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Total CO_2 output from Ischia Island volcano (Italy)

G. PECORAINO,* L. BRUSCA, W. D'ALESSANDRO, S. GIAMMANCO, S. INGUAGGIATO and M. LONGO

Istituto Nazionale di Geofisica e Vulcanologia—Sezione di Palermo, via Ugo La Malfa 153, 90146 Palermo, Italy

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The total amount of CO_2 released at Ischia Island has been estimated from soil gas flux measurements and from chemical composition of the gases released by fumaroles or dissolved in groundwaters. The preliminary results indicate an overall CO_2 output of about 15 kg s^{-1} from the entire island (46 km^2). The main contribution to the total output from diffuse soil degassing is about 14.8 kg s^{-1}, followed by dissolved CO_2 of about 0.3 kg s^{-1}. The contribution of fumaroles to the total output was found to be negligible (about 0.03 kg s^{-1}). Ischia's output, although being considerably less than that of open conduit volcanoes, is higher than many other volcanic systems, especially those related to volcanic arcs. The recent tensile tectonic regime of the area allows probably an easier upflow of CO_2 from the mantle sustaining the diffuse degassing of the island.

Keywords: JSCHIA, CO_2, output, soil CO_2, dissolved CO_2

INTRODUCTION

Determination of CO_2 emission rates from active volcanic systems is important both for volcanic surveillance and for the assessment of the role of magmatic CO_2 in the global carbon cycle. Although volcanism is one of the major natural carbon sources, its total contribution in atmosphere is far from being accurately assessed (Brantley and Koepenick, 1995; Arthur, 2000; Mörner and Etiope, 2002). The importance of CO_2 in forecasting eruptive activity derives from its high content in parent magmas, its early (deep) and efficient exsolution during magma uprise and its relative inertness (Bruno *et al.*, 2001; Symonds *et al.*, 2001). Volcanoes release CO_2 through active vents (open conduit craters or fumaroles) and through diffuse degassing from the soils. A significant part could also be discharged to the surface as dissolved carbon species by spring water (D'Alessandro *et al.*, 1997; Inguaggiato *et al.*, 2005). Passive degassing of volcanoes with open conduit activity are the major source of volcanic CO_2 to the atmosphere. Mt. Etna (Italy) and Popocatepetl (Mexico), for example, emit CO_2 from 400 to 1000 kg s^{-1} (Allard *et al.*, 1991; Goff *et al.*, 2001). But also quiescent volcanic systems display significant CO_2 emissions (see Table 3 for some examples). Both at active and quiescent volcanic systems, CO_2 emissions can be an important hazard to the people who live on it.

*Corresponding author (e-mail: g.pecoraino@pa.ingv.it)

The aim of the present work was to estimate the total output of CO_2 from Ischia Island, considering all the forms in which this gas is released at the surface. We carried out systematic measurements of CO_2 concentrations in fumarolic and bubbling gases, of diffuse flux of CO_2 through the soils over the entire surface of the island and of the total dissolved inorganic carbon (TDIC) content in groundwaters. Mörner and Etiope (2002) consider the quantification of CO_2 release to the atmosphere from natural sources an "urgent endeavour" for a better constraint of the global carbon cycle and this work will be a contribution to the worldwide data-set on CO_2 fluxes from volcanic areas.

STUDY AREA

Ischia Island (Fig. 1) has a surface area of 46 km^2 and is an active volcanic complex belonging to the alkali-potassic Quaternary Roman Volcanic Province of central-south Italy that includes the Phlegrean Fields and Mt. Vesuvius (Vezzoli, 1988). This volcanism is related to Plio-Quaternary extensional tectonics that formed the horst and graben structures that trend both NW-SE and NE-SW along the Tyrrhenian margin of the south Apennine chain (Molin *et al.*, 2003). Mt. Epomeo resurgent block (787 m a.s.l.; resurgence started about 33 ka b.p.) is the dominant morpho-tectonic feature of the island (Molin *et al.*, 2003), together with several eruptive centres that produced pyroclastic cones, lava cones, cinder cones and lava flows. Ischia's volcanic rocks are mainly composed of alkalitrachytes with subordinate trachybasalts, latites and phonolites (Vezzoli, 1988). The

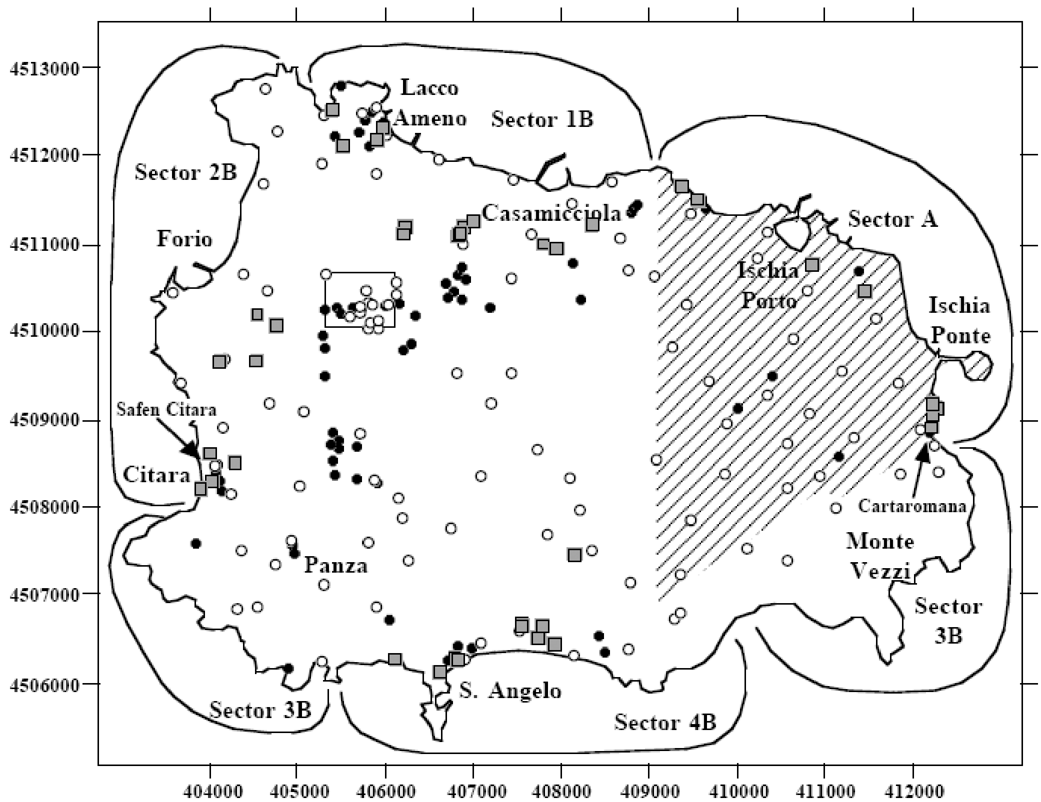

Fig. 1. Location of sampling points at Ischia. Open circles = soil flux measurements; Squares = groundwater sampling points. Rectangle encloses the 14 soil gas flux measurement points of the Pizzone–Mt. Nuovo area. Sectors refer to the hydrogeologic subdivision after Celico et al. (1999). Sector A = Ischia graben (hatched area); Sector B = Epomeo horst (subsectors 1 = Casamicciola–Lacco Ameno; 2 = Forio; 3 = Panza and Mt. Vezzi; 4 = S. Angelo). The two subsectors of Panza and Mt. Vezzi were grouped together by Celico et al. (1999) due to their similar hydrogeologic characteristics. Dots = active fumaroles location after Molin et al. (2003). Outer scale indicates the UTM coordinates in meters (grid zone 33 T). Safen Citara and Cartaromana are two bubbling gas sampling points.

oldest rocks are dated to 130–150 ka (Vezzoli, 1988) while the most recent activity took place at Mt. Arso in 1301. Afterwards, the persistent state of activity of Ischia magmatic system has been testified by the occurrence of shallow earthquakes, the last one in 1883 (I_0 = X MCS—Molin *et al*., 2003), and by the presence of an active geothermal system with temperature up to 250°C (Panichi *et al*., 1992; Inguaggiato *et al*., 2000), whose surface expression consists of numerous thermal springs (T up to 90°C) and fumaroles (T ≅ 100°C).

Carbon dioxide is present at Ischia as a separate gas phase in fumaroles, diffuse soil emissions and gas bubbles in spring waters and as Total Dissolved Inorganic Carbon (TDIC) in groundwater (divided among the dissolved species CO_2, HCO_3^- and CO_3^{2-} as a function of the pH of water). Based on carbon isotopic values of fumarolic CO_2 and of TDIC, both Caliro *et al*. (1999) and Inguaggiato *et al*. (2000) attribute the origin of CO_2 to a magmatic source with a δ^{13}C of about –2‰. This source would be a large magmatic body located at depth > 3 km (Inguaggiato *et al*., 2000). Such an isotopic value, which is higher than the usual magmatic range (–5 to –8‰), could be due either to crustal contamination of the shallow feeding system or to contamination of the deep mantle source through metasomatic processes, as already assessed for other volcanic systems of southern Italy (Parello *et al*., 2000).

Recently Chiodini *et al*. (2004) made a soil CO_2 flux survey of a restricted area (0.86 km^2) of the island on the western flank of Mt. Epomeo obtaining a total output of 0.38 kg s^{-1} of CO_2, 27% of which they attributed to the degassing of the hydrothermal system.

Sampling and Analytical Methods

Soil CO_2 flux

Measurements of CO_2 flux from soil and steamy ground were performed in early October 2002 using the method of the dynamic accumulation chamber (Chiodini *et al*., 1998; Farrar *et al*., 1995). The survey was made in

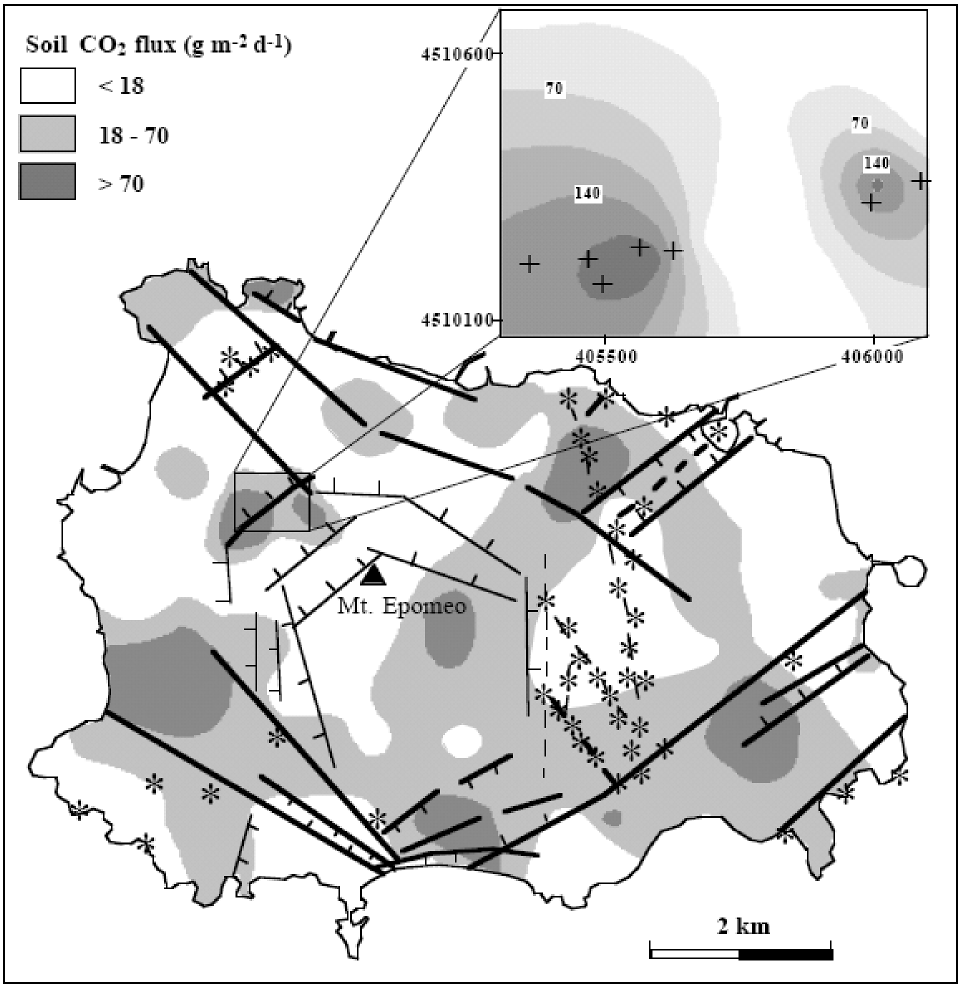

Fig. 2. Distribution of the anomalous degassing areas of Ischia. Areas with φ_{CO2} above 18 g m^{-2} d^{-1} are in light grey, while areas with φ_{CO2} above 70 g m^{-2} d^{-1} are in dark grey. Bold lines are regional tectonic structures, light lines local tectonic structures bounding the Mt. Epomeo resurgent bock (hatches on the downthrown side) and asterisks recent volcanic vents (Acocella and Funiciello, 1999). Inset: Pizzone–Mt. Nuovo area (crosses indicate fumarolic vents) with isolines interval of 35 g m^{-2} d^{-1} (outer scale indicates the UTM coordinates in meters).

a period of four days with stable weather conditions. Ninety-two flux measurements were carried out over Ischia Island, with a sampling grid of about 2 points per square kilometre (Fig. 1). In addition, 14 CO_2 flux measurements were made in the area of Pizzone–Mt. Nuovo (about 0.5 km^2), just NW of Monte Epomeo. In this area measurements were made with a higher sampling frequency because of a high density of tectonic structures and the presence of fumaroles, one of which (Pizzone–Mt. Nuovo) is regularly sampled for the geochemical surveillance of volcanic activity (Inguaggiato *et al.*, 2000). We could not make CO_2 flux measurements in most of the fumaroles of Ischia; hence we probably miss some information on the contribution of CO_2 from vent degassing. However, in the following discussion, we will make some assumptions to estimate this contribution. In each sampling point CO_2 flux measurements were performed in duplicate, and the arithmetic average of the two values was considered for budget calculations.

CO_2 dissolved in groundwater

The amount of volcanic CO_2 released in the ground water of Ischia was calculated on the basis of the estimates of ground water discharge to the sea and the values of dissolved TDIC determined in 46 ground water sampling points (Fig. 1). Values of TDIC were obtained summing up all dissolved inorganic carbon species. Bicarbonate was obtained from alkalinity values measured by titration with HCl 0.1 N. Dissolved CO_2 was measured by gas chromatography in the head space of vials sealed underwater at the sampling site and equilibrated in the laboratory with a fixed volume of pure argon (carrier gas).

The amount of dissolved CO_2 was subsequently recalculated taking into account the partitioning equilibrium of gaseous species between liquid and gas phase (Capasso and Inguaggiato, 1998).

RESULTS AND DISCUSSION

The values of CO_2 flux (φ_{CO2}) through the soils of Ischia Island range from 0 to 1082 g m^{-2} d^{-1}, with an average of 36.3 g m^{-2} d^{-1}. A similar range (0.1–4000 g m^{-2} d^{-1}) and average (43 g m^{-2} d^{-1}) was obtained by Chiodini *et al.* (2004) for a 0.86 km^2 wide are on the western flank of Mt. Epomeo.

The contour map of log φ_{CO2} for the 92-point survey (Fig. 2) shows that high φ_{CO2} values were measured mostly in the southern and eastern parts of the island. Maximum values roughly correspond to tectonic structures that can be referred to the regional tectonic system, but high diffuse degassing also occurs in the areas with the highest density of recent eruptive vents (east of Mt. Epomeo—Fig. 2). This pattern agrees well with the fact that active tectonic structures and areas of recent active volcanism are generally good pathways for gases of deep origin (Farrar *et al.*, 1995; Chiodini *et al.*, 1998). Chiodini *et al.* (2004) highlight also that CO_2 degassing in the area of the western flank of Mt. Epomeo is prevailingly connected to NW-SE striking normal faults. These tectonic features can be referred to the regional system (Acocella and Funiciello, 1999). Conversely, no diffuse degassing was found along the faults that bound the resurgent block of Mt. Epomeo to the north and to the west. These faults are preferred pathways for hydrothermal circulation whose surface expression are many fumaroles (Molin *et al.*, 2003). In these cases, therefore, fault permeability is probably lowered by self-sealing phenomena, which concentrate gas flux at the fumarolic vents. The contour map of logφ (CO_2 values for the 14-points survey at Pizzone–Mt. Nuovo (Fig. 2) shows, in fact, that the highest flux values are measured close to fumaroles.

The total output of CO_2 (Q_{CO2}) degassed from the soil of the surveyed areas was estimated using three methods: i) arithmetic averaging, ii) ordinary kriging, and iii) an anomaly threshold approach based on the statistical procedure of Sinclair (1974). In the first method Q_{CO2} was obtained by integrating the arithmetic average of the 92 φ_{CO2} values over the 46 km^2 surface of Ischia Island and the resulting value was 19.3 kg s^{-1}. The Q_{CO2} value obtained with ordinary kriging was 20.5 kg s^{-1}. In order to assess the anomaly threshold for soil CO_2 fluxes, a log probability plot was used for all 106 soil gas sample points at Ischia (Fig. 3). The plot indicates two evident inflection points, respectively at the 10th and 56th percentiles, indicating the presence of 3 distinct populations. Population A entails values below 18 g m^{-2} d^{-1}, which therefore

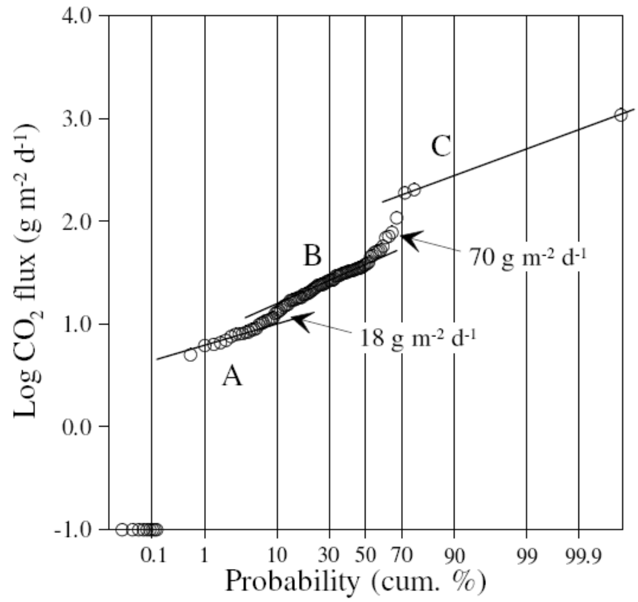

Fig. 3. Log probability plot for log soil CO_2 flux values measured at Ischia. The plot highlights the presence of three statistically distinct populations, indicated with capital letters.

can be set as the upper limit for background CO_2 flux level due to biological activity in the soil. Population B entails values between 18 and 70 g m^{-2} d^{-1}. Population C entails values above 70 g m^{-2} d^{-1}. Poputations B and C should include soil CO_2 fluxes due to degassing from the hydrothermal system. The mean φ_{CO2} of the three populations were 8.92 g m^{-2} d^{-1}, 31.5 g m^{-2} d^{-1} and 288.6 g m^{-2} d^{-1}, respectively. The CO_2 output from the background source was 2.44 kg s^{-1}, whereas that from both of the hydrothermal sources was 14.53 kg s^{-1}. The latter was estimated considering the average of the mean φ_{CO2} values of populations B and C (56.3 g m^{-2} d^{-1}) multiplied by the surface covered by the anomalous values (about 22.3 km^2).

For the Pizzone–Mt. Nuovo area, the Q_{CO2} obtained by integrating the arithmetic average of the 14 φ_{CO2} values over the 0.5 km^2 surface is about 0.22 kg s^{-1}, while applying the anomaly threshold approach we obtain a CO_2 output of 0.02 and 0.31 kg s^{-1} from the background source (i.e., below 18 g m^{-2} d^{-1}) and the hydrothermal sources (i.e., above 18 g m^{-2} d^{-1}) respectively.

The three methods applied for the estimation of the total soil CO_2 output gave results of the same order of magnitude but we consider the anomaly threshold approach, which excludes from calculation the background contribution (likely of organic origin), the most correct. Thus a reasonable estimate of the total hydrothermal CO_2 output from the soils of Ischia (14.84 kg s^{-1}) is obtained by summing the values both from the Pizzone–Mt. Nuovo

Table 1. Calculation of groundwater contribution to the total CO_2 flux of Ischia island

Sectors	A	1B	2B	3B	4B	sum	seawater	rainwater
N. of samples	7	19	9	2	9	46		
Mean TDIC (mg l^{-1})	976	1099	593	572	678		180	10
Water flow (l s^{-1})	129	60	54	111	54	408	151	257
CO_2 flux (kg s^{-1})	0.126	0.066	0.032	0.063	0.037	0.324	0.027	0.003

area and from the rest of the island surface.

The contribution of CO_2 from the fumaroles of Ischia is not easily quantifiable, mostly because the large majority of them are located in inaccessible areas. The only available data are from two sites (Cartaromana and Citara) where gas (almost pure CO_2) bubbles in thermal waters, and the respective measured output values yield about 2 and 0.1 g s^{-1} of CO_2. The soil CO_2 flux measurements that were made close to fumaroles gave an average value of 372 g m^{-2} d^{-1} (range between 0 and 1082 g m^{-2} d^{-1}). For comparison, the bubbling water sites would both give fluxes of more than 15,000 g m^{-2} d^{-1}, referred to the visible exhaling area (about 10 m^2 and 0.5 m^2, respectively). But these high flux values rapidly drop on moving away from the active vents. Referring the measured outputs to a surface of 100 m^2 we would obtain flux values of 1700 and 90 g m^{-2} d^{-1}, respectively, that are similar to the soil CO_2 flux measurements made close to some of the fumaroles of the island.

The estimate of CO_2 output from Ischia's fumaroles is based on the following assumptions: i) a single fumarole covers an average surface of approximately 100 m^2; ii) the mean soil CO_2 flux is 372 g m^{-2} d^{-1}; iii) the total number of fumaroles mapped is 60 (Molin *et al.*, 2003). The total CO_2 output obtained is, therefore, about 0.03 kg s^{-1}. Due to the large assumptions, this calculation must be considered only as an estimate of the order of magnitude of fumarole contribution to Ischia's CO_2 budget. The reasons for such small contribution lay in the small surface covered by each fumarole, but also in the high H_2O/CO_2 ratio (generally higher than 100—Panichi *et al.*, 1992; Chiodini *et al.*, 2004) and, concurrently, in the low steam flux that characterises most of fumarole emissions. Actually only few fumaroles have a detectable CO_2 content, the rest being almost pure water vapour with traces of atmospheric gases.

Carbon dioxide is rather soluble in the aqueous phase, and it can be significantly trapped by groundwaters flowing inside the permeable volcanic rocks. Therefore, CO_2 dissolved in groundwater must be taken into account when estimating the total output of this gas from an active volcanic system. Groundwaters with significant amounts of magma-derived volatiles dissolved have generally pCO_2 values largely exceeding those of atmosphere (3.3×10^{-4} atm) or soil air (10^{-2} to 10^{-3} atm). Groundwaters of Ischia are not an exception, as they display values ranging from 0.01 to 1.26 atm (average 0.24 atm), thus confirming the huge input of CO_2 of deep origin. Upon dissolution into groundwater, CO_2 hydrolizes forming also dissolved carbonated ions. Therefore, in the estimation of CO_2 flux through groundwater all dissolved inorganic carbon species ($CO_2 + HCO_3^- + CO_3^{2-}$) must be taken in account. TDIC values (expressed as CO_2 concentrations) in the sampled groundwaters range from 160 to 2100 mg l^{-1}. The total amount of CO_2 carried by the groundwaters of Ischia was obtained with the following equation:

$$Q_{TDIC} = \Sigma D_i \times C_i$$

where D is the average annual discharge to the sea and C is the mean content of TDIC expressed as CO_2. The suffix i indicates the sectors for which the calculation was carried out. According to Celico *et al.* (1999), Ischia Island can be divided into two sub-areas with different hydrogeological features: Mt. Epomeo horst (31 km^2) and Ischia graben (15 km^2). The former has been further divided in four sectors by the authors. Values obtained for each of the five sectors are displayed in Table 1. The obtained Q_{TDIC} value is 0.324 kg s^{-1}. As pointed out in the hydrogeology study of Celico *et al.* (1999), the seawater contribution to the total groundwater discharge along the coast is high (about 30%). Its significant carbon contribution (Q_{SW} = 0.027 kg s^{-1}) is not of endogenous origin and has been subtracted from the total flux. TDIC in rain waters in the study area is generally less than 10 mg l^{-1}, so contribution from the meteoric recharge can be neglected. The amount of CO_2 carried by groundwaters can thus be estimated at about 0.3 kg s^{-1}. This value is about 50 times lower than that released through diffuse degassing. Just to give an example of a different situation, the amount of CO_2 carried by groundwater at Mt. Etna is only 4 times lower than the CO_2 contribution from diffuse degassing through the flanks of the volcano (D'Alessandro *et al.*, 1997). The difference lies in the fact that groundwaters at Ischia are highly thermalised and much more saline than those flowing through Etna's edifice, and such conditions greatly lower carbon dioxide solubility in water (Capasso and Inguaggiato, 1998).

The high proportion of the total CO_2 output attributed to diffuse degassing (98%) with respect to fumarolic emission (0.2%) at Ischia is probably a typical feature of volcanic systems in a quiescent state. Pantelleria Island and Solfatara, in fact, display similar proportions (90% and 98%, respectively, for diffuse degassing and <2% and < 0.001%, respectively, for fumarolic degassing—Favara *et al*., 2000; Werner *et al*., 2003). Diffuse degassing, on the contrary, seems to be much less important in volcanoes with open conduit activity like Etna (about 7% of total CO_2 output—D'Alessandro *et al*., 1997), Oldoinyo Lengai (<2%—Koepenick *et al*., 1996), Mt. Erebus (<2%—Wardell *et al*., 2004), Stromboli (5%—Carapezza and Federico, 2000) and probably Popocatepetl (Varley and Armienta, 2001).

Table 2. Summary of the estimated contribution of CO_2 from the different types of gas emissions on Ischia island

Type of CO_2 emission	Output (kg s^{-1})	N	Surface (km^2)
Soil flux total	14.53	92	46
Soil flux Pizzone-Mt. Nuovo	0.31	14	0.5
Fumaroles	0.03	60	0.006
Dissolved	0.30	46	46

CONCLUSIONS

The total CO_2 output from Ischia can be estimated at about 15 kg s^{-1} (Table 2). Taking into account the quiescent state of Ischia island, its CO_2 output can be considered relatively high compared to other volcanic systems all around the world (Table 3). Higher values are, in fact, measured only in volcanoes with very strong open conduit activity (Mt. Etna, Popocatepetl, Kilauea, Oldoinyo Lengai), or volcanoes whose output estimate was made shortly after big explosive eruptions (Mt. Augustine, Mt. St. Helens, Mt. Redoubt). Its output is similar to other volcanic systems of southern Italy that display a quite similar activity status (Pantelleria, Solfatara) but significantly higher than volcanoes of the same area whose quiescent state lasts from much longer time (Ustica, Albani Hills). Volcanoes related to subduction zones display CO_2 outputs that are generally one order of magnitude lower

Table 3. CO_2 output from some volcanic and geothermal areas of the world

Mt. Etna (Italy)	450 kg s^{-1}	D'Alessandro *et al*. (1997)
Popocatepetl (Mexico)	450 kg s^{-1}	Goff *et al*. (2001)
Kilauea (U.S.A.)	100 kg s^{-1}	Gerlach *et al*. (2002)
Oldoinyo Lengai (Tanzania)	80 kg s^{-1}	Brantley and Koepenick (1995)
Mt. Augustine (U.S.A.)	70 kg s^{-1}	Symonds *et al*. (1992)
Cerro Negro (Nicaragua)	63 kg s^{-1}	Salazar *et al*. (2000)
Mt. St. Helens (U.S.A.)	56 kg s^{-1}	Harris *et al*. (1981)
Mt. Redoubt (U.S.A.)	54 kg s^{-1}	Hobbs *et al*. (1991)
Stromboli (Italy)	50 kg s^{-1}	Allard *et al*. (1994)
Masaya (Nicaragua)	34 kg s^{-1}	Burton *et al*. (2000)
Niragongo (D. R. Congo)	33 kg s^{-1}	Le Guern (1987)
Mt. Spurr (U.S.A.)	32 kg s^{-1}	Doukas (1995)
White Island (New Zealand)	30 kg s^{-1}	Wardell *et al*. (2001)
Rabaul (Papua N.G.)	28 kg s^{-1}	Perez *et al*. (1998)
Mt. Erebus (Antarctica)	22 kg s^{-1}	Wardell *et al*. (2004)
Galeras (Colombia)	20 kg s^{-1}	Stix *et al*. (1997)
Solfatara di Pozzuoli (Italy)	17.5 kg s^{-1}	Cardellini *et al*. (2003)
Ischia (Italy)	15.2 kg s^{-1}	this study
Pantelleria (Italy)	12.4 kg s^{-1}	Favara *et al*. (2000)
Ustica (Italy)	8.2 kg s^{-1}	Etiope *et al*. (1999)
Grimsvotn (Iceland)	6.0 kg s^{-1}	Agustsdottir and Brantley (1994)
Albani Hill (Italy)	5.9 kg s^{-1}	Chiodini and Frondini (2001)
Teide (Spain)	5 kg s^{-1}	Mori *et al*. (2001)
Mud Volcano (Yellowstone - U.S.A.)	4.4 kg s^{-1}	Werner *et al*. (2000)
Vulcano (Italy)	3 kg s^{-1}	Chiodini *et al*. (1996)
Mammoth Mountain (U.S.A.)	3 kg s^{-1}	Gerlach *et al*. (2001)
Naftia Lake (Italy)	3 kg s^{-1}	De Gregorio *et al*. (2002)
Usu (Japan)	2 kg s^{-1}	Hernandez *et al*. (2001a)
Yangbajain (China)	1.6 kg s^{-1}	Chiodini *et al*. (1998)
Miyakeijma (Japan)	1.5 kg s^{-1}	Hernandez *et al*. (2001b)
Nisyros (Greece)	1 kg s^{-1}	Cardellini *et al*. (2003)
Hakkoda (Japan)	0.86 kg s^{-1}	Hernandez *et al*. (2003)
Nea Kameni (Greece)	0.2 kg s^{-1}	Chiodini *et al*. (1998)
Iwoyama (Japan)	0.1 kg s^{-1}	Mori *et al*. (2001)

(Vulcano, Usu, Miyakeijma, Mykonos, Nea Kameni). The relatively high output of Ischia could be probably justified by the recent tensile tectonic regime that allowed the formation of pathways for an easier upflow of CO_2 from the mantle. The high CO_2 upflow from the mantle, which has also been recognised in nearby regions of western-central Italy (Chiodini *et al.*, 1999), was also attributed to the same regional tensile tectonic regime.

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