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CO₂ escapes in the Laacher See region, East Eifel, Germany: application of natural analogue onshore and offshore geochemical monitoring

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Abstract

Natural analogues studies have received growing interest during preceding years in a CCS perspective. There is a strong willing to deploy robust and reliable technologies to ensure the safety and integrity of CO₂ underground storages. Here we present a dataset acquired in the Eifel volcanic district, using geochemical monitoring methods focusing on both dissolved and gaseous species. Onshore and offshore monitoring (Lake Laacher See) were performed to depict spatial behaviour of CO₂ natural releases. Additional gaseous species, mainly helium and radon, were also monitored to better assess the shapes of gas vents, using methodologies that were learned from hydrological and tectonic applications. Lake water monitoring allowed the characterisation of the water body itself, in terms of lateral heterogeneities, to evaluate the impact of CO₂ deep degassing near the bottom of the lake. The use of a dedicated sensor for monitoring in situ CO₂ partial pressure did not provide more valuable information that was learned from more classical physico-chemical parameters. From those investigations, the usefulness of geochemical monitoring is still demonstrated, but the use of complementary approaches and methods is still needed to get a powerful set of techniques able to warn in case of leakages occurring from depth.

Keywords

Natural analogue monitoring
Soil gas
Dissolved gas
CO₂

1. Introduction

During last years, studies focussing on CO₂ sequestration have known growing interest as part of climate mitigation researches (Holloway et al., 2007; Wildenborg et al., 2009; Winthaegen et al., 2005). By them, studies dedicated to a better knowledge of natural analogues are of primary interest, as they focus either on sites where CO₂ is naturally stored at depth from many years (e.g. Gal et al., 2010; Holloway et al., 2007) or sites where underground gases migrate upwards (e.g. Battani et al.,
Researches performed on those analogues can bring useful information that have to be kept in mind when performing CO₂ sequestration in depleted oil/gas reservoirs or deep saline aquifers (Gale, 2004; Gapillou et al., 2009; Riding and Rochelle, 2005; Winthaegen et al., 2005).

Facing this perspective, several European nations have pooled their research efforts together through the Network of Excellence on Geological Storage of CO₂ “CO₂GeoNet”, under a 6th Framework Programme funded by the European Commission in 2004 (Czernichowski-Lauriol et al., 2009). Present work is part of the so-called Joint Research Activity Program “Monitoring Near Surface Leakage and its Impacts” (JRAP-18). Under this work package several methods were used, with special emphasize on soil/atmosphere gas monitoring with conventional and newly rapid surveying methods, microbiological impact studies and water column monitoring (Beaubien et al., 2008; Jones et al., 2009; Krüger et al., 2009). Here we present results acquired in 2007 and 2008 in the vicinity and within the water body of the Laacher See, a maar lake emplaced in Western Germany near Koblenz. The western shore of the lake was investigated using simple and robust methodologies in order to depict soil gas contents, whereas numerous in-situ / real-time loggings were performed in the lake itself. The goal of this work was to better understand migration pathways of gases – especially CO₂ – in a complex system (onshore unsaturated and saturated zone / offshore water mass), in order to assess the potential impact of CO₂ leaking from a deep seated storage into shallow regolith.

2. Site description

The Laacher See is a volcanic structure emplaced in the still uplifting Palaeozoic Rhenish Massif at 12,900 ± 560 yr. Before Present (Giggenbach et al., 1991; van der Bogaard, 1995) and forms part of the East Eifel volcanic district. Intra-plate alkali-basaltic lavas were produced within the upper mantle (Eifel plume), where partial melting enriched the lavas in gaseous species such as CO₂. During their rise up to the surface gases were partly released either in the lower crust or along faults and fractures in the upper crust. As the Palaeozoic basement was affected by NE-SW Variscan tectonics, the Pleistocene volcanic activity lead to the merge of numerous mineral waters in this area (van der Bogaard, 1995). Noble gases and carbon isotope ratios highlight a dominant mantle origin for the gases associated with mineral waters (Griesshaber et al., 1992).
As a result of volcanic activity, some maars are nowadays emplaced within the Eifel district. By them, the Laacher See represents a crater filled with water to form a 2.5 x 1.8 km – 3.31 km² area, 52 m maximum depth lake that covers 27% of its drainage area (Aeschbach-Hertig et al., 1996; Giggenbach et al., 1991). Lake water level has varied during historic times as a result of human reworks in the 12th century (lowering of 10 m of the water level) and in the 19th century (extra 5 m lowering).

Lake Laacher See has been studied for many years either by academics or local water authorities as it is part of an environmental protected area. The water body itself is presently classified as mesotrophic to eutrophic one, and experiences at least once a year a complete seasonal overturn (holomitic character). Contrary to other lakes set in similar geological context, such as Lake Pavin in France, Lake Laacher See probably did never have a meromictic character due to its hollow coefficient. Water is of hard type and several discharges of gases – mainly CO₂ of mantle origin (Aeschbach-Hertig et al., 1996; Griesshaber et al., 1992) – along the eastern shore are known, either within the water column (up to 99% CO₂ in the gaseous phase; Griesshaber et al., 1992) or in soils (up to 10% vol.; Langer, 1988). An annual release of about 5000 tons of CO₂ has been calculated by Aeschbach-Hertig et al. (1996). Sedimentation within the lake is a function of the water chemical state, varying from carbonate facies from 0 to 20-30 m depth, then clastic facies and last organic-rich clay facies in deeper parts (Bahrig, 1985).

As a result of human activities, some fields and pastures are emplaced along the western and southern shores of the lake. Especially along the western part some gas vents (mofettes) are emplaced, which were studied during the 2007 survey, whereas lake water characterization was performed during the 2008 survey (figure 1). During the 2007 survey soil gas studies were focussed in a meadow were rapid surveying methods using laser mounted on quad bike have highlighted the occurrence of CO₂ gas vents of limited extension (Jones et al., 2009). A second soil gas site, Obermendig, was also surveyed, located 5 km SW from the centre of the lake. In this site a carbogaseous spring merges (Erlenbrunnen spring), which is thought to have similar gaseous content than other springs emplaced in the Laacher See region, i.e. a dominant CO₂ phase, δ^{13}C ratios between -3 and -5‰ VDPB (Vienna Pee Dee Belemnite), low pH values, high conductivities and low redox potentials. The 2008 survey was dedicated to water logging using multi-parameter CTD (Conductivity – Temperature – Depth) probe, together with water and dissolved gases recovered from the lake.
3. Methodology

3.1 Soil gas analyses
As reported elsewhere (e.g. Battani et al., 2010; Gal et al., 2010), there is a wide set of surveying methods that could be deployed when studying natural analogues. Here we tried to deploy robust methods in order to get reliable results that would help to interpret data acquired with more recent devices. For the 2007 soil gas survey, quantifications of CO₂, O₂, CH₄, and ⁴He contents were made, as well as measurements of ²²²Rn activities. At given locations samples for further laboratory analysis (δ¹³C CO₂ isotope ratio determinations and gas chromatography measurements) were also taken in evacuated glass bulbs.

Determination of soil gas species were done in the field with portable InfraRed Gas Analysers (IRGA). LFG20 (ADC Gas Analysis Ltd.) and GA2000 (Geotechnical Instruments Ltd.) gas analysers allow to determine CO₂, CH₄ and O₂ concentrations. For LFG20, detection limit is 0.05% and precisions for CO₂ and CH₄ between 0 and 10% are ± 0.5%. For GA2000, the precisions are the same between 0 and 5%, rising up to ± 1% for CO₂ and CH₄ between 5 and 15%. Calibrations of IRGA were done at
laboratory and verified on site by using CO$_2$ labelled bottles (from 0.05 to 100% CO$_2$). Sampling was
done after drilling a small hole within the soil (c.a. 1 m depth, 1 cm in diameter) using a battery
powered drill and inserting a copper tube in the hole. Particular attention was given to properly seal
the copper tube, to avoid leakages and soil atmosphere contamination by atmospheric components.
Moreover sampling soil gas at such a depth considerably lowers risks of sampling gas that could have
interact with gas of atmospheric origin. Internal calibration of this sampling method has been done at
BRGM (Bureau de Recherches Géologiques et Minières, Orléans, France), reproducibility and results
being equivalent to those recorded using stainless steel probes progressively lowered down into the
soil by hand-hammer percussion. The copper tube was then connected to the IRGA and pumping
done at low flow rate (200 ml.min$^{-1}$). Equilibration of the gas flux occurred within one or two minutes,
the time needed to purge all the flexible pipes and then values were registered. Subsequently, two
other samples were taken for further analysis. For helium abundance measurements, a Tedlar bag
was connected at the exit connection of the IRGA, filled and rinsed prior getting a sample. Last, for
radon activity determinations, a vacuumed scintillating flask was filled by soil gas (c.a. 200 ml, internal
ZnS coating, Algade, France).
Helium ($^4$He) measurements were performed twice a day, using a modified Alcatel leaking mass
spectrometer (Adixen ASM102S). Values were 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
ppm $^4$He. Helium measurements were done on a half day basis, samples being analysed less than 4
hours after their collection. The linearity of the spectrometer in the 0.1 – 100 ppm range was checked
each time by circulating a 100 ppm reference gas.
Radon measurements ($^{222}$Rn) were done by alpha particles counting (Calen photomultiplier, Algade)
and expressed as activity data (Bq/m$^3$). Alpha photomultiplier background noise was less than 0.2
counts per hour. Counting was done during 180 seconds, stated reproducibility being better than
0.1%.
If relevant, additional samples were taken in vacuumed glass bulbs for laboratory gaseous
chromatography measurements (Varian 3400 gas chromatograph) and further isotope ratio
determination by mass spectrometry (Thermo Finnigan Delta S). Gas chromatography was used to
determine the proportions of the following gases: CO$_2$, Ar, O$_2$, N$_2$, CO, He, H$_2$, H$_2$S, C$_n$H$_{2n+2}$ (n = 1 to
6). Detection limits are ± 0.0002% for C$_n$H$_{2n+2}$, ± 0.001% for Ar, N$_2$, CO$_2$, O$_2$ and ± 0.005% for H$_2$ and
H$_2$S. As for the IRGA determination, percentages refer to volume ones. CO$_2$ isotopic measurements were done on a vacuum purified gas phase after freezing, to get a pure CO$_2$ fraction. This fraction was then analysed by classical dual inlet mass spectrometer. Stable carbon isotope ratio is expressed as $\delta^{13}C_{CO_2}$ with reference to the Vienna Pee Dee Belemnite standard (‰ VPDB). Analytical precision is ± 0.1‰.

3.2 Lake and mineral waters

The Laacher See water mass was investigated in June 2008 in order to characterise the water column and its chemical composition. Water logging was undertaken along an Eastern-Western transect, with some additional data acquisition near the eastern shore where CO$_2$ escapes were present. Continuous vertical profiling was augmented by *in-situ* spot sampling for chemical and gaseous determinands. Logging was performed using an Idronaut probe (Idro316Plus) recording the following parameters: water temperature, pH, redox potential (Eh), conductivity (expressed at 25°C), dissolved oxygen and CO$_2$ content (expressed as a mV value). Redox data are corrected from temperature influence and expressed with respect to the electro-motive force of the electrochemical reference cell. Water and dissolved gas sampling were performed using a nitrogen driven sampler, samples being taken each 10 m in depth. The stainless steel sampler was slightly over-pressurised (against the hydrostatic pressure existing at the desired sampling depth) at the surface, then gently lowered to the depth of sampling. Once the desired depth was reached, the pressure was slightly lowered to allow the opening of a valve and the filling of the sampler with 1l of water and dissolved species. Then the sampler is re-pressurised and recovered at the surface. Water was then transferred into vacuumed glass bulbs to avoid gas losses.

A set of 20 logs were acquired during the survey. Smaller ones extended up to less than 6 m depth on the Eastern shore and deeper ones up to 48 – 49 m depth in the central part of the lake (figure 1). Depth indicated by the probe may slightly differ from that reported on topographic maps, as “our” depth definition is based on sudden parameter changes induced by lowering the probe into unconsolidated sediments. Moreover, some profiles were performed at constant depth (respectively 1, 4, and 6 m depth) in order to evaluate any lateral discrepancy.
Collected water samples (lake and mineral waters) were analysed at laboratory for major ions by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) and chromatographic methods.
Dissolved gases were quantified using gas chromatography, using the same methodology as the one used for gaseous species determinations.

3.3 What can be learned from the use of the CO₂ sensor?
Since P_{CO₂} sensor are not yet frequently utilised in non-saline water bodies, laboratory testing was performed before in-situ deployment. The P_{CO₂} sensor is an adaptation of the Severinghaus electrode (Severinghaus and Bradley, 1958), which consists in a pH determination (expressed as a mV value) using one measuring electrode and one reference electrode, both merged in an electrolyte solution and protected by a gas permeable membrane. Response time should be 30 seconds for a working domain of 0.013 to 0.263 atm CO₂.
First tests were performed by circulating a gas flux of variable CO₂ concentration (0.05 to 100% vol.). The sensor clearly appeared to be better suited for low CO₂ concentrated environments (100 mV of potential difference for a 10% vol. CO₂ range and only 150 mV one for the 0 – 100% vol. range).
Moreover the potential difference was time dependent (Figure 2a) therefore correlation of the sensor electrical response with a defined gas concentration is not obvious. At the opposite, sensor behaviour when exposed to different CO₂ concentrations can be used to decipher between progressive enrichment or depletion, depending on the stated electric evolution with time.

Figure 2
(a) Evolution of the electrical response of the CO₂ sensor with time when exposed to progressive CO₂ enrichment (gas phase); (b and c): evaluation of the sensor’s equilibration time: (b) when exposed to tap water (low CO₂ content) at time 0 after equilibrating in CO₂-rich water; (c) when exposed to injection of 10% vol. of CO₂ gas in water (starting at time 0).
The time needed to achieve equilibrium state in aqueous environment has been evaluated under two schemes: 1) immersion of the probe from CO₂-rich water to tap water (Figure 2b) and 2) injection of a CO₂-rich gas phase in water (Figure 2c). The electrical potential evolved exponentially with time for case 1 and under polynomial regression for case 2. Time needed to reach 80% of the ending electrical signal was close to 2 minutes for CO₂ loss (case 1) and close to 3 minutes for CO₂ enrichment (case 2). This quicker time reaction for decreasing CO₂ concentrations than for increasing ones is conflicting with previous studies (Severinghaus and Bradley, 1958). Moreover, its implies to perform logging (probe deepening) at slow speed, typically between 0.5 to 2 m per minute in order to detect variations at a metric scale.

The evolution of the sensor response with temperature, that may induce variations of the CO₂ dissolved content (Diamond and Akinfiev, 2003), has been tested at 11 and 15°C, suggesting a lesser amount of dissolved CO₂ at higher temperature in agreement with calculated parameters based on gas saturated solution.

An in-situ test was conducted in the French Massif Central (Détente well; Renac et al., 2009). This 560 m deep well has been surveyed up to 400 m depth in order to explore both the two phase part (coexistence of dissolved and gaseous CO₂, from 0 to 115 m depth) and the deeper part (below 115 m depth) where only dissolved CO₂ is present (lundt and Robalo, 1990). Probe deepening was lesser than 2.4 m per minute in the 0 – 115 m depth interval and not larger than 5.1 m per minute downwards. Some stops were also made during lowering (Figure 3).

Stability of measurements was lesser in the two phase part of the well than in the deeper part, where no drift occurred when performing stops during probe lowering. Below 115 m depth, the mV evolution suggested a progressive enrichment in dissolved gas that was consistent with laboratory gas analyses (from 0.026 to 0.27 mol/l at depth) and with partial CO₂ pressures calculated from water chemistry (from 1.2 at surface to 12.8 atm at 260 m depth). There was no redhibitory instrumental drift with time. If we postulate that pH is mainly influenced by the CO₂ content, evolution of CO₂ data along with these pH data also suggested a consistent evolution, the progressive diminution of the pH value being more or less linked to enrichment in dissolved CO₂, especially below 250 m depth. Some discrepancies did exist between 115 and 250 m depth, as the CO₂ sensor suggested the existence of a less rich horizon. Dissolved CO₂ amounts and potential values from the CO₂ sensor were linked as follow:
\[ [\text{DCO}_2] = 44 \exp [-0.0658 \times \text{A} - 21.08]; \quad r^2 = 0.993; \quad n = 5 \quad (1) \]

with \([\text{DCO}_2]\) the dissolved \(\text{CO}_2\) concentration in mg/l and \(\text{A}\) the read of the \(\text{CO}_2\) sensor in mV.

Even if this preliminary in-situ testing was performed in \(\text{CO}_2\)-rich water, it has shown that the \(\text{CO}_2\) sensor can help in evaluating the relative quantities of dissolved gas, variations due to temperature and time being of secondary importance. Nevertheless no quantification of the dissolved amount appeared to be realistic (Figures 2 and 3).

Figure 3
Water logging of Détente well: plot vs. depth of water temperature, pH and \(\text{CO}_2\) (as mV value); dashes along the depth axis figure the depths where stops were made during logging. Lower right graphs represent the variation of the \(\text{CO}_2\) value as a function of water temperature and logging duration.
4. Soil gas data

4.1 External forcing

Even if this study was focussed on soil gas studies in the vicinity of gas vents (mofettes where an input of deep CO$_2$ is present), gas migration in near surface processes always depends on meteorological conditions (Toutain and Baubron, 1999). In order to get an overview of the main meteorological parameters before the September 2007 soil gas survey, we get daily means of these parameters from the Koblenz-Bendorf weather station, located 20 km ESE from Laacher See lake at 130 m a.s.l.
Figure 4 Meteorological parameters (air temperature, rainfall amount, barometric pressure, sunshine duration and relative humidity) before and during the survey; data from Koblenz–Bendorf weather station, http://www.weatheronline.co.uk/.
During the survey itself (24th – 27th of September 2007), atmospheric temperature experienced a sharp decrease, from 24 to 12°C for maximum ones and from 13 to 8°C for minimum ones. This was the consequence of the existence of a low pressure barometric system (1016 to 1008 hPa) that led to a great reduction of sunshine duration (from 6 hours on to 0), consequent rainfall amounts (3 mm on day 24, 33 mm on day 27) and a rise in relative humidity levels (from 73% to 94%).

During the weeks preceding the survey, air temperatures experienced a decrease directly linked to seasonal variation, from summer to autumn conditions. Rainfall amounts were low between end August to mid-September (less than 30 mm). As a consequence sunshine duration and barometric pressures exhibit quite high values, with relative humidity varying together with precipitations.

Radon contents in soils are dependent from those meteorological parameters (Finkelstein et al., 1998), as well as other gases such as CO₂ (Heinicke et al., 1993) or helium (Virk and Walia, 2001). Radon concentrations are e.g. dependent from diurnal variation linked to the sun rise on the morning, which is related to air temperature; from the possible partial dissolution of the gas into percolating water when raining; from changes due to barometric pressure fluctuations; from the effect of winds and ventilation.

Quantification of diurnal variations of gas contents within soils is not achievable as measurements were performed only once for a selected point. Barometric pressure variations are small (8 hPa) and their effect at one meter depth should be very low. Temperature variations are abrupt in the atmosphere (Figure 4), but similarly at depth they are likely to be attenuated and delayed. Soil humidity levels could be more variable as rainfalls occur at the end of the survey. Nevertheless, large amounts of rainwater are needed to modify soil gas concentrations (Wattananikorn et al., 1998). With regard to the meteorological evolution from August to September 2007, sudden changes on soil water content can be discarded for the Laacher See site and can only have influenced upper soil gas concentrations at the Obermendig site, where sampling was done during a 33 mm rainfall event.

Thus changes stated on soil gas concentrations must preferentially reflect heterogeneities linked to soil or tectonic structures affecting underlying rocks (Baubron et al., 2002; Ciotoli et al., 1999). In that sense measurements appear to be more related to the characterization of the geological framework rather than to rely on externally driven variations. Moreover, the Laacher See district is a nowadays
non-active area as no residual volcanic nor great tectonic activity is experienced, but it can neither be viewed as a pure non active area as gas fluxes from depth still occur, as highlighted by acquired data. Gas emanation should then be controlled by advection processes rather than by diffusion processes. Figure 5 favours this statement, as no correlation with meteorological evolutions was highlighted. Furthermore, soil gas data acquired away from areas with deep degassing would exhibit an opposite behaviour. For example, radon activities sometimes decline when atmospheric temperatures do or when barometric pressures rise (Kumar et al., 2009).

Figure 5
Plot of soil gas measurements vs. time of sampling.
4.2 Results and Interpretation

CO₂ concentrations on the western shore of the Laacher See (sampling between the 25th and the 26th of September) ranged between atmospheric values (0.03%) to 100% vol. They were associated with ²²²Rn activities from 120 to 30800 Bq/m³. Respective mean values were 13.8% and 8630 Bq/m³ (Table 1). Helium-4 concentrations plotted in a wide range, between 1.3 and 10.1 ppm, with a mean value slightly enriched relative to the atmospheric level. Such a helium distribution had a wider variability than reported for other leaking sites, e.g. Latera caldera in Italy (Beaubien et al., 2008), where concentrations lesser than 4 ppm were not monitored. Some additional measurements (Table 1) performed 5 km to the Southwest (Obermendig site), near the Erlenbrunnen mineral spring, revealed higher radon activities, similar CO₂ concentrations and confirmed the existence of negative helium anomalies (amounts lesser than the atmospheric value). No CH₄ was detected by the IRGA in the field.

Table 1

Soil gas measurements statistics: (a) Laacher See site; (b) Obermendig site.

<table>
<thead>
<tr>
<th></th>
<th>²²²Rn (Bq/m³)</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
<th>³⁶He (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Number of observations</td>
<td>70</td>
<td>87</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>Minimum</td>
<td>120</td>
<td>0.03</td>
<td>0</td>
<td>1.33</td>
</tr>
<tr>
<td>Maximum</td>
<td>30800</td>
<td>100</td>
<td>20.6</td>
<td>10.1</td>
</tr>
<tr>
<td>Median</td>
<td>6960</td>
<td>3.3</td>
<td>18.9</td>
<td>5.25</td>
</tr>
<tr>
<td>Mean</td>
<td>8630</td>
<td>13.8</td>
<td>17.2</td>
<td>5.44</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>6840</td>
<td>23.7</td>
<td>4.5</td>
<td>1</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>0.793</td>
<td>1.722</td>
<td>0.262</td>
<td>0.185</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) Number of observations</th>
<th>²²²Rn (Bq/m³)</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
<th>³⁶He (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>330</td>
<td>0.13</td>
<td>3.5</td>
<td>2.75</td>
</tr>
<tr>
<td>Maximum</td>
<td>81000</td>
<td>90</td>
<td>20.3</td>
<td>5.26</td>
</tr>
<tr>
<td>Median</td>
<td>18300</td>
<td>5.3</td>
<td>19</td>
<td>5.16</td>
</tr>
<tr>
<td>Mean</td>
<td>24500</td>
<td>14.5</td>
<td>17.2</td>
<td>4.93</td>
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<tr>
<td>Standard deviation</td>
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<td>4.5</td>
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<td>Coefficient of variation</td>
<td>0.999</td>
<td>1.664</td>
<td>0.261</td>
<td>0.136</td>
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</tbody>
</table>

Spatial distribution of CO₂ and radon on the western shore of Lake Laacher See are presented in Figure 6. Data interpolation was done using the natural neighbour algorithm as no well-defined variogram could be built to perform reliable krigging. This natural neighbour plot highlights the occurrence of a very emissive zone (gas vent) on the southern part of the monitored area (near points B and C) that is evidenced by high CO₂ contents and pronounced radon activities compared to
adjacent values. Another high gas content zone can be evidenced in the Northern part of the meadow. Decreasing of the CO₂ content back to non-anomalous values is done in a 20 m distance interval, close to spacing stated in Italy by Beaubien et al. (2008) if referring to their background value definition (concentrations lesser than 2.5% vol. CO₂). Here we prefer using another commonly used approach (Xue et al., 2008). An anomalous level was here defined by the “mean plus twice the standard deviation” parameter. For the Laacher See pasture, the thresholds were respectively 61.2% vol. for CO₂, 22,300 Bq/m³ for ²²²Rn and 7.44 ppm for ⁴He. Interestingly, frequency distribution histograms (Baubron et al., 2002) yielded to similar results, 93.1% of the CO₂ values being under 66% vol., 95.7% of the ²²²Rn values being under 21,700 Bq/m³ and 95.4% of the ⁴He values being under 7.44 ppm. Last, as often stated for soil gases, the CO₂ concentrations were ranged under log-normal distribution (probability of 94.3%), but both ²²²Rn and ⁴He were not, neither they were under normal distribution.

Only seven samples had a CO₂ concentration greater than 61%, lying between points B and C (Figure 6); by them 4 points also had anomalous helium content, and only one showed a conjoint CO₂-He-Rn anomaly. Two other samples had great radon activities without particular concentration in other gas species. Using such an approach may help to refine the definition of anomalies, i.e. there is only one true gas vent existing in the monitored area. Specifically, radon activities reaching values up to 20,000 Bq/m³ on the northern part of the surveyed area did not seem to be related to the existence of an active gas vent, even if CO₂ concentrations do reach few tens of % vol.

The contrasting behaviour of the ⁴He gas (Figure 6), with either enrichment or depletion relative to the atmospheric level, could then be interpreted as follow: the active centre of the vent allows the conjoint escape of both carbon dioxide and helium. As helium is co-eluted with other gases under great fluxes (> 500 g/m²/day for this vent; Jones, 2009, pers. comm.) and has a lower density than the air, it is drained out by the other gaseous species. As a consequence, soil formations existing close to the vent exhibit very low helium concentrations, that progressively come back to near atmospheric levels when moving away from the vent. Narrower helium anomalies compared to CO₂ ones were also stated in Italy (Beaubien et al., 2008). Helium originated from decaying of uranium-rich formations (Etiope and Martinelli, 2002) and at the opposite uranium-poor levels does not seem to be a valuable explanation, as spatial variations are too narrow and radon activities too small. Testing this hypothesis could be done in the future by performing helium isotope measurements (³⁴He ratio). As helium in the Laacher
See region is mainly of mantle origin (Aeschbach-Hertig et al., 1996, 1999), this pumping effect could be also evidenced by isotope ratios that would show a progressive rise of atmospheric component together with increasing distance from the vent.

Figure 6
Soil gas species along the western shore of lake Laacher See. Interpolation is done using natural neighbour computation, and is only valid near the set of 86 measurements (location represented by dots on central inset). Location of the western shoreline of the lake is indicated. Grid scaling: 20 m interval.

As a consequence of gas venting, there is a strong negative correlation between O₂ and CO₂ contents (Table 2), that could be explained by a progressive replacement of O₂ by CO₂ as the CO₂ concentration increases. The centre of the vent is then almost anoxic. There is also a slight correlation between ²²²Rn and CO₂. In this case, CO₂ could act as a carrier gas, allowing ²²²Rn transportation along its migration pathways (Heinicke et al., 1993). Nevertheless the depth where radon originates cannot be postulated, as it depends on the migration speed of the other mobile gases and on the soil physical parameters, which are different from one site to another.
Table 2

Correlation matrix—all data (Pearson coefficient).

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<tr>
<th></th>
<th>$^{222}$Rn (Bq.m$^{-3}$)</th>
<th>CO$_2$ (%)</th>
<th>O$_2$ (%)</th>
<th>$^4$He (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}$Rn (Bq.m$^{-3}$)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ (%)</td>
<td>0.579</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$ (%)</td>
<td>-0.596</td>
<td>-0.991</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$^4$He (ppm)</td>
<td>-0.165</td>
<td>0.047</td>
<td>-0.04</td>
<td>1</td>
</tr>
</tbody>
</table>

Such soil gas concentrations, especially those for CO$_2$ and $^4$He, are characteristic of emissive areas, similar to those known in the French Massif Central (Battani et al., 2010) or in Italy (Beaubien et al., 2008). Helium concentrations are nevertheless diluted regarding concentrations found in gas bubbles within the Laacher See itself (up to 20 ppm; Aeschbach-Hertig et al., 1996), whereas radon activities in France or Italy are much higher (up to thousands of kBq/m$^3$). This is could be attributed to different soils characteristics and to different basement geology. Those measurements might prove one of these effects linked to different soil structures. As said before, the Laacher See site is exposed to the atmosphere only since hundreds of years. Structures and organics layers inherited from underwater stage are still to be found within this soil (Krüger et al., 2009), while soils at Obermendig (sampling on the 27$^{	ext{th}}$ of September) have never been affected by such an evolution. Therefore this could partly result in observing similar carbon dioxide contents, especially above gas vents, but different radon levels.

Gas chromatography results revealed a good agreement between in-situ measurements and laboratory analyses (Table 3). Linear regression computations done on CO$_2$ and O$_2$ results lead to correlation’s coefficients of 0.992 and 0.991 respectively, IRGA measurements slightly overestimating laboratory ones. This could be an effect of the time delay needed to bring back samples to laboratory, as it’s especially noticeable for the high content samples. Other ubiquitous gaseous species were argon, with levels slightly lower than the atmospheric mean (0.93) and nitrogen. Two samples (D and E in Figure 6) had noticeable methane content (29 and 150 ppm respectively) that was well above atmospheric level (1.7 ppm). This enrichment could be the result of gas release together with CO$_2$ of deep origin. Beaubien et al. (2008) have noticed such methane enrichment in areas where CO$_2$ flux is greater than 500 g/m$^2$/day, methane oxidation processes becoming lesser noticeable. Methane enrichment was found in samples far away from the gas vent, preferably being the result of bacterial
activity in soils (methanotrophic species). Unfortunately, since none $\delta^{13}$C(CH4) measurement was performed, deciphering between those two hypotheses is not possible.

Table 3
Gas chromatography results; samples location is indicated in Fig. 3; d.l.: detection limit; precision of isotope ratio measurements is ±0.15‰ VPDB.

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>N2</th>
<th>CO2</th>
<th>CO2, IRGA</th>
<th>O2</th>
<th>O2, IRGA</th>
<th>He – H2 – H2S</th>
<th>CH4</th>
<th>CnH2n+2, n=2 to 6</th>
<th>$\delta^{13}$C (‰ VPDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d.l.</td>
<td>0,001</td>
<td>0,001</td>
<td>0,001</td>
<td>0,001</td>
<td>0,005</td>
<td>0,0002</td>
<td>0,0002</td>
<td>-1,9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt. A</td>
<td>0,55</td>
<td>47,2</td>
<td>39</td>
<td>39,2</td>
<td>12,5</td>
<td>12,3</td>
<td>&lt; d.l.</td>
<td>&lt; d.l.</td>
<td>&lt; d.l.</td>
<td>-4,1</td>
</tr>
<tr>
<td>Pt. B</td>
<td>0,87</td>
<td>73,3</td>
<td>5,75</td>
<td>6,38</td>
<td>19,5</td>
<td>19,1</td>
<td>&lt; d.l.</td>
<td>&lt; d.l.</td>
<td>&lt; d.l.</td>
<td>-1,5</td>
</tr>
<tr>
<td>Pt. C</td>
<td>0,41</td>
<td>36,7</td>
<td>52,2</td>
<td>61,6</td>
<td>9,75</td>
<td>7,9</td>
<td>&lt; d.l.</td>
<td>&lt; d.l.</td>
<td>&lt; d.l.</td>
<td>-2,6</td>
</tr>
<tr>
<td>Pt. D</td>
<td>0,8</td>
<td>68,1</td>
<td>13,3</td>
<td>14</td>
<td>17,7</td>
<td>16,8</td>
<td>&lt; d.l.</td>
<td>0,0029</td>
<td>&lt; d.l.</td>
<td>-2,6</td>
</tr>
<tr>
<td>Pt. E</td>
<td>0,32</td>
<td>24,4</td>
<td>67,4</td>
<td>77,5</td>
<td>6,63</td>
<td>5,5</td>
<td>&lt; d.l.</td>
<td>0,015</td>
<td>&lt; d.l.</td>
<td>-2,6</td>
</tr>
</tbody>
</table>

Laboratory results pointed out a dominant deep origin for the CO2 gas and argon concentrations suggesting a greater proportion of the deep gas flux. This deep origin was also indicated by carbon isotope ratio measurements. Ratios between -1.5 to -4.1‰ VPDB were measured (Table 3; mean value: -2.5‰) that agree well with those reported elsewhere for the CO2 escapes within the lake (-3.7 to -3.8‰ in Giggenbach et al., 1991; -3‰ in Griesshaber et al., 1992). The more negative ratios seem to be linked to a “deep origin” component (mantle and/or crustal degassing), also highlighted in non-emissive areas (Pauwels et al., 2007) and are clearly not related to interaction with CO2 produced by biological phenomena. Less negative ratios can perhaps be related to interaction within soil formations, e.g. with carbonate horizons.

5. Lake Laacher See and mineral springs

5.1 Chemical composition of Erlenbrunnen mineral spring and lake waters
Chemical composition of the Erlenbrunnen spring reflected the mean composition of mineral waters of the Eifel district (Griesshaber et al., 1992; van der Bogaard, 1995). This spring had a low discharge temperature (11.6°C), a Total Dissolved Solids (TDS) amount lesser than 4000 mg/l, high free CO2 gas content (calculated pCO2 = 1.13 atm), a slightly acidic pH and was of Ca-Mg-HCO3 type (respective concentrations of 305, 220 and 3800 mg/l). Chlorine content was less than 10 mg/l (Figure
Carbonate system was dominated by the $\text{H}_2\text{CO}_3/\text{HCO}_3$ couple. Erlenbrunnen water appeared to be slightly oversaturated with respect to Ca-CO$_3$ species (calcite, aragonite, dolomite) and slightly undersaturated with respect to Ca-SO$_4$ ones (anhydrite, gypsum). As a consequence, this spring will be considered as representative of the deep end-member even if local mineral waters are frequently mixture between old and young groundwaters (van der Bogaard, 1995).
Figure 7

Schöeller–Berkaloff diagram showing major ion contents of Erlenbrunnen mineral spring and Laacher See (LS) lake from near surface (~1.7 m) to bottom (~46 m); surface and bottom characteristics of Lake Pavin water (French Massif Central) are also indicated for comparison (BRGM, 2009, unpublished data).
Table 4

Chemical analyses of Laacher See water and Erlenbrunnen mineral spring; chemical balances are in the range −2 to +4%. For samples LSX refer to Fig. 1 for location; sampling depth is indicated after the hyphen. Saturation index (SI) and mmol/l concentrations of carbonated species (TDIC = Total Dissolved Inorganic Carbon = H2CO3 + HCO3 + CO3) are computed using Diagramme software (http://www.lha.univ-avignon.fr/LHA-Logiciels).

<table>
<thead>
<tr>
<th>Sample</th>
<th>TDS (mg/l)</th>
<th>T (°C)</th>
<th>pH</th>
<th>Cond. @25°C (μS/cm)</th>
<th>SICalcite</th>
<th>SIAragonite</th>
<th>SIDolomite</th>
<th>SIGypsum</th>
<th>SIAnhydrite</th>
<th>TDIC (mmol/l)</th>
<th>H2CO3 (mmol/l)</th>
<th>HCO3 (mmol/l)</th>
<th>CO3 (mmol/l)</th>
<th>pCO2 (atm)</th>
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<tbody>
<tr>
<td>LS5 bubbles</td>
<td>581</td>
<td>24.8</td>
<td>8.11</td>
<td>657</td>
<td>41.3</td>
<td>38.4</td>
<td>46.4</td>
<td>24.7</td>
<td>384.9</td>
<td>18.5</td>
<td>26.3</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS5-20cm</td>
<td>592</td>
<td>27.4</td>
<td>8.26</td>
<td>643</td>
<td>49.7</td>
<td>28</td>
<td>45.7</td>
<td>30.6</td>
<td>392.8</td>
<td>18</td>
<td>26.4</td>
<td>0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS4-1.7m</td>
<td>598</td>
<td>20.4</td>
<td>8.45</td>
<td>655</td>
<td>47.8</td>
<td>28.5</td>
<td>48.6</td>
<td>29.1</td>
<td>398.9</td>
<td>18</td>
<td>26.5</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS5-20m</td>
<td>592</td>
<td>20.5</td>
<td>8.26</td>
<td>644</td>
<td>44.6</td>
<td>38.1</td>
<td>49.3</td>
<td>22.9</td>
<td>392.2</td>
<td>16.3</td>
<td>26.2</td>
<td>0.55</td>
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<td></td>
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<tr>
<td>LS4-10m</td>
<td>601</td>
<td>3.2</td>
<td>8.12</td>
<td>665</td>
<td>37.9</td>
<td>38</td>
<td>51.1</td>
<td>26.5</td>
<td>402.6</td>
<td>18.4</td>
<td>26.3</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS4-20m</td>
<td>601</td>
<td>5.6</td>
<td>7.8</td>
<td>659</td>
<td>41.1</td>
<td>36.8</td>
<td>46.6</td>
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<td>405.7</td>
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<tr>
<td>LS3-30m</td>
<td>614</td>
<td>5.2</td>
<td>7.77</td>
<td>653</td>
<td>46.4</td>
<td>39.5</td>
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<tr>
<td>LS4-30m</td>
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<td>7.55</td>
<td>666</td>
<td>50.4</td>
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<td>48.2</td>
<td>28</td>
<td>394.7</td>
<td>18.1</td>
<td>25.9</td>
<td>0.55</td>
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<tr>
<td>LS4-40m</td>
<td>606</td>
<td>5.1</td>
<td>7.45</td>
<td>663</td>
<td>43.5</td>
<td>39.8</td>
<td>50.3</td>
<td>26.6</td>
<td>400.8</td>
<td>18.4</td>
<td>26</td>
<td>0.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS4-46m</td>
<td>603</td>
<td>5</td>
<td>7.35</td>
<td>617</td>
<td>50.4</td>
<td>24.8</td>
<td>47.4</td>
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<td>403.6</td>
<td>18.1</td>
<td>25.8</td>
<td>0.56</td>
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<tr>
<td>Mean</td>
<td>597.5</td>
<td>72</td>
<td>7.8</td>
<td>655.6</td>
<td>45.2</td>
<td>34.5</td>
<td>48.2</td>
<td>26.4</td>
<td>398</td>
<td>18.2</td>
<td>26.4</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>8.91</td>
<td>9.15</td>
<td>0.43</td>
<td>15.87</td>
<td>4.15</td>
<td>5.55</td>
<td>1.64</td>
<td>2.69</td>
<td>7.56</td>
<td>0.23</td>
<td>0.56</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean / SD</td>
<td>1.50%</td>
<td>76%</td>
<td>5.50%</td>
<td>2.40%</td>
<td>9.20%</td>
<td>16.10%</td>
<td>3.40%</td>
<td>10.10%</td>
<td>1.90%</td>
<td>1.30%</td>
<td>2.10%</td>
<td>1.40%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erlenbrunnen</td>
<td>3056</td>
<td>25</td>
<td>7.8</td>
<td>3100</td>
<td>45.2</td>
<td>34.5</td>
<td>48.2</td>
<td>26.4</td>
<td>398</td>
<td>18.2</td>
<td>26.4</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
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</table>

Laacher See waters had relatively high TDS contents (c.a. 600 mg/l) compared to those of e.g. Lake Pavin (Figure 7), set in a similar geological context (Aeschbach-Hertig et al., 1999), where TDS contents only reach 400 mg/l at lake’s bottom (BRGM, 2009, unpublished data). There were no significant TDS variations along the water column in Laacher See waters, dominant species being HCO3, Ca and Mg as for mineral waters (Table 4). Chlorine contents reached twice the value of the Erlenbrunnen spring and were almost constant throughout the water column as well as other anions contents (variations lesser than 2.1% of the mean / standard deviation ratio). Changes were greater
for cationic species, variations of 10% or more existing for Ca, K and especially Mg. As a consequence saturation indexes did vary with depth, waters being oversaturated with respect to Ca carbonated species at surface horizons and progressively becoming undersaturated with depth. Saturation changes appeared between 20 and 40 m depth (Table 4), in agreement with reported changes of sediment facies (Bahrig, 1985). The carbonate system was mainly governed by the bicarbonate specie which accounted for c.a. 98% of the Total Dissolved Inorganic Carbon (TDIC) from 0 to 10 m depth in, 90 to 95% from 20 to 45 m depth and c.a. 80% at the interface with unconsolidated sediments. Calculated CO$_2$ partial pressures were 2 to 3 orders of magnitude lesser than for the Erlenbrunnen spring, maximum pressure (0.023 atm) being reached at maximum depth. Similar values are only obtained under the chemocline barrier within Lake Pavin (Aeschbach-Hertig et al., 1999), suggesting a substantial enrichment of Laacher See waters, with respect to TDS values.

One intriguing point is the ubiquitous chlorine richness of the Laacher See waters. Lake waters appear to have contents similar to or greater than the majority of the neighbour mineral waters (Griesshaber et al., 1992). Chlorine content coming from rainwater can only reach few ppm even in near coastal environments (Koehler and Wassenaar, 2010). Chlorine coming from water/rock interactions in near surface environments is not believed to be an important supplier, as the Eifel district is not known for peculiar Cl-rich rock formations. Moreover in such a case water type should have been modified (e.g. rising of the Na or K concentrations) which is not identifiable, Na+K concentrations being lesser than those of mineral waters. Chlorine richness is not reported in crater lakes where CO$_2$ is known to accumulate, e.g. Lake Nyos (less than 1 mg/l; Giggenbach, 1990). Another option could be an input of gaseous chlorine, considerable amounts being reported in some volcanic districts (e.g. 800 to 7500 ppm in magmas; Aiuppa et al., 2009). However, the exsolution of chlorine (as HCl) is frequently concomitant with those of CO$_2$, and hence such an origin would also be characterised by strong CO$_2$ amounts. Excepted some onshore and offshore gas vents, there is no evidence of a strong and generalised degassing in the Eifel region. Moreover the gas phase measured on mofettes is mainly CO$_2$ (99 to 100% vol.) and chlorine abundances in the Eifel groundwaters is also consequently lesser than the one of CO$_2$ (resp. 0.3 – 0.6 and 55 – 60 kmol/l; Griesshaber et al., 1992).

If a dominant Cl origin from degassing can be discarded, Laacher See water enrichment towards local groundwaters remains unexplained. Surface water feeding of the lake, either by rain waters or streams, should not be the only purveyor. As suggested for Lake Pavin (Jézéquel et al., 2009),
underwater seepages of mineral waters, possibly of different chemical characteristics, may be one of the options to explain the peculiar chemical content of Laacher See waters. Complementary isotope analyses in the future may help to evaluate this hypothesis.

5.2 Lake water logging

Chemical data resulting from in-situ sampling were completed by diagraphies as described in section 3.2. Results are presented in Figures 8 to 10. Temperature and conductivity changes are expected to be linked to the physical characteristics of the lake body, and dissolved oxygen, pH and redox variations to be impacted by biological processes in this meso- to eutrophic lake.

Figure 8 is based on data acquired in the centre of the lake (see Figure 1), 200 m southward from the zone where measurements were performed by Aeschbach-Hertig et al. (1996). Temperature data were in good agreement with these previous data. Discrepancies that existed between 0 and 20 m depth could be attributed to the holomictic character of the lake. Since measurements were made in late June, waters have warmed during spring time but did not reach their thermal optimum that is frequently observed at the end of the summer time. There was a strong decreasing thermal gradient between 5 and 15 m depth (thermocline) all over the lake (Figure 9a), with some slight lateral heterogeneity that was probably related to non homogeneous mixing within the epilimnion. At 20 m depth 5.4 to 5.6 °C were reached, followed by a small temperature decrease in the hypolimnion, where 5°C represented the ubiquitous temperature. This bottom temperature was higher than the one reported by Aeschbach-Hertig et al. (1996) who gave a 4.3 – 4.5°C range, even if they found a slight warming in the last 5 m. As we found this 5°C value several times, we do think it reflected the real bottom temperature, suggesting a better vertical homogenisation during this 2008 spring than previously noticed.
Figure 8

Synthetic view of deepest logs acquired in the Laacher See. Labels in captions refer to Fig. 1. Data from May and September months are from Aeschbach-Hertig et al. (1996). The inset in $O_2$ vs. depth diagram shows the relationship between $O_2$ and pH.

Figures 9a and 9b

(a) Interpolation map drawn using the natural neighbour algorithm: evolution of temperature at selected depth; $X$-axis refers to longitude, $Y$-axis to latitude; crosses indicate location of data used for interpolation (also shown in the corner right inset). (b) Evolution of conductivity (at 25 °C) as a function of depth; same symbolism as for Fig. 9a.
Conductivity changes with depth (Figures 8 and 9b) were scarce as they ranged between 690 and 715 µS/cm (at 25°C). In the firsts 5 m, the lower conductivities were recorded probably resulting from efficient mixing (wind forcing) and relative dilution due to surface waters, especially rainfalls supply. One exception was the occurrence of ‘high’ conductivities near the eastern shore at one meter depth, in an area where gas bubbling occurs (Figure 1). Such an increase of the conductivity when CO₂ is present as a gas phase has already been stated when testing the probe in the Détente well (section 3.3; data not shown). Nevertheless this anomaly was only visible at 1 m depth and did not extend up to lake’s bottom where the gas did escape.

Further depth, conductivity increase was associated with the temperature drop in the thermocline (Figure 8) with some lateral heterogeneity that may be linked to gas bubbles migration which is a spot process all over the lake (Figure 9b). Under 15 m in depth, the conductivity began to stabilise, as the temperature did. Penetration into sediments resulted in drastic increases of the conductivity.
pH values ranged from slightly basic ones (8.5) at surface to near neutral ones at depth (Figures 8 and 10). Most changes occurred in the thermocline and in the hypolimnion, the upper 5 m experiencing only slight decrease of the pH value. Scarce influence of CO₂ degassing could be highlighted at 3 – 4 m depth near the Eastern shore where decreases of 0.2 to 0.5 pH units occurred between restricted water levels. Within the thermocline pH evolution was correlated with that of dissolved oxygen (Figure 8). This evolution should be linked to photosynthetic processes that are frequent in stratified lakes (Assayag et al., 2008). Two significant rises of the pH were noted between 6 – 8 m depth (+ 0.1 pH unit) and 9 – 11 m depth (+ 0.6 to 0.7 pH units), corresponding to increases of respectively 150-200 and ~10% of the dissolved oxygen content. The thermocline is indeed characterised by a low transport by turbulent dispersion. The resulting confined zone it represents allows the accumulation of oxygen, effect of photosynthetic activity being greater. Below the thermocline, pH values again decreased, lower part of the lake showing homogeneous water body. Even if measurements were performed during long sunshine duration days, light penetration at great depth is not sufficient to allow strong photosynthetic activity. As a consequence, respiration processes – organic matter oxidation – become dominant and contribute to lower both pH and dissolved oxygen values. Nevertheless some lateral variations did exist on pH between 15 and 35 m depth. These lateral variations suggest a slight acidification of the external parts of the lake while horizons overlying the deepest part of the maar appear to be more basic (Figure 10a). Such lateral variations can be partly explained by divers’ observations reported by Aeschbach-Hertig et al. (1996) who evidenced fast dissolution of bubbles coming from lake’s bottom near 25 m depth in. As this 15 – 35 m depth sequence is very important towards carbon species, those variations can impact the depth were the waters become undersaturated versus dolomite (pH < 7.86), aragonite (pH <7.67) and calcite (pH < 7.51). Below 35 m depth, lake water was always undersaturated towards these species.

Figures 10a, b, c, d
Figure 10a: interpolation map: evolution of pH as a function of depth; same graphical chart as in Figure 9a.
Figure 10b: evolution of dissolved oxygen as a function of depth; same graphical chart as in Figure 9a.
Figure 10c: evolution of redox potential as a function of depth; same graphical chart as in Figure 9a.
Figure 10d: evolution of dissolved CO$_2$ (expressed as an electrical potential value – warning: the absolute value is taken) as a function of depth; same graphical chart as in Figure 9a.

Figure 11: schematic representation of the CO$_2$-rich areas around or in the Laacher See; labels 19, 27 and 29 refer to bibliographic references.
Redox potential showed gradual increase along the water column (Figures 8 and 10c) without relation to the different lake’s compartments (epilimnion, thermocline, hypolimnion), rather showing a rapid increase of the potential from 0 to 10 m depth (+ 60 mV) and a gentle raise under 10 m depth (+ 20 mV down to bottom). A sudden decrease was stated when penetrating into unconsolidated sediments when the medium became reducing. At greater scale, logs performed along the Eastern shoreline suggested the presence of more oxidant waters than those encountered in the centre or near the Western shoreline especially in near surface horizons. Those parts of the lake being subject of CO₂ degassing, this was quite unexpected as the presence of a gaseous phase should strengthen oxygen stripping and consequently lower redox values.

As a consequence the entire water column was dominated by oxidant conditions but showed significant changes with depth (Figures 8 and 10b). Dissolved oxygen greatly evolved within the
thermocline, surface waters being less rich than thermocline waters and having same contents than deeper horizons. The 6 – 10 m depth interval was characterised by oxygen rich waters, especially on the Western part of the lake. This sudden dissolved oxygen change is not only related to the large temperature drop (a fall of 13 to 14°C) in the thermocline, which would favour gas dissolution, as the water below 15 m depth had a lower temperature and also a lower dissolved oxygen content. It should also be a consequence of the strong photosynthetic activity within this low turbulent dispersion zone (Jézéquel et al., 2009). In areas where CO₂ escapes as a gas phase, a lesser oxygen content was from place to place measured, maybe related to stripping processes, but this statement contradicts the one made using redox data. Nevertheless dissolved oxygen contents were comparable to those found on collected water samples (Table 5). They also exhibited a downward evolution mimicking the one reported by Rheinland-Pflaz water authorities (data not shown – database from 2005 to 2007 made available courtesy of I. Möller, Bundesanstalt für Geowissenschaften und Rohstoffe, BGR, Hannover), the levels around 10 m depth in having dissolved oxygen contents reaching 1.5 to 3 times the concentrations existing at the surface or at 20 m depth (depending on the season). Such stratification is also stated in Lake Pavin where thermocline waters are enriched in dissolved oxygen (Assayag et al., 2008).

Table 5
Dissolved gas contents (mol/l) measured on water samples taken from 10 to 46 m depth in the water column. LSX refer to samples location as indicated in Fig. 1; depth is indicated after hyphen; l.d.: limit of detection; l.q.: limit of quantification; n.d.: non-detected.

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS4-10m</td>
<td>1,40E-04</td>
<td>6,30E-05</td>
<td>2,10E-03</td>
<td>9,90E-03</td>
<td>9,80E-08</td>
</tr>
<tr>
<td>LS4-20m</td>
<td>2,40E-04</td>
<td>2,30E-05</td>
<td>6,60E-05</td>
<td>9,10E-04</td>
<td>1,80E-08</td>
</tr>
<tr>
<td>LS3-30m</td>
<td>5,80E-04</td>
<td>1,40E-04</td>
<td>3,30E-03</td>
<td>1,20E-02</td>
<td>6,50E-08</td>
</tr>
<tr>
<td>LS4-30m</td>
<td>2,60E-04</td>
<td>2,10E-05</td>
<td>1,20E-04</td>
<td>8,60E-04</td>
<td>n.d.</td>
</tr>
<tr>
<td>LS4-40m</td>
<td>5,10E-04</td>
<td>2,20E-05</td>
<td>6,80E-05</td>
<td>1,20E-03</td>
<td>n.d.</td>
</tr>
<tr>
<td>LS2-45m</td>
<td>1,20E-03</td>
<td>6,20E-05</td>
<td>9,70E-04</td>
<td>5,40E-03</td>
<td>2,10E-08</td>
</tr>
<tr>
<td>LS4-46m</td>
<td>1,20E-03</td>
<td>2,40E-05</td>
<td>3,00E-05</td>
<td>1,20E-03</td>
<td>n.d.</td>
</tr>
<tr>
<td>l.d.</td>
<td>3,50E-08</td>
<td>1,20E-08</td>
<td>1,10E-08</td>
<td>1,10E-08</td>
<td>2,20E-09</td>
</tr>
<tr>
<td>l.q.</td>
<td>5,30E-07</td>
<td>1,70E-07</td>
<td>1,70E-07</td>
<td>1,60E-07</td>
<td>3,30E-08</td>
</tr>
</tbody>
</table>

Qualitative evolution of dissolved CO₂ contents (Figures 8 and 10d) suggested the presence of CO₂-rich waters on the Western part of the lake, and less enriched waters in the Eastern part, except some higher values between 5 to 7 m depth. This statement contradicts information inferred from chemical
analyses (table 4), in-situ sampling (table 5) and man eye observations. It’s also in conflict with photosynthetic/respiration processes evolution along the water column, as the diminution of these processes should lead to CO₂ consumption and O₂ production rather than to CO₂ enrichment. No such O₂ enrichment is stated (Figure 10b). Moreover, the sensor did not react when immersed in lake compartments where bubbling occurs. The unique tendency that could partly reflect real processes is best highlighted by Figure 8, where CO₂ contents appeared to be greater at depth that in upper levels but far from concentrations really measured on samples (Table 4). For some of the profiles (labelled 5, 6 and 7), the minimum potential was recorded at depths where dissolved oxygen contents reached their maximum, which was a coherent behaviour. Last, there was another slight tendency exhibited by the sensor, consistent with a better CO₂ dissolution at depth where temperatures are colder than near the surface (Diamond and Akinfiev, 2003). As a consequence, and despite the information gathered during preliminary testing (eq. 1), data provided by this pCO₂ sensor are not enough reliable and too much dependent from depth and logging duration (e.g. for log 5 – 49 m depth, Pearson’s coefficients are 0.970 for CO₂-depth and 0.956 for CO₂-time). Therefore, evolution of the water CO₂ content within the lake must be based on sampling and subsequent gas analyses.

The carbonate system in the Laacher See should be principally dependent from the pH value (Stumm and Morgan, 1981), as waters evolve from relatively alkaline type at surface to nearly neutral one at depth. This progressive decrease of the pH values is mainly related to the growing content of H₂CO₃, as the CO₃ content becomes smaller with depth and the alkalinity (expressed as the HCO₃ content) remains stable (Table 4). Hence, there is a progressive increase of the partial CO₂ pressure along with depth, and some local enrichments in the dissolved CO₂ are encountered in areas where bubbling occurs (sample LS5 bubbles in Table 4). Even in near surface waters (1.7 m depth), there is a slight CO₂ enrichment towards the atmospheric equilibrium concentration, but the increasing gradient down to bottom is far from the one observed in Lake Pavin by Aeschbach-Hertig et al. (1999). The absence of lake water stratification, especially the absence of a monimolimnion, only allows the CO₂ equilibrium partial pressure to reach 0.023 atm at lake’s bottom. Depending on dissolved species, this pressure is still higher than the one calculated for Lake Pavin at similar depth (again 3 times enrichment) but does not favour at all degassing of the water. CO₂ remains far from saturation in the deepest parts of the lake (saturation concentration c.a. 94 mmol/l; Diamond and Akinfiev, 2003). There is no evidence of
degassing from the water body itself, all the bubbling coming from demixtion processes occurring deeper in the earth crust.

As often stated (Bakalowicz, 1994), CO$_2$ concentrations measured on samples (Table 5) are smaller than the ones coming from calculations (taken as the H$_2$CO$_3$ total content, i.e. the sum of CO$_2$(aq.) and H$_2$CO$_3$), but the highest discrepancy is lesser than a 2 times underestimation, and sometimes higher CO$_2$ contents are determined by the sampling method. As a consequence, we would no reject these analyses, as made by Aeschbach-Hertig et al. (1999) using data from Camus et al. (1993) concerning Lake Pavin. Moreover the total H$_2$CO$_3$ content takes into account both the CO$_2$(aq.) and H$_2$CO$_3$ contributions and can therefore explain, at least partially, the gap between the two dissolved CO$_2$ evaluations. Around 45 m depth, there is a good agreement between the two methods, calculations leading to a 0.975 – 1.485 mmol/l content, whereas two direct measurements give the same content (1.2 mmol/l), which is identical to the mean value arising from equilibrium considerations. Taking into account huge errors affecting these considerations (± 20 %; Aeschbach-Hertig et al., 1999), such an agreement should indicate that the sampling procedure and subsequent gas analyses fairly reflect the real dissolved gas contents.

Other detected gases were atmospheric ones (O$_2$, Ar, N$_2$) and punctually CH$_4$ (Table 5). Sample LS3-30m has been affected by sampling bias during sample recovery, its O$_2$ and N$_2$ contents reaching or exceeding gas saturation at specified temperature (saturation concentrations under atmospheric equilibrium: 3.5E-03 and 2.2E-03 mol/l respectively; Weiss, 1970). In lesser extent, same statement can be done for the 10 m depth sample, where N$_2$ was close to saturation. Secondary O$_2$ enrichment was stated near 30 m depth, accordingly with shapes illustrated by Figure 8. Remaining samples are far from saturation concentrations and showed a rather constant evolution along with depth except some higher values near the lake’s bottom (45 m) that were not confirmed 1 meter deeper (46 m). Very low amounts of CH$_4$ were measured from time to time with no consistent evolution with depth. The presence of CH$_4$ can be linked to the biological state of the lake (mesotrophic to eutrophic).

As a consequence, the dissolved gas measurements all suggest a strong influence of the atmospheric compartment, probably linked to seasonal overturn(s) experienced by the whole water body.

Underwater seepages were not clearly highlighted at the centre of the lake and the ones occurring on the Eastern shore did not have noticeable influence several hundreds of meters further to the West (Figure 11). Especially, the CO$_2$ gas vents emplaced along the Western shore do not have noticeable
effects on the water chemistry, whereas the CO₂ present along the Eastern shore imprints both the water chemistry and the soil gas contents. Nevertheless, the influence of this degassing appears to be restricted to surface water horizons (0 – 10 m depth), which are more sensitive to small chemical changes.

Figure 11
Schematic representation of the CO₂-rich areas around or in the Laacher see references ([Jones et al., 2009] and [Langer, 1988]).

6. Conclusion: what can be learned from CO₂ escapes in the Laacher See region?
This study of the Laacher See water body and its surroundings has dealt with two sets of monitoring approaches, based on terrestrial and offshore monitoring methods.
Terrestrial applications highlight the occurrence of several gaseous releases, with dominant CO$_2$ content (Figure 11). Some of them are clearly distinguishable within the environment (absence of grassland or presence of different grass species) whereas others can only be detected using in-situ gas analyses. Most of the known degassing structures around the lake are oriented along an N-S axis, which is consistent with the known geological structuration of the hercynian basement. Radon and helium were systematically co-eluted with this CO$_2$ phase. Radon transportation depends on the CO$_2$ flux but also on the soil mineral composition. In the areas with prominent CO$_2$ gas phase originated from depth, the relationship between CO$_2$ (vector phase) and the radon is less satisfactory than in areas with lesser CO$_2$ amounts. Whatever the radon production rate is, the existence of anomalies at 1 m depth in soils greatly depends on the velocity of the CO$_2$. In areas where the uprising flux is high, radon activities can be lowered as radon production is not high enough to supply amounts proportional to those of the CO$_2$. Moving away from mofettes centres, the CO$_2$ flux diminishes, but the radon exhalation should remain nearly the same in a few meters interval. The relationship between the two gases will then be different from the one stated in the centre of the gas vent. As a result, matrix calculations performed on the entire dataset, suggest a relatively poor relationship between CO$_2$ and radon, at least poorer than relationships that can be drawn for areas where deep gas influx are not known (Gal *et al.*, 2010). Same statement can be made using helium, even if this gas phase also comes from depth. A dilution effect should lower the helium concentrations at the apex of the gas vent, and have a lesser influence when moving outwards.

Offshore applications consisted in lake water monitoring and have revealed a homogeneous thermal stratification from the western to the eastern shorelines, with a rather constant electrical conductivity in the water column. This conductivity is quite high for lake waters emplaced in such geological environments and may be partly related to lake feeding by mineral water leaks, as is postulated for lake Pavin (Jézéquel *et al.*, 2009). Nevertheless, such seepages had neither been highlighted during the cruises made using Idronaut probe nor were able to explain the significant chlorine enrichment found in the samplings. Substantial bicarbonate content was found all along the water column, reaching levels rather characteristic of monimolimnion environments (e.g. lake Pavin) than purely freshwater feeding in non-sedimentary areas. Chemical equilibrium relationships for the carbonate system, as well as in-situ gas and water sampling, also suggested a gradual and progressive increase of the dissolved CO$_2$ content with depth. This may be linked to dissolution of CO$_2$ gas coming from
non-thermally disturbing underwater releases but these releases – which did exist as they are visible at the lake’s surface (Figure 11) – had low to very low impact on water electrical conductivity. From place to place pH parameter may be more impacted by the CO₂ but there may be an overlap with photosynthetic processes – and with O₂ production/consumption processes – which were not accounted for during this study. As no strong degassing areas were highlighted in the centre of the lake, nor potential underwater seepage, it was not possible to locate preferential leaking pathways beneath the lake bottom in its deeper parts.

In view of characterising, monitoring and subsequently insuring of the safety of CO₂ underground geological storages, above described results lead to the following comments:

- As structural control of potential leaks is one of the major issues to be addressed, one may be sufficiently confident to the ability of geochemical surveying methods to detect any variability of the fluid composition that may be related to processes other than naturally occurring ones. In the present case, a distinction has to be made between the lake itself and its surroundings. As in other locations, onshore monitoring methods allow to highlight areas with gas releases greater than the environmental background and to define the migration pathways in terms of intensity of gas feeding, using several species (e.g. CO₂, He, ²²²Rn) of different behaviours.

- Assessing the behaviour of gas releases in water bodies is much more complicated. Here we have used logging probes and sampling to the characterisation of the Laacher See which is an open water body that is easier to survey that groundwaters and deep aquifers. Even in such preferential conditions, it is highly difficult to clearly advocate of the location of deep gas and/or other fluid feedings. Indeed the surveying of open waters adds many contingencies that do not exist at deeper horizons, such as photosynthetic processes in the present case, but interrogations may exist regarding the capacity to highlight small variations in deeper aquifers and link them to CO₂ storage operations.

- Especially, as long-term monitoring is highly desirable, there is a complementary requirement that may not be totally addressed until now concerning the technological gap that exists for some monitoring parameters, such as months-long pH, dissolved oxygen or redox potential measurements. Long-term gas monitoring in the unsaturated zone or at the soil/atmosphere
interface is presently better technically constrained as sensor drifting may be overcome or biofouling effects may have lesser impacts on measurements.

As a consequence, geochemical monitoring techniques that are to be used for CO₂ storage characterisation and surveying must focus on several aspects rather than simply relying on a unique set of methods (i.e. focus on gas or water surveying). Gas monitoring with surface techniques would only be relevant if there are some geological structures that may allow gas migration. At the opposite, gas and water monitoring at depth, through dedicated monitoring boreholes, may allow to monitor gas migration e.g. via regular water logging, but suffers from a major drawback as boreholes only represent punctual structures compared to storage size. Despite this disadvantage, geochemical monitoring must be envisaged in such CO₂ storages, as it is the only method that is able to evaluate chemical changes resulting from CO₂ injection, as geophysical methods are best suited for monitoring plume migration along time.

Acknowledgments

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Figure captions

Figure 1: site location: green dashed area: soil gas survey done in 2007; labelled yellow points: emplacement of CTD probe logging; labelled blue squares: in-situ water sampling location

Figure 2: a) evolution of the electrical response of the CO₂ sensor with time when exposed to progressive CO₂ enrichment (gas phase); b) and c): evaluation of the sensor’s equilibration time: b) when exposed to tap water (low CO₂ content) at time 0 after equilibrating in CO₂-rich water; c) when exposed to injection of 10 % vol. of CO₂ gas in water (starting at time 0).

Figure 3: water logging of Détente well: plot vs. depth of water temperature, pH and CO₂ (as mV value); dashes along the depth axis figure the depths where stops were made during logging. Lower right graphs represent the variation of the CO₂ value as a function of water temperature and logging duration.

Figure 4: meteorological parameters (air temperature, rainfall amount, barometric pressure, sunshine duration and relative humidity) before and during the survey; data from Koblenz-Bendorf weather station, http://www.weatheronline.co.uk/.

Figure 5: plot of soil gas measurements vs. time of sampling.

Figure 6: soil gas species along the western shore of lake Laacher See. Interpolation is done using natural neighbour computation, and is only valid near the set of 86 measurements (location represented by dots on central inset). Location of the western shoreline of the lake is indicated. Grid scaling: 20 m interval.

Figure 7: Schöeller-Berkaloff diagram showing major ion contents of Erlenbrunnen mineral spring and Laacher See (LS) lake from near surface (-1.7 m) to bottom (-46 m); surface and bottom characteristics of Lake Pavin water (French Massif Central) are also indicated for comparison (BRGM, 2009, unpublished data).
Figure 8: synthetic view of deepest logs acquired in the Laacher See. Labels in captions refer to Figure 1. Data from May and September months are from Aeschbach-Hertig et al. [25]. The inset in O₂ vs. depth diagram shows the relationship between O₂ and pH.

Figure 9a: interpolation map drawn using the natural neighbour algorithm: evolution of temperature at selected depth; X-axis refers to longitude, Y-axis to latitude; crosses indicate location of data used for interpolation (also shown in the corner right inset).

Figure 9b: evolution of conductivity (at 25°C) as a function of depth; same symbolism as for Figure 9a.

Figure 10a: interpolation map: evolution of pH as a function of depth; same graphical chart as in Figure 9a.

Figure 10b: evolution of dissolved oxygen as a function of depth; same graphical chart as in Figure 9a.

Figure 10c: evolution of redox potential as a function of depth; same graphical chart as in Figure 9a.

Figure 10d: evolution of dissolved CO₂ (expressed as an electrical potential value – warning: the absolute value is taken) as a function of depth; same graphical chart as in Figure 9a.

Figure 11: schematic representation of the CO₂-rich areas around or in the Laacher See; labels 19, 27 and 29 refer to bibliographic references.

Tables

Table 1: Soil gas measurements statistics: a) Laacher See site; b) Obermendig site.

Table 2: Correlation matrix – all data (Pearson coefficient).
Table 3: gas chromatography results; samples location is indicated in Figure 3; d.l.: detection limit; precision of isotope ratio measurements is ± 0.1‰ VPDB.

Table 4: chemical analyses of Laacher See water and Erlenbrunnen mineral spring; chemical balances are in the range -2 to +4%. For samples LSX refer to Figure 1 for location; sampling depth is indicated after the hyphen. Saturation index (SI) and mmol/l concentrations of carbonated species (TDIC = Total Dissolved Inorganic Carbon = H₂CO₃ + HCO₃ + CO₃) are computed using Diagramme software (http://www.lha.univ-avignon.fr/LHA-Logiciels).

Table 5: dissolved gas contents (mol/l) measured on water samples taken from 10 to 46 m depth in the water column. LSX refer to samples location as indicated in Figure 1; depth is indicated after hyphen; l.d.: limit of detection; l.q.: limit of quantification; n.d.: non detected.