

## **The impact of methanotrophic activity on methane emissions through the soils of geothermal areas**

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Methane plays an important role in the Earth's atmospheric chemistry and radiative balance being the most important greenhouse gas after carbon dioxide. It has recently been established that geogenic gases contribute significantly to the natural CH<sub>4</sub> 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<sub>4</sub> (Cardellini et al., 2003; Castaldi and Tedesco, 2005; D'Alessandro et al., 2009; 2011; 2013). Due to the fact that methane soil flux measurements are laboratory intensive, very few data have been collected until now in these areas. Preliminary studies (Etiope et al., 2007) estimated a total CH<sub>4</sub> emission from European geothermal and volcanic systems in the range 4-16 kt a<sup>-1</sup>. This estimate was obtained indirectly from CO<sub>2</sub> or H<sub>2</sub>O output data and from CO<sub>2</sub>/CH<sub>4</sub> or H<sub>2</sub>O/CH<sub>4</sub> 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.

At the global scale, microbial oxidation in soils contributes for about 3-9% to the total removal of methane from the atmosphere. But the importance of methanotrophic organisms is even larger because they oxidise the greatest part of the methane produced in the soil and in the subsoil before its emission to the atmosphere. Environmental conditions in the soils of volcanic/geothermal areas (i.e. low oxygen content, high temperature and proton activity, etc.) have been considered inadequate for methanotrophic microorganisms. But recently, it has been demonstrated that methanotrophic consumption in soils occurs also under such harsh conditions due to the presence of acidophilic and thermophilic Verrucomicrobia. These organisms were found in Italy at the Solfatara di Pozzuoli (Pol et al., 2007), in New Zealand at Hell's Gate (Dunfield et al., 2007) and in Kamchatka, Russia (Islam et al., 2008).

Both the Italian and the Hellenic territories are geodynamically very active with many active volcanic and geothermal areas. Here we report on methane flux measurements made at Pantelleria (Italy) and at Sousaki and Nisyros (Greece). The total methane output of these three systems is about 10, 19 and 1 t a<sup>-1</sup>, respectively (D'Alessandro et al., 2009; 2011; 2013). The total emissions obtained from methane flux measurements are up to one order of magnitude lower than those obtained through indirect estimations. Clues of methanotrophic activity within the soils of these areas can be found in the CH<sub>4</sub>/CO<sub>2</sub> ratio of the flux measurements which is always lower than that of the respective fumarolic manifestations, indicating a loss of CH<sub>4</sub> during the travel of the gases towards earth's surface.

Furthermore laboratory methane consumption experiments made on soils collected at Pantelleria and Sousaki revealed, for most samples, CH<sub>4</sub> consumption rates up to 9.50 µg h<sup>-1</sup> and 0.52 µg h<sup>-1</sup> respectively for each gram of soil (dry weight). Only few soil samples displayed no methane

consumption activity.

Finally, microbiological and molecular investigations allowed us to identify the presence of methanotrophic bacteria belonging to the Verrucomicrobia and to the Alpha- and Gamma-Proteobacteria in the soils of the geothermal area of Favara Grande at Pantelleria. While the presence of the former was not unexpected due to the fact that they include acidophilic and thermophilic organisms that were previously found in other geothermal environments, the latter are generally considered not adapted to live in harsh geothermal environments. Their presence in the soils of Pantelleria could be explained by the fact that these soils do not have extremely low pH values (>5). Indeed thermotolerant methanotrophic Gamma-proteobacteria, have been previously found in the sediments of thermal springs in Kamchatka (Kizilova et al., 2012). Such species could find their niches in the shallowest part of the soils of Favara Grande where the temperatures are not so high and they thrive on the abundant uprising hydrothermal methane.

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