Evaluation of active and passive sampling techniques for determination of total volatile arsenic and its speciation in volcanic gases and biogases

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ABSTRACT

Volatile arsenic (As) species, so-called arsines, like AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As (Me = methyl group) are among other toxic trace elements known to be naturally emitted by volcanoes. Arsines have also been shown to occur at biogas plants. So far, only few studies exist about the emission of total As and its speciation on volcanoes due to the instability of arsines and thus challenging sampling. Therefore, the aim of the present study was to evaluate different techniques in the laboratory for sampling total atmospheric As and arsine species and to employ them on volcanic gas and biogas sampling.

In the first two studies of this thesis, moss bag monitoring was applied as field technique for emission screening of total As and other elements on several volcanoes. Studied volcanoes were the open conduit volcanoes Stromboli, Etna (both Italy), and Nyiragongo (Democratic Republic of the Congo), and the hydrothermal volcanoes Vulcano (Italy), Nisyros (Greece), and Yellowstone (USA). Moss was digested in 19.5% HNO_3/6% H_2O_2 and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). At the three hydrothermal volcanoes, volatile elements like As, S, Sb, Se, Tl, and Bi correlated with each other while they additionally correlated with Fe and Pb at the three open conduit volcanoes due to eruptive lava and ash emissions. Moss screening showed higher element accumulation rates at open conduit volcanoes than at hydrothermal volcanoes for most elements. The elements As, S, and Se, on the contrary were higher accumulated on moss bags exposed within the fumarolic field on Vulcano compared to the crater rims of the open conduit volcanoes, which is relevant for tourist exposure to these gases. Along a transect through the fumarolic field of Vulcano, As was revealed to be emitted as a volatile from the fumaroles with its maximum accumulation on the moss within the fumarolic field and its far downwind distribution. Its profile agreed with the other volatile elements and differed from soil-borne elements Fe, Co, and V.

The moss monitoring technique was evaluated for application on volcanoes revealing element accumulation patterns on the moss bags to be independent of exposure height (0.7-1.6 m), duration (3-9 weeks), and coverage of the moss bags. The moss shoot density and also moss species, however, influenced element accumulation and should therefore be normalized for comparability of different sampling areas and sites. In general, exposure of moss triplicates is recommended.

In the third study, moss was evaluated for species preserving trapping of AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As using batch experiments. Moss was extracted in 0.1 M HNO_3/3% H_2O_2 and analyzed by IC-ICP-MS for the respective pentavalent acids of the arsines while gas analysis was done by cryotrapping cryofocussing gas chromatography electron impact mass spectrometry split atomic fluorescence spectroscopy (CT-CF-GC-EI-MS/AFS). Me_2AsH and Me_3As were trapped on the moss and recovered as their respective pentavalent acids while $MeAsH_2$ was only partially trapped and inorganic As was not trapped at all. We propose the higher methylated arsines to be bound covalently to the moss surface. Consequently, moss monitoring can be employed to determine if methylarsines, besides As particles, occur in yet unknown As emissions.

In the last study different arsine species preserving sampling techniques were evaluated. Needle Trap Devices (NTDs) did not trap AsH_3, $MeAsH_2$, and Me_2AsH, released Me_3As only partially during GC analysis, and led to artifact formation of Me_2AsCl. These results question former studies sampling environmental gases using Solid Phase Micro Extraction fibers (SPME) equipped with the same sorption materials. Cryotrapping in dry ice only partially trapped Me_2AsH and Me_3As and did not trap AsH_3 and $MeAsH_2$. Silver nitrate traps were influenced in their arsine trapping efficiency by volcanic gases like water vapor and H_2S. Tedlar bag sampling remained the best field technique for sampling volatile As. It also samples matrix gases for which arsine stability was evaluated for the first time. Arsines were stable at 5°C in the dark for 19 days in dry N_2, for 11 days in 20% O_2, and for 19 days in 3800 ppm_V CO_2 (>80% recovery for every species). In H_2S, recovery of Me_3As was 67% after 21 days and in 100 ppm_V SO_2, 40% and 11% of Me_2AsH and Me_3As were recovered after 21 days, respectively. To remove CO_2, water vapor, and sulfur gases during Tedlar bag sampling of emissions from Vulcano and Solfatara (Italy), cooling traps and NaOH traps were employed. Inorganic AsH_3 was the predominant As species recovered with concentrations of $0.5\text{-}77\ \mathrm{ng\cdot m^{-3}}$. These concentrations suggest arsine emissions from volcanoes to be orders of magnitude lower than estimated based on previous studies. Occurrence of exclusively AsH_3 suggests microbial volatilization to be negligible at the fumaroles on Vulcano. On moss bags exposed on Vulcano, inorganic As was recovered, suggesting the additional presence of As particles deposited on the mosses. In gas from a wastewater treatment plant and biogas plants, on the contrary, predominantly methylarsines were recovered in Tedlar bags which were also recovered on moss bags.

All in all, the present study shows that (a) moss monitoring is a good sampling technique for screening of total As emissions and to gain information about its origin, distribution, potential occurrence of methylated arsines, and the respective volcano's emission activity and (b) Tedlar bag sampling proved the ideal species preserving quantitative sampling technique, even in volcanic gases, but requires elimination of these gases during sampling.

ZUSAMMENFASSUNG

Volatile Arsenspezies (As), sogenannte Arsine, wie AsH_3, $MeAsH_2$, Me_2AsH und Me_3As (Me = Methylgruppe) gehören zu den toxischen Spurenelementen, die natürlicherweise von Vulkanen emittiert werden. Arsine wurde ebenfalls in den Emissionen von Biogasanlagen nachgewiesen. Bisher wurden an Vulkanen aufgrund der Instabilität von Arsinen und der dadurch aufwendigen Probenahme nur in einigen wenigen Studien die Arsen-Gesamt- und Speziesgehalte bestimmt. Aus diesem Grund war das Ziel der vorliegenden Arbeit, verschiedene Probenahmetechniken für die As-Gesamtgehalts- und Speziesbestimmung im Labor zu testen und auf Vulkanen und an Biogasanlagen praktisch anzuwenden.

In den ersten beiden Studien dieser Arbeit wurde Moosbeutel-Monitoring zum Emissionsscreening von As und anderen Elementen an zwei Gruppen von Vulkanen angewandt: auf den eruptiven Vulkanen Ätna, Stromboli (beide in Italien) und Nyiragongo (Demokratische Republik Kongo) und auf den hydrothermalen Vulkanen Vulcano (Italien), Nisyros (Griechenland) und Yellowstone (USA). Nach dem Monitoring wurde das Moos in 19.5% HNO_3/6% H_2O_2 aufgeschlossen und mittels Massenspektrometrie mit induktiv gekoppeltem Plasma analysiert (ICP-MS). An den drei hydrothermalen Vulkanen korrelierten volatile Elemente wie As, S, Sb, Se, Tl und Bi miteinander, während sie auf den eruptiven Vulkanen zusätzlich aufgrund der Lava- und Ascheemission noch mit Fe und Pb korrelierten. Das Moos-Screening zeigte für die meisten Elemente höhere Akkumulationsraten auf Moosen von eruptiven Vulkanen als bei hydrothermalen Vulkanen, außer für As, Se und S, die im Fumarolenfeld auf Vulcano stärker akkumuliert waren als an den Kratern der eruptiven Vulkane. Dies ist besonders relevant für Touristen, die sich diesen Gasen aussetzen. Entlang eines Transekts durch das Fumarolenfeld auf Vulcano wurde As aufgrund der maximalen Akkumulation auf Moosbeuteln im Fumarolenfeld und der weiten Verteilung in Windrichtung als volatiles Element identifiziert. Das Profil für As stimmt mit den anderen volatilen Elementen S überein und unterscheidet sich von den bodenbürtigen Elementen Fe, Co und V.

Die Moos-Monitoring-Technik wurde für ihre Anwendung auf Vulkanen evaluiert. Dabei waren die Akkumulationsmuster verschiedener Elemente unabhängig von der Expositionshöhe der Moose (0.7-1.6 m), der Dauer der Exposition (3-9 Wochen) und der Abdeckung der Moose. Moosart und -dichte beeinflussten dagegen die Akkumulation und sollten zur Vergleichbarkeit unterschiedlicher Probenahmestellen und -gebiete vereinheitlicht werden. Generell wird die Verwendung von Moos-Triplikaten empfohlen.

In der dritten Studie wurde das Moos auf seine As-Spezies erhaltende Fähigkeit getestet. Dazu wurden Batch-Experimente mit AsH_3, $MeAsH_2$, Me_2AsH und Me_3As durchgeführt. Das Moos wurde

anschließend in 0.1 M HNO_3/3% H_2O_2 extrahiert und per Ionenchromatografie (IC) mit ICP-MS auf die den Arsinen entsprechenden fünfwertigen Säuren analysiert. Gas-Analysen wurden mit einem Gaschromatographen durchgeführt, gekoppelt an ein Elektronen-Impakt Massenspektrometer mit Split zur Atomfluoreszenzspektroskopie mit vorheriger Probenanreicherung durch Kryotrapping und Kryofokussierung (CT-CF-GC-EI-MS/AFS). Me_2AsH und Me_3As wurden auf dem Moos gebunden und als ihre jeweiligen fünfwertigen Säuren wiedergefunden während $MeAsH_2$ nur teilweise gebunden wurde und AsH_3 überhaupt nicht. Wir postulieren, dass die höher methylierten Arsine kovalent an die Moos-Oberfläche gebunden werden. Somit kann Moos-Monitoring in unbekannten As-Emissionen eingesetzt werden um zu bestimmen, ob neben As-Partikeln auch volatile methylierte As-Spezies vorkommen.

Die letzte Studie beschäftigt sich mit As-Spezies erhaltenden Probenahmetechniken. Needle Trap Devices (NTDs) konnten AsH_3, $MeAsH_2$ und Me_2AsH nicht binden. Während der GC-EI-MS Analyse konnten NTDs Me_3As nur teilweise wieder freisetzen und produzierten Me_2AsCl-Artefakte. Diese Ergebnisse stellen frühere Studien mit der Verwendung der gleichen Sorptionsmaterialien in Solid Phase Micro Extraction (SPME) in Frage. Kryotrapping in Trockeneis fixierte Me_2AsH und Me_3As nur teilweise und AsH_3 und $MeAsH_2$ überhaupt nicht. Silbernitratfallen wurden bei Arsinprobenahmen von den Vulkangasen H_2S und Wasserdampf beeinflusst. Die beste getestete As-Probenahmetechnik im Feld war die Nutzung von Tedlarbeuteln. Diese sammeln allerdings auch Matrix-Gase, in denen die As-Stabilität erstmals getestet wurde. Arsine waren bei dunklen Bedingungen und 5°C in trockenem N_2 19 Tage, in 20% O_2 11 Tage, und in 3800 ppm_V CO_2 19 Tage (>80% Wiederfindung für alle Spezies) stabil. In H_2S war nach 21 Tagen die Wiederfindung von Me_3As 67% und in 100 ppm_V SO_2 wurden nach 21 Tagen 40% und 11% Me_2AsH und Me_3As wiedergefunden. Um Wasserdampf, CO_2 und Schwefelgase während der Tedlarbeutel-Probenahme auf Vulcano und Solfatara (Italien) zu entfernen, wurden Kühlfallen und NaOH-Fallen verwendet. Anorganisches AsH_3 war mit 0.5-77 $ng \cdot m^{-3}$ die vorherrschende As-Spezies. Diese Konzentrationen legen nahe, dass vulkanische Arsin-Emissionen um Größenordnungen niedriger sind als in vorherigen Studien erwartet. Das Vorkommen von ausschließlich anorganischem AsH_3 deutet darauf hin, dass mikrobielle Volatilisierung in den Fumarolen auf Vulcano vernachlässigbar ist. Der Nachweis von As auf Moosbeutel von Vulcano und die Wiederfindung als anorganisches Arsen zeigen das zusätzliche Vorkommen von As-Partikeln an. Im Gas von Kläranlagen und Biogasanlagen dagegen wurden mittels Tedlarbeuteln überwiegend Methylarsine nachgewiesen, die auch auf Moosbeuteln wiedergefunden werden konnten.

Insgesamt zeigt die vorliegende Doktorarbeit (a) dass Moos-Monitoring eine gute Probenahmetechnik zum Screening für Gesamtarsen-Emissionen ist und um genauere Informationen über den

Ursprung, die Verteilung, die entsprechenden Vulkane und über das etwaige Vorkommen methylierter As-Spezies zu gewinnen und (b) dass Probenahme mit Tedlarbeuteln sich auch in Vulkangasen als ideale Spezies erhaltende Methode erwies, jedoch die Eliminierung dieser Gase während der Probenahme erfordert.

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LIST OF ABBREVIATIONS

AFS	Atomic fluorescence spectroscopy
“C“	Carboxen
CF	Cryofocussing
CT	Cryotrapping
“D“ or DVB	Divinylbenzene
EI	Electron impact
FEP	Fluorinated ethylene propylene
GC-(EI-)MS	Gas chromatography followed by (electron impact) mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
IC-ICP-MS	Ion chromatography coupled to inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
Me	Methyl group (used for methylarsines)
meq	Milli equivalent
MQ	Deionized ultrapure water
NTD	Needle Trap Device
“P“ or PDMS	Polydimethylsiloxane
ppm_V	Parts per million (volume)
SPME	Solid phase micro extraction fiber
UV light	Ultra violet light
WHO	World health organization
“X“	Carbopack X
XAS	X-ray absorption spectroscopy

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EXTENDED SUMMARY

1 INTRODUCTION

1.1 Overview on As chemistry in the atmosphere

Arsenic (As) is an ubiquitous element which occurs in soil and rocks, in surface and groundwater, and in the atmosphere where it is comparably less studied. In total, the atmosphere is estimated to contain 800-1,740 t As with a background concentration of 0.5-2.8 ng·m^{-3} in the northern hemisphere (Matschullat, 2000). The input sources for As to the atmosphere can be divided into diffusive and point sources, of which the latter ones have a higher impact. Wide-spread diffusive sources include microbial volatilization from soils, sediments, and waters, and sea spray dispersion. Point sources can be of anthropogenic and natural origin. Large anthropogenic sources are industry and coal/wood combustion (Σ 28,800 t·a^{-1}; Matschullat (2000)) while natural point sources are natural forest fires and, above all, geothermal and volcanic areas. The latter account for an annual impact of 17,150 t which is 100 times higher than natural forest fires (Matschullat, 2000).

Atmospheric As is dominated by particulate As (89-98.6%; Matschullat (2000)) which can e.g. be dust particles with half-lives of 7-10 days (Matschullat, 2000). The other part of atmospheric As are volatile gaseous molecules. Their most studied species are the inorganic arsine (AsH_3) and the organic species mono-, di-, and trimethylarsine ($MeAsH_2$, Me_2AsH, and Me_3As; Me = CH_3; chemical structures of all arsines in Figure 1) with boiling points of -62 or -55°C (AsH_3), -2 or +2°C ($MeAsH_2$), 35°C (Me_2AsH), and 52°C (Me_3As; boiling points from Ilgen and Huang (2013), Lide (2003), Pantsar-Kallio and Korpela (2000), and Planer-Friedrich et al. (2006)). In addition to these species, more exotic chlorinated and sulfonated As compounds like Me_2AsCl, $MeAsCl_2$, and Me_2AsSMe also have been shown to exist in nature (Planer-Friedrich, 2004). Chlorinated volatile As compounds like $AsCl_3$, $MeAsCl_2$, and $MeAsCl_2$ have even been generated in the laboratory in the presence of HCl and its vapor (Mester and Sturgeon, 2001).

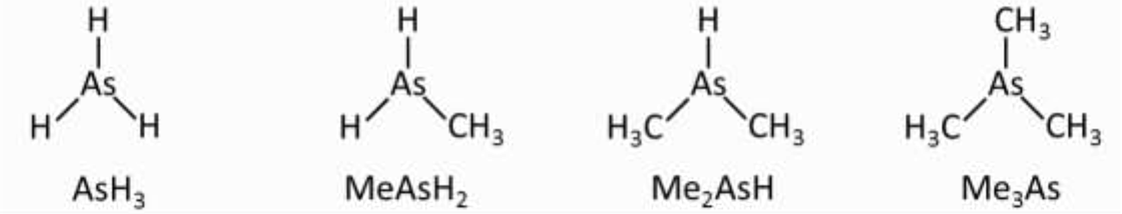

Figure 1: Chemical structures of volatile arsines arsine, mono- di-, and trimethylarsine.

In nature, volatile arsines are formed under reducing conditions. This can happen e.g. geothermally, but their volatilization can also be triggered by (micro)organisms. <u>Microbially</u>, As is volatilized by two different reaction pathways in waters and soils: (a) Aquatic As species are reduced and subsequently oxidatively methylated. By this alternating process of reduction and methylation, the methyl groups are added to the As compound one by one, which is often done by fungi. Every dissolved reduced methylated As species with a different amount of methyl groups ($H_{3-x}Me_xAs^{(+III)}O_{3-x}$; = 0-3) can be reduced further to volatilize it ($H_{3-x}Me_xAs^{(-III)}$; x = 0-3; Challenger (1945)). (b) The reduced dissolved As species are methylated directly without oxidation and subsequently volatilized (Mestrot et al. (2013a) and references therein). Volatilization of arsines was shown to take place e.g. in rice paddy soil (Mestrot et al., 2009), As-contaminated soil (Turpeinen et al., 2002), sediments of an As contaminated lake (Yuan et al., 2010), and biogas plants (Mestrot et al., 2013b). Inside the fermenters of biogas and wastewater treatment plants, temperature and nutrient conditions are adjusted to the optimum of the microbial community for CH_4 production. These conditions also render them predestinated sites for the occurrence of microbially produced volatile methylated arsines. In biogas plants and biogas plant digesters predominantly Me_3As has been detected (Hippler, 2013; Mestrot et al., 2013b).

The arsines' formation in geothermal and volcanic environments is less studied than the microbial one. Arsenic was predicted to be transported from the magma to the surface as AsS compound on Augustine Volcano (Alaska, USA) by the use of thermodynamic modelling (Symonds et al., 1992). In hydrogeothermal environments, thermodynamic equilibrium calculations over a wide temperature range from 25°C to 500°C predicted $As(OH)_3$ to be the major As species in the vapor phase while chlorinated and sulfonated As compounds were found to be negligible (Pokrovski et al., 2002). Volcanoes and geothermal systems most likely primarily volatilized inorganic As. The occurrence of methylarsines in geothermal gases (e.g. Hirner et al. (1998)) points to a secondary process taking place: biovolatilization. Basically, the same microbial processes could take place in these hostile environments as shown for soils. The only study identifying a responsible As volatilizing organism in geothermal environments so far took place in Yellowstone National Park where eukaryotic thermophilic algae were isolated from geothermal springs (Qin et al., 2009). These algae have been shown to methylate arsine species and to volatilize methylated aqueous As-species.

In geothermal and volcanic gases, which are the main study objects of this thesis, volatile arsenic was reported for the first time in emissions of hot springs in California (USA; Crecelius et al. (1976)). Several studies have shown the occurrence of As in emissions in the vicinity of geothermal power plants (Italy; Bargagli et al. (1997)), above geothermal hot springs in Yellowstone (USA; Planer-Friedrich and Merkel (2006)), and around several volcanic vents like mud volcanoes at Etna (Bonanno et al., 2012), Masaya volcano (Nicaragua), and Piton de la Fournaise (La Réunion, France; both in Martin et al. (2010)). In most studies only total volatile As was considered although speciation is important for geochemical properties of the volatile As. Speciation analysis was e.g. done in Yellowstone (Planer-Friedrich et al., 2006) revealing Me_3As and chlorinated or sulfonated As species. At hot springs in British Columbia (Canada), AsH_3, $MeAsH_2$, Me_2AsH, Me_3As and an unknown As species were found (Hirner et al., 1998).

To estimate the influence of arsines on the environment, however, it is important to know their atmospheric stability. The stability of arsines strongly depends on their speciation and concentration. At the beginning of the 20th century, several stability studies were conducted generating arsine in large concentrations from up to several grams of arsenic salts. Arsines were shown to react immediately and explosively with oxygen resulting in stability durations of a few seconds (Dehn, 1905; Dehn, 1908; Palmer, 1894; Palmer and Dehn, 1901). Environmentally relevant concentrations of arsines, however, are several orders of magnitude lower (Matschullat, 2000). In these lower concentrations, arsines are more stable. In moisturized air, the four arsines have been shown to be stable for at least 8 hours under oxidizing UV light and even longer than 7 days in the dark (i.e. in the absence of •OH radicals; Mestrot et al. (2011)). Temperature also has an influence on arsines: In moisturized air, stability of AsH_3, $MeAsH_2$, and Me_2AsH was reduced to 50% after 5 weeks at 50°C compared to 20°C (Haas and Feldmann, 2000). Independent of UV light and temperature conditions, AsH_3 was always the most stable species and methylarsines were less stable the more methylated they were (Haas and Feldmann, 2000; Jakob et al., 2010; Mestrot et al., 2011): Me_3As had a half-live of 2 days while half-live for AsH_3 even was up to 130 days. All in all, arsines can travel considerable distances without speciation changes, especially during the nights. This makes arsines more important to consider for biogeochemical cycles, global As-budgets but also regarding their environmental and health impact. Causing acute hemolysis, kidney failure and subsequent death at concentrations of 250 ppm (Pakulska and Czerczak, 2006), only recently, an occupational exposure limit has been proposed for arsines by the U.S. Environmental Protection Agency (NRC, 2000). Thus, the study of arsines becomes even more relevant for human health.

1.2 Sampling volatile arsines

Sampling volatile arsines is challenging due to the low stability of volatile As species. In consequence only few studies exist so far. Most of them employ sampling techniques for total atmospheric As, including volatile gaseous As (“arsines”) and particles, but some also use species preserving techniques. Sampling techniques employed so far are (a) passive sampling techniques without the need of active pumping like moss monitoring, trapping in oxidizing solutions like NaOCl, or solid phase micro extraction (SPME) by diffusion and (b) active sampling by pumping gas through trapping materials.

Moss monitoring is known from monitoring anthropogenic emissions of several pollutants (Adamo et al., 2003; Cao et al., 2009; Giordano et al., 2009). It utilizes the mosses' general natural large surface area (Brown and Bates, 1990) which naturally increases nutrient uptake by cation exchange at polyuronic acids on the outer cell walls (Clymo, 1963) or by uptake inside the moss cells (Raven et al., 1998). Uptake does not distinguish between toxic and beneficial substances (Brown and Bates, 1990). Most often, *Sphagnum* mosses are used (Ares et al. (2012) and references therein) due to their high surface area and high cation exchange capacity (0.9 – 1.5 meq·g^{-1}; Rühling and Tyler (1973)). Moss monitoring can either be applied by collecting and analyzing indigenous moss ("passive moss monitoring") which has been done at volcanoes like Masaya (Nicaragua) or Piton de la Fournaise (France; both Martin et al. (2010)) or by taking mosses from an uncontaminated area to the selected monitored sites ("active moss monitoring"). The latter technique was first employed in the 1970s for industrial emissions (Goodman and Roberts, 1971) and developed further by using non-indigenous moss packed in nylon bags ("moss bags"; Little and Martin (1974)). It has the advantages of being independent of the mosses' natural abundancy, and having variable and defined moss exposure times and known initial element concentrations (such as As). Just recently, moss bag monitoring has been applied for the first time on a volcano, monitoring total concentrations of As and 48 other elements on Etna (Calabrese and D'Alessandro, 2015; Calabrese et al., 2015). In *study 1* of this thesis, volcanic emission monitoring is applied on Vulcano to reveal element distribution patterns. The monitoring of 6 volcanoes and an evaluation of the application of moss monitoring on volcanoes are the topic of *study 2* of this thesis. Until now, moss has only been used for monitoring of total element emissions but not for its speciation which is addressed by *study 3* of this thesis.

Trapping volatile metal(loid)s in NaOCl solution was employed and evaluated as a passive sampling technique based on diffusion for geothermal emissions in Yellowstone National Park (Planer-Friedrich and Merkel, 2006). It employs the natural degassing pressure at geothermal features to bubble the emissions through the solution. Due to the oxidizing reaction to trap As, this method is limited to information on total As emissions and the emissions of other elements which are emitted in their reduced form.

Information on volatile arsine speciation can be gained by the use of Solid Phase Micro Extraction fibers (SPMEs) which are passive sampling devices, equipped with different sorption materials, relying on diffusion. Depending on the used materials or material combinations, any As species can be sampled. SPMEs have been applied to sample volatile arsine species from reduced soil in laboratory studies (Killelea and Aldstadt III, 2002) and from geothermal springs at Yellowstone (Kösters et al., 2003; Planer-Friedrich et al., 2006). Arsine species identification was done by injecting the SPME fibers into a gas chromatography coupled to mass spectrometry (GC-MS). Initial gas concentrations can be calculated by the Fick's first diffusion law like it has been done in Planer-Friedrich et al. (2006). However, several factors included in the calculation (e.g. diffusion coefficients) are difficult to measure and assumptions have to be made.

Active sampling techniques mostly require a pump and electricity. This can pose logistic challenges when sampling remote areas like volcanoes.

An often employed technique in volcanic emission monitoring is sampling by "filter packs" which has e.g. been employed on Etna (Calabrese et al., 2011), Stromboli (Allard et al. (2000); both Italy), Kilauea (Hinkley et al. (1999); Hawaii, USA), and Nyiragongo (Calabrese et al. (2014); Democratic Republic of the Congo). Basically, several cellulose filters (e.g. 0.2 µm) are used in a row during pumping of plume gases, particles, and aerosols. The first filter (which can also be made out of Teflon (Calabrese et al., 2014)) is an untreated filter and traps metal(loid)-containing compounds while the other filters are impregnated with an alkaline solution and trap acidic volcanic gases like SO_2, HCl, or HBr (Calabrese et al., 2014). This technique traps several metal(loid)s among others As, but does not preserve their speciation or differentiate between originally particulate and volatile As.

Needle Trap Devices (NTDs) are hollow stainless-steel needles equipped with the same sorption material as SPME fibers on their inner wall (Lord et al., 2010). Until now, NTDs have been applied for volatile organic compounds only (Wang et al., 2005) and have not been employed on arsines, yet which was done for the first time in *study 4* of this thesis. A defined volume of air can be sampled and arsine species are trapped (providing sorption capacity is not reached), making NTDs promising sampling devices. Trapping materials for arsines known from SPME fibers are the absorbing polymers polydimethylsiloxane (PDMS), divinylbenzene (DVB), and the mesh-structured molecule-sieve-like Carboxen (Planer-Friedrich et al., 2006). These sorption materials (among others) can be combined inside a single needle by using 1 cm packing of each material in its tip, with increasing trapping strength from the tip to the end of the NTD.

Silver nitrate traps ($AgNO_3$ traps) were evaluated for arsine sampling by Mestrot et al. (2009). Traps consist of silica gel filled glass tubes fixed with glass wool and are impregnated with silver nitrate. Silver nitrate has long been known to chemo-trap inorganic AsH_3 (Gutzeit method; Sanger and Black (1907)) and has been shown to trap the arsine and the methylarsines ($MeAsH_2$, Me_2AsH, and Me_3As) in a species preserving way (Mestrot et al., 2009). However, this method has only been validated for these four As species.

Cryotrapping in liquid nitrogen (-196°C) is an approved laboratory method to trap all volatile arsines (Feldmann et al., 2001; Ilgen and Huang, 2013) which all have boiling points below liquid nitrogen (section 1.1). However, in remote areas, the permanent availability of liquid nitrogen and its handling can pose logistic challenges.

All techniques mentioned so far enrich the sample during sampling. Tedlar bags, however, can sample different gas volumes but do not enrich the sample. Tedlar bags are made of an inert polyvinyl fluoride (=Tedlar®) and are equipped with a valve for tubing and an additional septum outlet. While all other presented sampling techniques remove matrix gases and only trap the arsines, Tedlar bags keep the arsines in their matrices until analysis. This requires stability of arsines in the respective matrices (section 1.1) which is elucidated in *study 4* of this thesis. Tedlar bag sampling has been applied for arsines in moisturized air before (Haas and Feldmann, 2000), recovering different volatile As species.

1.3 Objectives

The general aim of this PhD thesis was to investigate different active and passive sampling techniques for the determination of total volatile As and its speciation. These techniques (section 1.2) were tested in the laboratory for their arsine trapping and then employed on natural gases like volcanic emissions and biogas.

In summary, the objectives of the 4 studies of the present thesis were to

(1) investigate the emission and distribution patterns of As on Vulcano (Italy) and to compare them with other elements to elucidate the elements' origin and their potential way of distribution (*study 1*: Arndt et al. (2014)).

(2) study the element distribution patterns on 3 open conduit and 3 hydrothermal volcanoes (section 2), to reveal similarities between element distributions on open conduit and hydrothermal volcanoes, and to evaluate the moss monitoring technique for application on volcanoes concerning exposure height above ground, the usage of different moss types, coverage, and exposure duration (*study 2*: Arndt et al. (2017a)).

(3) determine the mosses' As species preserving trapping ability to gain additional information on volatile As speciation using moss monitoring and thus to elucidate its origin and potentially occurring processes in biogases and volcanic gases (*study 3*: Arndt and Planer-Friedrich (2018)).

(4) evaluate As species preserving sampling techniques like cryotrapping, NTDs, and Tedlar bags, to develop an As species preserving sampling technique for volcanic gases using Tedlar bags, and to investigate the stability of arsines in the presence of volcanic gases like O_2, CO_2, SO_2, and H_2S in comparison to N_2 (*study 4*: Arndt et al. (2017b)).

2 STUDY AREAS

2.1 Volcanoes

In the following, the studied volcanic areas Vulcano, Stromboli, Solfatara (all in Italy), and Yellowstone National Park (USA) are introduced briefly including their geology, volcanic activity, and known emissions, especially for As. In addition to these volcanoes, moss monitoring was also conducted on the volcanoes Nisyros (Greece) and Nyiragongo (Democratic Republic of the Congo) by Walter D'Alessandro and Sergio Calabrese. The results of their work and information on these volcanoes are published in *study 2*. For additional information on these two volcanoes the publications D'Alessandro et al. (2013) (Nisyros) and Calabrese et al. (2014) (Nyiragongo) and references therein are recommended.

2.1.1 Vulcano

Vulcano Island is the southernmost Island of the Aeolian Arc in the Tyrrhenian Sea north of Sicily (Italy). It developed due to the subduction of the African plate underneath the Eurasian one (Barberi et al., 1974) about 120,000 years ago (Pichler, 1981). Since Vulcano's last eruption in 1888, its most prominent feature is the 500 × 700 m wide crater of La Fossa. Today, Vulcano's activity consists of a passive degassing fumarolic field on the northern inner flank of the crater rim and some degassing at the harbor area and the harbor bay. Major gases emitted from the fumaroles are water vapor, CO_2, SO_2, H_2S, halogens, and NH_3, as well as trace elements like As (Signorelli et al., 1998). Emitted As has been investigated on Vulcano by condensate and sublimate sampling with subsequent modelling (Cheynet et al., 2000), postulating $AsCl_3$ to be the most frequent volatile As species, and by condensate sampling only, resulting in highest As concentrations on Vulcano compared to other volcanoes like Kilauea (Hawaii, USA), Teide (Canary Islands, Spain), and Stromboli (Italy; Signorelli (1997)).

During this PhD project, emissions from Vulcano were studied several times using different techniques. Vulcano was studied along a transect through the fumarolic field with 7 monitoring sites in 2013 using moss bags and active pumping with $AgNO_3$ traps, which were both analyzed for the volatile elements As, Sb, Se, Bi, and Tl, defined in *study 1*. The transect comprises one station in wind direction in front of the fumaroles, 2 stations within the fumarolic field, and 4 stations downwind of the fumaroles. Furthermore, in 2015, 2 triplicate moss bags were exposed for volatile As speciation monitoring within the fumarolic field and Tedlar bag sampling was done at 3 stations within the fumarolic field, at 2 stations downwind of the fumaroles, and at one station at the harbor.

2.1.2 Stromboli

Stromboli is the most northeastern Island of the Aeolian Islands (Italy) and characterized by the 924 m high basaltic stratovolcano of the same name. Its crater at 750 m height shows typical strombolian eruptions of lava, ash, and steam several times per hour. Trace elements have been investigated by rain water analysis in Stromboli town with As concentrations below the WHO threshold of 10 $\mu g \cdot L^{-1}$ (Madonia et al., 2013; WHO, 2011) and by filter sampling from the plume with As concentrations being as high as 3 $\mu g \cdot m^{-3}$ (Allard et al., 2000).

Until now, simultaneous monitoring of As and other trace element emissions in town and at the crater has not been conducted. In this PhD project, trace element emissions were monitored in spring 2013 for 3 weeks using triplicate moss bags at 10 stations in Stromboli town, on the way up to the crater, and at the crater. Additionally, soil and ash samples were taken at all sampling stations.

2.1.3 Solfatara

Solfatara is the most known geothermally active area of the Phlegraean Fields near Pozzuoli west of Naples, Italy. Beneath it, a 35,000 year old 12 km wide caldera is situated (Barberi et al., 1985) which is responsible for the Campanian Ignimbrite distributed in the whole Mediterranean area about 39,280 ± 110 years ago (Fedele et al., 2013). Emissions from the fumaroles at Solfatara are known to contain mainly water vapor, CO_2, and H_2S (Carapezza et al., 1984). Arsenic occurs in mineral precipitates at the vents like realgar (As_4S_4; Russo (2004)) and is thus known to be emitted, but volatile As has not been measured yet. During this PhD project, volatile arsines were sampled from three stations (big and small fumarole, and “sauna”) in triplicates using Tedlar bags.

2.1.4 Yellowstone National Park

The Yellowstone National Park (Wyoming, USA) is the caldera of the Yellowstone hotspot whose last eruption was 630,000 years ago. Today, the park hosts several geothermal features like hot springs, geysers, mudpots, geothermally influenced wetlands, and fumaroles. Waters in the park are known to contain high concentrations of As (Ball et al., 2002) and degassing of As and other trace elements is known to occur from several features (Planer-Friedrich and Merkel, 2006). Volatile As speciation has been estimated by passive sampling using SPME fibers and subsequent calculation using the Fick’s diffusion law (Planer-Friedrich et al., 2006), revealing the most frequent species to be Me_2AsCl besides Me_3As, Me_2AsSMe, and $MeAsCl_2$.

During this PhD project, several geothermal features of Yellowstone were sampled by moss monitoring (2013) and by active and passive sampling with $AgNO_3$ traps (2013 and 2014, respectively). Mudpots, hot springs, fumaroles, and geothermally influenced wetlands were sampled in the geothermal areas Norris Geyser Basin, Nymph Lake, West Nymph Creek Thermal Area, Gibbon Geyser Basin, and Lower Geyser Basin.

2.2 Biogas and wastewater treatment plants

The abundance and importance of biogas plants increased during the last years due to the production of renewable energy. Inside biogas plants, the reducing conditions, temperature, and nutrient supply present not only the optimum for microbial methane (CH_4) production but also for microbial production of methylated and hydrated metal(loid)s like arsines (section 1.1). Arsenic has already been shown to be contained in biogas besides the major gases CH_4, CO_2, and water vapor (Mestrot et al., 2013b).

Biogas samples were taken at one wastewater treatment plant and 2 different biogas plants near Bayreuth. Gas samples were taken from the top of the fermenter at the wastewater treatment plant. Gas samples from the pipes conducting the gas from the fermenter to the thermal power station were taken at the wastewater treatment plant and both biogas plants. One biogas plant, combusting mainly corn and grass silage, manure, and bruised grain, was used for moss monitoring inside the fermentation hall while the other 2 plants were sampled for their sludge to conduct incubation experiments with subsequent gas analysis.

3 METHODS

3.1 Generation of volatile arsine standards

For laboratory experiments and calibration standards, a gas mixture of 100 ng·L^{-1} per species of AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As was generated according to Ilgen and Huang (2013). Basically, the oxyanions and acids arsenite, monomethylarsonic acid, dimethylarsinic acid, and trimethylarsine oxide were dissolved in 5 mL 1 M H_3PO_4, before adding 3% $NaBH_4$ in 1% NaOH to volatilize them. Volatilized arsines were conducted through a NaOH trap to remove water vapor before entering a Tedlar bag. This generated gas was used in different dilutions for sampling with NTDs, for Tedlar bag experiments, and for calibration standards for analysis. For moss exposure experiments, each volatile As species was generated individually in a final concentrations of 10 µg·L^{-1} in a 1 L Tedlar bag.

3.2 Moss monitoring

3.2.1 Moss

Different species of Sphagnum moss were used for monitoring the different volcanoes: On Vulcano and Stromboli, *S. palustre* collected from a forest near Bayreuth was used, while for Nisyros and Nyiragongo a mixture of S. *tenellum, S. subsecundum, S. cuspidate, S. girgensonii,* and *S. fallax* collected at the "Schlöppnerbrunnen" in the Fichtel Mountains near Bayreuth was used. In Yellowstone, *S. palustre* (collected from a forest near Bayreuth) and commercial *S. palustre* (from Chile) were used for monitoring and comparison. These moss types differed by their shoot density. For monitoring biogas plants and for laboratory tests, the *Sphagnum* mixture from "Schlöppnerbrunnen" was used. Prior to monitoring, all mosses were cleaned from dirt particles, washed 3 times with deionized ultrapure water (MQ), dried in the drying oven at 40°C, and kept in closed plastic bags until further usage.

3.2.2 Set-up

For monitoring the volcanoes and biogas plants, 2 g of moss was packed in spherical bags with a diameter of approximately 7 cm using commercially 0.8-2 mm mesh mosquito nets. On the volcanoes, moss bags were tied to wooden sticks using nylon wire. They were exposed covered (Yellowstone), uncovered (Stromboli, Nisyros, Vulcano), or in both ways (Nyiragongo). Height above ground was chosen to be 1.6 m for most volcanoes except Vulcano Island, where moss bags were set up at 5 heights between 0.7 and 1.6 m above ground (Figure 2), and in Yellowstone where moss bags also were exposed below 1.6 m. Volcanoes were monitored for up to 12 weeks (*study 4*). For moss monitoring in the fermentation hall of the biogas plant, triplicate moss bags were exposed covered at the ceiling of the fermentation hall two times for a month each. After monitoring the volcanoes or biogas plants, the moss bags were recollected, sealed in plastic bags, and transported back to the laboratory.

Volatile As species preservation on the mosses was evaluated in the laboratory before testing natural samples. Therefore, 0.2 g moss was weighted into Schott bottles under N_2 atmosphere and 100 mL N_2 were replaced by 100 mL of individually generated volatile arsine species (10 µg·L^{-1}; section 3.1). Experiments were done in 5 replicates for all 4 arsine species at 5°C, and additionally for Me_2AsH at -20 and -80°C, and for $MeAsH_2$ at +45 and +80°C. After 10 days, the moss was removed and analyzed half for total As concentration, half for As speciation.

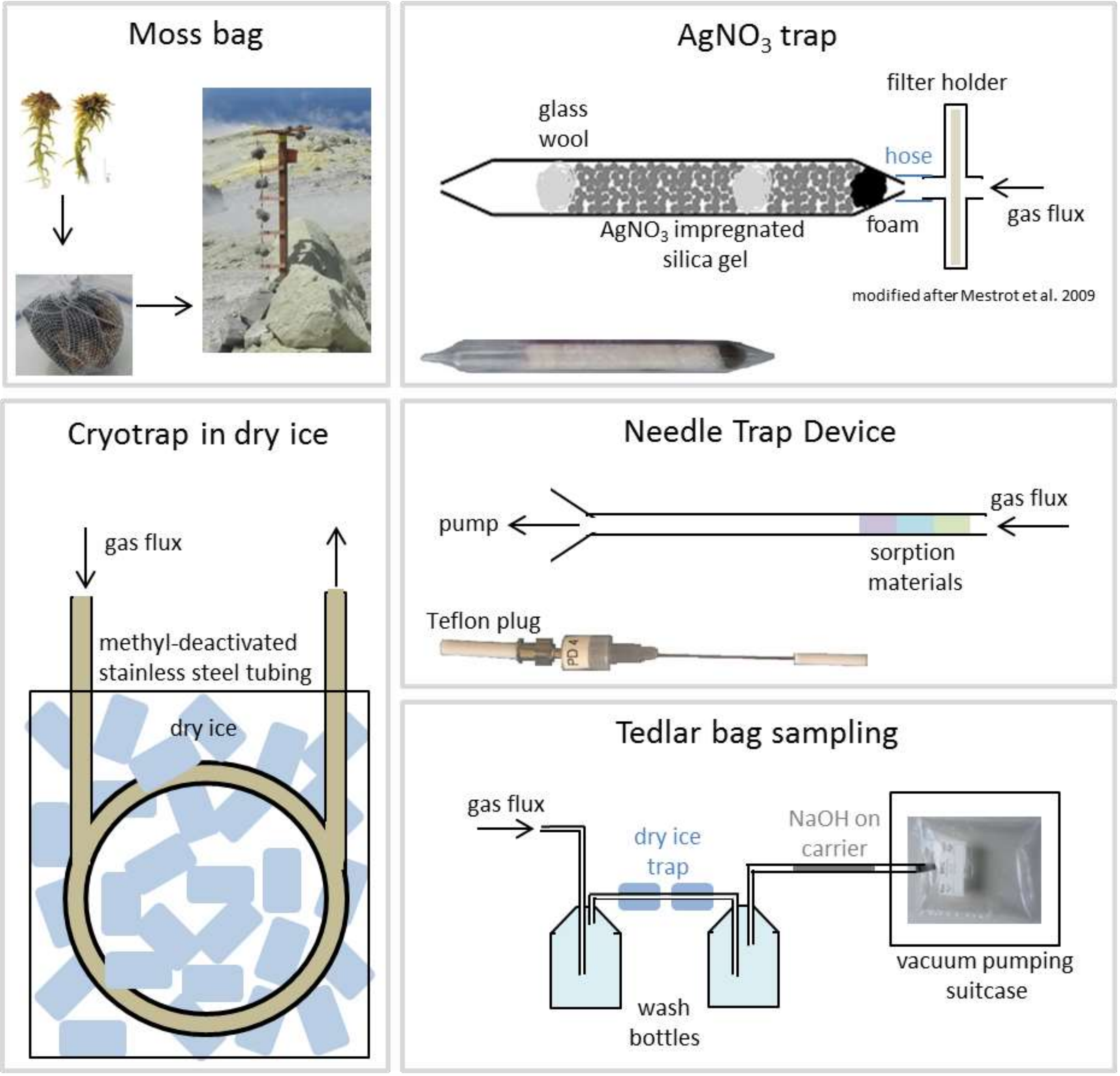

Figure 2: Overview of applied and evaluated sampling techniques: Moss bag monitoring, Cryotrapping, silver nitrate traps, Needle Trap Devices, and Tedlar bag sampling.

3.2.3 Analysis of moss for total element concentrations

Moss bags were unpacked, dried in the drying oven (40°C), ground, and 0.1 g of moss was digested in the microwave using 10 mL of 6% H_2O_2 in 19.5% HNO_3. Digests were filled to 25 mL with MQ, filtered (0.2 µm), and analyzed by quadrupole inductively coupled plasma mass spectrometry (ICP-MS; X-series2, Thermo Fisher) and by ICP with optical emission spectrometry (ICP-OES, Varian) for the elements As, Li, Mg, S, Cr, Fe, Co, Se, Sr, Mo, Sb, Ba, I, Tl, Pb, and Bi for all volcanoes. Moss exposed to biogas was analyzed for As only. To avoid polyatomic interferences standard-mode (Li, Mg, Mo, Sr, Sb, Ba, I, W, Tl, Pb, and Bi), kinetic energy discrimination (2 V, collision gas: 93% He with 7% H_2, for Cr, Co, Se, and Fe), and O_2 mode (reaction gas: 10% O_2 in He; for As and S) were used. Analysis of certified reference materials (TMDA-54.4 and 54.5) and spiked samples were added as quality control for analyses since 2015. Internal standards (Rh and Re; each 50 $\mu g \cdot L^{-1}$ per sample) and a repeatedly analyzed calibration standard were used for instrumental drift correction in every measuring sequence.

For better comparison of results from these passive sampling devices, accumulation rates were calculated per exposure time and weight of the moss ($\mu mol \cdot [g \cdot d]^{-1}$) for all elements on every moss.

3.2.4 As speciation analysis of moss samples

Species extraction of the moss was done for the As species arsenate, monomethylarsonic acid, dimethylarsininc acid, and trimethylarsine oxide which are the successors of the volatile arsine species AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As. Therefore, 0.1 g dried powdered moss was extracted in 10 mL 0.1 M HNO_3 in 3% H_2O_2 at 90°C for 90 min in a heating block, shaking every 30 min. H_2O_2 was added to completely oxidize arsenite to arsenate which otherwise would be indistinguishable to trimethylarsine oxide, due to very similar retention times (2.46 and 2.56 min for arsenite and trimethylarsine oxide, respectively). The used extraction technique is known to preserve arsenate, monomethylarsonic acid, and dimethylarsinic acid (e.g. from rice extraction; DIN-EN-16802 (2016)) and was tested for trimethylarsine oxide preservation before employing it on the mosses. It yielded recoveries between 105 and 107% for trimethylarsine oxide and was thus used for species preserving extraction of the mosses (*study 3*).

After extraction, solutions were filled to 10 mL with MQ, filtered (0.45 µm) and analyzed by ion chromatography (IC; ICS 3000 SP, Dionex) coupled to ICP-MS. IC was equipped with a PRP-X100 column (Hamilton) and used with an isocratic 1 $mL \cdot min^{-1}$ flow of 20 mM $NH_4H_2PO_4$ at pH 5.6, analogue to DIN-EN-16802 (2016).

3.3 Silver nitrate traps ($AgNO_3$ traps)

For preparation, the 7 cm long silica gel traps (SKC Inc., USA; Figure 2) were opened at both ends, impregnated with 1% $AgNO_3$ solution (Uroic et al., 2009), flushed with N_2, oven dried, and kept sealed with parafilm® in aluminum foil until application.

Traps were tested in the laboratory for their sensitivity to water vapor and H_2S influence on their trapping ability by exposure to one of these gases until they were either wet (water vapor) or black (due to AgS formation from H_2S exposure) before exposing them to freshly generated AsH_3. Between 5 and 50 ppb, AsH_3 trapping results were slightly lower than the ones of traps without prior water vapor exposure (85±7%), while for pre-exposure with H_2S, trapping even was increased slightly (up to 120%). These differences can also be based on analytical errors or upscaling during calculations. However, in volcanic gases, both gases exist which have oppositional effects on AsH_3 trapping. Despite these disadvantages, $AgNO_3$ traps were tested for sampling volcanic gases. In the field, traps were set up as active or passive samplers for species-preserving trapping.

Active sampling was used on Vulcano and at selected geothermal emission sources in Yellowstone (both 2013). Pumps (sera air 275 R plus, sera GmbH, Heinsberg, Germany) were mounted behind the $AgNO_3$ traps with cellulose filters in front of the traps (pore diameter: 2-3 µm; Rotilabo®, Germany) to distinguish between particles and volatile As species (Figure 2). Pump flow was adjusted to 1 $mL\cdot min^{-1}$ using a flowmeter (B-752, Porter Instrument Company, Hatfield, USA). Sampling durations and thus sampling volumes were adapted to visual emission strength between 100 and 460 L. Passive sampling with $AgNO_3$ traps was employed at selected sampling sites in Yellowstone 2014, exposing triplicates of $AgNO_3$ traps 1 m above the emission sources (see section 2.1.4). Traps were exposed for up to 30 days and shielded from rain by plastic beakers tied upside down to wooden sticks.

After sampling, all traps were sealed with parafilm® at their ends, wrapped in aluminum foil and sealed in plastic bags for transportation back to the laboratory. Filter papers were removed from the filter holders, folded in order not to remove particles from the filters and sealed in plastic bags, too. In the laboratory, traps were cut open and the silica gel was removed and homogenized. Half of it was used for total As analysis and the other half for As speciation. For total As analysis, silica gel was digested in the microwave in 19.5% HNO_3 and analyzed by ICP-MS (see section 3.2.3). For speciation, the silica gel was extracted in the microwave using 1% HNO_3, and analyzed by IC-ICP-MS (see section 3.2.4). Filters were cut in half and digested/extracted, and analyzed the same way as the silica gel. Concentrations of As were calculated per gram silica gel/filter and for active sampling also per sampled air volume.

3.4 Cryotrapping

Cryotrapping in liquid nitrogen (-196°C) is routinely applied to trap all volatile arsines for sample enrichment immediately before analysis (Feldmann et al., 1994; Ilgen and Huang, 2013). It was used as reference method to all other methods in this study and for analysis. For field use, especially in remote areas, it is rather impractical due to the necessity of liquid nitrogen availability and its difficult transport. Thus, dry ice (-78°C) was tested as a potential field applicable cooling agent for its arsine trapping efficiency using winded 1.2 m or 2.5 m long uncoated methyl-deactivated stainless steel tubing (Chrompack ultimetal tubing, inner diameter: 0.53 mm) immersed in dry ice (Figure 2). The arsine mix was conducted through the tubing for cryotrapping (5-10 $mL \cdot min^{-1}$) which was analyzed immediately after trapping by gas chromatography (section 3.6.2).

3.5 Needle Trap Devices (NTDs)

3.5.1 Sampling

Before sampling, Needle Trap Devices (NTDs) were heated in the GC injector for 15 minutes at 280°C minimum to remove potentially sorbed substances. Loading with volatile arsines was done by attaching the NTDs to a pump (Peli Products S.L.U.) and pumping a 50 $ng \cdot L^{-1}$ arsine mixture from the Tedlar bag through the NTDs (5 $mL \cdot min^{-1}$). The NTDs' inner walls are impregnated with different sorption materials and mixtures of them (compare section 1.2 and Figure 2) by the manufacturer. In this study, the sorption materials PDMS (abbreviated "P" in the following), DVB ("D"), and Carboxen 100 ("C"), which are known to trap arsines (Planer-Friedrich et al., 2006) were used. Additionally, Carbopack X ("X"), an adsorbing graphited carbon, was employed. NTDs were also tested on Vulcano for active sampling of fumarolic emissions by pumping and as passive sampling devices attaching them to wooden sampling poles for 24 h inside the fumarolic field.

3.5.2 Analysis of volatile As species from NTDs

For gas analysis, NTDs were injected in the gas chromatograph (injector equipped with a SPME liner heated to 220-280°C) and samples were inserted directly onto the column. Gas analysis was conducted according to Ilgen and Huang (2013). In short, volatile arsine species were separated chromatographically (30 m capillary column, 0.32 mm inner diameter, 4 µm film thickness; Rxi-1MS, Restek, USA). Then the sample was spilt and arsine species were detected by (a) electron impact mass spectrometry for molecule fragments (GC-EI-MS) and by (b) atomic fluorescence spectroscopy for total As (AFS). In some cases, an ICP-MS was used instead of the AFS (*study 4*). The gaseous calibration standards in N_2 matrix were inserted via cryotrapping and cryofocussing (see section 3.6.2).

3.6 Tedlar bags

3.6.1 Sampling set-up

Tedlar bags were used for stability experiments of volatile As species and for sampling fumarolic gases from Vulcano and Solfatara, Italy (*study 4*), and biogas.

Stability experiments were conducted over a duration of 21 days with a mixture of 2 ng·L^{-1} per As species (AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As) in the matrices of dry N_2, 3800 ppm$_V$ CO_2, 20% O_2, 100 ppm$_V$ SO_2, and H_2S. The 5 L Tedlar bags were kept at 5°C in the dark and only taken out of the refrigerator for triplicate analyzes (20 min each, at room temperature).

For fumarolic gas sampling, the 10 L Tedlar bags were placed in a vacuum pumping suitcase (SKC, Analyt-MTC, Germany). Dilution by air was minimized by placing a funnel approximately 50 cm above the fumaroles. The gas was conducted by a fluorinated ethylene propylene hose (FEP; Rotilabo®, Germany) first through one silanized glass wash bottle (used as water traps), then twice trough a dry ice cooling trap (-78°C), again through a wash bottle and finally through a NaOH trap into the Tedlar bag (Figure 2). The traps were used to remove water vapor (cooling and water traps), SO_2, H_2S, and CO_2 (NaOH trap) before entering the Tedlar bag. This is important as they would (a) destabilize the arsines in the sample and (b) freeze during cryotrapping in liquid nitrogen (-196°C) before analysis, causing blockage and disturb chromatographic As species separation (see section 3.5.2). In case of strong degassing activity, two consecutive NaOH traps were used.

Biogas samples were taken from the pipes in the wastewater treatment plant and biogas plants by using either the usual slight over-pressure in the pipes or the vacuum pumping suitcase (see section 2.2).

3.6.2 Analysis by CT-CF-GC-EI-MS/AFS

Samples from Tedlar bags (as well as calibration standards) were analyzed using the cryotrapping cryofocussing (CT-CF) system in front of the GC-EI-MS/AFS. For analysis, several trace and matrix gases like water vapor, H_2S, SO_2, CO_2, CH_4, and O_2 were eliminated due to their negative influence on either cryotrapping or chromatographic separation. To remove potential water vapor, sulfur gases, and CO_2 contained in natural samples, all samples and the calibration standards were conducted through a NaOH trap before cryotrapping in liquid argon (Ar, -183°C) which does not trap O_2. However, CH_4 was still trapped. To decrease the CH_4 concentration which would freeze in the traps and disturb chromatographic separation, biogas samples were diluted at least 1:10 before analysis. Calibration standards were prepared in dry N_2 for volcanic samples and in 6% CO_2 and 4% CH_4 mixture (rest: N_2; Riessner Gase, Germany) for biogas samples.

4 RESULTS AND DISCUSSION

4.1 Total emission monitoring of As and other elements

4.1.1 Moss bag monitoring on several volcanoes

4.1.1.1 Vulcano (study 1)

In this study, fumarolic emissions were monitored across the whole island of Vulcano (Arndt, 2012, unpublished) and along a transect through the fumarolic field (*study 1*). Moss monitoring showed accumulation of major elements like Mg, S, and Fe (up to 800,000 nmol·(g·d)$^{-1}$ at the crater stations), minor elements like Sr, Ba, Li, V, Cr, Se, and As, and trace elements like Co, Mo, I, W, Sb, Tl, Pb, and Bi (down to 0.01 nmol·(g·d)$^{-1}$ at the background stations) on the moss. Highest As accumulation on the moss was found at a station in the fumaroles (670 nmol·(g·d)$^{-1}$). Total element accumulation was not comparable between different monitoring periods (2012 and 2013) due to potential emission variations, weather (wind and precipitation) differences, and monitoring differences, but distribution patterns and rates could be compared.

Element distribution patterns of normalized accumulation rates per day revealed different element sources and kinds of distribution across the island (*study 1*): Clustering the elements enabled discrimination between volatile elements from the fumaroles (S, As, Sb, Se, Tl, Bi, and I), particulate soil-borne elements (Fe, Co, Pb, Cr, Mo, W, and Ba) predominantly from the crater, and sea-spray-borne elements (Mg, Sr, and Li).

Along the transect, highest As accumulation on the moss bags was found in the fumarolic field. The elements S, Sb, Se, Tl, and Bi also showed a clear peak at their emission source (i.e. the fumaroles) and, like As, decreased in wind direction with increasing distance from the fumaroles. Additionally, transect topography on the downwind side of the fumaroles with first a valley and then a hill was obvious in their distribution patterns: Accumulation rates decreased in the valley and increased on the hill again. The reason for this is transportation of the fumarolic As and other trace elements by wind over the valley to the next hill. Due to their distribution, these elements were defined as *volatile* emissions from the fumaroles (*study 1*). In contrast to fumarolic elements, soil-borne non-volatile elements like Fe, Co, and V had a continuous source and were distributed equally along the monitored transect with increasing accumulation at moss bags at the more wind exposed site at the end of the transect. The same was true for the sea spray-borne elements Li, Mg, and Sr. The distribution was even more continuous for the elements Pb, Cr, Mo, and Ba.

The elements grouped as volatiles from the fumaroles are known to occur in geothermal emissions: S, As, Sb, I, and Se have been detected in several studies (Aiuppa et al., 2005a; Aiuppa et al., 2005b;

D'Alessandro et al., 2013; Hirner et al., 1998; Planer-Friedrich and Merkel, 2006) and Tl has been postulated to occur on Vulcano as a volatile before (Cheynet et al., 2000). Differentiating between the fumarolic elements, As distribution patterns differ from iodine, which shows almost equally high accumulation rates at the monitoring stations in wind direction behind the fumaroles due to (a) the formation of halogen-metal(loid)-compounds (Cheynet et al., 2000), (b) its additional emission as hydrogen acid (Aiuppa et al., 2005a), and (c) its presence in sea water (Preedy et al., 2009) and thus in sea spray. Arsenic showed a similar distribution along the transect like Sb and S, to whom its chemical similarities and affinities are known: Arsenic is known to form thio-complexes in geothermal S-rich waters (Planer-Friedrich et al., 2007) which has also been shown for Sb (Planer-Friedrich and Scheinost, 2011) and even in the gas phase for As (Planer-Friedrich et al., 2006).

Consequently, moss monitoring as screening over the whole island and along a transect identified As to be emitted (among other elements) as a volatile on Vulcano.

4.1.1.2 Stromboli (study 2)

Moss monitoring on Stromboli was conducted in Stromboli town and on the way up to the crater. In parallel, soil and (if present) ash samples were taken from every monitoring station and analyzed for the metal(loid) elements grouped fumarolic in *study 1*.

In the moss, highest accumulation rates were found for the major elements Mg, Fe, and S (maximum 15,000 nmol·$(g\cdot d)^{-1}$) while concentrations of some trace elements were close to detection limits. Arsenic concentration was between 9.3 nmol·$(g\cdot d)^{-1}$ and 0.5 nmol·$(g\cdot d)^{-1}$ (crater and town, respectively). Most elements also had their maximum accumulations at the crater stations (Fe, Sr, Ba, Li, V, Cr, Co, Se, Mo, I, W, Tl, Pb, Bi, and As). This clearly defines the crater with its strombolian activity and emission of gases, lava, and ash as their origin. Only Sb was accumulated maximal in town. Sb is known to be emitted by traffic (Johansson et al., 2009) and was even detectable when monitoring marine particulate matter from a ship in the Mediterranean (Moreno et al., 2010). Thus, it can be concluded that Sb is emitted anthropogenically on Stromboli.

Distribution patterns of Pb, Fe, Co, Cr, and Ba (which were defined soil-borne on Vulcano (*study 1*) or refractory elements on Etna (Calabrese et al., 2015)) correlated with those of volatile elements like As. The reason for this difference to Vulcano is the additional emission of ash and lava which also occurs on Etna.

Arsenic was enriched in every soil sample more than two orders of magnitude compared to Sb, Se, Tl, or Bi (up to 65 µg·g^{-1} vs. maximum 0.8 µg·g^{-1} for the other elements). Its maximum accumulation in the moss was found at the crater while its maximum concentration in the soil was found further downhill at the hiking path up to the crater where plants were sketchy (*study 2*). This pattern also was found for Se, Tl, and Bi. The additional analysis of soil confirmed moss monitoring results. Based on these samples it can be said that As and the other elements are emitted at the crater and deposited as a particle further downhill. Antimony was the only volatile element for which moss and soil samples both had maximum concentrations at stations in town, confirming its anthropogenic origin.

In summary, moss monitoring results on Stromboli revealed several similarities of element distribution on Stromboli and Vulcano (like As being volatile), but also differences due to different volcanic activity.

4.1.1.3 Nisyros (study 2)

Moss monitoring showed highest As accumulation rates at Stefanos crater, which was 2 orders of magnitude higher than at the other 2 main fumarolic areas of Nisyros (3.8 nmol·(g·d)$^{-1}$). Most of the other monitored elements (Fe, Li, Co, Sr, Ba, S, Sb, Tl, and Bi) also were detected in their highest accumulations at this crater. The elements Se, Cr, Pb, and Mo were maximally accumulated at Polybotes crater (0.7, 4.5, 0.2, and 0.08 nmol·(g·d)$^{-1}$, respectively) while all element accumulations at Kaminakia crater were lower than at the other vents. The only two elements with higher accumulations at the background site were Sb and Co, which are both known from traffic emissions like brake ware abrasion and metal alloys (Johansson et al., 2009).

4.1.1.4 Nyiragongo (study 2)

At Nyiragongo, As, like all other monitored elements, was found in highest accumulation rates at the stations in wind direction from the plume at the crater rim compared to two downwind stations up to 12 km away (up to 3 nmol·(g·d)$^{-1}$; *study 2*). This clearly identifies the crater with its active lava lake and continuous degassing as the main source for all the elements monitored.

4.1.1.5 Yellowstone (study 2)

In Yellowstone, the commercial *Sphagnum palustre* was used for different geothermal features for As, Sb, Tl, and Bi emission only (section 3.2.1). Tl and Bi accumulations on the moss bags were below analytical detection limits at nearly all features (Hofmann, 2014, unpublished). Sb and As accumulations were close to field blanks at some monitored stations. At several features like the fumaroles at Nymph Lake or Conch Spring, however, As accumulation was significantly higher than at background sites, revealing that emission can have an effect on the geothermal features' immediate surrounding. In general, hot springs showed the highest mean As accumulation rates throughout the whole park, followed by fumaroles (0.82 nmol·(g·d)$^{-1}$ and 0.66 nmol·(g·d)$^{-1}$, respectively). Direct monitoring of the geothermal features contradicts monitoring of indigenous mosses and lichens

(Bennett and Wetmore, 1999) in Yellowstone National Park which concluded trace element emission to be negligible by monitoring background sites only.

In addition to emission screening, the difference between two types of mosses for monitoring was evaluated using As and Sb accumulation on the moss bags at three different features in Yellowstone (results see section 4.1.2, “Different moss”).

4.1.1.6 Comparison of different volcanoes by moss monitoring (study 2)

All the monitoring campaigns of the volcanoes presented above differ in the moss bags’ closest distance to the emission sources with distances of 1 m minimum for Vulcano, Nisyros, and Yellowstone and more than 100 m for Stromboli, Etna, and Nyiragongo due to accessibility.

On all volcanoes, the monitored elements were accumulated in larger concentrations than were found for the moss blanks with lowest differences on Nisyros and highest on Etna. The trace elements As and Se were even accumulated up to 5 and 4 orders of magnitude more in the fumarolic field on Vulcano (monitoring 2013) than at background sites. All of the volcanoes are frequented tourist destinations. Both elements are most toxic in their volatile form (Pakulska and Czerczak, 2006) and can thus affect tourists’ health.

Distribution patterns and emission sources were compared for all elements on every volcano. The elements As, S, and Se had their maximum accumulations in moss bags exposed at their emission sources (i.e. the fumaroles or craters) and distributed in downwind direction. This was observed on Vulcano and Etna before (*study 1* and Calabrese et al. (2015)), assigning these elements as volatiles emitted by the fumaroles. At the open conduit volcanoes Etna and Stromboli, As, Se, and S also correlated with Pb and Fe. Both elements have been shown to originate from bare soil on Vulcano (*study 1*) and were grouped as silica-related elements on Etna (Calabrese et al., 2015). Stromboli and Etna emit lava, ash, and gases, resulting in correlation of Pb and Fe with the volatile elements. This is not the case for the open conduit volcano Nyiragongo, which is less explosive due to its different geology (*study 2*). The elements Fe, Ba, and Sr correlated on all volcanoes except for Nisyros and the transect monitoring on Vulcano 2013. Their origin is bare soil (*study 1*), which on Nisyros and during the Vulcano 2013 transect monitoring consisted more of solid stone rather than of soil and ash particles which could be re-suspended by wind.

The open conduit volcanoes Etna and Stromboli show more similarities to each other than to Nyiragongo. There are two reasons for this: (a) the different geological settings which lead to less fractionated, more alkaline magma, and less explosive activity at Nyiragongo at the diverging African Rift Zone and (b) more rainfall and thus more deposition (see section 4.1.2, “Coverage”) at Nyiragongo compared to Stromboli and Etna. The monitored hydrothermal volcanoes also show some differences: Vulcano showed higher element accumulation rates and thus higher emission strength than Nisyros and Yellowstone. Low accumulation results in Yellowstone can originate from the different type of moss we used (section 4.1.2). Apart from monitoring differences, volcanic differences are that Yellowstone and Nisyros are in solfataric state with temperatures around or below 100°C while Vulcano has a high-temperature fumarolic field with temperatures up to 400°C (Paonita et al., 2013).

In general, many variables can influence moss monitoring of volcanoes like the geological setting, volcanic activity, climate and weather including rain and wind, the accessibility of the emission sources for monitoring, and finally the setup of the monitoring stations. However, a statement about the potential effect on tourists' health at the accessible sites, similar element distribution patterns, and element sources is possible. Moss bags can further be used as preliminary screening technique before employing highly sophisticated or species preserving sampling techniques.

4.1.2 Evaluation of the moss bag monitoring technique for volcanic areas (study 2)

During the monitoring campaigns on the volcanoes (see section 4.1.1), several factors influenced the monitoring results. Some factors like exposure height were already observed by studies monitoring anthropogenic emissions and a standard protocol was postulated for monitoring them (Ares et al. (2014) and references therein). However, volcanoes differ strongly from urban areas by their emission, and their surface influencing distribution. In this part of the study, the factors moss exposure height above ground, exposure duration, coverage and non-coverage, and the use of different types of moss were investigated.

The exposure in different heights above ground was evaluated on Vulcano (2013) along the transect through the fumarolic field (section 2.1.1). Moss bags exposed in triplicates at the heights of 0.7, 1.0, 1.2, and 1.5 m in general showed the same element distribution patterns along the transect as those exposed at 1.6 m (section 4.1.1.1) for elements emitted from the fumaroles like As: At all heights, maximum concentrations were found within the fumaroles, decreasing with increasing distance and reflecting the transect morphology with lower accumulations in the valley and higher ones on the hill downwind of the fumaroles. Accumulation rates showed no significant differences between the different exposure heights (Kruskal-Wallis test). At most stations, standard deviations of triplicates per height were larger than differences between the exposure heights. The independence of monitoring height on volcanoes is in line with the results of height evaluation in towns (Ares et al. (2014) and references therein). In big cities like Naples, however, "street canyons" are common which channel local winds and thus element distribution and make exposed moss bags yield different results depending on height (Adamo et al., 2011). Monitoring volcanoes like Vulcano without channeled element distribution by huge barriers is not dependent on monitoring height. Moss bags can be tied to available sticks and rocks between 0.7 m and 1.6 m height above ground which simplifies monitoring remote volcanoes. The use of moss bag triplicates at the same height is recommended as their accumulation variation is even larger than between different heights.

Different moss types of the same species *S. palustre* (section 3.2.1) were employed for monitoring 3 geothermal, degassing features in Yellowstone: one mudpot, a wetland, and a hot spring. The purchased moss (Chile) had a higher specific shoot density and thus a smaller potential element accumulation surface than the collected moss (Germany). At all sites, As and Sb accumulations were significantly lower for the moss from Chile (ANOVA, $p<0.001$) with differences up to 65%. Standardization of moss monitoring using the same moss has already been postulated by others before (Ares et al., 2012; Di Palma et al., 2016). In this study, the intra-species differences show that inter-comparison of different studies using different mosses is almost impossible and standardization would eliminate the problem.

Moss exposure duration was evaluated at 3 stations within the fumarolic field on Vulcano (2012) for durations from 3 days up to 9 weeks. Since S was accumulated in much larger amounts than As (maximum of 26,000 $\text{nmol}\cdot(\text{g}\cdot\text{d})^{-1}$ vs. 230 $\text{nmol}\cdot(\text{g}\cdot\text{d})^{-1}$, respectively) but was also classified as volatile element (*study 1*), exposure duration was evaluated for S. Sulfur accumulation increased linearly from 3 days to 3, 6, and 9 weeks with faster accumulation at the beginning of exposure. For anthropogenic emission monitoring, a minimum exposure time of 6 weeks was recommended (Capozzi et al., 2016). Our results show, that (a) accumulation can already be monitored after 3 weeks and (b) loading capacity is not exhausted after 9 weeks. Consequently, we recommend minimum exposure durations of 3 weeks for areas with a visible strong degassing activity and a longer exposure for areas with lower degassing or for background sites. Also, areas with temporally limited access profit from variability in moss exposure duration and their large accumulation capacity.

Coverage of moss bags was evaluated on Vulcano (monitoring 2012, *study 1*), Etna (monitoring campaign of Calabrese et al. (2015)), and Nyiragongo. These volcanoes differed in rain intensity during the monitoring period: There was no rain on Etna, some on Vulcano, and daily rain at Nyiragongo. In general, element distribution patterns were independent of coverage or non-coverage on all volcanoes and element concentrations were approximately 1 order of magnitude larger in uncovered moss bags on all volcanoes. Rain water chemistry monitoring on Vulcano showed comparable element distributions to moss bag monitoring. Thus, rain deposition did not lead to a washout (which is why the moss bags were covered precautionary) but to an increase in element concentrations. In addition to rain, uncovered moss bags also receive dust deposition. Our results are comparable to the results of Adamo et al. (2003), who also found washout to be negligible conducting moss monitoring in Naples (Italy). In summary, covering moss bags is not necessary because accumulation is faster for uncovered moss bags even in humid areas and seasons. Moss bag monitoring can be used as monitoring technique yielding equivalent results to rainwater monitoring and can especially be used in rain-poor areas/seasons to be independent of meteorologic conditions.

4.2 Evaluation of arsine species preserving field-applicable sampling techniques

4.2.1 Application of moss for arsine species monitoring (study 3)

Up to date, moss has only been used for total element monitoring. Its ability of preserving As species was unknown. In this study, moss was evaluated for volatile As species preservation by exposing it to single volatile arsine species. Self-made flow-through moss traps made out of fluorinated ethylene propylene hoses (FEP, Ø=12 mm) filled with 0.2 g moss did not trap the arsines when using a flow rate of 5 $mL \cdot min^{-1}$, presumably due to still too high flow rates and short exposure times. Thus, batch experiments in borosilicate Schott bottles were conducted (see section 3.2.2).

At +5°C, the volatile arsines Me_2AsH and Me_3As were trapped quantitatively on the mosses and were recovered as their respective acids (and/or oxyanions) after extraction. $MeAsH_2$ was only partially trapped on the mosses, while AsH_3 was not trapped at all. The reproducibility of these results for the arsines $MeAsH_2$ and Me_2AsH at temperatures below and above their boiling points, respectively, excludes temperature as reason for arsine recovery on the moss. If the surface of the borosilicate bottles had an effect on arsine stability, e.g. as “seed crystals”, arsine distribution would have been the same for bottles with and without moss (blanks). Stability experiments of arsines in Tedlar bags also could not explain recovery of Me_3As on the moss and AsH_3 in the gas (section 4.2.5.1, *study 4*). In glass bottles, Me_3As was even shown to be more stable than AsH_3 (Pantsar-Kallio and Korpela, 2000).

The exact precipitation mechanism of the arsines on the moss can either be physically or chemically. Physically, the arsines would enter the hyalocytes of the moss as was shown for phenantrene (Spagnuolo et al., 2017). The arsines’ molecule sizes thus would determine the amount taken up by the mosses. However, during grinding, the hyalocytes are opened and arsines would be released. Mosses analyzed 1 and 60 days after grinding yielded the same As concentrations contradicting the theory of physical trapping. We propose a chemical covalent bonding of the arsines to the moss surface. Arsines have a pyramidal structure with a free pair of electrons at the As atom (Figure 1). The AsH_3 molecule is unpolar (Meyer and Pietsch, 1952). Replacing H by CH_3 groups in which C has a higher electron negativity than H (2.55 and 2.18, respectively; Pauling (1960)) results in a lower electron density at the As atom. Thus, the molecule’s tendency to bind to electron-rich atoms becomes more likely the more methyl groups the molecule has. Electron-rich binding partners could e.g. be the polyuronic acids of the moss surface. To clarify the bonding mechanism of arsines to the moss surface, we propose micro-XAS (*study 3*).

We applied the tested species preserving moss monitoring on Vulcano and in the fermentation hall of a biogas plant. At both sites, matrix gases like SO_2 and H_2S are common which influence the arsines' stability (*study 4*), trigger their deposition, or lead to co-precipitation on the moss surface by bonding to deposited S on the moss due to the affinity of As for S. On moss exposed at Vulcano, we found predominantly inorganic As and <1% organic As while on moss exposed to biogas methylated As was predominant (95-100%). Up to 50% of AsH_3 were detected in gases emitted from Vulcano (*study 4*). Because AsH_3 is not trapped by moss (*study 3*), a large share of the As deposited on the moss must have been particles before. In biogas on the contrary, methylated arsines are known to exist (Mestrot et al., 2013b). Their recovery as acids (and/or oxyanions) on the moss means that the matrix gases of CO_2 and CH_4 do not significantly change the arsine trapping in comparison to N_2 in the batch experiments (CO_2: *study 4*).

Consequently, moss monitoring can be used as a screening tool to evaluate if emissions of methylated arsines are relevant besides particulate As. This method could be applied in parallel to common moss monitoring for total elements and prior to potential arsine speciation analysis.

4.2.2 Silver nitrate trap sampling of volcanic gases

Silver nitrate traps ($AgNO_3$ traps) were employed as active samplers at Vulcano and in Yellowstone (both 2013; Vulcano: Ehrenfels (2013, unpublished)) and as passive samplers in Yellowstone (2014). Arsenic accumulation on the traps can be influenced by volcanic matrix gases (section 3.3) and can thus differ from natural concentration. Nevertheless, speciation can be determined from $AgNO_3$ traps and accumulation gives a first hint for As emission comparison of several vents and is thus given in this section.

On Vulcano, active sampling using filters and $AgNO_3$ traps was conducted at the same sampling profile stations simultaneous to moss monitoring. This As sampling profile started with low total concentrations upwind of the fumaroles (station 1, west of the fumaroles: 0.01 $\mu g \cdot g^{-1} \cdot m^{-3}$), showed highest As concentrations within the fumarolic field (station 2: 8.8 $\mu g \cdot g^{-1} \cdot m^{-3}$), and again decreasing As concentrations with increasing distance to the fumaroles (station 4-7, east of the fumaroles: 0.5-0.03 $\mu g \cdot g^{-1} \cdot m^{-3}$). This defines the fumaroles as the clear source of As emissions and is consistent with moss monitoring results. Because $AgNO_3$ traps result in a short-term signal in contrast to moss monitoring (max. sampling duration 6 h vs. up to 3 weeks; see section 4.1.1.1), the morphology of the transect was not visible from total As concentrations on filters.

Arsenic was only found on the filters and not on the traps. Filters sample predominantly particles and were not evaluated for As species preservation. This matches the results of moss monitoring on Vulcano for As species, which showed predominantly inorganic As on the mosses that was attributed to particulate As (see section 4.2.1). The recovery of inorganic As on the filters during speciation analysis also suggests the appearance of As in the form of AsH_3 which was shown to occur by Tedlar bag sampling (section 4.2.5.2) but would not trap on the moss (section 4.2.1). Matrix gases like SO_2 and H_2S could also have an effect on its deposition. In contrast to As, the elements Se and Sb were found on traps and filters which leads to the conclusion that they either exist as gases and particles or that gases are partially sorbed by the filters. However, while filters are not validated for species preservation at all, $AgNO_3$ traps are validated for As only (Mestrot et al., 2009) and were not analyzed for speciation of other elements.

In Yellowstone (2013), active sampling showed As concentrations below detection limit on all sampled features in traps and most filters (detection limits: 76 $\mu g \cdot g^{-1}$ and 30 $\mu g \cdot g^{-1}$, respectively), except for the filters during duplicate sampling of one fumarole at Nymph Lake (mean: 41 $\mu g \cdot (g \cdot L)^{-1}$). Possibly, a total sampling volume of 100-450 mL was too low compared to emission strength. Passive sampling in 2014 over a duration of up to 25 days using $AgNO_3$ traps (without filters in the front) proved the passive technique to be functional with As concentrations above detection limit: Maximum accumulations were reached at the fumarole at Nymph Lake (3.5 $ng \cdot (g \cdot d)^{-1}$).

In general, the results of $AgNO_3$ traps in Yellowstone match the results of moss monitoring (see section 4.1.1.5): Arsenic emission concentrations at Yellowstone's geothermal features are very low compared e.g. to the fumaroles of Vulcano. However, the main disadvantage of $AgNO_3$ traps is their validation for inorganic and methylated arsines only and their trapping efficiency uncertainties of chlorinated and sulfonated arsines.

4.2.3 Cryotrapping on dry ice (Study 4)

Cryotrapping can theoretically trap all arsines depending on its temperature. However, liquid nitrogen (-196°C) is not easy to access in remote areas like volcanoes. Thus, dry ice (-78°C) was tested as a different cryotrapping agent. Me_2AsH, and Me_3As were only trapped partially while AsH_3 and $MeAsH_2$ were not trapped at all. To trap these species in dry ice, a longer trap and even lower flow rates would be necessary. However, this also would lead to a larger amount of dry ice needed, heavier equipment, longer pumping durations in the field, and eventually longer sampling campaigns. Consequently, this technique was not pursued any further.

4.2.4 Needle Trap Devices (study 4)

Sorption materials of Needle Trap Devices (NTDs) have shown to trap methylated arsines as well as chlorinated and sulfonated arsines on SPME fibers (Mester and Sturgeon, 2001; Planer-Friedrich et al., 2006). In contrast to SPME fibers, NTDs can sample a defined volume.

In laboratory tests, NTDs with different sorption material combinations (multi-bed needles equipped with PXC, PC, PCD, PX trapping materials and single-bed needles with C and X, only) were exposed to gas mixes of AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As (see section 3.1). None of the NTDs with different sorption materials trapped AsH_3, $MeAsH_2$, or Me_2AsH. Me_3As was the only As species from the generated gas recovered on the NTDs but desorption was incomplete. Instead, an additional As species was recovered that was not initially loaded onto the NTDs and was identified as Me_2AsCl by its EI mass spectrum. The masses for the molecules or fragments of $AsCl_3$ (180 and 145 without one Cl atom) and for $MeAsCl_2$ (160) were not detected. Thus, Me_2AsCl was the only chloro-arsenic species found. If it had been formed during hydride generation like shown in Mester and Sturgeon (2001), it would have been detectable in the gas mixture before NTD loading. Blank NTDs also did not show any Me_2AsCl peak. Thus, Me_2AsCl must have formed on the NTDs. The carboxen sorption material is known to be able to adsorb gaseous HCl on SPME fibers (Mester et al., 2000), but also to already contain small amounts of Cl that were detected by X-ray fluorescence (Dettmer and Engewald, 2002). Consequently, NTDs produce Me_2AsCl artifacts.

So far, chloro-arsine species have been found in nature only by SPME sampling using the same sorption materials like NTDs: PDMS and Carboxen (Killelea and Aldstadt III, 2002; Planer-Friedrich et al., 2006). Samples were taken from sediments and geothermal features in Yellowstone, respectively. In both cases, however, no direct gas analysis was done. Thus, the detection of chloro-arsines can also be an artifact of the used sorption materials.

Field applicability of NTDs was tested on Vulcano (2013) as active samplers (pumping rate: 5 $mL\cdot min^{-1}$) and as passive samplers despite of artifact formation. None of the NTDs with different sorption material combinations trapped any As revealing no Me_3As occurrence which is the only species that would be trapped if present. This is consistent with the results from moss monitoring for As species and from $AgNO_3$ traps (sections 3.2.4 and 3.3, respectively). However, As species which do not sorb on the NTDs can still be present.

A big disadvantage of NTDs in geothermal gas matrices containing SO_2 and HCl is the corrosive damage of the stainless steel needles. Besides this, artifact formation during arsine sampling excluded further tests using NTDs. It also questions As speciation of former reports using SPME sampling.

4.2.5 Tedlar bags

The use of Tedlar bags is an established quantitative species preserving sampling technique for volatile arsines (see section 1.2). However, it has up to now neither been validated nor applied for volcanic gases which contain several matrix gases like water vapor, CO_2, SO_2, and H_2S, but also O_2.

4.2.5.1 Arsine stability in Tedlar bags in the presence of volcanic gases (Study 4)

Stability of volatile arsines in Tedlar bags in dry N_2 matrix was used as a reference for all other gases. In N_2, the recovery of the total As was 98±4% after 19 days, while for the species AsH_3, $MeAsH_2$, and Me_2AsH recoveries were higher than 100% and for Me_3As recovery was 85% which is due to transformation to lower methylated As species. In the concentration range of 0.3-10 $ng{\cdot}L^{-1}$ As comparable to our experiments (2 $ng{\cdot}L^{-1}$ per As species), moisture does not cause As loss by adsorption onto the Tedlar bag walls (Haas and Feldmann, 2000; Mestrot et al., 2011). Thus, water vapor was not investigated any further.

For 20% O_2, 3800 ppm_V CO_2, and 100 ppm_V SO_2 matrix total volatile As recoveries were 92±1%, 91±2% and 60±2%, respectively. The losses in O_2 and CO_2 matrix are in the range of analytical uncertainties, while for SO_2 As losses are obvious.

Regarding As speciation in 20% O_2, recoveries were between 102% and 83% after 11 days. These results are in line with the recoveries of stability experiments in Tedlar bags at 20°C (Haas and Feldmann, 2000). After 24 h, recoveries were between 99% and 90% for AsH_3, $MeAsH_2$, and Me_2AsH and 86%, 73%, and 26% after 5 weeks, respectively. At higher temperatures (50°C), recoveries decreased. The even lower temperature of 5°C in our experiment can result in higher recoveries.

In the presence of 3800 ppm_V CO_2, recoveries of the arsines were between 95% and 88% after 19 days which are comparable to recoveries in N_2 matrix. This similarity can be explained by the low tendency of CO_2 to react with other gases.

In H_2S matrix, 67% of Me_3As were recovered after 17 days and 89%, 105%, and 123% of Me_2AsH, $MeAsH_2$, and AsH_3, respectively. Consequently, the missing Me_3As was transformed to lower methylated volatile As species, especially to AsH_3.

In 100 ppm_V SO_2, the lowest stability of arsine speciation was observed. After 21 days, only 72% AsH_3 and $MeAsH_2$, 41% Me_2AsH, and 11% Me_3As were recovered. This loss can also be seen in total volatile As concentration. In contrast to all other matrix gases evaluated in this study, SO_2 is very reactive and corrosive and can consequently oxidize the reduced volatile As species. This process is even faster than in the presence of the 200-fold concentration of O_2 (200,000 ppm_V O_2 vs. 100 ppm_V

SO_2). The process removing volatile As can either be adsorption to the Tedlar bag walls or precipitation e.g. by formation of As_2O_3 or As-S compounds (Meyer and Pietsch, 1952).

Independent of all matrix gases, the most stable volatile As species was AsH_3 and stability decreased with increasing methylation. Me_3As was the least stable species as a result of species conversion to AsH_3, adsorption, and/or precipitation. This sequence matches the ones found for arsines' stability in Tedlar bags with moisturized air matrix regarding storage temperature (Haas and Feldmann, 2000) and UV light exposition (Mestrot et al., 2011). In contrast to this, Me_3As was more stable than AsH_3 during 9 days of stability experiments in moisturized air matrix in glass bottles (Pantsar-Kallio and Korpela, 2000). However, no information is given about the influence of light during storage which was shown to be crucial for stability (Mestrot et al., 2011). The use of different containers (glass and Tedlar) can also have influenced the arsines' stability.

All in all, for sampling volatile arsines from volcanic gases using Tedlar bags, sulfur gases like SO_2 and H_2S should be removed during sampling to increase As stability. This was done using NaOH traps (see section 3.6.1).

4.2.5.2 Volatile As in volcanic gas samples (Study 4)

No significant loss of total volatile As or species transformation occurred in 8 days (section 4.2.5.1), which was the maximum transfer time between sampling and analysis. In the fumarolic field on Vulcano and at Solfatara, the predominant As species was AsH_3 at all sites. AsH_3 concentrations correlated with CO_2 concentrations, decreasing with decreasing CO_2 concentrations (by air dilution), which again confirms the volcanogenic origin of AsH_3. Its concentration ranged between 0.3 $ng \cdot m^{-3}$ and 74 $ng \cdot m^{-3}$ with highest concentrations occurring at a fumarole on the path through the fumarolic field of Vulcano. At Solfatara, AsH_3 concentrations were in the range of 1.2-2.2 $ng \cdot m^{-3}$. Besides the AsH_3 peak in all samples' chromatograms, an additional As peak occurred at the retention time of 3.56 min. At this time, Me_3As normally elutes from the column but could not been identified by its molecular mass fragments (EI-MS) due to its low concentrations of 0.07-2.9 $ng \cdot m^{-3}$. The species $MeAsH_2$ and Me_2AsH were not detected in any of the samples although they would have been detected if they were present concerning their stability (section 4.2.5.1). Thus, we can conclude their true absence in all volcanic gas samples from Vulcano and Solfatara.

Our results raise three aspects to discuss: (a) Why was only AsH_3 found in the fumarolic gases, (b) can total volatile As concentrations be realistic, and (c) what can we conclude from sampling fumarolic gases on Vulcano with different techniques?

(a): Regarding speciation, only inorganic As was found on Vulcano. Sampling volatile arsines with Tedlar bags above algae mats, Hirner et al. (1998) predominantly or even exclusively found methylarsines. Algae species are known to be able to volatilize methylarsines and even an eukaryotic thermophilic algae methylating arsine species and volatilizing methylated aqueous As-species has been isolated from geothermal environments in Yellowstone National Park (Qin et al., 2009). Volatile As speciation above a hot spring (maximum temperature: 50°C) had an even distribution of inorganic AsH_3 on the one hand and the methylarsines Me_2AsH and Me_3As on the other hand (Hirner et al., 1998). The sampled fumaroles on Vulcano and in Solfatara with even more hostile outlet temperatures of 150°C and water limitation showed inorganic AsH_3, only. The emission of solely methylarsines above algae mats, the emission of both, methylated and inorganic arsines, above hot springs and the only emission of inorganic AsH_3 from the fumaroles are evidence for the microbially catalyzed methylation. In contrast to inorganic AsH_3, methylarsines are not emitted directly by the volcanoes but are secondary microbial volatilization products.

(b): The total atmospheric background concentration of As on the northern hemisphere has been estimated to be 0.5-2.8 $ng \cdot m^{-3}$ with particulate As accounting for 89-98% of total As (Matschullat, 2000). Measured concentrations in this study were 1-2 orders of magnitude higher than the calculated background concentration for volatile As. In general, concentrations in our study are a conservative estimation because (1) volcanic activity undergoes natural variations and can be much higher than it was during sampling time, (2) given arsine concentrations are from daytime sampling but would be even higher during the nights due to their higher stability in environments without UV radiation (Mestrot et al., 2011), and (3) fumarolic gases do not emit methylarsines which are volatilized microbially in addition to inorganic arsines. All these factors lead to larger volatile As concentrations. However, volatile As concentrations in the $mg \cdot m^{-3}$ range (Planer-Friedrich et al., 2006) possibly are overestimated due to many assumptions made during calculation and potential trapping of particulate As in addition to volatile As.

(c): Employing all of the sampling methods on Vulcano, a clearer view of the ongoing processes and the present volatile As species is possible. Arsenic was shown to occur as AsH_3 by Tedlar bag sampling (see same section above). Filters in front of $AgNO_3$ traps and moss species analysis also reveal inorganic As (sections 4.2.1 and 4.2.1, respectively), although filters are not validated for volatile As species preservation and AsH_3 was shown not to be trapped by moss (section 4.2.1). This points to the emission of As in the form of AsH_3 and particle on Vulcano. Additionally, the volatile arsines' instability in the presence of SO_2 (section 4.2.5.1) can trigger deposition on the moss and the arsines' affinity to S can lead to particle formation and subsequent deposition or even its co-precipitation on the moss surface. In Tedlar bags, these sulfur gases are eliminated.

4.2.5.3 Volatile As in biogas

Besides volcanoes, biogas and wastewater treatment plants were sampled, but also emissions from satellite experiments with sludge incubation were taken using Tedlar bags. We experienced low temporal reproducibility of total volatile As and species concentrations. In general, Tedlar bag sampling shows a short-term signal in comparison to moss bag sampling. Thus, sampling with Tedlar bags is strongly influenced by the respective conditions of the biogas reactor (i.e. either the biogas/wastewater treatment plant or the satellite incubation reactor). However, speciation in wastewater treatment plants was dominated by AsH_3 while mainly methylarsines were found in biogas plants which is concurrent with Hippler (2013), who found Me_3As in 4 monitored biogas plants.

Duplicate incubation experiments with arsenite-spiked sludge from a biogas plant and a wastewater treatment plant differed by 3 orders of magnitude in their total gas and arsine production, as well as the color of the sludge differed at the end of the 14 days long incubation experiment. Slight changes in the microbial As community or in external conditions are difficult to influence in small satellite experiments and could be the reason for different CH_4 production and amounts of arsines. However, during all incubation experiments, predominantly AsH_3 was found, which can either be due to a lethal As dose for methylating volatilizing microorganisms or due to a yet incomplete As methylation process (section 1.1).

5 CONCLUSION

The aim of the present study was to investigate and evaluate several sampling techniques for total volatile As and its speciation. The special focus of this PhD thesis was arsine emission in volcanic gases which are rarely sampled in an As-species preserving way.

Moss bag monitoring, an easy-to-apply sampling technique for volcanic emissions, revealed not only total As but also several elements' distribution patterns from which conclusions to the elements' presence, their origin, and way of distribution were drawn (*study 1*). The analogue results to rain monitoring make moss bags an ideal technique to monitor within dry areas or during dry seasons. The independence of moss bag monitoring concerning exposure height (0.7-1.6 m) and duration (3-9 weeks) and its functionality without the need of covering the moss bags facilitates the application of this technique in remote volcanic and geothermal areas. For better comparison of element accumulations, the usage of the same moss and triplicate exposure for all sampling sites is recommended (*study 2*).

In addition to the monitoring of total As, moss is also able to trap higher methylated As species like Me_3As and Me_2AsH in a species preserving way, but traps $MeAsH_2$ only partially and does not trap AsH_3 at all. Arsines are eluted from the moss as their corresponding acids. Additionally, As particles are trapped on the moss, which can be identified by the recovery of inorganic As. We propose a covalent bonding of the arsines to the moss surface, however, verification e.g. by micro XAS is needed (*study 3*). Consequently, moss monitoring application can be extended to differentiation between methylarsines and As particles.

Needle Trap Devices (NTDs) did not trap AsH_3 and $MeAsH_2$ and did not release Me_2AsH and Me_3As quantitatively (*study 4*). Artifact formation of Me_2AsCl on their sorption materials questions former results of studies using the same materials on Solid Phase Micro Extraction fibers (SPME). Cryotrapping in dry ice also did not trap all arsine species. Active sampling using $AgNO_3$ traps with filters in front of them only trapped inorganic As on the filters which are not evaluated for species trapping in contrast to $AgNO_3$ traps.

Species preserving sampling of arsines by Tedlar bags was the best technique evaluated but requires stability of arsines in their matrix. At 5°C in the dark, arsines were stable up to 21 days in dry N_2 matrix and 3800 ppm_V CO_2 and for 11 days in 20% O_2. In volcanic gases like SO_2 and H_2S, arsines and especially methylarsines degraded. Thus, the removal of volcanic gases during sampling (e.g. by cooling and NaOH traps, that eliminate water vapor and CO_2 as well), cooled storage (5°C), and immediate analysis (max. after 8 days) is recommended (*study 4*). The arsines' stability in Tedlar bags, once volcanic gases are removed and storage conditions are optimized, makes Tedlar bag sampling a promising technique for future species preserving sampling to contribute to our knowledge about arsines in volcanic and geothermal gases.

In gas from biogas and wastewater treatment plants, volatile As was difficult to sample using Tedlar bags due to the low temporal reproducibility and the short-term non-accumulative signal of Tedlar bag sampling. However, at the wastewater treatment plant, predominantly AsH_3 was recovered while at biogas plants predominantly methylarsines were recovered. These were also recovered on moss bags (*study 3*).

On Vulcano, As was identified to be emitted as volatile element by its distribution pattern and fumarolic origin, together with the elements Sb, S, Se, Tl, and Bi using moss monitoring (*study 1*). The same conclusion could be drawn from monitoring the open conduit explosive volcanoes Etna and Stromboli and the less explosive Nyiragongo: At the former two volcanoes, the volatile elements correlated with lava and ash associated elements like Fe, Pb, and Sr (*study 2*). Regarding As speciation on Vulcano, As was trapped and eluted from the moss as inorganic As (*study 3*) as well as from the filters in front of $AgNO_3$ traps, postulating the presence of As particles. Tedlar bag sampling revealed a maximum of 74 $ng \cdot m^{-3}$ AsH_3 to be the predominant volatile As species on Vulcano besides small amounts of Me_3As. Recovery of inorganic As on filters in front of $AgNO_3$ traps and AsH_3 not being trapped on mosses (*study 3*), we propose the additional presence of As particles. The low recovery of methylarsines in fumarolic emissions of Vulcano makes biovolatilization a negligible process (*study 4*).

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CONTRIBUTION TO THE STUDIES IN THIS THESIS

Study 1: Active moss monitoring allows to identify and track distribution of metal(loid)s emitted from fumaroles on Vulcano Island, Italy

Master Thesis (Arndt, 2012, unpublished)	40%	concepts, field and laboratory work (screening 2012), first data interpretation
Arndt, J.	40%	concepts, field and laboratory work (transect monitoring 2013), data (re-)interpretation, manuscript preparation
Calabrese, S.	5%	discussion of results, comments on manuscript
D'Alessandro, W.	5%	discussion of results, comments on manuscript
Planer-Friedrich, B.	10%	concepts, discussion of results, comments on manuscript

Study 2: Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas

Arndt, J.	70%	concepts, monitoring of Stromboli and Yellowstone, laboratory work, data interpretation, manuscript preparation
Calabrese, S.	5%	monitoring of Nisyros and Nyiragongo, laboratory work, comments on manuscript
D'Alessandro, W.	5%	monitoring of Nisyros and Nyiragongo, laboratory work, comments on manuscript
Planer-Friedrich, B.	20%	concepts, discussion of results, comments on manuscript

Study 3: Moss bag monitoring as screening technique to estimate the relevance of methylated arsine emission

Arndt, J.	90%	concepts, laboratory experiments, data interpretation, manuscript preparation
Planer-Friedrich, B.	10%	concepts, discussion of results, comments on manuscript

Study 4: Evaluation of techniques for sampling volatile arsenic on volcanoes

Arndt, J.	70%	concepts, laboratory experiments, data interpretation, manuscript preparation
Ilgen, G.	10%	discussion of results, comments on manuscript
Planer-Friedrich, B.	20%	concepts, discussion of results, comments on manuscript

APPENDIX: PUBLICATIONS

Study 1: Arndt, J., Calabrese, S., D’Alessandro, W. and Planer-Friedrich, B., 2014. Active moss monitoring allows to identify and track distribution of metal(loid)s emitted from fumaroles on Vulcano Island, Italy. J. Volcanol. Geotherm. Res., 280: 30-39.
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Study 2: Arndt, J., Calabrese, S., D'Alessandro, W. and Planer-Friedrich, B., 2017. Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas. J. Volcanol. Geotherm. Res. 343: 220-232.
doi:10.1016/j.jvolgeores.2017.07.004

Study 3: Arndt, J. and Planer-Friedrich, B., 2018. Moss bag monitoring as screening technique to estimate the relevance of methylated arsine emission. Science of the Total Environment, 610-611: 1590-1594.
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Study 1: Active moss monitoring allows to identify and track distribution of metal(loid)s emitted from fumaroles on Vulcano Island, Italy

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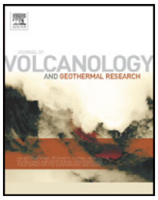

Active moss monitoring allows to identify and track distribution of metal(loid)s emitted from fumaroles on Vulcano Island, Italy

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ABSTRACT

Volatile metal(loid)s are known to be emitted from volcanoes worldwide. We tested the suitability of active moss monitoring for tracking volatile metal(loid)s released from the fumarolic field on Vulcano Island, Italy, and differentiated fumaroles from other sources of gaseous and particulate trace elements such as sea spray and soil. Metal(loid) accumulation on the mosses per day did depend neither on the state of the exposed moss (dead or living) nor exposure time (3, 6, or 9 weeks). After collection, mosses were digested with either HNO_3/H_2O_2 or deionized water and analyzed by ICP-MS. While for most elements both extraction methods yielded similar concentrations, higher concentrations were observed e.g. for Pb in the stronger HNO_3/H_2O_2 extracts, indicating the presence of particles, which were not digested and removed by filtration in deionized water extracts. Due to their ubiquitous detection in comparable concentrations at all 23 moss monitoring stations all over the island, Li, Mg and Sr were attributed to sea spray origin. Iron, Co, W, V, Pb, Cr, Mo, and Ba occurred predominantly at the crater, where the soil was not covered by vegetation, and thus likely represent soil-borne particulate transport. Arsenic, Sb, S, Se, Tl, Bi, and I showed a clear concentration maximum within the fumarolic field. Concentrations gradually decreased along a transect in wind direction from the fumaroles, which confirms their volcanic origin. Active moss monitoring thus proved to be an inexpensive and easy-to-apply tool for investigations of volcanic metal(loid) emissions and distributions enabling differentiation of trapped elements by their source of origin.

1. Introduction

Volatile metal(loid)s are metal(loid)s with a low boiling point and a high vapor pressure. They are released anthropogenically, e.g. during coal combustion (Miller et al., 2002) but also by natural processes. Besides low-temperature volatilization, which is mostly microbially catalyzed (Michalke et al., 2000; Smith et al., 2002; Mestrot et al., 2013), metal(loid) volatilization is common in volcanic areas. There, cooling and decompression of ascending magma lead to increasing separation of volatiles (mainly H_2O, CO_2, SO_2, H_2S, etc., but also metal(loid)s) into the vapor phase and liberation as passive quiescent (fumaroles) or eruptive magmatic degassing (volcanoes). Examples include hot springs in British Columbia, Canada (volatile As, Sb, Se, and I (Hirner et al., 1998) determined by collection in Tedlar Bags, cryo-focusing and analysis by low temperature GC-ICP-MS), or Yellowstone National Park (volatile Si, Ni, Cu, Zn, As, W, V, Ti, Mo, Ga, Ge, and Sb determined by trapping in an NaOCl oxidizing solution (Planer-Friedrich et al., 2006) and volatile As determined on solid-phase micro-extraction fibers (Planer-Friedrich and Merkel, 2006)) as well as the volcanoes Mt. Etna and Vulcano, Italy. On Mt. Etna, volatile As, Bi, Cd, Cs, Cu, and Tl were detected by sampling emissions by pumping plume air through filters and extracting them by using microwave digestion with HNO_3, HF and $HClO_4$ (Calabrese et al., 2011) whereas on Vulcano volatile Tl, As, Bi, Cd, Pb, and Zn were determined by thermochemical modeling after taking condensate and sublimate samples (Cheynet et al., 2000).

Seen from a global budget perspective, Nriagu (1989) suggested that volcanoes may contribute 40–50% of the natural annual atmospheric emission for Hg, Cd, As, Cr, Cu, Ni, Pb, and Sb. Besides a general understanding of element cycling, knowing about the metal(loid) release is also important from a toxicological point of view because many of the metal(loid)s are most toxic in their volatile form (e.g. AsH_3 (Pakulska and Czerczak, 2006)). Since it has recently been shown that volatile metal(loid)s can travel significant distances before converting into non-volatile oxidized species (Jakob et al., 2010), knowing their distribution around the releasing source is of special importance. For example, half-lives of gaseous arsenic were found to be approximately 8 h for methylarsines and even longer for inorganic arsine under day-time conditions (UV light) and up to weeks when tested in the dark (Mestrot et al., 2011).

Despite their significant release and potential relevance for widespread distribution, volatile metal(loid)s are often neglected in routine volcanic monitoring because complicated and expensive sampling techniques prevent monitoring at high spatial resolution. Further challenges, yet to be solved, are the preservation of samples for total and

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species analysis due to their instability toward hydrolysis, oxidation, or temperature-dependent conversion as well as analytical difficulties due to low total concentrations and a lack of standards for identification and quantification (Mestrot et al., 2013).

In the present study, we tested active moss monitoring as an inexpensive and easy-to-apply method to identify metal(loid)s release from a volcanic source and trace their distribution at any user-defined resolution. Bio-monitoring originally was used for monitoring anthropogenic air pollution and often used mosses (Adamo et al., 2003; Cao et al., 2009; Giordano et al., 2009). Not having roots, mosses take up nutrients with their entire surface (Brown, 1982). They have a high specific surface area (80.6 $m^2 \cdot kg^{-1}$ for *Hypnum cupressiforme*; Adamo et al. (2007)) with leaves consisting of one single cell layer where gases and particles can attach. Additionally, mosses have a high cation exchange capacity due to polyuric acids at their outer cell membranes (Clymo, 1963), which do not differentiate between uptake of nutrients or toxic substances (Brown and Bates, 1990). Active moss monitoring involves the use of non-indigenous mosses (Cao et al., 2009), which has (in contrast to passive biomonitoring) the advantage of known blank concentrations and exposure times, a user-defined choice of exposure sites, and its use even in “moss deserts”, i.e. areas where mosses do not grow naturally, which geothermal, volcanic areas normally are. Active moss monitoring has only recently been successfully applied on Mt. Etna, monitoring 49 elements (Calabrese and D'Alessandro, in press; Calabrese et al., in press).

Our study is focused on Vulcano Island, which is the southernmost Aeolian Island in the Tyrrhenian Sea north of Sicily, Italy. Together with the Aegean Island, the Aeolian Islands form one of two volcanic island arcs in the Mediterranean Sea that developed during the subduction of the African tectonic plate beneath the European plate (Barberi et al., 1974). Vulcano Island started to develop 120,000 years ago (Pichler, 1981). Today, the crater of the volcano La Fossa is the most prominent feature that characterizes Vulcano. It has a diameter of 2 km and a maximal height of 390 m. Since the last eruption of La Fossa in 1888, which lasted 2 years, Vulcano's volcanic activity has concentrated on fumarolic emissions at the northern rim and inner flank of the crater whereas minor activities can be found in the eastern harbor bay Baia di Levante.

The population of the island, outside the tourist season (June–September), is of only a few hundred people. Anthropogenic and industrial emissions have a minor or no impact due to no industry on the island. The traffic is never intense due to limitations in the summer and even around Vulcano Porto, the most inhabited area, we found no anomalies in accumulation of any metal(loid)s (Appendix, Table A2). Thus, anthropogenic emissions are neglected in the following.

The fumarolic gases mainly consist of CO_2 and H_2O (>98%) with S, halogens, B, NH_3 and trace elements (Signorelli et al., 1998) such as As, Sb, Tl, and Bi being minor components (Sortino et al., 2006). Trace element emissions have also been investigated by Cheynet et al. (2000) analyzing condensate and sublimate samples collected directly at the fumaroles of Vulcano. On average, they found concentrations of 2.1 $\mu g \cdot g^{-1}$ As and Pb, 0.4 $\mu g \cdot g^{-1}$ Bi, 0.14 $\mu g \cdot g^{-1}$ Zn, and 0.05 $\mu g \cdot g^{-1}$ for Cd and Tl. Up to 30 $\mu g \cdot g^{-1}$ As in fumarole condensates on Vulcano were the highest measured source concentrations worldwide exceeding concentrations at Mount St. Helens (<0.006 $\mu g \cdot g^{-1}$; USA), Stromboli (<0.006 $\mu g \cdot g^{-1}$; Italy), Kilauea (<0.06–1 $\mu g \cdot g^{-1}$; Hawaii) and Teide (3.8–4 $\mu g \cdot g^{-1}$; Canary Islands) according to Signorelli (1997).

To evaluate the distribution of the volatile metal(loid)s released from the fumarolic field of Vulcano over the whole island, Bargagli et al. (1991) used passive biomonitoring on pine needles and broom samples. They concluded that the environmental impact of Al, Co, Cr, Cu, Fe, Mn, and Pb from volcanic emissions was negligible. However, the selected plants were neither growing within the fumarolic field nor in the prevailing wind direction of the fumarolic gases. Thus, a large area located directly at the origin of potential volcanic trace element emissions was not even sampled. Varrica et al. (2000) also used passive monitoring on Vulcano Island on lichens. Even though they could not obtain samples within or directly downwind (eastward) of the fumarolic field but only in the southeast of the island, they concluded from enriched concentrations found on the lichens that fumarolic activity represents a significant and continuous source for trace elements like Cu, Au, and Zn.

In our study, we applied active moss monitoring on Vulcano Island as a uniform, simple, and inexpensive method to identify volatile metal(loid)s released from the fumarolic field, differentiated these from other metal(loid) sources and tracked their distribution depending on distance from the fumaroles and over the whole island.

2. Methods

Moss monitoring was done twice on Vulcano Island. The first monitoring was a screening in spring 2012 (12th April to 11th June) covering the whole island, which was also used to evaluate the moss monitoring method itself, using dead and living moss as well as covered and uncovered moss bags (Appendix, Fig. A1). The second monitoring was done along a transect through the fumarolic field using dead moss in uncovered bags in spring 2013 (30th April to 23rd May).

2.1. Preparation of moss bags

A mixture of different *Sphagnum* mosses (*Sphagnum tenellum*, *Sphagnum subsecundum*, *Sphagnum cuspidate*, *Sphagnum girgensonii*, *Sphagnum fallax*) was collected from an acidic fen in the Fichtelgebirge in Bavaria, Germany (“Schlöppnerbrunnen”, 50°08′14″ N/11°53′07″ E) approximately 1 month prior to exposure at Vulcano. Mosses were cleaned from dirt and larger particles and washed three times under constantly shaking with deionized water to remove adsorbed particles from the surface. Two different drying methods were applied. Freeze-drying the moss (−20 °C, 3 days) resulted in the destruction of the moss cells due to crystal formation during freezing. Oven-drying at low temperatures (max. 45 °C) keeps the mosses physically alive (Ares et al., 2012). Since the later results showed that accumulation per day and thus, distribution patterns, did not differ much between “dead”, freeze-dried, and “living”, oven-dried, mosses they were eventually treated as replicates. Polyester and nylon mosquito nets for the moss bags were obtained from a general household supply store and washed three times in acidified deionized water. For the spherical moss bags assembly, 1.5–2 g dry moss was weighed into each bag net (consisting of a polyester inner net (mesh size: 1.5 mm) and a nylon outer net (mesh size: 0.8 mm)). Moss bags were closed with a nylon wire and transported to Vulcano in closed plastic bags.

For the second monitoring in 2013, mosses (*Sphagnum palustre*) were collected in the forest around Bayreuth, Germany (49°54′42″ N/11°41′47″ E), and were treated as described above. To assure that all the mosses were dead and thus did not differ in accumulation mechanism, they were frozen (−20 °C) in wet state to destroy their cells and then oven-dried (40–45 °C, 1 day).

2.2. Sampling sites

Screening in 2012 included the evaluation of the moss monitoring technique. Moss bags thus were exposed for different times from 3 to 6 and 9 weeks. Differently prepared mosses (see Section 2.1) were employed, using living moss for the 6 week exposure and dead moss for all other exposure times. At 23 sites over the whole island of Vulcano (Fig. 1, GPS coordinates are provided in the Appendix, Table A1), poles were set up to which moss bags were tied at a height of approximately 1.60 m above ground. At every station, moss bags were set up covered and uncovered (Appendix, Fig. A1). Uncovered moss bags received additional deposition, but also washout by rain, as well as dust deposition from above and below, compared to covered moss bags. Six stations were monitored in triplicates.

At each moss monitoring station, SO_2 and H_2S were monitored by passive samplers under a plastic cover for the duration of 3 weeks for

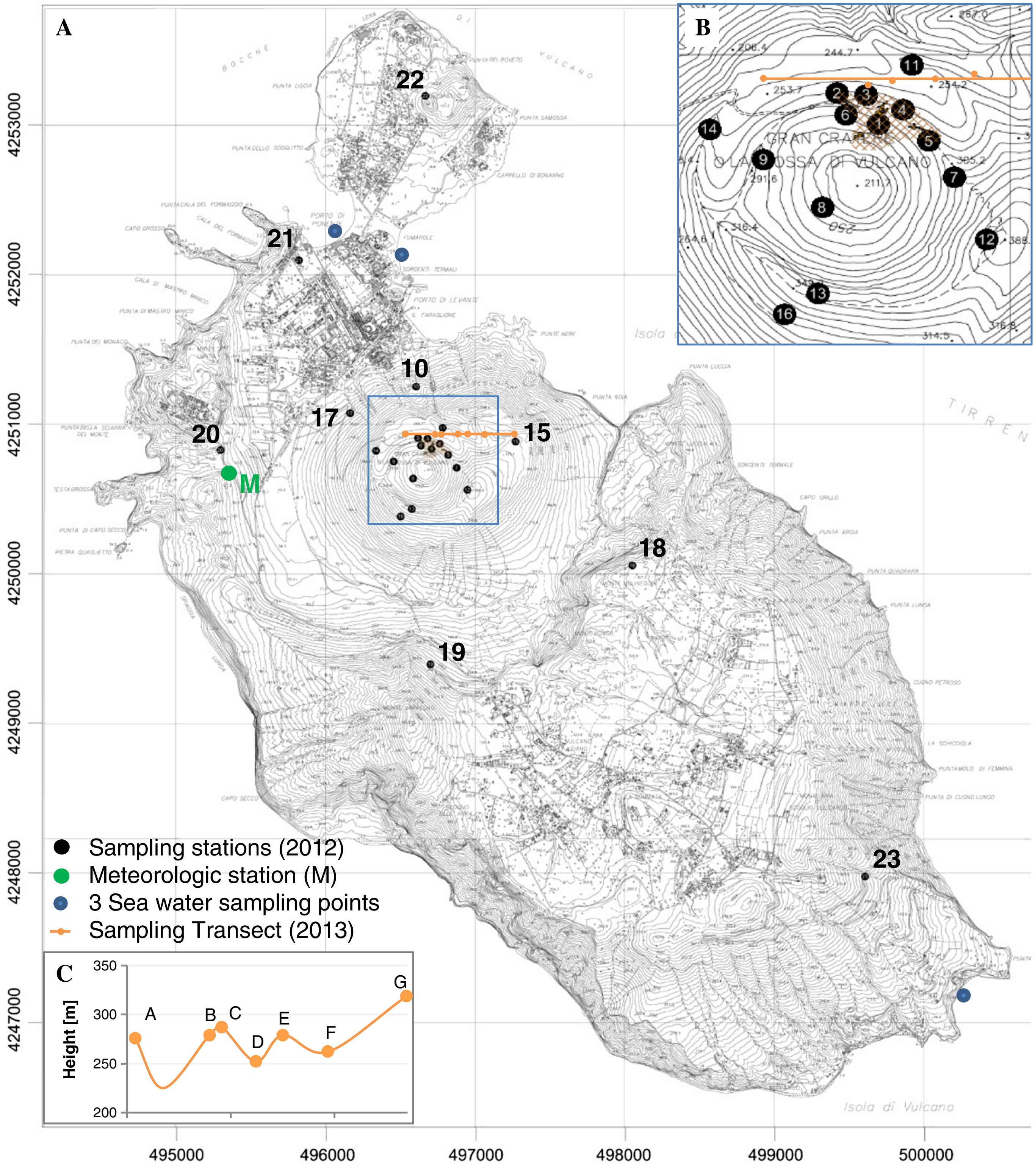

Fig. 1. Moss monitoring stations all over the island (2012) and along a transect (2013), as well as meteorological and sea water sampling stations on Vulcano Island (A, B). Fig. 1C shows the altitude for sampling sites A–G of the monitored transect.

all stations and additionally 3 days for 2 sites within the fumarolic field. The H_2S filters were impregnated with Zn acetate as sorbent, which reacts to ZnS with H_2S (Aiuppa et al., 2007). Diffusive samplers of polypropylene tubes were used to collect SO_2. The sorbent reacts with strong acids such as SO_2 but not with weak ones like H_2S (Aiuppa et al., 2004). The exact techniques of both passive samplers are described in Aiuppa et al. (2007).

Additionally, a triplicate of soil samples was taken at each station for comparison with dust deposition on the mosses. Sea water was sampled at three different sites around the island. The meteorological station marked in Fig. 1 provided hourly precipitation data as well as wind data.

For moss monitoring along a transect through the fumarolic field in 2013 only dead uncovered moss was exposed. Sampling was done in triplicates at 7 sites along the transect (Fig. 1, GPS coordinates in Table A1).

Since the main wind direction was western winds during the 2012 monitoring, the transect was designed with one station west of the fumarolic field (station A), 2 stations (station B, C) within, and 4 stations in wind direction from the fumaroles (station D, E, F, G). The setup of the moss bags was the same as mentioned above, soil samples and meteorologic data were taken as well.

2.3. Extraction methods

After exposure on Vulcano, moss bags were packed without further drying. They were transported in sealed evacuated plastic bags and stored in the dark at room temperature not longer than 3 weeks until extraction. In the laboratory, moss bags were unpacked and oven-dried (24 h at 40 °C). The mosses were treated with plastic instruments only, to avoid metal contamination. Mosses were ground in Zr vessels with a ball mill (Retsch MM 2000, 14 Hz, 3 min).

Samples from the 2012 screening were extracted twice, using HNO_3 and H_2O_2 for one extraction and ultrapure deionized water (MQ, 18.2 MΩ cm at 25 °C, <3 ppb total organic carbon, Merck Millipore) for the other one. Samples from the 2013 transect were only extracted with HNO_3/H_2O_2.

Deionized water extraction was done with 0.1 g moss powder and 20 mL MQ. The suspension was shaken for 2 h on an overhead shaker, centrifuged (5000 rpm, 5 min, Hettich Universal Centrifuge) and filtered at 0.2 μm (cellulose-acetate filter, Membrex). An aliquot of the filtered supernatant was used for pH measurement (HACH pH-meter HQ40d with PHC101 electrode). The HNO_3 extraction was performed after the screening (2012) and after monitoring the transect (2013). A total of 0.1 g of moss powder was used, 3 mL HNO_3 (65%), 2 mL H_2O_2 (30%), and 5 mL MQ were added and extraction was performed in closed pressure vessels in the microwave (CEM MARS Xpress). The heating was performed in steps of 10 min to 150, 200 and 220 °C, holding every temperature for 10 min. After extraction and cooling for 15 min, samples were filtered (0.2 μm) and stored at 4 °C until analysis. For HNO_3 digestion, no appropriate moss reference material existed. The few existing non-standardized moss reference materials were extracted by a different method than the one used in the present study (wet ashing compared to microwave extraction in the present study, Steinnes et al. (1997)) and thus were not suitable for direct comparison.

Soil samples were oven-dried at 65 °C for 24 h. A total of approximately 0.1 g of each soil sample was digested in aqua regia in the microwave (max. 160 °C, 15 min).

2.4. Analysis

For analysis, moss and soil extracts were diluted at minimum 1:10 for trace elements on mosses and up to 1:10,000 for Fe and Mg in soil samples. Total concentrations of As, Ba, Bi, Co, Cr, Cu, Fe, I, Li, Mg, Mo, Mn, Pb, S, Sb, Se, Sr, Tl, W, and Zn in all extracts were measured by quadrupole ICP-MS (X-Series2, Thermo Scientific). In 2013, V was analyzed additionally. For internal drift correction, a calibration standard was measured every 10–15 samples and data were corrected assuming a linear drift. Rhodium and Re were spiked to every sample as internal standard (50 $\mu g \cdot L^{-1}$ each). Arsenic and S were measured in reaction mode with 10% O_2 in He as reaction gas, while KED mode with 7% H_2 and 93% He as collision gas and a 2 V energy discrimination was used for Co, Cr, Fe, Mn, Se, and Zn.

2.5. Data evaluation and statistics

Although the used moss was washed before exposure, it contained small background concentrations of almost all elements analyzed. Background correction was done by extracting and analyzing unexposed moss and subtracting its concentrations as a blank value from all mosses exposed on Vulcano. Concentrations were calculated per gram moss but could not be referred to m^3 of air because the amount of air which passed the moss depended on diffusion, transport by wind, and turbulent eddies. These were too many factors to take into account using the Fick's first law, which is based on diffusive transport only. This was different for the passive samplers for SO_2 and H_2S, where the sampling material was enclosed in a tube with diffusion being the major factor controlling accumulation.

To account for different exposure times of the moss bags, accumulation rates per day [$\mu mol \cdot (g \cdot day)^{-1}$] were calculated. Since there were no significant differences between the accumulation rates per day for mosses exposed for 3, 6, and 9 weeks (Table A2a–d) under different rain fall conditions (Fig. A2), washout by rain was considered to have a minor effect on sampling of volatile metal(loid)s and their distribution patterns and is neglected in all following discussions. Mosses with different exposure times were thus treated as replicates as well as "living" and "dead" mosses (see Section 2.1).

For the determination of element distribution patterns and for comparison among the elements with different concentration ranges, all elements were normalized to the highest concentration obtained for each element and each monitoring interval. Covered and uncovered moss bags were considered separately. Data on maps and in cluster analysis given in percent of the maximal concentration for each element ignores absolute concentrations and thus allows emphasizing differences in element distribution patterns.

Data were clustered by calculating the Euclidean distances between each element distribution pattern and clustering elements hierarchical by the Ward, average linkage, and complete linkage method (program RStudio). Probabilities are given by the approximately unbiased p-value (Suzuki and Shimodaira, 2006). The wind rose was plotted by using Lakes Environmental software WRPLOT View™. Maps were produced by using ESRI geographical information system ArcMap 10.

3. Results and discussion

3.1. Method evaluation

3.1.1. Comparability of active moss monitoring with passive samplers

To evaluate the general suitability of mosses for monitoring the emission impact of fumaroles, the pH of MQ moss extracts was used as a first simple screening parameter. The pH of MQ extracts is a measure for the amount of acidic components being deposited on the mosses. It was lower for mosses exposed close to the fumaroles (higher concentration of acidic compounds released) than for mosses exposed at further distance from the fumaroles (Fig. 2a). Passive samplers for H_2S and SO_2 showed an opposite trend to pH: concentrations were highest within the fumarolic field (up to 10,000 $\mu g \cdot m^{-3}$) and decreased with increasing distance (Fig. 2b). The observed pattern corresponds to the expectations that SO_2 and H_2S as acidic gases are emitted by the fumaroles (Aiuppa et al., 2005b; D'Alessandro et al., 2013). The correlation of pH, SO_2, and H_2S thus shows that moss extracts are generally suitable to display the influence of the fumaroles.

Total S concentrations were also directly measured in the HNO_3 moss extracts which, in contrast to dissolution just by MQ, are a total digest of the moss powder. Comparing the measured S concentration [$\mu g \cdot (g \cdot d)^{-1}$] on the mosses with the actual total S concentration measured by passive samplers ($\mu g \cdot m^{-3}$, sum of SO_2 and H_2S) shows a positive correlation between both (Fig. 2b, R^2 of 0.74 and 0.73). Absolute concentrations cannot be compared because of the different reference system as explained in Section 2.5. The correlation with passive samplers is given for both, covered and uncovered moss bags, with uncovered moss bags having higher concentrations than covered ones. Consequently, mosses will allow drawing the same conclusions about spatial S distributions as well established passive samplers.

3.1.2. The effect of different extraction techniques

Two different extraction techniques were applied for the moss screening on Vulcano in 2012 to evaluate their respective extraction

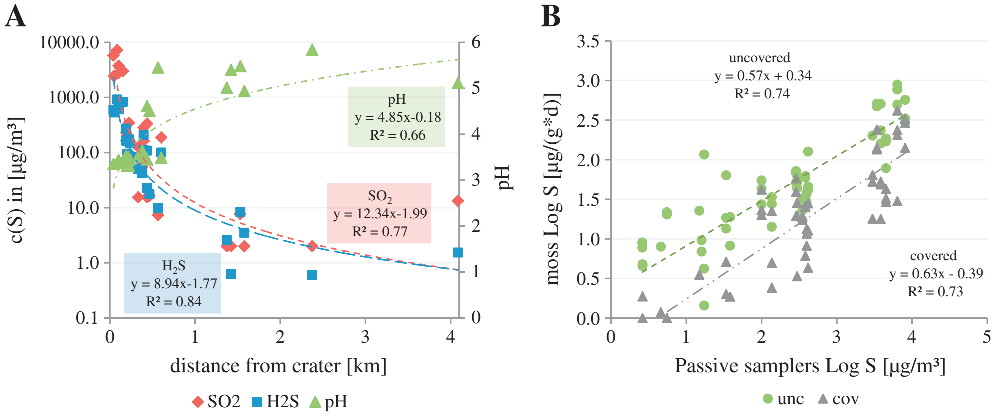

Fig. 2. SO_2 and H_2S concentrations on the whole Island of Vulcano, a: concentrations and pH of deionized water extracts of the moss bags as a function of the distance from the crater; b: relation between S concentration in passive samplers and moss bags.

efficiencies. Nitric acid results in a complete digestion of the moss powder which largely destroys particles or complexes >0.2 µm, if in solution. Deionized water extraction on the other hand is a soft extraction method, which mobilizes only weakly bound compounds and likely does not destroy particles and complexes. Before analysis, all solutions were filtered (0.2 µm). Comparing both extraction methods for all elements analyzed shows that MQ extraction dissolves a very variable ratio of the HNO_3 extraction, depending on the element. The two elements As and Pb are a clear example of the different extraction efficiencies. Arsenic was dissolved in MQ nearly as well as in HNO_3, resulting in largely comparable concentrations for both extraction techniques, whereas Pb showed significantly lower concentrations in MQ extractions (Fig. 3). The elements Tl, I, and S showed similar trends like As while Ba extraction efficiencies resembled Pb. As indicated above, less dissolution in MQ than in HNO_3 could point to the presence of particles or complexes >0.2 µm, which were not dissolved by MQ and therefore removed by filtration after extraction. These particles could e.g. be Pb and Ba sulfate salts, which are almost insoluble in the MQ extract, but can dissolve in the acidified hot water with a more oxic redox potential (due to H_2O_2 addition). Formation of carbonate salts is excluded by too acidic conditions. Dissolution of the exposed mosses in deionized water yielded pH values of 3.2 to 4 at and around the crater (Fig. 2a). Lead has often been considered a volatile element in geothermal systems (Planer-Friedrich and Merkel, 2006; Calabrese et al., 2011). If its source was a volatile release from the fumaroles at Vulcano, too, we must assume that the formation of Pb and Ba sulfates could have taken place after deposition on the moss. However, the spatial distribution, discussed in Section 3.3.2, points to a different source and, like for Ba, to transportation as particle.

All other elements showed some variations in concentrations between MQ and HNO_3 extraction, with HNO_3 extracts always showing higher concentrations than MQ extracts. Due to the discussed differences between HNO_3 versus MQ extractions for some elements, only the concentrations from HNO_3 extracts were used for data evaluation of all elements in the following sections.

3.2. Element distribution patterns

Screening over the whole island showed that all considered elements (As, Ba, Bi, Co, Cr, Fe, I, Li, Mg, Mo, Pb, S, Sb, Se, Sr, Tl, and W) except Zn, Mn, and Cu occurred at more than 50% of the sites in significantly larger concentrations than in the moss blank. Zinc and Cu were previously found to be enriched in lichens S and SE of the fumaroles (Varrica et al., 2000) where we had less monitoring stations. Our only station in that area (No 18) showed Zn concentrations below detection limit ($<0.15\ \mu g \cdot g^{-1}$). We detected Zn at some individual stations within the fumarolic field. However, in contrast to other elements, these Zn concentrations varied significantly between different monitoring periods (e.g. at station 3 where Zn was only found in covered moss bags after 6 weeks ($3\ nmol \cdot (g \cdot d)^{-1}$) and in one 9 weeks uncovered exposed moss bag of triplicates with $0.36\ nmol \cdot (g \cdot d)^{-1}$) and were thus not considered as representative. Manganese showed similar patterns, as it could only be detected at some single stations in single moss bags (of triplicates) and for only one single monitoring time at the crater area. Copper was found S and SE of the fumaroles (stations 13, 15, and 18) but had concentrations mostly below detection limit within the fumarolic field

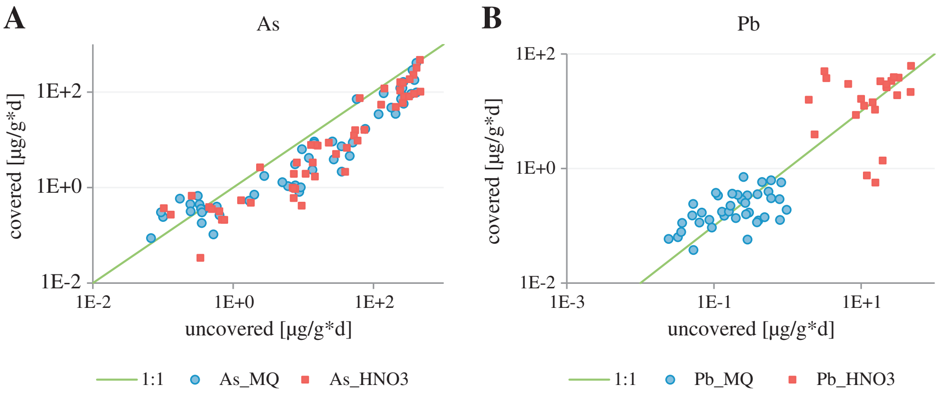

Fig. 3. Comparison of element concentration in covered and uncovered moss bags for As and Pb extracted once with HNO_3 and H_2O_2 and another time with MQ.

($<1.25\ \mu g \cdot g^{-1}$). Thus, Cu likely does not originate from the fumaroles. For further data evaluation neither Zn, Mn, nor Cu were considered.

All other elements were clustered using all 23 stations and data from the 3, 6, and 9 week monitoring with covered and uncovered moss bags to investigate similarities and differences in distribution patterns. All of the three different cluster methods applied, clearly separated As, Sb, S, I, Se, Tl, and Bi from Fe, Co, W, Pb, Cr, Mo, Ba, Li, Mg, and Sr (Appendix, Fig. A3a) which seems to correspond to fumarolic elements and non-fumarolic elements, respectively. Employing the average linkage method for clustering (which uses the averaged distance of all element pairs from different groups) separates Li from the rest of the group (Fe, Co, W, Pb, Cr, Mo, Ba, Sr, Mg) (Fig. A3b) indicating a somewhat different distribution. Clustering by complete linkage method shows three different groups with Li being grouped with Mg and Sr (Fig. 4). Except for Pb, the rest of the cluster is consistent with the cluster using average linkage method. The reason for picking the complete linkage cluster method for the following discussion is based on it delivering the best basis for our geochemical interpretation. Slightly different element source assignments might be obtained when selecting other cluster methods.

The first group contains the elements Li, Sr, and Mg, which were predominantly found outside the fumarolic field (Fig. 5, Appendix, Fig. A4). The elements Sr and Mg clustered together. The elements W, Co, Fe, Pb, Cr, Mo, and Ba belong to the second group and were found in higher concentrations primarily at the crater (Fig. 5, Fig. A6). Two sub-clusters can be found containing W, Co, and Fe on the one hand and Pb, Cr, Mo, and Ba on the other hand. The third group of elements clustered with a significant p-value of 96% and contained As, Sb, S, I, Se, Tl, and Bi. They were predominantly found within the fumaroles (Fig. 5, Fig. A5). That third group can further be divided into three sub-clusters grouping As, Sb, and S on the one hand, Se, Tl, and Bi on the other hand, with I forming its own third group. The transect across the fumarolic field monitored in 2013 reflects the similarity of distribution patterns for elements, which were clustered together based on the data of the screening (Fig. 6). Vanadium was only analyzed in 2013, thus not considered in the cluster analysis, but plotted with similar trends as W, Co, and Fe. In the following, we will first discuss the elements found predominantly outside the fumarolic field (group 1 and 2), then the fumarole-borne ones (group 3).

3.3. Elements not originating from the fumaroles

3.3.1. Sea spray-borne elements (group 1)

During the screening, Li, Mg, and Sr were found to be distributed almost equally all over the island (Fig. 5, Fig. A4). Such distribution suggests two possible main sources which are a geogenic or sea spray origin. Vulcano is an island, and thus, sea water could be one of these sources. Sea spray is known to be spread up to 1400 km (shown for Cl by Thornton et al. (2010)). The concentrations measured in sea water around Vulcano Island for Li are $17.7 \pm 11\ \mu mol \cdot L^{-1}$, which is in good agreement with general values for sea water analysis ($24.9\ \mu mol \cdot L^{-1}$ Li, (Schwochau, 1984)). Mg and Sr concentrations are reported to be $53{,}000\ \mu mol \cdot L^{-1}$ and $92\ \mu mol \cdot L^{-1}$, respectively (Schwochau, 1984).

In our study, Li shows highest concentrations at sites, which are at low altitudes above sea level and mainly lower concentrations on mosses at higher altitudes (Fig. 5). This might be an altitude effect as sea spray is likely to result in lower concentrations at the crater rim and other monitoring sites with higher altitudes in comparison to sites at lower altitudes. Consequently, the main source for Li is likely to be sea spray, covering the whole island.

In contrast to Li, Mg and Sr were found in high concentrations at all screening stations over the whole island as well as at elevated sites on the crater (Table A3). The only exceptions were stations directly within the fumarolic area, where concentrations dropped below detection limit (mean concentrations outside the fumarolic field of $5000\ \mu g \cdot g^{-1}$ and $126\ \mu g \cdot g^{-1}$ soil for Mg and Sr, respectively). Thus, soil is a likely additional source for these two elements besides sea spray. These results are consistent with Calabrese et al. (2011) who also pointed out a non-volcanic source for Mg and Sr at Mt. Etna, which could be geogenic dust or sea aerosols.

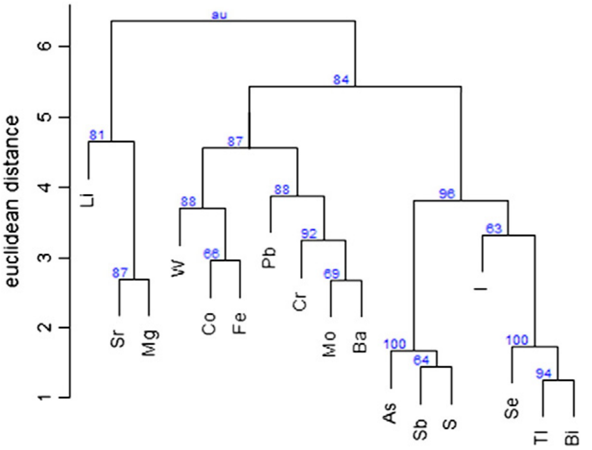

Fig. 4. Cluster analysis of distribution of elements in all moss bags on Vulcano Island. For clustering, all obtained data during screening (3, 6, 9 weeks, covered and uncovered moss bags) were used. Clustering was performed by using the complete linkage method in combination with the Euclidean distance as a measure of distance. Numbers indicate the approximate unibiased p-values [au, %] for each sub-cluster.

3.3.2. Soil-borne elements (group 2)

During the screening, Fe and its associates were predominantly found at the crater and in lower concentrations on the caldera rim and in the background (Fig. 5, Fig. A5). Along the transect, Fe, Co, and also V (which was measured in the 2013 transect samples only) were predominantly found outside the fumarolic field (station D–G), while W had an additional peak within the fumaroles (Fig. 6). The main characteristic, in which the crater and the background sites differed, was the presence of bare soil particles (no plants covering the soil). Moss bag samples with high Fe concentrations were derived from sites with bare soil, whereas low Fe concentrations were only found in combination with the presence of plants. Concentrations were also lower within the fumarolic field, where the ground was covered with crusts precipitated from fumarolic degassing. The monitored transect reflects these results with relatively low concentrations within the fumarolic field and higher concentrations outside the fumarolic field at wind exposed sites. Analysis of bare soil particle extracts and soil in the background revealed a high heterogeneity but in general higher concentrations of Fe and Co outside the fumarolic field (Appendix, Table A3). Bare soil particles can be easily wind-transported to the moss bags where they are deposited. Thus, Fe and its associates are likely to originate from soil particles. Investigating Mt. Etna, Calabrese et al. (2011) classified Co and Fe as refractory elements emitted from the volcano. However, in contrast to Vulcano, Mt. Etna's activity consists not only of fumarolic activity but also of frequent paroxysmal eruptions, which produce lava and ash.

The other elements in a sub-cluster in this group (Pb, Cr, Mo, and Ba) were also predominantly found at the crater area, but had a second maximum at transect station A on the upwind side of the fumarolic field and generally higher concentrations than the Fe-subgroup within the fumarolic field (Fig. 6; mean element concentrations in the moss are given in the Appendix, Table A5). The maximum before the fumarolic field might be explained by its location at the crater rim with bare soil. Lead and Ba being particulate elements agrees with extraction results, where both elements were shown to be present to a large extent as particles (Section 3.1.2). Tungsten from the first sub-group of this cluster shows a similar transect profile like Ba and Mo while Cr does not show higher concentrations at the fumaroles at the transect, but was

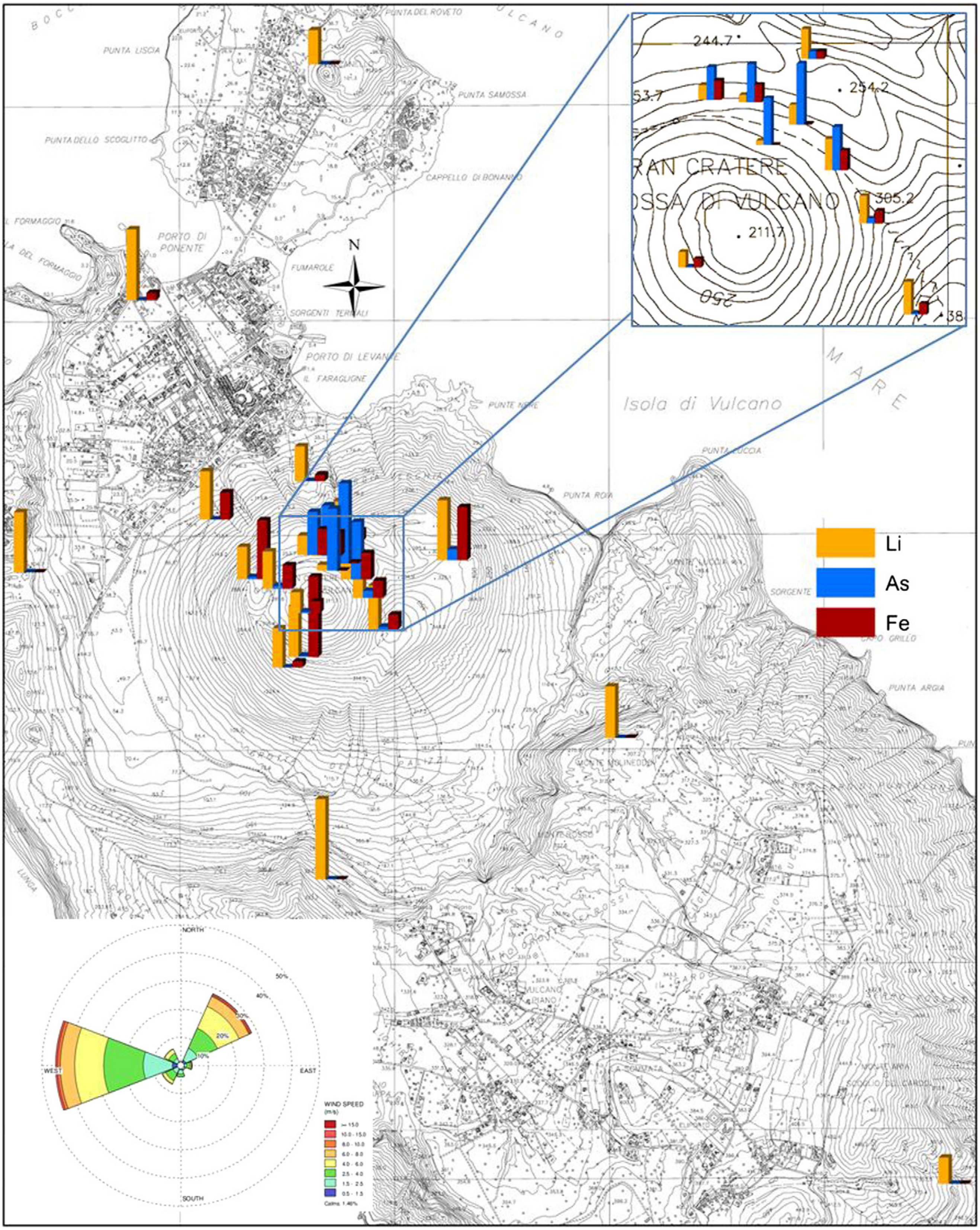

Fig. 5. Spatial distribution of Li, As, and Fe in moss bags (exposed uncovered for 9 weeks) including a wind rose of the monitoring period 2012.

found within the fumaroles during the screening (2012). Consequently, in this cluster, elements coming both from the fumaroles and from the soil can be found. Lead and Mo were previously detected as volatiles in the geothermal system in Yellowstone National Park, USA, using gas sampling chambers and NaOCl as oxidizing solution to trap volatile compounds (Planer-Friedrich and Merkel, 2006). Calabrese et al. (2011) also classified Ba as refractory rock-forming component on Mt. Etna, whereas Pb was classified as volatile element. Using moss as a sampling device

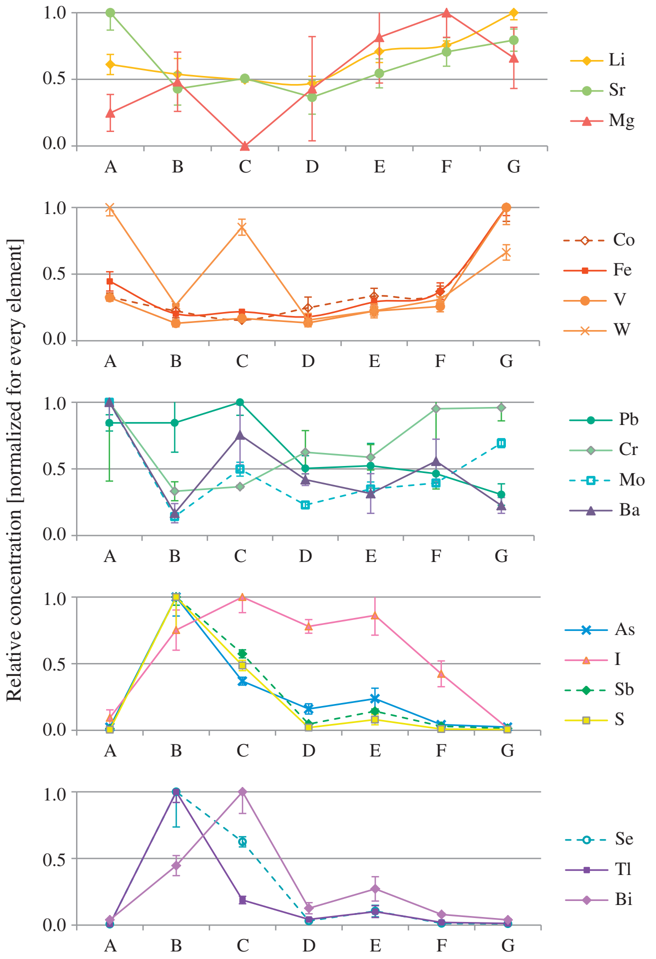

Fig. 6. Mean element concentrations of exposed moss bag triplicates along the transect. Concentrations of the triplicates were averaged and then normalized to the highest concentration obtained for each element.

does not directly permit a statement about the speciation and thus about the state of matter of each element. Only distribution patterns can be seen. If Mo and Pb are emitted as gases from the fumaroles at Vulcano, they must behave somewhat differently from the group of volatiles discussed in Section 3.4, e.g. have a much lower stability which can also lead to reduced transport distances.

3.4. Fumarolic elements

The last cluster of elements contains As, Sb, S, I, Se, Tl, and Bi (96% significance). These elements were predominantly found within the fumarolic field (Appendix, Fig. A6). Sulfur is known to be emitted from the fumaroles on Vulcano in gaseous form (see Section 3.1.1 and e.g. Aiuppa et al. (2005b)) and its characteristic odor is present within the whole fumarolic field. Thus, the other elements clustered with sulfur were also suspected to originate from the fumaroles.

To compare these elements with the soil-borne elements (identified in Section 3.3.2), hypothetical ratios between soil concentrations ($\text{nmol}\cdot\text{g}^{-1}$) and daily moss accumulation rates ($\text{nmol}\cdot\text{g}^{-1}\cdot\text{d}^{-1}$) were calculated (Appendix, Table A4). These ratios shall not be taken as absolute numbers but just help to visualize differences between sites and element groups. In contrast to soil-borne elements, which showed ratios between 1.1 up to 95,000 at all sites, the ratios for Sb, I, and Tl were between 0.22 and 0.5 at stations within the fumarolic field. This shows significantly higher accumulation rates per day for Sb, I, and Tl in the moss compared to absolute concentrations in the soil. Thus, these elements must have a different origin than the soil, which is another indication for their source being the fumaroles. For the elements As, S, Se, and Bi soil per moss ratios are larger (2.3–560). Sulfur obviously precipitates within the fumarolic field as yellow crystals and thus was contained in the analyzed soil. The other elements could undergo similar mechanisms or co-precipitate with sulfides, e.g. as orpiment (As_2S_3). In that context it is surprising that Sb does not follow the same trend, precipitating as stibnite, but no explication has yet been found.

The distribution of all elements in this clustered group (As, Sb, S, I, Se, Tl, and Bi) was found to depend on the prevailing wind direction. As Vulcano Island is located in the temperate zone, prevailing wind directions are westerly, so that fumarolic gases are transported to the east over the crater toward the sea. This was also true for both monitoring periods, in which the wind direction was predominantly from the west (Fig. 5). While monitoring the transect through the fumarolic field, wind direction monitoring was sketchy, but still showed predominantly western winds. During the screening, the elements of this group were additionally found at stations in wind direction from the fumaroles (Fig. 5). Monitoring the transect allows to have a closer look at the distribution of these elements (Fig. 6). All elements had low concentrations on the windward side of the fumaroles, a sharp increase in concentration within the fumarolic field (station B and C of the transect) and decreased in concentration behind the fumaroles. At station D, concentrations of all elements in this group decreased and increased again at station E, after which another concentration decrease followed at stations F and G. The distribution of the elements reflects the morphology of the transect (Fig. 1c). Station D was located in a valley and thus in the shadow of the crater rim, which mitigated the influence of the wind and the fumaroles. Station E was situated on the hill behind the valley of station D where the wind was not slowed down by morphology and thus showed higher concentrations than the station in upwind-direction. The following stations again were in a valley and on a hill but farther away from the fumaroles. Transport and dilution resulted in lower concentrations of As, Sb, S, I, Se, Tl, and Bi in the moss bags.

Though the elements were clustered together, there are some differences among their distribution transects. Iodine shows the most pronounced differences (Fig. 6). It was found in higher concentrations at stations D, E, and F, which were located behind the fumarolic field in wind direction, compared to the other elements of the group. This might be the reason for I to be clustered separately from the other elements. Iodine clusters with the volatile element group with a significance of 63%. It was accumulated on the moss in higher concentrations per day than it was concentrated in the soil during screening (Appendix, Table A4). Iodine has been shown to be emitted by fumaroles from Mt. Etna as HI (Aiuppa et al., 2005a) which could be present at Vulcano as well. Moreover, halogens are known to generate volatile compounds with metal(oid)s, which has also been shown on Vulcano for Cl (Cheynet et al., 2000). This fact can cause I to be grouped with As, Sb, S, Se, Tl, and Bi. A factor that separates I from the other elements can be the presence of I in sea water (Preedy et al., 2009) and thus its occurrence in sea spray. This is not given for the other elements of this group.

The remaining elements in this cluster are divided in two sub-clusters: As, Sb, and S ($p = 100\%$) and Se, Tl, and Bi ($p = 100\%$). Differences between these groups cannot be found in the transect, though. An explanation for As and Sb grouping together can be that these elements are chemically known to behave similarly: Both elements have been shown to have a high affinity to S and form thio-complexes in geothermal S-rich waters (Planer-Friedrich et al., 2007; Planer-Friedrich and Scheinost, 2011; Planer-Friedrich and Wilson, 2012). In volatile state, speciation of As compounds was investigated in Yellowstone National Park, where As–S complexes were detected as well (Planer-Friedrich et al., 2006). The occurrence of such compounds can cause As and Sb to group together with S. However, as was pointed out before, lower soil/moss ratios for Sb, compared to As, question its co-precipitation with S. Elements like As, Se, Sb, and I are also known to be emitted from geothermal systems as inorganic and methylated volatiles (Hirner et al., 1998;

Feldmann et al., 1999; Aiuppa et al., 2005a; Planer-Friedrich and Merkel, 2006). Thallium has been postulated to occur on Vulcano in gaseous form (Cheynet et al., 2000) and also was found to accumulate on uncovered mosses (during the screening) within the fumarolic field in higher concentrations per day than it had absolute concentrations in the soil. Investigating emissions from Mt. Etna by active moss monitoring and precipitation analysis, Calabrese et al. classified As, Tl, Se, Bi, and S as volcanogenic, volatile elements (Calabrese et al., 2011, in press). Consequently, all these elements are known to be emitted as gases from geothermal systems.

4. Conclusion

In the present study, active moss monitoring and clustering of distribution patterns were used to identify volatile metal(loid)s released from fumaroles at Vulcano Island. Elements occurring ubiquitously all over the island which originated from sea spray (Li, Sr, and Mg) and particles released from bare crater soil at exposed sites (W, Co, Fe, Pb, Cr, Mo, and Ba) could be clearly differentiated from volatile elements emitted by the fumaroles (As, Sb, S, I, Se, Tl, and Bi). Distribution of those elements could be tracked back to the source even over far distances and was shown to depend significantly on the morphology, with lower concentrations in calm depressions and increased concentrations at wind-exposed, higher sites. Moss-monitoring thus proved to be an ideal screening method to identify target elements, on which one can focus with more sophisticated and expensive methods if quantitative and species-selective sampling is required. Due to its low costs and easy application, moss-monitoring can cover large areas at high spatial resolution and quickly reveal the extent and emission impact of volatile metal(loid)s distribution away from their source.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jvolgeores.2014.04.016.

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Active moss monitoring allows to identify and track distribution of metal(loid)s emitted from fumaroles on Vulcano Island, Italy

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Appendix

Table A1: GPS coordinates of sampling points given in UTM WGS84 (zone 33S)

	sampling point	coordinates		altitude [m]
		E	N	
Screening Stations	1	496705	4250834	284
	2	496613	4250907	279
	3	496678	4250903	282
	4	496758	4250867	285
	5	496816	4250793	296
	6	496632	4250855	275
	7	496872	4250707	319
	8	496580	4250636	254
	9	496451	4250750	292
	10	496601	4251251	127
	11	496778	4250973	273
	12	496943	4250560	385
	13	496571	4250432	353
	14	496332	4250794	294
	15	497265	4250883	330
	16	496497	4250383	318
	17	496159	4251072	93
	18	498047	4250054	316
	19	496697	4249395	272
	20	495292	4250826	139
	21	495816	4252094	18
	22	496663	4253194	94
	23	499601	4247976	289
Transect Stations	A	496502	4250871	276
	B	496710	4250856	279
	C	496745	4250867	287
	D	496839	4250884	252
	E	496915	4250895	279
	F	497042	4250888	262
	G	497263	4250884	319

Table A2a: Mean element concentrations of 3, 6, and 9 weeks exposure during screening in uncovered moss bags at each sampling site extracted with HNO$_3$ [nmol·(g·d)$^{-1}$]. From all concentrations at every site moss blank concentrations were subtracted (section 2.5). Thus, some given concentrations may seem to be below detection limit, but actually are not.

Site	Li	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	Pb	Cr	Mo	Ba
DL*	1.1	1.2	450	0.27	0.028	610	0.55	0.038	$4.2\cdot10^{-3}$	$3.9\cdot10^{-3}$	$5.0\cdot10^{-3}$	0.11	190	1.8	0.31	0.043	2.04
1	6.5	1.5	160	120	6.3	< DL	5.8	1.9	0.32	0.55	0.01	< DL	200	< DL	1.20	0.03	0.91
2	7.8	4.9	1040	67	0.67	4300	6.9	1.1	0.76	0.75	0.02	0.03	220	2.5	0.51	0.02	1.5
3	4.4	4.4	720	75	2.6	< DL	9.8	3.5	1.7	1.4	0.01	0.10	320	3.9	7.5	0.13	4.0
4	12	1.4	980	130	3.4	< DL	11	4.7	0.96	0.53	0.01	< DL	15	0.15	0.21	0.02	0.63
5	21	4.9	1900	76	2.9	8900	4.5	1.0	0.38	0.24	0.01	0.08	520	0.64	1.3	0.04	1.5
6	33	4.2	1050	88	0.76	6500	5.9	0.78	0.29	0.17	0.01	0.06	430	< DL	0.68	0.03	2.2
7	20	4.2	2200	6.9	0.11	1600	2.4	0.06	0.02	0.01	0.00	0.04	170	2.6	0.36	0.01	1.2
8	13	4.0	1200	1.8	0.06	1000	2.1	0.03	0.00	0.00	0.00	0.04	460	1.3	0.27	0.01	2.3
9	25	3.1	730	4.1	0.12	720	3.4	0.07	0.01	0.02	0.03	0.09	470	1.0	0.32	0.02	0.90
10	22	1.3	540	0.19	0.04	440	0.85	0.02	0.00	0.00	0.00	0.01	170	4.5	0.23	< DL	0.68
11	15	4.6	2080	14	0.17	2300	3.9	0.17	0.10	0.05	0.01	0.04	270	2.1	0.78	0.03	1.7
12	14	3.7	1700	3.1	0.13	1300	3.9	0.11	0.02	0.02	0.01	0.03	190	2.3	0.57	0.03	1.5
13	19	11	1800	1.6	0.08	1700	1.4	0.18	0.01	0.01	0.03	0.25	1200	4.0	0.84	0.09	4.7
14	19	13	1200	3.8	0.08	1200	1.3	0.13	0.04	0.03	0.02	0.22	1400	3.0	0.95	0.08	5.2
15	22	8.9	2700	21	0.50	2600	3.7	0.43	0.17	0.11	0.02	0.17	810	0.5	0.57	0.06	2.3
16	17	3.4	1700	0.07	0.04	370	1.0	0.02	0.00	0.00	0.01	0.01	60	0.55	0.03	0.00	1.1
17	22	2.8	660	0.10	0.03	130	0.41	0.01	0.00	0.00	0.00	0.05	140	0.92	0.06	0.02	1.2
18	33	2.7	1500	0.09	0.06	710	0.94	0.01	0.00	0.01	0.01	0.22	25	0.92	0.01	0.03	1.0
19	26	0.92	400	0.06	0.04	180	0.59	0.00	0.00	0.00	0.00	0.02	39	0.38	0.05	0.01	0.04
20	33	1.2	480	0.01	0.03	140	1.1	0.00	< DL	< DL	< DL	< DL	< DL	0.43	< DL	< DL	0.11
21	28	3.7	1200	0.16	0.07	280	1.4	0.01	0.00	0.00	0.01	0.06	170	1.70	0.12	0.01	1.6
22	17	0.99	530	0.03	0.07	290	0.60	< DL	0.00	< DL	< DL	0.00	< DL	0.37	0.06	0.00	0.10
23	10	0.40	140	< DL	0.02	1000	0.70	0.10	< DL	< DL	< DL	0.01	< DL	0.87	0.14	< DL	< DL

* DL = Detection limit in nmol·g^{-1}·d^{-1}. Detection limits are given for the moss blank with a hypothetical exposition time of 9 weeks. The moss blank was used for blank correction when calculating daily accumulation rates for the mosses for every station.

Table A2b: Element concentrations of 3 weeks exposure during screening in uncovered moss bags at each sampling site extracted with HNO$_3$ [nmol·(g·d)$^{-1}$]. From all concentrations at every site moss blank concentrations were subtracted (section 2.5). Thus, some given concentrations may seem to be below detection limit (Table A2a), but actually are not.

Site	Li	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	Pb	Cr	Mo	Ba
1	< DL	2.7	160	230	11	26000	4.9	2.9	0.53	1.1	0.0061	< DL	< DL	< DL	3.0	0.068	< DL
2	< DL	6.1	1400	130	1.3	5500	11	1.9	1.1	1.4	0.039	< DL	11	3.1	0.58	0.014	0.60
3	0.27	3.7	730	87	2.7	8700	9.9	2.3	2.5	1.6	0.0066	< DL	35	5.7	0.99	0.031	0.34
4	< DL	2.7	980	150	4.4	14000	12	4.2	1.5	0.73	0.023	< DL	28	0.15	0.082	0.033	0.94
5	< DL	5.5	1560	78	1.8	4800	4.2	0.50	0.27	0.21	0.0035	< DL	< DL	< DL	0.10	< DL	< DL
6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
7	< DL	3.0	1300	4.9	0.14	1300	0.88	0.061	0.036	0.017	0.0050	< DL	54	7.1	0.35	< DL	1.1
8	< DL	5.1	840	0.81	0.070	890	1.5	0.0043	0.0054	0.0021	0.0023	< DL	139	< DL	0.18	< DL	4.4
9	< DL	2.4	405	4.4	0.21	707	5.2	0.078	0.012	0.041	0.057	< DL	49	1.5	< DL	0.027	< DL
10	< DL	1.0	480	< DL	0.053	< DL	0.81	< DL	< DL	0.0015	< DL	< DL	< DL	11	< DL	< DL	1.6
11	0.82	4.8	2200	18	0.20	1400	2.4	0.16	0.12	0.056	0.0084	0.0064	235	4.9	1.3	< DL	2.4
12	2.0	2.8	970	1.5	0.16	840	2.4	0.096	0.018	0.037	0.031	< DL	190	6.1	0.46	0.023	0.75
13	5.0	9.5	790	1.1	0.068	1500	1.2	0.19	0.0086	0.013	0.029	0.19	1400	4.0	0.93	0.043	6.5
14	14	25	1500	6.6	0.16	1900	0.65	0.29	0.084	0.083	0.050	0.45	3200	4.8	2.1	0.16	11
15	0.71	12	4300	33	0.66	3500	3.9	0.71	0.22	0.15	0.021	0.025	440	< DL	0.20	0.021	1.3
16	< DL	5.7	2800	< DL	0.045	37	1.7	0.036	0.0016	0.0030	0.020	< DL	95	< DL	< DL	< DL	2.1
17	< DL	2.9	1300	< DL	0.022	< DL	< DL	< DL	< DL	0.0016	0.0073	< DL	0.36	0.77	< DL	< DL	2.4
18	< DL	3.8	2100	< DL	0.033	< DL	0.57	0.0099	< DL	< DL	< DL	0.11	< DL	0.73	< DL	< DL	2.4
19	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
20	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
21	< DL	4.6	2600	< DL	0.052	< DL	1.9	< DL	< DL	< DL	0.00060	< DL	< DL	3.8	< DL	< DL	3.4
22	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Table A2c: Element concentrations of 6 weeks exposure during screening in uncovered moss bags at each sampling site extracted with HNO_3 [nmol·(g·d)$^{-1}$]. From all concentrations at every site moss blank concentrations were subtracted (section 2.5). Thus, some given concentrations may seem to be below detection limit (Table A2a), but actually are not.

Site	Li	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	Pb	Cr	Mo	Ba
1	10	1.1	< DL	74	3.0	16000	8.5	1.1	0.22	0.38	0.016	< DL	200	< DL	0.47	0.024	0.91
2	7.9	4.9	730	25	0.25	2500	4.6	0.43	0.63	0.33	0.0095	0.044	380	1.5	0.49	0.033	2.9
3	9.0	5.0	860	81	1.27	11000	12	3.1	1.37	0.95	0.020	0.17	680	4.6	19	0.25	8.7
4	13	0.86	< DL	140	3.1	16000	11	3.6	0.87	0.48	0.0043	< DL	5.3	< DL	0.30	0.021	0.36
5	25	4.4	2000	83	1.9	7600	5.8	0.85	0.28	0.16	0.0097	0.11	750	0.64	1.9	0.022	2.4
6	33	4.2	1100	88	0.76	6500	5.9	0.78	0.29	0.17	0.0058	0.060	430	< DL	0.68	0.029	2.2
7	25	5.0	2600	7.7	0.084	1600	3.1	0.061	0.020	0.010	0.0013	0.064	260	0.19	0.36	0.010	2.3
8	17	3.3	1400	2.6	0.064	1200	3.1	0.056	0.0025	0.0058	0.0028	0.055	1100	1.3	0.51	0.020	1.7
9	35	4.3	1000	4.6	0.084	970	3.0	0.11	0.012	0.015	0.025	0.090	1100	0.48	0.56	0.037	1.6
10	29	1.4	640	0.22	0.033	340	1.1	0.019	0.00062	0.0017	0.0013	0.0092	260	0.28	0.39	< DL	0.12
11	28	6.1	2400	13	0.19	4200	5.7	0.27	0.13	0.057	0.0085	0.10	450	0.33	0.80	0.045	2.1
12	22	4.5	2300	4.9	0.13	1900	5.6	0.14	0.017	0.011	0.0078	0.031	230	0.045	0.87	0.041	2.5
13	31	15	2300	2.3	0.11	2000	0.74	0.22	0.015	0.010	0.042	0.33	1300	< DL	0.88	0.15	5.5
14	29	6.5	1200	2.4	0.052	640	< DL	0.037	0.014	0.0085	0.020	0.12	430	< DL	0.30	0.033	2.8
15	41	11	2100	18	0.50	2500	1.4	0.31	0.18	0.099	0.023	0.37	1400	0.50	1.1	0.12	4.6
16	17	1.8	760	0.093	0.058	500	0.23	0.0086	< DL	< DL	< DL	0.0007	26	0.39	< DL	0.0010	< DL
17	25	1.4	120	0.10	0.031	130	0.48	0.0099	0.0027	0.00082	0.0010	< DL	130	1.1	< DL	0.015	0.061
18	45	2.2	880	0.14	0.086	780	< DL	0.019	< DL	0.0071	0.015	0.30	47	1.6	0.015	0.027	0.38
19	20	0.50	130	0.055	0.016	140	0.32	0.0048	0.00037	0.00016	0.0011	0.019	39	0.68	0.046	0.010	0.044
20	42	0.94	350	0.026	0.032	46	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.43	< DL	< DL	< DL
21	28	3.6	380	0.20	0.045	300	< DL	0.017	0.0012	0.0039	0.0039	0.075	250	0.72	0.21	0.020	0.82
22	19	0.92	490	0.033	0.084	320	< DL	< DL	0.001	< DL	< DL	0.0010	< DL	0.37	0.055	0.0011	< DL
23	10	0.22	39	< DL	0.016	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.17	< DL	< DL	< DL

Table A2d: Element concentrations of 9 weeks exposure during screening in uncovered moss bags at each sampling site extracted with HNO_3 [nmol·(g·d)$^{-1}$]. From all concentrations at every site moss blank concentrations were subtracted (section 2.5). Thus, some given concentrations may seem to be below detection limit (Table A2a), but actually are not.

Site	Li	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	Pb	Cr	Mo	Ba
1	2.3	0.67	< DL	72	5.1	22000	4.0	1.6	0.22	0.23	0.0016	< DL	< DL	< DL	0.027	0.0044	< DL
2	7.8	3.7	940	50	0.46	4800	4.9	0.91	0.59	0.56	0.0052	0.014	280	2.8	0.47	0.024	1.1
3	3.9	4.4	560	58	3.6	16000	6.8	4.9	1.3	1.64	0.013	0.019	250	1.6	2.6	0.099	3.1
4	10	0.56	< DL	93	2.7	15000	11	6.2	0.55	0.39	0.0071	< DL	10	< DL	0.26	0.013	0.59
5	17	4.9	2200	67	4.8	14000	3.5	1.7	0.60	0.36	0.0079	0.046	280	< DL	1.9	0.056	0.62
6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
7	14	4.7	2900	8.1	0.11	1800	3.4	0.070	0.014	0.011	0.0038	0.026	190	0.59	0.37	0.013	0.36
8	8.4	3.5	1300	1.8	0.048	1000	1.6	0.019	0.0030	0.0019	0.00046	0.018	130	< DL	0.13	0.0015	0.87
9	15	2.6	770	3.1	0.056	490	2.1	0.033	0.0051	0.0042	0.0047	< DL	250	< DL	0.088	0.0058	0.17
10	14	1.3	510	0.15	0.041	550	0.66	0.023	< DL	0.00011	< DL	0.011	70	2.2	0.063	< DL	0.32
11	15	3.0	1700	12	0.13	1100	3.8	0.078	0.066	0.036	0.0015	0.0083	110	1.1	0.21	0.0055	0.71
12	17	3.8	1800	2.9	0.10	1200	3.6	0.083	0.013	0.016	0.0021	0.024	160	0.67	0.40	0.019	1.1
13	21	7.7	2200	1.4	0.053	1600	2.2	0.12	0.010	0.0089	0.022	0.22	870	< DL	0.70	0.072	2.0
14	13	7.8	1000	2.5	0.037	950	1.9	0.057	0.014	0.0092	0.0053	0.090	640	1.1	0.40	0.037	2.2
15	24	3.8	1500	12	0.34	1900	5.9	0.27	0.097	0.089	0.013	0.11	570	< DL	0.45	0.039	1.0
16	16	2.7	1600	0.038	0.021	560	1.1	0.014	< DL	< DL	0.0029	0.020	63	0.70	0.025	0.0010	0.15
17	19	3.9	500	0.11	0.027	120	0.34	0.016	0.0017	0.0013	0.0030	0.053	290	< DL	0.059	0.016	1.3
18	21	2.0	1500	0.040	0.049	630	1.3	0.013	0.00065	< DL	< DL	0.26	3.6	0.41	< DL	< DL	0.41
19	32	1.3	680	< DL	0.073	220	0.85	< DL	< DL	< DL	< DL	< DL	< DL	0.084	< DL	< DL	< DL
20	24	1.5	600	0.0022	0.024	230	1.1	0.00043	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.11
21	29	3.0	710	0.12	0.11	260	0.87	0.0078	< DL	0.0046	0.011	0.045	78	0.51	0.027	0.0055	0.47
22	14	1.1	580	< DL	0.060	270	0.60	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.10
23	11	0.59	240	< DL	0.032	1100	0.70	0.098	< DL	< DL	< DL	0.0086	< DL	1.57	0.14	< DL	< DL

Table A3: Mean element concentrations in the soil at each sampling site during screening [nmol·g^{-1}]. Concentration of Li and Cr are NA, and are thus left out here.

Site	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	Pb	Mo	Ba
DL*	240	160	72	12	840	59	6.3	0.23	0.57	0.87	4.4	72	3.4	2.3	4100
1	150	< DL	780	1.4	4800000	2.1	110	0.16	1.3	1.7	0.38	< DL	47	2.6	1400
2	120	< DL	890	4.0	1300000	< DL	320	1.3	130	2.1	0.69	< DL	130	4.0	1200
3	110	< DL	1600	0.76	2300000	2.7	320	0.70	5.6	2.5	0.18	< DL	100	3.3	1200
4	130	< DL	760	0.98	8000000	5.0	130	0.17	1.3	3.4	0.18	< DL	28	5.1	1200
5	150	< DL	7200	3.2	5000000	14	540	0.69	6.1	2.0	0.42	< DL	40	2.6	820
6	84	< DL	150	1.3	7200000	< DL	13	0.09	1.0	7.3	0.27	< DL	29	9.2	970
7	120	< DL	200	< DL	25000	< DL	3.1	0.07	1.1	1.7	6.9	42000	29	6.5	5.8
8	1600	57000	180	0.05	170000	< DL	12	0.34	1.8	5.1	107	370000	55	21	600
9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
10	3200	180000	230	0.03	190000	7.3	19	1.3	1.4	4.1	130	420000	89	39	1800
11	740	54000	470	0.49	61000	< DL	9.0	0.31	1.8	5.9	81	310000	50	23	72
12	400	< DL	100	0.44	50000	< DL	3.9	0.05	0.36	3.5	13	64000	45	17	840
13	330	100000	120	1.6	46000	< DL	21	0.12	0.24	8.3	80	240000	44	31	< DL
14	270	180000	110	0.84	43000	< DL	12	0.15	0.29	3.1	147	300000	20	14	< DL
15	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
16	230	77000	79	0.87	31000	< DL	10	0.10	0.20	3.9	79	220000	28	22	< DL
17	630	190000	120	0.54	91000	< DL	13	0.68	1.2	3.5	150	300000	34	17	5.3
18	2500	650000	260	0.16	140000	13	62	15	0.32	4.7	1600	900000	60	18	3100
19	1200	280000	120	0.81	59000	< DL	13	1.20	0.46	3.0	210	330000	26	13	240
20	1700	290000	220	1.3	96000	12	20	7.4	8.2	5.0	310	540000	120	23	670
21	940	350000	180	2.1	95000	5.2	15	1.7	1.3	5.5	220	470000	72	22	560
22	3500	170000	130	0.84	650000	< DL	15	1.7	2.1	1.1	92	300000	43	11	1300
23	3000	350000	320	0.16	130000	7.4	40	2.20	0.79	6.4	670	1100000	86	22	2900

* DL = Detection limit in nmol ·g^{-1}. This detection limit is given for the extraction solution only (aqua regia). For the elements Mg, S, and Fe DL, extraction solution was measured without prior microwave digestion. These DLs were used for blank correction and thus subtracted from all measured concentrations. Consequently, some given concentrations in the table may seem below DL, but actually are not.

Table A4: Soil per moss ratios of soil mean concentrations [nmol·g^{-1}] and mean accumulation rates per day in mosses [nmol·(d·g)$^{-1}$)] during the screening 2012. Values given here are just for indication, not absolute. Missing values indicate either soil or moss concentration to be < DL. Chromium and Li are left out in this table due to no data for soil analysis.

Site	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	Pb	Mo	Ba
1	100		6.3	0.22		0.35	57	0.50	2.3	220				80	1600
2	23		13	6.02	300		300	1.7	170	120	24		54	170	800
3	25		21	0.30		0.27	91	0.4	4.0	190	1.8		26	26	290
4	92		6.0	0.29		0.45	27	0.18	2.5	300			190	230	1800
5	30		95	1.1	560	3.1	530	1.8	25	280	5.6		62	67	540
6	20		1.7	1.7	1100		16	0.32	5.6	1300	4.5			320	430
7	28		29		16		48	3.1	87	520	150	250	11	550	4.7
8	400	47	100	0.74	160		440	94	540	2700	2900	790	43	2000	260
9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
10	2500	330	1200	0.68	430	8.6	900	4200	1200	3100	13000	2500	20		2700
11	160	26	33	2.8	27		53	3.0	36	970	2100	1200	23	920	42
12	110		33	3.4	38		37	2.8	17	260	470	330	20	610	580
13	30	57	72	21	26		120	11	22	270	320	200	11	360	
14	21	140	28	10	37		91	4.1	8.7	130	680	210	6.9	180	
15	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
16	69	45	1200	21	85		530	65	67	350	7400	3600	50	22000	
17	229	310	1100	20	730		1000	310	1000	940	2800	2100	37	1000	4.3
18	930	430	2800	2.8	200	13	4400	23000	45	320	7200	36000	65	670	2900
19	1300	690	2200	18	330		2700	3200	2800	2800	11000	8600	68	1300	5400
20	1400	620	16000	45	700	11	48000						280		6200
21	250	280	1100	31	340	3.8	1300	1400	300	1100	3700	2800	43	1700	360
22	3500	330	3800	12	2200			1700			95000		110	9800	13000
23	7400	2500		6.7	125	11	410				77000		99		

Tabelle A5: Mean element concentrations of triplicates at each sampling station of 3 weeks exposure during the transect monitoring (2013) with uncovered moss bags at each sampling site extracted with HNO_3 [nmol·(g·d)$^{-1}$]. From all concentrations at every site moss blank concentrations were subtracted (section 2.5). Thus, some given concentrations may seem to be below detection limit, but actually are not.

Site	Li	Sr	Mg	As	Sb	S	I	Se	Tl	Bi	W	Co	Fe	V	Pb	Cr	Mo	Ba
DL*	1.5	5.8	2800	0.83	0.12	2000	2.4	0.11	0.010	0.011	0.017	0.25	350	0.66	0.72	0.71	0.091	12
A	23	34	1079	13	0.20	3538	1.0	0.47	0.04	0.05	0.05	0.98	4790	13	1.6	11	0.45	35
B	20	14	2096	561	17	792585	8.3	70	6.5	0.52	0.01	0.67	2179	5.4	1.6	3.5	0.06	5.8
C	19	17	< DL	207	9.6	385433	11	44	1.2	1.2	0.04	0.46	2333	7.0	1.9	3.9	0.23	26
D	18	12	1868	90	0.78	15901	8.6	2.2	0.28	0.15	0.01	0.73	1937	5.6	0.94	6.6	0.10	15
E	27	18	3546	133	2.4	63522	9.5	7.4	0.66	0.32	0.01	0.99	3127	9.2	0.97	6.2	0.16	11
F	29	24	4349	24	0.50	7312	4.7	0.89	0.13	0.09	0.01	1.1	4003	11	0.86	10	0.18	19
G	38	27	2874	13	0.23	4628	0.18	0.71	0.08	0.05	0.03	3.0	10757	41	0.57	10	0.31	7.8

* DL = Detection limit in nmol·g^{-1}·d^{-1}. Detection limits are given for the moss blank with an hypothetical exposition time of 3 weeks. The moss blank was used for blank correction when calculating daily accumulation rates for the mosses for every station.

Fig. A1: Moss bag exposure on Vulcano Island with uncovered moss bags, covered moss bags under the yellow plastic box and passive samplers for SO_2 and H_2S under the orange roof at the right side.

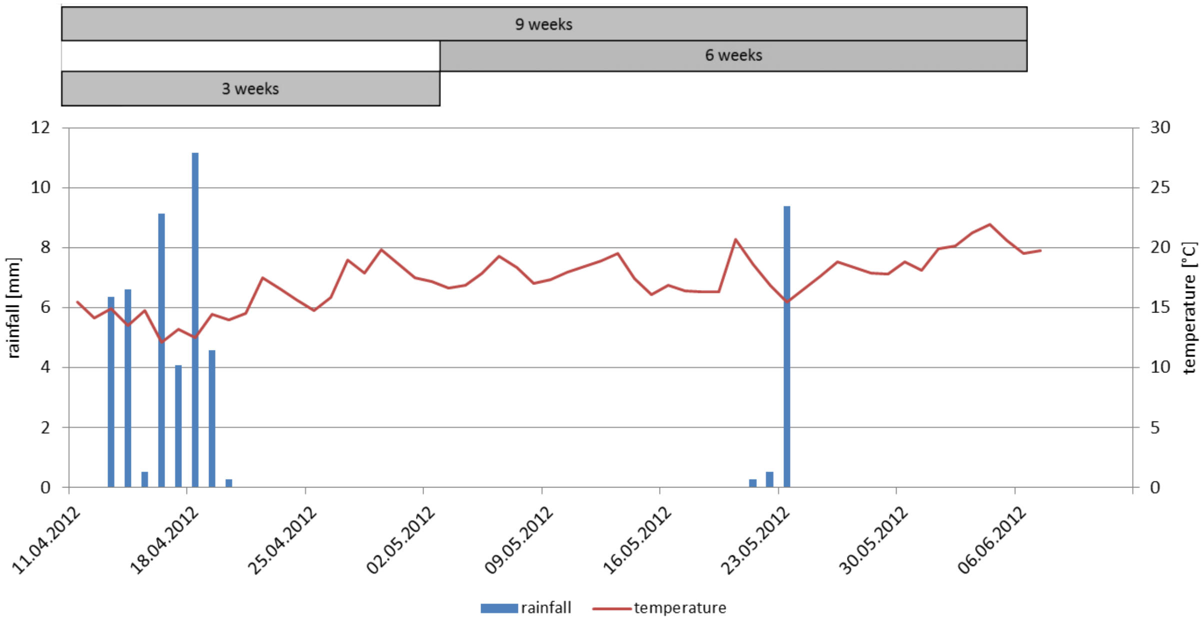

Fig. A2: Rain data for the moss monitoring time of the screening (spring 2012). The times for the moss bags exposed for 3, 6, and 9 weeks are indicated as bars above.

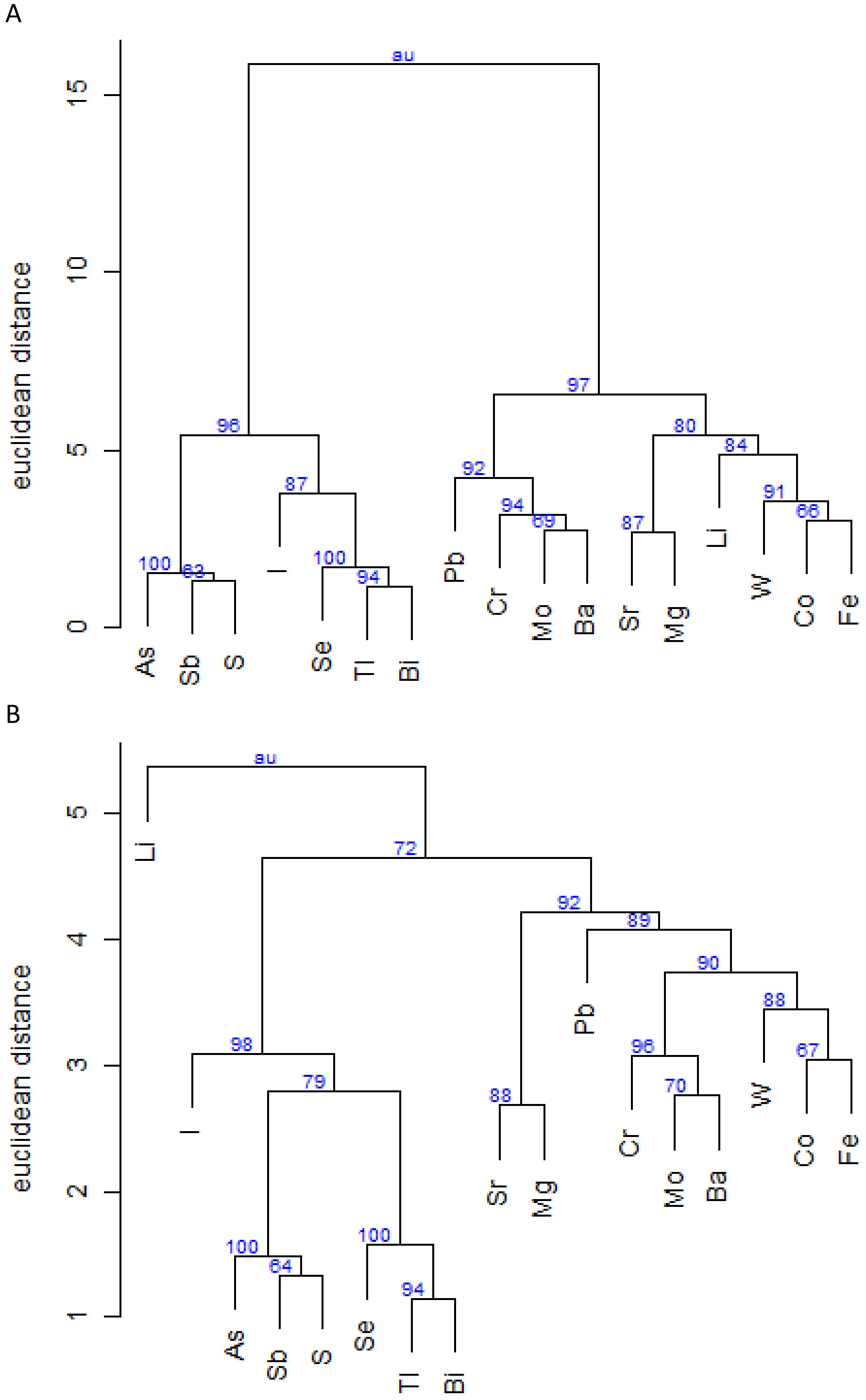

Fig. A3: Alternative cluster analysis of distribution of elements in all moss bags on Vulcano Island
For clustering all obtained data during screening (3, 6, 9 weeks, covered and uncovered moss bags) were used. Clustering was performed by using the Ward method (A) and the average linkage method (B), both in combination with the euclidean distance as a measure of distance. The approximate unbiased p-values [%] for each sub-cluster are given in blue.

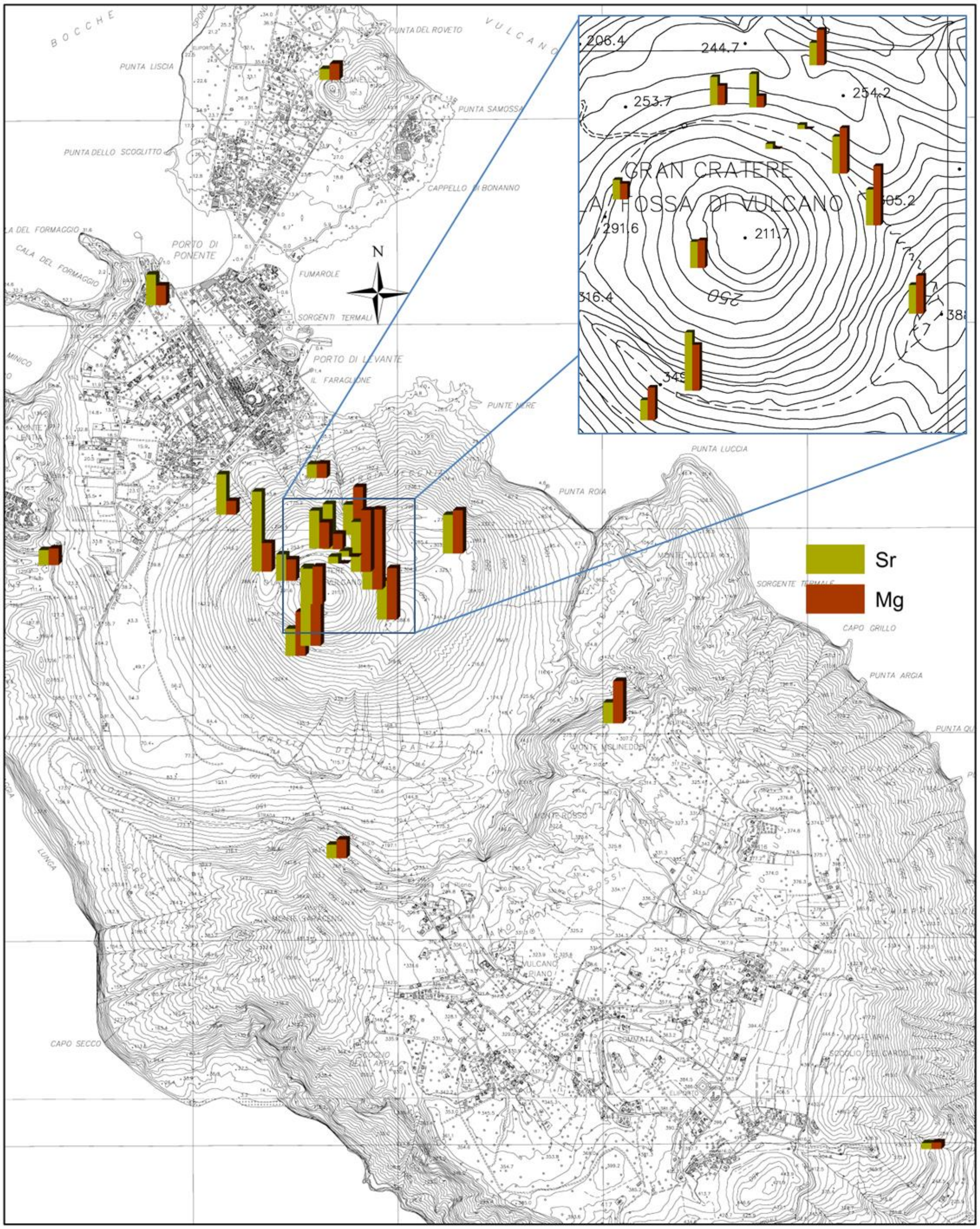

Fig. A4: Spatial distribution of Li, Sr, and Mg in moss bags (exposed uncovered for 9 weeks).

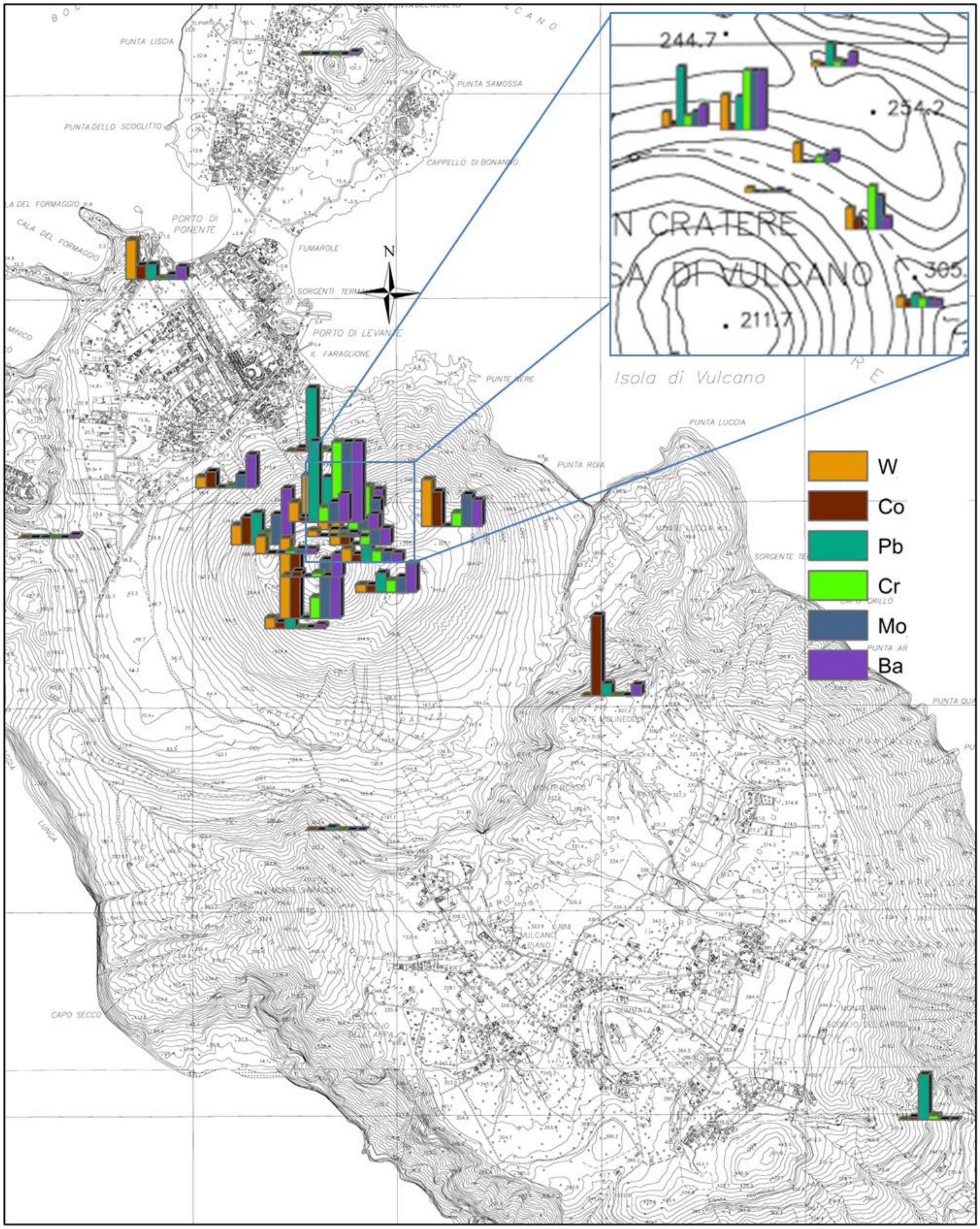

Fig. A5: Spatial distribution of W, Co, Pb, Cr, Mo, and Ba in moss bags (exposed for 9 weeks).

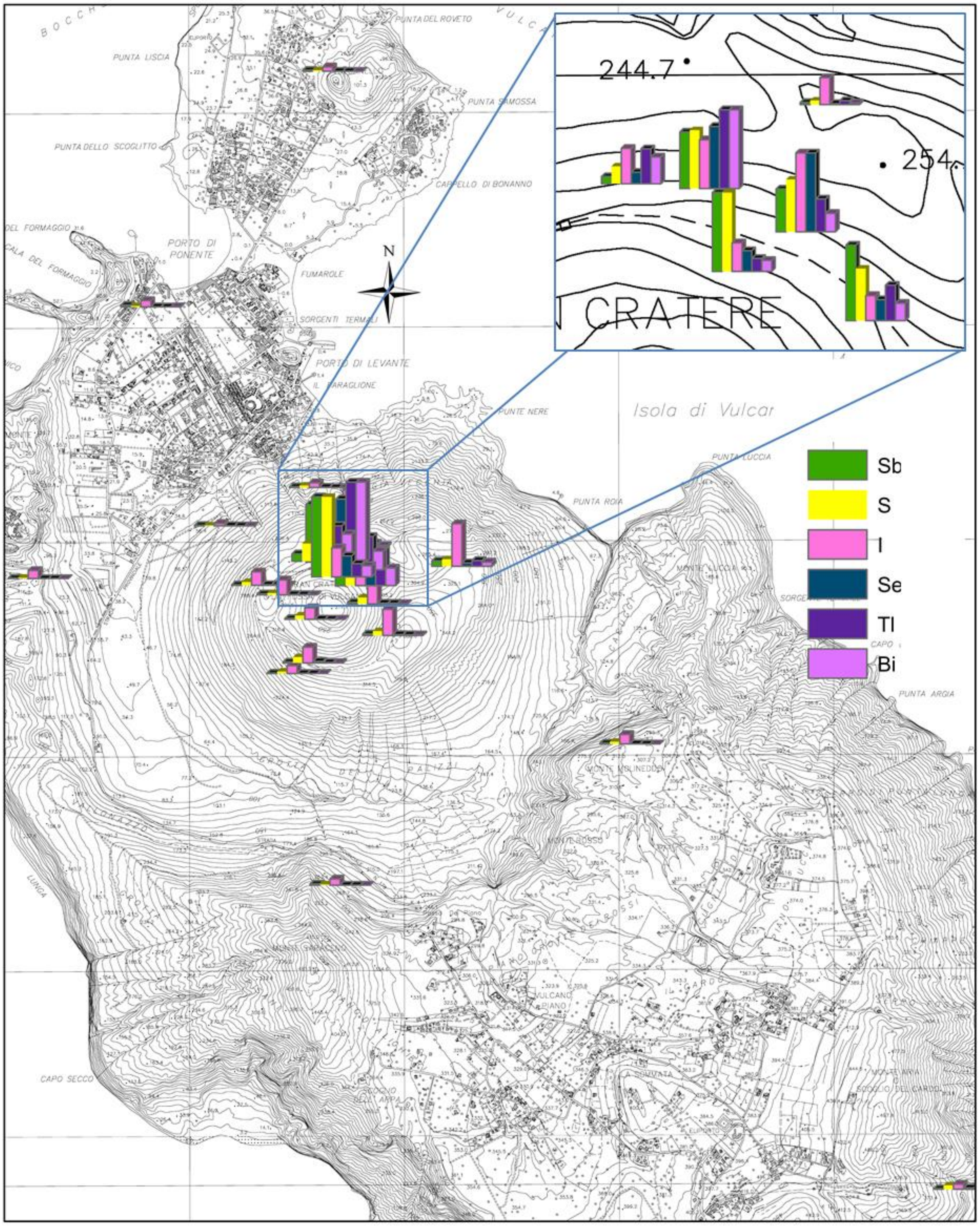

Fig. A6: Spatial distribution of Sb, S, I, Se, Tl, and Bi in moss bags (exposed for 9 weeks).

Study 2: Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas

Julia Arndt, Sergio Calabrese, Walter D’Alessandro, Britta Planer-Friedrich

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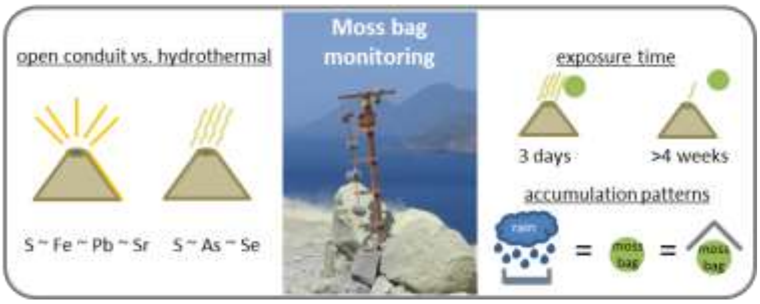

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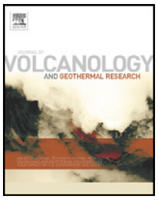

Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas

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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).

Table 1
Moss exposure details for all volcanoes.

Volcano	Survey year	Moss bag exposure	Height [m]	Duration [days]	Replicates	Moss species and collection site
Etna	2007	Covered & uncovered	1.6	1, 15, 27, 34	3 at selected stations	Sweden; *Sphagnum fuscum*, *S. tenellum*
Vulcano	2012	Covered & uncovered	1.6	3, 21, 40, and 69 ± 1	3 at selected stations mainly close to the fumaroles	Schlöppnerbrunnen, *S.* spp.[a]
Vulcano	2013	Uncovered	0.7, 1.0, 1.2, 1.5, 1.6	17–23	3 per station and height	Forest near Bayreuth; *S. palustre*
Stromboli	2013	Uncovered	1.6	23	3 per station	Forest near Bayreuth; *S. palustre*
Nisyros	2013	Uncovered	1.6	10–89	2 per station	Schlöppnerbrunnen; *S.* spp.[a]
Nyiragongo	2011	Uncovered	0.5–1.5	3–4	3 per station	Schlöppnerbrunnen; *S.* spp.[a]
Nyiragongo	2014	Covered & uncovered	0.5–1.5	4–30	3 per station	Schlöppnerbrunnen; *S.* spp.[a]
Yellowstone[b]	2013	Covered	0.4–1.6	15–21	3 per station	Forest near Bayreuth and Chile (bought); both *S. palustre*

[a] *S.* spp. = mix of *Sphagnum tenellum*, *S. subsecundum*, *S. cuspidate*, *S. girgensonii*, and *S. fallax*.

[b] In Yellowstone, only the elements As, Sb, Tl, and Bi were measured.

At Nyiragongo, 14 moss bags were exposed at the crater rim and at two down-wind distal sites (for a map with monitoring stations see SI 2). During the sampling periods (December 10th – 14th 2011 and October 26th–November 13th 2014), weather conditions were typically tropical with high temperatures and humidity during the days and heavy rainfall of about 50–100 mm within about 3 h each afternoon; prevailing winds were north-northeastern.

At Mount Etna, active moss monitoring survey was conducted in summer 2007 (Calabrese et al., 2015) at 28 stations (SI 3 and Calabrese et al., 2015). The monitoring period was characterized by passive plume degassing without significant paroxysmal explosive events, absence of rain, and prevailing northwestern winds (Calabrese et al., 2015).

At Stromboli, moss monitoring was conducted in the town and on the whole way up to the crater from May 1st to May 24th 2013 (SI 3). Volcanic activity on Stromboli showed typical continuous passive degassing as well as persistent Strombolian activity with emission of ash, scoriae, and gas around every 20 min. Weather was monitored on the close-by island Salina (40 km) and showed predominant wind directions from the west with a second maximum from the north-east. A total amount of 16.4 mm precipitation was measured on Salina during the exposure period.

At Vulcano, active moss monitoring was done in spring 2012 as an emission and deposition screening on the whole island (with *S.* spp. at a maximum exposure duration of up to 9 weeks) and in spring 2013 (with *S. palustre* for 3 weeks) along a transect through the fumarolic field (SI 3; Arndt et al., 2014).

At Nisyros, moss monitoring took place between June 3rd and 13th 2013 (SI 4). Only 2 moss bag replicates at the background station were exposed until September 16th 2013. No rain was measured during the whole monitoring period on the meteorological station of the island of Kos, 30 km north of Nisyros. Predominant wind directions were from the north-east to north with an additional maximum from the south-east (D'Alessandro et al., 2013).

At Yellowstone National Park, active moss monitoring was conducted directly at several geothermal features in Norris, Lower, and Gibbon Geyser Basin, in Nymph Lake and West Nymph Creek Thermal Area (map in SI 5) in June 2013 for 3–4 weeks. At each site, three moss bags of the commercial *S. palustre* (Chile) were exposed. Additionally, in each region a triplicate of moss bags was exposed as field blank for local background concentrations. Altogether, 3 geothermally influenced peatlands, 10 fumaroles, 6 mudpots, 26 geothermal springs, 1 geyser, and 6 background stations were monitored. The geyser and some mudpot stations were excluded from data evaluation because they were placed too close to the emission sources and were affected by splash water or mud and thus not usable for gaseous collected trace element analysis (compare SI 6). At three stations, a triplicate of *S. palustre* (Germany) was set up for moss comparison in addition to the triplicate of *S. palustre* (Chile) and at another station (Nymph), 2 triplicates of *S. palustre* (Chile) were exposed.

Furthermore to investigate other factors that could influence the uptake of volcanic emissions by the mosses we proceeded as follows. Moss bags were exposed covered (with a plastic box, put upside down above the moss bags) and uncovered (Table 1). Compared to covered moss bags, the uncovered moss bags received additional dry and wet (dust and rain) deposition, but were also subject to potential washout by rain. Covered moss bags were employed wherever rain was expected (Table 1). Moss bags were mostly attached at heights below 1.6 m. At Vulcano, the influence of 5 different exposure heights on element accumulation patterns was evaluated (Table 1). Exposure durations varied from 1 day up to 3 months, depending on distance from the emission source, wind direction, but also logistic constraints. A detailed list with information on employed moss species, moss bag coverage/non-coverage, exposure height, exposure duration, and replicates can be found in Table 1.

2.4. Moss digestion and elemental analysis

After exposure on the volcanoes, moss bags were brought back to the laboratory in sealed plastic bags. The moss was oven-dried (40 °C, ca. 24 h), powdered (Retsch MM 2000, 14 Hz, 3 min), and an aliquot of 0.1 g was digested in 3 mL 65% HNO_3, 2 mL H_2O_2, and 5 mL ultrapure water (MQ) according to Calabrese et al. (2015) and Arndt et al. (2014). Digests were filtered (0.2 μm) and analyzed (after a minimum dilution of 1:10) by inductively coupled plasma mass and optic emission spectrometry (ICP-MS and ICP-OES) for total element concentrations of Li, Mg, S, Cr, Fe, Co, As, Se, Sr, Mo, Sb, Ba, Tl, Pb, and Bi. Mosses from Yellowstone were analyzed only for the elements classified as volatile in Arndt et al. (2014): Sb, Bi, Tl, and As. Mg, S, and Fe were analyzed by ICP-MS for Vulcano (2012 and 2013), Stromboli, and Yellowstone and by ICP-OES for Etna, Nyiragongo and Nisyros. To avoid analytical interferences, analysis of As was done in O_2 mode (reaction gas: 10% O_2 in He; m/z: 91) for the first 3 volcanoes and in standard mode for the latter ones, and in KED mode (collision gas: 93% He with 7% H_2 and a 2 V energy discrimination) for Cr, Fe, Co, and Se. For measurement, a quadrupole ICP-MS (Xseries2, Thermo Scientific) with reaction/collision cell was used for all elements of moss extracts from Vulcano (2012 and 2013), Stromboli, and Yellowstone, while measurements of moss extracts from Etna, Nisyros, and Nyiragongo took place at the INGV Palermo using an ICP-MS for trace elements (Agilent 7500ce) and an ICP-OES for major elements (HORIBA Jobin Yvon Ultima II). For every volcano and monitoring period, unexposed moss blanks were treated the same way as the samples and an extraction blank (HNO_3, H_2O_2, MQ) was done with every extraction.

Moss from Yellowstone was diluted less during digestion to reach analysis results above detection limit (1 g moss + 10 mL; 1:2 dilution for analysis only).

2.5. Data evaluation

Element concentrations measured in the extraction blank were subtracted from all sample concentrations and the respective moss blank sample concentrations were subtracted from the moss samples. Data are calculated per gram of moss. To compare different exposure durations, data were calculated as accumulation rates per day (e.g. μmol·$(g \cdot d)^{-1}$). This of course does not visualize the immediate effect of rain but results in comparable long-term signals. For field triplicates, mean values were calculated. Relative standard deviation (%RSD) of triplicates was e.g. at the crater of Vulcano (2012 monitoring) between 8.5 and 27% with a mean value of 14.5%RSD. These values vary due to different small scale wind conditions and are in general higher for elements with low concentrations (which can be close to analytical detection limit). Statistical data evaluation was performed using the statistical program SPSS (Kruskal-Wallis test; Spearman rank correlation analysis). Maps are taken from Google Earth and edited by ESRI ArcGIS. Data for plots at the maps were normalized according to Arndt et al. (2014), representing the relative accumulation rate in respect to the highest accumulation rate measured for the respective element and volcano.

3. Results and discussion

3.1. Observed trace element emissions at the six different sites

3.1.1. Nyiragongo

At Nyiragongo, two monitoring stations were situated at distal sites in the towns of Goma and Kingi (Kingi: covered only), while all other stations were at the crater rim (map and coordinates in SI 2). All elements discussed in this paper had their maximum accumulations at the crater rim (Fig. 1) with Mg, Fe, and S being accumulated up to 20 μmol·$(g \cdot d)^{-1}$ (element accumulation rates for Nyiragongo can be found in SI 7). The background site in Goma, 12 km from the crater,

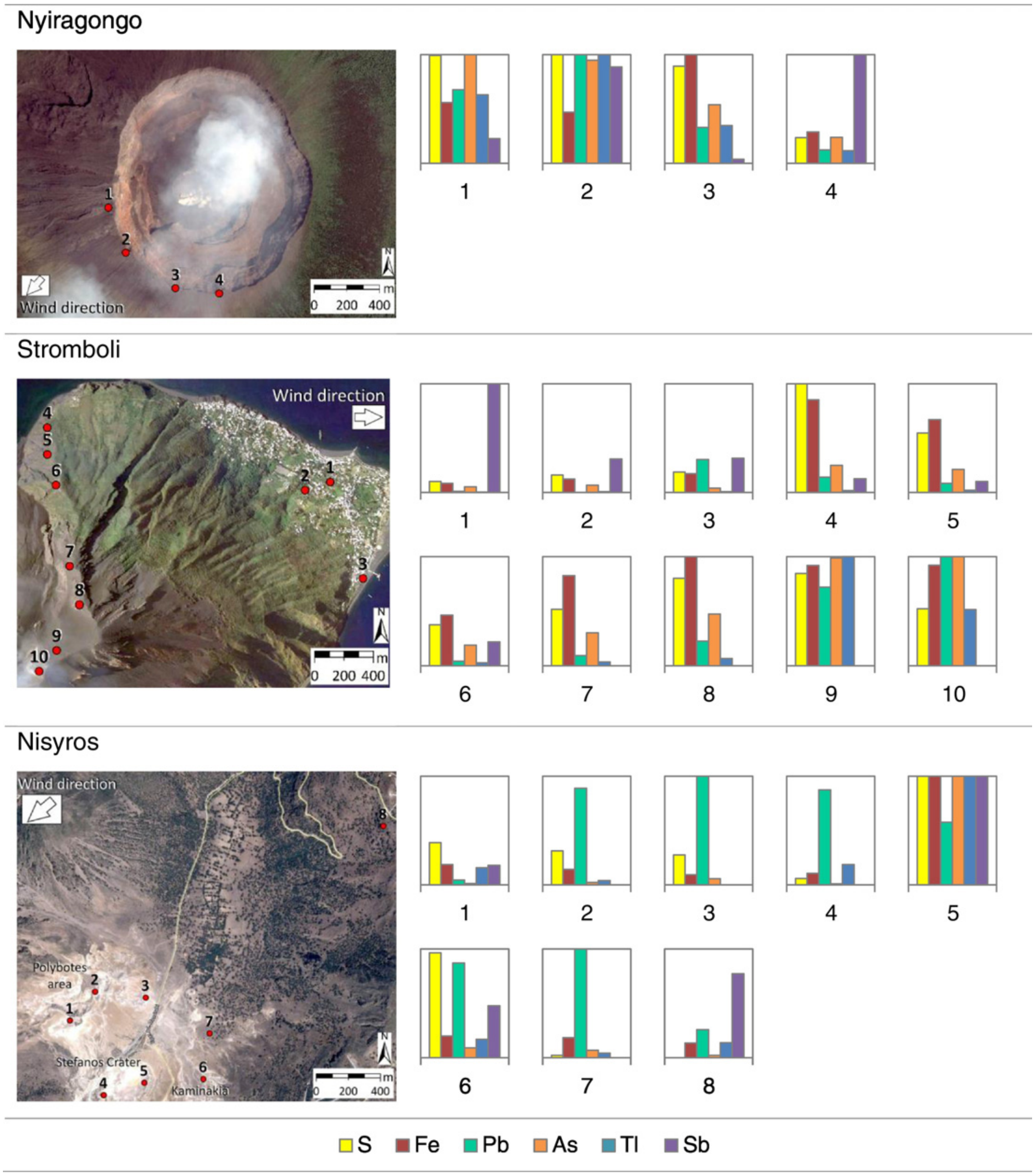


Fig. 1. Element distribution of S, Fe, Pb, As, Tl, and Sb in moss bags at Nyiragongo, Stromboli, and Nisyros. Data were normalized and thus present the relative accumulation rates in respect to the highest accumulation rate measured per element. Maps are from Google Earth edited by ArcGIS. Accumulation rates in nmol·$(g \cdot d)^{-1}$ are given in SI 7 for all elements and stations.

accumulated up to 39% of the maximum accumulation at the crater for Mg but <1% for all other elements (and thus is not presented in Fig. 1). Most of the elements shown in Fig. 1 showed highest accumulation rates at stations downwind (i.e. west) of the crater, while Fe was accumulated highest in the south west.

Despite the heavy daily rain on Nyiragongo (see Section 2.3), all elements show similar accumulation rates per day to most of the other volcanoes. This can be the result of wet deposition by rain as discussed in Section 3.3.4.

3.1.2. Etna

Etna has been described in detail before (Calabrese et al., 2015). Briefly, the monitoring station between two summit craters (about 100 m to each crater) reached the highest accumulation rates for all elements monitored with 72, 7.5, and 4.8 $\mu mol\cdot(g\cdot d)^{-1}$ for S, Fe, and Mg, respectively and 94, 42, 27, 20, 16, 5.7, and 5 $nmol\cdot(g\cdot d)^{-1}$ for Sr, Ba, As, Li, Se, Tl, and Pb, respectively (data can be found in the SI of Calabrese et al., 2015). The elements Fe, Mg, Sr, Ba, and Co had a second maximum at the stations downwind of the crater (station No. 25 and 16 in Fig. 1 of Calabrese et al., 2015). Mosses were also analyzed by SEM (Calabrese and D'Alessandro, 2015), but these results are not topic of the present study.

In comparison to Stromboli, there was no ash emission on Etna during the monitoring period, which resulted in lower accumulation rates of ash-derived elements like Fe, Mg, Sr, and Ba (Calabrese et al., 2015). Nevertheless, bare soil and ash were also present on the crater from former eruptions and contributed to the moss accumulation rates by dust deposition.

3.1.3. Stromboli

On Stromboli, one station was situated directly at the crater (map and coordinates in SI 3), where Fe, Se, Mo, Pb, and Bi had their maximum accumulation with Fe being accumulated up to 15 $\mu mol\cdot(g\cdot d)^{-1}$ (Fig. 1; mean element accumulation rates can be found in SI 7). The origin for Fe is the fine ash, which was accumulated in the moss bags at the crater. The two downwind stations showed maximum concentrations for Cr, Co, As, Ba, and Tl, but also were elevated for the elements with maximum at the crater and S and Sr. At the stations on the way up to the crater where some bare soil exists, but also some vegetation (with the amount of vegetation decreasing with decreasing distance from the crater) and which are neither directly up- nor downwind of the crater, the elements Li, Mg, S, and Sr had maximum accumulation rates per day, reaching up to 0.04, 20, 13, and 0.16 $\mu mol\cdot(g\cdot d)^{-1}$, respectively. Consequently, these elements are likely to originate either from the bare soil (and ash) on the whole volcano or from the emissions from the crater.

The three background stations situated at the coast and in Stromboli town, generally accumulated lower amounts of all elements, except Sb, which was maximally accumulated at one station in town. Sb previously has been attributed to traffic by Moreno et al. (2010) when monitoring marine particulate matter from a ship in the Mediterranean.

On Stromboli, the elements Fe, Mg, Ba, Sr, and Li showed higher accumulation rates compared to the other volcanoes. These elements were considered soil/ash and geogenic derived on Vulcano because of high concentrations in bare soil/ash and mosses exposed above these (Arndt et al., 2014) and also considered as being of volcanic-geogenic sources like pyroclastic material or dust for Etna (Calabrese et al., 2015).

3.1.4. Vulcano

The two monitoring campaigns in 2012 and 2013 on Vulcano Island have been described in Arndt et al. (2014). Briefly, during screening the whole island in 2012, highest accumulation rates of the fumarole-born elements S, As, Se, Sb, Bi, and Tl were found in the fumarolic field for all 3 monitoring durations (3, 6, and 9 weeks), reaching mean accumulations of 22,000, 130, 4.7, 3.4, 1.4, and 1.7 $nmol\cdot(g\cdot d)^{-1}$, respectively, and 600 m downwind from the fumaroles, reaching up to 12% of the maximum concentration in the fumarolic field for S, while the background accumulation rate was <1%. During transect monitoring in 2013, these elements reached accumulation rates of 970,000, 560, 70, 17, 0.52, and 6.5 $nmol\cdot(g\cdot d)^{-1}$ for S, As, Se, Sb, Bi, and Tl in the fumarolic field, respectively (datas 2012 and 2013 can be found in the SI of Arndt et al., 2014).

Regarding the two moss monitoring periods on Vulcano, an unexpectedly high difference in accumulation rates was discovered (see Section 3.2). Data were corrected for blanks and exposure duration. Thus, the differences can either be due to the fact that monitoring took place in different years and thus were exposed to different meteorological conditions (wind, rain), different mosses used (Table 1; discussion see Section 3.3.1), but also to the slight variations in monitoring stations (compare SI 3; Arndt et al., 2014), and potentially variations in geological emission.

3.1.5. Nisyros

The three fumarolic areas of Kaminakia crater, Stefanos crater, and Polybotes including the sampling stations are shown in Fig. 1 (map and coordinates in SI 4). Most elements were found in maximum accumulations per day at the monitoring station at Stefanos crater (Li, S, Fe, Co, As, Sr, Sb, Ba, Tl, and Bi), reaching up to 4000 $nmol\cdot(g\cdot d)^{-1}$ for S (Fig. 1; mean element accumulation rates can be found in SI 7). The elements Bi, As, Tl, and Ba were 1–2 orders of magnitude higher than on both other vent areas, while Sr and Co also were frequent in the background. The elements Cr, Se, Mo, and Pb were found maximum in the Polybotes area, reaching 6, 0.1, 0.6, and 5 $nmol\cdot(g\cdot d)^{-1}$, respectively. At the background station at a road, only Sb and Co reached accumulation rates of 77 and 60% of the maximum measured accumulation in the fumaroles. Both elements are known to be emitted from traffic (Sb from brake wear abrasion, Co from metal alloys; Johansson et al., 2009), although traffic on Nisyros is not a major emission source.

3.1.6. Yellowstone

At geothermal features in Yellowstone we were able to detect mean concentrations of 5 $nmol\cdot(g\cdot d)^{-1}$ As and 0.05 $nmol\cdot(g\cdot d)^{-1}$ Sb using moss monitoring (see Section 3.2). Tl and Bi were below detection limit of 0.05 and 0.048 $nmol\cdot g^{-1}$ at all sites. Monitoring hot springs, fumaroles, mudpots, and wetlands, mean accumulation rates of 0.82, 0.66, 0.48, and 0.03 $nmol\cdot(g\cdot d)^{-1}$ were detected for As and 0.17, 0.15, 0.18, and <0.01 $nmol\cdot(g\cdot d)^{-1}$ for Sb, respectively. A list of accumulation rates of all monitored sites including GPS data can be found in SI 6 and a map in SI 5. These concentrations are surprisingly low in comparison to a previous report of 1.2–200 $mg\cdot m^{-3}$ volatile As from diffusion-based calculations (Planer-Friedrich and Merkel, 2006). However, the potential overestimation of these volatile As concentrations in Yellowstone has already been discussed by Arndt et al. (2017).

3.2. Comparison of the different volcanic areas

For comparison of the different volcanic areas, we chose not to consider the background sites, but only the sites that were closest to the source of volcanic emission compatibly with accessibility and to compare uncovered bags only because covered bags were not exposed at all volcanoes. These closest-possible sites that we could sample at each volcanic site varied significantly in their distance from the true center of volcanic emission. At Vulcano, Nisyros, or Yellowstone, moss bags could be placed just meters above a degassing fumarole or hot spring while at Mount Etna the crater rim station was about 100 m away and 100 m higher than the source of emission. The same is true for Stromboli and Nyiragongo with distances of 240 and 500 m and height differences of 100 and 200 m, respectively.

Regarding all monitored areas, the major elements S, Fe, and Mg showed the greatest accumulation rates per day on all volcanoes (mean accumulation rates 86, 3.7, and 2.2 $\mu mol\cdot(g\cdot d)^{-1}$, respectively), while the trace elements Co, Tl, and Bi were lowest (0.0016, 0.00094, and 0.00065 µmol·$(g\cdot d)^{-1}$; Fig. 2). For the trace elements As, Sb, and Se highest accumulation rates were found on Vulcano (both, 2012 and 2013), while for Fe, Mg, Sr, and Ba the highest accumulation rates were found on Stromboli.

In general, mean element accumulations on moss bags like for S and the trace elements Mo, As, Sb, Se, and Bi differed over up to three orders of magnitudes between the volcanoes with the highest values for Vulcano 2013 and the lowest for Nisyros, except for Mo. For other elements, especially Cr and Pb, mean accumulation rates varied only about one order of magnitude for all volcanoes.

Element accumulation was considerably larger than the moss blank concentration for the elements S, As, Cr, Mo, Sb, Se, Tl, and Bi which have already been shown to be emitted from volcanoes (Arndt et al., 2014; Calabrese et al., 2015) and can be seen by calculation of the relative accumulation factor RAF (which is accumulation in comparison to the moss blank: $[c(x)_{\text{exposed moss}} - c(x)_{\text{ blank}}]\cdot c(x)_{\text{blank}}^{-1}$; SI 8). The lowest RAF values were found for Nisyros for nearly all of the monitored elements, while highest values on average were found for Etna.

Comparing element accumulation distribution at all volcanoes and different sites, we detected significant correlations for some elements, suggesting these to be of the same origin and to have similar distribution properties.

Sulfur shows highest concentrations at the emission sources and is distributed in downwind direction. Distribution patterns were similar e.g. for As and Se (Fig. 3a and b) which correlate with S concentrations on Etna, Stromboli, and Vulcano 2012 and 2013 ($p < 0.01$, very significant; for all correlation coefficients of Fig. 3 see SI 9) while there is no correlation on Nisyros and Nyiragongo. The correlation of these elements has already been shown for Vulcano (Arndt et al., 2014) and Etna (Calabrese et al., 2015) by moss monitoring.

Correlations of S and Pb are positive and significant for Etna and Stromboli (Fig. 3c; $p < 0.01$ and $p < 0.05$, respectively), while no correlation was found on the other volcanoes. The correlation of Pb and S has already been shown for Etna (Calabrese et al., 2015). Etna and Stromboli are both open conduit volcanoes emitting gas as well as ash and lava, while Vulcano and Nisyros only emit gases. Nyiragongo is the only alkaline volcano in this study and thus may show different element emission patterns, which is also known to occur for major gases like SO_2, CO_2, and water vapor (Textor et al., 2012). Being an alkaline volcano, Nyiragongo has less explosive activity than e.g. Etna and Stromboli and thus emits less silica particle related elements (e.g. Fe, Mg, Sr, and Ba), which are derived either directly from the magma or from ash being re-suspended in the air by winds. Due to the largest distance of our monitoring stations at the crater rim from the emission source, Pb concentration on the moss might be reduced too. Additionally, the low amount and variety of the four monitoring stations at the crater area can be the reason for the missing correlation.

Iron, which was categorized on Vulcano as an element from the bare soil and found in its maximal accumulation rates on the crater rim (Arndt et al., 2014), correlates with S on the two Mediterranean open conduit volcanoes Etna and Stromboli ($p < 0.01$; Fig. 3d). Thus, S, Pb, and Fe do have the same origin on both volcanoes which is the ash (and lava) emission.

Sr and Ba correlate with Fe nearly on all volcanoes except the Vulcano monitoring 2013 and Nisyros (Fig. 3e and f). The main Fe source which all volcanoes have in common is the bare soil, ash and dust on the crater areas in addition to eruptions at open conduit volcanoes like Etna, and Stromboli. The monitoring campaigns on Vulcano 2013 and on Nisyros have in common that they were both exclusively conducted at the emission sources which on both volcanoes show more solid stone than dust and bare soil particles, potentially causing the missing correlation.

Comparing the open conduit volcanoes (Fig. 2), accumulation rates on moss bags of Stromboli were highest for the volatile trace elements As, Se, and Tl and for the refractory elements Fe, Mg, Sr, and Ba while the elements Mo, Pb, and Cr are highest accumulated on Etna. Differences to Nyiragongo can either be due to additional rain deposition (compare Section 3.3.4) but also due to the fact that it is geologically different (highly alkaline lava lake and diverging African rift zone in comparison to converging tectonic plates in the Mediterranean; see Sections 3.1.1, 3.1.2 and 3.1.3). Despite its less explosive eruptions, its magma also shows less fractionation than at converging plate boundaries (Etna, Stromboli) and thus a different composition of trace elements (Henley and Berger, 2013; Textor et al., 2012).

Comparing the volcanoes grouped as hydrothermal in this paper (see Section 1), mosses exposed in the fumaroles of Nisyros show much lower amounts of trace elements like As, Se, Sb, Tl, and Bi than Vulcano Island (Fig. 2). Yellowstone also shows low amounts of the trace elements As and Sb (Fig. 2) which partly can be attributed to the moss we used (see Section 3.3.1). The large accumulation rates of

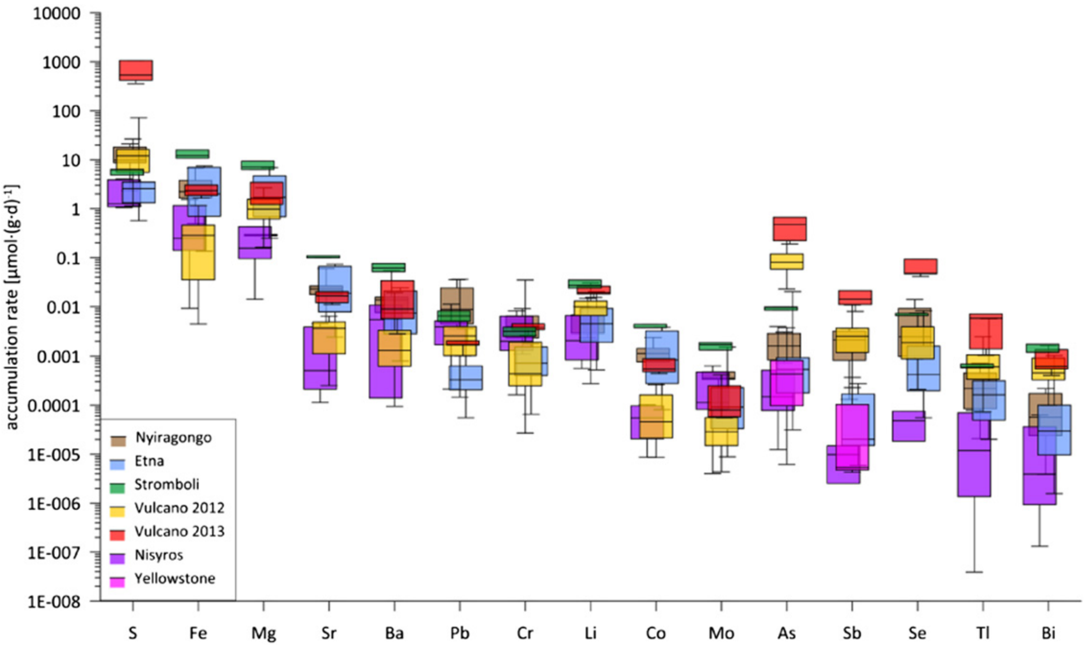


Fig. 2. Comparison of accumulation rates (in logarithmic scale) in uncovered moss bags at the emission source stations (stations at the craters/in the fumaroles).

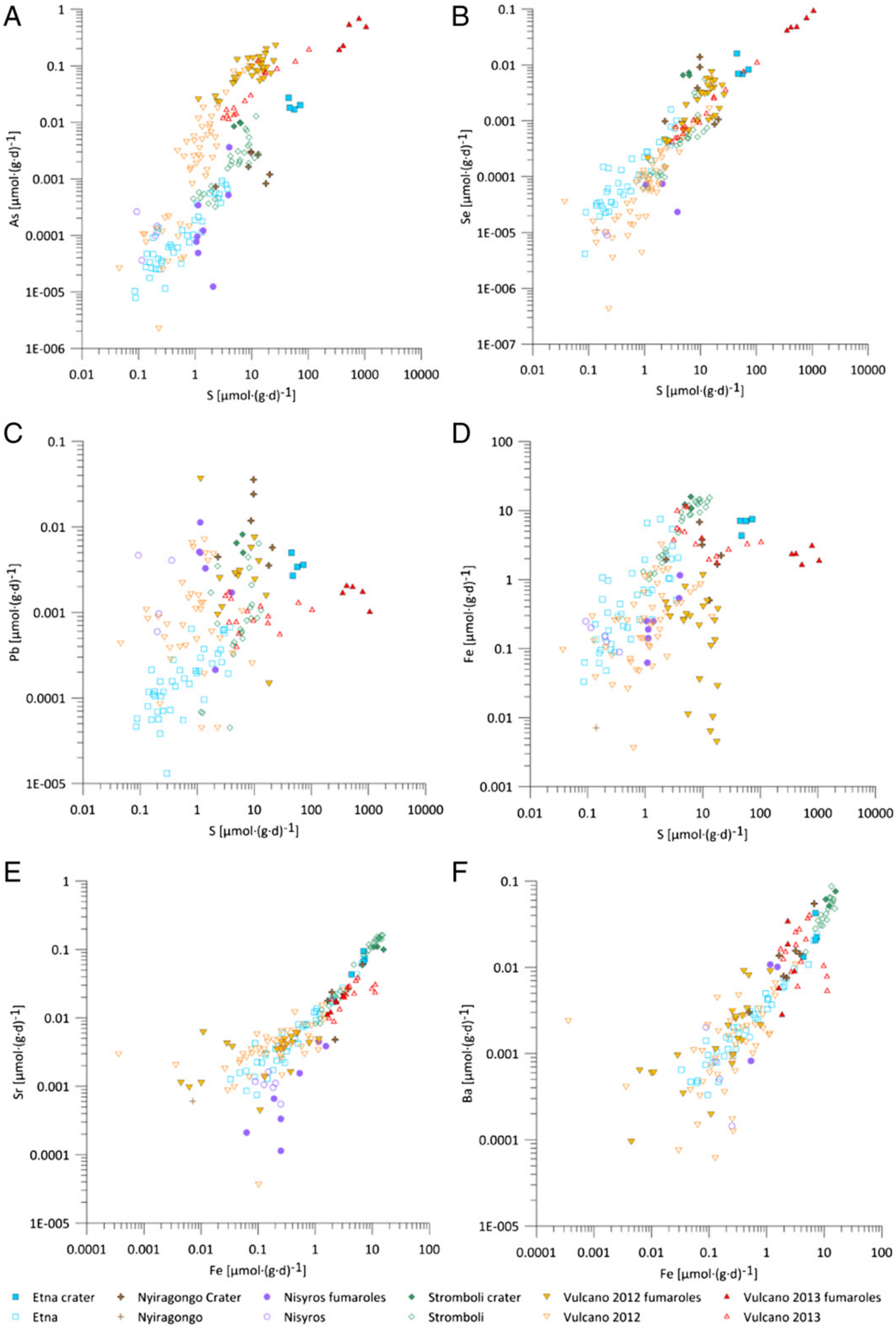


Fig. 3. Element correlations in µmol·(g·d)$^{-1}$.

trace elements found on Vulcano in both monitoring campaigns (2012 and 2013) in contrast to Nisyros and Yellowstone is mainly due to the differences in emission strength. It has to be considered that the three systems display very different fumarolic activity. Nisyros and Yellowstone are both in solfataric stage with emission temperature equal or less than boiling temperature of water. Condensation of water vapor, which is the major constituent of fumarolic gases, causes the more or less extended loss of elements or compounds due to dissolution in the condensed water before being emitted to the atmosphere. On the contrary Vulcano displays a large high temperature (up to 400 °C) fumarolic field and the fumarolic emissions are a mixture in different proportions of hydrothermal and magmatic components (Paonita et al., 2013).

In general, both, Yellowstone and Nisyros fit in our expectations of hydrothermal volcanoes to emit less trace elements than open conduit volcanoes. On Vulcano however, we found larger trace element accumulations than on Etna for the elements As, Se, Sb, Tl, and Bi. These are the elements classified as volatiles on Vulcano (Arndt et al., 2014). Etna is known to be a major emission source for several elements and has been estimated to contribute up to 16% and 19% of the global volcanic annual metal budget for heavy metals and alkali metals, respectively, during active periods and 2 and 4% in quiescent periods, respectively (Gauthier and Le Cloarec, 1998). However, in contrast to Vulcano, the moss bags at Etna had a larger distance to the emission source, which might be the reason for the smaller accumulation rates measured at Etna.

For improving global budget estimations, clearly a closer sampling to the emission sources using different more sophisticated quantitative methods would be necessary. However, our data reveal valuable information for risk assessment of human exposure to volcanic gases because all sampling sites were also easily accessible to tourists and tourists inhale the volcanic gases. On Etna, Nyiragongo, and Stromboli, guided tours can be booked, while Vulcano and Nisyros are accessible for everyone without a local guide and often without protective gear (Nyiragongo being not as frequented as the other volcanoes). Sulfur, the element with the highest concentrations measured, has an immediate impact on tourists, i.e. coughing due to SO_2 and H_2S gases, whose concentrations have already been evaluated by D'Alessandro et al. (2013). Sulfur was enriched in the moss bags at the crater up to three orders of magnitude (on Etna and Vulcano 2012; Fig. 4) while background concentrations differed <1 order of magnitude on Stromboli. Downwind stations had lower accumulation of S than the crater/fumarole stations at most sites. Trace elements were also enriched at the accessible sites on every volcano compared to the downwind and background stations monitored (Fig. 4). For Se and As, differences between crater/fumarole and background stations were 4 and 5 orders of magnitude, respectively. These elements are known to be emitted from the crater/fumaroles. Especially volatile As is known for its toxicity (Pakulska and Czerczak, 2006). While we cannot directly calculate from accumulation on moss to concentrations in μg/m^3 to compare with known toxicity thresholds, our data at least gives a clear ranking of site sensitivity with regard to potentially toxic elements such as As. For further health implications, detailed analysis on the basis of these moss data need to be conducted.

For Fe, an element from ash, dust, and soil re-suspension and subsequent deposition, background stations and crater stations do not show differences on all volcanoes because they are emitted from a larger area which can also involve the background station and crater stations also can have lower accumulation than background stations (e.g. on Vulcano and Nisyros, Fig. 4).

3.3. Evaluation of adaptations to the moss monitoring technique for volcanic areas

This last section summarizes lessons learned from monitoring different volcanic areas under different climatic conditions over a period of more than seven years. We show the effects of using moss with different shoot compactness, different exposure heights and durations and moss bag coverage versus non-coverage and what the observed effects might mean both for re-evaluation of previous results and future applications of moss monitoring.

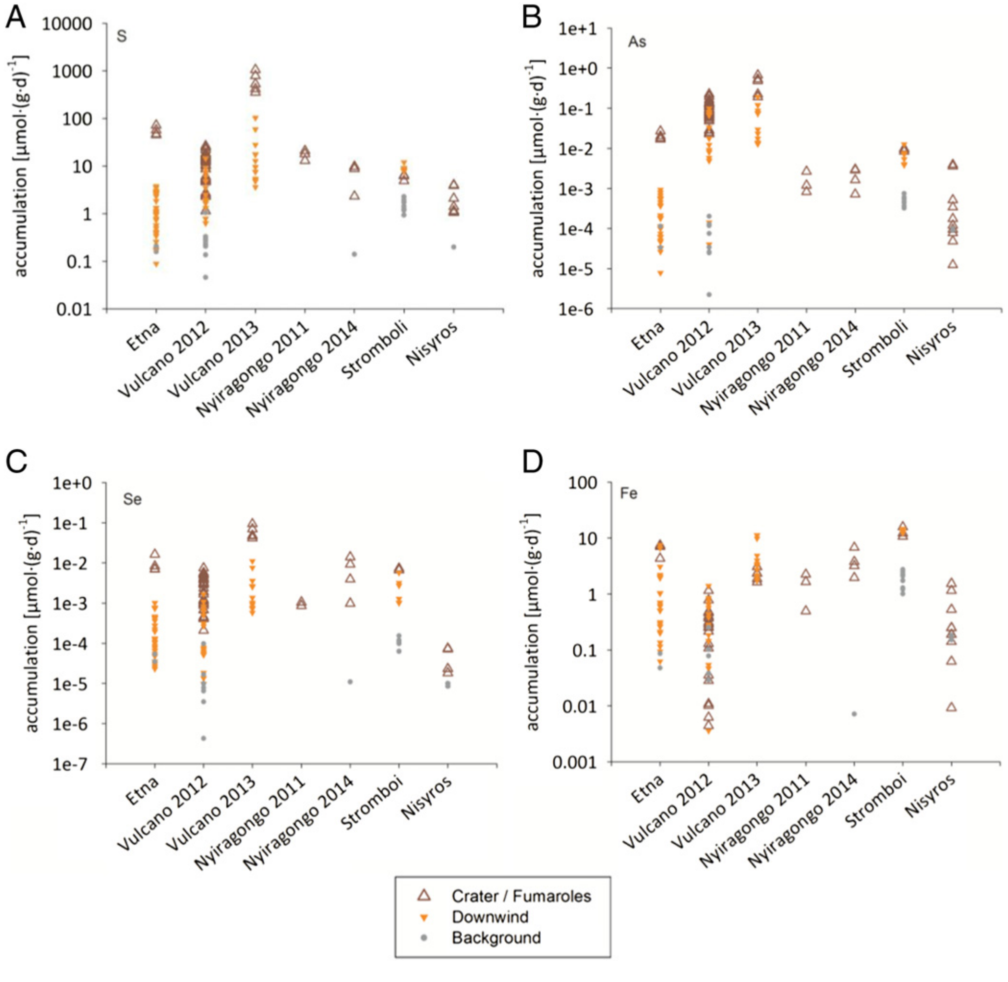


Fig. 4. Differences between accumulation rates in mosses at crater, downwind, and background stations for As, S, Se, and Fe.

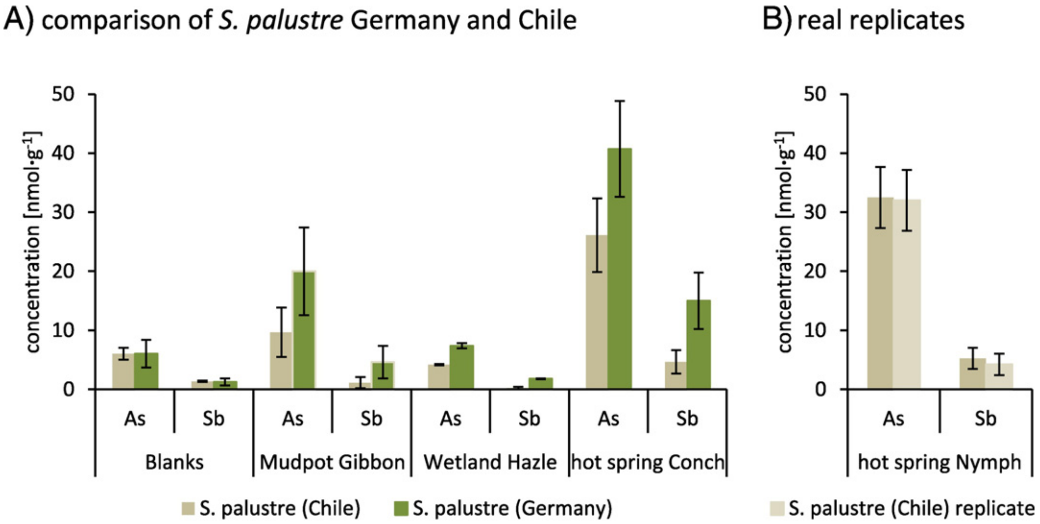
3.3.1. Effect of different mosses used for monitoring

Due to its quicker availability in large quantities we used commercial moss (called *S. palustre* (Chile) in the following) for emission screening at Yellowstone. In comparison to the collected *S. palustre* (called *S. palustre* (Germany)) used for monitoring Vulcano 2013, Stromboli, and part of Yellowstone springs (compare Table 1), *S. palustre* (Chile) accumulated significantly less As and Sb (decrease to 50–65% and 12–30%, respectively; $p < 0.001$; ANOVA; Fig. 5a, b). Results are blank corrected and the blanks for both mosses were very similar (As: 6.03 ± 1.01 vs. $6.03 \pm 2.33\ \text{nmol}\cdot\text{g}^{-1}$, Sb: 1.35 ± 0.11 vs. $1.23 \pm 0.6\ \text{nmol}\cdot\text{g}^{-1}$ for *S. palustre* (Chile) and *S. palustre* (Germany), respectively), so we can exclude that moss pre-treatment had any effect on the different results.

What we observed during moss pre-treatment was that *S. palustre* (Chile) was rather sturdy and much denser than *S. palustre* (Germany), resulting in a higher specific density of *S. palustre* (Chile) and thus in less exposure of its single leaves as potential element accumulation surfaces (Fig. 5c, d). We also noticed that grinding the dried *S. palustre* (Chile) for extraction needed twice as much time as for *S. palustre* (Germany) and the little stems were sturdier. With the *S. palustre* (Chile) being denser, weighting in 2 g of moss into the moss bag physically results to a lower amount of moss weighted in and thus less potential surface area than for moss with lower density (i.e. *S. palustre* (Germany)).

The observed differences are interesting to note. Obviously, when selecting an appropriate material for passive biomonitoring as well as for inter-comparison of studies not only the genus of the moss, but also the species matters. However, it seems there can still be intra-species differences concerning element accumulation properties. To date, most studies used mosses of the genus *Sphagnum* (Ares et al., 2012), though, sometimes without further specification on the species. Standardization of the moss used for biomonitoring has already been postulated by others (Ares et al., 2012; Di Palma et al., 2016). Comparison of different moss species or genus at the same sites rarely has been done. Most times, element accumulation of different moss species are used as complementary information as has also been done e.g. by Calabrese et al. (2015) on Etna using *Sphagnum fuscum* and *Sphagnum tenellum* (compare Table 1) or by Adamo et al. (2003) who used moss and lichen (*Sphagnum capilifolium* and *Pseudevernia furfuracea*) when monitoring the city Naples (Italy), discovering the lichen to accumulate larger amounts of metals than the moss during wet seasons.

Our results show that comparison of studies using different moss species should be made with caution. Recently, artificially grown clones of *Sphagnum palustre* for moss monitoring have been investigated in the framework FP7 European project MOSSclone, ensuring low uniform element composition and homogenous morphological characteristics.



C) *S. palustre* (Chile) D) *S. palustre* (Germany)

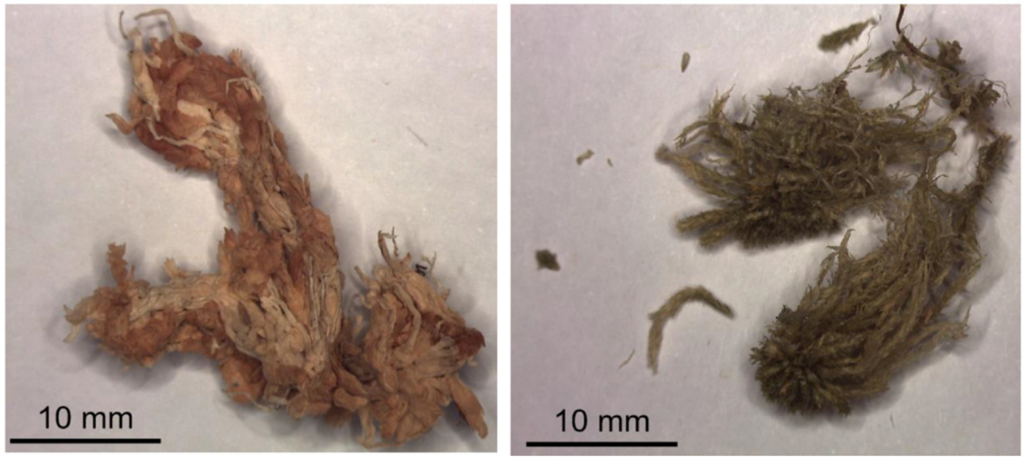


Fig. 5. Comparison of *S. palustre* (Chile) and *S. palustre* (Germany). A and B: As and Sb concentrations from the same emission sources. Each set consists of 3 moss bags. Triplicate moss bags of both mosses were exposed at 3 different sites; real triplicates (2 × 3 *S. palustre* (Chile) bags) were tested at the "Nymph" hot spring, too. Concentrations are given in $\text{nmol}\cdot\text{g}^{-1}$ moss, because exposure times were equal for both mosses at the same site and moss blanks were not exposed. C and D: microscope photos of both mosses showing the more dense and sturdier growth of the *S. palustre* (Chile) (C) in comparison to the *S. palustre* (Germany) (D).

These mosses have been tested with excellent results (Di Palma et al., 2016) and would overcome the shown monitoring variability.

3.3.2. *Effect of exposure height*

In volcanic areas, exposure height of the moss bags is often dictated by whatever natural material (larger rocks, dead trees, sticks) is available to tie the moss bags to, especially if the areas are remotely located and transportation of prepared poles is tedious. To see how much variation in exposure height affects the results, we sampled the seven stations of the 2013 transect at Vulcano at five different heights (0.7, 1.0, 1.2, 1.5, and 1.6 m). The transect consisted of one upwind station (A), two stations in the fumarolic field (B, C) and four downwind stations (D–G). Fig. 6a shows the height profiles for As, Se, Sb, Tl, Bi, and Te at station B. Differences between the heights were <20% for most elements. Some larger variations were observed e.g. at 0.7 m for Sb which was 50% lower than at the four other heights, at 1.5 m for Se which was 23% higher than at the four other heights, or at 1.6 m for As which was 22% higher and for Te which was 31% lower than at the four other heights. However, a Kruskal-Wallis test showed neither a significant trend over all heights nor for individual elements. The large standard deviations among one exposure height in comparison to mean accumulation rate difference between all exposure heights makes the latter ones negligible.

Looking at the profile (Fig. 6b: mean with standard deviation from the 5 height replicates, SI 10: individual profiles at different heights), one can see that in general the same interpretation will be reached concerning the concentration gradient along the transect, independent of the selected exposure heights: Station A shows the lowest concentrations, station B the highest concentrations (except for Bi and Se which peak at Station C), and concentrations decrease downwind from station C to G. Concentrations at station E were higher compared to station D because D is located in a valley, while station E is on the hill opposite of station C and receives more direct fumarolic emissions (Arndt et al., 2014). Taking variation over height into consideration, these general trends are not statistically significant for As between station D and E (due to low measured concentrations at 1.5 and 0.7 m at station E) and for Se between station B and C (due to high measured concentrations at 1.5 and 1.6 m at station C). All in all, variations of triplicates at the same height are often larger than variations over the heights from 0.7 to 1.6 m.

Our observations of exposure height having no significant influence on element accumulation is in line with previous observations from urban monitoring where no significant differences in accumulation of Cd, Cu, Hg, Pb, and Zn were found for moss exposure heights between 0.5 and 5 m (Ares et al., 2014), and in 4–10 m for the elements Ba, Cu, Ni, and Sr (Capozzi et al., 2016). In contrast, Adamo et al. (2011) reported anthropogenic traffic-borne elements like As, Ba, Co, Pb, V, and Zn to be enriched in moss bags exposed at 4 m height while Cd, Cu, Mo, and Ni, which were transported over longer distances, and sea-borne elements were enriched in moss bags exposed at 12 and 20 m height (Adamo et al., 2011). However, this study was done in a "street canyon" with houses up to 30 m height which poses a completely different and much more channeled morphology than our natural volcanic sampling sites with little morphological restrictions, apart from rocks or volcanic bombs with maximum heights of around 2 m. Overall, we summarize that at least for volcanic study areas exposure height differences from close to ground up to 1.6 m (a height still easily accessible in the field) do not have any significant influence on element accumulation. Using

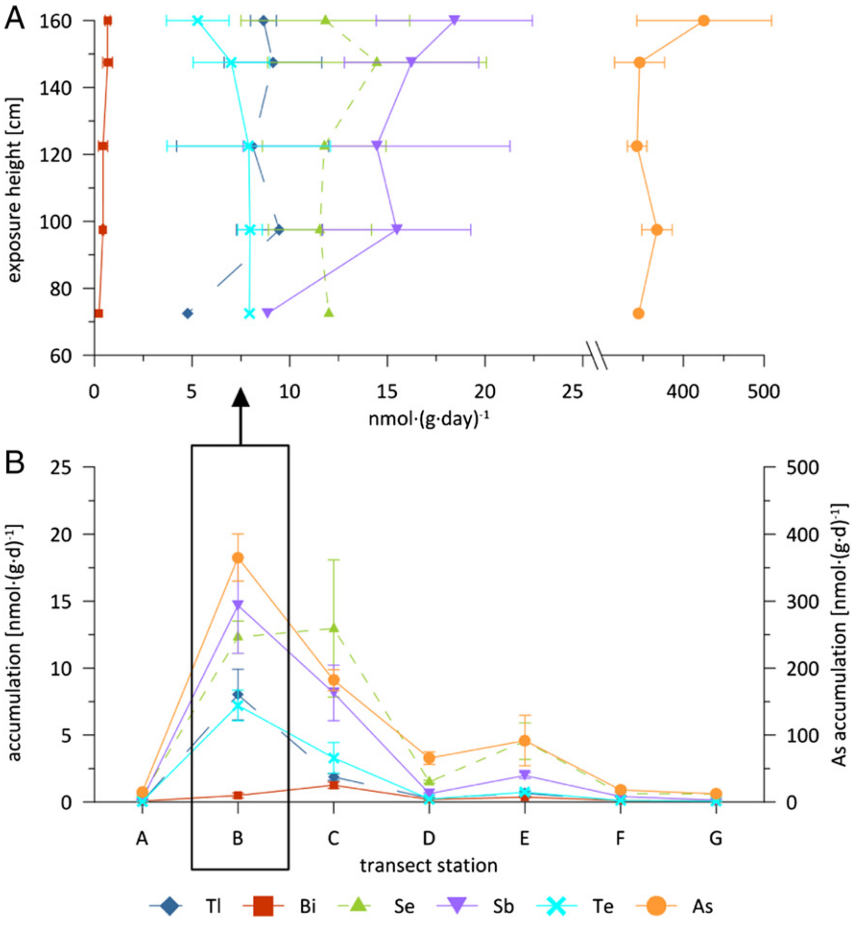


Fig. 6. A: Comparison of different moss bag exposure heights at station B within the fumarolic field. Standard deviation is shown for triplicate moss bags, whenever they were recovered from the field. B: Mean element concentrations along the transect for all exposure heights with standard deviation.

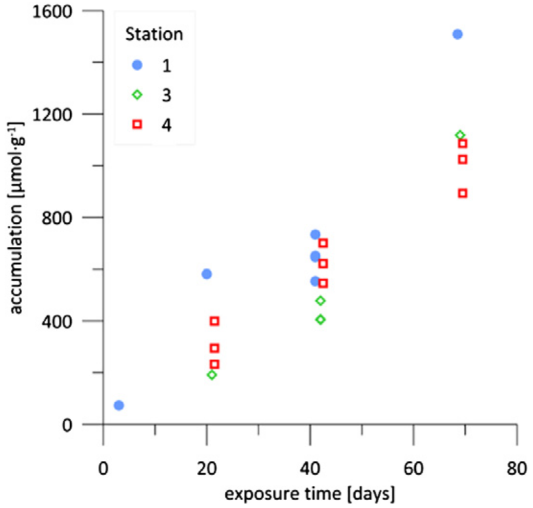


Fig. 7. Cumulative S accumulation of mosses with different exposure time at 4 stations within the fumarolic field of Vulcano during monitoring 2012. Triplicates are given as individual samples and data are given in μmol·g^{-1} without correction by exposure time. Station numbers are the same as in Arndt et al. (2014).

triplicates at approximately the same height will cover the natural variation expected from active moss monitoring sufficiently well.

3.3.3. Effect of exposure duration

Exposure duration of the moss bags is obviously crucial for element accumulation. The necessary minimum exposure duration depends extremely on the location and type of geothermal degassing. Sampling directly at the fumaroles on Vulcano, exposure times of as little as 3 days already reached element accumulations above detection limit, on the other hand the loading capacity of the moss was still not exhausted after as much as 9 weeks of exposure. Fig. 7 shows the linear increase for S accumulation from 3 days (73 μmol·g^{-1}) over 3 weeks and 6 weeks to 9 weeks (1500 μmol·g^{-1}). Calculated average accumulation rates were very similar for 3–9 weeks, while the one for 3 days was higher (24, 15 ± 7, 14 ± 3, and 16 ± 3 μmol·(g·d)$^{-1}$ for 3 days, 3, 6, and 9 weeks, respectively). Still, accumulation increases linearly, showing that loading capacity is not exhausted.

While for anthropogenic emissions exposure durations of a minimum of 6 weeks were recommended before (Capozzi et al., 2016), in volcanic areas a monitoring time of 3 weeks can be enough accumulation time if emission is strong enough and moss bags are exposed directly to the emission source, like on Vulcano. With accumulation being faster at the beginning as can be seen by the higher accumulation rate per day for the 3 day exposure, 3 weeks of minimum exposure time are recommended. However, in Yellowstone, accumulation over 3 weeks only reached values up to 0.003 μmol·(g·d)$^{-1}$ for As (SI 6). In combination with use of the commercial moss that had in general 50% less accumulation than the moss we collected in Bayreuth (compare Section 3.3.1), accumulated concentrations were very close to detection limit (compare Section 2.4) and extraction had to be adjusted for pre-concentration. Since the loading capacity is obviously not exhausted, yet, even after weeks of exposure, one is normally on the safer side with longer exposure times.

3.3.4. Effects of moss bag coverage during monitoring

Covering moss bags was assumed to be a necessity in those study areas where heavy rain falls could occur, i.e. either in boreal fully humid (Yellowstone) or tropical humid climates (Nyiragongo), to protect washout of accumulated elements from the moss bags. Uncovered moss bags could thus be expected to show lower element accumulation depending on rain intensity. Sure enough, uncovered moss also received higher primary element accumulation because of additional dust deposition and wet deposition from which covered moss bags are shielded. At all three sites where we tested covered versus uncovered exposure (Vulcano in 2012 (Arndt et al., 2014), Etna, and Nyiragongo), we observed the same general element distribution patterns independent of coverage or non-coverage (Nyiragongo: Fig. 8, Vulcano: Fig. 9, Etna: SI 11).

Calculating accumulation rate ratios in the mosses of covered versus uncovered exposure, we found ratios of 0.13 to 0.7 for Etna, 0.24 to 2.7 for Vulcano, and 0.13 to 0.92 for Nyiragongo. Despite the fact that there was a significant difference in rain intensity between the three areas (no rain at Etna, some rain on Vulcano, and re-occurring daily rain at Nyiragongo), there were no significant differences in these ratios. Over all

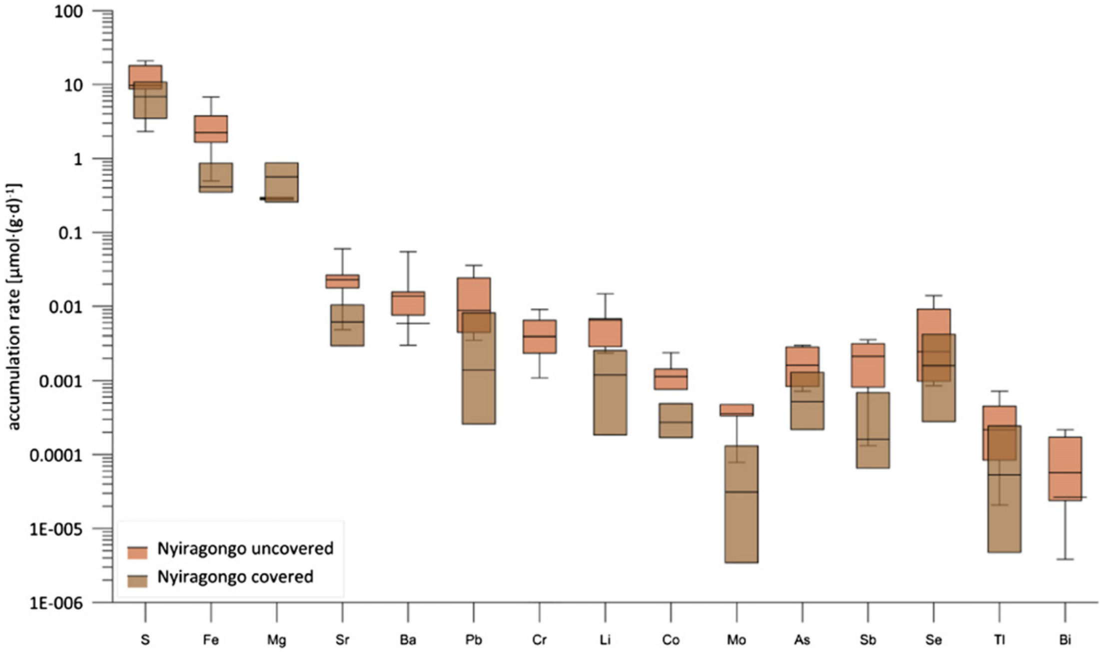


Fig. 8. Element accumulation rates in covered and uncovered moss bags at the crater of Nyiragongo.

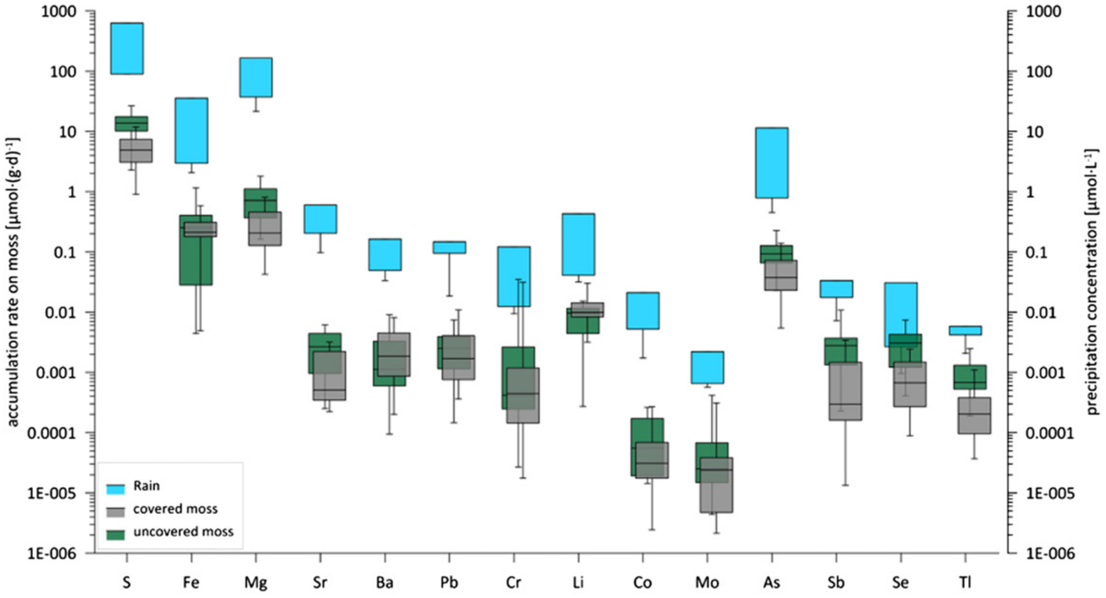


Fig. 9. Comparison of rain water concentrations with moss concentrations of covered and uncovered moss bags within the fumarolic field on Vulcano in 2012.

elements and all sites, concentrations in the uncovered moss bags were about one order of magnitude larger than those in the covered moss bags, indicating that any rain water washout effect is negligible, while additional dust and wet deposition is quite significant. The absence of washout by rain has also been stated by Adamo et al. (2003) who conducted moss bag monitoring in Naples (Italy).

Considering that we wash mosses with deionized water to remove adsorbed elements from the mosses prior to moss exposure (Section 2.2), it is at first glance surprising that rain water washout shows such little effect. However, rain water in volcanic areas washes out the atmosphere and takes trace elements and particles from the air with it. Comparing element distribution obtained from sampling rain water with the results from moss monitoring on Vulcano Island showed for all monitored elements the same patterns (monitoring 2012; Arndt et al. (2014); Fig. 9). This means, moss monitoring and rain water chemistry data yield complementary information.

In summary, covering moss bags proved unnecessary, even in humid climates. Uncovered, the moss bags trap higher concentrations in shorter times. If precipitation occurs during the sampling periods, samples could be taken to yield complementary information on element distribution. In areas where there is only sparse or seldom rainfall, moss monitoring is the easier technique to apply being independent of climate conditions.

4. Conclusions

The easy-to-apply low-budget moss bag monitoring technique was sensitive to monitor emissions in the six different studied active volcanic areas under different climate conditions. Considering the six monitored volcanic areas (Nyiragongo, Etna, Stromboli, Vulcano, Nisyros, and Yellowstone), characteristic element release and distribution patterns could be revealed. Differences could be attributed to the location of each monitoring station with a decrease of element concentrations with increasing distance to the emission sources, to geological context (magma and emissions' chemical composition), and the type of volcano with less silica particle (ash) related elements due to passive degassing in hydrothermal areas and more at open conduit volcanoes due to explosive activity. All the volcanoes had in common that volatile trace element concentrations were several orders of magnitude above background at sites that are easily accessible for tourists. For toxic volatile elements, such as As, this may pose a health threat and warrants further monitoring in the future.

Although there are still no standardized volcanic moss monitoring protocols available, this study shows the potentialities of the moss bags method, and provides new constraints to better define a protocol. From our experience over a total study duration of seven years, we can summarize the following suggestions for future studies:

- Moss selection turned out to be a sensitive parameter for later comparison of different studies because moss of physically higher shoot compactness accumulated only 50% of that of lower compactness. To eliminate the influence of moss characteristics on monitoring results standardized moss (i.e. moss clones) can be used.
- Exposure heights between 0.7 and 1.6 m above the emission sources revealed no significant differences in distribution patterns which means that moss bags can be tied to whatever is available on-site, eliminating the need of carrying extra poles along.
- Exposure times as short as three weeks are sufficient at sampling sites very close to the emissions (crater rims of open-conduit volcanoes or strongly exhaling fumaroles). On the other hand, moss accumulation capacities are high enough that sampling can be continued for at least nine weeks if for e.g. logistic reasons, samples cannot be recovered earlier.
- Covering moss bags proved unnecessary because rain washout was negligible, even in humid climates. Quite on the contrary, uncovered moss bags accumulated more because of additional dry and wet deposition.
- To cover for natural variations in emissions, exposing moss bags always in triplicates is recommended.

Surely, an ulterior effort is necessary to move towards a standard protocol of monitoring, that have to include a multidisciplinary approach, for example by collecting simultaneously rainwater and atmospheric particulates with consolidated techniques, while the moss bags are exposed, but also by merging knowledge from biology (the mosses), chemistry (sampled elements), and volcanology (activity).

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Appendix A. Supplementary data

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SUPPORTING INFORMATION

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

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SI 1: Description of monitored volcanoes

Open conduit volcanoes

Nyiragongo is a 3470 m high basaltic stratovolcano in the Democratic Republic of the Congo in the East African Rift System. Being a rift volcano (and also considered as hot spot volcano (Hamaguchi and Zana, 1990)), Nyiragongo is highly alkaline (36% SiO_2; Santo et al. (2003)). It currently hosts the largest permanent lava lake on earth (Sawyer et al., 2008) which was drained during its last eruption in 2002 (Tedesco et al., 2007) but refilled since then. Continuous degassing occurs from the lava lake forming a stable plume that constantly fumigates the southwestern sector of the volcano (Calabrese et al., 2014). Using Teflon filters to sample particles from 2400 L of volcanic plume gas, Calabrese et al. (2014) found the elements As, Bi, Cr, Mg, Mo, Pb, Tl, and Fe in median concentrations of 10, 20, 330, 790, 20, 24, 1, and 3300 $ng\cdot m^{-3}$. In rain water analysis from the crater during the same monitoring period, these elements were found in concentrations of 5.0, 0.01, 0.7, 4900, 0.48, 6.6, 3.2, and 10000 $\mu g\cdot L^{-1}$ (Calabrese et al., 2014).

Mount Etna is the largest European alkali basaltic stratovolcano with an elevation of 3329 m. It is located on Sicily (Italy), where the African continental plate collides with the Eurasian plate. Etna is characterized by continuous degassing from its 4 summit craters with some interrupting explosive events. Etna is known for emitting large amounts of major and trace elements to the atmosphere (Calabrese et al., 2016) and has been subject to various studies using different monitoring techniques for major volcanic gases (passive samplers for SO_2, HF, and HCl (Aiuppa et al., 2004)) and trace elements. Rain water sampling at the crater and in wind direction from the crater in Calabrese et al. (2011), showed that volatile elements (e.g. As, Bi, and Tl) and refractory elements (e.g. Ba, Co, and Fe) could be differentiated and more refractory than volatile elements were recovered in the precipitation on the crater. Particulate matter of the plume has been accessed by filtration, showing that the elements Pb, Mo, Se, Sb, Bi, and Tl were associated with sulfur in particles (Aiuppa et al., 2003). In another study, fluxes of 550, 125, and 35 $kg\cdot d^{-1}$ for Pb, Tl, and Bi, respectively, were calculated (Gauthier and Le Cloarec, 1998).

Stromboli is the most northeastern island of the Aeolian Islands (Italy). The 12.6 km^2 big island is characterized by the basaltic 924 m high stratovolcano with its crater at 750 m. The dispersion of volcanic emissions around the summit craters has been previously evidenced for major compounds measuring sulfur gases with passive samplers (D'Alessandro et al., 2013) and assessing the impact of emissions on rain for the halogens F and Cl (Bellomo et al., 2003) and for major ions in rain water like Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, and SO_4^{2-} (Liotta et al., 2006). Trace elements have been monitored in rain water in Stromboli town 3 km away from the crater and out of wind direction (Madonia et al., 2013), being below the WHO threshold concentrations for the elements Ba, Fe, As, Mo, Se, Sb, Cr, and Pb. The plume was sampled with dry filters directly at the crater and by aircraft (by pumping 1-8 m^3 air through the filters), resulting in concentrations as high as 3.0 μg·m^{-3} As, 1.3 μg·m^{-3} Pb, and 0.74 μg·m^{-3} Se during high eruptive activity in July 1994 (Allard et al., 2000). Up to date, trace element distribution from the plume on the crater and Stromboli town has not been investigated simultaneously.

Hydrothermally emitting volcanoes

Vulcano is the southernmost Aeolian Island in the Tyrrhenian Sea north of Sicily. Its volcanic island arc formed together with the Aegean Islands during the subduction process of the African plate beneath the European one (Barberi et al., 1974). Today, the 390 m high crater of La Fossa is the most distinct feature of Vulcano Island. Since Vulcano's last eruption 1888-90, its activity is characterized by a degassing high-temperature (>100°C) fumarolic field on the northern crater rim and some lighter degassing activity in the harbor bay. Volatile trace elements (As, Bi, Cd, Pb, Tl, and Zn) were already determined by condensate and sublimate sampling and subsequent thermochemical modelling (Cheynet et al., 2000) and by active sampling using Tedlar® bags for volatile As (Arndt et al., 2016). The impact of its fumarolic trace element emissions has been assessed through the analyses of indigenous lichens (Grasso et al., 1999) from the whole island except the crater area identifying the elements As, Sb, and Pb being of volcanic plume origin. Sampling lichens, Varrica et al. (2000) already came to the conclusion that fumarole activity represents a significant and continuous source of trace elements like Cu, Au, and Zn, however, the immediate crater area and the prevailing wind direction were left out.

Nisyros belongs to the Aegean Islands (Greece) west of Turkey, which form the 2nd island arc in the Mediterranean Sea that developed during subduction of the African plate beneath the European plate (Barberi et al., 1974). Since its last hydrothermal eruption in 1887 (Marini et al., 1993) its activity mainly consists of fumarolic degassing from 3 main active areas which are Kaminakia crater, Stefanos crater, and the area of Polybotes (consisting of Phlegeton, Polybotes Megalos and Micros craters, and Lofos Dome (from east to west)). Fumaroles in Nisyros show outlet temperatures around 100°C (Brombach et al., 2003). To our knowledge, no information about trace element emission has been published so far.

Yellowstone National Park, WY, USA, the caldera of the Yellowstone hot spot, formed 630,000 years ago. Its various geothermal features like hot springs, fumaroles, mudpots, geysers, and geothermally influenced peatlands, are known for high aquatic major and trace element concentrations (Ball et al., 2008; Ball et al., 2002; Ball et al., 2010) and also for volatile trace element emissions of which e.g. for volatile arsenic a maximum concentration of 200 mg As m^{-3} was calculated from passive sampling using Fick's law of diffusion (Planer-Friedrich and Merkel, 2006). This concentration is far above the average natural background concentration of 2.8 ng As m^{-3} calculated by Chilvers and Peterson

(1987). Until now, biomonitoring only has been done in Yellowstone outside the emission zones using indigenous lichens (Bennett and Wetmore, 1999), identifying the influence of geothermal emissions for the elements Fe, Co, As, S, and Mg as negligible. The geothermal emission zones were never monitored directly so far.

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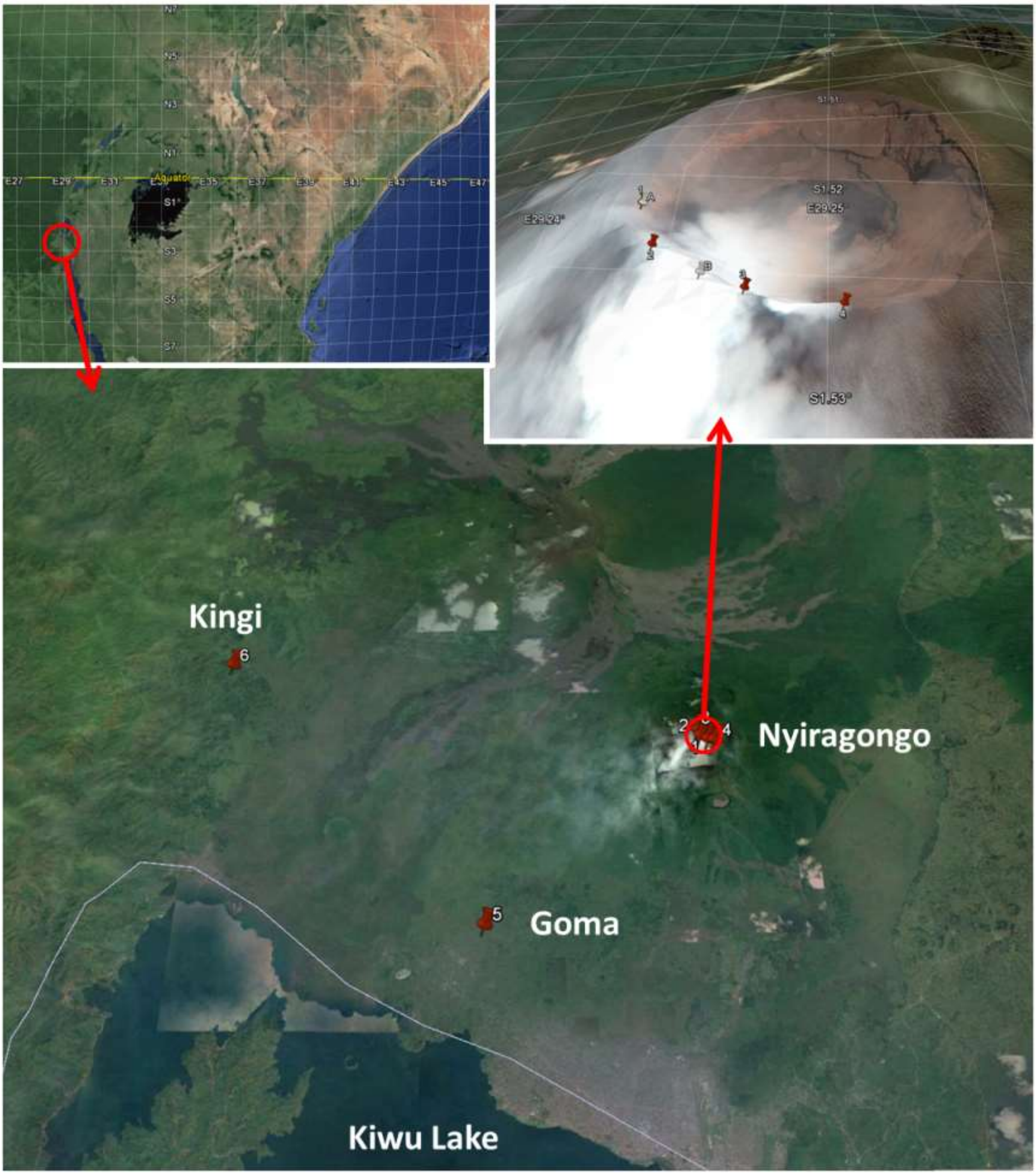
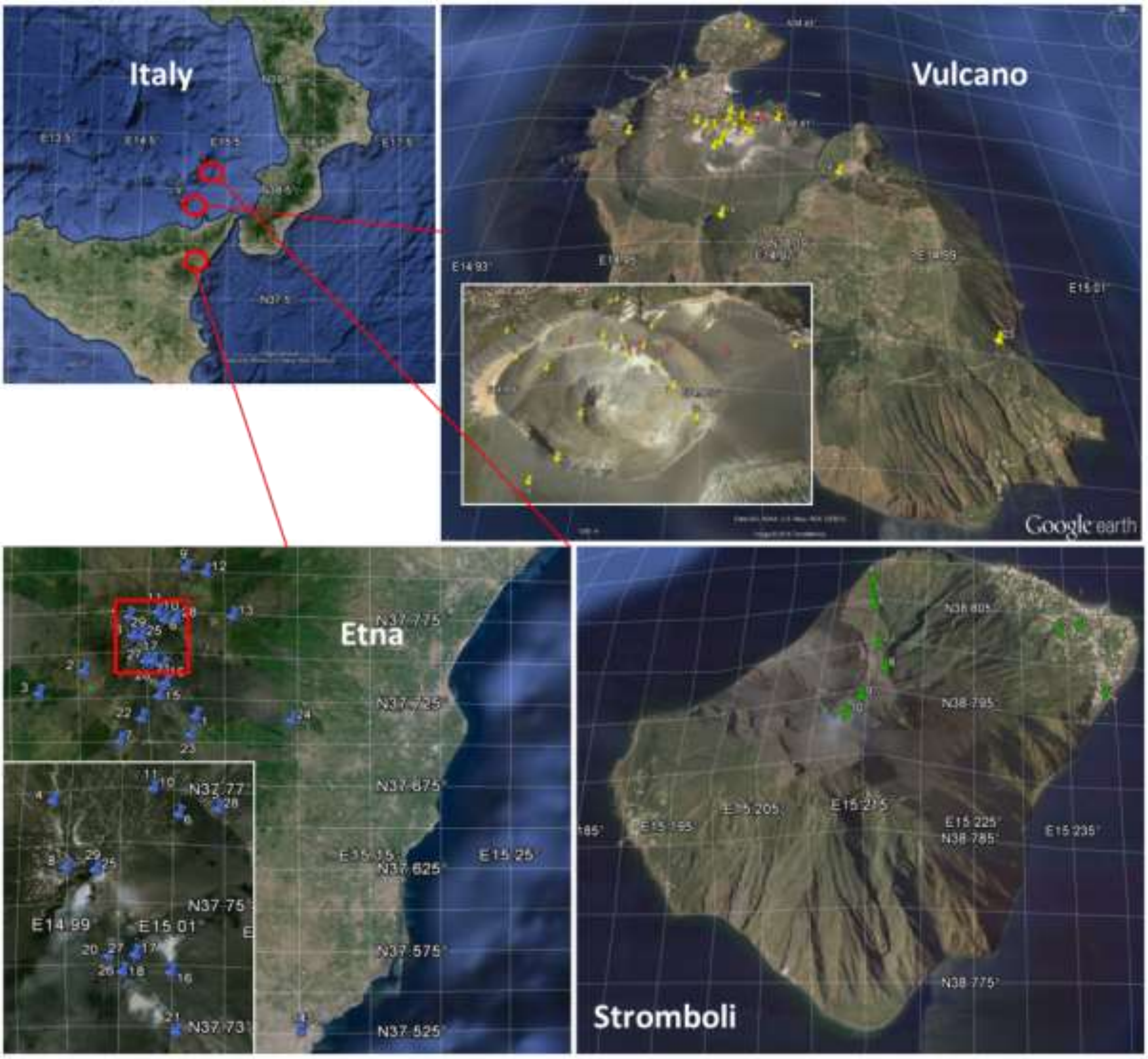
SI 2: Nyiragongo map and sampling points



Monitoring station	Coordinates (UTM WGS 84)		
#	Zone	S	E
1 Nyiragongo	35 M	749708	9831496
2 Nyiragongo	35 M	749814	9831221
3 Nyiragongo	35 M	750118	9831004
4 Nyiragongo	35 M	750386	9830972
5 Rusayo (Goma)	35 M	740637	9823147
6 Kingi	35 M	729116	9836004

SI 3: Map of all Italian Volcanoes with moss exposure points marked



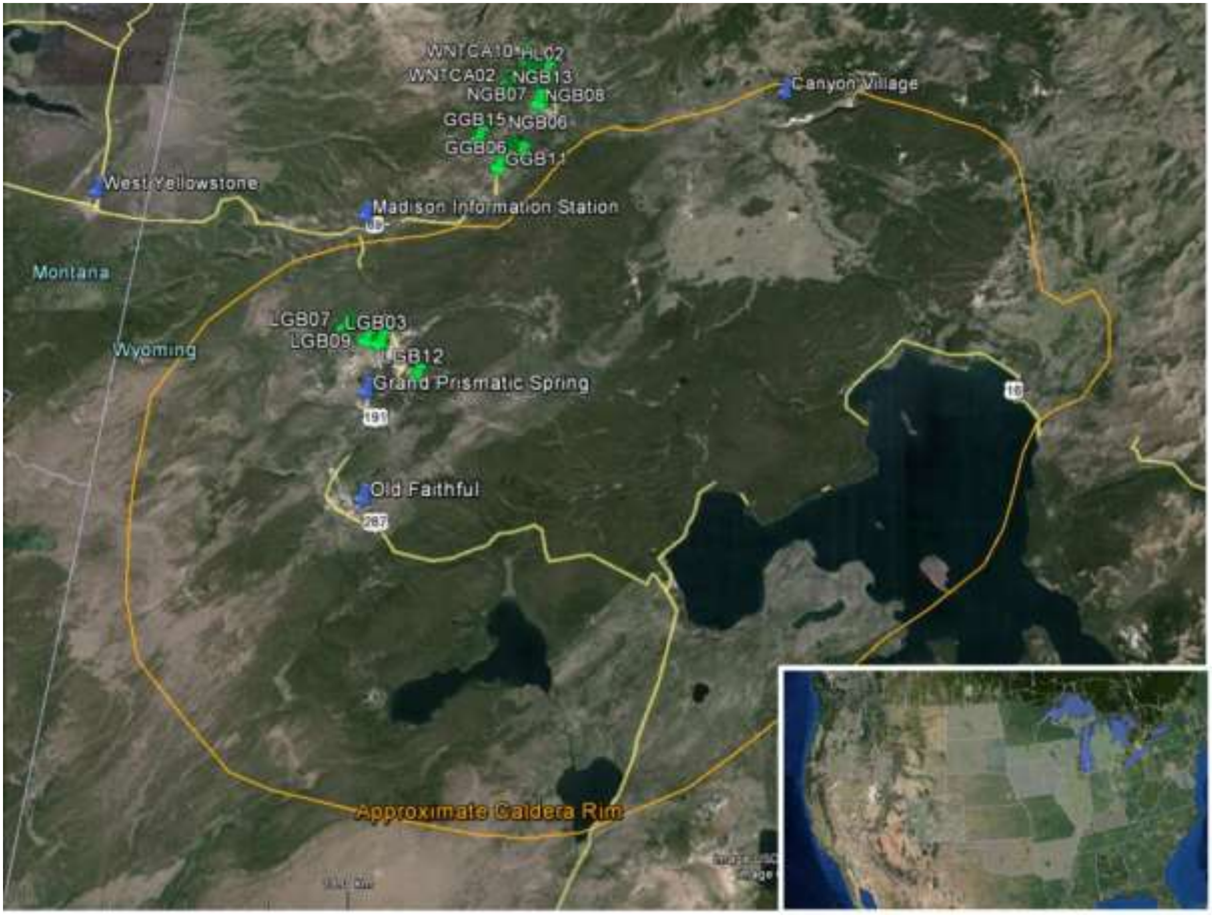
Stromboli			
Monitoring station	Coordinates (UTM WGS 84)		
	Zone	N	E
Str1	33 S	4294979	520503
Str2	33 S	4294923	520333
Str3	33 S	4294321	520727
Str4	33 S	4295350	518575
Str5	33 S	4295167	518575
Str6	33 S	4294957	518636
Str7	33 S	4294289	518728
Str8	33 S	4294142	518795
Str9	33 S	4293833	518639
Str10	33 S	4293691	518520

For coordinates of the Etna and Vulcano monitoring campaigns, please see Calabrese et al. (2015) and Arndt et al. (2014)

SI 4: Nisyros

Monitoring station	Coordinates (UTM WGS 84)		
	Zone	N	E
Phlegeton	35 S	514690	4048510
Andreas	35 S	514901	4048045
Kaminakia	35 S	515522	4048145
Stephanos	35 S	515154	4048122
Polybotes	35 S	514847	4048690
Pozzo Geotermico	35 S	515561	4048430
Lophos	35 S	515163	4048653
Belvedere	35 S	516644	4049722

SI 5: Yellowstone map including sampling points (green), the approximate caldera rim (orange), and some orientation points (blue).



SI 6: Moss accumulation rates in Yellowstone sampling sites for As and Sb [nmol·(g·d)$^{-1}$]

Area	Monitoring station name	type	Location Code	Coordinates		accumulation rate [nmol·(g·d)$^{-1}$]	
				N	W	As	Sb
Norris Geyser Basin	Crystal Spring	spring	NGB.01	44° 43.721	110° 42.718	0.45	< 0.01
	Fumarole near Crystal	fumarole	NGB.02	44° 43.720	110° 42.748	0.35	< 0.01
	The Gap	spring	NGB.03	44° 43.716	110° 42.787	0.46	< 0.01
	Kaolin Spring	spring	NGB.04	44° 43.695	110° 42.779	0.64	0.37
	Persnickety	spring	NGB.06	44° 43.670	110° 42.830	0.54	0.15
	Fumarole near Liveboat	fumarole	NGB.07	44° 43.659	110° 42.865	0.097	< 0.01
	Steam Engine	fumarole	NGB.08	44° 43.610	110° 42.994	0.67	0.23
	Elk Geyser	spring	NGB.09	44° 43.774	110° 42.708	0.26	< 0.01
	Mudpot near Beowulf	mudpot	NGB.10	44° 43.849	110° 42.678	0.26	0.26
	Beowulf Spring	spring	NGB.11	44° 43.886	110° 42.682	0.15	< 0.01
	Dragon Spring	spring	NGB.12	44° 43.909	110° 42.656	0.91	< 0.01
	Cinder Pool	spring	NGB.14	44° 43.947	110° 42.586	0.412	< 0.01
	Mudpot	Mudpot*	NGB.15	44° 44.011	110° 42.532	3.55	0.43
Gibbon Geyser Basin	fumaroles	fumaroles	GGB.04	44° 41.362	110° 43.714	0.16	< 0.01
	Whirlpool	spring	GGB.05	44° 41.225	110° 43.708	0.65	< 0.01
	Standard UGC Pool	spring	GGB.06	44° 41.221	110° 43.686	1.03	< 0.01
	Avalanche	Geyser*	GGB.07	44° 41.330	110° 43.664	208	2.4
	fumaroles	fumaroles	GGB.08	44° 41.367	110° 43.720	0.58	< 0.01
Lower Geyser Basin	Mudpot	mudpot	LGB.01	44° 33.783	110° 50.164	0.74	< 0.01
	Azure Spring	spring	LGB.02	44° 33.658	110° 49.979	0.43	< 0.01
	Conch Spring	spring	LGB.03a	44° 33.389	110° 49.927	0.71	< 0.01
	Conch Spring	spring	LGB.03b	44° 33.389	110° 49.927	3.74	< 0.01
	Boulder geyser	spring	LGB.04	44° 33.527	110° 50.640	1.90	< 0.01
	Mound Spring	spring	LGB.06	44° 33.891	110° 51.604	0.85	0.09
	Steep Cone	spring	LGB.07	44° 34.000	110° 51.792	0.93	0.12
	Mudpot at Boulder	mudpot	LGB.09	44° 33.509	110° 50.654	0.43	< 0.01
Nymph and Hazle Lake area	Frying Pan	spring	NL.01	44° 45.129	110° 43.346	< 0.01	< 0.01
	Nymph Creek	wetland	NL.02	44° 45.177	110° 43.446	< 0.01	< 0.01
	Roadside spring East	spring	NL.03	44° 45.210	110° 43.487	1.03	0.12
	Roadside spring West	spring	NL.04	44° 45.215	110° 43.518	0.49	< 0.01
	Fumarolic field	fumarole	NL.05	44° 45.102	110° 43.693	0.81	0.04
	Fumarole (new)	fumarole	NL.07a	44° 45.166	110° 43.745	1.00	0.30
	Fumarole (new)	fumarole	NL.07b	44° 45.166	110° 43.745	1.96	0.12
	Hazle Lake north	wetland	HL.01	44° 45.040	110° 42.755	< 0.01	< 0.01
	Hazle Lake south	wetland	HL.02	44° 45.005	110° 42.720	< 0.01	< 0.01
West Nymph Creek Thermal Area	Mudpot (north group)	mudpot	WNTCA.01	44° 44.615	110° 44.630	< 0.01	0.09
	The Hisser	fumarole	WNTCA.02	44° 44.545	110° 44.725	0.35	0.10
	Fumarole field (middle)	fumarole	WNTCA.03	44° 44.464	110° 44.607	< 0.01	0.10
	Boiler	spring	WNTCA.04	44° 44.349	110° 44.648	0.19	0.15
	the swamp	wetland	WNTCA.06	44° 44.291	110° 44.676	0.03	< 0.01
	Little Prismatic	spring	WNTCA.07	44° 44.257	110° 44.714	1.30	< 0.01
	Point of Youth	spring	WNTCA.08	44° 44.321	110° 44.579	0.088	< 0.01

* eliminated from data evaluation due to water/mud on the moss

SI 7: Mean element accumulation rates of uncovered moss bag triplicates exposed at Stromboli and Nyiragongo and duplicates at Nisyros [nmol·(g·d)$^{-1}$]. From all concentrations at every site moss blank concentrations were subtracted. Thus, some given concentrations may seem to be below detection limit, but actually are not.

	station	S	Fe	Mg	Sr	Ba	Pb	Cr	Li	Co	Mo	As	Se	Sb	Tl	Bi
	DL*	2700	450	4200	9.4	24	1.01	0.81	2.7	0.42	0.10	0.89	0.14	0.12	0.017	0.012
Stromboli	1	1100	1200	580	10	< DL	0.068	0.88	5.3	0.35	0.014	0.5	0.078	0.28	0.0035	0.0038
	2	1800	1700	1200	55	< DL	< DL	1.2	7.9	0.49	0.031	0.63	0.12	0.087	0.01	0.0063
	3	2100	2400	4400	21	< DL	2.0	1.5	6.7	0.94	0.041	0.37	0.12	0.089	0.01	0.0059
	4	11000	12000	16000	140	38	0.92	3.9	43	4.7	0.15	2.3	0.63	0.035	0.022	0.01
	5	6000	9400	11000	110	38	0.56	2.6	34	3.6	0.12	2.0	0.51	0.029	0.024	0.011
	6	4200	6500	5700	76	26	0.27	2.3	24	2.6	0.093	1.8	0.4	0.062	0.032	0.014
	7	5800	12000	9400	130	46	0.62	1.5	30	4.6	0.14	2.8	0.59	< DL	0.043	0.027
	8	8800	14000	9500	150	60	1.5	5.6	44	4.9	0.24	4.4	1.1	< DL	0.081	0.091
	9	9300	13000	12000	150	72	4.7	1.4	29	5.9	0.92	9.2	3.8	< DL	1.2	0.88
	10	5800	13000	7600	110	63	6.5	3.2	29	3.9	1.64	9.3	6.8	< DL	0.62	1.6
Nisyros	1	1600	250	160	0.34	0.14	0.21	4.5	2.6	0.033	0.082	0.045	0.073	0.0025	0.012	0.00053
	2	240	150	290	1.14	2	4.1	2.5	3.1	0.012	< DL	0.036	< DL	< DL	0.014	0.0037
	3	3900	270	< DL	1.5	0.8	4.1	2.6	3.6	0.096	0.29	0.35	0.023	0.0066	0.013	0.0056
	4	4000	1300	96	4.2	10	2.7	3.9	8.8	0.090	0.058	3.8	0.018	0.014	0.074	0.050
	5	1300	190	400	0.11	< DL	4.1	0.16	2.1	0.0086	< DL	0.085	< DL	< DL	0.0030	< DL
	6	93	250	220	0.55	0.14	4.7	3.5	1.8	0.038	< DL	0.26	< DL	< DL	0.0031	0.0013
	7	< DL	180	< DL	0.96	< DL	1.2	0.11	2.8	0.058	0.037	0.08925	0.0085	0.011	0.01	0.00022
	8	1100	130	14	0.44	< DL	8.2	1.7	0.92	0.021	0.4	0.22	< DL	< DL	< DL	0.0039
Nyiragongo 2014	1	9700	3800	NA	26	14	24	1.1	6.8	1.4	0.36	3.0	14	0.82	0.45	0.17
	2	9800	3200	NA	22	16	36	2.5	6.5	1.4	0.33	2.9	9.2	3.2	0.72	0.22
	3	8700	6800	280	60	55	12	9.1	6.5	2.4	0.37	1.6	3.9	0.13	0.25	0.066
	4	2300	2000	NA	24	7.9	4.4	3.9	2.4	0.83	0.48	0.72	0.98	3.6	0.084	0.0038
	5	140	140	190	2.8	0.74	1	< DL	0.22	0.083	0.0031	0.037	0.071	0.12	0.033	0.0018

* DL = Detection limit in nmol·(g·d)$^{-1}$. Detection limits are given for the moss blank with a hypothetical exposition time of 23 days (like on Stromboli). The moss blank was used for blank correction when calculating daily accumulation rates for the mosses for every station.

SI 8: Main relative accumulation factors (RAF) for the mosses exposed at the crater area/in the fumaroles. RAF is calculated by c(moss)-c(blank) / c(blank)

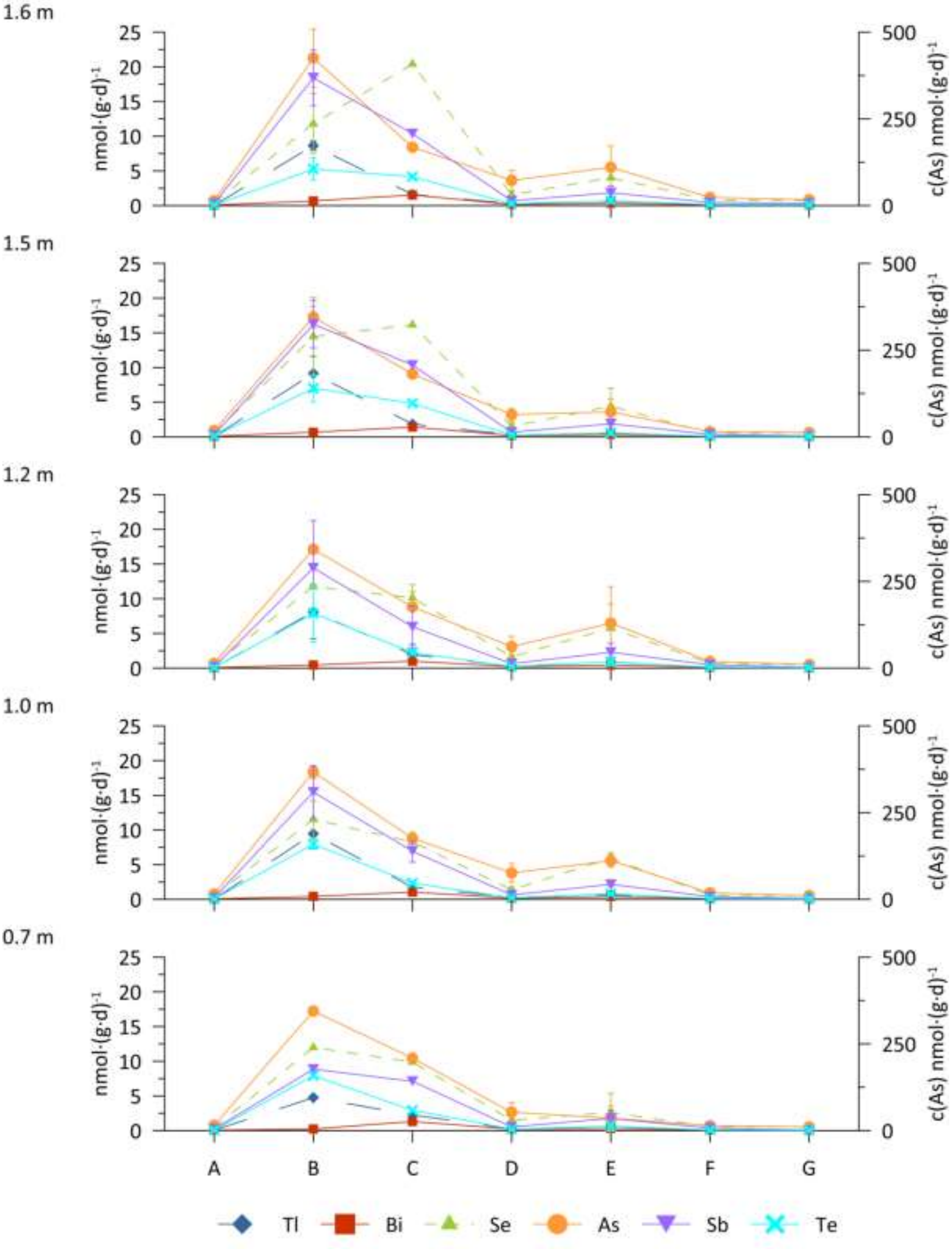
		S	Fe	Mg	Sr	Ba	Pb	Cr	Li	Co	Mo	As	Sb	Se	Tl	Bi
uncovered	Vulcano 2012	12	0.71	0.75	0.13	0.47	1.5	5.1	-0.07	0.64	190	4.6	42	53	100	87
	Vulcano 2013	240	5.0	0.29	1.8	0.94	2.1	10	1.8	1.1	380	4.0	400	89	340	55
	Stromboli	2.2	29	1.8	6.5	2.6	11	11	9.4	16	11	3.9	48	-0.14	36	130
	Nisyros	0.47	0.65	0.01	0.20	0.15	0.17	0.80	0.03	0.46	0.76	1.1	0.02	-0.01	1.1	0.52
	Nyiragongo	1.9	2.1	-0.11	8.7	0.73	0.29	1.9	1.8	0.68	3.9	0.89	11	30	97	1.7
	Etna	54	30	1.7	5.5	5.6	5.4	19	17	16	140	2.8	91	3.7	2000	290
covered	Vulcano 2012	5.4	0.29	0.31	0.42	0.60	0.33	6.0	5.3	0.12	0.32	98	14	13	33	25
	Nyiragongo	1.5	0.29	0.03	0.12	0.00	2.1	-0.23	0.54	0.58	0.09	1.6	6.4	4.6	37	-0.24
	Etna	6.5	12	0.81	2.7	2.6	1.1	0.86	4.4	6.9	2.6	31	2.6	27	240	39

SI 9: Correlation coefficients for presented element correlations for all volcanoes

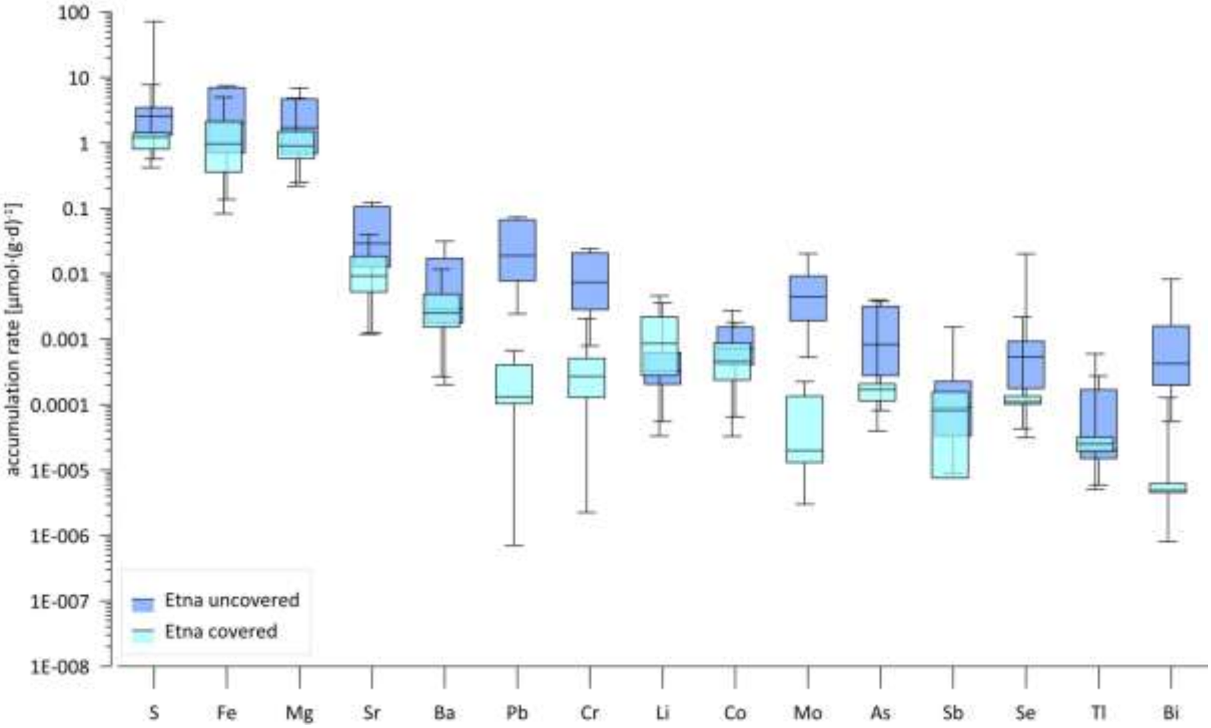
	elements		Volcano					
			Etna	Nyiragongo	Stromboli	Vulcano 2012	Vulcano 2013	Nisyros
Spearman correlation coefficient	S - As	R	0.914**	0.333	0.764**	0.933*	0.949**	0.418
		sign.	0	0.42	0	0	0	0.229
		N	44	8	30	81	20	10
	S - Se	R	0.886**	0.286	0.817**	0.945**	0.986**	-0.5
		sign.	0	0.535	0	0	0	0.667
		N	36	7	30	81	20	3
	S - Pb	R	0.768**	0.321	0.490*	0.305*	0.313	-0.548
		sign.	0	0.482	0.011	0.035	0.179	0.16
		N	44	7	26	48	20	8
	S - Fe	R	0.712**	0.048	0.876**	0.197	-0.729**	0.394
		sign.	0	0.911	0	0.102	0	0.26
		N	44	8	30	70	20	10
	Fe - Sr	R	0.894**	0.821*	0.911*	0.660**	0.901**	0.491
		sign.	0	0.023	0	0	0	0.125
		N	44	7	30	71	20	11
	Fe - Ba	R	0.905**	0.881**	0.912**	0.675**	0.131	0.6
		sign.	0	0.004	0	0	0.582	0.285
		N	44	8	21	67	20	5

R: Spearman-Rho correlation coefficient
sign.: 2-sided significance test
N: number of data available
*: correlation is significant on 0.05 level
**: correlation is significant on 0.01 level

SI 10: Influence of exposure heights on element accumulation in moss bags at every monitoring station (A-G). Arsenic is plotted on the 2nd y-axis. Standard deviations are given whenever triplicates were present.



196 **SI 11: Comparison of covered and uncovered moss bags exposed at the crater area on Etna**



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Study 3: Moss bag monitoring as screening technique to estimate the relevance of methylated arsine emission

Julia Arndt, Britta Planer-Friedrich

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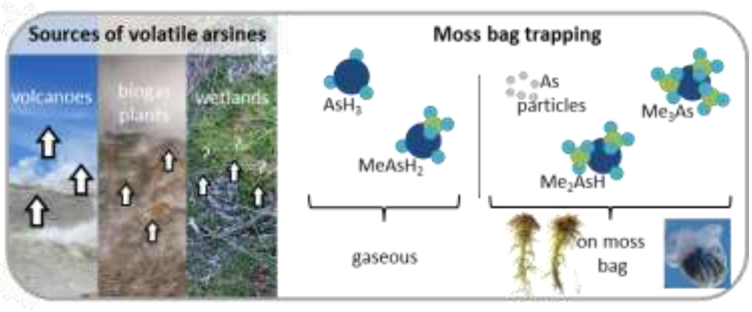

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Short Communication

Moss bag monitoring as screening technique to estimate the relevance of methylated arsine emission

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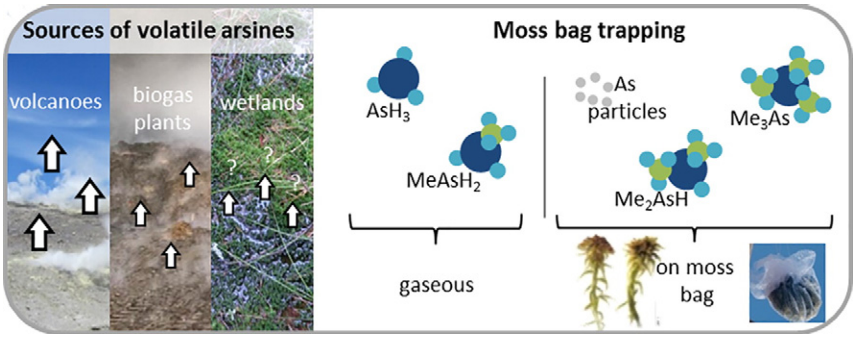
HIGHLIGHTS

- Volatile methylarsines can be recovered as respective oxyanions from *Sphagnum* moss.
- Moss bags can be used for screening the emission relevance of methylarsines.
- Volcanic emissions contain particulate As, recovered on the moss as arsenate.
- Biogas predominantly contains trimethylarsine, recovered as trimethylarsenoxide.

GRAPHICAL ABSTRACT



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ABSTRACT

Volatile arsenic (As) species, like arsine, mono-, di-, and trimethylarsine (AsH_3, $MeAsH_2$, Me_2AsH, Me_3As) are difficult to sample in remote areas without sophisticated equipment. The application of moss bags is an easy-to-apply screening technique which has been used for trapping total (mostly particulate) As from different emission sources before. We evaluated its potential for additional volatile As species screening. We found Me_2AsH and Me_3As in N_2 atmosphere to be quantitatively trapped on the mosses and to be recoverable as their respective pentavalent acids (and/or oxyanions) when ground mosses were heated for 90 min at 90 °C in 0.1 M HNO_3/3% H_2O_2. $MeAsH_2$ was trapped partially while AsH_3 was not trapped. The most likely mechanism is covalent bonding to the moss surface. While moss monitoring does not replace more sophisticated techniques for volatile As sampling, it can easily be used as screening technique to determine whether besides particulate As volatile methylated As species could have any relevance in environments with yet unknown As emissions.

1. Introduction

Arsenic (As) is an ubiquitous element and can often be found as volatile arsines in environmental gases like geothermal and volcanic exhalations (Arndt et al., 2014; Planer-Friedrich and Merkel, 2006) but also in diffusive degassing from soils and peatlands (Mestrot et al., 2013a), anthropogenic emissions like landfill degassing (Hirner et al., 1994), or biogas (Mestrot et al., 2013b). The main arsine species monitored are the inorganic AsH_3, and the methylated species mono-, di-, and trimethylarsine ($MeAsH_2$, Me_2AsH, and Me_3As; Me = methyl group) with boiling points (b.p.s) of −55 °C or −62.5 °C (AsH_3), −2 °C or +2 °C ($MeAsH_2$), +36 °C (Me_2AsH), and +52 °C (Me_3As; b.p.s from Ilgen and Huang (2013), Lide (2003), Pantsar-Kallio and Korpela (2000), and Planer-Friedrich et al. (2006)). Additionally, volatile chlorinated and sulfonated As compounds exist (Planer-Friedrich et al., 2006). Volatile As species have been sampled and determined by different methods which are listed in the supporting information (SI 1). All of

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the volatile arsines have in common their high toxicity (Pakulska and Czerczak, 2006) which is why their emissions are important to monitor.

Moss monitoring is often used for broad area screenings to estimate atmospheric total pollutant contents from natural and anthropogenic emissions. This technique uses the natural ability of mosses to take up nutrients as well as pollutants without differentiation by their large surface area (Brown and Bates, 1990), their cation exchange capacity with their outside cell walls consisting of polyuronic acids (Clymo, 1963), e.g. glucuronic acid (Popper and Fry, 2003), or even by uptake inside the moss cells (Raven et al., 1998). *Sphagnum* mosses are often used for moss monitoring studies (Ares et al. (2012) and references therein) due to their comparably large surface and cation exchange capacity (0.9–1.5 meq·g^{-1}; Rühling and Tyler (1973)). Moss monitoring can be applied as *passive* technique by collecting and analyzing indigenous mosses or as *active* technique by exposing mosses collected from an uncontaminated area packed as spherical moss bags at the desired monitoring sites. This method has the advantages of being independent of the natural abundance of moss in the monitored area, that initial element concentrations are known, and that any exposure duration can be selected. Monitoring by moss bags has been applied e.g. on anthropogenic emissions of industry and traffic (Adamo et al., 2003; Cao et al., 2009) and on volcanic emissions from Etna (Calabrese et al., 2015) and Vulcano (Arndt et al., 2014).

In this paper, we show that *Sphagnum* mosses can trap higher methylated volatile arsines in a species-preserving way and can thus be used to estimate their emission relevance.

2. Methods

2.1. Generation of volatile arsines

Volatile arsines were generated by hydride generation using the protocol of Ilgen and Huang (2013). Briefly, the respective As oxyanion salts (arsenite, monomethylarsonic acid ($MMAs^V$), dimethylarsinic acid ($DMAs^V$), and trimethylarsine oxide (TMAO); structures of all arsines and their corresponding pentavalent acids can be found in SI 2) in 1 M H_3PO_4 were reduced by 3% $NaBH_4$ (in 1% NaOH) and the produced gas containing the volatile arsines was conducted to a Tedlar® bag which was kept dark at 5 °C until the experiments. Individual arsine species were generated in gas concentrations of 10 μg·L^{-1} while for gas chromatography (GC) calibration standard, a mixture of all 4 arsines each at 100 ng·L^{-1} was generated (Arndt et al., 2017).

2.2. Moss exposure to individual arsine gases in N_2 atmosphere

A mixture of *Sphagnum* moss (*S. tenellum*, *S. subsecundum*, *S. cuspidate*, *S. girgensonii*, *S. fallax*) was collected, cleaned (Arndt et al., 2014), and kept dry in closed plastic bags until the experiments. Arsine gas exposure of the moss in dry N_2 matrix was done for 10 days in 4 replicates for each arsine species and for each temperature in 300 mL borosilicate shot bottles (VWR) sealed with a septum (chloro-isobutene-isoprene rubber, Ochs, Germany). Therefore, 0.2 g dried moss was weighted in each shot bottle before sealing and N_2 rinsing. Bottles were protected from light by aluminum foil. Experiments were conducted at 5 °C for AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As and additionally for $MeAsH_2$ below b.p. (−20 °C and −80 °C) and for Me_2AsH above b.p. (45 °C and 80 °C). Therefore, 100 mL N_2 per bottle were replaced by 100 mL of 10 μg·L^{-1} of the respective arsine. A "blank" shot bottle without moss was used for gas speciation comparison for every experiment set and moss only in N_2 matrix was used as moss blank. After 10 days with daily shaking, 500 μL gas per bottle was sampled and diluted max. 1:1000 for analysis. The total moss was ground (Retsch MM 2000, 14 Hz, 3 min) without distinguishing between stems and leaves, split into 2 parts for total As and speciation analysis, and kept frozen until immediate analysis.

2.3. Moss exposure to natural emissions

Dried *Sphagnum* moss was filled in commercial mosquito nets (2 g each), tied to spherical bags with nylon wire and kept in closed plastic bags until exposure. Bags were exposed in triplicates at two sites to fumarolic emissions on Vulcano (Italy; Arndt et al. (2014)) for 3 days in September 2015 and to biogas at the roof of the fermentation hall of a biogas plant (near Bayreuth, Germany) for a month each in September 2016 and February 2017. After exposure, moss bags were transported back to the laboratory in sealed plastic bags, dried, and ground for analysis.

2.4. Analysis

Gas analysis for arsines and speciation determination was done according to Arndt et al. (2017) using the GC protocol of Ilgen and Huang (2013). Briefly, gas samples were cryotrapped and cryofocussed (in liquid N_2, −198 °C) before gas chromatographic separation (Varian CP-3800, Varian, USA, capillary column: 30 m, 0.32 mm ID, 4 μm film thickness, Rxi-1MS, Restek, USA) and following split for detection of (a) arsine species by electron impact mass spectrometry (Varian Saturn 2000) and (b) total As by atomic fluorescence spectrometry (P.S. Analytical; with superlamp (193.7 nm wavelength); CT-CF-GC-EI-MS/AFS).

For **total As concentrations**, 0.1 g powdered moss was digested in the microwave (CEM MARS Xpress) using 10 mL 6% H_2O_2 in 19.5% HNO_3 (Arndt et al., 2014). Samples were filled to 25 mL with MQ (18.2 MΩ cm at 25 °C, <3 ppb total organic carbon, Merck Millipore), filtered (0.2 nm; cellulose-acetate, Membrex), and analyzed by quadrupole ICP-MS (X-Series2, Thermo Scientific) in reaction mode (10% O_2). For instrumental drift control, 50 μg·L^{-1} Rh per sample were used as internal standard and an As standard was measured every 15 samples. For quality control, the reference materials TMDA-54.4 and 54.5 ([As] = 43.6 and 45.1 μg·L^{-1}; Environment Canada) and pure and spiked measurements and digests were used. Recoveries were 98.5–116% for TMDA and 98–110% for spikes.

Arsenic speciation on the moss was analyzed after extracting 0.1 g powdered moss in 10 mL 0.1 M HNO_3 in 3% H_2O_2 at 90 °C for 90 min in a heating block (SCP Science) for the As species arsenate, $MMAs^V$, $DMAs^V$, and TMAO as the corresponding acids (and/or oxyanions) of originally trapped arsine, mono-, di-, and trimethylarsine shaking the vials every 30 min (method for foodstuff DIN-EN-16802 (2016)). The H_2O_2 was added to oxidize arsenite, the immediate successor of volatile arsine, to arsenate, because arsenite and TMAO have the same retention times with the used chromatographic separation technique and would be indistinguishable. Extraction solutions were weighted back to their initial weight with MQ, filtered (0.45 μm, hydrophilic Teflon®, SCP Science) and analyzed by ion chromatography (ICS 3000 SP, Dionex with PRP-X100 column and isocratic 1 mL·min^{-1} flow of 20 mM $NH_4H_2PO_4$ (pH 5.6)) coupled to ICP-MS. The extraction technique is known to quantitatively recover $MMAs^V$ and $DMAs^V$ and was evaluated prior to moss extraction for TMAO using spiked aqueous solutions with the methylated As salts (5 μg·L^{-1}).

3. Results

3.1. Extraction technique evaluation

Recoveries of arsenite, $MMAs^V$, $DMAs^V$, and TMAO were 94–107% which confirms no As loss during extraction (Table 1). Recoveries show the complete conversion of arsenite to arsenate (96.5% ± 2.4), $MMAs^V$ and $DMAs^V$ to remain stable (106–111%) which agrees with previous observations in DIN-EN-16802 (2016), and complete stability of TMAO (105.2% ± 1.5). Consequently, species separation of TMAO and arsenite is possible using anion chromatography and was applied for moss samples in this study.

Table 1
Recovery of species [%] after species extraction using 3% H_2O_2 and 0.1 M HNO_3.

		Recovered species[%]				
		TMAO	Arsenite	$DMAs^V$	$MMAs^V$	Arsenate
Initial species	Arsenite	0.0	0.2 ± 0.1	0.4 ± 0.2	0.2 ± 0.1	96.5 ± 2.4
	$MMAs^V$	0.0	0.0	0.3 ^{1}	106.7 ^{1}	0.0
	$DMAs^V$	0.0	0.0	111.5 ^{1}	0.0	0.0
	TMAO	105.2 ± 1.5	0.0	0.1 ± 0.1	0.3 ± 0.1	0.2 ± 0.0
	Mix of all 4	106.5 ± 0.4	0.0 ± 0.0	111.1 ± 2.3	102.6 ± 4.6	93.7 ± 3.9

For $MMAs^V$ and $DMAs^V$, species stability was shown before and duplicate extractions were done.

3.2. Moss exposure in N_2 matrix

Hydride generation from individual As salts resulted in gases containing only the respective individual volatile As species AsH_3, $MeAsH_2$, and Me_2AsH, while for Me_3As about 10% impurity of Me_2AsH was detected (Fig. 1A, "initial"). Total initial gas concentration was set to 100% As for every experiment set. Detailed information on the amounts of As are given in SI 3.

Arsenic gas speciation did not change after 10 days in the borosilicate bottles with or without moss (Fig. 1A, "remain" and "blank") for AsH_3, and $MeAsH_2$, while there was no Me_2AsH remaining in the gas after 10 days and also no Me_2AsH, but still Me_3As in the Me_3As experiment.

In all experiments at +5 °C (Fig. 1A), As gas concentration dropped significantly for all As species after 10 days with a stronger decrease for Me_2AsH and Me_3As (to 0 and 20%, respectively) than for AsH_3 and $MeAsH_2$ (to 61% for both). No As was found on the moss after 10 days of AsH_3 exposure, while there was about 7% of the initial As on the moss as $MMAs^V$ for $MeAsH_2$ exposure. Larger amounts of As were found on the moss for Me_2AsH (>50%) and for the Me_3As experiment (>60%), for which the total amount of present Me_2AsH was recovered on the moss. In general, the As speciation on the moss matches the initial gas speciation with all methylated arsines being converted to their respective pentavalent acids and/or oxyanions.

$MeAsH_2$ exposure repetitions below b.p. at −20 and −80 °C (Fig. 1B) resulted in no significant speciation changes in the gas or on the moss and in 19% and 7% of the As being recovered on the moss, respectively. Me_2AsH exposure repetitions above b.p. at +45 and +80 °C (Fig. 1C) showed no remaining As in the gas while recovered As on the moss matched the initial amount of volatile As added to the bottles. Seemingly, in N_2 matrix, Me_2AsH can be quantitatively recovered from moss as $DMAs^V$ over a wide temperature range exceeding the Me_2AsH b.p. by far.

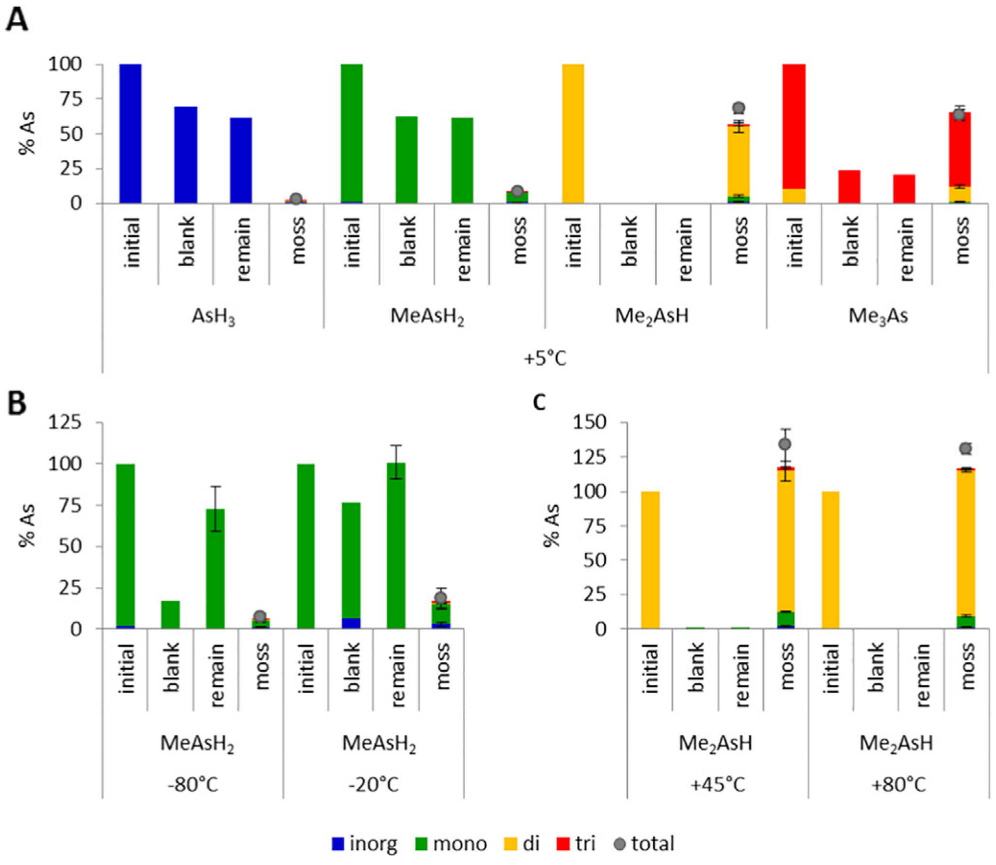

Fig. 1. Recoveries in percent of initial As gas after 10 days of moss exposure experiments at different temperatures. The initial total ng As in the gas was normalized to 100% for each experiment. The legend refers either to the gaseous As species (for the columns "initial", "blank", and "remain") or to the pentavalent As acids and/or oxyanions in 0.1 M HNO_3 (column "moss"). A: Moss exposure at +5 °C for AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As. B: Moss exposure to $MeAsH_2$ at −80 °C and −20 °C. C: Moss exposure to Me_2AsH at +45 °C and +80 °C.

Table 2
As speciation of moss bags from Vulcano [$mg \cdot g^{-1}$] and from biogas exposure [$\mu g \cdot g^{-1}$].

	Sample	Inorganic	$MMAs^V$	$DMAs^V$	TMAO	Total As[a]
Vulcano [$mg \cdot g^{-1}$]	A	67.5 ± 3.98	0.04 ± 0.02	0.00 ± 0.00	0.15 ± 0.01	NA
	B	22.8 ± 7.04	0.03 ± 0.00	0.01 ± 0.02	0.11 ± 0.03	NA
Biogas [$\mu g \cdot g^{-1}$]	16/09	<DL[b]	<DL[b]	2.00 ± 0.23	21.9 ± 0.39	33.8 ± 2.12
	17/02	0.04 ± 0.01	0.06 ± 0.01	0.14 ± 0.01	0.62 ± 0.07	0.96 ± 0.09

[a] Total As was determined after microwave digestion while species were determined after extraction (see methods section).

[b] Detection limit (DL) is <0.20 $\mu g \cdot g^{-1}$ for each species. From all concentrations of Vulcano and biogas exposed moss, moss blank concentrations were subtracted. Thus, some given concentrations may seem to be below detection limit, but actually are not.

3.3. Natural gases

Natural arsine gas sampling with mosses can be influenced by matrix gases, like e.g. O_2, CO_2, and CH_4. Moss exposed in the fumarolic field on Vulcano Island generally had As concentrations in the $mg \cdot g^{-1}$ range while As concentrations in moss exposed to biogas was in the $\mu g \cdot g^{-1}$ range (Table 2). On Vulcano, spatial differences in total As concentrations were high, but both mosses contained predominantly inorganic As and <1% organic As species. Moss bags from the moss monitorings on Etna 2007 and Vulcano 2012 and 2013 (Arndt et al., 2014; Calabrese et al., 2015) also showed >99% inorganic As (although moss was stored for >2 years and speciation might have changed; data not shown).

Moss exposed at the Bayreuth biogas plant in September 2017 and February 2016 showed As emissions in autumn to be 2 orders of magnitude higher than in spring, but the share of methylated As species on the moss was >70% in both cases.

4. Discussion

4.1. Binding mechanism of arsines on moss surface

In general, only the higher methylated arsines (Me_2AsH and Me_3As) were recovered on the moss, while $MeAsH_2$ was partially retained by the moss and AsH_3 was not trapped at all. This rises two questions: (a) why are arsines deposited and (b) how are they attached to the moss.

Boiling points could explain arsine deposition at 5 °C for Me_3As and Me_2AsH (b.p. 36 and 52 °C), their recovery on the moss and the recovery in the gas of AsH_3 (b.p. −55 °C) and $MeAsH_2$ (b.p. 2 °C close to 5 °C), but cannot explain the reproducibility of these results at different temperatures.

Sensitivity for surface as "seed crystal" could explain the disappearance of Me_3As and Me_2AsH from the gas phase in both blank and remaining gas phase in the moss batch. This would mean that deposition of the two arsines is independent of the moss presence and the surface of the borosilicate must have an influence on the arsines because this effect was not shown in Tedlar® bags (Arndt et al., 2017). In contrast, stabilization experiments in glass vials showed Me_3As to be the most stable species of all arsines (Pantsar-Kallio and Korpela, 2000) which does not match the gas phase results in the present study. Thus, the influence of the borosilicate surface on deposition remains unclear.

Binding mechanism to the moss could be physical deposition by impaction on the moss surface on which the arsines are trapped. Gases are able to enter moss hyalocytes by their large pores as has been shown for phenanthrene (Spagnuolo et al., 2017). The bigger the arsine molecule (the more methylated), the more is deposited on the moss or trapped inside the hyalocytes once entered. However, the moss is ground before extraction which breaks open hyalocytes and could release trapped arsines. Ground mosses from biogas exposure which were digested and analyzed after 1 and 60 days show the same results, which contradicts potential arsine degassing.

Chemical adsorption on the moss surface consisting of polyuronic acids is another possibility which is known from ion adsorption in water (Clymo, 1963; Popper and Fry, 2003). Arsine molecules are pyramidal with As at its top and H or CH_3 at the 3 bottom corners. AsH_3 has a free pair of electrons at the As, but is nonpolar (Meyer and Pietsch, 1952). Adding CH_3 groups, in which C has a higher electronegativity than As (2.55 and 2.18, respectively; Pauling (1960)) removes electron density from the As atom. Consequently, the more methyl groups the molecule has, the less electron density at the As atom and the more likely a reaction with electron-rich molecules. These could be the polyuronic acid groups on the moss surface.

In general, recovery of the arsines as their pentavalent acids and/or oxyanions could be either explained by adsorption (to oxygen) on the moss surface or by a reaction with water during extraction after being physically adsorbed. Due to potential degassing when trapped physically only, a chemical bonding is postulated here as most likely mechanism until further clarification e.g. by micro-XAS.

4.2. Implications for moss monitoring of natural gas

Being exposed to natural environments, mosses collect gases as well as particles. Matrix gases like sulfur gases of volcanic emissions can have a negative influence on arsine stability (Arndt et al., 2017) triggering their deposition or altering their sorption to the moss surface by S deposition and subsequent As sorption onto it due to the affinity of As to S. Gas analysis for As speciation during the moss monitoring (Arndt et al., 2017) showed 52% and 29% Me_3As for samples A and B, respectively. Thus, the moss shows that the fumarolic emissions have a larger share of As particles. Biogas is known to contain methylated arsines (Mestrot et al., 2013b) whose corresponding pentavalent acids were recovered on the moss. The matrix of CO_2 and CH_4 doesn't change arsine deposition significantly compared to N_2 matrix (CO_2: Arndt et al. (2017)).

5. Conclusion

Moss can trap higher methylated volatile arsines. Consequently, moss bags are an easy-to-apply tool for a fast screening for the occurrence of methylated volatile arsines or the predominance of particulate As. They can be applied to potentially As degassing environments e.g. wetlands to figure out if volatile (methylated) arsines occur and are important to be analyzed to understand element cycling or if particulate As is the predominant form of As in the atmosphere and gas speciation analysis can be omitted.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.06.123.

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Supporting material

Moss bag monitoring as screening technique to estimate the relevance of methylated arsine emission

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SI 1: Quantitative techniques for sampling volatile arsines species

Method	Short description and references for further information
$AgNO_3$ traps	Silica gel filled traps impregnated with silver nitrate sorb arsine and the three methylated arsine species. Species can be eluted as their respective oxyanions (Mestrot et al., 2009). Nothing is known so far about the trapping efficiency or potential artifacts of chlorinated / sulfonated arsine species.
Needle Trap devices (NTDs)	These hollow stainless steel needles with different sorption materials on their inside wall were shown to produce artifact chloro-arsines during quantitative trapping of arsines (Arndt et al., 2017), independent of the sorption material (polydimethylsiloxane (PDMS), divinylbenzene (DVB), carbopack X, Carboxen, or combinations of these materials).
Solid Phase Micro Extraction (SPME)	SPME fibers have been used as passive samplers for arsine emissions from geothermal springs (Planer-Friedrich et al., 2006) with subsequent concentration calculations via the Fick's diffusion law. It involves many uncertainties, potentially yielding too large concentrations (Arndt et al., 2017). Additionally SPME fibers use the same sorption materials as NTDs which were shown to produce artifacts (Arndt et al., 2017).
Tedlar bags	Stability of arsines in Tedlar bags has been shown several times in different gas matrices, temperatures, storage conditions and durations (Arndt et al., 2017; Haas and Feldmann, 2000; Mestrot et al., 2011), revealing higher stability at lower temperatures, in the dark without UV light, and without matrix gases like SO_2 and H_2S. In all cases, an immediate analysis is recommended.
Cryotrapping (-198°C)	Cryotrapping in liquid nitrogen currently is the best known method for trapping volatile arsines. However, this method is difficult to use in remote areas with limited access to liquid nitrogen supply. This technique e.g. was applied by Hirner et al. (1994).

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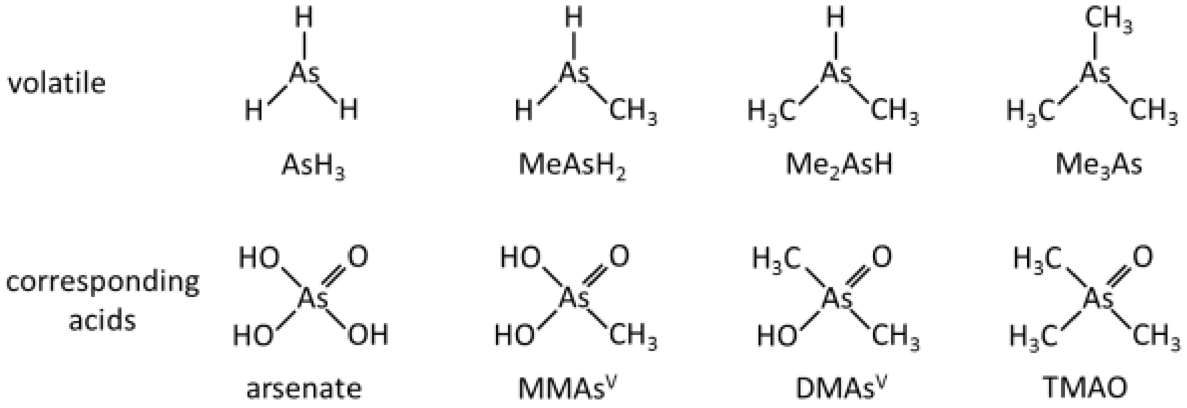
SI 2: Structures of the sampled arsines and the corresponding acids of the originally trapped arsines recovered in moss extracts



SI 3: As [ng] on the moss and in the gas after moss exposure to the individual gases in N_2 atmosphere

			inorganic	$MMAs^V$	$DMAs^V$	TMAO	Total
+5°C	AsH_3	initial	1103				
		blank	764				
		remain	682				
		moss	9.59 ± 4.18	3.20 ± 1.99	2.64 ± 1.82	5.98 ± 4.80	27.0 ± 14.0
	$MeAsH_2$	initial	5.60	739			
		blank	2.86	459			
		remain		457			
		moss	4.15 ± 1.01	52 ± 2.08	2.29 ± 1.99	1.93 ± 1.66	63.6 ± 10.5
	Me_2AsH	initial			337		
		blank					
		remain					
		moss	2.32 ± 1.29	14 ± 2.78	169.64 ± 13.8	5.29 ± 3.69	229 ± 11.7
	Me_3As	initial			81.7	692	
		blank				181	
		remain				158	
		moss	0.93 ± 0.75	4.97 ± 1.49	86.7 ± 7.25	414 ± 31.1	489 ± 31.0
-80°C	$MeAsH_2$	initial	6.50	376			
		blank		64.1			
		remain		278 ± 52.8			
		moss	4.72 ± 2.19	14.9 ± 2.85	1.43 ± 1.22	4.80 ± 3.36	27.4 ± 7.64
-20°C	$MeAsH_2$	initial		338			
		blank	21.0	239			
		remain		341 ± 34.0			
		moss	9.67 ± 3.56	41.8 ± 11.5	1.84 ± 1.34	5.39 ± 4.37	63.6 ± 19.6
+45°C	Me_2AsH	initial			315		
		blank	0.92	0.05			
		remain	0.80 ± 0.11	0.02 ± 0.03			
		moss	7.58 ± 1.94	31.6 ± 1.39	323 ± 23.2	7.29 ± 3.10	421 ± 37.2
+80°C	Me_2AsH	initial			590		
		blank					
		remain	0.56	0.24			
		moss	8.78 ± 2.27	48.3 ± 2.89	620 ± 8.09	9.19 ± 3.53	769 ± 24.7

Study 4: Evaluation of techniques for sampling volatile arsenic on volcanoes

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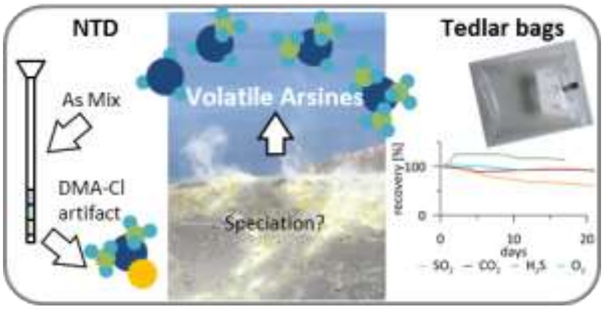

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Evaluation of techniques for sampling volatile arsenic on volcanoes

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Solfatara

ABSTRACT

Volatile arsenic (As) species, like arsine, mono-, di-, and trimethylarsine (AsH_3, $MeAsH_2$, Me_2AsH, Me_3As) are reported to be released from volcanoes but their determination is difficult because of low concentrations, low boiling points, and high reactivity, especially in the presence of volcanic gases like H_2S and SO_2. We tested needle trap devices (NTDs), cryotrapping, and Tedlar® bags for quantitative and species-preserving sampling. NTDs did not trap AsH_3, $MeAsH_2$, Me_2AsH, did not release sorbed Me_3As quantitatively, and lead to artifact formation of dimethylchloroarsine, which also questions the reliability of previous reports from solid phase micro extraction fibers using the same sorption materials. Cryotrapping in dry ice was insufficient to trap AsH_3 and $MeAsH_2$; Me_2AsH and Me_3As were only partially retained. Sampling in Tedlar® bags remained the best alternative. Stability of all four arsines was confirmed for dark storage at 5 °C for 19 days in a matrix of dry N_2, 11 days in 20% O_2, and 19 days in 3800 ppm_v CO_2 (>80% recovery for all species), while in the presence of H_2S, Me_3As recovery was only 67% and in the presence of SO_2, Me_2AsH and Me_3As recovery was 40 and 11%, respectively. Removing interfering reactive gases by a NaOH trap, we sampled natural volcanic emissions at fumaroles of Vulcano and Solfatara (Italy). Detected total arsine concentrations of 0.5–77 $ng \cdot m^{-3}$ were 1–2 orders of magnitude higher than the calculated background. Inorganic arsine was the dominant species suggesting that secondary microbially catalyzed methylation is a process of minor importance in the fumarolic gases.

1. Introduction

Arsenic is an ubiquitous element in nature, and due to its high solubility in high temperature fluids (Webster and Nordstrom, 2003) it is often found enriched in volcanic environments, i.e. fumarolic sublimates and incrustations, geothermal soils and waters, as well as in volcanic gases (Lantzy and Mackenzie, 1979; Nriagu, 1979, 1989; Nriagu and Pacyna, 1988). One review on global As budgets summarizes that terrestrial volcanoes contribute up to $1.7 \cdot 10^7$ $kg \cdot a^{-1}$ (plus $0.5 \cdot 10^7$ $kg \cdot a^{-1}$ release from submarine exhalations) to a total atmospheric input between 2.8 and $8.4 \cdot 10^7$ $kg \cdot a^{-1}$. The other important sources are low temperature natural volatilization from the pedosphere (up to $2.6 \cdot 10^7$ $kg \cdot a^{-1}$) and anthropogenic emissions (mainly from coal plants, Cu smelting, and wood fuel, up to $2.8 \cdot 10^7$ $kg \cdot a^{-1}$) (Matschullat, 2000). While the exact numbers have to be considered with care because different reports can vary for >2 orders of magnitude (Chilvers and Peterson, 1987), terrestrial volcanic exhalations and eruptions are without doubt the dominant source of natural As release from the lithosphere into the atmosphere.

The majority of studies on volcanic As release has focused on total As analysis in leachates from filters that collected deposits from passive degassing (Calabrese et al., 2014), condensate and sublimate samples (Cheynet et al., 2000), or moss monitoring (Arndt et al., 2014; Calabrese et al., 2015). None of these methods is designed to discriminate between particulate As (mostly As_2O_3) and volatile As ("arsines"). Very few studies focused so far on volcanic arsines (Planer-Friedrich et al., 2006; Planer-Friedrich and Merkel, 2006). Arsines comprise the inorganic species AsH_3 (boiling point b.p. −55 °C or −62.5 °C), the methylated species $MeAsH_2$ (b.p. −2 °C or +2 °C), Me_2AsH (b.p. 36 °C), and Me_3As (b.p. 52 °C; Me = methyl group, CH_3), as well as lesser known species such as chloroarsines (Me_2AsCl, $MeAsCl_2$, $AsCl_3$; b.p. 130 °C, >133 °C, and 133 °C, respectively; boiling points from Ilgen and Huang (2013), Lide (2003), Pantsar-Kallio and Korpela (2000), Planer-Friedrich et al. (2006)), or dimethylarsenomercaptane (Me_2AsSMe). One can find estimates in literature that in the troposphere, particulate As dominates with 89–98.6% as compared to volatile As (Matschullat, 2000). However, given the scarcity of studies focusing on volatile As, the reliability of these estimates is very questionable.

The special interest that we took in investigating volcanic arsines is based on a) the general scarcity of such information, b) the high toxicity of arsines (AsH_3 is the most toxic As compound known, acute hemolysis, kidney failure, and following death have been documented at concentrations of 250 ppm (Pakulska and Czerczak, 2006)), and c) more recent information showing that arsines at environmentally relevant low concentrations are much more stable than previously assumed (several hours to days under strong UV light and several weeks in the

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dark; stability decreases with an increasing number of methyl groups) and that they do not only affect the immediate area of emission but probably travel considerable distances (Mestrot et al., 2013).

The special challenges that measurements of arsines pose are the necessity of on-site protection from hydrolysis, oxidation, and temperature-dependent species conversion as well as analytical difficulties due to low total concentrations and a lack of commercial standards for identification and quantification. Volcanic emissions provide an additional challenge because they contain CO_2, SO_2, and H_2S, the reactivity of which with arsines is unknown.

The goal of the present paper was to find the best field-deployable technique for identification and quantification of known, and potentially also yet unknown volcanic arsines. Previously used, easy-to-apply techniques using chemo-trapping in oxidizing agents (Planer-Friedrich and Merkel, 2006) or on silver nitrate traps (Mestrot et al., 2009) were not suitable because they either only enable determination of total volatile As (Planer-Friedrich and Merkel, 2006) or selected As species (AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As; based on the assumption that they convert quantitatively in their respective oxyanion species) (Mestrot et al., 2009). Cryotrapping in liquid nitrogen (N_2, −196 °C) is an established technique to preserve arsines (Feldmann et al., 2001; Ilgen and Huang, 2013), however, difficult to organize and handle during field sampling in remote areas. In our paper, we used N_2-cryotrapping only as reference method. As easier-to-handle alternatives we tested cryotrapping in dry ice and a dry ice propanol mix.

Our main focus, however, was on testing sampling efficiency, desorption, and species stability on Needle Trap Devices (NTDs). NTDs are similar to solid phase micro extraction (SPME) fibers, which have previously been shown to trap volatile arsines including the previously unknown methylated chloroarsines (Mester and Sturgeon, 2001; Planer-Friedrich et al., 2006) and dimethylarsenomercaptane (Planer-Friedrich et al., 2006) in natural samples. SPMEs consist of a small fragile fiber which is exposed for sampling (picture see SI 1). The disadvantage of SPMEs, besides being very fragile for field applications, is that they are passive sorption devices, i.e. quantification of trapped As can only be done by calculating the diffusion flux which results in large uncertainties (Planer-Friedrich et al., 2006). NTDs in comparison to SPMEs are more sturdy for field applications because they consist of hollow stainless steel needles (picture see SI 1) which are impregnated on their inner wall using the same sorption materials which are used on SPMEs (Lord et al., 2010): polydimethylsiloxane (PDMS) and divinylbenzene (DVB), both being polymers and absorbing the sampled compounds, Carbopack X, a graphited carbon adsorbing the sampled compound and Carboxen, a mesh structured carbon working like a molecular sieve. In contrast to SPMEs, NTDs allow active pumping of a defined air volume through the needle with quantitative sorption (provided sorption capacity is not exceeded) and thus enable easy quantification. Similar to SPMEs, NTDs offer the opportunity to enrich the sample in the field before analysis. NTDs thus appear to be promising tools for quantitative and species-preserving sampling of arsines, but to the best of our knowledge they have so far only been used for sampling volatile organic compounds (Lord et al., 2010) and never been tested for sorption efficiency and sample stability with any volatile metal(loid)s.

As an alternative to NTDs we used Tedlar® bags in which we investigated the stability of arsines in the presence of O_2, CO_2, SO_2, and H_2S in synthetic samples. Tedlar® bags, bags consisting of inert Tedlar® (polyvinyl flouride) and an outlet with a septum (picture see SI 1), have been used for sampling arsines before (Haas and Feldmann, 2000; Jakob et al., 2010; Mestrot et al., 2011). In general, stability in Tedlar® bags is higher for AsH_3 (75% recovery after 7 days under UV light (Mestrot et al., 2011) and 50% recovery after 130 days in the dark (Jakob et al., 2010)) than for methylated arsines (50% recovery after 7–8 h under UV light in air-filled Tedlar® bags (Mestrot et al., 2011) and after 17 ($MeAsH_2$) and 67 days (Me_2AsH) in the dark (Jakob et al., 2010)). Comparing stability at 20 and 50 °C, it was found that the lower the storage temperature, the higher the stability, (Haas and Feldmann, 2000; Jakob et al., 2010). Adsorption of arsines on the walls of the Tedlar® bag is reported to be negligible (Haas and Feldmann, 2000). The major disadvantages of Tedlar® bags are the inability of enriching a sample and consequently the required large sample volumes to detect trace gases.

2. Methods

2.1. Preparation of a volatile As standard

Hydride generation of AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As was done according to Ilgen and Huang (2013) from 5 mL of a solution containing 100 $\mu g \cdot L^{-1}$ each of arsenite (Fluka; certified metal standard solution with 1000 $mg \cdot L^{-1}$), monomethylarsonic acid (≥97%; Argus, Vernio, Italy), dimethylarsinic acid (≥97%; Merck, Darmstadt, Germany), and trimethylarsinoxid (≥97%; Argus, Vernio, Italy). This solution was acidified using 1 M H_3PO_4 before 3% $NaBH_4$ (freshly prepared in 1% NaOH) was added as reducing agent. The produced gas was collected in a 5 L Tedlar® bag to yield an As mix stock gas (called "As mix" in the following) with a final concentration of 100 $ng \cdot L^{-1}$ of each of the 4 As species in dry N_2 atmosphere. To eliminate water vapor in the Tedlar® bag, the generated gas was conducted through a water trap filled with NaOH on a company-specific solid carrier material (Fluka Analytica, p.a.). NaOH did not sorb arsines in our own previous experiments (data not shown) which is in line with results of Svoboda et al. (2015). For sampling, the generated gas was diluted in N_2 (purity 5.0; Linde Gase) in a 1 L Tedlar® bag to the desired concentration of 2 $ng \cdot L^{-1}$ if not stated otherwise.

2.2. Test of different gas sampling methods in the laboratory

For the different tests on cryotrapping, a methyl-deactivated stainless steel tubing (Chrompack Ultimetal tubing, uncoated, methyl deactivated, 1.2 m length, inner diameter 0.53 mm) was used, which was winded and immersed in liquid nitrogen (−196 °C), dry ice (−78 °C), or a dry ice propanol mix (−75 °C), respectively. Because its suitability had already been established in previous studies (Feldmann et al., 2001; Ilgen and Huang, 2013), cryotrapping in liquid N_2 served as standard reference method against which the results of all other sampling methods were evaluated.

NTDs (PAS Technology, Magdala, Germany) containing the sorption materials PDMS, DVB, and Carboxen 1000 were chosen due to their previously proven adsorption ability of volatile arsine species using SPMEs (Mester and Sturgeon, 2001; Planer-Friedrich et al., 2006). Additionally, Carbopack X was tested, too. The following combinations of materials were tested: PDMS + Carboxen (PC), PDMS + DVB (PD), PDMS + Carbopack X (PX), and PDMS + Carboxen + DVB (PCD) and PDMS + Carbopack X + Carboxen (PXC), as well as two NTDs filled with Carboxen and Carbopack X only. Each sorption material had about 1 cm filling height in the NTDs. The Carboxen and Carbopack X NTDs were filled with 3 cm of each sorption material. One set of NTDs which already had been used for volatile As species determination in geothermal gases before was used for the experiments to evaluate reusability of NTDs. All NTDs were pre-treated by heating them in the GC injector for 15 min to remove any potentially adsorbed substances (280 °C for NTDs with sorption material PD and PCD; 300 °C for NTDs with PC, PX, and PXC, which is required for the materials Carboxen and Carbopack X (Trefz et al., 2012)) and rinsed with He during the heating. Blank NTDs analyzed after pretreatment resulted in no peaks and thus were considered as clean. Whenever NTDs were not in use, they were sealed with Teflon plugs at both ends. The As gas sampling on NTDs was done by pumping a concentrated "As mix" (50 $ng \cdot L^{-1}$) from a Tedlar® bag through the NTDs with 5 $mL \cdot min^{-1}$ (total load of 2 ng per As species per NTD) using a pumping suitcase (Peli™ 1400 Case, Peli Products; PAS Technology, Germany). Different desorption temperatures were tested. Initially, we used desorption temperatures that were identical to the pre-heating temperature for the respective NTD materials. However, because the thermal stability of

AsH_3 is reported to be 230 °C only (Meyer and Pietsch, 1952) we also tested desorption at a lower temperature (220 °C).

Tedlar® bags (picture see SI 1) were tested for species stability during storage by diluting the "As mix" (100 $ng \cdot L^{-1}$ per As species) in 5 L Tedlar® bags to 2 $ng \cdot L^{-1}$ in different matrix gases, using dry N_2, 3800 ppm_v CO_2 in N_2 (Riessner, Germany), 20% O_2 in N_2 ("synthetic air"; Riessner, Germany; ≙ 200,000 ppm_v), 100 ppm_v SO_2 in N_2 (Riessner, Germany), and H_2S in N_2. H_2S was generated from 130 mg FeS for H_2S generation (Merck) by reaction with H_3PO_4. Gas was led into a 5 L Tedlar® bag and diluted 1:2 for As stability experiments. CO_2, SO_2, and H_2S concentrations were adjusted to the maximum concentrations reported for fumaroles of Vulcano Island, Italy (Aiuppa et al., 2005): 3800 ppm_v for CO_2 and about 100 ppm_v for SO_2 and H_2S each. Stability samples were kept in the dark at +5 °C for 21 days and were taken out (room temperature) in dark plastic bags for 3 consecutive analyses at each day of analysis (20 min each; see Section 2.4). The As speciation in the dry N_2 atmosphere served as reference for each day. Stability in dry N_2 was confirmed by comparing an "As mix" (2 $ng \cdot L^{-1}$ per As species) in dry N_2 which was stored in the dark for 19 days to an "As mix" that was prepared freshly before each analysis (Section 2.4).

2.3. Field sampling

Volcanic gas sampling was done at 2 volcanic sites in Italy: Vulcano Island and the Phlegraean Fields. Vulcano is a volcanic island north of Sicily whose most prominent feature is the 390 m high and 500 × 700 m wide crater La Fossa. Since Vulcano's last eruption from 1888 to 1890, La Fossa emits fumarolic gases on its northeastern crater rim and in the harbor area, where the sampling took place (map and coordinates see SI 2). Fumarolic gases measured on the crater rim contain water vapor, CO_2, SO_2, and H_2S, halogens, and NH_3 (Signorelli et al., 1998). Emission of As (without differentiation between gaseous particles and volatile As species), has been reported from condensate sampling (Signorelli et al., 1998), condensate and sublimate sampling (Cheynet et al., 2000), and moss monitoring (Arndt et al., 2014) before.

The second sampling took place at the fumaroles of the Phlegraean Fields west of Naples, Italy (coordinates in SI 2) which is underlain by a 12 km wide, 35,000 year old caldera (Barberi et al., 1985). One of the Phlegraean Field's most known active areas is the Solfatara area with its fumaroles near Pozzuoli. Gaseous emissions (diluted by air) sampled above the fumaroles have been shown to contain a maximum of 1000 ppm_v CO_2 and 3.5 ppm_v H_2S (Carapezza et al., 1984) besides CH_4, B, NH_4 and halogens (Martini et al., 1991). Gaseous As emissions have not been measured, yet, but must exist because of the documented occurrence of As mineral precipitates around the fumaroles (Russo, 2004).

Tedlar® bags (SKC, Analyt-MTC, Germany) were filled using a vacuum pumping suitcase (Vacu Case™, SKC, Analyt-MTC, Germany) in which the Tedlar® bag was placed. Sampling was done by placing a funnel directly above the fumaroles (<50 cm distance) trying to minimize dilution of the fumarolic gases by air. In addition, on Vulcano Island, 2 sites downwind of the fumaroles at the crater were sampled (max. 20 m distance) where the funnel was placed in wind direction. From the funnel, a FEP (Fluorinated ethylene propylene) hose lead the volcanic gas to a silanized glass wash bottle as water trap and subsequently through dry ice cooling into a 2nd glass water trap, through a NaOH trap filled with NaOH on carrier material until finally entering the Tedlar® bag inside the pumping suitcase (Fig. 1). For strongly degassing fumaroles, 2 consecutive NaOH traps were used to increase trapping capacity. Wash bottles, dry ice, and NaOH traps were used to eliminate water vapor, H_2S, SO_2, and CO_2, because these gases would freeze in the N_2 cryotrap before analysis and cause blockage (Ilgen and Huang, 2013). Calculated concentrations of volatile arsenic in $ng \cdot m^{-3}$ refer to the gas volume collected in the Tedlar bag after passing the NaOH trap.

Tedlar® bags were kept in dark plastic bags because of the light sensitivity of volatile As (Mestrot et al., 2011) and stored cool until analysis (during transport at +4 to 15 °C; thereafter, in the refrigerator at +5 °C). At each sampling point, 3 × 10 L Tedlar® bags were filled for volatile As analysis and a 1 L foil bag (SKC, Analyt-MTC, Germany) was filled for CO_2 analysis without passing the NaOH-traps (which would trap the CO_2). Foil bags are non-permeable for CO_2 as they are made out of 4 layers of foil with an aluminum layer in the middle, but have the disadvantage to adsorb reactive gases like arsines. Sampling times were <5 min per sample.

2.4. Gas analysis

Volatile As species were analyzed using GC-EI-MS/AFS, i.e. gas chromatographic separation after which the sample is split to electron impact mass spectrometry (Varian CP-3800 with Varian Saturn 2000, Varian, USA) for molecular fragment information and atomic fluorescence spectrometry (P.S. Analytical; including a superlamp with the wavelength 193.7 nm) for total arsenic quantification.

Gas sample introduction was different for the different sampling techniques. For analysis from cryotraps, cryofocussing (CF) was done on a methyl deactivated capillary line immersed in liquid N_2 (−196 °C) before GC-EI-MS/AFS analysis (Ilgen and Huang, 2013). For analysis of NTDs, the NTDs, which were sealed on both ends with Teflon plugs immediately

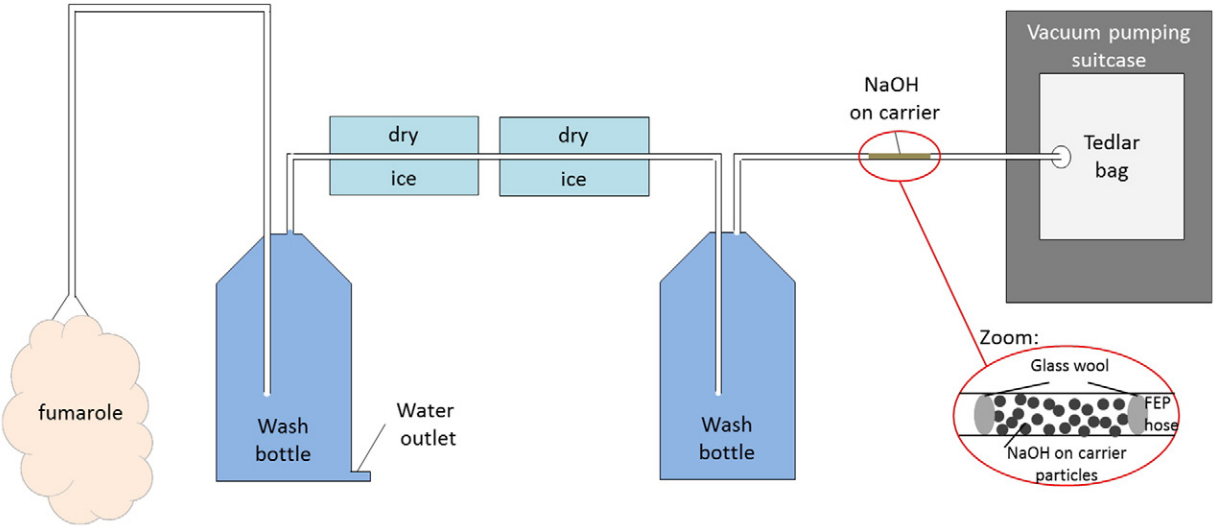

Fig. 1. Sampling setup scheme for volatile As in the fumaroles. A scheme of the NaOH trap is shown in the enlarged area.

after sampling, were opened at the front end directly before injection into the GC injector (injector type 1079, Varian; equipped with a SPME liner) for desorption at 280 °C, if not stated otherwise. For analysis from Tedlar® bags, the Tedlar® bag, kept in a dark plastic bag to avoid light influence, was connected to a cryotrapping (CT) and cryofocussing system and 50 mL of the 2 $ng\cdot L^{-1}$ As (dilution of the generated "As mix") were first cryotrapped, then cryofocussed in liquid N_2 (−196 °C) before being transferred to the GC column according to Ilgen and Huang (2013). For all analyses, a NaOH trap was employed before the CT-CF system. Whenever O_2 was present in analyzed gas samples from Tedlar® bags (stability experiments, samples from the field), the cryotrapping was done in liquid argon (−186 °C) and cryofocussing in liquid N_2 (−196 °C) to avoid oxygen interferences during trapping (boiling temperature: −183 °C).

The GC analysis followed the protocol by Ilgen and Huang (2013). Briefly, the analytical capillary column (30 m, 0.32 mm ID, 4 μm film thickness, Rxi-1MS, Restek, USA) was heated from 40 °C to 120 °C at a rate of 15 $°C\cdot min^{-1}$, followed by heating to 200 °C at 100 $°C\cdot min^{-1}$ and a holding time of 1 min before cooling down for the next sample. Column flow was constant at 5.5 $mL\cdot min^{-1}$. Detection limits of the CT-CF-GC-EI-MS/AFS system were determined by measuring "As mix" dilutions in dry N_2 with low concentrations. The lowest concentration at which peak integration was possible was defined as detection limit for the respective species. Detection limits were 10 pg for AsH_3, 5 pg for $MeAsH_2$ and Me_2AsH, and 20 pg for Me_3As, respectively.

In some cases, an inductively coupled plasma mass spectrometry (ICP-MS) was used instead of the AFS according to Ilgen and Huang (2013). Both techniques were evaluated using the same As standard which contained AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As and showed comparable peak areas. A detailed comparison of all As peak areas measured by cryotrapping and cryofocussing in triplicates by ICP-MS and AFS can be found in SI 3. Advantages of AFS compared to ICP-MS are fewer costs (purchase, maintenance, gas consumption, potential repair) and its easier handling. The difference to the setup with ICP-MS (Ilgen and Huang, 2013) is that after the split between EI-MS and AFS, a carrier gas of 25% H_2 and 75% Ar (Riessner Gase, Germany) was added with 150 $mL\cdot min^{-1}$ to the gas from GC separation. The carrier gas also served as flame gas for AFS detection. Total As detection limits between 5 and 20 pg As are comparable to ICP-MS (Ilgen and Huang, 2013). Thus, AFS was used whenever possible.

CO_2 and CH_4 concentrations in natural samples were analyzed by gas chromatography (SRI 8610C) using H_2 as carrier gas. After chromatography, CO_2 was reduced and measured as CH_4 by a FID detector (flame ionization detection). Detection limits were <380 ppm for CO_2 and <50 ppm for CH_4. In all samples, methane concentrations were below detection limit.

2.5. Data evaluation

Gaseous As standards are not commercially available and thus, concentration calculations were done using an "As mix" in dry N_2 (Ilgen and Huang, 2013) containing AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As with known As concentration (100 $ng\cdot L^{-1}$). A dilution of this stock (2 $ng\cdot L^{-1}$) was measured before each set of samples. Data evaluation and peak integration were performed using MS Data Review (Agilent) for ICP-MS data and Varian Interactive Graphics 6.9.1 for AFS data.

3. Results and discussion

3.1. Quality control

Cryotrapping our "As mix" in liquid N_2 showed the expected 4 As species AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As which are clearly identifiable by their EI-MS spectra (Fig. 2). Six replicates of the synthesized "As mix" showed that relative standard deviations (RSDs) in peak areas were below 10% for all arsine species analyzed (Table 1). Cryotrapping was therefore deemed suitable as reference method for all further tests.

3.2. Needle trap devices (NTDs)

3.2.1. Recovery of the As mix on NTDs

Trapping the "As mix" on different NTDs yielded a completely different picture than trapping in liquid N_2 as reference method (Fig. 3). Instead of observing sharp and clear peaks for AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As within the first 3.5 min (Fig. 3a), only two small peaks were observed after 3 and 4.5 min which are barely discernible from the background noise (Fig. 3b–e).

In samples with higher concentrations, the peak at 3 min could be identified as Me_3As by EI-MS (compare Section 3.2.2; data in SI 4). The shift to an earlier retention time in comparison to trapping in liquid N_2 (3.3 min; Fig. 3a) can be explained by the different injection systems for NTDs and cryotraps: NTDs were directly injected via the heated GC injector while the gas from cryotrapping was injected via cryofocussing to the GC column and therefore had a slightly longer traveling path (Ilgen and Huang, 2013). The identity of the peak after 4.5 min initially remained elusive (see Section 3.2.3 for further discussion) and we never observed any matching peak (with a later retention time than Me_3As) in chromatograms obtained with the reference method (Fig. 3a).

3.2.2. Test of single NTD sorption materials

After the initial failures of detecting arsines on multi bed NTDs, single bed materials were tested that consisted of 3 cm fillings of Carboxen 1000 or Carbopack X, only. A cryotrap (in liquid N_2) was mounted behind the NTD to trap the As passing the NTDs without sorption and a lower desorption temperature was tested (220 °C instead of 280–300 °C for the experiments described in Section 3.2.1) because of the thermal instability of AsH_3 above 230 °C (Meyer and Pietsch, 1952). Still, Me_3As was the only As species that could be recovered from the NTDs (Fig. 4a). The cryotraps mounted behind the NTDs showed the missing As species AsH_3, $MeAsH_2$, and Me_2AsH, but also part of Me_3As (Fig. 4b) which means that these species pass the NTDs without sorption, or in case of Me_3As, with only partial sorption. After triplicate sampling and analysis, each NTD was subjected to one final desorption step at a higher temperature (300 °C) and a large Me_3As peak was observed (Fig. 4c) which is the accumulated load of all the Me_3As which was trapped but not desorbed at 220 °C.

In summary, NTDs were no viable alternative to cryotrapping, because they were neither able to fully trap the 4 tested arsines nor completely release them at temperatures that do not exceed the stability range of the thermally most instable species (AsH_3).

3.2.3. Occurrence of As-Cl compounds

Apart from confirming their non-suitability for trapping AsH_3, $MeAsH_2$, Me_2AsH, and partially Me_3As, a further observation we made when using NTDs was formation of arsine artifacts which also requires critical re-evaluation of the some previous studies as outlined below. As already mentioned in Section 3.2.1, trapping the "As mix" on PXC, PC, PCD, and PX NTDs yielded one unexpected As peak at 4.5 min (Figs. 3, 5a, and b). Identification by EI-MS was only possible using the PXC NTDs (Figs. 3b, 5c), while concentrations were too low on the other NTDs. Using the NIST mass spectral database (version 2.0), the peak was identified as Me_2AsCl. The masses 141 and 139 represent the initial molecule, while the stepwise subtraction of 2 methyl groups results in the masses 124 and 109. The subtraction of Cl from the initial molecule or a demethylated fragment result in the masses 104 and 89, respectively, while mass 75 is the pure As atom (SI 5).

This Me_2AsCl peak was not observed when the same "As mix" from the Tedlar® bag was injected into the GC-EI-MS via CT-CF which also makes sense, because no Cl was added to the solutions we used for hydride generation (see Section 2.1). Therefore, Me_2AsCl in our experiments could not have formed during hydride generation, in contrast to

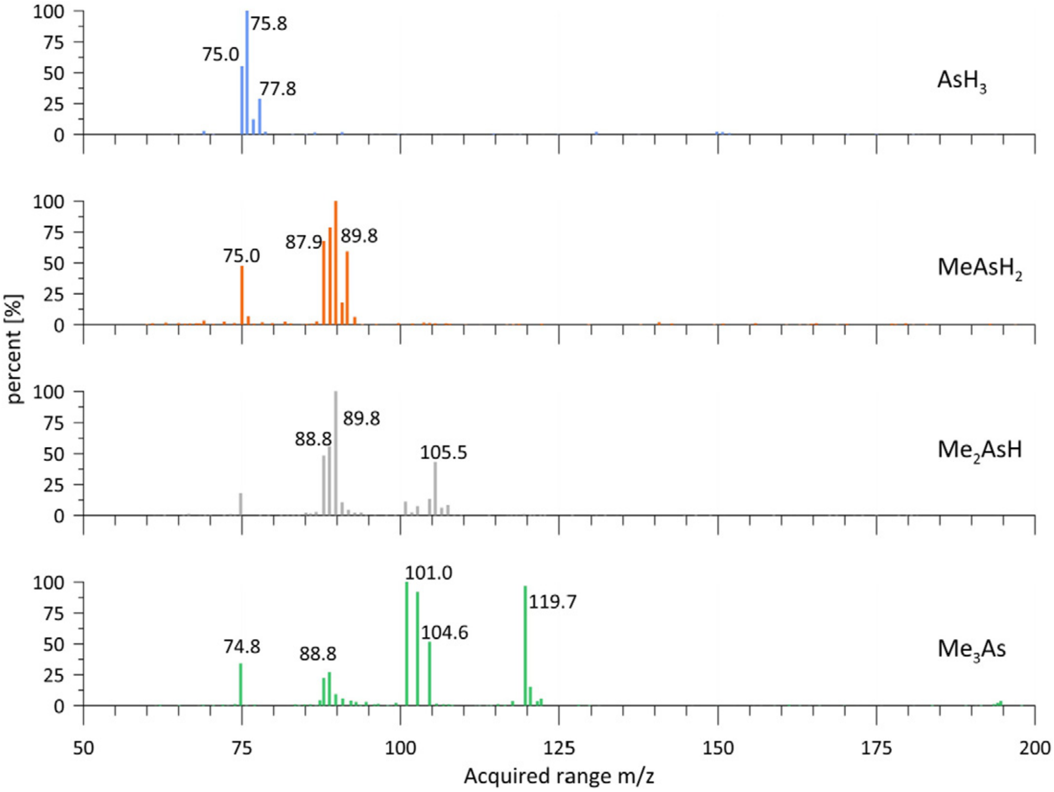

Fig. 2. EI-MS spectra of each arsine peak.

previous laboratory experiments, where chloro-arsines were intentionally produced during hydride generation from an HCl-containing solution and detected by SPME sampling as well as by direct gas injection (Mester and Sturgeon, 2001). Because Me_2AsCl in our experiments did neither occur using direct gas injection nor analyzing blank NTDs without As sampling, Me_2AsCl must have been formed on the NTDs during "As mix" sampling. Needle trap sorption materials consist of polymers only and supposedly are free of Cl according to the manufacturer (see Section 1), but small amounts of Cl have been measured by X-ray fluorescence on carboxen sorption material before (Dettmer and Engewald, 2002). SPME fibers with carboxen were also shown to adsorb gaseous HCl (Mester et al., 2000). Thus, there is also the possibility that Cl adsorbed on the multi-bed NTDs' sorption material from previous samplings and was not removed by NTD pre-treatment (see Section 2.2) might have reacted with the As loaded on the NTDs in the experiments shown in Figs. 3 and 5. The peak was not found on the single-bed Carboxen 1000 or Carbopack X NTDs, which had not been used for any other sampling before.

Me_2AsCl was the only chloro-arsine artifact that was observed. $MeAsCl_2$ and $AsCl_3$ were not observed, even though monomethylarsonic acid and arsenite were present in the solution used for hydride generation in the same concentrations as dimethylarsinic acid. The exact retention times of $MeAsCl_2$ and $AsCl_3$ with our instrumental settings are unknown. Since species are separated according to boiling points, $AsCl_3$ (boiling point 133 °C; see Section 1) might have a similar retention time as Me_2AsCl (boiling point 130 °C; see Section 1) and could therefore "hide" behind a Me_2AsCl peak. However, its molecular mass (180) or the characteristic mass fragment 145 (molecule without one Cl) are missing in the EI spectrum. Thus, it can be concluded that $AsCl_3$ has not formed. The boiling point of $MeAsCl_2$ is yet unknown (>133 °C; see Section 1). However, since we did not observe its distinct total molecule mass of 160, we exclude its presence (compare SI 5).

Interestingly, all reports that exist so far about natural occurrence of volatile As-Cl compounds are from studies with SPMEs (Killelea and Aldstadt, 2002; Planer-Friedrich et al., 2006) which use the same sorption materials as the NTDs we used in our study: PDMS and Carboxen. Me_2AsCl was identified by its EI mass spectrum in geothermal gas (Planer-Friedrich et al., 2006) and sediment samples (Killelea and Aldstadt, 2002) by SPME-GC-EI-MS. In both cases, direct gas injection to compare whether the observed As-Cl compounds were artifacts or real observations did not take place. We therefore suspect that the reported As-Cl compounds could also have been artifacts as we observed them in the present study with NTDs. The risk of artifact formation obviously excluded further tests and use of NTDs for field application. It also questions the reliability of previous reports of volatile As species on SPMEs using the same sorption materials like NTDs.

3.3. Cryotrapping arsines with dry ice

As an alternative to NTDs and liquid N_2 trapping, cryotrapping in dry ice (−78 °C) or a dry ice propanol mix (−75 °C) was tested. Cryotrapping in the dry ice propanol mix resulted in no trapping of arsines at all and all the arsines were found on the cryotrap in liquid N_2 (−196 °C) mounted behind the dry ice propanol cryotrap (data not shown). The cryotrapping with dry ice pellets physically had even less contact to the tubing than the dry ice propanol mix. Yet, the dry ice pellets cryotrap showed at least the two As species Me_2AsH and Me_3As on the cryotrap. However, in comparison to trapping the same amount on the cryotrap immersed in liquid N_2, much lower amounts of both As

Table 1
Peak areas of 6 AFS replicate measurements.

	Peak area	RSD (%)
AsH_3	83,254 ± 5740	6.9
$MeAsH_2$	221,446 ± 7930	3.6
Me_2AsH	208,715 ± 7624	3.7
Me_3As	151,268 ± 14,479	9.6

Number of replicates: 6.

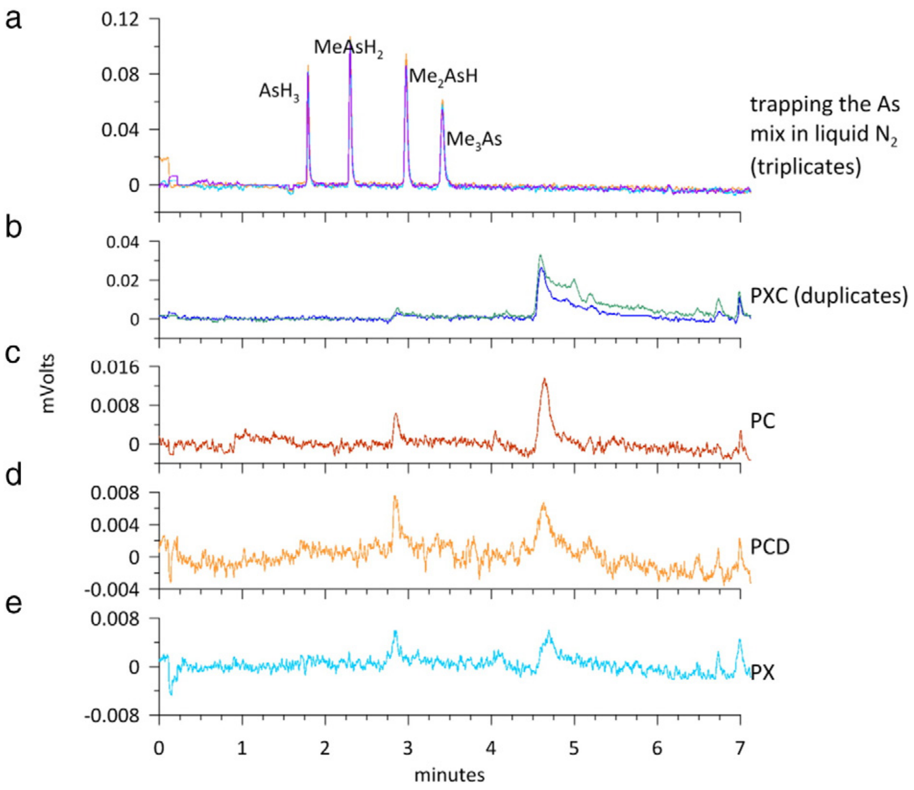

Fig. 3. Total element analysis results (AFS spectra) of NTDs with different sorption materials loaded with the As mix.

species were recovered and the two species AsH_3 and $MeAsH_2$ were missing completely (Fig. 6).

Obviously, the cooling efficiency of dry ice is insufficient for rapid, quantitative trapping of arsines, especially those with the lower boiling points (AsH_3: −55 °C, $MeAsH_2$: 2 °C). Ways of increasing the cooling efficiency are rather limited. Possibilities are enlarging the cryotrap (more than the presently used 1.2 m) to increase the way through the cooling or decreasing the gas flow (less than the presently used 5 $mL \cdot min^{-1}$) to increase cooling and reaction times. However, a longer cryotrap requires more dry ice for trapping, a stronger pump, and increases sample equipment demand. A slower gas flow rate will result in very long sampling times due to the required sample enrichment in the field and the need to pump large sample volumes. Consequently, both alternatives are not convenient for field use and were not pursued any further.

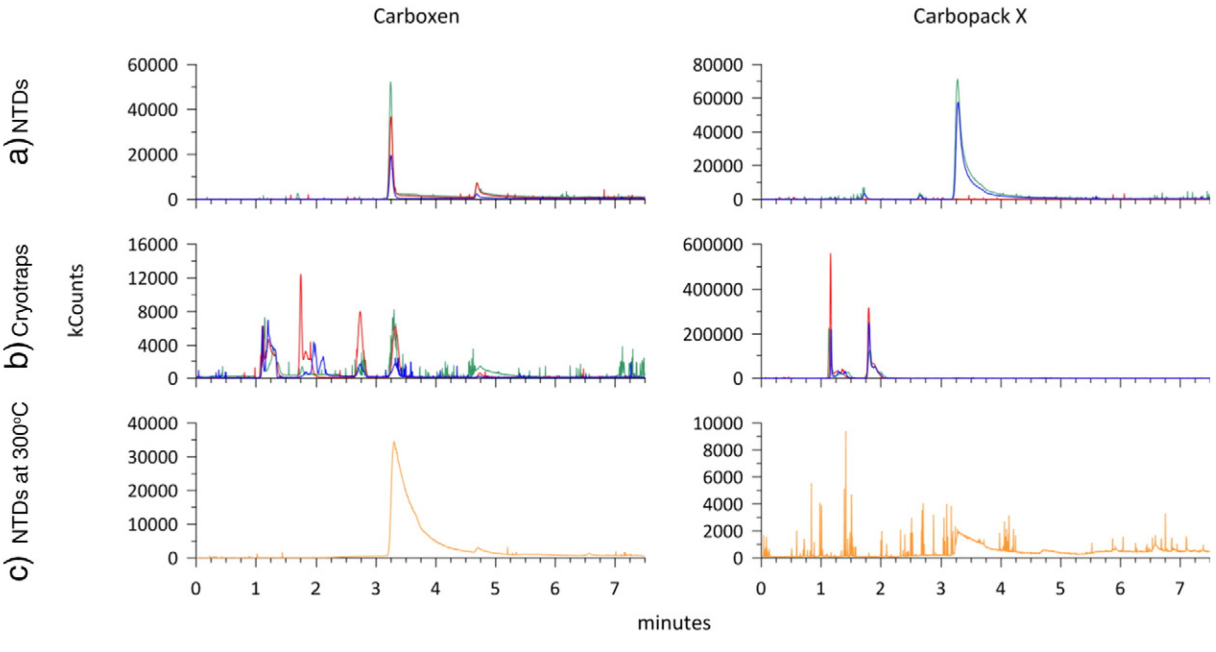

Fig. 4. ICP-MS spectra of m/z 75 of 2.5 ng As on a NTD filled with the sorption materials Carboxen 1000 or Carbopack X only (3 cm): a: NTD triplicate spectra, injected at 220 °C; b: triplicate spectra of cryotrapping in liquid N_2, which was mounted behind the NTD; c: NTD desorbed at 300 °C after triplicate accumulation of the experiments.

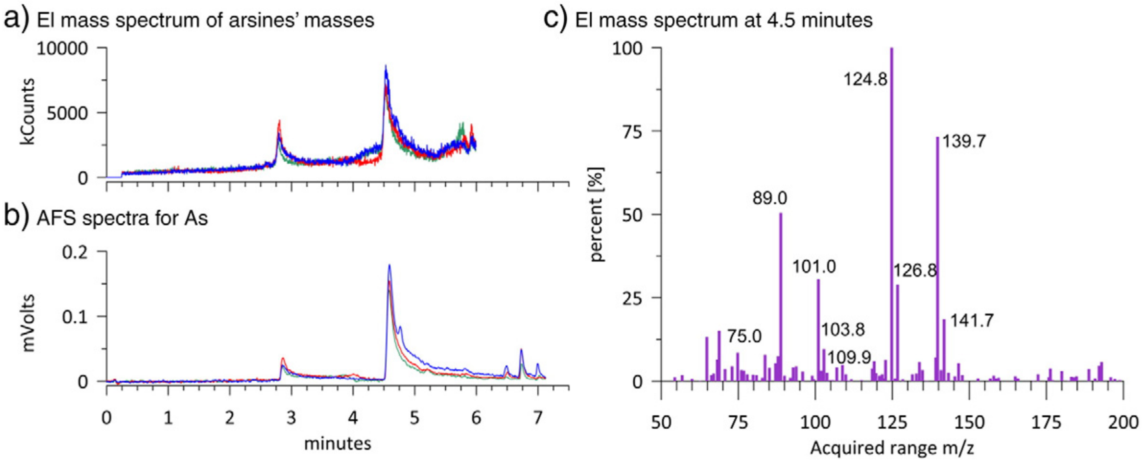

Fig. 5. Peak at 4.5 min from the PXC NTD filled with 1 cm of the sorption materials P, X, and C each (with increasing sorption capacities). a: EI-MS spectra of arsines' masses (75 + 76 + 89 + 90 + 92 + 101 + 105 + 106 + 119 + 120); b: AFS spectra for As; c: EI mass spectrum of the peak at 4.5 min which was identified as Me_2AsCl.

3.4. Laboratory stability of volatile arsines

Sampling in Tedlar® bags is an established technique for volatile As species (Haas and Feldmann, 2000) but has never been applied and validated for volcanic gases before. We therefore tested the stability of arsines in the presence of volcanic gases like CO_2, SO_2, and H_2S. Analysis of the reference "As mix" in N_2 confirmed no loss by sorption or precipitation in the Tedlar® bags over the monitoring time of 19 days with a total volatile As recovery of 98 ± 4% (Fig. 7). Recoveries of the individual species were excellent for AsH_3, $MeAsH_2$, and Me_2AsH with 106 ± 3, 103 ± 1, and 101 ± 4%, respectively (species concentrations in $ng \cdot L^{-1}$ can be found in SI 6). For Me_3As, we had a mean recovery of 85 ± 3% which indicates minor transformation to less methylated arsines and AsH_3. Volatile As recoveries in the presence of the gases O_2, CO_2, SO_2, and H_2S presented in the following are referenced to the respective As speciation in N_2 atmosphere.

In the presence of O_2, CO_2, and SO_2, total volatile As concentrations decreased slightly over time to 92 ± 1, 91 ± 2, and 60 ± 2%, respectively (compare SI 7). Previous experiments (Haas and Feldmann, 2000; Mestrot et al., 2011) did not find any losses when investigating gaseous As adsorption from moisturized air in Tedlar® bags in concentrations ($0.3–10\ ng \cdot L^{-1}$) comparable to our study ($2\ ng \cdot L^{-1}$). Our observations of small losses in the presence of O_2 and CO_2 might be in the range of analytical uncertainty, but SO_2 clearly induces As losses. The difference to behavior in air might be explained by the fact that SO_2 is a very reactive, corrosive gas, which can oxidize the reduced As gases faster than O_2 itself, despite a 200-fold lower applied concentration (100 ppm_v SO_2 versus 200,000 ppm_v O_2). Whether the dominant process is adsorption to the Tedlar® bag walls or precipitation (e.g. of As_2O_3 or As-S compounds (Meyer and Pietsch, 1952)) is unclear at the moment.

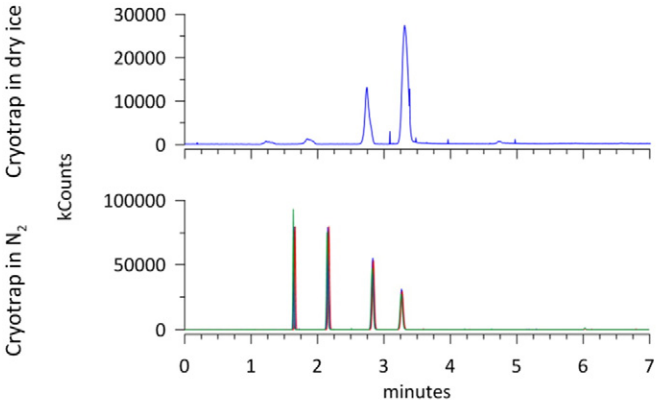

Fig. 6. Comparison of 2.5 ng of arsines trapped during cryotrapping in dry ice and liquid N_2. Total analysis was done by ICP-MS (*m/z* 75, As).

Regarding species transformations, in 20% oxygen ("synthetic air"), all the arsines showed recoveries between 102 and 83% after 11 days of storage at 5 °C in the dark (Fig. 7). This is comparable with the results of Haas and Feldmann (2000) who conducted stability experiments of arsines in Tedlar® bags filled with moisturized air and stored them at 20 °C. They found recoveries between 90 and 99% for AsH_3, $MeAsH_2$, and Me_2AsH after 24 h and 86, 73, and 26% after 5 weeks. Storage at a higher temperature of 50 °C resulted in lower recoveries for all three arsines tested in Haas and Feldmann (2000). Consequently, an even lower temperature in our study (5 °C versus 20 and 50 °C) can be the reason for our higher recoveries. In the presence of CO_2, the recoveries of arsines were 90% for AsH_3, 95% for $MeAsH_2$, 92% for Me_2AsH, and 88% for Me_3As after 21 days. These stability data are comparable to the arsine stabilities in N_2 which is plausible because CO_2 has a low tendency to react with other gases.

Both H_2S and SO_2 had a strong effect on species transformation. In the presence of H_2S, Me_3As showed a decrease in recovery to 67% after 17 days, while Me_2AsH and $MeAsH_2$ showed only slight variations and reached 89 and 105% recovery after 17 days, respectively. The AsH_3 recovery reached 123% after 17 days. Thus, the decrease in methylated species can be explained by the increase in AsH_3. In the presence of SO_2, only 72% of AsH_3 and $MeAsH_2$ were recovered after 21 days, only 41% of the higher methylated Me_2AsH, and 11% of Me_3As (Fig. 7). With regard to both total volatile As loss and species transformation we conclude that SO_2 must be eliminated from the matrix gases during Tedlar® bag sampling, which was done in the present study by NaOH traps (see Section 2.3).

Independent of the gas matrix, As stability decreased with increasing methylation. This sequence was also shown in previous stability experiments with moisturized air in Tedlar® bags in respect to UV light (Mestrot et al., 2011) and storage temperature (Haas and Feldmann, 2000). The fast decrease of Me_3As concentration (as a result of conversion to AsH_3 and precipitation/adsorption) is consistent with data from Mestrot et al. (2011) and Haas and Feldmann (2000) who also conducted stability experiments in Tedlar® bags and who both observed the fastest decrease for Me_3As during storage in Tedlar® bags. There is one published experiment where Me_3As was more stable than AsH_3 when stored in glass bottles filled with moisturized air for 9 days, but the authors do not state anything about light conditions during storage (Pantsar-Kallio and Korpela, 2000) which was shown to be crucial by

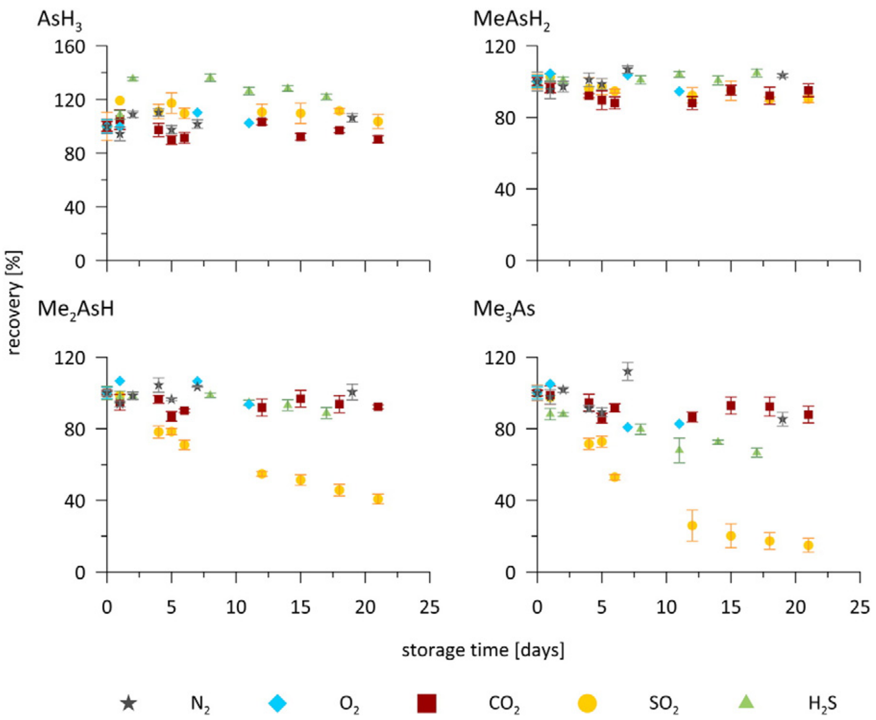

Fig. 7. Recovery of 2 ng·L^{-1} of AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As in dry N_2 (grey stars) and in the presence of the gases O_2, CO_2, SO_2 and H_2S in N_2 (blue diamonds, red squares, orange circles, and green triangles). The stored monitored "As mix" in dry N_2 (grey stars) was used for calibration and correction of instrument variations. All samples were kept in the dark at +5 °C. Calibration was done anew each day with a freshly prepared "As Mix" in dry N_2.

others (Mestrot et al., 2011). The different containers made of glass and Tedlar®, respectively, might also have had an effect.

3.5. Arsenic concentration in field samples

For analysis of natural samples from Vulcano and the Phlegraean Fields, we were able to realize a maximum transfer time from field site to laboratory of 8 days, during which, based on our laboratory stability tests (see Section 3.4), arsines in Tedlar® bags should undergo neither loss nor species transformations, provided that SO_2 is removed (see Section 3.4). The dominant arsine species in natural samples was AsH_3 with concentrations ranging from 0.3 to 74 ng As·m^{-3} (Table 2). The highest concentrations were detected at a fumarole on the path through the fumarolic field on La Fossa, Vulcano (GPS data in SI 2). Lowest concentrations were observed at stations downwind from the fumaroles (the more distant, the lower) and at the harbor of Vulcano Island. AsH_3 concentrations at Solfatara (Phlegraean Fields) were in the range of 1.2–2.2 ng·m^{-3} (Table 2). At all sites, AsH_3 concentrations correlated with CO_2 (SI 8), decreasing with decreasing CO_2 concentration due to dilution by air (and increasing distance to the fumaroles), which further confirms the volcanogenic origin of AsH_3.

Besides AsH_3, only one more peak was found in all samples from Vulcano and Solfatara. Its retention time of 3.56 min matched that of Me_3As and its detection by AFS confirmed that the molecule contained As. However, concentrations were too low (0.07–2.9 ng·m^{-3}) for a molecular identification by EI-MS (detection limit is 100 and 500 pg when injecting 1 L gas). $MeAsH_2$ and Me_2AsH were not detected in any of the natural samples. Based on the excellent stability of these species in the laboratory tests (Fig. 7), we assume that their non-detection in the natural environment is no sampling artifact, but true reflection of their non-occurrence at our sites.

Putting our results for volatile As speciation in fumarolic gases in context with those of Hirner et al. (1998) who also used Tedlar® bags for sampling volatile As species over algal mats in a geothermally influenced creek and over hot springs, we see the following sequence: Inside or directly above algal mats, methylarsines were the clearly dominant

Table 2

Arsenic and CO_2 concentrations at Vulcano and at the Phlegraean Field, Italy. CO_2 was sampled once and analyzed 3 times; standard deviation refers to analytical replicates. Standard deviation for As refers to sample replicates (3 samples were taken in the field).

	CO_2 [ppm$_v$][a]	AsH_3 [ng·m^{-3}]	Me_3As [ng·m^{-3}]	ΣAs [ng·m^{-3}]	Ratio CO_2/As
Vulcano					
V1	1930 ± 20	0.28 ± 0.1	0.83 ± 0.5	1.1 ± 0.6	$2.2\cdot10^{10}$
V2	1430 ± 10	0.94 ± 0.4	1.03 ± 0.9	2.0 ± 1.4	$4.9\cdot10^{9}$
V3	2250 ± 20	0.81 ± 0.4	1.1 ± 0.5	2.1 ± 0.8	$9.0\cdot10^{9}$
V4	4610 ± 70	3.2 ± 2.6	1.4 ± 0.8	4.7 ± 3.4	$4.7\cdot10^{9}$
V path	NA	74[b]	2.9[b]	77[b]	
V harbor	1950 ± 80	0.47 ± 0.1	0.069 ± 0.07	0.54 ± 0.04	$1.3\cdot10^{10}$
Solfatara (Phlegraean fields)					
S1	2550 ± 20	1.5 ± 0.8	0.97 ± 0.6	2.5 ± 1.2	$5.5\cdot10^{9}$
S2	4100 ± 30	1.2 ± 0.7	1.2 ± 0.8	2.4 ± 1.7	$1.1\cdot10^{10}$
S3	3610 ± 20	2.2 ± 0.7	1.1 ± 0.5	3.3 ± 1.2	$5.3\cdot10^{9}$

[a] Standard deviations for CO_2 are given for measurement replicates.

[b] No replicate samples were taken in the field, thus, no standard deviation is given.

or even exclusive volatile As species (Hirner et al., 1998). That algae can methylate arsines in geothermal environments has lately been confirmed by the identification of thermophilic eukaryotic algae in Yellowstone National Park that were able to volatilize Me_3As from geothermal aqueous arsenic (Qin et al., 2009). Directly above a hot spring (with a temperature maximum of around 50 °C) Hirner et al. (1998) found an almost even distribution of AsH_3 on the one hand and Me_2AsH plus Me_3As on the other hand pointing towards microbially catalyzed methylation. The fumarolic environments we sampled are even more hostile environments to methylating bacteria, because they are water-limited and temperatures at the fumarolic outlets are about 150 °C; these environments show a dominance of AsH_3. Taken together, this gives evidence that inorganic AsH_3 is a primary product of volcanic emissions, while methylarsines are secondary volatilization products, not released directly as a gas by the volcanoes but volatilized from aqueous arsenic species by (micro)organisms.

Putting the total concentrations of volatile As measured in our study ($0.5–77\ ng \cdot m^{-3}$, mostly between 1.1 and $4.7\ ng \cdot m^{-3}$) into context is difficult. Matschullat (2000) reports a total atmospheric As background concentration over land in the Northern hemisphere of $0.5–2.8\ ng \cdot m^{-3}$. No numbers exist specifically for volatile As, but assuming that particulate As dominates with 89–98.6% over volatile As (Matschullat, 2000), a calculated volatile As concentration would be $0.04–0.3\ ng \cdot m^{-3}$. In comparison, our measured releases from fumarolic gases are 1 to 2 orders of magnitude higher. We assume that this number is a very conservative estimate which could even be higher depending on variations in the volcanoes' natural activities. Furthermore, all our samples have been taken during day time while volatile As stability is reportedly higher in the dark; so night time values might be even higher. Last but not least, in environments more suitable for microbial communities or algae (see above) secondary volatilization from aqueous As might further increase total volatile As release over volcanic areas. However, previously reported concentrations of “volatile As” in the $mg \cdot m^{-3}$ range from passive sampling and trapping in oxidation solution from geothermal environments in Yellowstone National Park (Planer-Friedrich et al. (2006) are likely overestimations. Calculations were done by the 1st Fick's diffusion law which depends on the diffusion flux influenced by several factors like diffusion length and diffusion coefficients which are difficult to measure and for which assumptions had to be made. Furthermore, it cannot be excluded that particulate As has been trapped as well in that study (Planer-Friedrich et al. (2006), while the concentrations in the present study clearly only reflect volatile As species.

4. Conclusion

In summary, Tedlar® bags are a superior technique to sample volatile arsines in the field compared to cryotrapping in dry ice, which requires complicated logistics, and NTDs which do not trap arsines with lower boiling points, do not desorb trapped Me_3As, and produce artifact Me_2AsCl, questioning the reliability of previous reports using the same sorption materials on SPMEs. Stability of arsines in Tedlar® bags in the presence of different volcanic and air gases like SO_2, CO_2, H_2S, and O_2 was shown to be given for at least 11 days except for the higher methylated Me_3As in H_2S and Me_2AsH and Me_3As in SO_2, where degradation of the respective species was observed. Sampling with NaOH traps in combination with prior cooling of the gas eliminated arsine degrading matrix gases like SO_2.

Natural samples taken with Tedlar® bags from Vulcano and Solfatara (Italy) contained total volatile As concentrations of $0.5–77\ ng \cdot m^{-3}$ which exceed calculated natural background concentrations by at least 1–2 orders of magnitude. The predominant species was AsH_3 with concentrations between 0.3 and $74\ ng \cdot m^{-3}$. The absence of $MeAsH_2$ and Me_2AsH and the low concentrations of Me_3As ($0.07–1.4\ ng \cdot m^{-3}$) show that secondary microbially catalyzed methylation is a process of minor importance in the fumarolic gases.

While condensate and sublimate sampling or moss monitoring are easier to realize on a large scale and at higher spatial resolution and have the advantage of yielding integrative signals over longer time spans, they have the disadvantage of not being able to differentiate between particulate and volatile As. For a better understanding of the contribution of volcanoes to the global As budget, differentiation of these two fractions is important as well as a clear identification of those volatile inorganic As species that are directly released from volcanic gases and those that are volatilized from aqueous As in a secondary process. For the latter, the currently best method is sampling in Tedlar® bags eliminating reactive gases, short storage (cool and dark), followed by species-selective quantitative analysis by CT-CF-GC-EI-MS/AFS.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jvolgeores.2016.10.016.

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SUPPORTING INFORMATION

Evaluation of techniques for sampling volatile Arsenic on Volcanoes

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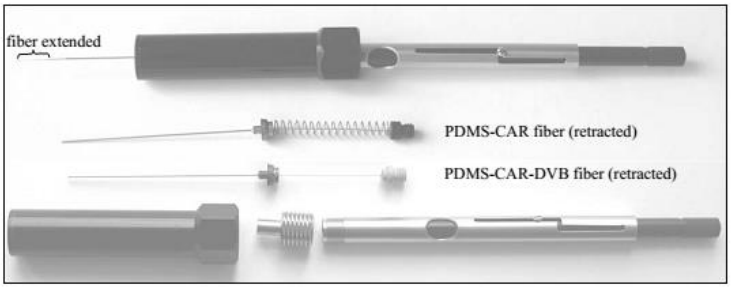
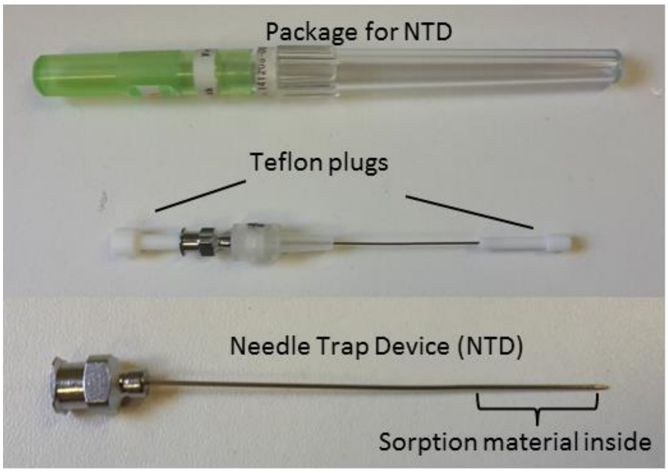
SI 1: Sampling device schemes: Solid phase micro extraction (SPME), Needle Trap devices (NTDs), and Tedlar bags.

SPME

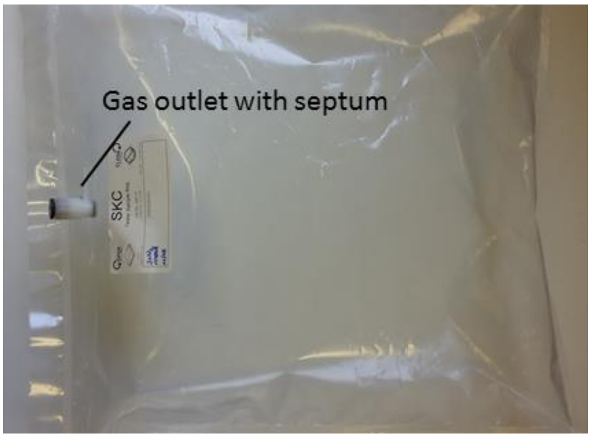


Picture from Planer-Friedrich (2004)

NTDs



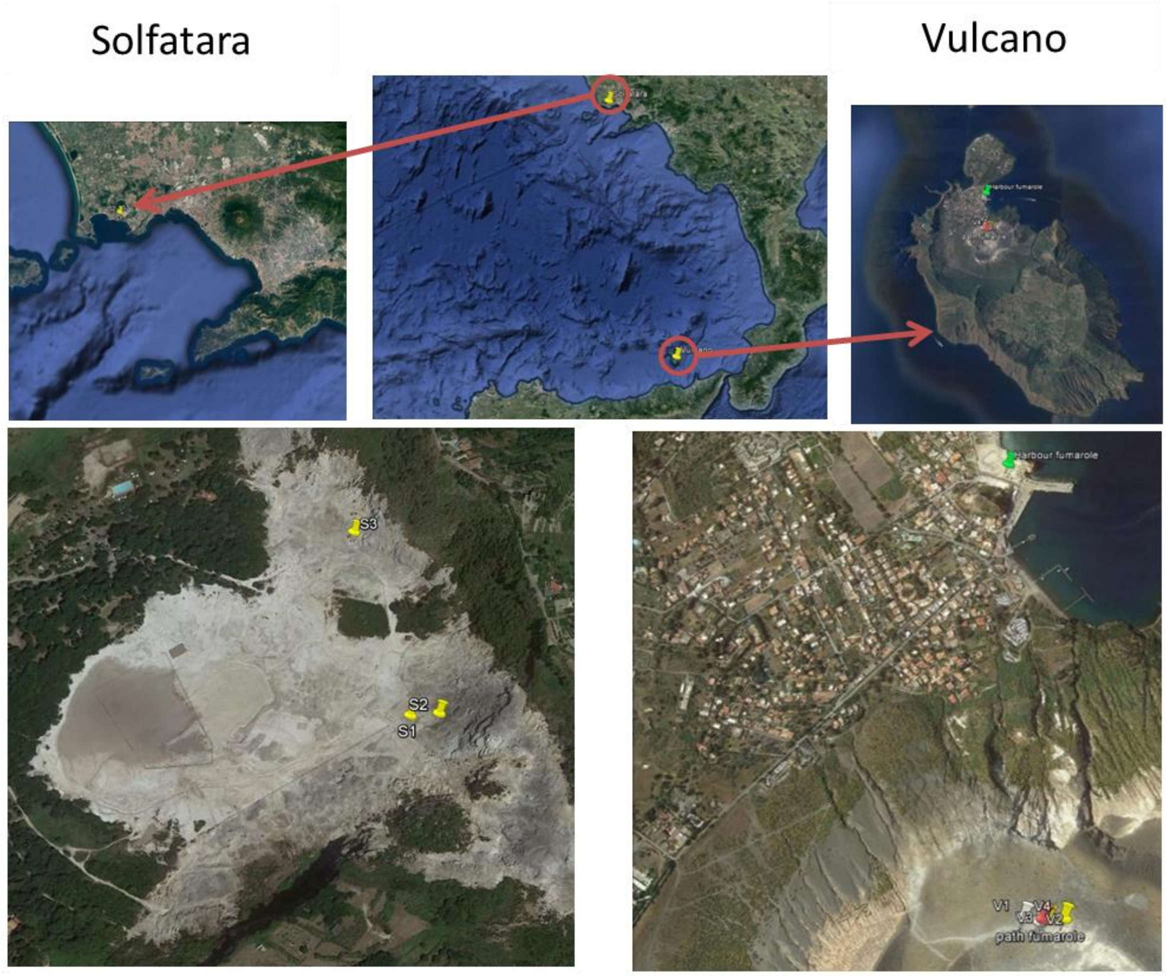
Tedlar bags



References:

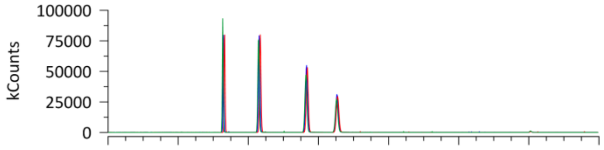
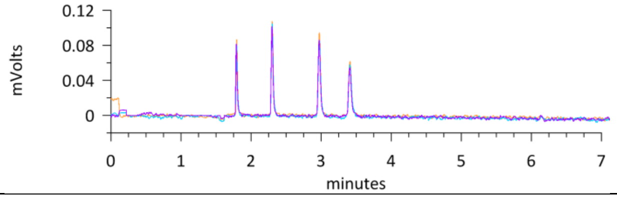
Planer-Friedrich, B., 2004. Volatile Arsenic in aquatic environments. PhD Thesis, TU Bergakademie Freiberg, Freiberg.

SI 2: Map of Vulcano and the Phlegraean Fields, Italy with sampling points and coordinates.

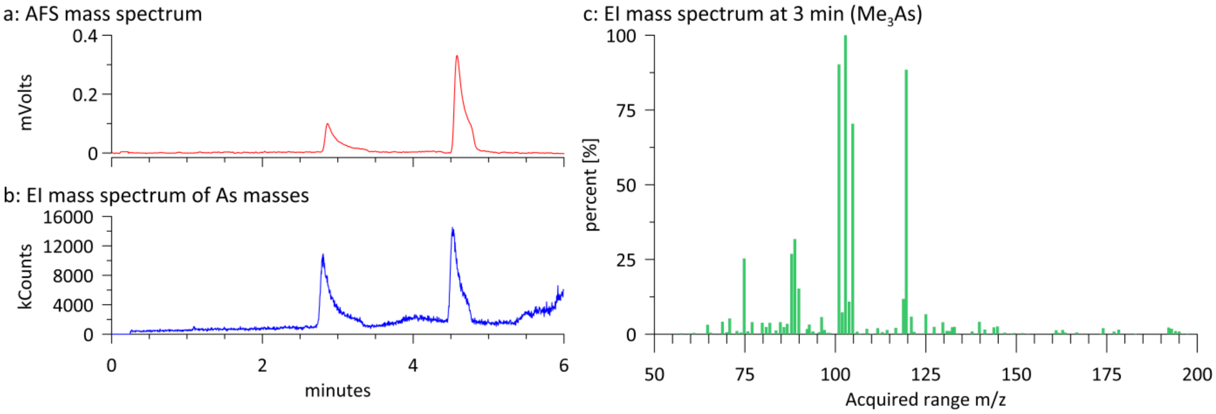


	Latitude N	Longitude E
Vulcano		
V1	38.40615	14.96103
V2	38.40609	14.96135
V3	38.40612	14.96152
V4	38.40614	14.96189
V path	38.40612	14.96145
V harbor	38.41573	14.96005
Solfatara (Phlegraean Fields)		
S1	40.82710	14.14160
S2	40.82711	14.14192
S3	40.82888	14.14079

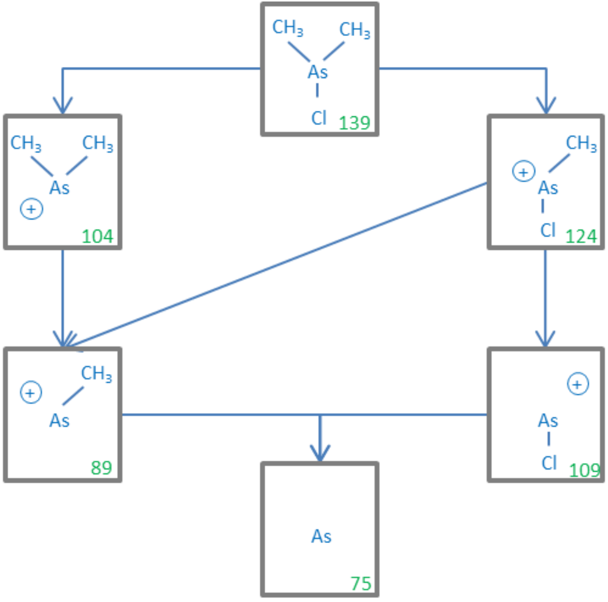
SI 3: Triplicate comparison of AFS and ICP-MS signals for the same As mix standard containing 2 ng of each AsH_3, $MeAsH_2$, Me_2AsH, and Me_3As

	Chromatograms	Peak area (kcounts for ICP-MS and mVolts for AFS)			
		AsH_3	$MeAsH_2$	Me_2AsH	Me_3As
ICP-MS		87,000 ±3,500	84,000 ±63,000	110,000 ±6,200	77,000 ±4,300
AFS		130,000 ±4,100	210,000 ±10,000	220,000 ±13,000	180,000 ±10,000

SI 4: Peak at 3 minutes from the PXC NTD filled with 1 cm of the sorption materials P, X, and C each (with increasing sorption capacities): a: EI mass spectrum of the As masses (75+76+89+90+92+101+105+106+119+120); b: AFS signal for As; c: EI mass spectrum of the peak at 3 minutes that can be assigned to Me_3As.



SI 5: Me_2AsCl fragments and their masses in EI-MS analysis

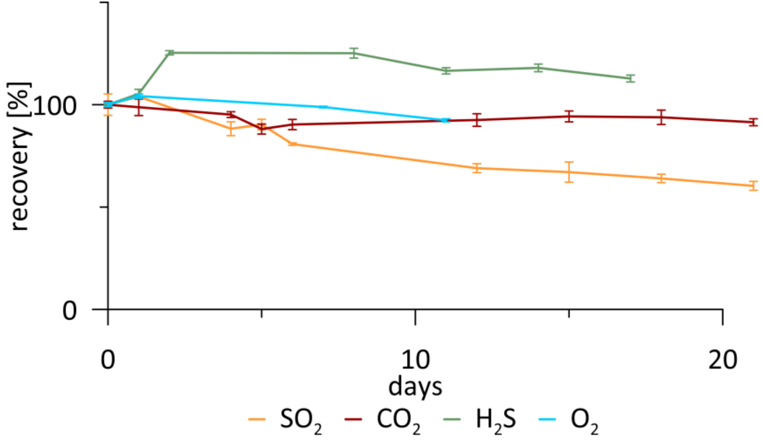


SI 6: Stability measurement data [ng As·L^{-1}]

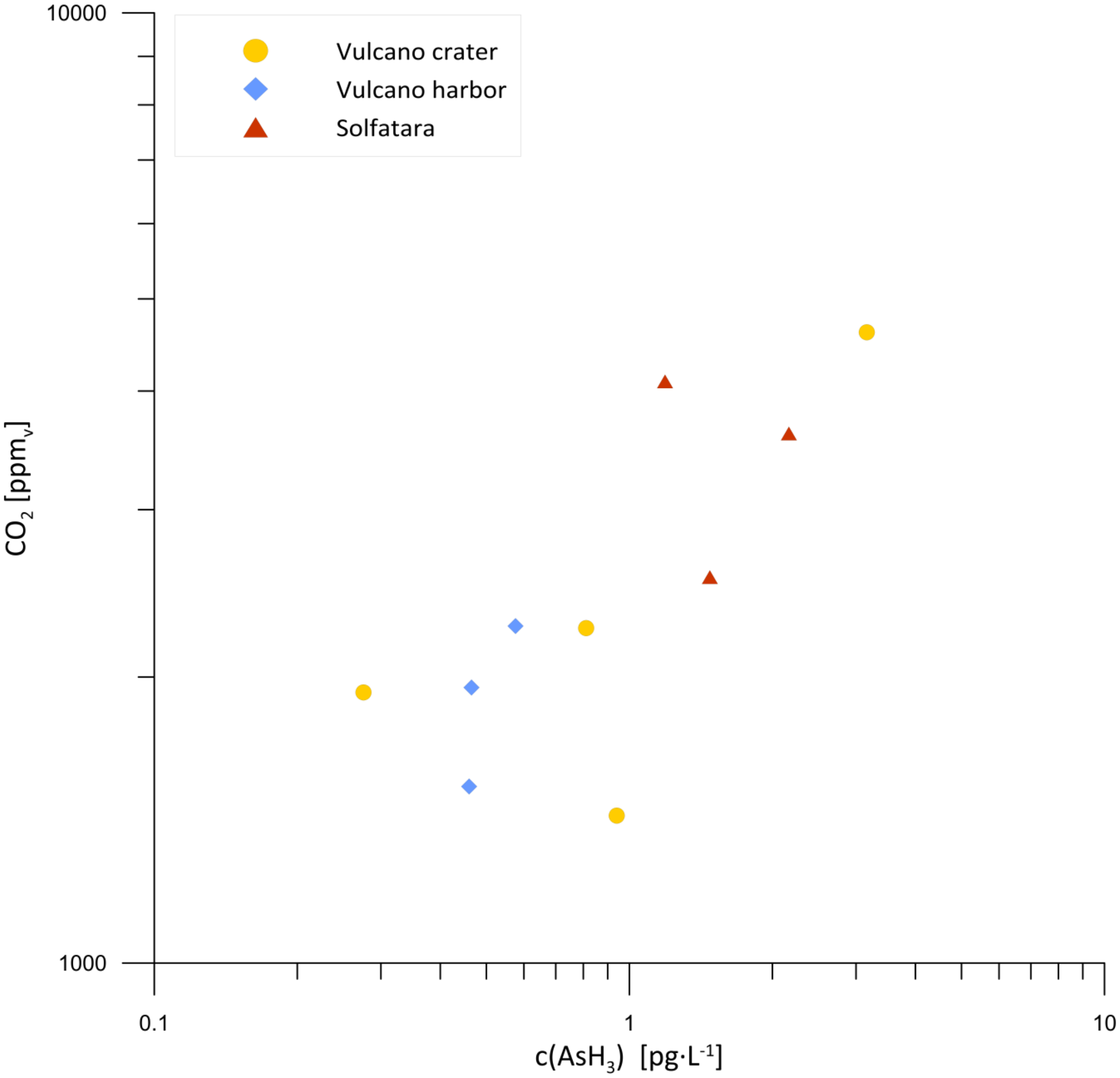
Matrix	Day	AsH_3	$MeAsH_2$	Me_2AsH	Me_3As
N_2	0	2.05 ± 0.11	2.14 ± 0.11	2.19 ± 0.04	2.39 ± 0.10
	1	1.94 ± 0.11	2.04 ± 0.11	2.06 ± 0.04	2.34 ± 0.10
	2	2.24 ± 0.05	2.08 ± 0.06	2.15 ± 0.05	2.43 ± 0.04
	4	2.26 ± 0.06	2.16 ± 0.08	2.28 ± 0.09	2.18 ± 0.04
	5	2.00 ± 0.06	2.11 ± 0.07	2.11 ± 0.02	2.13 ± 0.06
	7	2.09 ± 0.06	2.29 ± 0.06	2.26 ± 0.00	2.68 ± 0.12
	19	2.18 ± 0.07	2.21 ± 0.02	2.20 ± 0.01	2.04 ± 0.09
SO_2	0	1.69 ± 0.17	1.94 ± 0.08	1.98 ± 0.06	2.02 ± 0.09
	1	2.01 *	1.99 *	1.95 *	1.97 *
	4	1.87 ± 0.09	1.86 ± 0.12	1.55 ± 0.07	1.45 ± 0.06
	5	1.98 ± 0.13	1.88 ± 0.09	1.55 ± 0.03	1.47 ± 0.06
	6	1.85 ± 0.07	1.83 ± 0.02	1.41 ± 0.05	1.07 ± 0.03
	12	1.87 ± 0.10	1.79 ± 0.08	1.08 ± 0.03	0.52 ± 0.18
	15	1.85 ± 0.13	1.84 ± 0.10	1.02 ± 0.06	0.41 ± 0.14
	18	1.88 ± 0.03	1.75 ± 0.02	0.90 ± 0.07	0.35 ± 0.09
	21	1.75 ± 0.09	1.75 ± 0.04	0.81 ± 0.05	0.30 ± 0.08
CO_2	0	2.16 ± 0.08	2.14 ± 0.05	2.07 ± 0.02	2.08 ± 0.03
	1	2.27 ± 0.16	2.06 ± 0.06	1.96 ± 0.09	2.06 ± 0.11
	4	2.10 ± 0.11	1.97 ± 0.02	1.99 ± 0.04	1.97 ± 0.10
	5	1.94 ± 0.07	1.92 ± 0.11	1.79 ± 0.06	1.79 ± 0.06
	6	1.97 ± 0.09	1.89 ± 0.07	1.86 ± 0.02	1.91 ± 0.05
	12	2.23 ± 0.05	1.89 ± 0.08	1.90 ± 0.10	1.80 ± 0.06
	15	1.99 ± 0.05	2.04 ± 0.06	2.00 ± 0.10	1.93 ± 0.10
	18	2.10 ± 0.04	1.97 ± 0.10	1.94 ± 0.10	1.92 ± 0.11
	21	1.95 ± 0.06	2.04 ± 0.08	1.91 ± 0.02	1.83 ± 0.10
H_2S	0	19.91 ± 0.02	2.09 ± 0.06	2.09 ± 0.08	2.50 ± 0.08
	1	21.63 ± 0.65	2.13 ± 0.05	2.05 ± 0.07	2.20 ± 0.08
	2	26.96 ± 0.25	2.10 ± 0.04	2.07 ± 0.04	2.20 ± 0.03
	8	27.12 ± 0.54	2.11 ± 0.05	2.07 ± 0.03	1.99 ± 0.07
	11	25.14 ± 0.55	2.17 ± 0.03	1.98 ± 0.03	1.70 ± 0.17
	14	25.51 ± 0.41	2.10 ± 0.05	1.95 ± 0.06	1.81 ± 0.03
	17	24.28 ± 0.43	2.19 ± 0.05	1.86 ± 0.06	1.67 ± 0.06
O_2	0	1.97 ± 0.10	2.39 ± 0.08	2.42 ± 0.08	2.92 ± 0.09
	1	1.97 *	2.49 *	2.59 *	3.07 *
	7	2.18 *	2.47 *	2.58 *	2.36 *
	11	2.02 *	2.26 *	2.27 *	2.42 *

*Standard deviations are given for samples where triplicate measurements took place.

SI 7: Total As stability in Tedlar® bags in the presence of SO_2, CO_2, H_2S, and O_2



SI 8: Correlation of AsH_3 concentration with CO_2 at different sampling sites (Vulcano and Solfatara)



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