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Geofisica e Vulcanologia**

## **The application of soil gas technique to geothermal exploration: study of òhiddenö potential geothermal systems**

### **Final Report**

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## **1. Introduction**

Geochemical studies were conducted throughout soil gas and flux surveying for locating both permeable zones in buried reservoirs and the presence of possible gaseous haloes linked to active geothermal systems.

In this work we focused our interest on the distribution of soil gas concentrations (Rn, Th, He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S) in the soil air of the Tetitlan area considered a potential thermal field and characterized by scarcity of surface manifestations.

Radon is used as a tracer gas to provide a qualitative idea of gas transfer (velocity and flux), carbon dioxide and methane are believed to act as carriers for other gases (i.e., Rn and He), helium and hydrogen are used as shallow signals of crustal leaks along faults (Ciotoli et al., 2005). Methane is also considered both a characteristic biogenic indicator of organic matter deposits and a tracer of major crustal discontinuity. A total of 154 soil gas samples were collected in an area of about 80 square kilometres. The same area was investigated throughout a total of 346 of CO<sub>2</sub> and CH<sub>4</sub> flux measurements.

## **2. Objectives**

The main object of this work was to perform a geochemical study focused to the characterization of geothermal potential of the Tetitlan (Nayarit) area by means flux and soil gas concentration measurements. In particular, the location of diffuse degassing structures (Chiodini et al., 1995, 1998, 2000, 2001) using soil gas geochemistry, will allow to infer the leakage system of gases (such as helium, hydrogen and radon) that are considered fault and/or fracture tracers. The Tetitlan area has been considered, on the basis of previous CFE geochemical (water analysis) and geothermal studies, an "hidden" geothermal system as there are no superficial thermal evidences such as fumaroles and thermal springs. For this reason, a further study using the knowledge of the potential of gas geochemistry applied on the geothermal prospecting, was required.

## **3. Tectonic signature of soil gas leak and degassing**

Recent works observed anomalous gas concentrations over faults and confirmed these gases as a fault indicators (Quattrocchi et al., 1999; Mancini et al., 2000; Baubron et al., 2002; Ciotoli et al., 2005, 1999, 1998; Zhang and Sanderson, 1996; Lombardi et al., 1996; Klusman, 1993; Zhiguan, 1991).

Faults and fractures can favour gas leaks because they usually increase rock and soil permeability, and thus the presence of linear soil gas anomalies longer than several meters are often taken as strong evidence of tectonic features (Fridman, 1990). It is important to note that faults are typically wide fracture zones that can also be crosscut by other structures, thus resulting in diffuse or halo anomalies, respectively (Matthews, 1985; Sokolov, 1971). Recent research has demonstrated that the gas-bearing properties of faults are not necessarily continuous along a tectonic structure (Etiope et al., 2005; Ciotoli et al., 2005; Baubron et al., 2002; Lombardi et al., 1996; Ciotoli et al., 1998; Salvi et al., 2000; Pizzino et al., 2004; Voltattorni et al., 2006). In these cases isolated points with high concentration values (spot anomalies), are frequently observed. When multiple spot anomalies occur along a linear trend, one can infer that they lie along a structural feature which has a spatially discontinuous in terms of its gas-bearing properties (Ciotoli et al., 1998; Lombardi et al., 1996). Extensive experience in soil gas prospecting by the authors indicates that soil gas anomalies generally occur as linear, fault linked, anomalies, as well as in irregularly shaped diffuse or halo anomalies and irregularly spaced plumes or spot anomalies (Voltattorni et al., 2005; Beaubien et al., 2002; Lombardi and Voltattorni, 2003; Lombardi et al., 1996). These features reflect gas migration dominated by brittle deformation both at macroscale and/or microscale. Therefore spatial patterns of soil gases in faulted areas appear to be suitable tools for identifying tectonic structures also in areas characterized by thick clay cover whose plastic behaviour could mask the identification of faults by mean of other geological (field mapping) and geophysical methods.

## 4. Activities

### *4.1 Soil gas sampling and analysis*

Soil gas surveying consists of the collection and analysis of gas samples from the unsaturated, possibly dry, zones. In the present study samples were collected using a stainless steel probe driven into the ground to a depth of 0.5 m; this depth is considered below the major influence of meteorological variables (Hinkle, 1994; Segovia et al., 1987). Furthermore, the collection of a large number of samples statistically minimizes sampling/analytical error and bias caused by individual samples (Beaubien et al., 2003; Annunziatellis et al., 2003; Lombardi et al., 1996; Hinkle, 1994; Reimer, 1990). Radon and thoron are analyzed immediately in the field, due to their half-life (respectively of 3.8 days for radon and 55 sec for thoron), using a RAD7 DurrIDGE® alpha spectrometry instrument.

Radon ( $^{222}\text{Rn}$ ) and thoron ( $^{220}\text{Rn}$ ) values were measured every 15 minutes (third cycle reliable for the

final reading of the two components) pumping from the steel probe. The ionization chamber of the detector is protected by the > 10% humidity by a  $\delta$ drierite trap and a  $\delta$ gasoline type pre-filter. Radon and thoron particles generate positive charged  $^{218}\text{Po}$  and  $^{216}\text{Po}$  ions after entering the chamber and they are collected on the detector by electrical high-Voltage field sources. Radon calculation is based on the sum of  $^{218}\text{Po}$  and  $^{214}\text{Po}$  peaks, and thoron calculation is based on  $^{216}\text{Po}$  only because of the slow response of  $^{212}\text{Bi}/^{212}\text{Po}$ .

A 50 ml gas sample was placed in a previously evacuated, 25 ml volume, stainless-steel canister for transport and storage. Once in the laboratory, each gas sample was also analyzed for major ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ) and minor ( $\text{C}_{164}$  hydrocarbon,  $\text{He}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ) gas species using a *Perkin-Elmer AutoSystem XL* packed-column gas chromatograph.

A soil gas survey was performed over the Tetitlan area (about  $80 \text{ km}^2$ ) according to a regional sampling with a density of  $466 \text{ samples km}^2$  (100 samples, Figure 1, black dots). Furthermore, some high-resolution surveys (54 samples) were performed within detailed zones (Santa Isabel, Valle Verde and Tetitlan villages) across the area to enhance the chances of properly (on the basis of the radon and flux measurements results achieved directly on the field) recording the fault gas signal and to study fault influence on shallow soil gas distribution.

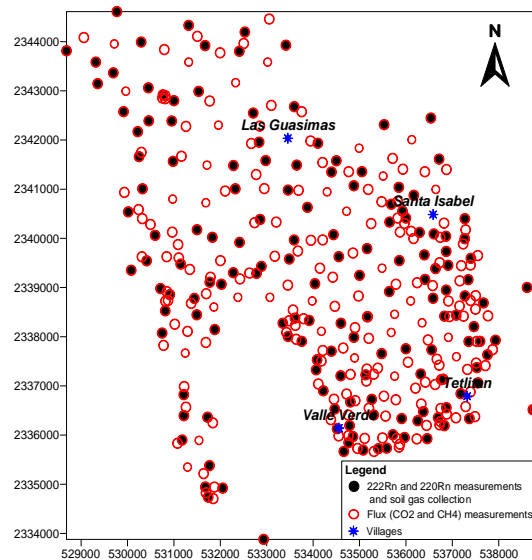


Figure 1 ó Sampling distribution: soil gas sampling and radon measurements in black dots, flux measurements in red dots.

#### 4.2 Flux measurements

In order to have a semiquantitative idea of the gas leakage in the faulted and unfaulted zones, 346 measurements of soil gas exhalation ( $\text{CO}_2$  and  $\text{CH}_4$ , Figure 1, red dots) were made by using a speed-portable "closed dynamic" accumulation chamber "time 0" (West System<sup>®</sup> instrument). The instrument is equipped of two sensors with different detection limit:  $0.01 \text{ gr/m}^2\text{day}$  for methane and  $0.2 \text{ gr/m}^2\text{day}$  for carbon dioxide. Accumulation chamber measurement techniques and flux-calculation methods have been widely described by many authors: Werner et al. (2000), Bergfeld et al. (2001) Chiodini et al., 1995, 1998, 2000, 2001, Chiodini and Frondini, 2001, Cardellini et al., 2003.

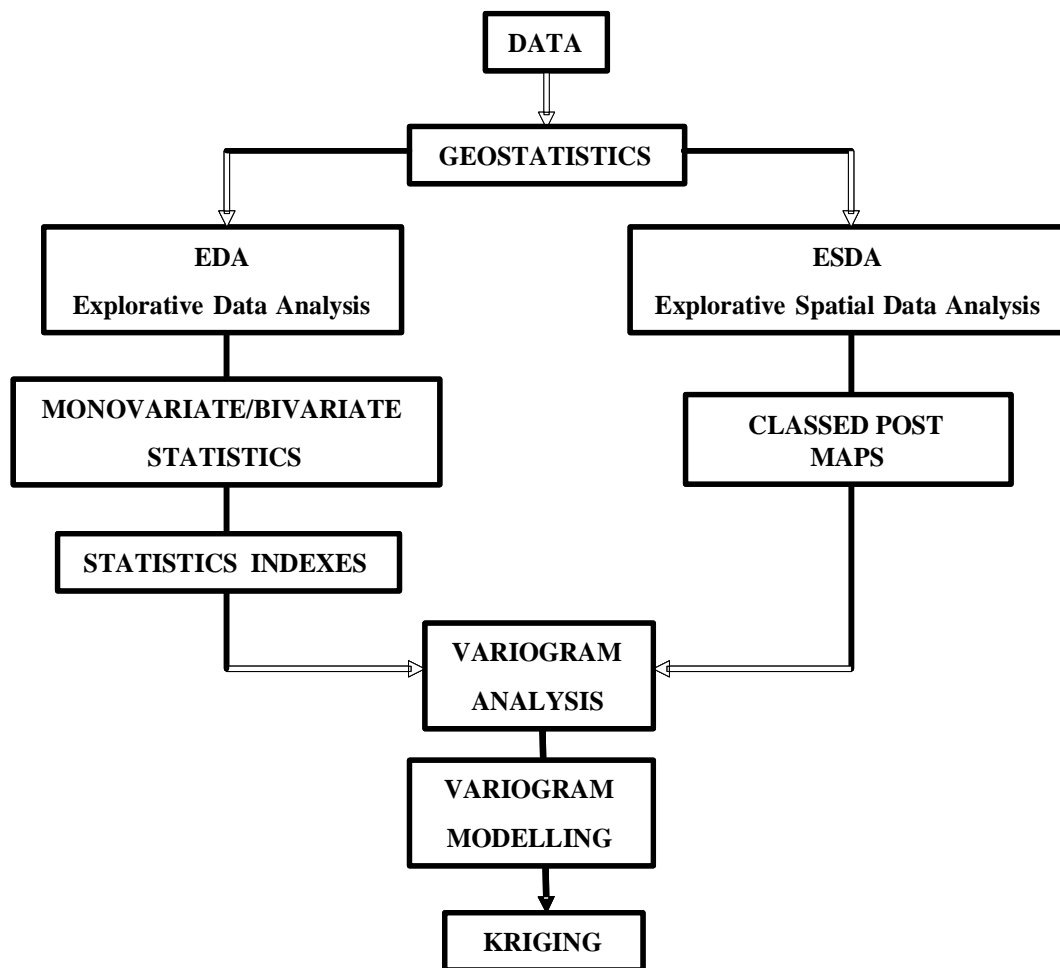


Figure 2 - Flowchart of the statistical and geostatistical techniques used for soil gas data elaboration and mapping procedure.

### ***4.3 Data interpretation***

Geostatistical techniques were applied for the study of spatially correlated data. The flowchart of the general steps followed in this study is shown in Figure 2. Exploratory data analysis (EDA) was first performed to evaluate the basic characteristics of the data (i.e., summary statistics and statistical distribution of each variable). Univariate and bivariate statistical and graphical methods were used to study each variable independently, the relationship between variable pairs, as well as to highlight the presence of multiple populations. Exploratory spatial data analysis (ESDA) consisted of preliminary spatial data representation by using classed post maps to show value distribution and to visualize the intersample distance, which is useful to determine the grouping intervals for experimental semivariogram calculation and to choose search radii in estimation routines (kriging). Variogram analysis is performed to check spatial continuity of the data values and the presence of anisotropies. Once spatial continuity is characterized it is modelled with variogram functions that form the basis for kriging.

Collected data were computer processed by using the following software: Statistica 6.0 (StatSoft, Inc.), Geostatistical Software for Environmental Science (Gamma Design Software, LLC) and Surfer 8 (Surface Mapping System, Golden Software, Inc.).

## **5. Results achieved**

### ***3.1 Soil gas concentrations***

The exploratory data analysis (EDA) shows that CO<sub>2</sub>, He, H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> have low dispersed distributions, as highlighted by the low value of the variance (Table 1). Otherwise, the wide ranges, as well as the high skewness values, for CH<sub>4</sub> and Rn indicate the presence of outliers. The mean and median values for CH<sub>4</sub> (30.32 ppm and 2.54 ppm), and Rn (2702.38 Bq/m<sup>3</sup> and 2180.00 Bq/m<sup>3</sup>) highlight that the frequency distribution of these gases are positively skewed (4.96 and 3.18, respectively), indicating an exponential or lognormal distribution.

These preliminary considerations indicate that active gas-bearing faults present in the area favour gas leakage. In particular, the high median values of Rn and CH<sub>4</sub> would confirm the presence of high gas microseeps. The low median values of He, H<sub>2</sub>, CO<sub>2</sub> concentrations could be due to dilution by major atmospheric components, i.e., nitrogen and oxygen. Furthermore, dilution by surface gases of biological origin may also alter CO<sub>2</sub> and CH<sub>4</sub> signatures. In this case the shallow distribution of fault-

related anomalies of these minor and trace species can be shown by spot values that could show a linear pattern. These soil gas anomalies, however, may display a complex character, both in space and time. For example, anomalies may differ according to the structure of the faults, such as fault gouges versus intensely sheared zones, resulting in a different shallow pattern due to the low gas permeability of fault gouge materials compared to high permeability of fractured rocks in the adjacent shear zones (King et al., 1996; Sugisaki et al., 1980). On this basis gas anomalies in correspondence of active faults can be either ÷direct leak anomalies÷ indicating a deep gas origin, or ÷secondary anomalies÷ linked to the shallower chemical-physical nature of the fault-constituting rocks.

*Table 1 - Main Statistics of Soil Gas Data*

	Samples	Mean	Median	Min Value	Max Value	Lower Quartile	Upper Quartile	Variance	Standard Deviation	Skewness
Radon (Bq/m <sup>3</sup> )	154	2702,38	2180,00	0,00	19200,00	1080,00	3490,00	5979312,66	2445,26	3,18
Thoron (Bq/m <sup>3</sup> )	154	6830,84	5120,00	289,00	24100,00	2960,00	9770,00	27268498,20	5221,92	1,11
He (ppm)	154	5,62	5,55	4,19	8,20	5,47	5,64	0,21	0,46	3,25
H <sub>2</sub> (ppm)	154	1,66	1,29	0,54	7,42	1,11	1,70	1,03	1,02	2,94
O <sub>2</sub> (%)	154	19,88	19,90	19,22	20,56	19,75	20,01	0,04	0,21	-0,39
N <sub>2</sub> (%)	154	77,38	77,30	76,77	78,68	77,14	77,57	0,13	0,36	1,03
CH <sub>4</sub> (ppm)	154	30,32	2,54	0,17	653,39	0,85	17,63	8340,08	91,32	4,96
CO <sub>2</sub> (%)	154	0,19	0,17	0,02	0,87	0,10	0,24	0,02	0,13	2,31

*The main statistics of soil gas data show that CO<sub>2</sub>, He, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> have low dispersed distributions as highlighted by the low value of the standard deviation. Otherwise, the wide ranges, as well as the high values of the skewness, for CH<sub>4</sub> and Rn concentrations indicate the presence of outliers. The mean and the median values for CH<sub>4</sub> and Rn highlight that the frequency distribution of these gases are positively skewed, indicating an exponential or lognormal distribution of these variables. In the case of skewed distributions, the median of CH<sub>4</sub> and of Rn, are better than the mean and the standard deviation to provide data dispersion and to highlight values that may be considered as anomalous.*

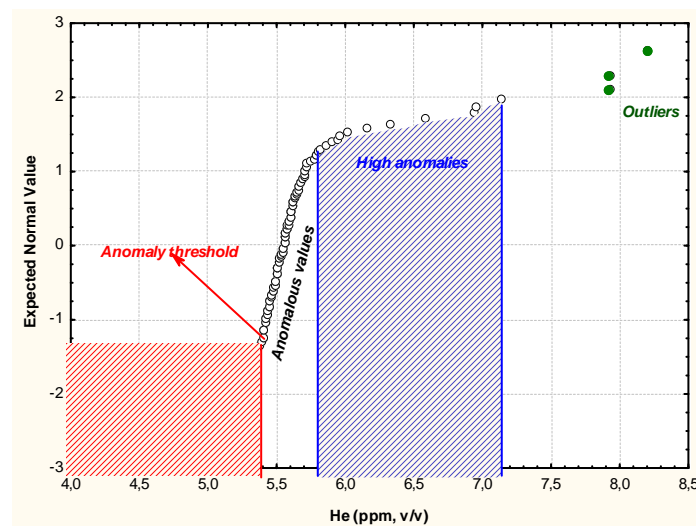
Because soil gases have a different abundance with respect to the atmospheric air, (0.01 kBq m<sup>3</sup> for <sup>222</sup>Rn, 0.036 for CO<sub>2</sub>, 1.4 ppm for CH<sub>4</sub>, 5.20 ppm for He, 78.08% for N<sub>2</sub>, 19.4% for O<sub>2</sub>, 0.5 ppm for H<sub>2</sub>), the detection of an anomaly threshold constitutes a fundamental step in the exploratory statistical analysis for further discussion about the possible sources of the studied gases. Various statistical methods can be applied to assess the anomalies relative to background (Ciotoli et al., 2005; Beaubien et al., 2003; Sinclair, 1991). In general, our experience highlights a strong correspondence between the



upper quartile and the anomaly threshold. It should be remembered, however, that soil gas anomalies cannot be fixed absolutely, but rather must be defined locally due to their complex origins.

According to Sinclair (1991) the normal probability plot (NPP) provides a good method to distinguish different, often overlapping, populations (i.e., background, anomalous values, and outliers) and a more objective approach to statistical anomaly threshold estimation. As an example, Figure 3 highlights how the anomaly threshold is calculated on the basis of achieved He results.

In order to study spatial patterns, data were visualized using classed-post maps (Figure 4). Anomalous carbon dioxide values agree well with the radon activity suggesting a fit with supposed local fault systems (Ferrari et al., 2003).



*Figure 3 ó Normal Probability Plot is used to evaluate the normality of the distribution of a variable, that is, whether and to what extent the distribution of the variable follows the normal distribution (in this last case, all values should fall onto a straight line). Data refer to He gas results achieved during the present study.*

This correlation supports the presence of buried gas-bearing channels in the area where the migration of CO<sub>2</sub> acts as carrier for trace species, suggesting a potential deep origin of these gases. This hypothesis is strengthened where methane and helium anomalies are also measured (particularly in the eastern sector, between Santa Isabel and Tetitlan villages and in the north-western sector, in proximity of Cerro San Pedro). However, to reinforce the hypothesis about the origin of CO<sub>2</sub>, carbon isotopic analyses are required.

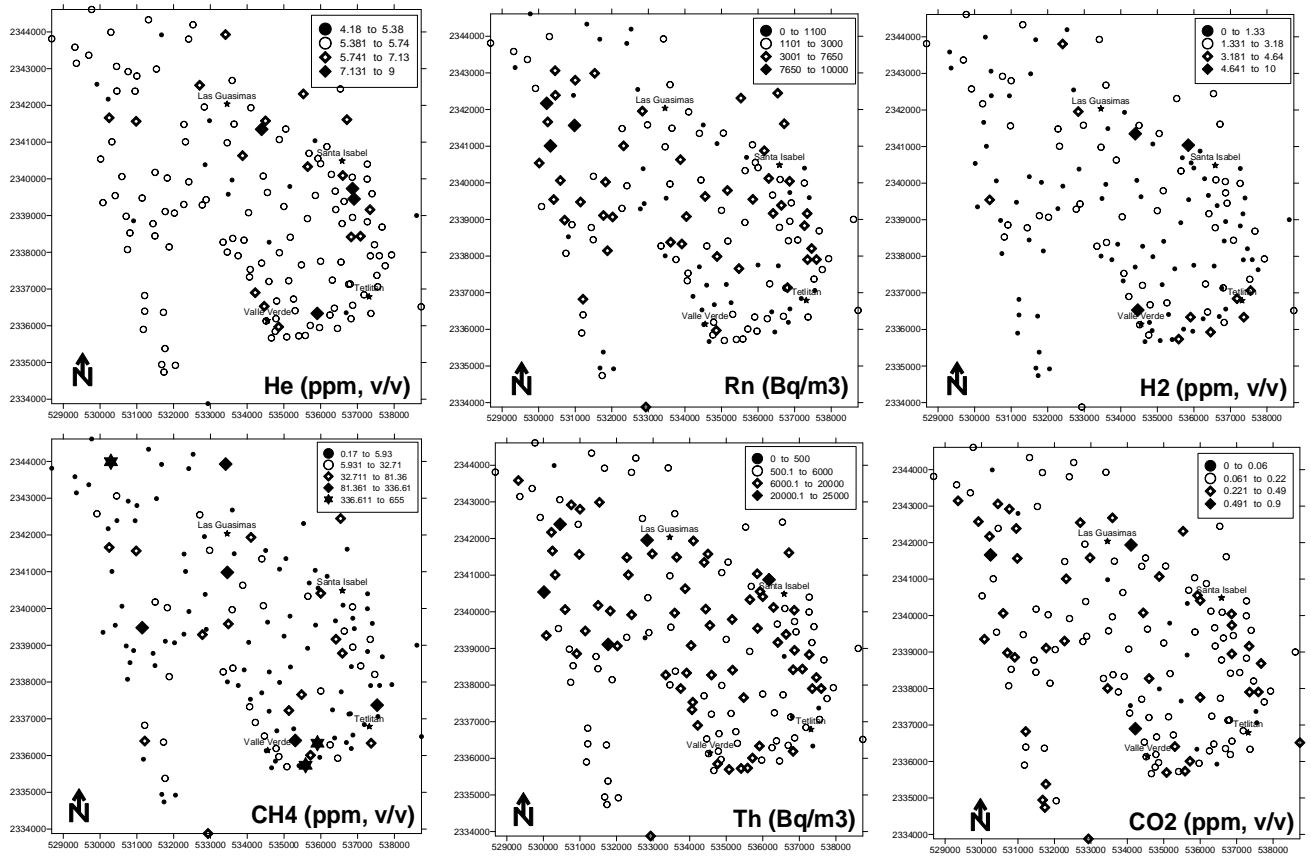


Figure 4 - Classed post maps show that radon and carbon dioxide anomalous values prevail in the eastern as well as in the north-western side of the studied area. Helium and methane distribution locally also corresponds a spot preferential pathway of degassing, although highest values are spreadly distributed between Valle Verde-Tetlitan-Santa Isabel villages.

The interpretation of CH<sub>4</sub> data is generally complex because this gas can be biologically produced in an-oxic sediments which are commonly rich in organic matter but can be biologically consumed in oxic soils. Figure 4 shows that anomalous values are located mostly in the southern side of the area in correspondence of Valle Verde village. The origin of methane can be interpreted based on isotopic signatures ( $\delta^{13}\text{C}$  and associations with other gases, e.g., heavier hydrocarbons). Anomalous values of H<sub>2</sub> often overlap methane ones suggesting a direct chemical correlation between the two soil gas species. The presence of thoron anomalous values spreading almost all over the sampled area suggests an interesting diffusion in the lower layers of the atmosphere.

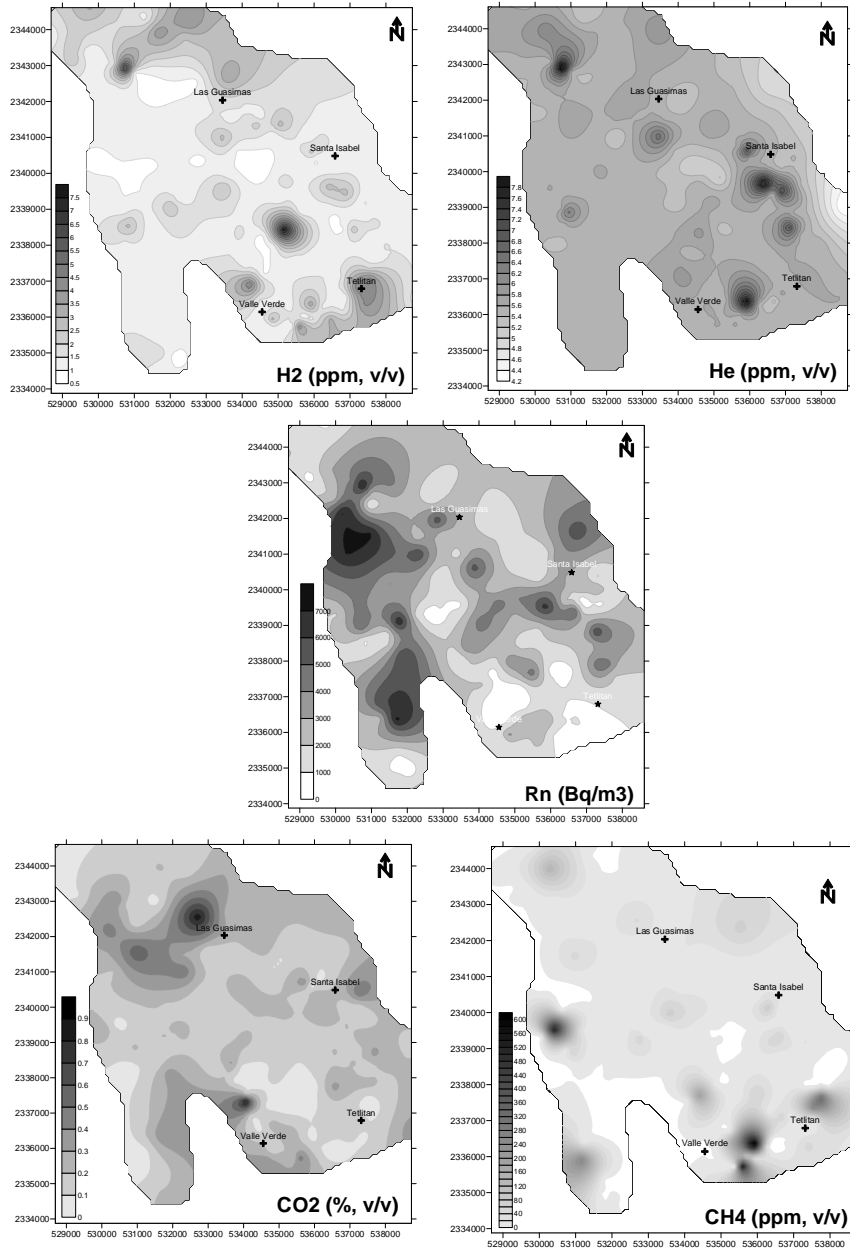
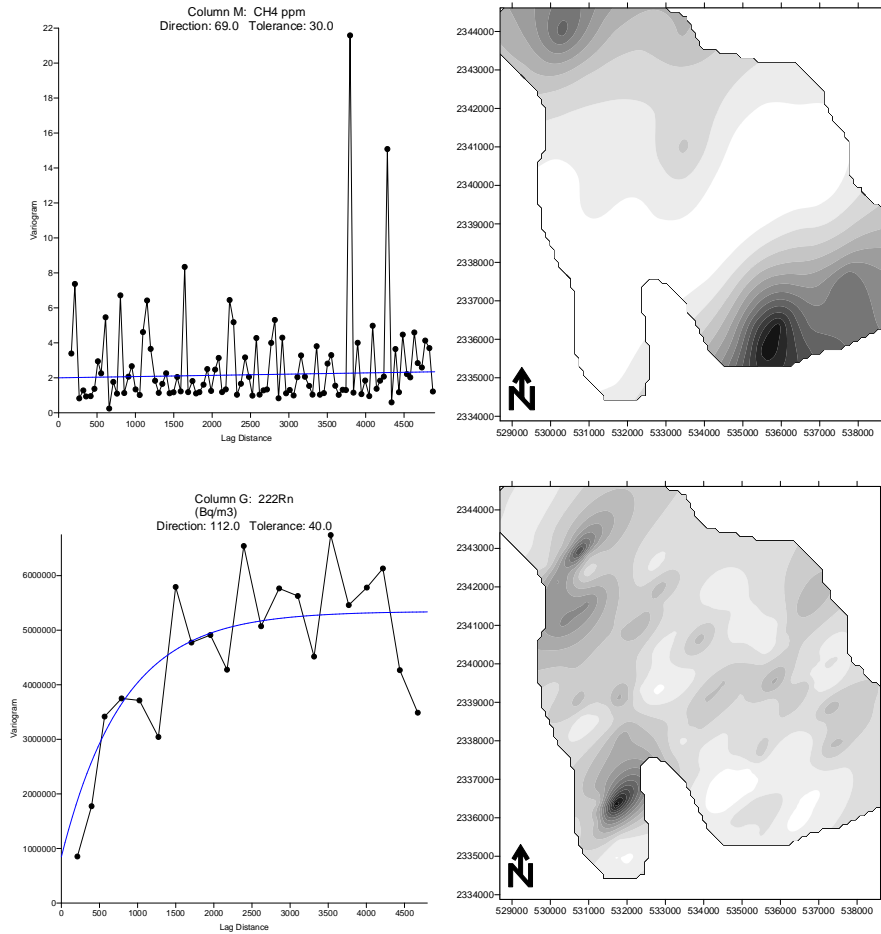


Figure 5 ó Soil gas concentration maps show a different distribution for each gas specie excepting in the north-western sector of the area where radon and carbon dioxide anomalous values are more concentrated.  $He$ ,  $H_2$  and  $CH_4$  have a more spotty distribution in the south- eastern sector.



*Figure 6 ó Methane and radon contour maps elaborated on the basis of modelled experimental variograms. The methane map highlights a major anomaly both in the southern and northern sector north oriented. On the contrary, the radon anomalies are evident along the western part of the studied area.*

Figure 5 shows the concentration maps of the analysed soil gas species. Excepting  $O_2$  and  $N_2$  having atmospheric values and for this reason not included in the discussion, it is well evident the distribution of anomalies for the other gas species. Rn and  $CO_2$  anomalies are present mainly in the north-western sector of the area, while the other gas species ( $He$ ,  $H_2$  and  $CH_4$ ) are more spotty distributed in the eastern and southern sector.

In order to study the different contribution of direction-specific versus random phenomena a geostatistical analysis was performed constructing experimental variograms in different direction for a better interpretation of anisotropies. In fact, directional variograms can differ in total sill value, highlighting a false zonal anisotropy. For this reason it is recommended to remove the proportional

effect by calculating  $\div$ relative variograms, where each pair difference is divided by the average of the individual pair of samples.

In linear geostatistics, as in conventional statistics, a normal distribution for the variable under study is desirable. Even though normality may not be strictly required, high skewness and outliers can impair the variogram structure and the kriging results. For this reason, the variographic study was performed only for Rn and CH<sub>4</sub>, because they constitute a typical carrier/trace gas association and because they show a less skewed data distribution than the other gases.

Figure 6 shows the contoured radon and methane values in sampled area using the parameters of the selected variogram models. The experimental variograms of CH<sub>4</sub> and Rn for the northern sector confirm the presence of anisotropy as they reach the same sill value at different ranges while, for the eastern sector, they highlight a quite different spatial domain showing a more complex structure.

## **5.2 Soil gas fluxes**

Carbon dioxide and methane fluxes were measured at 346 locations. Measurement spacing varied between 100 and 250 m including locations where soil gas concentration measurements were made at the same time. Data achieved directly on the field, were treated and calculated considering the variation of barometric pressure and temperature measured during the survey. Fluxes were analyzed using experimental variograms computed and modelled both for methane and carbon dioxide. Emission rates for each realization were calculated by summing the simulated flux across the grid and multiplying by the grid area. The average and standard deviations of the emission rates reported in Table 2 are calculated from the flux realizations.

Carbon dioxide and methane fluxes ranged from not detectable ( $<3 \text{ g/m}^2 \text{ d}^1$ ) to  $45,14 \text{ g/m}^2 \text{ d}^1$  and to  $9,00 \text{ g/m}^2 \text{ d}^1$  respectively. The means of the entire CO<sub>2</sub> and CH<sub>4</sub> flux data set were  $2.19$  and  $0,83 \text{ g/m}^2 \text{ d}^1$ , respectively. The data set had a coefficient of variation (CV: the standard deviation divided by the mean) of  $2,02$  for CO<sub>2</sub> and  $1,24$  for CH<sub>4</sub>, where CV values greater than 1 indicate a non-normal, potentially log-normal, population distribution (Singh and Engelhardt, 1997).

The distributions of fluxes within the area were skewed suggesting that CO<sub>2</sub> and CH<sub>4</sub> fluxes are spatially variable across the study area.

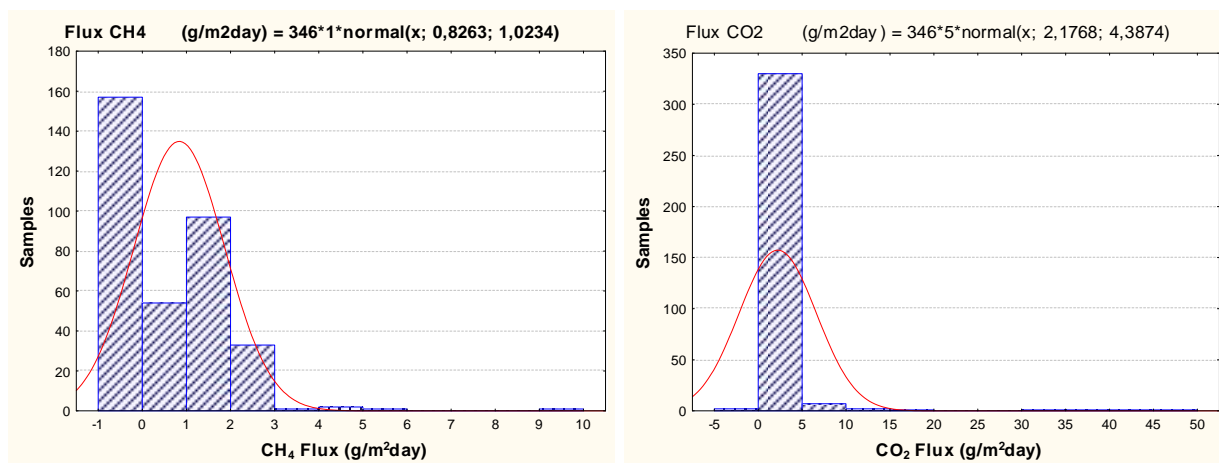
The contour maps (Figure 8) elaborated on the basis of the calculated experimental variograms, demonstrate that gas emission at the surface is not spatially heterogeneous within studied area. It is possible to infer that the variability of gas emissions is controlled by geological structures.

A comparison between the radon concentration map and the CH<sub>4</sub> flux distribution map (Figure 9) highlights an overlapping of the anomalous values: the methane flux acts as carrier gas for the radon rising along preferential pathways both in the north-western sector and in the central part of the area as well as the north-eastern.

*Table 2 - Main Statistics of Soil Gas Fluxes*

Flux	Samples	Mean	Median	Min value	Max Value	Std. Dev.	CV*
CO <sub>2</sub> (g/m <sup>2</sup> day)	346	2,18	1,34	0,00	45,14	4,39	2,02
CH <sub>4</sub> (g/m <sup>2</sup> day)	346	0,83	0,55	0,00	9,00	1,02	1,24

\*CV, coefficient of variation (standard deviation divided by the mean).



*Figure 7 - Histograms of the CO<sub>2</sub> and CH<sub>4</sub> fluxes (g/m<sup>2</sup> d<sup>1</sup>). The distributions are skewed indicating that gas emissions at the surface are not spatially heterogeneous within the studied area.*

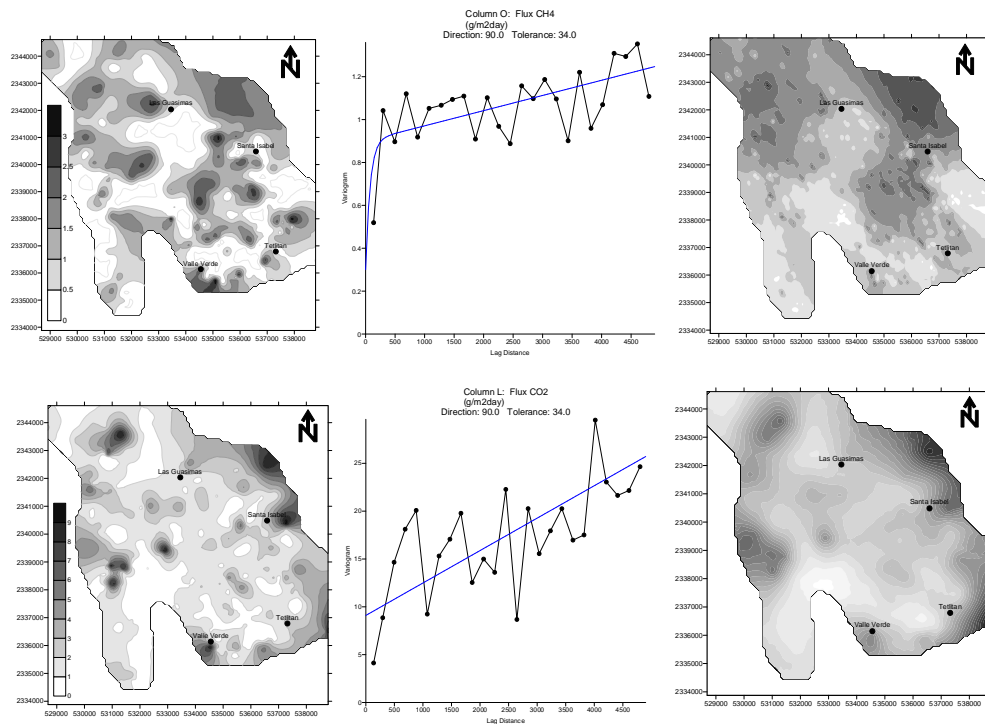


Figure 8 ó  $\text{CO}_2$  and  $\text{CH}_4$  flux concentration maps (on the left) and contour maps (on the right) elaborated on the basis of calculated experimental variograms. According to the latter maps, the methane flux is more evident in the north-western sector and in the central part of the area as well as the north-eastern. The carbon dioxide flux follow almost the same directions but has a more diffusive behaviour.

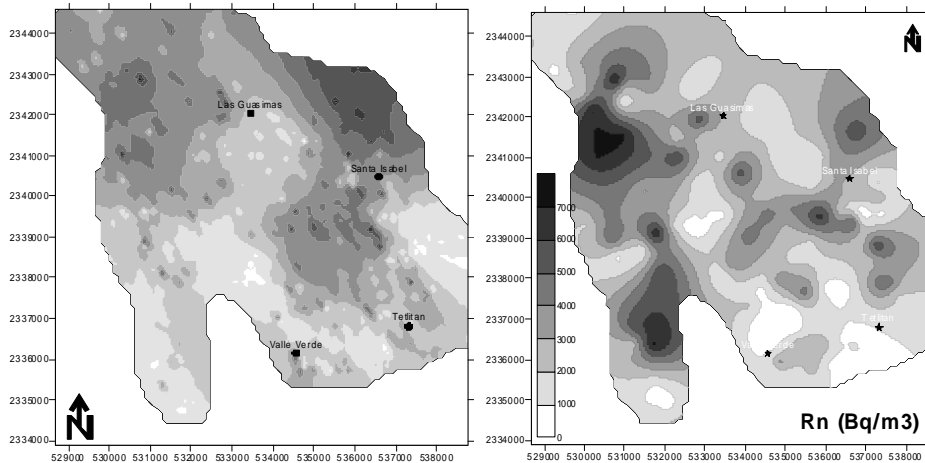


Figure 9 - A comparison between the  $\text{CH}_4$  flux distribution map (at the right) and the radon concentration map (at the left). There is a good overlapping of the gas anomalous values to NW of Las Guasimas and in the central part of the area as well as in the north-eastern (between Santa Isabel and Tetlitan villages) sector of the studied area.

## 6. Conclusions

The soil gas and flux geochemical surveys performed in the Tetitlan area highlighted a general upflow patterns of the local system, with the important implication that the highest CO<sub>2</sub> and CH<sub>4</sub> fluxes could be used in undeveloped geothermal systems to identify main upflow regions and areas of increased permeability due to structural control.

The largest areas of degassing were observed to the north-western of Las Guasimas village and in a large area surrounding the Santa Isabel village. Furthermore, some spot anomalies were found in proximity of Tetitlan and Valle Verde villages.

The spatial pattern of the main CO<sub>2</sub>, CH<sub>4</sub> flux anomalies as well as Rn, CO<sub>2</sub>, CH<sub>4</sub> and He soil gas anomalies suggests a structural control on degassing. Further investigations including a more detailed soil gas and flux surveys (e.g., local transects with a major spatial sampling density) are suggested in order to better understand the nature of spot anomalies. Moreover, it is strictly recommended to collect samples for isotopic analysis (in particular,  $\delta^{13}\text{C}$ ) both for methane and carbon dioxide so as to understand and define the origin of such gas species and, consequently, to give a more detailed interpretation of achieved data.

Furthermore, we stress the importance to compare the soil gas collected (fluxes and concentration) data with the data coming from the shallow aquifers (dissolved gases, CO<sub>2</sub> partial pressure, etc...) to discriminate the different behaviour of both the soluble and insoluble gasous species as well as their ratio in the different sectors of the studied area to better constrain the observed anomalies in the studied area.



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