Estimation of CO_2 release from thermal springs to the atmosphere

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Introduction

Geodynamically active regions have long been recognized as areas of anomalous Earth degassing [Irwin and Barnes, 1980]. Areas found at plate boundaries are characterized by seismic, volcanic and geothermal activity as well as ore deposition. These processes are enhanced by the circulation of hydrothermal fluids in the crust, which transport volatiles from the deep crust or mantle to the surface [King, 1986]. Kerrick and Caldera, [1998], were the first to indicate the significant contribution of the CO_2 degassing by extensional tectonic and hydrothermal activity in metamorphic belts during the Phanerozoic. Moreover, further studies concerning gas emissions from diffuse degassing tectonic structures on various geological regimes suggested in their majority elevated CO_2 concentrations [Klusman, 1993]. In fact, it is worth noting that the estimated global hydrothermal CO_2 flux from subaerial geothermal environments can be comparable to that of direct volcanic discharges [Kerrick et al., 1995; Seward and Kerrick, 1996].

Study Area

The back-arc geothermal fields of Greece include, among others, the Tertiary sedimentary basins of both Sperchios Basin and north Euboea, which are located in central Greece. Their tectonic activity contributes in crust thinning [Papadakis at al., 2016 and references therein] and elevated heat flow values [Fytikas and Kolios, 1979]. These geothermal anomalies due to the tectonic activity and the geological and volcanic regime are expressed as hot springs (Ypatis, Psoroneria, Thermopyles and Kamena Vourla in Sperchios Basin and Edipsos and Ilion in north Euboea). Tectonics of central Greece seems to be of particular interest as major fault structures are found in the area. Sperchios Basin was formed through the activity of WNW-ESE trending faults [Georgalas and Papakis, 1966; Marinos et al., 1973], whilst the Sperchios tectonic graben itself is considered to be the extension of the North Anatolia strike-slip fault. Moreover, in the north Euboean Gulf, the major fault structures are those of the Atalanti Fault Zone (AFZ) that consist of several segments of normal faults, trending about NW-SE [Pavlides et al., 2004].

Materials and Methods

Six groups of springs (Ypatis, Psoroneria, Thermopyles, Kamena Vourla, Edipsos and Ilion) were investigated in this study. Bubbling gases were sampled using an inverted funnel positioned above the bubbles and stored in glass flasks equipped with two stopcocks until analysis. Samples for dissolved gas analyses were collected in glass vials and were sealed underwater. In the laboratory, the concentrations of He, H_2, H_2S, O_2, N_2, CO_2 and CH_4, on the samples were analysed by an Agilent 7890B gas chromatograph with Ar as carrier.
The total CO_2 emitted through bubbling was measured at 6 different pools (Psoroneria, Psoroneria 2,

Thermopyles, Leonidas, Kamena Vourla and Ilion), whereas at other springs (Koniavitis-Sperchios Basin, Edipsos-Damaria and Edipsos-Thermopotamos) an estimation of the release was made by visual inspection. The CO_2 fluxes were measured using the floating chamber method [Mazot and Bernard, 2015] that was equipped with a portable fluxmeter (WEST Systems, Italy) based on the accumulation chamber method as suggested by Chiodini et al., [1998]. The flux data were processed with both the Graphical Statistical Approach (GSA) and the Stochastic Simulation Approach (SSA), with the latter being based on the algorithm of sequential Gaussian simulation [Deutsch and Journal 1998; Cardellini et al., 2003]. Zonal Statistics on the final CO_2 flux maps was obtained using the ArcMap 10.3 (ESRI) Spatial Analyst tool and were used to estimate the total CO_2 output to the atmosphere.

Results and Conclusions

Carbon dioxide is the prevailing gas species for the great majority of the under investigation sites, with only gases collected in the area of Kamena Vourla (Kamena Vourla and Koniavitis) being rich in N_2. The total bubbling CO_2 emission from the pools to the atmosphere ranged from 314 to 44,800 g/m^2/day. At sites with greater surfaces, the CO_2 release was estimated after performing direct measurements (28-Thermopyles, 74-Psoroneria) with the most elevated values being found in the areas of Thermopyles and Psoroneria (1 and 2 t/d, respectively) (Tab. 1); the maps were drawn following the SSA (Figure 1).

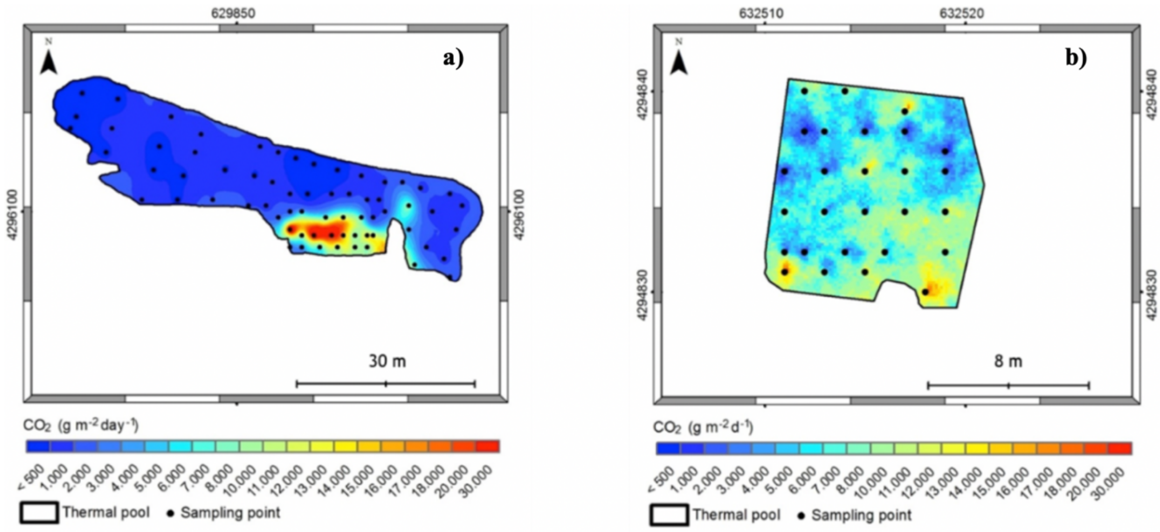

Figure 1 Maps of CO_2 output from Psoroneria (a) and Thermopyles (b) bubbling pools. Red areas represent the elevated free degassing.

The outgoing channels of the springs showed an elevated flow (> 250 l/s) of gas-charged water (> 15 mmol/l of dissolved CO_2). Even though no bubbling was visible along the stream, the dissolved CO_2 content sampled at different distances from springs of Psoroneria and Thermopyles, decreased up to an order of magnitude after few hundreds of metres, indicating an evident and intense, although not visible, CO_2 degassing versus the atmosphere. Physico-chemical parameters (temperature and pH) along the outlet channels were also measured at the same sampling points showing correlations (negative in terms of temperature; T decreased from 33.1 to 30.3 and 40.8 to 39 °C, respectively and positive in terms of pH; pH increased from 6.11 to 7.05 and 6.05 to 7.70, respectively) with the distance. The CO_2 output of the outgoing channels to the atmosphere was quantified considering the difference between the initial and the final content of the dissolved CO_2 as well as the water flow, obtaining values of > 10 t/d for Thermopyles and ~9 t/d for Psoroneria. Estimations were also made at Ypatis, Kamena Vourla, Koniavitis and Edipsos, where the mean values reached 1 t/d of CO_2 for each spring.

Spring *Methods*	**Degassing pool** *Accumulation chamber* t/d	**Outflow channel** *Dissolved gases* t/d	**Total** t/d
Ypatis	0.2	0.54	0.74
Psoroneria	**2.3**	**9.23**	11.53
Thermopyles	**0.67**	**12.5**	13.17
Leonidas	**0.12**		0.12
Koniavitis	0.2	1.5	1.7
Kamena Vourla	**0.02**	0.1	0.12
Ediposos	0.15	**0.69**	0.84
Ilion	**0.07**	**0.08**	0.15
Total	3.73	24.64	28.37

Table 1 CO_2 output of bubbling pools, outgoing channels and the total amount released. Measured values are found in bold. The remaining part was estimated.

The obtained CO_2 released from the bubbling pools to the atmosphere was directly compared with the one estimated from the outgoing channels (Tab. 1).

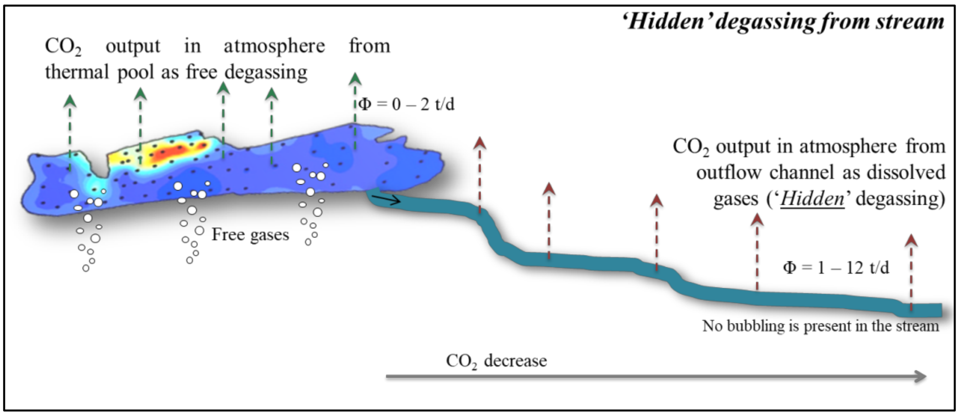

Figure 2 Concept model of total CO_2 output from spring to the atmosphere - stream system.

The degassing along the outflow channel was almost always higher than the corresponding bubbling pool, sometimes even an order of magnitude, suggesting that most of the degassing is "hidden". For each site the amount of CO_2 released versus the atmosphere was calculated as (Figure 2):

$$\Phi_{totCO_2} = \Phi_{pool} + \Phi_{stream} \qquad (1)$$

The total CO_2 released to the atmosphere as estimated for the study area is at ~ 30 t/d, with the major contribution deriving from the degassing along the outflow channels of the thermal springs. Such output is comparable and sometimes higher than that of each single active volcanic system along the South Aegean Volcanic Arc (15 - 38 t/d) and highlights the importance of "hidden" degassing along CO_2 - oversaturated streams.

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