

## Real-time measurements of Hg<sup>0</sup> in volcanic, geothermal and anthropogenic systems: a multi-methodological approach using Lumex<sup>®</sup> instrumentation

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Mercury represents a pollutant of global concern and strong environmental impact since is highly toxic. Hg is present in air in the oxidation states of 0 and +2, the former being the dominant species with a residence time of 1-2 years due to its high volatility, relatively low solubility and chemical inertness. Both volcanic/geothermal and anthropogenic systems are crucial contributor to the release of Hg<sup>0</sup> in the atmosphere. In this work, a Lumex<sup>®</sup> (RA-915M) was used to evaluate the environmental impact in air of Hg<sup>0</sup> from: i) the abandoned Hg mining site and geothermal areas from Mt. Amiata (Siena, Central Italy) and ii) selected Mediterranean volcanic and geothermal systems.

The Lumex<sup>®</sup> instrumentation, based on atomic absorption spectrometric technique with Zeeman effect, allows to measure Hg<sup>0</sup> at high frequency, in real-time and at a wide range of concentrations (from 2 to 50,000 ng/m<sup>3</sup>). Hg<sup>0</sup> measurements were coupled with those of other pollutants, such as CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub>. Carbon dioxide was measured using a Multi-GAS instrument manufactured by INGV-Palermo, whereas H<sub>2</sub>S and SO<sub>2</sub> using Thermo Scientific<sup>®</sup> Model 450i analyzer. GPS and meteorological parameters were continuously recorded, too. The data acquisition was carried out along transects at an approximately constant speed or at selected fixed points. Wherever possible, the analytical data were then converted into a spatial interpolation providing a qualitative model for the areal dispersion of the contaminants.

The Lumex<sup>®</sup> device was also applied to measure Hg<sup>0</sup> concentrations in interstitial soil gases collected from a probe inserted into the soil at 70 cm depth, in order to produce Hg<sup>0</sup> maximum concentration maps in Hg-polluted areas (e.g. Abbadia San Salvatore Hg mining area, Mt. Amiata). Diffuse Hg<sup>0</sup> soil fluxes were measured using a chamber positioned above the soil from which, at periodic time intervals, gases were extracted and injected into the Lumex<sup>®</sup> device. This instrument was also applied to measure Hg<sup>0</sup> concentrations along vertical profiles in thermal wells at Santorini (Greece) and Vulcano (Italy) by using a Rilsan<sup>®</sup> tube lowered into the wells at pre-defined depths. With this approach, a significant stratification of the air masses in terms of Hg<sup>0</sup>, strictly dependent on water temperature, air pressure and well depth, was observed. The efficiency of Lumex<sup>®</sup> for these different approaches demonstrated the reliability of this instrument to produce Hg<sup>0</sup> data that can be used to identify gaseous Hg-emitters in natural and anthropogenic environments, especially when coupled with other physical and chemical parameters.