

RESEARCH ARTICLE

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Key Points:

- Anomalous high soil temperatures were measured at the Terre Calde di Medolla
- A CO₂ and CH₄ isotopic decoupling was observed at 0.6 m depth
- Exothermic, oxidative CH₄ removal is the main mechanism of soil heating at TCM

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Ground heating and methane oxidation processes at shallow depth in Terre Calde di Medolla (Italy): Observations and conceptual model

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Abstract The toponym “Terre Calde di Medolla” (literally, “Warm Earths of Medolla”) refers to a farming area, located near the town of Modena (Emilia-Romagna region, northern Italy), which has always been known by the local population for the relatively high temperatures of the soil. This phenomenon is particularly evident in wintertime when the snow cover over this area rapidly melts. A detailed investigation, carried out after the devastating 2012 Emilia earthquake that affected this area, showed soil temperatures up to 44°C, i.e., 20–25°C above the local background value, together with diffuse soil fluxes of CH₄ (0–2432 g × m⁻² × d⁻¹) and minor, though significant, CO₂ (0–1184 g × m⁻² × d⁻¹), especially from subcircular (a few meters in diameter) zones. Ground heating and gas seepage appear spatially correlated, thus suggesting a close relationship between the two phenomena. The anomalous high ground temperature is not associated with an anomalous geothermal gradient or with the uprising of deep-seated hot fluids. According to the lateral and vertical distributions of the temperatures as well as the chemical and isotopic compositions of the soil gases, the most reliable explanation is the exothermic oxidation of diffusely uprising biogenic methane at very shallow levels (<1 m). Such a process occurs in the presence of free oxygen and methanotrophic bacteria and can then explain (i) the observed ground heating up, (ii) the diffuse emission from the soil of CO₂ characterized by an extremely negative isotopic (¹³C/¹²C) signature, and (iii) the lack of diffuse and low CH₄ fluxes. According to these hypotheses, the heating phenomena affecting the shallow groundwater and the ground surface, as described by several witnesses in the area of the May–June 2012 Emilia earthquake, could be related to either a coseismic or postseismic onset of new areas affected by CH₄ seepage or an increase in preexisting CH₄ fluxes.

1. Introduction

Methane, in spite of its relatively low, though growing, concentration in air (about 1800 ppbv [Kirschke et al., 2013, and references therein]), poses a severe environmental concern, since its global warming potential is 25 CO₂-eq in a 100 year time horizon [Cicerone and Oremland, 1988; Hansen et al., 1998]. The origin of CH₄ in the atmosphere is related to different anthropogenic (e.g., rice paddies, livestock farms, biomass burning, oil and gas mining, and waste disposal) and natural (e.g., wetlands, termites, oceans, freshwaters, and seepage from deep reservoirs in both sedimentary and volcanic environments) sources. Gas seepage from geological sources has traditionally not been considered important [Lelieveld et al., 1998]. Nevertheless, sedimentary basins account for 90% [Etiopie and Klusman, 2002] of the total geogenic CH₄, while those associated with geothermal and volcanic sources are less than 10% [Etiopie et al., 2007]. In faulted areas, CH₄ diffuse seepage from the ground may reach hundreds of mg × m⁻² × d⁻¹ [Etiopie, 2009], preventing biogeochemical oxidation processes in the soil to completely consume this gas uprising from depth.

The “Terre Calde di Medolla” (literally, the Warm Earths of Medolla, hereafter TCM) is a toponym used in a farming area of less than 1 km² located close to Medolla (Figures 1a–1c), a small municipality in the Province of Modena (approximately 45 km NW of Bologna, northern Italy). In this area, the occurrence of several small subcircular (<10 m in diameter) zones, characterized by anomalously high ground temperature (“warm Earth”) and clearly noticeable during wintertime as the snow cover quickly melts, has been known at least since the late nineteenth century [Spinelli, 1893; Spinelli and Cuoghi Costantini, 1893;

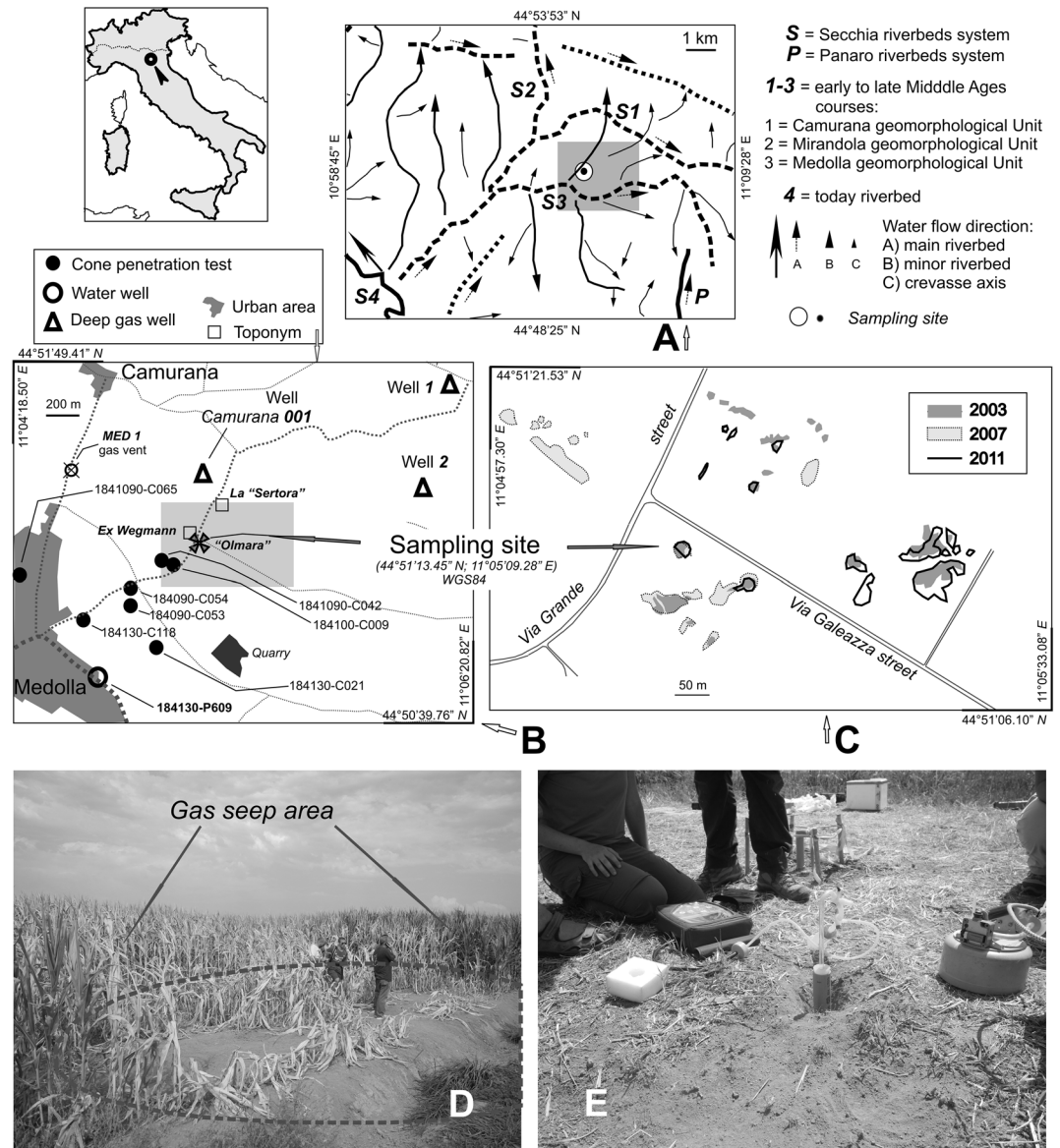


Figure 1. Locational settings of the study area. (a) Paleoriverbeds of the Secchia River in the Medolla area. (b) Location of the various boreholes and CPTs used to draw the stratigraphic log of Figure 2b: the numerical codes are referring to that figure. The location of the MED 1 gas emission is reported. (c) Planform of the vegetation anomalies due to the natural gas seep around the sampling site: The boundaries were outlined from satellite imagery (Google©) at various years after 2007. (d) The aspect of the sampled main gas seep site: The seeping area extends beyond the agrarian ditch on the lower right corner. (e) Gas sampling phase at the study site.

Gasperi and Pellegrini, 1981). Anomalous and occasionally abrupt temperature increases (up to 50–60°C) have also been reported to repeatedly occur in the shallow groundwater, such as recorded after the May–June 2012 Emilia seismic sequence that caused 27 fatalities and strong damages to residential dwellings, infrastructures, and local economy [e.g., Anzidei et al., 2012; Govoni et al., 2014]. The TCM area shows macroseeps; e.g., mud volcanoes [e.g., Tassi et al., 2012, and references therein]; microseepage, i.e., anomalously high soil CH₄ and, at a lesser extent, CO₂ fluxes [Sciarra et al., 2012, 2013]; and fossil wax (ozocherite) [Spinelli, 1893; Spinelli and Cuoghi Costantini, 1893]. The presence of these manifestations (Figure 1c) at the surface seriously affects the growth of some cultivated areas (Indian corn; Figure 1d). According to the description reported by Spinelli [1893] and Spinelli and Cuoghi Costantini [1893], the location of these gas seepages has remained relatively stable at least over the past 120 years.

The peculiar features of TCM, described and discussed in the present paper, represent an outstanding association between gas microseepage and soil heating, allowing us to (i) evaluate the amount of CH₄ released from this site, (ii) assess the geochemical relationships between CH₄ and CO₂, and (iii) understand the processes that favor the presence of anomalous temperature at the surface.

2. Geological Background

2.1. Geomorphological Setting

TCM is located (World Geodetic System 84: 44°51'13.45"N, 11°05'09.28"E) in the middle of the Po River plain (Figure 1), at an elevation of 21 m above sea level. It lies at the intersection of a number of alluvial ridges generated by the Secchia River paleochannels (Figure 1a). The whole domain of the Secchia alluvial ridges progressively covered the anabranching Po River alluvial plain [Cremonini, 2007; Bianchini *et al.*, 2014], which is characterized by sandy paleomeanders still out cropping a few kilometers northward.

2.2. Structural Setting

The northern Apennine orogenic front (Figure 2a) is composed of two geographic domains, i.e., an emerged (Apennine Chain in a strict sense) and outermost (*Dorsale Ferrarese*) part, buried beneath the Po River alluvial plain, located at about 50 km northward from the foothill chain [Consiglio Nazionale delle Ricerche (CNR), 1990; Cerrina Feroni *et al.*, 2002; Boccaletti and Martelli, 2004]. In particular, the *Cavone-Mirandola* thrust (Figure 2d) was the first anticline structure of the buried front to be generated in the outermost domain [Ghielmi *et al.*, 2010]. The double chain front is likely still active in response to the general compressive stress field [Michetti *et al.*, 2012] dating from the middle Pleistocene. This buried front is still undergoing a synsedimentary growth according to a decreasing rate of the tectonic uplift from 0.53 to 0.16 mm/yr during the last 1.4 Myr [Scrocca *et al.*, 2007; Picotti and Pazzaglia, 2008]. Owing to this growth, the top of the buried *Dorsale Ferrarese* tectonic folds in the area near Medolla and Mirandola, as well as near Ferrara (Figure 2a), lies at a very shallow depth beneath the alluvial plain, often less than 100 m [CNR, 1990].

The up-to-date activity of this sector of the buried Apennine front was confirmed by the May 2012 Emilia seismic sequence [Galli *et al.*, 2012; Ventura and Di Giovambattista, 2013; Cesca *et al.*, 2013]. During this seismic sequence, the vertical component of the deformation attained a relative maximum (112 mm) at the study site [Borgatti *et al.*, 2012; Galli *et al.*, 2012].

The schematic cross section in Figure 2d [International Commission on Hydrocarbon Exploration and Seismicity in the Emilia Region (ICHESE), 2014] intimately resembles the geological setting of the *Cavone-Mirandola* structural high [Nardon *et al.*, 1991; Carminati *et al.*, 2010].

2.3. Stratigraphic Setting

The stratigraphic details recorded in the surficial domain (Figure 3a) consist of proximal to median crevasse deposits related to the main paleo-Secchia *Unit of Medolla* and its younger geomorphologic subunits. The homogeneous grey-greenish color of the superficial layers is to be considered as a specific feature of the study area from where gas seepage occurs.

A medium-depth stratigraphic sequence (Figure 3b) has been obtained by merging stratigraphic data available within 1 km distance of the investigated area (Figure 1b). The prominent feature is the existence of two sandy river-channel facies, which can be referred to the Po riverbed due to both their thickness (14 m) and homogeneity. According to available data in the surrounding areas [Cremonini, 1993; Amorosi *et al.*, 2008], the whole sequence likely represents the entire Last Glacial period (Weichselian/Würmian: oxygen isotope stages (OISs) 2–5) up to a depth of 60 m. According to the stratigraphic model proposed by Amorosi and Colalongo [2005], the peaty clay layer lying at 61 m depth (Figure 3c) represents the most internal transgressive system tract deposits correlated with the maximum flooding surface of the Last Interglacial period (Eemian: OIS 5e). This would confirm its location as far as more than 60 km westward with respect to the homologue Holocene facies [Amorosi *et al.*, 2000]. The 33 m thick bank of sandy clay at 79–113 m in depth is the upper middle Pleistocene slope-shelfal-coastal deposit of the *Ravenna Formation* (*Prograding Complex*, after Ghielmi *et al.* [2010]). The lowermost 10 m of stiff clayey sequence can be regarded as the upper, eroded top of the marine Pliocene *Porto Garibaldi* Formation [Dondi *et al.*, 1982;

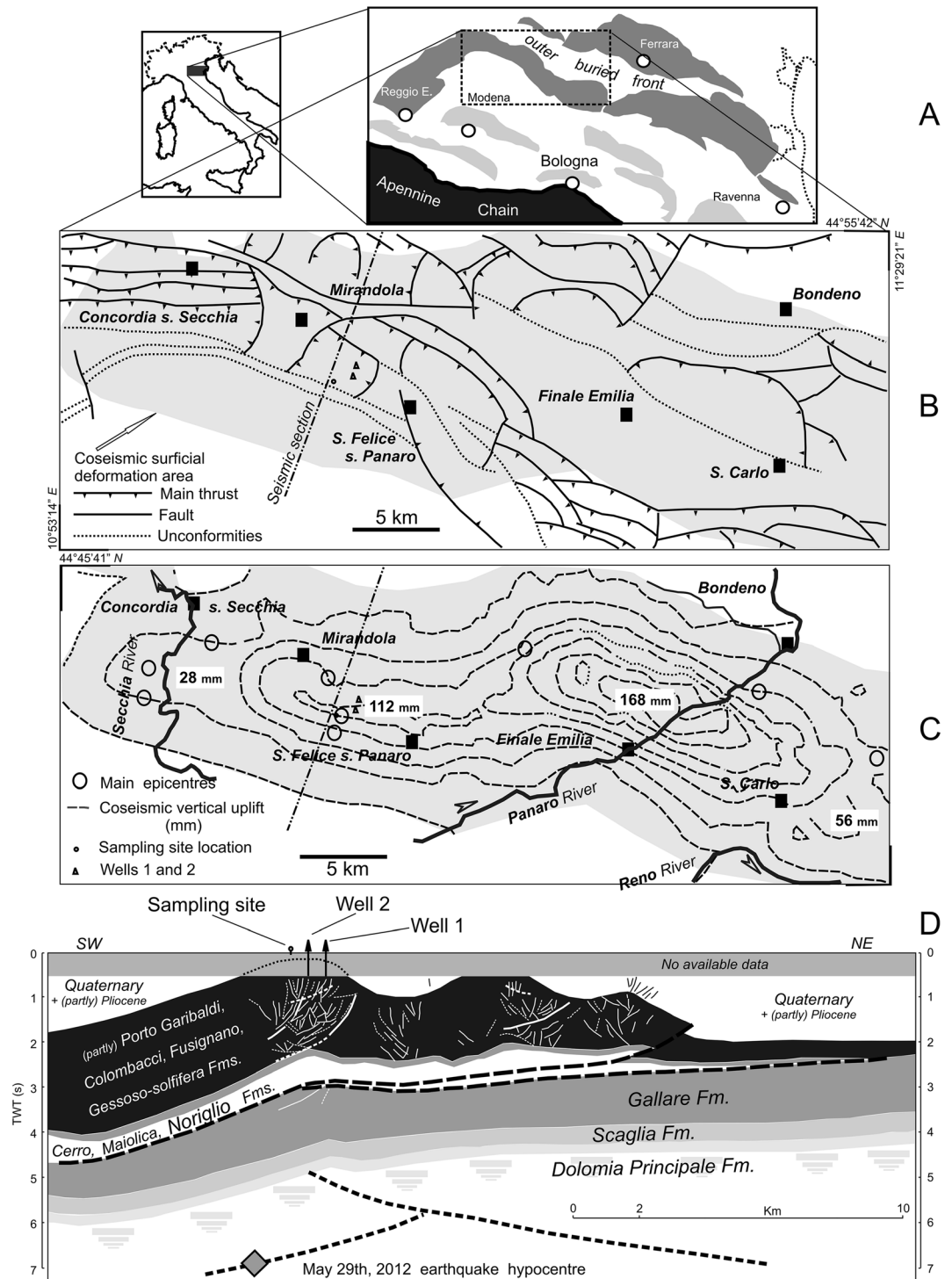


Figure 2. General tectonic setting of the Medolla area. (a) Main thrusts top of the buried Apennine Chain front (*Dorsale Ferrarese* and *Pieghe Romagnole*) and the emerged chain front in the Emilia Po Plain sector. (b) Detail of the *Dorsale Ferrarese* tectonic structures in the epicentral area of the 2012 May seismic sequence: The surficial deformation area is in grey tone (as in Figure 2c). The location of Well 1 and Well 2 of Figure 3 (black triangle) and of the sampling site (black circle) is also shown. (c) Total uplift of the May 2012 earthquake in the epicentral area (after *Borgatti et al. [2012]*, redrawn) and main shock epicenter location. (d) Interpretation of the seismic line MOD-74-19 (after *ICHESE [2014]*, Figure 7m: redrawn and modified). The projected location of Wells 1 and 2 was derived from Figure 1b. Possible minor faults (mainly, the white lines) are proposed.

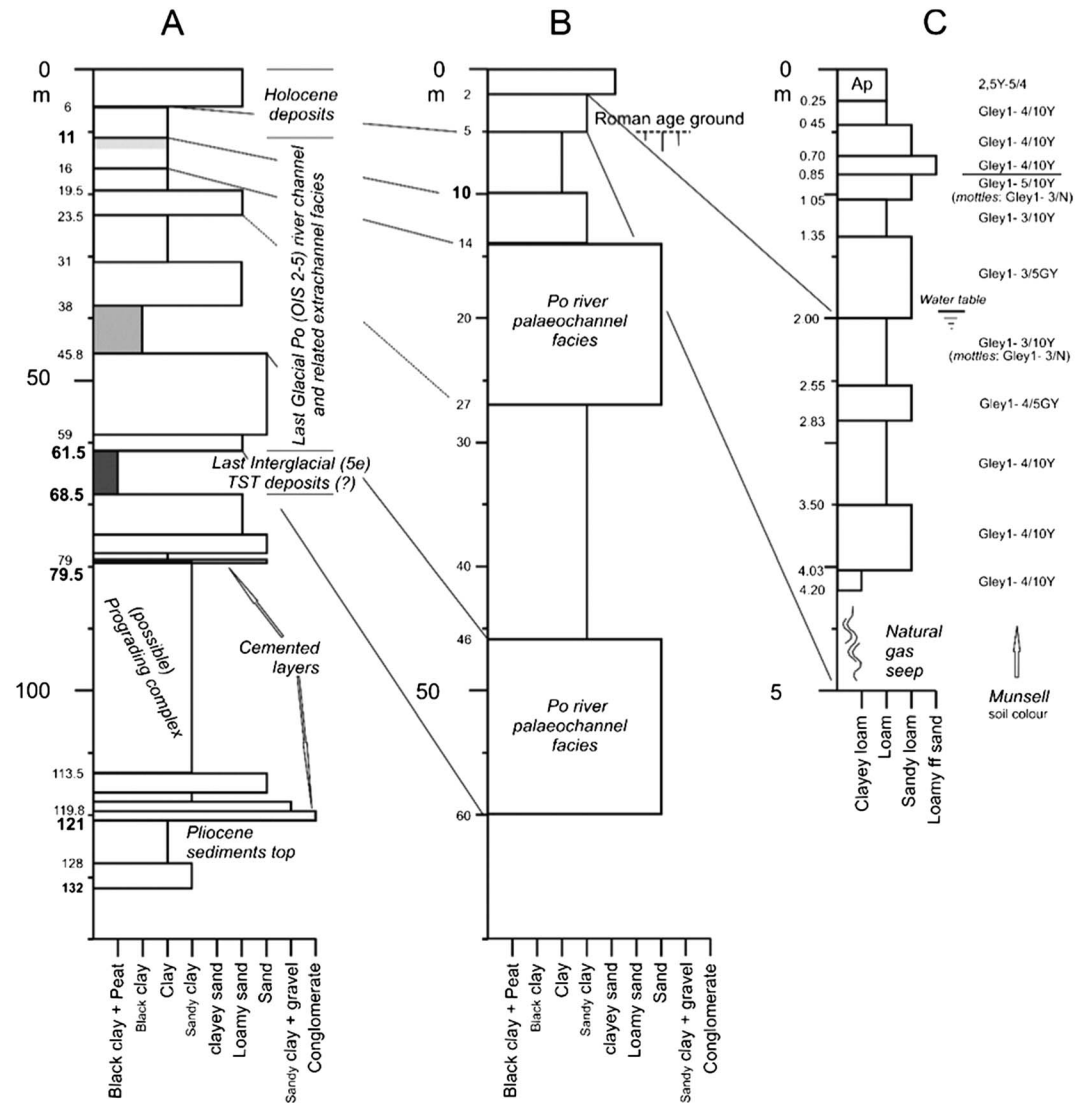


Figure 3. Stratigraphic logs at various depth scales available for the study site area. (a) Textural log from the handmade borehole used for sampling the natural gas seep: The Munsell soil color codes are also provided on the right. (b) Cumulative medium-depth stratigraphic log reconstructed from eight different points available near the sampling site. The single-log original codes (available at the same website of Figure 3a) are listed in Figure 1b. (c) Log of the well Region ER. 184130-P609 redrawn and simplified (available online at https://applicazioni.regione.emilia-romagna.it/cartografia_sgss/user/viewer.jsp?service=sezioni_geo).

Barchi et al., 2001; Fantoni and Franciosi, 2010; Ghielmi et al., 2010]. Well 1 (Figure 4) indeed shows a very thin layer (only 220 m) of Pliocene sediments due to the tectonic uplift of the *Dorsale Ferrarese* thrust system. The tectonic factor is further stressed by the existence of three to four reverse fault planes lying between 2000 and 2700 m (Figure 4). They are horizontal and consistent with the intense faulting linked to the tectonic thrust setting shown in Figure 2d. Brackish/salt water and CH₄-rich gas are mainly concentrated below the main fault planes, while no gas pockets or anomalous gas enrichments were recorded above them. The Well *Camurana 001* (Figure 1b), drilled 600 m north of the sampling point in 1943 and exploited for about 1 year, recorded a strong gas flow at 741–742 m and gas and slight mineral oil at 904–906 m in depth (<http://unmig.sviluppoeconomico.gov.it/vidempi/pozzi/consultabili.asp>). Furthermore, between 964 and 1113 m, the shale was described as “splintery (and) highly broken and slickensided,” thus suggesting the possible existence of a noticeable subvertical fault plane, as shown in Figure 2d.

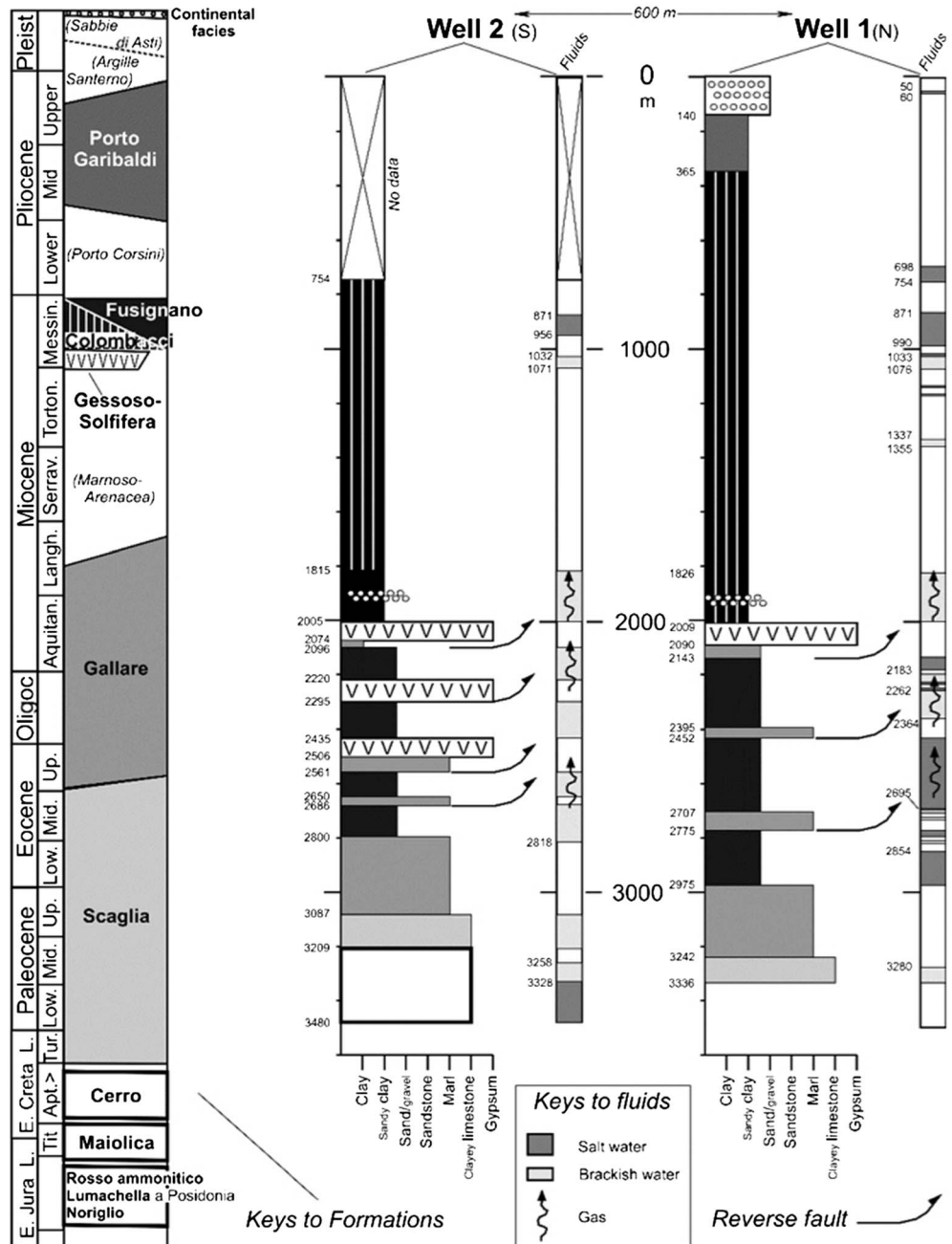


Figure 4. Stratigraphic log of two wells located 1.5 km NE of the study site. Each column was redrawn and simplified: The log Well 1 is available online at the website http://unmig.sviluppoeconomico.gov.it/deposito/pozzi/log/pdf/bignardi_001.pdf; the log Well 2 is available online at the website: http://unmig.sviluppoeconomico.gov.it/deposito/pozzi/log/pdf/bignardi_001_dir_bis.pdf. The first column on the left is the general stratigraphic scheme for the central Po River plain subsoil [Dondi et al., 1982] adopted for defining the formation names adopted in the well's log: The formation names in brackets are lacking in the studied area.

3. Materials and Methods

Diffuse CO₂ and CH₄ soil fluxes (microseepage) were measured in the TCM area in July 2008 (50 sites) and July 2013 (138 sites). During these two field campaigns, an area of ~260,000 m² was investigated. Gas flux measurements were based on the accumulation chamber "time 0" method [Norman et al., 1992, 1997; Chiodini et al., 1996, 1998, 2000; Rogie et al., 2000; Brombach et al., 2001; Cardellini et al., 2003]. The instrument used was a West System™ portable flux meter, equipped with two infrared spectrophotometer

detectors: (i) Licor 8002 for CO₂ and (ii) tunable laser diode with multipass cell for CH₄. During the 2013 campaign at the same sites, soil temperatures were also recorded at 10 cm depth with a digital thermometer equipped with a 20 cm long PT100 thermocouple.

A 2.5 m deep piezometer was drilled in the SW sector of the investigated area (Figures 1c and 1e), where an anomalously high CO₂ soil flux was measured (up to $103.4 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$). During drilling, soil temperatures, CH₄, and CO₂ fluxes as well as collection of gas samples for chemical and isotopic analyses were determined at intervals of 10 cm up to 80 cm depth and at intervals of 50 cm at greater depth. Flux measurements and collection of gas samples were carried out once a plastic tube (4.2 cm in diameter) was positioned in the hole and the internal volume was purged for 2'. A certain degree of uncertainty (± 5 cm, i.e., the length of the core barrel) affected the attribution to a specific depth of the flux measurements and gas collection. In October 2014, a gas sample (MED 1) with very high gas flux was measured and collected 1 km west of the TCM site. This new emission suddenly appeared during a CPT (cone penetration test) in an area where spontaneous gas seepages and phenomena of surface heating were not previously recorded.

Gas sampling was carried out using a preevacuated 150 mL flask, for both chemical and isotopic ($\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$) analyses. Inorganic gases and CH₄ were analyzed with a Shimadzu 15A gas chromatographic system equipped with a 9 m long molecular sieve column and thermal conductivity detector. The analytical error was <5%.

The $^{13}\text{C}/^{12}\text{C-CO}_2$ values (expressed as $\delta^{13}\text{C-CO}_2$ Vienna Pee Dee Belemnite (VPDB) ‰) were analyzed by mass spectrometry (Finnigan Delta S), after a two-step extraction and purification procedures of the gas mixtures by using liquid N₂ and a solid-liquid mixture of liquid N₂ and trichloroethylene. Internal (Carrara and San Vincenzo marbles) and international (National Bureau of Standards (NBS) 18 and NBS 19) standards were used to estimate external precision. The analytical uncertainty and the reproducibility were $\pm 0.05\text{‰}$ and $\pm 0.1\text{‰}$, respectively. The $^{13}\text{C}/^{12}\text{C-CH}_4$ values (expressed as $\delta^{13}\text{C-CH}_4$ VPDB ‰) were determined by mass spectrometry (Varian MAT 250) at International Organization for Standardization 4 laboratories according to the procedure reported by *Stump and Frazer* [1973] and *Schoell* [1980]. The analytical uncertainty was $\pm 0.15\text{‰}$.

4. Results

4.1. Microseepage of CH₄ and CO₂

Preliminary data analysis involved the calculation of standard statistical parameters to evaluate the basic features of the CH₄ and CO₂ flux data. Due to their lognormal distribution, the experimental data were rearranged by logarithmic transformation of the original emission rate. The CH₄ and CO₂ soil flux thematic maps were built by using the kriging interpolation method [e.g., *Bergfeld et al.*, 2001], and for this stochastic simulation, a Gaussian model was derived from the empirical semivariogram. Each estimated logarithm value was then backtransformed in computer worksheet format by extracting the emission rate estimated for each grid point. After identifying threshold values, the total emission rate was calculated according to the method suggested by *Chiodini and Frondini* [2001]. The threshold values were defined by using the graphic method of *Sinclair* [1991]. The normal probability plots defined two populations for CO₂ (Figure 5a) and three for CH₄ (Figure 5b) fluxes. The intersection points allowed recognition of the threshold values (10 and $30 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$, for CH₄ and CO₂, respectively) used for the calculation of the emission rates.

Descriptive statistical parameters and outputs ($\text{t} \times \text{d}^{-1}$) of the CO₂ and CH₄ emission rates (in $\text{g} \times \text{m}^{-2} \times \text{d}^{-1}$) measured in 2008 and 2013 and soil temperatures (measured at 77 sites in 2013) are reported in Table 1. Maps with the statistical interpolations of the CO₂ and CH₄ soil fluxes measured in 2008 and 2013 and temperatures measured in 2013 are reported in Figures 6a–6d and Figure 7.

In 2008, the CO₂ flux ranged from 0 to $139 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$ with a mean value of $25.1 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$, whereas those of CH₄ were from 0 to $51.8 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$ with a mean value of $6.6 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$. The anomalously high CO₂ and CH₄ fluxes (>30 and $>10 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$, respectively) were measured in two small ($<23,000 \text{ m}^2$) sites located in the southwestern border of the study area (Figures 6a and 6b). In 2013, about 1 year after the May–June 2012 seismic event, the CO₂ fluxes ranged from 0.8 to $1180 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$ with a mean

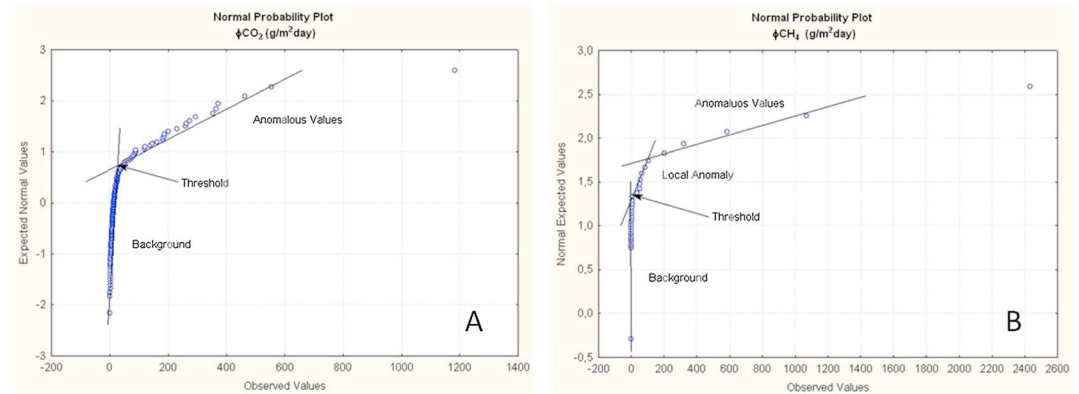


Figure 5. (a and b) The normal probability plot of the CO₂ and CH₄ fluxes for the 2013 survey, respectively.

value of $61.3 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$, ~50% of them being higher than those typically measured for a mature soil ($15 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$ [Capaccioni et al., 2011]).

Conversely, 92% of the measured CH₄ fluxes remained mostly below the detection limit ($<0.016 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$), although in few sites, CH₄ fluxes largely higher than those of CO₂ were measured (up to $2430 \text{ g} \times \text{m}^{-2} \times \text{d}^{-1}$) (Figures 6c and 6d). Thus, the CO₂ and CH₄ maximum fluxes measured in 2013 significantly increased with respect to those of 2008, and the zone characterized by anomalous soil CO₂ fluxes extending eastward reached values up to $\sim 38,000 \text{ m}^2$ (Table 1 and Figures 6a–6d). Accordingly, the total CO₂ and CH₄ emissions from the whole area increased by more than 1 order of magnitude, passing from 0.33 to 3.94 and from 0.17 to $1.93 \text{ t} \times \text{d}^{-1}$, respectively (Table 1). Soil temperatures, measured at 30 cm depth, showed a positive correlation with CO₂ ($r^2 = 0.69$), whereas no significant correlation with the CH₄ fluxes was observed (Figures 7 and 8, respectively).

Table 1. Descriptive Statistics of CO₂ and CH₄ Fluxes, Total Output, and Soil Temperature Measured in the Study Site Area

Population		Value Range	Mean	Median	Standard Deviation	Area (m ²)
ϕCO_2 (g × m ⁻² × d ⁻¹)						
2008 data	overall population	0–139	25.1	7.6	46.0	258,720
	Bg	0–30	7.1	7.3	2.7	236,155
	1	30–100	0.0	0.0	0.0	20,059
	2	>100	134.0	134.0	7.1	2,506
Output = $0.33 \text{ t} \times \text{d}^{-1} = 471.85 \text{ t} \times \text{yr}^{-1} \times \text{km}^{-2}$						
2013 data	overall population	0.8–1,184	61.3	15.0	135.5	258,720
	Bg	<30	11.7	9.7	7.7	220,021
	1	30–100	61.6	54.6	20.2	28,697
	2	100–210	163.0	216.9	29.6	7,018
	3	210–800	343.0	324.0	102.0	2,980
	4	>800	1184.0	1184.0	-	4
soil T (°C)		21.7–44.1	27.5	25.6	5.7	-
Output = $3.9 \text{ t} \times \text{d}^{-1} = 5,555 \text{ t} \times \text{yr}^{-1} \times \text{km}^{-2}$						
ϕCH_4 (g × m ⁻² × d ⁻¹)						
2008 data	overall population	0–51.8	6.6	0.0	15.9	258,720
	Bg	0–10	0.5	0.0	1.1	240,184
	1	10–30	0.0	0.0	0.0	14,559
	2	>30	43.1	43.1	12.3	3,977
Output = $0.2 \text{ t} \times \text{d}^{-1} = 241.6 \text{ t} \times \text{yr}^{-1} \times \text{km}^{-2}$						
2013 data	overall population	0–2,432	37.0	0.0	232.0	258,720
	Bg	0–10	0.3	0.0	1.2	243,697
	1	10–30	0.0	0.0	0.0	4,719
	2	30–210	81.8	60.2	53.1	7,525
	3	210–1,000	454.0	454.0	186.0	2,740
	4	>1,000	1751.0	1751.0	963.0	39
Output = $1.9 \text{ t} \times \text{d}^{-1} = 2717.9 \text{ t} \times \text{yr}^{-1} \times \text{km}^{-2}$						

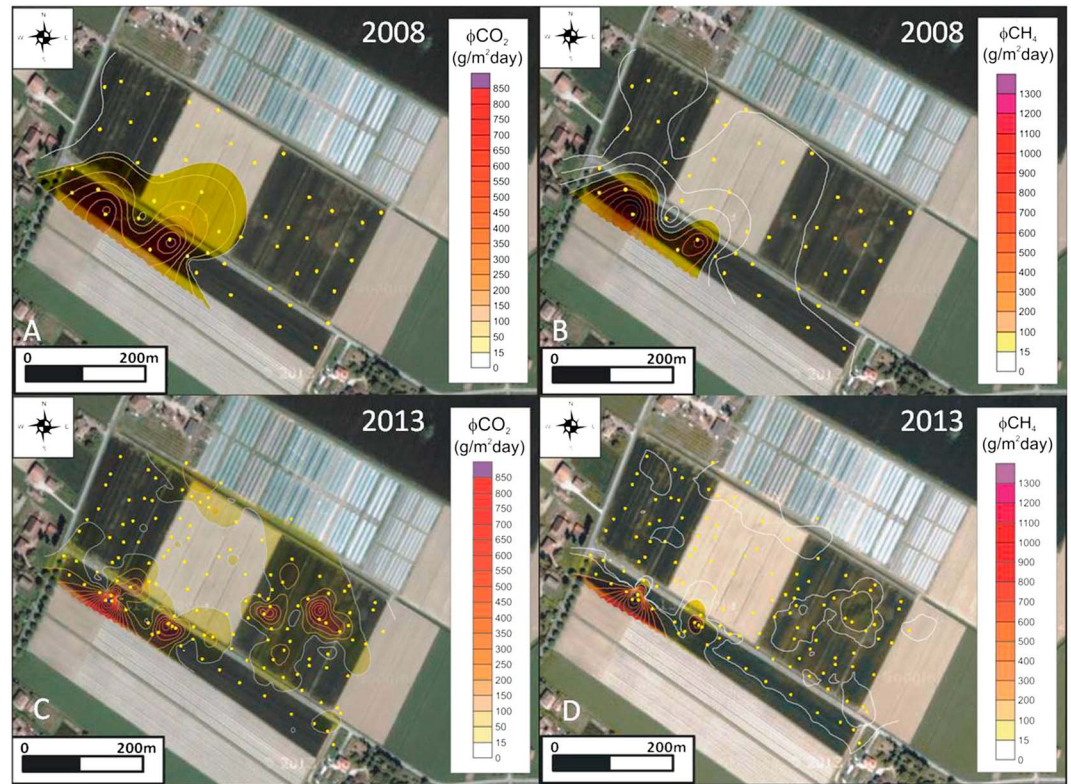


Figure 6. Contour maps of soil fluxes at the study site area: (a) CO₂ flux in 2008, (b) CH₄ flux in 2008, (c) CO₂ flux in 2013, and (d) CH₄ flux in 2013. The spatial distribution of the soil flux was computed by using the kriging estimation method. The location of measurement points are reported with yellow dots.

4.2. Physico-Chemical Parameters and Isotopic Data

The chemical and isotopic data of the soil gases collected during drilling of the 2.5 m deep piezometer are reported in Table 2 and plotted in Figure 9. The soil temperatures ranged from 36.4°C at the surface to 17.0°C at the bottom of the piezometer (–2.50 m), with a maximum measured temperature of 42.2°C at a depth of 0.6 m.

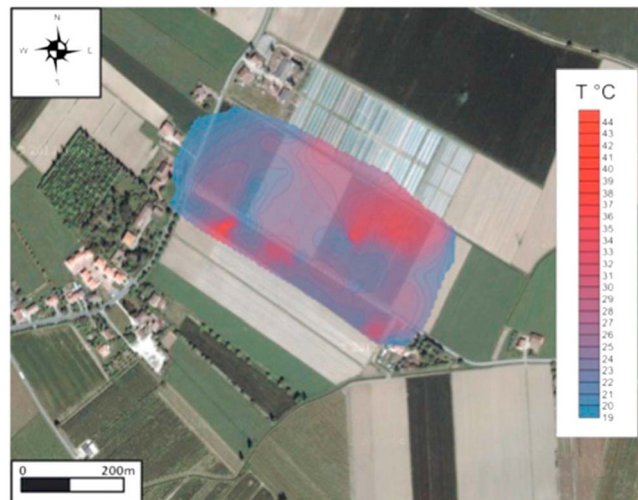


Figure 7. Contour maps of soil temperature at the study site area. Soil temperature was measured with a thermocouple at a depth of 0.30 m.

Within the first 20 cm, the temperature increased from 36.4 to 38.1°C. In this very shallow interval, the gas composition mainly consisted of atmospheric gases, with minor, though significant, amounts of CO₂ (up to 4.5 vol %), while CH₄ contents (<0.001 vol %) were negligible. At greater depth (0.30–0.70 m interval; Figure 9), the temperature reached its maximum value (42.2°C). Within this interval, the gas phase showed the highest CO₂ and the lowest O₂/N₂ ratio. The CO₂ contents reached a maximum of 17.1% at 30 cm depth, decreasing down to 6.9% at 0.70 cm depth. In the same interval, CH₄ passed from 0.34% to 51.0%, whereas a minimum value of 0.75% up to

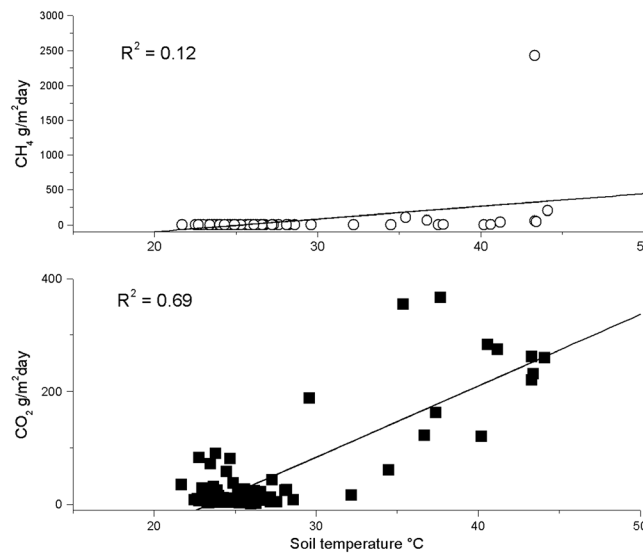


Figure 8. Soil temperatures collected at 30 cm depth versus CO₂ and CH₄ soil fluxes measured in the investigated area. The trend lines and the r^2 coefficients are also reported.

6.13% was recorded for O₂. As reported in Figure 9, in the 0.30–0.70 m interval, the O₂/N₂ decreases very rapidly from the atmospheric value (0.26) down to 0.009 at 0.5 m. From 0.70 to 2.50 m depth, the CH₄ contents showed no significant variations (~30%), whereas those of CO₂ were as low as 1.2%. The vertical profiles of the CO₂ flux (Table 2) displayed the maximum values within the interval of 0.50–0.80 m, where a relatively pervious loamy sandy layer was found (Figure 3). This suggests a control on gas flux exerted by the local permeability, whereas CH₄ flux steadily decreased from the maximum value at 2.5 m up to

negligible values ($<0.002 \text{ g} \times \text{d}^{-1}$) at <0.30 m depth. In Figure 10, the vertical variability of the measured CO₂/CH₄ flux ratio is plotted. Within the 0.6–2.5 m interval, the CO₂/CH₄ flux ratio was $\ll 1$, whereas at <0.60 m depth, the CO₂/CH₄ flux ratio rapidly increased up to 2000 (at ~ 0.20 m depth).

The $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-CO}_2$ values in the gases collected from the piezometer ranged from -72.3‰ to -62.5‰ and from -67.8‰ to -49.9‰ versus VPDB, respectively. The $\delta^{13}\text{C-CH}_4$ displayed a vertical variability with the lowest values ($<-68\text{‰}$ versus VPDB) measured at >0.70 m depth and the highest ones ($>-63.4\text{‰}$ versus VPDB) at shallower depths. The $\delta^{13}\text{C-CO}_2$ values showed an opposite behavior as the more positive values ($>-65\text{‰}$ versus VPDB) were measured at >0.70 m depths and the more negative ($<-65\text{‰}$ versus VPDB) were recorded at shallower depths. A striking “carbon isotopic inversion” between CH₄ and CO₂ (Figure 9) was recorded at depths <0.70 m, where the carbon isotopic signature of CO₂ was significantly lighter than that of CH₄.

The MED 1 gas sample (Figure 1b and Table 2) was also a CH₄-dominated gas emission, although characterized by higher flux ($13.45 \text{ g} \times \text{d}^{-1}$) and CH₄ contents (75.69 vol %) with respect to the TCM gases. The O₂/N₂ ratio was in good agreement with that of the atmosphere (i.e., no oxygen consumption), while the $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-CO}_2$ values were -78.0 and -23.2‰ , respectively.

5. Discussion

According to the geochemical and isotopic data, the gas seepage in the TCM area is characterized by the uprising of a N₂- and CH₄-dominated gas mixture with minor amounts of CO₂ and O₂. The N₂/Ar ratio is slightly higher ($82 \div 89$) with respect to that of the atmospheric gases (≈ 78), whereas O₂/N₂ is mostly lower. This suggests a minor addition of nonatmospheric N₂ (possibly organic) coupled with O₂ consumption likely caused by oxidation processes. A first arising question concerns how and where CH₄ is actually produced. As reported above, the TCM site is on top of the *Dorsale Ferrarese* tectonic fold located at <100 m depth below the alluvial cover (Figure 2a). Inspection of the subsoil stratigraphy has revealed the occurrence of gas and salty water seeps at depths ranging between 750 and $2000 \div 2300$ m. At ≈ 2000 m depth, the prevailing stratigraphic unit consists of upper Miocene marls and organic-rich clays. Above this depth, methanogenic organic-rich layers of significant thickness were not recognized in the stratigraphic sequence (Figure 4). The measured thermal gradient in the area is quite low ($1^\circ\text{C}/100$ m; Regione Emilia-Romagna (ER) report), with temperature not significantly exceeding 50°C at 2000 m depth. CH₄ can be produced and stored beneath the thrust surfaces from which it migrates upward along minor fault planes. As CH₄ rises up, it can also be stored within pervious horizons at shallower levels (such as the

Table 2. Depth, Temperature, CO₂, and CH₄ Fluxes (and Relative Ratios) From the Piezometer Expressed as Weight (g × d⁻¹) and Volume (L_{STP} d⁻¹; STP: Standard Temperature and Pressure) per Day (See Text for Further Explanations) and Chemical Composition (in vol %), CO₂/CH₄ Ratio, and Carbon Isotopic Composition (in VPDB ‰) of the Gases Collected From the 2.5 m Deep Piezometer Each 10 cm Down to 80 cm Depth and Each 50 cm at Greater Depth^a

ID	Depth (cm)	T (°C)	CO ₂ (g/d)	CH ₄ (g/d)	φCO ₂ /φCH ₄	L _{STP} /d CO ₂	L _{STP} /d CH ₄	CO ₂ % v/v	CH ₄ % v/v	CO ₂ /CH ₄ W/W	N ₂ % v/v	O ₂ % v/v	Ar % v/v	O ₂ /N ₂ V/V	δ ¹³ C _{CH₄} PDB ‰	δ ¹³ C _{CO₂} PDB ‰	δ ¹³ C _{CH₄} PDB ‰	δ ¹³ C _{CO₂} PDB ‰
0	0	36.4	0.203	0.000	1970.87	0.103	0.000							0.256				
1	10	36.7	0.131	0.000	276.37	0.067	0.001	1.26			78.1	19.69	0.95	0.252			-55.26	-65.91
2	20	38.1	0.191	0.000	1104.05	0.097	0.000	4.52			79.46	15.05	0.97	0.189				
3	30	38.5	0.189	0.002	102.58	0.096	0.003	17.14	0.328	143.70	77.55	4.04	0.94	0.052			-63.21	-65.24
4	40	38.1	0.275	0.009	29.53	0.140	0.013	13.99	0.93	41.37	82.93	1.22	0.93	0.015			-62.50	-66.71
5	50	39.8	0.317	0.027	11.64	0.161	0.038	14.14	2.385	16.30	81.78	0.75	0.95	0.009			-63.42	-67.71
6	60	42.2	0.425	0.653	0.65	0.216	0.915	8.38	25.29	0.91	63.31	2.27	0.75	0.036			-63.37	-67.83
7	70	38.4	0.314	1.191	0.26	0.160	1.669	6.91	51.47	0.37	35.09	6.13	0.4	0.175			-68.97	-65.91
8	80	34.6	0.518	1.109	0.47	0.264	1.553	7.51	31.55	0.65	54.44	5.86	0.64	0.108			-71.15	-55.21
10	100	31.6	0.484	0.982	0.49	0.247	1.376	4.09	35.22	0.32	55.89	4.15	0.65	0.074			-71.73	-61.36
11	150	28.1	0.315	1.053	0.30	0.160	1.475	4.85	31.83	0.42	60.55	2.07	0.7	0.034			-68.72	-49.86
12	200	21.5	0.342	1.510	0.23	0.174	2.115	3.48	30.16	0.32	64.06	1.55	0.75	0.024			-72.31	-52.47
13	250	17.0	0.232	3.137	0.07	0.118	4.395	1.19	31.59	0.10	63.62	2.87	0.73	0.045				
MED 1		14.0	0.640	13.45	0.05	0.326	18.836	1.99	75.69	0.07	17.43	4.54	0.29	0.260			-78.00	-23.19

^aMED 1 is a gas sample that suddenly appeared during a CPT on mid-October 2014 at ~1 km west of TCM.

sandy river-channel facies, possibly referred to the Po riverbed). Depending on the cover permeability, its thickness and the possible occurrence of diffuse fracture networks CH₄ can reach the surface, such as at TCM site.

The origin of CH₄ in natural environments is mainly related to (i) microbial activity (methanogenic archaea) and (ii) thermogenic degradation of preexisting organic matter. These two different CH₄ sources produce distinct ¹³C/¹²C ratios: (1) thermogenic CH₄ typically shows δ¹³C values ranging from -50 to -30‰ versus VPDB and (2) microbial CH₄ commonly has δ¹³C values < -50‰ versus VPDB [e.g., Schoell, 1980, 1988; Whiticar, 1999; McCollom and Seewald, 2007]. The δ¹³C-CH₄ values measured in the gas samples collected during drilling were < -70‰ versus VPDB, therefore suggesting a prevailing microbial origin of CH₄. As reported above, a source located at 2000 m depth should be at a temperature of ~50°C, which is within the typical range for biogenic production of CH₄ [Valentine et al., 2004]. Galand et al. [2010] showed that bacterial methanogenesis in peatland ecosystems produces a carbon isotopic fractionation between CH₄ and the coexisting CO₂ of 41‰ to 72‰. Whiticar [1999] suggested a larger carbon isotopic fractionation ranging from 49 to 95‰ depending on (i) temperature [Whiticar et al., 1986; Hornibrook et al., 1997], (ii) isotope composition of precursor organic substrate, and (iii) rate of methanogenesis [Zyakan, 1992]. The experimental results of Valentine et al. [2004] indicated that CH₄ production due to bacterial CO₂ reduction causes a carbon isotope fractionation of 22–58‰. The isotopic difference (expressed as (ΔCO₂-CH₄)) between the δ¹³C-CO₂ and δ¹³C-CH₄ values measured at TCM ranged from 20‰ at >0.50–0.60 m depths to -4.5‰ at shallower levels. Even when the highest recorded value (ΔCO₂-CH₄ = 20‰) is considered, the isotopic fractionation between CH₄ and the coexisting CO₂ cannot be related to fractionation processes due to bacterial methanogenesis at depth. The achievement of isotopic equilibrium between these two carbon species can also be ruled out, since temperatures higher than 350°C would be required [Giggenbach, 1997]. Moreover, the

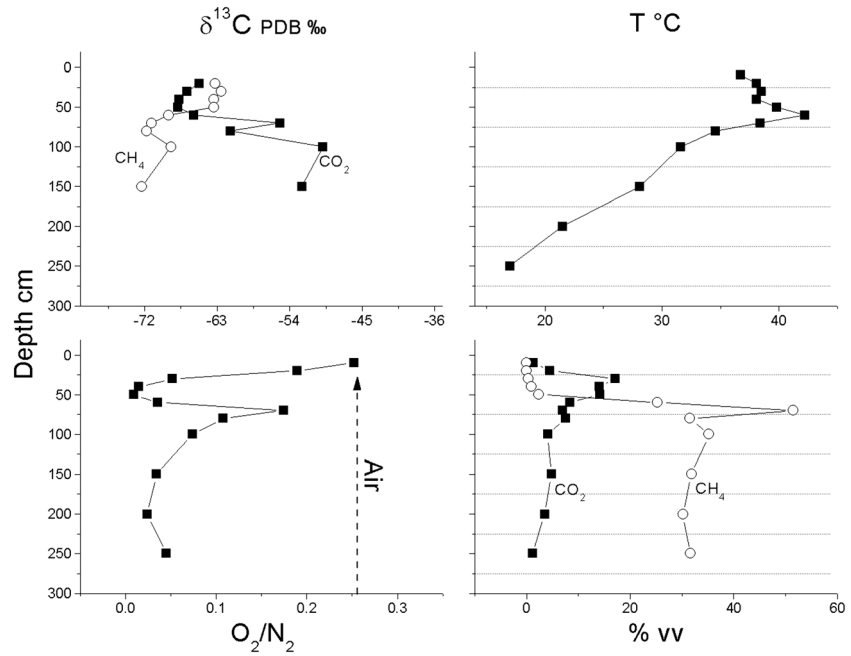


Figure 9. Vertical profiles of temperature and chemical and isotopic parameters on gases collected each 10 cm down to 80 cm depth and each 50 cm at greater depth.

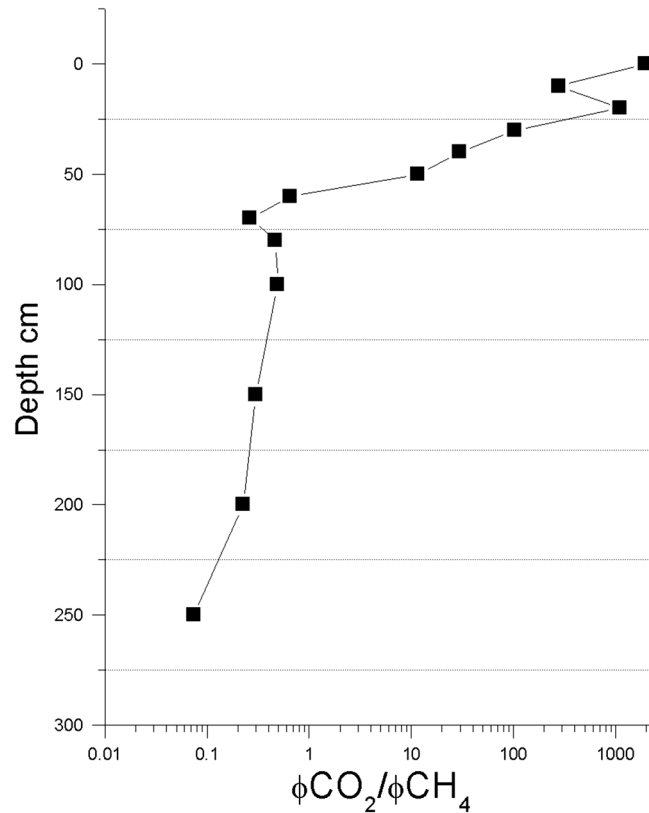


Figure 10. Vertical profiles of CO₂/CH₄ flux ratio measured during drilling of the piezometer. The respective measurements were carried out at depth intervals of 10 cm down to 80 cm depth and at intervals of 50 cm at greater depth. The strong increase of CO₂/CH₄ flux ratio at depth <50 cm appears meaningful.

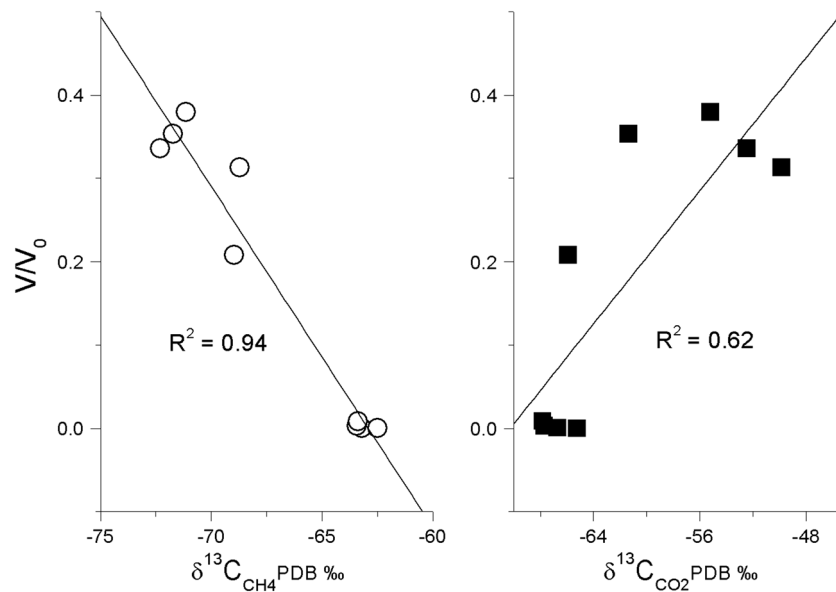


Figure 11. Residual volumetric fraction of CH₄ (see text for further explanation) of the gas phase collected each 10 cm down to 80 cm depth and each 50 cm at greater depth versus the measured δ¹³C-CO₂ and δ¹³C-CH₄ values. The trend lines and the r² coefficients are also reported.

composition of the gas sample (MED 1; Table 2), collected from a gas vent that suddenly appeared during a CPT ~1.0 km W of TCM, i.e., in an area previously free of both CH₄ seepages and anomalously high soil temperatures, is of particular interest. The chemical composition of MED 1 and TCM gases were similar such as their δ¹³C-CH₄ values (-78.0‰). Vice versa, a strikingly different δ¹³C-CO₂ value was measured in the MED 1 gas sample since it was significantly more positive (-23.2‰) than those measured at TCM. Both δ¹³C-CH₄ (-78.0‰) and the Δ_{CO₂-CH₄} (54.8‰) value of MED 1 is in good agreement with that expected for bacterial methanogenesis [Whiticar, 1999; Valentine *et al.*, 2004; Galand *et al.*, 2010].

Dunfield *et al.* [2007] observed that CH₄ concentrations at Tikitere (New Zealand), a geothermal area with diffuse CH₄-rich gas emissions, reached the lowest contents near the surface (0.10–0.20 m depth) due to oxidative CH₄ consumption by methanotrophic bacteria. A similar condition was also observed at the TCM site, where the CH₄ contents became negligible at very shallow depth (<0.6 m), whereas those of CO₂ reached the relative highest concentrations. Moreover, at <0.60 m depth, the δ¹³C-CO₂ values were more negative (~-68‰ versus VPDB) than those of δ¹³C-CH₄ (~-63‰). This was not recorded at >0.50–0.60 m depths, where δ¹³C-CO₂ ranged from -50 to -61‰ versus VPDB and δ¹³C-CH₄ from -68.7 to -72‰ versus VPDB (Figure 9).

The gradual depletion of ¹³C in CO₂ at shallower depth is consistent with a ¹³C/¹²C kinetic fractionation due to a partial CH₄ → CO₂ conversion. ¹²CH₄ is indeed oxidized slightly faster than ¹³CH₄ [Barker and Fritz, 1981], and therefore, the CH₄-derived CO₂ can significantly be enriched in ¹²C with respect to the residual CH₄. The residual volumetric fraction of CH₄, i.e., the ratio between the volumetric CH₄ fluxes measured at different levels (Table 2) and the maximum recorded volumetric CH₄ flux measured at the bottom of the piezometer (4.395 L_{stp} d⁻¹; Table 2), shows an inverse relation with the δ¹³C-CH₄ values, whereas it is directly related to those of δ¹³C-CO₂ (Figure 11). This behavior confirms the effect of the CH₄ → CO₂ conversion, which likely derives by isotopic fractionation processes during oxidative consumption of CH₄ at decreasing depths. This produces isotopically light CO₂ and, consequently, ¹³C-rich residual CH₄. In this context, the MED 1 emission may represent the pristine CO₂ and CH₄ isotopic compositions, likely before the growth of methane-utilizing bacteria (methanotrophs), whose metabolic activity promotes the CH₄ oxidation at shallow levels.

Summarizing, the measured carbon isotopic signature of CH₄ and CO₂ at TCM site is the result of the sequential combination of two processes:

1. Bacterial methanogenesis at depth (>2000 m), producing isotopically light CH₄ ($\delta^{13}\text{C}-\text{CH}_4 = -78.0\text{‰}$) and relatively heavy CO₂ ($\delta^{13}\text{C}-\text{CO}_2 = -23.2\text{‰}$);
2. Bacterial oxidation of CH₄ mainly within the most aerated loamy sandy layer located at very shallow depth, where isotopically lighter CO₂ (up to a $\delta^{13}\text{C}-\text{CO}_2 = -67.8\text{‰}$) and heavier CH₄ (up to $\delta^{13}\text{C}-\text{CH}_4 = -62.5\text{‰}$) are produced.

The fraction of the ¹²C-rich CO₂ systematically increases upward due to the increasing CO₂ contribution from CH₄ oxidation.

At TCM, the observed anomalous ground temperature, as well as the relatively high CO₂ and CH₄ soil fluxes, cannot be referred to neither an anomalous thermal flux nor uprising hot fluids. As previously described, this area is indeed an alluvial plain with a normal-to-low geothermal gradient (1°C/100 m; Emilia-Romagna Region [CNR, 1982]), and the documented deep groundwater has a temperature not exceeding 21°C at 500 m. In 2013, the maximum ground temperature (44.1°C) was recorded in the SW limit of the investigated area (Figure 7), in correspondence with the highest CO₂ and CH₄ soil fluxes (350 and 2428 g × m⁻² × d⁻¹, respectively; Figures 6c and 6d). As reported above, the spatial distribution of ground temperature is better related to the CO₂ flux than to that of CH₄. The spatial distribution of CH₄ fluxes appears to be characterized by few spots with very high fluxes (up to 2428 g × m⁻² × d⁻¹), whereas most data were below the detection limit. A similar condition was observed for biogas microseepage from the Municipal Solid Waste Landfill [Capaccioni *et al.*, 2011]. In these anthropogenic systems, biogenic CH₄ was completely removed by microbial activity within the soil cover in sites where the biogas fluxes (mainly consisting of CO₂ and CH₄) were <20–30 g × m⁻² × d⁻¹ [e.g., Tassi *et al.*, 2009]. Methane consumption progressively decreases as the CH₄ fluxes increase, likely due to kinetic effects. When biogas fluxes are >1000 g × m⁻² × d⁻¹, CH₄ is not significantly removed within the soil cover [Capaccioni *et al.*, 2011]. At TCM, the maximum soil temperature (42.2°C) was recorded at 0.60 m depth, which corresponds to the maximum removal of CH₄ and O₂ and the highest CO₂ production, i.e., to the level of maximum efficiency of the CH₄ → CO₂ conversion. In this context, the diffuse CO₂ seep is mainly the product of CH₄ oxidation at very shallow levels. Given the exothermic nature of the conversion process (800 kJ × mol⁻¹ [Ioannides and Verykios, 1997]), this appears as the only plausible mechanism able to cause the measured soil heating at TCM. This explains (i) the correlation between the spatial distribution of soil temperature and CO₂ fluxes and (ii) the absence of soil CH₄ flux, since its values are slightly above than the detection limit. Conversely, CH₄ is detected at surface only when its flux is sufficiently high to avoid the complete conversion to CO₂. The produced H₂O surplus could be responsible for the gleying process that exclusively characterizes the shallow sediments where the CH₄ → CO₂ conversion occurs.

6. Conclusions

At TCM, (i) soil temperature profile, (ii) compositional vertical patterns measured along the piezometer (Figure 9), and (iii) presence of metanotrophic bacteria in a soil sample collected at ~0.5–0.6 m depth (S. Fedi, personal communication) suggest the occurrence of exothermic, oxidative CH₄ removal as the main mechanism of soil heating at TCM. Oxidation of CH₄ is a highly exothermic process since 800 kJ × mol⁻¹ (CH₄) [Ioannides and Verykios, 1997] is produced. Methane oxidation can only occur in an aerobic environment [Lerner *et al.*, 2000]. It is difficult to verify whether oxidation and heating only occur in correspondence of a specific layer or spread throughout all the soil thickness. Nevertheless, it can be assessed that the CH₄ → CO₂ conversion achieved the highest efficiency close to the loamy sandy layer, which is the relatively more permeable and aerated strata within the studied soil profile.

The numerical simulation carried out by Nespoli *et al.* [2015] provides a good fitting between observed and simulated temperature profiles. It describes heat generation due to CH₄ oxidation within an unsaturated soil. The heat source is placed inside the more pervious layer at 0.6 and 0.7 m depths. Here CH₄ oxidation takes place, and the heat production is depending on the CH₄ flux. Numerical simulations consider different CH₄ fluxes, explore the efficiency of the process of CH₄ oxidation (producing different rates of heat generation), and take into account the seasonal effects.

According to the experimental results of Whalen *et al.* [1990], the kinetic constant of CH₄ oxidation, rather than the type of the microbial communities, depends on CH₄ concentration, temperature, and content of

the soil moisture. Sundh *et al.* [1995] described some parameters able to control the aerobic methane oxidation, as follows: ...the greater the vertical extension of aerated surface peat, the higher the methane oxidation capacity.These results suggest that the supplies of methane and oxygen largely control the biomass of methanotrophs across plant communities. This implies that changes in the groundwater table level (and hence in the supply of CH₄ and O₂ to the methanotrophs) could strongly affect the in situ oxidation rates and cause large temporal variation of the oxidized CH₄ fraction and, consequently, the amount of heat released by the exothermic reaction. The previously cited evidence provide a very shallow and local source for the anomalous heating at TCM related to the presence of CH₄ microseepage and oxidation at shallow soil levels due to methanotrophic bacteria.

According to Bonori *et al.* [2000] and Cremonini [2010], data on seismic profiles highlight the diffuse presence of uprising fluids, likely consisting of biogenic methane generated by bacterial degradation of organic matter at depth. Earthquakes may increase fluid propagation toward the surface by increasing both the pore pressure and/or opening new fractures that favor an increasing permeability. Despite the fact that only two CH₄ and CO₂ isoflux maps (2008 and 2013; Figure 6) are clearly not enough to identify any flux increase associated with the May–June 2012 Emilia earthquake, they nevertheless suggest that in the TCM area, the CH₄ and CO₂ fluxes have significantly changed in time and space and this variability should be investigated in more detail in the next future. Therefore, although direct relationships between gas fluxes, soil temperature, and the earthquake events of 2012 in the area cannot be definitively established, we can speculate that a possible increase of the CH₄ fluxes from depth may have caused a diffuse temperature increase of soil and shallow aquifers due to superficial CH₄ → CO₂ conversion. In our opinion, this mechanism may also explain the sudden and spontaneous phenomena, such as bubbling waters, heated soils and, occasionally, heated waters, reported by several witnesses in the area during and after the seismic sequence of the May–June 2012 Emilia earthquake. In a recent study, Qin *et al.* [2012] reported a series of preliminary data about the occurrence of a preseismic and coseismic thermal anomalies in the area revealed by satellite on 12 May 2012, i.e., 8 days before the 20 May 2012 earthquake (*M_L* 5.9) and on 24 May 2012, i.e., 5 days before the 29 May 2012 earthquake (*M_L* 5.8). These authors claimed for an increasing emission of greenhouse gases (CO₂ and CH₄) into the atmosphere from the ground, although according to the same authors, other possible heat sources such as the release of latent heat due to near-surface air ionization, stress-induced thermal effects due to friction, and uprising hot fluids could not be ruled out. In our opinion, a further heat source may be related to CH₄ oxidation processes at shallow levels. This implies that monitoring the occurrence of thermal anomalies in the Emilia region actually means to monitor the temporal evolution of CH₄ soil fluxes and the efficiency of its superficial oxidation. This aspect should be considered when monitoring surveys of seismic areas, such as those hit by the May–June 2012 events, are to be planned.

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