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Philippe de Donato, Jacques Pironon, Jérôme Sterpenich, Alain Laurent, Médéric Piedevache, et al.. CO2 flow baseline: Key factors of the geochemical monitoring program of future CO2 storage at claye-souilly (Paris basin). *Energy Procedia*, 2011, 4, pp.5438-5446. 10.1016/j.egypro.2011.02.529 . hal-02529905

HAL Id: hal-02529905

<https://hal.science/hal-02529905>

Submitted on 3 Feb 2021

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GHGT-10

CO₂ flow baseline: key factors of the geochemical monitoring program of future CO₂ storage at Claye-Souilly (Paris basin).

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Abstract

Two main deep saline aquifers have been identified in the Paris basin for possible CO₂ injection: carbonate reservoirs from the Dogger and Triassic sandstones. These two targeted reservoirs are located at convenient depths for supercritical CO₂ storage between 1500 and 2500 m in the center of the Paris basin and show good sealing properties on the upper cap rock. To control long term storage efficiency of CCS projects it is essential to design and implement an appropriate monitoring program that proves that CO₂ can be stored safely for a long time.

A future monitoring program will be focused on three main axes: a geophysical, geochemical and biological. This paper presents the global monitoring methodology developed to address geochemical aspects of future CO₂ storage sites. Three major compartments must be monitored for a well representative CO₂ flow baseline: the geosphere, biosphere and atmosphere compartments of the specific site. Viability of any CCS project is strongly dependent on the of our capacity to well establish a realistic quantitative baseline system integrating natural and anthropogenic contributions in each compartment. For these reasons, our technical strategy must a combination of in situ and continuous monitoring systems. On the basis of previous and present day research programs conducted on natural CO₂ storage sites, an in-situ monitoring combined methodology matrix adapted to CO₂ storage at Claye-Souilly site in Paris basin deep saline aquifer is argued. The presentation will also integrate the proposal of new development in optical sensors (Infrared, Raman and Laser) for gas quantification and traceability including the isotopic aspects.

Geosphere monitoring strategy must be mainly conducted through an original multi packers system allowing simultaneously reservoir, rock formations and strategic aquifers observations. In the reservoir, continuous acquisition of geochemical and hydrodynamic parameters is of first importance for adjusting and limiting the divergence criteria of the models and to adapt the injection procedure. In upper rock formations, establishment and modeling of gas transfer curves, will constitute a sensitive and powerful in-situ leakage detector tool. Biosphere survey strategy can be based on conventional accumulation chambers and dynamic flow chambers systems. The surface sampling network must be adapted on the basis of geological and structural characteristics of overburden rock as revealed by previous geophysical investigations. A remote infrared scanning sensing system combined with a laser remote system must support the

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atmosphere compartment survey strategy. The use of such combined remote system yields a spatial and temporal imaging of the CO₂ and its dynamics in air. Sensitivity of leakage detection will depend on the chosen sensing system and the amount of CO₂ injected. While variability of CO₂ flux and concentration vary with time and with geographic location, they will both depend on the investigated compartment, the natural carbon cycle and the anthropogenic events. Both, sensitivity and variability should be considered in order to establish the alert levels. Given the complexity of data, the time needed to quantify sensitivity and, variability aspects and to establish a base line system, must be longer than one year (one seasonal cycle). This aspect is of first importance to define and provide the remediation operations that must be applied in the case of CO₂ leakage on the basis of combined deep, surface and sub-surface measured gas data. Compilation of previous experiments strongly argued that our capacity to quantify variability of CO₂ flux/concentration baseline must be one major key factor in the choice of a future monitoring program for CO₂ storage site.

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Keywords: CO₂; geochemical monitoring; Claye-Souilly; Paris basin; waste storage.

1) Introduction

Veolia Environnement, which is already an international player in energy efficiency and the development of renewable energy, alternative fuels and all operating solutions that better respect the environment, is now committing resources and research teams to assess CCS technology as part of the fight against climate change.

Veolia Environnement began a research program in 2005 on the capture, transportation and storage of CO₂ with the aim of improving knowledge and developing solutions to suit the differing sizes and types of its clients' facilities. Potential sites for the CO₂ storage in France were identified and different preliminary studies were launched to select suitable monitoring program.

Veolia Environmental Services manages non-hazardous waste landfills in the Ile-de-France region, near Paris (Figure 1). From waste collection to the final phase in its transformation, all Veolia team efforts are directed at maximum environmental benefits. Ongoing research into innovative solutions and technical investments for each step in the chain have in just a few years turned our landfills into genuine resource recovery centers capable of limiting the percentage of waste landfilled and offering clean, safe processes.

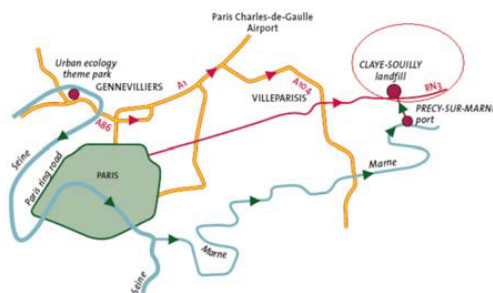


Figure 1 : Location of waste landfills in the Ile de France region (Claye Souilly site, France).

Residual wastes contain materials that are for the most part biodegradable. When they decompose in an anaerobic environment, they give off a biogas that contains about 40% of CO₂ and about 50% of methane, a more harmful greenhouse gas than carbon dioxide. Veolia goes far beyond the regulations requiring collection of this gas, and has been making substantial investments to exploit its energy potential and generate an increasing amount of electricity from the methane collected.

The CO₂ is produced by the existing biogas-to-energy units and different scenarios were studied to assess the possibility to inject the supercritical CO₂ into a saline aquifer targeted Triassic sandstones, located at a depth of more than 2000m. With close to 2 million tones of waste landfilled annually, these facilities are the

final and indispensable link in the municipal and industrial waste treatment chain.

Taking into account the specificities of the site and on the basis of previous monitoring results on natural analogs [1, 2, 3 and 4] and existing program (ANR SENTINELLE, National Research Program, 2007-2011, ref.: ANR-07-PCO2-007.), The main objectives of the future geochemical monitoring must be focused on the following points :

- o 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 level where storage could impact the environment:
- o At the level of the reservoir: verify that the evolution of the content in CO₂ is in accordance with the results of reservoir model predictions and to calibrate the modeling over time to have the most reliable possible predictive tool (together with the acquisition of the hydrodynamics parameters, P and T, K). At the level of the reservoir, the geochemical monitoring will be made at the point that will be affected by the CO₂ brine.
- o At the overburden aquifers, located above the targeted reservoir: be able to follow the natural CO₂ level to discover any abnormal variation that would be the consequence of a leak. Monitoring at the nearest overburden aquifer in order to detect any leak as soon as possible, and at the strategic aquifer to insure integrity.
- o At the surface: establish a network of surveillance and the alert thresholds with regard to the natural gas emission fluctuation linked to the natural concentration of CO₂ and its variability. The importance of surface monitoring program is amplified depending on the density of population around of the project site. An original methodology based on a triple combinatorial monitoring, geophysics, geochemical and from of the reservoir (-2,400 m) to the atmospheric compartment (up to 1,000 m).

The quantitative establishment of this initial baseline is an imperative element of the CO₂ storage project, with the aim to be able to distinguish the “conventional natural fluctuations” from the potential leak, as future CCS projects should provide the demonstration of the safety and the absence of leakage at all levels.

This paper is focused on the elaborations of the appropriate geochemical monitoring program that prove that CO₂ can be stored safely for a long time based on the best practices and lessons learned from existing natural CO₂ site and current CCS projects.

Particular efforts should be applied to elaborate the baseline that monitors the annular fluctuation of the flux of landfill gas in order to discriminate CO₂ sources and be able to trace the injected CO₂. Providing the environmentally effective and “climate friendly” waste management solutions is a challenge that a monitoring program should address to monitor and control the impact of each source of greenhouse gas.

2) Settings

Geological context

The Paris Basin is one of the three main onshore French basins (100,000 km²). Intensively explored for about fifty years, it contains a significant amount of oil produced by 39 oil fields. It's a well known area extensively described in different geological reports (IFP; BRGM, Geocapacity). According to the GEOCAPACITY European project conclusions, the Paris Basin, is the most advanced considering the CCS objectives, having the advantage of being a large reservoir system. Additionally, the saline Triassic aquifer has 2 levels of protection above (clay formations of Albian and Lias at 700 m and 1,600 m depth respectively) that limit leakage risks. A particular challenge of the CCS project in Paris Basin is the protection of the potable water Albien aquifers located at 800 m depth. As a source for energy, the Paris basin is presently producing about 25,000 bbls/d of oil, plus providing geothermal heat through numerous wells. One of the oil field named Ile de Gord is partially located at the Clay- Souilly site and the interaction of the 21 well of this oil field represents a particular challenge for the monitoring program

The geologic preliminary studies were carried out in order to obtain the infectivity, 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 reprocessing of 330 km of existing profiles are described in the GHGT 10 paper “Pertinence of the seismic reprocessing using existing seismic profiles in the Paris Basin“ . Each step of the construction of the geological model based on the data of Ile de Gord field (drilling report, reservoir maps, well logs ...) is presented in GHGT 10 the paper “Technical challenges in characterization of future CO₂

storage site in a deep saline aquifer in the Paris basin. Lessons learned from practical application of site selection methodology “.

Waste disposal of Claye-Souilly

To propose the appropriate monitoring program, the special features of the Claye-Souilly site should be identified to adjust the future monitoring program to reflect the site characteristics. A list of the particular characteristics and main associated technical challenges is provided below.

Biogas landfill gas at the shallow layers

There are five stages in the life of a landfill:

It all begins with quarrying – digging, screening and storage of materials that are sold for use in the construction industry. Once the approximately 1.6 million tons of materials have been removed, a huge cell remains for the disposal of residual wastes.

The second stage involves technical preparation of the cell, with the installation of waterproofing, drainage for the liquids (leachates) that percolate through the waste, and the landfill gas recovery system.

The third stage involves filling the cell with waste. The waste is compacted in horizontal layers, in which the landfill gas recovery system is installed. It takes four years from the decision to operate a cell to the end of cell operation, when nature begins to take over again. The average composition of recovered landfill gas is 50% methane, 35% carbon dioxide, 14% nitrogen and 1% oxygen. The biogas collects in the first 20 m of the shallow layers close to the surface that represent a important challenge for the elaboration of the monitoring program.

The fourth stage begins when the cell is full, when it is grassed over and planted with trees and shrubs indigenous to the area.

The fifth stage, post-closure, lasts 30 years, during which time all aspects are monitored and landfill gas and leachate collection continues.

Biogas-to-energy units

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 fire the energy production units.

The gas feeds steam boilers, which are equipped with burners that automatically adjust to the methane content of the gas.

The superheated steam drives a multi-stage condensing turbine. The mechanical power produced is transformed into electrical power by a generator. The electricity is transferred by a transformer to the EDF grid.

Urban area

Particular attention was required on the monitoring program as the Claye-Souilly site is located at the urban area only 10 km from the biggest Paris' airport, less than 550 m from the high speed train and near the medium size city.

3) Monitoring strategy

It is useful to make a bibliographical synthesis by compartments of the main original continuous geochemical types of monitoring and to clarify their sensibility. All these numerical values are relative to measures in real conditions in the natural environment.

The superficial Geosphere (-2400 to 0 m) monitoring concept is based on continuous measuring geochemical parameters at different levels including the target layer (Triassic reservoir: -2400m), the cap-rock and the main overburden aquifers (Lias, Dogger, Malm, Albien/Neocomien, Tertiary). The different horizons of interest are isolated in a borehole using a reliable multi packer ground water monitoring systems. A major innovation regarding in situ monitoring techniques is the use of miniaturized IR or Raman spectroscopy probes. These retrievable probes are placed directly within the ground water observation intervals, through access tubes. Probes are adapted to the pressure, temperature and water conditions and can be removed at any time to ensure maintenance and calibration. Data transfer is done through optical signal up to the surface. Besides the above-mentioned in-situ geochemical analysis tools the multi-packer system intervals are equipped

with pressure and temperature sensors. Additionally the multi-packer system allows carrying out hydraulic testing in order to determine the hydraulic conductivity and taking ground water samples under formation pressure for standard laboratory analysis. Two or three observation wells depending on the site specific hydrogeology, geology, infrastructure and at risk studies are probably needed for a reliable monitoring of a site. Figure 2 presents schematically the design for two multi packer systems for reservoir, cap rock and aquifers geochemical survey.

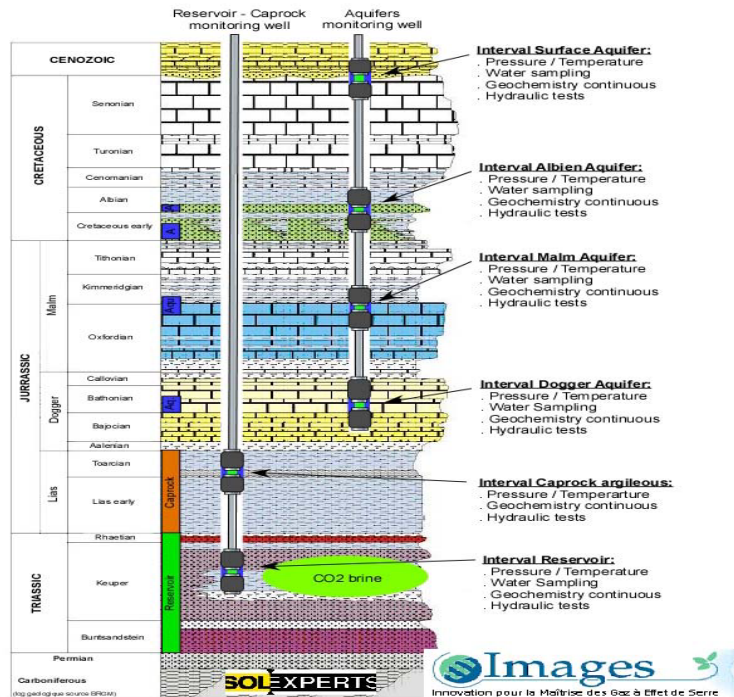


Figure 2: Typical design of two multi packer system for in-situ continuous and simultaneous geochemical monitoring of a) target layer and cap rock and b) overburden aquifers. These two completions are specific for CO₂ storage in the basin of Paris.

Specific Soil survey (0, -30m) will be developed through specific monopacker system.

In a shallow borehole, one observation interval is isolated from the surface with a mono-packer system. Within the packed off observation intervals the dissolved gases in the pore water are separated by a special collection chamber. These retrievable cells are connected to a closed noble gas filled circulation system linking the down hole cells with the analysis equipment at the surface.

Geochemical data will be mainly collected by optical technologies such as IR and RAMAN sensors and isotopic data will be collected mainly through micro gas chromatography combined to mass spectroscopy (μ GCMS) and wavelength scanned cavity ring down spectroscopy (WS-CRDS).

The sensor specifications are:

- o For wide spectral range infrared sensors (600-4000 cm⁻¹) combined to specific gas cell with variable optical path, the range of detection will go from 1 ppmv to 100 % of CO₂ with an

average error varying from 1 to 5 % [3], [5], [6] and [7]. More over, simulations of CO₂ leakage has shown that CO₂ detection at long distance (until 1000 m) is possible. [8], [9].

- For the Raman sensors equipped with optical fibers, the range of concentration goes from 400 ppmv to 100 % of CO₂ with a sensibility varying of 10 % (weak content) to 1 % (CO₂ > 2000 ppmv). [10]
- For the continuous isotopic measurement of ¹³CO₂, the range of average concentration of WS-CRDS goes from 10 ppbv to 2000 ppmv with neighbour's precision of 0,3%. [11]

Concerning the measurements of the vegetal area from soil surface to trees level (0 to 10 m), at the interface ground / air, the measures are made by typical chamber devices like accumulation chambers or dynamic chambers. The sampling strategy and the measurement grid must takes into the account geologic and biologic peculiarities of the site. At the level of the plant place setting, the measures of the dynamics of exchange are made by the method of turbulent correlations on a distance of 0 to 1,000 m. These measurements are subordinated to the continuous recording of the conventional meteorological parameters (temperature, atmospheric pressure, wind directions, moisture,...).

The sensor specifications are:

- For the accumulation chamber, the range of flux measurements spreads out from 0.05 to 4000 cm³.min⁻¹.m⁻² [8], [12]. With sensibility of gas sensors used (0,5 to 1 ppm), the threshold of detection for CO₂ and CH₄ fluxes 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 CO₂ flux detection, in comparison with the usual level of biogenic CO₂ emissions [9].
- Otherwise, technology operating with the method of turbulent correlations, is well developed and used as reference method for the measurements of the CO₂ exchanges between the biosphere and the atmosphere [13]. The ranges and the thresholds of sensibilities are equivalent to those indicated for sensors using an accumulation chamber. Other parameters are also continuously recorded, in particular those related anemometric data.

In the case of landfills, like studied Claye-Souilly site, it must be remembered that these detection limits can be strongly affected by the interaction with biogas leaks to the atmosphere.

The near atmosphere compartment (10 to 2,000 m) should be monitored because it is the final area of a migration of gas coming from the geological reservoir and the place where surface equipment failure can appear. Two main remote technologies are in strong development for atmospheric monitoring: visible laser and infrared emission remote technology. These innovative technologies are proposed as a part of global methodology. Monitoring approach is based on the use of two additional tools of 3D ground remote technologies: the remote sensing by Fourier-transform infrared emission spectroscopy typelike OPAG system and the remote sensing by laser like Lidar DIAL system. This last technology is also approached for satellite survey. The combination of infrared and laser remote technologies will provide dynamic 3D-4D fingerprints of the atmospheric gases. This will contribute to global control of the CO₂ and annex gases of the site.

The sensor specifications are:

- Infrared remote sensing was used in 2005 successfully for the analysis of the volcanic plume to foresee the eruptive potentialities of volcanoes [14]. It was also used in 2006 during the world cup of football in Germany, to survey the composition of gases in stadiums [15]. It allows an analysis of the composition of a gas mixture in long distance (0 to 2,000 m), in a volume 1 - 8 km³, and on a spectral range going from 600 to 5,000 cm⁻¹, with a spatial resolution of 10 m at 1,000 m of distance. The sensitivity for the CO₂ is better than 50 ppm.m (< on 1017 molecules.cm⁻²) with a nearby relative error of 5-10 %. [14], [15], [16]. This type of remote sensing is also sensitive to annex gases such as CH₄, NO_x, H₂S, H₂O, O₃, SF₆, ...
- For laser remote sensing, such as Lidar DIAL hétérodyme system, the measurements will be specific to CO₂ (wavelength of the laser at 2 μm). The average target is at 2,000 m. For a range of concentration varying from 300 to 1,000 ppm the precision is around +/-4 ppm. [13]

All these technologies exhibit a strong sensitivity compare to quantitative CO₂ detection. In these conditions, leakage detection limit will be mainly affected by natural and anthropogenic variability of CO₂ flux/concentration.

4) Preliminary surface results on Claye-Souilly site

Taking into account this road map for geochemical monitoring, first measurements on Claye-Souilly site were done in 2009. There were firstly focused on surface and were relative to CO₂ flux and concentration determination. Indeed, knowledge of CO₂ flux and concentration on a site before any injection is the first way for discriminating CO₂ sources. This baseline of CO₂ fingerprints will be used to identify any additional CO₂ contamination. This approach can be also extended to annex gases including artificial tracers. The 2D mapping of CO₂ concentration and flux obtained on Claye-Souilly site are given in figures 3 and 4 respectively. Increase of the measurement point network simulates the monitoring strategy around a planned injection area. Concentrations of CO₂ are acquired at 1m above the ground level using specific infrared CO₂ sensor. Flux of CO₂ are determined at the ground/atmosphere interface using an accumulation chamber device. This kind of 2D map will constitute the first bricks of baseline quantitative definition.

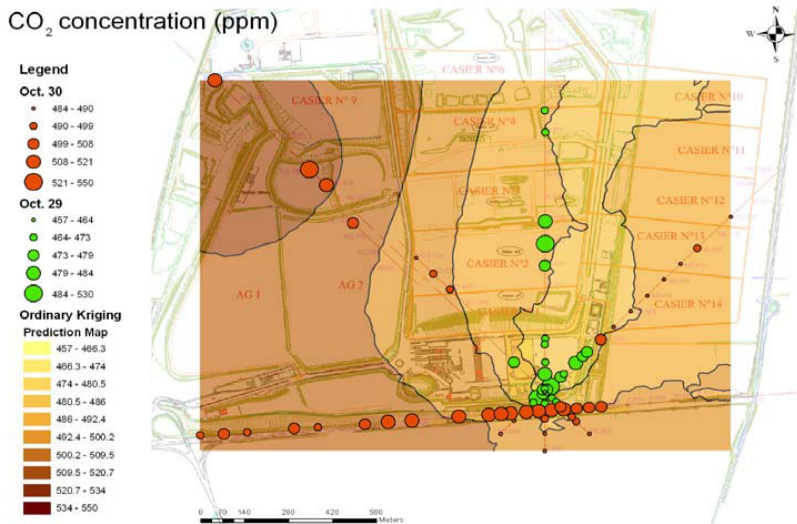


Figure 3: Typical 2D map of CO₂ surface monitoring concerning CO₂ concentration in ppm. Green and brown points indicate the two different date of measurements.

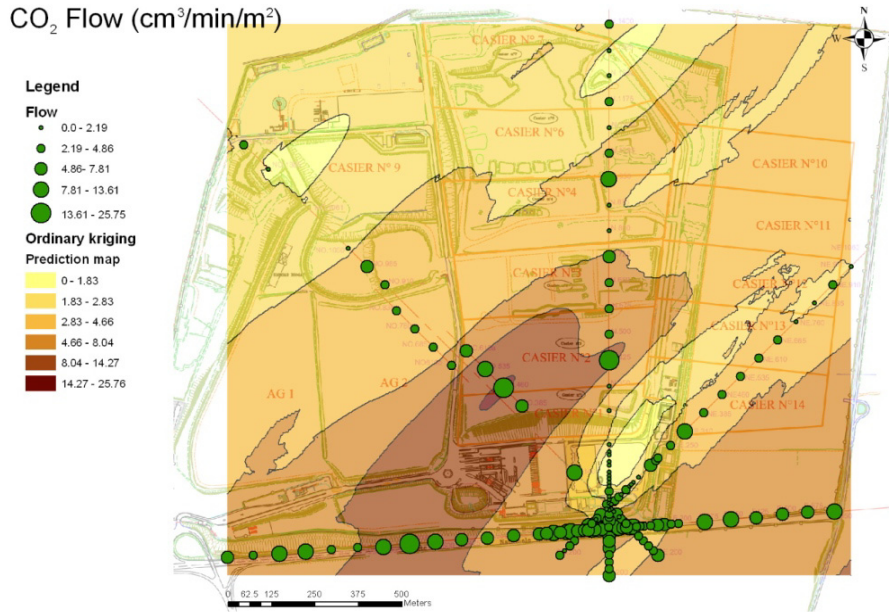


Figure 4: Typical 2D map of CO₂ surface monitoring concerning CO₂ flux in cm³.min⁻¹.m⁻². Green and brown points indicate the two different date of measurements.

8) Conclusions

The developed geological monitoring will allow:

- quantification of the flux/concentration parameters of CO₂
- identification of the isotopic signature of CO₂ for source discrimination
- identification of annex gases and tracers, markers of CO₂ migration,
- estimate of natural and anthropogenic gas flux/concentration variability,

All these information will be of first importance for quantitative baseline definition at the scale of:

- the reservoir level, where acquisition of geochemical and hydrochemical data are needed for limiting the divergence of the models and to adapt the injection characteristics if measured data are to far from calculated/predicted one,
- the overlying geological levels (cap-rocks and aquifers), where the establishments of the reference CO₂ (including annex gases) geological flux/concentration, must be determined in order to define the warning levels in case of CO₂ leakage,
- the surface level, where quantification of the natural and anthropogenic variability of CO₂ flux/concentration is one of the stronger argument for public acceptance of any sustainable CCS project.

The information collected by the implementation of the following monitoring program could be used to communicate to the authorities and to the population and to improve the acceptance of the risk related to the storage. Such procedure should demonstrate our capacity to act in a predictive way and to anticipate a potential incident and also to be able of setting up very quickly mitigation actions and risk management plan. The other advantage is to avoid any contesting on variations of the CO₂ concentration.

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