Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, τομ. XLVII , 2013
Πρακτικά 13ου Διεθνούς Συνεδρίου, Χανιά, Σεπτ. 2013

Bulletin of the Geological Society of Greece, vol. XLVII 2013
Proceedings of the 13th International Congress, Chania, Sept. 2013

HYDROTHERMAL METHANE FLUXES FROM THE SOIL AT LAKKI PLAIN (NISYROS ISLAND, GREECE)

D'Alessandro W.[1], Gagliano A.L.[2], Kyriakopoulos K.[3] and Parello F.[2]

[1] *Istituto Nazionale di Geofisica e Vulcanologia – Sezione di Palermo, Via U. La Malfa 153, 90146 Palermo, Italy, w.dalessandro@pa.ingv.it*

[2] *University of Palermo, Dept. DiSTeM, via Archirafi 36, 90123 Palermo, Italy*

[3] *National and Kapodistrian University of Athens, Faculty of Geology and Geoenvironment, Panepistimioupolis, 157 84 Ano Ilissia, Greece*

Abstract

Methane and CO_2 flux measurements from the soils were made with the accumulation chamber method in Lakki plain covering an area of about 0.06 km^2 including the main fumarolic areas of Kaminakia, Stefanos and Phlegeton. Flux values measured at 77 sites range from –3.4 to 1420 mg m^{-2} d^{-1} for CH_4 and from 0.1 to 383 g m^{-2} d^{-1} for CO_2. The three fumarolic areas show very different methane degassing patterns, Kaminakia showing the highest flux values. Methane output can be estimated in about 0.01 t a^{-1} from an area of about 2500 m^2 at Phlegeton, about 0.1 t a^{-1} from an area of about 20,000 m^2 at Stefanos and about 0.25 t a^{-1} from an area of about 30,000 m^2 at Kaminakia. The total output from the entire geothermal system of Nisyros should not exceed 1 t a^{-1}. Previous estimates of the CH_4 output at Nisyros, based on soil CO_2 output and CH_4/CO_2 ratios in fumarolic gases, were more than one order of magnitude higher. The present work further underscores the utmost importance of direct CH_4 flux data.

Key words: *accumulation chamber, soil degassing, hydrothermal systems, methane output.*

Περίληψη

Μετρήσεις φυσικής ροής μεθανίου και διοξειδίου του άνθρακα από το έδαφος πραγματοποιήθηκαν με τη μέθοδο συγκέντρωσης θαλάμου στην περιοχή Λακκί της Καλδέρας της Νισύρου, καλύπτοντας έκταση περίπου 0.06 km^2 συμπεριλαμβάνοντας τις περιοχές Καμινάκια, Στέφανος και Αλέξανδρο όπου παρατηρείται έντονη ατμιδική δραστηριότητας. Οι τιμές ροής που μετρήθηκαν σε 77 σημεία κυμαίνονται από –3.4 μέχρι 1420 mg m^{-2} d^{-1} για το CH_4 και από 0.1, μέχρι 383 g m^{-2} d^{-1} για το CO_2. Στις τρεις ατμιδικές περιοχές παρουσιάζονται διαφορετικοί ρυθμοί διαφυγής μεθανίου, ιδίως στα Καμινάκια όπου προέκυψαν οι μεγαλύτερες τιμές ροής. Η εξερχόμενη ποσότητα μεθανίου εκτιμάται σε 0.01 t a^{-1} από μια έκταση περίπου 2500 m^2 στον Αλέξανδρο, περίπου 1 t a^{-1} από μια έκταση περίπου 20,000 m^2 στον Στέφανο και περίπου 0.25 t a^{-1} από μια έκταση περίπου 30,000 m^2 στα Καμινάκια. Η συνολική εξερχόμενη ποσότητα από ολόκληρο το γεωθερμικό σύστημα της Νισύρου δεν πρέπει να υπερβαίνει το 1 t a^{-1}. Οι προηγούμενες εκτιμήσεις για την ποσότητα του εξερχόμενου μεθανίου από τη Νίσυρο, βασιζόμενες στην ποσότητα του CO_2 που διαφεύγει από το έδαφος και του λόγου CH_4/CO_2 των αερίων από τις φουμαρόλες,

ήταν περισσότερο από μία τάξη υψηλότερες. Στην παρούσα εργασία υπογραμμίζεται κυρίως η μεγάλη σημασία που παρουσιάζουν τα δεδομένα της απευθείας ροής του Μεθανίου.
Λέξεις κλειδιά: *Θάλαμος συγκέντρωσης, απαέρωση εδάφους, υδροθερμικά συστήματα, διαφυγή μεθανίου.*

1. Introduction

Methane plays an important role in the Earth's atmospheric chemistry and radiative balance being the second most important greenhouse gas after carbon dioxide (IPCC 2001). Methane is released to the atmosphere by a wide number of sources, both natural and anthropogenic, with the latter being twice as large as the former (IPCC 2001).

It has recently been established that geogenic gases contribute significantly to the natural CH_4 flux to the atmosphere (Etiope et al. 2008). Volcanic/geothermal areas contribute to this flux, being the site of widespread diffuse degassing of endogenous gases (Chiodini et al. 2005). In such an environment soils are a source rather than a sink for atmospheric CH_4 (Cardellini et al. 2003; Castaldi & Tedesco 2005; D'Alessandro et al. 2009; 2011). Preliminary studies (Etiope et al. 2007) estimated a total CH_4 emission from European geothermal and volcanic systems in the range 4-16 kt a^{-1}. This estimate was obtained indirectly from CO_2 or H_2O output data and from CO_2/CH_4 or H_2O/CH_4 values measured in the main gaseous manifestations. Such methods, although acceptable to obtain order-of-magnitude estimates, completely disregard possible methanotrophic activity within the soil. Furthermore at hydrothermal systems which display a rather large range in fumarolic CO_2/CH_4 values, like that of Nisyros (from 25 to 1600 in volume – Marini and Fiebig, 2005; Fiebig et al, 2009), the use of an average value could introduce a large uncertainty in the indirect estimation of the total CH_4 output to the atmosphere.

The Greek territory is geodynamically very active and has many volcanic and geothermal areas (Fytikas et al. 1995) which potentially contribute to the atmospheric CH_4 burden. Here we report on soil gas flux measurements made at Nisyros a currently quiescent active volcanic system with strong fumarolic activity due to the presence of a high enthalpy geothermal system. Measurements were used to estimate the total CH_4 output of this hydrothermal system.

2. Study Area and Methods

2.1. The Nisyros Volcanic and Geothermal System

The island of Nisyros belongs to the easternmost volcanic group of the South Aegean active volcanic arc. It was built up during the last 200 ka and is considered still active though at present in quiescent status (Vougioukalakis and Fytikas, 2005). Its volcanic activity has been characterized by (i) an early submarine stage, (ii) a subaerial cone-building stage, culminating in the formation of a central caldera, and (iii) a post-caldera stage, when several dacitic-rhyolitic domes were extruded (Keller, 1982). No historical magmatic activity is known on Nisyros and the most recent activity was of hydrothermal character (Marini et al. 1993). Such activity concentrated in the southern Lakki plain and on the southeastern flank of the Lofos dome both within the caldera. This hydrothermal activity formed a series of hydrothermal whose age decreases from southeast to northwest. The last events took place in 1871–1873 and 1887 partially destroying the small Lofos dome. A large fumarolic field is now present in this area mainly within the hydrothermal craters and being affected by fracturing along the main NW- and NE-trending active fault systems (Papadopoulos et al. 1998). Two deep explorative geothermal wells drilled in the Lakki plain revealed the existence of two distinct hydrothermal aquifers. The shallowest at about 500 m depth has temperatures around 150 °C while the deeper one (> 1500 m) reaches temperatures up to 340 °C (Brombach et al., 2003).

2.2. Sampling and Analytical Methods

Previous studies assessed a widespread CO_2 degassing in the whole fumarolic area and in the nearby areas (Caliro et al., 2005). The highest CO_2 fluxes (> 300 g m^2 day) were measured within the above described hydrothermal craters. Basing on these results we decided to concentrate our CH_4 flux measurements in the most representative craters (Kaminakia, Stefanos and Phlegeton) with some additional measurements in the fumarolic field of Lofos (outside any crater) and a few points in the low flux areas (Fig. 1a).

Measurements were made at 77 sites during two field campaigns (3-6 September 2009 and 24 August – 4 September 2010). At each sampling site the soil temperature was also measured at 20 and 50 cm depth and the soil CH_4 and CO_2 concentrations were determined at 50 cm depth.

Flux measurements were made with the accumulation chamber method (Livingstone & Hutchinson 1995; Baciu et al. 2008; D'Alessandro et al. 2009). The flux chamber has a cross-sectional area of 0.07 m^2 and height of 10 cm. The chamber top has two fixed capillary tubes, one used to collect chamber gas samples and the other used to balance the pressure between inside and outside. Three gas samples were drawn from the headspace in the chamber at fixed intervals after deployment (5, 10 and 15 min). The 20 mL samples are collected using a syringe and injected through a three-way valve and a needle into a 10 mL pre-evacuated sampling vial (Exetainer®, Labco Ltd.). The overpressured vials were sent to the laboratory for CH_4 and CO_2 analysis.

The flux of CO_2 and CH_4 from the soil can be calculated as the rate of concentration increases in the chamber:

Equation 1

$$\Phi = dC/dt \times V/A$$

where Φ is the flux of a gas, V is the volume of air in the chamber (m^3), A is the area covered by the chamber (m^2), C is the chamber concentration of a gas and dC/dt is the rate of concentration change in the chamber air for each gas. Volumetric concentrations are converted to mass concentrations accounting for atmospheric pressure and temperature. Flux values are expressed as g m^{-2} d^{-1} for CO_2 and as mg m^{-2} d^{-1} for CH_4. Positive values indicate fluxes directed from the soil to the atmosphere and negative values indicate flow from the atmosphere into the soil.

Ground temperature measurements were taken at 10 and 50 cm depth using thermal probes and a digital thermometer.

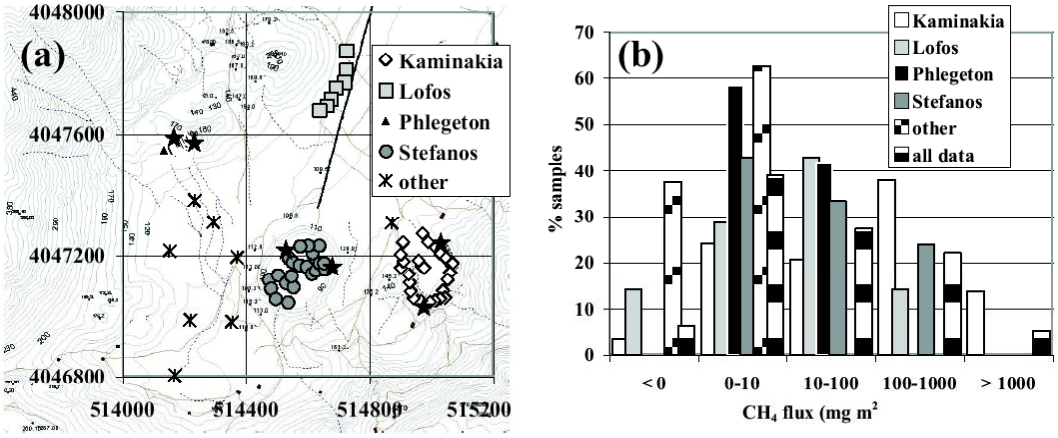

Figure 1 - (a) study area with CH_4 flux measurements points and sampled gas manifestations (stars). (b) Percent frequency distribution of CH_4 flux values.

Samples of soil gas were collected at each site at a depth of 50 cm through a Teflon tube of 5 mm ID using a syringe. During the 2009 campaign CH_4 and CO_2 concentrations were determined in the field with an IR gas analyser (LFG 20 - ADC Co Ltd). During the 2010 campaign soil gas samples were collected and stored for subsequent laboratory analyses in the same way as gases from the flux chamber.

Samples of the many fumarolic manifestations were collected during both campaigns with soda filled bottles (Giggenbach and Goguel, 1989) and analysed in the laboratory for H_2O, H_2S, He, H_2, O_2, N_2, CH_4 and CO_2. Two fumaroles for each of the craters investigated for soil CH4 fluxes were sampled both in 2009 and 2010.

Gas concentrations were measured using the GC Perkin Elmer Clarus 500 equipped with Carboxen 1000 columns, Hot Wire and Flame Ionisation detectors with methanizer. The gas samples were injected through an automated injection valve with a 1000 µL loop. Calibration was made with certified gas mixtures. Analytical precision ($\pm 1\sigma$) was always better than ±5%. The detection limit for CH_4 was about 0.1 µmol mol^{-1}.

Geographical distribution of the CH_4 flux values and the estimation of the total output have been made by using a GIS software (ArcMap™ 9.3, ESRI®).

3. Results

3.1. Geochemistry of the Fumarolic Gases

Results of the chemical composition of the fumarolic gases are shown in Table 1. All samples are dominated by water vapour that accounts for 91 to 99% of their composition. For the remaining gases the composition generally follows the order $CO_2 > H_2S > H_2 \approx N_2 \approx CH_4 \gg He > O_2 \approx CO$. Methane displays a wider range in composition with respect to the other gases which is reflected in the wide range in CO_2/CH_4 ratios (Table 1). The main difference between the three fumarolic areas can be summarised in a lower content in H_2O and H_2S and a higher CO_2 and CH_4 content in the fumaroles of Kaminakia (K6 and K7). This has been explained by previous authors (Marini and Fiebig, 2005) with condensation of water vapour close to the surface. Dissolution in the liquid phase changes the relative concentrations of the remaining gases depending on their solubility. This results in a depletion of the more soluble species (H_2S) and a relative increase of CO_2 and especially of CH_4.

3.2. Soil Flux Measurements

Results of the flux measurements are summarized in Table 2. Values range from –3.4 to 1419 mg m^{-2} d^{-1} for CH_4 and from 0.1 to 383 g m^{-2} d^{-1} for CO_2. To get insight in the methane output of the Lakki plain we focalised our measurements in restricted exhaling areas: Kaminakia, Stefanos and Phlegeton craters and the southeastern flank of the Lofos dome. Some measurements were also made in areas of lower hydrothermal output and indicated in the figures as other. The latter sites display the lowest CH_4 flux values (Fig. 2b) never exceeding 2.6 mg m^{-2} d^{-1} and frequent negative values. Of the investigated exhaling areas those where the most recent activity occurred show the lowest CH_4 flux values (Lofos and Phlegeton ~ 0-100 mg m^{-2} d^{-1}) while to the older craters reach progressively higher values (Stefanos up to 714 mg m^{-2} d^{-1} and Kaminakia up to 1419 mg m^{-2} d^{-1}).

4. Discussion

The CH_4 flux distribution maps have been used to estimate the CH_4 output of the three investigated craters. The three areas according to the very different flux values show also very different CH_4 outputs. Phlegeton shows an output of about 0.01 t a^{-1} from an area of approximately 2500 m^2, that of Stefanos is about 0.1 t a^{-1} from an area of some 20,000 m^2 and that of Kaminakia about 0.3 t a^{-1} from an area of approximately 30,000 m^2. Our flux measurements did not cover the whole exhalative area but likely the remaining areas would not add significant amounts of CH_4 to

the entire output of the geothermal system. In fact, of the remaining area the highest hydrothermal flux areas (Micro Polyvotis, Megalos Polyvotis, Logothetis), with strong fumarole emissions, have characteristics that are very similar to Phlegeton and their contribution will be of the same order of magnitude and thus probably negligible. A more substantial contribution could probably derive form the area northeast and southwest of Kaminakia along the caldera border where soil gases could be enriched in CH_4 in the same way as at Kaminakia. Previous studies on CO_2 soil degassing (Caliro et al., 2005) indicate that in these areas the fluxes tend to decrease rapidly away from the Kaminakia area especially in the southwest direction lowering their possible contribution to the total output.

Table 1 - Chemical composition of some selected fumaroles at Nisyros.

sample	date	H_2O	CO_2	H_2S	He	H_2	O_2	N_2	CO	CH_4	CO_2/CH_4
	dd-mm-yyyy	%				µmol mol^{-1}					
K6	03-09-2009	95.6	874811	96343	18	12572	0	3979	6	12272	71
K6	31-08-2010	91.2	890317	90278	28	7914	7	8006	2	3448	258
K7	03-09-2009	92.2	890682	73796	22	5217	8	7045	5	23226	38
K7	31-08-2010	94.7	890636	78563	51	10974	18	13386	1	6370	140
S15	31-08-2009	98.3	774458	211925	29	6640	8	4213	3	2723	284
S15	31-08-2010	99.0	740627	217953	22	7515	27	30830	1	3026	245
S4	31-08-2009	98.3	794665	190003	28	5372	13	6910	3	3006	264
S4	31-08-2010	99.1	736916	223931	24	6169	41	29539	1	3380	218
A13	04-09-2009	98.0	753938	227194	24	10830	0	7186	2	826	912
A13	30-08-2010	98.6	738197	245342	28	10303	3	5543	1	582	1268
AM	04-09-2009	97.9	755731	225266	25	11190	0	6968	2	818	924
AM	31-08-2010	97.9	739933	204683	25	8751	3	46073	47	485	1525

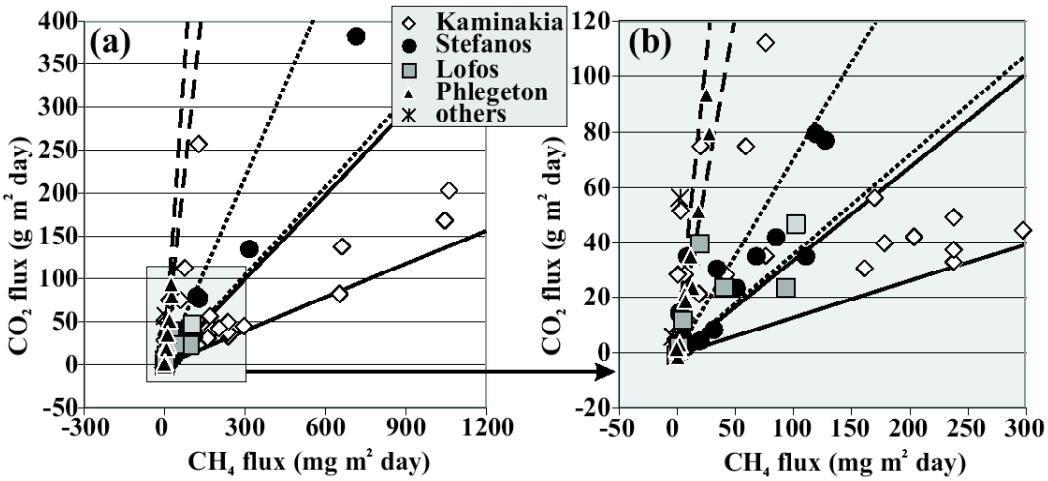

Figure 2 - CH_4 vs. CO_2 fluxes. The right graph is the enlargement of the left one. The black lines represent the range of CO_2/CH_4 concentration ratios in the Kaminakia fumaroles, the stippled line that of the Stefanos fumaroles and the dashed lines that of the Phlegeton fumaroles.

Table 2 - Soil gas and temperature measurements in the Lakki plain area.

Site	area	date	UTM coordinates		concentration		T°C	T°C	flux	
		d-mm-yy	easting	northing	CO_2	CH_4	@20cm	@50cm	CH_4	CO_2
			m	m	µmol mol^{-1}				mg m^2 day	g m^2 day
1	K	3-09-09	515021	4047221	447000	6500	44.2	64.4	238	32.7
2	K	3-09-09	515065	4047167	226000	3300	35.6	53.2	1062	203
3	K	3-09-09	515014	4047051	269000	5100	44.9	77.7	76.5	35.0
4	K	3-09-09	514946	4047060	197000	3400	37.2	54.2	238	37.2
5	K	3-09-09	514966	4047167	51300	800	41.5	45.7	3.4	51.3
6	K	3-09-09	514907	4047243	132000	2900	42.9	74.8	663	138
7	O	3-09-09	514871	4047306	23400	500	39.6	48.4	-3.4	5.5
8	S	3-09-09	514472	4047121	992000	5800	99.3	99.3	127	77.0
9	S	3-09-09	514479	4047093	992000	5400	92.5	100.4	314	135
10	S	3-09-09	514494	4047059	410000	1800	74.5	99.6	51.0	23.3
11	S	3-09-09	514534	4047047	615000	1000	54.0	86.8	110	35.0
12	O	4-09-09	514371	4047194	199000	3300	45.8	35.3	2.6	56.0
13	O	4-09-09	514295	4047308	13600	100	32.8	31.5	-0.9	1.5
14	O	4-09-09	514233	4047380	30500	100	43.2	34.7	-0.9	4.5
15	O	4-09-09	514153	4047215	1600	50	42.2	35.8	0.0	1.2
16	O	4-09-09	514219	4046989	1600	30	44.2	31.0	0.9	1.3
17	O	4-09-09	514169	4046795	2000	50	30.6	30.2	0.9	1.4
18	O	4-09-09	514353	4046983	25300	100	33.8	35.3	2.6	2.8
19	S	4-09-09	514502	4047137	992000	6500	74.2	99.0	1.7	0.5
20	S	4-09-09	514527	4047111	630000	3700	56.4	92.7	68.0	35.0
21	S	4-09-09	514551	4047097	992000	7100	70.7	98.8	6.0	4.7
22	S	4-09-09	514544	4047134	362000	3200	63.4	99.7	85.0	42.0
23	S	5-09-09	514537	4047192	662000	3500	63.2	97.2	34.0	30.3
24	S	5-09-09	514549	4047179	39000	300	32.7	41.5	2.6	14.0
25	S	5-09-09	514571	4047170	47000	300	30.4	36.0	1.7	14.3
26	S	5-09-09	514594	4047165	214000	1800	39.9	50.4	714	383
27	S	5-09-09	514611	4047141	12000	20	42.4	63.4	5.1	4.2
28	S	5-09-09	514624	4047151	63500	1000	52.2	91.0	68.0	35.0
29	S	5-09-09	514636	4047176	285000	1500	48.4	74.6	6.7	1.8
30	S	5-09-09	514654	4047155	784000	4000	99.0	100.9	20.0	4.3
31	S	5-09-09	514650	4047176	610000	3000	69.2	100.8	31.7	8.3
32	S	6-09-09	514613	4047209	152000	300	34.8	43.9	0.3	2.2
33	S	6-09-09	514635	4047233	212000	800	69.0	95.0	119	79.3
34	S	6-09-09	514599	4047233	85500	200	46.7	64.8	8.5	35.0
35	S	6-09-09	514573	4047231	24300	30	37.8	48.2	5.1	10.7
36	K	24-08-10	514971	4047271	52600	22	40.3	47.3	2.6	14.0
37	K	24-08-10	514988	4047244	56500	18	40.3	46.7	0.9	7.0
38	K	24-08-10	515012	4047226	32600	16	40.6	48.4	5.1	7.8

39	K	24-08-10	515029	4047205	167400	50	42.1	49.4	6.8	28.0
40	K	25-08-10	515046	4047191	271000	3841	41.4	51.5	1045	168
41	K	25-08-10	515068	4047174	536200	9215	57.4	69.6	297	44.3
42	K	25-08-10	515059	4047143	157000	1015	43.3	55.0	76.5	112
43	K	25-08-10	515052	4047120	155300	651	37.5	44.3	20.4	74.7
44	K	25-08-10	515037	4047084	253600	1368	53.5	62.7	59.5	74.7
45	K	25-08-10	515043	4047061	248800	5271	58.3	74.0	1419	154
46	K	25-08-10	515027	4047058	60600	847	60.2	66.0	654	81.7
47	K	27-08-10	515010	4047051	143500	1624	56.3	69.5	1419	261
48	K	27-08-10	514995	4047047	488900	7117	65.9	82.4	127	257
49	K	27-08-10	514965	4047050	22200	58	46.6	58.7	8.5	11.7
50	K	27-08-10	514942	4047060	257100	2750	44.4	57.6	170	56.0
51	K	27-08-10	514932	4047082	300400	3735	64.9	77.7	178	39.7
52	K	27-08-10	514929	4047111	660500	9890	63.5	87.0	238	49.0
53	K	27-08-10	514925	4047138	840000	13900	65.0	95.0	161	30.3
54	Ph	2-09-10	514219	4047572	749100	531	77.3	99.9	1.7	0.8
55	Ph	2-09-10	514206	4047584	739900	535	80.7	99.9	1.7	1.3
56	Ph	2-09-10	514199	4047572	17500	12	99.9	n.m.	13.6	23.3
57	Ph	2-09-10	514177	4047590	743500	515	63.2	87.5	6.8	21.0
58	Ph	2-09-10	514188	4047586	221600	156	51.0	70.3	7.7	18.7
59	Ph	2-09-10	514183	4047571	533	3	71.3	89.0	18.7	51.3
60	Ph	2-09-10	514175	4047566	496700	387	61.2	89.4	28.1	79.3
61	Ph	2-09-10	514165	4047573	661300	478	75.4	99.5	25.5	93.3
62	Ph	2-09-10	514155	4047570	n.m.	n.m.	62.2	n.m.	11.9	35.0
63	Ph	2-09-10	514157	4047552	21400	23	52.8	75.0	2.6	3.0
64	Ph	2-09-10	514148	4047551	1700	4	44.8	54.0	0.9	0.1
65	Ph	2-09-10	514134	4047552	3600	5	38.1	43.1	0.0	1.4
66	L	3-09-10	514724	4047872	121000	49	41.5	52.8	5.1	11.7
67	L	3-09-10	514723	4047809	535	3	33.9	41.6	-0.9	0.1
68	L	3-09-10	514717	4047770	33500	12	37.5	49.0	1.7	2.0
69	L	3-09-10	514690	4047753	74400	229	47.3	65.0	19.5	39.7
70	L	3-09-10	514674	4047717	82900	584	49.2	82.2	93.5	23.3
71	L	4-09-10	514661	4047692	414900	2892	48.6	76.4	40.4	23.5
72	L	4-09-10	514637	4047679	734600	5033	97.5	99.9	102	46.7
73	K	4-09-10	514901	4047159	112500	784	46.2	80.0	42.5	28.0
74	K	4-09-10	514908	4047180	142600	1376	47.0	77.0	19.1	21.0
75	K	4-09-10	514900	4047202	873800	14700	66.0	98.4	204	42.0
76	K	4-09-10	514958	4047183	1300	3	36.0	43.5	-0.9	4.7
77	K	4-09-10	514976	4047159	63800	4	36.0	43.8	0.9	28.0

Area: K=Kaminakia, S=Stefanos, Ph=Phlegeton, L=Lofos, O=other; UTM coordinates: reference system WGS84; n.m.=not measured.

Consequently our best estimation of the total CH_4 output of the geothermal system of Nisyros is about 1 t a^{-1}, which is more than one order of magnitude lower than the previous estimation (54 t a^1 - Etiope et al., 2007). The latter was made simply multiplying an estimated average CH_4/CO_2 ratio of the fumarolic emissions by the total CO_2 output obtained by Chiodini et al. (2005). As previously evidenced (D'Alessandro et al., 2009; 2011), part of the difference could be attributed to the disregarding of methanotrophic activity within the soils. Microbial activity has the potential to oxidize great quantities of CH_4 also within the soils of geothermal areas (Castaldi and Tedesco, 2005; Pol et al., 2007). Clues for methanotrophic activity in the soils of the study area can be evidenced in Figure 2 where, especially in the area of Kaminakia and Stefanos some of the sites show much higher CO_2/CH_4 ratios with respect to the relative fumarole gases.

Another source of error in the estimation of Etiope et al. (2007) derives from the great variability both in time and space of the CO_2/CH_4 ratios of the fumarole emissions at Nisyros (Table 1) as also evidenced by Marini and Fiebig (2005). Such great variability could introduce a great error in the CO_2/CH_4 ratio used to obtain the total CH_4 output. The CO_2/CH_4 ratio used by Etiope et al. (2007) is indeed low (167 by volume), close to the mean value of the Kaminakia crater, which is by no means representative of the whole area. Other strongly degassing areas show all considerably higher mean values accounting for a significant part of the difference in output estimation.

5. Conclusions

Flux measurements at Nisyros confirm that this geothermal system is diffusively degassing significant amounts of CH_4 (~1 t a^{-1}) through the soils. This study further confirms that volcanic/geothermal areas are significant sources of CH_4 to the atmosphere but also that probably their contribution has been overestimated. The present study indicates that the previous estimate (54 t a^{-1}) at Nisyros, made by cross-correlating CO_2 output data with the CO_2/CH_4 ratios of its gaseous manifestations, has been excessively large. This great difference derives from both disregarding methanotrophic activity within the soils and from an incorrect mean CO_2/CH_4 ratio of the fumarolic emissions used in the calculation of the total output.

6. Acknowledgments

We acknowledge the help of Jens Fiebig and Mika Gousgouni in the field and of Mauro Martelli and Francesco Salerno in the laboratory.

7. References

Baciu C., Etiope G., Cuna S. and Spulber L. 2008. Methane seepage in an urban development area (Bacau, Romania): origin, extent, and hazard, *Geofluids*, 8, 311–320.

Brombach T., Caliro S., Chiodini G., Fiebig J., Hunziker J.C. and Raco B. 2003. Geochemical evidence for mixing of magmatic fluids with seawater, Nisyros hydrothermal system, Greece, *Bull. Volcanol.*, 65, 505–516.

Caliro S., Chiodini G., Galluzzo D., Granieri D., La Rocca M., Saccorotti G. and Ventura G. 2005. Recent activity of Nisyros volcano (Greece) inferred from structural, geochemical and seismological data, *Bull. Volcanol*., 67, 358–369.

Cardellini C., Chiodini G., Frondini F., Granieri D., Lewicki J., Peruzzi L. 2003. Accumulation chamber measurements of methane fluxes: application to volcanic–geothermal areas and landfills, *Appl. Geochem.*, 18, 45–54.

Castaldi S., Tedesco D. 2005. Methane production and consumption in an active volcanic environment of Southern Italy, *Chemosphere*, 58, 131-139.

Chiodini G., Granieri D., Avino R., Caliro S. and Costa A. 2005. Carbon dioxide diffuse degassing and estimation of heat release from volcanic and hydrothermal systems, *J. Geophys. Res.*, 110, B08204.

D'Alessandro W., Bellomo S., Brusca L., Fiebig J., Longo M., Martelli M., Pecoraino G. and Salerno F. 2009. Hydrothermal methane fluxes from the soil at Pantelleria island (Italy), *J. Volcanol. Geotherm. Res.*, 187, 147-157.

D'Alessandro W., Brusca L., Kyriakopoulos K., Martelli M., Michas G., Papadakis G. and Salerno F. 2011. Diffuse hydrothermal methane output and evidence of methanotrophic activity within the soils at Sousaki (Greece), *Geofluids*, 11, 97–107.

Etiope G., Fridriksson T., Italiano F., Winiwarter W. and Theloke J. 2007. Natural emissions of methane from geothermal and volcanic sources in Europe, *J. Volcanol. Geotherm. Res.*, 165, 76 – 86.

Etiope G., Lassey K.R., Klusman,R.W. and Boschi E. 2008. Reappraisal of the fossil methane budget and related emission from geologic sources, *Geophys. Res. Lett.*, 35, L09307.

Fiebig J., Woodland A.B., D'Alessandro W. and Püttmann W. 2009. Excess methane in hydrothermal emissions is abiogenic, *Geology*, 37/6, 495–498.

Giggenbach W.F. and Goguel R.L. 1989. Collection and Analysis of Geothermal and Volcanic Water and Gas Discharges. *Report of the Dep. of Sci. and Ind. Res., Chem. Div.*, Petone, New Zealand, 81 pp.

Hanson R.S., Hanson T.E. 1996. Methanotrophic bacteria, *Microbiol. Rev.*, 60, 439– 471.

Intergovernmental Panel on Climate Change 2001. Climate change 2001, In: Houghton, J.T., Ding Y., Griggs D.J., Noguer M., van der Linden P.J., Dai X., Maskell K. and Johnson C.A., (Eds.), *The Scientific Basis*. Cambridge University press, UK.

Keller J. 1982. Mediterranean island arcs, In: Thorpe, R.S. (ed.) *Andesites*. Wiley, New York, pp 307–325.

Koschorreck M. and Conrad R. 1993. Oxidation of atmospheric methane in soil: Measurements in the field, in soil cores, and in soil samples, *Glob. Biogeochem. Cycles*, 7, 109– 121.

Livingston G.P. and Hutchinson G.L. 1995. Enclosure-based measurement of trace gas exchange: applications and sources of error, in: *Biogenic Trace Gases: Measuring Emissions from Soil and Water*. Methods in Ecology (Matson, P.A. and Harriss, R.C. eds.), pp. 14–51. Blackwell Science Cambridge University Press, London.

Marini L. and Fiebig J. 2005. Fluid geochemistry of the magmatic-hydrothermal system of Nisyros (Greece), *Mém. Géol*., 44, 192.

Marini L., Principe C., Chiodini G., Cioni R., Frytikas M. and Marinelli G. 1993. Hydrothermal eruptions of Nisyros (Dodecanese, Greece). Past events and present hazard, *J. Volcanol,Geotherm*. Res., 56, 71–95.

Papadopoulos, G.A., Sachpazi M., Panopoulou G. and Stavrakakis G. 1998. The volcanoseismic crisis of the 1996–97 in Nisyros, SE Aegean Sea, Greece, *Terra Nova*, 10, 151–154.

Pol A., Heijmans K., Harhangi H.R., Tedesco D., Jetten M.S.M. and Op den Camp H.J.M. 2007. Methanotrophy below pH 1 by a new Verrucomicrobia species, *Nature*, 450, 874-878.

Vougioukalakis G.E. and Fytikas M. 2005. Volcanic hazards in the Aegean area, relative risk evaluation, monitoring and present state of the active volcanic centers. In: Fytikas M., Vougioukalakis G.E. (Eds.), *The South Aegean Active Volcanic Arc*. Developments in Volcanology, vol. 7, 161–183.