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Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas

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ABSTRACT

Volcanoes emit SO_2, CO_2, and H_2S, but also trace elements gases and particles such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Sb. Active moss bag biomonitoring, an easy to apply and low budget method, was used to determine trace element release from volcanic areas of different geological context and climates. Exposure height variations (0.7–1.6 m above ground) due to different availability of natural tie points did not affect the results. Accumulation was linear for exposure durations from three days to nine weeks, so values were comparable by normalization to moss exposure time. Uncovered moss bags showed higher accumulation than co-exposed covered ones because of additional dust and wet deposition while washout by rain was negligible. The selection of a specific moss significantly affected element accumulation with moss of lower shoot compactness accumulating more. For all volcanic areas, highest accumulation was found for S (1–1000 $\mu mol\cdot(g\cdot d)^{-1}$), followed by Fe and Mg (0.1–10 $\mu mol\cdot(g\cdot d)^{-1}$), Sr, Ba, Pb, Cr, Li ($10^{-4}$–$10^{-1}$ $\mu mol\cdot(g\cdot d)^{-1}$), then Co, Mo and the volatile elements As, Sb, Se, Tl, Bi (10^{-6}–10^{-2} $\mu mol\cdot(g\cdot d)^{-1}$). For most elements, open conduit volcanoes (Etna, Stromboli, Nyiragongo) showed higher moss accumulation rates than more quiescent hydrothermal areas (Vulcano > Nisyros > Yellowstone National Park) and a correlation of S, Fe, and Pb from eruptive ash and lava emissions. For some volatile elements (S, As, Se), higher accumulation was observed within fumarolic fields compared to crater rims of open conduit volcanoes which is a relevant information for risk assessment of tourist exposure to volcanic gases.

1. Introduction

Since ancient times, volcanoes have been fascinating environments for mankind. Their emissions can affect humans during large violent eruptions but also on a very local scale where residents or tourists are exposed to continuous releases of major volcanic gases like SO_2, CO_2, H_2S, and water vapor from nearby volcanoes (D'Alessandro et al., 2013). The release of these gases is quite well studied by a wide range of different methods: direct sampling using Giggenbach's bottles (Giggenbach, 1975), alkaline gas traps (Wittmer et al., 2014), multigas detectors (Aiuppa et al., 2007), or remote sensing techniques using ultraviolet cameras (Pering et al., 2015), Fourier transform infrared spectroscopy (La Spina et al., 2013), or differential optical absorption spectroscopy (Galle et al., 2010). However, the emission of trace elements such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Sb is less studied, although some studies exist using e.g. rain water monitoring on Etna (Italy; Calabrese et al., 2011), filter sampling of particulate matter on Stromboli (Italy; Allard et al., 2000) or serial filter sampling of particles and acidic gases on Kilauea (Hawaii, USA; Hinkley et al., 1999). The lower number of studies for trace element emissions in comparison to major volcanic gases is all the more surprising considering both the attributed relevance of volcanic emissions in the global cycle of trace elements (up to >50% of all natural emissions (Nriagu, 1989)) as well as the toxicity of some of these elements in their volatile form (e.g. Hg, AsH_3). The lack of measurements is explained by a shortage of suitable sampling methods, largely because the instability of trace elements in their volatile form and their low concentrations require stabilization and enrichment during sampling. Especially where volcanoes are located in remote areas, which are difficult to access, there is no electricity or access to routine sample-preserving agents like liquid nitrogen and transport of sophisticated heavy equipment is difficult.

An easy-to-apply method comes from monitoring anthropogenic and industrial emissions: Moss monitoring is based on the property of the moss to take up nutrients as well as toxic substances (Brown and Bates, 1990) with their large surface and leaves consisting of a single cell layer where gases and particles can attach. Moss cells have polyuric acids on their outer cell wall that serve as cation exchange area (Clymo, 1963). Passive moss monitoring employs sampling of indigenous mosses as element emission collectors. It has been applied to monitor emissions from coal/petrol burning, chemical, and metal industry (Markert et al., 1996), or for general air quality screenings e.g. in

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Scandinavia (Rühling and Tyler, 1973) or Germany (Pesch and Schroeder, 2006). Passive moss monitoring has also been used to trace volcanic/geothermal emissions, e.g. on Etna (Lo Giudice and Bonanno, 2009), on Piton de La Fournaise (La Réunion, France) and Masaya Volcano (Nicaragua; both Martin et al., 2010), or at thermal springs at Mt. Amiata, Italy (Loppi and Bonini, 2000). Just recently, the additional ability of the moss to preserve higher methylated volatile As species has been shown (Arndt and Planer-Friedrich, 2017). Its major disadvantage concerning volcano monitoring, however, is the lack of naturally growing moss near the emission sources which causes data gaps in volcano surveys.

In the present study, we used active moss monitoring with non-indigenous mosses to monitor several volcanoes for trace element emissions. Active moss monitoring has been introduced by Goodman and Roberts (1971) and was adapted by Little and Martin (1974) using moss bags. Besides the flexibility of choosing any exposure site, active moss monitoring also has the advantages of known initial concentrations and defined moss exposure times (which can be adapted according to the emission strength). The moss monitoring technique is easy to apply on volcanoes due to its independence of electricity or preserving agents.

Most reports so far come from studies on anthropogenic and industrial emission sources (Adamo et al., 2011; Adamo et al., 2003; Cao et al., 2009). Only recently, active moss monitoring has also been used for investigating volcanic emissions at the open conduit volcano Etna, Italy (Calabrese and D'Alessandro, 2015; Calabrese et al., 2015), and the hydrothermally emitting volcano La Fossa, Vulcano, Italy (Arndt et al., 2014) using moss digestions for total element concentrations (Etna, Vulcano) and scanning electron microscope analysis (SEM; on Etna; Calabrese and D'Alessandro, 2015). Here, we present new data on trace element accumulation in moss bags from two further open conduit volcanoes (Nyiragongo in the Democratic Republic of Congo and Stromboli in Italy) as well as two further hydrothermally emitting volcanoes (Yellowstone National Park in the USA and Nisyros in Greece) and compare those to previous results from Etna and Vulcano. Details on the monitored areas can be found in Section 2.1 and SI 1.

While monitoring six different volcanic areas over a period of more than seven years in total, we experienced that different adaptations to the moss monitoring technique are necessary. We therefore also report here on some practical issues of active moss monitoring on volcanoes. In detail, we investigated the effects of using different mosses, different exposure heights above ground surface (often dictated by the availability of natural items like stones or sticks for moss bag fixation), different exposure durations (often dictated by site accessibility), and moss bag coverage versus non-coverage (mainly employed as a means to protect the moss bags from rain in boreal or tropical wet climate, however it also shields the moss from wind and thus potential deposition).

In summary, the objectives of this paper are to present (a) new data on gaseous trace element emissions of the volcanoes Stromboli, Nyiragongo, Nisyros, and Yellowstone, (b) a comparison of different element accumulation patterns observed at the different monitored volcanoes, and (c) an evaluation of the moss monitoring technique for active volcanic areas.

2. Methods

2.1. Study areas

The six volcanoes monitored can be divided into three open conduit volcanoes emitting gas, lava, and ash (Etna, Stromboli (Italy), and Nyiragongo (Democratic Republic of the Congo)) and three hydrothermal volcanoes emitting gas only (Vulcano (Italy), Nisyros (Greece), and Yellowstone (USA)). The three open conduit volcanoes differ in their geological settings: Etna and Stromboli are situated on a converging plate boundary while the alkaline Nyiragongo is a hot spot volcano (Hamaguchi and Zana, 1990) in the African Rift System. Etna has 4 summit craters and Stromboli one, while Nyiragongo hosts the largest lava lake on earth (Sawyer et al., 2008).

The three hydrothermal volcanoes can again be divided by their geology in a continental hot spot (Yellowstone) and two converging tectonic plate boundary volcanoes (Vulcano, Nisyros). One more difference is the degassing temperature with the fumarolic field on Vulcano having temperatures up to 400 °C (Paonita et al., 2013) while Nisyros shows temperatures around 100 °C (Brombach et al., 2003). The presence and absence of permanent liquid water can also be used for differentiating the hydrothermal volcanoes: in Yellowstone, fumaroles, hot springs, mudpots, geysers, and geothermally influenced peatlands are present while there are only fumarolic fields on Nisyros and Vulcano. A detailed description of all monitored volcanoes including former monitoring results of trace elements can be found in SI 1.

2.2. Preparation of moss bags

For all exposures, *Sphagnum* moss has been selected because it is known to have a large surface area, has been shown to have a very large cation exchange capacity (0.9–1.5 meq g^{-1}; Rühling and Tyler, 1973), and because of its widespread use in previous studies about industrial monitoring (Ares et al., 2012 and references therein), part of them only naming the genus, part of them also the species. Moss was collected at several sites for the different volcanoes monitored in this study (Table 1). For Vulcano in 2012, Nisyros, and Nyiragongo *Sphagnum* moss species (*S. tenellum*, *S. subsecundum*, *S. cuspidate*, *S. girgensonii*, *S. fallax*; called *S.* spp. afterwards) were collected from an acidic fen in the Fichtelgebirge in Bavaria, Germany ("Schlöppnerbrunnen", 50°08′14″ N/11°53′07″ E). For monitoring Etna, two Sphagnum species (*S. fuscum* and *S. tenellum*) were collected from Sweden (Calabrese et al., 2015), and for monitoring Vulcano 2013 and Stromboli *S. palustre* was collected from the forests around Bayreuth, Germany (49°54′42″ N/11°41′47″ E). For exposure in Yellowstone, commercial *S. palustre* from Chile was used; at a few stations, the collected *S. palustre* from Bayreuth was used in parallel for comparison.

Moss bags were prepared as described earlier (Calabrese et al., 2015). Basically, the moss was washed three times in deionized water (MQ, 18.2 MΩ cm^{-1}) to remove elements adsorbed on its surface. The washed moss was dried in the oven for 24 h at 40 °C. Approximately 1.5–2 g dried moss was loosely packed in spherical bags for exposure with a 0.8–2 mm mesh mosquito net. For the moss bags exposed on Vulcano (2012 and 2013), Stromboli, and Yellowstone, two nets with broader mesh were combined (Arndt et al., 2014). The moss bags were about 5 cm in diameter giving a moss weight to surface ratio between 20 and 25 mg cm^{-2}. Moss bags were kept in closed plastic bags until exposure on the volcanoes to avoid contamination.

Moss pictures were made using a stereo microscope (Leica M125) with 0.5× objective including a camera (IC80 HD).

2.3. Moss bag exposure

The choice of the geometry of the sampling network was mainly intended to evidence the distribution of the impact of volcanic emission. Therefore, compatibly with logistics, we tried to build up a concentric network around the main vent (open conduit craters or fumarolic fields) with a higher density and greater distances in the main downwind direction. Where the emission points were instead widely distributed and of low flux (Nisyros and Yellowstone) the sampling stations were positioned within few meters from the main emission points.

In all areas at least one background station was positioned following the criteria below: Absence of anthropogenic contaminations sources (like traffic or industry), distance from the main emission vents at least ten times the closest stations, in the up-wind direction of the main vents, within the area in which landscape is influenced by the volcanoes (e.g. presence of volcanic rocks).

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