Category		
NFR:	11.C	Geological seepage
SNAP:	1109 110900	Geological seepage Geological seepage
ISIC:		
Version	Guidebook 2023	

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Contents

1 Overview

Studies performed since 2000 have demonstrated that geologic emissions of methane are an important global greenhouse-gas source (Etiope, 2004; Kvenvolden and Rogers, 2005; Etiope et al, 2008). It is recognised that significant amounts of methane, produced within the Earth crust, are released naturally into the atmosphere through faults and fractured rocks. Major emissions are related to hydrocarbon production in sedimentary basins (microbial and thermogenic methane), through continuous exhalation and eruptions from more than 1 200 onshore and offshore mud volcanoes, more than 10 000 onshore and shallow marine seeps and through diffuse soil microseepage. Specifically, six source categories must be considered: mud volcanoes, gas seeps (independent of mud volcanism), microseepage (diffuse exhalation from soil in petroleum basins), submarine seepage, geothermal (non-volcanic) manifestations and volcanoes. Global emission estimates range from 42 to 64 Tg y^{-1} (mean of 53 Tg y^{-1}), almost 10 % of the total CH_4 emission, representing the second most important natural methane source after wetlands. Geo-CH_4 sources would also represent the missing source of fossil methane recognised in the recent re-evaluation of the fossil methane budget in the atmosphere (about 30 %; Lassey et al,, 2007; Etiope et al, 2008), which implies a total fossil methane emission much higher than that due to fossil fuel industry. The global geo-CH_4 emission estimates are of the same level as or higher than other sources or sinks considered in the Intergovernmental Panel on Climate Change (IPCC) tables, such as biomass burning, termites and soil uptake. Recent studies indicate that Earth's degassing also accounts for at least 17 % and 10 % of total ethane and propane emissions (Etiope and Ciccioli, 2009).

2 Description of sources

2.1 Process description

Geological seepage is the natural release of gas, mainly methane, produced in the lithosphere (Etiope and Klusman, 2002). Gas is released naturally into the atmosphere through gas permeable faults and fractured rocks, driven mainly by pressure (and density) gradients in the lithosphere. So far, the term "geological methane" has been used with reference to "fossil" methane (Etiope and Klusman, 2002; Kvenvolden and Rogers, 2005), which is radiocarbon free (older than about 50000 years) and can be distinguished from "modern" gas developed from recent organic material in soils or shallow sediments by radiocarbon (^{14}C-CH_4) analyses. However, the methane produced in late Pleistocene and Holocene sediments in estuaries, deltas and bays or trapped beneath permafrost, also could be formally considered geological even though this is not necessarily fossil. This 'recent' gas is widely discussed by Judd (2004), and Judd and Hovland (2007). Modern microbial methane produced by very recent and contemporary microbial activity should be considered in the literature and source categories of peatlands, wetlands and oceans.

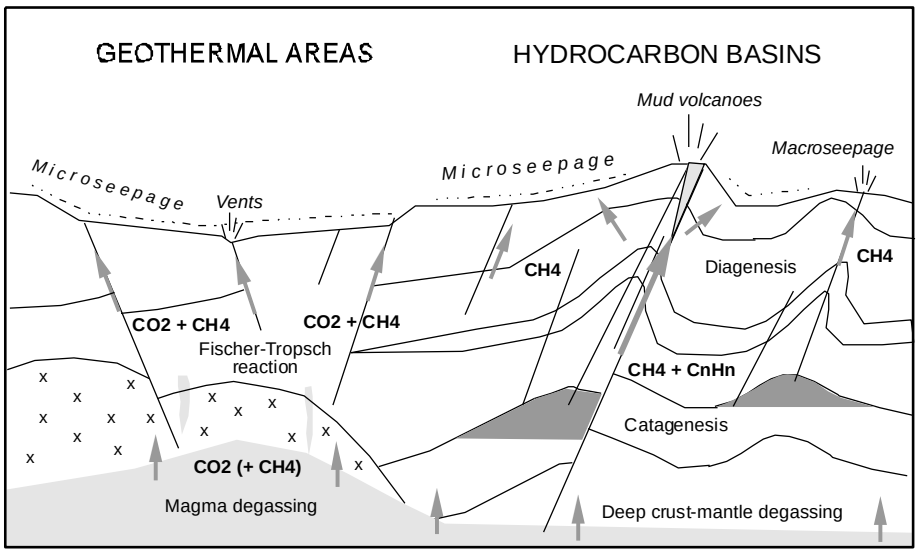
The production of fossil methane in sedimentary basins can be due to microbial and thermogenic processes. Microbial CH_4 is formed by bacterial breakdown of organic material in sediments, commonly with a distinctive $\delta^{13}C_{CH4}$ composition of –55 to –85 ‰. At greater depths, thermogenic CH_4 is produced by thermal breakdown of organic matter or heavier hydrocarbons with a $\delta^{13}C_{CH4}$ composition ranging from –25 to –50 ‰. Migration and accumulation in stratigraphic and structural traps is widely described in the petroleum geology literature (Hunt, 1996).

The largest expression of CH_4 release into the atmosphere is provided by macroseeps, in particular mud volcanoes. These cone-shaped structures are produced over faults by advective up-welling of sediments (mud) fluidised by gas and water. The gas is nearly always thermogenic CH_4 (Etiope et al, 2009). Mud volcanoes are developed over oil and gas reservoirs of Alpine-Himalayan, Pacific Ocean and Caribbean geological belts with more than 900 structures on lands and more than 300 on the ocean shelves. Gas is released through continuous (steady-state) exhalations from craters, vents and surrounding soil, intermittent blow-outs and eruptions (Kopf, 2002; Etiope and Milkov, 2004 and references therein).

Microseepage is the slow, continual loss of CH_4 and light alkanes from depths of 2–5 km in sedimentary basins where thermal degradation of indigenous organic matter is occurring (Etiope and Klusman, 2002). It is basically a pervasive, diffuse exhalation of methane from soil resulting from natural gas migration from underground hydrocarbon reservoirs. Microseepage may be responsible for positive fluxes or for a decrease in negative fluxes of methane in dry lands, indicating that methanotrophic consumption in the soil can be lower than the input from underground sources. The positive fluxes are typically of few units or tens of mg $m^{-2}d^{-1}$, but may be at the hundreds level over wide tectonised and faulted areas.

Seepage of thermogenic CH_4 in the marine environment operates somewhat differently from the terrestrial environment. Hydrocarbons passing through the sediments can be consumed by sulphate-reducing bacteria. Once in the water column, there will be partial to complete dissolution, followed by oxidation. The degree of dissolution in the seawater will depend both on the depth of water and the size of the bubbles rising toward the surface. Models and field data indicate that only submarine seeps occurring at depths less than 200–300 m can have significant impact on the atmosphere (Judd et al., 1997; Judd et al., 2002).

Figure 2-1 Scheme of geological seepage



Source: Etiope and Klusman, 2002

In contrast to the processes in sedimentary basins, CH_4 in geothermal fluids and related surface manifestations (fumaroles, mofettes) is present in low amounts (typically 0.001–1 %). The flux into the atmosphere nevertheless is not negligible. Anomalous concentrations of CH_4 are frequently found in soils over active geothermal areas. The higher CH_4 flux is generally found over faults that intersect the steam cap or the more extensive liquid-dominated portion of the geothermal reservoir (Etiope et al., 2007).

2.2 Techniques

Local flux measurements can be done by several techniques, including:

- closed-chamber system
- inverted funnel system
- flux-meters

associated with gas-chromatographic, infra-red, laser sensors.

These techniques are described by Etiope et al. (2002, 2004a) and Klusman et al., (2002a).

Emission from eruptions has been estimated in some cases by visual or indirect methods.

2.3 Emissions

Natural gas emissions are primarily methane (CH_4), but at a lower rate other alkanes (ethane, propane, butane) are also released. Global ethane and propane emission from geological sources account for about 10 % and 17 % of total emissions, respectively (Etiope and Ciccioli, 2009).

Typical compositions of gas released in sedimentary (hydrocarbon-prone) and geothermal areas are:

Sector	**CH_4 %v**	**CO_2 %v**	**N_2 %v**	**C_2H_6 %v**	**H_2S %v**
Sedimentary	90–99	0.1–10	0–5	0.0001–1	0–1
Geothermal	0.001–3	70–99	0.1–10*	< 0.004	0–3

Note:
In some conditions, geothermal and sedimentary gas can be enriched with N_2, with a concentration up to 90–95 %.

Emission mechanisms include:

- continuous degassing from macroseeps and soil microseepage (low daily and seasonal variability);
- intermittent degassing from macroseeps (bubbling pools, blow-outs);
- episodic eruptions from macroseeps (explosions from mud volcanoes or dry vents).

2.4 Controls

There are no controls to natural emissions by definition.

3 Methods

3.1 Choice of method

Due to the irregularities of emission patterns (both spatially and temporally), any advanced method to assess emissions will have to be based on measurements. Starting from knowledge on geologically relevant areas, typical techniques to cover area sources include accumulation chambers and laser sensors. A detailed description of the methodology used for flux measurements and emission derivations is reported by Etiope et al., (2002, 2004a, 2007) and Etiope and Milkov (2004).

The method depends on the emission type: microseepage, macroseep, submarine seepage and geothermal emission.

Emission calculation from microseepage is currently based on averaging field contribution from identifiable homogeneous areas (emission factor x seepage area).

Emission calculation from macroseepage zones is made by summing the macroseep flux component to the microseepage component.

Submarine gas fluxes are generally estimated on the basis of geophysical images (echo-sounder, seismic, sub-bottom profilers and side-scan sonar records) and bubble parameterisation (size of bubble plume and single bubbles) sometimes associated with geochemical seawater analysis (e.g., Judd et al., 1997).

For geothermal areas, in absence of direct CH_4 measurements, emission of methane can be estimated by knowing the CO_2 flux and CO_2/CH_4 concentration ratio or steam flux and steam/CH_4 concentration ratio (Etiope et al., 2007).

3.2 Tier 1 default approach

3.2.1 Algorithm

Emission calculation from microseepage is currently based on averaging field contribution from identifiable homogeneous areas, with calculations of the type:

$E = A \times \langle F \rangle$

where

A = the area in km^2 or m^2, and

<F> = average flux value (t km^{-2} y^{-1} or kg m^{-2} day^{-1}).

Emission calculation from macroseepage zones is made by summing the macroseep flux component ($E_{macro} = \Sigma F_{vent}$, sum of all vent fluxes, measured or estimated) to the microseepage component ($E_{micro} = A \times \langle F \rangle$).

3.2.2 Default emission factors

Even for the simpler methodology, the emission factors considered are based on disaggregating levels, depending on the type of source and its homogenous distribution. Emission factors and disaggregating levels are directly described in the Tier 2 section.

3.2.3 Activity data

Macroseeps and microseepage size, distribution and extent statistics is described by Etiope (2009), Etiope and Klusman (2002, 2009), Etiope and Milkov (2004), Etiope et al (2004a, b). These data derive basically from studies on petroleum geology and geochemistry, where hydrocarbon seepage is often an indication of underground petroleum reservoirs. It is evident that all seeps and microseepage zones occur within oil basin provinces and, in particular, within the Total Petroleum Systems (TPS, Etiope and Klusman, 2009)). Size of the individual area and point sources is provided by field and satellite observations.

3.3 Tier 2 technology-specific approach

3.3.1 Algorithm

The emission factor approach of Tier 1 (E = A x <F>) can be used but with higher disaggregation levels, as specified below.

3.3.2 Technology-specific emission factors

Hydrocarbon-basins fluxes

Microseepage emission factors can be divided in three main classes (Etiope, 2009; Etiope and Klusman, 2009):

- level 1: high microseepage (> 50 mg $m^{-2}d^{-1}$);
- level 2: medium microseepage (5–50 mg $m^{-2}d^{-1}$);
- level 3: low microseepage (0–5 mg $m^{-2}d^{-1}$).

Levels 1 and 2 occur mainly in sectors hosting macroseepage sites, and in the sedimentary basins in general, during winter. Over a database of 563 measurements performed in dry soils in different petroliferous basins in USA and Europe, 276 are positive fluxes (49 %); 5 % are in the level 1 range (mean of 210 mg $m^{-2}d^{-1}$); level 2 represents about 11 % of the surveyed areas (mean of 14.5 mg $m^{-2}d^{-1}$); level 3 is common in winter, far from macroseepage zones, accounting for about 33 % of the sedimentary zones surveyed (mean of 1.4 mg $m^{-2}d^{-1}$). Such emission factors and related percentage must, however, be better evaluated and refined by further measurements in different areas and soil types.

Macroseeps gas emission can cover a wide range. Single vents or craters of small mud volcanoes (1–5 m high) can release units to tens of tonnes/year. A whole mud volcano (hosting tens or hundreds of vents) can emit continuously hundreds to thousands of tonnes/year.

Eruptions of mud-volcanoes can release thousands of tonnes of CH_4 in a few hours. From 1810 until the present, more than 250 eruptions of 60 mud volcanoes have been observed in Azerbaijan.

In all mud volcanoes areas measured so far, the specific flux, including microseepage and macroseeps (excluding the eruptions), is generally between 100 and 1 000 t km^{-2} y^{-1}.

These data result from surveys performed in USA, Europe (Italy, Romania, Greece) and Azerbaijan, including more than 600 microseepage flux measurements and tens of macroseep flux measurements (Etiope , 2009; Etiope and Klusman, 2009).

Submarine seeps can release orders of 10^3–10^6 t y^{-1} for gas emission fields over 10^5 km^2 areas (Judd et al., 1997). The flux of an individual seepage or groups of bubble streams is on the order of 10^0–

10^4 t y^{-1}, but most seepages have outputs typically < 100 t y^{-1}. The main problem in regional and global estimates is the uncertainty in the actual area of active seepage.

Geothermal and volcanic fluxes

Volcanoes are not a significant methane source. Methane concentration in volcanic gases is generally in the order of a few units of ppmv, and the emissions, derived by CO_2/CH_4 or H_2O/CH_4 ratios and CO_2 or H_2O flux, range from a few units to tens of ton/year.

Instead, methane emission from geothermal fluids (where inorganic synthesis, thermo-metamorphism and thermal breakdown of organic matter are substantial), can be significant

The gas composition of geothermal vents, mofettes and bubbling springs is generally more than 90 % CO_2. The fraction of CH_4 is low, typically 0.01 to 1%, but the amount of the total gas released is on the order of 10^3–10^5 t y^{-1} . This may result in significant emissions of CH_4 into the atmosphere (10^1–10^2 t/y from individual vents). The specific flux of soil degassing is generally in the order of 1–10 t km^{-2} y^{-1} (Etiope et al., 2007)

Spatial disaggregation

Three main levels of spatial disaggregation can be defined:

- area including sites of verified flux;
- area including macroseeps (where microseepage is likely to occur);
- area including oil-gas fields (where microseepage is likely to occur).

This classification can be used for up-scaling procedures but, presently, there are no detailed maps or GIS data-sets available. The definition of the area used for emission calculation depends on the recognition of homogeneous identifiable areas and the spatial variability of the flux measured.

Temporal disaggregation

Constant emission flux is assumed, as otherwise temporal disaggregation would have to be based on observations, i.e. event-based. Qualitatively, it is known that microseepage is higher in winter and lower in summer, due to the different methanotrophic activity in the two seasons removing methane before it can reach the atmosphere.

Other short-term or seasonal variability can be due to meteorological and soil conditions.

Longer-time variability (years, decadal, centuries, millennia) can be induced by endogenic factors (changes of pressure gradients in the rocks, tectonic stress, etc.). New studies are necessary to define exactly the disaggregation criteria.

3.3.3 Abatement

Not applicable.

3.4 Tier 3 emission modelling and use of facility data

Emissions can also be estimated by process-based geological modelling, which, however, still needs to be developed. Such a modelling should be based on the assessment of the relationships between flux and factor such as soil, geology, and geophysics.

Specifically, four general models of methane seepage, from mud volcanoes, microseepage, shallow marine seeps and geothermal zones, should be developed. Knowing the main factors controlling the gas migration and release to the atmosphere (e.g. secondary permeability of rocks, fluid pressures,

soil properties, methanotrophic consumption; some parameters will be measured, other derived from various geological data) it will be possible to elaborate a process-level model able to predict the level of methane emission. Beyond geological factors, soil factors, e.g. microbial activity vs temperature vs soil water content, shall be considered.

4 Data quality

4.1 Completeness

A global database is available for microseepage flux, from which the emission factors are derived (Etiope and Klusman, 2009). It is based on hundreds of data from Europe, Eurasia and USA. Onshore macroseeps flux measurements are available mainly from manifestations in Europe and Azerbaijan (Etiope, 2009). A few estimates are reported for macroseeps in Asia and USA. Offshore emission data are available mainly from USA (offshore California, Gulf of Mexico), North Sea, Black Sea, Spain, Denmark, Taiwan and Japan. However, in many cases, the data refer to gas output from the seafloor to the water column, and not the fraction entering the atmosphere.

4.2 Avoiding double counting with other sectors

Natural geological gas seepage is quite well defined and generally there is no possibility of double counting with other sectors. In some cases, however, significant amounts of methane occurring in permafrost, lakes and recent marine sediments can be 'fossil', and therefore it should be considered geological and not counted in 'biological source' sectors.

4.3 Verification

Survey analysis in key areas can be performed periodically to check and measure the activity of gas manifestations (macroseeps) and the occurrence of microseepage from soil.

4.4 Developing a consistent time series and recalculation

No specific issues.

4.5 Uncertainty assessment

The main parameters used in the calculations are area data and emission factor. However, the uncertainties of these vary considerable if they are from micro- or macroseepage.

In the case of microseepage, most of the uncertainties originate from estimations of actual emitting area. Since the fields that emit methane are not delimitated, the exact size of emitting areas is hard to define. Currently, the estimation is done based on the distribution of oil fields and under the assumption that about 50 % of oil field areas have positive fluxes of CH_4 from soil. The area identified in oil-field maps is transformed in polygons that are later used in the calculations. The polygons drawn are a rough method to estimate emitting area. In addition, the use of polygons will most probably result in an over and/or under estimation of emitting areas. Somehow, in the overall scenario, the emission value obtained might be closer to reality than one might think because the errors in estimation of area are balanced.

For macroseepage, the main source of uncertainties is the temporal variation of emissions. The largest part of emissions from these occurs during 'individual' events/eruptions. These are difficult to simulate and the resultant emissions are also not easily quantifiable. Thus, calculations are

normally done using the assumption of continuous gas release from the counted vents. Moreover, the census of vents is an additional source of uncertainty. Sources belonging to macroseeps exist both in land and sea, with submarine vents being high contributors to the total emissions of this group. In land, the majority of big macroseeps have been identified and studied, but most of the smaller ones have not yet been surveyed or characterized.

Basically, the uncertainty of local flux measurements may range from 5 to 20 %. The uncertainty of emission factors can be assumed to be in the order of 10–50 %. The certainty of the 'typical value' is considerably better than the total emission range.

4.6 Inventory quality assurance/quality control QA/QC

Present flux inventories and emission factors are published in peer-reviewed journals.

4.7 Gridding

No specific issues.

4.8 Reporting and documentation

See section 6.

5 Glossary

Macroseep: visible manifestation of gas release at the earth surface in hydrocarbon-prone basins (methane dominant).

Microseepage: invisible exhalation of gas from the soil to the atmosphere in hydrocarbon-prone basins (methane dominant).

Mud volcano: cone-shaped manifestation of gas, water and mud emission (type of macroseep, in hydrocarbon-prone basins (methane dominant).

Gas vent: generic term of gas manifestation, but specifically adopted for geothermal/volcanic environment (to be distinguished from macroseeps in petroliferous areas).

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7 Point of enquiry

Enquiries concerning this chapter should be directed to the relevant leader(s) of the Task Force on Emission Inventories and Projection's expert panel on Agriculture and Nature. Please refer to the TFEIP website (www.tfeip-secretariat.org/) for the contact details of the current expert panel leaders.