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Natural emissions of methane from geothermal and volcanic sources in Europe

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Abstract

It has recently been demonstrated that methane emission from lithosphere degassing is an important component of the natural greenhouse-gas atmospheric budget. Globally, the geological sources are mainly due to seepage from hydrocarbon-prone sedimentary basins, and subordinately from geothermal/volcanic fluxes. This work provides a first estimate of methane emission from the geothermal/volcanic component at European level.

In Europe, 28 countries have geothermal systems and at least 10 countries host surface geothermal manifestations (hot springs, mofettes, gas vents). Even if direct methane flux measurements are available only for a few small areas in Italy, a fair number of data on CO_2, CH_4 and steam composition and flux from geothermal manifestations are today available for 6 countries (Czech Republic, Germany, Greece, Iceland, Italy, Spain). Following the emission factor and area-based approach, the available data have been analyzed and have led to an early and conservative estimate of methane emission into the atmosphere around 10,000 ton/yr (4000–16,000 ton/yr), basically from an area smaller than 4000 km^2, with a speculative upper limit in the order of 10^5 ton/yr.

Only 4–18% of the conservative estimate (about 720 ton/yr) is due to 12 European volcanoes, where methane concentration in volcanic gases is generally in the order of a few tens of ppmv. Volcanoes are thus not a significant methane source. While the largest emission is due to geothermal areas, which may be situated next to volcanoes or independent. Here inorganic synthesis, thermometamorphism and thermal breakdown of organic matter are substantial. Methane flux can reach hundreds of ton/yr from small individual vents. Geothermal methane is mainly released in three countries located in the main high heat flow regions: Italy, Greece, and Iceland. Turkey is likely a fourth important contributor but the absolute lack of data prevents any emission estimate.

Therefore, the actual European geothermal–volcanic methane emission could be easily projected to the 10^5 ton/yr levels, reaching the magnitude of some other natural sources such as forest fires or wild animals.
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Keywords: methane; natural emissions; geothermal systems; volcanoes; greenhouse-gas inventory

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1. Introduction

Atmospheric trace gases from natural sources contribute to atmospheric changes in the same way as those stemming from anthropogenic sources. Information on trace gas emissions from anthropogenic sources has greatly improved over recent decades as a consequence of countries' reporting requirements. The knowledge of natural emission still has large uncertainties (Simpson et al., 1999). As control activities have proved successful in decreasing anthropogenic emissions in many sectors over time, the relative importance of natural sources even increases. Thus, it is essential to improve our knowledge of all natural emissions.

Methane is both a greenhouse gas and reacting in the troposphere. An assessment of its natural emissions is thus important not only to understand its ozone forming potential, but also its greenhouse-relevant properties.

Gas seepage from geological origin has traditionally not been considered an important source significantly contributing to the atmospheric concentrations (e.g., Lelieveld et al., 1998; IPCC, 2001). Also in a European study (Simpson et al., 1999) gas seeps are not considered a major source. However, since 2001 there has been a growing body of evidence on the importance of geological seeps as global contributors of methane. New studies suggest that a wide class of geological sources, including onshore macro-seeps (e.g., mud volcanoes), microseepage, submarine seepage and geothermal seeps, are responsible for a surprisingly high global gas emission, in the order of 40–60 Tg/yr (Etiope and Klusman, 2002; Etiope, 2004; Etiope and Milkov, 2004; Etiope et al., 2004; Etiope, 2005; Kvenvolden and Rogers, 2005). Among the natural sources, only wetlands are considered more important. This increasing evidence also leads to consideration by organisations supporting a policy process: the UNECE Task Force on Emission Inventories and Projections (http://www.tfeip-secretariat.org), in a current revision of the UNECE/EMEP Atmospheric Emission Inventory Guidebook (EEA, 2004), is about to include geological sources with a new description and emission factors.

On the global scale, methane emission from geothermal and volcanic manifestations, which will be covered in this paper, seems to be less than 10% of total geological sources. The majority of geological emissions derives from the seepage from hydrocarbon-prone sedimentary basins (Etiope and Klusman, 2002). A first global geothermal emission was estimated to be in the range 1.7–9.4 Tg/yr by Lacroix (1993). Etiope and Klusman (2002) evaluated provisionally a continental geothermal (non-volcanic) source strength in the range 2.5–6.3 Tg/yr, on the basis of global heat flow data and a small data set of methane fluxes. On a country, regional or continental scale, the sedimentary/geothermal emission ratio can vary greatly depending on the geo-tectonic setting: in the regions of crustal rifting and plate subduction, geothermal and volcanic methane emission can be dominant.

The main constituents released by geothermal and volcanic manifestations are H_2O and CO_2. CH_4 occurs in very low amounts (from some ppmv to a few % units), produced either by inorganic reactions (like Fischer–Tropsch), magma degassing and/or thermal breakdown of organic compounds in crustal sediments (Welhan, 1988; Taran and Giggenbach, 2003; Fiebig et al., 2004). The total gas flux into the atmosphere however can be so high (orders of thousands of tonnes per year from individual gas vents) that also CH_4 fluxes may also become significant.

In Europe, 28 countries have geothermal systems (Lund and Freeston, 2001) and at least 10 countries host surface geothermal manifestations (hot springs, mofettes, gas vents). Data on gas composition and flux from these manifestations are available today for 6 countries (Italy, Iceland, Greece, Germany, Czech Republic and Spain); they are interpreted here to provide an early estimate of geothermal methane emission at European scale. This is the main task of this work. This emission was not considered by previous European inventories, neither by Simpson et al. (1999), nor the CORINAIR Inventory (see EEA, 2004). In this respect, specific emission and up-scaling calculation methods are proposed, following the concept of the EMEP/CORINAIR Guidelines, based on total gas flux data (CO_2 or steam) and on the amount of CH_4 occurring in the released gas.

2. Definitions

A discrimination of sources will be relevant only when abatement measures can be applied to specific sources, or when this discrimination allows for a better characterization of underlying physico-chemical processes and consequently also to improved assessment of fluxes into the atmosphere. In the context of anthropogenic emissions, the question of abatement and the application of measures to a specific source are of primary interest. For natural emissions as described here, the discrimination focuses towards a possibility to obtain better information on the underlying processes.

The geological sources considered in this work include both volcanoes and geothermal areas, which may be associated with, or independent of volcanoes.

This distinction is here made just because the term "volcanoes" is used in the methane source list of UNECE/EMEP Atmospheric Emission Inventory Guidebook (EEA, 2004). This work will show, however, how difficult the distinction of geothermal sources from volcanic sources is in areas where geothermal and volcanic systems are adjacent: in these cases, in fact, CH_4 released from the geothermal sector could be originated from fluids related to the close volcanic circulation system (or vice versa). For example, submarine flux data from Greece (Milos) are put under geothermal flux, since the gas is not directly from the volcanic edifice, even if the area is part of the Hellenic Volcanic Arc. However, it is not the ultimate purpose of this paper to derive the specific CH_4 origin, above what is required to determine the magnitude of emissions. To this aim, we will assume:

(a) volcanic emission: gas released from active, or historically active, volcanoes, either from craters or flanks. The gas, released from magma and emanating diffusely without ever being dissolved in a subcritical aqueous phase on the way to the surface, would typically have very high H_2O content and CO_2/CH_4 ratios.
(b) geothermal emission: gas released from ipo-magmatic (plutonic) or thermometamorphic environments, where there is no contemporary magma output at surface; the gas is generally released from an aqueous hydrothermal solution, by boiling or degassing. We include here gas manifestations in extinct volcanoes, paleo-volcanic zones and CO_2-rich "cold" vents in active tectonic zones, with gas coming from deep thermometamorphic processes and faults.

Accordingly, we will use always the generic term "geothermal" methane, both for volcanic and geothermal emissions, in order to distinguish it from the other large category of "sedimentary" methane, produced by microbial or thermogenic processes in the other tectonic domain of "cold" hydrocarbon-prone sedimentary basins (Etiope and Klusman, 2002), whose European emission estimate is the subject of a separate paper.

Geothermal methane can be released from localised sites (point sources: gas vents, mofettes, fumaroles, crater exhalation) and from diffuse and pervasive leakage throughout large areas (area sources). This diffuse degassing from soil is equivalent to the microseepage in sedimentary basins; the only difference is the CH_4 origin and abundance in the ascending gas-phase (CO_2 is dominant in geothermal diffuse degassing). But the term "microseepage" remains reserved to describe emissions from non-geothermal sources.

3. Up-scaling and emission calculation methods

Emissions may be most easily calculated as the sum of fluxes from individual sources. Such an approach requires knowledge on these individual fluxes. Thus it is generally available only for very large sources, which also have a very distinct spot of release: so-called point sources;

$$E = \sum_n F_n \tag{1}$$

where E is the emission, n the number of individual point sources and F the flux associated with the respective source. If fluxes are not available for all sources, a total flux may also be estimated from the available fluxes and the number of individual sources, assuming that fluxes from individual sources are similar:

$$E = nF_{\text{avg}} \tag{2}$$

with F_{avg}, the average flux for all measured point sources.

This approach can be generalized when not using the number, but another property associated with a source, estimating emissions using the so-called emission factor approach. The basic model to obtain an emission estimate utilizes the product of at least two variables, such as a specific emission factor and an activity indicator. This activity indicator is a parameter that can be assessed relatively easily from statistics, surveys or counts. The emission factor approach is widely used for sources that have their emissions measured only occasionally, for a few prototypes. These few measurements are then related to the activity indicators they are associated to, and form the emission factor. In the case of geothermal emissions, specifically diffuse emissions, we may use the areal extension of such phenomena to estimate emissions. The simplest equation for area sources (diffuse flux from soil) is then:

$$E = A\langle F_{\text{soil}}\rangle \tag{3}$$

where A is the homogeneous area and $\langle F_{\text{soil}}\rangle$ the average flux within A.

Emission factors are widely used in assessing emission inventories. Atmospheric emissions are estimated on the basis of measurements made at selected or representative sources, and then extrapolated also to all similar processes (see EEA, 2004). Area-based approaches as shown here

are typically applicable to agricultural or natural ecosystems.

The two most important preconditions to the applicability of emission factor approaches are the comparability of emission processes, and a limited temporal and spatial variability. Too often these conditions are not fulfilled. One way to deal with the problem is stratification, i.e. discriminating similar processes that exhibit very different emission behaviour, using different emission factors for each of the processes. The other option is to integrate over a larger, albeit inhomogeneous area, and expect at least the inhomogeneity to remain constant when the approach is being transferred.

A good sampling protocol will allow identification of the heterogeneity observed within a test area. Adequate more complex statistical techniques can be used, such as those based on lognormal distribution of data and related partitioning by probability graphs (e.g., Sinclair, 1974; Cardellini et al., 2003). Such techniques will allow to obtain information on the emission uncertainty. Still in order to apply emission fluxes to an area with no or few measurements available, assumptions must be taken on the distribution of the emission fluxes to be used. It is conceivable to also estimate the emission density distribution (often lognormal distribution may be expected), but it will be more practical to factor in this distribution into the estimated emission flux.

In practice, such a default emission flux will derive from measurements in other areas. Even if using the mean value which may be considerably less robust than using a median, the mean will be closer to the actual total when multiplied by the area, as it adequately considers those high data that contribute most significantly to the total. A median should be used only when also distributions are estimated, which, as stated above, is considered impractical.

The CH_4 flux (F_{CH4}) from individual geothermal point sources or area sources has been measured directly only in a few cases (Hernandez et al., 1998; Etiope, 1999; Etiope et al., 2002; Cardellini et al., 2003). However the CH_4 emission can be derived indirectly by knowing the flux of the total gas released (or of another gas, generally CO_2) and the CH_4 mixing ratio (or CO_2/CH_4 ratio) in the individual vents:

$$E_{CH4} = \sum_n \left(F_{gas\ n} \times C_{CH4\ n}\right) \quad (4)$$

where $C_{CH4\ n}$ is the volumetric fraction of CH_4 in the gas phase with respect to the total gas (or CO_2).

Furthermore, many publications already report regional estimates of CO_2 or steam emission from groups of vents and/or large areas. In this case, we can directly use these estimates and an average CH_4 concentration in the released gas to derive the regional CH_4 emission:

$$E_{CH4} = E_{gas} \times C_{CH4} \quad (5)$$

When CH_4 data do not allow calculation of the mean concentration, the value range is applied.

4. Data-sets

Two main types of data-sets, related to surface geothermal and volcanic manifestations, have been considered as input for the CH_4 emission calculation:

(a) CH_4 concentration (mixing ratio) in the gaseous-phase
(b) Flux of CO_2 and/or steam to the atmosphere

Both (a) and (b) are mainly available only for Iceland and Italy, and subordinately, for small areas in Greece, Czech Republic, Germany, and Spain (Canary Islands) (Fig. 1).

For the other 16 countries hosting significant geothermal systems (>100 GWh/yr of heat energy; Lund and Freeston, 2001), i.e., Austria, Bulgaria, Croatia, Finland, France, Hungary, Lithuania, Macedonia, Romania, Russia, Serbia, Slovak Republic, Slovenia, Sweden, Switzerland and Turkey, there are no data available. In the best cases only CO_2 flux data or only CH_4 concentrations in vents or soil are available. The available data refer to an area producing about 1/3 of

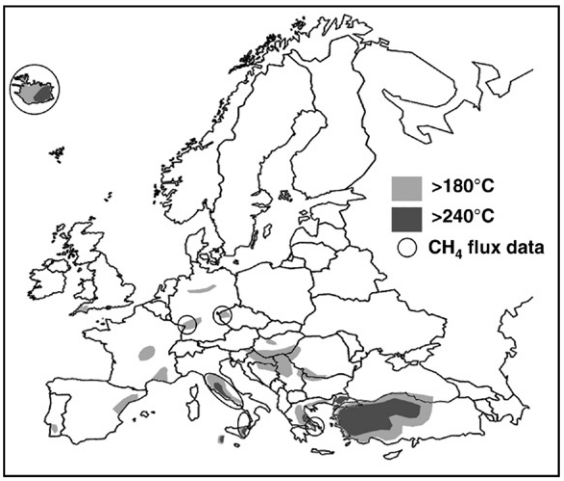

Fig. 1. Geothermal map of Europe, with temperatures at depth of 5000 m. It shows the areas with high potential of geothermal methane emission (redrawn from Hurtig et al., 1992, with additions).

Table 1
Estimates of CH_4 emissions from active European volcanoes

	CH_4 [1] (ppmv)	CO_2 [1] (%, v)	CO_2 emission (ton/yr)	CH_4 emission [2] (ton/yr)
Etna crater (Italy)	4 (1–6) [a, b]	23 (13–90) [b]	$\sim 13\times10^6$ [c]	82
Ischia (Italy)	48 (25–75) [d]	91 (77–97) [3 d]	479,000 [e]	9
Nisyros (Greece)	90 (10–470) [f]	1.5 (1–4.5) [f]	24,800 [f]	54
Pantelleria (Italy)	867 (829–890) [g]	2 [g]	2550 [f]	40
Phlaegrean Fields (Italy)	29 (19–35) [f]	15 [f]	540,000 [f]	38
Stromboli crater (Italy)	39 (1–190) [h]	80 (66–93) [3 h]	1.5×10^6 [i]	27
Teide, Tenerife (Spain)	4 [g]	17.4 [g]	229,000 [j]	2
Soil degassing only, 1996 [k]	–	–	–	*584* [4]
Soil degassing only, 2000 [l]	–	–	–	0.5
Vesuvio cone (Italy)	26 (13–74) [f]	9 (1.8–12) [g]	55,100 [f]	6
Vulcano (Italy)	88 (50–150) [g]	10 (5–15) [g]	65,000 [f]	21
Grímsvötn + Krafla + Askja (Iceland)	(see Tables 2a and 2b)			440
Total [5]				~720

[1] Average value from the data-set where both CH_4 and CO_2 data are available; range in brackets.
[2] Best guess calculated from the average CO_2/CH_4 concentration ratio found in the same data-set.
[3] Analysis of dry gas.
[4] Unreliable datum, not considered in the total and Table 6, because of the biogenic origin of CH_4, as suggested by light $\delta^{13}C$ values [k].
[5] Excluding datum (4) from reference k.
[a] Giammanco et al. (1998).
[b] D'Alessandro et al. (1997).
[c] Allard et al. (1991).
[d] Inguaggiato and Pecoraino (2000).
[e] Pecoraino et al. (2005).
[f] Chiodini et al. (2005).
[g] Chiodini and Marini (1998).
[h] Capasso et al. (2005).
[i] Allard et al. (1994).
[j] Castro et al. (2000).
[k] Hernandez et al. (1998).
[l] Lima et al. (2000).

total European geothermal heat energy, primarily by Iceland and Italy, the two major geothermal countries.

The input data-set (i.e. available pairs of gas-flux and CH_4 concentration) and related literature source, are included in Tables 1 2a 2b 3 4 5. Considering the possible wide ranges of the CO_2/CH_4 ratio for a given area and the uncertainty of total CO_2 flux (which is also variable over time), only the order of magnitude of CH_4 flux can be estimated. The list is updated to March 2006. A reader may alter the numbers, use better data – if any are available – or new data-sets. It will be easy to see that our results are so robust that the final figures will not change significantly, unless new emission areas are added.

5. Results

5.1. Volcanoes

Table 1 lists the available data for 12 active volcanoes in Europe. Data from some Icelandic volcanic centers are included in Tables 2a and 2b: since these estimates are derived from steam flux values covering the whole geothermal area surrounding the volcanic centers (with methane which can be derived from thermal breakdown of organic matter in layers located between lava flows), it is not possible to distinguish a simple volcanic emission. As first approximation, we may include the data from three well identifiable major volcanoes, Grímsvötn, Krafla, and Askja, in the category "volcanoes".

The typical concentration of CH_4 in the volcanic gases (fumaroles, crater exhalations) is on the order of a few units to some tens of ppmv. A world-wide data-base for 27 volcanoes (data from Chiodini and Marini, 1998; Taran and Giggenbach, 2003) indicates an average CH_4 concentration of about 50 ppmv and a median value of 6 ppmv. Flank degassing may have higher CH_4 concentrations. Gas flux emission data, generally in terms of CO_2 or steam flow, can be from the main craters and from the flank vents and soil, both ranging from thousands to millions of tonnes CO_2 per year. Considering the uncertainties of the CO_2/CH_4 ratio and total CO_2 flux, applying Eq. (4) to the 11 volcanoes gives provisionally a total European volcanic CH_4 emission in the order of 720 ton/yr.

5.2. Geothermal areas

5.2.1. Iceland

Methane emissions from Icelandic high-temperature geothermal systems have not been quantified directly. However, estimated heat loss from these systems and the observed CH_4 concentration in the geothermal steam can be used to evaluate the magnitude of their CH_4 emissions using a method initially developed by Arnórsson (1991) and Arnórsson and Gíslason (1994). Assuming that ascending steam is the dominant heat transport mechanism (Sorey and Colvard, 1994) the heat flow can be used

Table 2a
CH_4 emissions from Icelandic geothermal areas from which CH_4 data are available

Geothermal area	Areal extent (km^2)[a]	Steam flow (kg/s)[b]	Number of samples	Median CH_4 concentration (mmol/kg)	CH_4 emission (kg/yr)	Specific flux (ton km^{-2} yr^{-1})
Reykjanes	2	49[c]	7	0.03[d]	642	0.3
Krýsuvík	60	452	31	0.09[e]	20,069	0.3
Hengill	100	753	16	0.66[f]	248,962	2.5
Geysir	3	23	3	0.07[g]	741	0.2
Kerlingarfjöll	11	83	18	0.48[h]	20,006	1.8
Hveravellir	1	8	5	0.04[i]	144	0.1
Torfajökull	140	1055	22	0.22[j]	114,941	0.8
Köldukvíslarbotnar	8	60	6	3.87[k]	117,677	15
Kverkfjöll	25	621[c]	20	0.34[l]	107,557	4.3
Námafjall	7	53	26	1.08[m]	28,642	4.1
Krafla	30	226	15	0.36[m]	41,164	1.4
Theistreykir	19	143	38	0.83[n]	59,683	3.1
Total	406	3492	Weighted average 0.44		760,230	Mean 1.9

[a] Pálmason et al. (1985).
[b] Estimated assuming average heat flow of 20 W/m^2 for geothermal areas (Pálmason et al., 1985) except Reykjanes and Kverkfjöll.
[c] Computed from heat flow reported by Fridriksson et al. (2006; Reykjanes) and by Friedman et al. (1972; Kverkfjöll).
[d] Arnórsson and Gunnlaugsson (1985), J.Ö. Bjarnason (unpublished data).
[e] Arnórsson and Gunnlaugsson (1985), Arnórsson (1987).
[f] Torfason et al. (1983), Arnórsson and Gunnlaugsson (1985).
[g] Arnórsson and Gunnlaugsson (1985).
[h] Hjartarson and Ólafsson (2005a).
[i] Hjartarson and Ólafsson (2005b).
[j] Bjarnason and Ólafsson (2000).
[k] Fridleifsson et al. (1996).
[l] Torfason et al. (1993).
[m] Arnórsson et al. (1996).
[n] Gíslason et al. (1984).

to compute the mass flow of steam through the soil, $F_{S,\ H_2O}$ in kg s^{-1}, as:

$$F_{S,\ H_2O} = \frac{H_S}{(h_{s,100\ °C} - h_{w,t,r})}, \quad (6)$$

where $h_{s,\ 100\ °C}$ is the enthalpy of steam at 100 °C and $h_{w,t,r}$ is the enthalpy of water at 5 °C, the average annual temperature at Reykjanes ($2.676 \cdot 10^6$ and $2.1 \cdot 10^4$ J/kg, respectively; Schmidt and Grigull, 1979). If the concentration of methane in the geothermal steam is known the CH_4 emissions can be calculated from Eq. (4) by substituting F_{S,H_2O} for the more general E_{gas} (cf. Eq. (4)). Note that this method provides an estimate of the total methane emission from the respective geothermal manifestations, i.e. the sum of emissions via diffuse soil degassing and point source emissions. The resulting estimate of total CO_2 emissions from Iceland obtained by this method (Arnórsson, 1991; Arnórsson and Gíslason, 1994) is in good agreement with other estimates of total CO_2 emissions (see Ármannsson et al., 2005). Note also that this method assumes non-reactive transport of CH_4 through geothermal soil. If microbial oxidation of CH_4 is an important process in the geothermal soil this method will result in overestimation of the actual CH_4 emissions.

Approximately 25 to 30 high-temperature geothermal systems are currently active in the volcanic zone of Iceland. The estimated average heat flow from these systems is about 20 W/m^2 with the exception of Kverkfjöll and Grímsvötn, which have higher heat flow per unit area (Pálmason et al., 1985). The total aerial extent of the surface manifestations of these systems is about 600 km^2. Tables 2a, and 2b list estimated total steam flow from 24 Icelandic geothermal systems and the aerial extent of each system. The steam flow is computed using Eq. (6). The total heat flow for individual areas, used in Eq. (6), is the product of the aerial extent of a given system and the estimated average heat flow per unit area (Pálmason et al., 1985) with the exception of Reykjanes, Kverkfjöll, and Grímsvötn, for which the heat flow values are from Fridriksson et al. (2006), Friedman et al. (1972) and Ágústsdóttir and Brantley (1994), respectively.

Table 2a lists the 12 geothermal systems in Iceland from which data of methane concentration in steam are available. The steam samples were collected from steam

Table 2b
Estimated CH_4 emissions from Icelandic geothermal areas from which CH_4 data are not available

Geothermal area	Areal extent (km^2)[a]	Steam flow (kg/s)[1]	Median CH_4 concentration (mmol/kg)[3]	CH_4 emission (kg/yr)
Svartsengi	11	83	0.44	18,554
Brennisteinsfjöll	2	15	0.44	3374
Grímsvötn	65	1601[2]	0.44	358,435
Vonarskard	11	83	0.44	18,554
Askja	25	188	0.44	42,169
Fremrinámar	4	30	0.44	6747
Presthnúkur	1	8	0.44	1687
Tindfjallajökull	1	8	0.44	1687
Blautakvísl	7	53	0.44	11,807
Hrúthálsar	7	53	0.44	11,807
Gjástykki	7	53	0.44	11,807
Öxarfjörður	30	226	0.44	50,603
Total	171	2399		537,231

[a] Pálmason et al. (1985).
[1] Estimated assuming average heat flow of 20 W/m^2 for geothermal areas (Pálmason et al., 1985) except Grímsvötn.
[2] Computed from heat flow estimate by Ágústsdóttir and Brantley (1994).
[3] Median value for CH_4 concentrations in geothermal areas listed in Table 2.

vents at 100 °C with the exception of two samples from Kerlingarfjöll, which were collected at 140 °C. It can be seen from the table that the number of analyses ranges between 3 and 31 for individual systems. The value used as representative methane concentration in steam at a given system (C_{CH4} in Eq. (5)) is the median of the available analyses. The reason for using the median as opposed to the mean is that the mean is more sensitive to anomalously high gas concentrations that are commonly observed in samples from steam vents that are affected by partial condensation. For instance, Fridriksson et al. (2006) have described how gas concentrations in geothermal steam increase systematically away from the most intense steam vent activity at Reykjanes while the ratios of the non-condensible gases remain constant. This is a result of partial condensation of the steam in the less active parts of the field.

Table 2b lists the estimated CH_4 emissions from the 12 geothermal systems in Iceland from which data on CH_4 concentration in geothermal steam are not available. For these areas we used weighted average of the CH_4 concentrations from the other Icelandic geothermal systems shown in Table 2a. Inspection of Tables 2a and 2b shows that the estimated total CH_4 emissions from Icelandic geothermal systems are about 1300 ton/yr. Since this estimate is quite comprehensive and includes the diffuse soil degassing, the order of magnitude of the upper limit should remain within 10^3 ton/yr.

5.2.2. Italy

From a database of more than 70 gas vents distributed along the Tyrrhenian geothermal side of the Italian peninsula (Minissale et al., 1997; Rogie et al., 2000; Cardellini et al., 2003), the CH_4 concentration ranges from 1 to 132,000 ppmv, with a mean of 13,000 ppmv. CO_2 concentration is generally >90%. Tables 3 and 4 report the data used for emission calculation. In Table 3, the CH_4 flux from 13 vents is calculated individually by Eq. (4). Using an estimate that at least 100 geothermal vents occur in Italy (Rogie et al., 2000), we may assume 90 vents remaining to contribute additional emissions. Excluding the 2 largest vents (Mefite and Poggio Olivo), as no so big manifestations are known to occur elsewhere in Italy, the "mean" vent emits about 10 ton CH_4/yr; the remaining vents would then emit in total around 900 ton/yr. The total geothermal vent emission would be, therefore, on the order of 1300 ton/yr.

Table 4 reports a few direct measurements of CH_4 flux from diffuse soil degassing, performed by accumulation chambers, around some geothermal vents. The estimates

Table 3
Estimates of CH_4 emissions from geothermal vents in Italy

Geothermal vent	CO_2 concentration (% v)	CO_2 flux (ton/yr)	CH_4 concentration (ppmv)	CH_4 flux (ton/yr)
1 Bossoleto, Siena	96.1[a]	3500[b]	4280[c]	6
2 Castiglioni, Siena	99.1[a]	4400[d]	1100[e]	2
3 Manziana Caldara	97.4[f]	4800[f]	200[f]	0.4
4 Mefite d'Ansanto	98[f]	102,200[f]	2100[f]	80
5 Panarea (offshore)	99[g]	8500[g]	3000[g]	9
6 Pienza	94.2[f]	4015[f]	14,400[f]	22
7 Poggio Olivo	98.2[f]	73,000[f]	4030[f]	109
8 Rapolano Cecilia	96.3[f]	17,520[f]	4090[f]	27
9 Rapolano Ambra	94[a]	35,040[f]	1000[e]	14
10 San Sisto	97.7[f]	21,600[f]	3000[f]	24
11 Selvena	88.5[f]	2920[f]	80,400[f]	97
12 Telese	98.4[h]	20,000[h]	1000[h]	7
13 Umbertide	92.3[f]	5840[f]	2500[f]	6
Total		303,335	–	~400

[a] Etiope et al. (2005); [b] Raschi e Menegali, p.c.; [c] Bettarini et al. (1999); [d] Morner and Etiope (2002); [e] Etiope and Klusman (2002); [f] Rogie et al. (2000); [g] Caracausi et al. (2005); [h] Italiano et al. (2000).

Table 4
Measured CH_4 emissions from soil degassing in Italy

Soil degassing	Mean flux (mg m^{-2} d^{-1})	Area extent (km^2)	Output (ton yr^{-1})	Emission factor (ton km^{-2} yr^{-1})
Guardia dei Turchi (Ustica)[a]	4	0.25	0.4	1.5
Acqua Borra (Siena)[b]	24	0.12	1	8.7
Solfatara (Pozzuoli)[c]	155	0.5	3.4	6.8
Poggio Olivo (central Italy)[c]	19,420	1.5	15.7	10.4
Terme S. Giovanni (Rapolano)[d]				285
– High degassing sector (close to spring)	55,000	0.002	40	
– Low degassing sector (>50 m from spring)	230	0.2	17	

[a] Etiope et al. (2002); [b] Etiope (1999); [c] Cardellini et al. (2003); [d] Etiope, unpublished data.

by Cardellini et al. (2003) were based on lognormal distribution of data and related partitioning by probability graphs. The others were based on the emission factor and area source approach. The emission factor is derived by dividing the output estimated by the area investigated; it is not the mean flux, since the output derives from different mean values of homogenous sectors, i.e. Eq. (3) applied to high and low degassing sectors, or by the lognormal distribution statistics. The Ustica site does not include any vent. All other surveys suggest that positive CH_4 flux from soil to the atmosphere exists throughout relatively wide areas around the vents, in the order of 0.1–1 km^2, with a specific flux in the order of 10^1–10^2 ton km^{-2} yr^{-1}. The emission from the surrounding soil of all 100 vent sites (10–100 km^2) would be therefore in the range 100–10,000 ton/yr. The total geothermal emission (vent plus soil) could be then between 1400 and 11,300 ton/yr. Adding the volcanic component leads to a total country emission of 1600–11,500 ton/yr (let us say an order of 10^3 ton/yr).

A large scale estimate of geothermal CO_2 degassing from Italy, in the order of 9 Mt/yr for a sector 40,000 km^2 in area, has been proposed (Chiodini, 2005). If we assume that this degassing involves the mean concentration of methane in the Italian geothermal gases (13,000 ppmv), this would indicate a CH_4 output in the order of 43,000 ton/yr. We regard this figure a "speculative upper limit" of methane production.

5.2.3. Other countries

Table 5 reports the data available for Czech Republic, Germany, Greece. Czech data are from the Western Eger Rift hosting up to 140 mineral springs and up to 500 mofettes within 1500 km^2 (Weinlich et al., 1999). Data from Germany refer only to the West Eifel sector of the Rhine Graben (May, 2002). In both areas there is a wide range of CH_4 concentration in the mofettes, from a few ppmv to 1% v/v, and the CO_2 fluxes have also large uncertainties. The calculation of the CH_4 flux has thus to be considered as a first exercise, just to assess the possible order of magnitude. Assuming the lowest emission factor of soil diffuse leakage of 0.1 ton km^{-2} yr^{-1} (corresponding to CH_4 concentrations in the geothermal fluid of some tens of ppmv) and the areal extent of the manifestations (order of 1000 km^2), a speculative upper limit of the total emission from soil degassing in the order of 100 ton/yr can be provisionally proposed, both for West Eifel and West Eger.

The gas emissions from Milos (Greece) refer to submarine hydrothermal seeps, at water depths ranging from 3 to 113 m. It means that, due to dissolution in seawater, only a fraction of CH_4 emitted at deeper seabed enters the atmosphere. About 25% of the amount of gas emitted at seabed is from seeps occurring at 50–100 m water depth (Dando et al., 1995); from these depths roughly 50% of methane reaches the atmosphere (e.g., Leifer and Patro, 2002). So, if the total gas emission (at seabed) is $0.21–1.05 \cdot 10^{11}$ mol/yr and the average CH_4 concentration is 5000 ppmv (mean value from seeps where there is no significant biogenic CH_4

Table 5
Estimates of CH_4 emissions from other European geothermal areas

Geothermal area (vents)	Gas flux (ton/yr)	Average CH_4 concentration (ppmv)	Areal extent (km^2)	CH_4 emission (ton/yr)
West Eger Rift (Czech Rep.)	10,560[a]	70[a] [2]	1500	~0.3
West Eifel (Germany)	16,300[b]	300[b]	900	2
Milos submarine vents (Greece)	2,770,000[c]	5000[c]	34	600–3300[1]
Sousaki (Greece)	–	–	0.015	37[d]

[a] Weinlich et al. (1999); [b] May (2002); [c] Dando et al. (1995), CH_4 data (up to 9%) with significant biogenic component are excluded; minor biogenic CH_4 amounts are however likely in all seeps; [d] D'Alessandro et al. (2006).

[1] amount of CH_4 entering the atmosphere from seeps occurring at 50–100 m water depth (see text).

[2] The methane concentration has a wide range from 0 to 9000 ppmv. The average used is that of the major mofettes (CO_2 flux > 2000 l per hour), from the main four gas escape centers of West Eger.

production; Dando et al., 1995), the total amount of methane actually entering the atmosphere would be between 600 and 3300 ton/yr. But tens, if not hundreds, of similar submarine manifestations exist in Greece (Dando et al., 1995), indicating a potential of much larger emissions.

A further datum is available for the measured terrestrial degassing in a small area of the Sousaki geothermal field, around 37 ton/yr (D'Alessandro et al., 2006). Assuming the same CH_4 output for the other about 30 geothermal fields existing in Greece (mainly in Thrace, Macedonia and Aegean Islands; Fytikas et al., 2000) would suggest a total terrestrial emission in the order of 1000 ton/yr. Considering the numerous submarine manifestations similar to Milos, a speculative upper limit in the order of 10^4 ton/yr can be considered.

6. Conclusions

On the basis of the available data, the natural emissions of geothermal methane in Europe is today derivable almost entirely from the three countries located in the main high heat flow regions, Italy, Greece, Iceland, hosting the main volcanic and hydrothermal systems (Table 6). According to data on crustal temperatures at 5000 m depth (Fig. 1), Turkey is likely a fourth important contributor but the complete lack of data prevents any emission estimate.

The geothermal methane emission is provisionally and conservatively estimated in the order of 10,000 ton/yr (4000–16,000 ton/yr), basically from an area smaller than 4000 km^2. This refers to the area within which field measurements were actually carried out or local data were extrapolated. Therefore it is only part of the total emission from the entire European geothermal area.

Table 6
Summary of geothermal and volcanic CH_4 emissions from available data by country

	Area (km^2)	CH_4 output in the investigated areas (ton/yr)	Orders of magnitude of speculative estimates for the whole country (ton/yr)
Czech Rep.	1500	~0.3	10^2
Germany	900	2	10^2
Greece	34	~800–3500	10^4
Iceland	577	1300	10^3
Italy	~100	1600–11,500	10^4
Spain (only Teide volcano)	–	2	Not estimated
Total		~4000–16,000	10^5

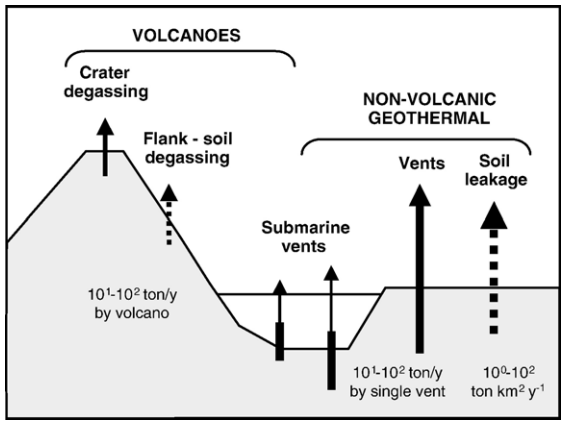

Fig. 2. Summary of geothermal methane emission types and related emission factors.

Only 4–18% of the output (about 720 ton/yr) is due to 12 European volcanoes, where methane concentration in volcanic gases is generally in the order of a few tens of ppmv. Volcanoes are thus not a significant methane source (Fig. 2). The largest emission is, instead, due to geothermal areas, next to volcanoes or independent, where inorganic synthesis, thermometamorphism and thermal breakdown of organic matter are substantial. Here, methane flux can reach hundreds of tons per year from small individual vents.

The actual total European emission, including all geothermal areas, could be likely in the order of 10^5 ton/yr, reaching the levels of some other natural sources such as forest fires or wild animals (Simpson et al., 1999). Still geothermal methane is not an important contribution of the top natural sources, such as wetlands and gas seepage in petroliferous areas (Etiope, 2004).

On a country level, the geothermal emissions are relatively high for Italy, Iceland and Greece. In Italy the speculative upper limit (43,000 ton/yr) is within the top 7 national sources (see ANPA, 1999), being higher than emissions from vehicles and several industrial activities (e.g., petroleum refineries).

The estimated anthropogenic methane emissions from Iceland in 2004, which are almost exclusively derived from agriculture and solid waste landfills, amount to 22,300 ton/yr (Hallsdóttir et al., 2005). Therefore the geothermal methane emissions from the country, 1300 ton/yr, amount to 6% of the anthropogenic emissions.

Obviously, more field measurements are necessary in order to refine the emission estimate, especially in countries where there is the complete lack of flux data but have high potential for geothermal methane emissions

(e.g., Turkey, Romania, Hungary, Slovenia, France, Russia), and in countries already explored but with a limited flux data set (e.g., Czech Republic, Germany, Greece, Spain).

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