



## **Diffuse soil emission of hydrothermal gases (CO<sub>2</sub>, CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>) at the Solfatara crater (Phlegraean Fields, southern Italy).**

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The Phlegraean Fields caldera, located in the Plio-Pleistocene tectonic depression of the Campanian Plain (southern Italy) and formed after the Neapolitan Yellow Tuff eruption (12-15 ka), is characterized by numerous (monogenetic) volcanic centers that testify a recurrent unrest. At least 61 eruptions after the Neapolitan Yellow Tuff emplacement occurred. The recent history of the Phlegran Fields is marked by ground surface movements due to volcano-tectonics and cycles of bradyseisms: vertical ground movements up to 12 m were evidenced at the Serapis Temple during the last 2200 years. More recently, ground movements, centered inside the Phlegraean Fields caldera, in 1969-1972 (+1.7 m), 1972-1975 (-0.2 m) and 1982-1984 (+1.8 m), occurred. The bradyseismic activity is likely triggered by periodic gas injection (mainly CO<sub>2</sub>) at the bottom of the hydrothermal system that feeds the fumarolic field of Solfatara.

The present study reports the results of CO<sub>2</sub>, CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> soil flux surveys, as well as chemical analyses of mono-aromatic compounds in fumaroles and air, carried out at the Solfatara crater in April 2012. The main aim is to investigate the distribution and behavior of these gases as they migrate from their source to the soil and the atmosphere. Soil flux distribution of the three investigated gas compounds has a good spatial correlation, suggesting that diffuse degassing is mainly controlled by local fractures. The calculated total output of diffuse C<sub>6</sub>H<sub>6</sub> from Solfatara is 0.10 kg day<sup>-1</sup>, whereas those of CO<sub>2</sub> and CH<sub>4</sub> are 79 × 10<sup>3</sup> and 1.04 kg day<sup>-1</sup>, respectively. Methane is affected by oxidation processes, which appear to be more efficient for low gas fluxes, i.e. the lower the gas flux the higher the residence time of the uprising hydrothermal gases within the crater soil. Benzene oxidation is independent on gas fluxes, whereas it is strongly controlled by presence of a shallow SO<sub>4</sub><sup>2-</sup>-rich aquifer located in the central and southwestern sectors of the crater, since sulfate acts as terminal electron acceptor during the reaction of benzene to produce benzoate. Relatively high benzene-toluene ratios, indicating a dominant hydrothermal origin, were measured in air close to the main fumarolic field of Solfatara crater. In this restricted area, benzene concentrations are more than one order of magnitude higher than the limit value for ambient air (5 μg m<sup>-3</sup>). This suggests that hydrothermal fluids have a strong impact on air quality in the immediate surroundings of the fumarolic vents. Significant concentrations of endogenous mono-aromatics were also detected in air samples collected from the northern and western sides of the crater. These gas compounds are mostly fed by the crater bottom soil, confirming that diffuse degassing plays a fundamental role for the energy release from the Solfatara crater.