Sampling strategies using the “accumulation chamber” for monitoring geological storage of CO_2

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ABSTRACT

Fundación Ciudad de la Energía (CIUDEN) is carrying out a project of geological storage of CO_2, where CO_2 injection tests are planned in saline aquifers at a depth of 1500 m for scientific objectives and project demonstration. Before any CO_2 is stored, it is necessary to determine the baseline flux of CO_2 in order to detect potential leakage during injection and post-injection monitoring.

In November 2009 diffuse flux measurements of CO_2 using an accumulation chamber were made in the area selected by CIUDEN for geological storage, located in Hontomin province of Burgos (Spain). This paper presents the tests carried out in order to establish the optimum sampling methodology and the geostatistical analyses performed to determine the range, with which future field campaigns will be planned.

Keywords:
Monitoring
Accumulation chamber
CO_2
Storage
Geostatistical

Contents

1. Introduction

Fundación Ciudad de la Energía (CIUDEN) is implementing research projects in Spain related to the capture and storage of CO_2. Since 2009, a group made up of Spanish and Italian universities has been taking part in a joint project called “Strategies for Monitoring CO_2 and other Gases when Studying Natural analogues”, which is coordinated by the company AMPHOS XXI. One of the primary objectives established was to set up a monitoring strategy using the accumulation chamber method for measuring diffuse flux of CO_2 into the atmosphere. The project involves measuring the CO_2 baseline within the area chosen as the site of a technological development plant, set up by CIUDEN, and injecting approximately 30,000 tonnes of CO_2 into a saline water-bearing stratum located at a depth of 1500 m. Determining the baseline before any CO_2 is injected is fundamental for the future control and detection of leakage during the injection and post-injection monitoring.

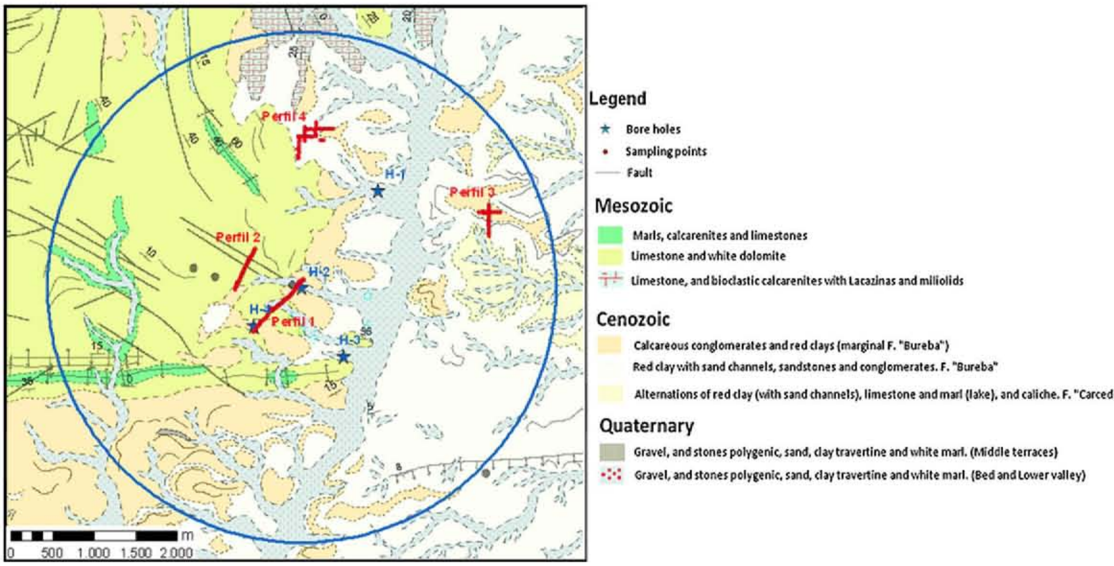

Fig. 1. Sampling areas at Hontomin.

The area chosen lies close to the village of Hontomín (Burgos, Spain). Until four years ago, a number of companies drilled for oil in this region, leaving 3 old test bore holes (Hontomín-2, -3 and -4), one of which might be used starting in 2011 as a monitoring well once the CO_2 has been injected into another bore hole (Hontomín-5), which will be drilled in the middle of 2011. This area is located in the northeastern part of the Duero's basin, and it is characterized by outcrops of Mesozoic, Cenozoic and Quaternary sedimentary rocks (Sheet 167/19-9 Montorio, Geological Map of Spain, scale 1:50.000 (IGME)).

During the site qualification phase soil and water analyses are planned, as are a 3D seismic campaign, magneto-telluric studies and the monitoring of CO_2 and trace gases (radon, helium, hydrogen, methane, etc.).

The first phase was to investigate the most suitable way of measuring CO_2 flux using the accumulation chamber. Although fast and simple, the actual value of the diffuse CO_2 flux measurements obtained using an accumulation chamber placed on the surface can be affected by a variety of causes: (a) an alteration of the air pressure inside the chamber; (b) a change in the degree of CO_2 concentration across the soil–air interface; (c) slow mixing in the chamber; (d) an increase in the amount of water vapour inside the chamber (Welles et al., 2001; Evans et al., 2001).

With regard to water vapour, the flux of water vapour might be 10–50 times the flux of CO_2. A good measuring system will automatically make a correction of the infrared spectral interference of H_2O on the measurement wavelength of CO_2. (Klusman, 2003a). We used a magnesium perchlorate ($Mg(ClO_4)_2$) absorbent to reduce the levels of water vapour.

It is important to evaluate the methodology used to record the flux of CO_2 as this can affect the qualification of the temporal and spatial variability of the flux in question. According to some authors (Lewicki et al., 2003), the methodology can influence the calculated value of CO_2 within the measurement area as well as the magnitude of the uncertainty associated with the estimator used. Likewise, in areas subject to strong winds, it is necessary to ensure that the contact between the bottom of the chamber and the ground is adequately sealed. If not, atmospheric air could enter the chamber and cause a dilution effect or cause an increased flux due to the Bernoulli effect. In some cases, a concentric protective screen is placed around the chamber or the chamber which is sunk a few centimetres into the ground. This modification of the physical properties of the ground can also contribute towards a potential change in the value of the CO_2 flux (Gerlach et al., 2001).

In short, the principal causes of variations in the flux of CO_2 are the sampling methodology used and the variability of the subsurface and surface parameters (porosity, permeability), biological respiration, meteorological parameters (atmospheric pressure and gradients, temperature, wind speed and direction) and the depth of the source of the CO_2 detectable at the surface. Therefore, it is considered of the utmost importance to determine the optimum methodology for measuring the flux of CO_2 in order to characterize the area investigated and calculate the base line CO_2 flux.

2. Materials and methods

2.1. Sampling design

Two campaigns were undertaken (C1 and C2). For both, the sampling area is approximately circular with a radius of 3 km with the village of Hontomin approximately at the centre. For campaign C1, 4 areas were chosen for measuring the flux of CO_2 (P1, P2, P3 and P4). The line of P1 runs in an N-45°-E direction and joins the locations of the Hontomín-2 and Hontomín-4 test bore holes. The approximate length of this line is 900 m, and the sampling was carried out at points 5 m apart. P2 is defined by a line running in an N-30°-E direction from the centre. It is 540 m long and sampled at 5 m intervals. The line runs in two diametrically opposed directions. One line runs north–south, is 375 m long with sampling points every 5 m, while the other line runs east–west, has a sampling length of 250 m with a distance between sampling points of 10 m. P4 consists of 3 lines running east–west and an additional 3 lines running north–south. The distance between the sampling points of the three east–west lines is approximately 10 m and they are 350, 160 and 50 m long, respectively. The north–south lines are 270, 170 and 180 m long and their sampling interval is 10 m (Fig. 1).

The C1 Campaign lasted 14 days distributed throughout 3 consecutive weeks in November 2009. The average accumulation time of a CO_2 flux measurement, including the measured complementary variables (pressure, humidity, etc.) and the georeferencing was between 5 and 10 minutes, including moving between sampling points. Ground temperature and humidity at a depth of 15 cm also determined, as were atmospheric pressure and wind speed and

Fig. 2. The CO_2 diffuse flux clearance and measurement process.

direction. A total of 768 CO_2 flux measurements were taken at 428 sampling points, together with the corresponding atmospheric and soil parameters.

A "sampling stratification level" was established in accordance with the geological characteristics shown on the geological map. This resulted in the identification of 3 "strata": Cenozoic, Mesozoic and Quaternary, to which a fourth was added, corresponding to the areas close to the test bore holes drilled during the search for oil. The C2 campaign was undertaken two months later in January 2010 in order to compare with the results obtained during C1.

2.2. Equipment

The "accumulation chamber" method was used to measure the diffuse emission of CO_2 into the atmosphere. This has been widely applied in volcanic and geothermal areas (Rodríguez and Gladis, 2008; Chiodini et al., 1998a; Farrar et al., 1999), as have CO_2 emissions due to the biological action in the soil (Yim et al., 2002). Other researchers (Klusman, 2003a,b, 2003c, 2005; Lewicki et al., 2005a) employ this technique for the diffuse emissions in CO_2 storage projects.

The theoretical concept is simple: the flux of CO_2 from the ground into the atmosphere is calculated from the increasing concentration of CO_2 taking place inside the chamber. This means it is possible to determine the flux by calculating the steepness of the concentration curve throughout time (dC/dt as ppmV/s) inside the chamber with an internal diameter of 200 mm (West Systems, 2009). In order to minimise the amount of humidity and particles entering the detector, which could interfere with the measurement, a magnesium perchlorate humidity filter is fitted followed by a 0.45-μm Teflon particle filter (PTFE) (Lewicki et al., 2005b; Chiodini et al., 1998b; West Systems, 2009).

In order to express the flux in g m^{-2} d^{-1}, we have to perform the following conversion:

$$\Phi(\text{g m}^{-2}\,\text{day}^{-1}) = \frac{dC}{dt}(\text{ppmV/s})\cdot\frac{V(\text{m}^3)}{A(\text{m}^2)}\cdot\frac{1\,\text{l}/(10^3\,\text{m}^3)}{1\,\text{ppmV}} \cdot\frac{86,400\,\text{s}}{1\,\text{day}}\cdot\frac{P(\text{bar})\cdot PM(\text{g/mol})}{R(\text{bar l}/(\text{K mol}))\cdot T(\text{K})}$$

where dC/dt = slope of the concentration curve against time; V = net volume of the chamber (including the volumes of the sensor, pump and connection tubes); P = atmospheric pressure, one standard atmosphere = 1.01325 bar; PM = molecular weight of the gas (for CO_2 = 44.01 g/mol); R = gas constant for an ideal gas (0.08314510 bar l K^{-1} mol^{-1}); T = air temperature (K).

The equipment used on this project is manufactured by the company WEST Systems (WS-LI820) and fitted with a LICOR (LI-820) infrared detector. This detector allows a range of 0–600 mol CO_2/m^2 per day to be determined. The LI-820 does not have automatic correction of the spectral interference of water vapor on the absorption band of CO_2, necessitating the use of magnesium perchlorate to remove water vapor. To illustrate the range of the instrument, the magmatic flux of CO_2 in the Horseshoe Lake area (California, USA), recently known to cause asphyxia of the trees located in the vicinity, was in the order of 200 mol m^{-2} day^{-1}. Therefore, we can affirm that the equipment used is valid for the measurement of significant fluxes of CO_2 in natural systems.

Some researchers (Klusman, 2011) have analyzed the advantages and limitations of the measures with accumulation chamber method. In this sense, there are different instruments with different chambers designs and different ways to water removal. For example, West Systems uses magnesium perchlorate to remove water while LICOR (LI-8100) automatically corrects this effect by direct measurement of CO_2 and H_2O. Among the future goals is the comparison between West Systems and LICOR, not only in CCS projects also in CIUDEN-PISCO2 project, a pilot project for CO_2 biomonitoring tools focusing on the development of biomonitoring of potential CO_2 leakages through testing biogeochemical effects of CO_2 injection in soils.

3. Results and discussion

3.1. Measurement protocols tested

Three different methodologies were tested for measurement of the diffuse flux of CO_2 using the "West System" equipment. (a) The "Clearance" Method (CM); (b) The "Non-Clearance" Method (nCM); and (c) The "Clearance and Waiting" Method (CWM). The method known as "Clearance" requires the following operations: (1) using a trowel, the sampling area to be covered by the collar is prepared by clearing away any vegetation and removing the first compact layer of topsoil, (2) the process is delayed until the concentration of CO_2 measured by the instrument is approximately equal to the atmospheric concentration, then the instrument then being set to that value. (3) The collar is then placed on the ground and the area of contact is sealed so as to prevent air from exchanging with the open atmosphere, (4) after placement of the chamber on the collar, the increase in the concentration of CO_2 is measured inside the chamber for the allotted time span (ppm/s) and, (5) the temperature and atmospheric pressure values are used to calculate the flux of CO_2 in gm^{-2} day^{-1} (Fig. 2). The "Non-Clearance" method is identical to the previous one except for the ground preparation phase. With this procedure, the chamber is placed directly on the ground on top of any vegetation, then the flux is measured. The final method tested is "Clearance and Waiting", which is also identical to the first except approximately 1 hour elapses between the ground clearance and sampling phases.

The comparison between the different flux measurement alternatives ("Clearance" Method and "Non-Clearance" Method) was

Table 1
Sampling models evaluated.

Models	Fixed factors	Random factors
Model 1	+ Ground measurement method (Clearance/Non-Clearance) + Sampling "stratum"	+ Measurement point coordinates + Clearance/Non-Clearance interaction with sampling point
Model 2	+ Ground measurement method (Clearance/Non-Clearance) + Sampling "stratum"	+ Sampling point coordinates
Model 3	+ Sampling "stratum"	+ Sampling point coordinates
Model 4	+ Ground measurement method (Clearance/Non-Clearance)	+ Sampling point coordinates

Table 2
The statistics of the four possible models.

Model	AIC	LogLik	p (df)
Model 1	4655.411	−2320.70	7
Model 2	4654.162	−2321.081	6
Model 3	4673.705	−2331.853	5
Model 4	4657.862	−2324.931	4

Table 3
Statistic of the fixed factors of Model 2.

Fixed effects			
Groups	Estimated	Standard error	t value
MODEL 2			
Intercepted	3.498	1.071	3.266
Clearance	4.900	1.036	4.729
Cenozoic stratum	0.880	0.584	1.507
Quaternary stratum	2.312	0.872	2.650

performed using a Mixed Linear Model statistical analysis and obtained via the "lme4" function of the "R" software (Bates and Maechler, 2009). Four models were evaluated in order to ascertain which best fits our objectives. This was done by determining how the clearance or non-clearance effect influences the measurement, analysing the different lithological strata where the measurement is taken and the spatial situation where the flux is measured. The following table defines which factors, fixed or random, were used in the corresponding models (Table 1).

When choosing a model, the Akaike Information Criterion or AIC (Akaike, 1974) is taken into account. The model chosen is the one that minimises the expression $\text{AIC} = -2\log(\text{lik}) + 2p$; where (lik) is the verisimilitude of the model and p the number of parameters of the model. The AIC Criterion values for each of the four models are included in the following table (Table 2).

The comparison between the models was made in accordance with the difference between the AIC values (Anderson and Burnham, 1999). If the difference (ΔAIC) is greater than 2, the model with the lesser AIC is chosen. However, if the difference between models in question is between 1 and 2, the models could be considered as being intimately linked. By applying these criteria, a clear difference can be observed between Models 1 and 2 compared with Models 3 and 4. The uncertainty lies, therefore, in which of the first two models (1 and 2) to choose, given that their ΔAIC is <2. The fact that Model 1 and Model 2 are similar is related to climate (temperature, moisture, and vegetation cover in that climate), rather than "strata." Therefore, climate is the most important control on CO_2 flux in the study area.

In order to differentiate between Models M1 and M2, a verisimilitude relation test is conducted (Faraway, 2006) in which the p-value is determined by calculating the probability, given that the null hypothesis is true, of obtaining a value equal to or greater than the maximum verisimilitude ratio of the models, expressed as $\text{LRT} = 2(\log\text{lik}(H_1) - \log\text{lik}(H_0)$ (in our case $H_1 = \text{M1}$ and $H_0 = \text{M2}$). To do this, data is generated in accordance with the null hypothesis, then compared with the null hypothesis and the alternative, and the LRT is calculated. This process is repeated a suitable number of times to enable the observation of the distribution of our LRT. Then the p-value is calculated as the proportion of times the value of the simulated LRT exceeds the observed LRT. Using this procedure the resulting p-value is 0.12, greater than the confidence level of 0.05, thereby validating the acceptance conclusion of the null hypothesis previously discussed.

It is worth pointing out in Table 3 that the measurement of the flux of CO_2 increases by more than $4\,\text{g}\,\text{m}^{-2}\,\text{day}^{-1}$ (Clearance = 4.9002) with respect to the flux obtained without first having cleared the vegetation, roots, etc. where the accumulation chamber is placed. This confirms that the sampling method used has an influence on the flux of CO_2 measured ("Clearance" Method and "Non-Clearance" Method). Having detected this difference in the flux measurement, it remains to determine which of the two methods is the most suitable for carrying out the sampling. Therefore, and assuming that the flux must vary over different lithological strata, an analysis was made of the importance of clearance prior to measurement of the flux of CO_2 from the ground. First, the flux data is separated into two groups in accordance with whether we clear the measurement location or not, and a linear model is made for each group so that the flux of CO_2 over the lithological strata which exist in the sampling area ("Cenozoic", "Mesozoic", "Quaternary") can be compared.

Significant differences were obtained between strata in the data corresponding to the "Clearance Method (CM)" group. On the contrary, this effect is not detected in the "Non-Clearance Method (nCM)". This result suggests the existence of a greater sensitivity in the flux measurements when the ground is cleared (CM) just before the CO_2 flux registration is taken. However, when no clearance takes place, the signal (nCM) is uniform throughout the entire sampling area irrespective of ground type, thereby possibly invalidating the previously suggested hypothesis. An alternative, when the ground is not cleared, the vegetative effect overwhelms the more subtle lithology effect.

To test the alternative, the variogram function (Ribeiro and Diggle, 2001) was calculated using the residuals of the linear models described above in order to determine whether there is any spatial dependency upon the flux of CO_2 by eliminating the effect of the stratum, with the result being shown in Fig. 3. The dotted lines envelop all semivariogram function computed by permutation of the data values on the spatial locations. Due to "Clearance Method (CM)" semivariogram is outside the envelope (dotted lines) it can be concluded that when the measurements were taken just after the ground was cleared there is a spatial relationship of the flux of CO_2.

However, some researchers (Lewicki et al., 2005b) expound that any alterations made to the ground must be minimized when the chamber is being positioned. If the ground has to be cleared (CM), the best solution would be to clear it at all the sampling points sequentially and, once this clearance has taken place, then measure the flux, point by point, in the same order. This means that there will be sufficient time for the gas flux to regain equilibrium following the alteration caused to the ground.

In this way, in light of the influence of, and the possible suitability of clearing the ground prior to taking the measurement, a second sampling campaign was planned in order to confirm which of the working methodologies is the most suitable. This involves taking three measurements at each point in accordance with the processes described above, namely with and without clearance, and a third

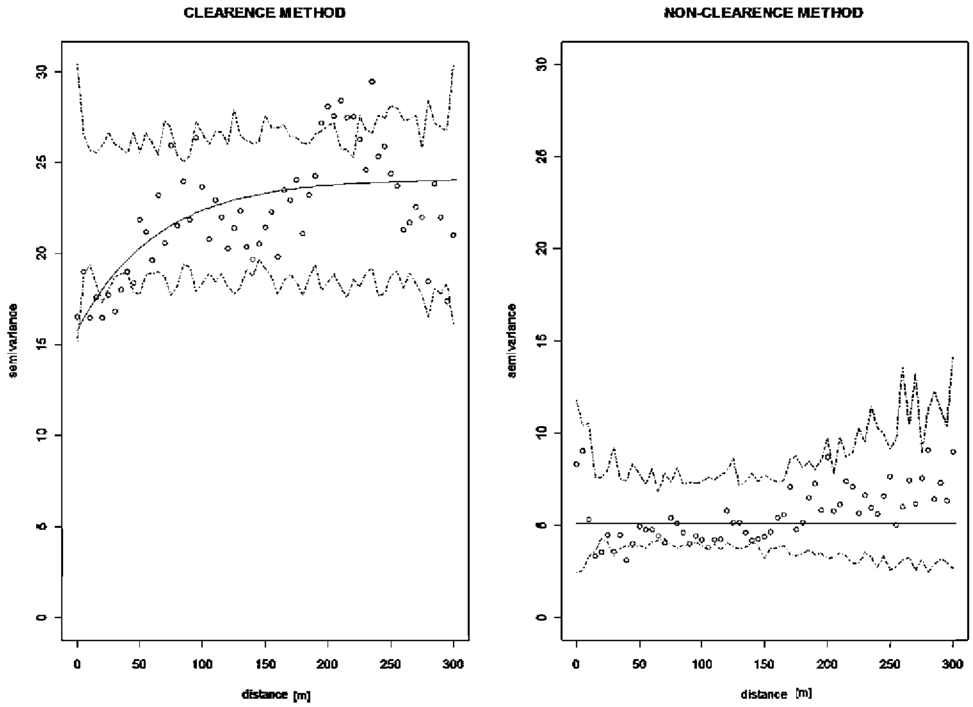

Fig. 3. Variogram functions using the CM and nCM methods.

for which the ground is cleared and the flux is given time to regain its equilibrium before the measurement is taken.

The time necessary for the re-equilibrium has been estimated at "one hour" as a result of the measurement protocol established by the authors at Hontomín: they would clean the measurement points along the profile and return to the starting point, which would take one hour. That value will obviously depend on the cleaning and measurement strategy, however it is recommended that the time between cleaning and measuring should be similar in all campaigns. So, the cleaning and measuring of CO_2 flow is made in the same day.

3.2. *Effect of atypical flux values*

The presence of several atypical high flux values were detected that might cause a distortion in the interpretation of the results. These atypical values might be due to either measurement errors, in which case they would have to be eliminated, or be interpreted as a significant anomaly (for example, the existence of a system of fractures through which the gas can migrate to the surface more easily, which is real and not eliminated from the data set).

In order to assess the validity of these values, it was decided to perform a comparative statistical analysis of the two measurement methods (CM and nCM) using all of the data, including the atypical, in the same way as in the case of the geo-statistical analysis. A check was made to ensure that the results of these two statistical analyses did not match and that these anomalous values had a strong influence upon the data (Table 4). Geologic knowledge applied to the distribution of the anomalous values can also be used to assess the validity of individual flux measurements.

The variance of the random error is equivalent to the nugget effect of the variographic analysis, with the observation that there is a small difference, between both (21.5 against 19.4). However, the variance at the sampling point would be equivalent to the value of the difference of the sill and of the nugget effect, given that its values are substantially different (13 and 6.8, respectively).

3.3. *Variogram analysis*

The cloud variogram in Fig. 4a shows the variances of all pairs of points separated from 0 m to 1400 m. In Fig. 4b the red lines are made with pairs of points that generate bigger variances in Fig. 4a. In order to reach a decision as to the appropriateness of retaining an atypical data point a variogram cloud was drawn up (Pebesma, 2004) (Fig. 4a). If several pairs of atypical data were to include an identical observation, this would indicate that the observation in question is substantially different from its neighbours and could therefore be considered as being a valid atypical value (outlier).

In Fig. 4a check is made as to whether there is a group of points in the upper part of the graph which is having a notable influence over the rest. If these are identified, it is checked if they coincide with the atypical values detected following the development of the Mixed Linear Model. As an example, one of these, which belongs to Sampling Subarea P2 and can be related with other measurement points located in Subarea P1, has been included (Fig. 4b). The red lines indicate the pairs of points that generate the greatest semivariance in the variogram cloud, noting that most of the red lines have a common point belonging to the subarea P2 that can be considered as an outlier.

Table 4
Dispersion statistics in the mixed linear analysis and in the variographic analysis.

	Variance of the residual random error	Nugget effect	Variance due to the value of the coordinates (sampling point variance)	Difference (sill – nugget effect)
Mixed linear model analysis	21.5		13	
Variographic analysis		19.4		6.8

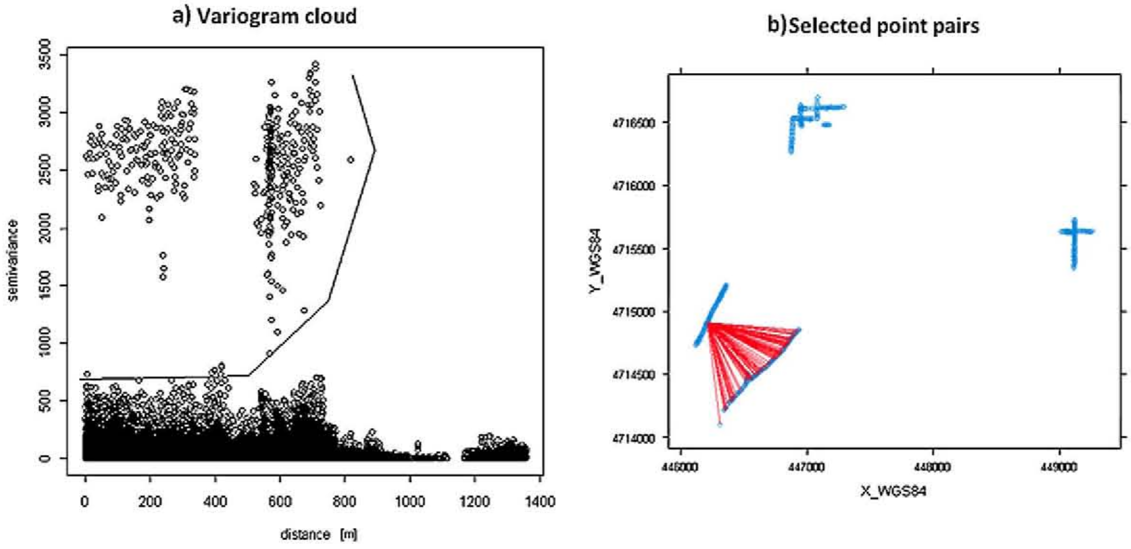

Fig. 4. (a) Variogram cloud. (b) The red lines joint atypical points, in terms of the distance between it and other points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In order to verify the influence these atypical values have over the rest, the data were corrected using a linear model so as to minimize the influence that clearance and the stratum beneath the sampling point have over the flux measurement. This was done by checking that the residual values separated by more than three standard deviations from the average correspond to the points which we consider as being possible anomalous values.

Given that it has once again been shown that the atypical values exert an extremely important influence over the rest of the observations, it was decided to eliminate them. The upshot of this was that by eliminating the effects of the anomalous values, the linear model with the most suitable mixed effects shows us that only the flux, not the sampling point, is influenced by the fixed clearance effect and by the random point change. Whatever the case, and although it is statistically insignificant (with a *p*-value greater than, but extremely close to 0.1), experience leads us to deem it suitable to maintain the influence of the stratum in the models, given that changes in soil conditions can have an influence on gas emissions. In our case, a possible cause for the stratum not being found to exert an influence might be that the flux of CO_2 is very low and the methodology is unable to detect that difference.

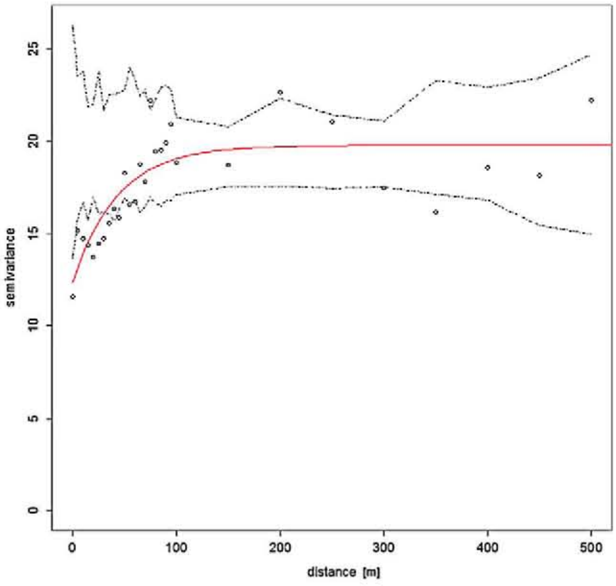

Fig. 5. Experimental and envelopment variogram.

3.4. *Geostatistical analysis*

One of the objectives set for Campaign 1 was that of calculating the "range", in other words the maximum distance which a spatial autocorrelation exists for the CO_2 flux values. The calculation of this value is extremely important given the fact that is used as the basis from which the following campaigns are designed by establishing the appropriate distance between consecutive sampling points.

Once the anomalous data had been eliminated, which interferes with the determination of the variogram, the flux data are corrected using a linear model (LM). This is done by eliminating the influence exerted on the flux measurement by the clearance and stratum factor, with the result being the variogram shown in Fig. 5.

Fig. 5 shows the experimental variogram obtained using the residual values of the linear model (points), the envelope (black dotted lines) of all those variograms that will be obtained after randomly permuting the data coordinates in such a way that if our experimental variogram is within it, no spatial relationship exists between the data. The red line shows the variogram adjusted using minimum squares measured in accordance with Cressie's principle (Cressie, 1993).

The variogram presents a nugget effect of 12.75 and a sill of 18.91. A variation due to the change of coordinates is 6.16 and the range is 107 m.

3.5. *The influence of the high flux values*

This involves studying the influence the highest flux values have over the remaining values. What is desired is finding some way to calculate the distances up to which a high CO_2 flux value could still exert an influence.

Given that it was decided that the geometry of the design of Campaign 1 was to be in accordance with lines and cross sections, rather than divided up into areas, it was assumed that the distances would correspond with concentric circumference radii to one with a high flux value as its centre. This simplification means accepting isotropy; however, isotropic distribution of fluxes is very unlikely because there is almost always a preferred orientation related to,

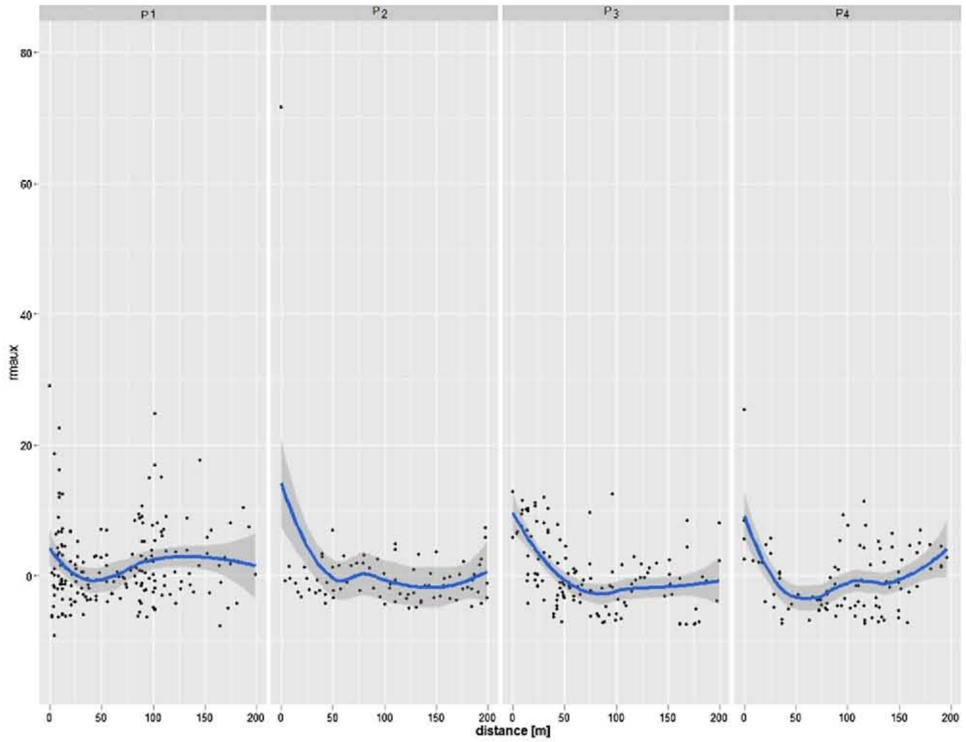

Fig. 6. Distance to the highest values. The Subareas P1, P2, P3 and P4 are represented from left to right.

and parallel to the orientation of faults and fractures. In future campaigns, when the measurement areas are made denser, it will be possible to evaluate whether isotropic behaviour does or does not exist.

This is represented by four graphs (Fig. 6) in which the residual values of the linear model (y-axis) are related with the distance between the highest flux value of each Subarea (P_i) and the rest of the sampling points (x-axis).

The choice of the residuals is explained by the fact that we wish to prevent the possible influence that these might have over the variable measured values such as the sampling methodology (clearance–non-clearance and the sampling stratum (lithology) The blue-coloured curve expresses the average of the values for each distance with a confidence interval of 95%. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

Interpreting Fig. 6 leads to the following conclusions:

- Subarea P1 is characterised as being that in which the most replications occurred. It is perhaps for this reason that it is the most confusing to interpret. On the other hand, it is also the area that has the largest number of high CO_2 flux values. The distance of influence with respect to high values could be estimated at around 50 m, as it corresponds with the change of gradient of the average values curve.
- Subareas P2 and P4 would appear to show more clearly a range of 50 m with respect to the high flux.
- However, in Subarea P3 the range appears to increase to in the region of 100 m.

Bearing in mind the diffuse emissions of CO_2, the range of which was previously estimated at 107 m and the highest flux, whose range is 50 m, it is worth pointing out the following:

- It is deemed interesting to make more CO_2 flux measurements in some of the Subareas sampled during Campaign 1 in order to validate the conclusions.
- Given that the CO_2 flux values in the Hontomín region are relatively low, it would be interesting to take measurements in areas with higher flux values with a view to repeating the statistical methodology applied.

In light of the two possible range values obtained (107 and 50 m) the choice is, from a conservative point of view, to make the distance between sampling points 25 m for the next campaigns.

3.6. *Second sampling campaign*

A second sampling campaign was carried out in order to confirm the results. As well as the sampling methods used in the first campaign (clearance and immediate measurement (CM), and non-clearance (nCM)). A third method was introduced involving the clearance and preparation of the sampling area, then waiting for approximately one hour before taking the measurement (CWM). Two different accumulation chambers were used, both made by West Systems (WS0825 and WS0834), and samples were taken at each point using the three techniques and with both types of equipment. The results obtained using the two types of equipment were not significantly different and will not be discussed further.

In the box diagram shown in Fig. 7, it is possible to observe in graph form that effectively clearing the sampling point, then taking the measurement (CM) gives a higher value than non-clearance (nCM), as had previously been shown during the first campaign. On the other hand, clearance and then waiting to take the measurement (CWM) results in the flux value dropping to similar values obtained using the "Non-Clearance" (nCM) procedure.

After performing another mixed linear model analysis, it was found that the model which best explains the results is that with the clearance method as its fixed effect and the point where the

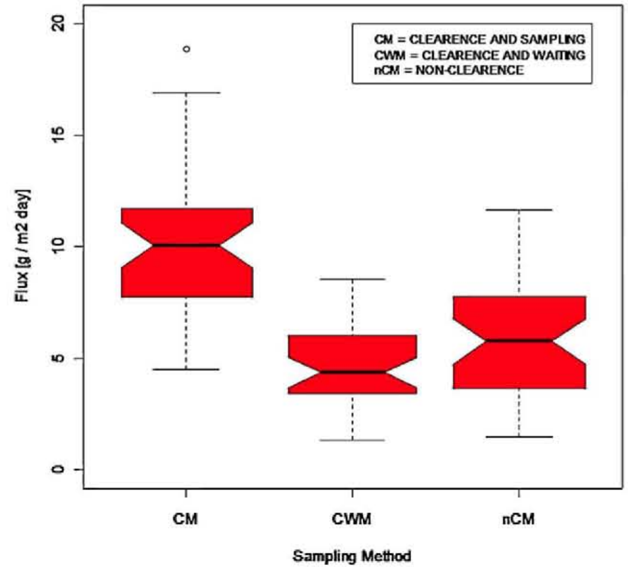

Fig. 7. Box plots according to sampling method.

sampling is carried out as its random effect. Furthermore, by using the CM procedure greater estimators of the average were obtained: the mean value obtained using the CM method is approximately 4.36 greater than that obtained using the nCM. This is a similar result to that obtained using the model of the first sampling campaign (4.9), and 5.53 greater than that of the CWM.

Finally, in order to confirm the hypothesis, a multiple comparison of the averages was carried out using the TukeyHSD test. This test showed that there was a significant difference between clearance and sampling (CM) and the two remaining techniques, namely clearance and waiting (CWM) and non-clearance (nCM). There was not a significant difference between (nCM) and (CWM).

In short, we conclude that the method used for determining the flux does indeed have an influence on the result, a claim proven by the fact that the greatest value is obtained by clearance and immediate sampling (CM). The reason behind these greater flux values could be due to the top layer of the ground being disturbed during clearance, thereby causing a temporary leakage of gases and a consequent overestimation of the emission value. By waiting for a long enough time, estimated at one hour, the flux values once more decreases to normal levels.

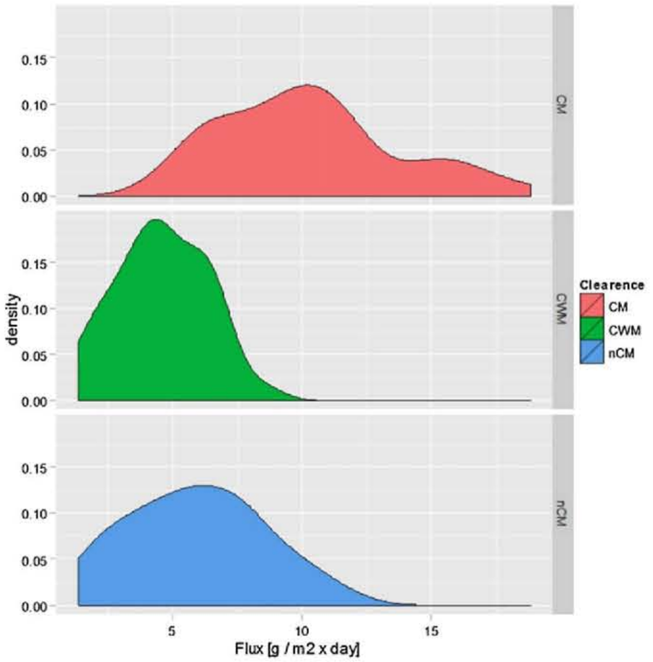

Fig. 8. Dispersion of flux values in accordance with the three clearance methods; CM: Clearance Method; nCM: No-Clearance Method; CWM: Clearance and Waiting.

These results mean that sampling could be done without clearance (nCM) or after clearance and waiting (CWM). In our case, the results obtained after clearance and waiting show less dispersion and this tells us that at this site this is the best technique to use. This is our conclusion due to the fact that the surface where we carry out the sampling is uneven and the constant wind in the area means that if we clear and leave a sampling area uniform and even, we achieve a better seal between the accumulation chamber and the ground, which justifies the increase in sampling time as it results in a more precise determination of the flux. The clearance prior to sampling removes vegetation, and the difference observed at another site may be influenced by the amount of vegetative cover and the season (Fig. 8).

4. Conclusions

Calculating the base line of the diffuse flux of CO_2 is essential when characterising a site where this gas is going to be stored underground. In the area investigated in this case (Hontomín, Burgos, Spain), the average flux values were low and uniform ($9.1\,g\,m^{-2}\,day^{-1}$ on average), and this made obtaining the most accurate values possible important. For this reason it was decided to conduct a study into the best methodology for sampling the flux of CO_2 using an accumulation chamber. This left us with three options: (a) prior clearance of the area on which the chamber is to be placed and then immediately sampling (CM); (b) not clearing the area, in other words placing the chamber on top of any vegetation that happens to be there (nCM); and (c) clearing the area but then waiting before sampling (CWM).

After performing a statistical analysis (Mixed Linear Model), we concluded that the method chosen has an influence on the flux value determined. The greatest values correspond to the clearance and immediate sampling (CM). The reason behind these greater flux values could be due to the top layer of the ground being disturbed during clearance, thereby causing a temporary leakage of gases and a consequent overestimation of the emission value.

Results mean that sampling could be done without clearance (nCM) or after clearance and waiting (CWM). However, the results obtained after clearance and waiting (CWM) show less dispersion and this tells us that CMW is the best technique for monitoring CO_2 Storage sites. All the sampling points were cleared sequentially. The team then returns to the first point from where it started, sequentially measuring the flux of gas. In this way enough time is provided for equilibrium to be restored between the ground and the gas flux to the atmosphere.

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