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Abstract

Methane and CO₂ gas emissions from a gas seep located in the French Alps, documented over two millenaries, have been quantified along with gas emissions from the miniseepage area contouring the main vent. Several tons per year of both gas phases are released in the atmosphere from the main seep (18 tons of CH₄ and 5.5 tons of CO₂) which has been modified by an old borehole. Diffuse seepage brings additional CH₄ (1 ton per year) and CO₂ (2.3 tons per year) which are emitted from a small area of 240 m². Secondary CH₄ oxidation processes are likely to occur near the surface. Biologically produced CO₂ is also found in the soil in the seepage area and the biological component becomes predominant as CO₂ concentrations drop lower than 2% vol. Soil gas CH₄+CO₂ enrichments are oriented along N45 and N170 pathways that represent the main structural directions of the area. Soil flux anomalies are more scattered because surface clay formations have been strongly reworked at surface. Variety of methods (IRGA, micro-GC, accumulation chamber flux measurements, IR-camera) were tested and are discussed in connection with environmental impact monitoring and the role of sampling conditions, with emphasis on shale gas and carbon storage baseline assessments. The role of potential leakage pathways represented by the old borehole structure is also discussed as an analogue with leaky shale gas wells.

27 **Highlights**

- 28 - Definition of the degassing pattern of a major CH₄+CO₂ gas seep in the French Alps.
- 29 - Quantification of greenhouse gas emissions to the atmosphere from this gas seep.
- 30 - Implications for containment and environmental baseline assessment related to
- 31 shale gas environmental impact.

32

33 **Keywords**

34 Methane – gas seep – natural degassing – environmental baseline assessment – shale gas

1. Introduction

Natural Earth degassing is a matter of concern and investigation since many years in various fields such as volcanology or geothermics. Often relying on the characterization of the gas species percolating from depth to shallow horizons and subsequently to the atmosphere, these studies have provided better constraints on the sources and amounts of gases released to the atmosphere and on potential migration pathways. Numerous studies have dealt with the evaluation of the amounts of CO₂ and other gases naturally released by volcanic structures (e.g. Greenland *et al.*, 1985; Hobbs *et al.*, 1991; Brantley and Koepenick, 1995; Halmer *et al.*, 2002) and the consequences such releases may have on human health (e.g. Sigurdsson *et al.*, 1987; Baxter *et al.*, 1999). Gas emissions from geothermal areas and from geothermal exploitation have also received growing interest as contribution to greenhouse gases (GHG) in the atmosphere (e.g. Capaccioni *et al.*, 1993; Cardenelli *et al.*, 2003a; Armannsson *et al.*, 2005). Furthermore, they induce direct risks for human dwellings (e.g. Durand and Scott, 2005). Gas releases may also be associated with emissions from hydrothermal resources (e.g. Battani *et al.*, 2010), from non-volcanic areas (e.g. Rogie *et al.*, 2000) or from other subsoil reservoirs (e.g. Etiope and Martinelli, 2002; Voltattorni and Lombardi, 2010): they are associated with mud volcanoes (e.g. Jud, 2005; Etiope *et al.*, 2011a) and with hydrocarbon plays (e.g. Etiope, 2015). The budgets of carbon emissions to the atmosphere have been assessed in the 2000's (e.g. Mörner and Etiope, 2002) and are regularly refined for CO₂ (e.g. Holloway *et al.*, 2007) or CH₄ (e.g. Etiope, 2015). Recently, methane emissions from igneous rocks (abiotic gas) have also been recognized as more widespread and more important than previously thought (e.g. Etiope, 2017).

Consequently, there is still need to better constrain methane emissions to the atmosphere given its elevated greenhouse power. As pointed out by Etiope (2015) in his landmark monograph, the importance of hydrocarbon seepage from onshore locations is far from negligible. The refinement of natural gas seepage contributions to the atmospheric methane budget thus contributes to better understanding the impacts on climatic forcing. Hydrocarbons released by gas seeps, miniseepages, microseepages and emissions from mud volcanoes are phenomena occurring worldwide, in Europe (Germany, Greece, Italy, Romania, Switzerland), Azerbaijan, Turkey, Asia (China, Japan, Taiwan), Australia and USA. Emissions from ophiolites or igneous intrusions (Etiope, 2015) are even more widespread. Methane seeps are also an important part of the geochemical baseline that needs to be defined when assessing the environmental impact of conventional and unconventional hydrocarbon exploration and exploitation (Humez *et al.*, 2016; Mayer *et al.*, 2015; Mayer *et al.*, 2016).

Emissions of alkanes in the alpine foreland are reported in Switzerland (Giswil, Northern Alps; Etiope *et al.*, 2010) taking the form of both diffuse degassing area and gas vents with large amounts of thermogenic gas released each year (more than 16 tons per year from 2 main seeps and diffuse degassing). Gas seeps in France are largely under-investigated (Etiope, 2009). Only one site is mentioned in the MAGA database (http://www.magadb.net/global_map/) even though methane point emissions do not seem to be an uncommon phenomenon in the French Subalpine Chains (Figure 1), apparently systematically related to outcropping or underlying Lower Jurassic argillaceous sediments.

We report investigations at the most prominent French alpine gas seep, known for at least two millenaries, the Fontaine Ardente du Gua site, south of Grenoble (hereafter referred to

as Fontaine Ardente). First measurements, in June 2015, aimed to define the shape of the gas emissions at surface and preliminary results can be found in Kloppmann *et al.* (2016) and in Gal *et al.* (2017a). Here we present more detailed investigations based on soil gas measurements and on soil gas flux measurements performed in October 2016, allowing a first quantitative assessment of CH₄ and CO₂ fluxes to the atmosphere.

Figure 1

2. Geological and historical settings

The Fontaine Ardente gas seep is situated 20 km South-West from Grenoble city (Isère department, France), at the foothill of the Urgonian limestone cliffs of the Vercors Massif (Figure 1Error! Reference source not found.). The gas emanates from Callovian claystones and argillaceous limestones (black shales) in a small thalweg in the main bed of the Vernant creek. Gas escapes are thought to be linked with faults but the geometry of these faults remains unclear and so does the origin of the gas phase. There has been a debate between a deep origin, linked to the existence of a deep fault reaching Triassic formations, and a near surface origin, linked to a minor fault only affecting shales (Mercier and Seguin, 1939), the region being rich in organic-rich sediments (coal seams of La Mûre or the Motte d'Aveillans coalfield; Berthier *et al.*, 1991).

The Fontaine Ardente seep is known from ancient times (as early as 426 AD) as “burning water” because the seep was initially observed in the stream bed of the Vernant creek (Figure 1). Following the rush in hydrocarbons exploitation in the US (especially in Pennsylvania) and Canada in the XIXth century, pro-parte based on the discovery of natural

gas associated with hydrocarbons, attempts to exploit the Fontaine Ardente gas have been made around 1880 (Piret, 1881). It was believed that there must be a considerable gas reservoir together with perennial gas production to allow leakage of methane at ground surface for such a long time – a volume of $1.73 \times 10^3 \text{ m}^3$ (3.1 tons at boiling point) of CH_4 per day was evaluated in the late XIXth century.

The composition of the gas phase was analyzed for the first time at the end of the XIXth century: 98.81% (vol.) of CH_4 , 0.58% of CO_2 , 0.48% of N_2 , 0.10% of O_2 and 0.03% of loss or bias during analysis (Piret, 1881). It was reevaluated in 1960, leading to the sole detection of CH_4 and CO_2 at 91.16% and 8.84% respectively (cited in AHPG, 2012). Traces of O_2 and N_2 previously described were attributed to atmospheric contamination during sampling.

In view of the exploitation of the gas phase, the primitive site was profoundly modified in the goal of focusing the patchy gas emissions into a unique emitting point (Piret, 1881). Infrastructure was built to deviate stream water and to allow the construction of a gasometer to collect gas without interaction with surface waters. From this gasometer the gas was piped uphill for further use to the plateau surrounding the thalweg where the fountain is located. The exploitation quickly ceased as the gas production could not be enhanced and floods repeatedly destroyed the surface infrastructure. The investigations related to these works concluded that the rock formations near the surface were altered down to a depth of 18 to 20 m below ground surface by the long-term percolation of the gas. Due to flooding in 1956, the site was covered by detrital sediments, the gas emission pathways have changed and the gas flux to the surface decreased.

In order to enhance and better constrain gas emissions, further works were undertaken in the 90's (Berthier *et al.*, 1991). After surveying soil gas (CO_2 soil gas concentration

prospecting at 0.5 m depth), 2 boreholes (FA1 and FA2) were drilled down to 35 m below ground level. Only one (FA2; Figure 1) was methane rich, main gas inflow occurring at about 10 m depth. Gas flowrate was measured at 130 l/min at 0.1 bars during 3 hours (borehole opened). Once closed, borehole pressure increased up to 0.6 bars. Exploitation of the gas had been expected to be possible at above 90 l/min but no exploitation was tried. Nowadays the FA2 borehole represents the main seep knowing that the wellhead has been destroyed and that additional reworking led to the building of a concrete platform around the former wellhead and to the flattening of the area close to FA2 borehole as shown by Figure 1

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3. Methods

Site investigations at Fontaine Ardente used two approaches: soil gas concentrations measurements at 1 m depth and soil gas flux quantification at the soil/atmosphere interface.

3.1. Soil gas measurements

Soil gas concentrations were measured according to a well-established methodology used *e.g.* for monitoring for Carbon Capture and Storage (CCS) sites (Gal *et al.*, 2014). A 1 m square mesh grid was used in 2015 (Figure 1). In 2016, the mesh grid varied from 1 x 1 m to 1 x 2 m. Some measurements were performed outside of this grid and outside of the Vernant river bed. These points serve as reference points for the evaluation of background characteristics of soil gas. Small holes (1 cm in diameter) were drilled down to 1 m depth. Such a small mesh size for systematic sampling is rarely used in similar studies (*e.g.* Bloomberg *et al.*, 2012) and is a direct consequence of the small size of the area to monitor.

Using a small mesh is also a way to lower the uncertainty in soil gas flux quantifications that may be related to the use of relatively small flux chambers (Parkin and Venterea, 2010). Owing to the presence of a concrete platform and surrounding rockwall (gabion wall), the area cannot be monitored totally.

For soil gas investigations, a sampling tube was inserted into the hole of 1 cm in diameter and an Infra-Red Gas Analyzer (IRGA, LFG20 by ADC Gas Analysis Ltd., UK) was plugged, pumping at low flow rate ($200 \text{ ml} \cdot \text{min}^{-1}$) and reaching steady state conditions within tens of seconds. No concentration changes on very short time scale (minutes) were observed. The IRGA allowed a direct estimate of CH_4 , CO_2 and O_2 gas concentrations in soils. Analytical precision for CO_2 and CH_4 was $\pm 0.5\%$ of the reading for low concentration range (0.01–10% vol.), $\pm 3\%$ of the reading for higher concentrations (10 to 50% vol.) and up to $\pm 5\%$ of the reading for the CO_2 sensor and $\pm 16\%$ for the CH_4 sensor for concentrations greater than 50% (a procedure is described in supplementary information to correct the bias for CH_4 concentrations). The precision for oxygen was $\pm 0.4\%$ full scale reading (0–25% vol.).

Complementary characterization of the gas phase was performed in 2015 using gas micro-chromatography (Agilent 3000) in order to increase the accuracy of CH_4 determinations (IR sensors exhibit non-linear absorption at high gas concentrations). Samples were stored in Tedlar[®] bags during site monitoring and analyzed by the end of the day. A quantitative assessment of the gas phase composition was then possible for permanent gases (CO_2 , O_2 , N_2 , Ar), alkanes (CH_4 , C_2H_6 , C_3H_8) and ^4He . Detection limits are 10 ppm for permanent gases, 2 ppm for alkanes and 50 ppm for helium. Precision of the measurement is better than 2% at full scale.

3.2. Soil flux measurements

Soil gas flux measurements were performed in 2016 on the 1 x 1 to 1 x 2 m mesh grid. At some locations, flux monitoring was not technically feasible as the ground was too pebbly, in the bed of the Vernant creek or strongly modified by the concrete platform and the rockwall (Figure 1). The accumulation chamber technique, with external recirculation, was used. Such closed chamber measurements are widely used for CO₂ flux quantifications (*e.g.* Chiodini *et al.*, 1998; Fridriksson *et al.*, 2006) and are also applied to CH₄ flux measurements (*e.g.* Etiope *et al.*, 2013a; Gal *et al.*, 2014). Reliable and representative estimates of the soil gas flux can be obtained as this technique does not rely on corrections depending on soil characteristics (Chiodini *et al.*, 1998, and references therein). The flux chamber system is a customized version of the soil gas flux system of Echo Instruments (Slovenia). The aluminum chamber has a semi-spherical geometry with a basal area of 0.0289 m² and a volume of 0.0018 m³ (soft ground) to 0.0023 m³ (hard ground). There is no anchor installation prior to measurement as the sharp-edged base of the chamber is shaped to be easily inserted in the ground. A fan with tunable speed ensures the required mixing of the headspace gas (Parkin and Venterea, 2010). Pressure, temperature and relative humidity inside the chamber, as well as pumping rate, are continuously monitored thus giving estimates on the possible influence of external parameters on the measurements. The following gas species are monitored: CO₂ and CH₄ by Non-Dispersive Infra-Red (NDIR) detectors (0 to 5000 ppmv ± 2% and 0 to 10000 ppmv ± 5% respectively), O₂ and H₂S by electrochemical cells (0 to 25% vol. ± 2% of the reading and 0 to 10000 ppmv ± 5% of the reading respectively). The measurements are performed directly on the soil surface without removal of the first centimeters of the soil as it was sometimes reported (Fridriksson *et al.*, 2006). Around two thirds of the fluxes were measured on bare soil or gravel soil, the rest on vegetated soil

(grass). This allowed quantification of the gas emissions to the atmosphere under undisturbed conditions (soil removal may artificially enhance gas emissions if performed shortly before measurement).

The flux measurement was based on the rate of CH₄ and CO₂ increases (positive fluxes), and possible opposite O₂ decrease (“negative” fluxes), in the chamber. Usually positive values indicate fluxes directed from the soil to the atmosphere and negative values indicate flow from the atmosphere into the soil (*e.g.* D'Alessandro *et al.*, 2018). Details on the procedure used to calculate flux is given as supplementary information.

4. Results and discussion

4.1. Meteorological conditions

The influence of meteorological conditions is a widely reported phenomenon (*e.g.* Toutain and Baubron, 1999). The two campaigns were performed under contrasted climatic conditions.

In June 2015, high rainfall amounts were recorded prior to the field acquisitions (40 mm on June 13 and 14). Such amounts can lower the soil gas concentrations in the upper part of the soil (0 to 40 cm depth) – and so the gas flux at the soil/atmosphere interface – as the result of a barrier effect that reduces gas emissions to the surface when water is percolating downwards and/or dissolving part of the soil CO₂ (Hinkle, 1994). At the opposite, increases of the concentrations by a “piston” accumulation effect can be observed deeper in the soil (Bouma and Bryla, 2000). Rainfall has less influence on CH₄ as it is less soluble in water than CO₂ (Weiss, 1974; Wiesenburg and Guinasso, 1979). Gas emission can also be affected by

pressure variations with possible anti-correlation of gas with air pressure (Toutain and Baubron, 1999) even if this relation has not been observed in all cases (*e.g.* Gal *et al.*, 2014).

The situation was opposite in October 2016. Only 4 mm of rainfall occurred during the two days preceding the measurements and August and September 2016 were drought months (only 37.8 + 37.1 mm precipitated compared to 67.2 + 105.7 mm on thirty-year average; <http://www.meteofrance.com/climat/france/grenoble/38384001/relevés>). Influence of rainfalls on gas emissions may be of secondary importance in 2016 as water uptake by vegetation and/or evaporation after rainfalls may preclude water to percolate deep in the soil. This period of drought also allowed enlarging the monitoring area by performing some data acquisitions directly in the river bed of the Vernant creek (Figure 1).

4.2. Statistical parameters

Main statistical characteristics of soil gas concentrations measured in the field by gas chromatography in 2015 and IRGA in 2016 are reported in Figure 2. The 2016 IRGA data were completed by some gas chromatography measurements (N_2 , 4He and C_2H_6) in order to cross-check high CH_4 concentrations measured by IRGA. The gas phases monitored in 2015 (Gal *et al.*, 2017a) and the gas phases monitored in 2016 are in good agreement:

- Soil gas concentrations cover a wide range of variation typically linked to the existence of a gas vent. Concentrations of the predominant gas in the main vent (CH_4) ranged from zero up to 90% vol.

- CO₂ exists across all the monitoring area with maximum values around 11% for the main vent and background values in the surrounding forest soils around 0.2% (Figure 1).
- Trace gases are detected less frequently. C₂H₆ and ⁴He appeared to be detectable in half of the samples in 2015 and their concentrations reached respectively 590 and 250 ppm. In a few samples, having a composition similar to that of the main seep (FA2 in Figure 1), very low amounts of C₃H₈ were measured close to the instrumental detection limit (2 to 3 ppm in the present case). Interestingly, H₂S has not been detected in 2015 but has been monitored at high concentrations in 2016 in four samples (up to 2.2% vol. in two samples; around 200 ppm in two other samples; below detection limit – 50 ppm – in the two last samples).
- Oxygen and N₂ concentrations varied from atmospheric concentrations down to near zero values for O₂ and residual content for N₂. The gas emitted at the main seep is composed by 89% CH₄, 9 to 9.5% CO₂, 1% residual N₂ and traces of Ar (less than 0.07%), ⁴He (0.018%) and C₂H₆ (0.0002%). H₂S measured in 2016 accounts for additional 2% vol. These values well match with the corrected IRGA measurements (respectively 92-93% CH₄, 9-9.2% CO₂ and 0% O₂). By comparison, a smaller gas seep reported locally (Meylan-Rochasson gas seep; Gal *et al.*, 2017a) is richer in CH₄ (94.5%), in C₂H₆ (1.9%) and C₃H₈ (0.3%), and has lower N₂ residual amount (0.35%), lower ⁴He (0.007%) and CO₂ contents (0.39%).

Main statistical characteristics of soil gas fluxes measured in 2016 are reported in Figure 2. Oxygen decrease over the duration of flux measurements (not reported in Figure 2) were measured on 9 points (of 69) and ranged between -3.5 and -20 g/m²/h. Both CO₂ and CH₄

fluxes reached values close to 16 to 17 g/m²/h at maximum. A CO₂ flux was always possible to monitor whereas CH₄ fluxes were measurable only on the four-fifths of the data.

Figure 2

4.3. Data analysis

All the gas concentrations measured in the soil are linearly correlated for all measured parameters (Gal *et al.*, 2017a):

- Strong positive correlations were found between CH₄ and ⁴He in 2015 (Pearson's coefficient of correlation of 0.970), CH₄ and C₂H₆ (0.981) and ⁴He and C₂H₆ (0.945);
- Weaker albeit statistically significant correlations were found between in 2015 between N₂ and O₂ (0.756), CO₂ and C₂H₆ (0.591), CO₂ and ⁴He (0.587) and in 2015 and 2016 between CO₂ and CH₄ (0.738);
- Reversely, strong anti-correlations were found in 2015 between N₂ and CH₄ (-0.989), N₂ and C₂H₆ (-0.988) and N₂ and ⁴He (-0.960);
- Last, reverse correlations were also found in 2015 between O₂ and ⁴He (-0.794), O₂ and C₂H₆ (-0.755), N₂ and CO₂ (-0.610) and in 2015 and 2016 between O₂ and CO₂ (-0.910) and O₂ and CH₄ (-0.810),
- Additional quantification of CO₂ and CH₄ fluxes allowed to add the following tendencies: strong correlation between CO₂ and CH₄ fluxes (0.918) but neither relation of CH₄ flux with CH₄ concentrations in soil gas (0.115) nor of CO₂ flux with CO₂ concentrations (0.014) when considering the whole dataset.

Among the dataset, about two thirds of the data clearly showed the influence of the gas seep (high CH₄, presence of ⁴He, C₂H₆ and CO₂).

4.3.1. CO₂-O₂ relationship

One of the most frequently studied relationships in soil gas studies is CO₂ vs. O₂ (*e.g.* Romanak *et al.*, 2012; Figure 3). Three main mechanisms result in linear correlations of both gases. By order of increasingly negative slopes of O₂ vs. CO₂ lines (Figure 3A), these are i) dilution, occurring when a deep CO₂ endmember dilutes the O₂+N₂ pool in near surface environments (slope of -0.2); ii) replacement, due to aerobic respiration in soil that consumes 1 mole of O₂ to produce 1 mole of CO₂ (slope of -1) ; iii) CH₄ oxidation in near surface environments where 2 moles of O₂ are needed to produce one mole of CO₂+H₂O (slope of -2). The linear regression line calculated using the 2015 and the 2016 measurements has a slope (-2.07) very close to this CH₄ oxidation line albeit data scattering is not negligible for CO₂ concentrations exceeding 3 to 4% vol. This suggests that CH₄ oxidation plays an important role in the appearance of CO₂ in the soil gas even if, in 2016, concentrations up to 4 to 5% of CO₂ (in the absence of CH₄) can still be attributed to near surface biological CO₂ production.

This 3 to 4% vol. CO₂ concentration range seems to be a threshold from which CH₄ oxidation process has a significant influence onto CO₂ production whatever the sampling period considered. At lower CO₂ concentrations, data are often lying in between the CH₄ oxidation line and the replacement line. This indicates a mixed origin with part of the CO₂ deriving from CH₄ oxidation and part of the CO₂ deriving from biological processes. The latter become predominant for CO₂ concentrations lower than 2% vol. Such concentrations levels can

reasonably be assumed as the mean biological background concentrations (*e.g.* Gal *et al.*, 2014 and references therein). Nonetheless, Figure 4 outlines that even at such low CO₂ concentrations the influence of CH₄ oxidation process may exist thus suggesting a complex behavior of gas emission towards the surface.

The CO₂ vs. O₂ plot allows the identification of another group of points that plots fairly well on the replacement line (Figure 3A). Their CO₂ concentrations reach more than 5% vol. and may represent soils with strong biological activity. Such concentrations are consistent with concentrations up to 8-10% of biologically derived CO₂ reported in the literature (*e.g.* Gal *et al.*, 2011, 2017b). These points are mainly located at the periphery of the monitoring zone (black dots in Figure 3B). This may suggest the maximum extension of the methane-derived CO₂-plume does not exceed a dozen of meters.

Figure 3

4.3.2. O₂-N₂ relationship

Processes are further constraint by O₂ vs. N₂ relationships (Romanak *et al.* 2012, 2017). Figure 3C indicates the existence of two distinct behaviors, evidenced mainly by the 2015 data (only 6 measurements of the N₂ concentration in 2016). The slope of the regression fit in green is close to -4 indicating quickly decreasing O₂ at near-constant, elevated N₂ concentrations. This corresponds to respiration processes and/or the presence of air as defined by Romanak *et al.* (2012, 2017). O₂ depletion on this line may be linked to biological processes, at least for O₂ concentration ranging from 21 down to 15-16% as suggested by the CO₂-O₂ plot. At O₂ concentrations close to 15-16%, the gas analyses still indicate that no

CH₄ is associated with N₂, O₂ and CO₂. When O₂ concentrations are lower than 15%, then the O₂ depletion becomes balanced by CH₄ and CO₂ concentrations increases (up to 12% and up to 9% respectively). Points having constantly high N₂ concentrations are located in the peripheral area surrounding the Fontaine Ardente main seep (black dots in the map; Figure 3C) where the influence of the gas seep becomes weaker. N₂ is only concerned by mixing with seeping gases, whereas O₂ is consumed by oxidation of both organic matter in the forest soil and of methane.

The second fit in Figure 3C (orange fit) has a slope of +0.265, close to the atmospheric O₂/N₂ ratio of 0.268, and represents the progressive mixing of air with N₂ and O₂ free gas vent (dilution line). The corresponding points are in the vicinity of the main seep. This location also well corresponds to points with a O₂ vs. CO₂ slope of ≥ 2 (Figure 3B) highlighting CH₄-oxidation. Some data (7 points, yellow black circles in Figure 3C) fall between these two main lines and they may correspond to some altered gas compositions. The spreading of these data is influenced by the CH₄ content of the soil gas phase (points with the lower N₂ concentrations are the most enriched in CH₄, up to 74 %). These points are subject to a variable influence of the gas vent with different rates of mixing between the geogenic and the biological endmembers. Plotted on the map (Figure 3C), these data are located at the peripheral of the gas vent highlighting the progressive – and non-linear – vanishing of the geogenic gas input, progressively hidden by the biological gas production in soil.

4.3.3. CO₂-CH₄ and O₂-CH₄ relationships

As CO₂ and O₂ are closely linked, the relationships between CH₄ concentrations and CO₂ or O₂ concentrations can be investigated in parallel (Figure 4). The CH₄ vs. O₂ relationship

shows less dispersion than the CH₄ vs. CO₂ relationship, as it is not affected by biological production of CO₂ in soil that may alter the compositional ratios in between gas phases.

The linear fits indicated in black in Figure 4A and Figure 4B represent the influence of atmospheric dilution. In the gas composition of the Fontaine Ardente main seep, no O₂ is present and the CH₄ concentration is close to 90%. If air is present in the soil (*c.a.* 78% of N₂ and 21% of O₂) then a decrease of the CH₄ concentration by 10% is accompanied by an increase of +2.1% in O₂ and of 7.8% in N₂ which corresponds to the atmospheric N₂/O₂ ratio.

The linear fits reported in blue in Figure 4A and Figure 4B correspond to rapid O₂ decrease accompanied by CO₂ increase at near constant CH₄ with a slope close to -2.4. The underlying process is oxidation of organic matter in the wood soil and root respiration, predominant in points located at the periphery of the gas seep. Minor contribution of CH₄ oxidation to the O₂ depletion and to the CO₂ enrichment may also exist. In the vicinity of the gas seep the dominant process is the seepage of methane and associated CO₂.

Figure 4

4.3.4. CO₂ flux – CH₄ flux relationship

Figure 5 shows the relation between CO₂ and CH₄ fluxes. The Pearson's coefficient of correlation, for the whole dataset, masks again a bimodal repartition of the data. Part of the data shows a good linear fit between the two parameters but this relation is mainly defined by a few high fluxes (3 data) whereas intermediate values are lacking (Figure 5A). In the present case study, a CH₄ flux is considered as high when it is greater than 2 g/m²/h. Point 17 has a CH₄ to CO₂ flux ratio close to 1, compared to 2.1 and 2.4 for the two other points (28

and 31), whereas the ratios between CH₄ and CO₂ concentrations are respectively 6.1 (point 17), 9.4 (point 28) and 8.6 (point 31). In the lower CH₄ flux range (grey dots in Figure 5B) CH₄ flux represents approximately half of the CO₂ flux.

Two conclusions come from these statements. The first is that the emission of CH₄ is highly variable over short distances albeit the higher fluxes are monitored in close vicinity to the main seep. The second is that there is no relationship between the soil concentrations at 1 m depth (Figure 4) and surface fluxes (Figure 5). This is a common observation in non-active areas – no volcanic nor geothermal activity (*e.g.* Gal *et al.*, 2014). In areas of deep gas fluxes (CO₂: *e.g.* Battani *et al.*, 2010; CH₄: *e.g.* Etiope *et al.*, 2011a) or where gas fluxes are intentionally induced (*e.g.* Schroder *et al.*, 2016), the link with concentrations may be stronger, even though complicated by transport through a thick soil column (*e.g.* Jones *et al.*, 2017).

The impervious geological substratum of the black shales would favor discrete gas flux on fractures rather than diffuse fluxes. Another preferential pathway might be drillholes that could have concentrated the formerly rather patchy gas leakage. At the surface level, the combination of former reworking and the existence of a clayey cover may lead to poor connection between CH₄ enrichment in the soil and CH₄ emission at the soil surface as the driving force is not sufficient for allowing stronger efflux.

Numerous points in Figure 5B show low to very low CH₄ fluxes (less than 0.1 g/m²/h excepted 1 sample at 0.18) and a wider scattering of the CO₂ flux (up to 4.5 g/m²/h). The locations of these points are generally randomly distributed all around the gas seep with the exception of some points (light blue and light blue-green dots in Figure 5B) which have CO₂ flux greater than 1 g/m²/h and which seem to surround the main seep a few meters away.

Even if the values of CH₄ fluxes are low, they are still influenced by the gas seep. Methane emissions quantified in forests or in grasslands are indeed frequently 1000 times lower (Jones *et al.*, 2005; Von Arnold *et al.*, 2005) and may rise up to 0.01 g/m²/h as a consequence of agricultural practices such as cattle slurry spreading (Jones *et al.*, 2005) or in wetlands (Le Mer and Roger, 2001). Similarly, CO₂ fluxes reaching 4.5 g/m²/h are still high compared to fluxes measured in standard environments where they are generally 10 times lower with the exception of agricultural spreading (up to 3.3 g/m²/h; Jones *et al.*, 2005) or enhanced emissions in clayey soils (up to 2.3 g/m²/h; Gal *et al.*, 2014). The measured CH₄ and CO₂ fluxes are then still influenced by the existence of the gas seep but there is no clear relation between the strength of the CO₂ flux and the location of the sampling point (Figure 5B). It is then complicated to distinguish between a CO₂ flux mainly linked to the gas seep (CO₂ produced by CH₄ oxidation) and a variable contribution to the CO₂ flux of biological origin.

Figure 5

A few points showed a progressive depletion in oxygen concentration during the flux measurement. These “negative” O₂ fluxes are reported in Figure 6 together with CO₂ and CH₄ fluxes. Locations having the highest CO₂ and CH₄ flux (points 1, 17, 28, 31 and 73) plot on linear fits thus suggesting that the O₂ depletion is intrinsically dependent from the strength of the CH₄+CO₂ emission to the surface. Each rise of one flux unit is related to a decrease of one unit of the O₂ flux with an intercept point at -3 to -4 g/m²/h, value under which the accuracy of electrochemical sensing cells is not sufficient to allow adequate monitoring of small changes of the O₂ concentration.

The most interesting case is point 73. At this location, the O₂ depletion is high (-10 g/m²/h), the CO₂ flux is high (4.5 g/m²/h) and the CH₄ flux is zero. In the soil, there is an O₂ depletion that is partially balanced by the presence of CO₂ (CO₂/O₂ = -1.5) and only traces of CH₄ are found. The classical way for interpreting this O₂ depletion is to consider that an oxygen flux from the atmosphere to the soil exists. Nevertheless, point 73 plots on the CO₂ flux – O₂ flux linear fit that is defined for locations where a CH₄ flux exists. The O₂ depletion monitored at this point thus represents the influence of the CH₄ gas seep and the genesis of O₂ depletion is a consequence of CH₄ oxidation that produces CO₂ that is to some extent mixed with biologically produced CO₂.

Figure 6

4.4. Data analysis

4.4.1. Qualifying and quantifying the CH₄ and related CO₂ emissions at the

Fontaine Ardente (main seep and peripheral areas)

4.4.1.1. Variability of the gas emissions

The variability of soil gas signals can be considered along three different time scales from short variations to daily variations and yearly changes. During the two field surveys, no strong daily variations of the soil gas signals were observed. This may be a consequence of the restricted emissive area. Similarly, between the two surveys, the gas anomalies in the soil had the same order of magnitude suggesting that the contrasting meteorological conditions in 2015 and in 2016 had little influence. Over longer time scales, Etiope *et al.* (2010) have highlighted thermal forcing on flux emissions in a gas seep in Switzerland but

they also established that air pressure and relative humidity have no influence onto long-term measurements.

The other time scale that can be considered is the 3 min duration of flux integration during chamber measurements. Gas emission of major species can also be variable over few minutes (Figure 7). Point 10 represents the routine situation with linear increase of the CO_2 concentration indicating constant gas emission. The situation was different for some monitoring points. Examples of varying flow are shown for points located close to the gas seep (Figure 7). We observe both examples of sudden and simultaneous increases of CO_2 and CH_4 fluxes (point 13) and decreases (points 15 and 17) that are not necessarily synchronous for both gases (point 17). Very short-term changes have also been observed (point 17). These variations may induce a bias in the estimation of fluxes. Of 69 CO_2 and 54 CH_4 flux measurements, respectively 17 and 12 showed variations, and for two in each case fluxes were potentially underestimated.

We could not perform repeated monitoring at these points so the bias linked to these short to very short term fluctuations of the seepage rate could not be precisely assessed. These fluctuations are also attested by the rapidly changing height of the flame as depicted in Figure 8. An estimation of the bias that may be related to this short term variability has been done by examining each gas accumulation curve during time. On the 69 CO_2 flux measurements, 17 showed temporal variation during the CO_2 accumulation phase among which only 2 were potentially underestimated. On the 56 CH_4 flux measurements, 12 showed temporal variation and by them 2 were also potentially underestimated. Thus, the flux measurements may rather lead to a slight overestimation of the global CO_2 and CH_4 budgets released into the atmosphere so that our estimates can be considered conservative.

Figure 7

Figure 8

4.4.1.2. Spatial distribution

Albeit our dataset is relatively limited compared to those that may be used e.g. in volcanic environments (*e.g.* Ciotoli *et al.*, 2016), such investigations on small areas can nevertheless yield to accurate estimates of both the gas emissions and the pattern of these emissions (Etiope *et al.*, 2010). As may be viewed from data available in the supplementary information, our dataset is skewed and neither ranges under normal nor log-normal data distributions. The existing bimodal distribution is a consequence of the existence of two distinct phenomena. The first is the presence of the gas seep and the second are common biological processes in soils. The definition of threshold values is thus done using quantile-quantile (Q-Q) plots (*e.g.* Ciotoli *et al.*, 2007) further allowing the calculation of the quantity of gas emitted to the atmosphere using Graphical Statistical Analysis (*e.g.* Bloomberg *et al.*, 2012, and references therein).

Variogram calculations were done for the data falling in the 20x20 m side square around the main seep (see supplementary information). All the data show an anisotropic pattern with the main axis elongated along the N45 direction with a length ranging from 6.5 to 13.7 m (9.2 m as a mean). Such a shape is in good agreement with the spatial extent of the gas vent that may be deduced directly from field measurements: high CH₄ values were found along the axis of the Vernant creek which flows to the NE and these high values were found in a narrow perimeter (less than 20 m of side).

Data are used to build classed post maps (shown in supplementary information) and interpolated maps (Figure 9). Classed post maps are presented for the entire monitoring area with detail for the vicinity of the main seep whereas contours maps only refer to this area of reduced size. These maps highlight once again that the majority of soil gas anomalies are located within few meters around the gas seep. From the classed post maps it is not obvious to define whether the degassing is structured along pathways inherited from structural or morphological features or if the degassing occurs randomly close to the vent.

A better definition of the spatial distribution of the degassing processes is given by contour maps (Figure 9). The N45 direction, which is the average flow direction of the Vernant creek and which was also highlighted by variogram calculations, suggests the existence of preferential pathways inherited from structural constraints. A second direction of degassing can also be defined using the helium gas contents in soil probably related to the ability of helium to laterally diffuse as a consequence of its low molecular weight (*e.g.* Toutain and Baubron, 1999). This second direction is close to N170, a direction that is commonly found in the limestones of the Vercors Massif. As for classed post maps, flux data do not allow defining or refining the structural shape of the gas emissions to the surface. Contour maps are dominated by a few outliers (high fluxes) which induce a peak-like interpolation. This may be a consequence of site alterations in the since the 19th century: the point where CO₂ and CH₄ emissions to the atmosphere are at their maximum value is indeed located on a break of slope, in front of the gabion wall that has been built to shelter the fountain, as visible on Figure 1 in the foreground of the panoramic photo.

Figure 9

505

506 **4.4.1.3. Gas emissions to the atmosphere**

507 Even if the Fontaine Ardente gas seep has a rather limited spatial extension – other seeps
508 may have considerably larger geographical manifestations (*e.g.* Etiope *et al.*, 2011b) – the
509 evaluation of the CH₄ and CO₂ emissions to the atmosphere is interesting. As shown by the
510 site monitoring, the main emission point is clearly the main seep itself, probably in strong
511 relation with the existence of the former FA2 borehole (Figure 1) that focuses the gas
512 emission by draining. Nonetheless, gas fluxes to the atmosphere are not restricted to the
513 former borehole and exist over a larger area that extends northeastwards from the seep and
514 their contribution has also to be quantified.

515 Estimations on the gas release at the seep mouth are done using the fire dynamics model of
516 methane flux vs. flame size (Etiope *et al.*, 2011b, and references therein) using the heat of
517 combustion given by Etiope *et al.* (2013a) for CH₄. Typology of the gas emission is taken from
518 flame height and diameter at emission point estimated using Figure 8. As the main seep
519 exhibits rapid changes in the flame height, the emission rate ranges between 15 kg per day
520 (flame of 38 cm height and 12 cm on diameter) and 84 kg per day (flame of 77 cm height and
521 24 cm on diameter). Based on the flame size variations that may be observed at the seep at
522 short time scale, the amount of CH₄ released in the atmosphere can be estimated to be
523 somewhere between 40 and 50 kg per day. The estimated release rate in the 90's, obtained
524 from pressure considerations (Berthier *et al.*, 1991), was 130 l/min giving approx. 120 kg of
525 CH₄ per day. Our present estimates, based on the flame height, may then be underestimated
526 *e.g.* as a consequence of short duration of the measurements. A significant uncertainty on
527 the result has been pointed out by Etiope *et al.* (2011b) especially when the gas emission is

high and turbulent. This new estimate may also represent a real decrease in the feeding rate of the borehole, the gas flux migrating along this preferential pathway changing with time.

The case of the Fontaine Ardente degassing area is also interesting insofar as this gas seep is CO₂-rich. Using the CH₄ flux estimated in the 90's and the proportion of CO₂ in the gas phase (approx. 11%), the quantity of CO₂ released in the atmosphere through the vent can be roughly estimated at 14 l/min *i.e.* 36 kg per day. Based on flame height estimates and still considering a proportion of CO₂ in the gas phase of 11%, then the estimate of the CO₂ release at the gas vent is close to 15 kg per day as a mean (range: 4.5 to 25 kg per day).

The CH₄ and CO₂ emissions from the soil are first quantified on a 84 m² area included in the larger 20 x 20 m area reported on Figure 9. The area is not a square area as the vicinity of the gas seep cannot be investigated (concrete plugs + gabion) but its geometry is likely to be representative as most of the efflux is located inside this small region (see Figure 9). This approach considers that the flux measured at one point is valid for 1 m²; in case the grid mesh is 2 x 1 m, then the value assigned in between two real measurements is the mean value of these two measurements. The sum of the fluxes is 44.8 g/h for CH₄ and 88.3 g/h for CO₂ leading to releases of 1.07 kg of CH₄ and 2.2 kg of CO₂ per day. A refined estimate is obtained using the interpolated maps. Integration of the anomaly is done using Surfer® software and indicates, for the whole flux monitoring zone (240 m²; Figure 9), a release of 2.83 kg of CH₄ and 6.27 kg of CO₂ per day. These estimates are in perfect agreement with those obtained using the 84 m² area [$1.07 \times (240/84) = 3.05$] suggesting that even the basic method could lead to realistic evaluation in the present case. Nonetheless this flux estimate doesn't take into account gas emissions that may occur with the area covered by concrete plugs which may be fissured and permeable to gas.

More sophisticated methods (*e.g.* Bloomberg *et al.*, 2012) or other spatial interpolation methods (*e.g.* Schroder *et al.*, 2017) may be used to quantify more precisely the leakage associated to the gas seep. Nonetheless, even well constrained data interpolation methods lead to biases in the emission estimates. During controlled release experiments, Schroder *et al.* (2017) report differences of 20 to 45% using the method that best fits the data. In the present case, the main emission is the gas seep itself, and errors on the soil emissions may be considered as negligible. Methane emission at gas vent ranges from 18 to 44 tons per year (2016 flame estimate / 1990 data) and CO₂ emission ranges from 5.5 to 13 tons per year. Referring to our measurements, the CH₄ emission from soils represents less than 6% of the CH₄ emitted at the seep (1.03 ton per year) whereas the CO₂ emission from soils accounts for 42% of the CO₂ emitted at the seep (2.3 tons per year) including biogenic soil CO₂. This biological component can be estimated to account for two thirds of the CO₂ release on the basis of volumes calculated using interpolated maps with a biological CO₂ production fixed at 1.25 g.m⁻².h⁻¹ (Werner and Brantley, 2003).

Conjoint emission of CH₄ and CO₂ in gas seep is not a common phenomenon. In the European database from Etiope *et al.* (2009) or the data from other countries (Etiope *et al.*, 2011a), which concern mud volcanoes, CO₂-rich emissions (8% vol. or more) are rare and linked to thermogenic CH₄. CH₄ seep rates associated to mini- and micro-seepages range from less than 10 up to 446 g/m²/day; associated CO₂ seep rates range from 3 to 535 g/m²/day (Etiope and Klusman, 2002). Maximum seep rates measured at point 17 are in this range (408 and 374 g/m²/day for CH₄ and CO₂ resp.). Abiotic methane emissions from ultrabasic rocks are associated with very low CO₂ emissions (Etiope *et al.*, 2011b). In such cases, CH₄ emissions can reach hundreds of g per day per m² but CO₂ emissions only reach 65 g/m²/day when soil litter is present and 10 g/m²/day when soil is absent. Eternal flames

from the USA (Etiope *et al.*, 2013a) or gas seeps reported in Switzerland (Etiope *et al.*, 2010) are not reported to be CO₂-rich but CH₄ emissions can reach 40 kg per day and 10 kg per day respectively in the US and in Switzerland (strong miniseepages, from hundreds of g/m²/day up to a few kg/m²/day). Similarly, studies of the large thermogenic gas seepage of Katakolo (Greece) only report CH₄ emissions (from 5.4 to 98.6 kg per day onshore; Etiope *et al.*, 2013b) albeit 6 to 8% vol. of CO₂ are monitored in the gas phase. Quantification of CO₂ emissions from natural methane seeps is rare, opposite to numerous studies of CO₂ emissions in volcanic or geothermal areas (*e.g.* Cardinelli *et al.*, 2003b).

The Fontaine Ardente area has thus a specific behavior that may partly be a consequence of the presence of a draining structure (borehole) and related impact onto surface properties of soil. Methane is found at high concentrations in the soil with moderate to weak leakage into the atmosphere. Most of the CH₄ is vented through the borehole that constitutes by itself an important gas seep. According to the terminology of Etiope (2015), miniseepage occurs around the gas vent but only accounts for 5% of the global budget of CH₄ emitted (compared to the lowest estimate of 18 tons/y). This differs from the gas emission reported in the Giswil by Etiope *et al.* (2010) where two thirds of the CH₄ are vented through two main seeps and one third is vented by miniseepage on a smaller area (115 m² compared to 240 m² at Fontaine Ardente area). The other specific character of the Fontaine Ardente seepage area is the richness of the gas phase in CO₂. At the scale of the miniseepage area, this leads to a quantity of CO₂ emitted being more than two times that of CH₄. This is a rather unique situation in the Alpine context and GHG emissions evaluations have to consider both CH₄ and CO₂ gas phases to be pertinent.

The other specificity of the Fontaine Ardente main seep is that it represents a unique analogue of a leakage situation. Hydrocarbon resources are rarely located at few meters below ground level. Here, a borehole intersects at c.a. 10 m depth geological formations which act as drain for CH₄+CO₂ gas mixture. The borehole as preferential pathway focuses gas emissions to the surface, similarly to degassing pipes like those in lakes Nyos and Monoun (Halbwachs *et al.*, 2004). The gas which is not vented through the borehole diffuses laterally in the subsurface layers through pathways whose geometry is likely to be influenced by the network of local fractures.

Old pictures, previous to drilling, clearly show numerous small vents, whereas at present there is a unique and dominant gas seep with only minor contribution of diffuse seepage. This highlights the impacts of small-scale works on gas flux patterns.

5. Implications for methane or CO₂ baseline assessment and monitoring

Several tens of tons per year of both CH₄ and CO₂ gas phases are naturally released in the atmosphere by the Fontaine Ardente main seep thus contributing to GHG emissions over at least two millenaries. Apart from gas released at the borehole mouth, the amounts of CO₂ emitted through soil degassing may largely exceed the range of natural CO₂ flux (from 7.6 to 76 g/m²/day; Klusman, 2015, and references therein) with maximum values greater than 350 g/m²/day. Similarly, CH₄ emissions reaching 10 g per m² per day around the main seep are considerably higher than those measured over grasslands during summertime with 4.86±22.8 mg per m² per day (mean + standard deviation) reported by Klusman (2015, and references therein). Apart from this quantification of GHG emissions, a second interest of this study was to test monitoring techniques and strategies to better assess the natural gas

baseline for impact studies. The production of unconventional natural gas has profoundly transformed the global energy game over the past ten years. Environmental stakes of shale gas exploration and exploitation show some similarities with the CCS thematic, specifically with the risk of leakage from geological formations from which CH₄ can be produced or in which CO₂ can be stored, albeit the gas species of interest have very different behavior in *e.g.* their reactivity or dissolution properties.

The example of the Fontaine Ardente seepage area makes it possible to investigate simultaneously methane and CO₂ migration on a unique natural analogue and to learn more about containment monitoring in settings where potential pathways to the surface exist (Jenkins *et al.*, 2015). It constitutes furthermore one of the rare examples of “eternal flames” directly emerging from shale formations, together with those from the Appalachians (Etiope *et al.*, 2013). More specifically, the Fontaine Ardente main seep case represents an example where the leakage is focused to a 1D pathway, represented by the former FA2 borehole. Here, the leakage does not occur from the casing itself, because of the presence of a concrete platform at surface, or from defective completion of the casing, which will be the most frequent occurrence of failure. Leakage occurs through the open borehole and this drillhole has strongly modified the gas emission on the site. From a spotty and rather diffuse leakage situation, attested by old photographs, it has been changed to a gas vent, with the borehole as main emitting structure, with minor contribution of diffuse degassing. It is thus possible that a hypothetical closure of the well will induce a highly different distribution of the seepage with strongly enhanced diffuse degassing, probably occur along fractures/faults following the main structural directions (Roberts *et al.*, 2015; Bond *et al.*, 2017).

This natural analogue highlights the potential difficulties of baseline assessment and site monitoring during exploration or exploitation of unconventional gas. The expected spatial extension of the leakage will condition the resolution of the monitoring grid (e.g. observation boreholes) and wrong initial hypotheses may lead to an incapacity to detect any anomaly related to leakage. The strongly focused fluxes at the Fontaine Ardente seepage area, further enhanced by the drilling, are somewhat similar to what might be expected in case of shale gas well failure, with a very restricted area of leakage around the borehole. Other leakage pathways, e.g. out-of-formation hydraulic fracturation, may lead to a much more diffuse pattern at surface, due to the predominantly diffusive or pervasive migration, from the host formation, via overlying deep aquifers to shallow formations. Timing of such migration can be also very different from direct pathways via leaking wells.

Transposed to a real shale gas or CCS site, the difficulty to anticipate and detect gas seepage areas will be a major challenge for baseline assessment and site monitoring. The area studied here is very small (around 240 m²), vegetated and set in a narrow thalweg. Surveying methods used directly at ground level may not be operative (too large mesh size) or they should require so much manpower that their cost will dramatically increase in case the grid has a very low mesh size. There is an extensive literature that points out the narrowness of gas emissions from faults and fractures and very recent data still agree with this feature (e.g. Jolie *et al.*, 2016; Bond *et al.*, 2017). The disadvantage of ground monitoring techniques may be overcome by airborne/UAV operated methods or methods having wider aperture (such as Eddy-Covariance – EC, laser operated methods...). Such methods are capable of giving better geographical coverage provided that they are appropriately settled. In the case of the EC method, changes of gas flux are monitored in an upwind direction. Nevertheless such methods may suffer from other disadvantages such as the decrease in sensitivity as a

function of distance to the emission point or the existence of photosynthetic processes on land surface or in the canopy (Klusman, 2015).

When working in a blind manner during baseline studies, in a setting similar to that of Fontaine Ardente area, it seems very difficult to detect gas anomalies related to minor or even major gas seeps. Topography and vegetation play an important role in the detectability of anomalies. Natural seeps from shale formations, as it is the case for the Fontaine Ardente, are frequently located on creeks, themselves following fault structures (Etiope *et al.*, 2013a). Their detectability by landborne methods may be simply limited by logistic obstacles and sampling resolution. With the available techniques, it seems virtually impossible to discover unknown seeps through a systematic research. Etiope *et al.*, (2013a) used the Tunable Diode Laser Absorption Spectroscopy (TDLAS) detectors in accumulation flux chambers to locate methane anomalies in ambient air but only in the vicinity of known eternal flames. Using a statistically stringent measurement pattern (grid) for landborne surveys would be hindered by (1) the accessibility of natural areas with rough terrain and (2) the possible resolution of such a grid compared to the size of anomalies. Some hope can be placed in vehicle-born surveys using CRDS (Cavity Ring-Down Spectroscopy) detectors but this approach fits best to urban areas with a high road density (Gallagher *et al.*, 2015) as well as to anthropogenic sources identified previously to the survey (Zazzeri *et al.*, 2015). It is unlikely that natural point-source emissions from gas seeps of a similar size to the Fontaine Ardente could be detected by such a technique. Airborne techniques, again using CRDS, are capable of detecting major methane plumes from known sources (e.g. landfills; Krautwurst *et al.*, 2017) at kilometeric scale but, again, their use in the present case seems to be highly limited by the vegetation cover and the topography.

To approximatively assess the vertical extension of the plume emitted by the Fontaine Ardente we used infrared cameras with specific lenses for targeting CH₄ or CO₂ gas phases (FLIR GF320). Such devices can image the gas plume emitted by the borehole and its dispersal in the atmosphere. Some wisps of gas do reach the base of the canopy, some meters above ground level, but they rather rapidly vanish afterwards (Figure 10). If the leakage flux rate is lower than the one of the Fontaine Ardente main seep (FA2 borehole), the detection by plume imaging becomes virtually impossible in practice. Thorough scanning of the miniseepage area did allow detecting a possible leakage area only after minutes of careful monitoring. It is established that such infrared cameras are not conceived for the detection of diffuse minor leaks in a natural environment (contrast problems) and that other monitoring techniques have considerably lower detection limits. Nevertheless, such cameras allow visualizing in real time the shape of the gas emissions especially vertically. Given our preliminary results, any other monitoring at the upper level of the canopy will be very difficult even using techniques with low detection ranges, including low-altitude airborne techniques.

Figure 10

The question on the best baseline and monitoring strategy for leakage assessment remains thus largely open. Landborne monitoring will always miss anomalies because of restricted accessibility – in our case the ability to perform accurate measurement in forested area – or because of lack of sensitivity – in our case quick dilution of the gas in the atmosphere. Consequently, appropriate monitoring strategy should rely on dense monitoring of structures and/or areas that are suspected to be potential pathways for leakage (known

712 faults, creeks...; Etiope *et al.*, 2013a). As dense monitoring cannot cover a large area,
713 monitoring should be adapted to the size and location of the expected leak. This requires a
714 realistic conceptual model of the leakage mechanisms and pathways, relying on a
715 statistically sound database of gas emissions in the context of the storage to monitor. The
716 temporal resolution of monitoring and its duration is another crucial issue, depending on (1)
717 the temporal variations of the baseline emissions and (2) the kinetics of potential gas
718 migration via the different suspected pathways (e.g. borehole failures, out-of-formation
719 fracturation..., existence natural fractured zones). In case of leakage allegation, even if the
720 alleged zone has not been surveyed before, the knowledge of local behavior of soil gas
721 emissions will allow to adequately identify an anomaly in the soil gas signals – an approach
722 defined as process-based approach by Romanak *et al.* (2012). The example on how the
723 leakage allegation in Weyburn was withdrawn shows how powerful such an approach can
724 be. Furthermore, it may not only apply to soil gas using the established CO₂ vs. O₂
725 relationship but also to soil gas fluxes using the derivative relation CO₂ flux vs. O₂ depletion is
726 the soil efflux.

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Figure captions.

Figure 1 A: Location of methane-rich gas seeps in the W-subalpine chains (Blavoux *et al.*, 1990, Etiope *et al.*, 2010, Gal *et al.*, 2017a) plotted on the geological map of France (1:1 000 000, BRGM). Geological formations in blue range from Lower Jurassic to Upper Cretaceous; B: close-up view of the Fontaine Ardente du Gua gas seep: different views in 2015 and 2016 showing the bare soil zone where CH₄ emissions occur and the pebbly area where the Vernant creek usually flows (arrow indicates the location of the Fontaine Ardente corresponding to the location of former wellhead of FA2 borehole); C: location of the sampling points in 2015 and in 2016 (satellite photograph from Google Earth).

Figure 2 : whisker plots for the 2015 and the 2016 surveys. CO₂, O₂ and CH₄ soil gas concentrations data: GC measurements (2015) and corrected IRGA measurements (2016). Other soil gas concentrations data: GC measurements only. Flux data are only available for 2016 (see supplementary information for details about flux calculation).

Figure 3: A: O₂ vs CO₂ binary plot; B: location of points as a function of the slope of the O₂ vs CO₂ relationship (inset: detailed location around the main vent). Blue circled points correspond to points labeled in **Error! Reference source not found.** C: left: O₂ vs N₂ binary plot showing two data distributions; equations of each linear fit are indicated; yellow points correspond to 2015 data plotting between the two distributions; right: location of points as a function of the slope of the O₂ vs N₂ relationship: grey dots for the orange linear fit (N₂+O₂ depletion line = dilution line); white dots for green linear fit (O₂ depletion line = respiration line).

Figure 4: A: CH₄ vs. O₂ binary plot; B: CH₄ vs. CO₂ binary plot. Plots are drawn using filtered data by reference to the N₂+O₂ depletion line and the O₂ depletion line defined in Figure 3.

The map (C) locates the points as defined by the linear fits in black and blue lines in the binary plots (points in black and blue respectively).

Figure 5: A: left: relation between CO₂ and CH₄ fluxes for all measurements; right: location of the measurements; B: left: relation between CO₂ and CH₄ fluxes for low CH₄ fluxes (lesser than 1 g/m²/h); the linear fit corresponds to the data plotted in grey circles; right: map showing the geographical distribution of high and low CO₂ fluxes (high fluxes are divided into 3 subgroups).

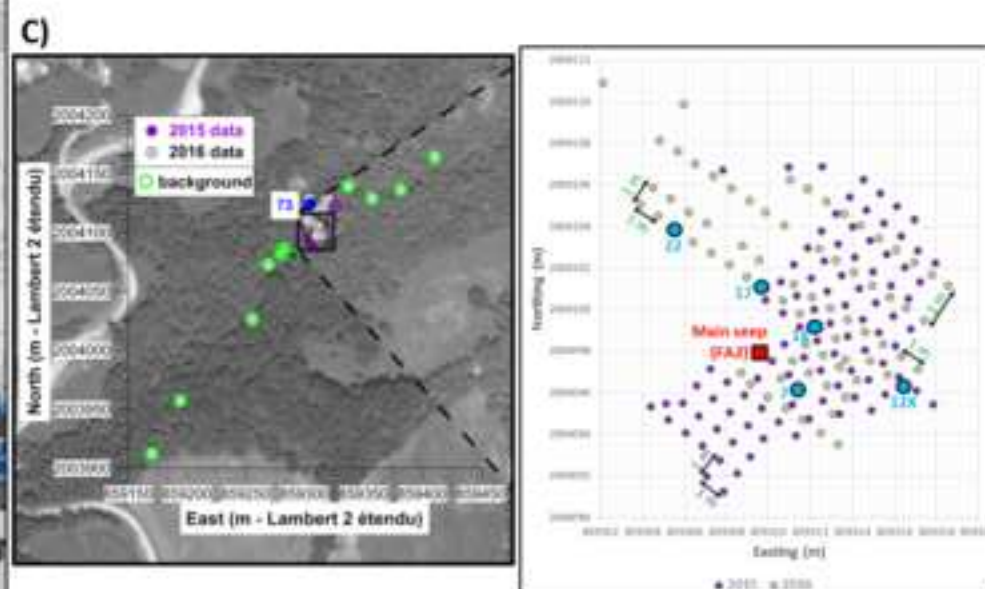
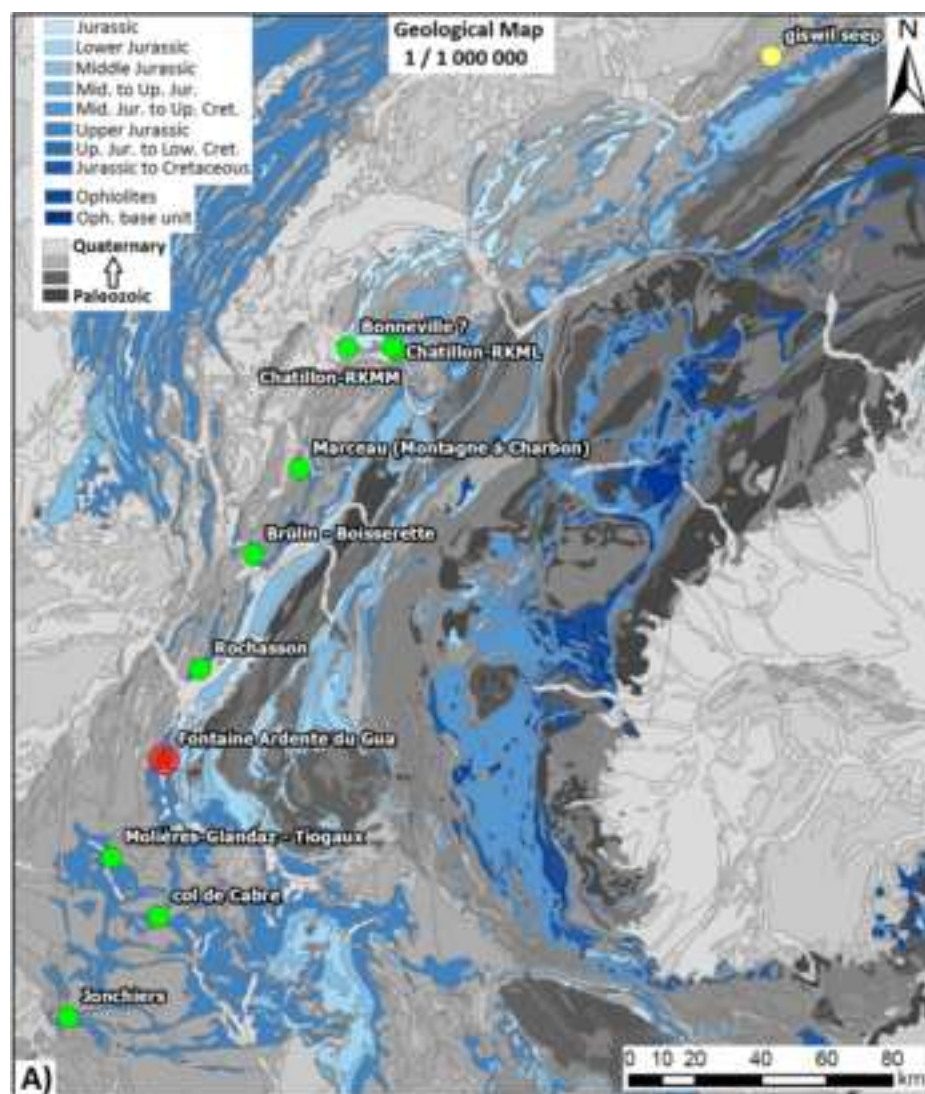
Figure 6: A: O₂ depletion as a function of CO₂ flux or CH₄ flux; B: geographical location of points showing O₂ depletion.

Figure 7: typology of CO₂ concentration increase and CH₄ concentration increase (shaded area) in the chamber during flux measurement. Blue lines represent the fits used for flux calculations; red lines represent the fits that are not used for flux calculations.

Figure 8: chrono-photography of the “Fontaine Ardente” gas seep in the manner of Étienne Jules Marey, French physiologist (end of XIXth) – 06 October 2016.

Figure 9: contour maps of soil gas species (concentrations in % vol.) and soil gas flux (in g/m²/h); kriging is done using data reported in supplementary information. Locations of measurements are reported on each map: area investigated during soil gas measurements: 400 m² (20x20 m); area investigated during soil flux measurements: 240 m² (dashed polygon in bottom maps). The red dot indicates the location of the “Fontaine Ardente”. The striped area in bottom right map shows the emplacement of the Vernant creek bed; the dark grey area shows the area (84 m²) used for quantification of the gas emissions (no flux measurement possible in the light grey area: old concrete plugs from former FA2 borehole).

971 Figure 10: infrared camera monitoring using specific lens sensitive to CO₂ (FLIR); the picture
972 in the right shows the conditions of monitoring, with shooting of the CO₂ plume just above
973 the flame (as can be seen in the background). The insets in the left show, from bottom to
974 top: the CO₂ plume directly issued from the burning seep; the CO₂ plume reaching the first
975 branches in the trees (3 to 4 m above ground); the dilution of the CO₂ plume at around 5 m
976 height.



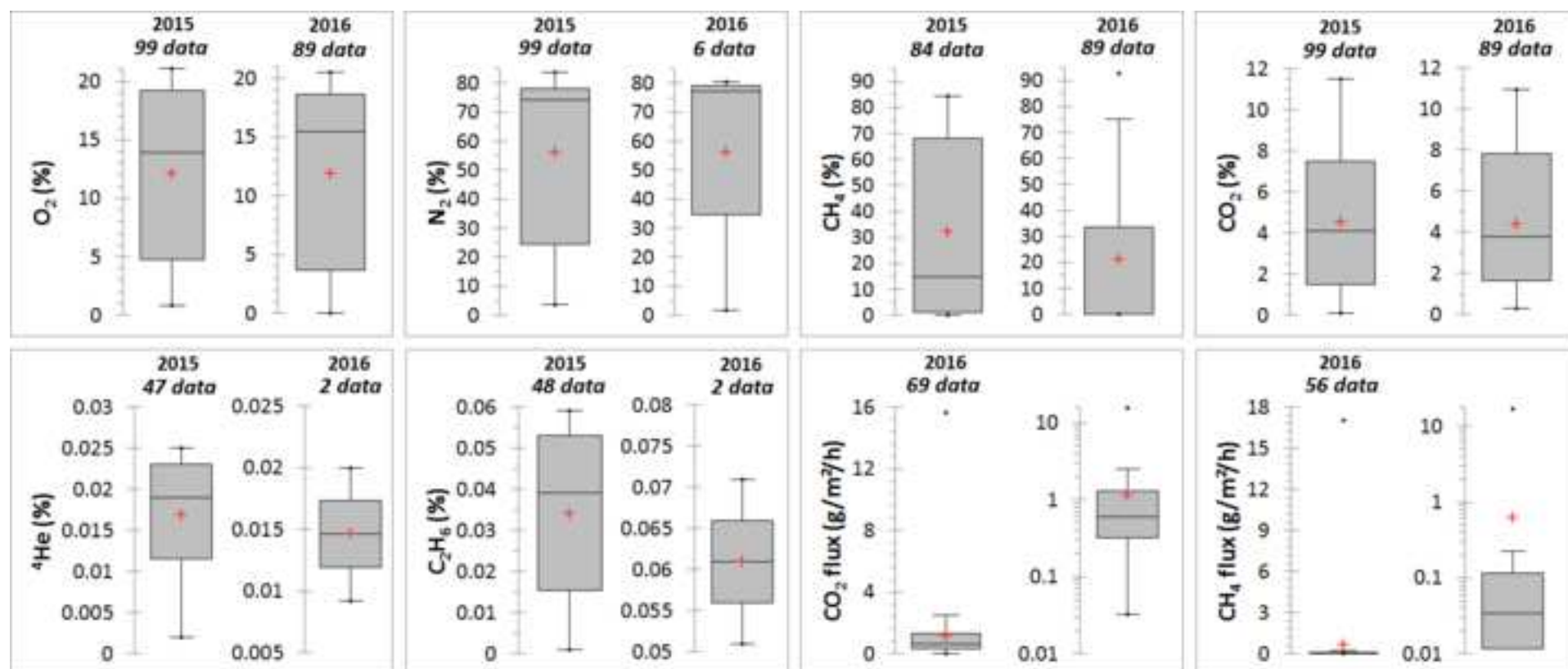
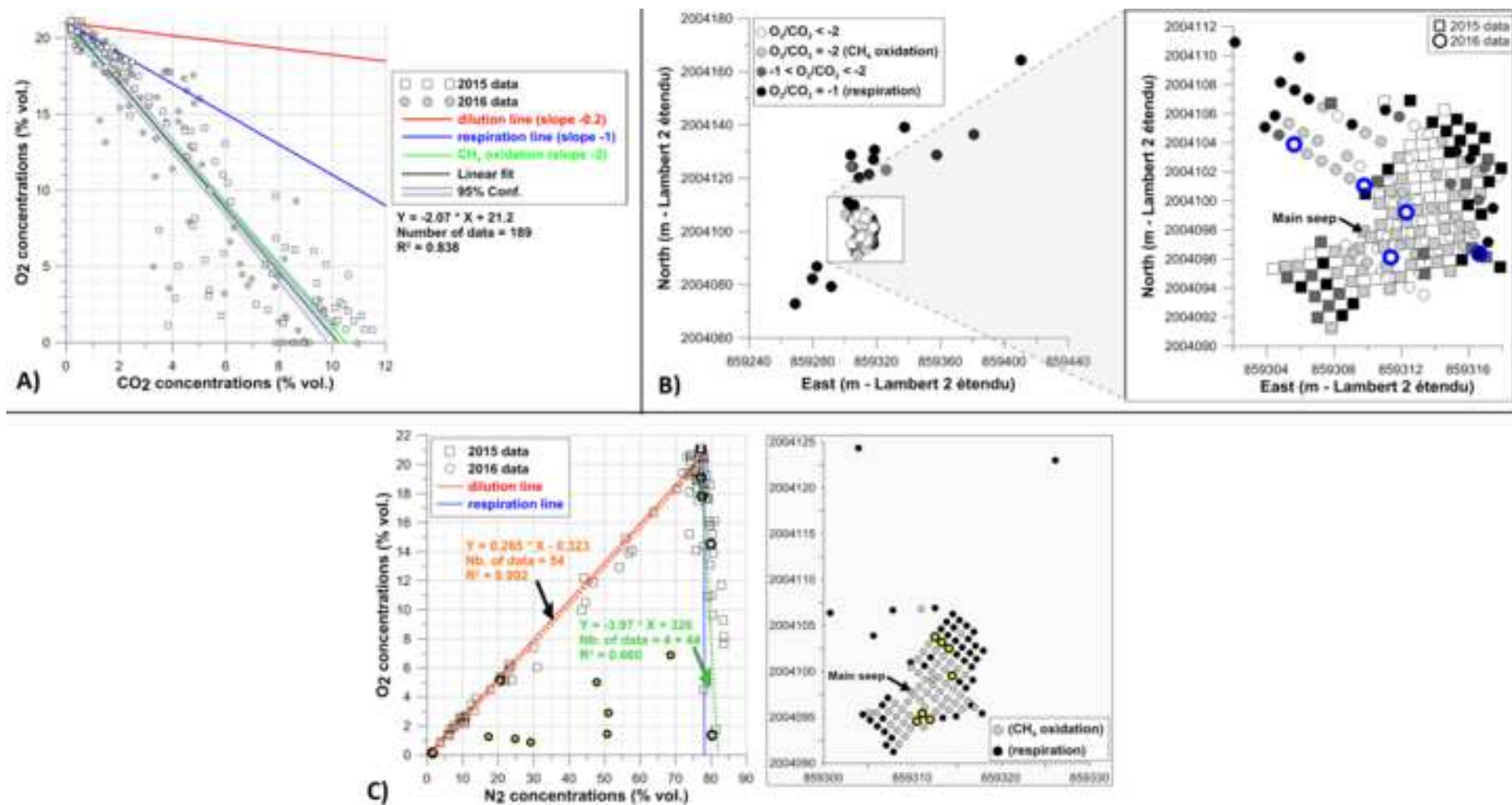


Figure 3

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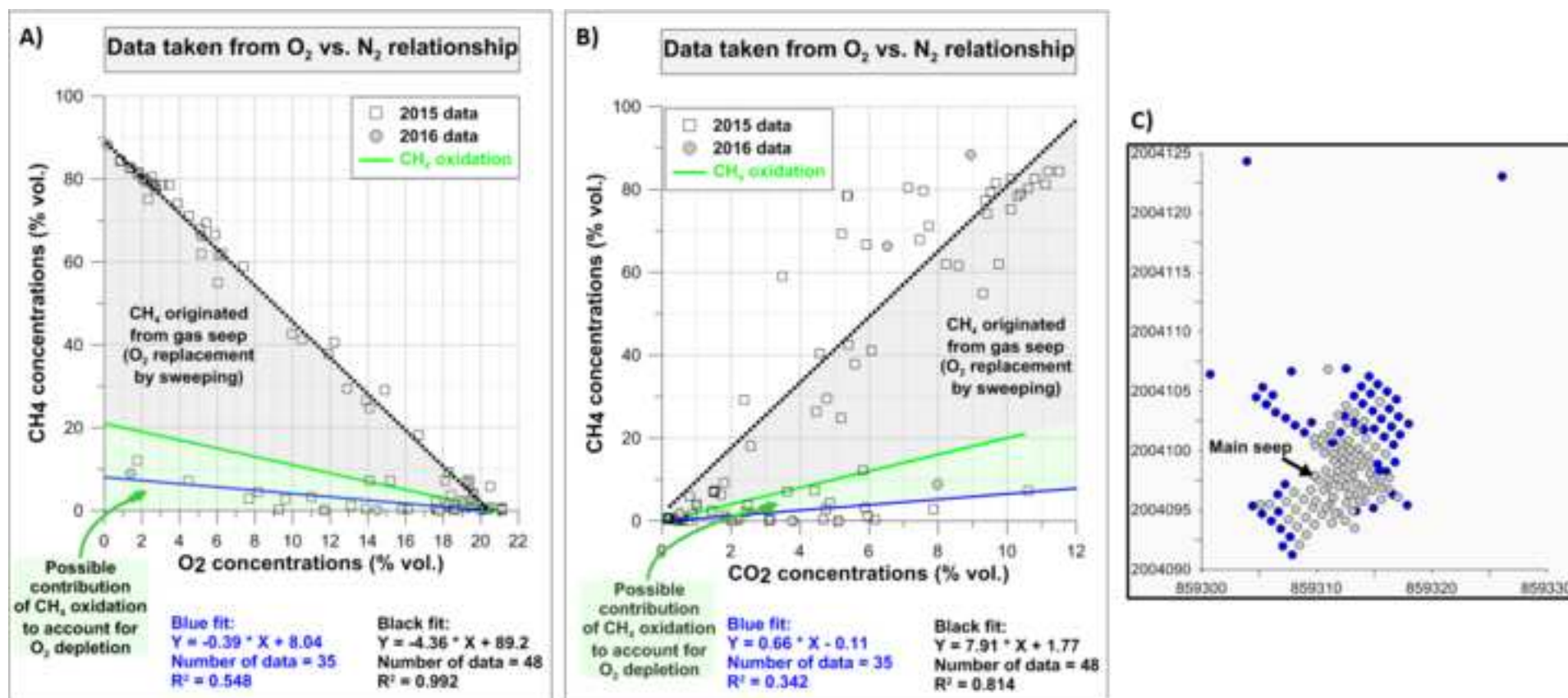


Figure 5

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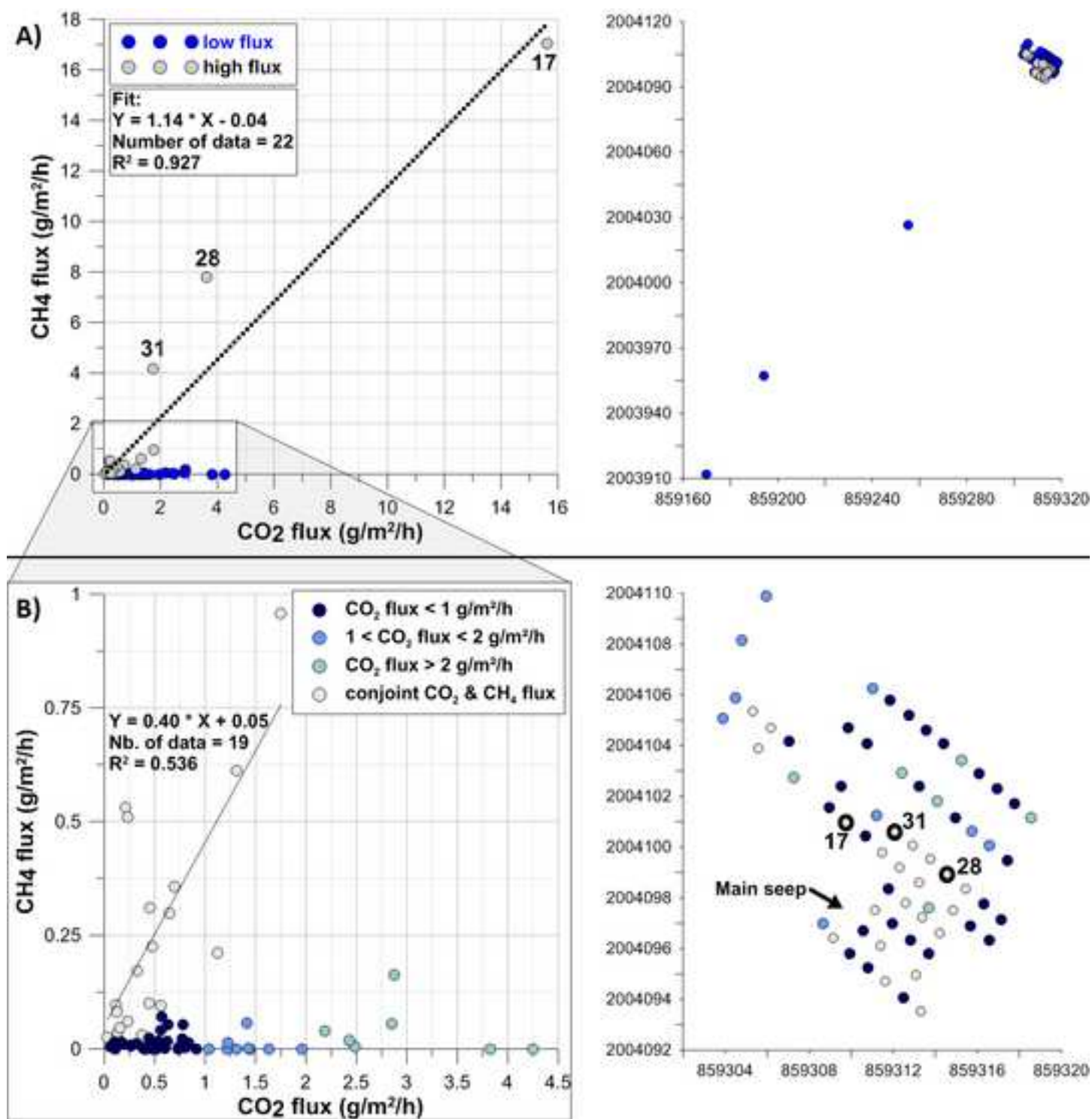


Figure 6

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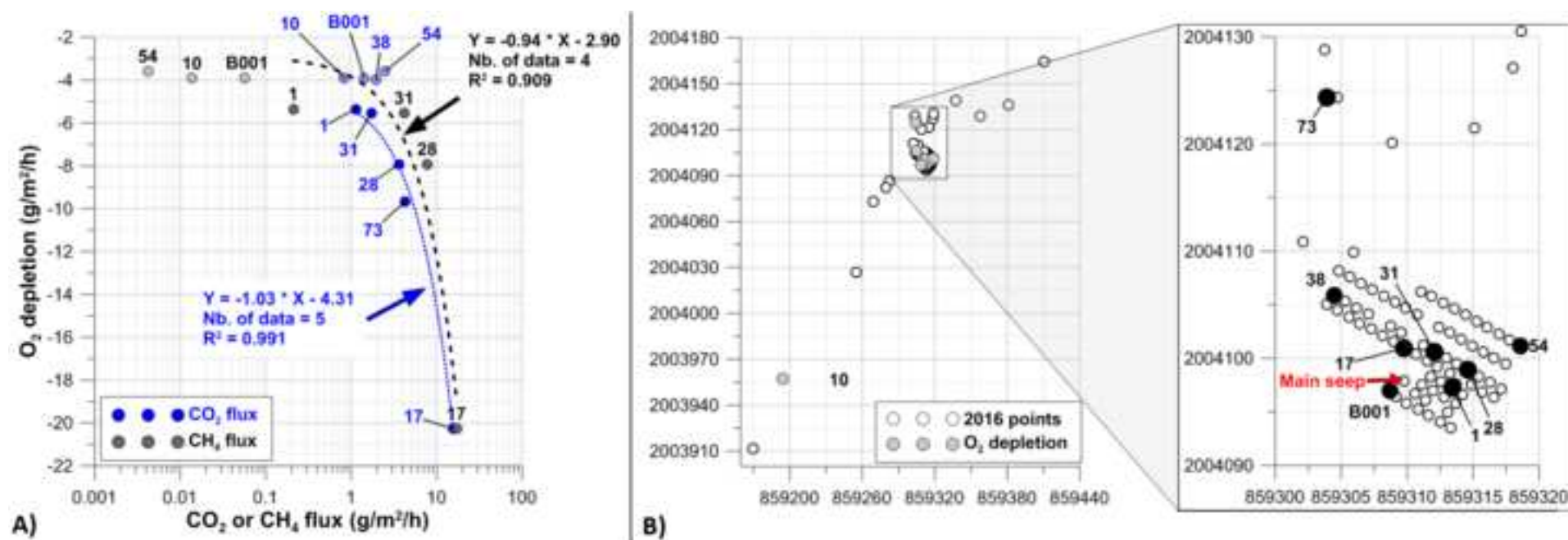


Figure 7

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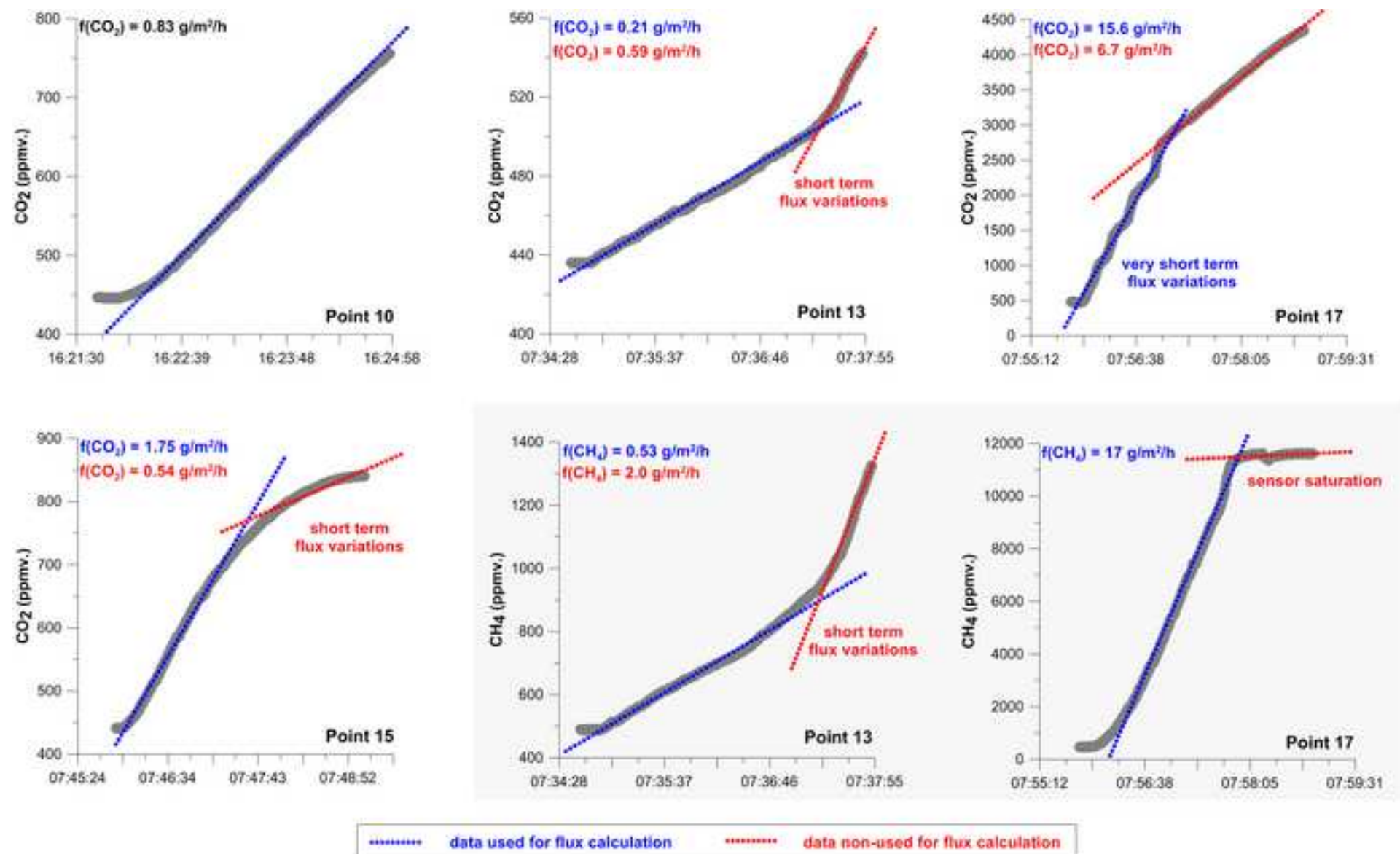


Figure 8

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Figure 9
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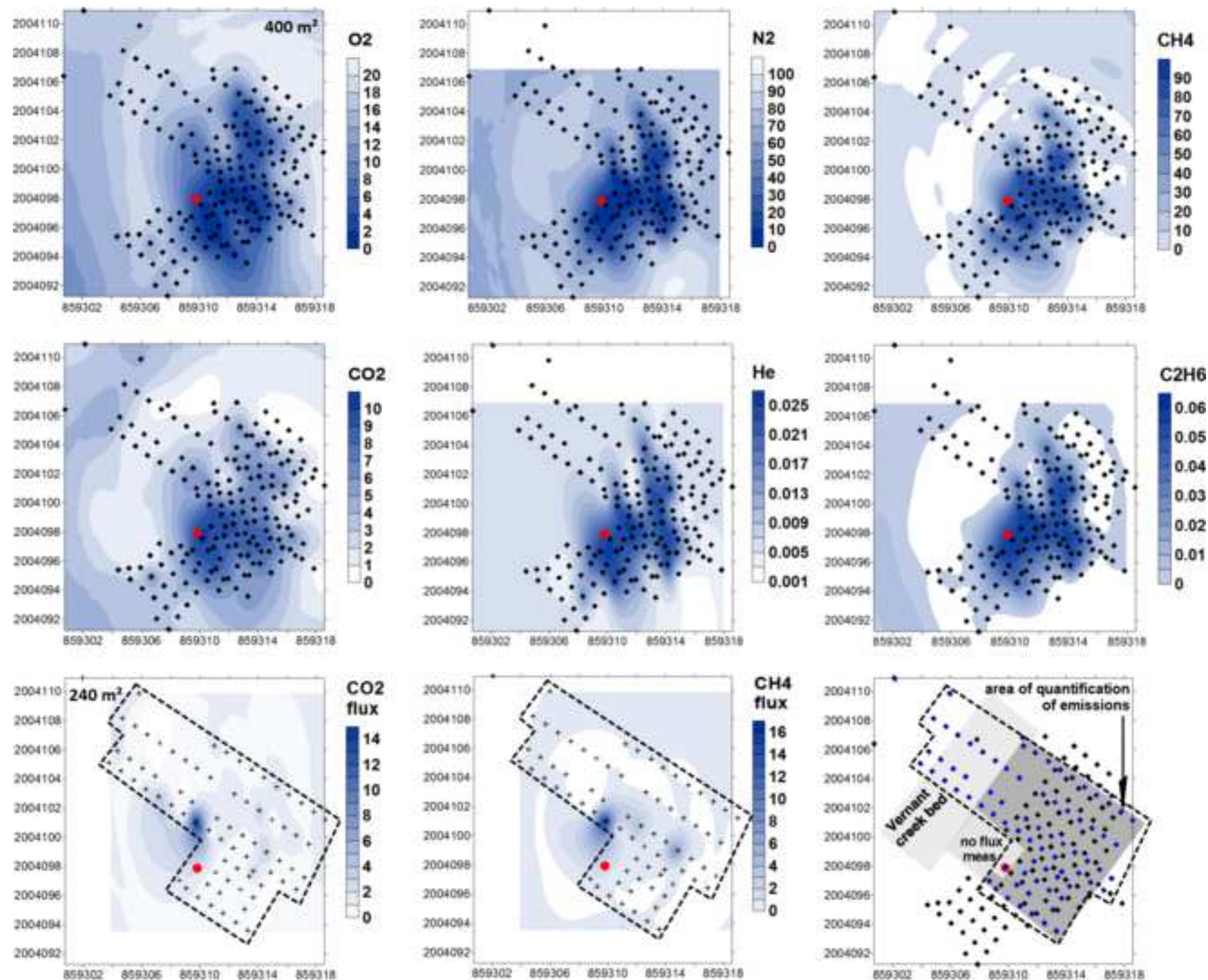
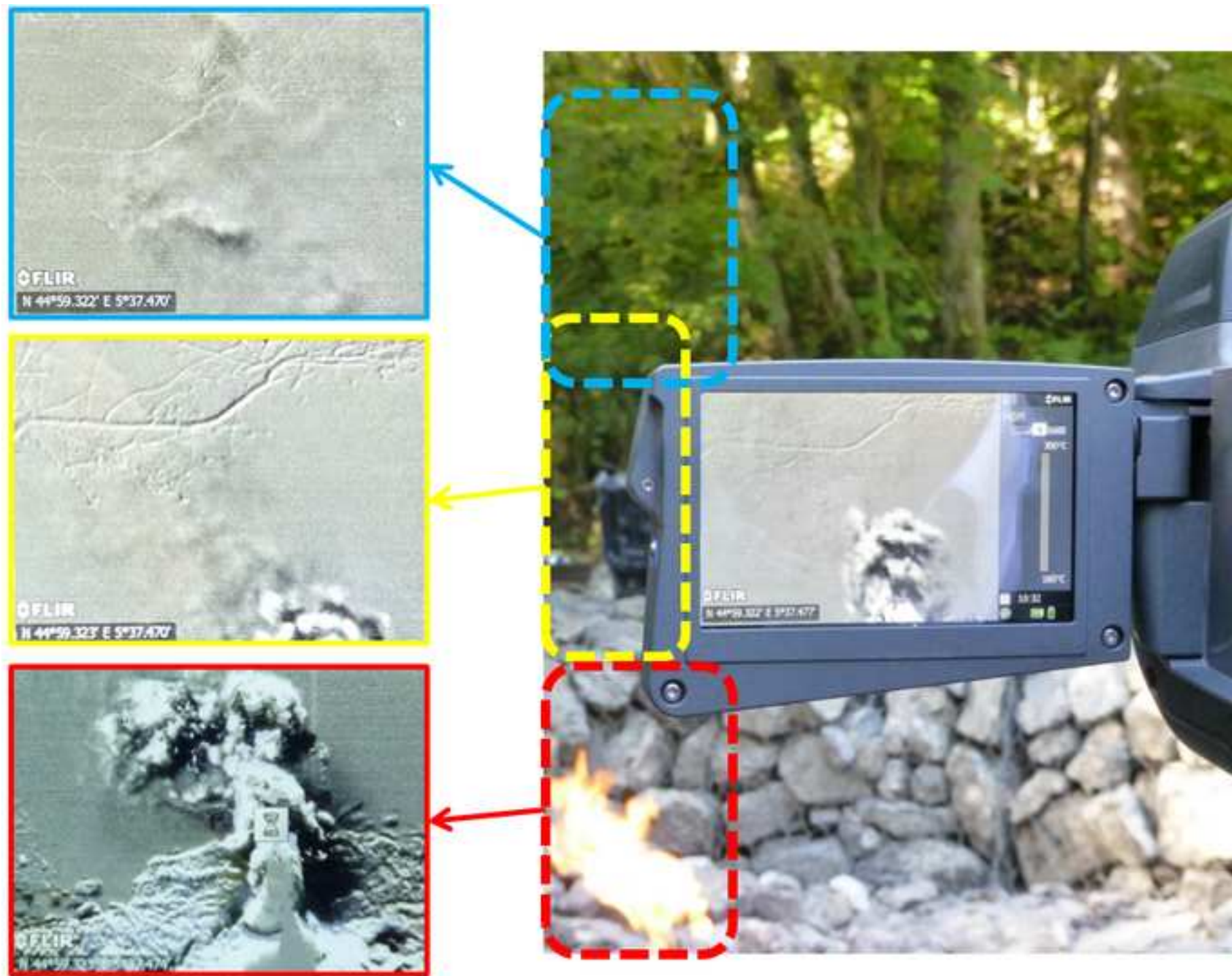


Figure 10

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Supplementary material

A.1 Methods

A.1.1 Soil gas measurements

In 2016, only IRGA device was used to monitor soil gas concentrations. In order to take into account of deviations from the gas concentrations resulting from these IRGA measurements, IRGA data were calibrated against gas chromatography data. Six samples, representative of the whole CH₄ concentration range as monitored in the field (from 0 to 77% vol.), were taken in appropriate containers (Isotubes®) and analyzed in the lab (Thermo Trace GC). This allowed correcting the bias inherent to IRGA analyses at high concentrations and to homogenize the 2016 dataset in view of comparing 2015 and 2016 campaigns. The same procedure was applied to CO₂ and O₂ gas concentrations. R² correlation coefficients between IRGA field measurements and laboratory analyses are 0.9952, 0.9941 and 0.9992 for CO₂, O₂ and CH₄ respectively (n=6). The mean error, evaluated using the slope of the linear fit between IRGA field measurements and lab measurements, is close to +4.8% for CO₂ (field data are slightly higher), -16.5% for CH₄ (field data are strongly underestimated) and +2.8% for O₂ (field data are slightly higher).

A.1.1 Soil gas flux measurements

The flux is calculated by considering the linear build-up of the gas concentration in the chamber during 3 minutes and by determining the initial slope of the gas concentration vs. time relationship, as described by many authors (*e.g.* Chiodini *et al.*, 1998; Etiope *et al.*, 2013a, and references therein). Fluxes were calculated according to the equation detailed by Lewicki *et al.* (2005) to correct the influence of pressure and temperature changes.

Uncorrected and P-T-normalized CO₂ fluxes only differ by 0.65% as a mean (uncorrected fluxes are slightly higher), the whole range being between -0.24% and +1.41% (69 CO₂ flux measurements). The influence of temperature and pressure changes is thus very low in the present case and the dataset can be considered as non- temperature or pressure dependent.

Not all the fluxes were calculated using the initial slope obtained from the 3 minutes duration of the build-up of gas concentrations inside the chamber. Contrarily to soil gas concentration measurements, some flux measurements were subject to short time scale variations of both the CO₂ and the CH₄ fluxes. In such cases, the fluxes have been calculated considering the linear fit that was prevailing during the major part of the acquisition. These short term variations concerned only a minor part of the data (respectively 17 of 69 CO₂ flux measurements and 12 of 56 CH₄ flux measurements).

Oxygen concentration decreases have been monitored at 10% of the monitoring points – this may be a consequence of a too short duration of the measurement sequence, typically set at 3 minutes in order to remain in the domain of linear increase (or decrease) of the gas concentrations. This may also be simply the consequence of low soil O₂ (progressive dilution by an oxygen-poor gas in the chamber). The point (label 17 in Figure 1) where O₂ concentration decrease was at maximum is also the unique point where the CH₄ sensor reached saturation within only 2 minutes thus the linear regression from which the flux is calculated was established only over this 2 minutes period.

As earlier reported (Chiodini *et al.*, 1998; Bloomberg *et al.*, 2012; Sanci *et al.*, 2009), soil moisture may also have a strong influence on the evaluation of gas emissions. The most obvious influence is via soil biological activity. In the present case – CH₄-rich seepage – this influence may eventually exist for the CO₂ gas phase but is less obvious for the CH₄ gas phase

as there are no potentially CH₄-emitting wetlands in the vicinity of the investigated sites. Field monitoring was performed during summertime thus the influence of humidity may be expected as reduced. Soil moisture directly influences soil gas concentrations through gas dilution by the water vapor content of the gas phase. Values of relative humidity of the air inside the chamber generally fall between 55% and 70% after the purge of the flux chamber depending on the hour of the day. Humidity variations measured during 3 minutes did not exceed +10% of the initial value and the observed maximum value was 75%. No apparent influence of moisture on CH₄, CO₂ or O₂ measurements has been stated during the graphical examination of raw data. This is consistent with the statement reported by Parkin and Venterea (2010). They found that an increase in relative humidity within a chamber from 0% to 100% will dilute the gas by only 3.05%. In the present case, it may be postulated that the influence of gas dilution will be considerably lower than 1% and can therefore be reasonably neglected.

Last, permanent visualization of the flow rate inside the system did not highlight any biases linked to the system itself during the measurement session. Nonetheless, such issues were sometimes encountered during CH₄ and H₂ measurements. A purge time is allocated between two measurements in order to refresh the air inside the system. The recovery of near atmospheric values is established in between 1 and 3 minutes for CO₂ and O₂. This may be somewhat longer for CH₄ as some memory effect on the sensor may delay the return to near zero values in case the atmospheric CH₄ background is elevated. This residual effect, sometimes reaching 200 to 300 ppm, may have induced some underestimates of CH₄ fluxes (no flux was measured instead of measuring a small flux).

A.2 Statistics

As shown by Figure A.2.a, the whole dataset is skewed for all gases. Consequently, the data are not distributed under normal law (Gaussian distribution) nor lognormal law (log-transformed data show Gaussian distribution). The situation is better when the dataset is reduced; He and C₂H₆ concentration distributions are then normal (p-values of 0.100 and 0.188 resp. using Kolmogorov-Smirnov test) and CO₂ and CH₄ fluxes distributions rather log-normal (p-values of 0.929 and 0.729 resp.). As the data measured hundreds of meters from the Fontaine Ardente main seep are likely not influenced by the gas seep (background data), the use of a dataset restricted to the vicinity of the seep (square of 20 m of side) is a way to better define data distribution. The only change by using sub-sampled dataset is the appearance of a slight tendency for CO₂ concentration to follow a normal distribution (p-value of 0.05). Another change is a higher p-value for CO₂ fluxes (0.965).

From Figure A.2.a it can be seen that data distribution is frequently bimodal. These poly-modal data distributions may exist *e.g.* for O₂ concentrations with a cut-off at 6.8% vol. or for CH₄ concentrations with a cut-off at 4.36%. One distribution is linked to the existence of the gas seep and the second is linked to common biological processes in soils. Consequently, the use of arithmetic parameters (mean and standard deviation), defined for a normal distribution, for the calculation of threshold levels cannot be used.

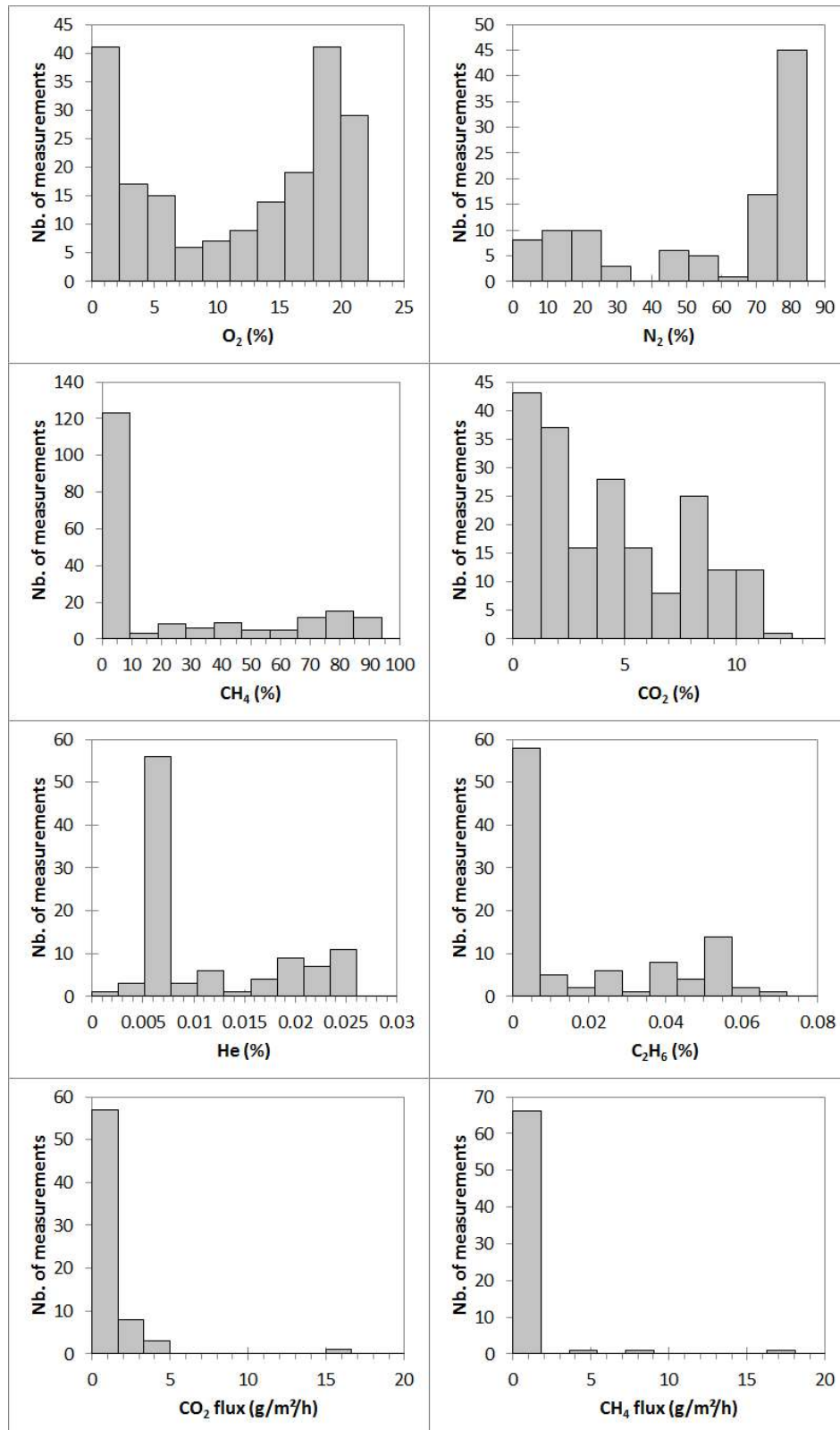


Figure A.2.a: histograms of soil gas data (2015 and 2016 data) and soil flux data (2016)

showing heterogeneous data distribution.

Here we refer to the quantile-quantile (Q-Q) plots to define threshold values (Figure A.2.b). The log-transformed data help to highlight changes in data distribution associated with strong deviations in the slope of the Q-Q plots. Anomaly thresholds are defined as follows: 17.5% vol. (O_2), 3.8 and 7.5% vol. (CO_2), 65% vol. (CH_4), 190 ppm (He) and 360 ppm (C_2H_6). As CO_2 and CH_4 flux data are linearly distributed, a clear definition of a threshold is not possible albeit deviations around the 0.25 quantile may have some significance (1.23 and 0.21 $g/m^2/h$ resp.). A reference to the thresholds obtained using the basic approach (mean + 2SD) gives levels of 5.14 and 5.66 $g/m^2/h$ respectively and such levels are not meaningful (only 1 point is above the CO_2 threshold and 2 points above the CH_4 flux threshold). Interestingly, the CO_2 and O_2 soil gas threshold levels (3.8% and 17.5%) are in good agreement with the pivot values defined in Figure 3 thus giving more confidence on the concentrations from which influence of the gas seep can be noticed.

Prior to establishing contour maps, variograms were calculated for each parameter on a restricted dataset (data falling in the 20x20 m side square around the seep). Results are given in Figure A.2.c and show the parameters of variogram calculation used for krigged maps.

Figure A.2.d presents classed post maps built using threshold levels given in Figure A.2.b.

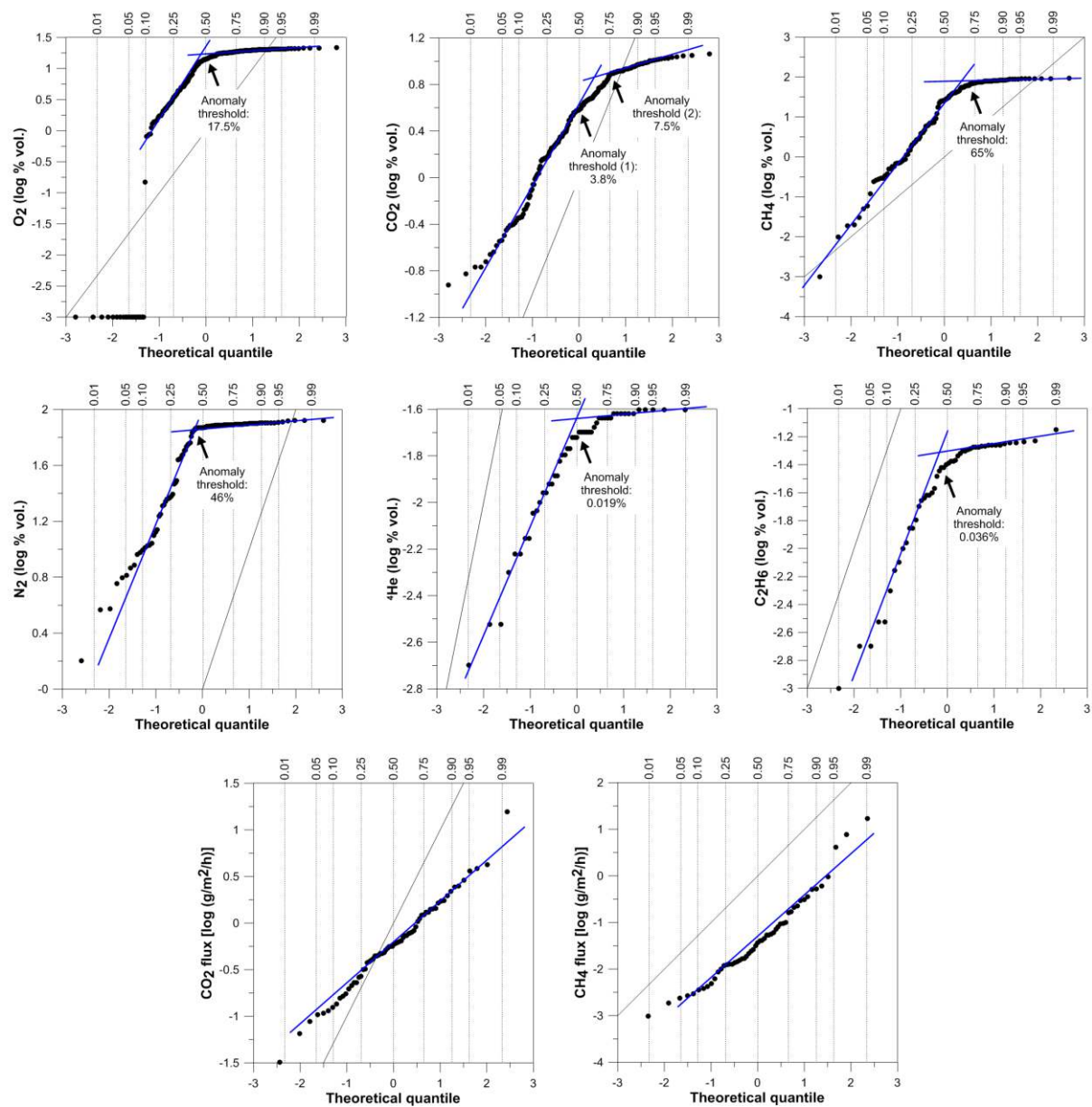


Figure A.2.b: quantile-quantile plots calculated for all the soil gas species and the CO₂ and CH₄ soil gas fluxes.

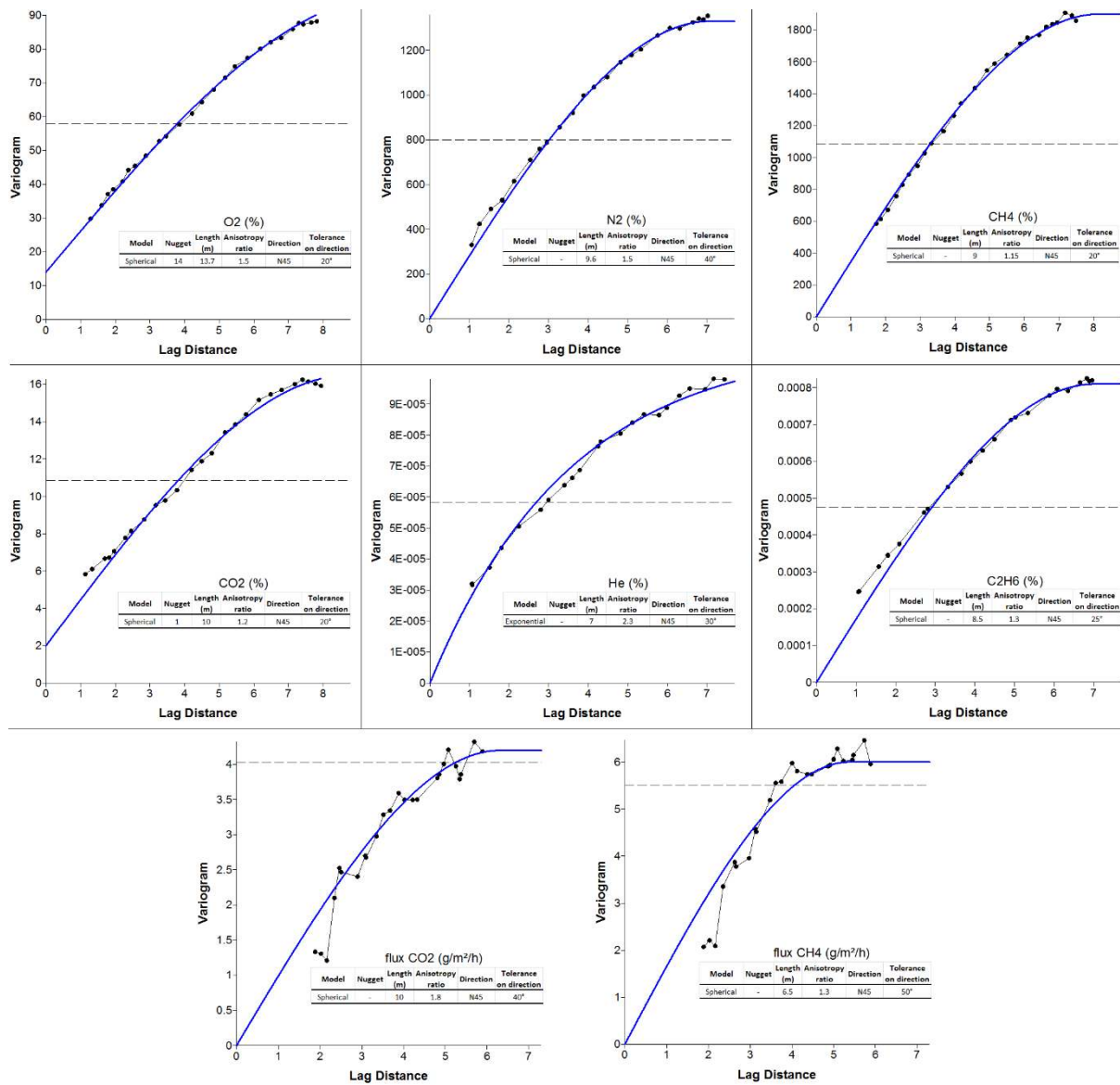


Figure A.2.c: variograms calculated for all the soil gas species and the CO₂ and CH₄ soil gas fluxes. Lag distance in meters.

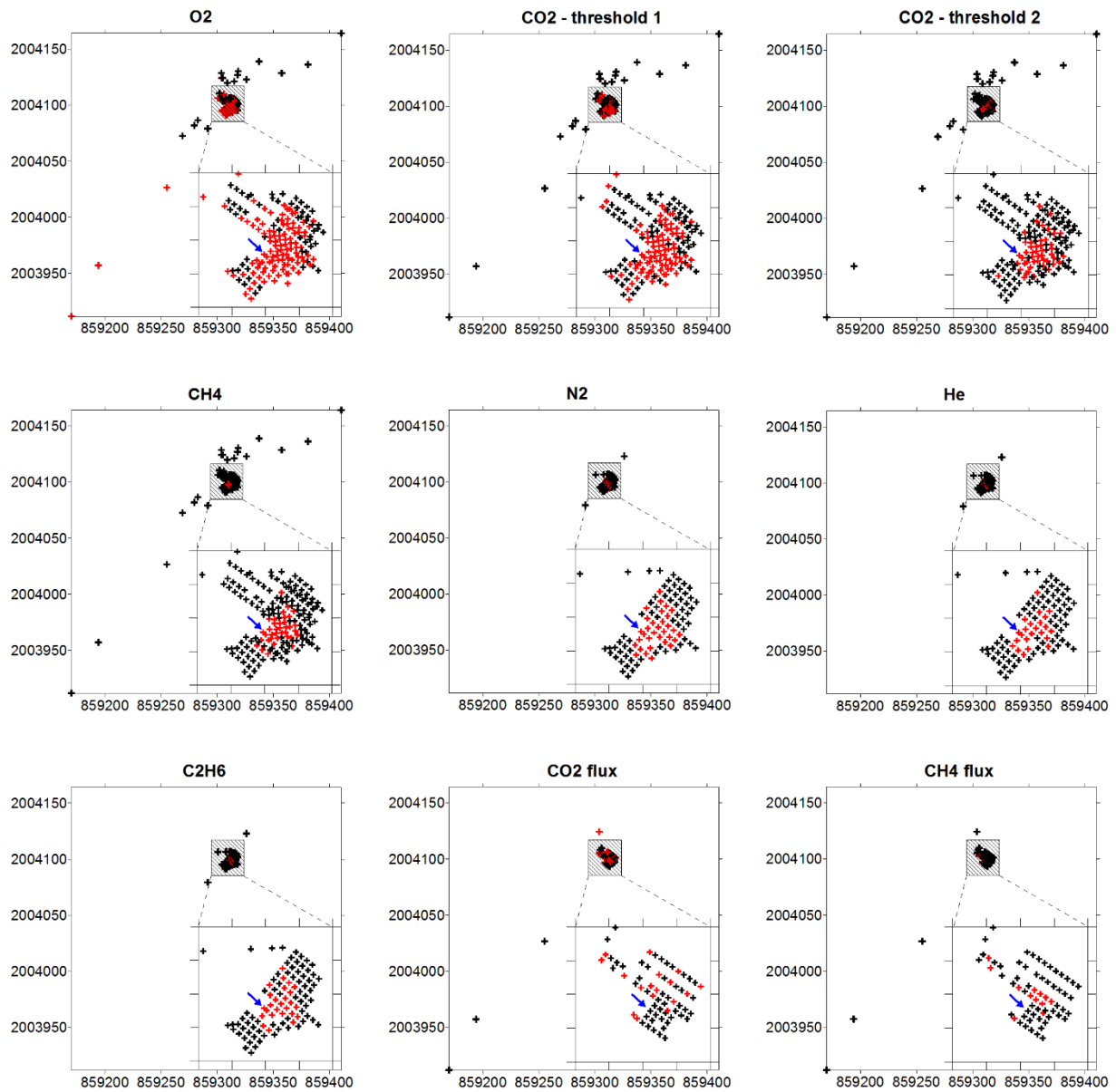


Figure A.2.d: classed post maps for the monitored parameters; insets in each map shows a detailed view of the 20x20 m side square near the gas seep. The blue arrow indicates the location of the Fontaine Ardente main seep. Red dots correspond to points that are above the threshold values defined in the text and in Figure A.2.b.

Supplementary material – References (if not cited in main text)

Lewicki J.L., Bergfeld D., Cardellini C., Chiodini G., Granieri D., Varley N., Werner C., 2005, Comparative soil CO₂ flux measurements and geostatistical estimation methods on Masaya volcano, Nicaragua, *Bull. Volcanol.*, 68, 76-90.

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