The Importance of Baseline Surveys of Near-Surface Gas Geochemistry for CCS Monitoring, as Shown from Onshore Case Studies in Northern and Southern Europe
Stan E. Beaubien, Livio Ruggiero, Aldo Annunziatellis, Sabina Bigi, Giancarlo Ciotoli, Paolo Deiana, Stefano Graziani, Salvatore Lombardi, Maria Chiara Tartarello

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**Dossier**
Edited by/Sous la direction de: F. Delprat-Jannaud

**Characterization of European CO2 Storage — European Project SiteChar**

*Caractérisation de sites européens de stockage de CO2 — Projet européen SiteChar*

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The Importance of Baseline Surveys of Near-Surface Gas Geochemistry for CCS Monitoring, as Shown from Onshore Case Studies in Northern and Southern Europe

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Abstract — The monitoring of the integrity of onshore geological carbon capture and storage projects will require an approach that integrates various methods with different spatial and temporal resolutions. One method proven to be quite effective for site assessment, leakage monitoring, and leakage verification is near-surface gas geochemistry, which includes soil gas concentration and gas flux measurements. Anomalous concentrations or fluxes, relative to the natural background values, can indicate the potential occurrence of a leak. However, the natural background can be quite variable, especially for CO2, due to biological production and accumulation in the soil that changes as a function of soil type, land use, geology, temperature, water content, and various other parameters. To better understand how these parameters influence natural, near-surface background values, and to examine the potential of different sampling strategies as a function of the survey goals, this paper reports results from two highly different case studies, one from northern Europe (Voulund, Denmark) and one from southern Europe (Sulcis, Sardinia, Italy). The small Voulund site, with its homogeneous soil, climate, and topography, was surveyed twice (in fall and in spring) within the EU-funded SiteChar project to examine the effects of different land use practices and seasons on baseline values. Forested land was found to have lower CO2 concentrations during both campaigns compared to cultivated and heath land, and higher CH4 values during the spring sampling campaign. Continuous monitoring probes showed much more detail, highlighting seasonal changes in soil gas CO2 concentrations linked primarily to temperature variations. The much larger Sulcis site, studied within an ENEA-funded project on potential CO2-ECBM (Enhanced Coal Bed Methane) deployment, was surveyed at the regional scale and on detailed grids and transects for site assessment purposes. Despite the completely different soil and climate conditions, the statistical distribution of the Sulcis data was similar to that of Voulund. Much higher soil gas CO2 anomalies were found at this site, however, due to the less permeable sediments (i.e., better water retention and greater gas accumulation) and the warmer temperatures. Detailed surveys at this site highlighted various
significant anomalies, some of which can be explained by near surface biological processes, whereas others, especially helium anomalies, were more difficult to explain. These results show the utility of baseline surveys, and highlight the need for follow-up studies to clarify any unexplained anomalies before any CO₂ storage.

Résumé — Importance des lignes de base pour le suivi géochimique des gaz près de la surface pour le stockage géologique du CO₂, illustration sur des pilotes situés à terre en Europe du Nord et du Sud — La surveillance de l’intégrité des projets de stockage géologique du CO₂ situé à terre requiert une approche intégrant diverses méthodes offrant différentes résolutions spatiales et temporelles. Parmi celles-ci, le relevé géochimique des gaz en surface s’est avéré très efficace pour l’évaluation des sites, la surveillance de fuites et la vérification de l’intégrité du stockage. Cette approche comprend des mesures de concentrations des gaz dans le sol et des mesures de flux de gaz. La détection de concentrations ou des flux anormaux est un signe éventuel de fuite. Toutefois, les concentrations en gaz et flux naturels peuvent être très variables, en particulier en ce qui concerne le CO₂, de par son processus de production biologique et de son accumulation dans le sol qui dépendent du type de sol, de l’usage des terres, de la géologie, de la température, de la teneur en eau et de divers autres paramètres. Avec pour objectif la compréhension de l’influence de ces paramètres sur les valeurs naturelles en surface ainsi que l’évaluation du potentiel des différentes stratégies de sondage, ce papier présente deux études de cas très différents, l’un dans le nord de l’Europe (Voulund, Danemark) et l’autre dans le sud de l’Europe (Sulcis, en Sardaigne, Italie). Le petit site de Voulund, avec son sol, son climat et sa topographie homogènes, a fait l’objet de deux sondages (en automne et au printemps) dans le cadre du projet SiteChar financé par l’UE afin d’appréhender les effets de différentes pratiques d’utilisation des terres ainsi que ceux induits par les variations saisonnières sur les valeurs de référence. On constate que les deux campagnes ont relevé de plus faibles concentrations en CO₂ dans les zones forestières que sur les terres cultivées et prospères, et que des valeurs plus élevées en CH₄ ont été mesurées au printemps. Des sondes permettant des mesures en continu fournissent plus de détails, et montrent notamment que les changements saisonniers des concentrations en CO₂ du sol sont principalement liés aux variations de température. Dans le cadre d’un projet financé par l’ENEA sur le potentiel de déploiement ECBM (Enhanced Coal Bed Methane) de CO₂, le site de Sulcis, beaucoup plus grand que le précédent, a été étudié à l’échelle régionale au moyen d’un échantillonnage détaillé à des fins d’évaluation du site. En dépit de conditions totalement différentes du sol et du climat, la distribution statistique des données de Sulcis était semblable à celle de Voulund. Beaucoup plus d’anomalies relatives à des concentrations élevées en CO₂ du sol ont été observées sur ce site, en raison de sédiments moins perméables (i.e. d’une meilleure rétention d’eau et d’une plus grande accumulation de gaz) et de températures plus élevées. Des sondages détaillés sur ce site ont mis en évidence diverses anomalies significatives, dont certaines peuvent être expliquées par des processus biologiques près de la surface, tandis que d’autres, en particulier les anomalies de la concentration en hélium, sont plus difficiles à expliquer. Ces résultats montrent l’intérêt des lignes de base, et confirment la nécessité des études de suivi pour clarifier les anomalies inexpliquées avant tout stockage de CO₂.

INTRODUCTION

The long term storage of anthropogenic CO₂ in deep geological reservoirs has been proposed (IPCC, 2005) as a short to medium term approach that will allow humanity to reduce greenhouse gas loading to the atmosphere, while giving time to migrate from the present fossil-fuel driven economy to one that is based more on renewable energy resources. Monitoring of such sites, be they offshore or on land, will be critical to ensure human health and ecosystem integrity as well as for carbon credit auditing purposes. Monitoring of onshore sites is required by legislation (e.g. EU Directives, OSPAR and London conventions) and will be particularly important to assure the public that geological Carbon Capture and Storage (CCS) is a viable and safe technology.
Of the numerous techniques that can be applied to terrestrial CCS monitoring, the measurement of soil gas concentrations and gas flux from the soil to the atmosphere is particularly useful due to the sensitivity of the method and the fact that the item of interest (CO$_2$ and associated gases) is measured directly in the realm in which it might have an impact (the biosphere). Numerous examples exist of the use of this methodology at industrial or test injection sites (Beaubien et al., 2013; Jones et al., 2011; Klusman, 2003, 2006; Loizzo et al., 2011; Risk et al., 2013). One of the challenges of the precise application of this technique is the need to separate a leakage signal from shallow, biogenic CO$_2$ background values or anomalies, which can vary as a function of water content, temperature, soil type, topography, etc (as reviewed in Beaubien et al., 2013). Baseline surveys, which measure the natural background concentration and flux values at a proposed CCS site prior to injection, have been proposed to help interpret monitoring results by defining the natural spatial and temporal variability of a site and the range of values that can typically be associated with local near-surface processes (Elio et al., 2013; Lescanne et al., 2011; Pironon et al., 2013).

Although it is clearly not possible to define all possible values for every location and for every environmental condition (Romanak et al., 2012) there are numerous reasons for conducting baseline studies. These include:

– defining different anomaly thresholds based on site variability (expected baseline values would likely be different for dry sandy highlands versus low-lying, organic matter rich, moist riparian areas);

– determining other potential sources of CO$_2$ (biogas);

– conducting site assessment and characterisation to ensure storage reservoir integrity (search for possible gas permeable faults);

– improving public awareness regarding the pre-injection values and conditions so as to prevent misinterpretation and false alarms during the injection phase; and

– fulfilling some regulatory requirements.

In addition, focused sampling strategies (such as at representative or high risk sites), combined with recent developments of autonomous monitoring systems for long-term deployment (Beaubien et al., 2013; Lewicki et al., 2010; Schloemer et al., 2012), have decreased the time and costs of conducting these surveys.

Results from two very different case studies are presented here from northern (Voulund, Denmark) and southern (Sulcis, Italy) Europe to address baseline-related issues, such as the spatial (land use) and temporal (seasonal) variability of near-surface gas baseline values, the influence that large-scale variables (climate, local geology) can have on site data, and what sampling strategies can be adopted.

1 SITE DESCRIPTIONS

1.1 Voulund, Denmark

The Voulund site in central Denmark (Fig. 1) was studied within the EU-funded SiteChar project. Although the Vedsted area is the main Danish study site within this project (Dalhoff et al., 2011), soil gas and gas flux baseline monitoring could not be conducted there due to access difficulties. The Voulund area was chosen as a substitute for this work, as it is similar in many ways (climate, soil, land-use, topography, etc.) and because its near-surface soil and hydrogeology processes have already been extensively studied by the Hobe Centre for Hydrology, the institute that maintains it (Jensen and Illangasekare, 2011). Clearly for a real storage project baseline surveys would need to be conducted on the chosen site itself and not on an analogue. Two surveys were conducted at the Voulund site, together with the deployment of autonomous, continuous CO$_2$ monitoring probes, to study the influence of land use and seasonal changes on baseline values.

The investigated area is located in the eastern upland part of the Skjern River catchment. The surface geology of this watershed is dominated by Quaternary glacial sediments, with outwash material from the last glaciation occurring in the central and eastern sectors (Stisen et al., 2011). These sediments are typically high-permeability coarse sands, and range from 20 to 40 m thick in the Voulund area. The Quaternary deposits overlay alternating marine, lacustrine, and fluvial deposits of Miocene age, which in turn overlay thick Palaeogene clay layers. The hydraulic conductivity of the Quaternary and Miocene sand formations is generally high, on the order of $10^{-4}$ to $10^{-3}$ m s$^{-1}$. The soil at the study site can generally be classified as a Spodosol, a coarse sand below a 0.30 m thick organic topsoil (Schelde et al., 2011). The upper 1 m of the soil has porosity values that range between 0.35 and 0.40, with water retention capacity around 19% in the top 20 cm of the organic topsoil but only 6% below. This necessitates frequent irrigation to maintain crop growth during most growing seasons. The groundwater table is located at a depth of approximately 5 m. Land use in the study area consists of three main types: cultivated agricultural land, tree plantations, and heath. As will be discussed later this subdivision was used to define sample
distribution and to study the influence of land use practices on baseline gas geochemistry values.

The climate of the area is maritime. The dominant westerly winds result in mild winters, cool summers and frequent rain, while south and east winds from the continent produce low temperatures in winter and high temperatures in summer. Mean annual temperature is 8°C, with a maximum average of 16.5°C in August and a minimum average of 1.4°C in January (Stisen et al., 2011). Precipitation rates vary seasonally, with a maximum in autumn and winter and a minimum in spring. Convective rain events in the summer have a significant influence on precipitation patterns, with the most intense rainfall events occurring between June to August with a maximum daily rainfall of up to 50 to 60 mm. The mean annual precipitation in the area is estimated to be about 1 050 mm.year⁻¹ (Stisen et al., 2011).

1.2 Sulcis, Italy

The Sulcis site in southern Sardinia, Italy (Fig. 2), was studied within an ongoing project funded by ENEA (the Italian Agency for New Technologies, Energy and Sustainable Economic Development) and in collaboration with the local mining company Carbosulcis S.p.A. At this site large coal reserves are mined at a depth of about 400 m, however the impracticality of mining the deeper extension of this unit has led to the study of their potential exploitation using CO₂ - Enhanced Coal Bed Methane (CO₂-ECBM) technologies. A single campaign was conducted at this location that consisted of both a regional survey and multiple detailed surveys. The regional survey was performed to define overall baseline values, while the detailed surveys were performed to define baseline values at proposed drilling locations and to study the potential gas permeability of inferred faults (site assessment).

The Sulcis Basin is filled by Palaeogene marine and continental deposits, Oligocene-Miocene calc-alkaline volcanics, and Neogene to Quaternary fluvial and lacustrine deposits. A regressive sequence within the Palaeogene deposits hosts the coal-bearing Produttivo Formation (Dreesen et al., 1997), which outcrops to the east of the investigated area, ranges in thickness from 40 to 70 m, and dips at 8-10° to the SSW. The Oligocene-Miocene volcanics consist of calc-alkaline, basaltic to intermediate lava flows, and calc-alkaline, dacitic to rhyolitic ignimbrites (Beccaluva and Civetta, 1985; Poli and Rosi, 2005). These ignimbrites outcrop throughout the study area in correspondence with topographic highs. Finally the Neogene to Quaternary sediments range from gravels and sands in the south and along the coast, to conglomerates with variable sand, silt and clay in the more northern parts of the study area. The Produttivo Formation has been affected by E-W and NNW-SSE oriented block faults related to rotation of the Corsica-Sardinian microplate (Poli and Rosi, 2005). Post-eruptive deformation of the volcanic succession is moderate, with vertical faulting causing offsets of up to 40 m (Dreesen et al., 1997). Although the major
regional structures occur outside the study area, a number of local fault systems have been recognised based on field observations, airphoto lineaments, and borehole results.

The studied area consists of generally flat plains (Quaternary sediments) that are interrupted by hills (calc-alkaline volcanics) that typically rise 20 to 100 m above the plains. Land use in the low-lying areas is primarily grain and animal feed crops, as well as extensive vineyards. The hilly areas are typically grass and brush covered. The climate is Mediterranean, with hot, dry summers and cool, wet winters. This area is classified as sub-arid, with annual rainfall averaging about 500 mm; rainfall is highly variable, often falling in torrential downpours during the autumn and spring (Schintu et al., 2005). The great majority of winds are from the northwest and the yearly average air temperature is 17°C.

2 METHODOLOGY

2.1 Sample Collection and Analysis

2.1.1 Soil Gas Concentrations

Individual soil gas samples were collected using a 6.4 mm (¼ inch), thick-walled, stainless-steel tube onto which two steel cylinders are welded to act as pounding surfaces when installing and removing the probe with a co-axial hammer (Beaubien et al., 2013; Ciotoli et al., 1998). The bottom end of the probe is fitted with a sacrificial tip to prevent blockage of the tube during its insertion into the soil. The probe is pounded down to the desired depth, a small aspirator bulb is attached to the upper end, evacuated, and then the probe is gently tapped upwards until the bulb fills with air (indicating that the probe bottom is free and within a gas permeable horizon). The aspirator bulb is pumped twice to clean the probe of atmospheric air and then the probe is sampled for field or laboratory analysis, as described below. All samples were collected at about 50-80 cm depth, which is sufficiently deep in most soils to avoid the influence of infiltrating atmospheric air (Hinkle, 1994).

Field analyses were conducted for CO₂, H₂S and H₂ by directly attaching the probe to a Multiwarn portable gas analyser (Draeger Instruments) and pumping until the measured values stabilised. The Draeger Multiwarn has a range up to 100% for CO₂, up to 100 ppm for H₂S detector and up to 1 000 ppm for H₂. Field analyses were also conducted at the Sulcis site for Rn by pumping gas directly from the probe into the Lucas cell of an RDA200 detector (EDA-Scintrex Instruments); not all points were measured for Rn due to the longer analysis time required. Samples were collected for laboratory analysis by injecting 60 mL of soil gas into a previously-evacuated, 25 mL stainless-steel canister sealed with a rubber septum. These containers were transported back to the laboratory and analyses performed within 1 month; note that tests conducted on these canisters have shown that storage up to at least 6 months has no adverse effects on sample gas concentrations. The samples were first analysed for He on a mass spectrometer (Varian Leak Detector) and then for other gases in a different laboratory on two Fisons 8000-series bench Gas
Chromatographs (GC) using helium as a carrier gas. One GC is equipped with a Flame Ionisation Detector (FID) for the analysis of CH₄, C₂H₂, C₂H₄, C₂H₆, and C₃H₈, while the other has a Thermal Conductivity Detector (TCD) for the analysis of CO₂, O₂ + Ar, and N₂. Note that O₂ and Ar are reported together as these two gases cannot be separated on the gas chromatograph column used for these analyses. The field instrument was calibrated prior to shipping to the field site. Comparison of field and laboratory CO₂ analyses of the same samples yielded a good agreement with a linear, high r² relationship with a slope close to unity.

2.1.2 Gas Flux

CO₂ flux measurements were made using an in-house developed flux system based on the closed-circuit, accumulation chamber technique. This system consists of an accumulation chamber of known volume (V) connected to an infrared detector within a control unit. Field measurement involves the removal of surface vegetation and the emplacement of the accumulation chamber directly on the soil to ensure a proper seal. The infrared detector measures the concentration of CO₂ within the chamber every second over a 100 s interval, resulting in a concentration trend reported in ppm/s. The concentration change over time is converted into CO₂ flux in g.m⁻².d⁻¹ using the formula:

\[ \frac{d[CO_2]}{dr} = k \frac{V T_0 P}{A T P_0} \]

(Lewicki et al., 2005), where k is a conversion constant (169.71 g.s.m⁻³.day⁻¹), V is volume (m³) and A is surface area (m²) of the accumulation chamber, T and T₀ are the measured and standard temperature (K), P and P₀ are the measured and standard pressure (bar), and (d[CO₂]/dr) is the rate of increase of CO₂ in the chamber during the measurement (ppm/s).

2.1.3 Monitoring Probes

The authors have developed small, inexpensive, autonomous gas sensing probes (GasPro) for the long-term, in situ monitoring of CO₂ concentrations (Beaubien et al., 2013); each unit consists of a CO₂ sensor behind a gas permeable membrane, a temperature sensor, batteries, and a control board housed in a 30 cm long, 8 cm diameter plexiglas tube. Deployment holes were augered to a depth of about 85 cm, the probe placed at the bottom with the gas-permeable membrane facing down, and the hole was back-filled with the removed soil.

2.2 Sampling Strategy

As stated, although both sites were surveyed to define baseline conditions using similar techniques, there were various differences due to site conditions and the scope of the studies. For example, a stratified sampling approach was used at the Voulund site, and it was possible to conduct two field campaigns during different seasons. In contrast, the Sulcis site covers a much larger area, and work involved both a regional survey as well as detailed sampling on regular grids to study small scale processes; only a single summer campaign was conducted at this site. Specific details regarding work done at each site is given below.

2.2.1 Voulund, Denmark

The Voulund site was sampled on two separate occasions, once in early fall from 7-14 September, 2011 (178 points) and once in late spring from 15-22 May, 2012 (200 points) to assess seasonal variability. The two sampling periods were chosen for their clearly different meteorological conditions. Based on data from the Danish Meteorological Institute (http://www.dmi.dk/vejr/arkiver/vejrarkiv/) for central and western Jutland, the actual weather conditions for the September 2011 and May 2012 sampling periods were relatively similar for average temperatures (13.8° versus 11.8°C), while total precipitation (134 mm versus 51 mm) and daylight hours (113 versus 248) were significantly different. In addition, crops were in the cultivated fields during the first campaign, whereas they had not yet been planted during the second.

A stratified sampling strategy was adopted to study the potential impact of land-use practices on near-surface baseline gas geochemistry, based on a subdivision of the area into cultivated, forest, and heath classes. With this approach an almost equal number of samples were randomly collected from each of the three classes (Tab. 1), with no attempt at re-sampling the same locations during the two campaigns (Fig. 1). The goal of this approach was to collect a statistically

| TABLE 1 |
|-----------------------------------------------|
| Number of samples collected during the two field campaigns at Voulund, divided also for land-use type |
|-----------------------------------------------|
| CO₂ flux total (cultivated/forest/heath)      | Soil gas total (cultivated/forest/heath) |
|-----------------------------------------------|
| Sept. 7-14, 2011                               | 90 (31/26/33)                             | 178 (64/56/58)                           |
| May 15-22, 2012                                | 191 (82/57/52)                            | 200 (75/65/58)                           |
representative sub-set of the land-use population without the need to cover large areas (which slows down sampling) and to avoid any difficulties associated with land access. The Voulund site is particularly well adapted to this approach because the area is relatively small with little topography, the sub-soil is quite consistent throughout (30 cm of black organic top soil overlying well sorted unconsolidated sand), there are no surface water bodies, and the water table is consistently deep (around 5 m).

Regarding the sampling itself, the sandy nature of the sub-soil typically meant that the ground was well drained and highly gas permeable, thus samples could be collected at almost all points at 80 cm depth, even during rainy periods. Instead the heavy rains encountered during the first campaign in September 2011 meant that CO₂ flux could not be measured (or gave poor results) at many points because of water logged conditions (Tab. 1).

Three GasPro CO₂ monitoring probes were deployed at the Voulund site, one in each land-use type, at locations chosen using the field-based CO₂ soil gas concentrations measured during the first sampling campaign (Fig. 1). The probes were deployed from September to December, 2011, and from March to August, 2012, with a programmed sampling interval of once every 6 hours. At the deployment depth diurnal concentration excursions were expected to be subtle, and thus this sampling frequency was chosen to prolong battery life for the monitoring of seasonal changes. Similar to the goals of the manual sampling campaigns, the probes were deployed to study the effect of land-use and seasonality on gas chemistry.

2.2.2 Sulcis, Italy

The Sulcis site was sampled once in the summer (June) of 2009. Based on archived data from a commercial weather site (http://www.ilmeteo.it/portale/archiviometeo/Carbonia/2009/Giugno) for the town of Carbonia, which is located about 3 km to the east of the study area, the conditions for the June 22-30, 2009 campaign consisted of an average daily temperature of 25°C and an average temperature maximum of 31°C, with essentially no precipitation.

{}\begin{table}
\centering
\caption{Number of samples collected during the Sulcis field campaign, divided also for survey type and land-use type} \\
\begin{tabular}{llll}
\hline
& CO₂ flux total (regional/cultivated/forest/other) & Soil gas total (regional/cultivated/forest/other) \\
\hline
June 22-30, 2009 & 90 (71/0/0/19) & 298 (70/75/66/87) \\
\hline
\end{tabular}
\end{table}

A total of 298 sample points were measured, divided into 3 general survey types: regional, grids, and transects (Fig. 2; Tab. 2). Stratified sampling was not used during this study, but rather the regional points were collected randomly over the entire studied area while the transects and grids were created using a regular sample spacing. The regional survey consisted of 70 samples collected over a 3 × 6 km area, for a sample density of about 4 samples per km²; this sampling was generally restricted to the sediment-filled plains due to the lack of significant soil cover on the volcanic hills. A total of 66 points were sampled amongst 3 small grids, chosen by Carbosulcis as potential future drilling sites, having 25 m node spacing. Finally, a total of 162 samples were collected over three transects. Each transect consisted of a series of parallel profiles (20 m sample spacing; 20-80 m profile spacing, depending on site conditions) that were conducted perpendicular to and across lineaments and inferred faults to search for leakage of deep gases associated with the coal bearing horizons. This was performed to test the integrity of the coal beds for eventual CO₂ storage. For the present work the entire dataset of 298 samples is used for site statistics and Transect 1 is used to examine possible approaches for baseline site assessment.

The subsoil at this site is much more variable than that at Voulund and thus although most samples were collected at 80 cm depth, some samples had to be collected at 50 to 60 cm depth because of hard ground or moist sediments. Unfortunately CO₂ flux could only be measured at about a third of the sampling points due to technical difficulties with one of the two instruments used; most of these measured points are on the regional grid (Tab. 2).

3 RESULTS AND DISCUSSION

3.1 Data Overview

{}\begin{figure}
\caption{Box-plots of \textit{CO₂} concentrations measured during the first sampling campaign at Sulcis (in green) and the two campaigns conducted at Voulund (in shades of blue).}
\end{figure}

The statistical distributions of the major soil gas species are presented in the box-plot of Figure 3, for both campaigns conducted at Voulund (in shades of blue) and the single campaign at Sulcis (in green). The box plots give the median as a horizontal line within a box defined by the upper and lower quartiles, a vertical line defining the upper and lower bounds of the non-outlier range, and symbols for the outliers. Except for a few additional outliers, the distributions of all three parameters are very similar for the two campaigns conducted at Voulund, despite the different sampling seasons; maximum values of about 6% CO₂ were observed during both campaigns.
The September 2011 dataset has a few more outlier values, with CO$_2$ and O$_2$ + Ar showing a mirrored distribution. N$_2$ presents a number of upper outliers compared to the almost normal distribution observed in the May 2012 dataset, with one sample having almost 86% N$_2$ (which is significantly higher than the atmospheric, and typical soil gas, concentration of approximately 78%). The bulk of the Sulcis data distribution is also very similar, however there are more (and more extreme) outliers for both CO$_2$ and O$_2$ + Ar, while the N$_2$ distribution is more symmetrical in terms of both upper and lower outliers. In particular, there are a number of quite high CO$_2$ values (with four samples exceeding 10%) and two extreme outlier values for N$_2$ (a low value at 71% and a high one at 86%).

The origin of the observed values for these major gas species can be inferred by plotting them together on a single scatterplot, since a given process or origin will influence the three gases in different ways (Beaubien et al., 2013; Riding and Rochelle, 2005; Romanak et al., 2012). All data from both Voulund campaigns are plotted in Figure 4a and all data from the Sulcis campaign are plotted in Figure 4b. Data from both sites clearly follow the theoretical trend calculated for soil respiration, which assumes that one molecule of O$_2$ is consumed for every molecule of biogenic CO$_2$ produced and that N$_2$ is not involved in the reaction. This contrasts clearly with the trend expected should CO$_2$ be added to the system (rather than produced in situ) via deep gas leakage, where both O$_2$ + Ar and N$_2$ would be diluted to zero as total CO$_2$ approaches 100%.

The scatter plots in Figure 4 again show the higher CO$_2$ concentrations at Sulcis, with eight Sulcis samples having values greater than the highest Voulund value of approximately 6%. This highlights the complex interplay between the processes that control in situ production and eventual accumulation or migration of CO$_2$ in the sub soil. For example, the sand at Voulund is highly permeable (thus minimising CO$_2$ accumulation) and its low water retention and low organic matter content will limit in situ CO$_2$ production. These two processes of production and accumulation in sandy sediments may limit the maximum amount of biogenic CO$_2$ that can occur at this site. In contrast, sampling at the Sulcis site was
conducted over a much larger area that encompassed a wide range of surface sediment types (most being clay-rich alluvium) and different soil moisture profiles (as controlled by topography and surface water) that clearly had a strong influence on the CO\textsubscript{2} content in the soil. Despite the fact that the climate is much drier at Sulcis, which could lead to greater gas permeability in the upper layers, the combination of sub-soil properties and the much higher temperatures encountered during the sampling has resulted in higher CO\textsubscript{2} soil gas concentrations. Similarly high CO\textsubscript{2} concentrations in the 5-20\% range have been documented at other locations in the context of CCS research and have been interpreted as resulting from near-surface biogenic processes (Beaubien et al., 2013; Lescanne et al., 2011).

Although the vast majority of data given in Figure 4 follows the expected respiration trend at both sites, a few points fall slightly outside. Three Vouland samples (all from the September, 2011 campaign) and one Sulcis sample show higher than expected N\textsubscript{2} values (up to 86\%) and lower than expected O\textsubscript{2} values; not only do these values lie outside of the biogenic trend, but they are opposite to what would be expected for the dilution trend. According to Romanak et al. (2012), lower than expected O\textsubscript{2} values may be due to the oxidation of CH\textsubscript{4} to CO\textsubscript{2}, however this reaction should again have no influence on N\textsubscript{2} (instead N\textsubscript{2} increases in these samples) and the samples should have high enough CH\textsubscript{4} concentrations to produce a significant effect. This mechanism is unlikely considering the low CH\textsubscript{4} concentrations in these samples (the three Vouland samples all have < 2 ppm CH\textsubscript{4}, while the Sulcis sample has 79 ppm). These same authors have suggested that excess N\textsubscript{2} can result from the greater solubility of CO\textsubscript{2}, thus leading to enrichment in the gas phase of the less soluble N\textsubscript{2}. This implies that there should be a similar enrichment in O\textsubscript{2}, which is only slightly more soluble than N\textsubscript{2}, however this does not appear to be the case in these samples. Denitrification, which produces N\textsubscript{2} gas as an end-product of nitrate reduction, is another potential explanation. This process is more important in low oxygen environments (Castaldi, 2000), and thus it may be more likely in the single Sulcis sample which is essentially anoxic and has elevated CH\textsubscript{4} (79 ppm). Instead microsite production, the tolerance of some denitrifying enzyme systems to O\textsubscript{2}, or the observation that denitrification increases exponentially with increasing O\textsubscript{2} consumption (Castaldi, 2000) are mechanisms that have been invoked to explain the observation of apparent “aerobic denitrification” (Amundson and Davidson, 1990); this may explain the three Vouland samples with elevated N\textsubscript{2} and reduced (but not negligible) O\textsubscript{2} concentrations. Ar data would be useful to better understand which of these various mechanisms is the most important.

Figure 4
Scatter plots comparing the concentrations of O\textsubscript{2} + Ar and N\textsubscript{2} against CO\textsubscript{2} for a) both campaigns at Vouland and b) the one campaign at Sulcis. The solid lines mark the expected trend due to respiration, and the dashed lines mark that expected due to dilution caused by deep gas leakage.
A single data point from the regional Sulcis survey (CO$_2$ $\approx$ 15%; Fig. 4b) lies between the dilution and respiration trends (closer to the former), but with normal values for the other gas species (e.g., CH$_4$ = 2.4 ppm, He = 5.3 ppm). This is an example of a sample point that requires some follow-up study. In this case, more detailed sampling around the point, combined with stable isotope analysis of CO$_2$ carbon, could be used to determine if deeper, natural CO$_2$ is leaking into the soil (which may be an indication of a gas permeable fault).

Two other points in this same dataset, having CO$_2$ concentrations on the order of 3-4%, appear to lie directly on the dilution trend. Given the small difference between the dilution and respiration trends at CO$_2$ concentrations below about 5% relative to an estimated analytical error for O$_2$ and N$_2$ of around 2%, it is likely that these plots cannot be used alone to distinguish the origin of CO$_2$ at values below this 5% threshold. As such, with the absence of anomalous values for the other measured parameters, these two samples are assumed to belong to the respiration trend.

The statistical distribution of CO$_2$ flux data is given in Figure 5a. At Voulund, median and quartile values are lower during the September 2011 campaign, and some negative values were even registered, likely due to the difficult and water logged soil conditions encountered during that campaign. The heavy rains during the sampling period created a barrier to gas flux, and surface water may have even dissolved CO$_2$ in the measurement chamber causing the observed negative fluxes. The May 2012 data from this site are, on the other hand, of much better quality, showing the vast majority of samples having flux rates below 40 g.m$^{-2}$.d$^{-1}$, which is typical for normal soil systems. The Sulcis data instead has a narrower, more normal distribution (less skewed) with values primarily below 25 g.m$^{-2}$.d$^{-1}$. These lower values are likely linked to the dry surface soil during the June sampling campaign; as is typical for the Mediterranean climate, grass turns yellow and surface soil productivity decreases during the hot dry summer months.

The plot of CO$_2$ flux versus soil gas CO$_2$ for Voulund (Fig. 5b) shows no correlation. The same plot for the Sulcis data (Fig. 5c) also shows very little correlation, although two sub-populations may have slightly different trends. While some studies have found a relationship between these two parameters (Jassal et al., 2005), they
are more often de-coupled from each other (Beaubien et al., 2013; Risk et al., 2002). The reason for this is related to the location of the CO₂ production zone, the gas permeability characteristics of the soil column down to the depth of the soil gas sample, and the balance between the storage and the migration of soil-produced CO₂. For example, the vast majority of biogenic-origin CO₂ is produced in the upper 20 cm (Risk et al., 2002) and thus this gas has a short and permeable pathway for its eventual migration and release to the atmosphere (as represented by the surface flux measurements). In contrast, increased water content and soil compaction with depth reduces gas permeability, leading to the potential for storage of elevated CO₂ concentrations despite the low production rates at that depth. In particular, rainfall events impact these processes in the short term (Maier et al., 2010). Keeping these processes in mind, the two weak trends in the Sulcis data (Fig. 5c) may be related to different near surface soil parameters (water content, land use) that influence gas migration/accumulation; it is not possible to assess any such correlations with the present dataset.

Results for some trace gas species measured at both sites are presented in Figure 6. Methane results at Voulund during the first campaign are almost all below the atmospheric concentration of approximately 1.8 ppm, as is expected due to the typical oxidation of atmospheric CH₄ in oxic sediments (Le Mer and Roger, 2001). Overall values were higher during the second campaign, and although the median value is still about 1 ppm, a number of outliers were measured that range between 3 and 5 ppm. This observed difference is discussed in Section 3.2. The Sulcis CH₄ distribution is similar to that of the second Voulund survey, with the difference being fewer outliers (apart from one significant outlier at 79 ppm). As mentioned above, this sample is associated with essentially anoxic conditions, and thus is likely due to in situ methanogenesis. The distribution of ethane for the Voulund surveys is similar to that for methane, while the Sulcis samples present generally lower values. The cause of the ethane distribution is not understood, considering that only CH₄ is thought to be produced biogenically; it should be noted, however, that most of the values are extremely low, with the upper quartiles of all surveys being below 0.025 ppm. Finally the He distribution for all three surveys is Gaussian and shows a median value close to the concentration of this gas in the atmosphere (5.22 ppm).
This normal distribution may be the result of instrument accuracy and reproducibility or may be due to shallow processes that can create minor anomalies. However, the very high value of 70 ppm measured at one of the detailed Sulcis grids (G10; Fig. 2) is very anomalous and difficult to explain via near surface processes. In addition, another two He outlier values were observed in Transect 1 (9.1 ppm) and grid 6 (8.5 ppm). Of these three He anomalies only that on T1 is near a mapped fault zone (Fig. 2), whereas the other gases in all three samples were not anomalous and the samples surrounding each He outlier value on the same grids (20 m spacing) did not have anomalous He values. Unfortunately it was not possible to return to verify the validity of these samples, however the occurrence of such values during a baseline survey would require a follow-up, detailed study to determine if they are due to deep gas migration along a permeable fault, shallow in situ production by uranium decay, or a sampling or analytical error. Note that normal He analytical error is less than 0.2 ppm, and only contamination from an external He source (such as that used for the gas chromatograph carrier gas) could explain such an extreme value as 70 ppm; to avoid this potential problem, samples were stored and analysed for helium in one laboratory and then subsequently transferred to a separate laboratory for GC analyses.

3.2 Seasonal and Land-Use Effects

Although an examination of the complete dataset from a campaign can yield important information on total concentration ranges, statistical trends and populations, and spatial distributions, the subdivision of data based on surface characteristics can help to explain how these parameters can influence baseline values. As the Voulund study site is small, with a uniform climate and geology, limited topography, and relatively homogeneous soil type, land-use was considered to be one potential variable which could influence gas concentrations and flux rates. To this end stratified sampling was conducted (during two different seasons) based on a division of the area into three land-use types:

- cultivated agricultural land (mainly wheat and barley);
- heath and scrub brush;
- forested tree plantations (coniferous pine trees) (Fig. 1).

Figure 7 shows the statistical distribution of some of this classified data.

The soil gas CO₂ results given in Figure 7a show similar trends for the two campaigns, with the cultivated and heath areas having similar distributions which are significantly higher than those of the forested areas. This observation is supported by an ANOVA analysis, which shows that there is a significant difference for the means as a function of land use type ($p = 0.000$) but that there is no significant difference for sampling season ($p = 0.498$).

The apparent influence of land use on soil gas CO₂ concentrations is likely related to vegetation canopy and root systems and how they can influence soil temperature and water content. For example, trees and the associated forest litter shade the forest floor, resulting in lower soil temperatures during the hotter months; this is clearly illustrated in temperature data from the three buried GasPro monitoring probes (Fig. 8a). In this plot,
the temperature values for all three probes are similar at the end of the winter (approximately 5°C in mid-March 2012), however over the course of the spring and summer the temperatures measured by the cultivated and heath probes increase along a similar trend whereas the forest probe rises much more slowly, resulting in a temperature difference of more than 4°C at the end of the monitoring period in mid July. Similar results using monitoring probes have been observed by others (Arevalo et al., 2010). Considering that soil biogenic CO₂ production increases exponentially with temperature (Hashimoto and Komatsu, 2006), such a temperature difference could have a significant effect on soil CO₂ concentrations. Trees can also influence soil moisture content by the capture and subsequent evaporation of precipitation in the canopy and via deeper roots that draw moisture from lower in the soil column via evapotranspiration. Finally, tree roots can also form cracks in the soil that create pathways for more direct, and rapid, migration of CO₂ from the soil to the atmosphere. In contrast, the root depths and shading characteristics of heath and planted crops are relatively similar, thus it is likely that similar processes control CO₂ soil production and migration in these two settings.

In contrast, the results reported in Figure 7a and supported by the ANOVA test indicate that there was little seasonal influence on the statistical distribution of CO₂ for the September and May datasets, a result which was not expected. After the heavy rains during the first campaign, the period of May was chosen specifically because it is typically the month with the lowest rainfall amount; this was observed during the actual sampling periods, with 134 mm in September, 2011 and only 51 mm in May, 2012. Although the average air temperatures for these two months were different by 2°C (13.8°C and 11.8°C, respectively), a close examination
of the soil temperature trends registered by the monitoring probes shows more detail and gives a better picture of the dynamics of the in situ soil conditions (Fig. 8a). Using the probe buried at the cultivated site as an example (i.e. the blue line in Fig. 8a), one can see how soil temperatures were constant at around 13°C just after the first sampling campaign from September 7-14, 2011, but that they rose rapidly from 10°C to 15°C during the second campaign from May 15 to 22, 2012 (almost 1°C/day). This, combined with the fact that the number of sunlight hours were much greater in May 2012 than September, 2011 (248 versus 113, respectively), would have a significant impact on plant growth and soil respiration (CO₂ production) over the sampling period.

Based on these observations one can propose that the similarity in the statistical distributions of CO₂ concentrations between the two different campaigns was due to similar temperatures, with the soil system being relatively stable during September but in dynamic increase during May. Although it is known that both temperature and water content play an important role in CO₂ generation and accumulation, the above discussion appears to indicate that temperature is the dominant factor, as supported in the literature (Moncrieff and Fang, 1999). Although no soil water content data are available, it should be remembered that the sand at this site has a very low water retention capacity (<6%), and thus the resulting excellent drainage towards the water table at 5 m depth means that heavy rains may have less of an impact on soil CO₂ production and accumulation compared to other sites.

Although differences in CO₂ concentrations are not evident at the statistical level between the two different seasonal sampling periods (apparently due to a coincidence of temperature and limited impact of different rainfall rates), continuous measurements at individual points using the three GasPro monitoring probes (Fig. 8b) do show that concentrations change both over the short term (caused by events like a brief heat wave) and long term (as controlled by seasonal patterns). The most complete GasPro dataset was obtained at the cultivated site. Here concentrations started high, near 5%, then dropped rapidly in correspondence with a similar decrease in soil temperature in the latter half of October 2011. Concentrations remained relatively constant around 1.5% for the first 2 months of the second deployment, followed by a significant peak (where concentrations increase by 1% over 2 weeks) in correspondence with the rapid temperature increase described above during the May 2012 field campaign. This implies that the statistical distribution of our manual sampling campaign in May, 2012 might have been much lower if it had been conducted just 1 or 2 weeks earlier, before the increase in temperature and the GasPro-measured CO₂ peak. Then from the beginning of June until middle July the concentration increased more slowly from about 1.5% to 2.4% over 6 weeks. These results support the importance of temperature as a dominant controlling mechanism of CO₂ production, as discussed above. Unfortunately the second deployment period did not extend past mid July, and thus it is not possible to assess year-on-year variability with respect to the high values observed in September, 2011.

The year-on-year variability can be assessed by multiple surveys during the same period during different years, as performed by Beaubien et al. (2013) at the Weyburn CO₂-EOR site. These authors conducted five different fall surveys, two in September (2002, 2003) and three in mid to late October (2004, 2005, 2011), that involved hundreds of samples being collected at the same differential-GPS-defined points during each campaign. This work showed slight differences in statistical CO₂ distributions that could be attributed in large part to different levels of precipitation for the various years. Although such an approach could be taken at other sites, the associated costs may limit the application of this approach. Instead a more cost-effective approach to yearly baseline definition may be to conduct four seasonal campaigns in one year (Lescanne et al., 2011), and to install multiple monitoring probes in different land use and soil-type settings for that year and beyond. By comparing data from the first year of joint manual and automatic monitoring, site specific relationships may be defined that would allow automatic monitoring in subsequent years at a limited number of points to be extrapolated (using also temperature and precipitation data) over the entire area of interest for an estimate of year-on-year baseline variability. To achieve this, however, a sufficient number of sensors must be deployed in well-chosen, statistically representative points.

GasPro CO₂ results from the heath site are much lower than those from the cultivated location (Fig. 8b), with a starting concentration of only about 1%. Values at this site during the second deployment are slightly lower, more variable, and show a slight tendency to increase towards the end of the monitoring period in May 2012. Interpretation of the results from this site is complicated by the fact that at some unknown time after deployment this heath land was tilled and cultivated, thus changing the soil conditions. Unfortunately the CO₂ sensor in the probe deployed in the forest site malfunctioned and only registered CO₂ data for the first two weeks; temperature data was, however, collected for the entire second deployment period. Instead the battery voltage in the heath probe decreased below the required threshold for CO₂ sensor operation in June 2012, although there
was sufficient power for continued temperature measurements.

The statistical distribution of the CO$_2$ flux data is presented in Figure 7b; it should be remembered that the data from the September 2011 campaign is likely biased by the difficulties encountered with waterlogged soil during this survey. Acknowledging these problems, it can noted that there is a clear difference between the three sites for this first campaign: measurements in the cultivated areas are much higher and present a wider statistical distribution than those observed in the other two land-use classes. This is in agreement with observations reported in the literature where farming practices such as tilling, fertilizers, irrigation, and liming have all been documented to increase CO$_2$ fluxes to the atmosphere (Arevalo et al., 2010; Carbonell-Bojollo et al., 2011). In contrast, the results from the May 2012 campaign show similar statistical distributions for all three classes, although the cultivated sites still show the most outlier values. This is likely the result of timing of farming interventions and coincident meteorological conditions. Note, as already discussed above, how the statistical distributions for soil gas CO$_2$ concentrations (Fig. 7a) and CO$_2$ flux (Fig. 7b) for the May 2012 campaign are clearly different, with higher concentrations in the cultivated and heath areas not translating into higher flux rates.

Finally the statistical distribution of CH$_4$ (Fig. 7c) is very similar for all three land use types during the September 2011 campaign, and it is again much the same during the May 2012 campaign for the cultivated and heath land-use types. In contrast, the samples during this latter campaign have higher values in the forested areas compared to all other groupings. According to Megonigal and Guenther (2008) some forests switch from being CH$_4$ sinks to CH$_4$ sources depending on soil water content, which may explain the observed results. Values slightly above the average atmospheric concentration (approximately 1.8 ppm) are likely due to in situ production, as methanogenesis has been documented in normally oxic soils that have been flooded for a brief period due to spring thaw or heavy rains (Kammann et al., 2001) or in anaerobic microenvironments (Kammann et al., 2009).

### 3.3 Site Assessment Surveys

Whereas work at Voulund concentrated on examining the potential effects of land use on near surface gas baseline values, study at Sulcis (a site actually proposed for CO$_2$-ECBM and CCS) focused on regional characterisation of the area and detailed surveys of potential leakage pathways (such as faults). This work is thus closely linked to the idea of site and risk assessment. Of the six detailed sites studied, only the results from Transect 1 will be presented here as an example. This transect is located in the centre of the regionally-mapped area, within Quaternary sediments but at the base of an ignimbrite hill, and near the intersection of two inferred faults and a 90° bend in a creek (Fig. 2). Although there is an apparent offset between the faults and the creek, this may be an artefact of the precision of the regional fault mapping. The precise location of the transect itself was chosen based on information available at the time (i.e., the mapped fault location) and land access. In particular, the survey was conducted on the east side of the road because this field was un-cultivated at the time and because the west side had a vineyard in which access was not granted. The sampled field was flat and planted with grass for animal feed.

Figure 9a shows how soil gas CO$_2$ concentrations are consistently low (<1.5%) in the northern 80% of the transect, but that a 60 m long anomalous area with CO$_2$ values between 4 and 12% occurs in the southern part near the creek bed. Some other parameters are also anomalous in this area, including O$_2$ minimums and individual, high-concentration values for N$_2$, CH$_4$ (Fig. 9b) and He (Fig. 9c). The low O$_2$ and high CO$_2$ values in this anomalous zone can be explained by in situ soil respiration processes. As described above, one of these points is particularly anomalous, with almost anoxic conditions, a position off the standard soil respiration trend (Fig. 4b), and anomalously high N$_2$ (86%) and CH$_4$ (79 ppm) concentrations. In normal soils N$_2$ values are typically near the atmospheric concentration of 78%, or can be less than that value if the soil gas is diluted by CO$_2$ leaking from deep volcanic/geothermal sources (Annunziatellis et al., 2008). Instead, the high N$_2$ in this sample is most likely due to the microbial process of denitrification, as described above, which converts NO$_3$ to N$_2$ through reduction reactions in anaerobic environments, although anammox processes (i.e., the anaerobic oxidation of NH$_3$ to N$_2$) are also possible (Stein and Yung, 2003). Similar to the N$_2$ anomaly, the observed CH$_4$ anomaly of 79 ppm in this sample (Fig. 9b) is also likely due to anaerobic microbial reactions (i.e., methanogenesis), as supported by the lack of any corresponding anomalies for the other measured hydrocarbon gases (not shown). Based on these results this anomaly could be related to a previous location of the near-by creek bed, in which the sub-soil contains much more organic-rich material. More difficult to explain, however, is the occurrence of a single helium anomaly of 9.1 ppm (Fig. 9c) located just 20 m to the west of the sample with anomalous CO$_2$, CH$_4$ and N$_2$. Helium is generally associated with deep magmatic or
mantle sources, although \(^4\)He is also formed via \(\alpha\)-decay in the U and Th series. It is thus possible that this anomaly has been caused by the accumulation of He produced as a result of high concentrations of these radiogenic elements in the near surface rhyolitic ignimbrites; although Rn data could give potentially support this interpretation, unfortunately this location was not analysed for this gas species.

This example clearly illustrates the need for follow-up surveys after a preliminary site assessment, required to concretely explain the occurrence of any observed anomalies in terms of either near-surface or deep leakage processes. In this case, it could include a structural examination to more precisely locate the mapped faults, vertical soil gas profiles (with isotopic analyses) to determine the source and genesis of the observed anomalies, and sampling on the transect border to look for continuation of the observed He anomaly. If a shallow origin is determined for something like coincident He and CO\(_2\) anomalies, this would be extremely important information during the site monitoring phase. Instead if natural deep-origin gas leakage is inferred (prior to CO\(_2\) injection) the associated gas-permeable pathway (a deep fault) would have to be taken into consideration when determining the viability and safety of such a site for CO\(_2\) storage.

**CONCLUSION**

The work performed at the two different sites has highlighted how baseline values can vary as a function of numerous parameters. In particular the influence of land-use at the Voulund Denmark site was clearly illustrated in the significantly lower soil gas CO\(_2\) values in forested areas compared to cultivated and heath areas, while continuous monitoring probes deployed in the soil highlighted seasonal variability due, in large part, to temperature changes. The measurements at Sulcis, Italy, instead showed how the entire dataset had a statistical distribution for various parameters that was actually similar to that for the Voulund dataset (despite different climate and geology), although the occurrence of soil gas CO\(_2\) outliers at the former illustrate how soil type (water content, gas permeability, organic matter content, etc.) and temperatures
can result in significant anomalies due to near surface processes. Detailed surveys at the Sulcis site also highlighted the usefulness of this method for site assessment purposes, testing inferred faults for deep gas migration, and measuring proposed deep drilling sites to create a pre-injection database.

It should be made clear that baseline surveys can serve two main purposes:

- defining the range of natural values due to near-surface processes to minimise false positives (i.e., natural, near-surface anomalies being incorrectly interpreted as leakage from the reservoir) or false negatives (an actual leakage signal not being recognised within the natural, biogenically mediated background noise);
- to search for pre-existing gas migration pathways that may represent a risk for the integrity of the storage site (gas permeable faults).

The use of stratified sampling, which consists of focused sampling on smaller areas that are representative of a certain “class” of characteristics (in this case near-surface parameters that can influence biogenic processes, like topography, land-use, soil type, water content, etc.), is well adapted to address the first point. In particular, it is a potentially useful way to reduce costs and time needed for site characterisation/baseline surveys, as this approach yields stationary variables and appears to define well the statistical distribution of values in different classes. In this way, it would not be necessary to cover the entire storage area for baseline purposes, but rather surveys would be conducted to ensure that each statistical population has been adequately sub-sampled. In contrast, a more spatially continuous, regional sampling approach may be more appropriate when trying to assess the existence and permeability characteristics of large-scale faults, although detailed transects across inferred structures (like those conducted at Sulcis) are another option.

The advantage of monitoring multiple soil gas species has been shown, for example by the discovery of a number of helium anomalies at Sulcis that require more detailed work. The types of gases to be measured should be decided based on the characteristics of the studied site. For example, ethane may prove useful at a site like Sulcis, because this gas can be found together with methane in coal deposits; if methane and ethane migrate upwards together, the latter can be used as a tracer since methane can be easily and rapidly oxidised. Finally, the deployment of long-term monitoring probes at the Voulund site has highlighted the utility of this technology to capture temporal variability that individual sampling campaigns cannot.

Based on these observations a rigorous but cost effective approach to baseline surveys can be recommended. Seasonal campaigns should be conducted at a proposed site prior to injection, with the number and actual timing depending on the local climate. For example, in a central continental climate a large campaign during the winter may be impractical because of deep snow and very cold temperatures, in tropical areas heavy rains during some periods may make soil gas sampling impossible because of saturated soil conditions, while in very arid, desert-like sites there may not be any seasonal biogenic variability. The first campaign will preferably be performed during the season with the lowest biogenic soil respiration production (i.e. the season during which subsequent monitoring will take place during the injection phase) and will consist of a complete regional survey for overall site characterisation and to search for large-scale gas permeable structures. Both field and laboratory analyses of a wide range of parameters will be performed on a large number of samples. At the end of this campaign, the field results will be interpreted (together with other available site information, like soil type, topography, water content) to choose areas for immediate but limited stratified sampling and monitoring probe deployment. In addition to choosing these sites to define the range of near-surface background values for a given class, these sites may also be chosen considering additional secondary purposes (e.g. future monitoring of abandoned borehole sites, inferred fault locations, etc.). This will be the longest and most costly campaign, however it will form the basis for all future baseline and monitoring work. The subsequent seasonal campaigns would only involve limited stratified sampling to define seasonal variability, with these results being integrated with those from the monitoring probes to give a more complete characterisation of spatial and temporal variability. By comparing data from the first year of joint manual and automatic monitoring, it may be possible to define site specific relationships that would allow automatic monitoring in subsequent years at a limited number of points to be extrapolated (using also temperature and precipitation data) over the entire area of interest for an estimate of longer-term seasonal and year-on-year baseline variability. To achieve this, however, a sufficient number of sensors must be deployed in well-chosen, statistically representative points.

In closing, near-surface gas geochemistry baseline studies should be considered as an important aspect of CCS site assessment and monitoring for onshore projects, to be deployed with all other investigative techniques applied in this field. In addition to defining a statistically robust dataset with which monitoring results can be compared, pre-injection surveys are also useful to assess the possible gas permeability characteristics of inferred faults, to create a legal basis for both
safety issues (study inferred leaks) and for carbon credit auditing (such as evaluating pre- versus post- CO2 flux rates to the atmosphere), and to increase public awareness and education regarding the natural pre-injection environment to avoid misinterpretation and false alarms during the injection phase. With focussed sampling and autonomous probes this work can be conducted in a timely and cost-effective way.

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