

Research Article

Towards a Better Knowledge of Natural Methane Releases in the French Alps: A Field Approach

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We report investigations performed at some hydrocarbon gas seeps located in the French Subalpine Chains in zones of outcropping Jurassic black shales, increasing the reported number of such occurrences in this part of the Alps. We present the characteristics of each of the seeps, based on soil flux measurements and soil gas measurements. Gases emitted are CH₄-rich (87–94%) with the exception of one site (78.5% CH₄ + 8.2% CO₂) where an active landslide may induce dilution by atmospheric air. CO₂ is generally measured at low levels (<1.6%). Concentrations in C₂H₆ are more variable, from less than 1% to more than 2.3%. Gas is emitted over areas of various sizes. The smallest gas emission area measures only 60 × 20 cm, characterized by a strong hydrocarbon flux (release of about 100 kg of CH₄ per year). At a second site, hydrocarbon emissions are measured over a surface of 12 m². For this site, methane emission is evaluated at 235 kg per year and CO₂ emission is 600 kg per year, 210 kg being related to gas seepage. At the third site, hydrocarbons are released over a 60 m² area but strong gas venting is restricted to localized seeps. Methane emission is evaluated at 5.1 tons per year and CO₂ emission at 1.58 tons per year, out of which 0.53 tons are attributed to gas seepage. Several historical locations remain uninvestigated at present, and numerous others may still be unknown. We outline strategies to search for such unrecorded sites. Considering the topography of the potential alpine and perialpine emission areas, the possibilities to detect gas emissions appear of the size recorded so far seem to be restricted to ground-based methods or to methods offering the possibility to point orthogonally to the soil towards the seep maximum. If such sites are to be investigated in the future in the frame of Environmental Baseline Assessment (EBA), even establishing appropriate monitoring protocols will be challenging.

1. Introduction

The occurrence of natural Earth degassing—and specifically hydrocarbon degassing—is known since very ancient times. In Europe, methane seeps are reported since the Roman period, e.g., in Greece [1], in Turkey [2], and in France [3]. Later, especially during the XIXth century, in conjunction with the hydrocarbon rush, some of these natural gas releases were investigated in more detail to assess their exploitability [3]. Nowadays, the growing interest for natural hydrocarbon seepage areas has two main angles: firstly, to better understand the production mechanisms of the hydrocarbon gas phases [4] and specifically to determine if the gas is produced by thermal or biological processes from organic matter [5, 6] or by abiotic reactions involving hydrogen [7]; secondly, to better describe the degassing patterns [8], to identify gas

migration pathways, and to quantify the amounts of gases released into the atmosphere [4, 9] and the related impacts onto the global atmospheric methane budget [10]. These investigations are in relation with environmental concerns related to the increasing share of unconventional gas exploitation [11] and to natural and man-induced gas emissions from hydrocarbon fields [12, 13] with a special focus on the integrity of gas and oil wells [14], including abandoned wells [15]. It is well established that gas seeps not only induce free gas emissions but also increase dissolved gas levels in aquifers [16–18] where their quantifications can be quite challenging [19, 20]. Here, we focus on the quantification of free gas leaks at the soil/atmosphere interface [10] where the influence of external parameters (temperature, soil properties, humidity, and so on) on the measurements of gas emissions needs to be taken into account [21].

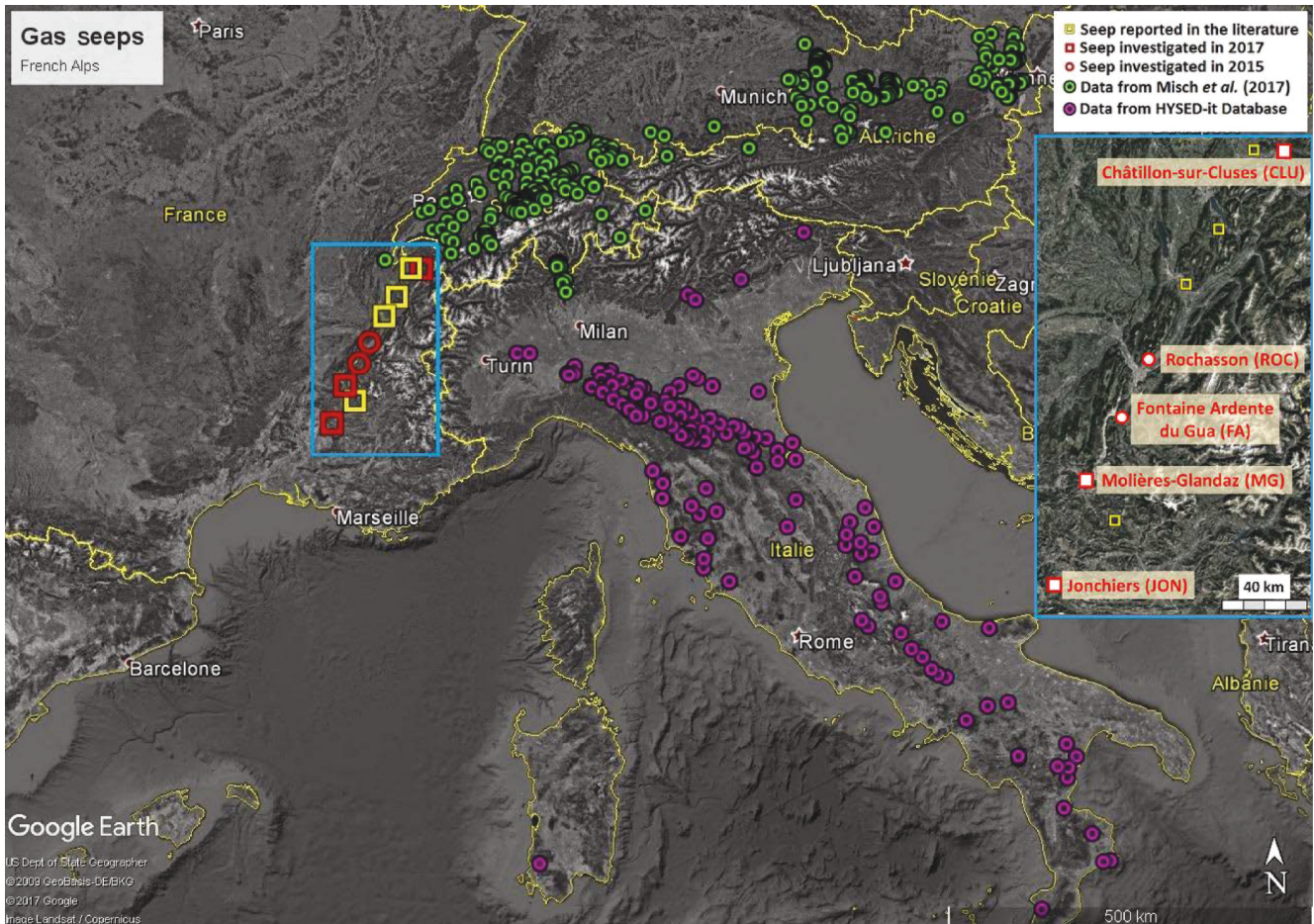


FIGURE 1: Gas seeps reported at the scale of the alpine chain. The blue inset details the locations of French CH_4 -rich seeps (in red: investigated locations).

Investigations of the most prominent French alpine gas seep, the Fontaine Ardente du Gua, have been recently reported [3] together with preliminary reconnaissance of a gas seep of lesser importance (Rochasson gas seep; [22]). When comparing the few known occurrences in the French Subalpine arc to the number of gas seeps reported for Italy (HYSED database; [23]) and for Switzerland, Germany, and Austria [5, 24, 25], mainly situated in the molasses basins, we suspect a significant knowledge gap, even though the lithological and tectonic contexts as well as the thermal history are not directly comparable. Thanks to an in-depth literature review, including “grey” historical literature, we localized several other sites prone to the release of hydrocarbon gases (Figure 1).

Here, we report field investigations performed at some of those newly localized sites (red symbols in Figure 1) as, from South to North, Jonchiers (JON), Molières-Glandaz (MG), and Châtillon-sur-Cluses (CLU). A fourth site (Rochasson (ROC)), already monitored in 2015, was investigated again because a landslide had modified its surface in 2016. Investigations were focused on the quantification and spatial patterns of gas emissions to the atmosphere as contributions to the greenhouse gas budget. Soil flux measurements using an accumulation chamber system were performed at all the sites

with the exception of JON. Soil gas analyses allowed estimating precisely the relative proportions of gas species.

2. Geological Settings

In their article in 1990, mainly focused on CO_2 emissions in the French southeast basin, Blavoux and Dazy [26] mentioned the occurrence of mofettes (natural gas seeps) among which some are methane-bearing including JON, MG, and the Fontaine Ardente du Gua (FA). For FA, we provided detailed information in Gal et al. [3]. Gas emissions reported at the Col de Cabre could not be investigated due to safety issues as these emissions were encountered during the drilling of a railway tunnel in 1887 [27]. Nonetheless, the probable source rocks for this site are black shale formations similar to those outcropping at Fontaine Ardente du Gua [3].

The Jonchiers site (JON; Figure 2) is located close to the town of Buis-les-Baronnies. This seep is associated with black shale formations of the Oxfordian age [27]. Local inhabitants discovered this methane seep indirectly by observing persistent flames after having practiced fire clearance (pers. comm.). Blavoux and Dazy [26] reported an analysis of the gas phase with dominant CH_4 (71.97%) and high concentrations in CO_2 (8.39%) and H_2 (5.19%), completed by N_2 (9.51%). These



FIGURE 2: Overview of the sites: from left to right and from top to bottom: Rochasson (ROC), Châtillon-sur-Cluses (CLU), Jonchiers (JON), and Molières-Glandaz (MG). FA: Fontaine Ardente du Gua (see [3]).

authors also reported an isotope analysis of the carbon of the methane ($\delta^{13}\text{C}_{\text{CH}_4} = -39.7\text{‰}$ vs. PDB), suggesting a dominant thermogenic origin for this gas phase. The location of this gas seep reported in the subsoil database BSS of the French Geological Survey (site BSS002BPZV; [28]) revealed to be erroneous (the real location is 730 m to the ESE).

The Molières-Glandaz site (MG; Figure 2) is not reported in any geological database. Blavoux and Dazy [26] only mentioned a location called “les Tiogaux” which corresponds to a farm. Nevertheless, they report a historical analysis from 1916: 70.16% of CH_4 , 14.05% of H_2 , 4.8% of C_2H_6 , 2.89% of N_2 , 1.2% of O_2 , and 0.3% of CO_2 . This alkane-rich gas is also seeping from black shale formations of the Callovian to Oxfordian age. Hints from the inhabitants oriented our investigations to a dry creek where we detected the seep organoleptically, through its characteristic hydrocarbon smell. Inhabitants have known the existence of this gas seep from immemorial times. It was discovered by observing gas bubbling in the creek during wet periods.

The Rochasson site (ROC; Figure 2) has been previously investigated [22]. This gas seep is again located in shale formations and has been only recently discovered in the 1970s in the course of geological investigations [29]. The gas phase is dominated by CH_4 (95%), with some C_2H_6 (1.9%) and only traces of CO_2 (0.4%), N_2 (0.35%), C_3H_8 (0.3%), and ^4He (0.007%). For comparison, the neighbouring Fontaine Ardente du Gua (FA) is less methane-rich (85 to 90%) and enriched in CO_2 (9 to 11%), other gas phases being N_2 (1%), Ar (<0.07%), ^4He (0.018 to 0.025%), and C_2H_6 (0.0002 to 0.058%), as measured in 2015 and 2016 [3].

The last investigated site is located much further in the north of the French Subalpine Chains, close to the municipi-

ality of Châtillon-sur-Cluses (CLU; Figure 2). Contrarily to the other seeps, it is not related to obvious Callovo-Oxfordian black shale outcrops. The existence of gas emission is reported since the XIXth century [30], and an analogy was made with the eternal flames occurring in the Caucasus or in Turkey (see references to Pliny the Elder in [2]). The gas was, at that time, collected at 16 m depth in argillaceous and gypsum formations covered by glacial deposits and used to light houses. Some decades later, a more detailed description was given by Omer [31]. Two locations were prone to gas emissions. The first emission zone was located in the backyard of a house, and some of the gas emerged from a crack of the floor inside a room. The second emission zone was located in a meadow and was discovered by a farmer who observed a bare surface of about 100 square meters, where the earth seemed “burned.” After having dug a hole in the ground, he heard a hissing gas, which caught fire instantly after approaching a burning match. These two locations are reported in the French BSS geological database (respectively, recordings BSS001RKMM and BSS001RKML; [28]). The gas phase is essentially methane, and production has been attributed in 1925, without proof, to the degassing of Eocene lignite-rich formations [32]. It can be noted that Lower Jurassic marls (Toarcian) outcrop near the site and have been noted as gas-bearing in a 45 m drillhole (BSS001RKML) even though their thickness cannot be compared to the sites further south. We report only the data from the first site, close to the house. The site owner provided instructive information on the zone (M. Dumont, pers. comm.): the area has been recently subject to a landslide which is currently monitored. Consequently, gas emissions to the atmosphere may be different from those described in the past.

3. Materials and Methods

The monitoring uses two well-established methods, soil gas flux measurements and soil gas concentration measurements. For all sites, soil gas flux measurements at the soil/atmosphere interface were performed. For most sites, these flux measurements were completed by soil gas measurements at 1 m depth. A detailed overview of these two techniques can be found in the literature [3, 33]; below, we provide a summary of the methods used.

Soil gas flux measurements were performed [using the accumulation chamber technique, with external recirculation] (Echo Instruments, Slovenia). The [...] 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) [and is equipped with a fan with tunable speed for mixing of the headspace gas]. Pressure, temperature and relative humidity inside the chamber are continuously monitored. CO₂ and CH₄ [are measured] 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 flux measurement was based on the rate of CH₄ and CO₂ accumulation (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 flow from the atmosphere into the soil. [Most flux measurements were performed directly on the clayey soil surface with little to absent soil litter. Flux measurements at CLU site were performed on a grassy soil surface.] [3]

Soil gas concentrations were measured [in a 10 mm hole drilled down to 1 m depth. A copper] sampling tube was inserted [...] and an Infra-Red Gas Analyzer (IRGA, LFG20 by ADC Gas Analysis Ltd., UK) was plugged, pumping at low flow rate (200 mL·min⁻¹).[...] [Readings (CH₄, CO₂ and O₂ gas concentrations) are taken once] steady state conditions [are reached, usually] within tens of seconds. Analytical precision for CO₂ and CH₄ was ±0.5% for low concentration range (0.01–10% vol.), ±3% for higher concentrations (10 to 50% vol.) and up to ±5% above 50% vol [...]. The precision for oxygen was ±0.4% full scale reading (0–25% vol.). [The most methane-rich samples were collected in Isotubes® for further laboratory characterization of the gas phase, encompassing] permanent gases (CO₂, O₂, N₂, Ar), alkanes (CH₄, C₂H₆, C₃H₈) 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]

Flux measurements preceded soil gas measurements to avoid introducing artefacts due to altered soil permeability. The only exception is the ROC site where soil gas was measured during a previous campaign in 2015. This site was subject to a landslide in between the two surveys in 2015 and 2017, so that the ground surface has been totally reshaped and the locations where soil gas concentrations had been measured two years before have disappeared.

4. Results and Discussion

4.1. Meteorological Conditions. Meteorological conditions are known to have adverse effect on soil gas emissions from the soil under certain conditions, especially when weather is rainy [21, 34]. The field survey was performed during one week in early September 2017. During this period, weather conditions were dry and no rainfall event occurred (Figure 3). The atmospheric pressure was particularly high. If high-pressure conditions are sometimes reported to reduce gas emissions [34], this may not be always the case [33]. During the survey, the pressure conditions were stable. If gas emissions were reduced by the effect of high-pressure conditions, this effect would have concerned the complete monitoring period so that a hypothetical variability of the gas emissivity linked to pressure effects would be very low. Some thunderstorms occurred some days before the survey, but the amounts of rainfall were highly variable from one location to the other (from less than 10 mm up to 30 mm). Thunderstorms are also events that have generally a local influence, and their impact at a distance of some kilometers to tens of kilometers may be low to inexistent. We used the indications of the relative humidity sensor inside the flux chamber to assess local humidity conditions (Figure 3). Relative humidity in the air pumped from the soil is low, between 31% and 74%, with a mean value of 50.6%. This is in accordance with limited rainfall amounts and a 10-day period without any rainfall event at the end of August. The effect of humidity on gas emissions is thus negligible.

4.2. Soil Gas Fluxes and Soil Gas Concentrations. Data are presented in Figure 4 as boxplots. Datasets are provided as supplementary material (available here). At the JON site, no methane flux measurements could be performed. Soil background CO₂ flux in the surroundings of the seep is generally low (<1 g·m⁻²·h⁻¹) and matches with the values reported for biologically produced CO₂ flux [35]. Only one measurement is higher but still falls in the range of biological CO₂ fluxes reported in summer in France [36]. The CO₂ concentrations are between 1 and 2% with slight O₂ depletion compared to the atmosphere. Soil gas emitted at the seep is diluted by atmospheric air as drilling into the clayey formations, and the subsequent measurements were only possible to 30 cm of depth. By correcting this dilution, assuming zero O₂, the gas composition was recalculated as follows: high CH₄ concentration (87%); abundant N₂ (10%); presence of CO₂ (1.6%), C₂H₆ (0.87%), and C₃H₈ (0.235%); and traces of C₄H₁₀ (0.071%), C₅H₁₂ (0.019%), and ⁴He (0.025%).

At the MG site, only soil gas flux was measured (Figure 4) with the exception of one soil gas measurement sampled at the vent immediately after the flux measurements. CO₂ flux measurements outside the gas seepage area yielded values similar to those measured at the JON site. For about one-third of the measurements, elevated CH₄ fluxes were measured, ranging from less than 30 to 220 g·m⁻²·h⁻¹. At the most emissive point, three repeated measurements obtained fluxes of 220, 182, and 204 g·m⁻²·h⁻¹. Intrinsic “pulsations” [5] of the seep can explain this variability as suggested by short-term changes of flame size [37]. Nonetheless, the variations are

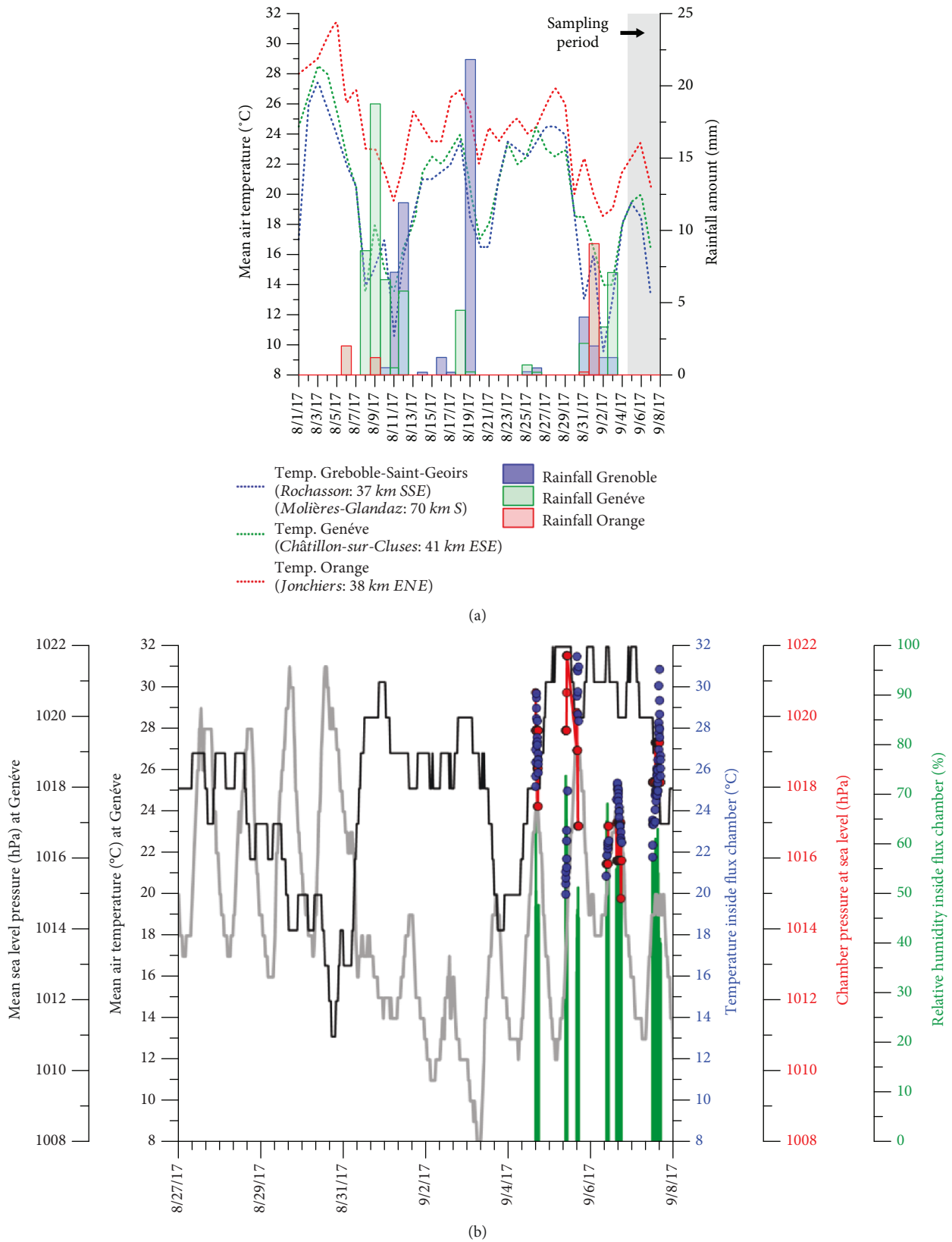


FIGURE 3: Meteorological parameters before and during the survey. (a) Daily mean air temperatures and rainfall amounts taken at the nearest airport weather stations (data from <https://freemeteo.fr>); distance between gas seeps and airports is indicated in the caption. (b) Hourly pressure and temperature data from Geneva (Genève) airport compared to temperature and pressure data measured using the flux chamber system during the measurements. Bar chart gives the relative humidity inside the chamber during the measurements.

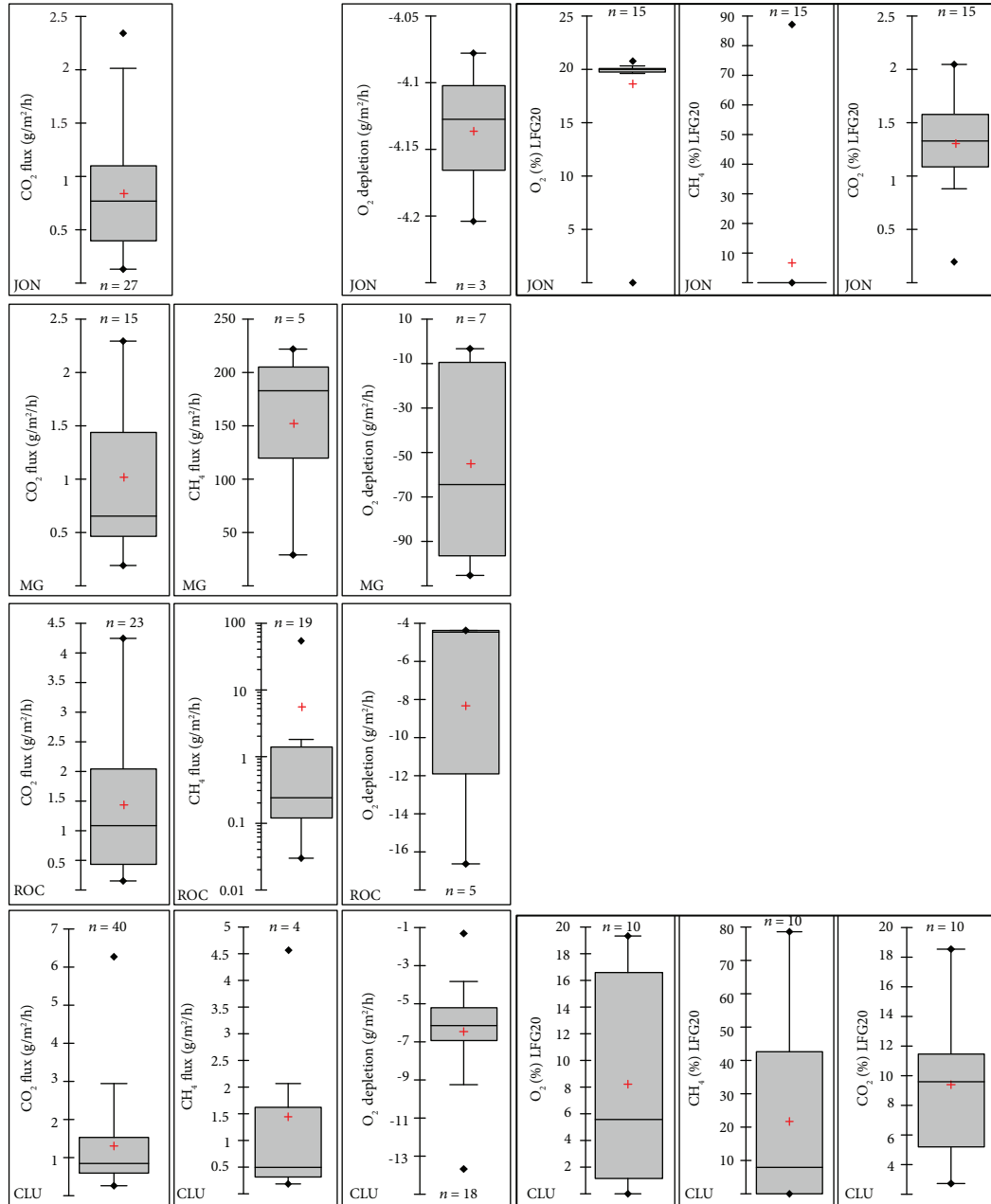


FIGURE 4: Boxplots for the four monitored locations; from left to right: CO₂ flux, CH₄ flux, O₂ depletion, and, if measured, O₂, CH₄, and CO₂ soil gas concentrations.

relatively weak with a standard deviation of less than $\pm 15\%$ [38], showing a good reproducibility of the flux measurements. If the lowest measured CH₄ flux is comparable to the upper range of diffuse seepage measured near the FA gas seep [3], the highest values are similar to some seeps reported by Etiope [2] in Greece or in Romania. In general, a strong depletion in oxygen in the chamber is linked to an increase in methane. The gas phase emitted at the MG site is CH₄-rich (94.2%), with abundant C₂H₆ (2.36%), residual N₂ (0.65%), and traces of CO₂ (0.31%), C₃H₈ (0.40%), C₄H₁₀ (0.056%), C₅H₁₂ (0.006%), and ⁴He (0.012%).

By comparison, the seepage intensity of the ROC site is apparently lower (maximum CH₄ flux of $54 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), but

the size of the degassing area is much larger (a CH₄ flux was detected for more than 80% of the points). The O₂ depletion inside the chamber is also lower. The CO₂ flux can punctually reach a relatively high value ($4.23 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) suggesting that part of the emitted CO₂ may originate from the seep. Strong CO₂ enrichment in the soil formations has been reported earlier at the ROC site [22].

The present-day methane emission at the CLU site is not as high as it could have been expected from historical literature. The highest value is only $4.56 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and only 4 points from 40 showed methane emission. Nevertheless, O₂ depletion in the chamber was monitored more frequently, suggesting that even in cases where the CH₄ flux is not

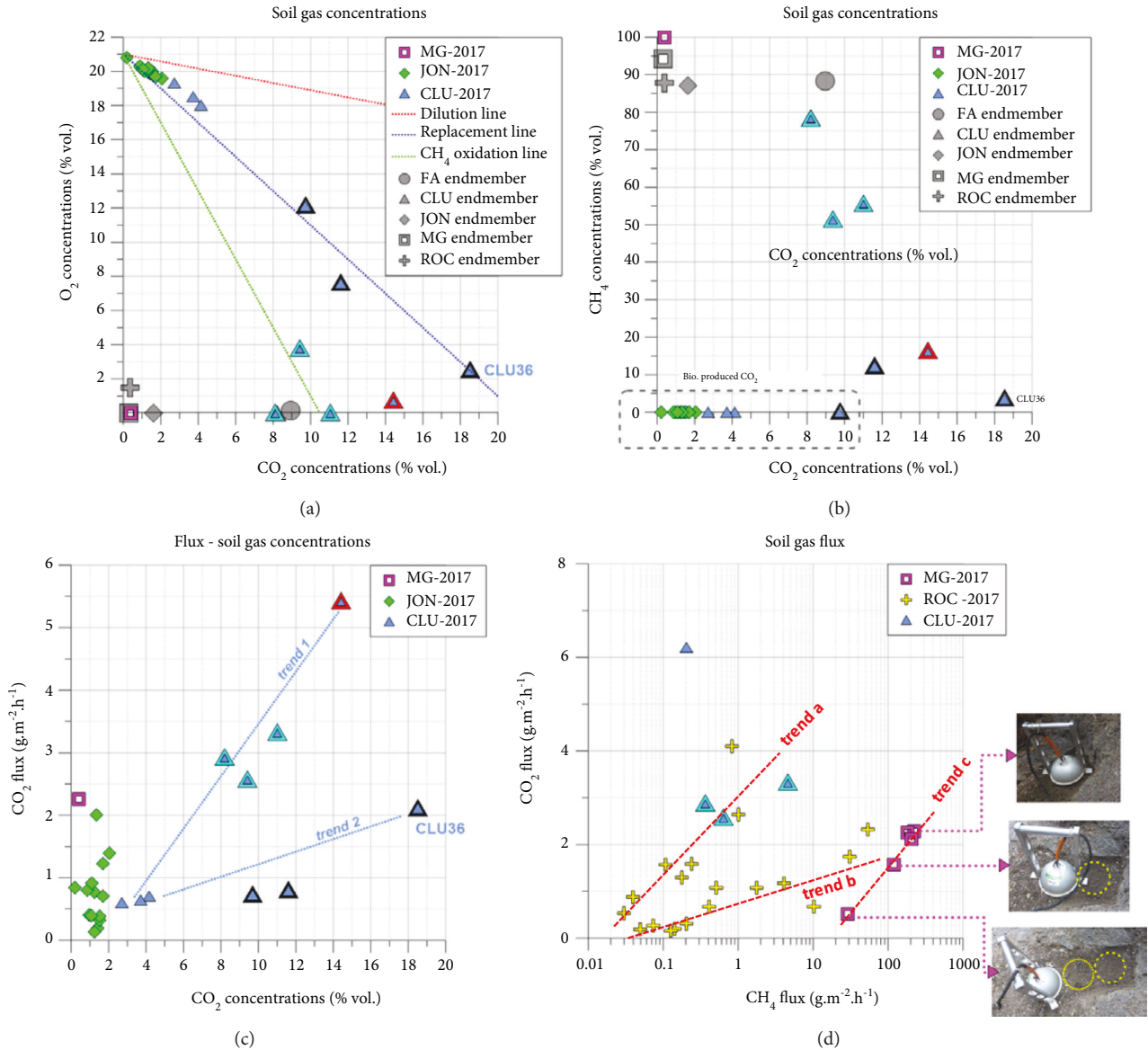


FIGURE 5: Binary plots showing (a) the O₂ concentrations vs. the CO₂ concentration, (b) the CH₄ concentration vs. the CO₂ concentration, (c) the CO₂ flux vs. the CO₂ concentration, and (d) the CO₂ flux vs. the CH₄ flux; diameter of the flux chamber: 20 cm. Lozenges: JON site, triangles: CLU site, squares: MG site, circle: FA site.

detectable, there is still an emission of deep oxygen-free gas diluting oxygen in the chamber volume [22]. This may be in relation with the active landslide that could have modified degassing patterns. Soil gas monitoring confirmed the existence of high CH₄ concentrations. The highest peak value was 78.5% monitored only during a short period. Lower CH₄ contents were measured in the laboratory (44.5%) accompanied by abundant nitrogen (47.8), CO₂ at 6.6%, and traces of C₂H₆ (0.60%), C₃H₈ (0.009%), C₄H₁₀ (0.0015%), and C₅H₁₂ (0.0002%). In spite of this supposed decline of methane supply, strong O₂ depletion and associated CO₂ enrichment were also monitored in soil.

4.3. Relationships between Gas Species. The binary plots in Figure 5 describe the relations between gas species. The

process-based approach [39] can be applied to the CO₂-O₂ relationship (Figure 5(a)). As expected, measurements at the JON site (green lozenges in Figure 5(a)) cover a reduced concentration range and plot close to the replacement line that characterizes respiration processes occurring in soils (aerobic respiration consumes 1 mole of O₂ to produce 1 mole of CO₂). The situation is different for the single sample taken at the centre of the JON gas seep (grey lozenge in Figure 5(a)), where O₂ is absent and CO₂ is present at ca. 2%. Similarly, only one point is available for the MG site (with on-site and laboratory measurements) so that it is not possible to characterize the CO₂-O₂ relation close to the MG gas seep.

Some of the measurements at the CLU site (small blue triangles in Figure 5(a)) plot on the replacement line

especially for relatively low CO_2 concentrations (<5%) which is common in summer in French soils [33]. At a CO_2 concentration greater than 9-10%, two behaviours exist. Some measurements (electric-blue-surrounded triangles in Figure 5(a)) plot close to the CH_4 oxidation line thus suggesting that part of the measured CO_2 is produced by CH_4 oxidation in the soil (2 moles of O_2 are needed to produce one mole of $\text{CO}_2 + \text{H}_2\text{O}$). This is coherent with the presence of CH_4 in sufficient amounts to allow for high CO_2 production in soil. Otherwise, with the exception of specific conditions, CH_4 amounts in soils are generally low [40]. Other measurements (black-surrounded triangles in Figure 5(a)) plot on the replacement line although their CO_2 concentrations may reach very high values (more than 18% for point CLU36). High CO_2 concentrations in soils, produced by biological processes, are sometimes reported (up to 12% [33]; up to 13% [41]; and up to 14% [42]) often in soils having high clay contents [43]. Higher concentrations seem to be exceptional even if locally excessive concentrations of CO_2 (up to 40% above the capillary fringe) are reported in the literature [44]. Point CLU36 being exactly on the replacement line, it must be hypothesized that there are local soil characteristics which allow the high concentrations of CO_2 may be in connection with the landslide phenomenon. Some of the CO_2 could be produced by CH_4 oxidation, but in amounts that are not sufficient for a noticeable deviation from the replacement line towards the CH_4 oxidation line. No influence of dilution of the $\text{O}_2 + \text{N}_2$ pool by a deep CO_2 endmember in near surface environments is visible from the CO_2 - O_2 binary plot.

Methane and CO_2 concentrations in soil are not well correlated for any of the sites (Figure 5(b)). Where biological processes in soil produce CO_2 by using O_2 (replacement line in Figure 5(a)), we would not expect elevated soil CH_4 (dashed rectangle in Figure 5(b) for the JON site and for some CLU points). The situation is different when some CH_4 is present in the soil gas. This is documented only for the CLU site. For the six measurements containing CH_4 , CO_2 appears inversely correlated to CH_4 . The existence of CH_4 oxidation in soil is only established for measurements with the highest CH_4 concentrations (electric-blue triangles in Figure 5(b)). These measurements also show the existence of a positive CH_4 flux at the soil surface (electric-blue triangles in Figure 5(d)). For these data, CH_4 oxidation may superpose to the biological production of CO_2 in soil. For the black-surrounded triangles, the CO_2 - O_2 relationship suggests that this is not the case (Figure 5(b)). Consequently, it is likely that biological processes are responsible even for very high CO_2 concentrations in soil (up to 18%).

A positive CO_2 flux was always measurable (Figure 5(c)). The positive correlation between CO_2 flux and soil CO_2 concentration is a common phenomenon in summer when biological activity is at its highest. The CLU site again shows a distinct behaviour. Biological CO_2 flux is less strong than at JON (blue triangles in Figure 5(c)). This can be a consequence of different soil conditions (texture, water content, and vegetation). Higher CO_2 flows (trend 1 compared to trend 2 in Figure 5(c)) demonstrate the additional production of CO_2 by CH_4 oxidation closer to the supposed CH_4 seepage areas.

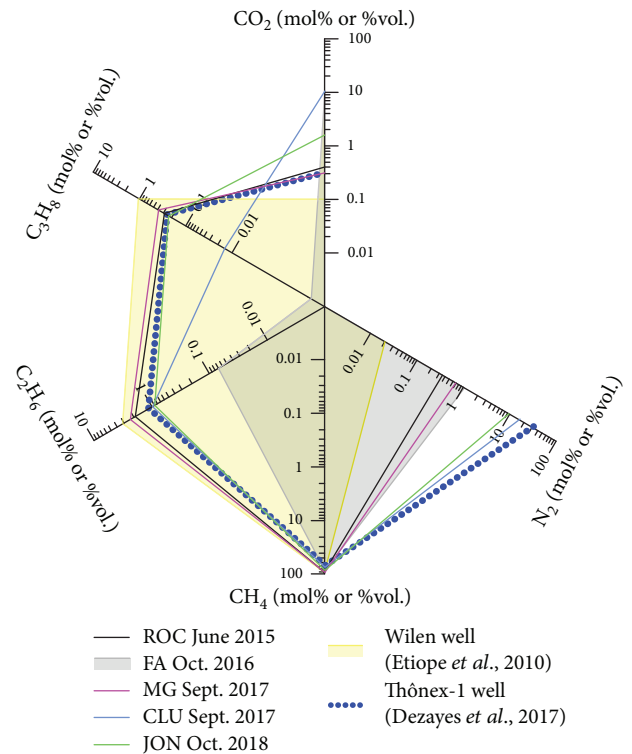


FIGURE 6: Radar diagram for the JON, MG, ROC, and CLU gas seeps; data from FA are indicated [3]. For comparison, data from two boreholes in Switzerland are reported [5, 45].

Figure 5(d) corroborates this assumption. The three measurements represented by electric-blue triangles have the highest CH_4 fluxes monitored at the CLU site. Part of the CO_2 release to the atmosphere is thus linked to CH_4 oxidation in soil. The CH_4 fluxes measured at the ROC site are more scattered. Below $10 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, it is difficult to define a clear relation between CH_4 and CO_2 fluxes. Two trends appear, one with relatively high CO_2 fluxes that also includes points from CLU (trend a) and one with a lower slope (trend b) reflecting different degrees of CH_4 oxidation. The trend for MG (trend c) has a similar slope to trend a and suggests, here again, a high rate of CO_2 production from CH_4 oxidation, at overall higher CH_4 fluxes, even though this is in apparent contradiction with the low CO_2 concentrations measured for this site (Figures 5(a) and 5(b)). Figure 5(d) shows the exponential decline of fluxes over a short distance (60 cm) from the main vent.

The gas dryness ratio ($= C_1 / (C_2 + C_3)$) provides some indication on the origin of alkane gases from the newly sampled methane seeps (Figure 6). The ratio is relatively low, from 34 (MG) up to 72-77 (CLU and JON, respectively). The ratio of ROC is in the same range (45) whereas the ratio of FA is much greater (1300). In the Western Alpine Arc, in Switzerland, ratios close to 50 are found in deep boreholes surrounding the Lemman lake (Thônex borehole; [45]), ratios close to 70 have been measured in gas seeps from the Giswil area [5], and ratios close to 20 were reported for boreholes located in the alpine flysch formations (Wilen well; [5]). Such ratios, lesser than 100, are often related to gas production

through thermogenic processes [46] whereas higher ratios may be related to a wider panel of production pathways or to secondary processes or mixing [47]. For the ROC, MG, and JON sites, situated in similar geological settings (lithology, geological age), similar mechanisms of light alkane production may be supposed. The situation may be different for the CLU site, with a comparable gas dryness ratios but where the seep likely to be associated with host rocks of different age and maturity, parameters known to be of prime importance [2]. For the FA site, if a genetic link of thermogenic methane generation with argillaceous host rocks, rich in organic matter, has certainly to be searched for, the higher dryness points potentially to secondary processes such as chemical fractionation upon transport or to biologically driven processes. This statement applies not only for alkane gas species but also for the origin of CO₂.

4.4. Gas Emissions to the Atmosphere. On the basis of the data from this study for the JON, MG, ROC, and CLU sites and previous results for ROC [22] and for FA [3], it is obvious that the FA site remains the most important spot source of greenhouse gases (GHG) so far reported in the French Subalpine Chains. Nevertheless, the other seeps cannot be neglected altogether, especially if we consider them as indicators of the diffuse flux potentially related to a large number of undetected macro- or microseeps (see discussion below).

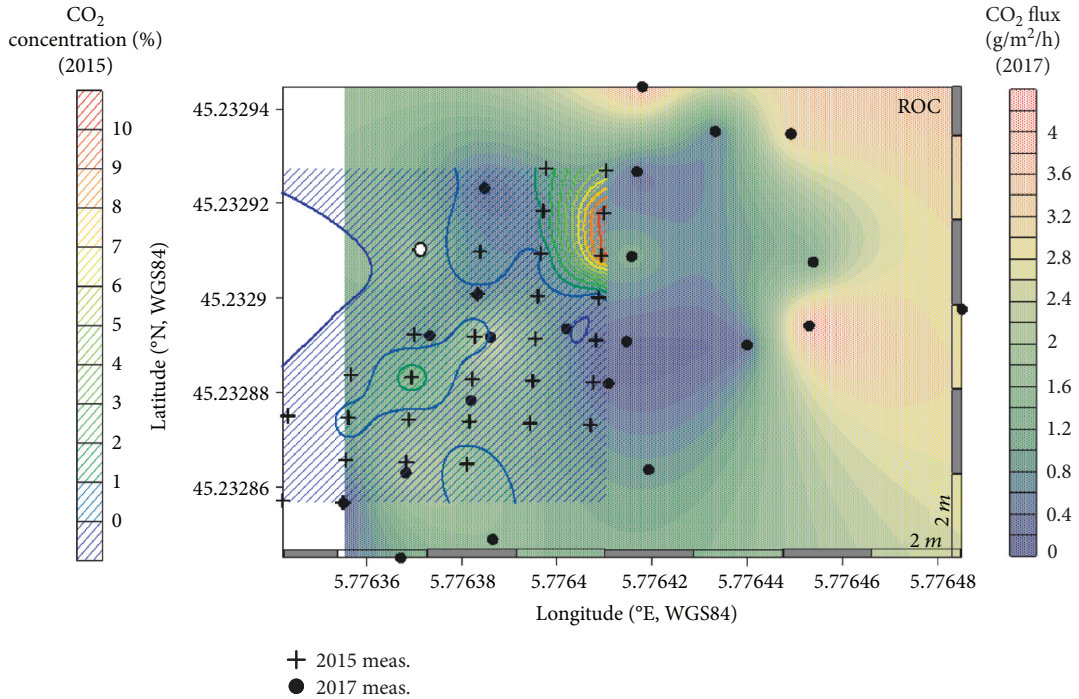
In the absence of flux measurements performed at the JON site, we refer to the other sites only. Nevertheless, the similarities in outcropping lithology, hydrographical, and topographic settings suggest that there may be comparable gas emission patterns for the JON and MG sites. Both are situated in creeks within the Middle Jurassic shales. The case of the MG site is particularly instructive. It is located in a very narrow riverbed (Figure 2), and the CH₄ emission was detected only in a 20 × 60 cm area (Figure 5(d)). As close as one meter away from this specific location, no CH₄ flux was measured at the soil surface. MG is thus the archetype of a tiny gas escape, with a very restricted seepage area, even though it falls in the macroseep category according to Etiope [2]. Calculation for MG is performed for the observed 0.12 m² emission area through which the gas is emitted (not extrapolated to 1 m²). Taking into account the variability of the flux measurement reported above, CH₄ emissions can be estimated between 95 and 100 kg per year (ca. 270 g/day), with minor CO₂ emissions (1 kg). This corresponds to the amount of CH₄ released in two days by the FA seep [3]. This is a negligible absolute contribution to the overall regional methane budget, but not imperceptible when considering the small degassing area. Indeed, Mörner and Etiope [48] reported CH₄ emissions of 20 kg per year at San Vincenzo la Costa (Italy) but for an area of 300 m² (gas emission from a mud volcano and not from shales). Etiope et al. [6] reported seeps in the Appalachians where CH₄ emissions may be as low as 1 g/day (Chestnut Creek). Given the size of the seepage area, the MG site is thus remarkable.

Flux measurements performed at the ROC site cover an area of ca. 110 m² over which a CO₂ flux was always measurable whereas a CH₄ flux was detected only on approximately half of the area (Figure 7). The 2015 dataset on soil gas

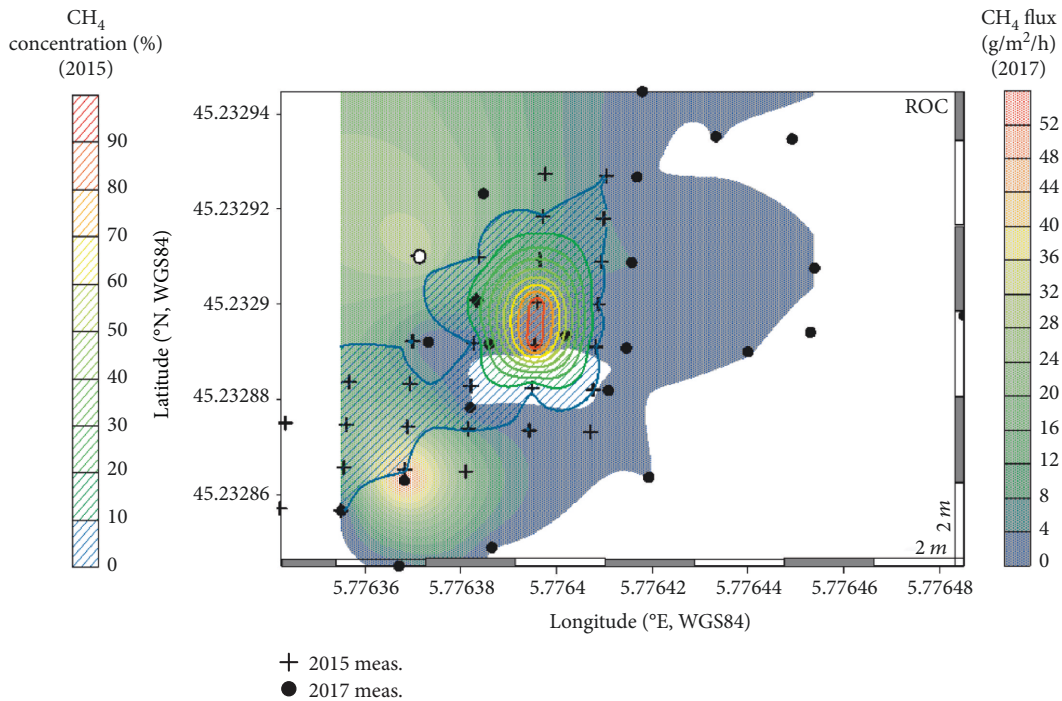
measurements is used for comparison [22]. Interpolation uses standard kriging options in Surfer® software (Golden Software). Volume calculation of the amounts of gas released is also done using Surfer® software. The dataset is reduced, the size of the area is limited, so that definition of the data distribution and calculation of a variogram may fail to be successful or representative. The 2015 soil gas data indicated that gas venting was restricted to patchy seeps and two of them were identified as macroseeps. The 2017 flux measurements also revealed patchy gas emissions and poor correlation between CO₂ emissions and CH₄ emissions. It is not possible to identify any clear pattern related to geological or morphological features. When looking at the alkane emissions, little correspondence is found between soil gas and soil flux data. This is likely the consequence of a large time span between the acquisitions and the occurrence of a landslide in between the two surveys (Figure 2). Nowadays, the ROC site is more emissive on its western part, which corresponds to the upper part of the shales' outcrop. Over an area of ca. 60 m², the global CH₄ emissions (macroseepage + miniseepage [2]) are evaluated at 5.1 tons per year. Gas seeps with similar annual releases are reported in Italy or in Romania [2]. The global CO₂ emission reaches 1.58 tons per year, 0.53 tons being related to gas seepage if a biological contribution to the CO₂ flux of 1.25 g·m⁻²·h⁻¹ is considered [35].

At the CLU site, our investigations followed a more regular grid thanks to the flatness of the grassy terrain. The area of interest is only 50 m² large (Figure 8). Concentration measurements were performed over a half of this area. A CO₂ flux was always perceptible whereas a CH₄ flux was measurable over a surface of 12 m² only. Some decrease of the O₂ content inside the chamber was nevertheless measured even where no CH₄ was noticeable, suggesting that O₂ can be used as a proxy when the CH₄ efflux is very low. This is the case in the vicinity of points CLU22 and CLU28. As for other seeps, the correspondence between the patterns of CH₄ and CO₂ fluxes is not always obvious: the highest CO₂ fluxes are measured in the northern part of the area, whereas the highest CH₄ fluxes lie in the southeast corner. There is also a poor coherence between patterns of soil CH₄ concentrations and CH₄ fluxes, especially close to point CLU11 (yellow arrow in Figure 8(a)), likely due to varying soil properties. As tortuous the gas emission patterns may be, methane emission in the atmosphere is not negligible on a yearly basis. Over 12 m², global methane emissions are evaluated around 235 kg per year. CO₂ emissions are larger (600 kg per year), a third of this value being related to the gas seep contribution if the biological contribution is assumed at 1.25 g·m⁻²·h⁻¹ [35]. This evaluation needs certainly to be refined as it was not possible to assess the impact of the landslide phenomenon onto the gas emission pattern by a sole 1-day monitoring. Given the historical records, methane emissions can be expected to occur at other locations around the investigated site so that the overall emissions would be currently underestimated.

4.5. Are there Other Seepage Areas in the French Alps? An interesting conclusion can be drawn from the above-mentioned measurements. The sum of ROC, CLU, and MG



(a)



(b)

FIGURE 7: ROC site: interpolated maps for soil gas concentrations (hatched fill; data from [22]) and fluxes (full fill); (a) CO₂ gas specie; (b) CH₄ gas specie. The light dot locates the main gas seep as represented in Figure 2 (no soil gas measurement done at this location).

contributions—and potentially the JON contribution if we assume it as similar to that of MG—to the CH₄ budget is close to 5.5 tons per year over a total degassing area of only 72 m². This represents 29% of the yearly CH₄ emission from the FA site [3], but the cumulated seepage area of the other sites is equal to 30% of the surface of the macroseepage and

diffuse seepage areas of FA. The similarities of the different sites in terms of outcropping source rocks, topography, gas composition, and emission patterns may lead to the conclusion that we can assume an average annual release of 75 to 80 kg of CH₄ per square meter at a typical subalpine black shale seepage site.

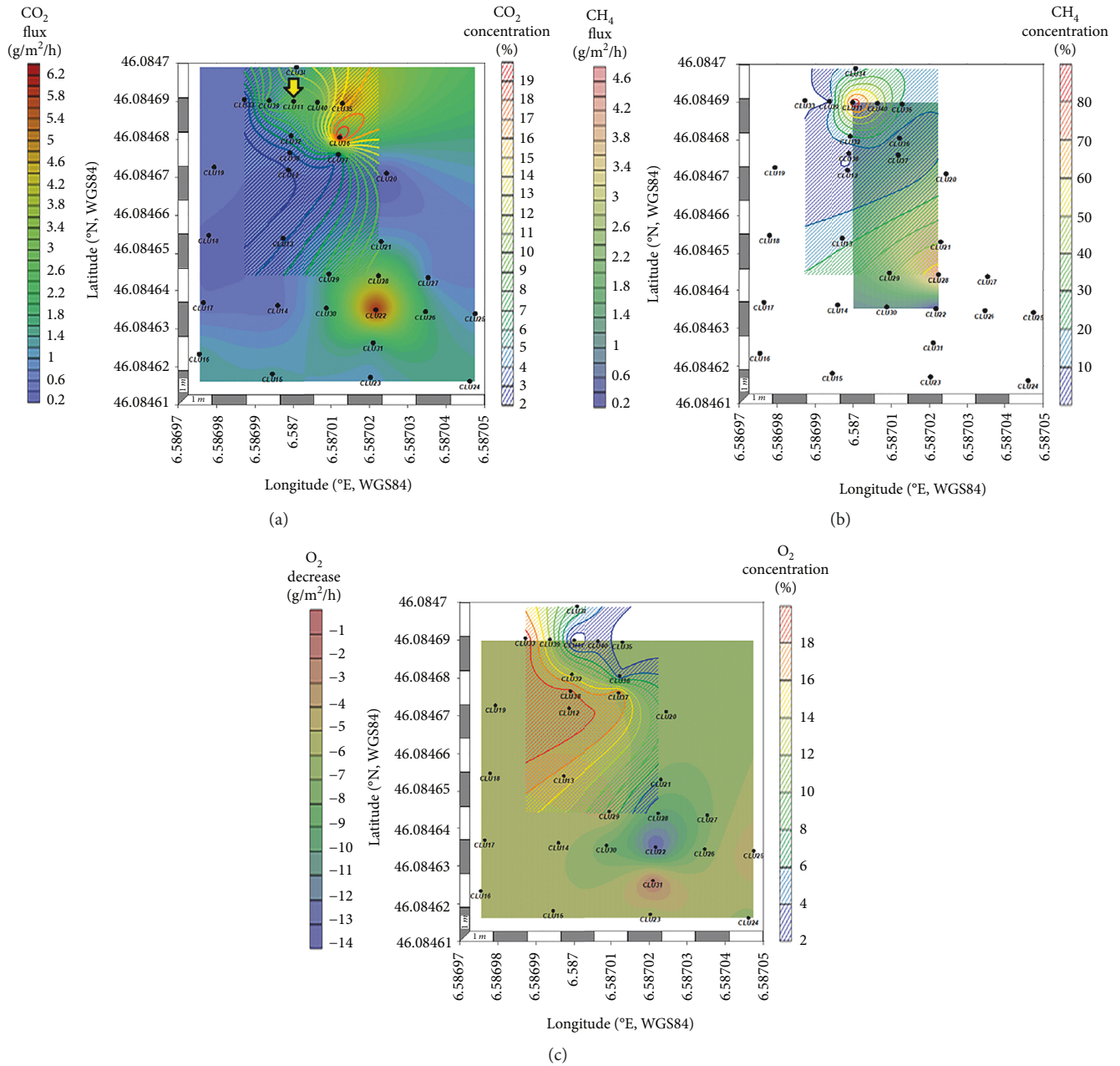


FIGURE 8: CLU site: interpolated maps for soil gas concentrations (lines) and fluxes (full fill); point CLU11 is located by the yellow arrow; (a) CO₂ gas; (b) CH₄ gas; (c) O₂ gas (for O₂, the data in g·m⁻²·h⁻¹ represent the decrease of gas content in the chamber during the measurement).

Several locations could not yet been localized and investigated (Figure 1), and many others may still be unknown or unreported. Black shale formations outcrop over hundreds of square kilometers in the French Subalpine Chains, and it is more than likely that other seepages exist in such a large area. Based on the knowledge gained on investigated seeps, the search of new degassing locations should probably focus on thalwegs and indented valleys crosscutting black shales. A rough estimate can be done in the case of the MG site. Over an area of 1 km², centred on the known gas seep, we can identify approximately 3.8 km (planar distance) of small valleys cutting into the outcropping black shales (Figure 9). Extrapolating this density to the total surface of black shale outcrops at the Subalpine Chains leads to tremendously high distances, which are, in most areas, only accessible by foot, given the rough topography and the dense vegetation on those agriculturally mostly unusable badlands.

The assessment of an environmental baseline with respect to potential uses of methane-containing argillaceous formations as well as any estimation of GHG releases from such formations would require a much more stringent approach to gas seep identification. Gal et al. [3] reported some aspects of gas detection in the context of environmental impact assessment-related shale gas exploration/exploitation.

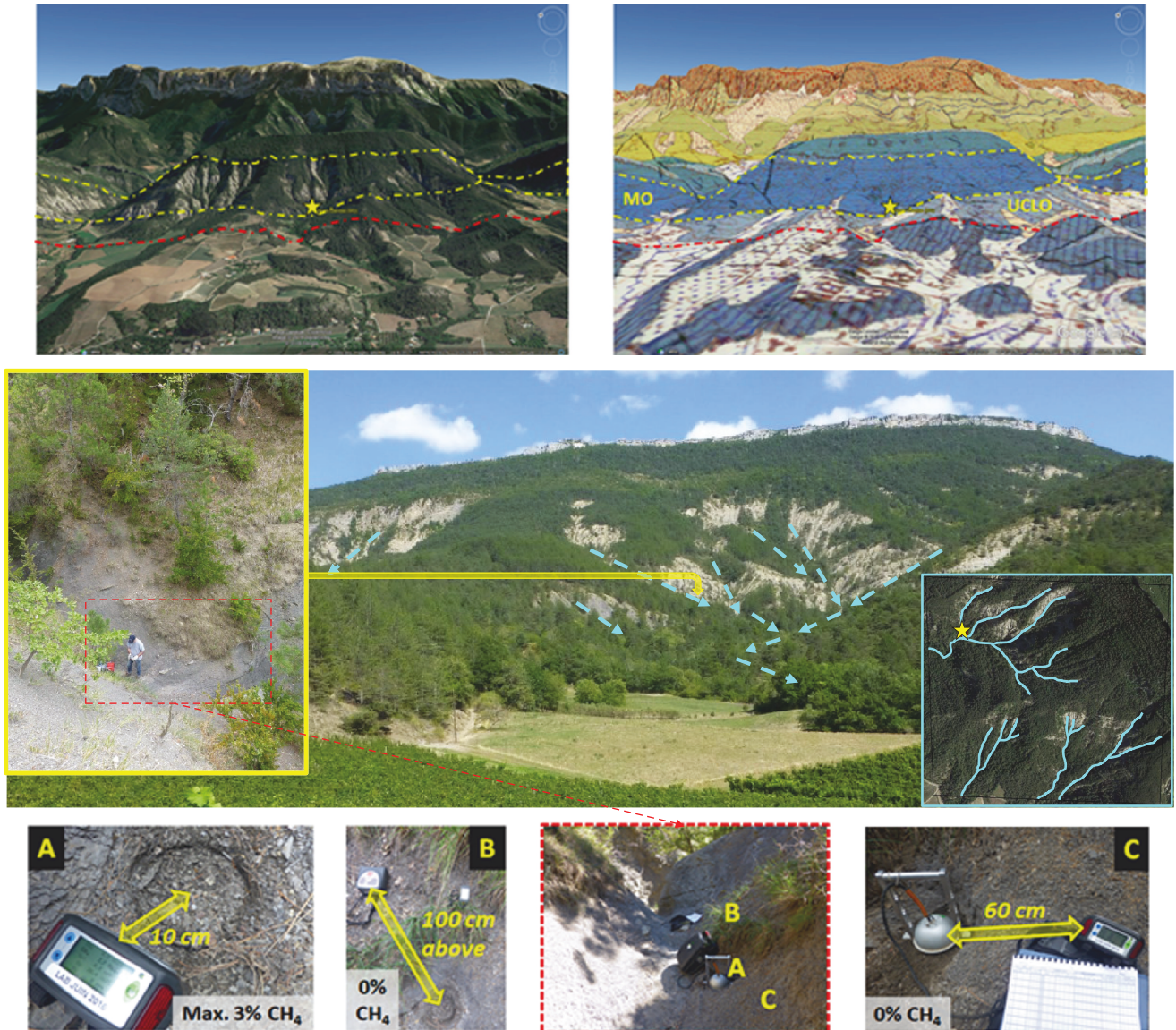


FIGURE 9: MG site: (top) overviews of reliefs surrounding the site and relief-shaped geological map (from Google Earth); location of the gas seep is indicated by the yellow star; MO: shales from the Middle Oxfordian age; UCLLO: black shales from the Upper Callovian to the Lower Oxfordian age. (Middle) Photograph of the site and main thalwegs (dotted lines); right inset: aerial view of thalwegs (from Google Earth); left inset: topography of the seepage area (the character is in front of the seep). (Bottom) Locations of passive atmosphere monitoring (A, B, and C) and results of CH_4 measurements.

The example of the MG seep is very illustrative in that perspective. Contrarily to the FA site, the MG site represents a small seepage, but the mechanism may be similarly linked to fault structures, given that leakage rates along faults may be highly heterogeneous [49]. The MG site can be considered as point source macroseep. The photographs presented in Figure 9 illustrate how difficult it is to locate such a seepage in the field, using currently available monitoring equipment. Given the natural air movements, a gas detector held 10 cm above the seep will record maximum CH_4 values of only 3%, in spite of the fact that there is enough CH_4 seeping to the soil surface to light a flame directly above the seep. We noted significant variability in the readings even for a very light wind blowing through the narrow channel formed by the creek

bed. Moving the gas detector some tens of centimeters away from the source precludes any detection of CH_4 . This makes it highly improbable to detect such gas vents with any method outside a very restricted volume around the point of gas emission. Indeed, the human nose is in the present case one of the best tools owing to its ability to detect trace gases, such as H_2S , at levels far below the detection limits of common portable equipment [50].

Future detection of unknown seepage areas will thus be a difficult task. At the scale we consider here, neither methods relying on air gas monitoring nor airborne methods will be easily applicable because of the rapid dispersion of the CH_4 in the air. The use of unmanned systems (e.g., drones) may be possible but the rugged topography and often dense

natural vegetation will limit their use in regions comparable to the investigated areas of the Subalpine Chains.

At the present technological state of the art, the best way to proceed will be a fastidious ground monitoring with regular stops to check for active leakage. Laser systems seem here to be more appropriate than other detection techniques. The low concentrations imply that the best results can be expected if the sensors integrated in the monitoring equipment point directly, orthogonally to the soil. Direct laser pointing will integrate a CH₄ content (often expressed in ppm) over the distance between the sensor and a reflective source (soil/rock). In the case of the MG site, our flux measurements show that several hundreds of ppm of CH₄ are emitted each second into the atmosphere at the seep (up to 1500 ppm·s⁻¹). Even for lower natural fluxes, a laser beam crossing the emission area, even at some distance, will detect such a release. Remote methane leak detectors built for pipeline leakage monitoring may be appropriate candidates. They often have a sensitivity of 5 ppm·m, a working range of 0 to 50,000 ppm·m or more, and working distances from a few decimeters to 30–80 m [51–55]. Some sensors also exist as drone-mounted versions [54]. In the case of the MG site, such sensors should be able to detect the observed seepage at 10 to 20 m of distance (corresponding to max. 150 ppm·m and 75 ppm·m, respectively), longer distances being not compatible with the lengths of the thalweg sections. The counterpart is that such kind of work implies a huge workload and is time and cost intensive. It is not adapted to operational day-to-day site surveillance of hydrocarbon plays.

5. Conclusions

The three newly investigated gas seeps situated in zones where argillaceous gas-bearing Jurassic host rock outcrop in the French Subalpine Chains complete our previous investigations reported for the most prominent alpine “eternal fire,” the Fontaine Ardente du Gua [3]. Again, methane is the dominant gas phase emitted to the atmosphere, over areas of variable size ranging from tens of square centimeters to tens of square meters. The integration of all data so far available for the French seeps leads to mean flux estimations with some statistical significance. Considering information from all macroseepage and miniseepage areas where a positive CH₄ flux is measured, mean CH₄ release is calculated at 76–79 kg per square meter per year. This is far above microseepage rates recently reported by Etiope et al. [9] thus confirming the superposition of diffuse and focused degassing processes at macroseeps, highlighting the role of faults and fractures in gas emissions even from shale formations. Contrarily to most oil- and gas-bearing sedimentary basins with known gas and oil seeps (e.g., the recent inventory for China [56]), the French alpine seeps seem not linked to tectonic trap structures, seeping through younger brittle deformations. All are directly related to outcropping argillaceous host rocks, but alpine thrusting and faults certainly play an important role in creating pathways for gas accumulation and migration, similarly to what was postulated for the Appalachian Mountains [6]. Linking structural analysis of fault patterns

to gas emissions is certainly one of the most promising approaches for targeting ground-based investigations aiming at discovering new emitting structures in the restrained time-frame of environmental baseline assessment. The gas seeps described so far were found accidentally, by local inhabitants through spontaneous or induced ignition, bubbling in water-bearing creeks or by detecting the particular smell of higher alkanes or H₂S. Systematic “blind” monitoring of black shale outcrops will probably fail to succeed if ground investigations are not guided, e.g., by airborne analysis of fault patterns. Future work will be oriented towards the testing of ground-based and airborne laser-based detectors to check their capacities of detection on known seeps. If these tests are conclusive, then trials in uncovered areas will be performed.

The systematic detection of seeps becomes crucial in the context of monitoring the potential impact of shale gas exploration or exploitation as well as of underground storage of natural gas and CO₂. Environmental baseline assessment is now a well-established prerequisite of Carbon Capture and Storage (CCS). As we attempt to demonstrate here, it is highly hypothetical that baseline investigations, as good as they may be from a technological point of view, will reveal all natural small-scale gas seeps. When then a site will shift to an operational stage, leakage from the exploitation infrastructure may be alleged if so far unreported natural seepage is discovered. This was the case at the CCS site of Weyburn in 2011 [57, 58]. Several studies have demonstrated the natural origin of the discovered CO₂ emission, related to specific processes in the soil formations close to the surface [59–61]. Nevertheless, eight years after the allegation has been raised, research is still ongoing aiming to discard or confirm CCS-induced leakage [62, 63]. In the context of shale gas, the situation is even more complex as the use of chemicals in hydraulic fracturing of the argillaceous host rocks has raised strong public concerns on health effects, both of flowback water spills and leaks to surface water or groundwater resources and of stray gas. [64, 65]. Much effort is put into optimizing water and groundwater monitoring [66, 67]. Monitoring during the activity of the site may be better focused than initial investigations of gas emission baselines over large areas. However, as shown for the Weyburn case, and other CCS test sites or demonstrators, as well as for areas with active unconventional gas exploitation, intrinsic fingerprinting of gas species as well as investigating chemical and isotopic characteristics of groundwater bears a great potential for system failure detection [68–73] and will usefully complete the identification and quantification of gas emanations.

Data Availability

Data are given as supplementary material.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Supplementary Materials

Soil gas flux values ($f\text{CO}_2$, $f\text{CH}_4$) are measured in the field, along with location and time of measurement. If a decrease of the O_2 concentration inside the chamber is measured together with an enrichment in CO_2 and/or CH_4 , then this depletion is reported. Soil gas concentrations (CO_2 , CH_4 , and O_2) are measured in the field, along with location and time of measurement. (*Supplementary Materials*)

References

- [1] G. Etiope, G. Papatheodorou, D. Christodoulou, M. Geraga, and P. Favali, "The geological links of the ancient Delphic Oracle (Greece): a reappraisal of natural gas occurrence and origin," *Geology*, vol. 34, no. 10, pp. 821–824, 2006.
- [2] G. Etiope, "Natural Gas Seepage," in *The Earth's Hydrocarbon Degassing*, Springer, 2015.
- [3] F. Gal, W. Kloppmann, E. Proust, and P. Humez, "Gas concentration and flow rate measurements as part of methane baseline assessment: case of the Fontaine Ardente gas seep, Isère, France," *Applied Geochemistry*, vol. 95, pp. 158–171, 2018.
- [4] G. Etiope and R. W. Klusman, "Geologic emissions of methane to the atmosphere," *Chemosphere*, vol. 49, no. 8, pp. 777–789, 2002.
- [5] G. Etiope, C. Zwahlen, F. S. Anselmetti, R. Kipfer, and C. J. Schubert, "Origin and flux of a gas seep in the northern Alps (Giswil, Switzerland)," *Geofluids*, vol. 10, no. 4, 485 pages, 2010.
- [6] G. Etiope, A. Drobniak, and A. Schimmelmann, "Natural seepage of shale gas and the origin of "eternal flames" in the northern Appalachian Basin, USA," *Marine and Petroleum Geology*, vol. 43, pp. 178–186, 2013.
- [7] G. Etiope and M. Schoell, "Abiotic gas: atypical, but not rare," *Elements*, vol. 10, no. 4, pp. 291–296, 2014.
- [8] G. Etiope and G. Martinelli, "Migration of carrier and trace gases in the geosphere: an overview," *Physics of the Earth and Planetary Interiors*, vol. 129, no. 3–4, pp. 185–204, 2002.
- [9] G. Etiope, G. Ciotoli, S. Schwietzke, and M. Schoell, "Gridded maps of geological methane emissions and their isotopic signature," *Earth System Science Data*, vol. 11, no. 1, pp. 1–22, 2019.
- [10] G. Etiope and R. W. Klusman, "Microseepage in drylands: flux and implications in the global atmospheric source/sink budget of methane," *Global and Planetary Change*, vol. 72, no. 4, pp. 265–274, 2010.
- [11] D. L. Pinti, Y. Gelinas, A. M. Moritz, M. Larocque, and Y. Sano, "Anthropogenic and natural methane emissions from a shale gas exploration area of Quebec, Canada," *Science of the Total Environment*, vol. 566–567, pp. 1329–1338, 2016.
- [12] D. R. Caulton, P. B. Shepson, R. L. Santoro et al., "Toward a better understanding and quantification of methane emissions from shale gas development," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 111, no. 17, pp. 6237–6242, 2014.
- [13] G. Etiope, L. A. Doezema, and C. Pacheco, "Emission of methane and heavier alkanes from the La Brea Tar Pits seepage area, Los Angeles," *Journal of Geophysical Research: Atmospheres*, vol. 122, no. 21, pp. 12,008–12,019, 2017.
- [14] S. Bachu, "Analysis of gas leakage occurrence along wells in Alberta, Canada, from a GHG perspective – gas migration outside well casing," *International Journal of Greenhouse Gas Control*, vol. 61, pp. 146–154, 2017.
- [15] G. Schout, J. Griffioen, S. M. Hassanizadeh, G. Cardon de Lichtbuer, and N. Hartog, "Occurrence and fate of methane leakage from cut and buried abandoned gas wells in the Netherlands," *Science of the Total Environment*, vol. 659, pp. 773–782, 2019.
- [16] M. Currell, D. Banfield, I. Cartwright, and D. I. Cendon, "Geochemical indicators of the origins and evolution of methane in groundwater: Gippsland Basin, Australia," *Environmental Science and Pollution Research*, vol. 24, no. 15, pp. 13168–13183, 2017.
- [17] P. Humez, B. Mayer, J. Ing et al., "Occurrence and origin of methane in groundwater in Alberta (Canada): gas geochemical and isotopic approaches," *Science of the Total Environment*, vol. 541, pp. 1253–1268, 2016.
- [18] J. T. Kulongoski, P. B. McMahon, M. Land, M. T. Wright, T. A. Johnson, and M. K. Landon, "Origin of methane and sources of high concentrations in Los Angeles groundwater," *Journal of Geophysical Research: Biogeosciences*, vol. 123, no. 3, pp. 818–831, 2018.
- [19] L. J. Molofsky, S. D. Richardson, A. W. Gorody et al., "Effect of different sampling methodologies on measured methane concentrations in groundwater samples," *Groundwater*, vol. 54, no. 5, pp. 669–680, 2016.
- [20] C. Rivard, G. Bordeleau, D. Lavoie, R. Lefebvre, and X. Malet, "Can groundwater sampling techniques used in monitoring wells influence methane concentrations and isotopes?," *Environmental Monitoring and Assessment*, vol. 190, no. 4, p. 191, 2018.
- [21] M. E. Hinkle, "Environmental conditions affecting concentrations of He, CO_2 , O_2 and N_2 in soil gases," *Applied Geochemistry*, vol. 9, no. 1, pp. 53–63, 1994.
- [22] G. Frederick, K. Wolfram, P. Eric et al., "Natural CH_4 gas seeps in the French Alps: characteristics, typology and contribution to CH_4 natural emissions to the atmosphere," *Energy Procedia*, vol. 114, pp. 3020–3032, 2017.
- [23] M. Pignone, "HYSED database," 2014, February 2019, <https://www.arcgis.com/home/webmap/viewer.html?webmap=03cc1bc26fd645228ad60bea403a1b26>.
- [24] E. Greber, W. Leu, D. Bernoulli, M. E. Schumacher, and R. Wyss, "Hydrocarbon provinces in the Swiss southern Alps—a gas geochemistry and basin modelling study," *Marine and Petroleum Geology*, vol. 14, no. 1, pp. 3–25, 1997.
- [25] D. Misch, W. Leu, R. F. Sachsenhofer, R. Gratzler, B. Rupprecht, and A. Bechtel, "Shallow hydrocarbon indications along the alpine thrust belt and adjacent foreland basin: distribution and implications for petroleum exploration," *Journal of Petroleum Geology*, vol. 40, no. 4, pp. 341–362, 2017.
- [26] B. Blavoux and J. Dazy, "Caractérisation d'une province à CO_2 dans le bassin du Sud-Est de la France," *Hydrogéologie*, vol. 4, pp. 241–252, 1990.

- [27] M. Gignoux and L. Moret, "Description géologique du bassin supérieure de la Durance," *Bulletin de la Société de statistique, des sciences naturelles et des arts industriels du département de l'Isère* 58(XVII), 1938, <https://gallica.bnf.fr/ark:/12148/bpt6k9610071m>.
- [28] BRGM, 2019, February 2019, <http://infoterre.brgm.fr/rechercher/default.htm>.
- [29] J. Debelmas, "Un dégagement de gaz naturel dans l'Oxfordien des environs de Grenoble (ravin du Rochasson, commune de Montbonnot, Isère)," *Géologie Alpine*, vol. 54, p. 15, 1978.
- [30] A. Favre, *Recherches géologiques dans les parties de la Savoie, du Piémont et de la Suisse voisines du Mont-Blanc, avec un atlas de 32 planches, Tome II, paragraphes*, Masson, 1867, February 2019, <http://docplayer.fr/34550274-Recherches-geologiques-dans-les-parties-de-la-savoie-du-piemont-et-de-la-suisse-voisines-du-mont-blanc-avec-un-atlas-de-32-planches-par.html>.
- [31] J. Omer, "Une source de gaz inflammable dans la Haute-Savoie," *La Nature, Revue des sciences et de leur application à l'art et à l'industrie*, vol. 1634, p. 246, 1904.
- [32] L. Moret, "Enquête critique sur les ressources minérales de la province de Savoie, précédée d'une esquisse géologique," *Bulletin de la Société Scientifique du Dauphiné*, vol. 46, no. 5, 1925.
- [33] F. Gal, K. Michel, Z. Pokryszka et al., "The SENTINELLE French research project: subsurface geochemical characterization prior CO₂ injection (baseline survey) – site of Rousse (TOTAL CCS pilot)," *International Journal of Greenhouse Gas Control*, vol. 21, pp. 177–190, 2014.
- [34] J. P. Toutain and J. C. Baubron, "Gas geochemistry and seismotectonics: a review," *Tectonophysics*, vol. 304, no. 1-2, pp. 1–27, 1999.
- [35] C. Werner and S. Brantley, "CO₂ emissions from the Yellowstone volcanic system," *Geochemistry, Geophysics, Geosystems*, vol. 4, no. 7, 2003.
- [36] Z. Pokryszka, F. Adelise, R. Farret, S. Lafortune, E. Michel, and S. Rupasinghe, "Valeurs de référence du flux de CO₂ et de CH₄ d'origine naturelle biogénique des sols, INERIS report DRS-17-164646-05731A," 2017, February 2019, https://www.ineris.fr/sites/ineris.fr/files/contribution/Documents/INERIS_DRS-17-164646-05731_Referentiel-flux-CO2-CH4-sols_ZPo.pdf.
- [37] G. Etiope, M. Schoell, and H. Hosgörmez, "Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars," *Earth and Planetary Science Letters*, vol. 310, no. 1-2, pp. 96–104, 2011.
- [38] G. Chiodini, F. Frondini, and B. Raco, "Diffuse emission of CO₂ from the fossa crater, Vulcano Island (Italy)," *Bulletin of Volcanology*, vol. 58, no. 1, pp. 41–50, 1996.
- [39] K. D. Romanak, P. C. Bennett, C. Yang, and S. D. Hovorka, "Process-based approach to CO₂ leakage detection by vadose zone gas monitoring at geologic CO₂ storage sites," *Geophysical Research Letters*, vol. 39, no. 15, 2012.
- [40] J. Le Mer and P. Roger, "Production, oxidation, emission and consumption of methane by soils: a review," *European Journal of Soil Biology*, vol. 37, no. 1, pp. 25–50, 2001.
- [41] G. Frédérick, P. Eric, B. Gaëtan et al., "What may be the consequences of a CO₂ leakage? Insights from soil gas measurements in an urban area – Clermont-Ferrand, French Massif Central," *Energy Procedia*, vol. 114, pp. 3006–3019, 2017.
- [42] N. R. Varley and M. A. Armienta, "The absence of diffuse degassing at Popocatepetl volcano, Mexico," *Chemical Geology*, vol. 177, no. 1-2, pp. 157–173, 2001.
- [43] R. H. Kiefer and R. G. Amey, "Concentrations and controls of soil carbon dioxide in sandy soil in the North Carolina coastal plain," *Catena*, vol. 19, no. 6, pp. 539–559, 1992.
- [44] H. Enoch and S. Dasberg, "The occurrence of high CO₂ concentrations in soil air," *Geoderma*, vol. 6, no. 1, pp. 17–21, 1971.
- [45] C. Dezayes, J. A. M. Mohammad, A. Bitri et al., "Application of exploration techniques on sedimentary basin fields, report IMAGE-D8.02, EU FP7 project IMAGE," 2017, February 2019, <http://www.image-fp7.eu/reference-documents/deliverables/IMAGE-D8.02-2017.09.18-Applications-of-Exploration-Techniques%20-%20public.pdf>.
- [46] B. B. Bernard, "Light hydrocarbons in marine sediments. PhD Dissertation," University of Texas, 1978, February 2019, <https://www.tdi-bi.com/wp-content/uploads/2015/04/BBB-1978-Diss-LIGHT-HYDROCARBONS-IN-MARINE-SEDIMENTS-r.pdf>.
- [47] A. V. Milkov and G. Etiope, "Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples," *Organic Geochemistry*, vol. 125, pp. 109–120, 2018.
- [48] N.-A. Mörner and G. Etiope, "Carbon degassing from the lithosphere," *Global and Planetary Change*, vol. 33, no. 1-2, pp. 185–203, 2002.
- [49] C. E. Bond, Y. Kremer, G. Johnson et al., "The physical characteristics of a CO₂ seeping fault: the implications of fracture permeability for carbon capture and storage integrity," *International Journal of Greenhouse Gas Control*, vol. 61, pp. 49–60, 2017.
- [50] INERIS, "Toxicological and environmental data sheet for chemical substances - hydrogen sulfide. Report DRC-07-83451-15432B," 2011, February 2019, <https://substances.ineris.fr/fr/substance/getDocument/2848>.
- [51] Focused Photonics, 2019, February 2019, http://www.fpi-inc.com/en/index.php/pro_info/19?ctype=34.
- [52] Gazomat, 2019, February 2019, <https://www.gazomat.com/en/products/gazoscan/>.
- [53] Heath Consultants, 2019, February 2019, <https://heathus.com/products/remote-methane-leak-detector/>.
- [54] Hesai, 2019, February 2019, http://www.hesaitech.com/en/laser-based_remote_methane_leak_detector.html.
- [55] Tokyo Gas, 2019, February 2019, http://www.tokyogas-es.co.jp/en/business/eq/laser_methane_mini.html.
- [56] G. Zheng, W. Xu, G. Etiope et al., "Hydrocarbon seeps in petroliferous basins in China: a first inventory," *Journal of Asian Earth Sciences*, vol. 151, pp. 269–284, 2018.
- [57] K. Brown, S. Whittaker, M. Wilson, W. Srisang, H. Smithson, and P. Tontiwachwuthikul, "The history and development of the IEA GHG Weyburn-Midale CO₂ monitoring and storage project in Saskatchewan, Canada (the world largest CO₂ for EOR and CCS program)," *Petroleum*, vol. 3, no. 1, pp. 3–9, 2017.
- [58] A. D. Boyd, Y. Liu, J. C. Stephens et al., "Controversy in technology innovation: contrasting media and expert risk perceptions of the alleged leakage at the Weyburn carbon dioxide storage demonstration project," *International Journal of Greenhouse Gas Control*, vol. 14, no. 2013, pp. 259–269, 2013.
- [59] S. E. Beaubien, D. G. Jones, F. Gal et al., "Monitoring of near-surface gas geochemistry at the Weyburn, Canada, CO₂-EOR

- site, 2001–2011,” *International Journal of Greenhouse Gas Control*, vol. 16, pp. S236–S262, 2013.
- [60] D. Risk, M. Lavoie, and N. Nickerson, “Using the Kerr investigations at Weyburn to screen geochemical tracers for near-surface detection and attribution of leakage at CCS/EOR sites,” *International Journal of Greenhouse Gas Control*, vol. 35, pp. 13–17, 2015.
- [61] K. Romanak, G. W. Sherk, S. Hovorka, and C. Yang, “Assessment of alleged CO₂ leakage at the Kerr farm using a simple process-based soil gas technique: implications for carbon capture, utilization, and storage (CCUS) monitoring,” *Energy Procedia*, vol. 37, pp. 4242–4248, 2013.
- [62] S. M. V. Gilfillan, G. W. Sherk, R. J. Poreda, and R. S. Haszeldine, “Using noble gas fingerprints at the Kerr farm to assess CO₂ leakage allegations linked to the Weyburn-Midale CO₂ monitoring and storage project,” *International Journal of Greenhouse Gas Control*, vol. 63, pp. 215–225, 2017.
- [63] C. D. Sandau, M. Prokipchuk, K. R. Dominato, and S. O. C. Mundle, “Soil gas investigation of an alleged gas migration issue on a residential farm located above the Weyburn-Midale CO₂ enhanced oil recovery project,” *International Journal of Greenhouse Gas Control*, vol. 81, pp. 11–20, 2019.
- [64] T. J. Centner and L. K. O’Connell, “Unfinished business in the regulation of shale gas production in the United States,” *Science of the Total Environment*, vol. 476–477, pp. 359–367, 2014.
- [65] Y. Yao, T. Chen, S. S. Shen et al., “Malignant human cell transformation of Marcellus shale gas drilling flow back water,” *Toxicology and Applied Pharmacology*, vol. 288, no. 1, pp. 121–130, 2015.
- [66] S. Gamper-Rabindran, “Information collection, access, and dissemination to support evidence-based shale gas policies,” *Energy Technology*, vol. 2, no. 12, pp. 977–987, 2014.
- [67] R. A. Howell, “UK public beliefs about fracking and effects of knowledge on beliefs and support: a problem for shale gas policy,” *Energy Policy*, vol. 113, pp. 721–730, 2018.
- [68] D. Györe, R. McKavney, S. M. V. Gilfillan, and F. M. Stuart, “Fingerprinting coal-derived gases from the UK,” *Chemical Geology*, vol. 480, pp. 75–85, 2018.
- [69] P. Humez, J. Lions, P. Negrel, and V. Lagneau, “CO₂ intrusion in freshwater aquifers: review of geochemical tracers and monitoring tools, classical uses and innovative approaches,” *Applied Geochemistry*, vol. 46, pp. 95–108, 2014.
- [70] P. Humez, P. Negrel, V. Lagneau et al., “CO₂-water-mineral reactions during CO₂ leakage: geochemical and isotopic monitoring of a CO₂ injection field test,” *Chemical Geology*, vol. 368, pp. 11–30, 2014.
- [71] B. Mayer, P. Humez, V. Becker et al., “Assessing the usefulness of the isotopic composition of CO₂ for leakage monitoring at CO₂ storage sites: a review,” *International Journal of Greenhouse Gas Control*, vol. 37, pp. 46–60, 2015.
- [72] B. Mayer, P. Humez, V. Becker et al., “Prospects and limitations of chemical and isotopic groundwater monitoring to assess the potential environmental impacts of unconventional oil and gas development,” *Procedia Earth and Planetary Science*, vol. 13, pp. 320–323, 2015.
- [73] P. Humez, B. Mayer, M. Nightingale et al., “Redox controls on methane formation, migration and fate in shallow aquifers,” *Hydrology and Earth System Sciences*, vol. 20, no. 7, pp. 2759–2777, 2016.



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