

## **Rain-ash interaction during paroxysmal events as potential input of toxic trace element in the environment: example from Mt. Etna Volcano**

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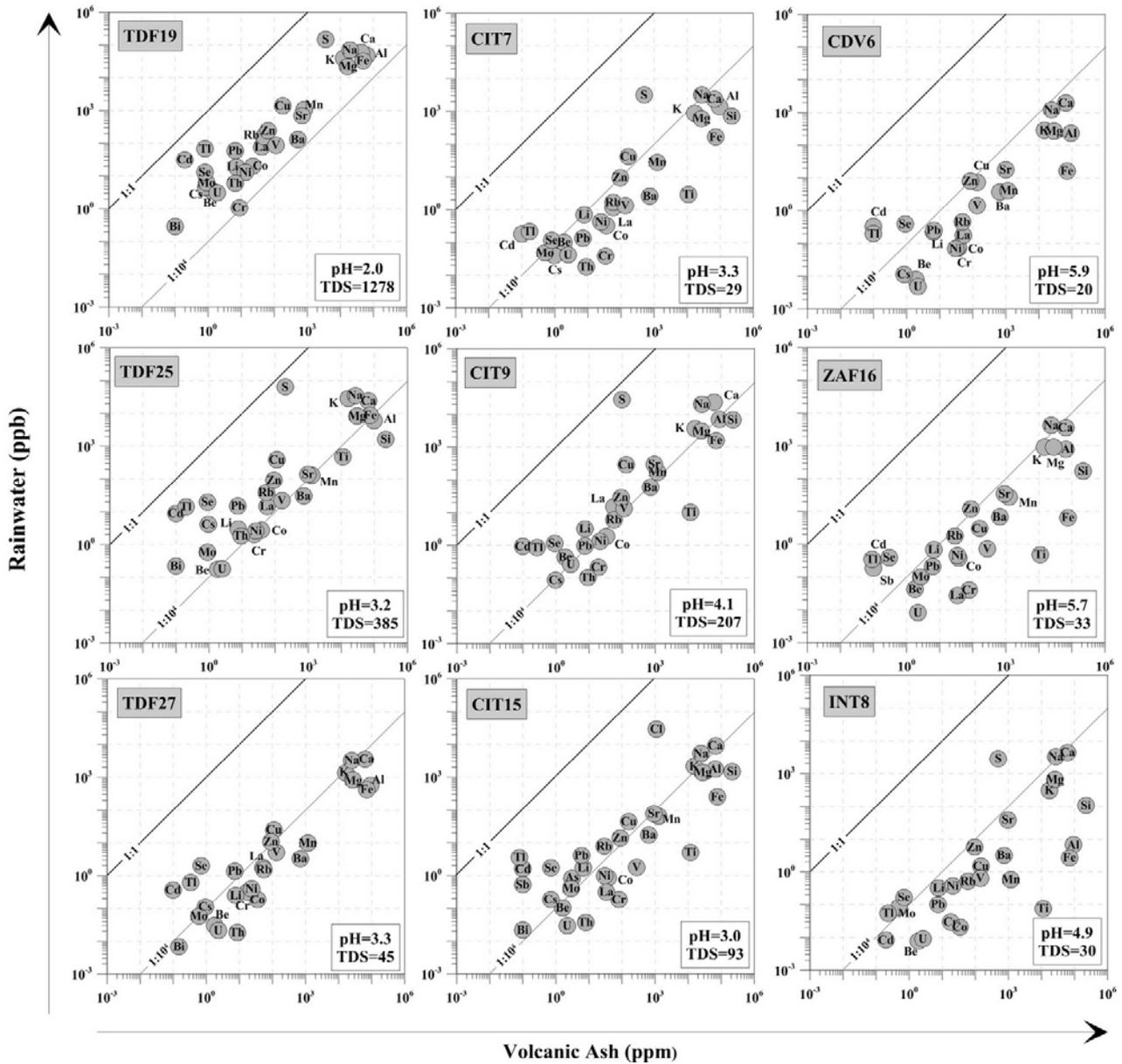
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Volcanic emissions represent one of the most relevant natural sources of trace elements to the troposphere, both during and between eruptions. Due to their potential toxicity they may have important environmental impacts from the local to the global scale.

Mount Etna, the largest European volcano and one of the most active volcano in the world, covers an area of about 1250 km<sup>2</sup> and reaches an altitude of about 3340 m. It has been persistently active during historical time, with frequent paroxysmal episodes separated by passive degassing periods. Atmospheric precipitation was collected approximately every two weeks, from April 2006 to December 2007, using a network of five rain gauges, located at various altitudes on the upper flanks around the summit craters of Etna Volcano. The collected samples were analysed for major (Ca, Mg, K, Na, F, SO<sub>4</sub>, Cl, NO<sub>3</sub>) and a large suite of trace elements (Ag, Al, As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Hg, La, Li, Mn, Mo, Ni, Pb, Rb, Si, Sb, Sc, Se, Sr, Th, Ti, U, V, Zn) by using different techniques (IC, SPEC, ICP-MS and CV-AFS). The monitoring of atmospheric deposition gave the opportunity to occasionally sample volcanic fresh ashes emitted by the volcano during the paroxysmal events. This was possible because the network of five rain gauges were equipped with a filter-system to block the coarse material. In this way, more than twenty events of ashfall were collected. Unfortunately, only half of these samples were suitable for a complete chemical analysis, because of the small amount of sample. In order to obtain elemental chemical composition of ashes, powdered samples were analysed by a combination of methods, including X-ray Fluorescence Spectroscopy (XRF), total digestion followed by Inductively Coupled Plasma Emission Mass Spectrometry (ICP-MS), Instrumental Neutron Activation Analysis (INAA), and infrared detection (IR).

The chemistry of rainwater reveals that most of the investigated elements have higher concentrations close to the emission vent of the volcano, confirming the prevailing volcanic contribution. Rainwater composition clearly reflects the volcanic plume input. Ash-normalised rainwater composition indicates a contrasting behaviour between volatile elements, which are highly-enriched in rainwater, and refractory elements, which have low rainwater/ash concentration ratios. The degree of interaction between collected ash and rainwater was variable, depending on several factors: (i) the length of the period in which tephra was present in the sampler (the ash fall may have occurred any day from the first to the last day of the rain collecting period); (ii) the amount of rainwater fallen on the collectors after the ash-fall event, and its acidity; (iii) the granulometry of the ash samples that was widely variable (from few centimetres to micrometric particles) increasing the interaction with decreasing dimensions of the grains; (iv) the distance of collector with respect to the craters. In order to investigate the role of volcanic ash on the evolution of the rainwater chemistry, absolute concentrations of rain and ash were plotted in binary plot diagrams (Figure 1). Each diagram corresponds to a single event, and pH and TDS of the solution collected is reported. The diagonal bars in the diagrams represent the rain/ash ratios (1:1 and 1:10000).

The results confirm that sulphate and halide salt aerosols are adsorbed onto ash particles, and their rate of dissolution in rainwater depends on solubility. Moreover, rapid chemical weathering of the silicate glass by volcanic acid (SO<sub>2</sub>, HCl and HF) can also explain the enrichment of several refractory elements (Na, K, Ca, Mg, Si, Al, Fe, Ti, Sc). Our observations highlight how explosive activity can increase enormously the deposition rate of several chemical elements, up to several km away from the emission vents.



**Figure 1.** Rainwater and volcanic ash concentrations for nine different ash emission events. Total dissolved solid (TDS) are expressed as mg/l.