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Diffuse emissions of Volatile Organic Compounds (VOCs) from soil in volcanic and hydrothermal systems: evidences for the influence of microbial activity on the carbon budget

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Soils in volcanic and hydrothermal areas are affected by anomalously high concentrations of gases released from the deep reservoirs, which consists of both inorganic (mainly CO_2 and H_2S) and organic (volatile organic compounds; VOCs) species. VOCs in volcanic and hydrothermal fluids are mainly composed of saturated and unsaturated hydrocarbons (alkanes, aromatics, alkenes, and cyclics), with variable concentrations of O- and S-bearing compounds and halocarbons, depending on the physicochemical conditions at depth. VOCs in interstitial soil gases and fumarolic emissions from four volcanic and hydrothermal systems in the Mediterranean area (Solfatara Crater, Poggio dell'Olivo and Cava dei Selci, in Italy, and Nisyros Island, in Greece) evidenced clear compositional differences, suggesting that their behavior is strongly affected by secondary processes occurring at shallow depths and likely controlled by microbial activity. Long-chain saturated hydrocarbons were significantly depleted in interstitial soil gases with respect to those from fumarolic discharges, whereas enrichments in O-bearing compounds (e.g. aldehydes, ketones), $DMSO_2$ and cyclics were commonly observed. Benzene was recalcitrant to degradation processes, whereas methylated aromatics were relatively instable. The chemical and isotopic ($\delta^{13}C$ in CO_2 and CH_4) composition of soil gases collected along vertical profiles down to 50 cm depth at both Solfatara Crater and Poggio dell'Olivo (Italy) showed evidences of relevant oxidation processes in the soil, confirming that microbial activity likely plays a major role in modifying the composition of deep-derived VOCs. Despite their harsh conditions, being typically characterized by high temperatures, low pH, and high toxic gases and metal contents, the variety of habitats characterizing volcanic and hydrothermal environments offers ideal biomes to extremophilic microbes, whose metabolic activity can consume and/or produce VOCs.
In the Solfatara Crater, microbial diversity was assessed by new generation sequencing (NGS) of 16S rDNA. Microbiological analyses of samples collected from selected vertical profiles in the soil, where temperatures were up to 60 °C, revealed total prokaryotic abundances ranging from 7.23×10^6 to 439×10^6 cell/g WW. The highest abundances were recorded in sites affected by the highest and the lowest CO_2 (3,350 and 110 $gm^{-2}day^{-1}$, respectively) and CH_4 (0.059 and 0.00021 $gm^{-2}day^{-1}$, respectively) soil fluxes, and H_2S concentrations ranging from 0.05 to 1.9 mmol/mol. The composition of both archaeal and bacterial communities showed remarkable changes depending on the sampling site, the most abundant phyla being represented by Proteobacteria, Firmicutes, Actinobacteria and Euryarchaeota at the highest inputs of hydrothermal fluids, corresponding to VOCs concentrations up to 898 nmol/mol (mainly alkanes and aromatics). Conversely, Proteobacteria, Acidobacteria, Firmicutes, Chloroflexi and Thaumarchaeota dominated in those sites where low gas fluxes and VOCs contents ($\leq$300 nmol/mol; mainly alkanes and O-bearing species) were recognized. The intimate relation between microbial distribution and hydrothermal gas concentrations and gas fluxes demonstrated the critical interplay between soil gases and microorganisms, remarking the potential biodegradation efficiency at extremely high VOCs concentrations in the soil.