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

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INTRODUCTION

Ustica is an inactive Pleistocene volcanic island and it is the only site in the southwestern part of the Tyrrenian sea (Figure 1) showing subaerial evidence of intraplate magmatism and Pleistocene tectonics related to the opening of the Tyrrenian 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/m²; Etiope et al., 1999). Therefore the degassing is referred in terms of invisible, diffuse exhalation from soil.

Soil CH₄ and CO₂ 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 of the major tectonic dislocation, the Arso fault, crossing the island from southwest 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
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$^\text{®}$ calibration standards. Reproducibility of the analytical results, computed over five days during which the instrument is turned on and off daily is within $\pm 6\%$ for CO$_2$ and $\pm 7\%$ 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 $\pm 5\%$ for He, and $\pm 3\%$ for the other species. To determine the $^3$He/$^4$He 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 $^3$He$^+$ from HD and H$^3$.

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

Soil degassing surveys in fault areas (Klusman, 1993; Etiope, 1999; Morner and Etiope, 2002, and references therein). This can be explained assuming that microseepage of endogenous CH₄ can exceed the capacity for methanotrophic oxidation in soil, mainly during drier and colder seasons, producing positive CH₄ fluxes to the atmosphere. Stable carbon isotopic measurements on CH₄ generally suggest that methanotrophic oxidation is higher in summer and that the geothermal CH₄ 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 CH₄ 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 CH₄.

The chemical composition of the soil gases displays an

### Table 1

Main statistics of soil-gas concentration and flux data

<table>
<thead>
<tr>
<th>Exhalation flux</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (t km⁻² y⁻¹)</td>
<td>1997</td>
<td>34,300</td>
<td>6,870</td>
</tr>
<tr>
<td></td>
<td>1999</td>
<td>24,926</td>
<td>3,890</td>
</tr>
<tr>
<td>CH₄ (mg m⁻² d⁻¹)</td>
<td>1997</td>
<td>15.5</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>1999</td>
<td>3.71</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

### Table 2

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

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>He</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>CO₂</th>
<th>R/Rₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>G.dei Turchi</td>
<td>02/01/98</td>
<td>5.7x10⁻³</td>
<td>2.07 x10²</td>
<td>7.91 x10²</td>
<td>1.12 x10⁻²</td>
<td>1.68</td>
<td>1.19</td>
</tr>
<tr>
<td>G.dei Turchi</td>
<td>17/06/98</td>
<td>5.8x10⁻³</td>
<td>2.09 x10²</td>
<td>7.89 x10²</td>
<td>6.20 x10⁻⁴</td>
<td>2.00</td>
<td>1.09</td>
</tr>
<tr>
<td>Arso</td>
<td>18/06/98</td>
<td>5.7x10⁻⁵</td>
<td>2.11x10²</td>
<td>7.88 x10²</td>
<td>9.87 x10⁻⁴</td>
<td>0.51</td>
<td>1.02</td>
</tr>
<tr>
<td>G.dei Turchi</td>
<td>18/06/98</td>
<td>6.3x10⁻³</td>
<td>2.12 x10²</td>
<td>7.87 x10²</td>
<td>1.58 x10⁻³</td>
<td>1.31</td>
<td>1.09</td>
</tr>
<tr>
<td>G.dei Turchi</td>
<td>25/06/98</td>
<td>6.7x10⁻³</td>
<td>2.13 x10¹</td>
<td>7.87 x10²</td>
<td>1.94 x10⁻¹</td>
<td>n.a.</td>
<td>1.01</td>
</tr>
<tr>
<td>G.dei Turchi2</td>
<td>25/06/98</td>
<td>6.1x10⁻⁵</td>
<td>2.07 x10²</td>
<td>7.93 x10²</td>
<td>1.95 x10⁻³</td>
<td>n.a.</td>
<td>1.02</td>
</tr>
<tr>
<td>Arso</td>
<td>25/06/98</td>
<td>6.0x10⁻³</td>
<td>2.06 x10²</td>
<td>7.94 x10²</td>
<td>9.51 x10⁻³</td>
<td>n.a.</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Concentrations in mmol/mol gas. R/Rₐ denotes the helium isotopic ratio compared to the atmospheric ratio (Rₐ atmospheric ³He/⁴He=1.39x10⁻⁶); n.a.: not analysed.
extensive atmospheric contamination, however a mixing with a deep-originated gas phase probably CO₂-dominated is also detectable. Assuming a ratio 1:1 between biogenic O₂ consumption and CO₂ production, and estimating the CO₂ produced in the soil by the equation (Etiope, 1999):

\[ \text{CO}_2^b = 100 \times \frac{\Delta \text{O}_2}{\text{CO}_2} \]

where \( \Delta \text{O}_2 \) is the oxygen depletion:

\[ \Delta \text{O}_2 = \left( \frac{\text{O}_2 \text{air}}{\text{N}_2 \text{air}} \right) \text{N}_2 - \text{O}_2 \text{soil} \]

the endogenous component of CO₂ (\( \text{CO}_2 = \text{CO}_2 \text{soil} - \text{CO}_2^b \)) is between 30 and 70% in the fault zone. Then, \( \text{CO}_2/\text{N}_2 \) ratios are in the range of 6.5x10⁻² - 2.5x10⁻¹, at least an order of magnitude above the atmospheric ratio, and the CO₂/CH₄ ratios are 3-4 orders of magnitude higher than the atmospheric ratio.

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.

**BIBLIOGRAPHY**


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