Diffuse and focused carbon dioxide and methane emissions from the Sousaki geothermal system, Greece

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[1] We report first data on chemical composition of the gas emitted by the geothermal system of Sousaki, Greece. Gas manifestations display typical geothermal gas composition with CO_2 as the main component and CH_4 and H_2S as minor species. Soil gas composition derives from the mixing of two end-members (atmospheric air and geothermal gas). Soil CO_2 fluxes range from <2 to 33,400 g m^{-2} d^{-1}. The estimated diffuse output of hydrothermal CO_2, estimated for an area of 0.015 km^2, is about 630 g s^{-1}, while a tentative estimation of CH_4 diffuse output gave a value of about 1.15 g s^{-1}. Point sources accounted for lower flux values of ~26 g s^{-1} of CO_2, ~0.1 g s^{-1} of CH_4 and ~0.02 g s^{-1} of H_2S. **Citation:** D'Alessandro, W., L. Brusca, K. Kyriakopoulos, S. Rotolo, G. Michas, M. Minio, and G. Papadakis (2006), Diffuse and focused carbon dioxide and methane emissions from the Sousaki geothermal system, Greece, Geophys. Res. Lett., 33, L05307, doi:10.1029/2006GL025777.

1. Introduction

[2] Mörner and Etiope [2002] have recently reported that the contribution of geothermal systems to lithospheric carbon degassing, although at present poorly constrained, is probably higher than volcanic degassing. An accurate quantification of CO_2 and CH_4 fluxes from low-enthalpy geothermal systems would therefore add important data for the accurate quantification of their contribution to the earth's carbon budget and to the global climate change. Both gas species have in fact important greenhouse effects and prediction of future climate scenarios rely heavily on a better quantification of their fluxes among all geochemical spheres.

[3] The Sousaki area (Figure 1) is located about 65 km west from Athens, near the Isthmus of Corinth and represents the NW end of the active Aegean volcanic arc. Here, sparse outcrops of dacitic rocks are the remnants of late-Pliocene to Quaternary volcanic activity (4.0–2.3 Ma [Pe-Piper and Hatzipanagiotou, 1997]), while widespread fumarolic alteration and warm (35–45°C) gas emissions are still recognizable. Drilling exploration assessed the presence of a low enthalpy geothermal field, revealing two permeable formations at shallow depth (<200 m) and one at deeper

levels (500–1100 m). All geothermal waters are of Na-Cl type and display temperatures in the range 50–80°C and salinities in the range 39–49 g/l [Fytikas et al., 1995]. The whole region comprised between Corinth and the Gulf of Saronikòs is geodynamically very active with frequent earthquakes, and even the geothermal degassing at Sousaki is likely controlled by active tectonic structures [Stiros, 1995].

[4] The aim of the present work is to present the first geochemical characterization of the main gas manifestation and of the soil gases of the geothermal field and also to estimate the total CO_2 and CH_4 output, considering both diffuse and focused degassing.

2. Study Area and Methods

[5] In the area showing the highest hydrothermal alteration, located along a narrow valley, several small caves were dug in the past century to extract hydrothermal alteration minerals (alunite, magnesite, sulfur). Some of these caves display at present hydrothermal gas emission from their floors. The gases, being denser than atmospheric air, flow on the floors of the caves and eventually spill out from the mouth of the caves dispersing in the atmosphere after descending the flanks of the valley. The gas flux seems to be almost constant with time creating a clear separation in the cave's atmosphere with an anoxic part on the floor, evidenced on the walls of the caves by a clear-cut line separating the lower fumarolic alteration products, mainly composed of native sulfur and sulfides, from the upper more oxidizing portion composed mainly of sulfates [Kyriakopoulos et al., 1990].

[6] Samples for gas analysis were taken from three caves, from an old exploration well and from 13 soil-sampling sites. Analyses were made in the laboratory with routine gas-chromatographic techniques, except for H_2S that was determined in the field with Dräger tubes. Results are shown in Table 1.

[7] The very strong gaseous flux in two of the caves (named ''small'' and ''big'') has been estimated in November 2005 in the following way. A tube was buried in the threshold of the caves and the speed of the gas escaping through the tube was measured with a hot-wire anemometer. The natural threshold of the caves was elevated and absence of gas spills was checked with a LFG 20 portable gas-analyzer (CO_2 and CH_4 with IR spectrometer and O_2 with chemical cell) and all measurements were made during stable weather conditions, in absence of wind. Total gas flux was obtained by multiplying the measured gas speed by the area of the cross-section of the tube.

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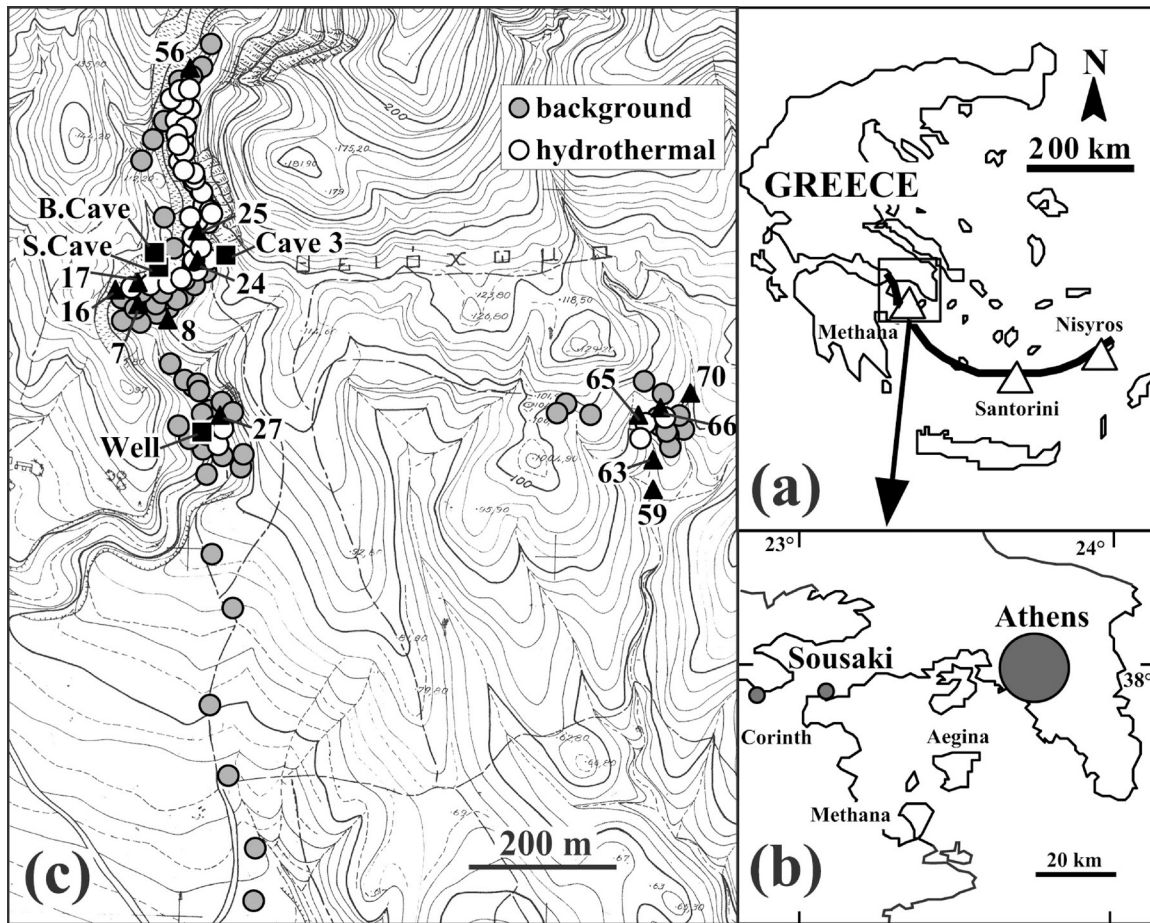
Figure 1. (a) Location of the Sousaki geothermal system with respect to the south Aegean volcanic arc (volcanoes with historical activity are evidenced with a triangle); (b) Area of the Isthmus of Corinth; (c) Study area with flux measurements points (subdivided in two sub-populations) and gas sampling points (squares = gas manifestations; triangles = soil gases; numbers as in Table 1).

[8] Many soil gases were also analyzed in the field for CO_2 and CH_4 with IR spectrometry during two field surveys (85 sampling points in October 2004 and 92 in November 2005). Soil gases were sampled with a syringe at a depth of 50 cm through a Teflon tube of 5 mm ID. Gases were injected in the IR cell through a three-way valve. Carbon dioxide concentrations were determined with an LFG 20 (ADC Co Ltd) instrument with a 0–100% by volume range. Samples with concentrations below 0.5% were checked with a GasCard II (Edimburg Instruments) with 0–0.5% range. Methane concentrations were determined with a GasCard II (0–5% range). Comparison with the results of gas-chromatographic analyses reveals a good agreement with differences never exceeding 10% for both gases.

[9] A total number of 101 diffuse CO_2 flux measurements were made on the 6th and 7th of November 2005. Most of the measurements were carried out in the geothermal altered area and in those areas that showed anomalous soil CO_2 values in the October 2004 survey. Sampling sites were spaced at around 20 m from each other, generally following the low-lying areas. Some large-spaced measurements were made far away from known manifestations to get a better insight on background values. Flux measurements were made with a portable CO_2 soil flux meter

(WEST Systems, Italy) based on the accumulation chamber method [*Chiodini et al.*, 1998]. Flux values (g m^{-2} d^{-1}) were determined at each site from the rate of CO_2 concentration increase in the chamber (area 0.031 m^2, volume 0.003 m^3) accounting for atmospheric pressure and temperature values to convert volumetric to mass concentrations. Using IR spectrometers with different sensitivity, the reproducibility was better than 10% in the range 10–20,000 g m^{-2} d^{-1}. Particular care was taken to fulfill the recommendations for measurements in volcanic-hydrothermal environments reported by *Lewicki et al.* [2005].

3. Results

3.1. Chemical Composition of the Gases

[10] Gases from the caves and from the well have a typical geothermal composition with CO_2 as the main component (>950 mmol/mol) and CH_4 and H_2S as minor components. The gases collected in the caves and at the wellhead display small but significant differences, the former being depleted in water-soluble gases (CO_2, H_2S). The gas collected at the wellhead is probably closer to the gas composition of the geothermal system, while the gases

Table 1. Chemical Composition of Gas Samples[a]

Sample	Date, dd-mm-yy	T, °C	He	O_2	N_2	CH_4	CO_2	H_2S
Small cave	11-12-03	n.m.	0.032	2.2	30.2	8.10	963	1.5
Small cave	02-10-04	42.0	0.031	2.6	32.6	10.30	959	0.9
Big cave	11-12-03	n.m.	0.034	<0.1	21.0	8.34	970	1.2
Big cave	02-10-04	44.0	0.037	<0.4	2.2	10.90	963	1.2
Big cave	05-11-05	37.0	0.022	16.1	92.9	8.88	865	1.2
Cave 3	07-11-05	n.m.	0.026	4.4	59.7	6.25	926	<0.01
Expl. well	02-10-04	n.m.	0.0011	<0.4	1.3	.034	981	5.0
Expl. well	08-02-05	n.m.	0.0017	1.5	18.8	0.047	974	5.5
Expl. well	10-06-05	n.m.	0.0012	0.4	2.6	0.059	982	n.m.
Expl. well	05-11-05	31.0	0.0009	2.1	11.5	0.040	972	5.5
Soil gas 7	01-10-04	n.m.	0.005	189	769	0.019	45.1	n.m.
Soil gas 8	02-10-04	n.m.	0.005	203	791	0.004	6.4	n.m.
Soil gas 16	02-10-04	n.m.	0.005	146	627	0.003	231	n.m.
Soil gas 17	02-10-04	n.m.	0.005	171	652	0.008	185	n.m.
Soil gas 24	02-10-04	n.m.	0.042	3.4	37.6	9.62	956	n.m.
Soil gas 25	02-10-04	n.m.	0.041	2.5	32.6	10.70	962	n.m.
Soil gas 27	02-10-04	n.m.	0.005	1.6	8.6	0.004	978	n.m.
Soil gas 56	02-10-04	n.m.	0.005	194	787	0.011	15.2	n.m.
Soil gas 59	02-10-04	n.m.	0.013	190	790	0.008	15.4	n.m.
Soil gas 63	03-10-04	n.m.	0.005	158	650	0.007	198	n.m.
Soil gas 65	03-10-04	n.m.	0.009	110	455	<0.001	436	2.0
Soil gas 66	03-10-04	n.m.	0.013	82.8	347	0.007	582	n.m.
Soil gas 70	03-10-04	n.m.	0.040	3.5	51.5	10.00	938	n.m.

[a]All concentrations in mmol/mol.

of the caves, loosing more soluble gaseous species during the interaction with shallow aquifers (Figure 2, arrow A), are enriched in less soluble gases (He, CH_4). The interaction can be confirmed by boron, an element highly enriched in geothermal fluids, which displays high contents in the shallow groundwaters of the area in the down-flow direction [*Kelepertsis et al.*, 2001].

[11] Soil gases collected in both surveys display CO_2 concentrations from 0.5 to 995 mmol/mol and CH_4, which displays values from 0 to 15 mmol/mol, was generally not detected when CO_2 concentration was lower than 950 mmol/mol. Soil gas composition reflects the mixing process between atmospheric air and a geothermal gas similar to that issuing from the caves (Figure 2, arrow B).

3.2. Focused Gas Flux

[12] Total gas flux from the two caves was estimated in $\sim$0.014 m^3 s^{-1}, with the small one accounting for about a quarter. Measurements were repeated after 1 day yielding the same values. In November 2004 a previous rough
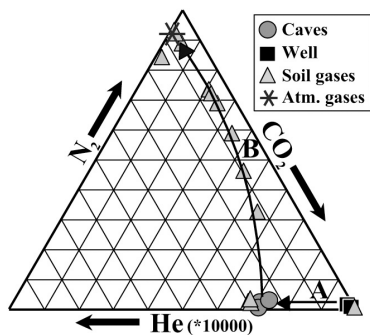
flux estimation from the small cave gave a similar result (0.004 m^3 s^{-1}) pointing to a relative stability of the cave's flux. The flux of the single species, obtained cross-correlating the total gas flux with the chemical composition, were $\sim$26 g s^{-1} of CO_2, $\sim$0.1 g s^{-1} of CH_4 and $\sim$0.02 g s^{-1} of H_2S.

3.3. Diffuse Gas Flux

[13] Measured CO_2 flux values range from lower detection limit ($\sim$1) up to 33,500 g m^{-2} d^{-1}. The probability plot (Figure 3) evidences two lognormal distributed populations. The first population, which can be defined as background, comprises about 60% of the measurements and displays a geometric mean of 29.5 g m^{-2} d^{-1}, while the second (hydrothermal contribution) has a geometric mean of 3630 g m^{-2} d^{-1}. Almost all points of the second population are distributed close to the two caves with high gas flux and in the narrow valley north of them that displays the most evident hydrothermal alteration (Figure 1). Only few anomalous points were found close to the sampled well and in a smaller area about 500 m to the east. Soil fluxes display a good positive correlation with CO_2 concentrations up to about 500 g m^{-2} d^{-1} when saturation of geothermal gas in soils at 50 cm depth is attained (Figure 4).

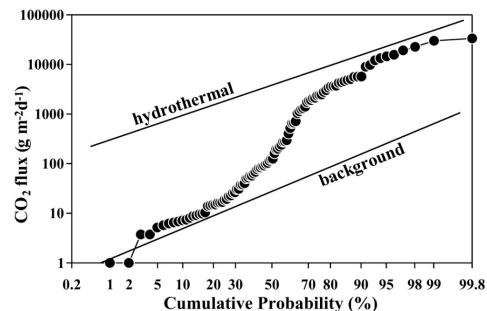**Figure 2.** He-N_2-CO_2 triangular diagram of gas samples collected at Sousaki. Arrow A indicates soluble gas depletion due to interaction with shallow groundwaters. Arrow B indicates mixing between hydrothermal and atmospheric gases.

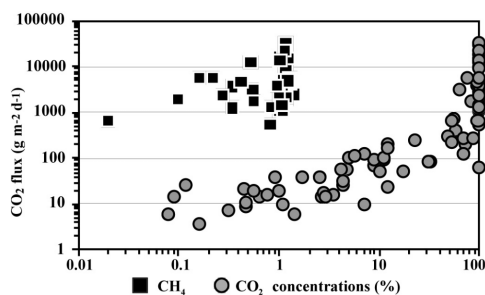**Figure 3.** Probability plot of CO_2 flux values.

Figure 4. Binary diagram of CO_2 flux values vs. CO_2 and CH_4 concentrations at 50 cm depth.

[14] Multiplying the area that encloses the measurement points belonging to the second population (0.015 km^2) by its mean flux we obtain a total hydrothermal CO_2 flux of $\sim$630 g s^{-1}. Although the sites of the background population that displays the highest values probably receive some contribution from the hydrothermal system, their output, estimated in $\sim$14 g s^{-1} over an area of about 0.04 km^2 and attributed to biological activity in the soil, has not been considered in the total hydrothermal output calculation.

4. Discussion

[15] As often observed in many other volcanic/geothermal systems [*Pecoraino et al.*, 2005], diffuse CO_2 flux is much greater than that released from point sources in the same area. This finding confirms the importance of measuring the diffuse gas emissions. The volcanic system of Sousaki, despite being extinct, displays a total CO_2 output of the same order of magnitude of two active volcanic systems of Aegean volcanic arc, such as Nisyros (total CO_2 output of 970 g s^{-1} [*Cardellini et al.*, 2003]) and Nea Kameni (total CO_2 output 170 g s^{-1} [*Chiodini et al.*, 1998]).

[16] Soil CH_4 fluxes reported in literature are generally slightly negative (in the order of -0.0005 to -0.002 g m^{-2} d^{-1}) due to atmospheric CH_4 consumption in the soil by methanotrophic bacteria, but in areas of volcanic/hydrothermal activity or of hydrocarbon accumulation it becomes positive, contributing to the CH_4 budget of the atmosphere [*Mörner and Etiope*, 2002]. *Castaldi and Tedesco* [2005] for example found a good correlation between CH_4 and CO_2 fluxes at the Solfatara di Pozzuoli, Italy. The instruments used at Sousaki did not allow us to measure diffuse degassing of CH_4, but considering that CH_4 was detected in soil gases only in sites whose CO_2 flux values belong to the anomalous

(hydrothermal) population (Figure 4), we made a very rough estimation of its flux values multiplying CO_2 fluxes by the CH_4/CO_2 mass ratio measured at the same site. The obtained values range from 0.02 to 145 g m^{-2} d^{-1} with a geometric mean of 6.6 g m^{-2} d^{-1}. Such values are unusually high for volcanic/hydrothermal environments where the highest values are generally in the order of 0.2–0.5 g m^{-2} d^{-1} [*Etiope et al.*, 1999; *Castaldi and Tedesco*, 2005], although values up to 12 [*Hernandez et al.*, 1998] and 31.3 g m^{-2} d^{-1} [*Vasarhelyi et al.*, 1997] were measured at Teide volcano (Tenerife) and at Matraderecske (Hungary), respectively. On the contrary, similar or even higher (up to 7000 g m^{-2} d^{-1}) were measured in soils close to active mud volcanoes emitting almost pure CH_4 [*Etiope et al.*, 2002].

[17] At Sousaki methanotrophic consumption in the shallowest 50 cm of the soil cannot be ruled out but, especially in the highest flux zones, it has to be considered improbable because of the unfavorable physico-chemical conditions (low O_2 concentrations in soil gas and low soil pH) for methanotrophic bacteria growth [*Bender and Conrad*, 1995]. Not considering the possible overestimation, the diffusive output of CH_4 at Sousaki is about 1.15 g s^{-1} and the total output, considering the contribution of the caves, is 1.25 g s^{-1}. Such an output (Table 2), although to be confirmed with specific measurements, is in the same order of the output measured at Ustica Island, Italy (1.6 g s^{-1} [*Etiope et al.*, 1999]) and of Solfatara di Pozzuoli, Italy (1.0 g s^{-1}) but one order of magnitude lower than Teide volcano, Spain (18.5 g s^{-1}). The relatively high CH_4 output at Sousaki (high CH_4/CO_2 output ratio) could possibly be explained by the higher CH_4 concentrations in the hydrothermal gas with respect to other volcanic/geothermal systems (Table 2).

5. Conclusions

[18] A soil gas survey of about 100 points allowed us to delimit a small area (0.015 km^2) of intense diffuse degassing at the Sousaki geothermal system. The diffusive output of CO_2 and CH_4 have been estimated in about 630 and 1.15 g s^{-1} respectively. Estimation of CH_4 output should be considered a first evaluation and has to be confirmed by further studies but provide evidence of importance of volcanic/hydrothermal systems in the total budget of natural CH_4 sources. Point sources in the same area, although contributing for less than 1/10 to the total output for both gases (26 and 0.1 g s^{-1}), represent an important source of gases dangerous to human health. Hazardous accumulation

Table 2. Methane Output From Volcanic/Hydrothermal System[a]

	CH_4 Output, g s^{-1}	CO_2 Output, g s^{-1}	Output Ratio, CH_4/CO_2	CH_4 Conc., mmol/mol	Conc. Ratio, CH_4/CO_2
Sousaki[b]	1.2	630	0.0018	15.0	0.0110
Solfatara[c]	1.0	17,600	0.0001	0.15	0.00015
Ustica[d]	1.6	8350	0.0002	0.005	0.00010
Teide[e]	18.5	4400	0.0042	8.5	0.0091

[a]CH_4 concentration and concentration ratio refer to samples less affected by atmospheric contamination.
[b]This work.
[c]*Castaldi and Tedesco* [2005] and *Cardellini et al.* [2003].
[d]*Etiope et al.* [1999].
[e]*Hernandez et al.* [1998].

of both asphyxiating (CO_2) and toxic (H_2S) gases has been observed at the main point sources.

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