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Soil degassing at Ustica Island: Comparison between 1997 and 1999 surveys

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RESUMEN

Se hicieron dos estudios de gas del suelo y de flujos de CO_2 y CH_4, en la Isla Ustica (arco sur del Mar Tirreno) en 1997 y 1999, para examinar el rol del degasamiento de sistemas de falla y fractura como una evidencia local de estructuras mayores de importancia regional. Los dos estudios muestran que la falla Arso que cruza la isla es la estructura de degasamiento principal.

Los flujos positivos de CH_4 relacionados con la falla confirman que el consumo metanotrópico del suelo es mayor en periodos más cálidos, pero parece ser insuficiente para consumir todo el CH_4 geológico que se fuga.

Los análisis químicos e isotópicos de los gases del suelo en los sitios de mayor degasamiento muestran que a pesar de la extensiva contaminación atmosférica, las concentraciones de He son siempre mayores que las atmosféricas. Las relaciones isotópicas $^3He/^4He$ sugieren también que una contribución de una componente que se origina en profundidad sigue siendo detectable en la isla.

PALABRAS CLAVE: Gas del suelo, dióxido de carbono, metano, helio, flujo de gas, degasamiento de fallas.

ABSTRACT

Two surveys of soil-gas and diffuse flux of CO_2 and CH_4 were carried out at Ustica Island (southern Tyrrhenian back-arc basin) in 1997 and 1999 to examine the degassing role of fault and fracture systems, as local evidence of wider structures of regional importance. Both surveys show that the Arso fault, crossing the island, is the main degassing structure.

Fault-linked positive CH_4 fluxes confirm that methanotrophic consumption in soil is higher in warmer periods but seems to be insufficient for consuming all leaking geologic CH_4.

Chemical and isotopic analyses of soil gases at higher degassing sites show that despite the extensive atmospheric contamination, He concentrations are always above the atmospheric level. $^3He/^4He$ isotopic ratios also suggest that a contribution of a deep-originated component is still detectable on the island.

KEY WORDS: Soil-gas, carbon dioxide, methane, helium, gas flux, fault degassing.

INTRODUCTION

Ustica is an inactive Pleistocene volcanic island and it is the only site in the southwestern part of the Tyrrhenian sea (Figure 1) showing subaerial evidence of intraplate magmatism and Pleistocene tectonics related to the opening of the Tyrrhenian back-arc basin (last activity 132 ka ago; De Vita *et al*., 1995; Etiope *et al*., 1999). The island is located about 66 km N-NW of the Sicily coast, on the southern edge of the oceanic domain of the Magnaghi-Vavilov and Marsili basins. There are no visible gas manifestations on the island and the heat flow is rather low compared to that measured in southern Thyrrhenian sea (less than 100 mW/m^2; Etiope *et al*., 1999). Therefore the degassing is referred in terms of invisible, diffuse exhalation from soil.

Soil CH_4 and CO_2 degassing throughout the island was investigated in 1997 (Etiope *et al*., 1999); the results indicated a structural control on the diffuse exhalation. Carbon dioxide fluxes above soil respiration (up to 93,750 t km^{-2} y^{-1}) and positive methane fluxes (up to 54.9 mg m^{-2} d^{-1}) were detected mainly in correspondence with the major tectonic dislocation, the Arso fault, crossing the island from south-west to north-east (Figure 1).

In this work we present the results obtained by a similar survey performed in a warmer period in 1999, and more complete chemical and helium isotopic analyses performed in 1998 in the higher-degassing sites.

METHODS

Soil-gas was sampled 0.6-0.8 meters below the surface by portable stainless steel probes (Etiope *et al*., 1999) at 36 points distributed as homogeneously as possible over the

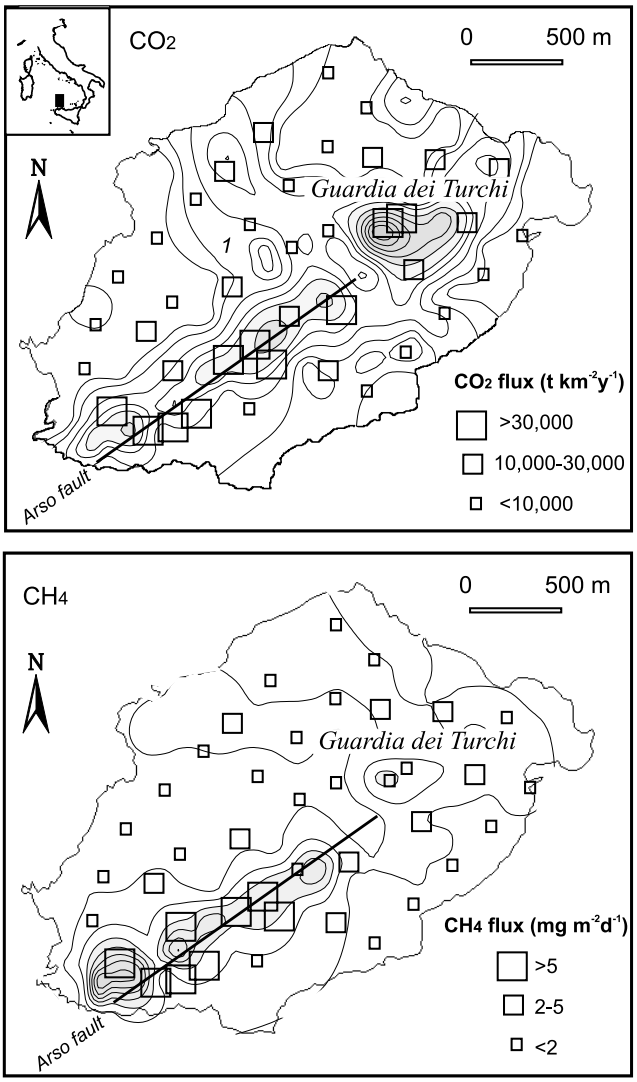

Fig. 1. Distribution of 1999 gas flux (squares) compared with 1997 soil-gas concentration from Etiope *et al.* (1999). Grey areas are major soil-gas anomalies (>3.8% CO_2 and >2.9 ppmv CH_4).

whole island (about 10 km^2). Gas exhalation (flux density from the ground to the atmosphere) was measured at 41 sites by the accumulation chamber method (Etiope, 1999). A 20L closed-static chamber was used, similar to the "Crill system" tested by Norman *et al.* (1997). In 1997 a 62.5 L box was used (Etiope *et al.*, 1999). Details on limitations and recommendations for the correct sampling strategy and interpretation of exhalation flux data are reported elsewhere (e.g., Hutchinson and Livingstone, 1993; Klusman, 1993; Norman *et al.*, 1997). An adjustment factor of 1.3 was adopted for CO_2 flux data as recommended by Norman *et al.* (1997).

Gas analyses were performed on the field by a portable, double-module, gas chromatograph (Chrompack), equipped with a micro-thermal conductivity detection (micro-TCD) system based on silicon micromachined technology (Etiope, 1997) and configured for analyses of CO_2 and CH_4. Analyses were performed in duplicate and a four point calibration curve was obtained by Scotty® calibration standards. Reproducibility of the analytical results, computed over five days during which the instrument is turned on and off daily is within ± 6% for CO_2 and ± 7% for CH_4. The sensitivity (or LOQ: Limit of Quantification) is about 7 ppmv for CO_2 and 0.4-1 ppmv for CH_4. In the sites of higher degassing found in 1997, soil-gas was also sampled for more complete laboratory analyses (including He isotopes) using 30 ml pyrex bottles sealed by two vacuum cocks at the ends. Chemical analyses of He, O_2, N_2, CH_4 and CO_2 were carried out with a Perkin Elmer 8500 gas-chromatograph equipped with a 4 m Carbosieve 5A column and double detector (Flame Ionization Detector and Hot Wire Detector). The detection limits are 5 ppmv for He, O_2, and N_2, 1 ppmv for CH_4. Analytical errors are ± 5% for He, and ± 3% for the other species. To determine the $^3He/^4He$ isotopic ratio, purified helium from 0.3 ml of the gas sample was admitted to a static mass spectrometer (VG5400TFT, VG Isotopes) modified by the addition of a "split flight tube". A resolving power of 600 al 5% peak height allows the separation for $^3He^+$ from HD and $H3^+$.

This machine, allowing the contemporary detection of ^3He and ^4He-ion beams, reduce the error of the $^3He/^4He$ ratios: typical uncertainties are about ±1% for $^3He/^4He$ ratios in the range of atmospheric values; below ±0.1% for high-^3He (e.g. volcanic) samples and below ±3% for low-^3He (radiogenic) samples.

RESULTS AND DISCUSSIONS

Table 1 lists the descriptive statistics of CO_2 and CH_4 soil-gas concentration and exhalation flux for both 1997 and 1999 surveys, while the chemical results at high degassing sites (1998) are listed in Table 2.

Figure 1 shows the 1999 distribution of CO_2 and CH_4 flux overimposed on the 1997 soil-gas concentration data from Etiope *et al.* (1999). The highest fluxes and concentration anomalies occur in correspondence with the Arso fault, confirming the results obtained in 1997. There is also a good correlation between CH_4 and CO_2 flux (Figure 2). Mean flux values, are however lower than those detected in 1997. In particular, more negative CH_4 fluxes have been found in 1999. This fact can be explained considering the role of methanotrophic activity in soil. Soil in drylands (aerobic environment) is generally an important sink for atmospheric methane due to methanotrophic consumption (e.g., Mosier *et al.*, 1991), with negative fluxes of the order of -0.5 to -2 mg m^{-2} d^{-1}. Nevertheless, concentrations of methane in dry soils higher than the atmospheric content are often reported

Table 1

Main statistics of soil-gas concentration and flux data

Exhalation flux					
		Mean	Min	Max	
CO_2 (t km^{-2} y^{-1})*	1997	34,300	6,870	93,750	(20 sites)
	1999	24,926	3,890	86,500	(41 sites)
CH_4 (mg m^{-2} d^{-1})	1997	15.5	2.9	54.9	(20 sites)
	1999	3.71	-0.4	21.30	(41 sites)
Soil-gas concentration					
		Mean	Min	Max	
CO_2 (%)	1997	1.78	0.09	11.3	(101 sites)
	1999	1.9	0.1	7.1	(36 sites)
CH_4 (ppm)	1997	1.74	1.1	5.7	(101 sites)
	1999	1.8	0.2	5.5	(36 sites)

* 1997 statistics does not include the highest value (243,300 t km^{-2} y^{-1}) found at Mt. Guardia dei Turchi (see Etiope *et al*., 1999).

Table 2

Chemical analysis of soil-gas at the sites with higher degassing

Site	**Date**	**He**	**O_2**	**N_2**	**CH_4**	**CO_2**	**R/R_a**
G.dei Turchi	02/01/98	$5.7x10^{-3}$	$2.07 x10^{2}$	$7.91 x10^{2}$	$1.12 x10^{-2}$	1.68	1.19
G.dei Turchi	17/06/98	$5.8x10^{-3}$	$2.09 x10^{2}$	$7.89 x10^{2}$	$6.20 x10^{-4}$	2.00	1.09
Arso	18/06/98	$5.7x10^{-3}$	$2.11x10^{2}$	$7.88 x10^{2}$	$9.87 x10^{-4}$	0.51	1.02
G.dei Turchi	18/06/98	$6.3x10^{-3}$	$2.12 x10^{2}$	$7.87 x10^{2}$	$1.58 x10^{-3}$	1.31	1.09
G.dei Turchi1	25/06/98	$6.7x10^{-3}$	$2.13 x10^{2}$	$7.87 x10^{2}$	$1.94 x10^{-1}$	n.a.	1.01
G.dei Turchi2	25/06/98	$6.1x10^{-3}$	$2.07 x10^{2}$	$7.93 x10^{2}$	$1.95 x10^{-3}$	n.a.	1.02
Arso	25/06/98	$6.0x10^{-3}$	$2.06 x10^{2}$	$7.94 x10^{2}$	$9.51 x10^{-3}$	n.a.	1.01

Concentrations in mmol/mol gas. R/R_a denotes the helium isotopic ratio compared to the atmospheric ratio (R_a atmosperic $^3He/^4He=1.39x10^{-6}$); n.a.: not analysed.

in fault areas (Klusman, 1993; Etiope, 1999; Morner and Etiope, 2002, and references therein). This can be explained assuming that microseepage of endogenous CH_4 can exceed the capacity for methanotrophic oxidation in soil, mainly during drier and colder seasons, producing positive CH_4 fluxes to the atmosphere. Stable carbon isotopic measurements on CH_4 generally suggest that methanotrophic oxidation is higher in summer and that the geothermal CH_4 transfer to the atmosphere is therefore higher in winter (Klusman *et al*., 2000). This phenomenon has been also observed in the Ustica Island where positive CH_4 flux decreased from a mean of 15.5 mg m^{-2} day^{-1} in colder period (late September, 1997; Etiope *et al*., 1999) to a mean of 3.71 mg m^{-2} day^{-1} in warmer period (late June, 1999). Anyway, even in the warmer period the bacterial activity is insufficient to consume all leaking CH_4.

The chemical composition of the soil gases displays an

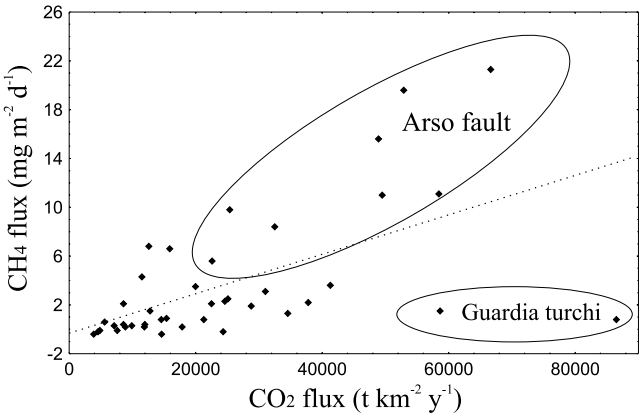

Fig. 2. Regression line for CH_4 and CO_2 flux.

extensive atmospheric contamination, however a mixing with a deep-originated gas phase probably CO_2-dominated is also detectable. Assuming a ratio 1:1 between biogenic O_2 consumption and CO_2 production, and estimating the CO_2 produced in the soil by the equation (Etiope, 1999):

$CO_2^{b} = 100 \times \Delta O_2^{soil}/CO_2^{soil}$
where ΔO_2^{soil} is the oxygen depletion:

$\Delta O_2^{soil} = (O_2^{air}/N_2^{air})\, N_2^{soil} - O_2^{soil}$

the endogenous component of CO_2 ($CO_2^{e} = CO_2^{soil} - CO_2^{b}$) is between 30 and 70% in the fault zone. Then, CO_2/N_2 ratios are in the range of 6.5×10^{-4} - 2.5×10^{-3}, at least an order of magnitude above the atmospheric ratio, and the CO_2/CH_4 ratios are 3-4 orders of magnitude higher than the atmospheric ratio.

The highest ratios were measured at the Mt. Guardia dei Turchi sampling site (central hill), where the presence of a vapour phase is sometimes detectable. This is also the site with the highest CO_2 flux. The isotopic ratio of helium in gas samples taken at this site displays the highest anomaly in the ^3He content, showing the helium isotopic ratio as high as 1.2 Ra without any correction for the atmospheric contamination. Total helium abundance is more than 1 ppmv above atmospheric level (5,200 ppbv). Weaker anomalies of the $^3He/^4He$ ratios, 1.01-1.02, were detected at the Arso fault, where CO_2 flux is lower.

CONCLUSIONS

This work represents one of the few examples available in the literature showing CO_2-CH_4 flux and soil-gas surveys, over a relatively wide territory (10 km^2), repeated few years apart (1997-1999).

The two surveys show qualitatively similar results (structural control by the Arso fault, with positive methane flux) but quantitatively different flux values, mainly for methane, whose flux into the atmosphere is lower in the warmer period. The reason is attributed to the different temperature-linked methanotrophic consumption in the soil, as found in other cases.

Anomalies of the helium isotopic ratio are quite low in comparison with those typical of active volcanic or geothermal areas, but significant for soil-gas of a "colder" area like Ustica, where biologic and atmospheric factors dominate soil-gas behaviour.

The presence of a deep-originated gas phase can be attributed to the residual degassing of the magmatic products of the island or to an active degassing due to local faulting of lithospheric interest. Further investigations, including carbon isotope analyses, may supply more information on both the flow rate variability and the genesis of the released gases and may help of improving the knowledge of this area of peculiar tectonic interest.

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