS Manual may be used.

19 RELEASE VERSION, DATE AND SOURCE

Version: Draft 3

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SNAP CODE:	**030301** **040209**
SOURCE ACTIVITY TITLE:	**PROCESSES WITH CONTACT** ***Sinter and Pelletizing Plants*** ***Sinter and Pelletizing Plants (Except Combustion 030301)***
NOSE CODE:	**104.12.02** **105.12.09**
NFR CODE:	**1 A 2 a** **2 C 1**
ISIC:	**2410** **2420**

1 ACTIVITIES INCLUDED

The sinter process is an ore pre-treatment step in the production of iron, non-ferrous metals and other special materials.

This chapter does not address sinter plants in the non-ferrous metal industry; these plants should be covered by the chapters in SNAP 040300.

With respect to the iron and steel industry, this chapter only addresses travelling grate sintering which is by far the most important technique for iron ore sintering. The discontinuous pan sintering process as well as the rotary kiln process are now used at very few plant and are not discussed here. In addition, other agglomeration processes like pelletisation, briquetting and nodulisation are not considered here.

2 CONTRIBUTION TO TOTAL EMISSION

Table 2.1: Contribution to total emissions of the CORINAIR 90 inventory (*up to 28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%] (including emissions from nature)**										
Sinter Plants		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	TSP*	PM_{10}*	$PM_{2.5}$*
Typical contribution	030301	1.3	1.0	0.1	0.1	4.9	0.4	-	-	1.82	1.96	2.97
Highest value										5.13	5.37	9.09
Lowest value										0.245	0.234	0.321

* EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006), contribution to total national emissions, excluding agricultural soils
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

Emissions of heavy metals and POPs from sinter plants are also relevant but limited information is available.

Table 2.2 gives the contribution of sinter plant to total emissions of heavy metals and POPs from the OSPARCOM-HELCOM-UNECE emission inventory. For many heavy metals and POPs, but particularly in the case of PCDD/Fs, contribution to total emission may vary significantly from country to country and could be large (up to 50%).

Sinter plant are unlikely to be a significant source of sulphurhexafluoride (SF_6), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs), (ETC/AEM-CITEPA-RISOE 1997, ref. 30).

Table 2.2: Contribution to total POP and heavy metal emissions of the OSPARCOM-HELCOM-UNECE emission inventory *(up to 39 countries)*

Source-activity	**SNAP-code**	**Contribution to total emissions (including emissions from nature) [%]**										
		As	Cr	Cu	Pb	Cd	Hg	Ni	Zn	PCBs	PCDD/Fs	PAH
Sinter plant	030301 / 040209	1.0	2.9	2.3	2.8	3.2	1.6	1.2	0.8	0.5	15	0

3 GENERAL

3.1 Description of activities

The sintering process is a pretreatment step in the production of iron where fine particles of metal ores are agglomerated by combustion. Agglomeration of the fine particles is necessary to increase the passageway for the gases during the blast furnace process. The strength of the particles is also increased by agglomeration.

The activities in the sinter plants include:

- treatment of the ores by crushing and sieving;
- mixing of treated ores, coke and flux compounds;
- combustion and agglomeration of a mixture of crushed ores, coke, small sintered agglomerates and flux compounds;
- sieving of the sintered agglomerates;
- cleaning of the combustion off-gases;
- transport and handling operations occurring between the above mentioned activities.

3.2 Definitions

Mixing of the ores	The ores are mixed with residual material, fuel (coke, breeze), and flux compounds. This is necessary for preparing the ore for the sintering process.
Crushing process	The ores are crushed to increase the contact area for the sintering. The sinter cake is crushed to improve the transportation to the furnace blasting process.

Sieving process	The crushed ores are sieved to prevent the ores which require further crushing from entering the sinter process. The crushed sinter cakes are sieved to prevent small sintered particles entering the furnace process.
Sintering process	During sintering ore particles, flux compounds and other material are agglomerated by the combustion of the coke / breeze. The temperature must stay below the melting temperature of the metals in the ores.
Air cleaning process	The air of the combustion and cooling process is cleaned by removing dust and sometimes other pollutants.
Basicity of sinter mixture	Basicity of the mixture may be an important parameter influencing the emissions of SO_2. It is defined by relation of the following compounds (fractions expressed as weight %): basicity = $(CaO + MgO)/(SiO_2 + Al_2O_3)$
POM	Polycyclic organic matter

3.3 Techniques used during the sintering process

The sintering process is used for several primary metal production processes, each having different designs. During sintering, fine-grained, smeltable ores, in particular iron ore, are agglomerated into compact lumps **by heating nearly to the melting or softening point**. Melting tends to occur at the grain boundaries leading to a caking of the material.

Before the sintering, the various substances are first mixed and, if desired, granulated. The iron ores are agglomerated on conveyor sinter installations, the conveyor belts consist of a large number of wagons. These wagons that have been linked up as an endless conveyor belt which can be as big as 4 m in width and 100 m in length. The fine ore to be sintered is moistened and fed on to the circulating grid together with coke breeze and additives such as limestone, quick lime, olivine or dolomite. Burners above a heat-resistant grate belt heat the material to the required temperature (1100-1200 °C). This causes the fuel in the mixture to be ignited. The combustion then is self supporting and provides sufficient heat, 1300 to 1480 °C, to cause surface melting and agglomeration of the mix. The carbon burns with the aid of the air sucked through the grid into the mixture, resulting in the flame front being moved through the sintering bed. On the underside of the sinter strand a series of windboxes is situated that draw combusted air down through the material bed into a common duct, leading to gas cleaning devices (ref. 1). The sintering processes are completed once the flame front has passed through the entire mixed layer and all fuel has been burnt.

The fused sinter is discarded at the end of the sinter strand, where it is crushed and screened. Undersize sinter is recycled to the mixing mill and goes back to the strand. The remaining sinter product is cooled in open air or in a circular cooler with water sprays or mechanical fans. The cooled sinter is crushed and screened for a final time, then the fines are recycled, and the product is sent to the blast furnaces to be charged (ref. 1).

The most common types of sinter coolers used include circular or straight line moving beds, quiescent beds, or shafts. Air or water is used as the cooling medium in these coolers, with air being prevalent in newer plants and water being dominant in older plants (refs. 2, 3).

Technical data which are typical for the plants operating in W-Europe are listed in Table 3.1:

Table 3.1: Range of technical parameters of European sinter plants

Parameter	Range	Ref.
width [m]	2,5-4,5	(ref. 4)
area [m²]	50-400 (1)	(ref. 4)
specific flue gas flows [m³/t sinter]	1800-2000	(ref. 5)
flue gas flows [million m³/h]	up to 1.5	(ref. 4)
height of sinter layer	ca. 250 -650 mm	(ref. 6)
coke input [kg/ton sinter]	38-55	

(1) some small installations are reported to be in operation in Poland, another one in Germany (sintering of iron containing return and filter materials)

The sinter plant plays a central role in an integrated iron and steel works for making use of production residues which would have to be disposed otherwise. Slags from steel production, filter dusts of diverse flue gas cleaning systems (including those applied to the sinter plant itself) and various iron-containing materials from residue treatment are recycled in the sinter plant. Recycling may lead to an enrichment of relevant compounds, particularly heavy metals. Some residue materials like roll mill scale may be contaminated with organic compounds (oils), being precursors for PAH and PCDD/F formation. An example of input material composition is shown in the Table 3.2 below.

Table 3.2: Example of input material composition to sinter plant

Material	% [1]
hematite	81.3
magnetite	2.7
returns	7.9
pellet abrasions	2.2
blast furnace dust	0.3
steel work dust	0.6
roll scale	1.3
limestone	9.4
olivine	3.5
coke breeze	5

[1] related to dry mixture

Chlorine compounds can enter into the sinter installation by means of the additive coke slack as well by the ore from its natural chloride contents. Furthermore, returned materials such as certain filter particles, scale and sludges from waste water treatment, which are added to the materials to be sintered, can also increase the chlorine content of the substances used. This is reflected in the waste gases from sinter installations which contain inorganic gaseous chlorine compounds.

An alternative process is pelletisation, where no combustion is necessary.

By 2010 a new technology called "converted blast furnace" or "melting-reduction technology" is expected to be operational. For this process sintering, pelletisation, and coke input will no longer be necessary (ref. 7).

3.4 Emissions

3.4.1 Emitted compounds

Of the 8 CORINAIR standard gaseous compounds, all except ammonia are known to be emitted by sinter plants.

- SO_2 emissions mostly originate from sulphur contained by the coke used as fuel. Actual emissions may be further dependent on the basicity of the mixture. With CaO dominated mixtures SO_2 production is decreased by increasing basicity. From MgO dominated mixtures about 97% of the sulphur content is converted to SO_2. The major fraction of the total SO_2 emission is generated in the hot part of the sinter belt (near the end), (ref. 5).
- Nitrogen oxides are mainly emitted as NO due to rapid downcooling of the flue gases. NO_X emissions originate from nitrogen contained in coke (ca. 80%) and iron ore (ca. 20%), (ref. 5).
- Raw materials contain heavy metals (HM). Dust emissions are generally associated with HM emission. During the sintering process some of the HM may be volatilised or converted into volatile compounds (e.g. chlorides) and can therefore be found in the flue

gas. This mainly concerns Zn, Pb, and Cd. Arsenic is emitted in gaseous form as As_2O_3, passing the dry gas cleaning facilities which are usually operated at 120 °C. Since these volatile compounds form or adsorb to fine particles which are removed by the gas cleaning facilities, they may be accumulated during the sinter return cycle. Moreover, fine particles passing the filters may have a much higher content of these metals than the raw gas dust or the sinter mixture (ref. 5).

- Polycyclic organic material (POM), eg. PAH and PCDD/F, may be formed from chlorine and precursor compounds like oily additives. Potentially, POM emissions may be released from the sinter machine windbox, from the sinter machine discharge point, and from sinter product processing operations (i.e. crushing, screening, and cooling). Because of the high temperatures used in sintering operations, it is probable that sinter plant POM emissions are in both gaseous and particulate matter forms (refs. 2, 8).
- Emissions of fluorides (sintering of ores recovered in Sweden) and hydrochloric acid (use of seawater moistening or coke treatment) have been observed (ref. 4)

3.4.2 Emission points

At a sinter plant, emissions may occur as ('direct') stack emissions and - to a minor degree - as fugitive ('indirect') emissions during all process steps mentioned above.

- Ambient air is sucked by several windboxes through the mixture to support the combustion process on the sinter belt. After passage of the belt the flue gases are collected, dedusted and released through the main stack.
- The main process steps (like coke crushing, raw material handling, belt charging and discharging, sintering) are usually done within encapsulated or semi-encapsulated housings. The housings may be equipped with suction hoods connected via flue gas cleaning devices to the main stack or to separate stacks. Thus, there may be more than one stack emission point at a given sinter plant.
- Fugitive dust emissions may arise during handling and transportation of the raw materials and of the cooled sinter as well as during maintenance and accidental interrupts of the cyclones or filters. More important, due to the strong thermal convection in the sinter hall' fugitive emissions through leakages in the roof are likely to occur particularly at the end of the sinter belt.

3.4.3 Abatement measures

Gaseous compounds

Limited information is available about specific control measures for gaseous emissions. A desulphurisation facility is operated at a German plant (ref. 9). Measures for SO_2 and NOx reduction are known from plants operated in Japan (ref. 4).

Dust

Abatement measures are directed to dust emissions. In principle, reduction of dust emission also leads to reduction of emissions for those compounds being bound to particulates. Sinter strand windbox emissions commonly are controlled by cyclone cleaners followed by a dry or wet electrostatic precipitator (ESP), high pressure drop wet scrubber, or baghouse. Crusher and hot screen emissions are usually controlled by hooding and a baghouse or scrubber.

Usually horizontal dry electrostatic precipitators are used; however, less efficient mechanical dedusting devices (e.g cyclone batteries) might be installed in old sinter plants if only protection of the blower wheel rather than environmental protection is intended. Some sinter plants located in CIS countries are reported to have only this low standard abatement technology, others are equipped with wet venturi washers (ref. 10).

POM
Since being identified as a relevant source of dioxins and furans some sinter plants have been equipped with special abatement technologies (e.g. ‘Airfine-system’, Austria; injection of activated charcoal or open hearth coke in connection with fabric filter) or optimised dedusting facilities (‘MEEP’ = ESP with rotating electrode), (ref. 6).

4 SIMPLER METHODOLOGY

4.1 Calculation of emission

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes (“activity rates”) and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

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[1] The term “Tier” is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

Emission = AR x EF

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tiers 3), to estimate emissions of gaseous pollutants from the cement production is based on measurements or estimations using plant specific emission factors - guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

An extensive measuring programme involving off-gas measurements at all relevant emission points is essential to get a clear picture of the actual emissions. Emission measurements should be performed at least at the main stacks connected to the windboxes of the sinter strand and to the hot crushing / sieving facility. This is particularly important concerning emissions of dioxins and furans since there is no way to date to estimate the emissions from different operating conditions.

Reference emissionfactors for comaprison with users own data are provided in Section 8.2.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of cement, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics. Standard international compilations of production statistics are available from

- EUROSTAT , Brussels (Iron and Steel, Yearly statistics, Theme 4, Series C);
- the International Iron and Steel Institute , Brussels;
- Wirtschaftsvereinigung Stahl, PO Box 10 54 64, 40045 Düsseldorf, Germany (Statistical Yearbook Iron and Steel Industry);
- National Statistical Yearbooks.

More details of these example data sources for activity statistics are given in Section 17 (References).

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities produced by various types of industrial technologies employed in industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 " Choice of activity statistics".

7 POINT SOURCE CRITERIA

Sinter plants usually are part of large integrated iron and steel plants connected to high chimneys (> 100 m), and should be regarded as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default emission factors for iron ore sinter plants - simple methodology

Table 8.1a: Emission factors for iron ore sinter plants

Pollutant	Emission factor	Units
Particulate matter Total suspended particulate	2	kg/t sinter
PM_{10}	0.8	kg/t sinter
$PM_{2.5}$	0.5	kg/t sinter
Arsenic	0.05	g/t sinter
Cadmium	0.08	g/t sinter
Chromium	0.5	g/t sinter
Copper	0.7	g/t sinter
Mercury	0.05	g/t sinter
Nickel	0.24	g/t sinter
Lead	4	g/t sinter
Selenium	0.02	g/t sinter
Zinc	0.9	g/t sinter
Dioxins and furans	15	µgTEQ/t sinter
Hexachlorobenzene	32	µg/t sinter
Polychlorinated biphenyls	200	µg/t sinter
Polyaromatic hydrocarbons	200	mg/t sinter

8.2 Emission Factors for Use With Detailed Methodology

This section provides reference emission factors for comparison with users own data.

The following emission factors are given in ref. 28 as recommended values for emission estimation concerning the compounds covered by the Corinair '90 inventory; they are based on the results reported by different sources in Western Europe and the U.S.A. (Annex 1); Emission factors reported for other sinter processes, other countries and additional compounds are given in Annex 1.

Since no assessment of uncertainty is given, data quality rating is generally assumed to be C.
N.B. It is assumed that the emission factors given in the following table were derived originally by relating the entire emission of a pollutant within a time period to the typical input of the mentioned fuels within the same time period, regardless of whether combustion of the fuel really causes any emission of the pollutant. While this procedure leads to chemically inconsistent emission factors it still enables the rough calculation of the entire emission of a plant when just knowing the input amount of one of the fuels used.

Table 8.2a: Emission factors for gaseous compounds

Compound	**Emission factor**	**Abatement type**	**Abatement efficiency**	**Fuel type (NAPFUE code)**
	[mg/GJ]		[%]	
SO_x	499	Uncontrolled	N/A	Coke breeze (107)
	658	Uncontrolled	N/A	Heating oil heavy (203)
	1410	Uncontrolled	N/A	heating oil light (204)
	4680	Uncontrolled	N/A	natural gas (301)
	5490	Uncontrolled	N/A	coke oven gas (304)
	8600	Uncontrolled	N/A	blast furnace gas (305)
		plus scrubber	90	all fuels
NO_x	500	Uncontrolled	N/A	Coke breeze (107)
	134	Uncontrolled	N/A	Heating oil heavy (203)
	100	Uncontrolled	N/A	heating oil light (204)
	530	Uncontrolled	N/A	natural gas (301)
	2350	Uncontrolled	N/A	coke oven gas (304)
	8050	Uncontrolled	N/A	blast furnace gas (305)
		low NOx technology	30	all fuels
		secondary measures (SCR)	70	all fuels
MMVOC	50	uncontrolled or with controls for SO_x and/or NO_x only	N/A	Coke breeze (107)
	5	uncontrolled or with controls for SO_x and/or NO_x only	N/A	Heating oil heavy (203)
	1.5	uncontrolled or with controls for SO_x and/or NO_x only	N/A	heating oil light (204)
	14	uncontrolled or with controls for SO_x and/or NO_x only	N/A	natural gas (301)
	26	uncontrolled or with controls for SO_x and/or NO_x only	N/A	coke oven gas (304)
	0.25	uncontrolled or with controls for SO_x and/or NO_x only	N/A	blast furnace gas (305)
CH_4	50	uncontrolled or with controls for SO_x	N/A	Coke breeze (107)

Compound	**Emission factor**	**Abatement type**	**Abatement efficiency**	**Fuel type (NAPFUE code)**
	[mg/GJ]		[%]	
		and/or NO_x only		
	4	uncontrolled or with controls for SO_x and/or NO_x only	N/A	Heating oil heavy (203)
	1.5	uncontrolled or with controls for SO_x and/or NO_x only	N/A	heating oil light (204)
	14	uncontrolled or with controls for SO_x and/or NO_x only	N/A	natural gas (301)
	257	uncontrolled or with controls for SO_x and/or NO_x only	N/A	coke oven gas (304)
	257	uncontrolled or with controls for SO_x and/or NO_x only	N/A	blast furnace gas (305)

N/A = not applicable, Data Quality = C

Table 8.2a: (continued) Emission factors for gaseous compounds

Compound	**Emission factor**	**Abatement type**	**Abatement efficiency**	**Fuel type (NAPFUE code)**
	[mg/GJ]		[%]	
CO	10500	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	14	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	13	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	2160	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	35000	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	84000	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)
	109000	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	78000	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	74000	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	55500	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	46000	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	200000	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)
	4	uncontrolled or with controls for SOx and/or NOx only	N/A	Coke breeze (107)
	10	uncontrolled or with controls for SOx and/or NOx only	N/A	Heating oil heavy (203)
	12	uncontrolled or with controls for SOx and/or NOx only	N/A	heating oil light (204)
	3	uncontrolled or with controls for SOx and/or NOx only	N/A	natural gas (301)
	2.3	uncontrolled or with controls for SOx and/or NOx only	N/A	coke oven gas (304)
	3	uncontrolled or with controls for SOx and/or NOx only	N/A	blast furnace gas (305)

N/A = not applicable

Data Quality = C

Table 8.2b: Emission factors for dust

Process	Emission factor [kg dust/ Mg sinter]	Data quality	Abatement type	Abatement efficiency	Country	Ref
Sintering	4	C	Unabated	0	D	ref. 5
Cooling	3.5	C	Unabated	0	D	ref. 5
Sintering	14	E	Cyclones	60-70 %	CIS	ref. 29
Cooling	3	E	Cyclones	60-70 %	CIS	ref. 29
Sintering	0.3	C	ESP	>90 %	EU	ref. 16
Cooling	0.05	C	multi cyclone,	>90 %	EU	ref. 16
Handling	0.1	D	ESP, bag filters	> 90 %	EU	ref. 16
crushing, blending, sintering	0.25	D	“after abatement”	N/A	EU	ref. 31
Cooling	0.2	D	Cyclones	N/A	EU	ref. 31
Cooling	0.06	D	bag filters	N/A	EU	ref. 31
Windbox	5.56	B	Uncontrolled	N/A	US	ref. 1
Windbox	4.35	A	Uncontrolled (after coarse particles removal)	N/A	US	ref. 1
Windbox	0.8	B	ESP (dry)	N/A	US	ref. 1
Windbox	0.085	B	ESP (wet)	N/A	US	ref. 1
Windbox	0.235	B	Venturi scrubber	N/A	US	ref. 1
Windbox	0.5	B	Cyclone	N/A	US	ref. 1
Sinter discharge	3.4	B	Uncontrolled	N/A	US	ref. 1
Sinter discharge	0.05	B	Baghouse	N/A	US	ref. 1
Sinter discharge	0.295	A	Venturi scrubber	N/A	US	ref. 1
windbox and discharge	0.15	A	Baghouse	N/A	US	ref. 1

Table 8.2b: (continued) Emission factors for dust / particulate matter (CEPMEIP)

Process type	**Abatement**	**Unit**	**TSP**	**PM_{10}**	**$PM_{2.5}$**	**Uncertainty**
Agglomeration plants: sinter	(multi-) Cyclone control only	kg/ton sinter	2	0.8	0.5	2
Agglomeration plants: sinter	Conventional installation with ESP	kg/ton sinter	0.6	0.3	0.25	2
Agglomeration plants: sinter	Fabric filter, high efficiency wet scrubbing or high efficiency ESP BAT	kg/ton sinter	0.2	0.1	0.1	2

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in table): The uncertainty in the emission factor for $PM_{2.5}$ from an plant with multicyclone only is 0.5 kg/ton sinter. The emission factor with uncertainty range will therefore be 0.5 kg per tonne sinter with an uncertainty range of 0.25 (0.5/2) to 1 (0.5x2).

8.2c Heavy metal emission

The following factors are based on the emission factors shown in Annex 1. They may be applied to estimate emissions from sinter plants in the western European countries that are commonly equipped with dedusting facilities. For calculation of the possible emission range refer to the values tabled in Annex 1. In view of the higher dust emission reported for sinter plants located in the CIS, higher emissions (about factor 2-3) of heavy metals are likely there.

Table 8.2c: Emission factors for heavy metals

Process	**Compound**	**Emission factor [g/ GJ sinter]**	**Data quality**
stack emission	As	0.05	C
	Cd	0.2	C
	Cr	0.2	C
	Cu	0.4	C
	Hg	0.05	C
	Ni	0.2	C
	Pb	8	C
	Se	0.02	C
	Zn	1	C

8.2d POP emissions

Since data on other POP were not available, only emissions of PCDD/Fs are included. Refer to Annex 1 to calculate potential emission range. It should be noticed that extremely high emissions from single plants may dominate the national emission. Therefore the simpler methodology should be applied cautiously.

Table 8.2d: Emission factors for PCDD/Fs

Compound	**Process**	**Emission factor** [1] **[µg I-TEQ/ Mg sinter]**	**Data quality**	**Abatement type**	**Abatement efficiency**	**Country /region**
PCDD/F	sintering	6	C	dedusting, ESP	0% [2]	WEu
PCDD/F	cooling	1	C	dedusting, ESP or cyclones	0% [2]	WEu
PCDD/F	sintering	1.5	D	'MEEP' (Moving ESP)	30-70%	D
PCDD/F	sintering	0.5	D	injection of adsorbents/fabric filters	up to 90%	D
PCDD/F	sintering	0.3	C	high performance washer (Airfine)	90%	A

[1] = Note that measurements have shown that there is a significant temporal variation in PCDD/F emissions from sinter plant (about a factor of 2). Also, at one German plant very high PCDD/F emissions were measured (nearly 100 µg I-TEQ/ Mg sinter), showing that variation between plant is likely.

[2] = no significant differences in PCDD/F content measured in raw and clean gas (ref. 6).

9 SPECIES PROFILES

As mentioned in section 3.4 the heavy metal profile of the dust emitted from the hot sintering and crushing/sieving processes are not necessarily related to the profile of the raw materials due to volatilisation and accumulation of some compounds. The following enrichment factors have been observed (ref. 5) :

Table 9.1: Enrichment factors for heavy metals at sinter plant

	Zn	**Pb**	**Cd**
$C_{\text{filter dust}}/C_{\text{Sinter mixture}}$	5	450	30
$C_{\text{clean gas dust}}/C_{\text{Sinter mixture}}$	20	1,300	90

PCDD/F profile information is available from a recent German study (ref. 6). Table 9.2 gives average mass fractions for PCDD/F homologues as revealed by measurement results obtained from 3 plants (5 measurements).

Table 9.2: Species data for PCDD/F from sinter plant

Homologue	**Range [%]**	**mean [%]**
TetraCDF	37-46	40
PentaCDF	26-32	28.5
HexaCDF	10-13	12
HeptaCDF	3.5-5	4
OctaCDF		0.5
TetraCDD	1-5	2
PentaCDD	4-6	4.5
HexaCDD	3-8	5
HeptaCDD	2-4	3
OctaCDD	0-2	1.5

The European IPPC Bureau (ref. 31) includes a graph showing the grain size and weight distribution of dust, based on samples from a number of sinter strands. There are two distinct maxima, one in the range 0.1 – 3 µm, one close to 100 µm. Particles smaller than 0.1 µm and between 3 µm and 80 µm make up a much smaller fraction of the total. The coarse dust can be separated in ESPs with high efficiency. However, the composition of the fine dust, alkali chlorides, reduces the efficiency of ESPs.

The EPA's AP-42 document (ref. 1) gives size distributions for particulate matter emitted from the various stages of sinter production. These are reproduced in Table 9.3.

Table 9.3: Particle size distributions and size-specific emission factors (ref. 1)

Process	Abatement technology	Particle size (µm)	Cumulative mass % < stated size	Cumulative mass emission factor (kg/t)	Quality rating
Windbox	uncontrolled (leaving gate)	0.5	4	0.22	D
		1	4	0.22	
		2.5	6.5	0.28	
		5	9	0.5	
		10	15	0.83	
		15	20	1.11	
			100	5.56	
Windbox	ESP (wet)	0.5	18	0.015	C
		1	25	0.021	
		2.5	33	0.028	
		5	48	0.041	
		10	59	0.05	
		15	69	0.059	
			100	0.085	
Windbox	Venturi scrubber	0.5	55	0.129	C
		1	75	0.176	
		2.5	89	0.209	
		5	93	0.219	
		10	96	0.226	
		15	98	0.23	
			100	0.235	
Windbox	cyclone	0.5	25	0.13	C
		1	37	0.19	
		2.5	52	0.26	
		5	64	0.32	
		10	74	0.37	
		15	80	0.4	
			100	0.5	
Windbox	baghouse	0.5	3	0.005	C
		1	9	0.014	
		2.5	27	0.041	
		5	47	0.071	
		10	69	0.104	
		15	79	0.119	
			100	0.15	
Discharge breaker and hot screens	baghouse	0.5	2	0.001	C
		1	4	0.002	
		2.5	11	0.006	
		5	20	0.01	
		10	32	0.016	
		15	42	0.021	
			100	0.05	

10 UNCERTAINTY ESTIMATES

The main uncertainty relates to the emission factors. The data quality for all emission factors given in this chapter is from C to E. Emissions are likely to vary greatly between different plant and some emission factors are likely to vary by a factor of at least 10. More information is required on the variation of emissions with different types and sizes of process, different abatement etc.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge on abatement techniques, dust removal efficiencies and operating techniques is limited. Emission of PCDD/F may depend strongly on operation conditions and raw material composition; hence, estimation may be very uncertain and measurements are required so that a realistic understanding of the emissions can be developed. Data for other POP remain to be collected.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

This section is not relevant because sinter plant are part of large integrated iron and steel works and therefore should be considered as point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

Sintering can be considered as a continuous process. However, emissions may vary with time (e.g. due to changes in raw material composition)

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

- Environmental Protection Agency: Compilation of Air Pollutant Emission Factors (AP 42);
- PARCOM-ATMOS Emission Factors Manual;
- Holtmann T., Rentz O., Samaras Z. Zachariadis T., Kulcke K, K.-H. Zierock: Development of a Methodology and a Computer Model for Forecasting Emissions from Relevant Mobile and Stationary Sources, Final Report 1995 (study on behalf of EC, DG XI,, Brussels).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done roughly for metal emissions by calculating the emissions using the factors from section 8 and comparing the results with a mean profile of the ore used. A mass balance over the entire plant may also be a useful check. In case of PCDD/Fs verification can only be done by measurements.

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Eurostat Information Office, Jean Monnet Building B3/88, L-2920 Luxembourg, Tel +352 4301 34567, Fax +352 4364 04

Eurostat Data Shop, Rue de la Loi 130, B-1049 Bruxelles, Tel +32 2 299 6666 Fax +32 2 295 0125

Statistisches Jahrbuch der Stahlindustrie. Published annually by Verlag Stahleisen, PO Box 10 51 64, D-40042, Dusseldorf, Contact Stahl Informations-Zentrum, PO Box 10 48 42, D-40213 Dusseldorf, Tel +211 829 0, Fax +211 829 231

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19 RELEASE VERSION, DATE AND SOURCE

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Source: JJM Berdowski, PFJ van der Most, JM Slager
TNO-MEP
The Netherlands

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Landesumweltamt Nordrhein-Westfalen
Germany

Further update by:
Martin Peirce
AEA Technology Environment
UK

Updated with emission factors (CEPMEIP) for particulates by:
Tinus Pulles and Wilfred Appelman

TNO
The Netherlands
May 2006

20 POINT OF ENQUIRY

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ANNEX 1 - BACKGROUND EMISSION MEASUREMENT INFORMATION

Emissions of gaseous compounds

Process type	**Iron ore sinter plants**								**Sintering of special materials**	
References	(ref. 11)	(ref. 7)		(ref. 12)		(ref. 13)	(ref. 14)	(ref. 15)	(ref. 7)	
Country or region	Int.	NL		USA		EU	Cz	P	NL	
Abatement	unknown	unabated	with abatement (abatement details unknown)	unknown		unknown	unknown	unknown	unabated	abated
Dimension	g/Mg product	g/Mg crude steel		g/Mg product		g/GJ (NAPFUE 107) (6)	g/GJ	g/Mg	g/Mg crude steel	
SO_x	2,000	857	86	1,250 (2)	70 (3)				1,181	118 (7)
SO_2						233-632		1200		
NO_x	1,500	388	66			300-702	137.9		450	90 (8)
NMVOC	108 (1)					8.5.	14.2	100	347	
VOC		254		700 (2)	25 (4)					
CH_4	292 (1)					15	38.4			
CO	20,000-40,000	15,367		22,000 (2)		272		12000	23,000	
CO_2		163,265				106			221,000	
N_2O						4				
Fluoride (5)		11.6	2					5 [6])		
HCl (5)		47	9							

[1] = general, 73 % CH_4 for VOC as 400 g/Mg; [2] = windbox; [3] = cooler; [4] = general for sinter process; [5] = dim: g/Mg sinter; [6] = in the document referred to also emission factors for other fuels are given (NAPFUE 203,204,301,304,305); [7] = with lime scrubber; [8] = with SCR

Dust emissions

[kg dust/Mg sinter produced]

Process type	Iron ore sinter plants														
References	(ref. 5)				(ref.10)	(ref. 7)		(ref.16) (6)			(ref. 31)				
Country or region	D				CIS	NL		D;I,B			EU				
Abatement (dust)	unabated		Two field ESP	ESP + fabric filter (3)	unknown (4)	unabated	abated	Dry ESP (3-4 fields)	multi cyclones	dry ESP (2-3 fields) or bag filters	“after abatement”	“after abatement”	“after abatement”	cyclones	bag filters
Dust	2-6 (1)	3-4 (2)	0.135-0.6	<0.006	10-24 (5)	0.675	0.165	0.12-0.34 (7)	0.03-0.12 (8)	0.05-0.2 (9)	< 0.0045	0.09-0.44	0.009-0.25	0.09-0.41	0.037-0.1

[1] = windbox emissions; [2] = crushing and screening; [3] = with injection of lignite activated charcoal and lime; [4] = see description given in 3.4.3; [5] = without sinter cooler 10-18 kg/t;

[6] = values calculated from given concentrations with spec flue gas flow; [7] = sintering process, Q_S assumed to be 2000 m³/Mg; [8] = Sinter cooling air (on strand) , Q_S assumed to be 700 m³/Mg; [9] = Sinter handling, Q_S assumed to be 1000 m³/Mg

Heavy metal emissions

[g/Mg sinter produced]

Process type	**Iron ore sinter plants**									
References	ref. 17	ref.18 (1)	ref.18 (2)	ref.19	ref. 20	ref. 21	ref. 7		ref. 5	ref. 6	ref. 22
Country or region	D	D		F	Int.	Int.			D (4)	D (3)	UK (4)
Abatement (dust)	electro-filters	electro-filters		electro-filters	electro-filters	cyclones	unabated	abated	electro-filters	electro-filters	unknown
Compound											
Arsenic (As)	-	0.025	0.009	-	-		0.05	0.01	0.026	0-0.038	
Cadmium (Cd)	-	$3*10^{-4}$	0.09	-	0.02-0.12	0.08	0.13	0.03	0.058	0.024-0.228	0.022
Chromium (Cr)	-	0.13	0.09	0.56	-	-	0.05	0.01	0.161	0.016-0.514	
Copper (Cu)	1	0.25	0.36	0.23	-	-	0.13	0.03	0.437	0.176-0.656	

n.r.a.= No range available

[1] = Diffuse sources, cold; [2] = Abated process emissions; [3]= calculated from given concentrations and spec. flue gas flow, [4]= calculated from reported annual emission with sinter production data

Heavy metal emissions (continued)

[g/Mg sinter produced]

Process type	**Iron ore sinter plants**										
References	ref.17	ref.18 (1)	ref.18 (2)	ref.19	ref. 20	ref. 21	ref. 7		ref. 5	ref. 6	ref. 22
Country or region	D	D		F	Int.	Int.			D (4)	D (3)	UK (4)
Abatement (dust)	electro-filters	electro-filters		electro-filters	electro-filters	cyclones	unabated	abated	electro-filters	electro-filters	unknown
Compound											
Mercury (Hg)	-	$6*10^{-5}$	0.01	-	-	-	0.04	0.01	0.012	0.010-0.106	
Nickel (Ni)	-	0.19	0.14	1.0	-	-			0.240	0.008-0.378	
Lead (Pb)	9	0.13	4.5	2.1	-	15.3	9.92	2.48	2.990	0.360-4.106	0.73
Selenium (Se)	0.02	$1*10^{-4}$	0.019	-	-	-			0.022		
Zinc (Zn)	-	0.13	0.9	2.1	-	-	0.37	0.09	0.678		
Manganese (Mn)									0.966	0.128-1.754	

n.r.a.= No range available

[1] = Diffuse sources, cold; [2] = Abated process emissions; [3]= calculated from given concentrations and spec. flue gas flow, [4]= calculated from reported annual emission with sinter production data

POP emissions

Data are available only for PCDD/Fs

µg I-TEQ/tonne of sinter produced (1)

Process type	**Iron ore sinter plants**									**Sintering of special materials**		
References	ref. 23		ref. 24	ref. 6			ref.25	ref. 26 (2)	ref. 27	ref.24 (8)	ref.25(9)	ref.25(10)
Country or region	A		D	D			NL	S	UK	D	NL	NL
Abatement (dust)	electro-filters	high performance wet scrubbing (‘Airfine’)	electro-filters	Moving electrofilters (‘MEEP’)	fabric filter, activated charcoal	fabric filter, hearth oven coke	electro-filters	electro-filters	electro-filters	electro-filter	fabric filter	washer
PCDD/Fs	4-5 (7)	0.4-1.0	1.3-27.7 (3) 5.9 (4) 0.88 (6)	1.4 (7)	0.24-4.95 (7)	0.04-4.2 (7)	0.3-17	1-2.8	1.2-9	338	0.3	4.5

[1] = I-TEQ: International toxicity equivalents according to NATO/CCMS; [2] = value given in N-TEQ (Toxicity equivalents, nordic model); [3] = windboxes, range except one-case maximum: 94.8 µg I-TEQ/t; [4] = typical value; [6] = sinter cooler; [7] = calculated from reported concentrations and estimate of specific flue gas volume (2000 m^3/t); [8] = sintering of iron containing residue materials; [9] = prod. of artificial gravel; [10] = prod. of phosphates

SNAP CODE: **040100**

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Overview

NOSE CODE: **105.08.00**

NFR CODE: **1 B 2 a iv**

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquid fuels (from motor gasoline to residual oil), by-product fuels and feedstocks (such as asphalt, lubricants, gases, coke), and primary petrochemicals (for instance, ethylene, toluene, xylene). Petroleum refinery activities start with the receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and terminate with storage preparatory to shipping the refined products from the refinery. (U.S. EPA 1985a and Poten and Partners Inc. 1988) The distribution and marketing of the products of a refinery are considered separately under SNAP sub-sectors 0504 and 0505.

Not all petroleum refinery processes that could result in the emissions to the air are included under SNAP code 0401. The following lists the major refinery processes and associated operations along with the SNAP code(s) most likely to apply to these operations (using currently available SNAP94 codes):

Table 1: Refinery Processes and Associated SNAP Codes.

	Process	SNAP	Description
1.	Feed Stock handling and storage	050401	Marine Terminals
		050402	Other Handling and Storage
2.	Separation Processes	040101	Petroleum Products Processing
3.	Petroleum Conversion Processes	040101	Petroleum Products Processing
4.	Petroleum Treating Processes	040101	Petroleum Products Processing
		060310	Asphalt Blowing
5.	Product Blending	040101	Petroleum Products Processing
6.	Product Storage and Handling	040104	Storage and Handling of Products in Refinery
		050501	Refinery Dispatch Station
7.	Auxiliary Facilities	030104	Combustion
		030105	Combustion
		010306	Process Furnaces
		040103	Sulphur Recovery Plants
		0405	Organic Chemical Production
		091001	Waste Water Treatment in Industry
		091002	Waste Water Treatment In Residential /Commercial Sector
		090202	Incineration of Industrial Wastes
7.	Auxiliary Facilities (Continued)	090203	Flaring in Oil Refinery
		090205	Incineration of Sludges From Water Treatment
		090400	Landfills
			Cooling Towers
			Vapour Recovery and Blowdown Systems

*this may be included with product storage and handling

Estimating NMVOC emissions due to spills and accidental discharges is considered outside the terms of reference for this manual, although a separate SNAP code could be created to record this information where it is available.

Petroleum refineries are significant sources of SO_2 and VOCs, with lesser emissions of particulate, NOx and CO.

In North America in 1985, the percent contributions to total anthropogenic emissions were estimated for non-combustion emissions from this sector as summarised in Table 2.

Table 2: 1990 Non-Combustion Emission from Petroleum Refineries Exposed as a Percent of Total Anthropogenic Emissions

Country	**Particulate***	**SOx**	**CO**	**NOx**	**NMVOC**
Canada		1.0	0.1		8.5
United States 1985		1.3	0.4	0.3	3.7

* = PM is detailed in the relevant individual chapters

See chapter ACOR and other relevant chapters for contribution from individual activities as listed above.

Percentage contribution to non-combustion VOC emissions from refineries in Canada in 1988 (CPPI and Environment Canada 1991) from the various non-combustion sources were estimated as in Table 2.

Table 3: Percent Contribution to Total Non-Combustion VOC Emissions - Canada 1988 (CPPI/Environment Canada 1991)

Process	Percent Contribution	Total Percentage
Process Sources (FCCU Only)		4.7
Fugitive Total		46.8
Pumps	5.1	
Compressors	1.5	
Valves	31.5	
Flanges	1.9	
P/R Valves	2.7	
O/E Lines	0.5	
Sampling System	0.4	
Drains	3.2	
Storage/Handling Total		25.9
Tanks	15.6	
Handling	10.3	
Waste Systems Total		22.6
Cooling Water	3.1	
Waste Water	18.8	
Land Farming	0.6	
Vent	<0.1	
Flare	0.1	
TOTAL		100

Swedish estimates of VOC emissions from oil refineries using the DIAL technique to quantify VOC emissions indicated that product storage represented a much larger portion of total emissions, in the order of 60 to 75 percent. Process emissions represented 25 to 35 percent, with water treatment emissions being under 5 percent.

Some work on NMVOC emissions from refineries has been done by the CONCAWE (for example, CONCAWE reports No. 2/86, 6/87, 52/87). In 1983 refineries contributed 2.2% and 2.4% to total anthropogenic NMVOC emissions in OECD Europe and EEC-10 countries, respectively. It is not clear if this includes combustion emissions from these sources. In

another CONCAWE report (52/87 1877), in which emissions from a typical refinery are reported, fugitive emissions contributed 53% by weight of non-combustion NMVOC emissions. Other sources included were tank storage, loading losses and wastewater treatment.
In Poland in 1992, refineries contributed 1% of total anthropogenic VOC emissions. In Russia, the oil and gas industry (mainly oil extraction and oil refining) emitted 1262 ktonnes VOC/year (year not specified) (Tsibulski 1993).

The simplest emission estimation method for petroleum refineries would be to use emission factors that estimate emissions from all of the above sources, based on the crude throughput, and assigning these emissions to SNAP code 0401.

A review of 29 Canadian refineries found a THC emission of 0.4 to 3.2 kg THC/m3 feed charged (CPPI and Environment Canada 1991), with an average of 1.1 kg/m3. VOC emission factors reported in a review for Corinair and EMEP (Veldt 1991) were (in kg/mg): Corinair 0.5, FRG 0.4, USA 0.65, Poland 0.88, USSR 12, Lithuania 2.4. The proposed default emission factor for NMVOC was 0.5 kg/mg. A Corinair report (CEC 1991a) stated that 11 West European refineries emitted an average of 0.35 kg VOC/t crude, ranging from 0.13 - 0.55 (source was not referenced). The default NMVOC emission factor for all refinery emissions in another Corinair report (CEC 1991b) was .225 kg/t of input for modern designs and .90 kg/t input for old designs. An overall VOC emission factor of 0.35 kg/m3 was calculated for an Austrian refinery (Winiwarter 1994).

The review of 29 Canadian refineries mentioned above (CPPI and Environment Canada 1991) also included estimates of 1988 emissions of particulate, SO_2, NOx and CO due to non-combustion sources at these refineries. These have been converted to emission factors, based on total refinery feed, as summarised in Table 4. These are very general emission factors in that the actual emissions for any given refinery will depend very heavily upon the portion of the total refinery feed that goes into specific processes.

Table 4: General Emission Factors for Non-combustion Emissions from Petroleum Refineries (CPPI and Environment Canada 1991)

Contaminant	**Emission Factor (kg/m^3 refinery feed)**	**Sources Considered**
Particulate	0.006	FCCU only
SOx	0.8	vac. tower, cat. cracker, fluid coking, S plant, S.W.S., incin., caustic regen., flares, vents, off gases, others.
NOx	0.05	catalytic cracking
CO	0.08	FCCU only

SNAP CODES: **040101**
040102

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Petroleum Products Processing
Fluid Catalytic Cracking

NOSE CODE: **105.08.01**
105.08.02

NFR CODE: **1 B 2 a iv**

1 ACTIVITIES INCLUDED

A basic refinery converts crude petroleum into a variety of sub-products. Principal products of a petroleum refinery include:

Table 1.1: Refinery Principal Products

Product Type	Principal Products
Liquid Fuels	Motor Gasoline
	Aviation Gasoline
	Aviation Turbine Fuel
	Illuminating Kerosene
	High-Speed Diesel
	Distillate Heating Fuel
	Medium-Speed Diesel
	Residual Oil
By-Product Fuels and Feedstocks	Naphtha
	Lubricants
	Asphalt
	Liquefied Petroleum Gases
	Coke
	Sulphur (Product of Auxiliary Facility)
	White Oils
Primary Petrochemicals	Ethylene
	Propylene
	Butadiene
	Benzene
	Toluene
	Xylene

The production of the latter group, primary petrochemicals, is, however, not included in this chapter, even if these chemicals are produced at a petroleum refinery. Please refer to the relevant chapters for sub-sector 040500 (chapters B451-B4522).

The petroleum refining industry employs a wide variety of processes. The types of processes operating at any one facility depend on a variety of economic and logistic considerations such as the quality of the crude oil feedstock, the accessibility and cost of crude (and alternative feedstocks), the availability and cost of equipment and utilities, and refined product demand. The four categories of general refinery processes are listed in Table 1.2.

Table 1.2: General Refinery Processes and Products

General Process	Products
Separation Processes	Atmospheric Distillation
	Vacuum Distillation
	Light Ends Recovery (Gas Processing)
Petroleum Conversion Processes	Cracking (Thermal and Catalytic)
	Coking
	Viscosity Breaking
	Catalytic Reforming
	Isomerization
	Alkylation
	Polymerization
Petroleum Treating Processes	Hydrodesulfurization
	Hydrotreating
	Chemical Sweetening
	Acid Gas Removal
	Deasphalting
Blending	Motor Gasoline
	Light Fuel Oil
	Heavy Fuel Oil

The major direct process emission sources of NMVOCs are vacuum distillation, catalytic cracking, coking, chemical sweetening and asphalt blowing (U.S.EPA 1985a). Process-unit turnaround (periodical shut-down of units) has also been reported as contributing to VOC emissions (CEC 1991).

Fugitive emissions from equipment leaks are also a significant source of NMVOC emissions from process operations at a refinery. Emissions from storage and handling are also classified as fugitive emissions. To avoid confusion, fugitive emissions from equipment leaks will be referred to as fugitive process emissions in this chapter.

Table 1.3 summarises significant sources of common pollutants from process and fugitive process emissions sources at refineries.

Table 1.3: Significant Process Emissions Sources at Petroleum Refineries (U.S. EPA 1985)

Process	**Particulate**	**NO_x**	**SO_x**	**CO**	**NMVOC**
Vacuum Distillation	x	x	x	x	X
Catalytic Cracking	**X**	x	x	**X**	X
Thermal Cracking	x	x		x	X
Sweetening					**X**
Blowdown Systems	x	x	x	x	**X**

X - Possibly significant sources (depending upon the degree of contract)
x - Minor sources

This section is a summary of the main products possibly produced at a refinery and the major processes that could be present, with an indication of the processes that are potentially significant sources of emissions to the air. All of these processes are currently under SNAP code 040101, with the exception of FCCs with CO boiler. However it is difficult to use this code separately from other processes, particularly for simpler emission estimation methods, which tend to encompass a wide variety of sources. It is therefore proposed that FCCs with CO boiler also be inventoried under 040101.

It is important to note that fugitive process emissions are somewhat difficult to characterise by their area (process vs. storage/handling vs. waste treatment), as they are estimated based on equipment counts and are not usually classified as to type of use or area of the refinery. Therefore fugitive process emissions for the entire refinery are inventoried under SNAP code 040101.

2 CONTRIBUTION TO TOTAL EMISSIONS

Table 2.1 summarises emissions from petroleum refining processes in the CORINAIR90 inventory. In a Canadian study (CPPI and Environment Canada 1991), the process/fugitive process sources contributed 51.5% (process 4.7% (Only FCCU estimated) and fugitive process 46.8%) of total VOC emissions for 29 refineries surveyed. Blending losses were not estimated separately. The process/fugitive process sources would represent approximately 2.6% of total anthropogenic emissions.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Petroleum Products Process.	040101	0.5	0.1	0.7	0	0	0.2	0.1	-	-
Fluid Catalytic Cracking	040102	0.4	0.1	0	-	0	0.1	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions
-

3 GENERAL

3.1 Description

3.1.1 Direct Process Sources

There are four main categories of processes in a petroleum refinery:

Separation Processes
Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons plus small amounts of impurities including sulphur, nitrogen, oxygen and metals. The first phase in petroleum refining operations is the separation of crude oil into common boiling point fractions using three petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing).

Conversion Processes
Where there is a high demand for high-octane gasoline, jet fuel and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions. Cracking, coking and visbreaking processes break large petroleum molecules into smaller petroleum molecules. Polymerization and alkylation processes rearrange the structure of petroleum molecules into larger ones. Isomerization and reforming processes rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecule size.

Treating Processes
Petroleum treating processes stabilise and upgrade petroleum products. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstocks prior to refining. Undesirable elements such as sulphur, nitrogen and oxygen are removed from product intermediates by hydrodesulphurization, hydrotreating, chemical sweetening and acid gas removal. Deasphalting is used to separate asphalt from other products. Asphalt may then be polymerised and stabilised by blowing (see SNAP code 060310).

Blending
Streams from various units are combined to produce gasoline, kerosene, gas oil and residual oil, and in some cases a few speciality items.

3.1.2 Fugitive Process Sources

Fugitive process emission sources are defined as NMVOC sources not associated with a specific process but scattered throughout the refinery. Fugitive process emissions sources include valves of all types, flanges, pump and compressor seals, pressure relief valves, sampling connections and process drains. These sources may be used in the transport of crude oil, intermediates, wastes or products.

Note that this category will actually include fugitive emissions from all such refinery sources, rather than those sources only associated with process emissions.

3.2 Definitions

3.3 Techniques

See section 3.1 (above).

3.4 Emissions/Controls

3.4.1 Direct Process Emissions

Vacuum distillation, catalytic cracking, thermal cracking, sweetening, blowdown systems, sulphur recovery, asphalt blowing and flaring processes have been identified as being potentially significant sources of SO_2 and NMVOC from those sources included under SNAP code 040101, with a relatively smaller contribution of particulate, NOx and CO. (U.S.EPA 1985a).

Vacuum Distillation
Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high-boiling-point hydrocarbons. The topped crude is separated into common-boiling-point fractions by vaporisation and condensation in a vacuum column at a very low pressure and in a steam atmosphere. A major portion of the vapours withdrawn from the column by steam ejectors or vacuum pumps are recovered in condensers. Historically, the non-condensable portion has been vented to the atmosphere.

The major NMVOC emission sources related to the vacuum column include steam ejectors and vacuum pumps that withdraw vapours through a condenser.

Methods of controlling these emissions include venting into blowdown systems or fuel gas systems, and incineration in furnaces (SNAP code 090201) or waste heat boilers (SNAP code 030100). These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions.

Note that the emissions from blowdown and vapour recovery systems have been included under this SNAP code rather than under SNAP code 090100 (see below).

Catalytic Cracking
Catalytic crackers use heat, pressure and catalysts to convert heavy oils into lighter products with product distributions favouring the gasoline and distillate blending components.

Fluidised-bed catalytic cracking (FCC) processes use finely divided catalysts that are suspended in a riser with hot vapours of the fresh feed. The hydrocarbon vapour reaction products are separated from the catalyst particles in cyclones and sent to a fractionator. The spent catalyst is conveyed to a regenerator unit, in which deposits are burned off before recycling.

Moving-bed catalytic cracking (TCC) involves concurrent mixing of the hot feed vapours with catalyst beads that flow to the separation and fractionating section of the unit.

Aside from combustion products from heaters, emissions from catalytic cracking processes are from the catalyst regenerator. These emissions include NMVOC, NOx, SOx, CO, particulates, ammonia, aldehydes, and cyanides.

In FCC units, particulate emissions are controlled by cyclones and/or electrostatic precipitators. CO waste heat boilers may be used to reduce the CO and hydrocarbon emissions to negligible levels.

TCC catalyst regeneration produces much smaller quantities of emissions than is the case for FCC units. Particulate emissions may be controlled by high-efficiency cyclones. CO and NMVOC emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater firebox or smoke plume burner.

SOx from catalyst regeneration may be removed by passing the flue gases through a water or caustic scrubber.

Thermal Cracking

Thermal cracking units break heavy oil molecules by exposing them to higher temperatures. In viscosity breaking (visbreaking), topped crude or vacuum residuals are heated and thermally topped in a furnace and then put into a fractionator. In coking, vacuum residuals and thermal tars are cracked at high temperature and low pressure. Historically, delayed coking is the most common process used, although fluid coking is becoming the more preferred process.

Emissions from these units are not well characterised. In delayed coking, particulate and hydrocarbon emissions are associated with removing coke from the coke drum and subsequent handling and storage operations. Generally there is no control of hydrocarbon emissions from delayed coking, although in some cases coke drum emissions are collected in an enclosed system and routed to a refinery flare.

Sweetening

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl disulfides in the presence of a catalyst. Conversion may then be followed by an extraction step in which the disulfides are removed.

Hydrocarbon emissions are mainly from the contact between the distillate product and air in the air-blowing step. These emissions are related to equipment type and configuration, as well as to operating conditions and maintenance practices.

Asphalt Blowing

Please refer to SNAP code 060310 for inventory methods for asphalt blowing.

Sulphur Recovery

Please refer to SNAP code 040103 for inventory methods for sulphur recovery plants.

Flaring

Please refer to SNAP code 090203 for inventory methods for flaring in a refinery.

Blowdown Systems

Many of the refining process units subject to hydrocarbon discharges are manifolded into a collection unit (i.e., blowdown system), comprising a series of drums and condensers, whereby liquids are separated for recycling and vapours are recycled or flared with steam injection. Uncontrolled blowdown emissions consist primarily of hydrocarbons, while vapour recovery and flaring systems (see SNAP code 090203) release lesser NMVOC and greater combustion products including SO_2, NOx and CO.

3.4.2 Fugitive Process Emissions

Fugitive process emissions sources include valves of all types, flanges, pumps in hydrocarbon service (packed or sealed), compressor seals, pressure relief devices, open-ended lines or valves, sampling connections, and process drains or oily water drains.

For these sources, a very high correlation has been found between mass emission rates and the type of stream service in which the sources are employed. For compressors, gases passing through are classified as either hydrogen or hydrocarbon service. For all other sources, streams are classified into one of three stream groups: gas/vapour streams, light liquid/two phase streams, and kerosene and heavier liquid streams. It has been found that sources in gas/vapour service have higher emission rates than those in heavier stream service. This trend is especially pronounced for valves and pump seals.

Of these sources of NMVOC, valves are the major source type. This is due to their number and relatively high leak rate.

Normally, control of fugitive emissions involves minimising leaks and spills through equipment changes, procedure changes, and improved monitoring, housekeeping and maintenance practices.

Applicable control technologies are summarised in Table 3.1.

Table 3.1: Control Technologies for Fugitive Sources (U.S. EPA 1985a)

Fugitive Source	**Control Technology**
Pipeline Valves	monitoring and maintenance programs
Open-Ended Valves	Instillation of cap or plug on open end of valve /line
Flanges	monitoring and maintenance
Pump Seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Compressor Seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Process Drains	Traps and covers
Pressure/Relief Valves	Rupture disks upstream of relief and/or venting to a flare

4 SIMPLER METHODOLOGY

The simplest inventory methodology is to combine the crude oil throughput of each refinery with either a single emission factor, or two emission factors (one for process and one for fugitive process emissions) for each refinery. The first approach would be the easiest to use if very limited information is available. However, the second approach would allow the user to in some way reflect the type of processes and related controls at the refinery as well as accounting for the sophistication of the fugitive emissions inspection and maintenance programs typical of the region and/or that particular refinery.

It is strongly recommended that the detailed methodology be used for petroleum refineries.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.[1]

5 DETAILED METHODOLOGY

The detailed methodology requires each refinery to estimate its process emissions for each process, using detailed throughput information and emission factors. Site specific emission factors or data would be preferable, wherever possible. Remote sensing, using Fourier transform techniques, is making it possible to measure total refinery emissions, although it may be difficult to identify the individual source strengths.

The state-of-the-art technology for estimating fugitive process emissions is to use an emission testing program to classify equipment into groupings and then estimate emissions using emission factors or algorithms (see section 16, Verification Procedures). However, this is a very expensive and time-consuming proposition and is considered beyond the resources of most inventory personnel. The methodology proposed below is a compromise between a testing program vs. estimates of the number of each type of equipment that might be in a refinery based on either its throughput or production data.

Fugitive process emissions, which are considered to be the major source of NMVOCs at a petroleum refinery, are inventoried using emission factors for each type of equipment and stream, based on a count of the number of sources, a characterisation of the NMVOC content of the stream in question and whether the refinery conducts an inspection and maintenance program.

The U.S. EPA has published a detailed protocol for equipment leak emissions estimates (U.S.EPA 1993). In the average emission factor method, the following unit-specific data is required:

1. the number of each type of component in a unit (valve, connector etc.);
2. the service each component is in (gas, light liquid, or heavy liquid);
3. the NMVOC concentration in the stream (weight fraction) and;
4. the number of hours per year the component was in service.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

The equipment is then grouped into streams, where all of the equipment within the stream has approximately the same NMVOC weight percent. Annual emissions are then calculated for each stream using equation 1 as follows:

$$\mathbf{NMVOCs = AEF * WFnmvoc * N} \qquad (1)$$

where:

NMVOCs = NMVOC emission rate from all equipment in the stream of a given equipment type (kg/hr)
AEF = applicable average emission factor for the equipment type (kg/hr/source)
WFnmvoc = average weight fraction of NMVOC in the stream and
N = the number of pieces of equipment of the applicable equipment type in the stream.

If there are several streams at the refinery, as is usually the case, the total NMVOC emission rate for an equipment type is the sum of emissions from each of the streams. The total emission rates for all of the equipment types are summed to generate the process unit total NMVOC emission rate from fugitive process sources.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a protocol such as that illustrated in the Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, the crude oil throughput of each refinery is required.
For the detailed methodology, specific data will be required on the throughput for each process area. For fugitive process emissions estimates, each emission source must be counted by type and process stream, and the NMVOC content for each stream must then be characterised. The number of annual hours of operation for each stream is also required. Finally it must be determined if an inspection and maintenance program is conducted at the refinery.

7 POINT SOURCE CRITERIA

All refineries are to be inventoried as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

The CONCAWE Air Quality Management Group identify a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR),

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.
The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

CONCAWE suggests a conservative overall fugitive emission factor of 0.30 kg NMVOC/metric tonnes refinery feed .

Total hydrocarbon emission factors based on an inventory of Canadian refineries in 1988 (CPPI and Environment Canada 1991) were 0.05 kg/m3 feedstock for process emissions and 0.53 kg/m3 for fugitive process emissions. Of the latter, valves accounted for 0.35 kg/m3 feedstock. Data was not available for NMVOC only. This inventory was based on a survey of individual refineries, in which some reported their own emission estimates and some reported base quantity data for which emissions were estimated using a variety of techniques.

The use of CONCAWE derived VOC emission factors, based upon a hypothetical 5 Mt/yr refinery, as follows was recommended as a default method for the Corinair 1990 project (CEC 1991). The emission factor for fugitive process emissions is 0.25 kg/t crude (0.21 kg/m^3 crude assuming specific gravity of 0.85 (BP 86)).

Sixty percent of these emissions are reported to be from valves. CONCAWE also indicates that average fugitive emissions in the same refinery with a maintenance and monitoring programme is 0.01% by weight (.085 kg/m3) of refinery throughput (CONCAWE Report 87/52 1987). The CORINAIR90 default emission handbook also reports a U.S.EPA factor of 0.18 kg/Mg crude (U.S.EPA 1985b) for process unit turnaround, and estimates that Western European refineries would emit half of this for turnaround, or 0.09 kg/Mg.

It is apparent that detailed emission inventory data is required for several refineries in differing regions in order to develop meaningful emission factors. Major factors affecting regional differences include crude characteristics, product demand (and hence refinery processes) and regulatory requirements.

Emission factors for non-combustion process sources of other contaminants were not identified, other than as provided in Table 4 of SNAP sector 040100.

8.2 Detailed Methodology

The more detailed methodology involves the use of process-specific emission factors based on the throughput of the unit and fugitive process emission factors based on equipment counts. Emission factors from CONCAWE in the following sub-section are the best available estimate. It is important to note that the factors presented below must be used with caution, as they do not account for regional differences in crude, product demand and regulatory requirements. Wherever possible, site-specific emission estimates based on monitoring should be considered.

8.2.1 Process Emission Factors

A 2006 schematic representation of process emission factors from CONCAWE are reported in Table 8.1 for main pollutants, Table 8.2 for heavy metals and 8.3 for Polycyclic Aromatic Hydrocarbons (PAHs).

The gaseous emissions from refinery blowdown systems are normally recovered and/or flared. The emission factors of Table 8.1 are referred at the case where these controls are not operational and the emissions are emitted to atmosphere.

The gaseous emissions from bitumen blowing are normally passed through a scrubber and then fed to an incinerator. The emission factors of Table 8.1 are referred at the case where these controls are not operational and the emissions are emitted to atmosphere.

Table 8.1: Uncontrolled (^) emission factors for petroleum refineries processes (Concawe, 2006)

Process	PM_{10}	SOx (as SO_2)	CO	NMVOC	NOx (as NO_2)	NH_3	C_6H_6
Catalytic cracking unit regenerators							
Full Burn Regeneration (°)	0.549	1.41	Neg	Neg	0.204	Neg	Neg
Partial Burn with CO Boiler (°)	0.549	1.41	Neg	Neg	0.204	Neg	Neg
Partial Burn without CO Boiler (°)	0.549	1.41	39,2	0.63	0.204	0.155	0.00105
Catalytic reforming unit units (°°)		0.00363	0,0416				
Fluid coking units (°°)							
Controlled with CO or Fired Waste heat boiler (°°)				Neg			Neg
Uncontrolled	0.765			0.046			0.000175
Uncontrolled blowdown systems (°°°)				1.65			0.00632
Uncontrolled bitume blowing (°°°°)				27,2			

(^) For PM10 emissions from *catalytic cracking unit regenerators* is assumed that there is a primary cyclone installed
(°) expressed as kg of mass emitted × volume of fresh feed to unit (in m^3)
(°°) expressed as kg of mass emitted × feed to unit (in m^3)
(°°°) expressed as kg of mass emitted × refinery feed (in m^3)
(°°°°) expressed as kg of mass emitted × mass of blown bitumen (in tonne)

Table 8.2: Heavy metals uncontrolled (^) emission factors for petroleum refineries processes (Concawe, 2006)

Process	As	Cd	Cu	Hg	Ni	Pb	Zn
Catalytic cracking unit regenerators (°)	0.0139	0.0625	0.139	0,0695	0.612	0.32	0.118
Fluid coking units (°)	2.16		0.015	0,03	0.57	0.045	0.045

(^) For emissions from *catalytic cracking unit regenerators* is assumed that there is a primary cyclone installed

(°) expressed as g of mass emitted × volume of fresh feed to unit (in m^3); for a unit with a primary cyclone installed

Table 8.3: PAHs uncontrolled emission factors for catalytic cracking unit regenerators (Concawe, 2006)

PAH	Emission Factor mg/tonnes of coke burned
Benzo(a)pyrene	2.966
Benzo(b)fluoranthene	2.915
Benzo(k)fluoranthene	2.892
Indeno(1,2,3-cd)pyrene	2.883
Benzo(g,h,i)perylene	2.886
Fluoranthene	5.471

For comparison, Table 8.4 lists emission factors for refinery processes based on tests conducted in the 1970’s, noting that overall, less than 1 % of the total hydrocarbons emissions are methane (U.S.EPA 1985a). The VOC emission factors listed in Table 8.5 were used to estimate emissions from processes in the United Kingdom (Passant n.d.).

Table 8.4: Emission Factors for Petroleum Refineries (U.S. EPA 1985a and 1995)

Process	Particulate	Sox (as SO_2)	CO	THC[a]	NOx (as NO_2)	Aldehydes	NH_3	Quality
Fluid catalytic cracking units								
Uncontrolled kg/10^3 liters fresh feed	0.695 (0.267-0.976)[b]	1.143 (0.286-1.505)	39.2	0.630	0.204 (0.107-0.416)	0.054	0.155	B
ESP and CO boiler kg/10^3 liters fresh feed	0.128 (0.020-0.428)	1.413 (0.286-1.505)	Neg[c]	Neg	0.204[d] (0.107-0.416)	Neg	Neg	B
Moving-bed catalytic cracking units								
kg/10^3 liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
Fluid coking units								
Uncontrolled kg/10^3 liters fresh feed	1.5	NA[e]	NA	NA	NA	NA	NA	C
ESP and CO boiler kg/10^3 liters fresh feed	0.0196	NA	Neg	Neg	NA	Neg	Neg	C
Blowdown systems								
Uncontrolled kg/10^3 liters refinery feed	Neg	Neg	Neg	1.662	Neg	Neg	Neg	C
Vacuum distillation column condensers								
Uncontrolled	Neg	Neg	Neg	0.052	Neg	Neg	Neg	C

Process	Particulate	Sox (as SO_2)	CO	THC[a]	NOx (as NO_2)	Aldehydes	NH_3	Quality
kg/10^3 liters refinery feed								
Uncontrolled kg/10^3 liters vacuum feed	Neg	Neg	Neg	0.144	Neg	Neg	Neg	C
Controlled	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

[a] Overall, less than 1 percent by weight of the total hydrocarbon emissions are methane

[b] Numbers in parenthesis indicate range of values observed

[c] Negligible emission

[d] May be higher due to the combustion of ammonia

[e] NA, Not Available.

Table 8.5: United Kingdom VOC Emission Factors (Passant n.d.)

Process		Emission Factor	Quality
Catalytic Cracker	Uncontrolled	628 g/m^3 feed	D
	Controlled	negligible	D
Fluid Coking	Uncontrolled	384 g/m^3 feed	D
	Controlled	Negligible	D
Vacuum Distillation	Uncontrolled	51.6 g/m^3 feed	D
	Controlled	negligible	D
Asphalt Blowing	Uncontrolled	27.2 kg/Mg asphalt	D
	Controlled	0.54 kg/Mg asphalt	D

8.2.2 Fugitive Process Emission Factors

Emissions factors for fugitive process emissions of NMVOC are expressed as losses per equipment unit per day. As previously discussed, the methods for estimating mass emissions from process equipment leaks range from the use of emission factors with equipment counts to comprehensive field measurement techniques. These methods have evolved from a number of studies of the organic chemical and petroleum refining industries for the U.S. EPA.

Concawe study (Concawe, 2006) provides separately emission factors for pressurized components (Table 8.4) and from low pressure equipment such as drains, oil-water separators and product storage tanks.

Table 8.4: Uncontrolled fugitive average emission factors for petroleum refineries for pressurized components (Concawe, 2006)

Equipment Type	Service	Emission Factor kg/hr/source
Valves	Gas	0.0268
	Light Liquid	0.109
Pump seals	Light Liquid	0.114
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.160

Flanges and non-flanged connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.015

The following algorithm provides an estimate for emissions from the entire refinery process drain system. Process drain openings (sumps, etc.) are normally fitted with an emission control device such as a water seal or sealed cover. An assessment needs to be made to establish how many of the drain covers are unsealed and vent directly to atmosphere.

$$E\ (kg) = 0{,}032 \times N \times h$$

where:

- N = number of unsealed covers in the refinery process drain system.
- h = period of emission estimate in hours e.g. for annual reports = 365 × 24.

If the total number of drains is unknown a drain count of 2.6 drains per pump in process areas can be used .

For oil-water separators, emissions are dependent on the type of separator installed.

$$E\ (kg) = F_{SEP} \times V_{WATER}$$

where:

- F_{SEP} = Emission factor for the type of separator given in Table 8.5.
- V_{WATER} = Volume of waste water treated by the separator (in m^3).

Emissions from basins and ponds that handle clean water or storm water are considered negligible. For ponds temporarily storing oily-water use the emission factor for an uncovered, gravity type separator in Table 8.5.

Table 8.5: Emission Factors for Oil-Water Separators (Concawe, 2006)

Separator type	**Emission factor (F_{SEP})**
Gravity type - uncovered	0.111
Gravity type - covered	0.0033
Gravity type – covered and connected to flare	0
DAF or IAF (°) - uncovered	0.004
DAF or IAF (°) - covered	0.00012
DAF or IAF (°) - covered and connected to flare	0

(°) DAF = Dissolved air floatation type, IAF = Induced air floatation type

Emissions from cooling water towers are considered negligible as sound refinery engineering practice ensures that oil is prevented from entering these systems.

For comparison, Table 8.6 provides U.S. EPA (1993) NMVOC emission factors for pressurized components.

Table 8.6: Process Fugitive Average NMVOC Emission Factors for Petroleum Refineries (U.S.EPA 1993)

Source		**Emission Factor (kg/hr-source)**	**Quality**
Valves	Gas	0.0268	
	Light Liquid	0.0109	

	Heavy Liquid	0.00023	
Open-ended Lines	All Streams	0.0023	
Connectors	All Streams	0.00025	
Pump Seals*	Light Liquid	0.114	
	Heavy Liquid	0.021	
Compressor Seals	Gas	0.636	
Sampling Connections	All Streams	0.0150	
Pressure Vessel Relief Valves	Gas	0.16	

* The light liquid pump seal factor can be used to estimate the leak rate from agitator seals

These emission factors, however, are in most cases considered to overestimate NMVOC emissions from sources in more modern facilities. The U.S. EPA allows a 75% reduction in emissions estimated by using these emission factors if an approved I and M program is conducted at the petroleum refining facility.

Passant (1993) used the VOC emission factors presented in Table 8.7, which were referenced to U.S.EPA 1988.

Table 8.7: Process Fugitive Emission Factors for Petroleum Refineries (Passant 1993)

Source		**Emission Factor (kg/hr)**	Quality
Valve	Gas	0.0056	D
	Light	0.0071	D
	Heavy	0.0023	D
Pump Seals	Light	0.0494	D
	Heavy	0.0214	D
Compressor Seals	all streams	0.2280	D
Pressure Relief Seals	all streams	0.104	D
Flanges	all streams	0.00083	D
Open-ended Lines	all streams	0.0017	D
Sample Connections	all streams	0.015	D

Although the derivation of the emission factors in table 8.4 is not given, it would appear that these are actually average synthetic organic chemical manufacturing industry (SOCMI) (1988) uncontrolled emission factors. These sets of factors are thought to be biased on the high side for petroleum refineries due to the inclusion of ethylene plants, which operate at 15,000 to 40,000 psig.

9 SPECIES PROFILES

9.1 Applicability of Generalised VOC Species Profiles

In both North America and Europe, VOC species profiles have been published based on measurements or engineering judgement. There is a need to produce generalised profiles for use by models, the alternative being to obtain refinery specific data. Generalised profiles can be generated at the most detailed process level, however, there are several important influences which should be considered in attempting to specify such generally applicable data. Some of these influences are:

<u>Meteorological and Climatological effects</u>: Ambient temperature and temperature ranges may have important influences on the emitted species profiles. Due to the logarithmic behaviour of vapour pressure, higher temperatures tend to favour the loss of the lower molecular weight compounds from storage vessels and some process streams.

<u>Variability of Raw Materials:</u> The type of crude oil being processed can influence the fraction of more volatile and more easily emitted compounds.

<u>Process Variability:</u> Different refineries will have process differences. Where the species profiles are based on individual operations, process differences can be allowed for. However, overall average refinery profiles will differ between refineries.

<u>Maintenance and Regulation:</u> Equipment maintenance and the enforcement of regulations will have significant effects on the overall emitted species distribution depending on which processes or operations are impacted by maintenance practices or by regulation.

The broad application of generalised profiles should be done with some caution. Where such profiles are necessary, consideration should be given to stratification of the data according to some of the major factors of influence such as climate, country, raw material etc.

9.2 Simplified VOC Speciation

For some applications, where there is no process detail, or where refineries are grouped as a single emission source, there is a need for a single overall species profile to characterise the emissions for modelling or other purposes. Process specific species profiles can be combined into a single overall refinery profile by appropriately weighting the individual profiles according to their relative contribution to the total refinery emissions.

Consideration should be given to stratification of the data according to some of the major factors of influence such as climate, country, raw material (crude) etc.
CONCAWE reports (Report 2/86) that refinery emissions are essentially saturated, with the saturated hydrocarbon content lying between 80 and 90% by weight. The balance of 10 to 20% is unsaturated and/or aromatic hydrocarbons, the actual values depending on the nature of the refinery processes installed. Several overall refinery species profiles are available, such as those reviewed by Veldt (1991) for application to the EMEP and CORINAIR 1990

emissions inventories. On the basis of this review, this chapter proposes an overall species profile for petroleum refining by mass fraction.

Table 9.1: CONCAWE Petroleum Refinery Speciation Profile

Species	**CONCAWE (%)**	**Quality**
Methane	0	(Unknown)
Ethane	5	
Propane	20	
n-Butane	15	
i-Butane	5	
Pentanes	20	
Hexanes	10	
Heptanes	5	
>Heptanes	5	
Ethene	1	
Propene	1	
Butene	0.5	
Benzene	2	
Toluene	3	
o-Xylene	0.7	
M,p-Xylene	1.3	
Ethylbenzene	0.5	
TOTAL	100	

The Air Emission Species Manual (AESM) for VOC (U.S. EPA 1994) provides an overall refinery species profile (Profile 9012: Petroleum Industry - Average, Data Quality E - based on engineering judgement) as summarised in Table 9.2.

Table 9.2: US EPA Petroleum Refinery Speciation Profile

Species	**CAS Number**	**Wt (%)**	**Quality**
Methane	74-82-8	13	E
Ethane	74-84-0	6.05	E
Propane	74-98-6	19.7	E
n-Butane	106-97-8	7.99	E
i-Butane	75-28-5	2.89	E
Pentanes	(109-66-0)	21.4	E
Hexanes	(110-54-3)	8.02	E
Heptanes	(142-82-5)	1.87	E
Octanes	(111-65-9)	2.13	E
Nonanes	(111-84-2)	1.01	E
Decanes	(124-18-5)	1.01	E
Cyclo-hexane	110-82-7	0.08	E
Cyclo-heptanes		2.27	E
Cyclo-octanes		0.66	E
Cyclo-nonanes		0.11	E
Propene	115-07-01	1.75	E
Butene	106-98-9	0.15	E
Benzene	71-43-2	0.38	E
Toluene	108-88-3	0.44	E
Xylenes	1330-20-7	0.19	E
Formaldehyde	50-00-0	8.88	E
Total		100.02	

The suggested applications are:

Blowdown system - vapour recovery./Flare
Blowdown system - without controls
Wastewater treatment - excl. Separator
Vacuum distillation - column condenser
Sludge converter - general
Fluid coking - general
Petroleum coke - calciner
Bauxite burning
Lube oil manufacturing

9.3 Detailed Process VOC Speciation

The most detailed speciation of VOC is achievable at the process level using the U.S. EPA AESM (U.S.EPA 1994). Such a detailed method is generally only applicable on an individual refinery basis where estimates of the emission contributions from the various process streams and operations are available. The generalised profiles, which are available for individual processes and operations, as well as fugitive process emissions, are summarised below. These profiles are based on United States data, and in many instances on data from California.

U.S. EPA petroleum refinery species profiles applicable to petroleum refinery process and fugitive process emissions are presented in Tables 9.3 through 9.8.

Table 9.3: Profile 0029: Refinery Fluid Catalytic Cracker.

CAS Number	**Name**	**Wt %**	**Quality**
	Isomers of hexane	13.00	C
74-82-8	Methane	36.00	C
50-00-0	Formaldehyde	51.00	C
TOTAL		100.00	

Table 9.4: Profile: 0031 Refinery Fugitive Emissions - Covered Drainage / Separation Pits.

CAS Number	**Name**	**Wt %**	**Quality**
	Isomers of hexane	12.20	C
	C-7 cycloparaffins	16.90	C
	C-8 cycloparaffins	5.20	C
	Isomers of pentane	10.10	C
74-82-8	Methane	2.90	C
74-84-0	Ethane	1.70	C
74-98-6	Propane	5.90	C
106-97-8	N-Butane	14.30	C
75-28-5	Iso-Butane	4.50	C
109-66-0	N-Pentane	12.00	C
110-54-3	Hexane	11.90	C
71-43-2	Benzene	2.40	C
TOTAL		100.00	

Used for: Fugitive hydrocarbon emissions - drains - all streams

Table 9.5: Profile: 0039 Description: Refinery Fugitive Emissions - Compressor Seals - Refinery Gas.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	1.00	D
	Isomers of heptane	0.10	D
	Isomers of pentane	8.60	D
74-82-8	Methane	13.30	D
74-84-0	Ethane	5.60	D
74-98-6	Propane	16.00	D
115-07-01	Propene	8.80	D
106-97-8	N-Butane	23.20	D
106-98-9	Butene	1.20	D
75-28-5	Iso-Butane	10.00	D
109-66-0	N-Pentane	7.60	D
110-54-3	Hexane	4.60	D
TOTAL		100.00	

Used for: Compressor seal - gas streams
Compressor seal - heavy liquid streams

Table 9.6: Profile: 0047 Description: Refinery Fugitive Emissions - Relief Valves - Liquefied Petroleum Gas

CAS Number	Name	Wt %	Quality
74-84-0	Ethane	4.10	D
74-98-6	Propane	90.40	D
115-07-01	Propene	5.10	D
75-28-5	Iso-Butane	0.40	D
TOTAL		100.00	

Used for: Vessel relief valves
Pipeline valves - gas streams
Pipeline valves - lt liq/gas streams
Pipeline valves - heavy liqd streams
Pipeline valves - hydrogen streams
Open-ended valves - all streams
Flanges - all streams
Vessel relief valves - all streams

Table 9.7: Profile: 0316 Description: Pipe / Valve Flanges

CAS Number	**Name**	**Wt %**	**Quality**
	C-7 cycloparaffins	0.20	C
	C-9 cycloparaffins	0.10	C
	Isomers of pentane	7.80	C
74-82-8	Methane	28.60	C
74-84-0	Ethane	5.80	C
74-98-6	Propane	11.50	C
115-07-01	Propene	0.10	C
106-97-8	N-Butane	18.30	C
75-28-5	Iso-Butane	7.40	C
109-66-0	N-Pentane	7.70	C
(10-54-3)	Hexanes	5.00	C
(42-82-5)	Heptanes	2.20	C
(11-65-9)	Octanes	2.20	C
(11-84-2)	Nonanes	1.10	C
(24-18-5)	Decanes	1.10	C
110-82-7	Cyclohexane	0.10	C
1330-20-7	Isomers of Xylene	0.20	C
71-43-2	Benzene	0.10	C
108-88-3	Toluene	0.50	C
TOTAL		100.00	

Used for: Pipeline - valves / flanges

Table 9.8: Profile: 0321 Description: Pump Seals – Composite.

CAS Number	Name	Wt %	Quality
	C-7 cycloparaffins	1.10	C
	C-8 cycloparaffins	0.10	C
	C-9 cycloparaffins	0.80	C
74-82-8	Methane	3.30	C
74-84-0	Ethane	1.20	C
74-98-6	Propane	3.70	C
106-97-8	N-Butane	8.10	C
75-28-5	Iso-Butane	0.80	C
109-66-0	Pentanes	17.70	C
(110-54-3)	Hexanes	16.50	C
(142-82-5)	Heptanes	12.60	C
(111-65-9)	Octanes	14.80	C
(111-84-2)	Nonanes	7.00	C
(124-18-5)	Decanes	7.00	C
(110-82-7	Cyclohexane	0.50	C
1330-20-7	Isomers of Xylene	1.30	C
71-43-2	Benzene	0.50	C
108-88-3	Toluene	3.00	C
TOTAL		100.00	

Used for: Pump seals - with/without controls
Pump seals - light liq/gas streams
Pump seals - heavy liqd streams
Sampling/purging/blind changing

10 UNCERTAINTY ESTIMATES

See next section on: Weakest Aspects/Priority Areas for Improvement in Current Methodology

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

More measurements of emissions from petroleum refineries should be done: based on testing programs in the United Kingdom, currently available emission factors have underestimated emissions typically by 30%.

Emission factors must be developed that can account for regional differences in the major sources of NMVOCs in refineries (see above and this part of section 040104). There are also difficulties in determining what the data really represents, as there is a wide variation in the definition of total hydrocarbons, hydrocarbons, non-methane hydrocarbons, VOCs and NMVOCs. There is a need to identify a standard method or definition of speciation of NMVOCS towards which all expert panels could work.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

No spatial disaggregation (of national emissions estimates) should be required since refineries are to be inventoried as point sources. However if data is not available on individual refineries, total regional or national crude processing data could be disaggregated based on refining capacity.

13 TEMPORAL DISAGGREGATION CRITERIA

No temporal disaggregation is possible if the simpler methodology is used.
If the detailed methodology is used, then individual refineries can indicate the temporal aspects of shutdowns.

None of the computational methods used to estimate fugitive leaks are based on parameters that show seasonal or diurnal changes. Therefore it is not possible to disaggregate fugitive process emissions at this time.

14 ADDITIONAL COMMENTS

In the European community, CONCAWE (1992) reports that the complexity of refineries has increased with the installation of additional conversion units (e.g. thermal crackers, catalytic crackers and hydrocrackers) as the demand for fuel oil production decreases and the demand for a higher yield of gasoline and other light products. This is shown on the table in which CONCAWE uses a system of refinery classifications that are based on increasing complexity.

Table 14.1:Concawe Petroleum Refinery Classification System

Year	No. of Refineries Reporting	Type I		Type II		Type III		Type IV	
		No.	**%**	**No.**	**%**	**No.**	**%**	**No.**	**%**
1969	81	34	42	31	38	16	20	-	-
1974	110	49	45	40	36	21	19	-	-
1978	111	50	45	36	32	25	23	-	-
1981	105	38	36	44	42	23	22	-	-
1984	85	18	22	47	54	20	24	-	-
1987	89	12	13	53	60	19	22	5	5
1990	95	9	9	53	56	22	23	11	12

Notes:

Type I:	Simple (non-conversion refinery: composed of crude oil distillation, reforming, treatment of distillate products, including desulphurization and/or other quality improvement processes (i.e. isomerization or specialty manufacturing).
Type II:	Type I plus catalytic cracking and/or thermal cracking and/or hydrocracking.
Type III:	Type II plus steam cracking and/or lubricant production within the refinery fence.
Type IV:	Refineries not in above categories, e.g. those producing only bitumen, lubes, etc. which import their feedstocks from other sources.

This classification system could be adopted for use in developing generic emission factors for application in the simpler inventory method. It could also be useful in developing generic speciation profiles.

15 SUPPLEMENTARY DOCUMENTS

There are no supplementary documents.

16 VERIFICATION PROCEDURES

There are more sophisticated and accurate methods to estimate fugitive process emissions, as developed by the U.S.EPA (1993). All of these methods involve the use of screening data, which are collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value is a measure of the concentration, in ppmv, of leaking compounds in the ambient air near the equipment in question. The EPA has detailed what is involved in an acceptable screening program in the protocol for equipment leak emissions estimation manual (U.S.EPA 1993).

The approaches to estimating equipment leak emissions based on screening data are:

1. Screening Ranges Approach
2. EPA Correlation Approach and
3. Unit -Specific Correlation Approach.

In the screening value approach, it is assumed that components having screening values greater than 10,000 ppmv have a different average emission rate than components with screening values less than 10,000 ppmv.

The EPA Correlation approach offers an additional refinement by providing an equation to predict mass emission rate as a function of screening value.

In the last approach, mass emissions rates are determined by bagging a specific type of equipment. The associated screening value can then be used to develop a leak rate/screening value correlation for that equipment in that process unit.

All of these methods are described in detail in the protocol document (U.S.EPA 1993).
As previously discussed, remote sensing monitoring programs can also provide verification of emissions estimates based on emission factors. However it is often difficult to differentiate between different refinery sources, and so this method would more often be used to verify total refinery emissions (i.e., more than just process and fugitive process emissions).

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19 RELEASE VERSION, DATE AND SOURCE

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Canada

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SNAP CODE: **040103**

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Sulphur Recovery Plants

NOSE CODE: **105.08.03**

NFR CODE: **1 B 2 a iv**

1 ACTIVITIES INCLUDED

H_2S is a by-product of processing natural gas and refining high sulphur crude oils. Sulphur recovery is the conversion of hydrogen sulphide (H_2S) to elemental sulphur. The Claus process is the most common sulphur recovery process used. Sulphur recovery plants may or may not be located at the processing or refining sites.

If this method is used to estimate emissions from sulphur recovery plants associated with natural gas processing, they should be coded under SNAP code 050301 (chapter B531).

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions from the CORINAIR90 inventory are summarised in table 1.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Sulphur Recovery Plants	040103	0.3	-	0	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006)[1].

3 GENERAL

3.1 Description

Sulphur recovery, used at both petroleum refineries and natural gas processing plants, converts by-product hydrogen sulphide (H_2S) in sour gas streams to an elemental sulphur product. During initial stages of high-sulphur crude oil or gas processing, process and fuel gases that contain significant amounts of H_2S are treated in a lean amine solution to absorb the sulphide components. The H_2S is subsequently stripped to provide either a feed gas to a

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

sulphur recovery plant or the stripped H_2S may be flared or incinerated at plants where sulphur is not recovered.

In the widely-used multistage Claus sulphur-recovery process, a portion of the H_2S in the feed gas is oxidized to sulphur dioxide (SO_2) and water in a reaction furnace with air or enriched oxygen. After quenching the hot gases to generate steam, the cooler gases are passed through a sulphur condenser to recover liquid sulphur and the gases are reheated. The remaining non-combusted fraction of the feed gas H_2S reacts with SO_2 in catalytic converters (e.g., using aluminium or bauxite catalysts) to form elemental sulphur, water and heat. Since each catalytic stage in the Claus plant recovers only a portion of the incoming sulphur, normally two or more stages are used to achieve up to 97% overall sulphur recovery. Tail gas from the final unit contains a variety of sulphur compounds and normally requires further tail gas cleanup to obtain higher recovery.

3.2 Definitions

3.3 Techniques

See section 3.1.

3.4 Emissions

Tail gas from a Claus sulphur-recovery unit contains a variety of pollutants from direct process oxidation reactions including SO_2 and unreacted H_2S, other furnace side reaction products such as reduced sulphur compounds and mercaptans (e.g., COS, CS_2) as well as small quantities of CO and VOC. These components may be emitted directly in older or very small uncontrolled Claus plants. The quantity and composition of sulphur components in the Claus plant tail gas are directly related to the sulphur recovery efficiency which will depend on factors such as: the number of catalytic stages, the concentration of H_2S and other contaminants in the feed gas, the stoichiometric balance of inlet gaseous components, operating temperatures, combustion efficiencies and catalyst maintenance. Typical Claus plant efficiencies range from 94-96% for two-stage units to 97-98.5% for four-bed catalytic plants and, because the process is thermodynamically limited, the tail gas still contains percent quantities of sulphur compounds which may be further treated for recovery and emission control. When feed gas flow is much lower than the dimensional flow for the Claus unit and when sour gas composition and flow is fluctuating between 80 and 90 % it can be difficult to achieve these high efficiencies. Efficiencies between 80 and 90 % have been reported for such difficult conditions.

3.5 Controls

Tail gas emission reduction from the Claus process is normally achieved by one of the three following types of control methods:

Claus Reaction Extension to Lower Temperature Liquid Phase Several processes are available which extend the Claus reaction into a lower temperature liquid phase, whereby enhanced conversion occurs at cooler temperatures in the catalytic stages. These processes result in overall higher sulphur recoveries (e.g. 98-99%) and correspondingly reduced sulphur compound emissions in the tail gas.

Tail Gas Scrubbing Although several types of tail gas scrubber variations exist, two generic types are used to reduce sulphur emissions from the sulphur recovery process - oxidation or reduction tail gas scrubbers. For example, the Wellman-Lord oxidation scrubber system is used in combination with tail gas incineration, whereby the Claus plant sulphur compounds are oxidized to SO_2 during combustion and this component is absorbed by sodium sulphite/bisulphite solution with associated release of the off gas. The bisulphite solution is then decomposed by boiling to produce a sodium sulphite precipitate for re-use and a regenerated SO_2 stream which is recycled back to the Claus process. Up to 99.9% sulphur recovery can be accomplished with the system. In reduction scrubbers, tail gas sulphur compounds are converted by hydrogenation to H_2S which is either removed by conventional amine scrubbers for regeneration/recycle back to the Claus process or converted to sulphur outside the Claus unit using the Stretford lean H_2S-to-sulphur process.

Tail Gas Incineration Claus plant emissions may also be directly incinerated to convert the more hazardous reduced sulphur compounds to SO_2 under proper combustion conditions for release to the stack.

4 SIMPLER METHODOLOGY

The simpler methodology would be to inventory using area source methods and assume that all sulphur recovery operations are two-staged and have no control technology for tail gas cleanup. Emissions of SO_2 would then be conservatively estimated by using the highest uncontrolled emission factor and the total amount of sulphur produced through sulphur recovery processes. This would provide an upper bound to the likely emissions, but in the absence of more detailed production information represents an acceptable estimation method to use.

5 DETAILED METHODOLOGY

The preferred methodology would involve either a sulphur mass balance or the measurement of emissions from each plant to develop site-specific emission factors or emissions data for all potentially significant sources.

In the mass balance approach, at minimum, the sulphur content and volumes of sulphur recovery plant feed gas materials (e.g., sour gas streams or absorption tower sulphide off-gas) are needed to define the mass of input sulphur. This may also comprise sulphur input from sour water stripping of waste-waters. In conjunction with the mass of elemental sulphur produced, the quantity of sulphur in tail gas emissions requires determination. This may be done by calculating the sulphur recovery efficiency with a knowledge of the number and type of sulphur recovery units including Claus plant catalytic stages and/or measuring the volume and sulphur content of the tail gas. Account should also be made of SO_2 emissions associated with catalyst regeneration, where practised on-site, as well as unaccounted losses to confirm the balance. Upon conversion to SO_2, the emissions from sulphur recovery operations (expressed as kg SO_2 per Mg pure elemental sulphur produced) may be calculated by:

$$SO_2 \ emissions \ (kg \ / \ Mg) \ = \ \frac{100 \ - \ \%recovery}{\%recovery} \ x \ 2000$$

In instances where the tail gas is treated further by scrubbers or incinerators, the emissions may be best determined by stack testing. Emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At this time, new site-specific emission factors should be derived based on testing or mass balance determinations.

Accordingly, the most reliable emission estimation alternative is to inventory each sulphur recovery installation as a point source, using site-specific process and production information. This would ideally include site-specific information on the average percent sulphur recovery, which can be used to derive site-specific emission factors by assuming that all sulphur is released as SO_2. If the sulphur recovery information is not available, the appropriate emission factors from section 8 should be used.

6 RELEVANT ACTIVITY STATISTICS

Emission factors are based on the production of elemental sulphur.

7 POINT SOURCE CRITERIA

The average production rate of a sulphur recovery plant in the U.S. varies from 50 to 200 Mg per day. Using a typical production rate per day of 124 Mg, an uncontrolled emission rate of over 4000 Mg SO_2 per year would be expected, while a similar facility with the highest level of control would emit just under 1000 Mg (see section 8 for emission factors). It is therefore recommended that all sulphur recovery facilities be inventoried as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

U.S. EPA emission factors for modified Claus sulphur recovery plants are summarised in Table 2.

The CONCAWE Air Quality Management Group (Concawe, 2006) has identified a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR),

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found

at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.
The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

For Sulphur Recovery Plants CONCAWE suggests the U.S. EPA methodology.

Table 2: Modified Claus Sulphur Recovery Plant Emission Factors (U.S. EPA 1994)

Number of Catalytic Stages	Average Percent Sulphur Recovery[a]	SO_2 (kg/Mg Sulphur Produced)	Emission Factor Rating
Two, uncontrolled	93.5[c]	139[b,c]	E
Three, uncontrolled	95.5[d]	94[b,d]	E
Four, uncontrolled	96.5[e]	73[b,e]	E
Two, controlled[f]	98.6	29	B
Three, controlled[g]	96.8	65	B

[a] Efficiencies are for feed-gas streams with high H_2S concentrations. Gases with lower H_2S concentrations would have lower efficiencies. For example, a 2- or 3-stage plant could have a recovery efficiency of 95% for a 90% H_2S stream, 93% for 50% H_2S and 90% for 15 H_2S.
[b] Based on net weight of pure sulphur produced. The emission factors were determined using the average of the percentage recovery of sulphur.
[c] Typical sulphur recovery ranges from 92 to 95 percent.
[d] Typical sulphur recovery ranges from 95 to 96 percent.
[e] Typical sulphur recovery ranges from 96 to 97 percent.
[f] Test data indicated sulphur recovery ranges from 98.3 to 98.8 percent.
[g] Test data indicated sulphur recovery ranges from 95 to 99.8 percent.

9 SPECIES PROFILES

Species profiles are not required for this sector.

10 UNCERTAINTY ESTIMATES

Emission factors for this sector are based on sulphur recovery ranges for typical operations. These indicate that, for a given process, total recovery rate variations range from as little as 0.5% to as much as 5%. Therefore, given accurate process and production information, estimates of SO_2 emissions from these facilities should be accurate to within 10 percent.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simpler methodology relies on emission factors that may not be representative of the process.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

All sulphur recovery plants should be inventoried as point sources. However, if the simpler methodology is used, emissions can be disaggregated based on plant production capacities.

13 TEMPORAL DISAGGREGATION CRITERIA

Sulphur balances are often conducted for petroleum refineries on a daily basis. Such plant-specific information may be used to temporally resolve emissions.

14 ADDITIONAL COMMENTS

SNAP Coding for sulphur recovery plants is somewhat awkward in that it is coded under petroleum refineries but is not exclusively found at these locations.

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

17 REFERENCES

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SNAP CODE: **040104**

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Storage and Handling of Products in Refinery

NOSE CODE: **105.08.04**

NFR CODE: **1 B 2 a iv**

1 ACTIVITIES INCLUDED

Only the emissions of NMVOC from the storage and handling of volatile intermediates and products are considered in this chapter. These intermediates and products are categorised as follows:

Table 1.1: Categories of Products

Category	Product
Liquid fuels	motor gasoline
	aviation gasoline
	aviation turbine fuel
	illuminating gasoline
	high-speed diesel
	distillate heating fuel
By product Fuels	Naphtha
	liquefied petroleum gases
	white oils
Primary petrochemicals	Ethylene
	Propylene
	Butadiene
	Benzene
	Toluene
	Xylene

The storage and handling of crude oil, the raw material of refineries, is dealt with in SNAP sub-sector 0502.

The storage and handling of refinery products outside a refinery is dealt with in SNAP codes 0504 and 0505.

2 CONTRIBUTION TO TOTAL EMISSIONS

Emissions from the storage and handling of intermediates and products typically contribute to between 1% and 6% of a country's total NMVOC emissions from anthropogenic sources. Table 2.1 and 2.2 summarise emissions of NMVOC from these sources.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Storage and Handling of Products in Refinery	040104	-	-	0.4	-	-	-	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Table 2.2: Emissions of NMVOC from Petroleum Product Storage at Petroleum Refineries in Canada

Country	NMVOC	
	Emissions (Mg)	% Total Anthropogenic
Canada (1988)	25280	5.16
Canada (1995)		

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

3 GENERAL

3.1 Description

Storage and handling of intermediates and products in a refinery is one part of the refining process.

Emissions arise as a result of evaporation from storage tanks, the displacement of vapour during volume changes, loading and unloading and spillage.

Intermediates and products may be stored in a variety of tanks. This chapter considers the following categories of tanks:

fixed roof tanks
external floating roof
internal floating roof
other tank types such as variable vapour space

Pressure tanks are considered to be minor sources and are not included in this chapter.

3.2 Definitions

3.3 Techniques

Fixed Roof Tanks - A typical vertical fixed roof tank consists of a cylindrical steel shell with a permanently affixed roof, which may vary in design from cone- or dome-shaped to flat. These tanks are either freely vented or equipped with a pressure/vacuum vent, which prevent the release of vapours during very small changes in temperature, pressure, or liquid level. This tank is considered the minimum acceptable equipment for storing organic liquids.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

Horizontal fixed roof tanks are constructed for both above-ground and underground service. These are generally small storage tanks with capacities with capacities of less than 40,000 gallons. Horizontal tanks are usually equipped with pressure-vacuum vents, gauge hatches and sample wells, and manholes. For underground storage tanks, emissions are associated mainly with changes in the liquid level in the tank.

External Floating Roof Tanks - An external floating roof tank typically consists of an open-topped cylindrical steel shell equipped with a roof that floats on the surface of the storage liquid. These tanks are equipped with a seal system, which is attached to the roof perimeter and contacts the tank wall. The floating roof system and seal act to reduce evaporative losses of the contents. Evaporative losses from the external floating roof design are limited to losses from the seal system and roof fittings (standing storage loss) and any exposed liquid on the tank walls (withdrawal loss).

Internal Floating Roof Tanks - An internal floating roof tank has a permanent fixed roof as well as an internal floating deck. Fixed roof tanks that have been retrofitted with an internal deck typically have the roof supported by vertical columns within the tank. Converted external floating roof tanks typically have a self-supporting roof. A newly constructed internal floating roof tank may have either. The deck may be a contact deck (floats directly on the liquid) or non-contact (floats on pontoons which float on the liquid surface). Both types incorporate rim seals and deck fittings. Evaporation losses from decks may come from deck fittings, non-welded deck seams, and the annular space between the deck and the wall. Circulation vents on the fixed roof allows these emissions to freely vent.

Variable Vapour Space Tanks - These tanks are equipped with expandable vapour reservoirs to accommodate vapour volume fluctuations due to temperature and barometric pressure changes. These are normally connected to the vapour space of one, or more, fixed roof tanks. Lifter roof tanks (a telescoping roof) and flexible diaphragm tanks are the two most common types of variable vapour space tanks. Losses occur from these tanks during tank filling when vapour is displaced by liquid.

3.4 Emissions

For all tanks, the total emission of NMVOC is the result of two types of losses. The first is the breathing or standing loss, which is the release of overhead vapours in the tank, due to changes in meteorological conditions such as temperature and pressure, without any appreciable change in the liquid level of the tank. The second is working or withdrawal loss resulting from the displacement of tank vapours occurring during filling or emptying. (CPPI and Environment Canada 1991)

3.5 Controls

All intermediates and final products should be stored in the appropriate container: pressure vessels for gases, floating roof tanks for volatile liquids, fixed roof tanks for heavy fuel oils and non-volatile liquids.

Improved operational procedures are an important part of a NMVOC emission control program. This may include such items as ensuring roof hatches etc are not opened unnecessarily; keeping storage temperatures as low as possible, frequent inspections and painting all tanks a light shade.

Vapour balancing, in which the vapours displaced during handling are collected and recovered or control, can have control efficiencies of 90 to 98 percent. Vapour recovery methods include vapour/liquid absorption, vapour compression, vapour cooling and/or vapour/solid adsorption. Efficiencies as high as 90 to 98 percent may be achieved, depending on the methods used, the design of the unit, the composition of vapours recovered, and the mechanical condition of the system. Control will involve thermal oxidation. Typically the air/vapour mixture is injected into an incinerator, with control efficiencies ranging from 96 to 98 percent. (U.S. EPA 1992)
Other control programs involve design changes and are more specific to the tank in question, as summarised, by tank type, below.

Fixed Roof Tanks - Fixed roof tank emissions vary as a function of vessel capacity, vapour pressure of the contents, utilisation rate of the tank and atmospheric conditions. Emissions can be controlled by the installation of an internal roof and seals, with a control efficiency of 60 to 99 percent. The control efficiency depends on the type of roof and seals installed as well as on the type of organic liquid being stored.

External Floating Roof Tanks - Efficiencies of primary seals may be improved through the used of weather shields. Additional control may be added through a secondary seal. External floating roof tanks may also be retrofitted with a fixed roof. Losses from roof fittings can be minimised through proper design, installation, maintenance and use.

Internal Floating Roof Tanks - Additional control of standing losses can be achieved through the installation of secondary seals. As for external floating roof tanks, losses from roof fittings can be minimised through proper design, installation, maintenance and use.

4 SIMPLER METHODOLOGY

The simplest methodology is to combine the crude oil throughput of each refinery with an emission factor. Emission estimates should be calculated for each refinery in the country and the emission factor used will depend on the type of tanks used to store volatile materials.

The storage and handling emission from each refinery may then be reported and assigned to a grid reference.

5 DETAILED METHODOLOGY

The detailed methodology requires each refinery to calculate the emission from each tank according to techniques developed by the American Petroleum Institute (API, 2002; 2003) (http://www.api.org/) or better. This methodology requires considerable input data and should be carried out by qualified engineers. The methodology allows typical diurnal and monthly variations to be reported.

The U.S. EPA has issued a new section for AP-42 which outlines all of the methods for estimating emissions from storage of organic liquids (Section 7, http://www.epa.gov/ttn/chief/). This may be more accessible for some people than API reports. API and the U.S. EPA have worked together to develop these modules.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, the crude oil throughput of each refinery is required, together with the proportion of different types of storage tanks used for volatile products.

For the detailed methodology, specific data on the throughput of the intermediates and products via each tank is required together with the physical properties of the intermediate or product. Other data required include such average meteorological data as the temperature, wind speed, barometric pressure and data specific to the tank such as type, dimensions, colour, seal type and condition of the tank.

7 POINT SOURCE CRITERIA

Each refinery should be considered as a point source.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

The Corinair1990 Default Emission Factor Handbook (CEC, 1992) proposed default emission factors of 0.25 g/kg crude oil throughput for a modern refinery (Data quality C) and 1.00 g/kg for an old refinery (Data Quality E).

The following emission factors are for the storage and handling of materials and are obtained by combining the Corinair Data with information obtained from Canada and the UK on proportion of losses from Storage and Handling.

Table 8.1: Canadian and UK Storage and Handling Losses

Refinery Type	Emission Factor (% of feedstock)	Quality
“Modern” Corinair	0.03	(Unknown)
Typical	0.05	(Unknown)
“Old” Corinair	0.12	(Unknown)

The following emission factors, together with conditions under which they should be used, have been developed by the U.S. EPA. However, they are considered dated and have a high uncertainty:

Table 8.2: EPA Emission Factors for Storage and Handling Losses

Emission Factor	Condition	Quality
0.17 g/kg	where the majority of volatile products are stored in floating roof tanks with secondary seals	(E)
0.67 g/kg	where the majority of volatile products are stored in floating roof tanks with only primary seals	(E)
4.9 g/kg	where the majority of volatile products are stored in fixed roof tanks	(E)

These emissions are intended to account for evaporative losses during storage and the displacement losses resulting from the loading and unloading of storage tanks.

8.2 Detailed Methodology

The CONCAWE Air Quality Management Group (Concawe, 2006) has identified a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR),

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.
The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

Concawe report suggests the use of the latest edition of API documents for Floating Roof Tanks (API,2003), and Vertical Fixed Roof Tanks (API, 2002). For Aboveground Horizontal Tanks, Concawe report suggests to use the latest edition of U.S. EPA methodology (U.S.EPA, 1995). Note that this reference normally contains the latest version of previously quoted API methodologies. An emission calculation software is available from the US EPA via their website, http://www.epa.gov, or on a CD-ROM (U.S.EPA, 2005). This CD also contains the EPA publication (U.S.EPA, 1995) and API documents (API 2002; 2003).

9 SPECIES PROFILES

Refinery products and intermediates vary considerably in the make up of emissions and only a very general speciated profile may be given. Where possible, speciated profiles should be obtained for each refinery. The U.S. EPA methodology provides a method for calculating tank-specific speciation factors.

10 UNCERTAINTY ESTIMATES

Uncertainties in throughput statistics are considered to be less than 5%.

Field measurements by the UK suggest that emission estimates based on API calculations underestimates emissions by factors of 2-4. Mass balance calculations carried out by the UK Institute of Petroleum suggest a similar scale of underestimate.

The emission factors relating crude oil throughput (feedstock) to emission vary by more than a factor of ten in some cases.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Simpler Methodology

This approach uses single emission factors to estimate emissions from an entire refinery. Little account is taken of the variation between refineries and changes in the quantity and type of volatile products manufactured. For example, NMVOC emissions from a refinery, which reduces production of kerosene and increases production of motor spirit, could be expected to change, even if the crude oil throughput remains the same.

As an illustration of how product output may vary, the table below shows the increase in the production of volatile products between 1980 and 1990, in the U.K.:

Table 11.1: UK Volatile Products Production

Year	Total Crude Processed (10^3 Mg)	Total Volatile Products (10^3 Mg)
1980	86393	28979
1990	88692	40455

In this example, using crude oil throughput as the activity statistic would result in a similar NMVOC emissions between 1980 and 1990. If emission factors could be derived for each of the volatile product outputs, then a significant change in emission estimates is likely.

Detailed Methodology

The U.S. EPA and API methodologies require detailed information from each oil refinery. However, emission estimates based on this method have been shown to differ significantly from measurements taken at refineries in the U.K. A detailed review of this discrepancy and the calculation of these emissions should be considered. If the U.S. EPA model appears promising for emission estimation, the addition of default climate parameters, for other regions of the world, to the TANKS model should be considered. This would ensure that different regions using the detailed method are calculating emissions in a consistent fashion. If a country did not have the resources to do a detailed emissions estimate, then the TANK model could be used to derive representative emission factors for a typical refinery for use in the simple methodology.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Each refinery should be considered a point source.

13 TEMPORAL DISAGGREGATION CRITERIA

No temporal disaggregation is possible if the simpler methodology is used.

If the detailed methodology is used, the refineries should report a typical diurnal variation (average hourly over 24 hours) and seasonal (average monthly over one year).

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

Compare estimates with mass balance calculations, i.e. the difference between crude throughput and products produced.

17 REFERENCES

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Carolina Chapter 7: Liquid storage tanks. (http://www.epa.gov/ttn/chief/ap42/ch07/index.html)

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18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE: **040105**

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Other

NOSE CODE: **105.08.05**

NFR CODE: **1 B 2 a iv**

Methodologies for activities covered by SNAPS 040101 – 040104 are detailed in previous chapters (see index). A specific methodology for other processes in petroleum industries (SNAP 040105) has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

(This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006)).[1]

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

SNAP CODE: **040202**

SOURCE ACTIVITY TITLE: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES**
Blast Furnace Charging

NOSE CODE: **105.12.02**

NFR CODE: **2 C 1**

ISIC: **2410**

1 ACTIVITIES INCLUDED

The charging of iron smelters is part of the production process for primary iron and steel.

2 CONTRIBUTION TO TOTAL EMISSIONS.

Blast furnace charging is a potential source of heavy metal emissions. The contribution to total emissions indicated in Table 2.2 refers to blast furnace operation in general. Information concerning the contribution of blast furnace charging is currently not available.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**										
Blast Furnace Charging	040202	SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	TSP*	PM_{10}*	$PM_{2.5}$*
Typical contribution		0	0	0	0	0.7	0.1	-	-	0.092	0.171	0.201
Highest value										0.235	0.413	0.444
Lowest Value										0.005	0.012	0.020

* for total blast furnace process (cowpers, charging and tapping), contribution to total national emissions, excluding agricultural soils, EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006),
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

Table 2.2: Contribution to total heavy metal emissions of the OSPARCOM-HELCOM-UN/ECE inventory for 1990 (up to 38 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Blast Furnace	040202	2.7	0.5	1.7	2.7	0.8	0.4	1.9	8.6

3 GENERAL

3.1 Description

In general, the blast furnace process can be subdivided into the following process steps:
- air heating (hot blast stove);
- blast furnace;
- tapping (casting bay);
- slag processing.

The *blast furnace* is a shaft furnace for producing pig iron from iron-containing raw materials, as iron sinter, pellets, and lump ore. The burden of the blast furnace, consisting of iron-containing raw materials and additives (Möller mixture), is fed alternately with coke through the top of the furnace in layers. For the production of a tonne of pig iron, 300-400 kg coke, and 1550-1600 kg of ore are needed. Air, heated up to 1,300°C, is blown through tuyeres into the lower part of the furnace. The combustion of the coke provides both the carbon monoxide (CO) needed for the reduction of iron oxide into iron and the additional heat needed to melt the iron and impurities. Auxiliary fuels such as fine coal, heavy oil, plastic waste and others may also be injected through the tuyeres. As the burden moves downward through the furnace, it is heated by the countercurrent upward flow of gases, that exit at the top of the furnace (Rentz et al., 1996).

The smelter is toploaded and works with an excess pressure of up to 2.5 bar depending on the type of furnace. To render possible energy recuperation, a dedusting of the top gas is necessary. With back-pressure furnaces the top gas is used in back-pressure turbines for power generation. The dedusted top gas is used as fuel for various applications in the iron and steel mill.

3.2 Definitions

Möller mixture	The complete package of basic materials for one smelter charge. A charge consists of a number of carriage loadings that are emptied into the smelter according to a specified scheme.
Pressure equalisation	The equalisation of pressure in the vapour lock at the blast furnace top with atmospheric pressure.

3.3 Techniques

The main techniques have been specified above in Section 3.1

3.4 Emissions

In the pressure equalisation stage some emissions of blast furnace top gas containing carbon monoxide, carbon dioxide, hydrogen, and hydrogen sulphide occur. The charging of the smelters produces a certain amount of dust during a short period of time. For CIS counties a dust content of 400 g/m^3 in the exhaust gas from the inter-cone space of the vapour lock is reported (Kakareka et al., 1998). The composition of the dust is related to the composition of the Möller mixture. It is a rather coarse dust with a particle size bigger than 10 micron. Although the dust contains heavy metals from the ore and the coke, the dust itself is rather inert due to the extensive pre-treatment activities like pelletising and sintering. In addition emissions may arise from conveying operations.

Table 3.1 shows selected values for the dust and heavy metal content of blast furnace top gas (Rentz et al., 1996).

Table 3.1: Dust and heavy metal content of blast furnace top gas (Rentz et al., 1996)

	Specific dust load $m_{Dust}/m_{Pig\ iron}$ [kg/Mg]	Specific waste gas volume $V_{Waste\ gas}/m_{Pig\ iron}$ [m^3/Mg]	Waste gas stream $V_{Waste\ gas}/t$ [m^3(STP)/h]	Dust load $m_{Dust}/V_{Waste\ gas}$ [g/m^3(STP)]	Weight composition of flue dust [wt.-%]
Blast furnace top gas	up to 17.5	1,400 - 1,700	100,000 - 550,000	up to 12.5	Pb up to 0.4 Zn up to 1.7

3.5 Controls

To reduce the escape of the basic materials during charging a vapour lock is installed on the top of the smelter. The lock is charged after pressure equalisation. Different constructions for this lock are in use. The sealed charging system can be a bell charging system or a bell-less charging system. In addition, the evacuation of gas at the top of the furnace and connection to the blast furnace gas treatment system can be used to control emissions (IPPC, 1999).

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

---

[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR} \times \text{EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

The blast furnace charging is a part of the primary iron and steel industry. The simplest method of emissions estimation is their assessment on the basis of the pig iron production from individual iron and steel plants or country production of pig iron in blast furnaces and average emission factors. Appropriate emission factors referring to statistical information on iron and steel production at national level are currently not available.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3), to estimate emissions of gaseous pollutants from the pig iron production is based on measurements or estimations using plant specific emission factors - Guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

6 RELEVANT ACTIVITIES STATISTICS

Information on the production of pig iron, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of pig iron produced by various types of industrial technologies employed in the cement industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 " Choice of activity statistics".

7 POINT SOURCE CRITERIA

Iron smelters in which the loading process is incorporated should be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The emission factor for coarse dust is generally about 20g/Mg pig iron (range 15-25 g/Mg, depending on the construction of the vapour lock). This information is produced by the Emission Inventory in The Netherlands, based on estimations from the steel plant managers.
Emission factors taken from four blast furnaces from four different EU Member States are available in (IPPC, 1999). For dust emissions to air from the charging zone an emission factor of 25 g/Mg liquid steel (LS) is proposed (range: 5-38 g/Mg LS; mean value and standard deviation: 14±13). Other air pollutants are considered to be of low significance. In (IPPC, 1999) a conversion factor of 940 kg pig iron/Mg liquid steel is used as a weighted average of all European basic oxygen steelworks.

Concerning blast furnaces in CIS countries heavy metal emission factors for blast furnace charging are proposed in (Kakareka et al., 1998). Table 8.1 shows these factors related to the removal efficiency of control devices.

Table 8.1: Heavy metal emission factors for blast furnace charging (Kakareka, 1998)

	Abatement type and efficiency		
	No Abatement 0 % efficiency	Venturi scrubbers or ESP 95 % efficiency	Includes dust suppression systems such as pressure equalisation 99.6 % efficiency
Cd [g/Mg pig iron]	0.009	0.0004	0.00004
Pb [g/Mg pig iron]	0.028	0.001	0.0001
Zn [g/Mg pig iron]	0.58	0.029	0.002
Ni [g/Mg pig iron]	0.052	0.003	0.0002

Table 8.2 shows emission factors for particulate matter.

Table 8.2: Emission factors for particulate matter in kg / ton pig iron (furnace charging and tapping, CEPMEIP*)

Technology	**Abatement**	**TSP**	**PM_{10}**	**$PM_{2.5}$**	**Uncertainty-factor**
Modern plant (BAT)	High efficiency ESP or equivalent to control primary sources; fabric filters for fugitive emission;	0.04	0.038	0.036	3
Conventional plant	Installation with average age; conventional dedusting: ESP, wet scrubber; some capturing of fugitives	0,24	0,192	0,12	2
Older technology	multi-cyclones only	2	1	0,5	2

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in Table 8.2): The uncertainty in the emission factor for $PM_{2.5}$ emissions from a modern plant is 3. The emission factor with uncertainty range will therefore be 0.036 kg per tonne pig iron with an uncertainty range of 0.012 (0.036 / 3) to 0.11 (0.036 x 3).

* Includes PM emission factors for the combination of both charging and tapping – see chapter B423 for Pig Iron tapping.

9 SPECIES PROFILES

A composition profile of used ore could give supporting information. No general profiles can be given.

Heavy metal content of dust collected in the charging zone of a blast furnace of a Russian iron and steel plant is given in Table 9.1 (Kakareka et al., 1998).

Table 9.1: Heavy metal content of dust from batch preparation (Kakareka et al., 1998)

	Cd [mg/kg]	Pb [mg/kg]	Zn [mg/kg]	Ni [mg/kg]	Cu [mg/kg]
Particulate matter from ESP (total sample)	0.15	900	14	5.26	12
Particulate matter from ESP (particle size < 4 µm)	2	7 - 10	145 - 200	10 - 13	15 - 20

10 UNCERTAINTY ESTIMATES

The uncertainty of the dust emission factors is estimated to be about 20%.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Information about emissions directly related to the individual process and the abatement methods is scarce. Emission factors for heavy metals should be improved.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Iron smelters should be considered as point sources (see section 7).

13 TEMPORAL DISAGGREGATION CRITERIA.

Emissions during charging are a discontinuous process. The temporal disaggregation depends on the production rate but quantitative information is not available.

14 ADDITIONAL COMMENTS

Charging of blast furnaces should be treated in connection with the pig iron tapping.

15 SUPPLEMENTARY DOCUMENTS.

US Environmental Protection Agency. Compilation of air pollutant emission factors AP-42

PARCOM (1992) Emission Factor Manual PARCOM-ATMOS. Emission factors for air pollutants 1992. P.F.J. van der Most and C. Veldt, eds., TNO Environmental and Energy Research, TNO Rept. 92-235, Apeldoorn, the Netherlands.

16 VERIFICATION PROCEDURES.

Comparing the composition profile of the ore used with the metal emissions calculated might serve as a verification process.

17 REFERENCES

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No additional documents.

19 RELEASE VERSION, DATE AND SOURCE

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Updated with emission factors (CEPMEIP) for particulates by:
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SNAP CODE: **040203**

SOURCE ACTIVITY TITLE: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES**
Pig Iron Tapping

NOSE CODE: **105.12.03**

NFR CODE: **2 C 1**

ISIC: **2410**

1 ACTIVITIES INCLUDED

Pig iron tapping is a part of the production process for primary iron and steel.

2 CONTRIBUTION TO TOTAL EMISSIONS

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**										
Pig Iron Tapping	040203	SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	TSP*	PM_{10}*	$PM_{2.5}$*
Typical contribution		0	0	-	0	0	-	-	-	0.092	0.171	0.201
Highest value										0.235	0.413	0.444
Lowest value										0.005	0.012	0.020

* for total blast furnace process (cowpers, charging and tapping), EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006), contribution to total national emissions, excluding agricultural soils,
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

Emissions of heavy metals from primary iron and steel industry, including pig iron tapping give a relevant contribution to the emissions on a national level. For heavy metal emissions, no specific figures for this source activity are available. The average relative contribution from the total iron and steel production industry and the production of pig iron, to the total emission of heavy metals has been presented for European countries in Table 2.2. Pig iron tapping is part of the production of pig iron. The data in Table 2.2 is according to Baart *et al.* (1995). /1/

Table 2.2: Average relative contribution of the production of iron and steel and the production of pig iron to the total emission of heavy metals in European countries

Compound	**Total iron & steel production (%)**	**Pig iron production (%)**
Cadmium	22	-
Chromium	36	3.7
Copper	16	-
Nickel	14	3.0
Lead	12	-
Zinc	33	-

- = not available

3 GENERAL

3.1 Description

The liquid molten iron and the sludge gathering in the bottom of the smelter are tapped on a regular basis. A smelter has usually three holes that are plugged with refractory material. After the process holes are bored by remote boring, and the mixture of pig iron and slag is guided by the trough to the skimmer where iron and slag are separated. The liquid pig iron is guided by the iron runner and the tilting runner to the mixer; the sludge is removed for granulation or dumping. After emptying the smelter the bore holes are closed again with refractory material. The fire resistant coating of the guides has a limited lifetime, and has to be exchanged regularly.

3.2 Definitions

Trough	Covered guide between the oven and the skimmer.
Skimmer	Tunnel shaped construction where the heavier pig iron is seperated from the lighter slag floating on the iron.
Iron run	Connection between the skimmer and the tilting runner.
Tilting runner	A bridge on the end of the iron runner where the mixers can be filled and exchanged. The mixer is a container placed on a railroad carriage used for transport to for instance the steel factory.(Basic Oxygen Furnace).
Refractory material	Material used for closing a tap hole. The refractory material contains in general coal and tar.
Runner coating	Fire resistant material used for coating the runners. This product also contains coal and tar.

3.3 Techniques

3.4 Emissions

The boring of the tap and the filling of the trough gives rise to dust emissions. These emissions mainly arise from contact between the hot metal and slag and ambient oxygen.Also dust emissions occur after the skimmer, but to a lesser extent than in the first part of the route. The dust contains some heavy metals. The particle size of the dust during the boring is mainly below ten micron. The size of the particles from the emissions from the roof is usually about 50 % bigger than ten micron.

After coating, the transport trough has to be heated. This gives volatile decomposition products. These decomposition products are also emitted by the heating of the plugging material.

Decomposition products from tar are polycyclic aromatic hydrocarbons (PAH) and benzene containing aromatics. The exact benzene content is not available. In principle the same products are produced by the heating of coal. The amount of coal used is however so small that these emissions can be neglected.

3.5 Controls

The trough, the skimmer, and the transport runners are usually covered. Dust and decomposition products are removed, and are passing fabric filters before emission into air. The part not captured passes through the roof. This emission is not abated. The total amount escaping through the roof is about 40 % of the total emission.

From the decomposition products of tar and coal only the condensable part of the PAH emissions is captured by the fabric filters.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR} \times \text{EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3), to estimate emissions of gaseous pollutants from the pig iron production is based on measurements or estimations using plant specific emission factors. Guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of pig iron production, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of pig iron produced by various types of industrial technologies employed in the iron and steel industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 " Choice of activity statistics".

7 POINT SOURCE CRITERIA

The emissions of the complete plant should be considered as a point source.

8 EMISSION FACTORS

The total air flowing from a representative smelter is between 540,000 and 660,000 m^3/hour. The dust content is measured from time to time. The emissions from the roof are based on information from a measurement campaign in a plant in the Netherlands. The emissions of hydrocarbons by decomposition of tar and coal from plugging mass and coating materials are based on expert estimations.

The emission factors presented in Table 8.1a are calculated by relating a measured dust production with the known production of the smelter in the same period (30.2 g dust per Mg pig iron produced).

Table 8.1a: Emission factors for the emission of heavy metals related to dust emissions from pig iron tapping

	Emission factor (in g Mg^{-1} pig iron produced)		
	total	unabated	fabric filters
Arsenic	0.0009	0.0003	0.0006
Cadmium	0.0003	0.0001	0.0002
Chromium	0.015	0.006	0.009
Copper	0.015	0.006	0.009
Lead	0.015	0.006	0.009
Mercury	0.0003	0.0001	0.0002
Nickel	-	-	-
Zinc	0.021	0.009	0.012

Table 8.1b shows emission factors for particulate matter derived from CEPMEIP.

Table 8.1b: Heavy metal emission factors for particulate matter in kg ton^{-1} pig iron (furnace charging and tapping, CEPMEIP*)

Technology	**Abatement**	**TSP**	**PM_{10}**	**$PM_{2.5}$**	**Uncertainty-factor**
Modern plant (BAT)	High efficiency ESP or equivalent to control primary sources; fabric filters for fugitive emission;	0.04	0.038	0.036	3
Conventional plant	Installation with average age; conventional dedusting: ESP, wet scrubber; some capturing of fugitives	0.24	0.192	0.12	2
Older technology	multi-cyclones only	2	1	0.5	2

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in Table 8.2): The uncertainty in the emission factor for $PM_{2.5}$ emissions from a modern plant is 3. The emission factor with uncertainty range will therefore be 0.036 kg per tonne pig iron with an uncertainty range of 0.012 (0.036 / 3) to 0.11 (0.036 x 3).

* Includes PM emission factors for the combination of both charging and tapping – see chapter B422 for Pig Iron Charging.

Although the amount of decomposition products is determined by the amount of tar and coal used, a relation can be established with the total amount of pig iron transported through the transport runners. This calculation results in the emission factors for organic compounds as presented in Table 8.2.

Table 8.2: Emission factors for the emission of organic compounds related to pig iron tapping.

	Emission factor (in g.Mg^{-1} pig iron)		
Substance	total	unabated	fabric filter
PAH	3.45	2.5	0.95
Aromatic hydrocarbons, including benzene	0.3	14.3	66
Benzene	2.5	0.45	2.05

9 SPECIES PROFILES

The dust emissions could be related to the profile of the ore. No general applicable information about ore compositions is available.

10 UNCERTAINTY ESTIMATES

The quality code of the emission factors is estimated to be C.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The only improvement measure for this part of the process is the exchange of tar with tar-free products in the plugging material and the coatings.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not applicable.

13 TEMPORAL DISAGGREGATION CRITERIA.

The tapping is a discontinuous process; the use of the smelter as such is a continuous process.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS.

Environmental Protection Agency, Compilation of air pollutants emission factors AP-42
PARCOM-ATMOS Emission factors Manual
W. Mulder, personnal communication, Delft, 1995.

16 VERIFICATION PROCEDURES.

A comparison between the metals profile of the ore and the emissions calculated might be used as a verification method.

17 REFERENCES

/1/ A.C. Baart, J.J.M. Berdowski, J.A. van Jaarsveld; Calculation of atmospheric deposition of contaminants on the North Sea; IWAD; ref. TNO-MW-R 95/138; TNO MEP; Delft; The Netherlands; 1995

/2/ Visschedijk, A.J.H., J. Pacyna, T. Pulles, P. Zandveld and H. Denier van der Gon, 2004, Cooordinated European Particulate Matter Emission Inventory Program (CEPMEIP), In: P. Dilara et. Al (eds), Proceedings of the PM emission inventories scientific workshop, Lago Maggiore, Italy, 18 October 2004, EUR 21302 EN, JRC, pp 163 - 174

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SNAP CODE: **040204**

SOURCE ACTIVITY TITLE: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES**
Solid Smokeless Fuel

NOSE CODE: **105.12.04**

NFR: **1 B 1 b**

1 ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions during coal carbonisation for the production of solid smokeless fuel. This type of fuel has been used for very long time by householders in open fire grates (Parker, 1978).

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Very limited information is available on to what extent emissions from the production of solid smokeless fuel contribute to the contamination of the air. It is expected that these emissions include sulphur and nitrogen oxides, VOCs, and volatile heavy metals and persistent organic compounds from coal. Coal carbonisation plant can be an important source of air contamination on a local scale.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Solid Smokeless Fuel	040204	-	-	0	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

3 GENERAL

3.1 Description

Coal carbonisation to produce solid smokeless fuel occurs at high temperatures reaching 1000° C. There are three methods of coal carbonisation which differ considerably from each other. In the first method, the coal is carbonised in tubular iron retorts heated externally by the gas produced. In the second, the coal is in a large chamber and is heated by direct contact with the products of combustion of the gas made. In both cases the product reactive coke is screened to obtain sizes suitable for the open fire and for closed stoves. In the third method, the coal is carbonised by fluidization with hot gas from combustion of the coal gas made, and the relatively small particles are pressed to form briquettes (Parker, 1978).

There are also systems for making solid smokeless fuel in which only certain types of coal, for example anthracite duff, are briquetted with pitch at a suitable temperature and then carbonised.

3.2 Definitions

Solid smokeless fuel - a product of coal carbonisation.

3.3 Controls

Modern coal carbonisation plants are equipped with electrostatic precipitators that remove at least 98 % of the particulate matter from exhaust gases.

4 SIMPLER METHODOLOGY

The application of emission factors with appropriate activity statistics can be regarded as a simple methodology for estimation of emissions during coal carbonisation. However, it should be noted that the chemical composition of coal used for carbonisation is one of the most important factors affecting the amount of these emissions.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.

5 DETAILED METHODOLOGY

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

No information is available from the international statistical yearbooks on the quantities of coal carbonised. It is expected that this information can be obtained directly from a given coal carbonisation plant.

7 POINT SOURCE CRITERIA

Coal carbonisation plants should be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

No information was found on the emission factors for coal carbonisation to produce solid smokeless fuel. However, Parker (1978) indicates that the waste gases from heating a range of retorts carbonising 1000 tonnes of coal per day would contain a quantity of sulphur dioxide of about 2.5 tonnes per day. Thus, the uncontrolled sulphur dioxide emission factor of 2.5 kg/tonne coal carbonised can be obtained on the basis of the above information.

9 SPECIES PROFILES

10 CURRENT UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/ PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Development of emission factors is necessary in order to obtain information needed for the estimation of emissions of various air pollutants during coal carbonisation.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

The production process in a coal carbonisation plant is continuous.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Parker A. (1978) Coal carbonisation for production of solid smokeless fuel, gas and by products. In: Industrial Air Pollution Handbook, A. Parker (ed.), Mc Graw-Hill Book Comp. Ltd., London.

16 VERIFICATION PROCEDURES

At present no specific verification procedures are available for estimation of atmospheric emissions from a coal carbonisation plant.

17 REFERENCES

Parker A. (1978) Coal carbonisation for production of solid smokeless fuel, gas and by products. In: Industrial Air Pollution Handbook, A. Parker (ed.), Mc Graw-Hill Book Comp. Ltd., London.

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SNAP CODE: **040205**

SOURCE ACTIVITY TITLE: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES**
Open Hearth Furnace Steel Plant

NOSE CODE: **105.12.05**

NFR CODE: **2 C 1**

1 ACTIVITIES INCLUDED

Steel production process in an open-hearth furnace is divided into five basic stages: furnace adaptation, furnace charging, melting, refining and cast finishing.

Individual stages differ from each other with respect to heat load, metallurgical reactions processing and duration. These differences directly influence the quality and quantity of emitted pollutants.

2 CONTRIBUTION TO TOTAL EMISSIONS

This process is being gradually phased out in particular in Western Europe and its percentage contribution to total pollutant emission should decrease. According to the OSPARCOM-HELCOM-UNECE inventory for 1990 almost all heavy metal emissions from this source category occur in Central and Eastern Europe (see Table 2-3). The share of steel smelting by the open hearth method in the CIS countries exceeds 60-65%, though there is a tendency for its decrease and transition to a converter method and electric arc smelting. (Kakareka et al; 1998).

Table 2-1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Open Hearth Furnace Steel Plant	040205	0	0.1	0	0	0	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

Table 2-2: Contribution to total heavy metal emissions of the OSPARCOM-HELCOM-UN/ECE inventory for 1990 (up to 38 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Open Hearth Furnace Steel Plant	040205	0.4	4.1	2.8	2.5	-	-	1.7	2.7

Table 2-3: Contribution of Central and Eastern European countries (19 countries) **to total sector emissions of the OSPARCOM-HELCOM-UN/ECE inventory for 1990**

Source-activity	**SNAP-code**	**Contribution to total sector emissions [%]**							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Open Hearth Furnace Steel Plant	040205	100	92	100	100	-	-	95	100

3 GENERAL

3.1 Description

This process covers the production of steel in an air furnace fired with gas or fuel oil. The basic metallic charge consists of pig iron and scrap. Ferroalloys, deoxidizers and ore are also used as charge.

Slag generation depends on limestone, lime, fluorite and bauxite used in the process. The composition of charge and the properties of added compounds influence the steel quality as well as the quality and quantity of air pollutants generated in the process. Fuel gas and air necessary in the process are heated up in the regenerator to a temperature of 1100^{o}C and then led to the working space of furnace, where after combustion the furnace gases reach a temperature of 1700 - 1800^{o} C and heat the charge in the oxidising atmosphere.

3.2 Definitions

pig iron	-	crude iron obtained directly from the blast furnace and cast in moulds
scrap method	-	re-use of metals as raw material for the process
deoxidizers	-	substances used for removing oxygen from molten metals
direct emissions		stack emissions (i.e. ducted gas flow), excludes fugitive emissions

3.3 Techniques

Metal smelting by the open-hearth method is performed on the bottom of the combustion reverberatory kiln supplied with regenerators (Kakareka et al.; 1998).
The construction of individual parts of the furnace depends on many factors, including the type of fuel and process as well as oxygen addition. Types of furnaces can vary with respect to the construction of heads, type of automatisation and lining with refractory materials of the furnace bottom, walls and roof.

As the basis for the classification of open hearth furnaces the following elements were assumed: furnace capacity, fuel type, bottom surface, calorific value of the fuel used, number of charging doors. Taking into consideration the calorific value of the fuel used and the roof lining, open-hearth furnaces can be divided into four groups:

- furnaces fired with low calorific value fuel with acidic roof;
- furnaces fired with low calorific value fuel with basic roof;
- furnaces modernised for high calorific value fuels;
- furnaces adapted for oxygen aiding.

Open-hearth furnace capacities range 100 to 900 tonnes. The most widespread are open-hearth one-bath furnaces with regenerators, which make up 65% of all furnaces used in CIS countries. In one-bath furnaces fuel together with air is previously heated up in regenerators then goes to the above-bath space, where it melts the metal by charge combustion. The products of combustion at a temperature of 1600-1700°C go to a reserve regenerator heating it up. Periodically the direction of a fuel-air mixture feed changes, thus, the temperature of blast is maintained in the range of 1000-1200°C. During the smelting process the following periods are distinguished: fettling, batch charging, warm-up, smelting, bath-boiling, finishing, deoxidisation and steel alloying. Dust emissions increase significantly in the period of smelting and bath boiling due to the process of intensive oxygen use.

As a whole, at operation of one-bath open-hearth furnaces the oxygen blow is used in 30 % of installations in CIS countries.

Double-bath furnaces represent the unit of two aligned and alternately blown down baths. The furnaces do not have regenerators and operate mainly without fuel burners, and CO formed in one bath is combusted above the second one. Double-bath furnaces are characterised by high productivity and high dust emissions. Thus, if in a usual furnace the duration of smelting depends on its capacity and varies from 8 to 15 hours, and at the increase of oxygen charge it takes 5-11 hours, then in double-bath – it is only 4-5 hours. (Kakareka et al.; 1998)

3.4 Emissions

Dust generation in open-hearth furnaces depends on three basic processes that take place in the working surface of the furnace:
- combustion
- mechanical impact of furnace atmosphere and charge,
- chemical processes

The furnace gases flow through the working chamber of the furnace with velocity of 1.5 - 2.5 m/s. This flow results in entrainment of fine particles of charge in the initial process of heating and in the refining process.
The chemical processes taking place in fluid metal actively increase dust-generation in the furnace gases. Especially in the process of intensive refining, rising CO bubbles throw particles to the surface of the melt which are then entrained by furnace gases increasing in this way the dust load.

Introduction of ore materials into the furnace as well as of dolomite and limestone affects slag generation and results also in an increase in furnace gas dust generation. Moreover, a considerable increase of furnace gas dust generation is observed during oxygen application for intensification of combustion and refining processes.

The concentration of dust in furnace gas heating changes during the process. Moreover, the concentration in individual periods depends on a whole range of factors, from which the following are the most important ones:

- type of charge material,
- type of process used,
- technical condition of the furnace,
- type of fuel,
- application of oxygen during the melting and refining processes.

The amount and temperature of furnace gases depends also on many factors including: furnace capacity, type of fuel, type of roof lining, furnace construction (stationary, tilting), type of heads and technical condition of a furnace. The SO_2 content in furnace gas is relatively low even in the case of using residual oil as a fuel.

3.5 Controls

In the case of purifying furnace gases from open-hearth furnaces the effectiveness of dust removal units should not be lower than 99%. That is why wet scrubbers, electrostatic precipitators or fabric filters are used for furnace gas dust removal.

The wet scrubbers were the earliest to be applied for furnace gas dust removal from open-hearth furnaces. They usually consist of two elements: dust coagulator and basic dedusting unit. The dedusting systems most often used in the case of open-hearth furnaces are electrostatic precipitators. Their efficiency is very high and usually exceeds 99%. Only in a few cases lower efficiencies (i.e. in the range 94-98%) are observed. However, obsolete equipment reduces cleaning efficiency to about 85%.

For flue gas cleaning at double-bath furnaces both wet and dry cleaning systems are applied. Dry systems are more widely used where gases are cooled and cleaned first in the waste heat boiler and in the scrubber and then in an electrostatic precipitator. (Kakareka et al.; 1998)

Recently, fabric filters have been applied to the purification of furnace gas from open-hearth furnaces. They allow to reach an efficiency of 99% or even higher, independently from the dust contents in furnace gas. Nonetheless, they require an especially precise design and proper selection of technical parameters.

4 SIMPLER METHODOLOGY

The simplest method of emissions estimation is their assessment on the basis of the amount of steel production from individual open-hearth furnace steel plants, or country production of steel in open-hearth furnace steel plants and average emission factors for a particular pollutant (one factor for systems without abatement and an alternative factor for systems with abatement).

The USEPA has published particulate size distribution data for open hearth steel making and these are summarised in Table 8.1.

5 DETAILED METHODOLOGY

The detailed methodology is based on emission factors as well and requires in addition the consideration of:

- type and capacity of furnace;
- type of charge (ore, scrap, ore + scrap);
- type of fuel used (residual oil, natural gas + residual oil, coke-oven gas + residual oil, generator gas + residual oil);
- type of emission control devices.

This method can be applied for the whole period of steel production process or to its separate stages, i.e.:

- charging
- melting
- refining
- finishing

In the detailed methodology, emissions are assessed on the basis of the data on the amount of steel production in open-hearth furnace processes for individual steel plant and adequate emission factors considering: furnace capacity, type of charge, type of used fuel and abatement devices used for the whole process or its separate stages.

Emissions can be also determined on the basis of emission measurements, covering the individual stages of the process.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, steel production in individual open-hearth furnace steel plants or on the country level is required.

For the detailed methodology of emissions assessment statistical data on steel production for individual steel plants with further split into furnace capacity, type of process and fuel used are required.

7 POINT SOURCE CRITERIA

Open-hearth furnace steel plants should be considered as point sources where relevant point source data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8-1: Open hearth steel-making PM emission factors

Process	Control	Emission factor, kg/Tonne		
		TSP	PM_{10}	$PM_{2.5}$
Open hearth steel-making	Unabated	10.55	8.76	6.33
	Electrostatic precipitator	0.14	0.07	0.05

Note that these emission factors are dated 1986 and may not be appropriate to facilities with modern abatement. The factors have the lowest USEPA quality rating (E).

Emission factors relevant for the whole process consisting of 5 stages are presented in table 8-2.

9 SPECIES PROFILES

A detailed chemical composition of furnace gas generated in the open-hearth furnace process is presented in table 9-1 for volatile organic compounds (VOC).

Table 9-1: Composition of open-hearth furnace gas

		according to Veldt (CORINAIR 1995)	Poland (Olczak (1993))
methane	C_1		89.13 %
ethane	C_2		2.9 %
propane	C_3		
butane	C_4		
ethylene	$C_{2=}$		
acetylene	C_2		
propylene	$C_{3=}$		
butylene	C_4		
hexane	C_6	7 %	

heptane	C7	36 %	
benzene	B	13.5 %	7.97 %
toluene	T	3.5 %	
xylene	K		
trimethyl-fluorosilane	tmFs	40 %	
Total		100 %	100 %

Concentrations of heavy metals in dust from various sampling points at an open-hearth furnace are presented in table 9-2.

Table 9-2: Content of heavy metals in open-hearth dust [mg/kg] (Kakareka et al.; 1998)

Sampling point	Hg	Cd	Pb	Zn	Ni	Cu
Collector of gas removal from the open-hearth furnace	-	269.2	7584	7553	85	390
Collector of gas removal from the drop separator	-	329.2	7856	10680	148	682
Spray catcher of Venturi scrubber	0.098	60.8	1083	2914	70	235

Table 8-2: Emission Factor Table

Compound	**Plant type**	**Emission factor**	**Data Quality**	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Country or region**	**Ref.**
SO_2	*Capacity up to 100 Mg*	0.09 kg/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	*Jarzebski(1970)*
SO_2	*Capacity > 100 Mg*	0.16 kg/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	*Jarzebski(1970)*
SO_2	*unknown*	0.09 kg/Mg steel	*E*	*n. a.*	*n. a.*	*gaseous*	*Poland*	*Jarzebski(1970)*
SO_2	*unknown*	0.18 kg/Mg steel	*E*	*n. a.*	*n. a.*	*residual oil*	*Poland*	*Jarzebski(1970)*
NO_x	*unknown*	55 – 96 g/GJ	*E*	*n. a.*	*n. a.*	*n. a.*	*Europe*	*CORINAIR(1995)*
NO_x	*unknown*	5.1 g/Mg steel	*C*	*n. a.*	*n. a.*	*n. a.*	*Poland*	*Jarzebski(1970)*
NMVOC	*unknown*	0.45 kg/Mg steel	*D*	*n. a.*	*n. a.*	*n. a.*	*Europe*	*CORINAIR(1995)*
NMVOC	*unknown*	0.02 kg/Mg steel	*C*	*n. a.*	*n. a.*	*n. a.*	*Poland*	*Fudala (1993)*
CH_4	*unknown*	0.005 kg/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Europe*	*CORINAIR(1995)*
CH_4	*unknown*	0.12 kg/Mg steel	*C*	*n. a.*	*n. a.*	*n. a.*	*Poland.*	*Olczak (1993)*
Particulates	*unknown*	10.55 kg/Mg steel	*A*	*uncontrolled*	*0 %*	*n. a.*	*USA*	*US EPA (AP-42)*
Particulates	*unknown*	0.142 kg/Mg steel	*A*	*controlled*	*n. a.*	*n. a.*	*USA*	*US EPA (AP-42)*
Particulates	*Capacity up to 100 Mg*	1.9 kg/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	*CORINAIR(1995)*
Particulates	*Capacity > 100 Mg*	2.5 kg/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Poland*	*CORINAIR(1995)*
Particulates	*unknown*	2.03 kg/Mg steel	*E*	*n. a.*	*n. a.*	*gaseous*	*Poland*	*CORINAIR(1995)*
Particulates	*unknown*	2.4 kg/Mg steel	*E*	*n. a.*	*n. a.*	*residual oil*	*Poland*	*CORINAIR(1995)*
As	*Capacity 50-370 Mg*	0.6 – 0.9 g/Mg steel	*E*	*n. a.*	*n. a.*	*liquid &/or gaseous*	*Poland.*	*Wessely (1993)*
Cd	*unknown*	0.5 – 0.9 g/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany*	*Jockel (1991)*
Cd	*Capacity 50-370 Mg*	0.2 g/Mg steel	*E*	*n. a.*	*n. a.*	*liquid &/or gaseous*	*Poland*	*Wessely (1993)*
Cd	*one-bath furnace, air*	0.12 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cd	*one-bath furnace, air*	0.008 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cd	*one-bath furnace,* O_2	0.40 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cd	*one-bath furnace,* O_2	0.03 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cd	*double-bath furnace*	0.59 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cd	*double-bath furnace*	0.04 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cr	*Capacity 50-370 Mg*	6.6 – 13.8 g/Mg steel	*C*	*n. a.*	*n. a.*	*liquid &/or gaseous*	*Poland*	*Wessely (1993)*

Table 8-2: continued

Cu	*Capacity 50-370 Mg*	3.6 – 7.8 g/Mg steel	*C*	*n. a.*	*n. a.*	*liquid &/or gaseous*	*Poland*	*Wessely (1993)*
Cu	*one-bath furnace, air*	0.23 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cu	*one-bath furnace, air*	0.015 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cu	*one-bath furnace,* O_2	0.78 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cu	*one-bath furnace,* O_2	0.05 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cu	*double-bath furnace*	1.18 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Cu	*double-bath furnace*	0.08 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Ni	*one-bath furnace, air*	0.05 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Ni	*one-bath furnace, air*	0.003 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Ni	*one-bath furnace,* O_2	0.18 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Ni	*one-bath furnace,* O_2	0.01 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Ni	*double-bath furnace*	0.27 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Ni	*double-bath furnace*	0.02 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Pb	*unknown*	7.0 – 18.0 g/Mg steel	*E*	*n. a.*	*n. a.*	*n. a.*	*Germany*	*Jockel (1991)*
Pb	*Capacity 50-370 Mg*	9.1 – 19.8 g/Mg steel	*C*	*n. a.*	*n. a.*	*liquid &/or gaseous*	*Poland*	*Wessely (1993)*
Pb	*one-bath furnace, air*	5.30 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Pb	*one-bath furnace, air*	0.35 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Pb	*one-bath furnace,* O_2	18.18 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Pb	*one-bath furnace,* O_2	1.21 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Pb	*double-bath furnace*	27.27 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Pb	*double-bath furnace*	1.82 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Zn	*Capacity 50-370 Mg*	73.3 – 150.2 g/Mg steel	*C*	*n. a.*	*n. a.*	*liquid &/or gaseous*	*Poland*	*Wessely (1993)*
Zn	*one-bath furnace, air*	7.81 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Zn	*one-bath furnace, air*	0.52 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Zn	*one-bath furnace,* O_2	26.77 g/Mg steel	*C*	*direct em.*	*85 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Zn	*one-bath furnace,* O_2	1.78 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*
Zn	*double-bath furnace*	40.15 g/Mg steel	*C*	*direct em.*	*85%*	*n. a.*	*CIS*	*Kakareka (1998)*
Zn	*double-bath furnace*	2.68 g/Mg steel	*C*	*direct em.*	*99 %*	*n. a.*	*CIS*	*Kakareka (1998)*

n. a.= not available
direct em = direct stack emissions (i.e. ducted gas flow), excludes fugitive emissions

10 UNCERTAINTY ESTIMATES

The uncertainty in the emission factors given in Section 8 varies, but in many cases a data quality rating of C has been assigned because process technologies and abatement efficiencies are documented. Uncertainty of estimates based on default emission factors without such a specification is high and only the order of magnitude may be assessed.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Priority for further work is low because the process is almost phased out in Western Europe and is being phased out in Eastern Europe.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not applicable because open-hearth furnace steel plant should be considered as point sources (see Section 7).

13 TEMPORAL DISAGGREGATION CRITERIA

The open-hearth furnace process is a continuous process.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

No supplementary documents are required.

16 VERIFICATION PROCEDURE

Verification would involve internal checking of completeness and consistency of the estimate (to see if all process steps are covered by emission factors in section 8) as well as a comparison to alternative estimates for this source category e. g. from other countries.

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19 RELEASE VERSION, DATE AND SOURCE

Version :	3.1
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SNAP CODE: **040206**

SOURCE ACTIVITY TITLE: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLERIES**
Basic Oxygen Furnace Steel Plant

NOSE CODE: **105.12.06**

NFR CODE: **2 C 1**

ISIC: **2410**

1 ACTIVITIES INCLUDED

The basic oxygen furnace is a part of the production process of primary iron and steel.

2 CONTRIBUTION TO TOTAL EMISSIONS

The emissions from the basic oxygen process are part of the primary iron and steel production.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity Basic Oxygen Furnace Steel Plant	SNAP-code 040206	Contribution to total emissions [%]										
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	TSP*	PM_{10}*	$PM_{2.5}$*
Typical contribution		0.2	0	0	-	1.5	0	-	-	1.05	2.16	3.69
Highest value										2.86	5.65	11.53
Lowest value										0.141	0.254	0.404

* contribution to total national emissions, excluding agricultural soils, EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006)
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

However, this chapter currently addresses only heavy metal and PM emissions.

3 GENERAL

3.1 Description

Pig iron contains 4 - 4.5 weight % carbon. In its solid state pig iron is hard and brittle, and rolling or forging is impossible. This can only be done by lowering the carbon content to below 1.9 weight %. This is the steel production process.

The first step in the conversion of iron steel is the removal of carbon.

This is feasible thanks to the strong attraction between carbon and oxygen. In the blast furnace process, the carbon released from the coke breaks the iron/oxygen bond in the ore by binding itself to CO and CO_2.

In the steel making process, the opposite occurs, the oxygen causing the carbon to leave the iron. It disappears from the converter in the form of carbon monoxide gas.

The oxygen-blown steel making process takes place in a pear-shaped vessel called a converter. This has a refractory lining and is mounted in such a manner that it can be tilted. Inside iron is turned into steel by blowing almost pure oxygen on to the surface of the molten metal, causing undesirable substances to be combusted. The refining process can be enhanced, where necessary, by “bottom stirring” with argon gas by porous bricks in the bottom lining in certain phases of the process. This produces a more intensive circulation of the molten steel and an improved reaction between the gas and the molten metal. The oxidation (combustion) of the various elements which escape from the bath is accompanied by the release of a great deal of heat. In many cases steel scrap is added at a rate of 10% - 20% to cool the metal. The gas, which is rich in carbon monoxide, is removed and used as a fuel.

A complete cycle consists of the following phases: charging scrap and molten iron, blowing, sampling and temperature recording, and tapping. In a modern steelwork, 300 tonnes of steel are produced in a 30 minute cycle.

At the end of the refining process the ladle filled with molten steel is conveyed to the continuous casting machine. Continuous casting, in which billets or slabs are cast direct from molten metal, replaces the traditional method of pouring molten steel into moulds to produce ingots which, when solidified, are reheated and rolled into slabs or billets.

Continuous casting not only saves time and energy, but also improves the quality of the steel and increases the yield.

3.2 Definitions

Primary dust removal	Oxygen blowing with a vertical converter
Secondary dust removal	Oxygen blowing with a tilted converter during loading and tapping

Unabated emissions	Emissions from roof ventilation with a tilted converter with no secondary dust removal
Refractory lining	Fire-resistant coating of the converter. The coating contains tar.

3.3 Emissions

The primary dust abatement produces in addition to CO and CO_2 mainly dust emissions. When the converter is provided with a fire resistant coating, this coating has to be preheated, producing PAH containing aromatic hydrocarbons. The amount of PAH is usually below the detection limit of the measuring technique. The dust contains a small amount of heavy metals. The secondary dust abatement produces dust with a higher heavy metal content than the primary dust. The same applies to the unabated dust emissions from ventilation through the roof.

The main part of the dust emissions consists of particles with a size smaller then 10 micron. For the dust emitted through the roof this is more than 50 %.

3.4 Controls

Primary dust abatement consists of a vapour cooler for separation of coarse dust and a washer for fine dust abatement. The secondary dust abatement is usually a fabric filter.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

Emission = AR x EF

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3), to estimate emissions of gaseous pollutants from the steel production is based on measurements or estimations using plant specific emission factors. Guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

For a local situation, the best approach would be to use extensive measurements, including the effects of abatement approaches. Reference emission factors for comparison with User's own estimates, are provided for selected pollutant releases, in Section 8.2

6 RELEVANT ACTIVITY STATISTICS

Information on the production of steel, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of steel produced by various types of industrial technologies employed in the iron and steel industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 "Choice of activity statistics".

7 POINT SOURCE CRITERIA

Primary iron and steel industry with a capacity above 3 million tonnes per year should be considered as a point source.

8 EMISSION FACTORS

8.1 Default Emission Factors For Use With Simpler Methodology

Table 8.1: Default Emission Factors (abatement type unknown/not specified)

Compound	**Emission factor (g/Mg)**	**Compound**	**Emission factor (g/Mg)**
Arsenic	0.015	Lead	1.5
Cadmium	0.025	Selenium	0.003
Chromium	0.1	Zinc	4
Copper	0.1	Dust	-
Mercury	0.003		
Nickel	0.05		

8.2 Reference Emission Factors For Use With Detailed Methodology

The data provided in Table 8.2 are based on a combination of six sources with abatement and two without abatement. The combination of this information is related to total production.

Table 8.2: Emission factors for dust and heavy metals from basic oxygen furnace production as reported by several countries/authors (in g/Mg)

Compound	**Germany [1]**	**Netherlands**		**France [4]**	**Pacyna [5]**	**Sweden [6,7]**	**Poland [8]**
abatement	partially abated	wet scrubbers fabric filters [2]	partially abated [3]	unknown	unknown	wet scrubbers fabric filters	abated
Arsenic	0.0040	0.02	0.0001	0.02	-	- -	
Cadmium	0.031	0.003	0.024	0.002-0.05	0.02	0.04 0.04	
Chromium	0.50	0.04	0.011	0.07	-	- 0.026	0.04-0.07
Copper	0.13	0.04	0.010	0.25	-	- 0.066	0.01-0.04
Mercury	-	0.004	0.002	-	-	0.001 0.00033	
Nickel	0.09	-	-	0.05	-	- 0.024	
Lead	1.30	2.3	1.08	0.9	1.6	4 4.6	0.08-0.14
Selenium	-	-	-	-	-	- -	
Zinc	3.3	4.1	2.7	4.1	3.9	6 6.4	0.4-0.8
Dust	-	100	53	-	-	- -	

- unknown

Table 8.3 lists emission factors for particulate matter (TSP, PM_{10} and $PM_{2.5}$) for different types of oxygen blow steel furnaces, derived from CEPMEIP (9).

Table 8.3 Emission factors for dust and heavy metals from basic oxygen furnace production as reported by several countries/authors (in kg/ton oxygen steel)

Technology	Abatement	TSP	PM_{10}	$PM_{2.5}$	Uncertainty
Conventional installation of average age	Primary dedusting by ESP, wet scrubbing; limited capturing of secondary dust emission	0.35	0.3325	0.315	2
Modern plant (BAT)	High efficiency ESP or added fabric filter to control primary sources; extensive secondary dedusting using fabric filters	0.12	0.12	0.12	5
Older plant	Primary dedusting by scrubber with removal efficiency around 97%; limited capturing of secondary dust emission	0.6	0.57	0.54	2

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in Table 8.3): The uncertainty in the emission factor for $PM_{2.5}$ from a conventional plant is 2. The emission factor with uncertainty range will therefore be 0.315 gram per tonne steel with an uncertainty range of 0.158 (0.315 / 2) to 0.630 (0.315 x 2).

9 SPECIES PROFILES

Information about the profile of the used ores might provide extra information. Generalised ore profiles are not relevant.

10 UNCERTAINTY ESTIMATES

The uncertainty in the emission factors may be estimated at about 50 %

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect in the methodology is the lack of sufficient information in relation to details of the processes used.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant if considered as point source.

13 TEMPORAL DISAGGREGATION CRITERIA

Although the different processes are discontinuous, steel production as such is a continuous process. Therefore for most purposes no temporal disaggregation is necessary.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency. Compilation of air pollutant emission factors AP-42
PARCOM-ATMOS Emission Factors Manual

16 VERIFICATION PROCEDURES

Verification of the heavy metal emissions by comparing with the profile of the ore could be useful.

17 REFERENCES

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18 BIBLIOGRAPHY

No additional bibliography.

19 RELEASE VERSION, DATE AND SOURCE

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Updated with emission factors (CEPMEIP) for particulates by:
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SNAP CODE: **040207**

SOURCE ACTIVITY TITLE: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES**
Electric Furnace Steel Plant

NOSE CODE: **105.12.07**

NFR CODE: **2 C 1**

1 ACTIVITIES INCLUDED

The electric steel furnace is a part of the production process for primary iron and steel. Figure 1.1 in the Introduction of the Guidebook shows a flow sheet of an integrated iron and steel plant. The block where scrap is added is where the electric furnace is situated. The figures 5.3 and 5.4 in the Guidebook Introduction show a more detailed picture of an electric furnace.

2 CONTRIBUTION TO TOTAL EMISSIONS

Electric furnaces contribute substantially to the total emission of particulates (PM), cadmium, chromium, zinc, hexachlorobenzene and dioxins and furans (see Tables 2.1-2.3).

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Electric Furnace Steel Plant	040207	0	0.1	0	-	0.6	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

Table 2.2: Contribution to total heavy metal (HM) emissions of the OSPARCOM-HELCOM-UNECE Emission Inventory (*38 countries*; Berdowski et al; ref. 17)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		dust[1]	Cd	Hg	Pb	As	Cr	Cu	Ni	Zn
Electric Furnace Steel Plant	040207	9	7	2	2	1	28	1	1	16

1) contribution of total iron and steel industry to total European (excluding the former U.S.S.R.) PM_{10} emission (ref. 18)
0 = emissions are reported, but the exact value is below the rounding limit (0.5 per cent)

\- = no emissions are reported

Table 2.3: Contribution to total POP emissions of the OSPARCOM-HELCOM-UNECE Emission Inventory (*38 countries*; Berdowski et al.; ref. 17)

Source-activity	SNAP-code	Contribution to total emissions [%]	
		Hexachlorobenzene	Dioxins/Furans
Electric Furnace Steel Plant	040207	3	3

0 = emissions are reported, but the exact value is below the rounding limit (0.5 per cent)

Electric furnace steel plant are unlikely to be a significant source of sulphurhexafluoride (SF_6), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs), (ETC/AEM-CITEPA-RISOE 1997; ref. 19).

3 GENERAL

3.1 Description

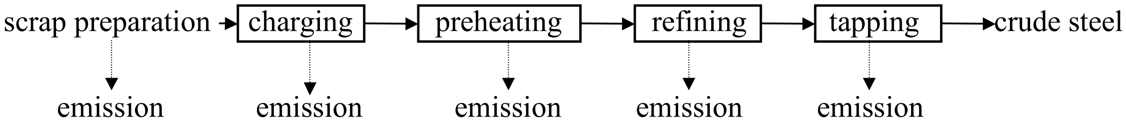
In an electric arc furnace non-alloyed, and low-alloyed steel is produced from polluted scrap. The scrap is mainly produced by shredding cars and does not have a constant quality.

Through carbon electrodes electricity is added to the scrap in the furnace, thus raising the temperature to 1700 ^oC. Lime, anthracite and pig-iron are then added. Depending on the desired quality of the steel, chromium, manganese, molybdenum or vanadium compounds can be added. The process is a batch process. Each cycle consists of the same steps: charging of scrap, preheating, refining with addition of other material and tapping (see figure 3.1).

Emissions are produced during each step of a cycle. Several abatement techniques are used to reduce the dust emissions (see Section 3.5).

The interior of the furnace is covered with fire-resistant coating.

Figure 3.1. The steps in a production cycle of an electric arc furnace.



3.2 Definitions

Electric arc furnace: A furnace equipped with carbon electrodes between which a high voltage is applied. The resulting electric arc melts the scrap.

Coating material:	Fire-resistant material covering the interior of the furnace. The coating is repaired from time to time and removed after a limited number of cycles. The coating material used can contain tar, but tar-free material is available.

3.3 Techniques

The techniques used are extensively described in literature.

3.4 Emissions

Besides carbon monoxide and carbon dioxide, dust is the main emission. Sixty percent of the dust particles are smaller than ten micron. Because polluted scrap is used, the dust contains heavy metals such as lead and zinc. Also copper, chromium, nickel, arsenic, cadmium, and mercury are present.

Small amounts of hexachlorobenzene and dioxins and furans are also emitted. Emissions of PAH depend on the coating material used, e.g. in the Netherlands PAH are not emitted, because tar-free materials are used for the coating.

3.5 Controls

Reduction of the emissions can be achieved by technological process changes as well as by abatement equipment. Varying the operating conditions or the design of the furnace may lead to a reduction in the amount of dust produced. Use of an ‘after burner’ reduces the amount of CO emitted. Use of equipment to capture the emitted particles, e.g. fabric filter or electrostatic precipitators (ESP), reduces the amount of dust emitted.

Fugitive emissions can be reduced by placing the furnace in a doghouse (a ‘hall’) and using abatement equipment to clean the effluent from the doghouse. Table 3.1 lists the overall efficiency of several abatement technologies.

Table 3.1. Abatement technologies and their efficiencies for complete electric furnace steel plants (assuming good housekeeping).

Abatement technology	efficiency (%)
fabric filter	95%[1]
electrostatic precipitators (ESP)	>95%[1]
doghouse, suction hood and fabric filter	>99.5%[1]
fibrous filter and post-combustion	>95%[1]

1) abatement for PM (and for most HM, but not for As and Hg)

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes (“activity rates”) and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (A) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The annual emission is determined according to Equation (1) by an activity and an emission factor:

$$E_i = EF_i \cdot A \qquad (1)$$

E_i annual emission of pollutant i
EF_i emission factor of pollutant i
A activity

The activity A and the emission factor EF_i have to be determined on the same level of aggregation by using available data.

5 DETAILED METHODOLOGY

Extensive measurements in a local situation will provide better information. Another way of estimating the emissions is using a mass balance. A third way is by estimating the emissions for each step of a production cycle.

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[1] The term “Tier” is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in the Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

The electric energy comes from an external power plant. For preheating of the scrap natural gas (heat content 31.65 MJ/m^3) is used. The amount used is about 3 - 7 m^3 per ton scrap.

Simpler methodology

The production statistics needed is the total secondary steel production of the country and a way to distribute this production over the plants (e.g. capacity per plant).

Detailed methodologies

Needed for: method 1 - Per plant measurements
method 2 - All flows going in and out of each plant
method 3 - The amount of product in each step of the production cycle
For the third methodology some information is presented in the tables.

7 POINT SOURCE CRITERIA

All electric (arc) furnace plants should be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

From the smelters in the Netherlands about 2,800 ton dust a year is captured. The dust production can be calculated to be about 11.6 kg/ton steel. The abated dust emission is about 0.64 kg/ton steel produced (abatement efficiency 95%). From this figure emission factors for heavy metals have been calculated. The BAT Reference document for production of iron and steel gives a dust range of 0.001-0.780 kg/tonne and USEPA gives a filterable PM range of 0.009-0.05 kg/tonne.

Table 8.1. Emission factors for (in)direct greenhouse gases plus SO_x from electric arc furnaces.

Plant type	Compound	Emission factor g/Mg	Data Quality	Abatement type	Abatement efficiency	Fuel type	country or region	Ref.
us[7]	SO_x	350	D	*unknown*	*unknown*	*unknown*	USA	15
stack, cs[6]	SO_x	350	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	SO_2	28-350[1]	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	SO_2	130	D	*unknown*	*unknown*	*unknown*	Switzerland	5
us[7]	SO_2	130	D	*unknown*	*unknown*	*unknown*	Netherlands	3
us[7]	NO_x	200	D	*unknown*	*unknown*	*unknown*	*unknown*	15
stack, cs[6]	NO_x	50	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	NO_x	80-820[2]	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	NO_x	220	D	*unknown*	*unknown*	*unknown*	Switzerland	5
us[7]	NO_x	470	D	*unknown*	*unknown*	*unknown*	Netherlands	3
us[7]	NMVOC	90	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	NMVOC	170	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	NMVOC	33-180[3]	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	NMVOC	80	D	*unknown*	*unknown*	*unknown*	Switzerland	5
charging, us[7]	VOC	0.5	D	*unknown*	*unknown*	*unknown*	*unknown*	15
tapping, us[7]	VOC	1	D	*unknown*	*unknown*	*unknown*	*unknown*	15
stack, cs[6]	VOC	175	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	VOC	58	D	*unknown*	*unknown*	*unknown*	Netherlands	3
us[7]	CH_4	10	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	CH_4	10	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	CO	10000	D	*unknown*	*unknown*	*unknown*	*unknown*	15
carbon steel	CO	9000	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	CO	1000-11500[4]	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	CO	1000	D	*unknown*	*unknown*	*unknown*	Switzerland	5
us[7]	CO	1500	D	*unknown*	*unknown*	*unknown*	Netherlands	3
us[7]	CO_2	150000-220000	D	*unknown*	*unknown*	*unknown*	Denmark	6
us[7]	CO_2	2000-100000[5]	D	*unknown*	*unknown*	*unknown*	*unknown*	15
us[7]	CO_2	100000	D	*unknown*	*unknown*	*unknown*	Switzerland	5
us[7]	CO_2	1400000	D	*unknown*	*unknown*	*unknown*	Netherlands	3
us[7]	N_2O	5	D	*unknown*	*unknown*	*unknown*	*unknown*	15

1) suggested value: 130 g/Mg
2) suggested value: 200 g/Mg
3) suggested value: 90 g/Mg
4) suggested value: 10000 g/Mg
5) suggested value: 50000 g/Mg
6) cs is carbon steel
7) us is unknown type of steel

Table 8.2. Emission factors for heavy metals from electric arc furnaces.

Plant type	Compound	Emission factor g/Mg	Data Quality	Abatement type	Abatement efficiency	Fuel type	country or region	Ref.
ccs[1]	As	0.1	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Cd	0.25	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Cr	1	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Cu	0.8	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Hg	0.15[1]	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Ni	0.25	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Pb	14	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Se	0.05	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ccs[1]	Zn	50	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	As	0.015	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Cd	0.07	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Cr	15	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Cu	0.5	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Hg	0.15[1]	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Ni	5	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Pb	2.5	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Se	0.05[1]	E	*unknown*	*unknown*	*unknown*	Netherlands	1
ss[2]	Zn	6	E	*unknown*	*unknown*	*unknown*	Netherlands	1
us[3]	As	0.048	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	As	0.002	E	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Cd	0.086	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Cd	0.004	D	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Cd	0.39	E	*unknown*	*unknown*	*unknown*	} United	12
us[3]	Cd	0.22	E	*unknown*	*unknown*	*unknown*	} Kingdom	12
us[3]	Cd	0.23	D	*unknown*	91%	*unknown*	Switzerland	5
us[3]	Cr	0.61	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Cr	0.03	D	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Cr	0.12 - 7.9	E	*unknown*	*unknown*	*unknown*	Poland	4
us[3]	Cu	0.55	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Cu	0.03	D	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Cu	0.05 - 3.1	E	unknown	*unknown*	*unknown*	Poland	4
us[3]	Hg	0.0048	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Hg	0.0002	E	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Hg	1	E	*unknown*	*unknown*	*unknown*	Switzerland	5
us[3]	Ni	0.086	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Ni	0.004	D	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Pb	18	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Pb	1	D	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Pb	0.08 - 5.5	E	unknown	*unknown*	*unknown*	Poland	4
us[3]	Pb	21	E	*unknown*	*unknown*	*unknown*	} United	12
us[3]	Pb	12	E	*unknown*	*unknown*	*unknown*	} Kingdom	12
us[3]	Pb	31	D	*unknown*	91%	*unknown*	Switzerland	5
us[3]	Zn	190	E	uncontrolled	0%	*unknown*	Netherlands	3
us[3]	Zn	11	D	fabric filter	95%	*unknown*	Netherlands	3
us[3]	Zn	0.37 - 24	E	*unknown*	*unknown*	*unknown*	Poland	4
us[3]	Zn	94	D	*unknown*	91%	*unknown*	Switzerland	5

1) ccs is carbon & construction steel
2) ss is stainless steel
3) us is unknown type of steel

Table 8.3. Emission factors for dust from electric arc furnaces.

Plant type	Compound	Emission factor g/Mg	Data Quality	Abatement type	Abatement efficiency	Fuel type	country or region	Ref.
charging, us[4]	dust	100 - 300	E	*unknown*	*unknown*	*unknown*	France	11
tapping, us[4]	dust	60 - 130	E	*unknown*	*unknown*	*unknown*	France	11
ccs[1]	dust	60 - 200	E	*unknown*	*unknown*	*unknown*	Sweden	2
stack, cs[2]	dust	25000	E	*unknown*	*unknown*	*unknown*	*unknown*	15
ss[3]	dust	30 - 900	E	*unknown*	*unknown*	*unknown*	Sweden	2
us[4]	dust	120 - 150	D	filter	*unknown*	*unknown*	Denmark	6
us[4]	dust	6000 - 20000	E	*unknown*	*unknown*	*unknown*	France	11
us[4]	dust	11000 - 23000	E	uncontrolled	*unknown*	*unknown*	Germany	9
us[4]	dust	610	E	uncontrolled	0%	*unknown*	Netherlands	3
us[4]	dust	30	D	fabric filter	95%	*unknown*	Netherlands	3
us[4]	dust	1300	D	*unknown*	91%	*unknown*	Switzerland	5

1) ccs is carbon & construction steel
2) cs is carbon steel
3) ss is stainless steel
4) us is unknown type of steel

Table 8.4. USEPA Particulate matter emission factors* for electric arc furnaces (g/Mg) (ref. 20)

Process	**Control**	**Emission factor, g/Mg**				
		PM	**Rating**	**PM_{10}**	**$PM_{2.5}$**	**Rating**
Electric arc furnace(steel minimills AP-42 Chapter 12.5.1 (2004)						
Charging, melting, slagging, tapping	Shell evacuation and roof canopy to fabric filter	0.050	D	*0.038*	*0.038*	*E*
Charging, melting, slagging, tapping, ladle transfer to ladle furnace, ladle preheater, alloy addition, ladle furnace melting	Shell evacuation and roof canopy to fabric filter	0.030	E	*0.023*	*0.023*	*E*
Charging, melting, slagging, tapping, continuous caster	Shell evacuation and roof canopy to fabric filter	0.009	E	*0.007*	*0.007*	*E*
Charging, melting, slagging, tapping, ladle transfer to ladle furnace, ladle preheater, alloy addition, ladle furnace melting , continuous caster	Shell evacuation and roof canopy to fabric filter	0.034	E	*0.026*	*0.026*	*E*
Electric arc furnace steel production AP-42 Chapter 12.5 (1986)						
Melting and refining	Uncontrolled carbon steel	19000	C	11020	8170	D
Charging, tapping, and slagging steel	Uncontrolled emissions escaping monitor	700	C	*400*	*300*	*E*
Melting, refining, charging, tapping, and slagging	Uncontrolled – alloy steel	5650	A	*3280*	*2430*	*E*
	Uncontrolled – carbon steel	25000	C	*15000*	*11000*	*E*
	Building evacuation to baghouse for alloy steel	150	A	*110*	*110*	*E*
	Direct shell evacuation (plus charging hood) vented to common baghouse for carbon steel	21.5	E	16	16	E

* = In the absence of more appropriate data use the AP 42 emission factors, figures in italics for PM_{10} and $PM_{2.5}$ derived from USEPA particle size profiles for uncontrolled and fabric filter.

Table 8.5. Emission factors for dioxins and furans and benzo(a)pyrene from electric arc furnaces.

Plant type	Compound	Emission factor µg I-TEQ/Mg	Data Quality	Abatement type	Abatement efficiency	Fuel type	country or region	Ref.
us[1]	dioxins/fur.	5[4]	E	*unknown*	*unknown*	*unknown*	Belgium	13
us[1]	dioxins/fur.	6	E	*unknown*	*unknown*	*unknown*	France	7
us[1]	dioxins/fur.	0.15 - 1.8	C	fabric filter	*unknown*	*unknown*	Germany	13
us[1]	dioxins/fur.	0.068 - 0.23	C	ESP	*unknown*	*unknown*	Germany	13
us[1]	dioxins/fur.	2	E	semi-abated	*unknown*	*unknown*	Netherlands	16
us[1]	dioxins/fur.	20	E	semi-abated	*unknown*	PVC cont.	Netherlands	16
us[1]	dioxins/fur.	0.7	E	*unknown*	*unknown*	no Cl_2	} United	13
us[1]	dioxins/fur.	10	E	*unknown*	*unknown*	high Cl_2	} Kingdom	13
us[1]	dioxins/fur.	0.2 - 8.6[2]	E	*unknown*	*unknown*	*unknown*	Sweden	13
us[1]	dioxins/fur.	11	E	*unknown*	*unknown*	*unknown*	Switzerland	5,13
us[1]	B(a)p[3]	17[3]	E	*unknown*	*unknown*	*unknown*	Czech Rep.	8

1) unknown type of steel
2) ng NTEQ/Mg
3) B(a)p (benzo(a)pyrene) in mg/Mg
4) value based on data from Sweden and the Netherlands; the range is 0.1 - 50 µg I-TEQ/Mg

9 SPECIES PROFILES

Comparison of species profiles with local information about ore and scrap compositions might be useful for verification purposes. However, no generalised information is available. See Table A.2 in Annex A for an example of dust composition.

10 UNCERTAINTY ESTIMATES

The uncertainty differs per compound. It varies between a factor of 1.5 and 3.5.

Since most material is on Western European countries, it can only be applied to Southern and Central and Eastern European countries when no better information is available.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect of the methodology is the lack of measurements in relation to the type of steel produced, the composition of the scrap/ore used in the furnace and the abatement.

For the simpler methodology a formula to calculate an emission factor based on ore/scrap composition used, steel type produced and abatement used would be very useful. Ideally the formula would be in this form:

$E.F. = \text{å} \bullet [x]_{in} \bullet f_x \bullet PM \bullet \text{ç}_x$ with å is an enrichment factor, $[x]_{in}$ is concentration of metal x in ore/scrap, f_x is a factor depending on concentration of metal x in steel produced, PM is the amount of particulates emitted and ç_x is the abatement efficiency for compound x.

Not enough information is available to breakdown the emission factors for the total production cycle to emission factors for each step of a production cycle.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

The basic steel plants are to be regarded as point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

Although the electric arc furnace is a discontinuous process, the smelter operation as such is a continuous process. The plant is operating 24 hours a day and 7 days a week.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

US Environmental Protection Agency, Compilation of air pollutant emission factors AP-42

16 VERIFICATION PROCEDURE

Verification of heavy metal emissions by comparing the profile of the emissions with ore and scrap compositions could be used as a verification method. A mass balance over the complete plant (one of the detailed methods) can be used as verification method.

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No additions to the general literature about iron and steel production.

19 RELEASE VERSION, DATE AND SOURCE

Version :	3.3
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20 POINT OF ENQUIRY

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ANNEX A: CONCENTRATION DATA FOR COMPOUNDS IN FLUE GASES AND DUST

Table A.1. Compound concentration in the flue gas of electric arc furnaces.

Plant type	Compound	Concentration mg/m3	Data Quality	Abatement type	Abatement efficiency	Fuel type	country or region	Ref.
us[3]	SO_2	5 - 50	D	*unknown*	*unknown*	*unknown*	France	11
us[3]	NO_x	50	D	*unknown*	*unknown*	*unknown*	France	11
us[3]	dust	0.08	D	filter	*unknown*	*unknown*	Denmark	6
us[3]	dust	500 - 15000	E	uncontrolled	*unknown*	*unknown*	Germany	
us[3]	dust	0.7 - 13.5	D	}	97.4%	*unknown*	Germany	9
us[3]	As	-	-	}	-	*unknown*	Germany	9
us[3]	Cd	<0.001 - 0.015	C	} doghouse &	>92.5%	*unknown*	Germany	9
us[3]	Cr	<0.001 - 0.008	C	} spark arrester	>98.4%	*unknown*	Germany	9
us[3]	Ni	<0.001 - 0.003	C	} & bag &	>90%	*unknown*	Germany	9
us[3]	Pb	0.04 - 0.7	C	} pocket filters	>93.6%	*unknown*	Germany	9
us[3]	Zn	0.23 - 0.7	C	}	>98.5%	*unknown*	Germany	9
us[3]	dust	2	C	)	99.9	*unknown*	Germany	9
us[3]	As	<0.001	C	)	>95	*unknown*	Germany	9
us[3]	Cd	<0.002	C	) doghouse &	>99.8	*unknown*	Germany	9
us[3]	Cr	<0.002	C	) suction hood &	>99.9	*unknown*	Germany	9
us[3]	Ni	<0.001	C	) fabric filter	>99.6	*unknown*	Germany	9
us[3]	Pb	0.08	C	)	99.9	*unknown*	Germany	9
us[3]	Zn	0.8	C	)	99.9	*unknown*	Germany	9
us[3]	dioxins/fur.	0.016 - 0.26[1]	C	fabric filter	*unknown*	*unknown*	Germany	13,14
us[3]	dioxins/fur.	0.010 - 0.040[1]	C	ESP	*unknown*	*unknown*	Germany	13,14
us[3]	dioxins/fur.	2.3[1]	D	fibrous filter	*unknown*	*unknown*	Luxembourg	13
us[3]	dioxins/fur.	0.77[1]	D	fibrous filter & post-combustion	*unknown*	*unknown*	Luxembourg	13
us[3]	dioxins/fur.	0.04[1]	E	*unknown*	*unknown*	*unknown*	Netherlands	13
us[3]	dioxins/fur.	0.1 - 1[2]	E	*unknown*	*unknown*	*unknown*	Sweden	13

1) ng I-TEq/m^3
2) ng NTEQ/m^3
3) unknown type of steel

Table A.2. Concentration of heavy metals in dust (in wt.%).

	Cd	Cr	Cu	Ni	Pb	Zn	Country	Ref.
Low alloy steel	0.1	0.14 - 0.6	0.4	0.1	6.1-7.0	17 - 31	France	11
Stainless steel	0.03	13.7	0.3	3.8	1.9	1.9	France	11
Steel	0.017	*unknown*	*unknown*	*unknown*	2.3	7.0	Switzerland	5
Steel	0.02 - 0.1	*unknown*	*unknown*	*unknown*	1.3-3.7	*unknown*	UK	10

Table A.3. Concentration of dioxins/furans in filter dust.

Plant type	Compound	Emis. Factor µg I-TEq/Mg filter dust	Data Quality	Abatement type	Abatement efficiency	Fuel type	country or region	Ref.
us[2]	dioxins/fur.	1000[1]	E	*unknown*	*unknown*	*unknown*	Sweden	13
us[2]	dioxins/fur.	150	E	*unknown*	*unknown*	*unknown*	Netherlands	13
us[2]	dioxins/fur.	74 - 1500	D	*unknown*	*unknown*	*unknown*	Germany	13

1) ng NTEQ/Mg filter dust
2) unknown type of steel.

SNAP CODE: **040208**

SOURCE ACTIVITY: **PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES**
Rolling Mills

NOSE CODE: **105.12.11**
105.12.12
105.12.13

NFR CODE: **2 C 1**

1 ACTIVITIES INCLUDED

Rolling mills are part of the production process from primary iron and steel. The products are sections and concrete reinforcing rods.

2 CONTRIBUTION TO TOTAL EMISSIONS.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Rolling Mills	040208	0	0	0	-	0	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

The emissions from rolling mills are a relevant part of the primary iron and steel production on all geographical levels. For heavy metal emissions, specific figures for this source activity are available from Baart *et al.* (1995). /1/. The average relative contribution from the total iron and steel production industry and the rolling of iron to the total emission of heavy metals has been presented for European countries in table 2.

Table 2: Average relative contribution of the production of iron and steel and the production of pig iron to the total emission of heavy metals in European countries

Compound	Total iron & steel production (%)	Rolling mills (%)
Cadmium	22	-
Chromium	36	3.6
Copper	16	-
Nickel	14	0.8
Lead	12	-
Zinc	33	-

- = not available

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Long products such as sections and concrete reinforcing rods can be produced by hot-rolling steel ingots. The huge reduction in thickness is accompanied by changes in structure and recrystallization, leading to a material with a very fine crystal structure. This is necessary in regard to the requirements for strength and deformability. This procedure is part of the traditional method of pouring molten steel into moulds to produce ingots which, when solidified, are reheated into slabs or billets. This method has in many cases been replaced by continuous casting.

However it is impossible to achieve these large degrees of re-rolling with continuously cast billets, and this applies also to the continuously cast strip. This problem can be solved by mounting conductive coils round the casting apertures. The electromagnetic stirring of the still molten core of the billet produces a very fine, homogeneous structure without segregation. This makes it possible to accept a lower degree of rolling without loss of quality.

The continuous cast slabs are transported to the hot strip mill without waiting for them to cool, and rolled immediately. The hot rolling of steel slabs has long been used as a “flattering process”. This term does not, however, apply to modern hot strip mills. By a subtle combination of chemical composition, reheating, deformation rate speed of cooling after hot rolling and strip temperature during coiling, a variety of steel grades can be produced, ranging from high-strength steel alloys to ultra-low carbon, super-deformable steel. In principle, it is even feasible to carry out heat treatment during hot rolling. This is achieved by cooling the strip rapidly to 200 - 300 ^{o}C after the last stage of deformation, producing a dual phase microstructure which ensures a unique combination of high strength and high deformability.

The hot slabs are prepared for rolling by heating in walking-beam furnaces to rolling temperature (about 1200 ^{o}C). The roughing mill train consists of five stands placed in tandem, where the slabs are rolled to achieve both the desired width and thickness. In a seven stands finishing train the product takes on the desired dimensions and shape and flatness of the strip are largely determined. As it passes over the run-out table, the strip is cooled to the desired temperature by means of water, after which it is coiled.

There are limits to the purposes for which thin sheet produced from hot-rolling mills can be used. Besides the fact that the requirements in terms of surface quality cannot be met by hot-rolling material, however carefully it is rolled, the thickness can be a physical problem. Therefore much of the hot-rolled strip is destined for further reduction of the thickness in cold rolling reduction mills.

As a first step it is put through the pickling line to remove the mill-scale. Immediately after pickling the necessary lubricant is applied by electrostatic machines. After cold reduction, which greatly improves the strength of the material, it is annealed to restore the desired deformability. This process is now largely carried out in continuous furnaces, but also batch annealing is used. Gradual heating and cooling results in recrystallization of the steel, restoring its deforming properties. During this process, which takes several days, nitrogen or hydrogen is passed through the furnace to prevent oxidation of the steel.

After annealing, the material is passed through the tempering mill and coiled for further processing.

3.2 Definitions

Continuous casting	Slabs or non-flat products (billets) are cast directly from molten metal. Continuous casting not only saves time and energy, but also improves the quality of the steel and increases the yield. Moreover, the process is more controllable. At the end of the refining process the ladle filled with molten steel is conveyed to the continuous casting machine. From a ladle mounted above the caster, the molten steel enters the tundish, from whence it flows into the moulds. If necessary, certain alloying elements which become unstable when exposed to oxygen in the atmosphere, or which act only for a brief period, can be added at the last minute by introducing cored wire into the mould.
VHO-gas	Smelter gas enriched with coke oven gas with a varying composition. Both products contain small amounts of hydrogen sulfide, left over from cleaning processes.

3.3 Techniques

3.4 Emissions

Hot-rolling of slabs and non-flat products (billets) produces hydrocarbon emissions from lubricating oils. Preheating of material and annealing after rolling results in emissions of nitrogen oxides and carbon monoxide. When VHO gas is used some sulfurdioxide will also be emitted. Pickling before cold-rolling produces emissions of hydrochloric acid. Cold-rolling gives emissions of hydrocarbons and decomposition products of lubricant oil. Gradual heating and cooling gives emissions of nitrogen oxides and carbon monoxide. Protection gas contains polycyclic aromatic hydrocarbons.

3.5 Controls

Hydrochloric acid from pickling is removed by a washing tower. Hydrocarbon vapours from rolling are captured by lamelle filters. Protection gas containing PAH's can be burned in afterburners.

4 SIMPLER METHODOLOGY

A simpler method would be to relate emissions to economic or production statistics. However, information for using this default method is not yet available.

5 DETAILED METHODOLOGY

Extensive measurements related to the individual process and the applied abatement methods will give a more individual picture of the emissions.

6 RELEVANT STATISTICS

In the Netherlands natural gas is used. For batch annealing sometimes enriched smelter gas is used. (VHO-gas).

7 POINT SOURCE CRITERIA

The emissions from primary steel production of capacity greater than 3 million tonne steel per year should be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

• Pickling	Hydrochloric acid (HCl): 2 g/Mg	
• Hot-rolling, Billets	VOC: 1 g/Mg	
- Fuel	1 - 1.2 GJ/Mg ==>	NO_x: 80 - 120 g/Mg
		CO: 100 - 120 g/Mg
• Hot-rolling, Slabs	Lubricating oil 2 - 5 g/Mg	
- Fuel	1.5 - 2 GJ/ton ==>	NO_x: 100 - 150 g/Mg
		CO: 220 - 250 g/Mg
• Cold-rolling	Lubricating oil: 10 - 100 g/Mg	
	VOC: 20 - 30 g/Mg	
	Decomposition products of oil: 10 - 20 g/Mg	
- Fuel, natural gas	0.4 - 2 GJ/Mg ==>	NO_x: 40 - 100 g/Mg

CO: 40 - 200 g/Mg

- VHO gas 1 - 2 GJ/Mg ==> NO$_x$: 20 - 50 g/Mg

CO: 0.3 - 1 g/Mg

SO2: 30 - 60 g/Mg

- Annealing PAH: 1.7 g/Mg (125 mg/Mg Borneff PAH).

9 SPECIES PROFILES

No generally applicable species profile is available.

10 UNCERTAINTY ESTIMATES

The uncertainty in the emission factor is estimated to be C.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect is the lack of adequate measurements related to the abatement methods.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

The primary iron and steel industry is expected to be regarded as a point source.

13 TEMPORAL DISAGGREGATION CRITERIA

Most of the processes described are continuous.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency, Compilation of air pollutant emission factors AP-42
PARCOM-ATMOS Emission factors Manual

16 VERIFICATION PROCEDURES

The emissions of VOC and PAH as calculated can only be verified by representative measurements.

17 REFERENCES

/1/ A.C. Baart, J.J.M. Berdowski, J.A. van Jaarsveld; Calculation of atmospheric deposition of contaminants on the North Sea; IWAD; ref. TNO-MW-R 95/138; TNO MEP; Delft; The Netherlands; 1995

18 BIBLIOGRAPHY

No additional bibliography

19 RELEASE VERSION, DATE, AND SOURCE

Version : 2.1

Date : November 1995

Source : J.J.M.Berdowski, P.F.J.van der Most, W.Mulder, P.Verhoeve
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SNAP CODE: **040301**

SOURCE ACTIVITY TITLE: **PROCESSES IN NON-FERROUS METAL INDUSTRIES**
Aluminium Production (electrolysis)

NOSE CODE: **105.12.21**
105.12.22

NFR CODE: **2 C 3**

1 ACTIVITIES INCLUDED

Production of primary aluminium, excluding alumina production.

2 CONTRIBUTION TO TOTAL EMISSIONS

Table 2.1 Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Aluminium Production	040301	0.1	0	0	-	0.4	0.1	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

For heavy metal emissions, specific figures for this source activity are available from Baart *et al.* (1995). /1/ The average relative contribution from the primary aluminium production industry to the total emission of heavy metals has been presented for European countries in table 2.

Table 2.2 Average relative contribution of the production of aluminium and the total non-ferrous industry to the total emission of heavy metals in European countries

	Contribution (%)	
Compound	Total non-ferrous industry (%)	Primary Aluminium production (%)
Cadmium	24	0.12
Chromium	0	-
Copper	11	-
Nickel	0	-
Lead	2.7	-
Zinc	28	0.004

- = not available

3 GENERAL

3.1 Description

Primary aluminium is produced by electrolytic reduction of alumina. The electrolytic process occurs in steel cells lined with carbon. Carbon electrodes extend into the cell and serve as anodes whereas the carbon lining of the cell is the cathode. Molten cryolite functions both as electrolyte and as a solvent for the alumina. Molten aluminium metal is deposited at the cathode and periodically tapped.

3.2 Definitions

Pots	Shallow rectangular cells lined with carbon.
Paste	Petroleum cake mixed with pitch binder.
Butts	Anode blocks prepared from paste by baking.

3.3 Techniques

Modern aluminium plant manufacture aluminium using pre-baked anodes, in older plant the Soderberg process is used. Other emissions include the anode preparation and, aluminium refining and casting activites.

3.4 Emissions during production activities

The main substances emitted are particulate matter, gaseous fluoride and particulate fluoride. The fluorides originate from the electrolyte. Emissions from the baking ovens include PAHs from the pitch binder. The dust produced contains some heavy metals.

3.5 Controls

Emission controls include wet scrubbers and fabric filters, the latter can incorporate a dry sorbant system for HF removal. Fugitive emissions from the pot room, particularly on older plant, can be significant.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1&2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR} \times \text{EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

5 DETAILED METHODOLOGY

If an extensive measuring program is available, the emissions can be calculated on the basis of the measurements of the dust emission and the composition of compounds over the total process.

The detailed methodology (equivalent to Tiers 3), to estimate emissions of gaseous pollutants from the cement production is based on measurements or estimations using plant specific emission factors - guidance on determining plant specific emission factors is given in the Measurement Protocol Annex.

The detailed methodology to estimate emissions of trace elements from the cement production is similar to the simpler one. However, more information on the type of the process, e.g. wet and dry kilns, as well as on the type of the industrial technology should be made available. This information shall be used to estimate specific emissions for at least a specific industrial technology.

Measurements of the emission rate and chemical composition of fine particles with < 1.0 μm diameter are often carried out at major cement kilns world-wide. The results of these measurements are then used to estimate atmospheric emissions of several trace elements contained as impurities in the raw materials and fuel.

Reference emission factors for comparison with users own data are provided in Section 8.2.

6 RELEVANT ACTIVITY STATISTICS

Standard national or international production statistics should be used.

7 POINT SOURCE CRITERIA

The primary aluminium plants usually are connected to high chimneys and can be regarded as point sources if plant specific data are available.

8 EMISSION FACTORS

8.1 Default Emission Factors For Use With Simpler Methodology

Table 8.1ai Emission factors for the electrolysis process

Substance	**Emission factor (g/Mg aluminium produced)**
Fluoride (gas)	350
Fluoride (particles)	950
Fluoranthene	4.5
Benz(a)pyrene	0.12
Sulfurdioxide	14200
Carbondioxide	1550000
Carbonmonoxide	135000
Nitrogenoxides	2150
Cadmium	0.15
Zinc	20
Nickel	15

Particulate emission factors are provided in Table 8.1aii from USEPA AP42 with ‘expert judgement’ estimates of PM_{10} and $PM_{2.5}$.

Table 8.1aii PM Emission factors for the electrolysis process

Activity	Abatement	Emission factor, g/tonne material produced		
		TSP	PM_{10}	$PM_{2.5}$
Electrolysis	Uncontrolled	49,000	37,000	25,000
	Fugitive	5,000	2,900	1,400
	Spray tower	56,000	42,000	28,000
	Dry alumina fabric filter	900	900	900
	ESP/dry + secondary scrubber	400	400	300

Table 8.1b Emission factors for the anode production process

Substance	**Emission factor (g/Mg aluminium produced)**
Fluorides (gas)	40
Fluorides (particles)	2
Fluoranthene	30
Benz(a)pyrene	1.4
Sulfurdioxide	900
Carbon dioxide	2200
Carbon monoxide	400
TSP	380
PM_{10}	280
$PM_{2.5}$	190

8.2 Reference Emission Factors For Use With Detailed Methodology

The emission factors presented are derived from the SPIN document, based on the Emission Inventory in the Netherlands. Particulate emission factors are from USEPA AP42 with estimates of PM_{10} and $PM_{2.5}$ based on USEPA speciation profiles and 'expert judgement'.

Table 8.2ai Emission factors for the electrolysis process

Substance	**Emission factor range** (g/Mg aluminium produced)
Fluoride (gas)	200-500
Fluoride (particles)	400-1500
Fluoranthene	3-6
Benz(a)pyrene	0.10-0.14
Sulfur dioxide	11000-17500
Carbon dioxide	1500000-1600000
Carbon monoxide	120000-150000
Nitrogen oxides	1300-3000
Cadmium	0.1-0.2
Zinc	15-25
Nickel	10-20

Table 8.1aii PM Emission factors for the electrolysis process

Activity	Abatement	Emission factor, g/tonne material produced		
		TSP	PM_{10}	$PM_{2.5}$
Electrolysis	Uncontrolled	47,000	24,000	16,000
Prebake cell	Fugitive	2,500	1,500	700
	Multicyclone	10,000	5,800	4,000
	Dry alumina scrubber fabric filter	900	900	900
	ESP + spray tower	2,300	1,300	600
	Spray tower	56,000	32,000	16,000
	Floating bed scrubber	56,000	32,000	16,000
	Coated fabric filter	900	900	900
	Crossflow packed bed	13,200	7,700	3,700
	Dry + secondary scrubber	400	400	400
Soderberg cell	Uncontrolled	49,000	25,000	16,000
(horizontal)	Fugitive	5,000	1,600	850
	Spray tower	11,000	6,400	4,400
	Floating bed scrubber	10,000	5,800	4,000
	Scrubber + wet ESP	900	900	900
	Wet ESP	900	900	900
	Dry alumina scrubber	900	900	900

Table 8.2b Emission factors for the anode production process

Substance	**Emission factor range** (g/Mg aluminium produced)
Fluorides (gas)	10-80
Fluorides (particles)	n.a.
Fluoranthene	20-40
Benz(a)pyrene	1.0-1.8
Sulfur dioxide	800-1000
Carbon dioxide	2000-2400
Carbon monoxide	n.a.
TSP	380
PM_{10}	280
$PM_{2.5}$	190

9 SPECIES PROFILES

A profile for PAH emissions from a single aluminium plant in the Netherlands is given in table 5. This table can be used to get at least a first estimation of PAH emissions for cases where only information about a single substance (in most cases benz(a)pyrene) is available.

Table 9.1 Relative profile for PAH emissions from aluminium production (Benz(a)pyrene put at one)

Substance	Relative amount
Naphthalene	90
Anthracene	5
Phenanthrene	20
Fluoranthene	20
Chrysene	3
Benz(a)anthracene	3
Benz(a)pyrene	1
Benz(k)fluoranthene	3
Benz(ghi)perylene	0.3

10 UNCERTAINTY ESTIMATES

The overall 'Uncertainty' in national emission inventories may be significant – as illustrated in Table 9.1.

Table 9.1 Uncertainty estimate for selected pollutants in the UK air emission inventory (NAEI, 2005).

Pollutant	Estimated Uncertainty (%)
PM_{10}	-20 to +50
$PM_{2.5}$	-20 to +30
$PM_{1.0}$	-10 to +20
$PM_{0.1}$	+/- 10
Sulphur Dioxide	+/- 3
Oxides of Nitrogen	+/- 8
NMVOCs	+/- 10
Ammonia	+/- 20

There is uncertainty in both the aggregated emission factors and activity data used to estimate emissions i.e. the imprecision and error to be expected from the application of an 'average' emission factor or activity statistic to estimate emissions from a specific sector - an artificial grouping of 'similar' sources.

The uncertainty is partly the result of how emission factors are developed and applied. In the case of primary particulate matter, the expanded statistical uncertainty is made up of: between plant variance, within plant variance, and uncertainties associated with the measurement methodology used and the aggregation of data. The measurement data in Annex 1 illustrates the variability in emission factors that occurs from between plant variance.

Process measurements, from which emission factors are developed at individual facility level, are subject to both systematic and random errors in the determination of mass concentration, mass emission, size distribution, and analytical errors etc.

In addition bias may exist in emission factors arising from:

1. Assumptions made about the abatement used on ‘typical’ industrial installations. For example emission factors ‘age’, the factors widely used in the Guidebook and hence by many countries as default emission factors in their national inventories become out of date. Recent measurement work suggests that they may overestimate emissions from the industrial processes subject to more modern industrial emissions regulation. They may, however, still be fully representative for older plant, small plant, or for poorer fuels;
2. Assumptions about the relationship between TSP and PM10/$PM_{2.5}$. The technical literature is comprehensive for TSP and the data quality can be good if measurements have been made using the international standard methods that are available (typically the 95% confidence limit ~10%). But a variety of methods are used for particle size fractionation and as yet there are no harmonised international standards to ensure comparability. Published measurement data for PM10 is sparse, that for $PM_{2.5}$ emissions more so. An added complication is that the methodology for the determination of TSP differs from that of PM10 and $PM_{2.5}$ and so the two need not correlate directly.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The contribution of heavy metals from the dust and the PAH emissions are the weakest aspects at the moment.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Primary aluminium production can be considered as a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

Environmental Protection Agency, COMPILATION OF AIR POLLUTANT EMISSION FACTORS AP 42, Chapter 12.1

Spindocument Productie van primair aluminium ; RIVM (report no. 736301131); November 1992 (in Dutch)

PARCOM-ATMOS Emission Factors Manual Actualised version 1993.

16 VERIFICATION PROCESSES

17 REFERENCES

1. A.C. Baart, J.J.M. Berdowski, J.A. van Jaarsveld; Calculation of atmospheric deposition of contaminants on the North Sea; IWAD; ref. TNO-MW-R 95/138; TNO MEP; Delft; The Netherlands; 1995
2. AP 42 (5th edition), October 1998, US Environmental Protection Agency. http://www.epa.gov/ttn/chief/ap42/ch12/index.html

18 BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP 42 or the PARCOM-ATMOS Manual may be used.

19 RELEASE VERSION, DATE AND SOURCE

Version:	3.1 (draft)
Date:	April 2001
Source:	J. J .M. Berdowski, P.F.J.van der Most, W. Mulder, J. PJ . Bloos TNO The Netherlands

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SOURCE ACTIVITY TITLE: PROCESSES IN NON-FERROUS METAL INDUSTRIES

ACTIVITY	SNAP CODE	NOSE CODE	NFR CODE
Ferro Alloys	**040302**	**105.12.41-42**	**2 C 2**
Silicium Production	**040303**	**105.12.23**	**2 C 5**
Magnesium Production (Except 030323)	**040304**	**105.12.24-25**	**2 C 5**
Nickel Production (Except 03024)	**040305**	**105.12.26**	**2 C 5**
Allied Metal Manufacturing	**040306**	**105.12.45**	**2 C 5**
Galvanizing	**040307**	**105.01.02**	**2 C 5**
Electroplating	**040308**	**105.01.03**	**2 C 5**
Other	**040309**	**105.12.59**	**2 C 5**

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006)

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SNAP CODE: **040401**

SOURCE ACTIVITY TITLE: **PROCESSES IN INORGANIC CHEMICAL INDUSTRIES**
Sulphuric Acid

NOSE CODE: **105.09.10**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

This sector covers emissions released from sulphuric acid production plants. Emissions released from all process steps are taken into account.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from sulphuric acid production plants to the total emissions in the countries of the CORINAIR90 inventory are given as follows:

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Sulphuric Acid	040401	0.7	0	0	-	0	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Sulphuric acid manufacture is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

This chapter covers all production steps within the plant and hence include the production of sulphur dioxide, sulphur trioxide, sulphuric acid and "oleum". The following figure provides an example of a flow sheet of a double contact sulphuric acid plant:

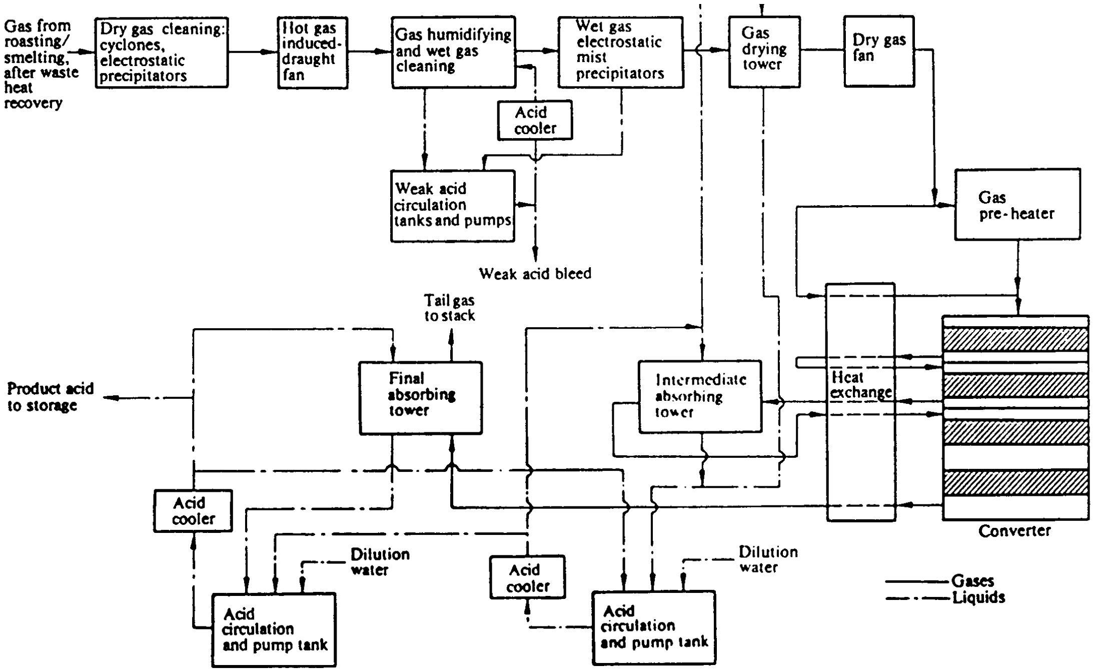

Figure 1: Double contact sulphuric acid plant (schematic, based on /7/)

For SO_2 emissions the relevant process units are the cleaning of SO_2-containing raw gas, the converter, the final absorbing tower, and scrubbers (see also section 3.4). Scrubbers may be installed for the cleaning of raw gas and behind the tail gas cleaning (see also section 3.3).

3.2 Definitions

Oleum	highly concentrated sulphuric acid (a solution of uncombined SO_3 dissolved in H_2SO_4).

3.3 Techniques

In principle the commercial production of sulphuric acid includes the following steps:

- Production of gases containing SO_2 and cleaning of the gases obtained if necessary,
- Oxidation of SO_2 to SO_3 and absorption of the SO_3 obtained.

3.3.1 Production of gases containing SO_2 /cf. 3/

Sulphur dioxide is produced by the oxidation of elemental sulphur with air, by the roasting of sulphidic ores with the addition of air, or by the decomposition of sulphates and spent sulphuric acids etc. in air. Elemental sulphur, which is obtained either from natural deposits (e.g. Frasch-process sulphur) or from the desulphurisation of natural gas or crude oil (recovered sulphur), is burned at temperatures between 900 °C and 1,800 °C; the SO_2 content of the combustion gases is generally up to 18 vol.-%. The sulphur content of sulphidic ores is converted into SO_2 by roasting it with air at more than 600 °C; the SO_2 content of the roaster gases is normally between 3 and 15 vol.-%. The usual types of furnaces are multiple-hearth furnaces, rotary kilns, fluid bed roasters, pyrite fines furnaces, sinter roasters and flash smelters, depending on the roasting material.

Roaster gases containing dust are fed to a gas cleaning system: wet separators and electrostatic precipitators, either single or in combination.

100 % sulphur dioxide is obtained

- by scrubbing the gases containing SO_2 with appropriate solvents (e.g. alkaline absorbents) and subsequently driving out the dissolved SO_2 by heating it (it is then dried, compressed and liquefied by refrigeration),
- by means of combined compression and separation of the gas containing SO_2,
- by conversion of 100 % SO_3 or oleum with elemental sulphur or hydrogen sulphide.

The waste gas containing SO_2 from the production of 100 % sulphur dioxide is generally fed to a sulphuric acid plant or cleaned by scrubbing at a pH value of between 5 and 6. The by-product is a sodium sulphite/sodium bisulphite solution, which may be added to the scrubber liquid.

The waste gas coming from the liquefaction process of sulphur containing gases is in general fed to a sulphuric acid plant.

3.3.2 Oxidation of SO_2 to SO_3 and absorption of the SO_3 obtained /cf. 3/

A distinction is made between plants for the production of sulphuric acid and plants for the processing of products containing sulphur. The end product is always sulphuric acid.

The contact process without intermediate absorption, the single contact process, is used to process SO_2 gases with low and widely varying SO_2 contents. The gases containing SO_2 are oxidised to SO_3 in the presence of catalysts containing alkali and vanadium oxides. The SO_3 is absorbed (by oleum and water) and converted to sulphuric acid.[1]The contact process with intermediate absorption, the double contact process, is widely used and has a primary conversion efficiency of 85 to 93 %. After cooling the gases, the SO_3 obtained is absorbed in the intermediate absorber by means of sulphuric acid with a concentration of 98 to 99 wt.-%. The SO_3 formed in the second stage is absorbed in a final absorber. In general, SO_2 gases containing 8 to 10.5 vol.-% SO_2 are used for this process.

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[1] Older process types also exist which today are of lower relevance. These older process types can be summarised as "nitrogen oxide processes": The production and the cleaning of the SO_2 gases are comparable to the contact process. However, for the conversion of the SO_2, nitrogen oxide is used as a catalyst which operates as an oxygen carrier. Depending on the lining of the reaction chamber, two processes are known: the lead chamber process (which is no longer in operation) and the tower process (brick lined chamber, advanced "lead chamber"-process).

The wet contact process is mainly used to process gases containing hydrogen sulphide from coke ovens, gasworks or oil refineries. The gases containing 15 to 100 vol.-% sulphides (e.g. hydrogen sulphide) etc. are burned autothermally with excess air in a combustion furnace. After cooling the SO_2 is oxidised to SO_3 in a converter (with alkali/vanadium oxide). After condensation or absorption, sulphuric acid with a concentration of 78 wt.-%, is generally obtained. A modified wet contact process is used for the direct processing of hot gases with low SO_2 contents (< 1.0 vol.-%) and high water contents e.g. from Claus plants. Sulphuric acid is obtained with concentrations of 78 to 93 wt.-%. The wet/dry contact process with intermediate condensation is based on sulphur combustion and is used in the processing of waste air contaminated with sulphur compounds (e.g. hydrogen sulphide). The SO_2 gases are converted in wet contact stages and then absorbed. The sulphuric acid obtained is cleaned in different steps. For processing oxygen-free gases to sulphuric acid, the lowest possible content per unit volume varies between 40 to 120 g sulphur per m^3, depending on the components in the input gas.

The waste gas containing SO_2 from the contact process can be fed into an intermediate absorption process, which reduces SO_2 emissions by approximately 80 %. Further reduction can be achieved by lowering the gas velocity in the contact process or by installing a fifth contact bed. SO_2 emissions from the double contact process can be reduced by up to 30 %, if a 5-bed system is installed instead of a normal 4-bed system.

The reduction of sulphuric acid aerosols can be achieved with for example candle filters, electrostatic precipitators or venturi scrubbers.

By applying an oxidising gas scrubbing process (e.g. Peracidox) for the waste gas cleaning downstream of a double contact process, SO_2 emissions can be reduced by up to 90 % and SO_3 emissions by up to 50 %. The oxidising agent is either peroxosulphuric acid or hydrogen peroxide. No waste products are obtained.

To reduce emissions of SO_2 and SO_3 from the contact process without intermediate absorption, a NH_3 tail gas scrubbing can be installed; the reduction efficiency for SO_2 emissions is up to 75 % and for SO_3 emissions up to 50 %. The products of this process are ammonium sulphite or ammonium bisulphite (for SO_2) and ammonium sulphate (for SO_3).

3.4 Emissions

The main relevant pollutants are sulphuric oxides (SO_x), which include sulphur dioxide (SO_2) and sulphur trioxide (SO_3). For CORINAIR, SO_2 and SO_3 should be reported together expressed as SO_2. Relevant process steps are listed below in Figure 1. Emissions of nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC)[2], carbon monoxide (CO)

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[2] The production of organic compounds gives rise to spent sulphuric acid which may contain organic compounds, salts etc. Depending on the type and degree of contamination, spent sulphuric acid is decomposed and processed to sulphuric acid in a contact plant. Slightly contaminated dilute acids can be concentrated to between 65 and 75 wt.-% and then subsequently evaporated to a concentration of ca. 96 wt.-%. /3/

and ammonia (NH_3) are negligible[3,4]. Emissions of heavy metals (e.g. from roasting sulphur in the smelter gas) are not relevant due to the fact that most of them are particle bound and separated by the wet gas cleaning (e.g. electrostatic precipitation). Heavy metals remaining in the flue gas are mostly absorbed by the sulphuric acid formed in the converter.

SO_2 emissions are released from the production of gases containing SO_2 (raw gas preparation)[5], the oxidation of SO_2 to SO_3 (converter) and the absorption of SO_3 obtained (H_2SO_4 production).

Nearly all sulphur dioxide emissions from sulphuric acid plants are found in the exit stack gases. In addition to these, small quantities of sulphur oxides are emitted from storage tank vents as well as from tank truck vents during loading operations, from sulphuric acid concentrators, and through leaks in process equipment. Few data are available on the quantity of emissions from these non-stack sources /1/.

3.4.1 Production of gases containing SO_2 (raw gas) /cf. 3/[5]

Extensive analysing of sulphur dioxide emissions released by the stacks of sulphuric acid plants shows that the major part of the SO_2 emissions is an inverse function of the sulphur conversion efficiency (SO_2 oxidised to SO_3). This conversion is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentration of the reactants (sulphur dioxide and oxygen). /1/ The efficiency of converting sulphur dioxide to trioxide is for the single contact process about 97 to 98 % and for the double contact process usually 99.5 % /cf. 7/. Depending on the raw material and the process, the waste gases contain up to 0.12 g SO_3 per m^3 before scrubber /3/.

Exhaust gases from the absorption process have an SO_2 concentration of 2,500 to 3,000 mg/m^3. The residual gas from the separation of the liquefaction process has an SO_2 concentration of up to 300 g/m^3. No exhaust gases occur when reducing SO_3 with sulphur or H_2S. Emissions from raw gas cleaning may occur.

3.4.2 Oxidation of SO_2 to SO_3 and absorption of the SO_3 obtained (H_2SO_4 production)

SO_2 emissions are relevant for the process steps: converter, final absorption tower and scrubbbers (if installed). The emissions are released through the stack.

Large quantities of sulphuric acid mist may be formed by the combustion of hydrogen sulphide (e.g. from coke ovens) and during decomposition processes, due to the oxidation of nitrogen compounds /3/. Concerning mist emissions an unpublished report by the US-EPA found that uncontrolled mist emissions from oleum plants burning spent acid range from 0.5

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[3] Oleum plants also produce mist emissions of sulphuric acid.

[4] For sulphuric acid production only SO_2 is relevant. Other pollutants may be released from the preparation of SO_2 feed gas (roasting, smelting etc.), which are not covered here.

[5] Emissions from the production of raw gases containing SO_2 are not considered here.

to 5.0 kg/Mg. 85 to 95 wt.-% of the mist particles from oleum plants are less than two microns in diameter, compared to only 30 wt.-%. /1/

3.5 Controls

Control measures are an integral part of the production process (see sections 3.3.1 and 3.3.2 and figure 1). Control measures include the oxidising gas scrubbing process and the tail gas scrubbing with NH_3.

4 SIMPLER METHODOLOGY

For the production of sulphuric acid only a simpler methodology is provided; a detailed methodology is not proposed (see section 5). Here "simpler methodology" refers to the calculation of emissions based on emission factors and activities. The simpler methodology covers the pollutant SO_x.

The annual emission is determined by an activity and an emission factor:

$$E_i = EF_i \cdot A \qquad (1)$$

E_i annual emission of pollutant i
EF_i emission factor of pollutant i
A activity rate

The activity rate A and the emission factor EF_i have to be determined on the same level of aggregation by using available data (e.g. production of sulphuric acid, see also Section 6).

Emission factors for emissions of SO_2 and SO_3 are given in Table 2 based on literature data. The required unit of the emission factors according to CORINAIR90 is mass pollutant/mass product [g/Mg].

5 DETAILED METHODOLOGY

A detailed methodology is not proposed, due to the low emission relevance of the production of sulphuric acid compared to the total anthropogenic emissions (see Section 2). Emission measurements appear to be not necessary for inventory purposes.

6 RELEVANT ACTIVITY STATISTICS

The activity according to CORINAIR90 should be reported in mass product/year [Mg/a]. The total production of sulphuric acid can be derived directly from statistics available on an European level. For individual point sources, data from national sources (e.g. associations of chemical industries) should be used.

The following statistics contain data concerning the production of sulphuric acid:

- United Nations (ed.): Industrial Statistics Yearbook 1991; Vol. I, Commodity Production Statistics, New York 1993; ISIC 3511-47 (production of sulphuric acid)

The following statistics on a European level contain only economic variables, such as number of enterprises, number of employees, turnover for the "Manufacture of basic industrial chemicals and manufacture followed by further processing of such products".

- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992
- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1994

7 POINT SOURCE CRITERIA

According to the CORINAIR90 methodology, sulphuric acid plants should be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 2 contains emission factors for the relevant pollutants SO_2 and SO_3 based on literature data. Emissions are expressed with reference to different compounds. Emission factor are given in relation to SO_2, SO_3, SO_x, and SO_4^{2-}.

Table 2: Emission factors for the production of sulphuric acid (expressed as 100 % acid)

Process	Emission factors in terms of production of 100 % H_2SO_4 [g/Mg]							
	SO_2		SO_3		$SO_x$$^{8)}$		SO_4^{2-}	
	range	value	range	value	range	value	range	value
Contact process without intermediate absorption (single absorption)	10,000 - 25,000$^{2)}$	17,000$^{7)}$ 14,000$^{2)}$ 17,500$^{2)5)}$	400 - 600$^{7)}$		1,100 - 17,000$^{3)}$	9,050$^{3)}$		
Contact process with intermediate absorption (double absorption)	1,500 - 4,000$^{2)6)}$	<1,000$^{4)7)}$ 2,700$^{2)6)}$			1,000 - 5,000$^{2)}$ 1,900 - 7,200$^{3)}$	3,000$^{2)}$ 4,550$^{3)}$	100 - 300$^{2)6)}$	200$^{2)6)}$
- with constant gas conditions		2,600$^{7)}$	100 - 150$^{7)}$					
- with fluctuating gas conditions	3,300 - 6,600$^{7)}$		300 - 400$^{7)}$					
- Decomposition plants (spent sulphuric acid)		6,600$^{7)}$		400$^{7)}$				
Wet contact process								
- 78 % sulphuric acid		17,000$^{7)}$		350$^{7)}$				
- 98 % sulphuric acid		17,000$^{7)}$		400$^{7)}$				
Wet/dry contact process with intermediate condensation/ absorption		3,300$^{7)}$	100 - 150$^{7)}$					

1) AIRS, EPA /6/;
2) CORINAIR /2/;
3) RIVM /4/;
5) old contact process, average conversion of 97.3 %
6) for Germany and the
8) SO_x: mixture of SO_2 and SO_3; proportions are not specified
Contact process absorber conversion 99.9 % 2,000$^{1)}$ absorber conversion 97 % 20,000$^{1)}$

[4] Swedish plants (in general) /5/;	Netherlands; [7] based on /3/;	absorber conversion 99.5 % absorber conversion 99 % absorber conversion 98 %	3,500[1] 7,000[1] 13,500[1]	absorber conversion 96 % 27,500[1] absorber conversion 95 % 35,000[1] absorber conversion 94 % 41,000[1] absorber conversion 93 % 48,000[1]

9 SPECIES PROFILES

The emissions contain sulphur dioxide (SO_2) and sulphur trioxide (SO_3) depending on the efficiency of converting sulphur dioxide to sulphur trioxide (see also Section 3.4).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors. Technique specific emission factors are provided in table 2. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested in the analysis of measured data in order to decrease the range of emission factors given or to provide a further split of emission factors taking into account further technical specifications.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) should provide a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from sulphuric acid plants can be obtained by taking into account the time of operation.

However, data for the annual time of operation should take into account, that sulphuric acid plants produce during the whole year, and the production of sulphuric acid is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on "Concepts for Emission Inventory Verification" different verification procedures can be recommended. Verification procedures considered here are principally based on the verification of emission data on a national level and on a plant level.
Verification on a plant level takes into account, e.g. the number of sulphuric acid plants considered, and relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

Emission data for sulphuric acid production can be verified on national level by comparing annual emissions related to the territorial unit to independently derived emission estimates (e.g. obtained by using population equivalents).

17 REFERENCES

/1/ US-EPA (ed.): Compilation of Air Pollutant Emission Factors, Vol. 1: Stationary Point and Area Sources, 1986, AIR CHIEF Version 2.0 Beta, April 1992

/2/ CITEPA (ed.): CORINAIR - Emission Factor Handbook, pat 1: Default Emission Factors from stationary sources; 1992

/3/ Verein Deutscher Ingenieure (ed.): Emission Control Sulphuric Acid Plants; Nr. 2298; Düsseldorf (Germany); 1984

/4/ Bol, B; Kohnen, E. A. E. M.: Produktie van Zwavelsuur; RIVM-report 736301143; RIZA-report 92.003/43; Maart; 1993

/5/ Ms. Froste; Mr. Kvist; Ms. Haclund; personal communication; February 1995 (Swedish EPA)

/6/ EPA (ed.): AIRS Facility System; EPA-Document 450/4-90-003, Research Triangle Park; March 1990

/7/ Parker, Albert: Industrial Air Pollution Handbook; London; 1978

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 2.1

Date : December 1995

Source : Otto Rentz, Dagmar Oertel
University of Karlsruhe
Germany

Updated with particulate matter details by:

Mike Woodfield
AEA Technology
UK
December 2006

20 POINT OF ENQUIRY

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SNAP CODE: **040402**

SOURCE ACTIVITY TITLE: **PROCESSES IN INORGANIC CHEMICALS INDUSTRIES**
Nitric Acid

NOSE CODE: **105.09.11**

NFR CODE: **2 B 2**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from nitric acid production plants, whereby all process steps are taken into account.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from nitric acid plants to the total emissions in the countries of the CORINAIR90 inventory is given as follows:

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Nitric Acid	040402	-	0.6	0.1	-	0	-	5.4	0.1

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

For the production of nitric acid, ammonia is oxidised catalytically. Nitrous gases are obtained, which are converted into nitric acid (together with oxygen and water). The following figure shows a flow sheet of a nitric acid plant:

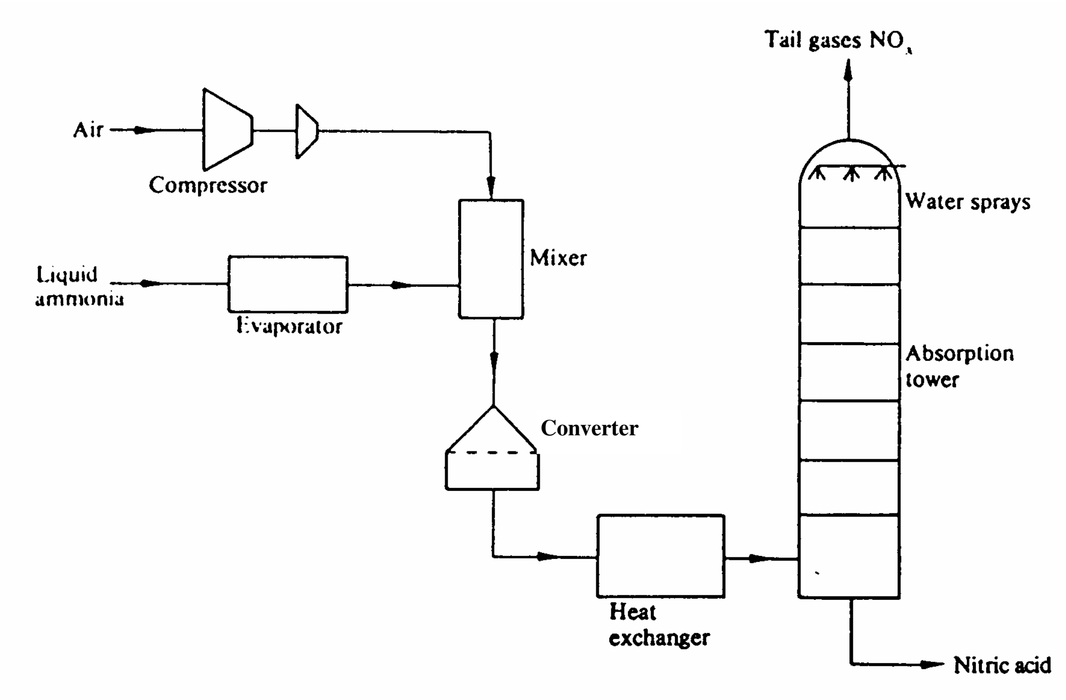

Figure 1: Nitric acid plant (weak acid about 50 wt.-%) - schematic (based on /5/)

For NOx emissions the relevant process units are the absorption tower and the tail gas cleaning units (e. g. SCR, SNCR). Small amounts of NOx are also lost for acid concentrating plants.

3.2 Definitions

Highly concentrated acid:	nitric acid with a concentration of about 98 wt.-%.
Weak acid:	nitric acid with a concentration of about 50 to 75 -wt.-%.

3.3 Techniques

Nitrogen monoxide (NO) is formed by catalytic oxidation of ammonia with atmospheric oxygen. NO is oxidised to nitrogen dioxide (NO_2) by adding further air. The reaction of NO_2 with water and oxygen forms nitric acid (HNO_3) with a concentration of generally 50 to 75 wt.-% ("weak acid").

For the production of highly concentrated nitric acid (98 wt.-%), first nitrogen dioxide is produced as described above. It is then absorbed in highly concentrated acid, distilled, condensed and finally converted into highly concentrated nitric acid at high pressure by adding a mixture of water and pure oxygen. /cf. 3/

The following production steps should be distinguished /3/:

- Production of nitrogen monoxide:
  Ammonia is oxidised with air in the presence of catalysts of platinum-rhodium alloy. The yield of nitrogen monoxide (normally between 95 and 98 % /1/) depends on the reaction conditions (such as pressure and temperature).
- Further treatment of nitric oxides:
  Nitrogen monoxide is oxidised to nitrogen dioxide. Nitrogen dioxide is then absorbed and reacts with water to form nitric acid.
- Upgrading of nitric acid.

Plants for the production of nitric acid can be designed as low pressure (< 1.7 bar), medium pressure (1.7 - 6.5 bar) and high pressure (> 8 bar) plants. New plants are only built for pressure ranges above 4 bar.

3.3.1 Weak Nitric Acid Production

Medium pressure plants (1.7 to 6.5 bar) can achieve NOx contents (see Section 3.4) of 600 to 800 ppm by volume in the exhaust gas. High pressure plants (above 8 bar)) can achieve NOx contents of 200 to 400 ppm by volume in the exhaust gas. /cf. 3/ Taking into account the ammonia combustion as described above, two plant types can be further distinguished:

- single-pressure plant	NH3 oxidation and absorption take place at the same pressure; compression takes place before the NH_3 oxidation (medium pressure).
- dual-pressure plant	Absorption takes place at a higher pressure than the NH3 oxidation; an NO compressor is required.

3.3.2 High Strength Nitric Acid Production

The reaction of nitrogen dioxide with water and pure oxygen takes place at high pressure. The reaction water from the combustion gases has to be condensed by cooling and then discharged. Nitrogen monoxide (NO) is oxidised with air and then with highly concentrated nitric acid to form nitrogen dioxide. NO_2 is scrubbed by means of highly concentrated nitric acid. The nitrogen dioxide and the dinitric tetroxide (N_2O_4, obtained by dimerisation) are mixed with nitric acid containing water. This mixture is converted to nitric acid (98 to 99.5 wt.-%) at high pressure (e.g. 50 bar). The NOx content of the waste gas depends on the temperature of the last absorption stage. /cf. 3/

3.3.3 Process-integrated emission reduction facilities

The two most common techniques used in order to control NOx emissions are:

- extended absorption by alkali solutions, and
- catalytic reduction.

Here, controls refer to reduction facilities which are normally an integral part of a nitric acid plant (see Section 3.3).

Extended absorption reduces nitrogen oxide emissions by treatment of the waste gas either with sodium hydroxide or with ammonia.

By treatment of the waste gas with sodium hydroxide, NO and NO_2 are absorbed and sodium nitrite ($NaNO_2$) is formed. Under certain conditions a NOx content in the waste gas of 200 ppm by volume can be achieved (absorption pressure of more than 4.5 bar, NOx content by volume of less than 600 ppm etc.) /3/.

Catalytic purification can be divided into a non-selective and a selective process. Both processes for waste gas treatment require a minimum temperature and a minimum pressure, conditions which often cannot be achieved in old plants /3/.

In non-selective reduction processes, the waste gas reacts with a reduction agent (hydrogen and/or hydrocarbons e.g. natural gas, waste gas from ammonia plants or naphtha) by passing a catalyst (which contains platinum, rhodium or palladium). Depending on the reduction conditions (amount of reduction agent) the reduction product is either nitrogen monoxide or nitrogen. The utilisation of hydrocarbons has the disadvantage that the waste gas contains carbon monoxide as well as hydrocarbons in a non-converted or partially converted state. /3/

In the selective reduction process the reduction agent, ammonia, reacts with nitric oxides to form nitrogen and water. The catalysts used are for example vanadium pentoxide, platinum, iron/chromium oxides mixtures or zeolites. According to the stoichiometric conditions of the reaction an excess of ammonia is necessary. This process can offer economical advantages for plants with small capacities (less than 100 t of N per day). /3/

A seldom used alternative control device for the absorption of tail gas is the use of molecular sieves. This process can be used for nitric acid plants with high-pressure absorption, where nitrogen dioxide is absorbed from the waste gas at an ambient temperature. /3/

3.4 Emissions

Relevant pollutants are nitrogen oxides (NOx) and nitrous oxide (N_2O). Emissions of ammonia (NH_3) and non-methane volatile organic compounds (NMVOC) are of less relevance. Emissions of carbon monoxide (CO) are not relevant.[1, 2]

Basic reactions for the production of nitric acid, according to the "Ostwald"-process (oxidation of ammonia, see section 3.3), are:

I $4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$

II $2\,NO + O_2 \rightarrow 2\,NO_2$

$2\,NO_2 \rightleftarrows N_2O_4$

III $3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$

---

[1] Trace amounts of HNO_3 can also be emitted.

[2] Emissions of NMVOC and CO reported in CORINAIR90 are not specified with regard to process technology.

Concerning the formation of N_2O only step I is of relevance. By using suitable catalysts about 93 - 98 % of the ammonia is converted into NO. The rest of the ammonia is converted into nitrogen, mostly in secondary reactions, but also to nitrous oxide according to /6/:

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 4\ O_2 \rightarrow 2\ N_2O + 6\ H_2O$$

Based on literature data it can be assumed that about 1.5 % of the ammonia is converted to N_2O; modern processes need about 283 kg NH_3/Mg HNO_3 produced. /6/

Emissions released by the stacks contain mainly a mixture of nitrogen oxides (see section 9). In general, the quantity of NOx emissions is directly related to the kinetics of the nitric acid formation reaction and the design of the reduction equipment. Here, NOx emissions contain nitrogen monoxide (NO), dinitric trioxide (N_2O_3), nitrogen dioxide (N_2O), and dinitric tetroxide (N_2O_4). Emissions are mostly expressed as NO_2.

The design of the absorption process in a nitric acid plant is decisive for NOx emissions. The process parameters of influence are for example pressure, temperature, the design of the reaction chamber, the (low) solubility of nitrogen monoxide in water or nitric acid, the efficiency of the absorption column etc. NOx emissions may increase when there is for example an insufficient air supply to the oxidiser and absorber, low pressure (especially in the absorber), or high temperatures in the cooler condenser and absorber. NOx emissions can also increase due to operation at high throughput rates or faulty equipment, such as compressors or pumps which lead to lower pressures or leaks and thus decreasing plant efficiency. /1, 3/

Comparatively small amounts of nitrogen oxides are lost from acid concentrating plants. These losses (mostly NO_2) originate from the condenser system, but the emissions are small enough to be easily controlled by absorbers. Acid mist emissions do not occur from the tail gas of a properly operated plant. The small amounts that may be present in the absorber exit gas streams are removed by a separator or collector before entering the catalytic reduction unit or expander. The acid production system and storage tanks are the only significant sources of visible emissions at most nitric acid plants. Emissions from acid storage tanks may occur during tank filling. /1/

A very high contribution to total emissions of nitrous oxide (N_2O) from nitric acid plants has been reported within the CORINAIR90 inventory (see Table 1). This high relevance of N_2O emissions has not yet been reported in the literature (except CORINAIR90).

3.5 Controls

Control measures are an integral part of the production process of nitric acid (see section 3.3.3). Control measures are e.g. the treatment of the waste gas with sodium hydroxide, non-selective catalytical purification (SNCR), selective catalytical purification (SCR) or the use of molecular sieves.

4 SIMPLER METHODOLOGY

For nitric acid plants only a simpler methodology is given; a detailed methodology is not proposed (see section 5). Here “simpler methodology” refers to the calculation of emissions based on emission factors and activities. The simpler methodology covers the relevant pollutants NOx, N_2O and NH_3.

The annual emission is determined by an activity and an emission factor:

$$E_i = EF_i \cdot A \qquad (1)$$

E_i	annual emission of pollutant i
EF_i	emission factor of pollutant i
A	activity rate

The activity rate A and the emission factor EFi have to be determined on the same level of aggregation by using statistical data (e.g. production of nitric acid, see Section 6).

Emission factors are given in Table 2 (section 8) based on literature data.

5 DETAILED METHODOLOGY

A detailed methodology is not proposed, due to the low relevance of emissions from nitric acid production compared to the total anthropogenic emissions (see section 2). Emission measurement appears to be not necessary for inventory purposes.

6 RELEVANT ACTIVITY STATISTICS

The activity rate according to CORINAIR90 should be reported in mass product/year [Mg/a]. The total production of nitric acid can be derived directly from statistics available on a European level. For point sources, individual data from national sources (e.g. association of chemical industries) should be used.

The following statistics contain data concerning the production of nitric acid:

- United Nations (ed.): Industrial Statistics Yearbook 1991; Volume I: Commodity Production Statistics; New York 1993; ISIC 3511-49 (production of nitric acid)

The following statistics on a European level contain only economic variables, such as the number of enterprises, number of employees, turnover, for the “Manufacture of basic industrial chemicals and manufacture followed by further processing of such products”:

- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992,
- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1994.

7 POINT SOURCE CRITERIA

According to the CORINAIR90 methodology, nitric acid plants have to be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 2 contains emission factors for relevant pollutants based on literature data. Nitrogen emission factors vary considerably depending on the type of control equipment and the process conditions.

Table 2: Emission factors for nitric acid production (expressed in 100% acid)

Type of process	Emission factors in mass/mass 100 % acid [g/Mg]					
	NO_x[1]		N_2O[9]		NH_3	
	range	value	range	value	range	value
Low pressure	10,000 - 20,000[2][5][6] 3,600 - 8,600[3]	12,000[2][5][6] 3,500[3]		800[2][7]		
Medium pressure	5,000 - 12,000[2][5][6]	7,500[2][5][6]		800[2][7]		
High pressure	1,500 - 5,000[2][5][6]	3,000[2][5][6]		800[2][7]		
Direct strong acid process	100 - 1,000[2]	5,000[3]				
No specification	664-75,000[8]		1,000-79,000[8]		1- 5.000[8]	10[8]

[1] no specification into NO, NO_2, etc. has been reported

[2] CORINAIR /2/; data are from French and W.-German plants

[3] EPA data /1/

[4] Swedish data /4/

[5] Control by catalytic reduction: range 10 - 800 g/Mg; value 400 g/Mg

[6] Control by extended absorption: range 400 - 1,400 g/Mg; value 900 g/Mg

[7] French value as used for the "taxe parafiscale"; not further specified as low, medium or high pressure process

[8] CORINAIR90 data

[9] Emission measurements from the so called DuPont Process have led to emission factor ranges of 2 - 9 g N_2O/kg HNO3 /7/.

9 SPECIES PROFILES

The NO_x emissions ("nitrous gases") contain a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2), dinitric oxide (N_2O_3) and dinitric tetroxide (N_2O_4). Emissions of N_2O have to be reported separately (see also section 3.4).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors. Technic specific emission factors are provided in Table 2. CORINAIR90 data can only be used in order to give a range of emission factors. Further work should be invested in the analysis of measured data in order to decrease the range of emission factors given or to provide a further split of emission factors.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) provides a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from nitric acid plants can be obtained by taking into account the time of operation of different process types (see table 2).

However, data for the annual time of operation should take into account, that nitric acid plants produce during the whole year, and that the production of nitric acid is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on "Concepts for Emission Inventory Verification" different verification procedures can be recommended. Verification procedures considered here are principally based on the verification of emission data on a national level and on a plant level. Verification on a plant level takes into account e.g. the number of nitric acid plants considered and relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

Emission data for the nitric acid production can be verified on national level by comparing annual emissions related to the territorial unit to independently derived emission estimates (e.g. obtained by using population equivalents).

17 REFERENCES

/1/ US-EPA (ed.): Compilation of Air Pollutant Emission Factors, Vol. 1: Stationary Point and Area Sources; 1986; AIR CHIEF Version 2.0 Beta; 1992

/2/ CITEPA (ed.): CORINAIR - Emission Factor Handbook, part 1: Default Emission Factors from stationary sources; 1992

/3/ Verein Deutscher Ingenieure (ed.): Emission Control Nitric Acid Production; Nr. 2295; Düsseldorf (Germany); 1983

/4/ Ms. Froste; Mr. Kvist; Ms. Haclund: personal communication; February 1995 (Swedish EPA)

/5/ Parker, Albert: Industrial Air Pollution Handbook; London; 1978

/6/ Schön, M.; Walz, R.: Emissionen der Treibhausgase Distickstoffoxid und Methan in Deutschland; Umweltbundesamt (Hrsg.); Berlin, 1993

/7/ Olivier, J. G. J.: Nitrous oxide emissions from industrial processes; in: Methane and Nitrous Oxide - Methods in National Emission Inventories and Options for Control; Proceedings of an international IPCC Workshop; Amersfoort (The Netherlands); 3-5 February 1993

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 2.1

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Source : Otto Rentz, Dagmar Oertel
University of Karlsruhe

Updated with particulate matter details by:
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20 POINT OF ENQUIRY

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SOURCE ACTIVITY TITLE: PROCESSES IN INORGANIC CHEMICAL INDUSTRIES

ACTIVITY	SNAP CODE	NOSE CODE	NFR CODE
Ammonia	**040403**	**105.09.01**	**2 B 1**
Ammonium Sulphate	**040404**	**105.09.22**	**2 B 5**
Ammonium Nitrate	**040405**	**105.09.23**	**2 B 5**
Ammonium Phosphate	**040406**	**105.09.24**	**2 B 5**
NPK Fertilisers	**040407**	**105.09.25**	**2 B 5**
Urea	**040408**	**105.09.27**	**2 B 5**
Carbon Black	**040409**	**105.09.41**	**2 B 5**
Titanium Dioxide	**040410**	**105.09.36**	**2 B 5**
Graphite	**040411**	**105.09.42**	**2 B 5**
Calcium Carbide Production	**040412**	**105.09.43**	**2 B 4**
Chlorine Production	**040413**	**105.09.02**	**2 B 5**
Phosphate Fertilisers	**040414**	**105.09.26**	**2 B 5**
Storage & Handling of Inorganic Chemical Products	**040415**	**105.09.49**	**2 B 5**
Other	**040416**	**105.09.48**	**2 B 5**

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Updated with particulate matter details by:
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Leaders of the Combustion and Industry Expert Panel

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SNAP CODE: **040501**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Ethylene

NOSE CODE: **105.09.50**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Ethylene is produced by thermal cracking of nafta fractions.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of ethylene plants according to Corinair 90 were 0.00 to 0.06% to the total NMVOC emission in the reporting countries.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Ethylene	040501	0	0	0.3	0	0	0.1	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

(This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006)).[1]

3 GENERAL

3.1 Description

The feed is preheated in heat exchangers and brought to the reaction temperature of 750 - 850° Celsius by adding hot products and steam to the reaction furnace. Additional steam isadded to dilute the reaction mixture. The residence time is kept short (about 0.1 sec.) to limit side reactions (coke formation).

After the reaction the gas mixture is quenched with cold oil, which in turn is used to produce steam. The oil gas steam mixture is separated in different fractions in a rectification section. In several steps the most important products of the mixture are separated. The low boiling products ethylene, propylene and the butylenes are separated after drying, compression and distillation.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

For many applications ethylene must not contain acetylene. The acetylene is removed from the ethylene by selective hydrogenation.

After separation from the reaction mixture, ethane and propane are recycled to the reaction furnace feed, methane is used as fuel gas and hydrogen is used for hydrogenation (of acetylene).

The C-4 mixture is used as feed for the butadiene production.

The typical feed (ethane to heavy petroleum distillates) results in a production of about 36% ethylene, 13% propylene, 8% butylenes and 7% aromatics.

3.2 Definitions

Not relevant.

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are CO2, NOx, CO and hydrocarbons. The first three compounds are produced during the combustion of fuel gases in the reaction furnace, the hydrocarbons are mostly emitted by leakage and flaring of the residual gases.

For the Netherlands all cracking processes together produced in 1986 4000 tons of VOCs per year. Ethylene production is estimated by a proportional share, being 36% of the total VOC emission. This emission, 1440 ton, is related to a production capacity of about 2700 kton ethylene per year and a realized production of about 2400 kton ethylene per year.

Emissions can be subdivided as follows:

Emission source	**[1]**	**[2]**
leakage losses from appendages, pumps, etc.	72%	75%
flaring, disruptions	18%	5%
losses due to storage and handling	1%	13%
combustion emissions	5%	<1%
other process emissions	4%	7%

About 73% of the VOC emissions can be considered as production independent (leakage etc. plus losses due to storage etc), but process operation time dependant (i.e. production capacity dependant). The other 27% is production dependant.

In a Canadian report [3] a subdivision specific for the emission from ethylene plants is given:

Process	51%
Fugitive	46%
storage and loading	1%
Spills	1%

3.5 Controls

The losses due to leakage can be limited by use of better seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an default emission factor for ethylene production emissions where the amount of emitted VOC is directly related to the ethylene production. For the Netherlands, 4000 ton VOC emission related to the thermal cracking activity, 36% ethylene in the thermal cracking product, and 2400 kton ethylene produced this would give an overall emission factor of 0.6 ton VOC/kton ethylene produced.

5 DETAILED METHODOLOGY

A more detailed method would be using emission factors for each piece of equipment, such as valves, flanges, etc. This way a total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. Hence, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

In a Canadian study [3] the use of this methodology instead of the simpler one resulted in a considerably lower estimate of the process emissions.

6 RELEVANT ACTIVITY STATISTICS

Relevant statistics are the production capacity for ethylene and the realised ethylene production. Table 6.1 lists ethylene capacity and Table 6.2 production in several countries and regions (note that the countries statistics may not add up to the regional figures, since various sources of information have been compiled).

Table 6.1.: Ethylene capacities for some countries and regions for 1990

Country/Region	ktons/y	Source
China	1928	ChemWeek 12/2/92
Korea, South	1155	ChemWeek 12/2/92
Japan	5976	ChemWeek 12/2/92
Taiwan	845	ChemWeek 12/2/92
Thailand	315	ChemWeek 12/2/92
Africa + Middle East	3500	EurChemNews 23/3/92
Asia/Pacific	10900	EurChemNews 23/3/92
Eastern Europe	7900	EurChemNews 23/3/92
South America	3200	EurChemNews 23/3/92
USA + Canada	22000	EurChemNews 23/3/92
Western Europe	16500	EurChemNews 23/3/92

Table 6.2.: Ethylene production for some countries and regions for 1990

Country/Region	ktons/y	Source
Australia	1054	Chem&EngNews 29/6/92
Canada	2434	Chem&EngNews 29/6/92
China	1572	Chem&EngNews 29/6/92
Czechoslovakia	619	Chem&EngNews 29/6/92
France	2246	Chem&EngNews 29/6/92
Germany, West	3075	Chem&EngNews 29/6/92
Hungary	234	Chem&EngNews 29/6/92
Japan	5810	Chem&EngNews 29/6/92
Poland	308	Chem&EngNews 29/6/92
Romania	243	Chem&EngNews 29/6/92
Taiwan	776	Chem&EngNews 29/6/92
U.K.	1496	Chem&EngNews 29/6/92
U.S.A.	16556	Chem&EngNews 29/6/92
U.S.S.R.	3065	Chem&EngNews 13/4/92
Western Europe	14400	EurChemNews 27/4/92
Western Europe	12223	UN Statistics 1990

Table 6.3 Ethylene production in 2004 in kiloton/year (International Petrochemical Information Forum)

	Asia	Western Europe	North America	South America
Ethylene	18.406	21.408	31.772	3.723

7 POINT SOURCE CRITERIA

Ethylene production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

As stated in section 4, an overall VOC emission factor for the ethylene production in the Netherlands is 0.6 ton VOC per kton ethylene produced.
An example of a more detailed emission factor calculation is given below:

Based on the data presented in section 3.4 and an ethylene percentage of 36 of the product from the typical feed (sections 1, 3.1) the emission factor of VOC for the ethylene production (without taking notice of other products) can be estimated in more detail as follows:

1 0.389 ton VOC/kton ethylene production capacity (leakage and losses)

Namely, 0.36 * 0.73 * 4000 ton VOC per 2700 kton ethylene production capacity for leakages and losses during handling and storage (together 73% of emissions).

2 0.162 ton VOC/kton ethylene produced (combustion, flaring, other processes)

Namely, 0.36 * 0.27 * 4000 ton VOC per 2400 kton ethylene produced
Part of these emissions is already dealt with under other SNAP codes (combustion and flaring): 0.138 ton VOC/kton ethylene produced : 0.36 * (0.18 + 0.05) * 4000/2400.

In Table 8.1 emission factors used in different countries are presented.

Table 8.1.: Emission factors for ethylene

Source	Factor (kg/ton)	Quality Code
Information from ethylene plant 1987 [4]	2 (new plant)	C
Information from ethylene plant 1987 [4] Handbook of emissionfactors (1983) (8)	5 (old plant) 2 -3.5	C C
Internal report from US origin [5]	10[1]	C/D
Environment Canada [3]	0.9, 1.8, 5.1, 8.2	D
Borealis AB [2]	2 - 7	C

[1] with an estimated capacity of 200 kton/y

The World Bank Handbook (ref 7) gives as emissions from a naphtha cracker 0.6 to 10 kilograms per metric ton of ethylene produced, depending on the quality of the abatement methods applied. These figures are consistent with the figures from the Netherlands

9 SPECIES PROFILES

Table 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: Composition of the VOC emissions for different sources [1]:

	methane	ethylene	propylene	Benzene	others HC's
leakage loss	70%	5%	3%	1%	21%
flaring and disruptions	10%	40%	25%	1%	24%
storage and handling loss	0%	0%	0%	1%	99%
Combustion	75%	10%	0%	1%	14%
other process emissions	70%	5%	3%	1%	21%

Table 9.2: Overall VOC emission profile for ethylene plants

	TNO ER [1]	EPA [6]
Methane	58.8%	12.5%
Ethane	-	37.8%
Ethylene	11.5%	-
Propane	-	23.9%
Propylene	6.8%	-
n-butane	-	15.0%
n-pentane	-	8.1%
Benzene	1.0%	2.1%
Toluene	-	0.5%
Methanol	-	0.3%
other HC's	22.0%	-

The World Bank Handbook (1998) gives 75% of alkanes, 20 % of unsaturates hydrocarbons (half of them ethylene) and 5 % aromatics.

10 UNCERTAINTY ESTIMATES

As the data on which the proposed emission factors are based are rather old they should only be used as default factors with the appropriate uncertainty.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

- The emission factors given are mainly based on internal information gathered by TNO during the emission inventory in the Netherlands. Comparison with data from other countries should improve the quality. The probably newer world bank data are consistent with these data.
- These data assume an average feed and an average composition of the production process in which a wide range of other commodities are produced in addition to ethylene.
- The leakage losses are estimated with emissions factors used for the chemical industry as a whole. No subdivision within the chemical industry is made.
- The flaring emission is based on an assumed combustion percentage. The measurement of the amount of gas flared is inaccurate and in most cases only roughly estimated.
- One factor is used for all countries. It would be more accurate to use a different factor for each country or each group of countries.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The ethylene plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

Detailed reports from USEPA and UNECE on refinery processes.

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Communication from ethylene producing company in the Netherlands (1992).

2 Borealis AB, Sweden, personal communication 1995.
3 Environment Canada: Emissions of Volatile Organic Compounds from selected organic chemical plants, B.H. Levelton & Associates Ltd., 1990.
4 Communication from ethylene producing company in the Netherlands (1987).
5 Internal report of an ethylene producing company from American origin.
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- International petrochemical information forum: 2004 Western European market review

19 RELEASE VERSION, DATE AND SOURCE

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TNO
The Netherlands

Update by:
P.F.J. van der Most

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SNAP CODE: **040502**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)** ***Propylene***

NOSE CODE: **105.09.51**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Propylene is produced by thermal cracking of nafta fractions.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of propylene plants according to Corinair 90 were in 1990 0.01% of the total NMVOC emission in the reporting countries.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Propylene	040502	-	-	0.2	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

3 GENERAL

3.1 Description

The feed is preheated in heat exchangers and brought to the reaction temperature of 750 - 850° Celsius by adding hot products and steam to the reaction furnace. Additional steam is added to dilute the reaction mixture. The residence time is kept short (about 0.1 sec.) to limit side reactions (cokes formation).

After the reaction the gas mixture is quenched with cold oil, which in turn is used to produce steam. The oil gas steam mixture is separated in different fractions in a rectification section. In several steps the most important products of the mixture are separated. The low boiling

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

products ethylene, propylene and the butylenes are separated after drying, compression and distillation.

After separation from the reaction mixture, ethane and propane are recycled to the reaction furnace feed, methane is used as fuel gas and hydrogen is used for hydrogenation (of acetylene).

The C-4 mixture is used as feed for the butadiene production.

The typical feed (ethane to heavy petroleum distillates) results in a production of about 36% ethylene, 13% propylene, 8% butylenes and 7% aromatics.

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to the air are CO2, NOx, CO and hydrocarbons. The first three compounds are produced during the combustion of fuel gases in the reaction furnace, the hydrocarbons are mostly emitted due to leakage and flaring of the residual gases.

For the Netherlands all cracking processes together produce 4000 ton of VOC's per year. Propylene production is estimated by a proportional share, being 13%, of the total VOC emission. This emission, 520 ton, is related to a production capacity of about 975 kton propylene per year and a realized production of about 870 kton propylene per year.

Emissions can be subdivided as follows [1]:

leakage losses from appendages, pumps, etc.	72%
flaring, disruptions	18%
losses due to storage and handling	1%
combustion emissions	5%
other process emissions	4%

About 73% of the VOC emissions can be considered as production independent (leakage etc. plus losses due to storage etc.), but process operation time dependant (i.e. production capacity dependant). The other 27% is production dependant.

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of a default emission factor for the propylene production emissions. The amount of emitted VOC is directly related to the propylene production. For the Netherlands, 4000 ton VOC emission related to the thermal cracking activity, 13% propylene in the thermal cracking product, and 870 kton propylene produced this gives a default emission factor of 0.6 ton VOC/kton propylene produced. .

5 DETAILED METHODOLOGY

A more detailed methodology would be using emission factors for each piece of equipment, like valves, flanges, etc.The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of that type of equipment. So, for this method it is necessary to know how many valves etc are present in the plant.

In a Canadian study [2] the use of this methodology instead of the simpler one resulted in a considerably lower estimate of the process emissions.

6 RELEVANT ACTIVITY STATISTICS

Relevant statistics are the production capacity for propylene and the realized propylene production. Table 6.1 lists propylene capacity and Table 6.2 propylene production in several countries and regions.

Table 6.1: Propylene capacity in some regions for 1990 or 1991

Region	ktons/y	source	year
Western Europe	9400	EurChemNews 27/4/92	1990
World	36600	EurChemNews 27/4/92	1991

Table 6.2: Propylene production in some countries and regions for 1990

Country/Region	ktons/y	source
Australia	608	Chem&EngNews 29/6/92
Canada	765	Chem&EngNews 29/6/92
France	1433	Chem&EngNews 29/6/92
Germany, West	1829	Chem&EngNews 29/6/92
Japan	4215	Chem&EngNews 29/6/92
Taiwan	398	Chem&EngNews 29/6/92
U.K.	750	Chem&EngNews 29/6/92
U.S.A.	9918	Chem&EngNews 29/6/92
U.S.S.R.	1366	Chem&EngNews 13/4/92
Western Europe	8800	EurChemNews 27/4/92
Western Europe	6880	UN Statistics 1990

Table 6.3: Propylene production in 2004 (according to the 2004 World Petrochemical Production Report)

	Asia	Western Europe	North America	South America
Propylene	12.969	15.123	16.711	1.852

7 POINT SOURCE CRITERIA

Propylene plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

As stated in section 4, an overall VOC emission factor for the propylene production in the Netherlands is 0.6 ton VOC per kton propylene produced.

Based on the data presented in section 3.4 and an propylene percentage of 13 of the product from the average feed (sections 1, 3.1) the emission factor of VOC for the propylene production (without taking notice of the other products) can be estimated in more detail as follows:

1 0.389 ton VOC/kton propylene production capacity (leakage and losses).
Namely, 0.13 * 0.73 * 4000 ton VOC per 975 kton propylene production capacity for leakages and losses during handling and storage (together 73% of emissions).

2 0.162 ton VOC/kton propylene produced (combustion, flaring, other processes).
Namely, 0.13 * 0.27 * 4000 ton VOC per 870 kton propylene produced.

Part of these emissions are already dealt with under other SNAP codes (combustion and flaring): 0.138 ton VOC/kton propylene produced.
Namely, 0.13 * (0.18 + 0.05) * 4000/870.

For propylene the same emission factors are used as for ethylene (see ethylene for other factors) except in the 1985 NAPAP Emission Inventory (0.45 kg/ton for propylene and 0.40 for ethylene). Following this approach the World Bank report (1998) would give 0.6 to 10 kilograms per metric ton propylene produced, depending on the quality of the abatement methods applied.

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1.: The composition of the VOC emissions for the different sources is [2] :

	methane	ethylene	propylene	benzene	others HC's
leakage loss	70%	5%	3%	1%	21%
flaring and disruptions	10%	40%	25%	1%	24%
storage and handling loss	0%	0%	0%	1%	99%
combustion	75%	10%	0%	1%	14%
other process emissions	70%	5%	3%	1%	21%

Table 9.2.: The overall VOC emission profile for plants

	TNO ER [2]
Methane	58.8%
Ethylene	11.5%
Propylene	6.8%
Benzene	1.0%
other HC's	22.0%

10 UNCERTAINTY ESTIMATES

The data on which the proposed emission factors are based are rather old. They should only be used as default factors with the appropriate uncertainty.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

- The emission factors given are mainly based on internal information of producers gathered by TNO during the emission inventory in the Netherlands. Comparison with data from other countries should improve the quality.
- These data so far assume an average feed and an average composition of the production process in which besides propylene also a wide range of other commodities are produced.
- The leakage losses are estimated with emissions factors used for the chemical industry as a whole. No subdivision within the chemical industry is made.
- The flaring emission is based on an assumed combustion percentage. The measurement of the amount of gas flared is inaccurate and in most cases only roughly estimated..
- One factor is used for all countries. It would be more accurate to use a different factor for each country or each group of countries.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The propylene plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

Detailed reports on refinery processes can be found on the sites of for instance USEPA and UNECE.

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Communication with propylene producing company in the Netherlands (1992).
2 Emissions of Volatile Organic Compounds from selected organic chemical plants, B.H. Levelton & Associates Ltd., 1990.

3. World Bank group Pollution prevention and abatement Handbook Petrochemicals Page 371 and 372 (1998)

18 BIBLIOGRAPHY

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- Winnacker-Küchler, Chemische Technologie, Organische Technologie I, Band 5, 4. Auflage (1982) (in German).
- International Petrochemical Information Forum : 2004 World Petrochemical Production Report

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.3

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Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
TNO
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Update by:
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SOURCE ACTIVITY TITLE: PROCESSES IN ORGANIC CHEMICAL INDUSTRIAL (BULK PRODUCTION)

ACTIVITY	SNAP CODE	NOSE CODE	NFR CODE
1,2 dichloroethane (Except 040505)	**040503**	**105.09.57**	**2 B 5**
Ethylene Oxide	**040516**	**105.09.74**	**2 B 5**
Formaldehyde	**040517**	**105.09.70**	**2 B 5**
Storage & Handling of Organic Chemical Products	**040522**	**105.09.99**	**2 B 5**
Glyoxylic Acid	**040523**	**105.09.73**	**2 B 5**
Halogenated Hydrocarbons Production	**040524**		**2 B 5**
Pesticide Production	**040525**	**105.09.95**	**2 B 5**
Production of Persistent Organic Compounds	**040526**	**105.09.79**	**2 B 5**
Other (Phytosanitary...)	**040527**	**105.09.96**	**2 B 5**

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Updated with particulate matter details by:
Mike Woodfield
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Leaders of the Combustion and Industry Expert Panel

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SNAP CODE: **040504**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Vinylchloride

NOSE CODE: **105.09.58**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Most vinylchloride is produced in the balanced process (see chapter B455). An alternative route is the addition of HCl to acetylene.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of vinylchloride plants contribute according to Corinair 90 on average 0.02% to the total NMVOC emission in the reporting countries.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Vinylchloride	040504	-	-	0	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

3 GENERAL

3.1 Description

HCl and an acetylene containing mixture are fed to a reactor containing Hg_2Cl_2 on carbon as catalyst. Reactor operation conditions are: T: 150 - 180°C; p: 500 - 1500 kPa.

Mixtures of acetylene and ethylene can be fed to the reactor, since ethylene does not react under the operation conditions used.

3.2 Definitions

Not relevant

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

3.3 Techniques

See section 3.1

3.4 Emissions

Emissions from a vinylchloride plant are mainly NMVOC.

3.5 Controls

The fugitive emissions can be abated by use for instance by better types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the vinylchloride production emissions. The amount of emitted VOC is then directly related to the vinylchloride production.
The World Bank handbook gives some figures for that.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1.: Vinylchloride production in some countries and regions for 1990 :

Country or Region	kton/y	source
U.S.A.	4826	Chem&EngNews 29/6/92

7 POINT SOURCE CRITERIA

Vinylchloride production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The World Bank Handbook gives an emission factor of 0.02 – 2.5 kg per metric ton product, depending on the quality of the abatement methods applied. The quality code might be B or C.

9 SPECIES PROFILE

According to the World Bank Handbook the VOC emissions from vynylchloride production should be 45 % ethylenedichloride , 20 % vinylchloride , and 15 % other chlorinated hydrocarbons and 20 % other hydrocarbons.

10 UNCERTAINTY ESTIMATES

The emission factors given should be used as default values with the appropriate accuracy.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

No supplementary documents

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1. World Bank group. Pollution Prevention and Abatement Handbook. Petrochemicals manufacturing Page 371 and 372 (1998)

18 BIBLIOGRAPHY

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 23, third edition (1983).
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

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Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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Update by:
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SNAP CODE: **040505**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
1,2 Dichloroethane + Vinylchloride (Balanced Process)

NOSE CODE: **105.09.59**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

This main process used for vinylchloride production is the balanced process. This is the only process for which emissionfactors have been found sofar..

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of vinylchloride plants contribute in 1990 according to Corinair 90 on average 0.02% to the total NMVOC emission in the reporting countries.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
1,2 Dichloroeth. + Vinylchl. (balanced process)	040505	-	-	0.02	-	-	-	-	-

- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

3 GENERAL

3.1 Description

The balanced process is described in great detail on the sites of USEPA and some companies.A short description is given below..

The balanced process consists of two routes operated simultaneously; in the direct chlorination route, chlorine is added to ethylene to form 1,2-dichloroethane; in the oxychlorination route, ethylene reacts with hydrogen chloride under oxidative conditions (presence of oxygen) also to form 1,2-dichloroethane. The reaction equations are:

direct chlorination: $CH_2{=}CH_2 + Cl_2$ ® CH_2ClCH_2Cl

---

[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

oxychlorination: $CH_2{=}CH_2 + 2\ HCl + \frac{1}{2}\ O_2$ ® $CH_2ClCH_2Cl + H_2O$
1,2-dichloroethane: $2\ CH_2ClCH_2Cl$ ® $2\ CH_2{=}CHCl + 2\ HCl$

overall: $2\ CH_2{=}CH_2 + Cl_2 + \frac{1}{2}\ O_2$ ® $2\ CH_2{=}CHCl + H_2O$

- Direct chlorination:
  Ethylene and chlorine are dissolved in 1,2-dichloroethane with $FeCl_3$. The reaction is limited by ethylene absorption. The selectivity to 1,2-dichloroethane is >99%.. The formation of 1,1,2-trichloroethane by-product is suppressed by using oxygen or DMF as inhibitor.

  The reactor can be operated in two ways:
  - reactor temperature 50 - 65 °C; after the reactor the 1,2-dichloroethane is washed with water to remove $FeCl_3$ or the $FeCl_3$ is adsorbed on a solid, e.g. activated carbon.

  - reactor temperature is equal to the boiling temperature of 1,2-dichloroethane; the evaporation of 1,2-dichloroethane removes the heat of reaction from the reactor. The reactor effluent, crude 1,2-dichloroethane, contains no $FeCl_3$, so no washing is needed.

- Oxychlorination:
  This is a vapour phase process using $CuCl_2$ with additives on porous support, e.g. alumina, as catalyst. Both dry air and dry oxygen are in use. The use of pure oxygen has the advantage of reducing purge streams and it allows the use of reduced (reaction) temperatures. Good temperature control is necessary because the reaction is highly exothermic.

  Operation conditions for fluid beds are: T: 220 - 235 °C; p: 250 - 600 kPa.
  Operation conditions for fixed beds are: T: 230 - 300 °C; p: 250 - 1500 kPa.
  1,2-Dichloroethane selectivity is 93 - 96%.

  The 1,2-dichloroethane is quenched with water or cooled with a heat exchanger, so the 1,2-dichloroethane and water in the effluent are condensed. The 1,2-dichloroethane and water are separated by a decantation. The remaining gas (containing 1 - 5% 1,2-dichloroethane) is further processed to recover all 1,2-dichloroethane.

  1,2-Dichloroethane of both routes is sent to a purification section, where light and heavy impurities are removed.

The purified 1,2-dichloroethane is fed to a reactor where it is pyrolyzed to form vinylchloride. Operation conditions are: T: 500 - 550 °C; p: up to 2500 - 3000 kPa.

A 1,2-dichloroethane conversion of 50 - 60% per pass is used.

After cracking, rapid cooling is required to suppress by-product formation. This is done by contacting the effluent, with cold 1,2-dichloroethane. From the quench tower effluent first the hydrogen chloride and then the vinylchloride is removed. The hydrogen chloride is recycled to the oxychlorination reactor. The unreacted 1,2-dichloroethane is purified and recycled. All waste streams contain chlorinated compounds. From the fluid waste streams useful by-products can be recovered. The remaining waste streams can be vented or first incinerated or catalyticly oxidated and then vented. The oxidation product stream containing hydrogen chloride can be recycled to the oxychlorination reactor (where the hydrogen chloride reacts with ethylene).

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: 1,2-dichloroethane, vinylchloride, and other chlorinated hydrocarbons. The sources are mainly fugitive sources..

The VOC emission can be subdivided as follows:

Emission source	**[1]**
leakage losses from appendages, pumps, etc.	91%
flaring, disruptions	0%
losses due to storage and handling	4%
combustion emissions	2%
other process emissions	3%

3.5 Controls

The losses due to fugitive sources leakage can be limited by use of for instance more sophisticated types of seals

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the production emissions. The amount of emitted VOC is then directly related to the production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA:

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each

equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1: Vinylchloride production in the USA in 1990 :

Country	kton/y	source
U.S.A.	4826	Chem&EngNews 29/6/92

7 POINT SOURCE CRITERIA

These plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Emission factors for 1.2 dichloroethane

In the criteria document for 1.2.dichloroethane (4) an emission factor of 10 kg/ton product is proposed based on data from 1981.

Table 8.2: Emission factors for vinylchloride (balanced process)

Source	factor (kg/ton)	Quality Code
Information from vinylchloride plant TNO 1992 [1]	0.76	C
Information from vinylchloride plant TNO 1987 [2]	2.2	C

The criteriadocument for vinylchloride (5) (1981) gives an emissionfactor of 4-5 kg/ton for uncontrolled emissions and 0.13 kg/ton for best available technology.
The Handbook of emissionfactors (6) gives 0.1-0.2 kg/ton for abated emissions.

The World Bank Handbook gives emission factors of 0.02- 2.5 kg VOC per metric ton product, depending on the applied abatement which are consistent with the factors for individual plants mentioned above..

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1.: The composition of the VOC emissions for the different sources is [1]:

	Methane	**Ethylene**	**1,2-dichloroethane**	**toluene**	**ClHC's**	**other HC's**
leakage loss	0%	9%	42%	0%	48%	1%
flaring and disruptions	-	-	-		-	-
storage and handling loss	0%	0%	96%	0%	4%	0%
combustion	60%	10%	0%	1%	0%	29%
other process emissions	0%	82%	10%	6%	0%	2%

Table 9.2: The overall VOC emission profile for plants

	TNO Emission inventory [1]
Methane	1.2%
Ethylene	10.9%
1,2-dichloroethane	42.3%
Toluene	0.2%
Other Chlorinated hydrocarbons	43.8%
Other hydrocarbons	1.6%

The World Bank Handbook (3) gives the following profile: 45% ethylene dichloride, 20% vinyl chloride 15 % other halogenated hydrocarbons , and 20 % other hydrocarbons

10 UNCERTAINTY ESTIMATES

The uncertainty depends on the information available about the applied abatement methods

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is present..

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

No supplementary documents

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.
See Verification Chapter for further details.

17 REFERENCES

1 Communication to TNO from vinylchloride producing plant in The Netherlands (1992.)
2 Communication to TNO from vinylchloride producing plant in The Netherlands (1987).
3 World Bank group Pollution Prevention and Abatement Handbook Petrochemicals Manufacturing Page 371 and 372 (1998)
4 Criteria document 1.2. dichloroethane . Reported by RIVM Nr……. Year 1983
5. Criteria document vinylchloride Reported by RIVM Nr …..Year 1983
6 Handbook of Emissionfactors Part 2 Industrial Sources Ministry of Housing, Spatial Planning and the Environment M.E.Reinders (editor)(1983)

18 BIBLIOGRAPHY

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 23 3rd edition (1983)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).
- USEPA Locating and estimating air emissions from sources of ethylenedichloride plants.

Report EPA 450/4-84-007

- Siemens AG Gas Analysis in VCM (Vinylchloride monomer)Production Plants

http://www.processanalytics.com

19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODES:	**040506** **040507**
SOURCE ACTIVITY TITLES:	**PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)** ***Polyethylene Low Density*** ***Polyethylene High Density***
NOSE CODE:	**105.09.80** **105.09.81**
NFR CODE:	**2 B 5**

1 ACTIVITIES INCLUDED

This section includes the manufacture of polyethylene. Three types are produced; low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE).

This section includes all emissions during the processing of chemical feed-stocks to produce polyethylene, including process and fugitive emissions. Emissions from storage of feed-stocks, intermediates and products are not included.

Note. ‘Polyethylene’ and ‘Polythene’ are synonymous and the terms may be used interchangeably.

2 CONTRIBUTION TO TOTAL EMISSIONS

The CORINAIR 1985 inventory gives emission estimates for LDPE and HDPE production (Eurostat, 1992). Emissions are total hydrocarbon. LDPE production typically represents 0 to 1% of a countries national emission of VOCs (including methane), whereas HDPE production typically represents 0 to 0.3%. No data are available for LLDPE production.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Polyethylene is a polymer of ethylene and has the general empirical formula $(-CH_2CH_2-)_n$. The manufacturing process used depends upon the type of polymer produced.

3.2 Definitions

LDPE is a tough waxy polymer, with approximately 2% branching between polymer chains and has a density of about $0.92 t/m^3$.

LLDPE is a crystalline polymer with no chain branching and a density comparable to that of LDPE.

HDPE is a crystalline polymer with no chain branching and a density of about 0.96t/m^3.

3.3 Techniques

LDPE
LDPE is generally produced by high pressure and high temperature catalytic polymerisation of ethylene in a tubular or autoclave reactor.

LLDPE
A low pressure method is generally used in which ethylene and a co-monomer such as butene or hexene are catalytically polymerised.

HDPE
HDPE is produced by low pressure polymerisation of ethylene in a reactor containing a liquid hydrocarbon diluent and in the presence of Ziegler catalysts. The polymer produces a slurry as it forms and is filtered from the solvent.

3.4 Emissions/Controls

The major emissions to air are NMVOC - un-reacted monomer (i.e. ethylene), some partially reacted monomer (alkenes and alkane) together with small amounts of additives.

NMVOCs are emitted primarily through leakages, and may be production time dependent rather than production dependent.

Control techniques are primarily through replacement of leaking valves etc, and regular maintenance.

4 SIMPLER METHODOLOGY

The simpler methodology relies on the use of an emission factor for each type of polyethylene production combined with national activity statistics.

5 DETAILED METHODOLOGY

The detailed methodology involves the use of several emission factors for different types of emission sources combined with activity statistics relating to individual plants.

The assessment of individual plants may be verified through measurements.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, the national annual production of each of the three types of polyethylene is required.

For the more detailed methodology, data on the throughput of individual plant is required.

7 POINT SOURCE CRITERIA

Polyethylene production is carried out at a limited number of sites throughout Europe (for example three production sites have been identified in the UK). These sites should therefore all be considered point sources, regardless of the size of the emission.

For the simpler methodology, if the production from each site is not known, then the national emission estimate may be proportioned according to the relative production capacities of each plant.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

Emission factors are in kgVOC/t polyethylene produced and are tabulated below:

Process	Emission factor	Quality Code	Reference
PE manufacture	2 kg/t (new plant)	D	UN ECE, 1990
	10 kg/t (old plant)	D	UN ECE, 1990
LDPE manufacture:	3 kg/t	D	UN ECE, 1990
	2 kg/t	D	ChemInform, 1993
LLDPE manufacture	2 kg/t	D	ChemInform, 1993
HDPE manufacture:	6.4 kg/t	D	UN ECE, 1990
	5 kg/t	D	ChemInform, 1993

8.2 Detailed Methodology

Emission factors for the detailed approach are based on the USEPA Protocol for Generating Unit Specific Emission Estimates for Equipment leaks of VOC and VHAP. For example one of the protocols involves the use of the Synthetic Organic Chemical Manufacturing Industry (SOCMI) average emission factor model. SOCMI factors are combined with component counts to give an overall fugitive emissions from a plant. The SOCMI average emission factor method does not involve on-site monitoring whereas the other approaches considered by the USEPA protocol do require on-site monitoring.

Further information may be obtained from the USEPA, Research Triangle Park, Rayleigh, North Carolina, United States.

9 SPECIES PROFILES

Species present will depend upon the process used and the stage of the process. No detailed speciation has been found. In the absence of further information, it may is assumed that the NMVOC emission is 100% ethene.

10 UNCERTAINTY ESTIMATES

For the simpler methodology, the range of emission factors between old and new plant and the relatively low data quality suggest that the potential uncertainty in emission estimates is large i.e more than factor 2.

For the detailed methodology, the uncertainty is not known. However in a study by Environment Canada, use of SOCMI average factors tended to give considerably higher emission estimates than were obtained using other more detailed methods in the USEPA protocol referred to above (Edwards 1990).

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect of the methodology is the use of general emission factors whose accuracy needs to be confirmed through measurement.

In addition the emission factors do not distinguish between methane and non methane VOCs. No speciated data appears to be available for the emission from these plants. Various organic compounds may be present including methane.

The priority areas for improvement are suitable measurement programme to assess emissions from whole plants and thus enable accurate comparison between the different methodologies used for estimating VOC emissions. Such a programme should also establish the speciated profile of emissions from polyethylene production plants.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

All sources should be considered point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

In the absence of better information, it may be assumed that Polyethylene production is carried out as a continuous process. No temporal variation is considered, except for shutdowns of plants for maintenance. Where available, monthly production statistics should be used to establish any possible temporal variations.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

USEPA Protocol for Generating Unit Specific Emission Estimates for Equipment Leaks of VOC and VHAP.

16 VERIFICATION PROCEDURES

Verification is through comparison with emission estimates from other countries together with a measurement programme for selected sites.

17 REFERENCES

Eurostat (Statistical Office of the European Communities), Environment Statistics, Luxembourg, 1992

UN ECE VOC Task-force, Emissions of Volatile Organic Compounds from Stationary Sources and Possibilities for their Control, July 1990

Edwards W.C., Quan R.G., Lee N.P., Emissions of Volatile Organic Compounds from Selected Organic Chemical Plants, Unpublished Report, Environment Canada, Industrial Programmes Branch, Ottawa. October 1990.

ChemInform, The Organic Chemical Industry and VOC Emissions, Unpublished report for Warren Spring Laboratory, March 1993. Available from AEA Technology, NETCEN, Culham Laboratory, Abingdon, Oxon, UK. OX14 3DB.

18 BIBLIOGRAPHY

Chemical Intelligence Services produce various publications relating to the chemical industry. Their address is: 39a Bowling Green Lane, London EC1R 0BJ.

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Updated with particulate matter details by:
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December 2006

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SNAP CODE: **040508**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Polyvinylchloride

NOSE CODE: **105.09.82**

NFR CODE: **2 B 5**

DRAFT REVISION 2006 Version 0.3

1 ACTIVITIES INCLUDED

Polyvinylchloride is made by polymerizing vinylchloride. Several processes are available: mass polymerisation (8%), emulsion polymerisation (12%) or suspension polymerization (80 %) .

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of polyvinylchloride plants contributed less than 0.01% to the total NMVOC emission in the reporting countries.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Polyvinylchloride	040508	-	-	0.1	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

3 GENERAL

3.1 Description

The different processes are:

- Mass polymerization; a batch process.
  This is a two stage process. In the first stage, the liquid vinylchloride monomer with an initiator is prepolymerized for 1 - 1.5 hours until 7 - 10% monomer conversion is reached. The grains resulting from this stage function as skeleton seeds for growing in the second stage.

In the second stage, a mixture of the effluent from the first reactor, extra monomer and initiator are fed to an autoclave. The reaction is stopped as the pressure drops and no free liquid monomer is available; the free liquid monomer is needed for heat removal by a condensor. The unreacted monomer, adsorbed in the polymer grains, is removed by vacuum and recovered by vapor compression and condensation in a recycle condensor. The reaction temperature is 50 - 70 °C.

- Suspension polymerization; a batch process.
  Vinylchloride monomer is dispersed in water by agitation. Polymerization starts by adding monomer-soluble initiators and addition of suspension stabilizers and suspending agents minimizes coalescence of the grains. The reaction temperature is used for the control of the M_w and varies between 45 - 75 °C. Reactor pressure is between 800 - 1200 kPa. Reaction is carried out till 85% conversion is reached.

  After polymerization most unreacted monomer is recovered in a dump tank. The remaining monomer is stripped from the polymer with steam. The waste water is separated in a centrifugator. The PVC resin is dried with hot air and stored.

- Emulsion polymerization; batch, semi-continuous or continuous.
  Vinylchloride monomer is emulsified in water by means of surface-active agents. The monomer is thus present as droplets and a small fraction is dissolved in micelles. Water-soluble initiator is added and polymerization starts in the micelles. Monomer is added to the latex particles (=micelles) by diffusion from the emulsion droplets through the aqueous fase.

  Batch: all components in reactor; polymerization is stopped when the yield is reached.

  Semi-continuous: emulgator is continuously added during the polymerization.

  Continuous: water, initiator, monomer and emulgator are added at the top of the reactor. The PVC latex is removed at the bottom of the reactor. The latex is degassified and dried; the resulting solid PVC is stored.

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: vinylchloride and methane. Methane is emitted due to combustion and vinylchloride due to leakage and storage loss.

For the Netherlands, the VOC emission due to polyvinylchloride production is 55 ton/y. This emission is related to a production of 387 kton/y and a capacity of 409 kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Emission source	**[1]**
Leakage losses from appendages, pumps, etc.	94.4%
Flaring, disruptions	0 %
Losses due to storage and handling	5.5%
Combustion emissions	0.1%
Other process emissions	0 %

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

The simpler methodology involves the use of an overall emission factor for the PVC production to estimate total emissions. The amount of emitted VOC is thus directly related to the PVC production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1.: Polyvinylchloride capacity in some countries

Country or Region	**kton/y**	**source**	**year**
Latin America	1410	EurChemNews 13/4/92	1991
Indonesia	164	EurChemNews 1/6/92	1990?

Table 6.2.: Polyvinylchloride production in some countries and regions for 1990

Country or Region	kton/y	source
France	1028	Chem&EngNews 29/6/92
Germany, West	1323	Chem&EngNews 29/6/92
Italy	618	Chem&EngNews 29/6/92
U.K.	349	Chem&EngNews 29/6/92
Japan	2049	Chem&EngNews 29/6/92
Korea, South	541	Chem&EngNews 29/6/92
Taiwan	921	Chem&EngNews 29/6/92
U.S.S.R.	606	Chem&EngNews 13/4/92
Poland	199[1]	EurChemNews 9/12/91

1) Production in 1989

7 POINT SOURCE CRITERIA

PVC production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1.: Emission factors for Polyvinylchloride production :

Source	factor (kg/ton)	Quality Code
Communication to TNO 1992 [1]	0.14	C
Communication to TNO 1987 [2]	3 (emulsion)	C
Communication to TNO 1987 [2]	1.5 (suspension)	C
Environmental protection agency AP42 [3]	8.5	E

The handbook (6) gives emission factors of 2 to 20 kg/ton, depending on the process and the abatement. The criteria document (5) gives 4 kg/ton for uncontrolled emissions and o,7 kg/ton for best available technology. Older literature from Germany mentions for 1974 emissions of 40 to 50 kg /ton.

Table 8.2: AP 42 Particulate matter emission factor* for Polyvinylchloride (kg/Mg) [7]

Source	PM (kg/Mg)
Polyvinylchloride – controlled with fabric filter	17.5

* = In the absence of more appropriate data use the AP 42 emission factor[1]

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1.: The composition of the VOC emissions for the different sources is [1]:

	Methane	ethylene	vinylchloride	benzene	other HC's
Leakage loss	0%	0%	100%	0%	0%
Flaring and disruptions	-	-	-	-	-
Storage and handling loss	0%	0%	100%	0%	0%
Combustion	60%	10%	0%	1%	29%
Other process emissions	-	-	-	-	-

Table 9.2.: The overall VOC emission profile for polyvinylchloride plants

	TNO ER [1]	EPA [4]
Methane	0.1%	-
Ethylene	0%	-
Vinylchloride	99.9%	100%
Benzene	0%	-
Other HC's	0%	-

10 UNCERTAINTY ESTIMATES

As the emissions are mostly fugitives the accuracy depends on the degree of abatement applied.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Net relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 23, 3rd edition (1983)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Communication from PVC producing company to TNO (1992)
2 Communication from PVC producing company to TNO (1987)
3 US Environmental protection agency AP-42
4 US Environmental protection Agency Airchief 1991
5 Criteria document vinylchloride (1983)
6 Handbook of emissionfactors Part 2 Industrial sources Ministry of Housing, Spatial Planning and the Environment M.E.Reinders (editor)(1983)
7 US EPA (1996) Compilation of Air Pollutant Emission Factors Vol.1 Report AP-42 (5th ed.)

18 BIBLIOGRAPHY

No specific documents

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.3

Date : September 2006

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
TNO
The Netherlands

Update by:
P.F.J. van der Most

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SNAP CODE: **040509**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Polypropylene

NOSE CODE: **105.09.83**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Polypropylene is produced by polymerization of propylene. This can be done in several ways: all using a Ziegler-Natta catalyst. Most ways use a solvent, either propylene or hexane/heptane. In one process type the polymerization is operated in the gas-phase.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of polypropylene plants according to Corinair 90 were on average about 0.1% of the total NMVOC emission in a the reporting countries.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Polypropylene	040509	-	-	0.1	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
*** = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions**

3 GENERAL

3.1 Description

All processes use a Ziegler-Natta catalyst. A commonly used Ziegler-Natta catalyst is $Al(CH_2CH_3)_2Cl$ complexed with $TiCl_4$.
The different processes are:

- Gas-phase polymerization.
  The propylene is led through a reactor with catalyst. Liquid propylene is used for cooling (interstage cooling). Unreacted propylene is recovered and recycled. Reactor operation temperatures are 70 - 90°C.

- Solvent polymerization.

- solvent is propylene.
  Liquid propylene and catalyst are led into the reactor. After the reactor solid isotactic polypropylene is separated from the unreacted propylene, which contains dissolved atactic polypropylene and catalyst. The polypropylene is dried with nitrogen. The unreacted propylene is recovered and recycled. During the propylene recovery the atactic polypropylene is recovered as deposition.

  Reactor operation conditions are: T: 50 - 70°C; p: 2500 - 4000 kPa.

- solvent is hexane or/and heptane.
  Solvent, catalyst and propylene are added to the reactor. The reactor effluent is flashed to recover the unreacted propylene. Then the effluent is washed with alcohol to extract the catalyst and the alcohol phase and solvent phase are separated. The solid isotactic polypropylene is separated from the solvent in a centrifuge. The isotactic polypropylene is dried before storage. Reactor operation conditions are: T 50 - 90°C; p 500 - 1500 kPa.

  The solvent is recovered, during which the atactic polypropylene forms a slimy mass at the bottom of the apparatus. The atactic polypropylene can be recovered.

- The newest process (the Montedison-Mitsui high yield process) differs from the process described above in that a better catalyst with a higher yield is used, so less catalyst is needed. This has as advantage that no separate catalyst phase exists. After the flashing the effluent is split using a centrifuge in two fractions: one with solid isotactic polypropylene and `trapped’ solvent, the other with solvent and dissolved atactic polypropylene. The solvent from both fractions is recovered and recycled; the isotactic polypropylene is dried with nitrogen; the atactic polypropylene is also recovered.

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emission to air is: propylene.
For the Netherlands the VOC emission due to the polypropylene production was in 1992 304 ton/y. This emission can be related to a production of 353 kton/y and a capacity of 371 kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Emission source	[1]
Leakage losses from appendages, pumps, etc.	94 %
Flaring, disruptions	0.2%
Losses due to storage and handling	6 %
Combustion emissions	0 %
other process emissions	0 %

3.5 Controls

The losses due to fugitives can be limited by use of modern abatement methods.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the polypropylene production to estimate total emissions. The amount of emitted VOC is then directly related to the polypropylene production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1.: Polypropylene capacity in some countries

Country or Region	**kton/y**	**source**	**year**
Latin America	830	EurChemNews 13/4/92	1991
Indonesia	10	EurChemNews 1/6/92	1990?

Table 6.2.: Polypropylene production in some countries and regions for 1990

Country or Region	kton/y	source
France	779	Chem&EngNews 29/6/92
Germany, West	509	Chem&EngNews 29/6/92
U.K.	296	Chem&EngNews 29/6/92
U.S.A.	3773	Chem&EngNews 29/6/92
Japan	1942	Chem&EngNews 29/6/92
Korea, South	574	Chem&EngNews 29/6/92
Australia	19	Chem&EngNews 29/6/92
U.S.S.R.	127	Chem&EngNews 13/4/92

7 POINT SOURCE CRITERIA

Polypropylene production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for polypropylene

Source	factor (kg/ton)	Quality Code
Information from plant in the Netherlands1987 [2]	8 (5 - 12)	C
Information from plant in the Netherlands 1992 [1]	0.86	C
EPA 1989? [3]	0.35	E

The Emission factors Handbook (4) gives the following emissionfactors:

Table 8.2 Emissionfactors for polypropylene (1983)

Substance	emissionfactor
saturated hydrocarbons	5-10 kg/ton
propylene	0.5-1.5 kg/ton
polypropylene	0.1-0.2 kg/ton
butanol 2	0.1-0.2 kg/ton

Table 8.3 AP 42 Particulate matter emission factor* for polypropylene (kg/Mg) [5]

Source	**PM (kg/Mg)**
Polypropylene (uncontrolled)	1.5

* = In the absence of more appropriate data use the AP 42 emission factor[1]

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile for the different sources and the overall profile.

Table 9.1.: The composition of the VOC emissions for the different sources is [1]:

	propylene	**isobutanol**	**other HC's**
leakage loss	0%	4%	96%
flaring and disruptions	1%	0%	99%
storage and handling loss	0%	0%	100%
combustion	-	-	-
other process emissions	-	-	-

Table 9.2.: The overall VOC emission profile for polypropylene plants

	TNO ER [1]
methane	0%
ethylene	0%
isobutanol	3.8%
other hydrocarbons	96.2%[1]

[1] most likely all propylene.

10 UNCERTAINTY ESTIMATES

The uncertainty depends on the fit of the proposed default emission factors with the real process.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 16, 3rd edition (1981)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Communication to TNO from polypropylene producing plant 1992
2 Communication to TNO from polypropylene producing plant 1987
3 Environmental Protection Agency, AP-42
4. Handbook of Emissionfactors Part 2 Industrial Sources. Ministry of Housing, Spatial Planning and the Environment M.E.Reinders (editor) (1983)
5 US EPA (1996) Compilation of Air Pollutant Emission Factors Vol.1 Report AP-42 (5th ed.)

18 BIBLIOGRAPHY

The processes are extensively described on many sites for instance from the USEPA or the chemical industry.

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.3

Date : September 2006

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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Update by:
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SOURCE ACTIVITY TITLE: PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES

ACTIVITY	SNAP CODE	NOSE CODE	NFR CODE
Chipboard	**040601**	**105.06.02**	**2 D 1**
Lime (Decarbonizing)	**040614**	**105.11.26**	**2 A 2**
Batteries Manufacturing	**040615**	**105.13.01**	**2 A 7**
Extraction of Mineral Ores	**040616**	**105.02.01**	**2 A 7**
Other (Including Asbestos Products Manufacturing)	**040617**	**105.11.61**	**2 A 7**

A specific methodology for these activities has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

If you have information contrary to this please contact the expert panel leaders.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Updated with particulate matter details by:
Mike Woodfield
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December 2006

Leaders of the Combustion and Industry Expert Panel

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SNAP CODE: **040602**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK & OTHER INDUSTRIES**
Paper Pulp (Kraft Process)

NOSE CODE: **105.07.01**

NFR CODE: **2 D 1**

1 ACTIVITIES INCLUDED

Pulp and paper production has three major processing steps: pulping, bleaching, and paper production. The type of pulping and the amount of bleaching used depends on the nature of the feedstock and the desired qualities of the end product. Kraft (sulphate) pulping is one of the chemical pulping processes that can be used. It is the most widely used pulping process and is typically used to produce strong paper products. The Kraft pulping process includes wood digestion in a water solution of sodium sulphide and sodium hydroxide, pulp washing, bleaching, chemical recovery, and by-product recovery.

Not all Kraft pulping and related processes that could result in the emission of significant amounts of NMVOC, SO_x, particulates, NO_x and CO are included under SNAP code 040602. Other significant sources are listed in Table 1.

Table 1.1 Other Relevant SNAP Codes for Paper Pulping - Kraft Process

Source	SNAP CODE
Combustion in boilers	03 01 xx
Lime kilns	03 03 12
Paper-mill industry (drying processes)(paper machines)	03 03 21
Waste water treatment	09 01 xx

In addition to more conventional fuels such as wood/bark, coal, oil and natural gas, boilers at pulp and paper mills may combust non-condensable gases, wastewater treatment sludge (from both virgin pulp and recycle operations), non-recyclable recovered paper, tire-derived fuel, old corrugated container materials etc (NCASI 1993).

It is assumed that these non-conventional fuels that are combusted in boilers will be covered in SNAP group 03.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions inventoried from Kraft pulp and paper processes are summarized in Table 2.1 and 2.2 below.

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Table 2.1 Contribution to Total Emissions of the CORINAIR90 Inventory *(28 countries)*

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Paper Pulp	040602	0.1	0.1	0.1	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
= no emissions are reported

Table 2.2 1990 Emissions from Paper Pulping Kraft Process

Country	Particulate		PM 10		PM 2.5		Hg		Pb		Cd	
	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]
Canada[2] 1995	17901	1.5	12059	1.7	10013	2.3		0.01				
United States (1985)	112480						1.62[3]	1.1[4]				

Country	SO_x		NO_x		CO		NMVOC		PAH	
	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]
Canada[2] 1995	5473	0.2	11092	0.5	24726	0.3	2757	0.1		
United States (1985)	112480	0.2			557867	0.6				

[1] As a percentage of total anthropogenic emissions for given country.

[2] Percentage Excludes Open Sources: Road Dust, Forest Fires, Wind Erosion, Construction, Prescribed Burning.

[3] 1994 - 5: US EPA 1997, Locating and Estimating

[4] 1995: US EPA 1997, Report to Congress.

Sources contributing to Kraft pulping emissions of VOCs in Canada in 1990 are summarised in Table 2.3.

Table 2.3 Sources of VOCs in Paper Pulping in Canada (CPPA n.d.)

Source	Percent of Total Kraft Emissions	Percent Total Pulp and Paper
Recovery boiler stack	42	16
Digester relief and blow tank	31	12
Lime kiln stack	8	3
Multiple effect evaporators	6	2
Black liquor oxidation system	5	2
Washers and screen	4	2
Smelt dissolving tank vent	3	1
Fluid bed calciner	0.3	0.1

3 GENERAL

3.1 Description

In Kraft pulping, white liquor, a water solution of sodium sulphide and sodium hydroxide, is used under high temperature and pressure to chemically dissolve the lignin that binds the cellulose fibres of the wood together. After the wood chips are subjected to this digestion, the wood pulp is washed, screened and dried to unbleached pulp or further delignified in an oxygen stage and bleached in a bleach plant. The inclusion of a bleaching step depends upon the intended use of the product. The remainder of the Kraft processes are designed to recover chemicals and heat. The spent cooking liquor, containing process chemicals and water and spent chemicals from the wood, is combined with pulp wash water to form what is called black liquor. This black liquor is concentrated through evaporation and then combusted in a recovery furnace, where heat from the combustion of organics is recovered for process use and for the generation of electrical power; inorganic chemicals are recovered as molten smelt. Water and quicklime are used to convert this smelt back to white liquor in a causticizing tank. The lime mud which precipitates from the tank is calcined in a lime kiln to regenerate quicklime. Kraft recovery systems may also receive spent liquor from neutral sulphite semi-chemical pulping mills.

3.2 Definitions and 3.3 Techniques

The main process steps involved in Kraft pulping are briefly described below. It is important to note that some of the main air emission sources for Kraft pulping are inventoried under separate SNAP codes (see section 1 above).

3.2.1 Stripping

Wet or dry barking techniques may be used.

3.2.2 Digestion

Wood chips are cooked in a digester with white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). There are two types of digester systems: batch and continuous. Once cooking is complete in either a batch or continuous process, the chemical mixture (black liquor) and pulp are discharged into a blow tank - a low pressure vessel. Vapours from the blow tank may be vented to an accumulator or a vapour sphere for collection. The vapours may be incinerated, stripped, or recovered for resale as turpentine or tall oil.

3.2.3 Washing

The pulp from the blow tank is washed to remove the black liquor from the pulp. There are several types of washers, including counter-current vacuum, diffusion, rotary pressure, horizontal belt filters, chemiwashers, wash press, and dilution/extraction. The black liquor extracted from this process is diluted with wash water, and so is called weak black liquor.

3.2.4 Delignification

In many mills, delignification is done in the digester. However additional reductions in lignin may be achieved through oxygen delignification and/or ozone bleaching.

3.2.5 Bleaching

The pulp is produced as a slurry after removal of spent cooking chemicals and dissolved wood organics. Bleaching chemical pulps is generally complex and uses several chlorine-based chemicals. Not all pulp is bleached.

3.2.6 Turpentine Production

The vapours discharged from the digester contain up to about 6 kg turpentine per tonne of pulp, depending upon wood species and cooking conditions. These vapours are normally condensed as part of the odour control system. Turpentine has a different specific gravity than water, and so can be decanted or recovered by other processes based on the density differences. The recovered turpentine is purchased by refining companies, or is used as fuel in the mill, most commonly in the lime kiln (see SNAP Code 03 03 12) (Environment Canada 1983).

3.2.7 Tall Oil Recovery

Tall oil precursors can be recovered from black liquor cooling and evaporation. The black liquor can have soap and other tall oil precursors skimmed from the surface of weak, intermediate, or strong black liquor storage tanks and from the black liquor oxidation process. The soap can then be sold or processed into tall oil by acidification (U.S. EPA 1991).

3.2.8 Chemical Recovery

The primary functions of the Kraft recovery system are: converting sulfur compounds in the black liquor to Na_2S; regenerating NaOH; generating large quantities of steam from combustion of organic by-products; and reducing or eliminating a potential pollution source by destroying the organic substances (mostly lignin) dissolved during the cooking. The key steps in the black liquor recovery are: evaporation or concentration; black liquor oxidation (optional); combustion/oxidation in a recovery furnace; recausticizing; and calcining in a lime kiln (the latter is described in SNAP Code 030312) (U.S.EPA 1991).

3.2.9 Evaporation

The majority of water removal from the weak black liquor, to about 55 percent solids, is usually carried out in multiple effect evaporators. This is a series of evaporators operated at different pressures so that the vapour from one evaporator body becomes the steam supply to the next evaporator. The vapour from the final evaporator is condensed in either a large heat exchanger (surface condenser) or by direct contact with water in a barometric condenser. A surface condenser requires a small vacuum system to remove non-condensable gases from the system.

Direct contact evaporators may then be used to further concentrate the black liquor to about 65 percent solids by bringing the liquor into direct contact with the flue gases from the recovery furnace. Alternatively, a forced circulation indirectly heated steam-heated evaporator, generally known as a concentrator, may be used.

3.2.10 Black Liquor Oxidation

Generation of H_2S results in the direct contact evaporator when sodium sulphide in black liquor comes in contact with carbon dioxide in the recovery furnace gases. This can largely be eliminated by oxidising the sodium sulphide with air, or oxygen, to sodium thiosulphite. Black liquor oxidation is not required if indirect evaporator concentrators are used (U.S. EPA 1991).

3.2.11 Recovery Furnace

The black liquor recovery furnace further concentrates the liquor solids. The heavy black liquor from the evaporators is heated and sprayed into the furnace. Water is evaporated from the liquor solids and the organics are burned to reduce oxidised sulphur components to sulfide. The inorganic black liquor chemicals form a molten smelt.

3.2.12 Recausticizing

In recausticizing, sodium carbonate (Na_2CO_3) in the smelt is converted into NaOH, an active cooking chemical. The smelt from the recovery furnace is dissolved in a tank with weak wash to form green liquor. After clarification, the green liquor is mixed with reburned lime to form a slurry and agitated at high temperatures to form lime mud. White liquor is clarified from the lime mud by decantation. The lime mud then goes to the lime kiln for calcination (SNAP CODE 030312).

Currently, research in new pulping processes based on organic solvents is directed to reduce the environmental effects and to reduce operating and investment costs. These organosolve processes result in lower gaseous emissions of sulphur dioxide and odorous compounds. However, these processes are generally characterised by high reaction temperatures and pressures, complicated pulp washing and recovery systems, and inferior pulp strength.

3.4 Emissions

Emission sources at Kraft pulp and paper mills are summarised in Table 3.1 (NCASI 1993, U.S. EPA 1985). Sources that are inventoried under separate SNAP Codes (marked *) have been included to provide an overall picture of these operations.

The term non-condensable gases is applied to the gases emitted from the pulping and black liquor evaporation processes, including digester relief gases, digester blow gases, evaporator gases and condensate stripper gases. These gases, which are stored in a tank, consist of a mixture of terpenes, total reduced sulphur (TRS) compounds and methanol along with a variety of less significant organics. Strictly speaking, these gases are all condensable, but the term is used to distinguish them from the vapours which do condense in the relief vent, blow heat recovery vent and evaporator non-condensable extraction system under normal conditions of operation. (Environment Canada 1983) In some cases these non-condensable gases are not collected, and so are considered as emission sources at the point of creation (i.e. digester, evaporator). However, they are, in North America and Scandinavia, typically collected and incinerated in the lime kiln or a dedicated boiler. In certain circumstances, however, about 2% of the time, these gases may be vented to the atmosphere, although in Scandinavia there is usually a second or back-up system for collection and destruction of non-condensable gases, which means that these gases are directly vented to the atmosphere less than 0.5% of the time. The non-condensable gases, collected but not incinerated, must be considered a potential source of VOCs. (NCASI 1993) Thus in Table 3.1 the digestion and evaporators will not be sources of VOCs if non-condensable gases are collected.

Table 3.1 Emission Sources in Paper Pulping - Kraft Process

Source							
	TPM	**PM 10**	**PM 2.5**	**SO_2**	**NO_x**	**VOC_s**	**CO**
Stripping						x	
Digestion				X[1]		x	
Washing				X[1]		x	
Bleaching						x	
Non-condensable gases:							
-- Collected, not incinerated				X[2]		X	
-- Incinerated				X[2]	x		
Turpentine Production						x	
Tall Oil Recovery						x	
Chemical Recovery							
-- Evaporation				x		x	
-- Black Liquor Oxidation						X	
-- Recovery Furnace			X	X	X	X	x
-- Recausticizing			X	x	x	x	
-- Lime Kiln[3]			X	x	X	X	x
Pulp Drying[3] (this will have to be confirmed based on SNAP code 03 03 21)						x	
Boilers (fuel-dependent)[3]			X	X	X	X	
Wastewater Treatment[3] (this will have to be confirmed based on SNAP code 09 01 xx)					X		

Major sources are marked with an X, minor sources are marked with an x.

1. Depending on if the gases are collected.
2. Depending on if the emissions are treated in a scrubber or if the incineration takes place in the lime kiln.
3. Recorded under separate SNAP codes.

Although these contaminants are emitted in varying quantities, the major problem for this industry is odour related due to TRS emissions.

3.5 Controls

This summary only refers to those Kraft pulp and paper processes that are included under SNAP Code 040602.

Emissions control at these mills is a major consideration in the design of a Kraft pulping mill and will, to a large extent, depend on the methods used to control odours. Control may include process modifications and improved operating conditions, as well as add-on emissions control.

For example, particulate control on recovery furnaces is achieved in a number of ways. In mills with either a cyclonic scrubber or cascade evaporator as a direct contact evaporator, particulate control efficiencies of 20 to 50% are achieved for the recovery furnace if gases from the recovery furnace are routed to these processes. An electrostatic precipitator or venturi scrubber and possibly auxiliary scrubbers may then be added to achieve the desired reduction of 85 to 99% (U.S. EPA 1985).

Since the particulate material that is released is largely sodium sulphate and sodium carbonate, the recovery through the use of ESPs or scrubbers is normally practised for economic reasons on all recovery furnaces (Environment Canada 1983).

Sulphur dioxide is emitted mainly from oxidation of reduced sulphur compounds in the recovery furnace, The U.S. EPA (1985) reports that the direct contact evaporator absorbs about 75% of these emissions, and that further scrubbing can provide additional control. Other methods may also be used to decrease the SO_2 emissions from the recovery boiler (SEPA 1992):

- changed combustion conditions;
- increased dry solids content of the strong liquor;
- decreased sulphur-to-sodium ratio in the furnace;
- decreased load of inert compounds;
- improved process control.

The major cause of carbon monoxide emissions from the recovery furnace is furnace operation well above rated capacity, which results in failing to maintain oxidising conditions.
Non-condensable gases are usually incinerated. In some cases the non-condensable gases are incinerated in a dedicated incinerator, which is effective but usually requires auxiliary fuel to maintain combustion. More recent installations incinerate the gases in the lime kiln, the power boiler or the recovery furnace. Incineration of these gases does result in the emission of SO_2. Scrubbers may be used to recover sulphur for the pulping process prior to incineration (Environment Canada 1983).

The reader is referred to European Commission 2001, Environment Canada 1983, and Swedish Environmental Protection Agency 1992 for more details.

4 SIMPLER METHODOLOGY

Emissions from Kraft pulping, tall oil and turpentine may be inventoried using the default emission factors provided in Table 8.1. These emission factors represent the high end of typical emission factors, and assume limited control technology is in place.

As an alternative method one can make use of emission calculation programmes which usually are based on average emission factors of typical mill configurations. In annex I there is a short description of a programme which can be used to calculate SO_2, TRS and NO_x emissions of Scandinavian or Iberian Kraft pulp mills.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.

5 DETAILED METHODOLOGY

The preferred methodology is the use of continuous measurement data, which, in some countries, is available for major sources of SO_2, TRS and NO_x. This is particularly the case for modern Kraft mills, where there is collection of strong and dilute gases and as such there are a limited number of emission points to be monitored.

In older Kraft mills there are usually numerous emission sources and it is not economically possible to measure them all continuously. In these cases, the facilities are inventoried as point sources using total production statistics for each plant in combination with the most appropriate emission factors from Table 8.2. The selection of these factors will involve: a basic knowledge of the technology used at that facility (direct or indirect contact evaporator, the use of black liquor oxidation towers); some knowledge of the air pollution control techniques where choices are available for emission factors (primarily for the recovery furnace); a knowledge of by-product recovery facilities (turpentine and/or tall oil); and information on the occurrence of releases of non-condensable gases.

To facilitate the estimation of the fine particulate fraction of Total Particulate matter released the US EPA has developed software which will apply the effects of control devices on the fine fractions. Portions of the information contained in the software have been put into tables in this document for ease of use. This software is available on the Internet at: http://www.epa.gov/ttn/chief/index.html

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

Most emission factors are based on the production of air dried tonnes of pulp. Production of tall oil and/or turpentine in tonnes and tonnes of black liquor solids recausticized may also be relevant statistics.

7 POINT SOURCE CRITERIA

All Kraft pulping facilities could be inventoried as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

A summary of default emission factors for use with a simpler methodology for estimating emissions are provided in Table 8.1. The emission factors are extracted from the Integrated

Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001) and are relative to existing plants as shown in Table 8.4. Emissions reported here are average values. Value for Carbon Monoxide is from EPA (EPA, 1985).

Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and 040602.

Table 8.1 Emission Factors for Kraft Pulping

Pollutant	kg/ADt pulp *
Total suspended particulate	1
NOx	1
SO_2	2,5
VOC	2
CO	5.5

* ADt = air dried tonnes of pulp

8.2 Detailed Methodology

Table 8.2 is a summary of reference emission factors for the detailed methodology for inventorying emissions from Kraft pulping processes. The values in this table are based mainly on the NCASI up-date of factors (NCASI 1993). For some processes, the most recently available data are from AP-42 (US EPA 1985 or Stanley 1991). Where data ranges are available, these are provided in the table immediately below the mean value. For particulate emissions, both controlled and uncontrolled emission factors are provided. The type of particulate control device used is provided in the table and applies only to the TSP emissions; the emissions of the other species are provided without specification of any control method. NO_x, SO_2 and CO emissions are expressed as NO_2, SO_2 and CO respectively.

Care must be exercised when using the VOC emission factors; the VOCs in the table are defined as the total gaseous non-methane organics (TGNMO). The NCASI factors are expressed in terms of kilograms of carbon per tonne air dry pulp and include both hydrocarbons such as turpentine (turpenes) and methanol as well as reduced sulphur compounds such as methyl mercaptan, dimethyl sulphide and dimethyl disulphide. The VOC emission factors in the table from AP-42 represent reduced sulphur compounds only, expressed in terms of sulphur. In either case, the average molecular weight of the gaseous mixture is required in order to permit a mass based emission factor to be calculated.

Table 8.2 Kraft Pulping Processes - Emission Factors

		TSP (Note 2)							
Source and Description	**Units (Note 1)**	**Uncontrolled**	**Controlled**	**Control Device**	**Ref**	**NOx (Ref) (Note 4)**	**SO2 (Ref) (Note 5)**	**VOC (Ref) (Note 3)**	**CO (Ref)**
Digestion	kg/Adt							0.6 (b) 0 (c)	
Washing									
- clean condensates used	kg/Adt					0 (a)	0 (a)	0.045 (a) (0.001-0.085) (a) 0.025 (b)	
- foul condensates used	kg/Adt					0 (a)	0 (a)	0.49 (a) (0.45-0.52) (a) 0.2 (b)	
Bleaching	kg/Adt					0 (a)	0 (a)	0.05 (a) (0.004-0.2) (a)	
Non-condensible gases									
- collected, not incinerated	kg/Adt							0.5 (a)	
- incinerated	kg/Adt						3 (a) (1.0-10.0) (a)		
Turpentine Production	kg/tonne turpentine							0.25 (b) 0.05 (c)	
Oxygen delignification reactors	kg/Adt					0 (a)	0 (a)	0.041 (a) (0.016-0.075) (a)	
Tall Oil Recovery	kg/tonne TO					0 (a)	0 (a)	2.0 (a) (0.1-4.9) (a)	
Chemical Recovery:									
Evaporation								0.05 (b)	
Black Liquor Oxidation	kg/Adt					0 (a)	0 (a)	0.17 (a) (0.12-0.22) (a)	
Recovery Furnace									

		TSP (Note 2)							
Source and Description	**Units (Note 1)**	**Uncontrolled**	**Controlled**	**Control Device**	**Ref**	**NOx (Ref) (Note 4)**	**SO2 (Ref) (Note 5)**	**VOC (Ref) (Note 3)**	**CO (Ref)**
- Without Direct Contact Evaporator	kg/Adt	115	1	ESP	b	1.16 (a) (0.85-2.0) (a)	2.1 (a) (0.005-43) (a)	0.14 (a) (0-0.8) (a)	5.5 (b)
- With Direct Contact Evaporator	kg/Adt	90	24 1 7.5 1.5	VS ESP VS/AXS ESP/AXS	b b b b	0.9 (a) (0.45-1.7) (a)	1.7 (a) (0.02-8.6) (a) 3.5(b)	0.53 (a) (0.005-1.13) (a) 1.5 (b)	5.5 (b)
Recausticizing	kg/tonne BLS	3.5	0.5 0.1	MP S	b b	0.017 (a) (<4E-4-0.075) (a)	0.008 (a) (0.0-0.038) (a) 0.1 (b)		
- With clean condensates	kg/tonne BLS							0.031 (a) (1.E-5-0.107) (a) 0.01 (b)	
- With dirty condensates	kg/tonne BLS							0.88 (a) (0.72-1.2) (a) 0.15 (b)	

Note 1: ADt = air dried tonnes of pulp. BLS = black liquor solids. TO = tall oil.

Note 2: Control device applies only to TSP emissions; no control devices specified for other species; ESP = electrostatic precipitator, VS = venturi scrubber, AXS = auxiliary scrubber, MP= mesh pad, S = packed tower scrubber.

Note 3: Units for Reference (a) are expressed as carbon; Units for Reference (b) are expressed as sulphur; VOC is defined as total gaseous non-methane organics (TGNMO) which includes reduced sulphur compounds.

Note 4: Ranges given in brackets apply to the value immediately above: emissions expressed as NO_2.

Note 5: Ranges given in brackets apply to the value immediately above: emissions expressed as SO_2.
REFERENCES: (a) NCASI, 1993; (b) US EPA, 1985; (c) Stanley, 1991

Quality Rating:

AP-42 factors are reported to have an A class quality rating at the time they were published in 1986; this rating may need to be reviewed in the light of process changes and particularly in terms of more recent control requirements. The NCASI emission factors would likely warrant an A quality rating.

The table below lists the US EPA FIRE 6.22 Emission factors from the processes in Kraft mills. These emission rates are for different control devices so care must be taken to use the appropriate emission rate.

Table 8.3 Emission Rates for Criteria and Toxic Pollutants (US EPA 1999)

Process	Pollutant	Control	Emission Rate	Units	Material	Quality
Digester Relief and Blow Tank						
	Methyl alcohol	None	8.50E-01	kg/Mg	ADt	U
	Methyl ethyl ketone	None	7.00E-03	kg/Mg	ADt	D
Washer/Screens						
	Sulfur oxides (SOx)	None	5.00E-03	kg/Mg	ADt	A
	Volatile organic compounds (VOC)	None	1.00E-01	kg/Mg	ADt	U
	Methyl ethyl ketone	None	1.35E-02	kg/Mg	ADt	D
Multi-effect Evaporator						
	Methyl ethyl ketone	None	1.35E-02	kg/Mg	ADt	D
Recovery Furnace/Direct Contact Evaporator						
	PM, filterable	None	9.00E+01	kg/Mg	ADt	U
	PM10, filterable	None	8.40E+01	kg/Mg	ADt	U
	PM 2.5 (AP-42, EPA 95)	None	7.5E+01	kg/Mg	ADt	C
	Carbon monoxide	None	5.50E+00	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	3.50E+00	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	9.75E-01	kg/Mg	ADt	U
	Hexachlorodibenzo-p-dioxins, total	ESP	1.10E-03	mg/Mg	ADt	U
	Methyl ethyl ketone	None	7.50E-03	kg/Mg	ADt	D
	Nitrogen oxides (NOx)	None	1.00E+00	kg/Mg	ADt	U
	Pentachlorodibenzo-p-dioxins, total	Misc.	3.80E-04	mg/Mg	ADt	U
	Tetrachlorodibenzo-p-dioxins, total	Misc.	2.90E-04	mg/Mg	ADt	U
	2,3,7,8-Tetrachlorodibenzofuran	ESP	3.40E-05	mg/Mg	ADt	U
Smelt Dissolving Tank						
	PM, filterable	None	3.50E+00	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	1.00E-01	kg/Mg	ADt	U
	PM10, filterable	None	3.10E+00	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	5.00E-01	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	8.00E-02	kg/Mg	ADt	U
Lime Kiln						
	PM10, filterable	None	4.70E+00	kg/Mg	ADt	U
	PM, filterable	None	2.80E+01	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	1.50E-01	kg/Mg	ADt	A
	Carbon monoxide	None	5.00E-02	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	1.40E+00	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	1.25E-01	kg/Mg	ADt	U
	Nickel	None	6.45E-05	kg/Mg	ADt	U
	Mercury	None	1.45E-07	kg/Mg	ADt	U
	Lead	None	5.44E-05	kg/Mg	ADt	U
	Copper	None	1.40E-05	kg/Mg	ADt	U
	Chromium	None	2.33E-04	kg/Mg	ADt	U
	Cadmium	None	1.01E-06	kg/Mg	ADt	U
	Arsenic	None	2.34E-07	kg/Mg	ADt	U
	Selenium	None	2.02E-07	kg/Mg	ADt	U

Process	**Pollutant**	**Control**	**Emission Rate**	**Units**	**Material**	**Quality**
	Manganese	None	1.75E-05	kg/Mg	ADt	U
	Beryllium	None	3.90E-06	kg/Mg	ADt	U
	Fluoranthene	None	<1.74E-6	kg/Mg	ADt	U
	Acetaldehyde	None	3.70E-05	kg/Mg	ADt	U
	2,3,7,8-Tetrachlorodibenzofuran	None	0.00E+00	kg/Mg	ADt	U
	Polychlorinated dibenzofurans, total	None	4.23E-10	kg/Mg	ADt	U
	Polychlorinated dibenzo-p-dioxins, total	None	1.42E-09	kg/Mg	ADt	U
	Pentachlorodibenzofurans, total	None	5.37E-11	kg/Mg	ADt	U
	Octachlorodibenzo-p-dioxins, total	None	8.76E-10	kg/Mg	ADt	U
	Tetrachlorodibenzofurans, total	None	1.27E-10	kg/Mg	ADt	U
	Hexachlorodibenzofurans, total	None	4.20E-11	kg/Mg	ADt	U
	Heptachlorodibenzofurans, total	None	8.31E-11	kg/Mg	ADt	U
	Hydrogen chloride	None	1.10E-06	kg/Mg	ADt	U
Turpentine Condenser						
	Methyl ethyl ketone	None	4.50E-03	kg/Mg	ADt	D
	Volatile organic compounds (VOC)	None	3.50E-02	kg/Mg	ADt	U
Fluid Bed Calciner						
	PM10, filterable	None	2.52E+01	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	1.50E-01	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	1.40E+00	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	1.25E-01	kg/Mg	ADt	U
Liquor Oxidation Tower						
	Sulfur oxides (SOx)	None	1.00E-02	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	2.25E-01	kg/Mg	ADt	U
	Methyl ethyl ketone	None	5.00E-03	kg/Mg	ADt	D
Recovery Furnace/Indirect Contact Evaporator						
	PM, filterable	None	1.15E+02	kg/Mg	ADt	U
	PM10, filterable	None	1.15E+02	kg/Mg	ADt	U
	Carbon monoxide	None	5.50E+00	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	9.50E-01	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	4.00E-01	kg/Mg	ADt	U
Other Not Classified						
	Chloroform	None	9.25E-03	kg/Mg	ADBt	U
	Formaldehyde	None	3.23E-03	kg/Mg	ADBt	U
	Ethylene dibromide	None	< 2.01E-4	kg/Mg	ADBt	U
	Dichloromethane	None	6.91E-05	kg/Mg	ADBt	U
	Methyl alcohol	None	2.68E-03	kg/Mg	ADBt	U
	Chlorine	None	1.07E-06	kg/Mg	ADBt	U
	Carbon tetrachloride	None	4.07E-04	kg/Mg	ADBt	U
	Benzene	None	9.12E-05	kg/Mg	ADBt	U
	Acetaldehyde	None	5.47E-06	kg/Mg	ADBt	U
	Methyl alcohol	None	3.91E+00	kg/Mg	ADBt	U
	Methyl alcohol	None	8.44E-04	kg/Mg	ADBt	U
	Methyl ethyl ketone	None	1.50E-03	kg/Mg	ADBt	D
	1,1,1-Trichloroethane	None	1.57E-04	kg/Mg	ADBt	U
	Trichloroethylene	None	3.32E-05	kg/Mg	ADBt	U
	Acetaldehyde	None	7.01E-06	kg/Mg	ADBt	U
	Acetaldehyde	None	3.61E-04	kg/Mg	ADBt	U

ADt - tonnes Air Dried Unbleached Pulp; ADBt - tonnes Air Dried Bleached Pulp

The emission factors, for recovery furnaces, extracted from the IPPC BREF (European Commission, 2001) are reported in Table 8.4. Typical emissions are the emissions from existing plants. best available techniques (BAT) for reducing emissions to air included in BREF are:

- SO_2 emissions are controlled by firing high dry solids concentration black liquor in the recovery boiler and/or by using a flue gas scrubber;
- NO_x emissions ensuring proper mixing and division of air in the boiler, and for new or altered installations also by appropriate design;
- flue gases are cleaned with efficient electrostatic precipitators to mitigate dust emissions.

In the table the BAT emission levels to air from the process that are associated with a combination of these techniques are shown. The emission levels refer to yearly averages and standard conditions.

Table 8.4 IPPC BREF Emission Factors for Kraft Pulping (recovery furnaces)

Source	**Units***	**TSP**	**NO_x**	**SO_2**	**VOC**
Typical	kg/ADt	0.1-1.8(1)	0.6-1.8	1-4 (2) 0.1-0.4 (3) 0.2-0.5 (4)	0.1 (5) 0.4 (6)
BAT	kg/ADt	0.2-0.5	1-1.5	0.2-0.4	
Chips store	kg/m^3 of wood				0.2-0.3 (7)

* ADt = air dried tonnes of pulp
(1) after electrostatic precipitator
(2) without scrubber and 63-65% dry solids of black liquor
(3) with scrubber and 63-65% dry solids of black liquor
(4) without scrubber and 72-80% dry solids of black liquor
(5) softwood kraft
(6) hardwood kraft
(7) mainly turpenes, emitted to the atmosphere from wood chips stored in heaps outdoors the process

Table 8.5 below lists the latest US EPA emission percentages for the fine particulate fraction of Total Suspended Particulate (TSP) from the PMCALC software for estimating PM 10 and PM 2.5 emissions.

Table 8.5 Fine Particulate Fractions of Total Suspended Particulate. (US EPA 1997)

	Fine Particulate Fraction [%]		
Process	**PM10**	**PM6**	**PM2.5**
Digester Relief and Blow Tank	94.0	91.0	78.0
Washer/Screens	94.0	91.0	78.0
Multi-effect Evaporator	94.0	91.0	78.0
Recovery Furnace/Direct Contact Evaporator	93.3	92.2	83.3
Smelt Dissolving Tank	88.6	85.7	74.3
Lime Kiln	16.8	13.6	10.4
Turpentine Condenser	85.0	62.0	30.0
Fluid Bed Calciner	70.0	60.0	40.0
Liquor Oxidation Tower	94.0	91.0	78.0
Recovery Furnace/Indirect Contact Evaporator	100.0	80.5	78.3

	Fine Particulate Fraction [%]		
Process	**PM10**	**PM6**	**PM2.5**
Liquor Clarifiers	94.0	91.0	78.0
Other Not Classified	94.0	91.0	78.0

Control Devices:

The US EPA PMCALC program for calculating PM 10, PM 6, and PM 2.5 emissions based on TPM emissions lists the following control percentages for control devices:

Table 8.6 Fine Particulate Control Efficiencies (US EPA 1997)

Control Device	**Control Efficiencies [%]**		
	PM 10	**PM 6**	**PM 2.5**
None	0.0	0.0	0.0
None	0.0	0.0	0.0
Wet scrubber - hi-efficiency	99.0	95.0	90.0
Wet scrubber - med-efficiency	95.0	85.0	25.0
Wet scrubber - low-efficiency	90.0	80.0	20.0
Gravity collector - hi-efficiency	6.0	5.0	3.6
Gravity collector - med-efficiency	4.8	4.0	2.9
Gravity collector - low-efficiency	3.7	3.2	1.5
Centrifugal collector - hi-efficiency	95.0	95.0	80.0
Centrifugal collector - med-efficiency	85.0	75.0	50.0
Centrifugal collector - low-efficiency	50.0	35.0	10.0
Electrostatic precipitator (high efficiency)	99.5	99.0	95.0
Electrostatic precipitator - med-efficiency	97.0	90.0	80.0
Electrostatic precipitator - low-efficiency	90.0	80.0	70.0
Mist eliminator - high velocity >250 FPM	90.0	75.0	10.0
Mist eliminator - low velocity <250 FPM	75.0	40.0	5.0
Fabric filter - high temperature	99.5	99.5	99.0
Fabric filter - med temperature	99.5	99.5	99.0
Fabric filter - low temperature	99.5	99.5	99.0
Liquid filtration system	85.0	75.0	50.0
Packed-gas absorption column	99.0	95.0	90.0
Tray-type gas absorption column	95.0	85.0	25.0
Spray tower	90.0	80.0	20.0
Venturi scrubber	99.0	95.0	90.0
Process enclosed	3.7	3.2	1.5
Impingement plate scrubber	99.0	95.0	25.0
Dynamic separator (dry)	99.0	95.0	90.0
Dynamic separator (wet)	85.0	75.0	50.0
Mat or panel filter - mist collector	97.0	94.0	92.0
Multiple cyclone w/fly ash reinjection	20.0	15.0	10.0
Metal fabric filter screen	90.0	65.0	40.0
Dust suppression by water sprays	90.0	65.0	40.0
Dust suppression by chemical stabilizer or wetting	80.0	5.0	0.0
Wet cyclonic separator	97.0	90.0	80.0
Gravel bed filter	90.0	20.0	10.0
Annular ring filter	50.0	35.0	10.0

Control Device	Control Efficiencies [%]		
	PM 10	**PM 6**	**PM 2.5**
Fluid bed dry scrubber	85.0	75.0	50.0
Single cyclone	95.0	95.0	80.0
Multiple cyclone w/o fly ash reinjection	85.0	75.0	50.0
Water curtain	90.0	45.0	10.0

9 SPECIES PROFILES

The U.S. EPA (1994) generic VOC speciation profile for the Kraft Pulping classification under the Pulp and Paper Source Category (Profile 9001, External Combustion Boilers - Industrial - Average) is presented in Table 9.1.

Table 9.1 U.S. EPA VOC Speciation Profile for Kraft Pulping (U.S. EPA 1994)

Species Name	Mol. Wt.	% Wt.
Isomers of hexane	86.17	0.89
Isomers of heptane	100.2	0.37
Isomers of octane	114.23	0.67
Isomers of pentane	72.05	2.07
C7-C16 paraffins	156.31	5.62
Methane	16.04	23.35
Ethane	30.07	11.41
Ethylene	28.05	1.67
Propane	44.09	4.19
Propene	42.08	2.65
Acetylene	26.04	2.32
n-Butane	58.12	9.24
Butene	56.1	0.87

This profile is applied to washers/screens, recovery furnaces (with or without direct contact), recausticizing, turpentine condensers and black liquor oxidation. A quality rating of E is provided with this profile.

It is important to note that the definition of VOCs used by the U.S. EPA excludes reduced sulphur compounds and halogenated organics. The National Council of the Paper Industry for Air and Stream Improvement Inc. (NCASI) (1993) VOC definition is based on TGNMO and includes organo-sulphur compounds such as methyl mercaptan, dimethyl sulphide and dimethyl disulphide. A typical VOC content of non-condensable gas emissions provided by NCASI (1993) is summarised in Table 9.2.

Table 9.2 NCASI VOC Speciation Profile for Kraft Pulping (NCASI 1993)

Species	**Composition % by volume**
Methyl mercaptan	2.1
Dimethyl sulphide	2.1
Dimethyl disulphide	1.7
Turpentine	0.1
Methanol	0.2

If these sulphur compounds are incinerated and the combustion vented without scrubbing, then the sulphur dioxide produced by combustion should be added to the SO_2 emissions.

The U.S. EPA has published a particulate matter speciation profile for Kraft recovery furnaces (available through the CHIEF bulletin board system). Part of this particulate profile number 23103 is presented in Table 9.3.

Table 9.3 U.S. EPA Partial Profile for Particulate Emissions from Kraft Recovery Furnaces with ESP and Wet Scrubber - (Profile 23103 - Data Quality D)

Species	**% weight**	**Uncertainty**
Arsenic	0.004	0.003
Cadmium	0.018	0.013
Chromium	0.016	0.010
Copper	0.004	0.004
Mercury	0.002	0.003
Nickel	0.026	0.042
Lead	0.026	0.017
Selenium	0.005	0.004
Zinc	0.017	0.014

Emissions from stripping and chip storage operations consist of terpenes.

The Swedish Environmental Protection Agency (SEPA 1992) reports that over sixty compounds have been identified in Kraft condensates, at concentrations between trace levels and 1% by weight. The impurities include:

Bivalent sulphur compounds	- hydrogen sulphide
	- methyl mercaptan
	- dimethyl sulphide
	- dimethyl disulphide
Alcohols	- methanol
	- ethanol
Ketones	- acetone
Terpenes	- pinene
	- terpineol
Phenolics	- phenol
	- guaiacols
	- cresols

Methanol is the main impurity, with a total emission of about 5 to 10 kg/ADt.

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simpler methodology relies on emission factors that may not be representative of the process. The detailed methodology is more detailed but still relies on typical emission factors, and may still not result in accurate estimates. The preferred methodology would involve the measurement of emissions from each plant to develop site-specific emission factors for all potentially significant sources. These emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At this time, new site-specific emission factors should be derived based on testing. However, this program is costly and time consuming. Continuous measurements are required in some countries (see section 5).

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emissions estimate can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Kraft pulping facilities normally run year-round. It may be assumed that emissions occur uniformly over diurnal and annual cycles, barring unusual operational disruptions.

14 ADDITIONAL COMMENTS

While organo-sulphur compounds have, in some cases, been included under the VOC classification, in some circumstances these compounds should be classed as sulphur dioxide emissions depending on the application of the inventory data. Reduced sulphur compound are a source of odour and toxic effects and where considerations are focused on the impacts of emissions on local to urban scales, it is appropriate to consider these compounds separately and not to group them in the VOC class. Where impacts on regional, continental or global scales are of concern, the reduced sulphur compounds should probably be classed with sulphur dioxide emissions since they are fairly rapidly oxidised in the atmosphere yielding SO_2, which participates in other chemical reactions in the atmosphere to produce acidification.

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

17 REFERENCES

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19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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SNAP CODE: **040603**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES**
Paper Pulp (Acid Sulphite Process)

NOSE CODE: **105.07.02**

NFR CODE: **2 D 1**

1 ACTIVITIES INCLUDED

Pulp and paper production has three major processing steps: pulping, bleaching, and paper production. The type of pulping and the amount of bleaching used depend on the nature of the feedstock and the desired qualities of the end product. Sulphite pulping is one of the chemical pulping processes that can be used. It involves chemically pulping the wood using SO_2 adsorbed in a base solution. Sulphite pulping produces a weaker paper than some other types of pulping, but the pulp is less coloured, making it more suitable for printing, often with little bleaching.

The production of sulphite pulps (European Commission 2001) is much smaller than the production of kraft pulps and sulphite pulps are more used in special purposes in papermaking rather than being an alternative market pulp grade for kraft pulps. Very little unbleached sulphite pulp is made and the yield is a little higher which can be attributed to the lower pH in the cooking.

Not all sulphite pulping and related processes that could result in the emission of significant amounts of NMVOC, SOx, particulates, NOx and CO are included under SNAP Code 040603. Other significant sources are summarized in Table 1

Table 1: Other Relevant SNAP Codes for Paper Pulping - Acid Sulphite Process

Source	SNAP CODE
Combustion in boilers	03 01 xx
Paper-mill industry (drying processes)	03 03 21
Waste Water Treatment	09 01 xx

In addition to more conventional fuels such as wood/bark, coal, oil and natural gas, boilers at pulp and paper mills may combust red liquor (see section 3 below), small quantities of wastewater treatment sludge (from both virgin pulp and recycle operations), no-nrecyclable recovered paper, tire-derived fuel, old corrugated container materials etc. (NCASI 1993)

It is assumed that these non-conventional fuels that are combusted in boilers will be covered somewhere in SNAP group 03.

This section is under review by Scandinavian participants. Changes are anticipated as more information becomes available. These will be incorporated in a future edition of this manual.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Table 2 summarises emissions reported from acid sulphite pulp and paper processes.

Table 2a: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Paper Pulp (Acid Sulphite Process)	040603	0.2	0	0.1	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Table 2b: Emissions from Paper Pulping - Acid Sulphite Process

Country	**Particulate**		**SOx**		**NOx**		**CO**		**NMVOC**	
	Emissions (Mg)	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**
Canada (1985)	2163	0.1	32591	0.9	130	<0.0				
United States (1985)			22000							

[1] % of total anthropogenic emissions.

3 GENERAL

3.1 Description

In the acid sulphite process, a caustic solution (cooking liquor) is used under high temperature and pressure to chemically dissolve the lignin that binds the cellulose fibres of the wood together. The caustic solution is SO_2 adsorbed in a base solution. The bases commonly used are calcium, magnesium, ammonia or sodium. After digestion, the wood pulp is washed and dried for sale as market pulp, or further treated by refining, cleaning and addition of other pulps and chemicals, and made into paper on-site. Depending on the intended use of the product, the pulp may or may not be bleached. Heat and/or chemical recovery may also be done, depending on the cooking liquor used. An acid plant will normally be necessary to supply the mill sulphite requirement.

3.2 Definitions

3.3 Techniques

The main process steps involved in acid sulphite pulping are briefly described below. It should be noted that some of the main sources for acid sulphite pulping are inventoried under other SNAP codes (see section 1 above). (Environment Canada 1983, U.S. EPA 1985 and U.S. EPA 1991)

Digestion Digestion is carried out under high pressure and high temperature, in either batch mode or continuous digesters, in the presence of a sulphurous acid/bisulphite cooking liquid (see acid plant below). The delignification is accomplished by sulphonation and hydrolysis reactions which form soluble ligno-sulphates. When this is completed, the contents of the digester are either discharged at high pressure into a blow pit or pumped into a dump tank at lower pressure. A blow pit is a tank with a finely perforated bottom to allow liquids to drain out while retaining the pulp. A blow tank is commonly an atmospheric cyclone. The spent sulphite liquor (sometimes called red liquor) is drained, and discharged or treated and incinerated or sent to a plant for recovery of heat and/or chemicals.

Washing The pulp is then washed with fresh water to further remove dissolved chemicals. This water is usually routed to recovery operations.

Bleaching The pulp is produced as a slurry after removal of spent cooking chemicals and dissolved wood organics. Bleaching chemical pulps is generally complex. Strictly speaking, bleaching is part of the paper making process, as opposed to pulping, but has been included under this SNAP code for complete coverage of the pulp and paper industry as a whole.

Chemical Recovery More than a dozen types of recovery systems, using widely different processes, are in operation around the world. The variety of systems for heat and/ or chemical recovery is largely due to the variety of cooking bases used.

The sulphite cooking process is based on the use of aqueous sulphur dioxide (SO_2) and a base -calcium, sodium, magnesium or ammonium. The specific base used will impact upon the options available within the process in respect of chemical and energy recovery system and water use. Today, the use of the relatively cheap calcium base is outdated because the cooking chemicals cannot be recovered. In Europe (European Commission, 2001) there is still one mill (FR) using ammonium as a base. The dominating sulphite pulping process in Europe is the magnesium sulphite pulping with some mills using sodium as base. Both magnesium and sodium bases allow chemical recovery. The lignosulphonates generated in the cooking liquour can be used as a raw material for producing different chemical products.

In calcium base systems, chemical recovery is not practical, and the spent liquor is usually discharged or incinerated. In ammonium base operations, heat can be recovered by combusting the spent liquor, but the ammonium base and sulphur are lost. In sodium or magnesium base operations, the heat, sulphur and base may all be recovered.

The first step in all recovery systems is the concentration of red liquors in a multiple effect evaporator, and possibly a direct contact evaporator, to anywhere from 35 to 60 percent solids, depending upon the type of combustion unit to be used. The >strong= liquor is then sprayed into a furnace and burned, producing steam to operate the processes or other power requirements.

When only heat recovery is practiced, the recovery process might actually be considered conventional combustion and inventoried under snap code 03 as mentioned in section 1.

When magnesium base liquor is burned, the combustion products are a carbon-free MgO ash and SO_2. The gases pass through a series of multiple cyclones where the ash is collected and flushed with water to a retention tank. The MgO slurry is then converted to $Mg(OH)_2$ in the slaking system and used for absorption of the SO_2 in a series of venturi scrubbers. The overall chemical recovery of sulphur and $Mg(OH)_2$ is around 80%.

When sodium base liquor is burned, the inorganic compounds are recovered as a molten smelt containing sodium sulphide and sodium carbonate. This smelt may be further processed and used to adsorb SO_2 from the flue gas and sulphur, or sold to a kraft mill as raw material for producing green liquor. It is not suitable for reuse in sulphite cooking.

Acid Plant In an acid plant, sulphur is normally burned in a rotary or spray burner. The gas produced is then cooled by heat exchangers and a water spray and then absorbed in a variety of different scrubbers containing either limestone or a solution of the base chemical. In the past, limestone was used exclusively in the gas absorption tower, serving both as a packing and a chemical source of calcium. More recently, soluble bases such as magnesium, sodium and ammonium are used for environmental reasons as well as improved pulp strength. Before the raw acid is used in pulping it is fortified with relief SO_2 from the digester. The fortification takes place in the low and high pressure accumulators, which are pressurized to increase the solubility of SO_2 in the liquor.

3.4 Emissions

SO_2 is usually considered the major pollutant from acid sulphite processes. The digester and blow pit (or blow tank) system is a major source of SO_2. It is present in the intermittent digester relief gases, as well as in the gases released when the digester is discharged into the blow pit or blow tank. SO_2 is also released from the recovery system, the various pulp washing, screening and cleaning operations, as well as from evaporators and acid fortification towers. (Environment Canada 1983 and U.S. EPA 1985).

Particulate may be released from the absorption system handling the recovery furnace exhaust. Ammonium base systems generate less particulate than do magnesium or sodium base systems. (U.S. EPA 1985)

The recovery furnace is a source of VOCs (Stockton and Stelling n.d.) Bleaching operations may also be minor sources of VOCs. (NCASI 1993)

In a magnesium sulphite mill (European Commission 2001) the main source for sulphur oxide emissions is the recovery boiler. After the recovery boiler, magnesium oxide ash is collected from the flue gas in electrostatic precipitators and washed with water forming magnesium hydroxide. This liquid is used in venturi scrubbers to absorb SO_2 and SO3 from the recovery boiler (and in a few mills also from the digesters, washers and evaporators). The absorption system is made up with a number of scrubbers, normally three, four or five.

3.5 Controls

Many mills have separate blow tanks, or pits, and emission stacks for each digester. Water showers may be installed in the blow tank vents to control the blowing SO_2 emissions, or a scrubber may be used. The latter may achieve an efficiency of as high as 99 percent. (Environment Canada 1983).

Magnesium, sodium and ammonium base recovery systems all use absorption systems to recover SO_2 from sources such as the recovery furnaces, acid fortification towers and multiple effect evaporators. Generally these recover better than 95 percent of the sulphur for reuse, by scrubbing with the base chemical slurry or solution. (Environment Canada 1983, U.S. EPA 1985)

Depending on local conditions the following devices and systems can be found in sulphite pulp mills for collecting and purifying emissions to the atmosphere (European Commission 2001):

- Cyclone for chip blowing,
- The gases from the continuous pressure control relief of the digesters are led to combustion in the recovery boiler.
- Collecting system for aerating gases from digesters, blow tanks, knot screens, washing filters, all weak and thick liquor tanks and fibre filters. These gases are led to combustion in the recovery boiler,
- Scrubbers for the absorption of sulphur dioxide in aerating gases from the bleach plant.
- Non-condensable gases from the evaporation are led to combustion in the recovery boiler.
- Absorption of SO_2 in the flue gases leaving the recovery boilers in the acid preparation plant (venturi-scrubber system).
- Collection system for ventilation gases from the boiler house's liquor and condensate tanks, weak liquor filter and mix tank. The gases are led to combustion in the recovery boiler.
- Dust separation from flue gases from the auxiliary-boiler (burning bark, oil or other fuels) with electrofilter (ESP) and wet scrubber.
- NO_x-reduction in the bark boiler by injection of urea.

4 SIMPLER METHODOLOGY

Acid sulphite pulping facilities are inventoried as point sources using total production statistics for each plant in combination with the most appropriate emission factors. Default emission factors are provided in section 8.1.

5 DETAILED METHODOLOGY

The preferred methodology would involve the measurement of emissions from each plant to develop site-specific emission factors for all potentially significant sources. These emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At this time, new site-specific emission factors should be derived based on testing.
Reference emission factors for comparison with users own data are provided in Section 8.2.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a protocol such as that illustrated in the Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

Most emission factors are based on the production of air-dried tonnes of unbleached pulp.

7 POINT SOURCE CRITERIA

A recent report (Stanley 1993) indicated that six sulphite mills in Canada emitted a total of 456 Mg of NOx and 1597 Mg of NMVOC in 1990. Unfortunately, neither a breakdown of this information nor production information was supplied. However, this would seem to indicate that sulphite pulping processes should be inventoried as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

A summary of default emission factors for use with the simpler methodology for estimating emissions is provided in Table 8.1. Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and 040603.

Table 8.1 Default emission factors from Paper Pulp (Acid Sulphite Process)

Pollutant	**Emission factor**	**Units**
Particulate matter Total suspended particulate (TSP)	1	kg/tonne (unbleached dried pulp)
PM_{10}	0.75	kg/tonne (unbleached dried pulp)
$PM_{2.5}$	0.67	kg/tonne (unbleached dried pulp)
SO_2	4	kg/tonne (dried pulp)
NO_x	2	kg/tonne (dried pulp)
VOC	0,2	kg/tonne (dried pulp)

The value for SO_2, NO_x and VOC are extracted from the Integrated Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001) and are relative to existing plants as shown in Table 8.4. Emissions reported here are average values. Values for Particulate Matter are from U.S. EPA (EPA, 1985). Because of its importance in terms of capacity and numbers of mills running in Europe in Table 8.1 the focus is on magnesium sulphite pulping.

8.2 Detailed Methodology

Long term particulate and SO_2 average emission factors for sulphite pulping are summarized Table 8.2 (U.S. EPA 1985).

Table 8.2 Particulate and SO2 Emission Factors for Sulphite Pulping (U.S. EPA 1985)

			Emission Factor (kg/Mg air dried unbleached pulp)		
Source	**Base**	**Control**	**Particulate**	**SO2**	**Rating**
Digester/blow[a] pit	All	None	neg	5 to 35	C
	MgO	Process Change[b]	neg	1 to 3	C
	MgO	Scrubber	neg	0.5	B
	MgO	Process change/scrubber	neg	0.1	B
	MgO	All exhaust to recovery	neg	0	A
	NH_3	Process Change	neg	12.5	D
	NH_3	Process Change/scrubber	neg	0.4	B
	Na	Process Change/scrubber	neg	1	C
	Ca	Unknown	neg	33.5	C
Recovery system[c]	MgO	Multicyclone/venturi	1	4.5	A
	NH_3	Ammonia absorption/mist	0.35	3.5	B
	Na	Sodium Carbonate Scrubber	2	1	C
Acid Plant[d]	NH_3	Scrubber	neg	0.2	C
	Na	Unknown[e]	neg	0.1	D
	Ca	Jenson Scrubber	neg	4	C
Other[f]	All	None	neg	6	D

Notes

a. Factors represent emissions after cook is completed and when digester contents are discharged into blow pit or dump tank. Some relief gases are vented from digester during cook cycle, but these are usually transferred to pressure accumulators and SO_2 therein reabsorbed for use in cooking liquor. In some mills, actual emissions will be intermittent and for short periods.

b. May include such measures as raising cooking liquor pH (thereby lowering free SO_2), relieving digester pressure before contents discharge, and pumping out digester contents instead of blowing out.

c. Recovery system at most mills is closed and includes recovery furnace, direct contact evaporator, multiple effect evaporator, acid fortification tower, and SO_2 absorption scrubbers. Generally only one emission point for entire system. Factors include high SO_2 emissions during periodic purging of recovery systems.

d. Necessary in mills with insufficient or no recovery systems.

e. Control is practiced, but type of system is unknown.

f. Includes miscellaneous pulping operations such as knotters, washers, screens, etc.

These emission factors are cited as being from: Background Document: Acid Sulfite Pulping. EPA-450/3-77-005.U.S. EPA January 1977.

A publication from the Canadian Pulp and Paper Association (Stanley 1991) summarized available NOx and VOC emission factors from Stockton and Stelling n.d.: as provided in Table 8.3.

Table 8.3 NOx and VOC Emission Factors for Sulphite Pulping (Stockton and Stelling n.d.)

Source	Base	Control	Emission Factor (kg/tonne air dried pulp)		
			NOx	VOC	Rating
Acid Plant	NH_3		0.0[a]	0.0[b]	
	Na		0.0[a]	0.0[b]	
	Ca		0.0[a]	0.0[b]	
Digester/blow[a]	Ca		0.0[a]	neg[c]	
pit or dump tank	All others		0.0[a]	neg[c]	
	NH_3	Process Change, scrubber	0.0[a]	neg[c]	
	MgO	Process Change, scrubber	0.0[a]	neg[c]	
	MgO	Recovery System	0.0[a]	neg[c]	
	Na	Process Change, scrubber	0.0[a]	neg[c]	
Other Misc. Sources			0.0[a]	neg	
Recovery	NH_3		0.0[a]	1.8[d]	
System	MgO		0.0[a]	1.8[d]	
	Na		0.0[a]	1.8[d]	

Notes

a. No test data available. NOx emissions expected to be zero due to low temperatures of operation.

b. Based on VOC emissions for sulphuric acid plant.

c. Based on data from U.S. state files specifically for the ammonia digester/blow pit/dump tank but should be similar for other digester/blow pit/dump tanks.

d. Based on NCASI (National Council of the Paper Industry for Air and Stream Improvement Inc., U.S. referenced in Stockton and Stelling n.d.) data. Data were specific to the MgO process but levels should be similar to those at any acid plant. These data are an approximation in the absence of better information.

An emission factor of 0.05 (range 0.004 - 0.14) kg VOC (as C)/tonne air dried pulp is reported by the NCASI (1993) for pulp bleaching. This is based on tests of one to eleven vents at thirteen sources. The type of pulp is not specified.

Although ratings for these NOx and VOC emission factors are not given, a D or E rating would seem appropriate.

Following the Integrated Pollution Prevention and Control Reference Document on Best Available Techniques (European Commission, 2001), emissions are about 4 - 6 kg SO_2 per tonne of pulp when three scrubbers are used and 2 - 3 kg/t when four are used. Each scrubber reduces the concentration by about 70%. There are also less concentrated SO_2 emissions from the bleach plant, the digesters, washing and the auxiliary boilers.

Emissions of NO_x (European Commission, 2001) from sulphite pulp mill recovery boilers are generally higher than those from kraft pulp mills because of the higher temperature in the recovery boiler. NO_x emissions range normally from 100 - 200 mg/MJ or about 1.5 - 3 kg/t of pulp. Table 8.4 summarises typical ranges for SO_2 and NO_x from recovery boilers.

Table 8.4 Emissions from sulphite pulp recovery boilers and corresponding concentrations (European Commission, 2001)

Unit	S	NO_x
Kg/t	0.5 – 3	1.0 – 3
(mg/m^3)*	(100 - 400)	(200 - 500)

* at a gas flow of about 6000 - 7000 m^3/t (NTP, dry gas)

Emissions of furfural mercaptanes and H_2S might cause odour and emissions of gaseous sulphur may also cause annoyance. At some mills emissions of malodorous gases are collected and burnt in the recovery boiler.

The reported ranges of total emissions to the atmosphere from European sulphite pulp mills are shown in Table 8.5.

Table 8.5 Atmospheric emissions from European sulphite pulp mills as yearly average (European Commission, 2001)

Unit	Total gaseous S [kg/ADt*]	NO_x [kg/ADt*]
Recovery boiler	0.5-5	1-3
Bark boiler	0.02-0.06**	0.1-1**
Total emissions from mills	0.55-5**	1.2-4.2**

* ADt = air dried tonnes of pulp

** For the bark boiler estimated figure (bark boiler recorded under separate SNAP codes). Any use of fossil fuel in the bark boiler is not included

Emissions of VOC from the process are about 0.2 kg/t of sulphite pulp (European Commission, 2001). The chip-heaps also contribute to emissions of VOC.

Depending on the type of the specific process-integrated measures implemented and the technical character of the mill the emissions associated with the use of best available techniques (BAT) in Table 8.6 can be generally achieved.

Table 8.6 should be read together with the following additional explanations. As far as concentrations of emissions are given they refer to daily averages and standard conditions of 273 K, 101.3 kPa and dry gas. The reference oxygen content is 5% for recovery boilers.

In sulphite pulp mills, emission of particulates is controlled by electrostatic precipitators and multi-stage scrubbers. Dust emissions for recovery boilers between 5 – 20 mg/Nm^3 or 0.02 - 0.15 kg TSP/ADt (with a gas flow of 6000 - 7000 m^3/ADt) can generally be achieved by use of ESP and scrubbers.

Reduction of SO^2 emission from flue gases by absorption in alkaline liquid is considered BAT. A removal efficiency for SO^2 of 95 + % is achievable. From recovery boilers equipped with multi-stage scrubber SO^2 emissions between 50 - 150 mg S/Nm^3 or 0.3 - 1.0 kg S/ADt are achievable.

The emission of nitrogen oxides can be controlled by burner design (low NO_x burners) and modified combustion conditions (primary methods). The design of the recovery boiler (staged air feed systems) can result in relatively low NO_x concentrations. Achievable emission levels are in the range of 200 - 300 mg NO_x/Nm^3 or 1.0 - 2.0 kg NO_x/ADt respectively.

Table 8.6 Emission levels from the pulping process (recovery boiler and fugitive emissions) associated with the use of a suitable combination of best available techniques (emissions from any auxiliary boiler are not included) (European Commission, 2001)

Parameters	Units	Bleached sulphite pulp mills
TSP	kg/ADt	0.02-0.15
SO_2 as S	kg/ADt	0.5-1.0
NO_x as NO_2	kg/ADt	1.0-2.0

9 SPECIES PROFILES

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simpler methodology relies on emission factors that may not be representative of the process. The detailed methodology is costly and labour intensive, and may still not result in accurate estimates of emissions. However, continuous measurements are thought to be too costly in view of the total contribution to emissions from this sector.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emissions estimate can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Acid sulphite pulping facilities normally run year-round. It may be assumed that emissions occur uniformly over diurnal and annual cycles, barring unusual operational disruptions.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

17 REFERENCES

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19 RELEASE VERSION, DATE AND SOURCE

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Source: Marc Deslauriers
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SNAP CODE: **040604**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES**
Paper Pulp
(Neutral Sulphite Semi-Chemical Process)

NOSE CODE: **105.07.03**

NFR CODE: **2 D 1**

1 ACTIVITIES INCLUDED

Pulp and paper production has three major processing steps: pulping, bleaching, and paper production. The type of pulping and the amount of bleaching used depend on the nature of the feedstock and the desired qualities of the end product. Neutral sulphite semi-chemical pulping (NSSC) is one of the chemical pulping processes that can be used. It involves partial delignification of hardwood feedstock using a buffered sodium sulphite solution, with completion of the pulping process by mechanical means. NSSC pulps are used in corrugating media and in certain writing and printing papers.

Not all neutral-sulphite pulping and related processes that could result in the emission of significant amounts of NMVOC, SOx, particulates, NOx and CO are included under SNAP code 040603. Other significant sources are listed in Table 1.

Table 1: Other Relevant SNAP Codes for Paper Pulping - Neutral Sulphite Semi-Chemical Process

Source	SNAP CODE
Combustion in Boilers	03 01 xx
Paper-mill industry (drying processes)	03 03 21
Waste water treatment	09 01 xx

In addition to more conventional fuels such as wood/bark, coal, oil and natural gas, boilers at pulp and paper mills may combust non-condensable gases, small quantities of wastewater treatment sludge (from both virgin pulp and recycle operations), non-recyclable recovered paper, tire-derived fuel, old corrugated container materials etc. (NCASI 1993)

It is assumed that these non-conventional fuels that are combusted in boilers will be covered somewhere in SNAP group 03.

This section is under review by Scandinavian participants. Changes are anticipated as more information becomes available. These will be incorporated in a future edition of this manual.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions inventoried from neutral sulphite semi-chemical pulp and paper processes are summarized in Table 2.

Table 2: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Paper Pulp (Neurtral Sulphite Semi-Chem. Proc.)	040604	0.1	-	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

In the NSSC process, a cooking liquor is used under high temperature and pressure to chemically dissolve the lignin that binds the cellulose fibres of the wood together. The main cooking agent is sodium sulphite, buffered with sodium bicarbonate to maintain a neutral solution. This prevents alkalinity and acidity from degrading the hemicelluloses in the pulp, but also retards delignification. Thus after blowing from the digester, the pulping is completed using mechanical disc refiners. The pulp is then cleaned and thickened and dried for sale as market pulp or further processed into paper products on-site. Spent liquor handling methods vary widely. Options include disposal, recovery of heat and/or chemicals or transfer of the spent liquor to conventional kraft recovery mills for cross recovery.

The Integrated Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001) describe the process but not indicate specific emission factors for it. The IPPC BREF document declare that THE dominating sulphite pulping process in Europe is the magnesium sulphite pulping with some mills using sodium as base.

3.2 Definitions

Blowing - evacuation of a vessel (the digester) under pressure.

3.3 Techniques

The main process steps involved in neutral sulphite semi-chemical pulping are briefly described below. It should be noted that significant emission sources for this process are inventoried under separate SNAP codes (see section 1).

Digestion Digestion is carried out under high pressure and high temperature, in either batch mode or continuous digesters, in the presence of a buffered sodium sulphite cooking solution (liquor). Delignification occurs by lignin sulphonation and hydrolysis. Buffering, usually by the addition of sodium carbonate to the cooking liquor, retards the delignification process. When about half the lignin is dissolved. delignification tends to slow down considerably. The pulp is blown to a blow pit at this point and dewatered. Pulping is completed using mechanical disc refiners. This method achieves yields as high as 60 to 80 percent, much higher than the 50 to 55 percent yields for other chemical processes.

The pulp may then be dried for sale as market pulp or further refined, cleaned and made into paper on-site. Most of the pulp used for the manufacture of printing products is bleached.

Bleaching Bleaching chemical pulps is generally complex and uses several chlorine-based chemicals. Strictly speaking, bleaching is part of the paper making process, as opposed to pulping, but has been included under this SNAP code for complete coverage of the pulp and paper industry as a whole.

Chemical Recovery In some NSSC processes, chemical recovery is not practiced. In other cases, NSSC spent liquor is delivered directly to a conventional kraft recovery system, a technique known as cross recovery. This is only feasible when a kraft mill is close by and where chemical losses in the kraft mill warrant cross recovery.

In some cases, however, chemical recovery is practiced on site. Fluidized-bed reactors are used to combust the spent liquors after preconcentration in multiple effect evaporators to 30-35% solids. The inorganic chemicals and sodium organic salts are chiefly oxidized to sodium sulphate and sodium carbonate pellets. This matter is removed from the reactor and can be sold to a kraft mill for use as its chemical make-up, if a suitable market exists.

Acid Preparation Plant

In an acid plant, sulphur is normally burned in a rotary or spray burner. The gas produced is then cooled by heat exchangers and a water spray and passed to an absorber tower.

3.4 Emissions and Controls

Particulate emissions are a only potential problem when a fluidized bed reactor is used for chemical recovery. However, particulate controls are usually installed to improve chemical recovery rates, since the particulate is mainly sodium sulphate and sodium carbonate.

Absorbing towers, digester/blow tank systems and the recovery furnace are the main sources of SO_2. These sources are normally controlled with scrubbers.

The fluid bed reactor has been reported as a minor source of NOx and VOCs. Bleaching plants may also be minor sources of VOCs.

4 SIMPLER METHODOLOGY

Due to a lack of emission factors, it is not possible to recommend a simple inventory methodology for neutral sulphite semi-chemical plants at this time.

5 DETAILED METHODOLOGY

The preferred methodology would involve the measurement of emissions from each plant to develop site-specific emission factors for all potentially significant sources. These emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At that point, new site-specific emission factors should be derived based on testing.

6 RELEVANT ACTIVITY STATISTICS

Emission factors for this sector would normally be based on tonnes of air dried pulp.

7 POINT SOURCE CRITERIA

A recent report (Stanley 1993) indicated that one semi-chemical mill emitted 24 Mg of NMVOC. Unfortunately, no production information was supplied for this facility. However, this would seem to indicate that NSSC facilities should be inventoried as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

There is a very limited data base available for NSSC. No particulate or SO_2 emission factors were found. Available NOx and VOC emission factors (kg/tonne air dried pulp) are summarized in Table 3.

Table 3: NOx and VOC Emission Factors for Neutral Sulphite Pulping (kg/tonne air dried pulp)

Source	NOx	VOC	Reference
Sulphur burners/absorbers	0.0*	0.0**	Stockton and Stelling n.d.
Digester/dump tank/blow pit	0.0*		Stockton and Stelling n.d.
Evaporator	0.0*		Stockton and Stelling n.d.
Fluid bed reactor	0.5***	0.1***	Stockton and Stelling n.d.
Bleach Plant		0.05^{+}	NCASI 1993

* No NOx because of low temperature.

** No apparent source of VOCs.

*** Factor transferred from kraft mill processes.

$^{+}$ This is on an as carbon basis. Range: 0.004 - 0.14 kgg/tonne air dried pulp. Based on tests of one to eleven vents at thirteen sources. The type of pulp is not specified. It was indicated that it was NMVOC. (NCASI 1993).

With the exception of the bleach plant emission factor, all factors would have a quality rating of E.

9 SPECIES PROFILES

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

An emission factor compilation should be done for this sector so that a simpler methodology can be recommended. This database must be detailed enough to accommodate the wide variety of processes that may be present at one of these facilities.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Neutral sulphite semi-chemical processes are inventoried as point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

Neutral sulphite semi-chemical pulping facilities normally run year-round. It may be assumed that emissions occur uniformly over diurnal and annual cycles, barring unusual operational disruptions.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

17 REFERENCES

Environment Canada, 1983. AThe Basic Technology of the Pulp and Paper Industry and Its Environmental Protection Practices.@ Training Manual, EPS 6-EP-83-1. Environment Canada, Ottawa.

European Commission (2001), Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques (BREF) in the Pulp and Paper Industry, December 2001

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Pinkerton, J., 1993. AEmissions of SO_2 and NOx from Pulp and Paper Mills.@ Air & Waste, 43: 1404-1407.

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19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODE:	**040605**
SOURCE ACTIVITY TITLE:	**PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES** ***Bread-making & Other food manufacturing***
NOSE CODE:	**105.03.02**
NFR CODE:	**2 D 2**

1 ACTIVITIES INCLUDED

This chapter addresses NMVOC emissions from food manufacturing, except emissions from vegetable oil extraction (060404), tobacco products and alcoholic beverages (040606, 040607, 040608). Emissions are included from all processes in the food production chain which occur after the slaughtering of animals and the harvesting of crops.

2 CONTRIBUTION TO TOTAL EMISSIONS

There is considerable uncertainty over the contribution to total emissions from this sector. Nevertheless, preliminary estimates suggest that bread-making and other food manufacturing may contribute up to 2% of the UK's total emission of NMVOCs (Passant 1993). This contribution will vary significantly from country to country.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Food manufacturing may involve the heating of fats and oils and foodstuffs containing them, the baking of cereals, flour and beans, fermentation in the making of bread, the cooking of vegetables and meats, and the drying of residues. These processes may occur in sources varying in size from domestic households to manufacturing plants.

3.2 Definitions

to land	to bring to port a catch of fish or other seafood
feed	food for animals
compound feedstuffs	animal feed based on the processing of other animals and plants

3.3 Techniques

Food processing may occur in open vessels without forced ventilation, closed vessels with periodic purge ventilation or vessels with continuous controlled discharge to atmosphere. In the larger plants, the discharges may be extremely odorous and consequently emission may be controlled using end-of-pipe abatement.

3.4 Emissions/Controls

Emissions occur primarily from the following sources:

the cooking of meat fish and poultry, releasing mainly fats and oils and their degradation products;
the processing of sugar beet and cane and the subsequent refining of sugar;
the processing of fats and oils to produce margarine and solid cooking fat;
the baking of bread, cakes biscuits and breakfast cereals;
the processing of meat and vegetable by-products to produce animal feeds;
the roasting of coffee beans.

Where cooking or putrefaction are not involved, such as the production of fresh and frozen foods, emissions are considered negligible. Emissions from the pasteurisation of milk and the production of cheeses are also considered negligible

Control techniques typically involve incineration or biological treatment, resulting in more than 90% destruction of NMVOCs.

4 SIMPLER METHODOLOGY

The simpler methodology divides food manufacture into seven categories each with its own emission factor. These categories are:

meat, fish and poultry
sugar
margarine and solid cooking fats
bread
cakes, biscuits and breakfast cereals
animal feeds
coffee roasting

To obtain an emission estimate for NMVOCs from each of these categories, national production statistics are multiplied by default emission factors presented in section 8. It is assumed that no controls of emissions are in place.

5 DETAILED METHODOLOGY

A detailed methodology for emission from bread-making requires production statistics for the following types of bread:

sponge dough
white bread
white bread, shortened process
wholemeal bread
light rye bread
dark rye bread

In addition, information about the extent of control of emissions from each of the major sectors is required.

6 RELEVANT ACTIVITY STATISTICS

6.1 Simpler Methodology

The relevant activity statistics are based on national production figures.

total production of home-killed meat, including meat subsequently canned
total fish and seafood landed
total production of poultry meat
total sugar production
total production of fats excluding butter
total production of bread
total production of cakes, biscuits and breakfast cereals
total production of compound feedstuffs for cattle, pigs, poultry and other animals
total weight of beans roasted to produce coffee

The principal information source will be the country's national statistics of production.

6.2 Detailed Methodology

Requires all the activity statistics given in paragraph 6.1 together with:

total production of bread by the sponge-dough process
total production of white bread by the shortened process
total production of wholemeal bread
total production of light rye bread
total production of dark rye bread

A national trade association relating to the manufacture and production of bread would be the principal source of information for these activities.

7 POINT SOURCE CRITERIA

Only a few food processing plants are likely to be large enough to be considered point sources.

To qualify for consideration as point sources, the following levels of production should be obtained:

Foodstuff	Production rate (tonne per year)
Bread	300 000
Meat etc.	1 500 000
Sugar	150 000
Margarine etc	150 000
Animal feed	1 500 000
Coffee roasting	2 700 000

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Background Data

The following emission factors have been used to derive default emission factors for the simple and detailed methodologies:

Process	NMVOC Emission Factor	Quality Code	Source
Grain drying	1.31 k/t(grain)	E	USEPA,1985
Coffee roasting	0.55 k/t(beans)	D	Rentz et al, 1991
Animal rendering (uncontrolled)	0.326 k/t(meat)	D	Passant, 1993
Fish meal processing (uncontrolled)	1.04 k/t(fish)	D	Passant, 1993
Sponge-dough	8 k/t(bread)	D	Henderson, 1977
White bread	4.5 k/t(bread)	D	Bouscaren 1992
White bread, shortened process	2.0	D	Bouscaren 1992
Wholemeal bread	3.0	D	Bouscaren 1992
Light Rye bread	3.0	D	Bouscaren 1992
Dark Rye bread	0	D	Bouscaren 1992

The sponge dough process used in the manufacture of bread is not typical of Europe.

8.2 Default Emission Factors

Foodstuff	**Default Emission Factor**		**Quality Code**
	Simple	Detailed	
Bread (Europe)	4.5 k/t(bread)		E
Bread (North America)	8 k/t (bread)		E
Bread (sponge dough)		8 k/t(bread)	D
Bread (white)		4.5 k/t(bread)	D
Bread (wholemeal and light rye)		3 k/t(bread)	D
Bread (dark rye)		0 k/t(bread)	E
Cakes, biscuits and breakfast cereals	1 k/t(product)		E
Meat, Fish and Poultry	0.3 k/t(meat etc)		E
Sugar	10 k/t(sugar)		E
Margarine and solid cooking fats	10 k/t (product)		E
Animal feed	1 k/t		E
Coffee roasting	0.55kg/t(beans)		D

It is assumed that abatement equipment reduces emissions by 90% when used. Hence to obtain a default emission factor from a controlled source, multiply the uncontrolled emission factor by 0.1.

If, for example, the extent of control is 75%, assign 25% of the activity to an uncontrolled emission factor, and 75% of the activity to a controlled emission factor.

Note, since most domestic cooking of meat is within ovens, grills etc, emissions to the environment are likely to be very low. This source may be considered controlled.

9 SPECIES PROFILES

Emissions from the processing of cereals is known to involve a range of NMVOC including alcohols, ethers, aldehydes, aromatics, aliphatics, dimethyl sulphide and carboxylic acids (See SNAP codes 040606, 040607, 040608 Alcoholic Beverages).

The NMVOC emission from breadmaking is 95% ethanol arising from the fermentation process. The remaining 5% may include acetaldehyde and pyruvic acid (2-oxopropanoic acid) (Henderson, 1977). The following species profile of animal rendering has been produced, based on reports by a number of workers (Passant, 1993):

Compound	**%wt**
Aromatics	33
Alkanes	30
Aldehydes	21
Sulphur Compounds	13
Alcohols	3

In the absence of better data, the following default species profile may be used for emissions from the food industry as a whole, with a data quality E.

Compound	**%wt**
Ethanol	20
Other alcohols (e.g. propanol)	10
Aldehydes (e.g. acetaldehyde)	20
Sulphur Compounds (e.g. dimethylsulphide)	10
Carboxilic acids (e.g. pyruvic acid)	10
Alkanes	10
Aromatics	10
Ethers	10

10 UNCERTAINTY ESTIMATES

Uncertainty in the emission estimates is greater than a factor of 2.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect of the methodology is the quality of the data for emission factors. Those sectors with the largest emission estimate and data quality E for the default emission factor should be considered first. For the UK, the priority order would be as follows:

1. Sugar
2. Animal feeds
3. Margarine and solid cooking fats
4. Meat, fish and poultry

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

The proportion of the emission remaining once the contribution of point sources has been removed should be disaggregated by population.

13 TEMPORAL DISAGGREGATION CRITERIA

Assume continuous emission over 24 hours and throughout the year, unless better information is available.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

Verification of the methodology is through the measurement of emissions from selected point sources.

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19 RELEASE VERSION, DATE AND SOURCE

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SNAP CODES:	**040606** **040607** **040608**
SOURCE ACTIVITY TITLES:	**PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES** ***Wine*** ***Beer*** ***Spirits***
NOSE CODE:	**105.03.03** **105.03.04** **105.03.05**
NFR CODE:	**2 D 2**

1 ACTIVITIES INCLUDED

Emissions are included from the production of alcoholic beverages, specifically wine, beer and spirits. Emissions from the production of other alcoholic drinks are not covered in this edition.

Emissions from the distribution of alcoholic beverages should be included, but in this edition are not considered.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution to total national emissions of NMVOC emissions from the production of alcoholic beverages lies in the range 0 to 2% (based on information given in Passant et al., 1993). In general, spirit production tends to be the largest source and this may be considered very country specific.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

When making any alcoholic beverage, sugar is converted into ethanol by yeast. This is fermentation. The sugar comes from fruit, cereals or other vegetables. These materials may need to be processed before fermentation. For example, in the manufacture of beer, cereals are allowed to germinate, then roasted and boiled before fermentation. To make spirits, the fermented liquid is then distilled. Alcoholic beverages, particularly spirits and wine, may be stored for a number of years before consumption.

3.2 Definitions

beverage	drink
cask	container in which drinks are stored to mature.

to decant	to pour from one container into another. This verb is often used to imply that only part of the contents of the first container are poured into the second.
distillate	product of distillation; the more volatile substances.

3.3 Techniques

3.3.1 Preparation of feedstock

Cereals used in the production of beer and some spirits are usually allowed to germinate before use. This process is called malting, and results in the conversion of starch into sugars.

Germinated cereals may then be roasted. The length of roasting varies depending on the type of grain and the type of beverage to be produced.

Before fermentation, cereals are often boiled in water to produce wort, which is then filtered to separate out the solid residues.

Grapes and other fruit used to make alcoholic beverages, are pressed to recover their juice, which is filtered to remove solid residues. Red wine is fermented with the grape skins remaining in the vat for the initial fermentation. The liquid wine is run off when the required colour and tannin have been obtained, and the remainder of the liquid is obtained by pressing.

The solid residues may be further processed into food for animals.

3.3.2 Fermentation

Fermentation occurs in large fermenting vessels and typically lasts for from one to three days. Some vessels are sealed, recirculating the carbon dioxide. Others, normally in smaller plants, vent to atmosphere via a water trap.

The yeast strain used for fermentation depends on the beverage.

The specific gravity of the fermenting mixture is measured regularly as an indication of the sugar content and thereby the degree of fermentation. Temperature controls may need to be used as most fermentation will only take place at 5-30^{o}C.

3.3.3 Distillation

After separating solids from the fermented product, distillation may be used to recover the alcohol and other volatile organic species. Additional flavourings may be added either before or after distillation. More than one stage of distillation may be used. The final distillate can now either be diluted to give a standard alcohol content and bottled, or, in the case of whisky, brandy, some gins and other spirits, undergo a period of storage (maturation) during which the flavour develops.

3.3.4 Maturation

Wine is transferred to wooden casks after fermentation. Every 3 months the wine is decanted ("racked") from one cask to another to remove the sediment which collects during maturation. After maturation, which may take from a few weeks to several years, the wine is bottled (Burroughs and Bezzant, 1980).

Some spirits are transferred to wooden casks after distillation. Whisky and brandy are stored for a minimum of three years (usually longer). Some other spirits, such as gin, may occasionally be stored for shorter periods before sale. The final product is diluted to the appropriate alcohol strength and bottled.

3.4 Emissions/Controls

Emissions may occur during any of the four stages which may be needed in the production of an alcoholic beverage.

During preparation of the feedstock, the most important emissions appear to occur during the roasting of cereals and the drying of solid residues. Techniques for controlling emissions during the drying of residues exist and may involve condensers or bio-filters.

During fermentation, alcohol and other NMVOCs are carried out with the carbon dioxide as it escapes to atmosphere. In some cases, the carbon dioxide may be recovered, reducing the emission of NMVOC as a result.

During the distillation of fermentation products emissions are to be expected, but very little data is available. Losses occur as a result of poor maintenance and the use of old plant.

During maturation NMVOCs evaporate from the stored beverage. The mass of emission will be proportional to the length of the maturation period. Few if any control technologies are known.

Some losses of spirit are to be expected during transfer of spirit to barrels for storage. The UK Customs & Excise allow for a maximum loss of 0.1% of alcohol production (Passant, 1993).

4 SIMPLER METHODOLOGY

The simpler methodology involves combining readily available national data on the production of wine, beer and spirits with default emission factors based on all the currently available information. The default emission factors are designed to ensure that the resulting emission is not underestimated.

The annual production in hectolitre is multiplied by the relevant 'emission factor' to give the annual emission:

Emission Factor (kg/hl) x Annual Consumption (hl/a) = Annual Emission (kg/yr)

kg/yr = kilogram per year
kg/hl = kilogram per hectolitre
hl/yr = hectolitre per year

Emission factors for a variety of alcoholic beverages are given in paragraph 8.3.

5 DETAILED METHODOLOGY

The detailed methodology involves the acquisition of more detailed data on the production of red and white wine, and the types of spirit produced. These data are combined with default emission factors as described in the simpler methodology.

6 RELEVANT ACTIVITY STATISTICS

6.1 Simpler Methodology

Total production of wine
Total production of beer and cider
Total production of spirits

International statistics for these activities are given in World Drink Trends, 1993. NTC Publications Ltd, ISBN 1 870562 63 1, price £25.

6.2 Detailed Methodology

Total production of red wine
Total production of white wine
Total production of beer
Total production of whisky and the typical maturation period
Total production of brandy and the typical maturation period
Total production of other spirits and the typical maturation period

The principle information source will be the country's national statistics of production.

7 POINT SOURCE CRITERIA

The criterion proposed for consideration as a point source is an emission of 1.5 kt NMVOC per year. This is equivalent to a point source producing 19 000 000 hl of wine, 43 000 000 hl of beer, 100 000 hl(alcohol) of whisky, 430 000 hl(alcohol) of brandy, or 4 000 000 hl(alcohol) of other spirits. Hence it would be unusual for an individual production unit to create such a significant emission

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Background Data

The following emission factors were used to derive default emission factors for the simpler and detailed methodologies.

Process	Emission factor	Quality code	Reference
Barley malting	550 g/t (barley)	E	Passant, 1993
Hop processing	0.0055-0.011 kg/t(beer)	C	UBA, 1981
Fermentation	2 kg/t (alcohol)	D	Passant, 1993
Casking	0.5 kg/t (alcohol)	D	Passant, 1993
Maturation	20 kg/a/t (alcohol)	C	Passant, 1993
Grain drying	1310 g/t (grain)	E	USEPA, 1985
Wine	200 g/tonne	D	Rentz et al, 1991
Red Wine	0.1-1.2 kg/m^3	E	Jourdan et al, 1990
White Wine	0.1-0.3 kg/m^3	E	Jourdan et al, 1990
Red Wine	0.81 g/kg	D	Veldt,1991
White Wine	0.34 g/kg	D	Veldt, 1991

0.15 tonne of grain is required to produce 1 tonne of beer (Passant, 1993).

Malt whiskies are typically matured for ten years. Grain whiskies are typically matured for six years. It is assumed that brandy is matured for three years and that other spirits are not matured.

Beer is considered to be typically 4% alcohol by volume and to weigh 1 tonne per cubic metre.

If no better data is available, assume spirits are 40% alcohol by volume.

Alcohol (ethanol) has a density of 789 kg/m^3

8.2 Default Emission Factors

Beverage	Emission Factor		Quality
	Simple	Detailed	
Wine (unspecified colour)	0.08 kg/hl(wine)		E
Red Wine		0.08 kg/hl(wine)	D
White Wine		0.035 kg/hl(wine)	D
Beer (including de-alcoholized)	0.035 kg/hl(beer)		D
Spirits (unspecified sort)	15 kg/hl(alcohol)		E
Malt Whisky		15 kg/hl(alcohol)	C
Grain Whisky		7.5kg/hl(alcohol)	C
Brandy		3.5 kg/hl(alcohol)	D
Other Spirits		0.4 kg/hl(alcohol)	D

9 SPECIES PROFILES

Emissions from most processes in the manufacture of alcoholic beverages are likely to consist almost entirely of ethanol.

Emissions from the processing of cereals is known to involve a range of NMVOC including alcohols, ethers, aldehydes, aromatics, aliphatics, dimethyl sulphide and carboxylic acids (Rapport et al., 1983; Gibson et al., 1994; Buckee et al., 1982; Lukes et al., 1988; Seaton et al., 1982)

Methanol and dichloromethane may be used in the extraction of hops for the flavouring of beer. However, emissions from this process contribute very little to the total.

Little is known of actual emissions during the fermentation of wine, however 98% of all NMVOC in must (fermenting grapes and grape skins) is ethanol, so the primary species emitted from fermentation is likely to be ethanol, with the remaining species primarily alcohols, aldehydes and esters (Passant et al., 1993; Jourdan et al., 1990; Lichine, 1975)

Emissions from the fermentation of beer are >90% ethanol, with the remaining 10% are made up of hexanal, benzaldehyde, ethers, esters, acetates, acids.

Emissions from distillation and maturation are expected to be entirely ethanol.

Unless better information is available, the composition of emissions from the production of wine and spirits is assumed to be 100% ethanol.

The following default emission profile for beer production may be used, with a data quality of E:

Compound	**% contribution to total emission**
Ethanol	59%
Propanol	10%
Hexanal	10%
Dimethyl Sulphide	10%
Acetic Acid	10%
Dichloromethane	1%

10 UNCERTAINTY ESTIMATES

The uncertainty in emissions from the production of wine and beer is expected to be greater than a factor of 2.

The uncertainty in emissions from spirits will also be greater than a factor of 2 unless the type of spirit produced is identified. If this is the case, then the uncertainty in emissions from spirits will be less than a factor of 2.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspect of the methodology is the accuracy of the emission factors. Which factor should receive most attention depends on the relative proportions of wines, beers and spirits in a country's production. Hence, for example, in the United Kingdom, where a large volume of spirits (matured for several years) is manufactured, uncertainty in the emission factor for maturation is the largest source of uncertainty. In Germany, where more beer and a smaller volume of spirits (matured for less time) are made, the emission factors for cereal processing are also important. More accurate emission factors may be obtained through a programme of measurements from a range of selected plant.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

The manufacture of most beverages is associated with particular regions of a country. The lowest level of accuracy is obtained by disaggregating the net emission according to population density. Greater accuracy is achieved by identifying regions where particular beverages are produced and confining the distribution of emissions to those regions.

13 TEMPORAL DISAGGREGATION CRITERIA

The lowest accuracy assumes that emissions do not vary temporally.

Greater accuracy is achieved if it is assumed that the processing of feedstock and fermentation occur primarily in three months of the year, namely August, September and October. Distillation and maturation occur during all months of the year.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

World Drink Trends, 1993. NTC Publications Ltd, ISBN 1 870562 63 1, price £25.

16 VERIFICATION PROCEDURES

Verification procedures involve the measurement of emissions from specific plant and in particular emissions during the processing of cereals and fermentation.

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18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 2.2

Date : March 1995

Source : M A Emmott, S J Richardson.
AEA Technology Environment

Updated with particulate matter details by:
Mike Woodfield
AEA Technology
UK
December 2006

POINT OF ENQUIRY

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SOURCE ACTIVITY TITLE: PRODUCTION OF HALOCARBONS AND SULPHUR HEXAFLUORIDE

ACTIVITY	SNAP CODE	NOSE CODE	NFR CODE
	040801	105.09.60	-
	040802	105.09.61	-
	040803	105.09.62	-
	040804	105.09.63	-
	040805	105.09.64	-
	040806	105.09.65/66	-

A specific methodology has not been prepared yet as this is a new sub group. Please contact the expert panel leaders if you have relevant information.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Updated with particulate matter details by:
Mike Woodfield
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SNAP CODE:	**030311** **040612**
SOURCE ACTIVITY TITLE:	**PROCESSES WITH CONTACT** ***Cement*** ***Cement (decarbonizing)***
NOSE CODE:	**104.11.02** **105.11.21**
NFR CODE:	**1 A 2 f** **2 A 1**
ISIC:	**2394**

1 ACTIVITIES INCLUDED

This chapter covers emissions from both the combustion and mechanical processes used to produce cement.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of gaseous emissions released from the production of cement to total emissions in countries of the CORINAIR90 inventory is presented in Table 2.1.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (***28 countries***)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**										
Cement	030311	SO_2	NOx	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	TSP	PM_{10}	$PM_{2.5}$*
Typical contribution		0.8	2.3	0	0	0.2	2.1	0.3	-	11.8	5.96	3.60
Highest value										48.2	23.1	14.5
Lowest value										1.70	1.08	0.68

* EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006), contribution to total national emissions, excluding agricultural soils

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

\- = no emissions are reported

The emitted dust may contain heavy metals, particularly so when wastes are burnt as fuel, see Baart et al. (1995). The average relative contribution from the cement production industry to the total emission of heavy metals has been presented for European countries in Table 2.2.

Table 2.2: Average relative contribution of the production of cement to the total emission of heavy metals in European countries (Baart et al., 1995)

Compound	**Contribution (%)**
Cadmium	1.2
Chromium	1.5
Nickel	1.7
Lead	0.23

Cement production may be an important source of mercury as well as the metals presented in Table 2.2. It was estimated that on a global scale cement contributes with about 1.0 % to the total emissions of the element emitted from anthropogenic sources (Pacyna and Pacyna, 1996). However, Table 2.3 gives the contribution of cement to total emissions of heavy metals and POPs from the OSPARCOM-HELCOM-UNECE emission inventory, and the estimate for mercury is a 15 % contribution.

Table 2.3: Contribution to total POP and heavy metal emissions of the OSPARCOM-HELCOM-UNECE emission inventory (up to 39 countries)

Source-activity	**SNAP-code**	**Contribution to total emissions (including emissions from nature) [%]**										
		As	Cr	Cu	Pb	Cd	Hg	Ni	Zn	PCBs	PCDD/Fs	PAH
Cement	040612	0.5	1.2	0	0.1	0.5	15	0.3	0.3	0	0.2	0

3 GENERAL

3.1 Description

The “standard” cement is Portland cement, which accounts for about half of the EU/EEA consumption (European IPPC Bureau, 2000). The raw materials for Portland cement clinker are limestone, sand, shale, clay and iron oxide. Other cements are composite cements and blast furnace cement, which substitute blast furnace slag or other materials for a portion of the raw materials. In each case, the processing is largely the same, and the clinker is later combined with gypsum to create the final cement. The main process stages are:

- Handling of raw materials, intermediate products and final product;
- Fuel grinding if solid fuel is used;
- Kiln feed preparation;
- Pyroprocessing in a rotary kiln to form clinker;
- Clinker cooling;
- Milling (grinding and blending with gypsum).

Types of fuels used vary across the industry. Cement kilns are highly energy-intensive and fuel costs have a critical effect on profitability. Historically, some combination of coal, oil, and natural gas was used, but over the last 15 years, most plants have switched to coal.

However, in recent years a number of plants have switched to systems that burn a combination of coal and waste fuel.

3.2 Definitions

Portland cement	a type of hydraulic cement usually made by burning a mixture of limestone and clay in a kiln
Kiln	a furnace for burning fuel and cement clinker

3.3 Techniques

Portland cement can be produced either by dry or wet milling. In the case of wet milling the raw cement clinker is first mixed with water; this mixture is fired into a rotary kiln and finally milled. In the dry process the mixing with water is omitted. The dry process requires less energy than the wet process.

The raw materials are first brought to site; some will normally be conveyed from nearby quarries or open pits. The materials are then mixed, crushed and ground to produce a raw mix (raw meal) of the correct particle size and chemical properties. The raw meal is converted into cement clinker by pyroprocessing in rotary kilns. These consist of a refractory lined cylindrical steel shell slightly inclined to the horizontal and rotating at 1 – 3 rpm. Raw material is fed in at the upper end and gradually moves downward towards the lower end where there is a burner providing counter-current heating.

Most cement kilns now use the dry process, in which raw mill material is fed into the rotary kiln dry. Before passing into the kiln the material may be preheated in a vertically arrayed multi-cyclonic preheater, in which the rising hot gases exiting the kiln contact the downward flowing raw materials. Some dry processes also employ a precalciner stage beneath the preheater, just before the raw material enters the kiln. Preheaters and precalciners often have an alkali bypass between the feed end of the rotary kiln and the preheater to remove undesirable volatile components.

The use of the wet process, where the ground meal is mixed with water and fed into the kiln as a slurry, is now less common. The wet process uses about 40% more energy than the dry process.

The last stage involves cooling the clinker. As the hot clinker comes off the lower end of the kiln it is rapidly cooled by ambient air in a clinker cooler. There are many different designs of cooler, the most common of which is a travelling grate with under-grate fans that blow cool air through the clinker. Some of this air can be used for combustion, but some is vented to atmosphere or used for drying solid fuels and raw materials.

Finally, the cooled clinker is then mixed with gypsum and, for composite cements, other materials such as blast furnace slag, and ground to a fine homogeneous powder to produce the final product, which is then stored in silos prior to bulk transportation or bagging.

3.4 Emissions

Dust emissions result from activities such as handling raw materials; on site transportation; firing of clinker; milling; and shipment. The largest emission sources are the three units of kiln operation: the feed system, the fuel firing system, and the clinker cooling and handling system. The most desirable method of disposing of the collected dust is injection into the kiln burning zone and production of clinker from the dust. If the alkali content of raw materials is too high, however, some of the dust is discarded and leached before returning to the kiln. In many instances, the maximum allowable cement alkali content of 0.6 % (calculated as sodium oxide) restricts the amount of dust that can be recycled.

Nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon monoxide (CO), and carbon dioxide (CO_2) are the primary emissions in the manufacture of portland cement. Small quantities of volatile organic compounds (NMVOC, methane (CH_4)), nitrous oxide (N_2O), and ammonia (NH_3) also may be emitted (see also Table 8.1). Emissions may also include residual materials from the fuel and raw materials or products of incomplete combustion that are considered to be hazardous. Because some facilities burn waste fuels, particularly spent solvents, in the kiln, these systems also may emit small quantities of additional hazardous organic pollutants (IPCC, 1995).

Oxides of nitrogen are generated during fuel combustion by oxidation of chemically bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. As flame temperature increases, the amount of thermally generated NO_x increases. The amount of NO_x generated from fuel increases with the quantity of nitrogen in the fuel. In the cement manufacturing process, NO_x is generated in both the burning zone of the kiln and the burning zone of a precalcining vessel. Fuel use affects the quantity and type of NO_x generated. There is a marked increase in the amount of oxides of nitrogen (mainly nitric oxide) that is formed at temperatures above 1,400 °C. The formation of nitric oxide is also a function of the excess air (IPCC, 1995; EPA, 1995).

Sulphur dioxide may be generated both from the sulphur compounds in the raw materials and from sulphur in the fuel. Here only emissions from combustion are taken into account originating from the sulphur in the fuel. The sulphur content of both raw materials and fuels varies from plant to plant and with geographic location. Sulphur is normally present in the form of metal sulphide and sulphates. The amount of sulphur present will vary widely according to the nature of the deposits used. During the calcining operation, sulphur dioxide is released.

Compounds of sulphur are common constituents of most fuels and levels of sulphur may be as high as 5 wt%. Sulphides and organic sulphur compounds in the raw materials will normally be oxidised to sulphur dioxide and pass through the burning zone of the kiln with the process gases. For practical purposes sulphur in the kiln exhaust may be assumed to be emitted as sulphur dioxide, although there is usually some sulphur trioxide formed. Where this sulphur dioxide is formed at temperatures lower than the calcium carbonate calcination, it will be emitted from the kiln and preheater system to a significant extent. Some absorption may take place in the precipitator or raw mill. In most circumstances, only a small fraction of the sulphur dioxide generated within the kiln from the fuel is released to atmosphere, since it is mainly incorporated into the cement clinker by chemical combination. (IPCC, 1995; EPA, 1995).

The CO_2 emissions from portland cement manufacturing are generated by two process steps: As with most high-temperature, energy-intensive industrial processes, combusting fuels to generate process energy releases substantial quantities of CO_2. Substantial quantities of CO_2 are also generated through calcining of limestone or other calcareous material. This calcining process thermally decomposes $CaCO_3$ to CaO and CO_2. The amount of CO_2 released in the calcining process is about 500 kilograms (kg) per Mg of portland cement produced. Total CO_2 emissions from the pyroprocess depend on energy consumption and generally fall in the range of 0.85 to 1.35 Mg of CO_2 per Mg of clinker. Carbon dioxide comprises at least 20 % of the dry combustion gases and is produced from the carbon content of fuels and from calcination of the calcium carbonate (IPCC, 1995; EPA, 1995). IPPC BREF document (EUROPEAN COMMISSION, 2001) report an estimated emission of CO_2 at 900 to 1000 kg/tonne clinker, related to a specific heat demand of approximately 3500 to 5000 MJ/tonne clinker, but also depending on fuel type.

Fuel combustion at portland cement plants can emit a wide range of pollutants in smaller quantities. If the combustion reactions do not reach completion, CO and volatile organic pollutants (VOC) can be emitted. Incomplete combustion also can lead to emissions of specific hazardous organic air pollutants, although these pollutants are generally emitted at substantially lower levels than CO or VOC (IPCC, 1995).

Carbon monoxide is formed by the incomplete combustion of carbonaceous fuels and even with good combustion control small amounts of carbon monoxide will be present in combustion gases. When operating near to stoichiometric conditions in the kiln, there is localised generation of carbon monoxide (HMIP, 1992).

Heavy metal emissions from cement plants depend on their content in fuels and raw materials, industrial technology (e.g. combustion temperature), and emission control measures. During the cement production process at high temperatures many heavy metals present in the fuel and the raw materials evaporate and then condense on the clinker and partly on fine particles in the flue gas. The latter portion of the metals finds its way to the atmosphere after passing through the emission control equipment.

Fluorine compounds in the feed constituents are partly volatised into gaseous acidic fluorides at the high temperatures in the kiln. However, such acidic compounds are immediately neutralised (in the form of solid calcium fluoride) by the alkaline constituents in both the clinker and the feed. Thus, 88 - 98 % of the fluoride content of the feed materials is trapped in the clinker and the remainder deposits on dust particles and is mainly removed by the dust control devices. Chlorine compounds behave in a similar manner to those of fluorine.
Some kilns do burn hazardous waste as supplemental fuel. Other types of non-hazardous liquid and solid wastes used as supplemental fuels include tyres, waste oil, and wood chips. Dioxins (PCDDs) and furans (PCDFs) were first detected in stack emissions from portland cement kilns in the early 1980s (e.g. EPA, 1994). They were detected at low concentrations and were thought to be caused by the co-firing of liquid hazardous waste with conventional fossil fuels. Recently more information has become available on the possible formation

mechanisms of dioxins in the portland cement kilns. The following mechanisms have been suggested:

- some primary combustion fuels and fuel supplements used to sustain elevated temperatures in the kiln to form clinker may also produce aromatic hydrocarbon compounds that can later become chlorinated ring structures. The oxidation of HCl gas has been shown to provide chlorine available for ring substitution;
- the chlorinated aromatic compounds may act as precursor molecules to the thermalytic formation of CDD/CDFs on the active surface of carbonaceous particles;
- de novo synthesis of CDD/CDFs on the active surface of carbonaceous particles in the presence of a catalytic agent (e.g. metal ions);
- post-kiln temperatures of the combustion gases are often within the range of temperatures that promote the continued formation of CDD/CDFs;
- co-firing of liquid hazardous organic wastes with coal and petroleum coke may lead to an increase in the amount of CDD/CDFs formed in the post-combustion zone.

3.5 Controls

Emission reduction is usually obtained by reducing the dust emissions. Electrostatic precipitators (ESPs) and fabric filters (FFs) are most widely used on both kilns and clinker coolers. For electrostatic precipitation dust concentrations of 30 - 40 mg/m^3 can be achieved. For fabric filters a value of 20 to 50 mg/m^3 is common. A few gravel bed filters have also been used to control clinker cooler emissions. Fugitive emission sources are normally captured by a ventilation system and fabric filters used to collect the dust.

A portion of heavy metals in the flue gas will also be removed with particles. However, the most volatile heavy metals are present on very fine particles, often penetrating both ESPs and FFs. It is proposed that further reduction of dust concentrations in the flue gas to 10 mg/m^3 should be achieved in order to obtain reasonable reduction of heavy metals.

Emissions of sulphur dioxide are best reduced by use of low sulphur raw materials. Removal of sulphur dioxide from the exhaust gases is possible using injection of calcium hydroxide into the air stream - after the preheater for minor reductions, or by a separate fluid bed absorber for significant reductions. However, the alkaline nature of the cement provides for direct absorption of SO_2 into the product, thereby mitigating the quantity of SO_2 emissions in the exhaust stream. Depending on the process and the source of the sulphur, SO_2 absorption ranges from about 70 percent to more than 95 percent. However, in systems that have sulphide sulphur (pyrites) in the kiln feed, the sulphur absorption rate may be as low as 70 percent without unique design considerations or changes in raw materials. Fabric filters on cement kilns are also reported to absorb SO_2 (IPCC, 1995; EPA, 1995).

Flue gas desulphurisation equipment also reduces the concentration of gaseous mercury present in the flue gas. This reduction can be as high as 50 %. Further reduction of up to 85 % can be achieved through the application of very expensive measures such as injection of activated carbon or application of activated carbon beds.

Oxides of nitrogen can be reduced by applying the following techniques (EPA, 1995):

- Use of low-NO_x-burners where practicable, the principle of which is the avoidance of localised hot spots.
- Avoidance of over-burning of the clinker. The temperature in the burning zone can be limited to that necessary to produce a free lime content which gives acceptable clinker quality. Cements kilns can be fitted with on-line oxides of nitrogen sensors which form the basis of an automatic kiln control system. The prevention of over-burning not only gives reduced oxides of nitrogen levels but also provides some worthwhile energy savings.

The formation of carbon dioxide should be minimised by the use of energy efficient systems and techniques (HMIP, 1992).

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR} \times \text{EF}$$

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3), to estimate emissions of gaseous pollutants from the cement production is based on measurements or estimations using plant specific emission factors - guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

The detailed methodology to estimate emissions of trace elements from the cement production is similar to the simpler one. However, more information on the type of the process, e.g. wet and dry kilns, as well as on the type of the industrial technology should be made available. This information shall be used to estimate specific emissions for at least a specific industrial technology.

Measurements of the emission rate and chemical composition of fine particles with < 1.0 µm diameter are often carried out at major cement kilns world-wide. The results of these measurements are then used to estimate atmospheric emissions of several trace elements contained as impurities in the raw materials and fuel.

Reference emission factors for comparison with users own data are provided in Section 8.2.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of cement, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of cement produced by various types of industrial technologies employed in the cement industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 " Choice of activity statistics".

7 POINT SOURCE CRITERIA

Cement production plants are regarded as point sources if plant specific data are available. When emissions care is needed to distinguish ground level emissions (from mechanical processes) from combustion related emissions released via a chimneystack.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors For Use With Simpler Methodology

A summary of default emission factors for use with a simpler methodology for estimating emissions are provided in Table 8.1a and Table 8.1b. The emission factors are mainly extracted from the Integrated Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001). Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030311; fuel used in the process does not have to be taken into account in 0301.

Table 8.1a: Emission Factors for Cement production

Pollutant	**Emission factor**	**Units**
Particulate matter (1)		
TSP	600	g/tonne cement
PM_{10}	510	g/tonne cement
$PM_{2.5}$	180	g/tonne cement
Nitrogen oxides		
Average (3)	2100	g/tonne of clinker (2)
BAT (3, 4)	700	g/tonne of clinker
Sulphur oxides (4)		
raw materials with little or no volatile sulphur	20	g/tonne of clinker
raw materials with high volatile sulphur		
average	2400	g/tonne of clinker
BAT (5)	600	g/tonne of clinker
Volatile organic compounds(3)	110	g/tonne clinker

(1) When information on type of facilities and abatement used is available, the corresponding emission factors for particulates (CEPMEIP) in Table 8.2g can also be used in the simple methodology. The here referred emission factor for particulate matter is for the most used technology in the EU; Conventional Cement production plant with an ESP on the main stack and smaller fabric filters for moderate control of fugitive sources

(2) Production capacities for clinker (intermediate product) and cement slightly differ and a correction factor needs to be used to transform the emission factor to cement. This factor is in order of magnitude of 0.8 [IPPC, BREF].

(2) Mean value of NOx emission measurements at more than 50 preheater rotary cement kilns from "*British Cement Association, Prevention and abatement of NOx emissions, International Cement Review, p. 51-59, October 1997*" as reported in *EUROPEAN COMMISSION, 2001*

(3) Using average of ranges in mg/m^3 and exhaust gas volumes around 2000 m^3/tonne of clinker from *EUROPEAN COMMISSION, 2001*

(4) The BAT for reducing NO_x emissions are a combination of general primary measures, primary measures to control NO_x emissions, staged combustion and selective non-catalytic reduction (SNCR) as reported in *EUROPEAN COMMISSION, 2001*"

(5) The best available techniques for reducing SO_2 emissions are a combination of general primary measures and absorbent addition for initial emission levels not higher than about 1200 mg SO_2/m^3 and a wet or dry scrubber for initial emission levels higher than about 1200 mg SO_2/m^3.

Table 8.1b: Metal and specific VOCs Emission Factors for Cement production

Pollutant	**Emission factor**	**Units**
Arsenic	0.2	g/tonne cement
Cadmium	0.01	g/tonne cement
Chromium	1	g/tonne cement
Copper	0.4	g/tonne cement
Mercury	0.1	g/tonne cement
Nickel	0.1	g/tonne cement
Lead	0.2	g/tonne cement
Selenium	0.002	g/tonne cement
Zinc	2	g/tonne cement
Dioxins and furans	0.2	µg TEQ/tonne cement
Hexachlorobenzene	11	µg TEQ/tonne cement
Polyaromatic hydrocarbons	3	mg/tonne cement
Polychlorinated biphenyls	1	µg/tonne cement

8.2 Reference Emission Factors for Use With Detailed Methodology

Table 8.2a contains reference emission factors for the production of cement based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg clinker), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a value for the specific energy consumption of 13 GJ/Mg product has been reported.

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030311; fuel used in the process does not have to be taken into account in 0301

Table 8.2a: Emission factors for the production of cement (fuel related)

Type of fuel				NAPFUE code	Emission factors						
					SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
s	coal	hc	coking	101	$569^{1)}$, $85\text{-}165^{2)}$	$701^{1)}$, $450\text{-}709^{2)}$		$1^{1)2)}$		$86^{1)2)}$	
s	coal	hc	steam	102	$44\text{-}880^{1)}$, $35\text{-}600^{2)}$	$150\text{-}170^{1)}$, $0.4\text{-}575^{2)}$	$15^{1)}$, $15\text{-}33^{2)}$	$14.7\text{-}15^{1)}$, $0.3\text{-}15^{2)}$	$10\text{-}110^{1)}$, $18\text{-}100^{2)}$	$93\text{-}94^{1)}$, $78\text{-}101^{2)}$	$12^{1)}$, $3\text{-}12^{2)}$
s	coal	hc	sub-bituminous	103	$134\text{-}154^{1)}$, $1{,}260^{2)}$	$57^{1)}$ $820\text{-}1{,}300^{2)}$			$22^{1)}$	$99^{1)}$, $320\text{-}420^{2)}$	$8^{2)}$
s	coal	hc	brown coal/lignite	105	$25^{2)}$	$575^{2)}$	$15^{2)}$	$15^{2)}$		$100\text{-}113^{2)}$	$3.5^{2)}$
s	coal	hc	briquettes	106	$11^{2)}$	$575^{2)}$	$15^{2)}$	$15^{2)}$	$100\text{-}260^{2)}$	$97\text{-}98^{2)}$	$3.5^{2)}$
s	coke	hc	coke oven	107	$25^{2)}$	$575^{2)}$	$15^{1)}$, $0.5^{2)}$	$15^{1)}$, $0.5^{2)}$	$110^{1)}$, $100^{2)}$	$108^{1)}$, $100\text{-}105^{2)}$	$14^{1)}$, $4^{2)}$
s	coke		petroleum	110	$355\text{-}511^{1)}$, $85\text{-}1{,}200^{2)}$	$300\text{-}568^{1)}$, $0.4\text{-}575^{2)}$	$1.5^{1)}$, $1.5\text{-}15^{2)}$	$1.5^{1)}$, $1\text{-}15^{2)}$	$10\text{-}70^{1)}$, $15\text{-}100^{2)}$	$99\text{-}102^{1)}$, $97\text{-}102^{2)}$	$14^{1)}$, $3\text{-}14^{2)}$
s	waste		municipal	115	$161^{1)}$	$200^{1)}$	$15\text{-}40^{1)}$	$15\text{-}40^{1)}$	$70^{1)}$	$100\text{-}121^{1)}$	$5\text{-}12^{1)}$
s	waste		industrial	116	$135^{2)}$	$0.4\text{-}568^{2)}$		$0.2^{2)}$	$1429^{2)}$	$83^{2)}$	$4^{2)}$
l	oil		residual	203	$131\text{-}1{,}030^{1)}$, $16\text{-}1{,}079^{2)}$	$150\text{-}220^{1)}$, $0.4\text{-}575^{2)}$	$3^{1)}$, $3\text{-}10^{2)}$	$1\text{-}3^{1)}$, $1\text{-}5^{2)}$	$15\text{-}20^{1)}$, $8\text{-}79^{2)}$	$76\text{-}79^{1)\,2)}$	$2\text{-}15^{1)\,2)}$
l	oil		gas	204	$4\text{-}1{,}410^{2)}$	$0.4\text{-}575^{2)}$	$1.5^{1)}$, $1.5\text{-}2.5^{2)}$	$1\text{-}5^{1)}$, $1\text{-}8^{2)}$	$12^{1)}$, $12\text{-}79^{2)}$	$74^{1)}$, $73\text{-}74^{2)}$	$12^{1)}$, $2\text{-}14^{2)}$
l	gasoline		motor	208			$2.5^{1)}$	$2.5^{1)}$	$12^{1)}$	$72^{1)}$	$12^{1)}$
l	oil		shale-oil	211						$78^{1)}$	
g	gas		natural	301	$0.1\text{-}135^{2)}$	$175^{1)}$, $60\text{-}560^{2)}$	$2.5^{1)}$, $2.5\text{-}18.4^{2)}$	$2.5^{1)}$, $0.4\text{-}5^{2)}$	$20^{1)}$, $10\text{-}120^{2)}$	$53\text{-}56^{1)}$, $55\text{-}69^{2)}$	$3^{1)}$, $1\text{-}3.7^{2)}$
g	gas		liquified petroleum gas	303	$0.04^{2)}$	$100^{2)}$	$2.5^{1)}$, $2.1^{2)}$	$2.5^{1)}$, $0.9^{2)}$	$20^{1)}$, $13^{2)}$	$65^{1)2)}$	$3^{1)}$, $1^{2)}$
g	gas		coke oven	304	$0.6^{2)}$	$575^{2)}$	$2.5^{2)}$	$2.5^{2)}$	$10^{2)}$	$44^{2)}$	$1.5^{2)}$
Data quality rating					B	B	D	D	C	C	D

1) CORINAIR90 data, area sources
2) CORINAIR90 data, point sources

Technique related emission factors are listed in Tables 8.2b through 8.2g for sulphur dioxide, nitrogen oxides, non-methane VOCs, CO, methane, and particulate matter. Only for particulates (Table 8.2g) some information exists on the type and efficiency of abatement techniques. All other factors in these tables seem to be valid for emissions from uncontrolled processes.

Table 8.2b: Emission factors for SO_2 from cement production

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Dry process kiln	N/A	N/A	N/A	kg/tonne product	5.1	E	USA
Wet process kiln	N/A	N/A	N/A	kg/tonne product	5.1	E	USA
Cement production	N/A	N/A	N/A	kg/tonne cement	0.2-0.3	E	USA
Clinker production	N/A	N/A	N/A	g/gJ	0.02-50.0	E	USA

Table 8.2c: Emission factors for NO_x from cement production

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Dry process kiln	N/A	N/A	N/A	kg/tonne product	1.4-2.1	E	USA
Wet process kiln	N/A	N/A	N/A	kg/tonne product	1.1-1.4	E	USA
Semi-wet process kiln	N/A	N/A	N/A	kg/tonne product	1.8	E	USA
Clinker production	N/A	N/A	N/A	g/GJ	1.2	E	USA
Clinker production (80% NO_x reduction, 20% energy saving)	N/A	N/A	N/A	kg/tonne clinker	0.6	E	USA
Cement production	N/A	N/A	N/A	g/GJ	130-220	E	USA
Cement production	N/A	N/A	N/A	kg/tonne cement	1.3-1.4	E	USA
Cement/lime industry, kiln	N/A	N/A	Natural gas	kg/GJ	1.1	E	USA
Cement/lime industry, kiln	N/A	N/A	Oil	kg/GJ	0.5	E	USA
Cement/lime industry, kiln	N/A	N/A	Coal	kg/GJ	0.5	E	USA

N/A - Data not available

Table 8.2d: Emission factors for NMVOC from cement production

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Dry process kiln	N/A	N/A	N/A	g/tonne product	10.0	E	USA
Cement production	N/A	N/A	N/A	kg/tonne cement	50.0	E	USA

N/A - Data not available

Table 8.2e: Emission factors for CO from cement production

Process type	**Abatement type**	**Abatement efficiency**	**Fuel type**	**Unit**	**Emission factor**	**Data Quality Code**	**Country or region**
Cement/lime industry, kiln	N/A	N/A	Natural gas	g/GJ	83.0	E	USA
Cement/lime industry, kiln	N/A	N/A	Oil	g/GJ	79.0	E	USA
Cement/lime industry, kiln	N/A	N/A	Coal	g/GJ	79.0	E	USA

N/A - Data not available

Table 8.2f: Emission factors for CH_4 from cement production

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor	Data Quality Code	Country or region
Cement/lime industry, kiln	N/A	N/A	Natural gas	g/GJ	1.1	E	USA
Cement/lime industry, kiln	N/A	N/A	Oil	g/GJ	1.0	E	USA
Cement/lime industry, kiln	N/A	N/A	Coal	g/GJ	1.0	E	USA

N/A - Data not available

Table 8.2g: Emission factors for particles from cement production

Process type	Abatement type	Abatement efficiency	Fuel type	Unit	Emission factor			Data Quality Code*	Country or region
					TSP	PM_{10}	$PM_{2.5}$		
Cement production (conventional plant)	ESP on main stack and smaller fabric filters for moderate control of fugitive sources	N/A	N/A	g/tonne cement	600	510	180	E (1,5)	EU (CEPMEIP)
Cement production	Limited control fugitive sources; ESP in main stack	ESP < 97%	N/A	g/tonne cement	2000	800	300	E (1,5)	EU (CEPMEIP)
Cement production (modern facility)	Addional fabric filters on the oven stack; effective control of fugitive sources	N/A	N/A	g/tonne cement	200	180	80	E (1,5)	EU (CEPMEIP)

N/A - Data not available

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in Table 8.2g): The uncertainty in the emission factor for $PM_{2.5}$ from a conventional cement production plant with an ESP on the main stack and smaller fabric filters for moderate control of fugitive sources is 1.5. The emission factor with uncertainty range will therefore be 510 gram per tonne cement with an uncertainty range of 340 (510/1.5) to 765 (510x1.5).

The emission factors for particles are dominated by the PM emissions arising from the kilns. Emissions for manufacturing of raw material and the processing and handling of the product are significantly lower. Emission factors for milling where emissions are controlled are in the range of 4 – 14 g TSP / ton material processed (AP42, table 11.6-3).

The emission factors for heavy metals are determined by the composition of the raw material and the type of fuels used for firing. An illustration of the range of emission factors to be expected is given in Table 8.2h. This table is derived from the PARCOM-ATMOS Emission Factors Manual (van der Most and Veldt, 1992). Unfortunately, no information is available on the abatement efficiency for these data.

Table 8.2h: Examples of emission factors for heavy metals from cement production in g/Mg cement (van der Most and Veldt, 1992)

Substance	**Coal and oil fired**	**Proportion of waste oil**	**Fuel unknown**	**Fuel unknown**	**Fuel unknown**
Arsenic	-	-	-	0.012	-
Cadmium	-	-	0.04	0.008	< 0.001
Chromium	0.006-0.02	0.02-0.3	-	0.105	-
Lead	0.006	0.012-0.2	1.1	0.216	<0.033
Mercury	-	-	-	0.275	-
Nickel	-	-	-	0.111	-
Selenium	-	-	-	0.002	-
Zinc	-	-	-	0.293	0.003-0.47

- Data not available

Similar results were reported for the UK cement industry (Salway, 1997).

In the CIS countries cement plants operate mostly using the wet process, and in this way 83 % of cement is produced. Some preliminary emission factors suggested for these countries are within the ranges presented in the above tables (EMEP-MSC-E, 1997). The same can be concluded for the emission factors developed in the Netherlands.

Concentrations of dioxins and furans in the flue gas after passing the control equipment in the cement production are presented in Table 8.1b after a compilation of data by the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Emission Control Committee in Germany (Umweltbundesamt, 1996) and information obtained from Schreiber et al. (1995), EPA (1994), and (Quass, 1997).

Emission data from kilns in operation coming from IPPC BREF document (EUROPEAN COMMISSION, 2001) is given in Table 8.2i. The emission ranges within which kilns operate depend largely on the nature of the raw materials, the fuels, the age and design of the plant, and also on the requirements laid down by the permitting authority. Mass figures are based on 2000 m^3/tonne clinker and 1 million tonnes clinker/year. Emission ranges are one-year averages and are indicative values based on various measurement techniques. O_2-content is normally 10%.

Typical kiln exhaust gas volumes expressed as m^3/tonne of clinker (dry gas, 101.3 kPa, 273 K) are between 1700 and 2500 for all types of kilns. Suspension preheater and precalciner kiln systems normally have exhaust gas volumes around 2000 m^3/tonne of clinker (dry gas, 101.3 kPa, 273 K).

There are also releases of particulates from all milling operations i.e. raw materials, solid fuel and product. There is potential for the release of particulates from any outside storage of raw materials and solid fuels as well as from any materials transport systems, including cement product loading. The magnitude of these releases can be significant if these aspects are not well engineered or maintained and being released at low level can lead to local nuisance problems.

Table 8.2i: Emission ranges from European cement kilns from IPPC BREF document (EUROPEAN COMMISSION, 2001)

Pollutant	**mg/Nm^3**	**kg/tonneclinker**	**tonnes/year**
NO_x (as NO_2)	<200–3000	<0.4-6	400-6000
SO_2	<10–3500	<0.02-7	<20-7000
Dust	5–200	0.01-0.4	10-400
CO	500–2000	1-4	1000-4000
CO_2	400-520 g/Nm^3	800-1040	0.8-1.04 million
TOC	5-500	0.01–1	10-1000
HF	<0.4-5	<0.8-10 g/t	<0.8-10
HCl	<1-25	<2-50 g/t	<2-50
PCDD/F	<0.1-0.5 ng/Nm^3	<200-1000 ng/t	<0.2-1 g/year
Metals:			
Σ(Hg,Cd,Tl)	0.01-0.3 (mainly Hg)	20-600 mg/t	20-600 kg/year
Σ(As,Co,Ni,Se,Te)	0.001-0.1	2-200 mg/t	2-200 kg/year
Σ(Sb,Pb,Cr,Cu,Mn,V,Sn,Zn)	0.005-0.3	10-600 mg/t	10-600 kg/year

9 SPECIES PROFILES

An analysis of dust emissions from clinker firing in the Netherlands gave results presented in Table 9.1. The composition is given in mg per tonne cement:

Table 9.1: Composition of dust from clinker firing

Substance	**Concentration in dust (g/tonne of cement)**
Antimony	6
Arsenic	4
Cadmium	6
Chromium	5
Copper	8
Lead	6.5
Mercury	9
Nickel	4
Selenium	3
Tellurium	5
Thallium	3
Uranium	3
Vanadium	5
Zinc	4

EPA (1995) gives size distributions for particulate matter emitted from various cement production processes. These are reproduced in Table 9.2. The profiles for controlled dry process kilns and controlled clinker coolers seem most appropriate for the EU and suggest that particulate matter emissions comprises about 80% PM_{10}.

Table 9.2: Particle size distributions and size-specific emission factors (EPA 1995)

Process	Abatement technology	Particle size (µm)	Cumulative mass % less than stated size
Kilns, wet process	Uncontrolled	2.5	7
		5	20
		10	24
		15	35
		20	57
		total	100
Kilns, wet process	ESP	2.5	64
		5	83
		10	58
		15	91
		20	98
		total	100
Kilns, dry process	Uncontrolled	2.5	18
		10	42
		15	44
		total	100
Kilns, dry process	Fabric filter	2.5	45
		5	77
		10	84
		15	89
		20	100
		total	100
Clinker coolers	Uncontrolled	2.5	0.54
		5	1.5
		10	8.6
		15	21
		20	34
		total	100
Clinker coolers	Gravel bed filter	2.5	40
		5	64
		10	76
		15	84
		20	89
		total	100

In general, no reliable information exists at present on physical and chemical species of trace elements emitted during the cement production. It can be assumed that the majority of trace elements volatilised from the raw material and fuel enter the atmosphere on fine particles.
Very general information collected by Pacyna (1987) appears to indicate that elemental forms, oxides and sulphates are the major chemical forms of atmospheric trace elements from the cement production.

10 UNCERTAINTY ESTIMATES

It is rather difficult to assess current uncertainties of emission estimates for pollutants emitted during the cement production. The uncertainties of sulphur dioxide emission estimates can be assessed in a similar way as the uncertainties of the estimates for the fossil fuel combustion (see chapter B111).

Recently it was concluded that up to 50% of uncertainties may be assigned to the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Similar uncertainty can be assigned for emission estimates of these compounds from the cement production.

Uncertainties associated with the emissions of $PM_{2.5}$ are indicated in Table 8.2g.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge of abatement techniques, dust removal efficiencies and operating techniques is limited; measurement data of composition of dust is poor.

The fuel specific emission factors provided in Table 8.1 are related to point sources and area sources without specification. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested to develop emission factors, which include technical or fuel dependent explanations concerning emission factor ranges. Emission factors also need to be generated, which specifically relate to different levels of abatement on different types of plant.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Cement production plants should be considered as point sources if plant specific data are available. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Cement production can be considered as a continuous process.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

Emission inventory in The Netherlands, 1992. Emission to air and water

Personal information and experience during emission inventories 1975 - 1995

Emission factors to be used for the building industry, TNO report 89/091

Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP 42

PARCOM-ATMOS Emission Factors Manual

16 VERIFICATION PROCESSES

Verification of the emissions can be done for metal emissions by calculating the emissions using the factors from the PARCOM ATMOS manual and comparing the results with a mean profile.

17 REFERENCES

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1 ACTIVITIES INCLUDED

The activities described under chapter 040613 regard the process emissions during the production of different types of glass (flat glass, container glass, glass wool and other glass {including special glass}). The activities concerned with the combustion and the resulting emissions are described in the chapters 030314, 030315, 030316 and 030317. The emissions treated in this chapter are carbon dioxide emissions from the carbonisation process and emissions of micropollutants, heavy metals and dust, partly resulting from the combustion of fossil fuels, partly from the basic materials. For micropollutants, heavy metals and dust separate emission factors for combustion and process emissions are not available. The factors given are to be used as default values for the whole process.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of emissions released from the production of glass to total emissions to air in countries of the CORINAIR90 inventory is given as follows:

Table 2.1: Contribution to total emissions to air of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Typical contribution to total emissions [%] (lowest value – highest value)									
		SO_2	NO_x	NMVOC	CH_4	CO	N_2O	NH_3	TSP*	PM_{10}*	$PM_{2.5}$*
Flat Glass	030314	0.1	0.3	0	-	0	-	-	0.004 (0.001 - 0.008)	0.222 (0.008 - 0.74)	0.352 (0.011 - 1.073)
Container Glass	030315	0.1	0.2	0	-	0	-	-	0.113 (0.004 - 0.367)	0.222 (0.008 - 0.74)	0.352 (0.011 - 1.073)
Glass Wool	030316	0	0	-	-	-	-	-	0.022 (0 - 0.043)	0.043 (0.001 - 0.077)	0.051 (0.002 - 0.084)
Other Glass	030317	0	0.1	-	-	0	-	-	0.073 (0.032 - 0.114)	0.144 (0.059 - 0.23)	0.227 (0.121 - 0.333)

* contribution to total national emissions, excluding agricultural soils, EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006)
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

Table 2.2: Contribution to total emissions to air (OSPAR-HELCOM-UNECE Emission Inventory)

Source-activity	Contribution to total emissions [%]							
	Arsenic	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
Glass industry	1.3	1.3	0.9	0.1	0.1	0.1	0.9	0.2

Table 2.3: Contribution from the carbonisation process

Source-activity	Contribution of carbon dioxide to total emissions [%]
Glass industry	

The emission of fluorides are also important.

3 GENERAL

In the production of glass products can be distinguished, for instance flat glass, container glass, special glass, glass wool, continuous filament fibres, water glass and tableware. The smelting process for the different product groups is similar.

The production of flat glass, container glass, glass fibres and commodity glass is dominated by large multinational companies, whereas domestic glass production (manufacture of table and decorative ware) take place in small- and medium-sized enterprises. Unlike technical glass production, domestic glass production is characterised by a great diversity of products and processes, including hand forming of glass. (Rentz et al., 1991; Eichhammer et al, 1994).

3.1 Description of Activities

The manufacturing process of glass consists of the following steps (Schmalhorst E.; Ernas T., 1995; Rentz et al., 1991; Eichhammer et al, 1994):

- *Selection and controlling of raw materials.*
- *Preparation of raw materials:* preparation consists essentially of a weighing and mixing operation.
- *Melting:* the raw materials undergo fusion at high temperature in a furnace.
- *Forming:* the molten glass is given a shape and allowed to solidify (production of flat and container glass); the formation of fibres into glasswool mats is carried out (production of glasswool).
- *Curing:* the binder-coated fibreglass mat is allowed to cure (production of glasswool).
- *Annealing:* internal stresses are removed by heat treatment.
- *Finishing:* finishing includes in particular quality control and cutting (production of flat and container glass); finishing includes cooling the mat, and backing, cutting, and packaging the insulation, as well as quality control (production of glasswool); finishing includes quality control, cutting, and for hand-shaped glass, further decorative treatment such as engraving or polishing (special glass).

A large variety of glass with differing chemical composition is produced, and therefore a great diversity of raw materials is used in glass manufacturing (VDI Kommission Reinhaltung der Luft, 1997). Main raw materials are silica sand, lime, dolomite and soda for the production of soda lime glass, as well as lead oxide, potash and zinc oxide for the production of special glass (Rentz et al., 1991; UN/ECE, 1995). Glass wool is a boro-silicate glass, which is manufactured from sand, limestone, dolomite, boric-oxide and other oxides. Refining agents such as antimony oxide, nitrates, sulphates, and colouring agents like metal oxides and sulphides enter also in the composition of special glass, e.g. TV glass, crystal glass, etc. (VDI Kommission Reinhaltung der Luft, 1997).

Nowadays, approximately 85 % of the glass produced in Europe is made up of soda lime, and consists principally of flat and container glass. The remaining 15 % of the European glass production include glass wool and special glass such as hand-shaped glassware, lighting, TV-screen, optical glasses. (Abraham et al. 1997)

Recycled glass is also largely used in the manufacturing of glass and represents typically between 20 and 25 % of the quantity of melted flat glass and up to 80 % of the quantity of melted container glass. Throughout the industry, virtually all internally generated cullet is reused. The poor quality and contamination of external cullet virtually eliminates its use for flat, commodity and domestic glassware, but much external cullet (with treatment) can be used in the container glass industry. (Abraham et al. 1997)

Currently, the majority of raw material is delivered to the glass production site in a prepared form; only broken glass pieces from recycling undergo processing steps such as sieving. The different materials are weighed and mixed, and the mixed batch is transferred to the melting furnace. (Rentz et al., 1991)

3.2 Definitions

Borosilicate glass	a silicate glass that is composed of at least five percent oxide of boron and is used especially in heat-resistant glassware.
Crown glass	alkali-lime silicate optical glass having relatively low index of refraction and low dispersion value.
Fibreglass	glass in fibrous form used in making various products (as glass wool for insulation).
Flint glass	heavy brilliant glass that contains lead oxide, has a relatively high index of refraction, and is used in lenses and prisms.
Float glass	flat glass produced by solidifying molten glass on the surface of a bath of molten tin.
Glass wool	there exist two types of glass fibre products, textile and wool, which are manufactured by similar processes. Here only glasswool is taken into account: glass fibres in a mass resembling wool and being used especially for thermal insulation and air filters.
Lead glass	glass containing a high proportion of lead oxide and having extraordinary clarity and brilliance.
Optical glass	flint or crown glass of well-defined characteristics used especially for making lenses.

3.3 Techniques

For container glass production, the melting stage can be preceded by a pre-heating of the mixed batch (Rentz et al., 1991); however, this is not commonly done: around 10 batch preheaters are currently in operation world wide (Abraham et al. 1997).

The melting process is the most important step with regard to quality and quantity of glass, which depend on the furnace design (Eichhammer et al., 1994). In the melting furnaces, the glass is melted at temperatures ranging from 1,500 °C to 1,600 °C (the flame temperature achieving more than 2,000 °C) and are transformed through a sequence of chemical reactions to molten glass. Although there are many furnace designs, furnaces are generally large, shallow, and well-insulated vessels that are heated from above. In operation, raw materials are introduced continuously on top of a bed of molten glass, where they slowly mix and dissolve. Mixing is effected by natural convection, gases rising from chemical reactions, and, in some operations, by air injection into the bottom of the bed. (EPA, 1994) In the glass production, both continuously and batch-wise operated melting furnaces are in use. In large glass manufacturing installations as it is the case for flat and container glass production, and where the forming processes are fully automated, refractory lined tank furnaces are operated in the continuous mode. For the production of smaller quantities of glass, especially for hand-shaped glassware, the batch operating mode is preferred since molten glass has to be removed from the pot furnace by hand. (Eichhammer et al., 1994; VDI Kommission Reinhaltung der Luft, 1997)

Some characteristics of the above mentioned furnaces are summarised in the following table.

Table 3.4: Some characteristics of furnaces used in glass production (VDI Kommission Reinhaltung der Luft, 1997; Landesgewerbeanstalt Bayern, 1994)

Type of Furnace	**Type of Firing**	**Energy Source**	**Operating Mode**	**Capacity [Mg/d]**
Single or multi-pot	flame or electrically heated	gas, oil, electricity	batch	0.1 – 35
Day tank	flame or electrically heated	gas, oil, electricity	batch	0.1 – 3
Tank furnace	flame or electrically heated	gas, oil, electricity	continuous	2 - 900

In order to achieve a higher energy efficiency and a higher flame temperature, the combustion air is preheated. Air preheaters in use are recuperative or regenerative (Rentz et al., 1991; Nolle G., 1997; Teller A.J.; Hsieh J.Y., 1992). Glass melting furnaces use natural gas and/or oil as a fuel, since the use of hard coal or lignite would result into an import of molten ash in the glass phase, and would subsequently lead to a lower product quality and would block the refractory lattice of the regenerators or the recuperators (Rentz et al., 1991; Abraham et al. 1997). For the production of container glass, approximately 70 % of the furnaces are operating with oil and 30 % with natural gas. City gas or liquified gas are used in isolated cases (VDI, 1998).

The furnace most commonly used within flat glass production is a cross-fired furnace with regenerative preheating working in the continuous mode; very few exception with end-fired furnaces do exist in the production of printed glass (Abraham et al. 1997). In container glass production, mostly regeneratively heated furnaces are in use (Abraham et al. 1997).

Additional electric heating is frequently employed to increase output and to cope with peak-load demands. Between 5 to 30 % of the total energy is passed in the form of electrical energy directly into the glass batch through electrodes. (VDI, 1998).

Table 3.5: Specific energy demand for the production of glass

Type of Glass	Specific Energy Demand [GJ/Mg glass]
Flat glass	7
Container glass	6
Glass wool	12
Special glass	25

However, more advanced glass furnaces do exist with lower specific energy demands (for example around 4 GJ/Mg (VDI, 1998) in the production of flat glass).

Glass Wool Manufacturing Process

In the "indirect" melting process, molten glass passes to a forehearth, where it is drawn off, sheared into globs, and formed into marbles by roll-forming. The marbles are then stress-relieved in annealing ovens, cooled, and conveyed to storage or to further processing in other plants. In the "direct" glass fibre process, molten glass passes from the furnace into a refining unit, where bubbles and particles are removed by settling, and the melt is allowed to cool to the proper viscosity for the fibre forming operation (EPA, 1995).

During the formation of fibres into a wool fibreglass mat (the process is known as "forming" in the industry), glass fibres are made from molten glass, and a chemical binder is simultaneously sprayed on the fibres as they are created. Although the binder composition varies with product type, typically the binder consists of a solution of phenol-formaldehyde resin, water, urea, lignin, silane, and ammonia. Colouring agents may also be added to the binder. Two methods of creating fibres are used by the industry. In the rotary spin process, centrifugal force causes molten glass to flow through small holes in the wall of a rapidly rotating cylinder to create fibres that are broken into pieces by an air stream. This is the newer of the two processes and dominates the industry today. In the flame attenuation process, molten glass flows by gravity from a furnace through numerous small orifices to create threads that are then attenuated (stretched to the point of breaking) by high velocity, hot air, and/or a flame (EPA, 1995).

3.3.1 Gas- and Oil-Fired Glass Melting Furnaces with Regenerative Air Preheating

The common feature of all tank furnaces is a large ceramic tank which serves as a melting container. In general, tank furnaces are operated by alternating flame-heating based on the regenerative principle. (VDI, 1988)

Regenerative air preheaters use a lattice of brickwork to recover waste heat from the exhaust gas. The regenerators are made up of two chambers, each of them consisting of a refractory lattice; the chamber walls and the mentioned lattice represent the heat storing material, which transfers the heat from the waste gas to the combustion air. The waste gas is lead from the furnace to one of these chambers, whereby the lattice is warmed up. The combustion air enters the furnace via the other chamber. The combustion air flow and the waste gas flow are then reversed: the combustion air flows then through the hot chamber and is heated there, while the waste gas flows through the second chamber, reheating the refractory lattice. The temperature of the incoming air achieves up to 1,350 °C, and the waste gas leaves the regenerative chambers with a temperature of about 500 – 550 °C. (Rentz et al., 1991; VDI Kommission Reinhaltung der Luft, 1997;, Kircher U., 1993)

Depending on the arrangement of the burners and the position of the flames, one differentiates between cross-fired and end-fired tanks. (VDI, 1988) Because of the higher number of burner necks and the larger regenerator chambers, the specific energy consumption is higher for cross-fired furnaces than for comparable end-fired furnaces. (VDI Kommission Reinhaltung der Luft, 1997) Small and medium-sized tanks are built as end-fired tanks, larger ones as cross-fired burner tanks. In both arrangements, the flames flow closely over the molten glass surface and transmit heat to it, primarily by radiation. (VDI, 1988)

Cross-fired furnaces give better control of melting chamber temperatures and oxidation state and therefore predominate in the larger throughput and ”quality glass” furnaces. Cross-fired furnaces are used exclusively in float glass furnaces and in the larger container furnaces, whereas for melting surfaces up to 120 m^2 more and more are laid down as end-fired furnaces, since they show a simpler arrangement, a lower price and a higher energy efficiency than comparable cross-fired furnaces. (VDI Kommission Reinhaltung der Luft, 1997)

3.3.2 Gas- and Oil-Fired Glass Melting Furnaces with Recuperative Air Preheating

Another configuration of the tank furnace is the recuperatively heated glass melting tank. Recuperative air preheaters use most commonly a steel heat exchanger, recovering heat from the exhaust gas by exchange with the combustion air; the preheating temperature can reach up to 800 °C (VDI Kommission Reinhaltung der Luft, 1997). Here, the hot waste gas and the cold combustion air flow through two parallel, but separated ducts, and the heat exchange is performed via the separation wall. Unlike regenerative heating furnaces, the combustion is not interrupted and the waste gas is continuously recuperated via the heat exchanger. In order to achieve an optimal energy use, the recuperators are often connected to waste heat boilers for steam or hot water generation (Rentz et al., 1991; Kircher U., 1993). The lower flame temperatures achieved (compared with those from regenerative systems) eliminates them from use in the higher quality glasses (e. g. float glass) or high specific pull (many container glasses). Recuperatively heated furnaces are generally of cross-fired configuration. (Abraham et al. 1997)

3.3.3 Pot Furnaces

The use of pot furnaces is confined to manually worked specialty glasses, with intermittently operation and melting temperatures under 1,460 °C. One furnace usually is comprised of several pots permitting simultaneous melting of several types of glass. Flame-heated regeneratively and recuperatively-operated furnaces as well as electrically heated furnaces, are put to use here. City gas, natural gas, liquefied gases and light oil as well as electricity are used as heat energy. The specific heat consumption (relative to glass production) of pot furnaces is comparatively high and averages 30 GJ/Mg glass produced (Jockel W., Hartje J., 1991).

3.3.4 Electric Furnaces

Electric furnaces melt glass by passing an electric current through the melt. Electric furnaces are either hot-top or cold-top. The former use gas for auxiliary heating, and the latter use only the electric current (EPA, 1994). Electric heating is used either for additional heating (electric boost) or almost exclusively in small- and medium-sized furnaces for the manufacturing of special glass such as lighting glass, glass fibres, crystal glass (Rentz et al., 1991; Nolle G., 1997; Teller A.J.; Hsieh J.Y., 1992). One case of soda lime glass manufacturing via electric heating is currently known, but is restricted to low furnace outputs and special composition glasses (Abraham et al. 1997). Further information on electric heating is given later in this chapter.

3.4 Emissions

3.4.1 Combustion-related Emissions

Pollutants released during the manufacture of glass are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2) and nitrous oxide (N_2O). Also emissions of hydrogen chloride, hydrogen fluoride, particulate matter and heavy metals are produced by the melting process. Emissions of particulate matter can also result from handling raw materials. Heavy metals will be present in the particulate matter. According to CORINAIR90 of these, the main relevant pollutants are SO_2, NO_x, and CO_2 (see also Table 1).

The waste gases released from melting furnaces consist mainly of combustion gases generated by fuels and of gases arising from the melting of the batch, which in turn depends on chemical reactions taking place within this time. The proportion of batch gases from exclusively flame-heated furnaces represents 3 to 5 % of the total gas volume. (VDI, 1998)

Sulphur Oxides

The amount of SO_2 released during glass manufacturing is mainly determined by the sulphur content of the fuel, the sulphate content of the molten batch and the sulphur absorption ability of the glass produced (VDI, 1988; Gitzhofer K.-H., 1993).

The sulphur contained in the batch is partly bound in the glass as SO_3. Glass contains up to 0.4 wt.-% SO_3 (VDI, 1998). The SO_3-content is 5 to 10 % of the SO_2-content. The amount of SO_3 depends on the excess air and the combustion temperature. (VDI, 1988)

The SO_2 content in the off-gas is also determined by the operating conditions of the glass melting tank. With tank furnaces operated by alternating flame heating, based on the regenerative principle, an increase of the SO_2 content in the off-gas during the firing interval is observed. This is most likely due to a decrease in the sulphur absorption ability of the molten glass with an increasing temperature in the upper zone of the furnace, and evaporation of already condensed sulphurous species in the air preheater (Gitzhofer K.-H., 1993). The oxygen content in the upper zone of the furnace also has an impact on the SO_2 content of the off-gas: if the amount of excess air is decreased, in order to minimise fuel input and to suppress NO_x formation, an increase in the SO_2 content of the off-gas is observed. This is due to the fact that the sulphur absorption ability of the molten glass decreases with a decreasing oxygen content in the upper furnace zone (Gitzhofer K.-H., 1993).

Since natural gas and city gas contain only trace amounts of sulphur, a lower SO_2 content in the off-gas of glass melting tanks fired with gaseous fuels is observed compared to oil fired glass melting tanks. (Rentz et al., 1991)

Nitrogen Oxides

The relevant NO_x emission process step within the production of glass is the melting stage. NO_x emissions released by glass furnaces are nitric oxides (NO to about 90 % due to the near stoichiometric operation of the furnaces, the remainder being nitrogen dioxide NO_2). The concentrations of nitrous oxide in glass furnace waste gases are in general below the detection limit (Quirk R. , 1997).

Four main NO_x formation mechanisms exist: three of them are combustion related and include thermal, fuel and prompt NO_x formation; the fourth mechanism (the ‘batch’ NO_x formation) results from the use of nitrates in the raw materials for certain glasses. (Quirk R. , 1997) In the glass melting furnace, the temperature ranges from 1,500 °C to 1,600 °C (VDI Kommission Reinhaltung der Luft, 1997), leading to flame temperatures above 2,000 °C (Abraham et al. 1997). This explains the presence of high NO_x concentrations, almost exclusively due to thermal NO_x formation (according to the Zeldovich mechanism). Several parameters influence the mechanism of thermal NO_x formation: flame temperature, oxygen content in the reaction zone, and retention time of the combustion gas in high temperature zones of the flame. These parameters are in direct relation with operating parameters as for example burner and melting furnace design, amount of excess air, mixing of fuel and combustion air, etc. (Kircher U., 1993; Flamme M., 1993; Flamme M.; Haep J., 1994). Prompt NO_x is relatively small, and when firing natural gas, fuel NO_x is sensibly zero (Quirk R. , 1997).

The conversion of nitrogen compounds contained in the raw materials and in the refining agents contributes also to NO_x emissions due to the batch NO_x formation. The quantity of nitrogen oxides arising from the feed material (see also chapter B4614) will be affected by the concentration and composition of the nitrates in the feed. (Her Majesty´s Inspectorate of Pollution, 1992) For example, certain tinted glasses in the flat glass sector require the use of nitrates, which produce additional NO_x-emissions almost as great as uncontrolled emissions from a clear flat glass operation: typical emissions might be 2,500 mg/Nm^3 for clear glass, 4,000 mg/Nm^3 for tint glass (UN/ECE, 1998). It must be acknowledged that such tints are only occasionally manufactured.

When using gas fired glass melting tanks, the achieved flame temperature is higher compared to oil. As a consequence, oil fired tanks emit less NO_x than gas fired tanks. Moreover, as end-fired furnaces allow a more favourable flame characteristic than cross-fired glass melting furnaces, the first show lower NO_x emissions. Recuperative furnaces induce lower NO_x emissions than regenerative furnaces, due to their lower preheating temperature (Rentz et al., 1991; Kircher U., 1993).

Following table gives the NO_x-concentrations for some types of furnaces.

Table 3.6: NO_x Emissions for some types of furnaces (Rentz et al., 1991; Kircher U., 1993b)

Type of Furnace / Fuel	NO_x-Emission* [mg/Nm^3]
Oil fired recuperatively heated furnace	400 – 1,400
Gas fired recuperatively heated furnace	400 – 1,600
Oil fired regeneratively heated furnace	
• end-fired furnace	1,000 – 2,400
• cross-fired furnace	1,600 – 3,600
Gas fired regeneratively heated furnace	
• end-fired furnace	1,400 – 3,000
• cross-fired furnace	1,600 – 4,000

* These values refer to an O_2-content in the waste gas of 8 vol.-%.

3.4.2 Process-related Emissions

The most important source of atmospheric emissions is the hot furnace. The heavy metals from the raw materials or the fuel partly vaporize in the hot furnace. The heavy metals which are emitted to air are mainly arsenic, cadmium, chromium, lead, tin, and selenium.

If fuel oil is used in the combustion process also nickel and vanadium may be found. In south and eastern Europe fluorspar is often used in the melting process. If recycled glass originating from these countries some fluorine may be emitted.

Basic materials for glass production are silicium oxide and oxides of alkalimetals. The alcali metal oxides are produced during the process from dissociation of carbonates. The emission factors given under (Leendertse, A., 1998) are calculated from the amount of carbonates added in general in the production process of the different types of glass, assuming that all metal oxides have their origin in carbonates and that no recycled glass is added. If however oxides, hydrocarbonates, sulfates, or a relevant amount of recycled glass are used corrections must be made.

3.5 Controls

3.5.1 NO_x-Emission Reduction Measures

3.5.1.1 Primary Emission Reduction Measures

3.5.1.1.1 Lowering the Amount of Excess Air

Technical Aspects

This relatively simple measure aims at achieving near stoichiometric combustion, resulting in a lower oxygen concentration in the reaction zone, and consequently in a reduction of nitrogen oxides. Sealing of the furnace against inleaked (false) air is an additional measure to lowering the amount of excess air. NO_x emission reduction efficiencies between 30 and 70 % (depending on the initial level) are achievable (Kircher U., 1993). Further a slight decrease in specific energy consumption is observed (Abraham et al. 1997).

However, it may be noted that a move to near stoichiometric combustion can give a significant reduction in NO_x, but may lead on the other hand to an increase of the emissions of other pollutants (e. g. CO, dust) as well as to a slight increase of energy demand. Furthermore, the quality of the product and the furnace lifetime can both be influenced by the O_2-content in the upper zone of the glass melting furnace. (Rentz et al., 1991)

Side-Effects

Near stoichiometric combustion (as performed when lowering the amount of excess air) lowers the nitrogen oxides formation, but in the same time induces slightly increased emissions of measured SO_2.

3.5.1.1.2 Reduced Air Preheating

Preheaters have originally been used to improve the heat transfer from flame to batch, and have proved to lead to savings in energy consumption (Abraham et al. 1997).

Technical Aspects

By reducing the air preheating temperature, the flame temperature is reduced and consequently the formation of nitrogen oxides. Reduction of the preheating temperature can be carried out by using recuperative air preheaters instead of regenerative air preheaters (Rentz et al., 1991). However, when switching from a regenerative to a recuperative preheater, the melting capacity is reduced, inducing the need of larger facilities and thus higher costs. Furthermore, recuperative air preheaters achieve lower energy efficiencies. (Abraham et al. 1997)

Side-Effects

The use of recuperative air preheaters instead of regenerative ones results in a reduction of flame temperature and hence glass quality, pull rate and energy efficiency (Abraham et al. 1997).

3.5.1.1.3 Staged Combustion

In a classical combustion facility, the totality of fuel and air/oxygen is injected at the same place. The resulting flame is then composed of a hot and oxidising primary zone located at the flame root and a colder secondary zone located at the flame end. The primary zone generates most of the NO-emissions, which increase exponentially with the temperature, whereas the contribution of the secondary zone is rather modest. Staged combustion aims at decreasing the temperature in the primary zone. Therefore, only a part of the fuel or of the air/oxygen is injected at the burner, the rest being injected downstream of the main combustion zone.

Emission reduction rates in the range of 50 to 70 % can be achieved by combining staged combustion with other primary measures. It is estimated that about 30 to 50 % of the reduction may originate from staged combustion alone. Concentrations around 700 mg/Nm^3 may be reached in the best cases (Delacroix et al., 1996).

Air/Oxygen Staging

The KORTING air staging process (Barklage-Hilgefort, H., Sieger W., 1989) has been tested at three furnaces in Germany at the beginning of the 90s, but has been abandoned meanwhile.

Maintenance problems have appeared on the air ejector at high temperatures, and anyway this technique does not allow as good reduction efficiencies as do state-of-the-art low-NO_x burners (Delacroix et al., 1996; Kircher U.; 1995).

Oxygen staging with the Oxygen Enriched Air Staging (O.E.A.S.) process (Joshi M.L. et al.1994) is still in a state of development (three test furnaces are running in the USA) and it is therefore impossible to conclude about efficiency and applicability(Delacroix et al., 1996). Due to the high costs of oxygen, this technique will most probably not be generally applied (Abraham et al. 1997).

Fuel Staging

A lack of fuel in the primary zone decreases the flame temperature. The fuel-rich secondary zone becomes reducing, generating hydrocarbon radicals reducing NO into molecular nitrogen. About 8 to 10 % of the fuel is injected into the combustion air in the port neck, resulting in sub-stoichiometric conditions in the main flame, and therefore leading to reduced NO_x formation. The remaining fuel is injected within the furnace and ensures complete burnout. NO_x concentrations below 800 mg/m^3 have been reported with initial values between 1,800 and 2,200 mg/m^3. (Rentz et al., 1991)

Fuel staging has proven to be rather attractive: it has been implemented at 12 German glass melting tanks for nitrogen oxides abatement (Rentz et al., 1991); however, this measure is expected to be phased out with the installation of new low-NO_x burners (Abraham et al. 1997).

Side-Effects

No side-effects have been observed.

3.5.1.1.4 Flue Gas Recirculation

Technical Aspects

This technology is in principle similar to staged combustion: NO_x-emissions are reduced by lowering the flame temperature. Secondary air is mixed with a part of the flue gas, and this oxygen lacking air is injected as combustive agent in the furnace.

Three tests of flue gas recirculation have been performed in the glass production sector (Abraham et al. 1997). NO_x emission abatement rates between 16 and 44 % could be achieved, but this technology proved to be difficult to be implemented, and has meanwhile been abandoned (Delacroix et al., 1996).

Side-Effects

No side-effects have been observed, but it must be acknowledged that the experience is very limited.

3.5.1.1.5 Reburning / 3R Process

The reburning process and the 3R process are similar technologies, based on the same principle. In the literature, both processes are either considered as primary NO_x-emission reduction measures or as secondary NO_x-removal options. In the framework of this report, the reburning / 3R process will be presented as a primary measure, since it can be compared to the fuel-staging process.

Technical Aspects

In both the reburning and 3R processes, NO or its precursors (HCN, NH_y) formed in the combustion zone undergo reduction by injection of natural gas or fuel as the waste gases enter the regenerators from the melting chamber. In the 3R process, hydrocarbon fuel is injected into the waste gas downstream of the glass melting furnace tank (Shulver I.; 1994). The added fuel does not burn, but pyrolyses to form radicals converting the nitrogen oxides in the waste gas into nitrogen and water. A major advantage of this process is the possibility of using all kinds of hydrocarbon fuels (natural gas, fuel oil...) (Abraham et al. 1997), (Quirk R. , 1997). Air is added downstream of the denitrification zone to ensure burnout of residual ”fuel” fragments.

Reburning is at an experimental stage, whereas the 3R process has been installed at one German float glass production site, achieving nitrogen oxides concentrations below 500 mg/m^3 (Kircher U., 1995). According to Quirk R., 1996 and Koppang R., 1996, 3R has been successfully operated on float furnaces in Finland and California, and demonstrated on furnaces in the TV glass production (in Korea (Abraham et al. 1997)), container, and shaped glass. In all cases, a nitrogen oxides abatement up to 85 % could be achieved. One further furnace has been equipped with 3R at a float glass production site in the UK. This technology is now applied by two float glass companies in the USA (Abraham et al. 1997).

Side-Effects

As this process is based on hydrocarbon fuel injection, an increased energy consumption is to be expected. Nevertheless, this technology ensures burnout of residual fuel fragments; subsequently, achievable levels of CO may be lower than with conventional combustion. Moreover, if supplementary heat recovery is available, the additional CO_2 originating from the increased use of fuel can be compensated by the reduction that would have arisen from fossil fuel boilers or from the power station (Quirk R. , 1997).

3.5.1.1.6 Low-NO_x Glass Melting Furnaces

Technical Aspects

In recent years, new melting furnaces have been developed achieving low NO_x emissions: the FlexMelter® and the LoNOx® melter (Quirk R., 1996; Pabst R., 1994).

The LoNOx® melter is a combined electrical/fossil fuel fired melting tank with recuperative air preheating, including a batch preheating step. For this melting furnace, energy efficiency has been increased to compensate for the lower thermal efficiency of the air preheater compared with the regenerator and so the heat consumption of this modified recuperatively fired furnace can be compared to conventional regeneratively fired furnaces: waste gas from the melting furnace is first fed to the recuperative air preheater and afterwards used to preheat the cullet. Air temperatures of about 750 °C are reached (Gitzhofer K.-H., 1993). This melting furnace allows to achieve NO_x concentrations below 500 mg/m^3 in the waste gas (Flamme M.; Haep J., 1994; Kircher U., 1995; Shulver I., 1994; Pabst R., 1994). This type of low NO_x melter is exclusively used in the container glass manufacturing at about 70 – 80 % cullets undergoing preheating (Abraham et al. 1997).

The FlexMelter® has originally been developed for discontinuous production, but is operated nowadays both in the continuous and discontinuous mode. Typical applications are glass fibres for insulation, automobile lighting, and other special glass such as crystal glass. The relatively low flame temperatures from recuperative air preheaters precludes their use for typical flat glass and most container glass production (Abraham et al. 1997).

Currently, three low-NO_x melting furnaces with a total capacity of approximately 800 Mg/d glass are operated in Germany. (Abraham et al. 1997)

Side-Effects

No side-effects have been observed.

3.5.1.1.7 Oxy-Fuel Firing

Technical Aspects

By this very effective, but also very expensive technology, preheated combustion air is replaced by high purity oxygen and there is thus no need for regenerators. Even though the resulting nitrogen oxide concentration in the flue gas is higher with oxy-fuel firing, mass emissions of NO_x are lower. Therefore, the actual mass flow has to be considered. Oxy-fuel firing can be applied to pot furnaces and day tanks (UN/ECE; 1998). The conversion from air to 100 % oxygen may result in a 50 - 60 % reduction of energy consumption (UN/ECE, 1998). As regards the achievable NO_x reduction rate, (Barklage-Hilgefoot H.J.; Sieger W., 1989) quotes a 80 to 95 %-reduction for oxy-fuel firing over 100%-air firing (50 % in the worst case of existing furnaces with poor sealing conditions (UN/ECE, 1998).

About one hundred furnaces are run world-wide on the oxy-fuel mode, representing approximately 4 % of the whole glass production. Since the beginning of the 90s, oxy-fuel combustion has gained importance mainly in the USA, where it represents nowadays about 10 % of the number of glass melting furnaces. The reason why oxycombustion is so popular in the USA is mainly due to economical reasons: sometimes nitrogen can be used for non-melting applications in the factory or associated products and then the overall cost of the oxygen is reduced. Furthermore, when applying this technology, an increase in capacity can be observed as well as an improvement of the product quality (UN/ECE, 1998). In Germany, two container glass melting furnaces are operated in the oxy-fuel mode, and several others are planned, among which two special glass production sites (Rentz et al., 1991; Kircher U., 1995; Abraham et al. 1997). The application fields of oxy-combustion are basically the glass fibre, TV glass, container and special glass industries (Her Majesty´s Inspectorate of Pollution, 1992).

Besides the environmental aspect, since regenerators and recuperators can be omitted, low investment is a further advantage increasing the interest of glass producers in oxy-fuel firing. Moreover, the change from a recuperatively heated furnace to oxy-fuel firing is very easy (Abraham et al. 1997). For an energy balance, production of oxygen has to be considered, and energy savings can be achieved in the case of an effective heat recovery. It should however be mentioned that the related operating costs are higher compared to 100% air firing, due to the high price of oxygen and that this technology is not yet applicable to every field of glass production (Shulver I., 1994; Delacroix et al., 1996). Furthermore, oxy-fuel firing is not effective when nitrate containing batches are melted, since only thermal NO_x is being reduced by oxy-combustion (Quirk R. , 1996). Another problem which had been reported several times is the corrosion of the furnace superstructure and crown due to higher concentration of volatiles in the furnace. (Abraham et al. 1997)

Side-Effects

Besides NO_x, other pollutants can be abated via oxy-fuel firing: volatile components allowing substantial savings in batch materials and particulates in special glass (e. g. borosilicates). Energy savings can be expected when no consideration of the oxygen production is made. However, since electricity is required for the production of oxygen, the total energy consumption is the same as with conventional fired furnaces. (Jockel W., Hartje J., 1991; Abraham et al. 1997; Delacroix et al., 1996) Furthermore, it must be mentioned that a transfer of pollution occurs upstream towards electricity production, therefore not solving the pollution problem.

3.5.1.1.8 Electric Melting

Technical Aspects

Molten glass is an electricity conductor and thus can be heated via electrodes immersed in the bath of glass. These electrodes are generally made up of molybdenum or platinum, and are located either at the top, at the bottom or at the walls of the furnace tank. In electrically heated furnaces, no direct emissions are released. Furthermore, compared to conventional regeneratively fired furnaces, electric melting furnaces show several advantages such as good temperature control and preheating of the batch inherent to the system, but the following drawbacks should be mentioned:

- the pollution is transferred upstream, towards electricity production;
- the lifetime of an electric melting furnace is reduced compared to a conventionally fired one;
- the furnace size is limited;
- an incompatibility between glass and electrodes occur for some glass compositions;
- high operating costs related to energy costs may be expected. (VDI Kommission Reinhaltung der Luft, 1997)

Electric melting is currently limited to production of special glass, especially crystal glass, and to glass fibre production (UN/ECE, 1995; Delacroix et al., 1996).. Very small units have been constructed in the float industry for specially formulated glasses only (Abraham et al. 1997).

Side-Effects

Via electric melting, pollution is transferred upstream towards electricity production.

3.5.1.2 Secondary Emission Reduction Measures

Even though high NO_x emission reduction can be achieved by primary measures, especially via combustion modifications and the reburning/3R process, secondary measures can be used in some cases to meet more stringent standards. Proven NO_x-abatement measures in the glass industry are the selective non-catalytic (SNCR) and catalytic (SCR) reduction processes.

3.5.1.2.1 Selective Non Catalytic Reduction (SNCR)

Technical Aspects

Ammonia is injected at an over-stoichiometric ratio into the waste gas stream of the glass melting furnace within a temperature window ranging from 850 to 1,100 °C. This temperature window is the most important parameter with regard to satisfactory NO_x conversion, in parallel with avoiding an increased ammonia slip. In regenerative glass melting furnaces, the above given temperature window can generally not be met. Therefore, this secondary measure is rather suitable for recuperatively heated furnaces, although SNCR technology can be found also in regeneratively fired glass melting furnaces (Kircher U., 1993; Kircher U., 1995).

The NO_2 conversion and the NH_3 slip are function of the amount of NH_3 injected: an appropriate NH_3 distribution in the waste gas is required to obtain a satisfactory conversion rate and ammonia slip. (Rentz et al., 1991)

The SNCR process is characterised by relatively high costs with regard to a rather low NO_x-removal efficiency, typically around 50 % (Abraham et al. 1997; Quirk R. , 1997), which is not sufficient as regards European regulations.
Today in Germany, 6 glass melting plants are equipped with SNCR technology, and three further installations are planned (Kircher U., 1995). Two further installations are located in the USA, and one in Switzerland (Delacroix et al., 1996). Operational parameters of the six German plants are given in Table 3.7.

Table 3.7: Operational parameters of 6 SNCR installations in the European glass production sector (Kircher U., 1995)

Plant	1	2	3	4	5	6
Furnace	Recuperative	recuperative	recuperative	Regenerative	recuperative	regenerative
Technical / Experimental	Technical	technical	technical	Technical	technical	technical
Fuel	Natural gas	natural gas	heavy oil	natural gas / heavy oil	natural gas	natural gas
Glass	Special	special	container	Water	special	soda lime
Waste gas flow rate	10,000 m^3/h	10,000 m^3/h	25,000 m^3/h	25,000 m^3/h	10,000 m^3/h	20,000 m^3/h
Ammonia feeding	Downstream Recuperator	downstream recuperator	between two recuperators	downstream first regenerator	downstream recuperator	middle of regenerator
Dissolved / gaseous NH_3	Gaseous	gaseous	gaseous	solution	gaseous	gaseous
Start of operation	1989	1992	1992	1989 / 1990	1994	1994
Efficieny	84 %	86 %	75 %	50 – 60 %	ca. 80 %	50 – 60 %
Ammonia slip	6 mg/m^3	23 mg/m^3	< 30 mg/m^3	< 30 mg/m^3	< 30 mg/m^3	< 30 mg/m^3
NO_x content in the cleaned gas*	180 mg/m^3	470 mg/m^3	<500 mg/m^3	<800 mg/m^3	350 mg/m^3	650 mg/m^3

* These values refer to an O_2-content in the waste gas of 8 vol.-%.

Side-Effects

Neither emissions to water, nor solid waste occur. But an increase in energy consumption and an ammonia slippage can be observed. The use of ammonia on-site is a potential safety hazard.

3.5.1.2.2 Selective Catalytic Reduction (SCR)

Technical Aspects

Here, the reduction of nitrogen oxides is based on the injection of gaseous or aqueous ammonia in a near stoichiometric ratio into the waste gas of the glass melting furnace in the presence of a catalyst and within a temperature window between 300 and 400 °C. A NO_x-abatement up to 90 % can be achieved. Some years ago, in glass production, catalyst lifetime was reduced by the presence of sodium sulphate in the waste gas which blocks and poisons the catalyst, but nowadays a catalyst can already achieve up to 4 years lifetime, and therefore, SCR has reached the status of a proven technology (Kircher U.; 1995). However, the SCR applied in the glass manufacturing industry is always operated with an electrostatic precipitator, in order to achieve concentrations of soda dust below 10 mg/m^3, which may be a poison to the catalyst. For the same reason of catalyst poisoning, natural gas is preferred over oil as a fuel. (Abraham et al. 1997)

Six SCR installations at glass melting plants are implemented in Germany, mainly in the field of special glass production (e. g. TV screen glass) (Abraham et al. 1997). In Hombourg (France), a SCR facility has been started in 1997 in the float glass production (Quirk R., 1997, Genuist G., 1996).. Table 8 gives an overview of the operational parameters of SCR at six German glass production plants.

Table 3.8: Operational parameters of 6 SCR installations in the German glass production sector (Schmalhorst E., Ernas T., 1995;, Kircher U., 1995, UN/ECE, 1998)

Plant	**1**	**2**	**3**	**4**	**5**	**6**
Furnace	Regenerative	regenerative	regenerative	regenerative	regenerative	regenerative
Fuel	Natural gas	natural gas	natural gas	natural gas	natural gas	natural gas
Type of Glass	Container	special	special	container	special	special
Waste gas flow rate	50,000 m^3/h	50,000 m^3/h	40,000 m^3/h	60,000 m^3/h	40,000 m^3/h	40,000 m^3/h
Dissolved / gaseous NH_3	Solution	solution	gaseous	solution	solution	gaseous
Catalyst	Zeolithe	V_2O_5/TiO_2	V_2O_5/TiO_2	V_2O_5/TiO_2	V_2O_5/TiO_2	V_2O_5/TiO_2
Number of layers	1	1	1	2	2	1
Start of operation	1987	1989	1991	1994	1994	1994
Efficiency	55 %	75 %	70 %	76 %	n. a.	75 %
Ammonia slip	28 mg/m^3	< 30 mg/m^3	< 30 mg/m^3	2 mg/m^3	< 30 mg/m^3	< 30 mg/m^3
NO_x content in the cleaned gas	480 mg/m^3	1,000 mg/m^3	1,350 mg/m^3	500 mg/m^3	< 1,500 mg/m^3	< 1,000 mg/m^3

n. a. = data is not available

The installation at plant 1 was stopped in June 1997 in favour of primary measures (Abraham et al. 1997). The only SCR installed at a container glass production plant is currently running at PLM Glashütte Münder, where clean gas concentrations of 500 mg/Nm^3 are achieved (low NO_x burners are already installed) (Schmalhorst E., Ernas T., 1995; UN/ECE, 1998).

Side-Effects

SCR generates solid waste via deactivated catalyst, but it can often be reprocessed by the manufacturer or be used as combustion material. As for SNCR, the increased energy consumption and ammonia slippage have to be accounted for. The use of ammonia on-site is a potential safety hazard.

3.5.2 SO_x-Emission Reduction Measures

3.5.2.1 Primary Emission Reduction Measures

The most important option for the reduction of SO_2 emissions from glass melting furnaces is the use of fuels with a lower sulphur content. SO_2 emissions from gas fired glass melting tanks are lower than the emissions from oil fired furnaces, since gaseous fuels have a lower sulphur content than liquid fuels. (Rentz et al., 1991) However, the selection of fuels depends on their availability and on the furnace design in place. (VDI, 1998)

Furthermore, the melting furnace should be operated in such a way that the sulphur absorption ability of the melt is not decreased: it it thus necessary to obtain a certain oxygen concentration in the upper zone of the furnace. (Rentz et al., 1991)

3.5.2.2 Secondary Emission Reduction Measures

Emissions of sulphur oxide from the off-gases of glass melting furnaces can be removed via sorption, e.g. by supply of appropriate sorbents (dry sorbent, or calcium and sodium based sorbents). Besides sulphurous compounds, hydrogen chloride, hydrogen fluoride, and gaseous heavy metals are also removed by this process. Removal efficiency for the different compounds is mainly determined by the amount of sorbent used and by the temperature at which the reaction takes place. A higher temperature leads to higher removal rates for SO_2 and hydrogen chloride. The removal of hydrogen fluoride is slightly lower at higher temperatures. (Gitzhofer K.-H., 1993)

3.5.3 Emission Reduction Measures for Other Pollutants

Measures for decreasing air emissions from the combustion process will also result in a reduction of the heavy metal and dust emissions. Dust emissions from handling raw materials can be reduced using fabric filters or using different improved handling techniques. The emissions of carbon dioxide from the carbonisation process can be reduced by adding more recycled glass or using non-carbonate basic materials.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR} \times \text{EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8.1. Note: The values given for the carbonisation process are very much dependant on the local situation and can only be used if no information is available.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3), to estimate emissions of gaseous pollutants from the glass production is based on measurements or estimations using plant specific emission factors - Guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

Note: a detailed calculation should be based on individual plant information about the amounts of substances added. Also the amount of recycled glass used should be available. However these data are often confidential. Also fuel information and information about local abatement methods should be available.

6 RELEVANT ACTIVITY STATISTICS

Information on the production of glass, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of glass produced by various types of industrial technologies employed in the glass industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 " Choice of activity statistics".

7 POINT SOURCE CRITERIA

The production of glass is usually connected to medium size stacks that may be regarded as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors for Use With Simpler Methodology

In Table 8.1 and Table 8.2 are reported default emission factors for glass production (including, where applicable, also emission from non-melting activities). The emission factors on Table 8.2 was elaborated from Integrated Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001). Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030314; fuel used in the process does not have to be taken into account in 0301.

Table 8.1: Emission factors (kg/Mg glass melted) for glass production (European Commission, 2001) (1)

Substance	Flat glass production	Container glass production	Glass wool (2)	Other (3)
NO_x	4.6	2.4	3.9	4.8
SO_x	5.3	2.5	0.23	0.7
PM	0.4	0.4	2.74	0.4
VOC			1.51	
NH_3			3.16	

(1) Emissions factors without secondary abatement
(2) Combined fossil fuel-electric melting furnace including non-melting activities
(3) Domestic soda lime-glass as reference

For carbonization process an average emission factor of 137 kg/Mg glass can be used (the value derive from the detailed methodology emission factors, an IPPC BREF evaluation of the European production composition and an IPPC BREF evaluation of post consumer cullet in production of different kinds of glass).

Table 8.2: Emission factors to air in [g/Mg glass] for heavy metals and micropollutants for glass production in general

Substance	Default value	Range
Arsenic	0.10	0.1 - 0.25
Cadmium	0.15	0.05 - 0.25
Chromium	2.5	0.5 - 5
Copper	0.5	0.4 - 1.1
Lead (1)	10	2 - 24
Mercury	0.05	0.04 - 0.07
Nickel	2	1.2 - 2.6
Selenium	20	2.5 - 24
Zinc	10	5 - 24
Dichloromethane	5	0 - 11
Fluorine	30	5 - 70
Dust	400	3 - 800

The emission of lead is mainly determined by the amount of recycled glass used (Beerkens, R.G.C., 1991).

8.2 Reference Emission Factors for Use With Detailed Methodology

The emission factors in Table 8.3a give the theoretical amount of carbon dioxide emitted. Especially for container glass the amount of recycled glass may be up to 85 %.

IPPC, BREF (European Commission, 2001) reports an average of 40% of post consumer cullet in container glass production while the total cullet introduced in flat glass furnaces is typically around 20% (process cullet and sometimes also post consumer cullet).

Table 8.3a: Theoretical process emission factors for carbon dioxide from the carbonisation process in [kg/Mg product] in relation to the alcaline content of the product

Glass type	sodium oxide (wt %)	potassium oxide (wt %)	Magnesium oxide (wt %)	calcium oxide (wt %)	barium oxide (wt %)	carbon dioxide
Container glass	12-14	0.3-0.5	0.5-3	10-12	-	171-229
Flat glass	13.6	0.3	4.1	8.6	-	210
Continuous filament fibres						
E-fibres	< 2	< 2	20-24	20-24	-	157-203
AR-fibres	13-15	13-15	4-6	4-6	-	92-172
R/S-fibres	< 1	< 1	9-16	9-16	-	71-182
D-fibres	< 4	< 4	0	0	-	0-28
C-fibres	15-20	15-20	10-30	10-30		149-470
ECR-fibres	< 1	< 1	22-27	22-27	-	173-302
A-fibres	12-15	12-15	10-15	10-15		135-270
Special glass						
CRT panel	6.6-9.4	6.6-8.4	0-1.2	0-3.2	0	78-144
CRT tube	5.8-6.7	7.8-8.1	0.6-2.2	0.9-3.8	0	91-139
Glass tube, earth alk	12.5	2.5	2	4	0	154
Glass tube, borosilicate	3.5-6.5	0.5-1.5	0.01-0.5	0.01-1	0	27-66
Borosilicateglass	3.5-6.5	0.5-1.5	0.01-0.5	0.01-1	0	27-66
Opaque lighting glass	13.6	1.8	0	9.4	0	178
Lamb bulb	3-4	1.5-2.5	0.5	0.5	0	38-49
Glass ceramic	0.5-10	0	0-1	0.5-7	0	7.5-137
Quartz	0	0	0	0	0	0
Boron crown optical	0-5	12-18	0	0-0.3	0	56-122
Fluorine crown optical	0	0	0	0	20	57
Waterglass sodium sil.	22.5-24	0	0.008	0/008	0	160-171
Waterglass potassium silicate	0	27-32	0.008	0.008	0	126-150
Glass wool	12-18	12-18	8-15	8-15	0	119-292
Stone wool	0.5-5	0.5-5	30-45	30-45	0	238-527

Table 8.3b gives emission factors for particulate matter (TSP, PM10 and PM2.5) for glass production derived from CEPMEIP.

Table 8.3b: Emission factors for particulate matter in glass production [kg/Mg glass product] (CEPMEIP)

Glastype	**Technology and abatement**	**TSP**	**PM_{10}**	**$PM_{2.5}$**	**Uncertainty**
Flat glass, blown or drawn glass and container glass	Electrically heated, ESP, scrubber or fabric filter	0.03	0.027	0.024	5
Flat glass, blown or drawn glass and container glass	Gas or fuel oil-fired, uncontrolled or limited emission control	0.5	0.45	0.4	3
Flat glass, blown or drawn glass and container glass	Uncontrolled; old plant	2	1.8	1.6	3
Glass fibres	Electrically heated, ESP	0.5	0.45	0.35	3
Glass fibres	Gas or fuel oil-fired, uncontrolled	1	0.9	0.7	2
Glass fibres	Uncontrolled; old plant:	2	1.8	1.4	3

NOTE: The uncertainty range (95% confidence) in the emission factor is expressed as a factor. The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example (first row in table): The uncertainty in the emission factor for $PM_{2.5}$ for flat glass production with an electrical is 5. The emission factor with uncertainty range will therefore be 0.024 kg per tonne glass with an uncertainty range of 0.048 (0.024 / 5) to 0.120 (0.024 x 5).

8.2.1 Production of Flat Glass

Reported emission levels from IPPC, BREF (European Commission, 2001) are given in Table 8.4. The table shows figures separately for unabated furnaces and furnaces with secondary abatement techniques installed. The data covers both gas and oil fired furnaces making clear float glass under normal operating conditions and includes measurements from 1996 and 1997 only. The term unabated furnaces refers to furnaces operating normally with no specific pollution control technology.

Table 8.4: Total emission ranges[1] reported for flat glass sector furnaces with primary and secondary abatement measures (European Commission, 2001)

Parameter	**Unabated Furnaces**		**Abated Furnaces Primary/Secondary Methods**	
	mg/Nm^3	**kg/t glass melted**	**mg/Nm^3**	**kg/t glass melted**
NO_x	1800 – 2870	1.7 - 7.4	495 - 1250	1.1 - 2.9
SO_x	365 – 3295	1.0 - 10.6	218 - 1691	0.54 - 4.0
PM	99 – 280	0.2 - 0.6	5.0 - 40	0.02 - 0.1
HCl	7.0 – 85	0.06 - 0.22	4.0 - 30	<0.01 - 0.08

Parameter	**Unabated Furnaces**		**Abated Furnaces** **Primary/Secondary Methods**	
	mg/Nm^3	**kg/t glass melted**	**mg/Nm^3**	**kg/t glass melted**
HF	<1.0 - 25	<0.002 - 0.07	<1.0 - 4.0	<0.002 - 0.01
Metals	<1.0 – 5.0	<0.001 - 0.015	<1.0	<0.001

[1] Reference conditions are: dry, temperature 0°C (273K), pressure 101.3 kPa, 8 % oxygen by volume.

The on-line coating processes applied to flat glass are very case specific and the raw materials used and the pollutants emitted will vary. However, emissions will typically contain acid gases (HF, HCl) and fine particulate matter (e.g. oxides of silicon and tin). This type of process is usually subject to the general local environmental legislation and abatement is installed accordingly. For example, HCl 10 mg/m3, HF 5 mg/m3, particulate 20 mg/m3, and tin compounds 5 mg/m3 (European Commission, 2001).

The range of energy consumption encountered within the sector is quite narrow, because there is relatively little variation in the type of furnace used. Energy levels for melting are typically 5.5 to 8.0 GJ/Mg of glass melted, with specific energy requirements for the process as a whole generally less than 8.0 GJ/Mg (European Commission, 2001).

For the situation in the Netherlands, the following emission factors for flat glass in kg/Mg glass was proposed:.

handling/shipping:

dust:	0.15 kg/Mg

melting oven:

SO_2	3.0 kg/Mg
CO_2	140 kg/Mg
F_g	0.055 kg/Mg
Cl_g	0.06 kg/Mg
dust	0.37 kg/Mg

fuel:

SO_2	3.0 (fuel oil) kg/Mg
CO_2	530 kg/Mg
NO_x	5.5 kg/Mg
CO	0.09 kg/Mg

Heavy metals are incorporated in the dust emissions. The available information about compositions is scarce. The only consistent information is based on the work of Jockel and Hartje (Jockel W.; Hartje J., 1991), also incorporated in the PARCOM-ATMOS Manual. This information, based on the situation in Germany, is given in Table 8.5.

Table 8.5: Emission factors for glass production in [g/Mg glass] generalised for the situation in Germany.

Substance	**Emission factor [g/Mg glass]**	**Range [g/Mg glass]**
Arsenic	0.12	0.1-0.24
Cadmium	0.15	0.06-0.24
Chromium	2.4	0.5-5
Copper	0.6	0.4-1.1
Lead	12	2-24
Mercury	0.05	0.036-0.072
Nickel	1.9	1.2-2.6
Selenium	18	2.4-24
Zinc	11	4.8-24

The following Table 8.6 contains fuel related emission factors for container glass production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product) are listed in footnotes.

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030314.

Table 8.6: Emission for flat glass production 6)

Type of fuel				**NAPFUE code**	**Emission factors**						
					SO_2 3) [g/GJ]	**NO_x 4) [g/GJ]**	**NMVOC 5) [g/GJ]**	**CH_4 [g/GJ]**	**CO [g/GJ]**	**CO_2 [kg/GJ]**	**N_2O [g/GJ]**
s	Coal	hc	Steam	102	650 1)	300 1)	15 1)	15 1)	100 1)	93 1)	4 1)
s	Coal	bc	brown coal/lignite	105	500 1)	300 1)	15 1)	15 1)	100 1)	113 1)	3.5 1)
s	Coal	bc	Briquettes	106	220 1)	300 1)	15 1)	15 1)	100 1)	98 1)	3.5 1)
s	Biomass		Wood	111	25 1)	130 1)	48 1)	32 1)	160 1)	105 1)	4 1)
l	Oil		Residual	203	930-1,470 1,400 2)	98-1,800 1) 180 2)	3-4 1) 3 2)	3-4 1) 3 2)	10-320 1) 15 2)	72-78 1) 78 2)	2-14 1) 14 2)

Type of fuel				NAPFUE code	Emission factors						
					SO_2 3) [g/GJ]	NO_x 4) [g/GJ]	NMVOC 5) [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
l	Oil		gas	204	85-1,410 1) 600 2)	100-450 1) 180 2)	1.5-4 1) 1.5 2)	1.5-4 1) 1.5 2)	10-12 1) 12 2)	73-74 1) 74 2)	2-12 1) 12 2)
g	Gas		natural	301	0.5-8 1)	60-570 1) 100 2)	2.5-10 1) 2.5 2)	2-3 1) 2.5 2)	10-120 1) 13 2)	53-56 1) 53 2)	1-3 1) 3 2)
g	Gas		coke oven	304	12 1)	400-450 1)	2.5 1)	2.5 1)	10 1)	44-49 1)	1.5 1)

1) CORINAIR90 data, area sources

2) CORINAIR90 data, point sources

3)	SO_x:	1,500	g/Mg product	Melting furnace (Loos, B. 1992)
		2,246	g/Mg product	General (EPA, 1990)
		1,675	g/Mg product	General, with venturi scrubber (EPA, 1990)
		1,182	g/Mg product	General, with low energy scrubber (EPA, 1990)
		2,800	g/Mg beaded glass	Ground cutlet beading furnace (Loos, B. 1992)
4)	NO_x:	8.6-10	kg/Mg product	General (Bouscaren, 1992)
		2,920	g/Mg product	General (EPA, 1990)
		4,000	g/Mg product	Melting furnace (Loos, B. 1992)
		4,250	g/Mg product	Ground cutlet beading furnace
		800	g/Mg product	General, (FRG, GDR, 1990) (BUNDESUMWELTMINISTERIUM, 1994)
5)	VOC:	50	g/Mg product	Melting furnace (Loos, B. 1992)
		150	g/Mg beaded glass	Ground cutlet beading furnace (Loos, B. 1992)

6) It is assumed, that emission factors cited within the table are related to combustion sources in flat glass production. Footnotes may also include emission factors for other process emissions.

8.2.2 Production of Container Glass

Reported emission levels from IPPC, BREF (European Commission, 2001) are given in Table 15. The source of this table is a statistical study made among members of the container glass trade association FEVE on data from 228 fossil fuel fired furnaces, with and without electric boosting, from the entire spectrum of furnace and product types. Data refers to measurements made in 1996 and 1997. Sampling and measurement techniques are not standardised and the data can only be considered as indicative of the range of actual emissions at the time of the survey. The data for metals emissions was supplied for only 42 % of the furnaces and the metals included may differ.

About 30 % (72/228) of the container glass furnaces in the FEVE study are equipped with secondary abatement. The secondary abatement referred to is in all cases dust abatement, by an Electrostatic Precipitator or (less frequently) a bag filter, generally with upstream desulphuring. Filter dust is recycled in all cases into the glass melt, within the limits imposed by possible substitution of raw materials. Overall reduction of sulphur oxide emissions thus corresponds in current practice to the substitution of sulphate in raw materials. The desulphuring is considered as secondary abatement for other acid gases (HCl & HF) with similar limitations on the overall effect due to recycling of filter dust. Secondary abatement of NOx (by SCR) is only installed in one EU container plant (4 furnaces).

The data for Table 8.7 from the same FEVE study as for Table 8.8 report the 80 % middle range (from Percentile 10 to Percentile 90) and is an indication of the performance of the majority of EU-wide installations in 1996 – 1997.

Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030315.

Table 8.7: Total emission ranges reported for container glass sector furnaces with primary and secondary abatement measures (European Commission, 2001)

Parameter	Without Secondary Abatement With or without primary measures		With Secondary Abatement	
	mg/Nm^3	kg/t glass melted	mg/Nm^3	kg/t glass melted
NO_x	400–5000	0.6-11.7	<400	<0.74
SO_x	100–4500	0.2-9.8	100-1637	0.2-3.4
PM	40–800	0.1-1.9	1-32	0.002-0.22
HCl	5–62	0.01-0.12	7-30	0.01-0.07
HF	1–70	≤0.16	≤1-6	≤0.02
Metals	≤1–16	≤0.017	≤1-3	≤0.003
Cullet Rate	5-95 %			
Typical Load	25-600 t/day			
Specific Energy Melting only incl. Boosting	3.2-12.2 [GJ/t]			

[1]Reference conditions are: dry, temperature 0°C (273K), pressure 101.3 kPa, 8 % oxygen by volume.

The application of hot surface coatings and cold surface treatments can give rise to emissions of fume and vapours, principally HCl and tin compounds (European Commission, 2001). The levels of emissions will vary between processes and will depend on many factors. Mass emissions are quite low due to the low amounts of substance used, and concentrations will depend heavily on the amount of extraction air applied. To date, the control of these substances seems to have concentrated on the control of workplace exposure levels.

Table 8.8: Total emission ranges reported for Middle 80 % (P10 to P90) container glass sector furnaces with primary and secondary abatement measures (European Commission, 2001)

Parameter	Without Secondary Abatement With or without primary measures		With Secondary Abatement	
	mg/Nm^3	kg/t glass melted	mg/Nm^3	kg/t glass melted
NO_x	600-2000	1.2-3.9	<400	<0.74
SO_x	250 - 3200	0.5 - 7.2	230 - 1500	0.4 - 2.8
PM	100 - 270	0.2 - 0.6	2 - 32	0.002 - 0.05
HCl	10 - 40	0.02 - 0.08	7 - 30	0.01 - 0.06
HF	1 - 11	≤0.027	≤1 - 5	≤0.011
Metals	0.2 - 8	≤ 0.016	≤ 1	≤ 0.002
Cullet Rate	18 - 80 %			
Typical Load	100 - 360 t/day			
Specific Energy Melting only incl. Boosting	3.9 - 6.4 [GJ/t]			

[1] Reference conditions are: dry, temperature 0°C (273K), pressure 101.3 kPa, 8 % oxygen by volume.

Wherever, HCl containing waste gas from hot end coating is combined with waste gas with a significant organics content, consideration must be given to the potential for the formation of dioxins and furans. The forming processes are highly mechanised which can give rise to mists of lubricating oils but these are controlled according to workplace exposure levels and do not represent a significant emission to air (European Commission, 2001).

For the situation in the Netherlands, the following emission factors for container glass can be proposed:

handling/shipping:

dust:	0.03 - 0.15 kg/Mg glass

melting oven:

SO_2	1.2 kg/Mg glass
CO_2	150 kg/Mg glass
F_g	0.014 kg/Mg glass
Cl_g	0.05 kg/Mg glass
dust	0.30 kg/Mg glass

fuel:

SO_2	3.0 (fuel oil) kg/Mg glass
CO_2	265 kg/Mg glass
NO_x	3.8 kg/Mg glass

The dust is the main source of heavy metals. The emissions are largely determined by the composition of the basic materials and the product. Jockel and Hartje (Jockel W.; Hartje J., 1991) produced some generalised emission factors for the situation in Germany. These factors, also used in the PARCOM-ATMOS Manual, are given in Table 8.9 in g/Mg glass:

Table 8.9: Emission factors for glass production in [g/Mg glass] generalised for the situation in Germany

Substance	**Emission Factor [g/Mg glass]**	**Range [g/Mg glass]**
Arsenic	0.12	0.1-0.24
Cadmium	0.15	0.06-0.24
Chromium	2.4	0.4-1.1
Copper	0.6	0.4-1.1
Lead	12	2-24
Mercury	0.05	0.036-0.072
Nickel	1.9	1.2-2.6
Selenium	18	2.4-24
Zinc	11	4.8-24

The following Table 8.10 contains fuel related emission factors for container glass production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product) are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 6 - 100 GJ/Mg product has been reported.

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030315.

Table 8.10: Emission factors for container glass production[7]

Type of fuel			**NAPFUE code**	**Emission factors**						
				SO_2[2] [g/GJ]	**NO_x[3] [g/GJ]**	**NMVOC[4] [g/GJ]**	**CH_4[4] [g/GJ]**	**CO[5] [g/GJ]**	**CO_2[6] [kg/GJ]**	**N_2O [g/GJ]**
1	oil	residual	203	143-1,470[1]	100-570[1]	3[1]	3-8[1]	12-20[1]	73-78[1]	2-10[1]

Type of fuel			**NAPFUE code**	**Emission factors**						
				SO_2[2] [g/GJ]	**NO_x[3] [g/GJ]**	**NMVOC[4] [g/GJ]**	**CH_4[4] [g/GJ]**	**CO[5] [g/GJ]**	**CO_2[6] [kg/GJ]**	**N_2O [g/GJ]**
l	oil	Gas	204	55-1,410[1]	100-570[1]	1.5[1]	1.5-8[1]	12-20[1]	73-74[1]	2[1]
g	gas	natural	301	0.3[1]	80-570[1]	2.5-4[1]	2.5-4[1]	13-176[1]	53-57[1]	1[1]
g	gas	Liquified petroleum gas	303	0.04[1]	100[1]	2.1[1]	0.9[1]	13[1]	65[1]	1[1]

[1] CORINAIR90 data, area sources

[2]	SO_x:	2,246	g/Mg product	General (EPA, 1990)
		1,700	g/Mg product	Melting furnace (Loos, B. 1992)
[3]	NO_x:	4.3-5	kg/Mg product	General (Bouscaren, 1992) (spec. fuel consumption 7.5 GJ/Mg glass)
		2,920	kg/Mg product	General (Loos, B. 1992)
		3,100	kg/Mg product	Melting furnace (Loos, B. 1992)
[4]	VOC:	100	g/Mg product	Melting furnace (Loos, B. 1992)
[5]	CO:	100	g/Mg product	Melting furnace (Loos, B. 1992)
[6]	CO_2:	423	g/Mg product	General (EPA, 1990)

[7] It is assumed, that emission factors cited within the table are related to combustion sources in container glass production. Footnotes may also include emission factors for other process emissions.

8.3 Production of Glass wool

Reported emission levels for melting from IPPC, BREF (European Commission, 2001) are given in Table 8.11 and Table 8.12. Table 8.11 shows the full range of melting emissions from glass wool plants in the EU. Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030316.

Glass wool products usually contain a proportion of phenolic resin based binder. The binder solution is applied to the fibres in the forming area and is cross-linked and dried in the curing oven. The forming area waste gas will contain particulate matter, phenol, formaldehyde and ammonia (European Commission, 2001).

The particulate matter consists of both organic and inorganic material, often with a very small particle size. Lower levels of VOCs and amines may also be detected if they are included in the binder system. Due to the nature of the process the gas stream has a high volume and high moisture content. The releases from the oven will consist of volatile binder materials, binder breakdown products, water vapour and combustion products from the oven burners. After exiting the oven the product is cooled by passing a large quantity of air through it. This gas is likely to contain glass wool fibre and low levels of organic material. Product finishing involves cutting, handling and packaging, which can give rise to dust emissions (European Commission, 2001).

Table 8.11: Total emission ranges reported for glass wool melting activities (European Commission, 2001)

Substance	**Electric Melting Glass**		**Flame Fired Furnaces**		**Combined Fossil fuel / electrical melting**	
	mg/m3	**kg/Mg of melt**	**mg/m3**	**kg/Mg of melt**	**mg/m3**	**kg/Mg of melt**
PM	2 – 250	0.004 - 1.0	10 - 1000	0.02 - 4.0	10 - 1000	0.02 - 4.0
SO_2			20 - 1000	0.05 - 4.0	20 - 1000	0.05 - 4.0
NO_x	15 - 500	0.002 - 0.03	100 - 1500	0.5 - 6.0[1]	100 - 1500	0.5 - 6.0
HF	0.5 - 5	0.003 - 0.03	0.5 – 5	0.002 – 0.02	0.5 - 5	0.002 - 0.02
HCl	0.2 - 5	0.001 - 0.03	1 – 30	0.004 – 0.08	1 - 30	0.004 - 0.08
CO_2	30 – 150 $*10^3$	100 - 300	150-190$*10^3$	400 – 500	150-190$*10^3$	400 – 500

[1]The lower levels of NOx are from an oxy-gas fired furnace.

Table 20 shows the estimated middle 80 % middle range (from Percentile 10 to Percentile 90) and is an indication of the performance of the majority of EU-wide installations.

Table 8.12: Total emission ranges reported for Middle 80 % (P10 to P90) for glass wool melting activities (European Commission, 2001)

Substance	**Electric Melting Glass**		**Flame Fired Furnaces**		**Combined Fossil fuel / electrical melting**	
	mg/m3	**kg/Mg of melt**	**mg/m3**	**kg/Mg of melt**	**mg/m3**	**kg/Mg of melt**
PM	25 - 220	0.08 - 0.9	30 – 200	0.06 – 0.8	30 - 200	0.06 - 0.8
SO_2			20 – 100	0.05 – 0.4	20 - 100	0.05 - 0.4
NO_x	200 - 400	0.02 - 0.025	500 - 1200	2.5 - 4.8	500 - 1200	2.5 - 4.8
HF	0.5 - 1.0	0.003 - 0.006	1.0 - 5.0	0.004 – 0.02	1.0 - 5.0	0.004 - 0.02
HCl	0.5 - 1.0	0.003 - 0.006	1.0 - 15.0	0.004 – 0.04	1.0 - 15.0	0.004 - 0.04
CO_2	30 – 150 $*10^3$	100 - 300	150-190$*10^3$	400 – 500	150-190$*10^3$	400 - 500

[1]The lower levels of NOx are from an oxy-gas fired furnace.

An important factor that has a major impact on emissions from forming, curing and cooling is the level of binder applied to the product, as higher binder content products will generally result in higher emission levels. Binder derived emissions depend essentially on the mass of binder solids applied over a given time, and therefore high binder content, and to a lesser extent high density products may give rise to higher emissions (European Commission, 2001).

Table 8.13 shows the full range of emissions from downstream operations of mineral wool plants in the EU, with figures for kg/Mg of product in brackets. Table 8.14 shows the estimated middle 80 % of the range.

Table 8.13: Total emission ranges reported for glass wool after melting activities (European Commission, 2001)

Substance	**Combined fiberising, forming and curing**		**Fiberising and forming**		**Product curing**		**Product cooling**		**Product finishing**	
	mg/Nm	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**
PM	10 - 200	0.3 - 6.0	10 - 200	0.3 - 6.0	5.0 – 55	0.01 - 0.18	10 - 50	0.04 - 0.3	1.0 - 50	0.005 - 0.4
Phenol	2.0 - 50	0.05 - 1.6	2.0 - 50	0.05 - 1.5	2.0 – 40	0.004 - 0.11	1.0 - 10	0.004 - 0.06		
Formaldehyde	2.0 - 30	0.05 - 1.2	2.0 - 30	0.05 - 1.0	2.0 – 60	0.004 - 0.17	1.0 - 10	0.004 - 0.06		
Ammonia	20 - 250	0.6 - 8.8	20 - 250	0.5 - 7.6	30 – 460	0.06 - 1.9	1.0 - 50	0.004 - 0.3		
NO_x					50 – 200	0.1 - 0.6				
VOC	5.0 - 150	0.1 - 5.0	5.0-150	0.1 - 4.6	5.0 – 150	0.01 - 0.43	1.0 - 30	0.004 - 0.2		
CO^2					20 – 80 * 10^3	40 - 230				
Amines	1.0 - 40	0.1 - 1.3	5.0 - 40	0.1 - 1.2	5.0 - 20	0.01 - 0.06	1.0 - 5.0	0.004 - 0.03		

Table 8.14: Total emission ranges reported for Middle 80 % (P10 to P90) for glass wool after melting activities (European Commission, 2001)

Substance	**Combined fiberising, forming and curing**		**Fiberising and forming**		**Product curing**		**Product cooling**		**Product finishing**	
	mg/Nm	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**	**mg/Nm**	**kg/Mg of product**
PM	10 - 50	0.9 - 1.9	10 - 50	0.6 - 3.5	5.0 - 25	0.01 - 0.07	10 - 30	0.04 - 0.2	5.0 - 20	0.03 - 0.16
Phenol	5.0 - 25	0.2 - 1.3	5.0 - 25	0.1 - 0.8	5.0 - 15	0.01 - 0.04	1.0 - 5.0	0.004 - 0.03		
Formaldehyde	5.0 - 20	0.15 - 0.43	5.0 - 20	0.1 - 0.6	5.0 - 30	0.01 - 0.09	1.0 - 5.0	0.004 - 0.03		
Ammonia	40 - 150	1.8 - 5.4	40 - 150	1.0 - 4.5	50 - 200	0.1 - 0.6	2.0 - 20	0.007 - 0.12		
NO_x					50 - 150	0.1 - 0.4				
VOC	10 - 80	0.2 - 2.7	10 - 80	0.3 - 2.4	10 - 80	0.02 - 0.23	1.0 - 10	0.004 - 0.06		
CO^2					$20 – 80 * 10^3$	40 - 230				
Amines	5.0 - 20	0.1 - 1.0	5.0 - 20	0.1 - 0.6	5.0 - 10	0.01 - 0.03	1.0 - 5.0	0.004 - 0.03		

For the situation in the Netherlands, the following emission factors for several compounds in kg/Mg glass wool can be proposed::

handling/shipping:

dust:	0.03 - 0.15 kg/Mg glass

melting oven:

SO_2	0.5 kg/Mg glass
CO_2	450 kg/Mg glass
F_g	0.006 kg/Mg glass
Cl_g	0.01 kg/Mg glass
dust	0.04 (after dust collector) kg/Mg glass

spinning/wool manufacturing:

formaldehyde	0.9 kg/Mg glass
phenol(s)	0.3 kg/Mg glass
ammonia	4.5 kg/Mg glass
VOS	0.6 kg/Mg glass

fuel:

SO_2	5.0 (fuel oil) kg/Mg glass
CO_2	670 kg/Mg glass
NO_x	2.8 kg/Mg glass

Emissions of heavy metals may be contained in the dust. No specific information for glass wool production is available. For a first estimation the factors referred to above for flat glass and container glass may be used.

The following Table 8.15 contains fuel related emission factors for the production of glass wool based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg material), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 4.3 - 100 GJ/Mg product has been reported.

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030316.

Table 8.15: Emission factors for the production of glass wool[7]

				Emission factors						
	Type of fuel		NAPFUE code	SO_2[2] [g/GJ]	NO_x[3] [g/GJ]	NMVOC[4][5] [g/GJ]	CH_4[5] [g/GJ]	CO[6] [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
l	oil	Residual	203	840-1470[1]	150-450[1]		8[1]	20[1]	76-77[1]	2[1]
l	oil	Gas	204	55-1410[1]	50-100[1]		81)	20[1]	73-74[1]	2[1]
g	ga s	Natural	301	8[1]	60-150[1]	10[1]	2-3[1]	20-30[1]	53-55[1]	1-3[1]

[1] CORINAIR90 data, area sources (preliminary data)

[2]	SO_x:	2,246	g/Mg product	General (EPA, 1990)
		5,000	g/Mg material processed	Regenerative furnace and recuperative furnace (Bouscaren, 1992)
		20	g/Mg material processed	Electric furnace
		300	g/Mg material processed	Unit smelter furnace
[3]	NO_x:	5,400-6,000	g/Mg product	General (Bouscaren, 1992)
		2,500	g/Mg material processed	Regenerative furnace (Bouscaren, 1992)
		850	g/Mg material processed	Recuperative furnace (Bouscaren, 1992)
		135	g/Mg material processed	Electric furnace (Bouscaren, 1992)
		245	g/Mg material processed	Forming, rotary spin (Bouscaren, 1992)
		550	g/Mg material processed	Alting oven: rotary spin (Bouscaren, 1992)
		150	g/Mg material processed	Cooling (Bouscaren, 1992)
		150	g/Mg material processed	Unit smelter furnace (Bouscaren, 1992)
		1,000	g/Mg material processed	Cursing: flame attenuation (Bouscaren, 1992)
[4]	NMVOC:	5,000	g/Mg product	(Loos, B. 1992)
[5]	VOC:	100	g/Mg material processed	Regenerative furnace, recuperative furnace and electric furnace (Bouscaren, 1992)
		3,500	g/Mg material processed	Forming: rotary spin (Bouscaren, 1992)
		1,500	g/Mg material processed	Cursing oven: rotary spin (Bouscaren, 1992)
		150	g/Mg material processed	Forming: flame attenuation (Bouscaren, 1992)
		3,500	g/Mg material processed	Cursing: Flame attenuation (Bouscaren, 1992)
[6]	CO:	0-500	g/Mg glass	For electric melting (Loos, B. 1992)
		100-600	g/Mg glass	For other furnaces (Bouscaren, 1992)
		125	g/Mg material processed	Regenerative furnace (Bouscaren, 1992) and recuperative furnace (Bouscaren, 1992)
		25	g/Mg material processed	Electric furnace (Bouscaren, 1992)
		850	g/Mg material processed	Cursing oven: rotary spin (Bouscaren, 1992)
		125	g/Mg material processed	Unit melter furnace (Bouscaren, 1992)
		1,750	g/Mg material processed	Cursing: flame attenuation (Bouscaren, 1992)

[7] It is assumed, that emission factors cited within the table are related to combustion sources in glasswool production. Footnotes may also include emission factors for other process emissions.

8.4 Production of Other Glass

The emission levels from IPPC, BREF (European Commission, 2001) are given in Table 8.16 (domestic glass) and Table 8.17 (examples of special glass processes).

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030317.

Table 8.16: Summary of emission averages and ranges reported for domestic glass furnaces (European Commission, 2001)

Substance	Soda-lime glass				Lead Crystal[1]			
	mg/m3		kg/Mg of melt		mg/m3		kg/Mg of melt	
	Range	Average value	Range	Average value	Range	Average value	Range	Average value
PM	0.5 – 400	200	0.001 – 0.8	0.4	2 - 10	5	0.001 - 0.1	0.02
SO_2	50 – 1000	250	0.1 - 2.8	0.7			0.1 - 1	0.2
NO_x	140 – 5500[2]	2300	0.9 - 11	4.8	1000 - 2000	1500	0.9 - 5.0	1
HF	<5				0.1 - 1.0	0.5	0.0002 - 0.004	0.0003
HCl	<10				0.5 - 5.0	2.0	0.001 - 0.003	0.002
Metals[3]	<5				0.05 - 0.5	0.2	0.0001 - 0.035	0.01

(1) These data relate to conventional furnaces (i.e. not electrical)

(2) Some high results relate to the use of nitrates in the batch or to other specific conditions (e.g. very low pull rate).

(3) Including lead

Table 8.17: Summary of emission factors (kg/Mg) reported for special glass specific example processes (European Commission, 2001)

Substance	Water glass	TV funnel glass	TV panel glass
PM	0.212	0.0061	0.0326
SO_2	1322	0.0714	0.0817
NO_x	2028	12000	2700
HF	400	0.00137	0.0013
HCl	24	0.00924	0.0026

For emissions of heavy metals some specific information are derived from the PARCOM-ATMOS Emission Factors Manual and the literature mentioned there:

- For the production of lead crystal glass an emission factor of 60 g lead/Mg product is mentioned, using bag filters as abatement method. Without abatement the emission factor is estimated to be 1% of the lead content of the glass (UK Energy Efficiency Office, 1994).
- For coloured glass an emission factor of 0.11-0.15 g cadmium/g glass is mentioned.
- For the situation in Germany some specific information is given by Jockel and Hartje (Jockel W.; Hartje J., 1991). This information is given in Table 8.18.

Table 8.18: Emission factors for heavy metals from special glass production in Germany in [g/Mg product]

Substance	Emission Factor [g/Mg product]	Range [g/Mg product]
Arsenic (lead crystal glass)	140	22-310
Arsenic (crystal glass)	96	-
Cadmium	0.15	0.06-0.24
Chromium	2.4	0.5-5
Copper	0.6	0.4-1.1
Lead (lead crystal glass)	2700	2200-3200
Lead (crystal glass)	480	-
Mercury	0.05	0.036-0.072
Nickel	1.9	1.2-2.6
Selenium	18	2.4-24
Zinc	11	4.8-24

The following Table 8.19 contains fuel related emission factors for the production of other glass based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, g/Mg material processed), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 25 - 6.000 GJ/Mg product has been reported.

In each case, care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and emissions reported here in activity 030317.

Table 8.19: Emission factors for the production of other glass[6]

					Emission factors						
	Type of fuel			**NAPFUE code**	**SO_2[2] [g/GJ]**	**NO_x[3] [g/GJ]**	**NMVOC[4] [g/GJ]**	**CH_4[4] [g/GJ]**	**CO[5] [g/GJ]**	**CO_2 [kg/GJ]**	**N_2O [g/GJ]**
s	Coal	hc	steam	102	787[1]	150[1]	15[1]	15[1]	10[1]	94[1]	14[1]
s	Biomass		wood	111		200[1]	50[1]	30[1]		92[1]	14[1]
l	Oil		residual	203	960-1,470[1]	132-370[1]	3-19[1]	0.1-3[1]	15-19[1]	76[1]	14[1]
l	Oil		gas	204	138-1,410[1]	80-100[1]	2[1]	1[1]	12[1]	73[1]	14[1]
l	Kerosene			206	69[1]	80[1]	2[1]	1[1]	12[1]	71[1]	14[1]
l	Gasoline		motor	208	45[1]	80[1]	2[1]	11)	12[1]	71[1]	14[1]
g	Gas		natural	301	8-260[1]	32-622[1]	10-26[1]	0.4-3[1]	8.5-95[1]	53-56[1]	1-3.7[1]
g	Gas		liquified petroleum gas	303	2[1]	20-40[1]	1-4[1]	1-4[1]	13[1]	60-65[1]	3[1]

[1] CORINAIR90 data, area sources

[2]	SO_x:	2,246	g/Mg product	General (Loos, B. 1992)
		1,500	g/Mg material processed	Textile fiber, regenerative furnace and recuperative furnace (EPA, 1990)
		2,800	g/Mg product	Pressed and blown glass, melting furnace (EPA, 1990)
		2,800	g/Mg beaded glass	Ground cullet beading furnace (EPA, 1990)
[3]	NO_x:	3,500-6,000	g/Mg product	General (Bouscaren, 1992)
		10,000	g/Mg material processed	Textile fiber; regenerative furnace, recuperative furnace and unit smelter furnace (EPA, 1990)
		1,300	g/Mg material processed	Textile fiber; curing oven (EPA, 1990)
		4,250	g/Mg product	Pressed and blown glass, melting furnace (EPA, 1990)
		4,250	g/Mg beaded glass	Ground cullet beading furnace (EPA, 1990)
[4]	VOC:	100	g/Mg material processed	Textile fiber: regenerative furnace and recuperative furnace (EPA, 1990)
		0	g/Mg material processed	Textile fiber: unit smelter furnace (EPA, 1990)
		150	g/mg product	Pressed and blown glass, melting furnace (EPA, 1990)
		150	g/Mg beaded glass	Ground cullet beading furnace (EPA, 1990)
[5]	CO:	100	g/Mg product	Pressed and blown glass, average (Bouscaren, 1992)
		100	g/Mg product	Pressed and blown glass, melting furnace (EPA, 1990)

[6] It is assumed, that emission factors cited within the table are related to combustion sources in other glass production. Footnotes may also include emission factors for other process emissions.

9 SPECIES PROFILES

An analysis of dust emissions from a melting oven in the Netherlands is available. The major constituents from this analysis are given in g/Mg glass:

Table 9.1: Composition of dust from glass melting oven

Substance	**Concentration [g/Mg glass]**
Aluminium	1.3
Chromium	0.15
Cobalt	0.05
Copper	0.15
Iron	2.4
Lead	0.30
Manganese	0.05
Nickel	1.0
Titanium	0.08
Vanadium	1.90
Zinc	0.25

These components are present as sulphates.

10 UNCERTAINTY ESTIMATES

If the simplified approach is used the results may differ very much from the real situation. A classification C-D is appropriate in this case. If more detail about the individual plant are available the factors should be corrected e in classifications in the B to C range.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The default calculation could be very much improved if information about the basic materials used is available.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant if treated as point source. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment or population statistics.

Production of special glass is usually done in small plants. They may be treated as an area source by disaggregating national emission estimates on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The production of flat glass, container glass, and glass wool can be considered as a continuous process. The production of special glass is usually a discontinuous process but no information is available on temporal profile.

14 ADDITIONAL COMMENTS

No additional comments.

15 SUPPLEMENTARY DOCUMENTS

- Emission inventory in The Netherlands, 1992. Emission to air and water
- Personal information and experience during emission inventories 1975 - 1995
- Emission factors to be used for the building industry, TNO report 89/091
- Environmental Protection Agency, Compilation of Air Pollutant Emission Factors AP-42
- PARCOM-ATMOS Emission Factors Manual
- SPIN document "Productie van glas ,glasvezel, en glaswol", 1992 (in Dutch)
- LEENDERTSE, A.: Dutch notes on BAT for the Glass and Mineral Wool Industry. prepared for the Ministry of Housing, Spatial Planning and the Environment. Directorate for Air and Energy Draft version October 1998
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16 VERIFICATION PROCESSES

Verification should be applied by comparing calculated emissions with measured emissions at an individual plant.

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19 RELEASE VERSION, DATE AND SOURCE

Version : 2.2

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Updated with emission factors (CEPMEIP) for particulates by:

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20 POINT OF ENQUIRY

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SNAP CODE: 040210

SOURCE ACTIVITY TITLE: PROCESSES IN IRON & STEEL INDUSTRIES & COLLIERIES *Other*

NOSE CODE: 105.12.19

NFR CODE: 2 C 1

Methodologies for activities covered by SNAPS 04021 – 040209 are detailed in previous chapters (see index). A specific methodology for other processes in iron and steel industries and collieries (SNAP 040210) has not been prepared because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant

If you have information contrary to this please contact the expert panel leaders.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Updated with particulate matter details by:
Mike Woodfield
AEA Technology
UK
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Leaders of the Combustion and Industry Expert Panel

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SNAP CODE: **040510**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Styrene

NOSE CODE: **105.09.53**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Styrene can be made from ethylbenzene in two ways, either by the dehydrogenation process or the oxidation process. The first route is used in the majority of plants.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emissions of styrene plants according to Corinair 90 were on average smaller then 0.01% to the total NMVOC emission in the reporting countries.

(This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006)).[1]

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Styrene	040510	-	-	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

The hydrogenation process can be operated in two ways; in both processes steam is used for heat addition to the feed and for retarding coke deposition.

- The adiabatic process.
  Preheated ethylbenzene is mixed with superheated (800 - 950°C) steam (ratio 1:<14) and led over the catalyst. Operation conditions are: T: 610 - 660°C; p: <138 kPa.

  This process is the most common.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

- The isothermal process.
  A tubular reactor with catalyst is used. Reaction heat is provided by indirect heat exchange. Operation conditions are: T: 580 - 610°C; p: <138 kPa. Ethylene/steam ratio is 1: 6 - 8.

The catalyst used in both processes is Fe_2O_3 with Cr_2O_3 as stabilizer and K_2CO_3 as coke formation retardant. After the reactor a settler separates vapor (vent gas; mostly hydrogen), water (saturated with aromatics) and liquid hydrocarbons (crude styrene).

In the purification section, which operates under vacuum, inhibitors are used to suppress polymerization of styrene. Benzene is recovered and recycled to the ethylbenzene plant; the residue is used as fuel. Ethylbenzene is recovered and recycled to the reactor feed.

The oxidation process is a three stage process.

In the first stage ethylbenzene is oxidized to form ethylbenzene hydroperoxide. Air is bubbled through liquid ethylbenzene, no catalyst is required. A series of reactors is used, each operating at a different temperature: in the first reactor the temperature is 135 - 160°C, in the last 125 - 155°C. The temperature is reduced to reduce formation of by-products (decomposition). The operating pressure is 800 - 1500 kPa.

In the second stage the hydroperoxide formed in the first stage reacts with propylene to form 1-phenylethanol and propylene oxide. The catalyst used are compounds of metal, e.g. Mo, W, V. Reaction temperature is 100 - 130°C.

In the third stage the 1-phenylethanol is dehydrated to form styrene.

3.2 Definitions

Not relevant

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: methane, styrene, toluene. Methane is emitted due to combustion, styrene and toluene due to leakage and storage loss.

For the Netherlands the VOC emission due to styrene production is 230.2 ton/y. This emission is related to acrylonitrile production of 928 kton/y and a capacity of kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Cause of the emission	**[2]**
leakage losses from appendages, pumps, etc.	65.4%
flaring, disruptions	0.1%
losses due to storage and handling	19.0%
combustion emissions	15.5%
other process emissions	0 %

In a Canadian report [1] a subdivision specific for the emission from styrene plants is given:

Process	0.6%
Fugitive	89.1%
storage and loading	7.7%
Spills	2.6%

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the styrene production to estimate total emissions. The amount of emitted VOC is then directly related to the styrene production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant. In a Canadian study [1] the use of this methodology instead of the simpler one resulted in a considerably lower estimate of the process emissions.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1.: Styrene production in some countries and regions for 1990

Country or Region	kton/y	Source
U.S.A.	3640	Chem&EngNews 29/6/92

7 POINT SOURCE CRITERIA

Styrene production plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1.: Emission factors for styrene

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [2]	0.25	C
Canada [1]	0.7	?
USA [3]	18	?

The Worldbank Handbook (5) gives a range of 0.25 to 18 kg/ton product, depending on the quality of the abatement. The Handbook of emission factors (6) gives for the situation in the Netherlands a range of 0.05 to 0.5 kg/ton product, probably with good abatement.

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: The composition of the VOC emissions for the different sources is [2]:

	methane	Ethylene	styrene	benzene	toluene	other HC's
leakage loss	7%	0%	17%	4%	33%	39%
flaring and disruptions	0%	0%	0%	0%	0.2%	99.8%
storage and handling loss	0%	0%	39%	1%	22%	38%
Combustion	40%	10%	0%	0.2%	0.2%	50%
other process emissions	-	-	-	-	-	-

Table 9.2: The overall VOC emission profile for styrene plants

	TNO ER [2]	Canadian [1]	EPA [4]
Methane	10.8%	-	21.7%
Ethylene	1.6%	-	24.4%
Styrene	18.5%	7.6%	4.9%
Benzene	2.8%	0.3%	23.3%
Toluene	25.8%	0.0%	9.2%
Ethane	-	-	6.5%
ethylbenzene	-	-	9.9%
other hydrocarbons	40.5%	92.1%	-

10 UNCERTAINTY ESTIMATES

As the influence of the applied abatement is rather big the use of a default overall factor can result in a rather high uncertainty if the real abatement is not known.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 21, 3rd edition (1983).
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Emissions of Volatile Organic Compounds from selected organic chemical plants, B.H. Levelton & Associates Ltd., 1990.
2 Communication with styrene producing plant by TNO during emission inventory 1992.
3 Internal report from styrene producing company.
4 US Environmental Protection Agency Airchief 1991.
5 World Bank Group Pollution prevention and abatement Handbook Petrochemicals Manufacturing (1998)
6 Handbook of emission factors Part 2 Industrial Sources Ministry of Housing ,Spatial Planning and the Environment M.E.Reinders (editor) (1983)

18 BIBLIOGRAPHY

Many detailed describtions of the process on internet.

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.3

Date : September 2006

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
TNO
The Netherlands

Update by:
P.F.J. van der Most

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SNAP CODE: **040511**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Polystyrene

NOSE CODE: **105.09.84**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Polystyrene is made by polymerizing styrene monomer. Most polystyrene is produced by free-radical polymerization.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of polystyrene plants contributes on average 0.01% to the total NMVOC emission in a country.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Polystyrene	040511	-	-	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Polystyrene can be polymerized via several mechanism: free-radical, anionic and cationic and with Ziegler-Natta catalyst. Commercially free-radical polymerization is most important.

Styrene acts as its own free-radical initiator, when heated. A commonly used temperature is 100 °C.

The process has a high yield; the product a high purity, because no additions are needed.

The key-problems are: heat removal and pumping the highly viscous solutions.

3.2 Definitions

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: styrene and other hydrocarbons.

For the Netherlands, the VOC emission due to the polystyrene production is 342.3 ton/y. This emission is related to a production of 131.4 kton/y and a capacity of 194 kton/y (data for 1992).

The VOC emission can be subdivided as follows:

Emission source	**[1]**
leakage losses from appendages, pumps, etc.	94.5%
flaring, disruptions	0 %
losses due to storage and handling	5.5%
combustion emissions	0 %
other process emissions	0 %

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the polystyrene production to estimate total emissions. The amount of emitted VOC is then directly related to the polystyrene production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.
Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Tables 6.1 and 6.2 list relevant capacities and production data for several countries and regions for 1990.

Table 6.1: Polystyrene capacity in some countries

Country or Region	kton/y	source	year
Latin America	590	EurChemNews //92	1991
Indonesia	27.5	EurChemNews //92	1990?

Table 6.2: Polystyrene production in some countries and regions for 1990

Country or Region	**kton/y**	**source**
France	542	Chem&EngNews 29/6/92
Italy	353	Chem&EngNews 29/6/92
Canada	215	Chem&EngNews 29/6/92
U.S.A.	2280	Chem&EngNews 29/6/92
Japan	2097	Chem&EngNews 29/6/92
Korea, South	592	Chem&EngNews 29/6/92
U.S.S.R.	515	Chem&EngNews 13/4/92

7 POINT SOURCE CRITERIA

Polystyrene production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for polystyrene

Source	**factor (kg/ton)**	**Quality Code**
TNO Emission Registration 1992 [1]	2.6	C
EPA [2]	0.6 - 2.5 batch	C/D
EPA [2]	0.2 - 3.3 cont.	C/D
EPA [2]	5.4 expandable	C/D

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: The composition of the VOC emissions for the different sources is [1]:

	methane	**ethylene**	**styrene**	**HCFC's**	**other HC's**
leakage loss	0%	0%	>2%	0%	<98%
flaring and disruptions	-	-	-	-	-
storage and handling loss	0%	0%	>17%	0%	<83%
combustion	-	-	-	-	-
other process emissions	-	-	-	-	-

Table 9.2: The overall VOC emission profile for polystyrene plants

	TNO ER [1]	**EPA [3]**
methane	0%	-
ethylene	0%	-
ethylbenzene	-	10%
styrene	>3%	90%
other HC's	<97%	-

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 23, third edition (1983).
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 TNO Emission Registration, 1992
2 EPA, AP-42
3 EPA, Airchief, 1991

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.2

Date : October 1995

Source : J J M Berdowski, W J Jonker & J P J Bloos
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Updated with particulate matter details by:
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SNAP CODES: **040512**
040513
040514

SOURCE ACTIVITY TITLES: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Styrene Butadiene
Styrene Butadiene Latex
Styrene Butadiene Rubber

NOSE CODE: **105.09.85**
105.09.86
105.09.87

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

The process described or the polymerisation reaction to produce styrene-butadiene copolymers, is the emulsion polymerisation.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of all styrene butadiene (SB) plants contributes on average 0.02% to the total NMVOC emission in the to Corinair 90 reporting countries.

(These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006)).[1]

3 GENERAL

3.1 Description

The copolymerization of styrene and butadiene can be done in several ways. In this guidebook two ways are distinguished: styrene butadiene latex and styrene butadiene rubber.

SB latex

- SB latex is made by emulsion polymerization. The reaction is started with free-radical initiators. The emulsion consists for 5 - 10 wt.% of non-rubber, more than half being emulsifiers (others components: initiators, modifiers, inorganic salts, free alkali and short stops). A polymer string consists of random blocks of styrene and butadiene.
- Another way of producing SB latex is emulsification of SB rubber: SB rubber particles are dissolved in water with dispersing and wetting agents.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

<u>*SB rubber*</u>

The production of SB rubber can be done in several ways:

- anionic polymerization.
  The reaction can be started with reaction of the initiator with either styrene or butadiene.
  - When the reaction starts with styrene, the propagation can be with styrene or butadiene.
    Reaction conditions:
    - in an inert hydrocarbon solvent under a nitrogen blanket (no water or oxygen may be present).
    - temperature: 5 °C ('cold'); conversion 60 - 80%.
    - temperature: 50 - 65 °C ('hot'); conversion >90%.
  - When the reaction starts with butadiene, all butadiene will first react and then the styrene to form a block copolymer of the type SB and/or SBS.
    The length of the polymer can be varied by varying the amount of initiator.
    Statistical (random) copolymerization is possible by adding 'donators' like ether or tertiary amines.
- polymerization with redox-system.
  The redox-system: oxidizing compounds (peroxides), reducing compounds and heavy metalions, like Fe^{2+}.

  Operation temperature is 5 °C; the low(er) temperature contributes to the regular structure of the polymer (the polymer has more styrene blocks in the 'backbone', more *tert*-1,4-butadiene is incorporated, the branches are shorter and the percentage of gel in the polymer is lower.

3.2 Definitions

Latex:	a colloidal aqueous emulsion of an elastomer.
Synthetic latex:	latex with in situ polymerised elastomer.
Artificial latex :	latex from reclaimed rubber polymers.

3.3 Techniques

See section 3.1.

3.4 Emissions

The VOC emission from SB rubber production can be subdivided as follows:

Cause of the emission	**[1]**
leakage losses from appendages, pumps, etc.	99.9%
flaring, disruptions	0.0%
losses due to storage and handling	0.0%
combustion emissions	0.0%
other process emissions	0.1%

3.5 Controls

The losses due to leakage can be limited by use better abatement methods.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the SB production (latex or rubber) emissions. The amount of emitted VOC is then directly related to the SB production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, such as valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by first multiplying each equipment emission factor by the number of pieces of that type of equipment, than adding up the emission for each type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

The Rubber Statistical Bulletin provides relevant data on SB polymer production.

7 POINT SOURCE CRITERIA

SB plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for SB polymer

Source	**Emission factor (kg/ton)**	**Quality Code**
Netherlands Emission Inventory 1987 [1]	5 - 10	E
US Environmental Protection Agency AP-42 [2]	5.8 - 8.6	E
US Environmental Protection Agency Airchief 1993 [3]	2.9 - 7.8	E

The World bank handbook (5) gives for an SBR plant a factor of 3 to 10 kg/ton product.
The Handbook of Emission factors (6) gives factors for butadiene an emission factor of 0.1 to 0.5 kg/ton and for styrene 0.1 to 2.0 kg/ton.

**Table 8.2 Emission factors for Emulsion polymerisation of SB polymer. (4)
US Airchief gives for 1995 the following table (quality class B):**

Process step	Emission styrene and butadiene gr/kg product
Monomer recovery uncontrolled	2.6
Absorber vent	0.26
Blend coagulation tank uncontrolled	0.42
Dryers	2.51

Table 8.3: Emission factors for SB latex

Source	**factor (kg/ton)**	**Quality Code**
Netherlands Emission inventory 1987 [1]	10	E
US Environmental Protection agency AP-42 [2]	8.55	E
US Environmental Protection Agency Airchief 1993 [3]	7.8	E

Table 8.4 Emission factors for Emulsion polymerisation of SB latex according to US Airchief 1995. (quality class B) (4)

Process step	
Monomer removal condenser vent	8.45 gr/kg
Blend tanks uncontrolled	0.1 gr/kg

Table 8.5: Emission factors for SB rubber

Source	**factor (kg/ton)**	**Quality Code**
Netherlands Emission Inventory 1992 [1]	3.7	C
Netherlands Emission Inventory 1987 [2]	5	C
US Environmental Protection Agency AP-42 [3]	5.8	E
US Environmental Protection Agency Airchief 1993 [4]	2.9	E

9 SPECIES PROFILES

Table 9.1 lists the overall VOC profile for SB latex.

Table 9.1: The overall VOC emission profile for SB latex plants

Compound	NL Emission Inventory(1)
Styrene	75 %
1,3-butadiene	25 %

Tables 9.2 and 9.3 list the VOC profile respectively for the different sources and the overall profile for SB rubber.

Table 9.2: The composition of the VOC emissions for the different sources is [1]:

	ethylene	acrylonitrile	styrene	Toluene	other HC's
Leakage loss	0.1%	0.0%	86.8%	0.1%	13.0%
flaring and disruptions	-	-	-	-	-
storage and handling loss	-	-	-	-	-
Combustion	-	-	-	-	-
other process emissions	0%	0%	0%	0%	100%

Table 9.3: The overall VOC emission profile for plants

	NL Emission Inventory [1]	NL Emission Inventory [2]
Styrene	87	95 %
1,3-butadiene	incl. in HC’s	5 %
other HC's	13	-

10 UNCERTAINTY ESTIMATES

Depending on the fit of the overall emission factors

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant,

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 20, 3rd edition (1984) & Volume 9, 4th edition (1994).
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Emission Inventory in the Netherlands 1987
2 US Environmental Protection agency AP-42, 1985
3 US Environmental Protection Agency Airchief 1993
4 US Environmental Protection Agency Airchief 1995
5 World Bank Group Pollution Prevention and Abatement Handbook (1998)
6 Handbook of Emission Factors Part 2 Industrial sources. Ministry of Housing Spatial Planning and the Environment M.E.Reinders (editor) (1983)

18 BIBLIOGRAPHY

Detailed process descriptions to be found on Internet

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.1

Date : September 2006

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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Update by:
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SNAP CODE: **040515**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Acrylonitrile Butadiene Styrene (ABS) Resins

NOSE CODE: **105.09.88**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Acrylonitrile butadiene styrene (ABS) is a combination of a graft copolymer and a polymer mixture.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of ABS plants contributes on average of less than 0.1% to the total NMVOC emission in a country.

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

ABS can be produced in three ways:

- Emulsion polymerization.
  This is a two step process. In the first step a rubber latex is made, usually in a batch process. In the second step, which can be operated as batch, semi-batch and continuous, styrene and acrylonitrile are polymerized in the rubber latex solution to form an ABS latex. The ABS polymer is recovered through coagulation of the ABS latex by adding a destabilizing agent. The resulting slurry is filtered or centrifuged to recover the ABS resin. The ABS resin is then dried.

- Mass (or bulk) polymerization.
  Two or more continuous flow reactors are used in this process. Rubber is dissolved in the monomers, being styrene and acrylonitrile. During the reaction the dissolved rubber is replaced by the styrene acrylonitrile copolymer (SAN) and forms discrete rubber particles. Part of the SAN is grafted on the rubber particles, while another part is occluded in the particles. The reaction mixture contains several additives, e.g. initiator, chain-transfer agents, these are needed in the polymerization.

  The product is devolatilized ro remove unreacted monomer, which are recycled to the reactor, and then pelletized.

- Mass-suspension.

This batch process starts with a mass polymerization (see above) which is stopped at a monomer conversion of 15 - 30%. Then a suspension reaction completes the polymerization. For this reaction the mixture of polymer and monomer is suspended in water using a suspending agent and then the polymerization is continued.

Unreacted monomers are stripped, then the product is centrifuged and dried.

3.2 Definitions

Graft polymer: a polymer with a ‘backbone’ of one type of monomer and with ‘ribs’ of copolymers of two other monomers.

3.3 Techniques

See section 3.1.

3.4 Emissions

The VOC emission can be subdivided as follows:

Cause of the emission	[1]
leakage losses from appendages, pumps, etc.	99.4 %
flaring, disruptions	0.00%
losses due to storage and handling	0.4 %
combustion emissions	0.1 %
other process emissions	0.0 %

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the ABS production emissions. The amount of emitted VOC is then directly related to the ABS production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA:

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each

equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

7 POINT SOURCE CRITERIA

SB plant can be considered as point source if individual plant data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1. Emission factors for ABS production

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1990 [2]	5	C
TNO Emission Registration 1992 [1]	1.4	C
EPA Airchief 1993 [3]	27.2	E

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile for the different sources and the overall profile respectively.

Table 9.1. The composition of the VOC emissions for the different sources [1]

	methane	ethylene	acrylonitrile	styrene	other HC's
leakage loss	0%	0%	12%	70%	18%
flaring and disruptions	-	-	-	-	-
storage and handling loss	0%	0%	16%	81%	3%
combustion	21%	5%	3%	43%	28%
other process emissions	-	-	-	-	-

Table 9.2. The overall VOC emission profile for ABS plants

	TNO ER [1]	TNO ER [2]	NAPAP [4]
methane	0%		0%
ethylene	0%		0%
acrylonitrile	12%	40	60%
styrene	70%	40	40%
1,3-butadiene	-	20	-
other HC's	18%		0%

10 UNCERTAINTY ESTIMATES

At the time of publication there were not enough data to establish an uncertainty estimate.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Emission factors need to be confirmed or improved.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 1, 4th edition (1991)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.
See Verification Chapter for further details.

17 REFERENCES

1 TNO Emission Registration 1992
2 TNO Emission Registration 1990
3 EPA AIRCHIEF 1993
4 NAPAP 1985

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.1
Date : October 1995

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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Updated with particulate matter details by:
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SNAP CODE: **040518**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Ethylbenzene

NOSE CODE: **105.09.54**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Ethylbenzene can be produced both in liquid- and in vapour-phase. All processes use a catalyst with aluminium.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of ethylbenzene plants contributes on average <0.01% to the total NMVOC emission in a country.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Ethylbenzene	040518	-	-	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

The liquid-phase ethylbenzene production can be operated in two ways:

1 The Union Carbide/Badger process.

Ethylene is sparged in the reactor containing a mixture of benzene, catalyst ($AlCl_3$) and a promotor (monochloroethane or sometimes HCl). The reaction mixture is agitated to disperse the catalyst-complex and operated at low temperature and pressure. Almost complete conversion of ethylene is obtained. In the reactor polyethylbenzenes are transalkylated to ethylbenzene.

The reactor effluent is cooled and led into a settler. From the settler the catalyst-complex is recycled to the reactor and the organic phase is washed with water and a caustic solution to remove any remaining catalyst. The waste aqueous phase (from the treatment of the organic phase) is neutralized and aluminum hydroxide is recovered and disposed as landfill or calcinated to recover aluminum oxide.

After the washing treatment the ethylbenzene is purified. Recovered benzene and polyethylbenzenes are recycled. The heavier compounds are used as fuel.

2 The Monsanto process.

Resembles the Union Carbide/Badger process. The reaction is operated at higher temperature, so less catalyst is needed. No catalyst complex phase is present, since all catalyst is dissolved, resulting in higher selectivity and higher overall yield.

Two reactors are used: one with only dry benzene, ethylene, catalyst and promotor; the second with the effluent from the first reactor plus (recycled) polyethylbenzenes.

The effluent of the second reactor is washed with water and a caustic solution to remove the catalyst complex. Further processing as above.

The vapour-phase operation of ethylbenzene can be operated in several ways:

- The simple process.
  A solid catalyst e.g. alumina on silica gel is used. Operation temperatures are >300 °C; pressures >6000 kPa. High benzene/ethylene ratios are used to minimize formation of higher alkylated ethylbenzenes. A small dealkylation unit, like the liquid phase process, is used to obtain higher overall yield.

- The Mobil/Badger process.
  Fresh ethylene, preheated benzene and recycled alkyl-aromatics are led to a single fixed bed reactor containing a ZSM-5 catalyst. In the reactor simultaneous transalkylations occur. Operation conditions are: high temperatures and moderate pressures.

  Two reactors are used: one in use, the other being regenerated.

  After the reactor a prefractionator is used to separate benzene, volatile components and ethylbenzene and high boilers. The top of the prefractionator is cooled; the condensate (mainly benzene) is recycled to the reactor, the uncondensable components are vented or used as fuel. The bottom product consists of crude ethylbenzene; this crude product is purified and recovered benzene and polethylbenzenes are recycled to the reactor. The residue from the purification is used as fuel.

- The Alkar process.
  This process is used for feeds with low ethylene concentrations. The reactor contains a solid acid catalyst of activated alumina with some BF_3.

  A separate transalkylation reactor is used to reform polyethylbenzenes.

Before the purification the non-reactive gasses are removed in a flash drum. During the purification of ethylbenzene, benzene and polyethylbenzenes are recovered and recycled.

3.2 Definitions

See section 3.1.

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: methane, ethylene, benzene and toluene. Methane is released due to combustion, ethylene due to leakage loss and combustion, benzene due to leakage loss and toluene due to leakage and storage loss.

For the Netherlands, the VOC emission due to ethylbenzene production is 75.4 ton/y. This emission is related to a production of 989 kton/y and a capacity of 1429 kton/y (1992 data).
The VOC emission can be subdivided as follows:

Emission source	**[1]**
leakage losses from appendages, pumps, etc.	92%
flaring, disruptions	0%
losses due to storage and handling	1%
combustion emissions	7%
other process emissions	0%

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the ethylbenzene production to estimate total emissions. The amount of emitted VOC is then directly related to the ethylbenzene production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each

equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1: Ethylbenzene production in some countries and regions for 1990

Country or Region	kton/y	Source
U.S.A.	3800	Chem&EngNews 29/6/92

7 POINT SOURCE CRITERIA

Ethylbenzene production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for ethylbenzene

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [1]	0.1	C
TNO Emission Registration 1987 [2]	0.6	C
USA [3]	1 - 2	?

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: The composition of the VOC emissions for the different sources is [1]:

	methane	ethylene	benzene	toluene	formal-dehyde	other HC’s
leakage loss	0%	8%	48%	11%	0%	33 %
flaring and disruptions	-	-	-	-	-	-
storage and handling loss	0%	0%	0%	11%	0%	89%
combustion	37%	10%	0.1%	0.1%	0.3%	53%
other process emissions	-	-	-	-	-	-

Table 9.2: The overall VOC emission profile for ethylbenzene plants

	TNO ER [1]	EPA [4]
methane	2.6%	-
ethylene	8.1%	-
benzene	44.2%	-
toluene	10.2%	-
ethylbenzene	-	100%
other HC's	35.1%	-

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume edition (19)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 TNO Emission Registration, 1992
2 TNO Emission Registration, 1987
3 American Report
4 EPA, Air Chief, 1991

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 1.2

Date : October 1995

Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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Updated with particulate matter details by:
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SNAP CODE: **040519**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Phthalic Anhydride

NOSE CODE: **105.09.75**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Phthalic anhydride is manufactured from either *o*-xylene or naphtalene. Several types of oxidation are used to produce phthalic anhydride.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of phthalic anhydride plants contributes on average of about 0.1% to the total NMVOC emission in a country.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Phthalic Anhydride Production	040519	0	-	0.1	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Using *o*-xylene as feed two processes are used:

- Fixed bed vapor-phase oxidation.
  The feed is led into a multitubular reactor. This is operated at 380 - 400 °C and ambient pressure. The catalyst used is vanadium oxide with titanium dioxide on a non-porous carrier.

  The *o*-xylene inlet concentration in the air feed is above the explosion limit of *o*-xylene. The yield is 1.09 kg phthalic anhydride per kg pure *o*-xylene.

- Liquid-phase oxidation.
  As solvent acetic acid is used. The operation temperature is 150 - 245 °C and the catalyst is a mixture of cobalt, manganese and bromine salts. Under these conditions *o*-xylene is oxidated to phthalic acid. In the next step phthalic acid is dehydrated to phthalic anhydride.

  This process has as advantage high yield, but as disadvantage high capital costs.

Using naphtalene as feed also two processes are used:

- Fixed bed vapor-phase oxidation.
  Operation conditions are the same as for the *o*-xylene fixed bed oxidation, except for the catalyst. Vanadium oxide and alkali metal on silica support is used as catalyst.

  The yield is 0.9 - 0.96 kg phthalic anhydride per kg naphtalene.

- Fluidized bed vapor-phase oxidation.
  This is a process at lower temperature: 340 - 385 °C. A low activity catalyst of vanadium oxide on silica gel is used. The yield is lower as for the fixed bed process.

Phthalic anhydride recovery and purification from vapor-phase oxidations.

The reactor outlet is fed to a switch condensor. The tubes in the condensors first are cooled to solidify the phthalic anhydride on the outside of the tubes, then hot oil is circulated through the tubes. This causes the phthalic anhydride to melt and the liquid is collected in a tank.

The purification section consists of two columns. Both are operated under vacuum. The first column removes the low boiling by-products (maleic, benzoic, phthalic and citraconic acid) and the second the high boiling products.

Total by-product production is less than 1 wt.% of the phthalic anhydride production.

3.2 Definitions

3.3 Techniques

See section 3.1.

3.4 Emissions

The VOC emission can be subdivided as follows:

Cause of the emission
leakage losses from appendages, pumps, etc.
flaring, disruptions
losses due to storage and handling
combustion emissions
other process emissions

No data are available on relative distribution of emissions from these sources.

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the phthalic anhydride production emissions. The amount of emitted VOC is then directly related to the phthalic anhydride production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA:

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Relevant statistics are published by the UN Statistical Office.

7 POINT SOURCE CRITERIA

SB plant can be considered as point source if individual plant data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 2: Emission factors for phthalic anhydride

Source	**factor (kg/ton)**	**Quality Code**
o-xylene oxidation factor, EPA [1]	1.3	C
naphthalene oxidation factor, EPA [1]	6.0	C

9 SPECIES PROFILES

The emitted products from the *o*-xylene oxidation process are: phthalic anhydride, maleic anhydride and benzoic acid.

The emitted products from the naphthalene oxidation process are: phthalic anhydride, maleic anhydride, naphthaquinone and products from the thermal incinerator (when present).

10 UNCERTAINTY ESTIMATES

At the time of publication there were not enough data to establish an uncertainty estimate.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Emission factors need to be confirmed or improved.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 17, 3rd Edition (1982).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

See Verification Chapter for further details.

17 REFERENCES

1 US EPA, AP-42.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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Source : J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos
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SNAP CODE: **040520**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Acrylonitrile

NOSE CODE: **105.09.76**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Acrylonitrile is made by the catalytic ammoxidation of propylene in the vapour-phase. This process was developed by Standard Oil of Ohio (Sohio).

Some plants still use the older route, namely addition of hydrogen cyanide to acetylene.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of acrylonitrile plants contributes on average <0.01% to the total NMVOC emission in a country.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Acrylonitrile	040520	-	-	0	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Acrylonitrile is produced by reaction of propylene with ammonia and oxygen. For this process a fluid bed reactor with a solid catalyst is used. It is a single pass process meaning that no recycling is used. The propylene conversion is 98%. Operating conditions are: Temperature 400 - 510 °C; p 150 - 300 kPa; the catalyst used is a mix of metal oxides, most commonly bismuth and molybdenum oxides with traces of other metal oxides.

The reactor effluent is quenched with water in a countercurrent absorber and unreacted ammonia is neutralised with sulphuric acid. The resulting ammonium sulphate can be recovered (and used as a fertiliser).

The absorber off-gas containing primarily nitrogen, carbon monoxide, carbon dioxide and unreacted hydrocarbons is vented or passed through an incinerator to combust the hydrocarbons and carbon monoxide and then vented.

The acrylonitrile-containing solution from the absorber is separated in several columns to produce: acrylonitrile, crude hydrogen cyanide, crude acetonitrile and a fraction with heavy impurities. The acetonitrile is either incinerated or purified for use as solvent.

3.2 Definitions

Ammoxidation Oxidative reaction of ammonia with an aliphatic group:
$R\text{-}CH_3 + NH_3 + 1.5\ O_2 \rightarrow R\text{-}CN + H_2O$
R = aromatic or olefin

3.3 Techniques

Other processes, now obsolete, are:

- ethylene oxide + $HCN \rightarrow HOCH_2CH_2CN \rightarrow CH_2{=}CH\text{-}CN$

For the first step a base-catalyst is, e.g. diethyl amine; The temperature is 60 °C. For the second step a catalyst of alkali(ne) metal salts of organic acids, e.g. $MgCO_3$ is needed. The temperature is 200 °C.

- $CHCH + HCN \rightarrow CH_2{=}CH\text{-}CN$

Cuprous chloride is used as a catalyst.

3.4 Emissions

The major emissions to air are acrylonitrile, ethylene, methane and halogenated hydrocarbons. The halogenated hydrocarbons are released due to cleaning; the acrylonitrile is released in several sections of the plant; methane is released due to leakage; ethylene is released due to combustion.

For the Netherlands the VOC emission due to the acrylonitrile production is 73 ton/y. This emission is related to a production of 166 kton/y and a capacity of 183 kton/y (1992 data).
The VOC emission can be subdivided as follows:

Emission source	**[1]**
leakage losses from appendages, pumps, etc.	62%
flaring, disruptions	35%
losses due to storage and handling	2%
combustion emissions	0.1%
other process emissions	1%

3.5 Controls

The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the acrylonitrile production to estimate total emissions. The amount of emitted VOC is then directly related to the acrylonitrile production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, like valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by multiplying each equipment emission factor by the number of pieces of that type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

Table 6.1: Acrylonitrile production in some countries and regions for 1990

Country or Region	**kton/y**	**Source**
Western Europe	1200[1]	Kirk-Othmer Vol. 1 ‘91
Mexico	60[1]	Kirk-Othmer Vol. 1 ‘91
Far East	200[1]	Kirk-Othmer Vol. 1 ‘91
U.S.A.	1217	Chem&EngNews 29/6/92
Japan	593	Chem&EngNews 29/6/92

[1] figures for 1988

7 POINT SOURCE CRITERIA

Acrylonitrile production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for acrylonitrile

Source	**factor (kg/ton)**	**Quality Code**
TNO Emission Registration 1992 [1]	0.44	C
EPA AIRCHIEF 1993 [2]	100	C/D

The proposed emission factor for use in calculating the VOC emission from an acrylonitrile plant is 1 kg/ton.

9 SPECIES PROFILES

Table 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1: The composition of the VOC emissions for the different sources is [1]:

	methane	**ethylene**	**acrylonitrile**	**HCFC's**	**other HC's**
leakage loss	2%	3%	25%	0%	70%
flaring and disruptions	0%	4%	0.2%	0%	96%
storage and handling loss	0%	0%	99.6%	0%	0.4%
combustion	59%	10%	0%	0%	31%
other process emissions	0%	0%	0%	100%	0%

Table 9.2: The overall VOC emission profile for acrylonitrile plants

	TNO ER [1]	**EPA [2]**
methane	1%	0%
ethylene	3%	0%
acrylonitrile	18%	100%
HCFC's	1%	0%
other HC's	77%	0%

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 1 4th edition (1991)
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 TNO Emission Registration 1992
2 EPA, AIRCHIEF CD-ROM 1993

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE, AND SOURCE

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Date :	October 1995
Source :	J.J.M. Berdowski, W.J. Jonker & J.P.J. Bloos TNO The Netherlands

Updated with particulate matter details by:
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SNAP CODE: **040521**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Adipic Acid

NOSE CODE: **105.09.72**

NFR CODE: **2 B 3**

1 ACTIVITIES INCLUDED

This chapter covers emissions from the bulk production of adipic acid using the intermediates cyclohexanol and cyclohexanone. The mixture of these intermediates is sometimes known as KA.

2 CONTRIBUTION TO TOTAL EMISSIONS

There is uncertainty in national emission estimates for N_2O and it is not possible to give an accurate figure for the contribution of adipic acid production to total emissions.

It has been estimated that the increase in the concentration of N_2O in the earth's atmosphere is 0.2% and that growing adipic acid production accounts for up to 10% of this increase (Theimans and Trogler, 1991). From this it is not clear if adipic acid production is considered a major contributor to national emissions, compared with natural and other anthropogenic sources.

Global adipic acid production is estimated to be 2.2×10^9 kg, and that just under one mole of N_20 is emitted for every mole of adipic acid produced (Theimans and Trogler, 1991), suggesting that global emissions of N_2O from adipic acid production is of the order of 0.5×10^9 kg.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Adipic Acid	040521	-	0	-	-	-	-	12.4	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description

Adipic acid is a colourless, odourless, sour tasting crystalline solid. Little of this dicarboxylic acid occurs naturally. Aqueous solutions of the acid are corrosive. Adipic acid is produced from cyclohexane. Cyclohexane is used to produce KA, a mixture of cyclohexanol and cyclohexanone. KA is then oxidised with nitric acid to produce adipic acid. Adipic acid is primarily used for the manufacturing of 6.6-nylon.

3.2 Definitions

3.3 Techniques

The first reaction stage is the production of the intermediates cyclohexanone and cyclohexanol (usually abbreviated to KA, KA oil, ol-one or anone-anol). The KA, after separation from unreacted cyclohexane and reaction by-products, is then converted to adipic acid by oxidation with nitric acid via nitrolic acid intermediates.

All current industrial adipic acid production processes use nitric acid in the final oxidation stage. Growing concern with air quality may exert further pressure for alternative routes as manufacturers seek to avoid NO_x abatement costs, a necessary part of processes that use nitric acid.

There are variations of the cyclohexane oxidation process. However, the process is still fundamentally the same as originally developed in the early 1940s. Cyclohexane is oxidised with 40-60% nitric acid in the presence of copper and vanadium catalysts. The reaction is exothermic and produces the following major by-products: dicarboxylic acids, glutaric, succinic acids and CO_2. Nitric acid is reduced to a combination of NO_2, NO, N_2O and N_2.

The most industrially significant reaction of adipic acid is with diamines, specifically 1,6-hexanediamine. A water soluble polymeric salt is formed initially upon mixing solutions of the two materials; then heating with removal of water produces the polyamide, nylon-6,6.

3.4 Emissions

The principle emissions of concern from these processes are related to nitric acid, either as the various oxides of nitrogen or as a very dilute solution of the acid itself.

Nitrous oxide is produced during the conversion of cyclohexanol to the ketone, and also upon oxidation of aldehyde and alcohol impurities usually accompanying the KA and arising in the cyclohexane oxidation step. This oxidation step has an associated emission factor (for unabated emissions) of 300g N_2O/kg adipic acid produced.

Of all the intermediates the nitrolic acid is the only one of sufficient stability to be insoluble under very mild conditions. It is hydrolysed to adipic acid in one of the slowest steps in the sequence. Nitrous oxide is formed by further reaction of the nitrogen-containing products of nitrolic acid hydrolysis. The NO and NO_2 are reabsorbed and converted back to nitric acid, but N_2O cannot be recovered in this way, and thus is the major nitric acid derived by-product of the process.

About 20% of the reaction occurs by the vanadium oxidation of 1,2-dioxygenated intermediates; this path does not produce the non-recoverable nitrous oxide.

The nitric acid oxidation step produces three major waste streams: an off-gas containing oxides of nitrogen and CO_2, water containing traces of nitric acid and organics from the water removal column; and a dibasic acid purge stream containing adipic, glutaric and succinic acids.
Adipic acid may also be dispersed as a dust when it is subject to normal dust explosion hazards. The material is also an irritant, especially upon contact with the mucus membranes.

3.5 Controls

Off gases may be treated in a reductive furnace to reduce NO_X emissions, this treatment also destroys N_2O.

Nitric acid may be removed by distillation, the copper and vanadium catalyst are recovered by ion-exchange treatment.

4 SIMPLER METHODOLOGY

The simpler methodology involves multiplying the national production data for adipic acid with an emission factor.

5 DETAILED METHODOLOGY

The detailed methodology involves gaining site specific data on the production of adipic acid and emissions of N_2O, other oxides of nitrogen and compounds such as CO_2.

6 RELEVANT ACTIVITY STATISTICS

The relevant activity statistic is the national production of adipic acid in metric units (eg kg, metric tons). There was an adipic acid demand of nearly two billion metric tons per year world-wide in 1989. World-wide production in 1986 reached 1.6×10^6 metric tons (3.5×10^9 lb) and in 1989 was estimated at more than 1.9×10^6 metric tons. Adipic acid is a large volume organic chemical. It is one of the top fifty chemicals produced in the United States in terms of volume, with 1989 production estimated at 745 000 metric tons.

7 POINT SOURCE CRITERIA

There are relatively few adipic acid manufacturing plants and they should be treated as point sources when plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Emission Factor	Quality Code	Reference	Comments
300g/kg N_2O produced	C	Thiemans and Trogler 1991	Based on laboratory experiments designed to simulate industrial production

9 SPECIES PROFILES

For the simpler methodology, it is assumed that the emission profile is 100% N_2O. For the detailed methodology, the emissions profile is obtained directly from site measurement data. Note, other compounds believed to be emitted include CO_2 and possibly NO and NO_2.

10 UNCERTAINTY ESTIMATES

The range of production of N_2O from the laboratory measurements was between 0.7 and 1.06 moles per mole of adipic acid produced. This suggests the uncertainty in the emission factor is about ±20%. However, it is not clear how representative of the possible range in emissions the laboratory measurements are and so an absolute uncertainty cannot be stated.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simple methodology relies on one emission factor, no account is taken of slightly differing processes, abatement equipment etc. The more detailed methodology requires measurement data from the plant, but this is not widespread practice.

Improving the emission factors requires measurements to be taken from a range of representative industrial plants.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant as plants are to be considered point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

Unless further information is available, it is assumed that emissions are constant, both on a diurnal and seasonal basis.

14 ADDITIONAL COMMENTS

During the late 1980’s and early 1990’s adipic acid production continued to increase globally, particularly in the Far East, as demand for nylon increased.

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

Verification procedures are through site specific measurements. With few emission factors available, comparison with other countries is likely to show up differences in production statistics rather than in actual emissions.

17 REFERENCES

IPCC Guidelines for National Greenhouse Gas Inventories. Greenhouse Gas Inventory Manual. Vol. 3, 1995.

Kirk-Othmer 1991 Encyclopaedia of Chemical Technology. Fourth Edition. Pub. Wiley Interscience.

Thiemans M.H., Trogler W.C. 1991. Nylon Production: An Unknown Source of Atmospheric Nitrous Oxide, Science Volume 251 pp 932 - 934.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version:	1.3
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Source:	S. Pittman and S. Richardson AEA Technology UK

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SNAP CODE: **040610**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES**
Asphalt Roofing Materials

NOSE CODE: **105.16.17**

NFR CODE: **2 A 5**

1 ACTIVITIES INCLUDED

The asphalt roofing industry manufactures saturated felt, roofing and siding shingles, and roll roofing and sidings. Most of these products are used in roofing and other building applications. This section covers emissions of NMVOC, CO and particulate material from all related facilities, with the exception of asphalt blowing, which is inventoried separately under SNAP code 060310.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Table 1 summarises emissions from asphalt roofing manufacturing facilities. Emissions of SOx and NOx are most likely related to combustion to produce steam or to process dryers and if so should be included under SNAP sector 0301.

Table 1: Emissions (Mg) from Asphalt Roofing Manufacture in 1990

Country	Particulate		Sox		NOx		CO		NMVOC	
	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]	Emissions (Mg)	%[1]
Canada	20073	1.6	-	-	-	-	27763	0.3	707	0
Corinair90	-	-	~1000*	0	<100	0	-	-	~11000	0.1

[1] % of total anthropogenic emissions for that particular country.
* Reported as SO_2
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
\- = no emissions are reported

The source is believed to be <0.1% of the total PM emissions for most countries.

3 GENERAL

3.1 Description

Asphalt felt, roofing and shingle manufacture involves the saturation or coating of felt. Heated saturant and/or coating asphalt is applied through dipping and/or spraying. Key steps in the process include asphalt storage, asphalt blowing (see SNAP code 060310), felt saturation, coating and mineral surfacing. When glass fibre is used in place of paper felt, the saturation step is eliminated.

3.2 Definitions

3.3 Techniques

For asphalt-saturated felt, a typical manufacturing line consists of a paper feed roll, a dry looper section, a saturator spray section (may not be used), a saturator dipping section, steam-heated drying-in drums, a wet looper, water cooled rollers, a finish floating looper, and a roll winder.

For asphalt shingles, smooth rolls and mineral-surfaced rolls, the manufacturing line is similar to the felt line, with the addition of a filled asphalt coater, a granule applicator, a press section, water cooled rollers, a finish floating looper, and either a roll winder or a shingle cutter and stacker. Filled asphalt coating is prepared by mixing heated coating asphalt with a mineral stabilizer (filler), which may or may not be pre-dried.

Detailed descriptions of these processes may be found in U.S. EPA 1980.

3.4 Emissions

The processes which contribute to emissions from asphalt roofing manufacturing are:

- the roofing manufacturing line;
- the delivery, transfer, and storage of asphalt and mineral products used in the manufacture of roofing products;
- the blowing of asphalt (see SNAP code 060310 for the latter).

Emission sources included under SNAP code 040610 are summarized in Table 2.

Table 2: Asphalt Roofing Manufacture - Sources of Emissions

Emission Source	Pollutant
saturator	particulate and gaseous hydrocarbons
wet looper	gaseous hydrocarbons
coater-mixer tank	particulate hydrocarbons, gaseous hydrocarbons, and inorganic particulates
coater	particulate hydrocarbons, gaseous hydrocarbons, and inorganic particulates
surface application	inorganic particulates
sealant strip application	gaseous hydrocarbons
asphalt storage tank	gaseous hydrocarbons and particulate

Emission Source	Pollutant
materials handling	inorganic particulates
filler dryer	inorganic particulate, combustion gases

3.5 Controls

The following process controls can be used to minimize emissions:

1. dip saturators, rather than spray or spray-dip saturators;
2. asphalts that inherently produce low emissions;
3. reduced temperatures in the asphalt saturant pan; and
4. reduced asphalt storage temperatures.

Add-on emission controls are summarized in Table 3.

Table 3: Emission Controls for Asphalt Roofing Manufacture.

Emission Sources	Control Devices	Comments
saturator, wet looper and coater	afterburner, high energy air filter, electrostatic precipitator, mist eliminators, fabric filters, or wet scrubbers	These sources usually share a common enclosure and are ducted to a common control device.
coater-mixer	high velocity air filter	Fumes may be routed to common control device (see above).
asphalt storage tanks	mist eliminator	may be routed to common control device during production periods.
mineral surfacing and granule application	bag-house, wet scrubber, cyclone	
granule and mineral delivery, storage, and transfer	bag-house(s), wet scrubber, cyclone	Storage and conveyors are usually enclosed to prevent moisture pick-up.

4 SIMPLER METHODOLOGY

The simplest inventory methodology is to combine total national production statistics with average emission factors to estimate total emissions. Emission factors used should reflect the level of control for the region being inventoried.

5 DETAILED METHODOLOGY

The detailed methodology would involve the measurement of emissions from each plant to develop site-specific emission factors. This would be the case where asphalt roofing manufacturing plants are considered to be point sources. If they are considered to be area sources, then there is no detailed methodology.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a protocol such as that illustrated in the Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

In order to estimate emissions, production data by plant or for the sector are required. The relevant activity statistic is the production of shingles.

7 POINT SOURCE CRITERIA

In a report by the U.S. EPA (1980), a large asphalt roofing plant was identified as having an annual production rate of 280,000 Mg per year. Table 4 summarizes releases for this facility calculated with emission factors from section 8.

Table 4: Estimated Annual Emissions from a Large Asphalt Roofing Manufacturing Facility (Mg)

	Uncontrolled	Controlled
particulates	168 - 448 (a)	4.5 - 9.8 (b)
carbon monoxide	3	no data
total organic compounds	13 - 36 (a)	13 - 45 (b)

a. Depending upon the technology
b. Depending upon the technology and the type of control.

The release estimates given in Table 4 do not include asphalt blowing, which, although it is often done at the roofing manufacturing location, is inventoried under a different SNAP code. The U.S. EPA reports that blowing still has the highest total emissions of any of the emission sources in an asphalt roofing plant (U.S. EPA 1980). For the large asphalt plant referred to above, about 120,000 Mg/yr of asphalt would be blown.

Emissions calculated with emission factors from AP-42 (see SNAP code 060310) and assuming approximately half saturant and half coating blowing (U.S. EPA 1985) are presented in Table 5.

Thus, based on non-combustion emissions, asphalt roofing manufacturing plants would likely not qualify as point sources of criteria pollutants in the CORINAIR 1990 project, where emissions must be in excess of 1000 Mg in a year for SO_2 and NOx and 1500 Mg of NMVOC.

Table 5: Estimated Emission from a Blowing Still associated with a Large Asphalt Roofing Manufacturing Facility (Mg)

	Uncontrolled	**Controlled**
Saturant Blowing		
particulates	216	15
carbon monoxide	8.4	36
total organics (as CH_4)	43.8	0.9
Coating Blowing		
particulates	804	27
carbon monoxide		264
NMVOC	111	3

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 6: Emission Factors for Asphalt Roofing Manufacture (U.S. EPA, 1994)

Shingle Saturation Process	**Emission Factors (Emission Factor Rating) (kg/Mg shingle produced)**		
	Particulate[a, b]	**TOC**[c]	**CO**
Dip saturator[d] - Uncontrolled	no data	no data	0.0095 (D)
Dip saturator[e] - Uncontrolled	0.60 (D)	0.046 (D)	no data
Dip saturator[e-] ESP	0.016 (D)	0.049 (D)	no data
Dip saturator – HEAF[f]	0.035 (D)	0.047 (D)	no data
Spray / dip saturator[g] - Uncontrolled	1.6 (D)	0.13 (D)	no data
Spray / dip saturator[g] - HEAF	0.027 (D)	0.16 (D)	no data

a. As measured using EPA Method 5A: that particulate collected on or prior to the filter.

b. assume representative of TSP, PM_{10} and $PM_{2.5}$ - USEPA states that PM is primarily due to condensed asphalt fume in which case the emission can be reasonably considered as 100% PM_{10} and also likely to be all $PM_{2.5}$

c Total organic compounds as measured with EPA Method 25A (or equivalent) sampling train.d.With drying - in drum section and coater.e.With drying - in drum section, wet looper and coater.f.With drying - in drum section, wet looper and High-Energy Air Filter.g.Spray/dip saturator, drying-in drum section, wet looper, coater and storage tanks.

Emission factors are all rated D. The controlled CO emission factor is based on tests at one plant only, with an afterburner as a control device.

9 SPECIES PROFILES

No NMVOC speciation profiles specific to asphalt roofing manufacture were identified. However, Passant (1993) used the general speciation profile for emissions from petroleum refineries to characterize emissions from asphalt blowing, as summarized in Table 7.

Table 7: Speciation Profile for Asphalt Roofing Manufacture

Compound	% Weight
Ethane	6.0
Propane	18.8
Butanes	30.5
Pentanes	17.2
Hexanes	8.4
Heptanes	9.8
Octanes	7.4
Cycloparaffins	1.9
Benzene	0.1

UN ECE groups: 2% group I; 73% group II; 25% group III.
POCP factor:43

This profile could be used as a default profile for the asphalt roofing industry. The reader is also referred to generalized species profiles provided chapter B411 (Petroleum Refining).

The U.S. EPA (1994) indicates that polycyclic organic matter comprises approximately 1.1 per cent of particulate matter for saturators.

10 UNCERTAINTY ESTIMATES

It is not possible to estimate the accuracy of estimates based on the emission factors summarised in section 8. Based on the low data qualities and the large differences in emission factors, the level of uncertainty is high. Comments received from other panel members suggest that the uncertainty is greater than a factor of 2.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

It is recommended that better emission factors be developed for these sources. Separate emission factors for felt vs shingle/roll products should be considered, as well as accounting for the level of control for this industry.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Asphalt roofing manufacturing plants are likely to be within reasonable (i.e. cost effective) shipping distances of asphalt producers or distributors. If this data is not available, population may also be used to disaggregate these emissions.

13 TEMPORAL DISAGGREGATION CRITERIA

In the absence of data on the operational characteristics of the industry, it may be assumed that the emissions are continuous (24 hour operation).

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

17 REFERENCES

U.S. Environmental Protection Agency (U.S. EPA), 1980. “Asphalt Roofing Manufacturing Industry Background Information For Proposed Standards.” EPA-450/3-80-021a. PB 80 212111. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

U.S. Environmental Protection Agency (U.S. EPA), 1994. “11.2 Asphalt Roofing” Supplement to Compilation of Air Pollutant Emission Factors: Stationary Point and Area Sources. AP-42, Fourth Edition. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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SNAP CODE: **040611**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES**
Road Paving with Asphalt

NOSE CODE: **105.16.31**

NFR CODE: **2 A 6**

1 ACTIVITIES INCLUDED

Asphalt surfaces and pavements are composed of compacted aggregate and an asphalt binder. The asphalt binder may consist of heated asphalt cement (hot mix) or liquefied asphalts (cutback or emulsified). This section covers emissions from asphalt paving operations as well as subsequent releases from the paved surfaces.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Information on U.S. and Canadian NMVOC emissions are not available at this time. Estimates based on U.S. asphalt sales in 1991 as reported by the Asphalt Institute (1992) and the maximum available emission factors (please see section 8) indicate a maximum emission of approximately 460,000 Mg VOC from liquefied asphalt paving, which would represent about 0.2% of total estimated emissions from all sources (U.S. EPA 1993a).

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Road Paving with Asphalt	040611	-	-	0.1	-	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

3 GENERAL

3.1 Description

Asphalt roads are a compacted mixture of aggregate and an asphalt binder. Natural gravel, manufactured stone (from quarries) or byproducts from metal ore refining are used as aggregates. Asphalt cement or liquefied asphalt may be used as the asphalt binder.

3.1.1 Asphalt Cement

Asphalt cement is semisolid, and must be heated prior to mixing with the aggregate. This is done in hot mix plants, which, are considered to be potential sources of common and toxic pollutants. Hot mix plants are normally fixed bulk manufacturing plants. After the hot mix is produced, the mixture is very low in volatile hydrocarbons and is not thought to be a significant source of NMVOC during paving operations (U.S. EPA 1985).
In order of development, hot mix asphalt paving materials can be manufactured by: batch mix plants; continuous mix plants; parallel flow plants; and counterflow plants. Continuous mix plants are thought to constitute a small portion of production.

In the batch process aggregate is dried, sorted, stored and then mixed in a separate pug mill with heated asphalt cement.

In the parallel flow drum mix process, the dryer is used to not only dry the aggregate but also mix the heated and dried aggregates with the liquid asphalt cement. This combined mixing process means that mixing in the discharge end captures a substantial portion of the aggregate dust. The disadvantage is that, because the mixing of aggregate and liquid asphalt occurs in the hot combustion product flow, organic emission (gaseous and liquid aerosol) may be greater than in other processes.

In the counterflow plant, the material flow in the drum is opposite to the direction of exhaust gases. Because the liquid asphalt cement, and aggregate are mixed in a zone removed from the exhaust gas stream, counterflow drum mix plants are likely to have organic emissions (gaseous and liquid aerosol) that are lower than parallel flow drum mix plants, in addition to greater capacity to accomodate recycled pavement and improved thermal efficiencies.

3.1.2 Liquefied Asphalt

Liquefied asphalts may be used as a pavement sealant, as a tack coat, in priming roadbeds for hot mix application and for operations up to several inches thick. Liquefied asphalts are considered to be significant sources of NMVOCs during the mixing and subsequent paving operations. The two types of liquefied asphalt used for road paving are cutback asphalt and emulsified asphalt.

Cutback asphalt is prepared by blending or “cutting back” asphalt cement with various blends of petroleum distillates. The three categories of cutback asphalt are rapid cure (RC), medium cure (MC) and slow cure (SC). SC, MC and RC cutbacks are prepared by blending asphalt cement with heavy residual oils, kerosene-type solvents, or naphtha and gasoline solvents, respectively. Depending on the viscosity desired, the proportions of solvent generally range from 25 to 45 percent by volume. (U.S.EPA 1985)

Emulsified asphalts are prepared with a blend of water with an emulsifier, which is generically referred to as a soap. The blend consists of 94 to 98 percent water and 2 to 6 percent soaps. As for cutback asphalts, emulsified asphalts can be classified as rapid set (RS), medium set (MS) or slow set (SS) depending on the application and blend percentage. The blend proportions are dependent upon the specific application and operating parameters. It has been reported that emulsified asphalts may have as high as 12 percent VOC content

(U.S. EPA 1993b). Emulsified asphalts may also be classified as either anionic (highfloat) or cationic through the use of particle charge testing. (U.S.EPA 1993a)

3.2 Definitions

Asphalt - this is commonly called bitumen in some European countries. Macadam is another term for as laid asphalt.

3.3 Techniques

3.4 Emissions

3.4.1 Hot Mix Plants

The most significant source of ducted emissions from batch mix plants is the dryer, which emits particulate matter and small amounts of VOCs derived from combustion exhaust gases. Aggregate dust, VOCs and a fine aerosol of liquids are also emitted from the hot-side conveying, classifying and mixing equipment. Vented emissions from these areas may be controlled by equipment ranging from dry mechanical collectors to scrubbers and fabric collectors. Organic vapour and its associated aerosol are also emitted directly to the atmosphere as process fugitives during truck loadout and from the bed of the truck during transport. In addition to low molecular weight VOC, these organic emission streams may contain small amounts of polycyclic compounds. The ducted emissions from the heated asphalt storage tanks may include VOC and combustion products from the tank heater. Other fugitive sources of particulate include vehicular traffic and aggregate materials handling.

In parallel flow drum mix plants, the most significant ducted source of emissions is the rotary drum dryer. Emissions include particulate and small amounts of VOCs resulting from incomplete combustion and from the heating and mixing of liquid asphalt cement inside the drum.

Counterflow plants have similar emissions to parallel flow drum mix plants, although VOC emissions are likely to be lower because liquid asphalt cement and aggregate are not in contact with the hot exhaust gas stream. The organic compounds that are emitted are likely to be the result of inefficient combustion.

Process fugitive emissions for parallel and counterflow plants are much lower than batch plants**.** However VOC emissions from transport, handling and loadout of the hot mix are likely to be similar.

3.4.2 Liquefied Asphalt

For any given amount of asphalt, total emissions are believed to be the same, regardless of stockpiling, mixing and application times. The major source of NMVOCs from the use of liquefied asphalts is the cutback asphalt.

For cutback asphalt, the two major variables affecting both the quantity of NMVOC emitted and the time over which emissions occur are the type and quantity of petroleum distillate used as a diluent. Long term emissions from cutback asphalts can be estimated by assuming that

95 percent of the diluent evaporates from rapid cure (RC) cutback asphalts, 70 percent from medium cure (MC) cutbacks, and about 25 percent from slow cure (SC) asphalts, by weight percent.

Limited test data suggest that, from RC asphalt, 75 percent of the total diluent loss occurs on the first day after application, 90 percent with the first month and 95 in three to four months. For MC, evaporation is slower, with about 20 percent loss in the first day, 50 percent in the first week and 70 percent after three to four months. Although no data is available for SC, the total losses are believed to be in the order of 25 percent, considerably less than for RC or MC, and occur over a considerably longer period of time. (U.S.EPA 1985)

3.5 Controls

3.5.1 Hot Mix Plants

Dryer exhaust and vent line control equipment ranges from dry mechanical collectors to scrubbers and fabric collectors. Attempts to use electrostatic precipitators have been largely unsuccessful.

The dryer and other potential sources may also be routed to primary dust collection equipment with large diameter cyclones, skimmers or settling chambers. These chambers are often used as classifiers to return collected material to the process. To capture the remaining particulate matter, the primary collector is ducted to a secondary collection device such as a baghouse or a venturi scrubber**.**

3.5.2 Liquefied Asphalts

Emulsions are typically used in place of cutback asphalts to eliminate emissions of NMVOC. Limits on the volatile hydrocarbon content of emulsions can be put in place to limit NMVOC emissions.

4 SIMPLER METHODOLOGY

It is important to obtain information on asphalt sales for the purposes of paving that are broken down into hot mix, cutback and emulsified classifications. This then permits a generally realistic emission estimation based on reasonable emission factors for each category.
The selection of average emission factors for each of hot mix, cutback and emulsified asphalt will then depend on the level of regulation in the inventory area. For example, for liquefied asphalt, levels of VOCs in the asphalt may be regulated and emission factors used would reflect the upper limits of the allowable practice. In the case of hot mix plants, a knowledge of the industry and its controls would permit the selection of the most appropriate emission factor from those presented in Section 8. In the absence of any such information, however, the emission factors for batch mix plants should be selected.

If only total asphalt sales are available, it should be assumed that the entire amount is rapid cure cutback asphalt at 45% percent by volume of diluent , with the appropriate emission factor from Section 8.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.

5 DETAILED METHODOLOGY

Detailed information on the use of each of hot mix, cutback asphalt and emulsified asphalt should be obtained. These may be available from paving associations.

For hot mix asphalt, emission factors are based on total product, which includes the weight of the aggregate. Therefore, a survey of the types of hot mix plants by production (or at the very least capacity) and type of control, would facilitate the breakdown of hot mix asphalt use into categories matching the available emission factors. If this detailed production survey is not possible, then the production can be estimated by assuming that the total asphalt cement used represents 8 percent of the total product. (U.S. EPA 1994)

For liquefied asphalts, the detailed emission estimation methodology is to estimate emissions from basic principles using detailed product specification and use information. It is assumed that, over the long term, 95 % of the diluent in RC evaporates. Similarly 70% of MC and 25% of SC are assumed to evaporate. If the product specification is given that specifies the weight percent of VOCs in asphalt the calculation of VOCs is fairly straight forward. It is common, however, to specify the diluent content on a percent by volume basis. An example calculation for this situation follows (U.S.EPA 1985):

Example: Local records indicate that 10,000 kg of RC cutback asphalt, containing 45 percent diluent by volume, was applied in a given area during the year. Cutback asphalt is a mixture of diluent and asphalt cement. To determine the VOC emissions, the volume of diluent present in the cutback asphalt must first be determined. Because the density of naphtha (0.7 kg/l) differs from that of asphalt cement (1.1 kg/l), the following equations must be solved to determine the volume of diluent (x) and the volume of asphalt cement (y) in the cutback cement:

$$10{,}000 \text{ kg cutback asphalt} = (x \text{ l diluent})\ (0.7 \text{ kg/l}) + (y \text{ l asphalt cement})(1.1 \text{ kg/l})$$

and

$$x \text{ liter diluent} = 0.45\ (x \text{ litre diluent} + y \text{ l asphalt cement})$$

From these equations, the volume of diluent present in the cutback asphalt is determined to be about 4900 litres, or about 3400 kg. Assuming that 95 percent of this is evaporative VOC, emissions are the 3400 kg x 0.95 = 3200 kg (i.e., 32% by weight, of the cutback asphalt eventually evaporates).

These equations can be used for MC and SC asphalts by assuming typical diluent densities of 0.8 and 0.9 kg/litre, respectively, unless actual density values are available from local records. If actual diluent contents are not known, a typical value of 35 percent may be assumed for inventory purposes.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

The annual weight of asphalt used in road paving is required as a minimum to prepare estimates of maximum likely emissions of NMVOCs from this source. If more detailed information is available on the breakdown of this total annual usage (i.e. cement asphalt for hot mix, cutback asphalt and emulsified asphalt) and the diluent contents of the same, then progressively more accurate emissions estimates may be done. Details on the type of information that may be obtained are provided in Section 5.

7 POINT SOURCE CRITERIA

It is not likely that hot mix plants will qualify as point sources of common pollutants. Therefore road paving with asphalt should be inventoried as an area source.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Hot Mix Plants

The U.S. Environmental Protection Agency has recently completed a detailed review of the hot mix industry (U.S.EPA 1994). Emission factors for particulate matter, CO, NOx, SO2 and total organic compounds (TOC) from this review are summarized in Tables 2 and 3. The organic emissions are reported as TOC as methane, based on EPA Method 25A test data. Detailed organic compound emission factors are provided in Tables 4 and 5. It can be seen that NMVOCs generally represent less than half of the TOC, depending on the type of control.

8.2 Liquefied Asphalt

Emission factors can be developed for the use of liquefied asphalts if sufficient information is available, as described in section 5. Alternatively, default emission factors are provided in Table 6 (U.S. EPA 1985).

Table 2: Emission Factors for Batch Mix Hot Mix Asphalt Plants (kg/Mg of Product) [c]

Process	Particulate[b] Matter	CO	NOx	SO_2	TOC[c]
Natural gas-fired dryer					
Uncontrolled	16 (E)	0.17 (D)	0.013 (D)	0.0025 (D)	0.0084 (D)
Fabric Filter	0.02 (D)				
Oil-fired dryer					
Uncontrolled	16 (E)	0.035 (D)	0.084 (D)	0.12 (D)	0.023 (D)
Fabric Filter	0.04 (D)				

[a] The emission factor rating is supplied in brackets after the emission factor.
[b] The sum of filterable PM and total condensible PM emission factor.
[c] Factors represent TOC as methane, based on EPA Method 25A test data.

Table 3: Emission Factors for Drum Mix Hot Mix Asphalt Plants (kg/Mg of Product)[c]

Process	Particulate[b] Matter	CO	NOx	SO_2	TOC[c]
Natural gas-fired dryer					
Uncontrolled	9.4	0.028	0.015	0.0017	0.025[d]
Fabric Filter	0.0089				
Oil-fired dryer					
Uncontrolled	9.4	0.018	0.038	0.028	0.035[d]
Fabric Filter	0.020				

[a] The emission factor rating is D for all factors. Drum Mix refers to both parallel flow and counterflow plants. Tests included dryers that were processing reclaimed asphalt pavement (RAP). Because of limited data, the affect of RAP processing on emissions could not be determined.

[b] The sum of filterable PM and total condensible PM emission factor.

[c] Factors represent TOC as methane, based on EPA Method 25A test data.

[d] Organic compound flows are expected to be smaller.

Table 4: Emission Factors for Organic Pollutant Emissions from Batch Mix Hot Mix Asphalt Plants[a]

Emission Factor Rating: D

Process Pollutant	Emission Factor kg/Mg	% of TOC
Natural Gas-fired dryer		
2-Methylnaphthalene[b]		0.00
Acenaphthene[b]		0.0041333
Acenaphthylene[b]		0.00
Acetaldehyde		2.13
Acetone		21.33
Anthracene[b]	1.50e-07	0.000133
Benzaldehyde	6.40e-05	0.43
Benzene	1.70e-04	1.13
Benzo(a)anthracene[b]	2.30e-09	0.000015
Benzo(b)fluoranthene[b]	2.30e-09	0.000015
Benzo(k)fluoranthene[b,c]	1.20e-08	0.000080
Butyraldehyde/Isobutyraldehyde	1.50e-05	0.10
Chrysene[b]	3.10e-09	0.000021
Crotonaldehyde	1.50e-05	0.10
Ethyl benzene	1.60e-03	10.67
Fluoranthene[b]	1.60e-07	0.000067

Process **Pollutant**	**Emission Factor kg/Mg**	**% of TOC**
Natural Gas-fired dryer		
Fluorene[b]	9.80e-07	0.01
Formaldehyde	4.30e-04	2.87
Hexanal	1.20e-05	0.08
Methane	6.00e-03	40.00
Naphthalene[b]	2.10e-05	0.14
Phenanthrene[b]	1.60e-06	0.01
Pyrene[b]	3.10e-08	0.00021
Quinone	1.40e-04	0.93
Toluene	8.80e-04	5.87
Xylene	2.10e-03	14.00
Total for Natural gas-fired dryer	1.50e-02	99.80

Oil-fired dryer		
2-Methylnaphthalene[b]	3.00e-05	0.77
Fluoranthene[b]	1.20e-05	0.31
Formaldehyde[c]	1.60e-03	40.92
Methane	2.20e-03	56.27
Naphthalene[b]	2.20e-05	0.56
Phenanthrene[b,c]	1.80e-05	0.46
Pyrene[b]	2.70e-05	0.69
Total for Oil-fired dryer	3.91e-03	99.97

[a] Factors kg/Mg of hot mix asphalt produced. Factors represent uncontrolled emissions, unless noted.
[b] Controlled by a fabric filter. Compound is classified as polycyclic organic matter (POM).
[c] Emission Factor Rating: E

Table 5: Emission Factors for Organic Pollutant Emissions from Drum Hot Mix Asphalt Plants[a]

Emission Factor Rating: D

Process **Pollutant**	**Emission Factor kg/Mg**	**% of TOC**
Natural Gas-fired dryer		
2-Chloronaphthalene[c]	8.90e-07	0.00086
2-Methylnaphthalene[c]		0.03558
Acenaphthene[c]	3.80e-05	0.000615
Acenaphthylene[c]	6.20e-07	0.00000
Anthracene[c]	4.30e-07	0.000096
Benzene	3.20e-04	0.58
Benzo(a)anthracene[c]	3.20e-03	0.000096
Benzo(a)pyrene[c]	4.60e-09	0.000004
Benzo(b)fluoranthene[c]	5.10e-08	0.000049
Benzo(e)pyrene[c]	5.20e-08	0.000050
Benzo(g,h,i)perylene[c]	1.90e-08	0.000018
Benzo(k)fluoranthene[c]	2.60e-08	0.000025
Chrysene[c]	1.80e-07	0.000173
Dibenz(a,h)anthracene[c,e]	1.30e-09	0.000001
Ethyl benzene[e]	1.50e-04	0.14
Fluoranthene[c]	3.00e-07	0.0003
Fluorene[c]	2.70e-06	0.000
Formaldehyde	1.80e-03	1.73
Formaldehyde[d,e]	7.90e-04	0.76
Ideno(1,2,3-cd)pyrene[c]	3.60e-09	0.000003
Methane	1.00e-01	96.15
Methyl chloroform[e]	2.50e-04	0.24
Naphthalene[c]	2.50e-05	0.02
Perylene[c,e]	6.20e-09	0.00001
Phenanthrene[c]	4.20e-06	0.000
Pyrene[c]	2.30e-07	0.00022
Toluene	1.00e-04	0.10
Xylene	2.00e-04	0.19
Total for Natural gas-fired dryer	1.04e-01	99.96

Oil-fired dryer[c]		
2-Methylnaphthalene[c]	8.50e-05	0.63
Acenaphthylene[c]	1.10e-05	0.08
Acetaldehyde	6.50e-04	4.78
Acetone	4.20e-04	3.09
Acrolein	1.30e-05	0.10
Anthracene[c]	1.80e-06	0.01
Benzaldehyde	5.50e-05	0.40
Benzene	2.00e-04	1.47
Butyraldehyde/Isobutyraldehyde	8.00e-05	0.59
Crotonaldehyde	4.30e-05	0.32
Ethylbenzene	1.90e-04	1.40
Fluorene[c]	8.50e-06	0.06
Formaldehyde	1.20e-03	8.82
Formaldehyde[d,e]	2.60e-04	1.91
Hexanal	5.50e-05	0.40
Isovaleraldehyde	1.60e-05	0.12
Methane	9.60e-03	70.59
Methyl Ethyl Ketone	1.00e-05	0.07
Naphthalene[c]	1.60e-04	1.18
Phenanthrene[c]	2.80e-05	0.21
Propionaldehyde	6.50e-05	0.48
Pyrene[c,e]	1.50e-06	0.01
Quinone	8.00e-05	0.59
Toluene	3.70e-04	2.72
Valeraldehyde	3.40e-05	0.25
Xylene	8.20e-05	0.60
Total for Oil-fired dryer	1.36e-02	100.27

[a] Factors kg/Mg of hot mix asphalt produced. Table includes data from both parallel flow and counterflow drum mix dryers. Organic compound emissions from counterflow systems are expected to be less than from parallel flow systems, but the available data are insufficient to quantify accurately the difference in these emissions.

[b] Tests included dryers that were processing reclaimed asphalt pavement (RAP). Because of limited data the effect of RAP processing on emissions could not be determined.

[c] Controlled by a fabric filter. Compound is classified as polycyclic organic matter (POM).

[d] Controlled by a wet scrubber.

[e] Emission Factor Rating: E

Table 6: Evaporative VOC emissions from cutback asphalts as a function of diluent content and cutback asphalt type[a]

Type of Cutback[b]	Percent, by Volume of Diluent in Cutback[c]		
	25%	**35%**	**45%**
Rapid cure	17	24	32
Medium cure	14	20	26
Slow cure	5	8	10

[a] These numbers represent the percent, by weight, of cutback asphalt evaporated. Factors are based on References 1 and 2.

[b] Typical densities assumed for diluents used in RC, MC, and SC cutbacks are 0.7, 0.8 and 0.9 kg/liter, respectively.

[c] Diluent contents typically range between 25-45%, by volume. Emissions may be linearly interpolated for any given type of cutback between these values.

9 SPECIES PROFILES

9.1 Hot Mix Plants

For hot mix asphalt plants, total organic emission factors are expressed as methane, and it is indicated that this may consist of low molecular weight VOCs and polycyclic compounds. Speciation of the TOC has been provided in Tables 4 and 5.

9.2 Liquefied Asphalt

If the detailed emission estimation method has been used for the liquefied asphalts, species profiles could be based on typical profiles for the diluent. Otherwise species profiles for these sectors have not been identified.

10 UNCERTAINTY ESTIMATES

The largest source of uncertainty in these estimates will be the level of detail available in terms of the relative breakdown of asphalt into asphalt cement, cutback asphalt and emulsified asphalt. As an example, in the U.S. in 1991, 86 percent of total asphalt sales was asphalt cement for hot mix use. If this was assumed to be RC cutback at an average of 45 percent, total emissions would be 6,448,174 tonnes VOC. In comparison, total organic emissions (expressed as methane) from hot mix plants would be 8815 Mg for an equivalent amount of asphalt cement, assuming that asphalt cement is 8 percent of hot mix. Therefore, the simpler estimation can greatly overestimate emissions of VOCs.

The state-of-the-art estimations will, however greatly improve the estimates as the detail of the base quantity estimates and characterizations improve.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

There is no available information on which to base a more realistic average emission factor for the simpler methodology. Therefore emission estimates may be grossly overestimated using this methodology.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Since most of the emissions occur at the paving locations, emissions can be disaggregated based on percent of total paved road surfaces. If this information is not available the emissions can be disaggregated based on mobile source emission estimates or population.

13 TEMPORAL DISAGGREGATION CRITERIA

Available information indicates that VOC emissions occur within four months of paving, with the majority of this within one month (U.S.EPA 1985).

In climates where cold weather prevents paving for a portion of the year, paving emissions should be spread over this shorter season.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

It may be possible to verify asphalt sales estimates through comparison with figures on road construction. Emissions estimates for hot mix plants may be verified by emission testing.

17 REFERENCES

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18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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Environment Canada
Canada

Updated with particulate matter details by:
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20 POINT OF ENQUIRY

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SNAP CODE: **040618**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES**
Limestone and Dolomite Use

NOSE CODE: **105.11.25**

NFR CODE: **2 A 3**

A specific methodology for this activity has not been prepared yet as it is a recent addition. It will be investigated this year.

The expert panel leaders for this activity are listed below.

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Updated with particulate matter details by:
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SNAP CODE: **040619**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK AND OTHER INDUSTRIES**
Soda Ash Production and Use

NOSE CODE: **105.07.07**

NFR CODE: **2 A 4**

A specific methodology for this activity has not been prepared yet as it is a recent addition. It will be investigated this year.

The expert panel leaders for this activity are listed below.

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

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