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Real-Time Measurements of Hg⁰ and H₂S at Solfatara Crater (Campi Flegrei, Southern Italy): an Innovative Approach to Investigate the Distribution of Gaseous Contaminants in Air

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The emission of gaseous contaminants from volcanic and geothermal systems can cause severe concerns for the natural environment and human health, especially in nearby densely populated areas. The Solfatara Crater (Campi Flegrei, Southern Italy) is a hydrothermally altered tuff-cone characterized by intense emission of endogenous fluids from low-to-medium temperature fumaroles and soil degassing. The crater is located within the town of Pozzuoli, thus these volcanic fluids are supposed to have a significant impact on local population. The present study focuses on two potential air contaminants, i.e. gaseous mercury and hydrogen sulfide, which occur in the Solfatara fluids at relatively high concentrations.

Mercury has a strong environmental impact, since it is a toxic pollutant of global impact. Volcanic degassing accounts for a significant part of the natural mercury emissions. Gaseous elemental mercury (GEM or Hg⁰), the dominant form of mercury in the atmosphere (~98%), is characterized by high volatility and residence time of 1-2 years due to its relatively low solubility and chemical inertness. Hydrogen sulfide (H₂S) quantitatively represents the third-most-prevalent gas species emitted from hydrothermal systems after H₂O and CO₂. It is a toxic acidic gas, as it is irritating and suffocating although it is detectable by humans at very low concentrations due to the distinctive unpleasant odor.

The concentrations of Hg⁰ and H₂S in the air strongly vary both in time and space, being dependent on meteorological conditions, such as wind, humidity, temperature, as well as on photochemical reactions. According to our approach, real-time measurements of these two gaseous species were carried out within the Solfatara Crater coupling, respectively, a portable Zeeman atomic absorption spectrometer with high frequency modulation of light polarization (Lumex RA-915M) and a pulsed fluorescence gas analyzer (Thermo Scientific Model 450i). The two instruments were synchronized and set to high-frequency acquisition. A multigas analyzer (manufactured by INGV-Palermo) was also used to measure in real-time the CO₂ concentrations. The measurements were carried out along a pre-determined systematic path at walking speed and they were repeated for several days, in order to evaluate the influence of meteorological conditions on the distribution in air of selected gases. The simultaneous acquisition of GPS signal provided the spatial coordinates for the gaseous concentration values. Meteorological parameters were continuously measured using a Davis Vantage Vue weather station located close to the measurement path.

Our results indicate that this approach is highly efficient, providing reliable and reproducible concentrations of Hg⁰ and H₂S that can be used to construct detailed maps showing the contaminants distribution in air. The method can be thus applied to investigate the behavior of these pollutants released from both natural and anthropogenic sources.