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1. Technical references

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2. ABSTRACT

This report describes the results achieved in task 3.2.2: - Linking volcanoes and climate change. This task aimed at fostering novel multi-disciplinary understanding of submarine volcanic CO₂ seep environments, as natural proxies for global-change related ocean acidification. Acid gas deposition from subaerial volcanic plumes was also studied as proxy for anthropogenic gas-related impact on land.

In these three years, we conducted a systematic survey across the Pozzuoli Bay. We characterized degassing activity in the Campi Flegrei caldera (CFc) offshore by measuring CO₂ partial pressure (pCO₂) in the seawater column performing 273 vertical profiles. Our large dataset (520 punctual measurements) constrains the mean and median pCO₂ well above (574 and 505 μatm , respectively ± 1 standard deviation of 502 μatm) the typical atmospheric equilibrium pCO₂ value of 420 μatm , indicating the existence of an additional CO₂ source. In this third year, the main result is the generation of a detailed map illustrating the spatial distribution of pCO₂ in seawater across Pozzuoli Bay. High concentrations are observed at 5 "hotspots": Secca delle Fumose (SdF), Baia Castle beach, Capo Miseno, Academia-Bagnoli coast and Nisida. Additionally, geochemical pCO₂ surveys were coupled with fluid collection for microbial diversity description. Divers collected the hydrothermal fluid and biofilm samples directly emitted from SdF vent at 10m depth and from colder emissions in the same hydrothermal area. Seawater column samples were also collected along N–S and E–W transects centered on the SdF vent (n = 9 water columns). Here, we combine fluid geochemistry, in situ pCO₂ measurements, 16S amplicon sequencing and shotgun metagenomics to demonstrate that SdF acts as localized biogeochemical hotspot that restructures microbial communities and promotes niche partitioning without disrupting broader ecosystem function. These findings show that while shallow vents exert strong local chemical forcing, their wider ecological footprint extends to nearby locations. By resolving how chemical and biological transitions unfold across a vent-seawater gradient, this study underscores the value of SdF as natural laboratories for studying microbial adaptation and resilience to environmental extremes.

Atmospheric deposition represents a primary pathway for the entry of chemical species—including volcanic ash, anthropogenic particulates, and polycyclic aromatic hydrocarbons—into environmental compartments. We utilized volcanic emissions from Mt. Etna as a proxy to evaluate the environmental impacts of persistent volcanic degassing. Based on a comprehensive three-year monitoring campaign (n=300 bulk deposition samples), our results demonstrate that volcanic emissions are characterized by significantly elevated loads of major ions (F⁻, SO₄²⁻, Cl⁻, Mg²⁺, NH₄⁺, and K⁺) and trace elements (Al, Fe, Ti, Tl, Te, and V) relative to regional background levels. While this volcanogenic signature is most pronounced at proximal sites, its influence remains detectable in distal urban and industrial zones, such as Catania and Priolo Gargallo, as well as the rural highlands of the Nebrodi Regional Park. To further elucidate the interaction between meteoric precipitation and volcanic particulates, Rare Earth Element (REE) concentrations were normalized to chondritic values and compared with the lithological signature of Mt. Etna's source rocks. The observed REE fractionation patterns closely mirror the trend of the volcanic substrate, exhibiting prominent positive Yttrium (Y) anomalies. Minor deviations, specifically negative Cerium (Ce) and Europium (Eu) anomalies in lower-concentration samples, suggest secondary fractionation during transport. These geochemical trends are attributed to enhanced acid-driven leaching of volcanic ash within the plume, which facilitates the mobilization of REEs into the soluble fraction and increases their total flux in bulk deposition. This research underscores the necessity of monitoring volcanic proxies to refine source apportionment models and assess environmental health risks across local and regional scales.

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4. First Section

4.1 Submarine CO₂ degassing at Campi Flegrei caldera (CFc)

This activity aimed at using shallow water hydrothermal vents for investigating the dynamics of acidification of the marine environments and their influence on the ecosystems. Hydrothermal gas seepage in the Pozzuoli bay, in the Campi Flegrei caldera offshore, was used as a proxy for a man-induced oceanic acidification.

The seawater results from the Pozzuoli Bay were obtained during nine different surveys performed from June 2023 to November 2025 using appropriate underwater CO₂ sensors: the HydroCTM CONTROS System and Solutions (Kiel, Germany) and the CO₂-Pro™ OCEANUS CV Submersible pCO₂ Sensor (Fietzek et al., 2014; Di Napoli et al., 2016). Both sensors are compact submersible systems developed for in-situ determination of the partial pressure of carbon dioxide (pCO₂) in seawater. The final map generated after the last survey confirmed a large spatial heterogeneity in pCO₂ values across the Pozzuoli Bay, suggesting that such excess CO₂ is not uniformly distributed, but rather focussed in specific areas (Fig. 4.1.1); in fact, approximately 80% of seawater measurements fall within a relatively narrow range, from approximately 376 µatm to 600 µatm. However, significantly higher concentrations are observed at a number of sites, revealing a "hotspot" distribution. These localized, high-concentration zones cluster in 5 main areas where CO₂-rich hydrothermal vents have been reported in the seafloor, these are: Secca delle Fumose (SdF), Baia Castle beach, Capo Miseno, Accademia-Bagnoli coast and Nisida. Among the five hotspots, SdF site exhibited the most extreme pCO₂ conditions. In fact, a vertical profile was conducted in the SdF area, right above the SdF vents, each consisting of pCO₂ measurements at 2, 6, and 10 m depth (Fig. 4.2.2a). This profile demonstrates a steep CO₂ vertical gradient along the water column which leads to a rapid decline in seawater pH. At 2 m, pCO₂ ranges from 500–520 µatm (pH = 8.02), suggesting only moderate enrichment relative to ambient seawater. At 6 m, concentrations increase substantially, reaching 1400–1600 µatm (pH = 6.94). The highest values are recorded at 9-10 m, where pCO₂ peaked between 6800 and 9000 µatm (pH = 5.77).

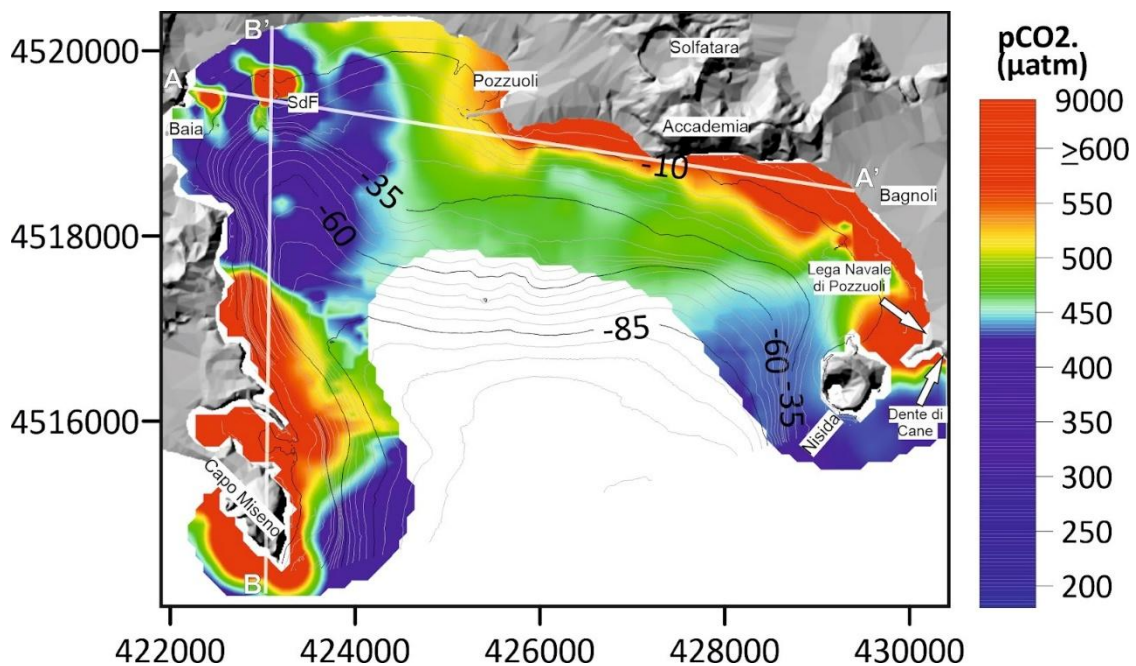


Figure 4.1.1. Distribution of pCO₂ in seawater along the Pozzuoli Bay. Major anomalies were found in SdF (up to 9000 µatm), Accademia-Bagnoli-Nisida coast (up to 4420 µatm), Baia Castle beach (up to 850 µatm) and

Capo Miseno (up to 2300 μatm). Black and gray solid lines represent bathymetry which is given in meters. Solid white lines represent the profile A-A' of Fig. 4.2.2.

Our map also allowed a preliminary quantification of the total CO_2 output sustained by the CFc offshore. To this aim, we rely upon the pCO_2 results illustrated in the cross-section of Fig. 4.2.2b that, stretching in a E-W direction across Pozzuoli Bay, is roughly perpendicular to the dominant N-S seawater current direction. We interpolate and integrate the Total Dissolved Inorganic Carbon in excess (TDIC_{excess}) results across the whole cross-sectional area of Fig. 4.2.2b, using a Sequential Gaussian Simulation (Deutsch and Journel, 1998) to obtain an integrated Excess Carbon content of $2.7 \pm 0.03 \text{ mol}\cdot\text{m}^2/\text{kg}$. Current measurements in the Pozzuoli Bay are sparse, but observations during our campaigns indicate an average current speed of $\sim 0.05 \text{ m/s}$ (given the limited information available, we consider a possible range of 0.01 to 0.1 m/s in the calculations below). From this, the total Excess Carbon flux is estimated at $136 \pm 2 \text{ mol/s}$, or $516 \pm 6 \text{ tons CO}_2/\text{day}$ (range, 103 to 1031 tons/day), from the combination of integrated Excess Carbon and current speed.

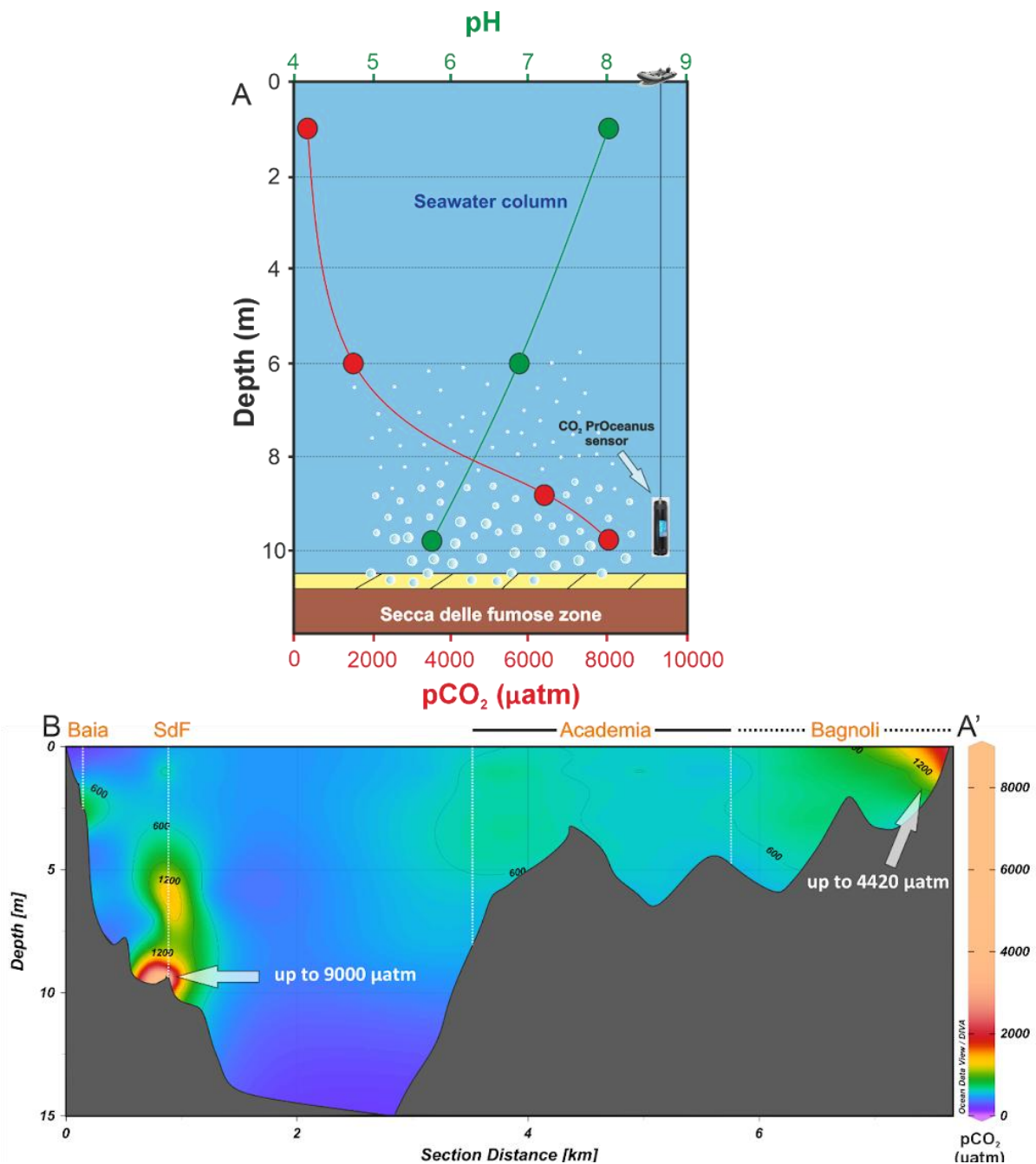


Figure 4.2.2. A) Vertical variability of pCO₂ and pH in seawater above the SdF zone. B) Profile AA' (SEE Fig.1) showing the variability of pCO₂ in the seawater column and the distribution of the main hydrothermal hotspots along the Pozzuoli Gulf.

4.2 Impact of CO₂ degassing on ecosystems

Geochemical pCO₂ surveys were coupled with fluid and seawater sampling to investigate the effects of venting on microbial diversity. Between June and July 2023, divers collected hydrothermal fluids (72 °C) and biofilm samples directly emitted from the SdF vent at 10 meters depth and from lower temperature emissions (40 °C) associated with diffuse venting in the same hydrothermal area. In October 2024, seawater column samples were collected across N-S and E-W transects centering on the SdF vent (n = 9 water columns points, for a total of 27 samples in total at different depths; Fig. 4.1.3). Seawater column samples were collected via Niskin bottles from the boat as follows: i) only at one depth if the seafloor was shallower than 6 m bsf; ii) at two depths if the seafloor was between 6 and 8 m bsf; and iii) at three different depths if the seafloor was deeper than 8 m bsf. The maximum depth reached was 15 m. In total we collected 27 samples for biological analyses: biofilm (n=5), hydrothermal fluid (n=1) and seawater (n=21). SF1D13_B1 and SF1D13_B2 are orange biofilm samples collected from SdF emission site in June and July 2023, respectively; SF2A_B1, SF2B_B1, and SF2C_B1 are white biofilm samples collected from colder seafloor areas marked by diffuse hydrothermal venting; SF1D13_F2 is the hydrothermal fluid sample collected from the emission site at SdF; TxDy samples were collected from the seawater column surrounding SdF, from distinct sites and depths (x = transect site, y = depth). Shotgun metagenomic sequencing generated a total of 6,997 million reads across all samples, on average 259 million reads per sample, of which 99% passed quality filtering and were retained for downstream analyses. Of these, on average, 802 million paired reads across all samples were taxonomically annotated.

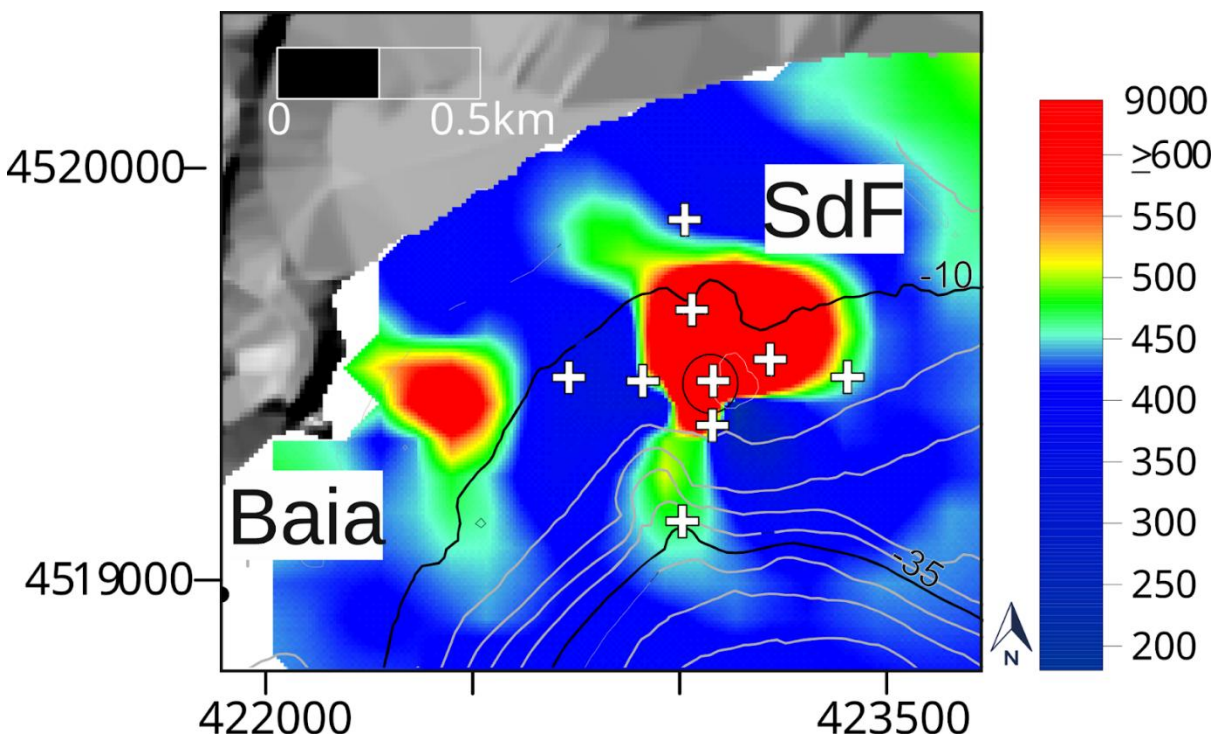


Figure 4.2.3. Close up of the SdF hydrothermal area. The crosses indicate sites where pCO₂ probing was coupled to biological samples collection to assess the effect of SdF vent (circled cross) pCO₂ anomaly on

microbial diversity. Samples from seawater column were collected along two transects, one N-S (sites T1, T2, T4, T5) and one W-E (sites T6, T7, T8, T9), both having SdF as their center (site T3).

The SdF was defined as a hot vent, acidic, low in salinity and Mg^{2+} , and enriched in CO_2 , Mn, Fe, and reduced gases, reflecting a magmatic-hydrothermal source modified by water-rock interaction and vapor-phase separation. These anomalies corresponded to sharp shifts in microbial composition (Fig. 4.1.4): for instance, the vent hosted thermophilic chemolithoautotrophs and was enriched in genes for CO_2 fixation, hydrogen and sulfur oxidation, anaerobic respiration, and arsenic detoxification. Despite large differences between the venting fluid and surrounding seawater taxonomic and functional diversity, microbial taxa and functions typical of hydrothermal fluids were present in the surrounding water column, thus suggesting a spill-over of microbial diversity and chemolithoautotrophic carbon to neighboring ecosystems. Overall, SdF acts as localized biogeochemical hotspot that restructures microbial communities and promotes niche partitioning without disrupting broader ecosystem function.

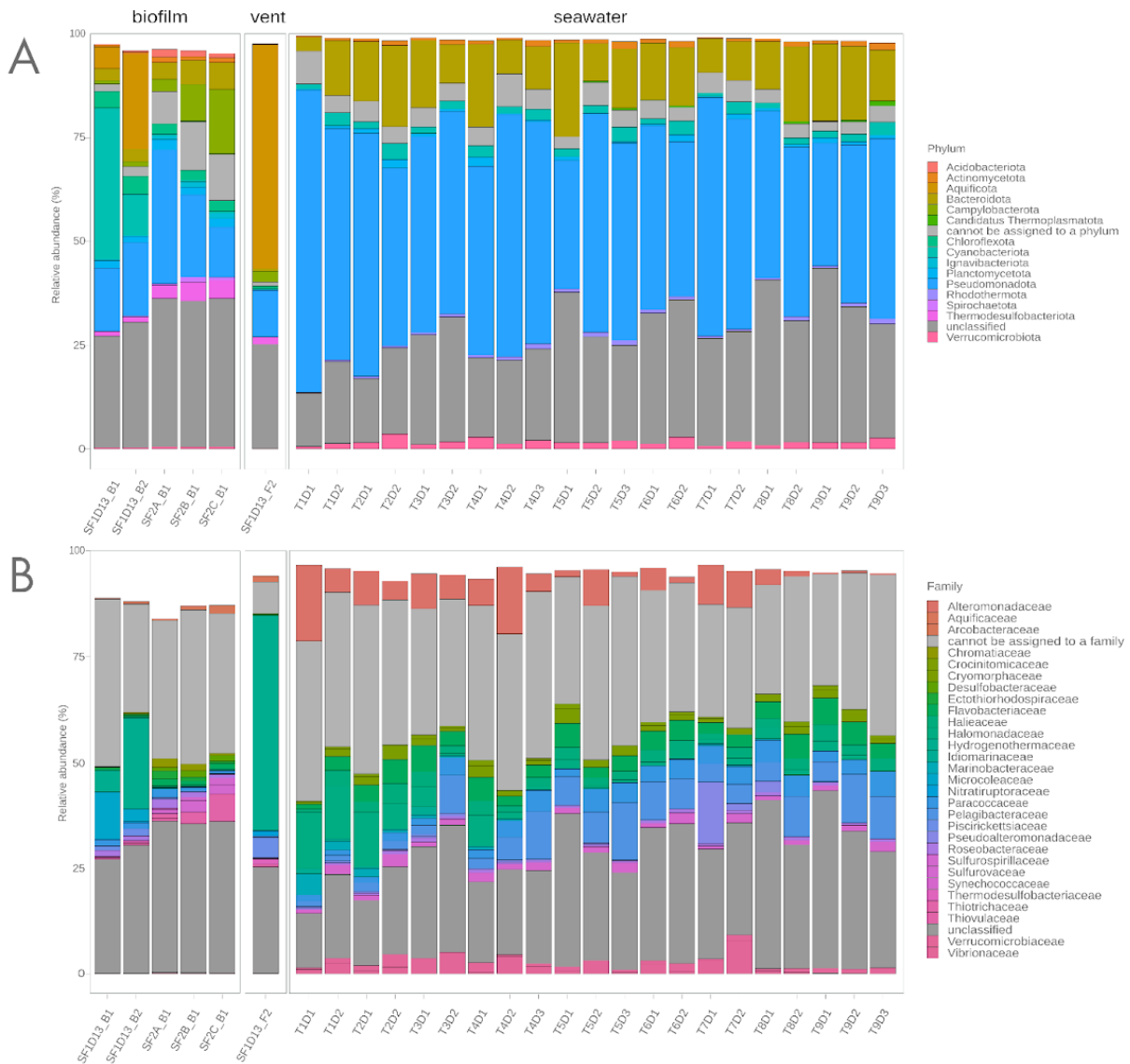


Figure 4.1.4. Microbial composition obtained from the sampling at SdF

4.3 Acid gas deposition from volcanic plumes

In recent years, Mt. Etna has been characterized by a frequent succession of paroxysmal episodes, resulting in significant tephra dispersal and widespread ash fallout. To evaluate the geochemical footprint of these events on atmospheric chemistry, this study compares daily depositional fluxes during syn-eruptive periods against quiescent intervals. Monitoring was conducted across a strategic network of proximal (volcanic), rural, urban, and industrial sites, providing a cross-sectional view of depositional dynamics at varying distances from the emission source. Volcanic plumes act as potent sources of acid-precursor gases, primarily sulfur dioxide (SO₂), hydrogen chloride (HCl), hydrogen fluoride (HF), and hydrogen bromide (HBr). These acid species drastically alter the natural acidity of meteoric water. Near Mt. Etna, precipitation frequently exhibits pH values well below the pristine threshold of 5.6, with observed ranges extending from highly acidic (pH 3.0–4.5) to circumneutral-alkaline (pH 7.7) depending on plume grounding and neutralization dynamics (Fig 4.2.1).

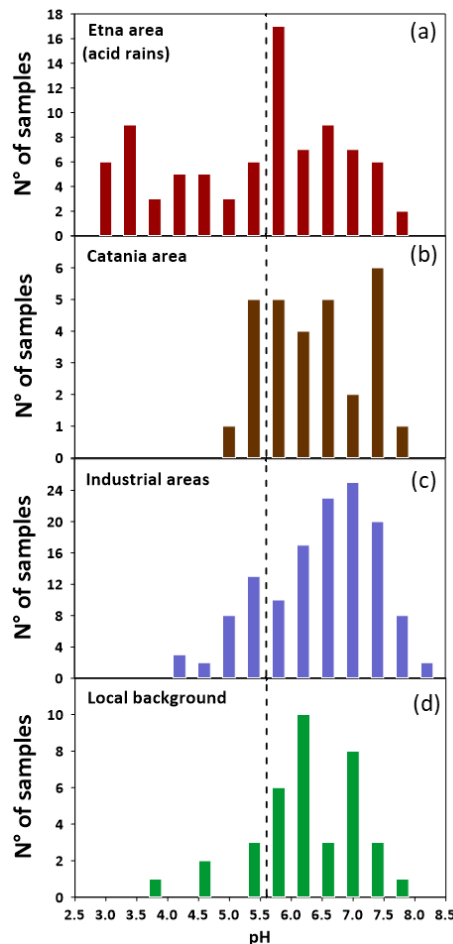


Figure 4.2.1. Rainwater acidity (pH) at Etna (a), Catania (b), Industrial areas (c) and Local background (d).

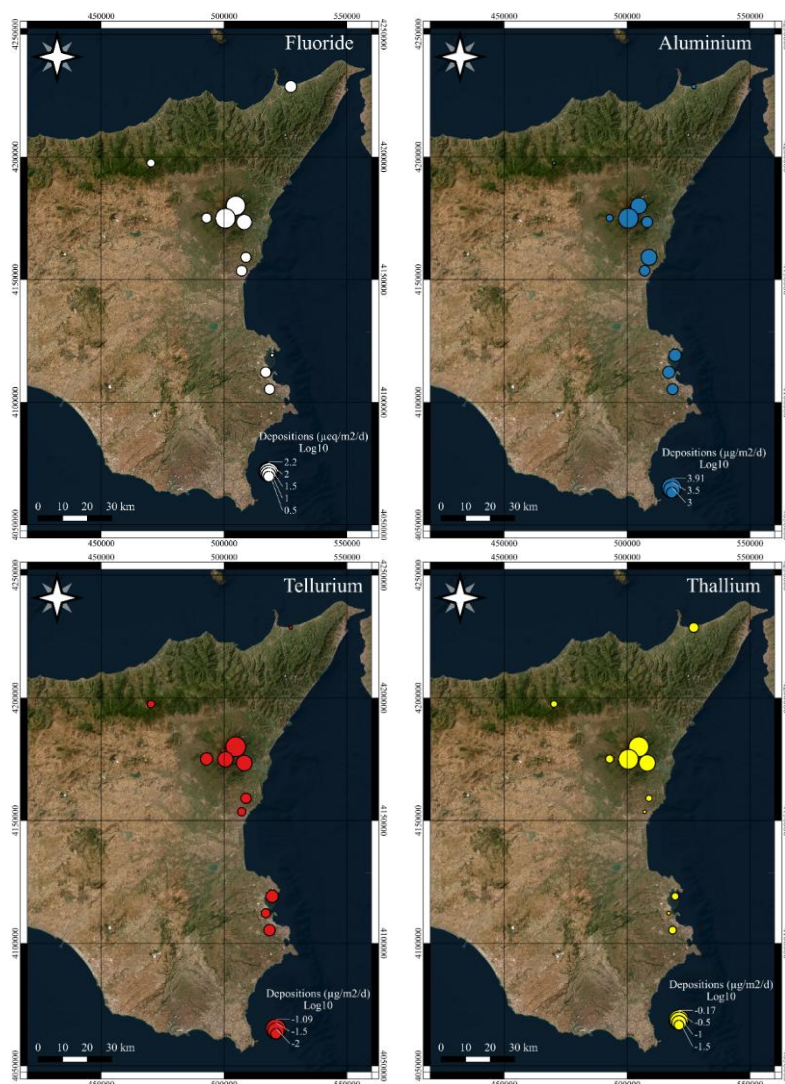


Figure 4.2.2. Fluoride ($\mu\text{eq m}^2 \text{d}^{-1}$), Aluminum ($\mu\text{g m}^2 \text{d}^{-1}$), Tellurium ($\mu\text{g m}^2 \text{d}^{-1}$), and Thallium ($\mu\text{g m}^2 \text{d}^{-1}$) atmospheric deposition fluxes on eastern Sicily.

The interaction between acidified hydrometeors and volcanic particulates facilitates the incongruent dissolution and leaching of volcanic ash. This process enriches the bulk deposition with a suite of trace metals, including aluminum (Al), iron (Fe), titanium (Ti), thallium (Tl), tellurium (Te), and vanadium (V) (Fig. 4.2.2 and 4.2.3). Spatial and temporal variability in plume dispersion dictates the depositional patterns; sites proximal to the active craters consistently exhibit the highest concentrations and fluxes of F, S, Cl, and associated lithophile elements. For instance, fluoride deposition rates at proximal sites reached $681 \mu\text{eq m}^2 \text{d}^{-1}$, while sulfate fluxes peaked at $2567 \mu\text{eq m}^2 \text{d}^{-1}$, reflecting the massive magnitude of volcanic SO_2 scavenging. The potential for atmospheric neutralization in volcanic regions is often overwhelmed by the high flux of volcanic halogens. The dominance of these acidic species effectively counteracts the buffering capacity typically provided by crustal or marine cations, such as non-sea-salt calcium (nss- Ca^{2+}) and magnesium (nss- Mg^{2+}). This persistent acidity enhances the mobility of trace elements and Rare Earth Elements (REEs), further perturbing local geochemical cycles.

Statistical analysis reveals significant intra-site variability driven by diverse emission sources and meteorological forcing. The volcanic proximal sites were dominated by primary volcanic degassing and ash leaching, showing peak values for acidic species and chalcophile elements. Industrial areas were characterized by elevated fluxes of Br, B, Ni, Mo, Cr, Sb, and Zn, resulting from a synergy of marine aerosols, petrochemical emissions, and domestic combustion. Urban areas exhibit high variability influenced by lithogenic dust and anthropogenic markers, such as Sb, which is primarily attributed to vehicle brake-wear particulates. Finally, rural sites reflect a more balanced contribution from marine and crustal-natural sources, with sporadic volcanic influence during specific wind regimes.

In conclusion, the dynamics of acid gas deposition from Mt. Etna's plumes exert a profound influence on regional environmental compartments, including soil chemistry and water quality. Understanding these depositional pathways is imperative for quantifying the ecological consequences of persistent volcanism and for developing robust mitigation strategies in volcanically active and densely populated regions.

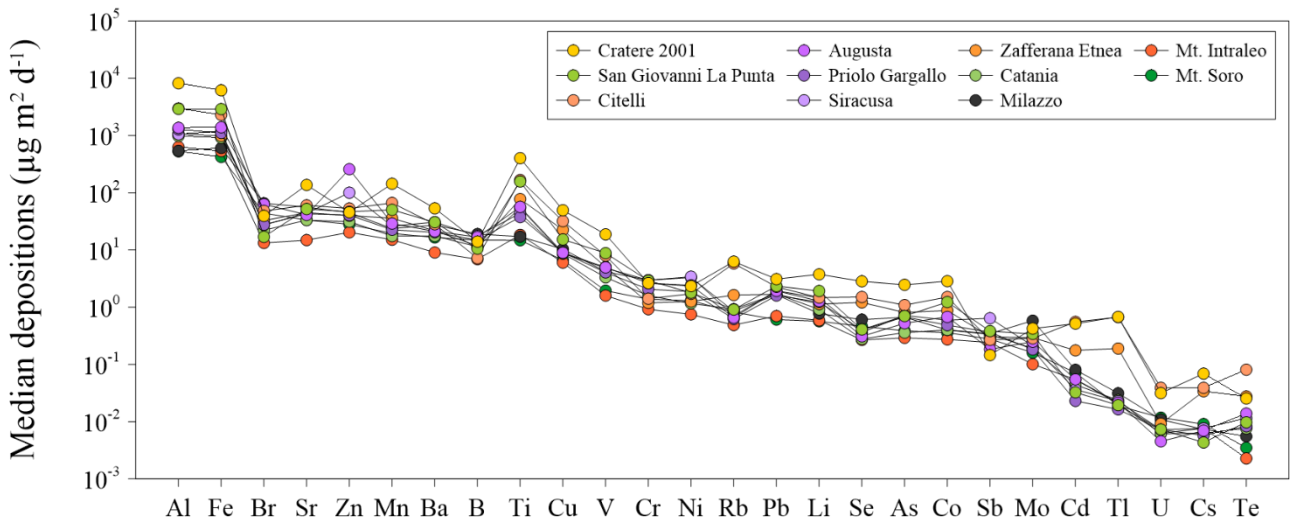


Figure 4.2.3. Median atmospheric depositions ($\mu\text{g m}^{-2} \text{d}^{-1}$) of trace elements in Volcanic (Cratere 2001, Citelli, Zafferana Etnea), urban (San Giovanni La Punta, Catania), Industrial (Augusta, Priolo Gargallo, Siracusa, Milazzo), and Rural (Mt. Intraleo and Mt. Soro) sampling sites.

5. Conclusions

Repeated pCO₂ surveys conducted between June 2023 and November 2025 demonstrate a marked spatial heterogeneity of CO₂ in Pozzuoli Bay. Approximately 80% of seawater measurements (n=fall within 376–600 µatm, but five localized hydrothermal hotspots—Secca delle Fumose (SdF), Baia Castle beach, Capo Miseno, Academia-Bagnoli coast, and Nisida—show substantially elevated values. SdF exhibits the most extreme conditions, with a strong vertical gradient: pCO₂ increases from 500–520 µatm at 2 m depth (pH 8.02), to 1400–1600 µatm at 6 m (pH 6.94), and peaks at 6800–9000 µatm at 9–10 m (pH 5.77). Integration of excess dissolved inorganic carbon ($2.7 \pm 0.03 \text{ mol}\cdot\text{m}^{-2}\cdot\text{kg}^{-1}$) with estimated current velocities ($\sim 0.05 \text{ m/s}$) yields a CO₂ flux of $516 \pm 6 \text{ tons CO}_2/\text{day}$ (range 103–1031 tons/day). Metagenomic analyses of 27 samples (5 biofilms, 1 hydrothermal fluid, 21 seawater), generating 6,997 million reads (99% retained after quality filtering), show that SdF vent fluids (72 °C) are acidic, low in salinity and Mg²⁺, and enriched in CO₂, Mn, Fe, and reduced gases. Geochemical anomalies at SdF correspond to strong microbial shifts, with enrichment of thermophilic chemolithoautotrophs and genes involved in CO₂ fixation, hydrogen and sulfur oxidation, anaerobic respiration, and arsenic detoxification. Vent fluids and surrounding seawater differ markedly in taxonomic and functional composition; however, hydrothermal taxa and metabolisms extend into the water column, indicating ecological spill-over. Overall, SdF functions as a high-flux biogeochemical hotspot that drives localized carbon enrichment and microbial niche partitioning while maintaining broader ecosystem resilience.

The investigation of acid gas deposition from the volcanic plumes of Mt. Etna's leads to the following key conclusions. Volcanic emissions significantly depress rainwater pH (3.0–4.5), bypassing the atmospheric neutralization capacity typically provided by marine and crustal cations. The interaction between acidic precipitation and volcanic ash promotes the mobilization of lithophile and trace elements (Al, Fe, Ti, Tl, Te, V), significantly altering local geochemical cycles and REE distribution patterns. A clear spatial gradient exists where proximal sites are dominated by magmatic degassing, whereas distal urban and industrial areas exhibit a complex synergy of volcanic, petrochemical, and traffic-related (e.g., Sb from brake wear) pollutants. The observed fluxes of F⁻ (up to $681 \mu\text{eq m}^2 \text{ d}^{-1}$) and SO₄²⁻ (up to $2567 \mu\text{eq m}^2 \text{ d}^{-1}$) underscore the role of Mt. Etna as a primary regional source of environmental acidification, with direct implications for ecosystem resilience and human health.

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Conferences and dissemination

- Dissemination Workshop RETURN, Turin, 1–2 February 2024 – Poster presentation
- National Biodiversity Forum (NBFC), University of Palermo, 20–22 May 2024 – Poster presentation
- European Marine Biology Symposium (EMBS), Naples, 16–20 September 2024 – Oral presentation

Publications

Under submission:

- Dominech, S., Brugnone, F., Calabrese, S., Brusca, L., Parello, F., D'Alessandro, W. Rare Earth Elements and Trace Critical Elements in atmospheric deposition from urban, industrial, volcanic and rural areas in Sicily (Italy).
- Sandoval-Velasquez A., Migliaccio, F., Diana, S. C., Caliro, S., Di Vito, M.A., Milazzo M., Giovannelli, D., Aiuppa, A. Volcanic CO₂ degassing and microbial carbon fixation in a caldera offshore, submission to *Scientific Reports* (Nature Portfolio Collection: Volcanic Calderas).
- Migliaccio, F., Diana, S. C., Sandoval-Velasquez A., Brusca, J., Pellicciari-Silva, A., Taccaliti, E., Cascone, M., Bassolino, I., Di Iorio, L., Cordone, A., Milazzo, M., Aiuppa, A., Giovannelli, D. Shallow-water hydrothermal vent impact on the surrounding water column microbial diversity, submission to *Frontiers in Earth Science* (Special Issue: Biogeochemistry and Ecology of Extreme Microbial Habitats).