GEOPHYSICAL RESEARCH LETTERS, VOL. 34, L14303, doi:10.1029/2007GL030341, 2007

Methane seeps and mud volcanoes in Italy: Gas origin, fractionation and emission to the atmosphere

Giuseppe Etiope,[1] Giovanni Martinelli,[2] Antonio Caracausi,[3] and Francesco Italiano[3]

Received 11 April 2007; revised 17 May 2007; accepted 4 June 2007; published 17 July 2007.

[1] Molecular composition, CH_4 isotopes and gas flux of all main terrestrial mud volcanoes and other methane seeps in Italy are being assessed for the first time. Whereas 74% of the Italian gas reservoirs are biogenic, about 80% of the seeps release thermogenic gas. Dry-seep gas generally maintains the reservoir $C_1/(C_2 + C_3)$ "Bernard" ratio while mud volcanoes show molecular fractionation likely occurring during advective migration. Accordingly, a simple and direct use of the "Bernard" parameter might be misleading when applied to mud volcanoes as it could not always reflect the reservoir composition. Methane flux into the atmosphere from macro-seep areas is in the order of 10^2–10^6 t km^{-2}y^{-1}. Microseepage is widespread throughout large areas and, on a regional scale, it provides the main methane output. A first emission estimate for the total hydrocarbon-prone area of Italy suggests levels of 10^5 t y^{-1}, comparable to national sources from fossil fuel industry. **Citation:** Etiope, G., G. Martinelli, A. Caracausi, and F. Italiano (2007), Methane seeps and mud volcanoes in Italy: Gas origin, fractionation and emission to the atmosphere, *Geophys. Res. Lett.*, *34*, L14303, doi:10.1029/2007GL030341.

1. Introduction

[2] Italy is the 7th European producer of natural gas, with reserves for 220 billion cubic metres [*Eni*, 2004]. About 74% of this gas is biogenic, 14% thermogenic and 12% mixed [*Mattavelli and Novelli*, 1988]. The gas fields are spread out in sedimentary basins affected by Neogene tectonics which, beyond creating favourable conditions for structural traps, produced a network of dislocations, very permeable to secondary gas migration, leakage and ascent to the Earth surface. As a result, about a thousand of surface gas seeps formed, including small mud volcanoes, hydrocarbon rich springs and dry-seeps. Most seeps are today extinct but they have historically driven the national petroleum exploration, like in other countries [*Link*, 1952]. Presently, understanding seep gas origin may contribute to tectonic and petroleum geology studies (depth of gas-bearing faults [*Italiano et al.*, 2000]; definition of the Petroleum Seepage System [*Abrams*, 2005]), assist hydrocarbon exploitation (geochemical and pressure variations during fluid extraction) and support environmental impact studies (aquifer contamination, underground gas storage). Gas seepage is also an important natural source of "fossil" methane for the atmosphere, as recently recognised on a global scale [*Etiope*, 2004]. Nevertheless, only a few seeps in Italy have been investigated so far. In this work we report a full-scale frame including quite a complete compositional and isotopic CH_4 analysis of all main seeps still active today. Diagrams based on $\delta^{13}C_{CH4}$ vs δD_{CH4} and $\delta^{13}C_{CH4}$ vs $C_1/(C_2 + C_3)$ are used to assess gas origin, differences among seep typologies and from reservoir gas. Methane flux from macro-seeps and soil microseepage is then assessed, leading to a first estimate of national CH_4 seepage output to the atmosphere.

2. Occurrence of Natural Gas and Seeps

2.1. Gas Reservoirs

[3] Hydrocarbon generation and accumulation in the Italian sedimentary basins are the result of Neogene tectonics with Apennines orogenesis, leading to the formation of three main tectono-sedimentary domains, corresponding to three parallel bounds which divide the Italian peninsula longitudinally (Figure 1): Chain, Foredeep and Foreland. About 77% of gas is located along a band between orographic front and the outer Foredeep line drawn in Figure 1, including the folded Foredeep front. About 82% of such a gas is biogenic ($-76 < \delta^{13}C < -60$; $-223 < \delta D < -171$; $C_{2+} < 0.5\%$), stored in Plio-Pleistocene sediments; 3% is thermogenic ($-50 < \delta^{13}C < -30$; $-215 < \delta D < -153$; $C_{2+} > 0.5\%$), in pre-Pliocene reservoirs; 15% is mixed ($-60 < \delta^{13}C < -50$; $-217 < \delta D < -176$; $0.1 < C_{2+} < 13\%$); 10% of gas is in the Foreland (99% biogenic, 1% thermogenic) and 13% in the Chain (97% thermogenic, 3% mixed) [*Mattavelli and Novelli*, 1988]. In the northern Apennine, a number of thermogenic reservoirs occur at shallow depth (<1200 m), where gas migrated vertically from deeper horizons [*Borgia et al.*, 1988]. A large part of these shallow occurrences are relatively dry, due to cracking or chemical fractionation during migration.

2.2. Seeps

[4] More than 1000 macro-seeps were catalogued in 1950 [*Martinis*, 1962]. Fifty mud volcanoes were catalogued by *Martinelli and Judd* [2004]. After more than one century of hydrocarbon exploitation, today most seeps are disappearing and becoming inactive: gas flux is being significantly reduced compared to the past, often leaving only a weak but diffuse microseepage at the old manifestation. Around 30 seeps still show continuous or episodic, strong or weak gas emissions. All seeps are clearly related to tectonic and neotectonic faults. Most seeps occur along the external margin of the Apenninic chain (orographic boundary or inner folded foredeep; Figure 1) and should result from migration of gas from Mesozoic limestone

---

[1] Section of Roma 2, Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy.

[2] Environmental Protection Agency of the Emilia Romagna Region, Bologna, Italy.

[3] Section of Palermo, Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy.

0094-8276/07/2007GL030341$05.00

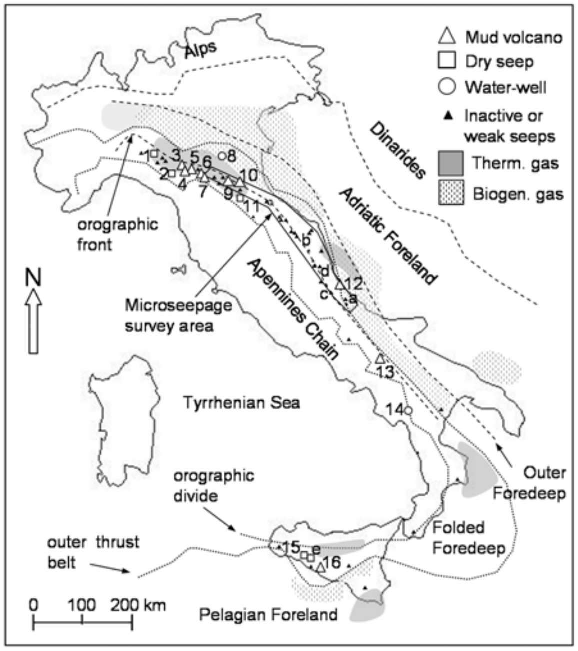

Figure 1. Location of investigated gas seeps, microseepage survey area and biogenic-thermogenic reservoirs in the tectono-stratigraphic domains in Italy. Numbers of sites are those in Table 1. Letters "a–e" are sites where only gas flux was measured (see Table 2).

substratum and Miocene structural and stratigraphic traps. Minor amounts of gas may mix with biogenic pools in Pliocene and Quaternary rocks. A few seeps fall in the external Foredeep, so they should mainly result from biogenic gas migration from Pliocene-Quaternary sandy reservoirs in compressive anticlines. Everywhere, under-compacted and overpressured sediments, with brackish waters and clays, may lead to the formation of mud volcanoes.

3. Seep Description, Sampling and Analysis

[5] In 2005 and 2006 we surveyed all main active seeps in Italy, merely related to hydrocarbon sedimentary zones. Data related to 4 seeps investigated in 1998 in North Italy [*Minissale et al.*, 2000] and 2001 in Sicily [*Etiope et al.*, 2002; *Grassa et al.*, 2004] are re-called for completeness. Gas manifestations with significant amounts of methane (unit or tens of %Vol) but with partial signatures of volcanic or geothermal processes are not considered in this work. In total 30 seeps were found to release gas but only 16 (listed in Figure 1 and Table 1) allowed safe sampling of gas in sufficient amounts for isotopic analyses. They include 10 mud volcanoes (hereafter referred as MV), 4 dry-seeps, 2 bubbling water-wells (Figure 1). Italian MVs are much smaller (up to 2–3 m high) than others occurring along the Alpine-Himalayan belt (Romania, Azerbaijan, Pakistan etc.). The vents (gryphons, small craters, bubbling pools) generally cover areas of 10^2–10^3 m^2. Maccalube in Sicily, 1.4 km^2 wide, is the largest Italian MV. Dragone MV (9 in Figure 1) is different from others because it is weakly emitting only a gas-phase, without water or mud release. Higher gas flux and mud release occurred in the past. Dragone is likely in a long quiescent phase or may have begun its way to extinction. The dry seeps are gas vents without water release, naturally crossing the soil horizon (Censo fire, 15) or collected by abandoned shallow bore-holes (Monte Busca, 11; Montechino 1; Miano 2). Corporeno (8) and Tramutola (14) are wells built on shallow water occurrences, in which free gas is ascending through bubbles.

[6] Gas was collected in 50 ml pyrex bottles sealed by two vacuum cocks. All samples were analysed for C_1–C_6 hydrocarbons, $\delta^{13}C_1$, δDC_1, He, H_2, Ar, O_2, CO_2, N_2, by

Table 1. Chemical Composition of Gas Seeps and CH_4 Isotopes[a]

Site	Type	N_2	O_2	Ar	CO_2	He	CH_4	C_2	C_3	C_{4-6}	$\delta^{13}C_1$	δDC_1
1 - Montechino	DS	0.42	0.05	0.01	0.05	0.0017	95.30	2.460	1.020	0.691	−33.98	−132.6
2 - Miano	DS	0.91	0.03	0.02	0.44	0.0019	98.44	0.153	<0.001	<0.001	−39.38	−168.4
3 - Rivalta	MV	0.42	0.01	0.01	1.24	0.0034	98.32	0.018	<0.001	<0.001	−41.38	−180.6
4 - Torre[b]	MV	0.40	0.04	0.01	2.73	0.0013	96.79	0.037	0.0004		−39.10	
5 - Regnano	MV	0.92	0.01	0.01	2.12	0.0016	96.78	0.150	0.004	<0.001	−45.72	−152.6
6 - Nirano	MV	0.97	0.12	0.01	0.58	0.0020	98.26	0.051	0.005	<0.001	−45.65	−185.5
7 - Ospitaletto	MV	1.07	0.09	0.01	2.16	0.0026	96.62	0.044	<0.001	<0.001	−45.60	−183.3
8 – Corporeno[c]	SWW	26.53	1.30	0.51	5.10	<0.001	66.52	0.038	<0.001	<0.001	−65.98	−174.1
9 - Dragone	DMV	4.15	0.05	0.01	2.90	<0.001	88.85	3.007	1.001	0.030	−58.40	−219.0
10 - Bergullo	MV	0.89	0.15	0.02	0.27	<0.001	98.61	0.046	<0.001	0.014	−69.43	−180.2
11 - M. Busca	DS	37.96	0.48	0.06	0.45	0.163	58.44	1.550	0.504	0.376	−35.81	−160.9
12 - Pineto	MV	5.40	0.02	0.11	0.36	0.0016	94.13	0.036	<0.001	<0.001	−73.11	−188.2
13 - Malvizza	MV	1.94	0.039	0.03	1.66	0.025	95.64	0.670	<0.001	<0.001	−59.09	−163.8
14 - Tramutola	SWW	15.12	0.01	0.01	2.17	0.0026	82.61	0.267	<0.001	<0.001	−42.12	−193.8
15 - Censo fire[d]	DS	17.4	3.8		1.8		76.40	0.591	0.083		−35.10	−146.0
		9.66	2.03		2.2	0.0367	86.00					
16 – Maccalube[d]	MV	6.46	1.27		0.73		91.20	.045	0.002		−48.07	189.6
		1.15	0.29		0.90	0.0071		0				–

[a] Gas composition is given in %Vol. CH_4 isotopes are given in ‰ vs PDB and SMOW. MV: Mud Volcano; DMV: Dry Mud Volcano; DS: Dry Seep; SWW: Seep Water Well.

[b] *Minissale et al.* [2000].

[c] Gas in solution in water.

[d] First line from *Grassa et al.* [2004]; average of 3 Maccalube samples); second line from *Etiope et al.* [2002].

Table 2. Methane Flux From Macro-Seeps and Related Microseepage[a]

Site	Seep Type	Measured Area, m^2	N. Vents	Macroseep Output, t y^{-1}	Microseepage Output, t y^{-1}	Total Output, t y^{-1}
1- Montechino	DS	200	1	100	0.15 [8]	100
2- Miano	DS	100	1	200	0.03 [5]	200
3- Rivalta	MV	2500	7	1.2	10.8 [8]	12
5- Regnano	MV	5800	8	5	29 [11]	34
6- Nirano	MV	10000	18	6	26.4 [6]	32.4
7- Ospitaletto	MV	1000	4	0.8	0.6 [7]	1.4
9- Dragone	DMV	2000	2	0.2	0.15 [5]	0.3
10- Bergullo	MV	1	3	1	nm	1
11- M.Busca fire	DS	100	1	7	2.2 [8]	9.2
12- Pineto	MV	10000	1	0.1	2.6 [18]	2.7
14- Tramutola[b]	SWW	1	1	2400	nm	2400
15- Censo fire[c]	DS	80	1	4.2	2 [2]	6.2
16- Maccalube[c]	MV	1.4×10^6	69	20	374 [9]	394
a- Lanciano Frisa	MV	5000	1	0	1.9 [11]	1.9
b- Serra de Conti	MV	15000	3	0.3	3 [15]	3.3
c- Astelina	MV	5000	1	0	0.5 [5]	0.5
d- Offida	MV	7000	1	0	1.8 [9]	1.8
e- Occhio Abisso[c]	MV/DS	1000	4	2.2	0.49 [13]	2.7
Total						3203

[a] Number of microseepage measurements is in brackets. Numbers of sites are those in Figure 1 and Table 1. Sites (a–e) are not included in Table 1; nm means not measured.

[b] *Italiano et al.* [2000].

[c] *Etiope et al.* [2002].

gas chromatography (Carle AGC 100–400 TCD-FID GC; detection limit: CO_2, N_2, Ar, O_2: 40 ppmv; He and HC: 10 ppmv; accuracy 2%; 10% at the detection limit) and mass spectrometry (Finnigan Delta Plus XL; accuracy ±0.1 per mil on ^{13}C and ±2 per mil on ^{2}H) at Isotech Labs Inc. (Illinois, USA).

[7] Methane output was evaluated from macroseeps (MV craters and gryphons, bubbling pools and dry vents), from the surrounding microseepage and far from macro-seep zones. Measurements were made at 10 analysed macro-seeps plus other 4 smaller and weaker seeps in central Italy (a–d in Table 2). Output of the bubbling gases was measured by means of a stainless-steel funnel connected to a overturnable bottle of known volume and counting the time required to displace water out. Gas flux in those vents not accessible for direct measurement was estimated using a calibrated plot of bubble flux vs. bubble size vs. bubble frequency [*Etiope et al.*, 2004a]. Gas flux from Miano well-seep was assessed by a wet-test (drum type) gas flow meter (Ritter®). Gas output from weaker vents and soil microseepage was measured by closed-chamber method [*Etiope et al.*, 2004a]. Gas accumulated in the chamber was analyzed by gas chromatography with Flame Ionization Detector (Autofim II, Telegan; detection limit 0.1 ppm, accuracy 4–5%). In 2006 microseepage measurements were also performed by directly connecting the chamber on line with a portable solid state CH_4 detector (METREX 2, Huberg; detection limit 5 ppmv, accuracy 10%). Far from macro-seeps, a regional scale microseepage survey (76 points homogeneously distributed throughout 9000 km^2; Figure 1) was made along the whole gas/oil field zone from the central Adriatic coast to the northern Apenninic margin, (data of the central Adriatic sector are reported by *Etiope and Klusman* [2007]). Total gas emission was computed summing up macro-seep and microseepage outputs following the up-scaling and emission factor calculation procedures recommended by the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook [*Etiope et al.*, 2007].

4. Results and Discussion

4.1. Gas Origin and Fractionation

[8] Table 1 lists the compositional and isotopic data of sampled gas, including 3 literature data. All seeps, as expected, are CH_4-dominated and show typical compositions of natural gas. Monte Busca dry-seep shows the highest N_2 and He concentrations (38% and 0.16%), which are comparable to analyses performed in 1998 (36% and 0.27%) [*Minissale et al.*, 2000]. The highest ethane and propane concentration (with $C_2 + C_3 > 4\%$) was found in the ‘‘dry’’ Dragone MV, coherently with the previous analysis performed 8 years before.

[9] The diagrams traditionally used to assess methane origin, i.e. $\delta^{13}C_{CH4}$ vs δD_{CH4} [*Schoell*, 1983] and $\delta^{13}C_{CH4}$ vs $C_1/(C_2 + C_3)$ [*Bernard et al.*, 1978] are reported in Figure 2. The ‘‘Schoell’’ diagram shows that all seeps occurring along the Chain (within the orographic front) are thermogenic, except Malvizza and Dragone which are mixed; some MVs however fall in an ambiguous sector of the ‘‘Bernard’’ diagram, which could suggest alteration due to secondary post-genetic processes, such as oxidation of biogenic gas or molecular separation during migration. Only two MVs (Bergullo and Pineto) display a gas which is clearly biogenic. All dry seeps along the Chain are unequivocally thermogenic. In both diagrams, we have compared the seep gas with the corresponding reservoir gas, represented by thermogenic Apenninic and biogenic Po Plain fields (Figure 2) [*Mattavelli and Novelli*, 1988]. Whereas the dry-seeps maintain the thermogenic signature of the Apenninic gas, all MVs, except the two mixed, are shifted towards higher $C_1/(C_2 + C_3)$ ratios, falling also outside the thermogenic field. A specific comparison is shown (Figure 2a), as an example, for Ospitaletto MV, whose reservoir has a higher ethane + propane concentration

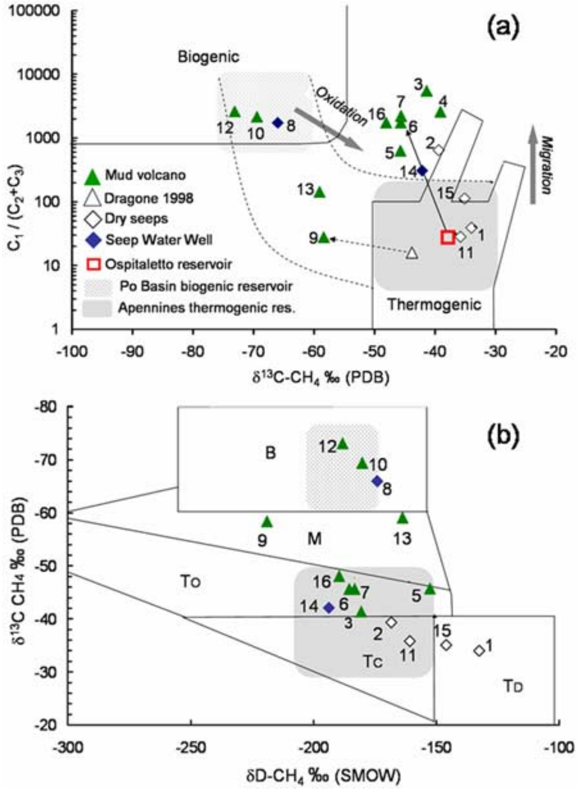

Figure 2. (a) Carbon isotope vs. alkanes ratio [*Bernard et al.*, 1978]. Two mixing lines are plotted by assuming microbial Po Plain end-members ($\delta^{13}C = -76$ to -60‰, $C_1/(C_2 + C_3) = 600$ to 10000), and Apenninic thermogenic end-members ($\delta^{13}C = -50$ to 30‰, $C_1/(C_2 + C_3) = 4$ to 200). Arrow shows the molecular fractionation in the Ospitaletto MV. Dashed arrow shows the isotopic shift of Dragone MV from 1998 to 2006. (b) Carbon and hydrogen isotope diagram [*Schoell*, 1983]. B: biogenic gas; M: mixed; To: thermogenic with oil; Tc: thermogenic with condensate; T_D: dry thermogenic. Biogenic and thermogenic fields are from *Mattavelli and Novelli* [1988]; Ospitaletto reservoir is from borehole data from *Borgia et al.* [1988].

[*Borgia et al.*, 1988]. It suggests that a molecular fractionation occurred in MV gas. Overall, no significant isotopic fractionation is observed. Basically the difference between "dry" seepage (only gas phase) and the typical MV seepage (gas + water + mud) is clear. Such a fractionation cannot be explained only by diffusion, which is important in the early gas migration from source rock to reservoir and between multi-level reservoirs [*Schoell*, 1983; *Prinzhofer and Battani*, 2003], because the seep is rather the result of a rapid ascent of gas by two-phase advection driven by pressure and density gradients (microbubbles, bubbles and slugs) [*Etiope and Martinelli*, 2002]. Advective separation of alkanes was observed also in the Trinidad mud volcanoes, where the dryness of the gas was interpreted as due to a segregation process during migration to the surface related to differential adsorption on the solid grains of the mud, and solubility processes [*Deville et al.*, 2003]. Similarly, petroleum seepage studies observed a "chromatographic effect" of lower concentrations of higher molecular weight hydrocarbons as the distance from reservoir increases [*Price*, 1986].

[10] We also observe that molecular fractionation seems to be inversely correlated with the gas flux, as shown in Figure 3: the higher the flux, the higher the velocity, the lower the time available for gas-water-mud interaction, the lower the fractionation. Consistently, the "Bernard" parameter should be lower during MV eruptions, as shown by Regnano MV in 1998 (Figure 3). The same phenomenon was observed in Trinidad where the C2+ concentration was higher in the MVs with more recent eruptions [*Deville et al.*, 2003]. In dry-seeps the gas ascent mechanism (mainly one-phase system) is not perturbed by water or mud. Accordingly, the $C_1/(C_2 + C_3)$ "Bernard" ratio cannot be a reliable diagnostic parameter for the origin of MV gas. Dragone appeared to be the most thermogenic MV in 1998, when its activity was much more vigorous; in 2006 it shifted towards the mixing trend (Figure 2a). It is likely, therefore, that the decrease of fluid pressures implied a reduction of the deeper (heavier CH_4) component against a relative increase of shallow biogenic components.

4.2. Methane Flux

[11] Table 2 summarises methane flux from macro-seeps and surrounding microseepage. Flux from individual MV vents (gryphons, bubbling pools) may reach 1–2 t y^{-1}. A significant microseepage exists around the vents, in the order of 10^3–10^6 mg m^{-2} d^{-1}. The two biggest MVs in northern Italy, Regnano and Nirano, emit at least 34 and 32 t y^{-1}, respectively. The biggest MV of Italy, Maccalube, emit about 400 t y^{-1} [*Etiope et al.*, 2002]. For all MVs the specific flux (total output divided by area) is in the order of 10^2–10^3 t km^{-2} y^{-1}. Dry-seeps have a higher specific flux, up to 10^5–10^6 t km^{-2} y^{-1}. The very high flux of seep-wells should be considered "artificial", due to the gas channelling along the borehole, so it cannot be compared to other seeps. The total flux induced by macroseepage is above 3000 t y^{-1}.

[12] The regional-scale microseepage survey detected positive methane flux from soil in 39% of the sites, 31% in the range 1–50 mg $m^{-2}d^{-1}$ (mean 10) and 8%, closer to

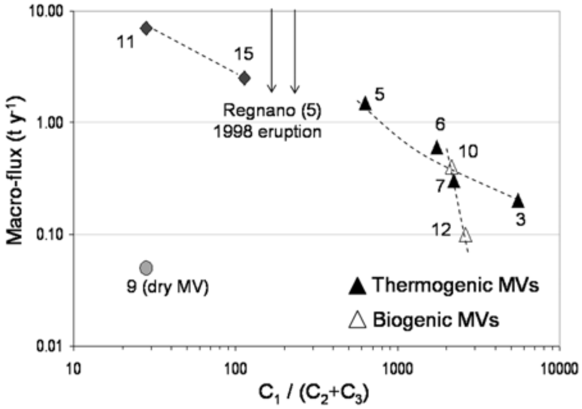

Figure 3. Alkane composition vs macro-seep flux of the analysed vent. Vertical arrows show the "Bernard" parameter values of two Regnano samples during an eruption in 1998 [*Capozzi and Picotti*, 2002]. Numbers of sites are those in Table 1.

the gas-oil fields, from 50 to 200 mg $m^{-2}d^{-1}$ (mean 80). Application of the two emission factor averages for the respective areas gives a total emission in the order of 30000 t y^{-1}. In Italy the potentially microseepage area, i.e. the area of the so-called Total Petroleum Systems, is about 150000 km^2; so the actual emission of geologic methane into the atmosphere from the entire hydrocarbon-prone area of Italy could reach levels of the order of 10^5 t y^{-1}. For comparison, national anthropogenic sources due to fossil fuel industry and distribution emit 214 kt CH_4 y^{-1} (GAINS model) [*Höglund-Isaksson and Mechler*, 2005].

5. Conclusions

[13] About 80% of the active seeps in Italy release thermogenic methane, produced in deep reservoirs along the Apenninic sector; most of these reservoirs, and related cap rocks, are therefore crossed by active and permeable faults. Biogenic reservoirs are more preserved being less affected by brittle tectonics. Whereas dry seeps maintain the reservoir $C_1/(C_2 + C_3)$ ratio, mud volcano gas is generally fractionated, lighter than reservoir. Accordingly, conventional diagrams based on the "Bernard" ratio [$\delta^{13}C_{CH4}$ vs $C_1/(C_2 + C_3)$], when applied to mud volcanoes, must be interpreted with caution.

[14] Most MVs today have a weaker gas flux than in the past and much lower than that stemming from the bigger MVs of Romania or Azerbaijan. However, due to the intense microseepage surrounding the vents, the specific methane flux into the atmosphere is still in the order of 10^2–10^3 t km^{-2} y^{-1}, which is the same range shown by all MVs investigated so far [*Etiope et al.*, 2002, 2004a, 2004b]. On a regional scale, microseepage independent from macroseeps is the main geologic CH_4 source. This work, like those performed in other MV and seep zones (e.g., Azerbaijan, Romania) [*Etiope et al.*, 2004a, 2004b] showed in fact that microseepage exists at low levels (units or tens of mg m^{-2} d^{-1}) throughout vast zones of the petroliferous basins, independently from the occurrence of macro-seeps. In total, CH_4 emission into the atmosphere from the hydrocarbon-prone areas can be one order of magnitude above the natural emission from geothermal areas [*Etiope et al.*, 2007], and it could have the same order of magnitude of national anthropogenic sources related to fossil fuel industry. Microseepage surveys in other petroliferous zones are needed to refine the total emission estimate.

[15] **Acknowledgments.** Thanks are due to two anonymous reviewers for helpful comments, and to A. Dadomo for support in the field survey. The work was funded by INGV-DPC (Dipartimento per la Protezione Civile), V5 Project.

References

Abrams, M. A. (2005), Significance of hydrocarbon seepage relative to petroleum generation and entrapment, *Mar. Pet. Geol.*, *22*, 457–477.

Bernard, B. B., J. M. Brooks, and W. M. Sackett (1978), Light hydrocarbons in recent Texas continental shelf and slope sediments, *J. Geophys. Res.*, *83*, 4053–4061.

Borgia, G. C., C. Elmi, and T. Ricchiuto (1988), Correlation of genetic properties of the shallow gas seepages in the Emilian Apennine (northern Italy), *Adv. Org. Geochem.*, *13*, 319–324.

Capozzi, R., and V. Picotti (2002), Fluid migration and origin of a mud volcano in the northern Apennines (Italy): The role of deeply rooted normal faults, *Terra Nova*, *14*, 363–370.

Deville, E., A. Battani, R. Griboulard, S. H. Guerlais, J. P. Herbin, J. P. Houzay, C. Muller, and A. Prinzhofer (2003), Mud volcanism origin and processes. New insights from Trinidad and the Barbados Prism, in *Surface Sediment Mobilization*, edited by P. Van Rensbergen et al., *Spec. Publ. Geol. Soc. London*, *216*, 475–490.

Eni (2004), *World Oil and Gas Review*, 209 pp., Rome.

Etiope, G. (2004), GEM—Geologic emissions of methane, the missing source in the atmospheric methane budget, *Atmos. Environ.*, *38*(19), 3099–3100.

Etiope, G., and R. W. Klusman (2007), Microseepage in drylands: Flux and implications in the global atmospheric source/sink budget of methane, *Global Planet. Change*, in press.

Etiope, G., and G. Martinelli (2002), Migration of carrier and trace gases in the geosphere: An overview, *Phys. Earth Planet. Inter.*, *129*(3–4), 185–204.

Etiope, G., A. Caracausi, R. Favara, F. Italiano, and C. Baciu (2002), Methane emission from the mud volcanoes of Sicily (Italy), *Geophys. Res. Lett.*, *29*(8), 1215, doi:10.1029/2001GL014340.

Etiope, G., C. Baciu, A. Caracausi, F. Italiano, and C. Cosma (2004a), Gas flux to the atmosphere from mud volcanoes in eastern Romania, *Terra Nova*, *16*, 179–184.

Etiope, G., A. Feyzullaiev, C. Baciu, and A. V. Milkov (2004b), Methane emission from mud volcanoes in eastern Azerbaijan, *Geology*, *32*(6), 465–468.

Etiope, G., T. Fridriksson, F. Italiano, W. Winiwarter, and J. Theloke (2007), Natural emmissions of methane from geothermal and volcanic sources in Europe, *J. Volcanol. Geotherm. Res.*, doi:10.1016/j.jvolgeores.2007.04.014, in press.

Grassa, F., G. Capasso, R. Favara, S. Inguaggiato, E. Faber, and M. Valenza (2004), Molecular and isotopic composition of free hydrocarbon gases from Sicily, Italy, *Geophys. Res. Lett.*, *31*, L06607, doi:10.1029/2003GL019362.

Höglund-Isaksson, L., and R. Mechler (2005), The GAINS model for greenhouse gases—Version 1.0: Methane (CH_4), *Interim Rep. IR-05-054*, Int. Inst. for Appl. Syst. Anal., 82 pp., Laxenburg, Austria.

Italiano, F., M. Martelli, G. Martinelli, and P. M. Nuccio (2000), Geochemical evidence of melt intrusions along lithospheric faults of the southern Apennines, Italy: Geodynamic and seismogenic implications, *J. Geophys. Res.*, *105*, 13,569–13,578.

Link, W. K. (1952), Significance of oil and gas seeps in world oil exploration, *Am. Assoc. Pet. Geol. Bull.*, *36*, 1505–1540.

Martinelli, G., and A. Judd (2004), Mud volcanoes of Italy, *Geol. J.*, *39*, 49–61.

Martinis, B. (1962), Manifestazioni petrolifere, in *Enciclopedia del Petrolio e del Gas Naturale*, edited by C. Colombo, pp. 1251–1265, Eni, Rome.

Mattavelli, L., and L. Novelli (1988), Geochemistry and habitat of natural gases in Italy, *Org. Geochem.*, *13*, 1–13.

Minissale, A., G. Magro, G. Martinelli, O. Vaselli, and G. F. Tassi (2000), Fluid geochemical transect in the northern Apennines (central-northern Italy): Fluid genesis and migration and tectonic implications, *Tectonophysics*, *319*, 199–222.

Price, L. C. (1986), A critical overview and proposed working model of surface geochemical exploration, in *Unconventional Methods in Exploration for Petroleum and Natural Gas IV*, edited by M. J. Davidson, pp. 245–309, SMU Press, Dallas, Tex.

Prinzhofer, A., and A. Battani (2003), Gas isotopes tracing: An important tool for hydrocarbon exploration, *Oil Gas Sci. Technol.*, *58*(2), 299–311.

Schoell, M. (1983), Genetic characterization of natural gases, *Am. Assoc. Pet. Geol. Bull.*, *67*, 2225–2238.

A. Caracausi and F. Italiano, Section of Palermo, Istituto Nazionale di Geofisica e Vulcanologia, via Ugo La Malfa 153, I-90146 Palermo, Italy.

G. Etiope, Section of Roma 2, Istituto Nazionale di Geofisica e Vulcanologia, via Vigna Murate 605, I-00143 Rome, Italy. (etiope@ingv.it)

G. Martinelli, Environmental Protection Agency of the Emilia Romagna Region, Via Po 5, I-40139 Bologna, Italy.