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How to establish CO₂ flow/concentration warning levels based on the geochemical monitoring baseline: specific case of CO₂ storage at Claye-Souilly (Paris basin).

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Abstract

An appropriate monitoring program proving CO₂ can be stored safely for a long time is a key factor in controlling long term storage efficiency of CCS projects. A site in the Paris basin near Claye-Souilly area was identified for a future CCS pilot project. Baseline acquisition is deeply complex due to the presence of multi CO₂ sources (biogas, vehicles, industrial operations, natural sources). Campaigns of measurement have demonstrated the feasibility of such strategy to detect gas transfers from subsurface equipment. Survey of CO₂ storage is greatly affected by site activity and requires the development of efficient sensors in deep boreholes.

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Keywords: CO₂ flow, CO₂ concentration; monitoring program; biogas; baseline; waste cell

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1. Introduction

Considering the objectives of the greenhouse gas emission reduction, Veolia Environnement began in 2005 a research program on the capture and storage of CO₂ with the aim of improving knowledge and developing site specific solutions to suit the differing sizes and types of its client's facilities. Managing roughly 100,000 sites throughout the world, including combustion facilities and non-hazardous waste landfills, Veolia Environment Research & Development launched an assessment of a geological storage

experiment to identify the technological and economical validity of CCS implementation and define a baseline strategy.

A non-hazardous waste landfill in the Île-de-France region was identified for a possible CCS pilot project in 2008. With close to 2 million tons of waste landfilled annually, the waste disposal of Claye-Souilly is one of the most important non-hazardous waste landfills in Europe. The waste is compacted in shallow horizontal layers in waste cells. Each cell is equipped with waterproofing, drainage for the liquids (leachates) that percolate through the waste, and a landfill gas recovery system. Residual wastes contain materials that are for the most part biodegradable. When they decompose in an oxygen free environment, they give off a biogas that is mainly composed of CO₂ and methane, a more harmful greenhouse gas than carbon dioxide. This biogas, collected in the first 20 m of the shallow layers of the waste cells, presents an important challenge for the elaboration of the monitoring program.

Veolia goes beyond the regulations requiring collection of this biogas and generates an increasing amount of electricity from it. Claye-Souilly site has a combined-cycle gas turbine, boiler and steam turbine that recover 17,000 Nm³ per hour of landfill gas used to supply the energy production units. In total, the biogas combustion plant generates about 0.1 Mt/y of CO₂.

On the basis of a preliminary site selection study, detailed studies were carried out to confirm that the selected site was adequate to store 100 000 t of CO₂ per year. The CO₂ is produced from a waste-supplied thermal power plant and could be captured by the special units. Different scenarios were studied to assess the possibility to inject the supercritical CO₂ into a saline aquifer in targeted Triassic sandstones, located at a depth of more than 2000 m. The geological preliminary studies were carried out in order to determine the injectivity, the storage capacity and the cap rock integrity to insure the technical feasibility of CO₂ storage in the targeted rock Triassic formation.

The results of the seismic Claye Souilly site, reprocessing of 330 km of existing profiles, are described in [1]. Each step of the construction of the geological model based on the data of the Ile de Gord field (drilling report, reservoir maps, well logs ...) is presented in a separate paper [2]. Once Claye Souilly site was identified for potential CO₂ storage, different preliminary studies were launched to select suitable monitoring program.

The quantitative establishment of this initial baseline is an imperative of any CO₂ storage site to be able to distinguish the “conventional fluctuations” from any abnormal CO₂ emission, as future CCS projects should provide the demonstration of the safety and the absence of leakage at all levels [3], [4]. This paper is focused on the monitoring program in a very challenging environment and provides the results of the appropriate geochemical monitoring baseline that monitors the seasonal fluctuation of the gas flux/concentrations of landfill CO₂. Providing the environmentally effective and “climate friendly” waste management solutions is a challenge that monitoring program can solve by controlling the impact of each source of greenhouse gas.

2. Specificities of Claye-Souilly site

To define a monitoring program on the basis of the site characteristics, three main specificities and associated technical challenges were considered:

- Biogas at shallow depth in “modern” isolated waste cells

The average landfill gas is made of: 50% methane, 35% carbon dioxide, 14% nitrogen and 1% oxygen. The gas occupies the first 20 m of the shallow layers close to the surface and represents an important challenge for the elaboration of the monitoring program by comparison to other CCS projects.

- Ancient non equipped waste deposit below or near the shallow waste cells

Before the implementation of the biogas collection program, the Claye-Souilly site has stored similar wastes without confinement and gas collectors.

- Urban area

A particular attention was required on the monitoring program as the Claye-Souilly site is located in a dense urban area only 10 km from the biggest French airport (Paris-Charles de Gaulle) with a high way that goes along the industrial site and less than 550 m from the high speed train, and near the medium size city of Claye-Souilly.

Taking into account the specificities of the site and on the basis of previous monitoring results on natural CO₂ production site [4, 5, 6 and 7] and existing French research program [8], the main objectives of the future geochemical monitoring is to control, test, optimize and validate the various types of technologies or combinations of technologies, appropriate to guarantee the safety of the CO₂ storage site at all levels where storage could impact the environment. At the surface, the initial goal was to establish a network of surveillance points and the alert thresholds with regard to the natural emission, impact and variability of CO₂ from biogas. The additional important information, expected from the baseline measurements was the assessment of the seasonal fluctuation of CO₂ near the location on the possible injection well.

3. Geochemical monitoring techniques applied to surface gases

Following monitoring tools and technologies were used for the baseline geochemical monitoring:
Conventional accumulation chambers method and CO₂ mobile infrared sensor

Previously measurements have shown the necessity of associating conventional accumulation chambers and mobile IR sensor (MSR PTC 82-1160) for surface CO₂ mapping.

This whole portable device is supported by a specific mobile device dedicated to the immediate measurement of the surface atmospheric CO₂ (+1 m), the temperature and the atmospheric moisture content. The precision of this sensor to CO₂ is of +/-30 ppm in a range of concentrations going from 30 to 9000 ppm.

Concerning the measurements of CO₂ flux at the soil/atmosphere interface, the measurements are made by accumulation chambers (INERIS CARE method) connected to high-resolution sensors [9], [10]. These measurements are subordinated to the continuous recording of the conventional meteorological parameters (temperature, atmospheric pressure, wind directions, moisture...).

With using measuring devices, the range of flux measurements spreads out from 0.05 to 4000 cm³.min⁻¹.m⁻². The threshold of detection for CO₂ is located between 0.01 and 0.05 cm³.min⁻¹.m⁻², according to the local conditions of the site. This establishes a very low limit of detectability of CO₂ flux that is below the usual level of biogenic origin emissions as observed in Europe [10], [11].

Based on the detailed topographical characteristics of the site and the waste cells locations, the specific measurement network was proposed and each landmark, associated to the measurement point has been geo-referenced to ensure the Claye Souilly repeatability of each measurement campaign.

The measurement network applied on Claye Souilly site is presented fig. 1. The position of 162 measurement points distributed on about ten square km have been defined as follow:

- 50 points on a limited area around the position of the possible CO₂ injection well, located at the North West part of the site.
- 100 points distributed on the different waste cells
- 10 points distributed on a natural soil outside of the Claye-Souilly landfill site.
- 2 points located on geological fault area.

It must be remembered that gas flux and concentration measurements can be strongly influenced by the interaction with biogas produced on Clay Souilly site.

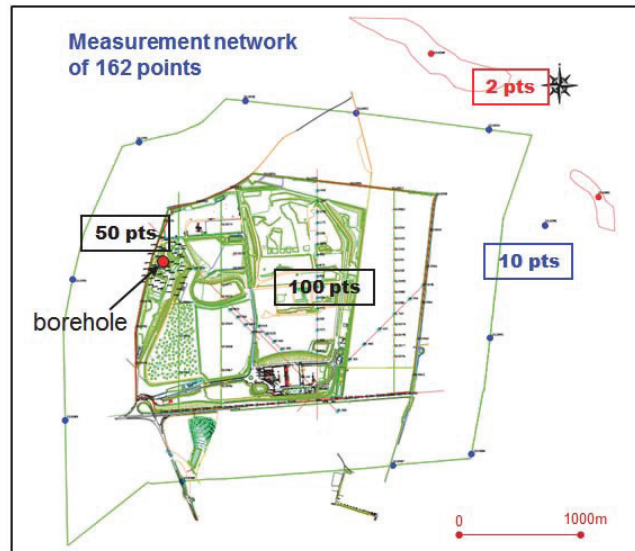


Fig.1: Claye-Souilly site with the location of the measurement network and the borehole

The geochemical platform for continuous gas measurements in boreholes.

The constant optimization of the continuous measurements of the gases from an instrumented drilling is a regular activity of SOLEXPERTS Company. In partnership with the Université de Lorraine, a geochemical platform for continuous soil gases measurements was set up. The figure 2 shows the principle of the gas continuous measurement module constituted by three parts: 1) the completion, 2) the circulation gas system and 3) the Fourier transform infrared sensor.

The completion is equipped with a chamber isolated of the rest of the column by a packer (Fig. 2) and allowing gas collection and circulation towards the IR sensor. The inside borehole temperature, gas pressure and pumping flow rate are also monitored. The system is connected to a circulation gas module with numerous removing sampling cells. The monitoring borehole is located in the North West part of the site, near to the possible location of the CO₂ injection well.

The infrared sensor (Bruker, Alpha spectrometer single compartment) is equipped with a gas cell with a fixed 5 cm optical path. Spectra are recorded in transmission mode on the range 5500-500 cm⁻¹ with a 1 cm⁻¹ spectral resolution and a 2 zero filling. Each measurement is the average of 10 scans and is recorded each hour.

Calibration of IR sensor was acquired at Université de Lorraine laboratory using a procedure described in [12] and the following limits of sensitivity have been established:

- For CO₂: +/-8 % for a concentration from 150 ppm to 294 000 ppm in total ranges of pressure from 950 to 1050 mbar. +/-7 % for a concentration from 102 000 ppm to 330 000 ppm in ranges of total pressures from 950 to 1050 mbar.
- For CH₄: +/-6 % for a concentration from 0 to 200 000 ppm to total ranges of pressure from 950 to 1050 mbar.

The experimental protocol includes two interfaces of measurements (OPUS -Bruker Optics and GEOMONITOR-Solexperts) and a friendly interface of display (WEB DAVIS-Solexperts). The interface OPUS, is used for managing the parameters of the IR sensor and the measurement. Quantitative treatment

of transmission IR spectra is made through a specific laboratory software [14], [15]. This will lead to the establishment of a specific tool to appreciate any abnormal deviation of the CO₂ concentration with regard to a standard state behavior.

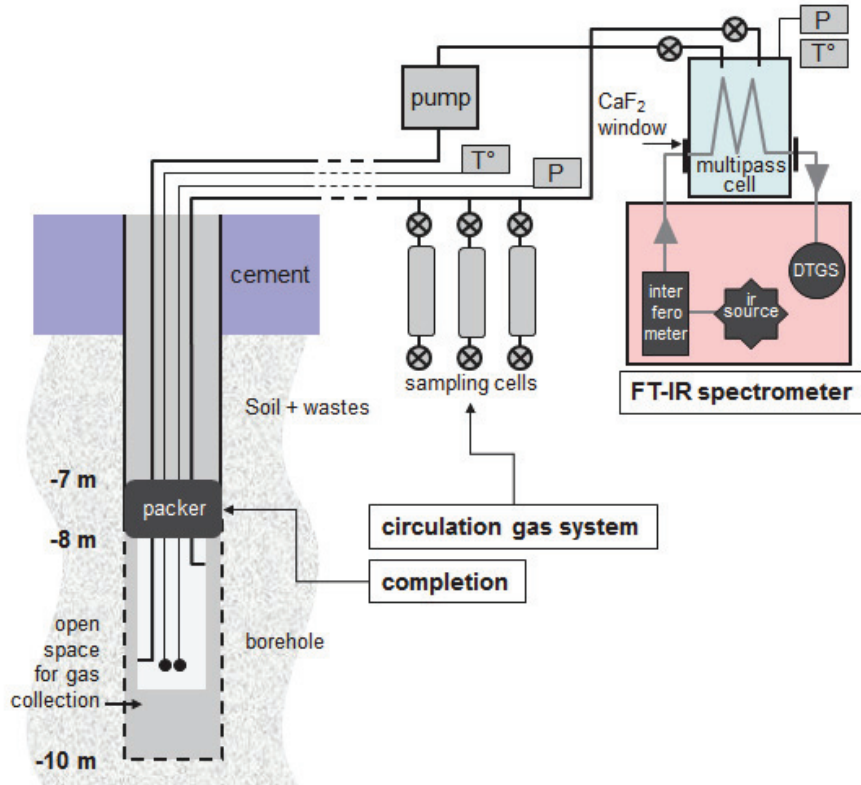


Fig. 2: The geochemical platform for continuous gas measurements in borehole

4. Sub-surface gas measurement results

Biogas:

Gas from collector before the gas plant has been sampled. Average chemical analysis of biogas for October 2009 is given in table 1. Main gases are CH₄ and CO₂ with some complementary minor organic gases. Some small variations can be noticed as a function of the type of the waste cell, with a maximum variation of +/- 18% for major and +/- 110% for minor gas concentration. Biogas is methane dominated. The N₂/O₂ is O₂ depleted compared to the atmosphere.

Table 1: Average chemical analysis of biogas

	CO ₂	CH ₄	N ₂	O ₂	Propane	n-Butane	i-Butane	Propene
Major (%vol)	34.9	42.7	19.4	3.1				
Minor (vpm)					4.2	5.5	3.3	8.4

CO₂ fluxes and atmospheric CO₂ concentrations at the soil/air interface

The first measurements on Claye-Souilly site were performed during one seasonal cycle period (October 2009, March 2010 and September 2010) in order to appreciate climate seasonal variations of CO₂ flux and concentration levels on the site of Claye-Souilly before any injection operations. They were firstly focused on surface (0 to +1m) and were relative to CO₂ flux (0m) and surface atmospheric concentration determination (+1m).

A 2D/3D illustration of typical GOCADTM interpolated map of CO₂ flux obtained on Claye-Souilly site in March and September 2010 (Fig. 3). Quick overview of fig. 3 indicates that biogas capture system developed on the site is effective with CO₂ fluxes variations included between 0 and 253 cm³.min⁻¹.m⁻². This aspect will be developed further. Map of CO₂ flux of March 2010 and September 2010 show clear differences (high flux in the central part in March, and along the high way in the southern part in September) and some similarities (high flux at the eastern part of the area of measurements). Some of these variations are passing (central) and some other are persistent (eastern part). This approach can be also extended to annex gases including artificial tracers. This kind of 2D/3D interpolated map will constitute the first step of gas baseline quantitative definition allowing to estimate the temporality of gas transfer processes.

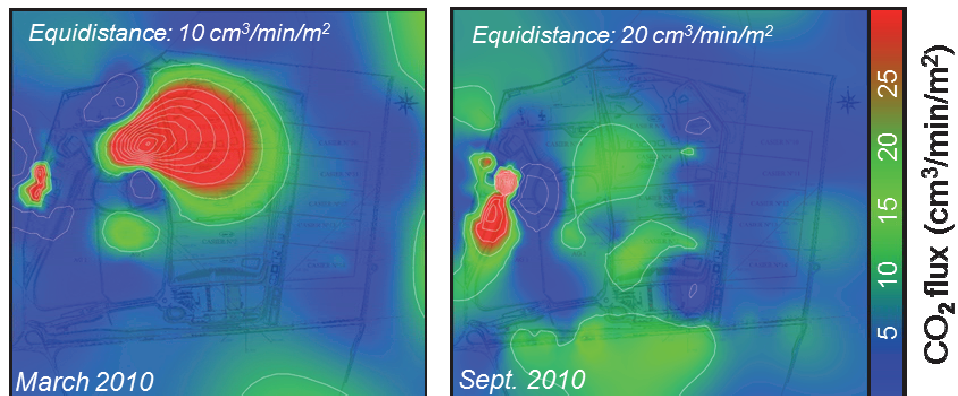


Fig. 3: Typical 2D/3D interpolated map of CO₂ fluxes measured at the air/soil interface of the landfill site of Claye-Souilly.

Fig. 4 shows two maps of CO₂ concentration obtained on North-West part of Claye-Souilly site at 1 m above the soil in March and September 2010. CO₂ concentrations vary from 390 to 580 ppm. Comparisons of concentration maps for March 2010 and September 2010 show that atmospheric concentration was different for the two periods of time.

The campaign of September 2010 has allowed distinguishing three spots of emission with CO₂ flux around 30 cm³.min⁻¹.m⁻² (fig. 3). These three spots are more or less superimposed to the maximum of atmospheric CO₂ concentration (> 560 ppm). They can be assigned to gas leakages from old waste cells

non-equipped with liners at the time of waste deposition. The highest CO₂ concentrations are located in topographic depressions.

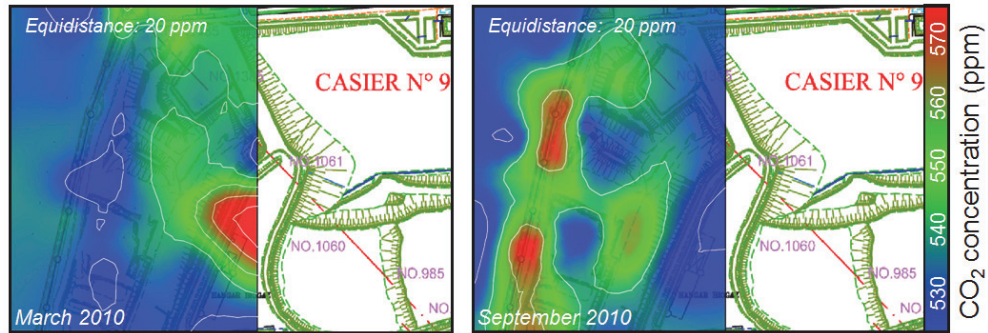


Fig. 4: Typical 2D/3D interpolated map of CO₂ concentrations measured at the air/soil interface of the landfill site of Claye-Souilly.

This explains that gases are present in the soil by diffusion from neighboring waste cells and can be exchanged with the atmosphere. Such 2D/3D maps strongly argue for the existence of abnormal emissive areas in the north-west segment of the Claye-Souilly site.

Gas from the borehole

Previous CO₂ flux/concentration observations in the North West part of the site have been confirmed by soil gas continuous measurements at -10 m depth. CO₂ and CH₄ concentrations in the borehole are similar to those of the biogas. CH₄ concentration remains more or less constant during a period of measurement of 14 months. CO₂ concentration increased during the same period of time. These gases at 10 m depth have similar composition to biogas but show an increase of the CO₂/CH₄ ratio with time, probably due to changes in microbiological activity. High concentrations of CO₂ and CH₄ in soil have been also detected, mainly around the borehole and near the highway. No isotopic difference has been detected with $\delta^{13}\text{C}\text{O}_2$ varying between -12 and -16‰, $\delta\text{C}^{18}\text{O}_2$ between 28 and 33‰, and $\delta^{13}\text{C}\text{H}_4$ varying between -42 and -53‰. This definitively concludes that biogas is still present in the soil at this North-West part of the Claye-Souilly site and is partly exchanged with the atmosphere. However, the gas concentrations in surface air stay very low and do not present a danger for human health or safety.

Seasonal evolution of the average CO₂ fluxes and concentrations

Average natural CO₂ flux vary in France between 2 and 8 cm³.min⁻¹.m⁻², according to the season, and normal CO₂ concentration in the atmosphere is situated between 390 and 500 ppm. [12] [13]. Figure 5 shows the variations of temperature, relative humidity and CO₂ concentration for the three campaigns of measurements. It appears that the dispersion of CO₂ concentration data is weak when temperature and relative humidity dispersion data were the weakest in September 2010. This explains the good correlation between CO₂ flux and CO₂ concentration only observed for the third campaign of measurements.

Despite some anomalous emission zones indicated in fig. 4 and 5, the data show clearly that average CO₂ fluxes and atmospheric concentrations in studied Claye Souilly site are similar to reference values in natural environment. These results show the very good efficiency of the biogas collection in most parts of the site.

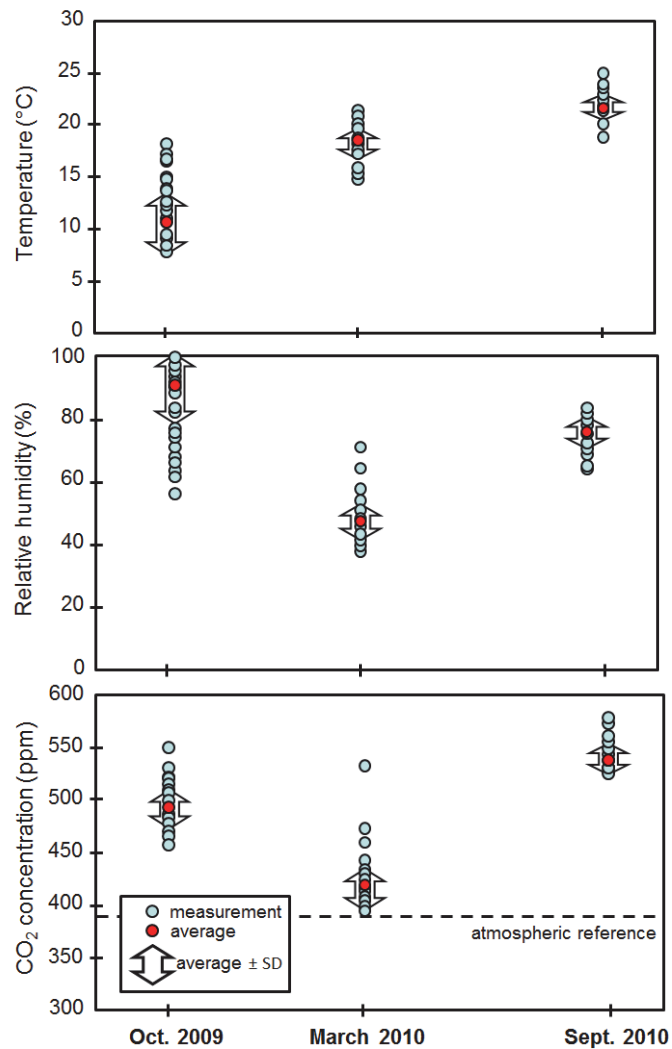


Fig. 5: Temperature, relative humidity and CO₂ concentration recorded for the three periods of measurements for the landfill site of Claye-Souilly.

5. Discussion and conclusion

On the base of our results obtained on the Claye-Souilly site and focused in the possible CO₂ injection well area, tables 2 and 3 collect the average values (Ave) of each campaign as well as the standard deviation (σ) for CO₂ flux and concentration respectively. The values of threshold of vigilance (Tv) for every campaign are indicated as well as the global average standard deviation. The threshold of vigilance

is defined as the level from which the flux or concentration of CO₂ is judged acceptable range of variability. For CO₂ flux, Tv can be written as follow:

$$Tv = (\text{Max} - \text{Ave}) / \sigma.$$

For CO₂ concentration, it must be taken into account the standard CO₂ atmospheric content (390 ppm) and Tv becomes:

$$Tv = (\text{Max} - \text{Ave}) / \sigma + 390$$

Table 2: Threshold of vigilance for CO₂ fluxes in the area of the CO₂ injection well of the Claye-Souilly site.

Campaign	Average Ave (cm ³ .min ⁻¹ .m ⁻²)	Standard deviation σ (cm ³ .min ⁻¹ .m ⁻²)	Flux Min-max (cm ³ .min ⁻¹ .m ⁻²)	Maximum range of variability Rv	Threshold of vigilance Tv _{flux} (cm ³ .min ⁻¹ .m ⁻²)
Oct. 2009	5,3	4.4	0,0 - 25,8	4.6 σ	25.5
March 2010	8,6	23,4	0,7 - 129	5.1 σ	34.6
Sept. 2010	14,8	40,6	0,0 - 253	5.9 σ	254.3

Table 3: Threshold of vigilance for CO₂ concentration in the area of the CO₂ injection well of the Claye-Souilly site.

Campaign	Average Ave (ppm)	Standard deviation σ (ppm)	Concentration Min-max (ppm)	Maximum range of variabilityRv	Threshold of vigilance Tv _{concentration} (ppm)
Oct. 2009	492	17,5	460-554	3.6 σ	607
March 2010	416	20,8	390-540	6 σ	540
Sept. 2010	539	13	535-573	2.6 σ	573

The baseline measurements indicate that the average levels of CO₂ fluxes and concentrations on the whole Claye-Souilly site, except for points of evidences of biogas contribution, are close to the average background level of flux and concentration [12], [13] in similar climatic areas. Moreover, weak gas exchanges between soil and atmosphere can be revealed by such monitoring approach.

On the base of the results of tables 2 and 3 and in spite of the existence of located areas of stronger emissivity, we can note that the seasonal variability combined with the industrial activity of the site, does not strongly disrupt the threshold of vigilance for CO₂ flux and concentration.

Nevertheless, the definition of “threshold of vigilance” and of “threshold of alert” needed for the operator to have the tangible indicator of the site monitoring program still remains, at this stage of the study, a difficult notion to define and to quantify because of four fundamental reasons:

- transfer of biogas from soil to atmosphere can be superimposed to natural CO₂ flux from soil, then, the variability from a point to another of the railing, for the same seasonal period, can reach six times the standard deviation,
- presence of biogas is clearly detected down to 10 m depth in North-West area of the site,
- biogas composition at -10 m varies with time,
- the CO₂ flux and concentrations in deeper levels (from 10 to 2500 m depth) are unknown,
- the measurement campaigns did not allow covering more than one seasonal cycle,
- at the surface, the variability between wintry / autumnal season and summer season is important.

By consequence, thresholds of vigilance determined in tables 2 and 3 cannot be used for an efficient survey of such a site.

Special challenges of the Claye-Souilly site can classify this specific site as the “worst case” for the monitoring environment. They can be summarized in 5 main following categories:

- Presence of biogas at shallow depth,
- Multi CO₂ sources (natural emission from soil, airport, highway, power plant, biogas),
- Operating industrial site [1 km x 1 km] dedicated to waste repository with accessibility restrictions,
- Neighboring operational oil field,
- Urban area located near the industrial site

To propose an appropriate monitoring program, two years’ work has allowed us to establish a complex monitoring program that addresses all aspects of geochemical monitoring. The undertaken work combined different well-known and advanced measurement technologies. The sampling strategy and the measurement grid of 162 points took into account geologic, industrial and biologic characteristics of the site. It allowed us to construct CO₂ flux and concentration maps. Chosen surface technical strategy was a combination of in-situ monitoring sensors at different levels. Nevertheless leakage detection in such site needs deeper monitoring systems below the biogas-rich zone. It can be proposed an additional monitoring borehole and great depth equipped with 1 multi chambers completion for the continuous monitoring of the intermediate aquifers at several hundred meter depth.

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