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# Monitoring of fumarole discharge and $CO_2$ soil degassing in the Azores: contribution to volcanic surveillance and public health risk assessment

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**Abstract**

Fluid geochemistry monitoring in the Azores involves the regular sampling and analysis of gas discharges from fumaroles and measurements of $CO_2$ diffuse soil gas emissions. Main degassing areas under monitoring are associated with hydrothermal systems of active central volcanoes in S. Miguel, Terceira and Graciosa islands. Fumarole discharge analysis since 1991 show that apart from steam these gas emissions are $CO_2$ dominated with $H_2S$, $H_2$, $CH_4$ and $N_2$ in minor amounts. Mapping of $CO_2$ diffuse soil emissions in S. Miguel Island lead to the conclusion that some inhabited areas are located within hazard-zones. At Furnas village, inside Furnas volcano caldera, about 62% of the 896 houses are within the $CO_2$ anomaly, 5% being in areas of moderate to high risk. At Ribeira Seca, on the north flank of Fogo volcano, few family houses were evacuated when $CO_2$ concentrations in the air reached 8 mol%. To assess and analyse the $CO_2$ soil flux emissions, continuous monitoring stations were installed in S. Miguel (2), Terceira and Graciosa islands. The statistical analysis of the data showed that some meteorological parameters influence the $CO_2$ flux. The average of $CO_2$ flux in S. Miguel stations ranges from 250 g/m$^2$/d at Furnas volcano to 530 g/m$^2$/d at Fogo volcano. At Terceira Island it is about 330 g/m$^2$/d and at Graciosa 4400 g/m$^2$/d.

**Key words** *volcanology – geochemistry – soil degassing – monitoring – risk*

## 1. Introduction

The Azores Archipelago comprises nine volcanic islands in the Atlantic Ocean where the American, African and Eurasian lithospheric plates meet (Searle, 1980; fig. 1). The Mid-Atlantic Ridge clearly defines the northern and southern branches of the Azores Triple Junction (Lourenço *et al.*, 1997) but the location and geodynamic relations of the boundary between the Eurasian and African plates, corresponding to the so-called Terceira Rift (Machado, 1959), is still controversial (Madeira and Ribeiro, 1990). The complexity of this geological setting, reflected by the seismic and volcanic activity, may bear on the inferred existence of a mantle plume (White *et al.*, 1976).

During more than 500 years of history about thirty important destructive earthquakes and twenty-eight volcanic eruptions have been reported in the archipelago, causing thousands of

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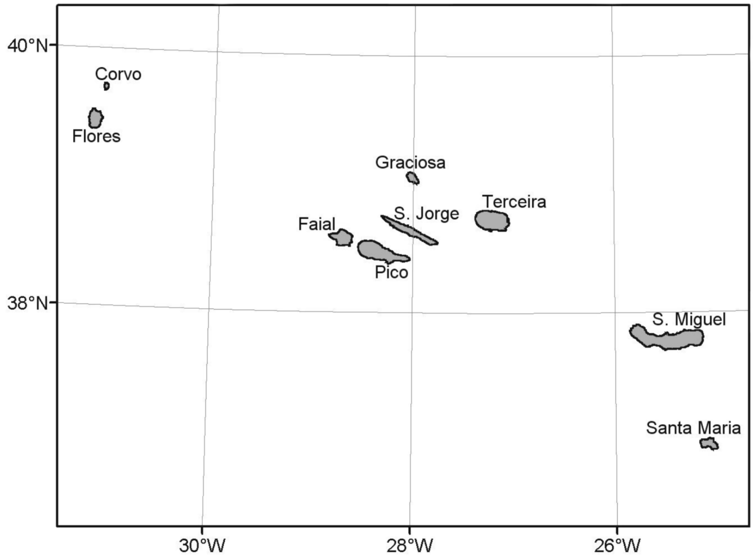


**Fig. 1.** Geographic location of the Azores Archipelago.

deaths and severe damage. The July 9, 1998 Faial earthquake (Senos *et al.*, 1998) and the 1998-2001 submarine eruption west of Terceira Island (Gaspar *et al.*, 2003) were the most recent events.

Present-day volcanic activity in the Azores is marked by highly active fumarolic fields, hot springs and soils diffuse degassing phenomena. This paper reports the fluid geochemistry monitoring programme that is being undertaken for volcanic surveillance and public health risk assessment in the region. Special attention is given to the $CO_2$ diffuse emissions whose significance in the total degassing of volcanic areas is of major importance (Allard *et al.*, 1991).

## 2. Degassing areas

Degassing areas in the Azores are related to hydrothermal systems (Ferreira, 1994). The most important zones of degassing are located in S. Miguel, Terceira and Graciosa islands and at some submarine volcano-tectonic structures along the Terceira Rift. Less significant degassing fields exist in Faial, Pico, S. Jorge and Flores islands (Ferreira, 1994; Viveiros, 2003). There are no reported gas emanations in Santa Maria or Corvo islands.

The monitored degassing areas in S. Miguel Island are associated with the Furnas and Fogo active central volcanoes. Furnas village (M-FV) and Furnas Lake (M-FL) fumarolic fields are located inside the Furnas caldera (fig. 2) defining a WNW-ESE path compatible with a major regional tectonic trend that traverse the island (Gaspar *et al.*, 1995). Pico Vermelho (M-PV), Caldeira Velha (M-CV) and Caldeiras da Ribeira Grande (M-CRG) fumaroles are on the northern flank of the Fogo volcano associated with the NW-SE Ribeira Grande graben (fig. 3).

In Terceira Island monitoring is focussed in the Furnas do Enxofre (T-FE) fumarolic field (fig. 4). The area covers a part of the Galhardo trachytic lava dome and extends beyond its crater being located in the intersection of NW-SE, E-W and NNE-SSW faults (Lloyd and Collis, 1981).

At Graciosa Island the main hydrothermal area under surveillance is within the Furna do Enxofre lava cave (G-FE). This volcanic structure was formed at the end of an intracaldera lava lake episode and is part of the main conduit of the Caldera volcano, controlled by NE-SW and NW-SE faults (Gaspar, 1996; fig. 5).

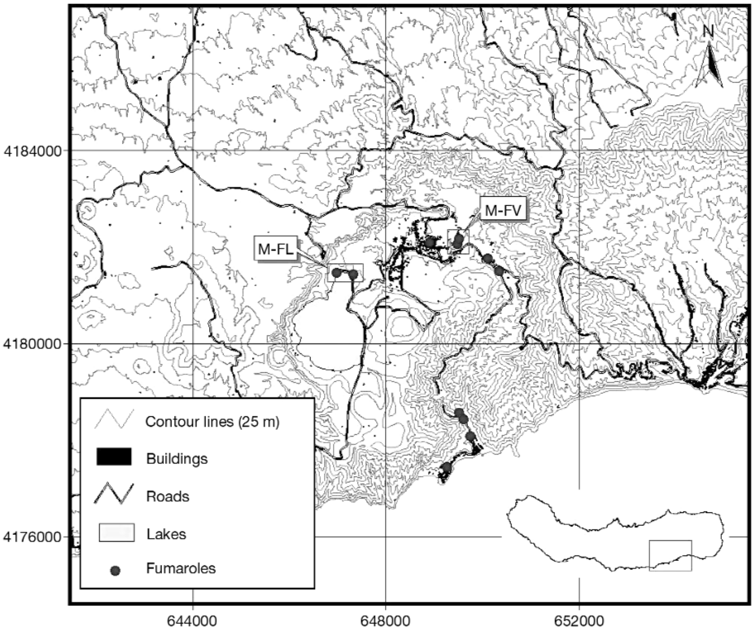


**Fig. 2.** Furnas volcano, S. Miguel Island, fumarolic fields (M-FL – Furnas Lake; M-FV – Furnas Village).

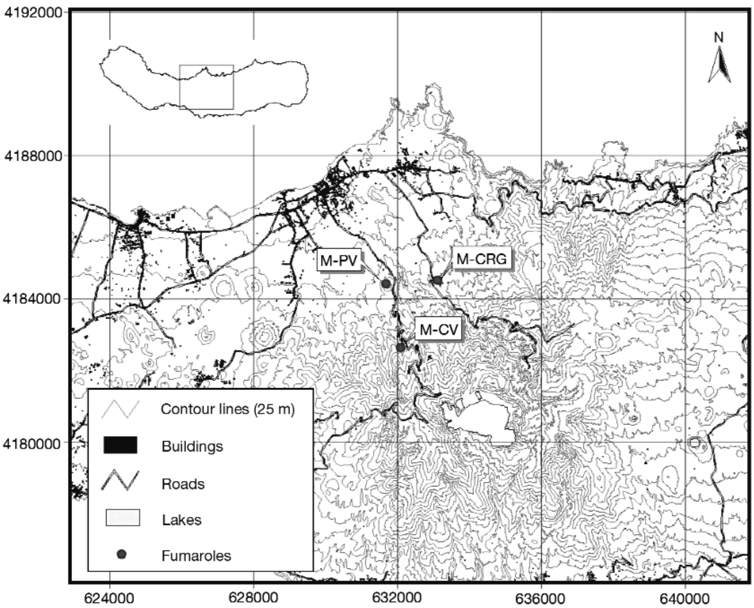


**Fig. 3.** Fogo volcano, S. Miguel Island, fumarolic fields (M-PV – Pico Vermelho; M-CRG – Caldeiras da Ribeira Grande; M-CV – Caldeira Velha).

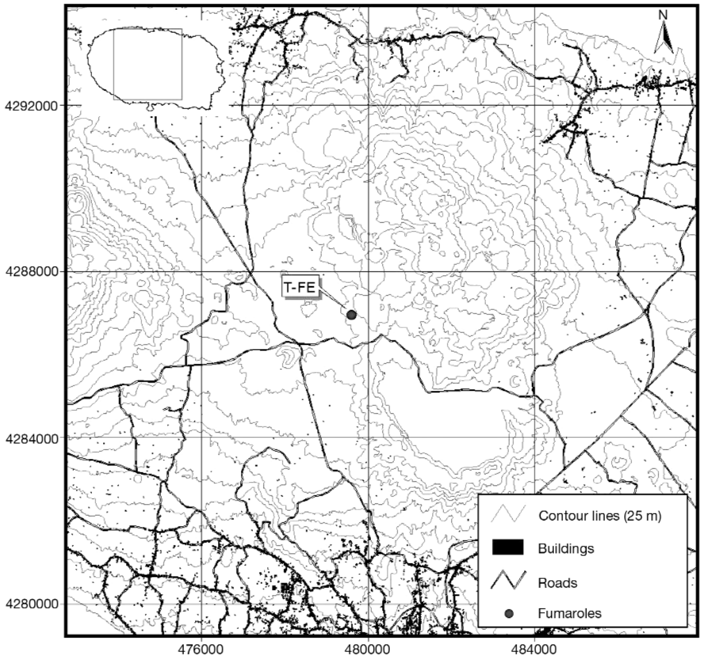


**Fig. 4.** Furnas do Enxofre fumarolic field at Terceira Island (T-FE – Furnas do Enxofre).

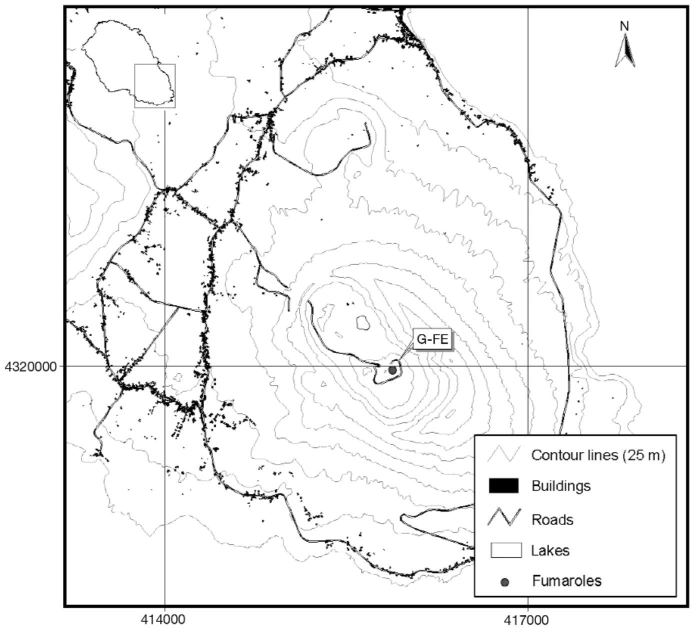


**Fig. 5.** Furnas do Enxofre fumarolic field at Graciosa Island (G-FE – Furnas do Enxofre).

## 3. Fumaroles regular monitoring programme

### 3.1. *Sampling and analytical processes*

The procedures for fumarole gas sampling are described in Ferreira (1994) and Ferreira and Oskarsson (1999) and follow the so-called Giggenbach methodology (Giggenbach and Gogel, 1989) using a known volume of a strong KOH solution (12 M) for adsorption of the acid gases. The samples are collected by placing a funnel, connected to a silicone tubing sampling train, over the steam vents. Gas flowing through the tubing system is collected into an evacuated borosilicate sample-bottle containing a measured weight of the KOH solution. $CO_2$ and $H_2S$ are adsorbed in this solution, which becomes diluted with the condensed steam, while the fixed gases $H_2$, Ar, $CH_4$, $N_2$ and $O_2$ fill the remaining space.

After being equilibrated to atmospheric pressure, gases in the sample-bottle are analysed with a gas chromatograph (Perkin-Elmer) with thermal conductivity detector, automated fixed sample loop, molecular sieve column and He as carrier gas. Ar is analysed in a separate run after washing the gas sample with basic pyrogallol solution.

$CO_2$ and $H_2S$ dissolved in the basic solution are quantified by titrimetric methods. $CO_2$ is determined by automated titration with hydrochloric acid and $H_2S$ is titrated with mercury acetate using dithizone for end point detection. A small volume of the basic solution is weighted for density determination, needed for mass balance involved in total gas analysis quantification.

### 3.2. *Results*

Occasional monitoring of S. Miguel (M-FL, M-FV, M-CV, M-CGR), Terceira (T-FE) and Graciosa (G-FE) fumaroles started in 1991 but regular measurements were started within the present programme. The available data show that $CO_2$ is the main constituent of the total gas in the steam discharges, representing 94 to 99.6 mol%. $H_2S$ and $H_2$ are the other major components contributing for 0.1 to 3 mol% of the total gas. Nitrogen concentration is below 1.5 mol% in all samples, the highest values being found at T-FE. $CH_4$ values are in general lower than 0.08 mol% except at T-FE where they can be 10 times higher.

All monitored fumaroles have discharges of broadly similar composition. However, on Ter-

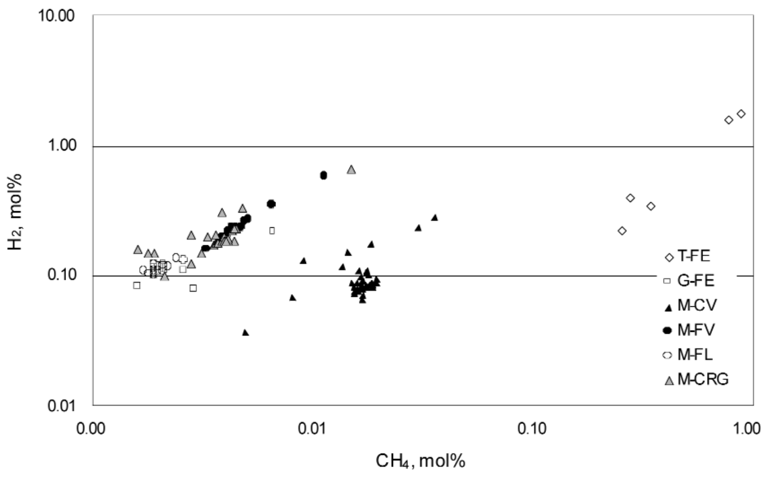


**Fig. 6.** $H_2/CH_4$ relation for the fumaroles under monitoring at the Azores Archipelago. References as in text.

ceira Island fumaroles are richer in $H_2$ and $CH_4$. The differences between gas compositions are better displayed using the ratio $H_2/CH_4$. In fact these gases show the most regular abundances of all the analysed components allowing a discrimination between the fumarolic fields (fig. 6). Based on equilibrium relations of $H_2$ and $CH_4$ and assuming a deep origin for these gases a simple model was applied to S. Miguel fumarole discharges considering a binary carbon dioxide-steam system (Ferreira and Oskarsson, 1999). According to this model these gases are derived from supercritical conditions, presumably equilibrated within hot rocks below the hydrothermal systems.

## 4. Mapping of $CO_2$ soil concentrations

### 4.1. *Methodology*

Analysis of $CO_2$ soil concentrations at the Azores follows the methodology applied by Baubron *et al*. (1994) and Ferreira and Gaspar (1997). An iron probe 1 m long is buried in the soil at a depth of 50-70 cm and the gas is pumped into a portable $CO_2$ analyzer with an infrared detector. The instrument is calibrated to measure concentrations between 0 and 100 mol%. Soil temperature is measured at the same sites as the $CO_2$ using a digital thermometer with 0.1ºC precision.

The distance between sampling sites depends on the observed values, being shorter, in the order of a few meters, where the concentrations are above the ground noise level (0 to 1.5 mol%). The collected data are inserted in a GIS and the anomaly grid maps are produced for $CO_2$ and temperature by means of the kriging statistical method.

### 4.2. *Results*

$CO_2$ soil concentration maps have been produced in the Azores for hazard and risk assessment. Baubron *et al*. (1994) showed the existence of an important anomaly in Furnas village, within the Furnas Caldera in S. Miguel Island, and Baxter *et al*. (1999) discussed the public health risk associated with such hydrothermal area.

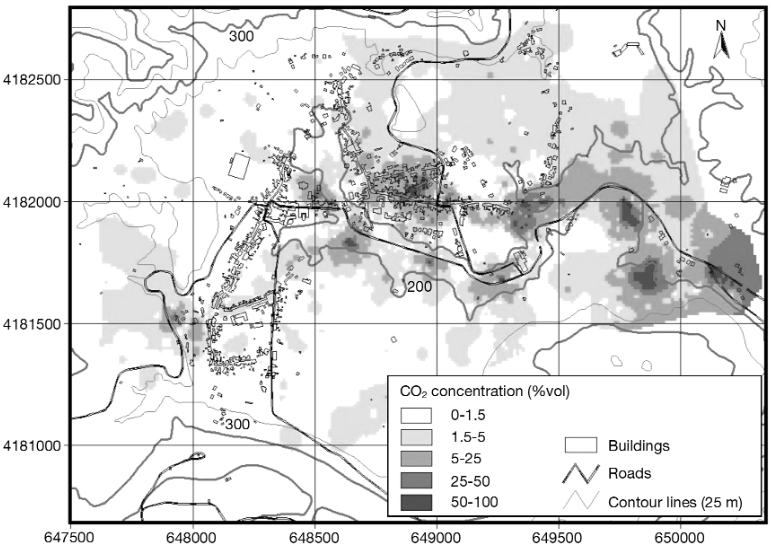


**Fig. 7.** $CO_2$ soil concentrations at Furnas village, S. Miguel Island (modified from Sousa, 2003).

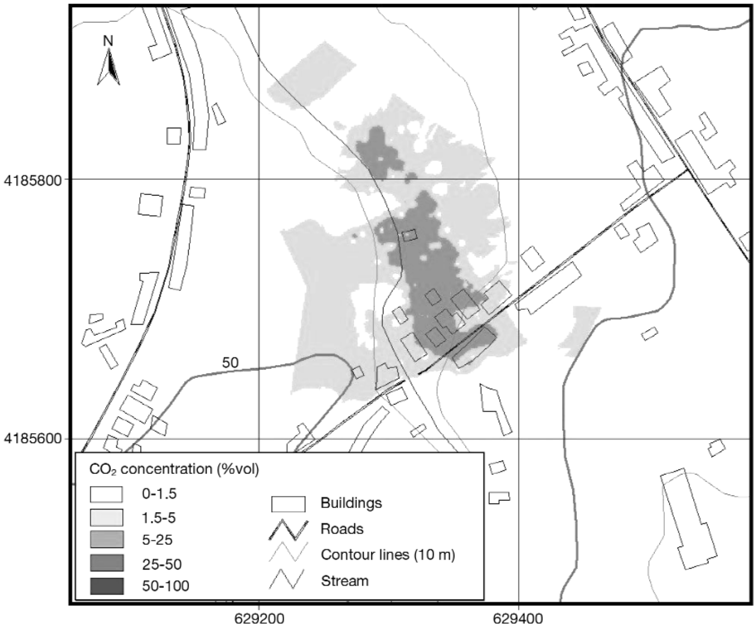


**Fig. 8.** $CO_2$ soil concentrations at Ribeira Seca in 1998, S. Miguel Island (modified from Ferreira, 2000).

A new survey recently performed in the same zone led to the conclusion that the general shape and magnitude of the anomaly remain almost identical 10 years later (fig. 7). Soil $CO_2$ concentrations reach 95 mol% in some areas and soil temperatures can be as high as 100ºC. These observations indicate that on a large temporal scale the Furnas village anomaly map can be used as a reference level concerning Furnas volcano surveillance. With respect to public health risk assessment, Sousa (2003) calculate that 62% of the 896 houses at Furnas village are within this geochemical anomaly, 5% being located in areas of moderate to high risk according to the classification of Baubron *et al.* (1994).

Public health risk at S. Miguel Island was also reported by Ferreira and Gaspar (1997) at Ribeira Seca village, about 3 km NW of the Pico Vermelho geothermal area. In April 1997 a $CO_2$ geochemical anomaly affecting an area of approximately 250 $m^2$ was detected but regular observations until the end of 1997 revealed that the anomaly pattern remained unchanged. At that time the maximum $CO_2$ soil concentration was about 13.5 mol% and measured soil temperatures reached 50°C. In March 1998 a new survey carried out in the zone showed that the anomaly increased to an area of about 10000 $m^2$ (fig. 8). $CO_2$ soil concentration levels of 24 mol% and soil temperatures of 50°C were then detected and four families were evacuated from their residences because $CO_2$ concentrations inside houses reached values of 8 mol% (Gaspar *et al.*, 1998). Regular monitoring surveys done since then show a slight decrease of the anomaly area but the maximum observed values remain similar.

$CO_2$ soil concentration maps are also useful for identification of major active tectonic faults (Sugisaki *et al.*, 1983; Giammanco *et al.*, 1998; Baubron *et al.*, 2002). In the Azores, this technique has proved to be very efficient considering that young pyroclastic deposits often bury the active fault areas of the main trachytic central volcanoes (Faria *et al.*, 2003; Marcos *et al.*, 2003).

## 5. $CO_2$ soil flux continuous monitoring

### 5.1. *Monitoring network and sampling*

Continuous monitoring of $CO_2$ soil diffuse degassing at the Azores started in October 2001. The first permanent station was installed on S. Miguel Island in a large degassing area that extends into Furnas village (station GFUR1) inside the caldera of the Furnas volcano. A second station was set up on the island on February 2002 in the northern flank of the Fogo volcano, within the Pico Vermelho geothermal area (GFOG1). On December 2002 two other stations were installed at Terceira Island, in Furna do Enxofre fumarolic field (GTER1), and at Graciosa Island, inside the Furna do Enxofre lava cave (GGRC1).

All $CO_2$ soil flux continuous monitoring stations are based on the accumulation chamber method (Chiodini *et al.*, 1998). The station GGRC1 is also equipped with a sensor for $H_2S$ flux measurements. All the stations include additional sensors to record information on meteorological and environmental parameters such as barometric pressure, air temperature, air humidity, wind speed and direction, rainfall, soil water content and soil temperature.

Flux stations are configured to read data every hour. Each $CO_2$ flux measurement is made during a time period of 1-3 min and the value is registered at the same time as the data from all the above-mentioned sensors. Additional information on the operating *status* of the equipment is also available. Data transmission links from the field stations to the volcanological Observatory of the Azores University, on S. Miguel Island, were established using GSM (GFUR1), freewave (GFOG1 and GTER1) and UHF plus freewave (GGRC1).

### 5.2. *Results*

The Azores climate is typically oceanic such that low pressure areas are followed by increased wind speed and increased precipitation that strongly affect the soil degassing. Knowledge of how meteorological parameters interfere with diffuse soil degassing at any particular monitoring site is crucial to recognise changes due to deep processes. The influence of external factors on $CO_2$ flux is gauged by applying multiple regression analysis (Draper and Smith, 1981) and time series analysis modelling (Box and Jenkins, 1976).

For S. Miguel Island the results obtained show that the main influencing parameters do not act in the same way on each monitoring site (Viveiros *et al.*, 2003). At GFUR1 barometric pressure, rainfall, soil water content, air temperature and soil temperature are the parameters that have significant statistical connection to $CO_2$ flux fluctuations. At GFOG1 station wind speed, barometric pressure, soil temperature, soil water content and rainfall are the statistically relevant influencing parameters (Viveiros, 2003). The average of $CO_2$ flux at GFUR1 is near 250 $g/m^2/d$ while at GFOG1 it is around 530 $g/m^2/d$.

The recent $CO_2$ flux data of Terceira and Graciosa islands are still under analysis. However, the preliminary study of the obtained data showed that the average $CO_2$ flux is about 330 $g/m^2/d$ at GTER1 and 4400 $g/m^2/d$ at GGRC1.

In a general way, the $CO_2$ flux averages observed in the above mentioned hydrothermal zones are lower than the ones reported for other volcanic areas, such as Solfatara and Vesuvio (Granieri *et al.*, 2003). The Furna do Enxofre soil degassing area at Graciosa Island is the exception.

## 6. Future developments

The Volcanological Observatory of the Azores University is responsible for the seismic and volcanic monitoring of the Azores region using geophysical, geodetic and geochemical techniques. Geophysical monitoring includes the management of a seismological network of more than 40 seismic stations, run in collaboration with the Meteorological Institute. Geodetic monitoring is based on a GPS network of several permanent receivers and complemented by regular GPS field surveys. As discussed, the actual geochemistry monitoring programme involves the regular sampling and analysis of gas discharges in fumaroles and the study of $CO_2$

diffuse soil gas emissions. To a minor extent, hot springs, geothermal and water wells are also under observation.

The development of the Azores seismovolcanic network comprises the set up of warning and alert systems based on the integration of all the monitoring data. This strategy implies the extension of the monitoring programme to all the islands and will benefit from the data transmission system that is being installed in the archipelago for civil protection activities.

The recognition of hazardous zones due to the permanent diffuse soil degassing in several inhabited or tourist places requires the installation of alarm sensors in order to reduce the public health risk. Such preventive measure is already being implemented at Furna do Enxofre lava cave, where two people died in 1992 due to an increase in $CO_2$ in the atmospheric air (Ferreira *et al*., 1993; Gaspar, 1996).

## Acknowledgements

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