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Surface Gas Geochemistry above the Natural CO₂ Reservoir of Montmiral (Drôme, France), Source Tracking and Gas Exchange between the Soil, Biosphere and Atmosphere

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Résumé — Échanges gazeux et géochimie des gaz à la surface du réservoir naturel profond de CO₂ de Montmiral (Drôme) — Une des options envisagées pour réguler les concentrations de gaz à effet de serre dans l'atmosphère est le stockage souterrain du CO₂. Dans ce domaine existe un fort besoin de renforcer et de développer des méthodes susceptibles d'être utilisées tout au long de la durée de vie de ces stockages souterrains, afin de s'assurer de leur sécurité et de pouvoir suivre l'évolution du panache de CO₂ injecté. Parmi elles, les méthodes géochimiques peuvent jouer un rôle important. Nous décrivons ici les résultats acquis dans le cadre du programme de recherche « Géocarbonate-Monitoring » financé en partie par l'Agence Nationale de la Recherche sur l'analogie naturel de Montmiral dans le Sud-Est de la France. D'autres résultats obtenus dans le cadre de ce même programme de recherche sont rapportés dans un autre article présent dans ce volume.

Des méthodes d'échantillonnage ponctuelles permettant une grande couverture géographique et des mesures en continu sur certains points sélectionnés ont été entreprises en 2006 et 2007, afin de permettre la détermination des concentrations en gaz du sol et des flux, ainsi que des déterminations des rapports isotopiques du carbone. Sans aucune preuve d'une fuite de CO₂ profond, à la fois les concentrations et les flux de CO₂ semblent être plus élevés que ne pouvant s'expliquer par l'effet des seules activités biologiques. Des études plus approfondies sont donc nécessaires pour mieux comprendre l'évolution des gaz tout au long de l'année.

Abstract — Surface Gas Geochemistry above the Natural CO₂ Reservoir of Montmiral (Drôme, France), Source Tracking and Gas Exchange between the Soil, Biosphere and Atmosphere — One of the options considered to mitigate greenhouse gas concentrations in the atmosphere is underground storage of CO₂. There is a strong need for enhancing and developing methods that would help throughout

the duration life of such underground storage, to ensure the safety and able to monitor the evolution of the injected CO₂ plume. Among these, geochemical methods can play an important role. Here, we describe results acquired under the research programme “Géocarbonate-Monitoring”, partially funded by the French National Research Agency, on the Montmiral natural analogue in South-Eastern France. Other results obtained under the same research programme in the French Massif Central are reported elsewhere in this volume.

Spot sampling methods allowing a great geographical coverage and continuous measurements on selected points were undertaken in 2006 and 2007, in order to determine soil gas concentrations and fluxes as well as carbon isotope ratio determinations. One important result is that without any evidence of deep CO₂ leakage, both CO₂ concentrations and fluxes appear to be higher than can be explained only by biological activities. Further investigations are thus needed to understand the gas evolution better throughout the year.

INTRODUCTION

Underground storage of CO₂ is one of the options considered to be realistic for mitigating greenhouse gas concentrations in the atmosphere (*e.g.* Winthaege *et al.*, 2005; Holloway *et al.*, 2007; Wildenborg *et al.*, 2009). Several types of storage sites can be used such as depleted oil or gas reservoirs, saline aquifers and deep brine-filled layers, cavities in salt layers and/or domes, and unmineable coal beds (*e.g.* Hitchon *et al.*, 1999; Jean-Baptiste and Ducroux, 2003; Gale, 2004; Winthaege *et al.*, 2005). Nearly depleted oil and gas reservoirs represent one of the most frequently used storage sites, as CO₂ infilling can enhance oil and gas recovery (EOR/EGR operations). Among them, the ongoing Weyburn EOR project (started in 1997) uses anthropogenic CO₂ to enhance hydrocarbon production (Preston *et al.*, 2005; Riding and Rochelle, 2005). Initially not designed in a GHG emission mitigation perspective, this North-American project represents one of the major sequestration demonstration projects, enhancing knowledge and understanding of the mechanism by which CO₂ is sequestered in a carbonate onshore reservoir (Preston *et al.*, 2005). Since then, other onshore projects have been launched but not in a EOR/EGR perspective, such as the CO₂CRC Otway basin project in Australia (Michael *et al.*, 2009; Urosevic *et al.*, 2009), using a depleted methane reservoir for supercritical CO₂ injection (starting date April 2008), and the Lacq CO₂ pilot in France, where injection will be done in a former CH₄ field too (Gapillou *et al.*, 2009). Sequestering CO₂ in the ground instead of venting it into the atmosphere is also achieved in some offshore projects. In the North Sea (K12-B, Netherlands), the CO₂ resulting from gas extraction and subsequent purification is re-injected into the reservoir (Winthaege *et al.*, 2005). The feasibility of CO₂ geological storage in saline aquifers has also been proven by the experience of both CO₂ injection in pilot projects (Frio, Ketzin, Nagaoka) and existing commercial operations (Sleipner, Snøhvit, In Salah) (Michael *et al.*, 2009; Nance *et al.*, 2005; Wildenborg *et al.*, 2009). Frequently, large-scale operations use the CO₂ separated from the extracted fluid to

be re-injected into an aquifer (Sleipner: Kongsjorden *et al.*, 1997; Torp and Gale, 2004; Steeneveldt *et al.*, 2006; Winthaege *et al.*, 2005; Holloway *et al.*, 2007; In Salah, Snøhvit: Michael *et al.*, 2009; Wildenborg *et al.*, 2009).

CO₂ storage programmes must also meet safety rules, as public acceptance is strongly dependent on this key parameter. Indeed, one needs to ensure that the injected CO₂ is absent or present at very low concentrations within the reservoir overburden, by using appropriate monitoring technologies looking into deep horizons and near-surface ones (*e.g.* Sharma *et al.*, 2009; Winthaege *et al.*, 2005; White and Johnson, 2009). One way to understand and evaluate the safety and the integrity of such sites is to study natural analogues, where huge amounts of nearly pure CO₂ (*e.g.* Winthaege *et al.*, 2005; Anping *et al.*, 2009) are trapped at depth for a long time (*e.g.* South France, Otway basin in Australia, Colorado Plateau and Southern Rocky Mountains in the US, and Bohai Bay basin in China). Under favourable conditions, such natural CO₂ reservoirs are thought to retain CO₂ for millions of years (Holloway *et al.*, 2009). In a complementary perspective with the study of naturally leaking analogues (Annunziatellis *et al.*, 2008; Battani *et al.* in this volume), lessons learned from the study of deep CO₂ reservoirs provide a unique opportunity to strengthen the applicability of existing monitoring technologies and to develop new powerful tools.

In the South-Eastern part of France, some CO₂ entrapments were discovered during oil exploration in the 60s, that revealed several CO₂ accumulations with minor CH₄ content. Among them, the Montmiral CO₂ reservoir belongs to the so-called carbogaseous province, tectonically inherited from the alpine orogeny (Blavoux and Dazy, 1990). Such a province is characterised by waters of local origin quickly infiltrated from the surface, the presence of CO₂ mainly of magmatic origin (mantellic and/or deep crustal) and the existence of gas in sedimentary reservoirs due to migration through major fault systems. Previous work has been done to characterise chemical and isotope compositions of fluids from the reservoir up to the surface, under the framework of the

European project NASCENT (Natural Analogues for the Storage of CO₂ in the Geological Environment; Czernichowski-Lauriol *et al.*, 2002; Pauwels *et al.*, 2007; Pearce *et al.*, 2002, 2003). The Montmiral site offers a unique opportunity to study the long-term CO₂-water-rock interactions, particularly processes that could help to understand and estimate the integrity of storage sites better. One of the key results was the possible discovery of a prior leakage affecting Rhaetian and Hettangian limestones and attributed to post-Pyrenean tectonic relaxation (Pearce *et al.*, 2003). Less documentation exists regarding the possible impacts of the Montmiral CO₂ reservoir on the surface, either near the well or a few kilometres away. To help give a better understanding of its behaviour, funding was obtained from the French Research Agency (ANR) for the so-called “Géocarbone-Monitoring” research programme. By using both geophysical and geochemical monitoring methods, this programme is intended to help establish a synthetic view of the reservoir and its influence on the near surface and surface. As CO₂ leakages at the surface have never been reported, the Montmiral CO₂ accumulation is thought to be in a stable state. Therefore, the major goal of the geochemical study of this site is to monitor natural soil gas concentrations and establish their temporal and spatial variability, to give reference values that will be helpful for permit delivery regarding underground CO₂ storage in similar geological settings. Robust as well as innovative methods were therefore used.

1 SITE DESCRIPTION

1.1 Geological Settings

The Montmiral CO₂ accumulation belongs to the French South-Eastern basin, a graben formed in the alpine foreland (Rhône valley), between the French Massif Central basement and the Alpine belt. This natural reservoir was discovered by drilling for oil exploration in Mesozoic formations: in 1961 a CO₂-rich fluid was encountered at the V.Mo.2 borehole at ca. 2400 m depth. The CO₂ commercial exploitation began in 1991.

The reservoir itself comprises Triassic sandstones and Rhaetian to Hettangian fractured carbonates and dolomites, all characterised by matrix porosity. Reservoir fluids are essentially gases (98.55% on a 10-year basis) with minor water (1.33%) and oil (0.12%). The gas phase is mainly CO₂ (97%) with (by order of importance) traces of methane, nitrogen, helium and ethane (Pearce *et al.*, 2003). The CO₂ accumulation is overlaid and confined by a thick sedimentary pile (Jurassic limestones and marls, Tertiary detritic sediments).

Whole rock, rock-forming minerals and fluid geochemistry have been intensely studied under the NASCENT project (*e.g.* Pearce *et al.*, 2003), due to the availability of both

fluid and rock samples from this CO₂-rich reservoir. Water collected at the V.Mo.2 wellhead nowadays has a high salinity (75 g.L⁻¹), resulting from mixing between the CO₂-H₂O gas mixture and the reservoir brine, whose expected salinity, based on a stable oxygen isotope methodology, is around 85 g.L⁻¹ (Pauwels *et al.*, 2007). Calculation of this reservoir brine chemical composition allowed the identification of chemical reactions induced by CO₂ interactions within the reservoir. The main identified reactions are K-feldspar dissolution and subsequent kaolinite precipitation, suspected anhydrite dissolution and Mg-Ca carbonate precipitation, although not observed in existing core samples.

On a wider scale (Tersanne and Montmiral areas, see *Sect. 1.2*), outcropping of Oligocene to Miocene formations, partly consisting of molassic sediments, do not show great tectonic structuration at the surface. Major hidden faults were recognised by seismic profiling, along NE-SW and NW-SE directions, inherited from geological constraints imposed on the West by the Massif Central relief and on the East by the alpine fore-belt (Vercors). Those major tectonic features are mainly related to tertiary tectonic events and crosscut geological strata up to lower Miocene ones. This induced directions varying from N160°E to N-S and N40°E (Pearce *et al.*, 2003).

Lastly, the North-Western part of the studied area, near Tersanne, is close to a non-permanent underground methane storage, operated in salty caverns at around 1500 m depth (Durup *et al.*, 2007). If leakages do occur in this zone, the monitoring devices used should be able to detect them.

1.2 Investigated Zones

Geochemical investigations undertaken under the “Géocarbone-Monitoring” programme are separated into two groups. The first one comprises spot sampling using portable devices and/or in situ sampling, and the second involves more complex technologies that cannot be easily moved on the field. This implies that the whole set of methods was used in the vicinity of the V.Mo.2 well, *i.e.* in the plant protected area. A lighter set of more flexible methods was used within a perimeter of ca. 15 km radius, following transects whose directions were learned from major tectonic directions (*i.e.* along E-W profiles in the so-called Montmiral-Tersanne area; *Fig. 1*).

Two field campaigns were done in June 2006 and April 2007, both exploring the restricted area and wider transects crosscutting tectonic directions. As a consequence of this scale discrepancy, sampling spacing is shorter in the small-scale zone (from 2 to 20 m) and larger (between 500 and 1000 m) in the Montmiral-Tersanne area. Those adapted scales should be sufficient to establish:

- if some leakages are occurring and, if so;
- where they are emplaced relative to tectonic features.

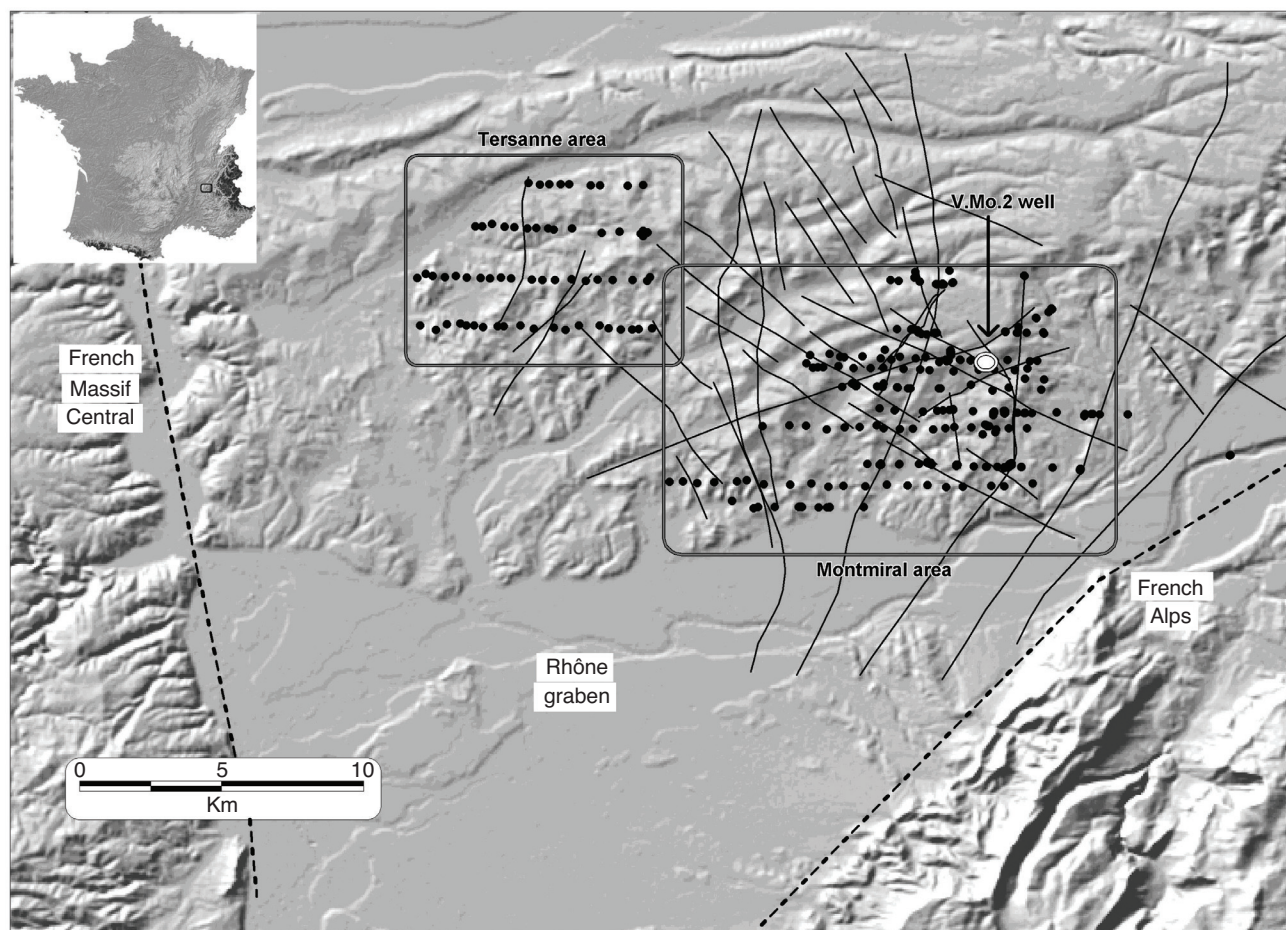


Figure 1

Location of the studied zone; black dots indicate the location of the E-W profiles used for soil concentration and flux measurements. The white circle indicates the emplacement of the V.Mo.2 well and its vicinity, where measurements of concentrations and fluxes, and continuous monitoring were performed. Dashed lines indicate respective locations of the French Massif Central, Rhône graben and French Alp domains. Black lines indicate surface projection of major hidden faults highlighted by seismic studies.

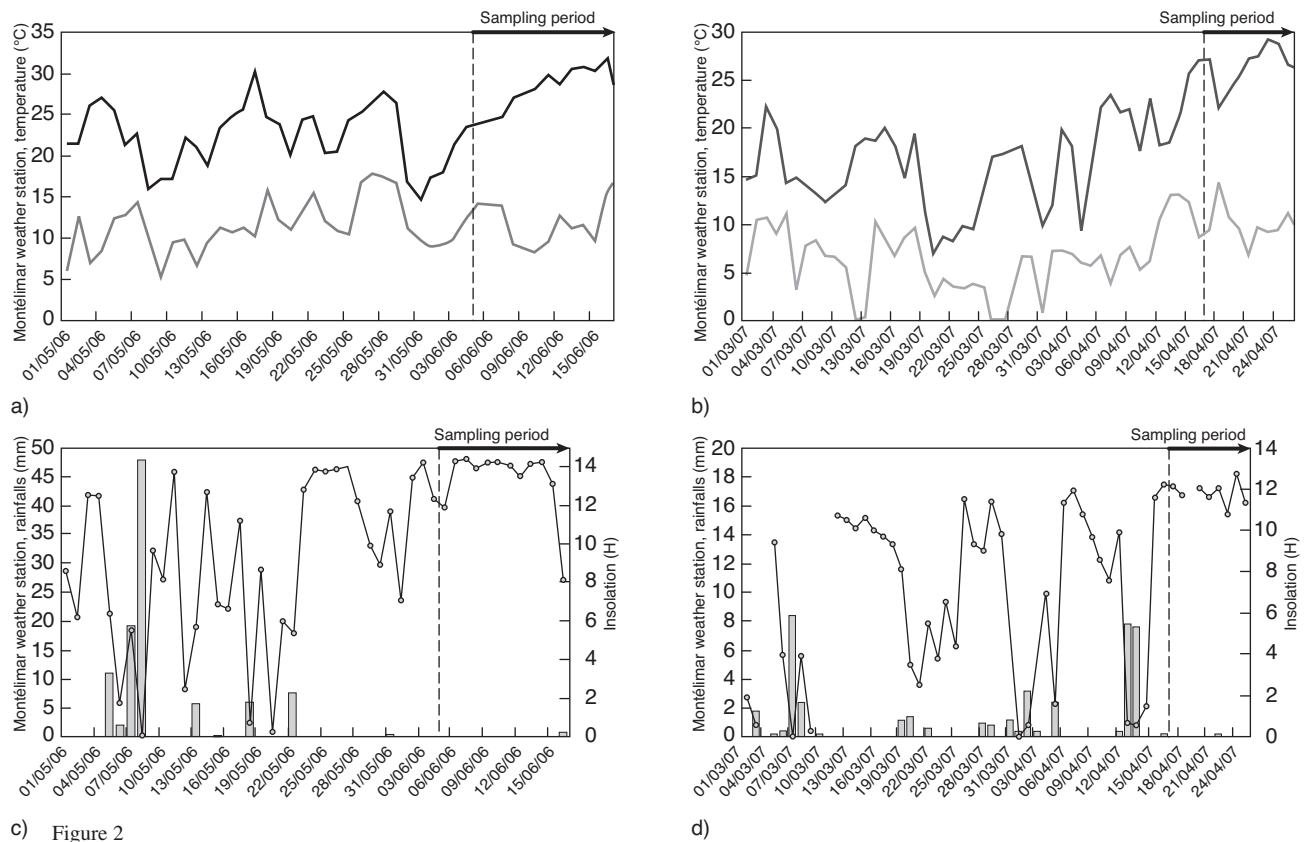
The two field trips were done at the same time by all the implied partners, namely BRGM, IFP, INERIS and INPL. As a consequence, all the data were acquired under the same meteorological conditions and can thus be considered as forming a consistent database, using a wide range of soil gas monitoring methods.

1.3 Meteorological Conditions Prevailing During Field Studies

As previously mentioned, two campaigns were performed under the “Géocarbone-Monitoring” research programme at Montmiral. The first samplings were done between the 5th and the 16th of June 2006. A second trip was carried out in 2007, between the 17th and the 26th of April. As no local weather station was deployed, we refer to existing

meteorological data available from the Météo-France database (<http://france.meteofrance.com/>) and from regional airports (<http://www.meteociel.fr/>). Three nearby cities were considered: Montélimar, 70 km SSW of Montmiral, Grenoble (70 km ENE) and Lyon-Saint-Exupéry (100 km to the North). Those cities, respectively, belong to the Rhône valley, the external alpine domain and the northern part of the Rhône valley. Such locations allow one to fully describe Montmiral’s weather, as dominant rainfalls originate, respectively, from Mediterranean, continental and orographic domains (*e.g.* Vincent and Hirsch, 1966). As rainfall amounts were greater in Montélimar in May and June 2006, as well as in March and April 2007, we tried to only represent this city in Figure 2.

During sampling, mean atmospheric temperatures were slightly higher at the end of the 2006 spring (19.8°C) than at



c) Figure 2

Weather conditions before and during sampling in Montélimar (70 km SSW of Montmiral); a) minimal and maximal atmospheric temperatures recorded in May and June 2006; b) minimal and maximal atmospheric temperatures recorded in March and April 2007; c) rainfall amounts and sunshine duration recorded in May and June 2006; d) rainfall amounts and sunshine duration recorded in March and April 2007.

the beginning of the 2007 spring (18.2°C), which is not surprising. Very scarce rainfall events occurred during the two sampling periods: 0.8 mm in 2006, and 4.2 mm in 2007. With respect to the sunshine duration (160 hours and 100 hours, respectively), there is undoubtedly no influence of the rainfalls on the measurements performed within the soils (*see sect. 2*). Dry conditions prevailed during the 15 preceding days in 2006, but an amount of 15 mm of water was precipitated during the week preceding sampling in 2007. Nevertheless, no water-saturated and only a few wet soils in scattered locations were encountered during the measurements, suggesting a relatively low influence of those rainy days.

2 METHODS

As mentioned previously, several techniques were used. Some of them are commercially available, whereas others were developed during the “Géocarbone-Monitoring” research programme. A general overview will be given below.

2.1 In Situ Spot Soil Gas Analyses

2.1.1 Concentration Measurements

Determination of soil gas species was done in the field with portable InfraRed Gas Analysers (IRGA). LFG20 (*ADC Gas Analysis Ltd.*) and GA2000 (*Geotechnical Instruments Ltd.*) allow one to determine CO₂, CH₄ and O₂ concentrations. For LFG20, the detection limit is 0.05% and precision for CO₂ and CH₄ between 0 and 10% is ±0.5%. For GA2000, the precision is the same between 0 and 5%, rising up to ±1% for CO₂ and CH₄ between 5 and 15%. Calibrations of IRGA were done at the lab and verified on-site by using CO₂-labelled bottles at 0.05, 0.238, 0.965, 10.2 and 100% CO₂. Sampling was done after drilling a small hole in the soil (ca. 80 cm depth, 1 cm in diameter) using a battery powered drill, and inserting a copper tube in the hole. Particular attention was given to properly sealing the copper tube, to avoid leakages and soil atmosphere contamination by atmospheric components. Moreover, sampling at 1 m depth considerably lowers risks of sampling gas that could have interacted with



Figure 3
Varian mobile microchromatograph in acquisition.

gas of atmospheric origin (Lewicki *et al.*, 2003). Internal calibration of this sampling method has been done at BRGM, the reproducibility and results being equivalent to those recorded using stainless steel probes progressively lowered down into the soil by hand-hammer percussion. Using electrically-powered instruments also permits one to save time. The copper tube is then connected to the IRGA, and pumping is done at low flow rate ($200 \text{ mL}/\text{min}^{-1}$). Equilibration of the gas flux occurs within one or two minutes, then values are registered. Subsequently, two other samples are taken for further analysis. For helium abundance measurements, a Tedlar bag is connected at the exit connection of the IRGA, filled and rinsed at least once prior

to getting a sample. Lastly, for radon activity determination, a vacuum scintillation flask is filled by soil gas (ca. 200 mL, internal ZnS coating, *Algade*, France).

Helium measurements were performed twice a day, using a modified *Alcatel* leaking mass spectrometer (*Adixen* ASM102S). Values are measured as mV data and then expressed in ppm with reference to the atmospheric value, set to 5.24 ppm. Sensitivity is 0.1 ppm in the range 0.1 ppm - 100% He. Helium measurements were made on a half-day basis, samples being analysed less than 4 hours after their collection.

Radon measurements were done by alpha particle counting (*Calen*, *Algade*) and converted into activity data (Bq/m^3) using the manufacturer's spreadsheet. Alpha photomultiplier background noise is less than 0.2 blps per hour. Counting was done for 180 seconds, the stated reproducibility being better than 0.1%.

If relevant, additional samples are taken in vacuum glass bulbs or stainless steel canisters for laboratory gaseous chromatography measurements and further isotope ratio determination. During the year 2006 the first in situ tests were performed by using a mobile Varian micro-gas chromatograph (*Fig. 3, 4*). This μGC is equipped with 3 independent modules. The first one allows the analysis of the usual components of the air (CP-4900 Backflush Column Module, 10 m MS5). The second module is used to measure CO_2 and light hydrocarbons (CP-4900 Module, 10 m PPQ Heated Inj.). Lastly, the third module is dedicated to measuring CO_2 (CP-4900 Module, 6 m 5CB Heated Inj.). Each module contains its own injector, column and detector. Thermal Conductivity Detectors (TCD) are known for their very good linearity from a few ppm to 100% (V/V). The



Figure 4
Illustration and photographs of micro-GC sampling.

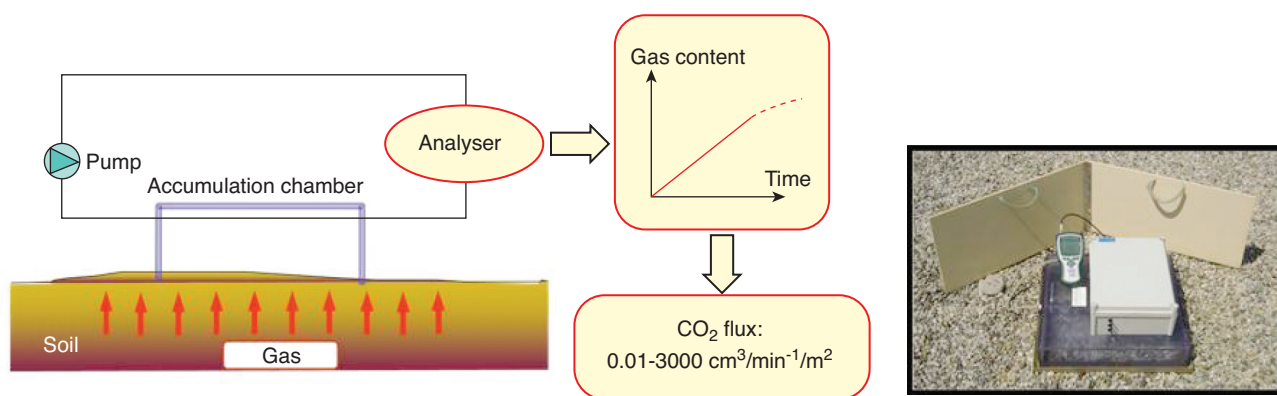


Figure 5

INERIS flux chamber measurement device (patent number 96-05996).

working temperature of the columns is about 40°C. This temperature limits the consumption of energy in winter and remains in most cases lower than the temperatures encountered in summer. The complete separation of the components and their quantification by the software takes less than 2 minutes (including the access to the individual chromatogram peaks). Equipped with a specific carriage (Fig. 3), this apparatus can easily move from one point to another. The batteries and gas bottles easily ensure a whole day of measurements.

This first study mainly focuses on N₂, O₂+Ar, CO₂, CH₄, C₂H₆ and C₃H₈. Calibration and metrology considerations were carried out in the laboratory with various gas mixtures containing CO₂, CH₄, C₂H₆, C₃H₈ and C₄H₁₀. The proportion of each gas ranges between 50 ppm and 5%. We used different samplers for collecting gases (Fig. 4). The soil gas probe shown in Figure 4 is equipped with a packer which limits gas exchanges between the soil and the atmosphere. Moreover, it allows direct measurements of gases in porous rocks (outcrop, for example). After drilling, this probe is inserted in the soil and the packer is inflated with a manual pump. A short delay is then needed in order to reach soil/gas equilibrium. After this delay, the µGC sampling pump allows one to collect the soil gas. The low flow rate (10 mL/min) does not unbalance the soil gas proportions. Moreover, as TCD is a non-destructive detector, it is possible to check the quality of the sample injected in the µGC and to collect it for further analyses (e.g. laboratory isotopic measurements). This kind of approach is used for collecting gas bubbles from gaseous waters. To ensure the capture of the bubbles is fully achieved, decreases in N₂ and Ar+O₂ peaks are followed.

2.1.2 Fluxes

Flux measurements were performed with a home-made accumulation chamber that avoids perturbing the environment too much (Fig. 5). The chamber is fitted onto

the soil, allowing the natural escape of the gas from the soil into the atmosphere. As the system is hermetic, soil gas accumulates in the chamber. It is then possible to study and monitor gas dynamics and how the in-chamber atmosphere becomes enriched in gas. To quantify gas species and amounts, a sample of the gas accumulated within the chamber is drawn into an infrared analyser and then flows back into the chamber. By monitoring the rate at which the re-circulated mixture is enriched in the gas, it is possible to deduce the local gas flow at a given point. Chamber size and operating parameters were optimised at the design stage at the lab, using a test rig and known gas flows. This measurement system is relatively simple to operate. The time needed for a single measurement ranges between 5 and 10 minutes, so that a large number of acquisitions can be made daily (from 30 to 60 points, depending on sampling site accessibility). The exact procedures involved in this method are protected by the 96-05996 patent "Measurement of gas flows through surfaces".

More than 260 measurements were made during the 2006 and 2007 field campaigns, both within the Montmiral plant area (ca. 90 measurements near the V.Mo.2 borehole plus 90 other measurements, especially in the eastern part of this perimeter - see Sect. 2.3) and along E-W profiles (ca. 80 measurements). As the meteorological conditions remained stable during those two campaigns (Fig. 2), comparison of data would not suffer from strong atmospheric temperature influence, as pointed out by Lewicki *et al.* (2003) during their survey in California.

2.2 Laboratory Chemical Analyses

2.2.1 Gas Content

Gas phase chromatography allows determination of proportions of the following gases: CO₂, Ar, O₂, N₂, CO, He, H₂, H₂S,

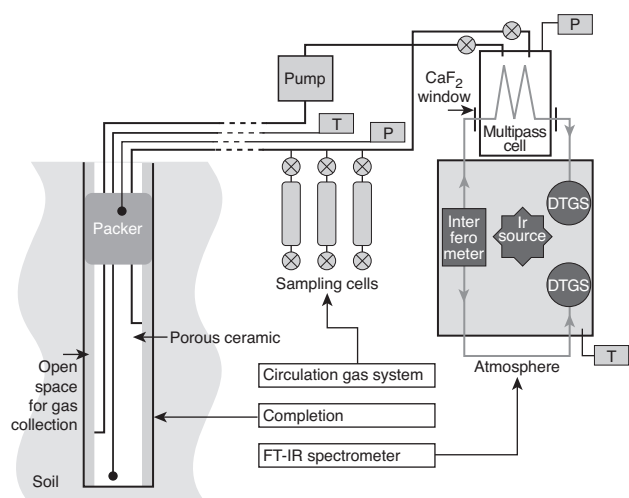


Figure 6

Scheme of the borehole completion used for FT-IR measurements; the completion is linked to a circulation gas system and a FT-IR spectrometer for on-line CO₂ measurement (T: temperature sensor, P: pressure sensor).

CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂ and C₆H₁₄. Detection limits are $\pm 0.0002\%$ for C_nH_{2n+2} (n = 1 to 6), $\pm 0.001\%$ for Ar, N₂, CO₂ and O₂ and $\pm 0.005\%$ for H₂, H₂S and He. As for IRGA determination, percentages refer to volume ones. Helium cannot be detected by laboratory measurements, as the detection limit is ten times higher than the atmospheric content.

2.2.2 Isotopic Measurements

Isotopic measurements were carried out on CO₂ and noble gases. For CO₂ isotopic measurements, the gas phase is purified under vacuum after freezing, to get a pure CO₂ fraction. This fraction is then analysed by a classical dual-inlet mass spectrometer. The stable carbon isotope ratio is expressed as $\delta^{13}\text{C}_{\text{CO}_2}$ with reference to the Vienna Pee Dee Belemnite standard (‰ VPDB). Analytical precision is $\pm 0.1\%$.

2.3 Continuous Monitoring

A permanent 1.3-m depth borehole was implemented for continuous gas phase monitoring. It was located 80 m to the East of the V.Mo.2 well, but still within the plant's protected area. The soil was reworked during the plant's construction and is now grassland with 5- to 10-m-high trees (false acacias and poplars). This soil shows a high biological activity (significant population of earthworms) and is clay-rich (swelling behaviour during rainy periods).

The well completion (Fig. 6), manufactured and established by the *Solexperts Company*, is made of porous ceramics that protects a temperature sensor and two gas lines. The diameter of the ceramics is slightly lower than the diameter of the borehole, creating an open space dedicated to gas collection. An inflatable packer is emplaced on the top of the completion, in order to isolate the gas collection volume from the atmosphere. The water pressure into the packer is constant and fixed at 4 bars. The temperature of the borehole is recorded with the same time step as the IR spectra.

This completion is linked to a gas circulation system equipped with a pump and several stainless steel sampling cells (100 mL each). At 1 m depth, the soil air is pumped at 20 mL/min and reaches the IR gas cell prior to being re-injected into the borehole. The gas inflow is located 30 cm above the bottom of the completion in order to avoid water income. The IR gas cell consists of a multipass[®] Bruker cell with an IR beam length varying from 0.25 to 1 m. The gas cell and the Fourier Transform Infrared (FTIR) spectrometer are equipped with CaF₂ windows in order to avoid alteration by humidity. The Bruker[®] Tensor spectrometer is composed of one interferometer, one IR source and two compartments with two DTGS detectors. One compartment is dedicated to the analysis of borehole gas and the other allows open path recording of the atmospheric gases, 0.7 m above the soil surface. Spectra are recorded between 5500 and 900 cm⁻¹ for one minute (20 scans) with a spectral resolution of 2 cm⁻¹. A spectrum of natural gas from the CO₂ Montmiral reservoir is also recorded after collection in the gas cell from the V.Mo.2 well. Temperature and gas pressure in the gas cell are also recorded.

Gas concentrations were calibrated at the laboratory from several known gas mixtures at various CO₂ partial pressures and bulk gas pressures. Calculation of CO₂ concentrations were calibrated from the stretching ν_3 vibration centred at 2350 cm⁻¹ for concentrations lower than 0.5%, from the combination band ($2\nu_2 + \nu_3$) centred at 3609 cm⁻¹ for concentrations between 0.5 and 35% and from the combination band ($\nu_1 + 2\nu_2 + \nu_3$) centred at 4984 cm⁻¹ for concentrations between 0.7 and 100%. Spectra of soil gases and of the atmosphere were successively recorded each hour and stored in the hard disk of the computer. Area integrations and procedures of recording were developed using[®] OPUS software from Bruker.

The spectrometer was emplaced in a garden shelter in the vicinity of the borehole, to be protected from atmospheric perturbations (wind, rainfalls, etc.). The continuous records presented here extend from April the 5th and May the 15th of 2007. Rainfalls were registered on-site the week before the recording started, between April the 26th and May the 5th, and on May the 15th (Fig. 2).

3 RESULTS AND DISCUSSION

3.1 Vicinity of the CO₂ Reservoir

3.1.1 Produced Gas Phase

In 2006 the exploited gas at the Montmiral plant was sampled at the producing wellhead (V.Mo.2). Gas chromatography analysis reveals a high CO₂ content (91.9%), and significant amounts of CH₄ (1.14%) and noble gases (Ar: 0.06%; He: 0.054%), the rest being essentially nitrogen (5.11%) and oxygen (1.03%) with hydrocarbon traces (C₂ to C₆). Nevertheless, this analysis suggests some differences to those performed by Pauwels *et al.* (2007), that showed a greater CO₂ enrichment (97.2%), together with non-negligible N₂ content (0.76 to 1%). As pointed out by those authors, such variations may be linked to changes in the exploitation conditions, or to the horizons of the reservoir that are under production. If those slight changes in the gas production could explain some amount variations, they are not thought to impact other chemical parameters. Among them, the carbon isotope ratio of the CO₂ phase should remain nearly the same, as the CO₂ always comes from the same reservoir in depth. This was indeed the case with the 2006 sample: the carbon isotope ratio is at -2.6‰ VPDB, in good agreement with the 3 analyses performed earlier by Pauwels *et al.*, 2007 (-2.7‰ VPDB). Moreover, additional isotope measurements performed on helium and neon all suggest a deep origin with a consequent mantle contribution, as noticed earlier (*e.g.* Blavoux and Dazy, 1990; Pearce *et al.*, 2003). The high content of radiogenic helium measured in this gas phase also suggests a non-negligible amount of ⁴He originating from ²³⁸U, ²³⁵U and ²³²Th crustal disintegration.

3.1.2 Spot Sampling and Flux Measurements

In the protected area surrounding the V.Mo.2 well, soil gas mapping was undertaken in June 2006 and repeated in April 2007. The soil gas analyses give very similar results from one year to another. In 2006, CO₂ concentrations range between close to atmospheric values (0.08%) and about 2.16%, associated with ²²²Rn activities from 11 to 6620 Bq/m⁻³, with respective mean values of 0.6% and 1,675 Bq/m⁻³ (28 measurements). In 2007, ²²²Rn activities range between 0 and 37860 Bq/m⁻³ and CO₂ concentrations between 0.03 and 6.82%. The associated mean values are, respectively, 3670 Bq/m⁻³ and 1.03% (59 measurements). This slight increase in radon and CO₂ mean values between 2006 and 2007 is linked to the spatial distribution of the measurements, as more data were acquired in 2007 in the Eastern part of the Montmiral plant, where maximum values are recorded. The influence of the seasonal cycle is not thought to be of primary importance, as measurements were performed during the growing season in both years (Riding and Rochelle, 2009). This spatial arrangement is depicted in Figure 7, that corresponds to the

mathematical interpolation of 2006 and 2007 results, based on a krigging approach. As the Eastern part of the site has a better spatial definition than the others, partly related to less human reworking and buildings, caution must be taken when interpreting contour plots. Nevertheless, a possible “high values” alignment could exist around N40°E to N60°E, compatible with directions inferred from structural analysis (*see Sect. 1.1*). Moreover, the immediate vicinity of the V.Mo.2 well appears to be a non-emissive area, CO₂ concentrations and radon activities being less than 2% and 5000 Bq/m⁻³, respectively.

This spatial arrangement of CO₂ concentrations is also depicted when dealing with fluxes (*Fig. 8*). Both in 2006 and in 2007, the Eastern part of the site is more emissive, fluxes reaching 40 to 50 cm³/min/m², whereas the V.Mo.2 surroundings are characterised by lower values from 0 to 15 cm³/min/m², most of the measurements plotting under the natural background (ca. 3 cm³/min/m²). As mentioned in Figure 8, the vicinity of the V.Mo.2 well is covered by a concrete pavement. To obtain comparable data, the same measurement device was used within this area, measurements being focused on fractures and cracks affecting the concrete. The contact area between the flux chamber and the concrete was cautiously covered with adhesive tape material, in order to produce an accumulation effect within the chamber. Such a procedure should have allowed one, if relevant, to notice leakage directly resulting from V.Mo.2 well completion. As no such CO₂ flux was observed at the surface, then there is no noticeable well leakage or leakages originating from horizons between the deep reservoir and the surface. The more elevated flux measurements correspond to grass area measurements not covered with concrete.

Figure 9 shows the flux measurement evolution when the distance increases from the V.Mo.2 well. Measurements made far from the V.Mo.2 borehole area (*i.e.* at a distance of ca. 150 m in the SE direction - *see Fig. 7*) show the more elevated fluxes. Indeed, the recorded values in the eastern part of the plant area reached 40 to 50 cm³/min⁻¹/m⁻² in 2006. This more emissive zone was investigated in more detail in 2007 (*Fig. 8, 9*). All the flux measurements plot far above the mean natural background, thought to range between 3 and 4 cm³/min⁻¹/m⁻² (Jones *et al.*, 2005; Von Arnold *et al.*, 2005). As a consequence, this increase could not only be explained by the natural background, and further investigations are needed to fully understand the processes that lead to such an enrichment.

The spatial arrangement highlighted by CO₂ fluxes also exists when dealing with CO₂ concentration and radon activity measurements (*Fig. 7*). This is also suggested by *in situ* (*Fig. 10*) and laboratory chromatography measurements, where no significant leakages from the V.Mo.2 well are noticed. Maximum CH₄ amounts are very low (0.006%) and far from the content of the produced gas (1.4 to 1.8%; Pearce

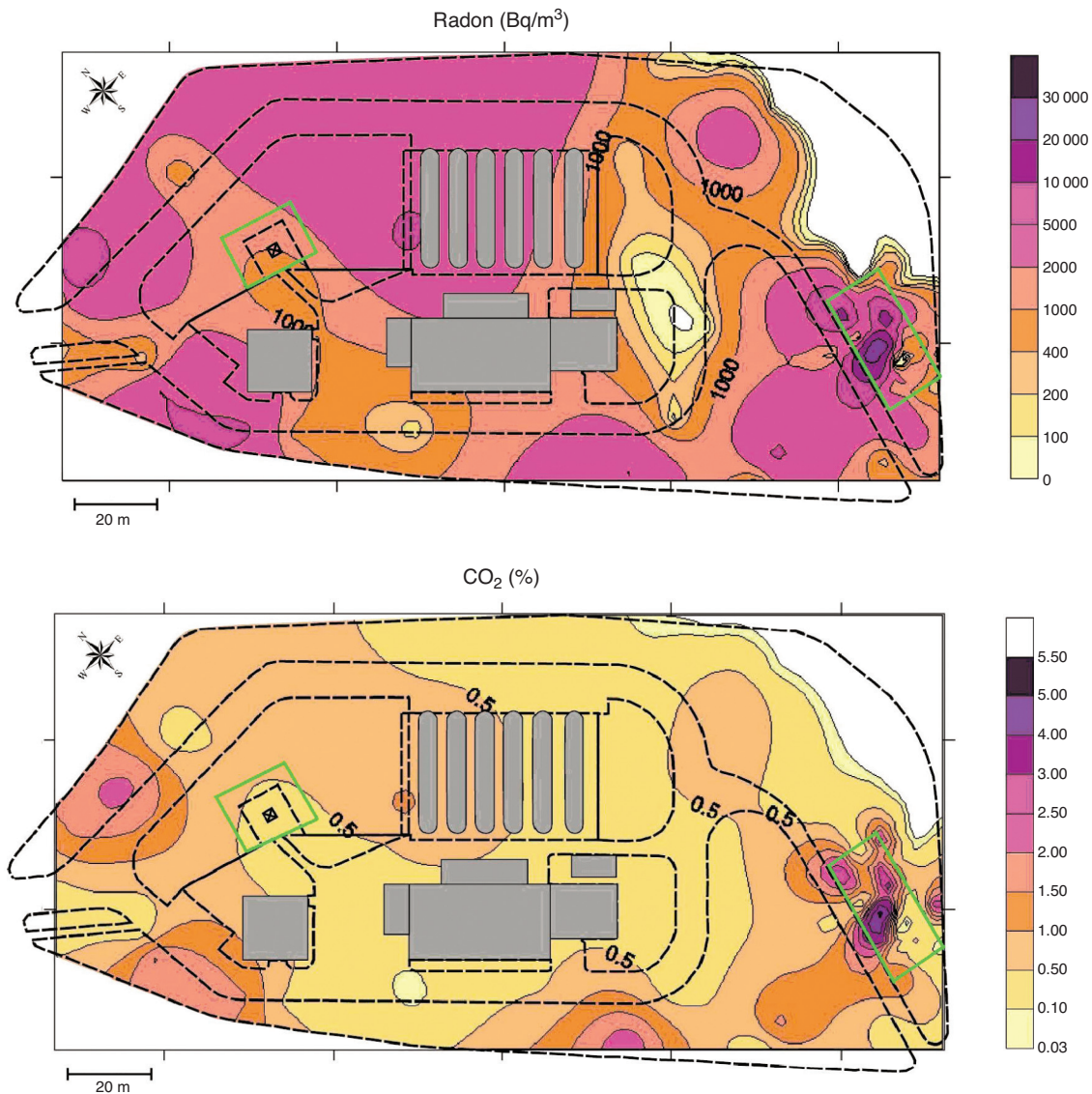


Figure 7

Interpolation (kriging method) of radon (top) and CO₂ (bottom) soil gas measurements around the Montmiral plant. Green squares represent areas of flux measurements depicted in Figure 8 (left one: vicinity of V.Mo.2 well; right one: vicinity of small borehole equipped with a completion).

et al., 2003) and can thus be related to methanotrophic processes within the soil. Helium contents follow the same behaviour: micro-chromatography and spectrometric measurements range between 5.16 and 5.3 ppm, the mean value being close to the atmospheric one (5.23 ppm; 59 measurements). Only one helium value plots out of this range, but showing a negative anomaly (4.98 ppm) and thus once again not linked to the reservoir content (0.0324 to 0.072%; Pearce *et al.*, 2003). As a consequence, helium measurements suggest the absence of caprock imperfections (Heath *et al.*, 2009).

3.1.3 Continuous Recording

Figure 11 shows representative FT-IR spectra recorded in the same analytical conditions (the same gas cell with the same spectral resolution) on the gases at Montmiral from three different environments: gas from the atmosphere, gas from the CO₂ geological reservoir and gas from the soil at 1.3 m depth. These spectra point out specific characteristics for each compartment:

- the gas from the air is water vapour-rich, and shows the presence of CO₂ and sometimes of CO due to the plant activity;

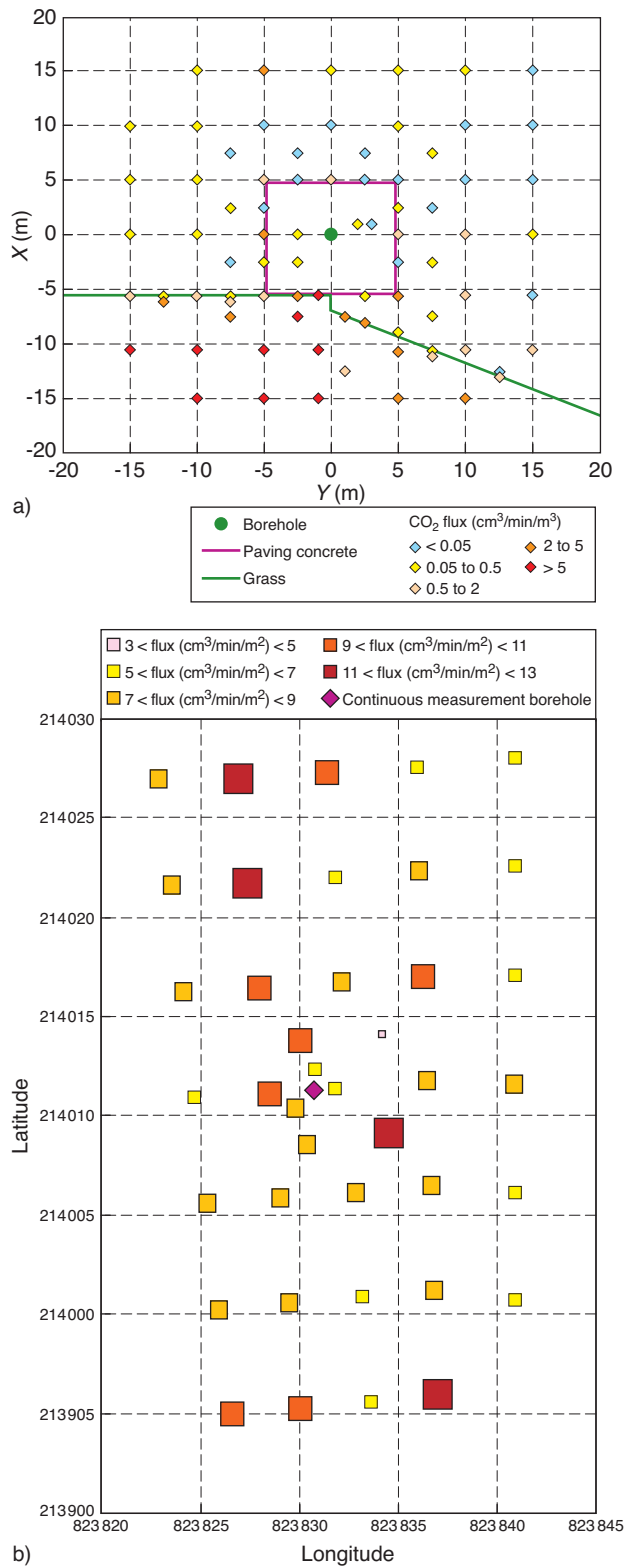


Figure 8

Top: flux measurements carried out in 2006 close to borehole V.Mo.2 (metric scale); Bottom: flux measurements carried out in April 2007 on the eastern part of the site (vicinity of small borehole equipped with a completion). Location of sampling areas is indicated in Figure 7.

- the gas from the CO₂ geological reservoir is dominated by the presence of CO₂ and shows a weak CH₄ contribution, no water vapour being detected;
- the gas from the soil is CO₂-rich and water vapour-rich, with no CH₄ trace.

The recorded 2006 CO₂ concentrations within the soil failed to give exploitable results, as the performance and use of such complex methodologies require step by step developing and testing. Nevertheless, the data acquired in 2007 are fully exploitable and highlight great variations in the CO₂ content at 1.3 m depth. Diurnal changes are well recorded, as well as sudden variations in the atmospheric compartment (Fig. 12). Indeed, CO₂ concentrations vary from 350 ppm to 1,600 ppm in this atmospheric compartment. Daily variations, from 400 to 700 ppm (mean ca. 500 ppm) are essentially due to biological activity controlled by plant respiration and photosynthesis. The minimum CO₂ concentration is recorded at around 5:00 am and the maximum twelve hours later (around 5:00 pm). The maximum of the morning/afternoon fluctuations is observed at the beginning of April and the minimum at the beginning of May. These fluctuations are probably linked to the variation in the photosynthesis intensity. In the atmosphere, some sharp peaks in the CO₂ concentration record are noticed for very short periods (less than one hour; Fig. 12). These sudden increases appear to be well linked to CO₂ discharge within the atmosphere caused by the plant activity. Considering the soil compartment, variations in CO₂ concentrations range from 1 to 9% during the investigated period. Maximum values are reached during spring (April) and minimum ones during summer (July). For the April-May 2007 period (Fig. 12) CO₂ concentrations vary from 3 to 8%.

Soil CO₂ concentrations monitored within the dedicated borehole (the Eastern part of the plant area) experience a series of charges and discharges which are probably linked to the soil water saturation state. When the soil is saturated by rainfall, its porosity is filled by water and therefore the CO₂ coming from a deeper source tends to accumulate below the saturated layer. In contrast, when the soil is dry, the porosity is more likely open to the atmosphere and the previously accumulated CO₂ can be released to the atmosphere. Such behaviour is an interesting parameter to model, but remains a challenging task as it involves several unknown parameters such as soil properties (porosity, permeability and heterogeneity) as well as time-dependent data (rainfall and sunshine exposure of the site, which control the saturation state of the soil). In addition, the recorded soil concentration shows daily fluctuations which can be linked either to the daily atmospheric CO₂ concentration fluctuations or to the biological activity of the soil.

Nevertheless, the exponential-like trends of the recorded concentration suggest that the dominant mechanisms of mass

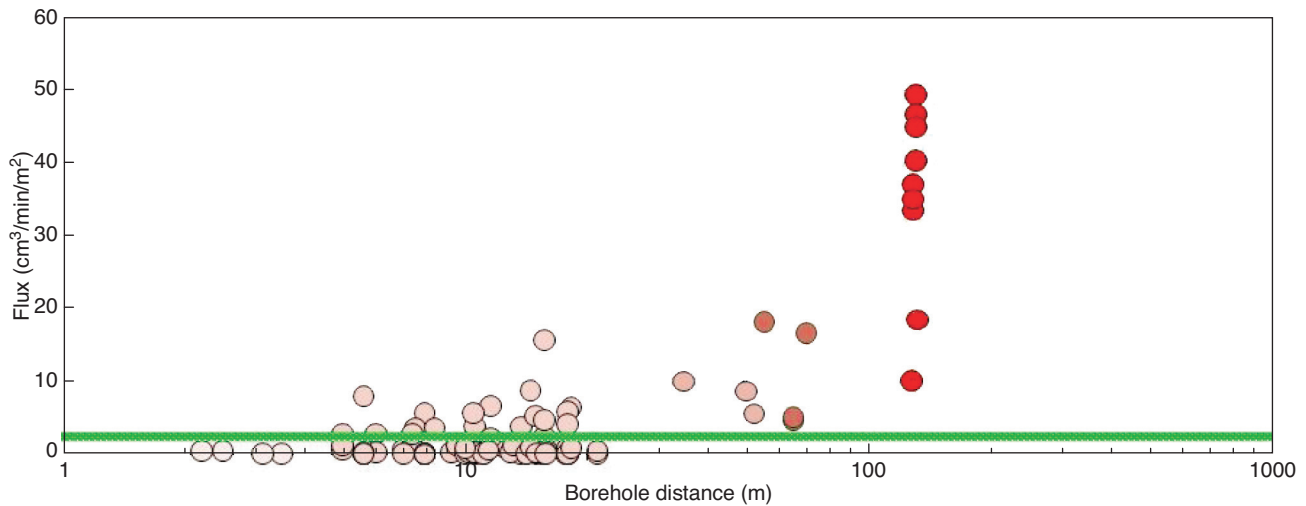


Figure 9

Evolution of CO₂ fluxes as a function of the borehole distance (V.Mo.2 well) expressed on a logarithmic scale. The three colours used (brown, dark brown and red) represent the following distance ranges: 0 to 50 m; 50 to 100 m and larger than 100 m. The green line represents maximal natural CO₂ flux (extracted from bibliographic data).

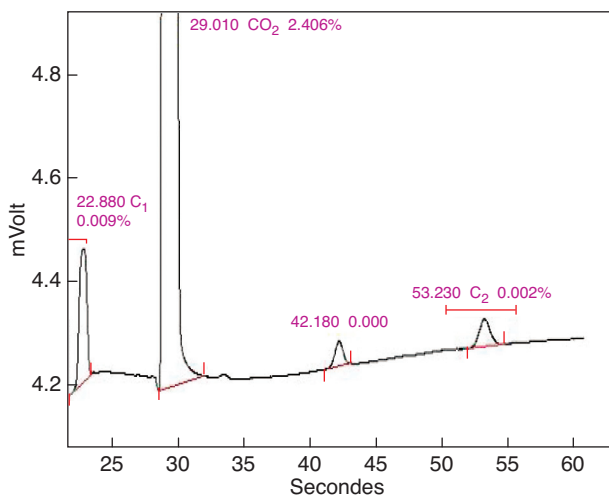


Figure 10

Example of micro-gas chromatography plot with the soil probe equipped with a packer: small methane and ethane amounts are detected (lower than 100 ppm).

transfer can be described by a simplified mass balance approach (cf. Battani *et al.*, 2009) which leads to the following equation:

$$C(t) = C_f + (C_o - C_f) \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where C is the measured concentration, C_f the final concentration, C_o the initial concentration, t the time and τ a time constant characteristic of the speed of the charge/discharge process.

The result of this modelling is shown in Figure 12 for the first 30 days of recording. A charge phase appears to be the dominant process during the first 15 days. During this phase, the soil appears to be poorly connected to the atmosphere, allowing a CO₂ concentration increase. For this first phase the following parameters are obtained:

$$C_o = 38400 \text{ ppm} \quad C_f = 79500 \text{ ppm} \quad \tau = 2.2 \text{ days}$$

Afterwards a discharge phase is observed, suggesting that the soil becomes dry, allowing the release to the atmosphere of the accumulated CO₂. For this phase the following parameters are obtained:

$$C_o = 79500 \text{ ppm} \quad C_f = 38400 \text{ ppm} \quad \tau = 5 \text{ days}$$

For this second phase, the time constant is more than two times higher than that of the first phase. This suggests that the CO₂ circulated more slowly from the soil to the atmosphere than from deeper horizons to the soil. One important parameter could be connectivity, which seems to be higher during the first phase than during the second one. Moreover, it is worth noting that modelled initial and final concentrations are compatible with the ones measured by soil gas sampling in the vicinity of the 1.3-m depth borehole. Lastly, similar observations (soil drying / permeability increase / greater diffusion) have been made at Weyburn, but on the CH₄ phase (Riding and Rochelle, 2009).

Unfortunately, there are not enough data available to fully characterise these processes and to suggest accurate

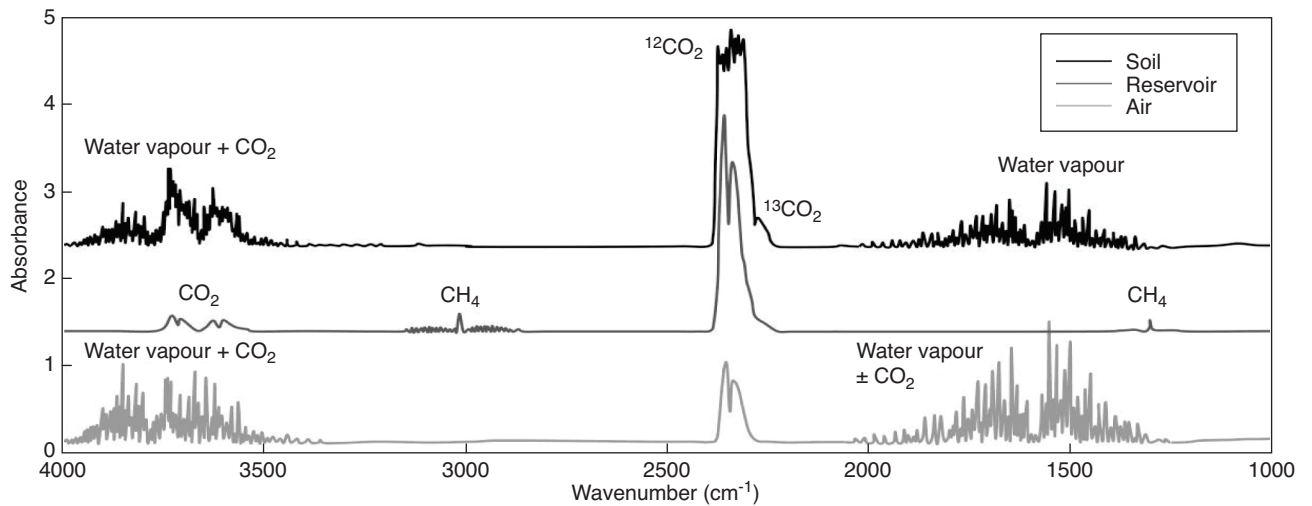


Figure 11

FT-IR spectra of the three investigated systems (soil gas, deep gas reservoir, free atmosphere) showing the presence of CO₂ and water vapour in the soil and in the air, and CO₂ and CH₄ in the gas reservoir.

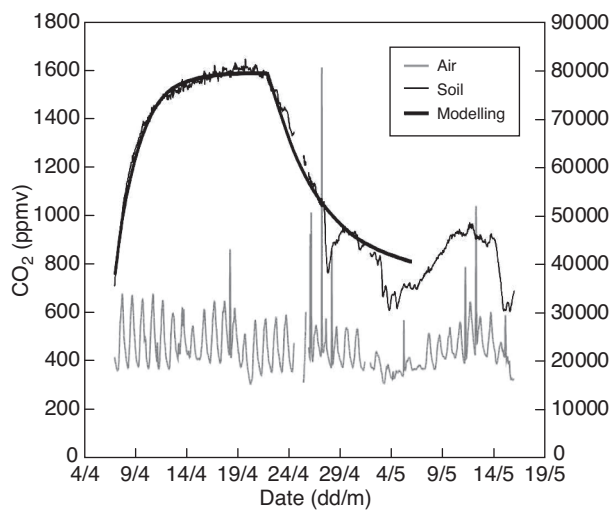


Figure 12

Evolution of the CO₂ content of the free atmosphere at 70 cm above the surface (grey curve) and of the soil gas atmosphere at 1.30 m depth (black curve) from April the 5th to May the 15th of 2007. A modelling curve has been superimposed on the evolution of the concentration of CO₂ (see text for explanations).

explanations for these discrepancies. Moreover, soil concentration shows strong fluctuations between April the 28th and May the 4th that are difficult to explain. Therefore, no further modelling was carried out beyond this period. Nevertheless, even the results of such simplistic modelling (Eq. 1) are useful, as they suggest a way to improve future work for such concentration recordings. Indeed, this modelling has highlighted the need to also monitor the soil

water saturation. This parameter thus appears to be another key one that could be very helpful in order to quantify and validate connectivity assumptions. Extended soil physical characterisation (porosity, texture, composition, etc.) and in situ real-time meteorological monitoring (wind speed, soil humidity, etc.) could also provide useful additional information (e.g. Lewicki *et al.*, 2003; Beaubien *et al.*, 2008).

3.1.4 Comparison of the Methods

Concerning only the CO₂ phase, three kinds of information come from the performed measurements. Two investigating methods were used to characterise the Montmiral plant area, by defining CO₂ fluxes and concentrations. Once these were done, additional CO₂ concentration measurements were performed on a continuous basis using a dedicated borehole. The information provided by those methods is fully complementary, but should not be considered as a unique dataset, rather as various inputs helping to understand soil gas migration and emanation processes better. Indeed, it remains difficult to crosscut and correlate flux measurements made at the soil surface and concentration measurements performed at depth, since these last measurements were precisely undertaken at a depth where atmospheric influence is very low. For example (Fig. 7-9), fluxes can reach 5 cm³/min⁻¹/m² in the grassland surrounding the V.Mo.2 well, which is quite an elevated value (Jones *et al.*, 2005; Von Arnold *et al.*, 2005). In the same area CO₂ concentrations only reach 1%, which is quite a low value for spring measurements under a temperate climate. However, both methods infer that no leakage is noticeable around the V.Mo.2 wellhead. On the whole Montmiral plant scale, a different situation exists. Both spot flux and concentration measurements rise to more

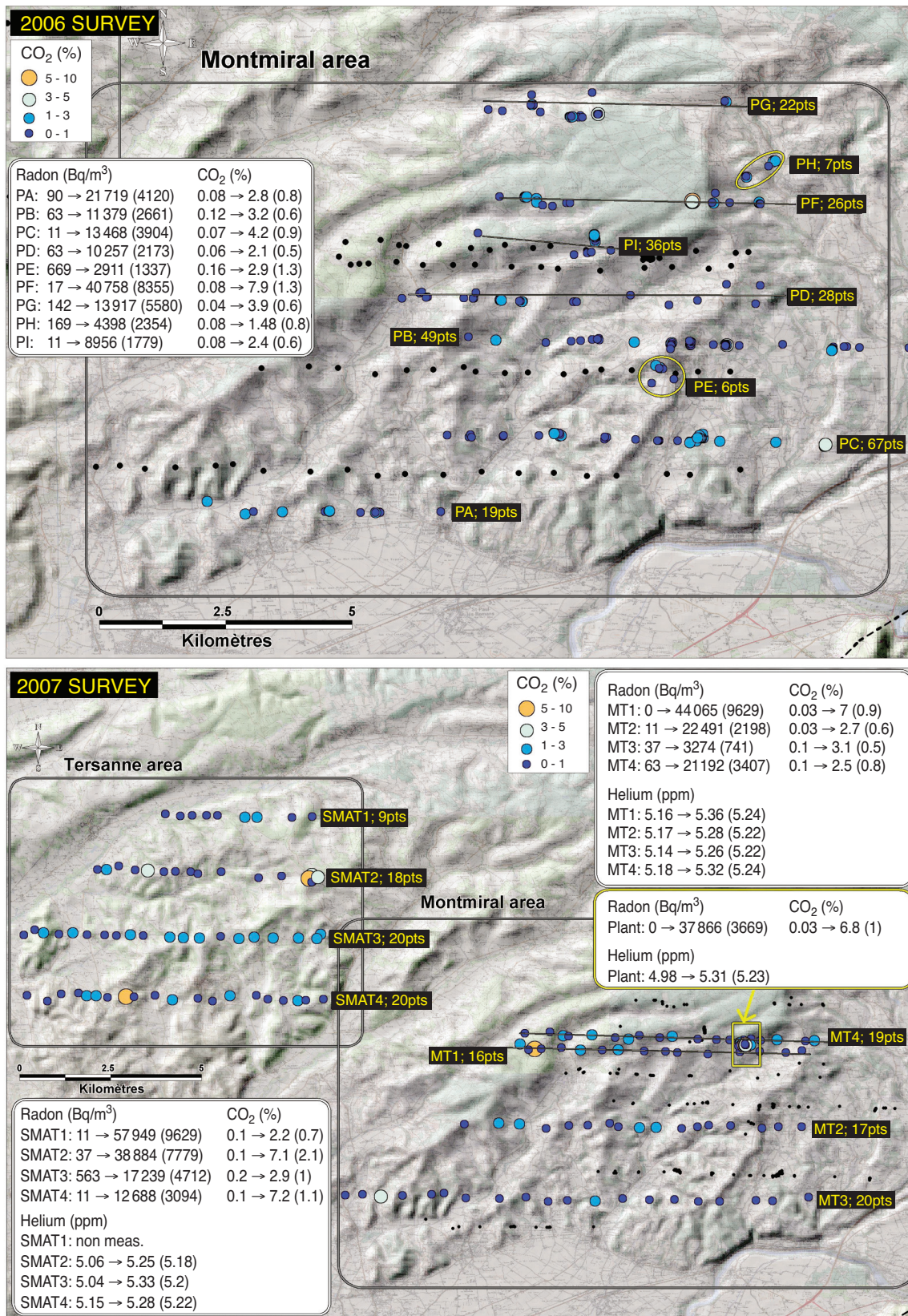


Figure 13

Soil gas concentration results: 2006 (top) and 2007 (bottom). Variation range for CO₂ (%), helium (ppm) concentrations and radon activities (Bq/m³) are indicated for each profile, as well as mean values (between brackets). Background cartographic maps are from IGN (1/25 000th scale).

elevated values (up to 50 cm³/min⁻¹/m² and 5.5%, respectively), which are confirmed by long-term monitoring using FT-IR spectrometry (soil CO₂ content varying between 3 and 8%). Moreover, both methods highlight a “more emissive, more rich” CO₂ zone, whose direction cannot be defined precisely due to an insufficient number of data.

Nevertheless, this area does not appear to be an anomalous zone with CO₂ coming from depth, as suggested by carbon isotope data (*see Sect. 3.2*). Considering all the acquired data in this small perimeter, it is therefore difficult to define values or levels that should be considered as anomalous ones. In totally different geological contexts, Beaubien *et al.* (2008) and Möller *et al.* (2008) come to similar conclusions, highlighting the great spatial variability in fluxes and soil gas concentrations, on scales of less than 5 m spacing, which is the grid spacing used at Montmiral. Measurements should thus be considered as a dataset acquired under similar meteorological conditions, that give similar spatial distribution between 2006 and 2007, but whose levels can significantly vary during the year due to several parameters (biological activity, rainfalls, wind, etc.). Extrapolating to surveys of carbon dioxide underground storage sites, this implies a very good spatial definition of the monitored points and the conjoint use of both spot and continuous monitoring methods.

3.2 Gas in the Montmiral and Tersanne Areas

The Montmiral perimeter was investigated both in 2006 and 2007, whereas the Tersanne area was only monitored in spring 2007 (*Fig. 1*). In those two zones, soil CO₂ concentrations range from close to atmospheric values up to 7.2-7.9% (*Fig. 13*). Mean content appears to be greater at Tersanne than at Montmiral (1 vs 0.8%), and the spatial distribution of maximum values does not reflect known tectonic structures. Radon activities show the same arrangement, higher at Tersanne than at Montmiral (ca. 3940 vs 3510 Bq/m³), extreme values ranging between 11-0 and 40760-57950 Bq/m³ in 2006 and 2007, respectively.

On all geographic scales, there is a good correlation between soil CO₂ content and radon activities in soils (Pearson's coefficient: 0.734), but greater contents do not appear to be related to geological structures. There is also an anti-correlation between CO₂ and O₂ contents (Pearson's coefficient: -0.857), suggesting that carbon dioxide enrichment is directly linked to a decrease in the oxygen content via reactions in which oxygen is consumed, and subsequently suggesting that the CO₂ is mainly of biogenic origin (*e.g.* Beaubien *et al.*, 2008; Riding and Rochelle, 2009).

Contrary to areas belonging to the French carbo-gaseous province where helium leakages do occur (Annunziatellis *et al.*, 2008; Battani *et al.*, in this volume), neither significant

helium anomalies nor methane ones were highlighted. Mass spectrometric helium measurements range between 5.04 and 5.36 ppm, with a mean at 5.21 ppm, close to atmospheric content (5.24 ppm). More precisely, near Tersanne, where non-permanent methane underground storage is carried out, soil methane content is less than 10 ppm (accuracy of infrared detectors) and mean helium content is slightly lower at 5.2 ppm. As a consequence, neither the Montmiral nor Tersanne areas appear to experience significant CH₄ leakages, even though the CH₄ content in the reservoir can reach 1.6 to 1.8% (Pauwels *et al.*, 2007). The same observation can be made for helium contents, ranging between 320 and 420 ppm within the reservoir. No leakage can be evidenced either in the V.Mo.2 well vicinity or on a greater geographic scale regarding CH₄ and helium contents.

To help refine these observations, flux measurements were made in 2007 on a kilometric scale around the V.Mo.2 well (*Fig. 14*). CO₂ fluxes range between 2 and 20 cm³/min/m². Only two measurements are under the limit of the biological background. A large part of the fluxes measured cannot be only linked to biosphere activity, as they fall within the background values defined, for example, in the Latera district (0 to 60 g/m²/day), which is known to be an emissive area (Annunziatellis *et al.*, 2008). Measurements performed along profiles (*Fig. 14*) only show a group of dots with no correlation with the geological structures or borehole position. A similar trend with no relation to known structures was already shown by the measurements made in the vicinity of the V.Mo.2 well.

As previously mentioned, the comparison between flux measurements and soil gas contents is difficult to undertake, as soil lithology, humidity, porosity, plant activity, etc. greatly influence emanation of CO₂ from 1 m depth to the surface. As a consequence (*Fig. 13 and 14*), measurements performed at the same time along the same profile and at the same location can give scattered results, even if low CO₂ concentrations often correspond to low fluxes between the soil and the atmosphere. Along profiles MT1 (13 measurements) and MT4 (15 measurements), Pearson's coefficients do not show any correlation between these two datasets (-0.119 and 0.056, respectively). On the contrary, along the profile MT3, a slight correlation is noticeable (Pearson's coefficient: 0.612), but this could also be due to a smaller number of measurements (only 7).

The measured fluxes cannot only be explained by CO₂ fluxes coming from biological activity, typically reaching a maximum of 13 to 16 g/m²/day over temperate grasslands and croplands (Lewicki *et al.*, 2003). Indeed, some of those fluxes and CO₂ concentrations and fluxes remain high regarding mean levels inferred from other studies. Annunziatellis *et al.* (2008) give a mean CO₂ amount in Italy of 1.93%, with a median value of 0.83% based on more than 16000 data, including a lot of work performed around or within active areas. The median value for fluxes in the Latera

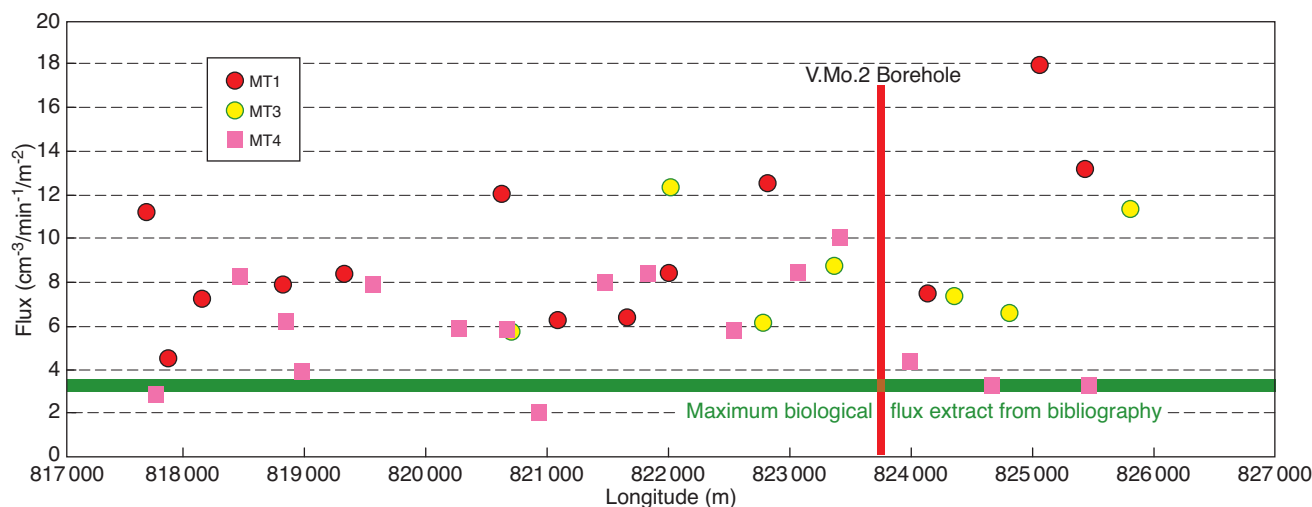


Figure 14

Projection on the same axis of flux measurements made along profiles MT1, MT2 and MT3 (see Fig. 13 for profiles' location). Geographical position of the borehole is indicated by the red line (longitude reported in metric scale under Lambert II projection).

district is close to 5 g/m²/day (Annunziatellis *et al.*, 2008) and between 6 and 21 g/m²/day near the Stromboli volcano (Carapezza *et al.*, 2009), whereas the data acquired during this study range from 5.5 to 56 g/m²/day. Similar background noise values have been stated at less than 2% for CO₂ concentrations and less than 10 g/m²/day for CO₂ fluxes for the Latera district (Beaubien *et al.*, 2008). Associated with the San Andreas Fault, King *et al.* (1996) found CO₂ anomalies only reaching 5% associated with creeping segments. Associated radon activities were lower than those measured in the Montmiral – Tersanne area, less than 40000 Bq/m³. Nevertheless, as radon-222 is thought to mainly originate from near-surface processes, and as no mineralogical investigations were done during our surveys, it is difficult to assign a systematic anomalous character to those elevated activities. Moreover, during studies performed at Weyburn, repeated ²²²Rn measurements over many years have shown that in some cases radon can be originated in situ with very little to absence of transport (Riding and Rochelle, 2005, 2009).

In the above-mentioned areas, especially the Italian ones, the origin of the CO₂ can account for the participation of a deep CO₂ end-member, but here we have no evidence of the geological origin of this CO₂ flux excess. Based on these observations, some ¹³C_{CO2} data were therefore acquired. The carbon isotope ratio is known to be representative of the C origin, as it quickly fractionates and equilibrates fast. In 2007, 11 gas samples were taken in various localities, to reflect CO₂ (from 1.4 to 7.2‰) and radon-222 (from 6100 to 39000 Bq/m³) content and activity variations. Carbon stable isotope ratios range from -21.4‰ to -25.9‰ VPDB, the mean value being

-23.9‰. Mean δ¹³C is the same at Montmiral, whereas the Tersanne area appears slightly depleted (-24.3‰). In all occurrences, these data plot far from the isotopic composition of the exploited CO₂ phase (-2.6‰) and strongly suggest a probable organic origin resulting from the C₃ photosynthetic cycle. Mixing between a hypothetical highly depleted C pool and enriched CO₂ from the reservoir (*e.g.* Prinzhofer *et al.*, 1995) should be discarded, as no deep CO₂ leak is found near the V.Mo.2 well and no methane is found within the soil gas atmospheres. Moreover, depleted isotopic ratios are registered at locations where the soil atmosphere is enriched in CO₂, also suggesting a near-surface gas origin. Nevertheless, a slight uncertainty remains as such biogenic values can be found even near the San Andreas Fault system, where a mantle CO₂ flux is known to exist (Lewicki *et al.*, 2003).

As a consequence, such high CO₂ concentrations (7 to 8%) appear to be elevated, even though measurements were made during spring vegetation bloom. But at this time, all the acquired data do not show spatial trends clearly related to the structural sketch. Performing new data acquisition in winter months would certainly give indications, biological activity being less developed in winter than in spring and summer. Repeated measurements should also be made on a regular time basis, to define precisely diurnal variations in both CO₂ concentrations and fluxes. In the same way, rock analyses should be performed in order to quantify uranium and thorium contents. This would help to decipher between a shallow radon origin or a deeper one, migration thus being done along fractures. Lastly, additional information could also come from carbon isotope ratio measurements performed on the soil CO₂ flux component, as recent investigations suggest that such measurements can give

interesting results when applied in areas with various carbon end-members (Chiodini *et al.*, 2008).

CONCLUSION

The Tersanne – Montmiral area, delineated by tectonic structures, does not appear to experience noticeable deep degassing. On the other hand, CO₂ fluxes, CO₂ soil concentrations and soil radon activities could become significant. In the same way, the most elevated CO₂ fluxes cannot be only explained by the CO₂ produced by biological activity. These contradicting results have to be refined in the future, but highlight the need for performing multi-component baseline analyses and recording prior to establishing an underground CO₂ storage site, to constrain natural variations in soil gas atmosphere compositions better. Lastly, as already pointed out by Pauwels *et al.* (2007), geochemical analyses of local aquifers and rocks are as important as soil gas analyses to understand migration pathways of soil gases better, mainly radon and CO₂, and should therefore be developed when considering the study of underground CO₂ storage.

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