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The geochemical cycle of Tellurium in volcanic environments

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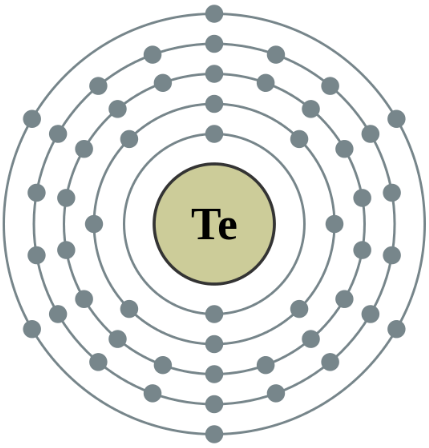

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DOTTORATO DI RICERCA IN GEOCHIMICA XXVI CICLO
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A Chiara e a Simone

Abstract

This research is focused on the geochemistry of Tellurium (Te) in active volcanic environments. To this end concentrations of Te have been measured on different matrices (plume, ashes, soils, atmospheric depositions and plants). Samples were collected from different volcanoes around the world: volcanic aerosols from Etna and Vulcano (Italy), Turrialba (Costa Rica), Myakejima, Asama and Aso (Japan), Mutnovsky and Gorely (Kamchatka, Russia), Copahue (Argentina), Nyamuragira and Nyiragongo (D.R. Congo); atmospheric depositions from Etna and Vulcano (Italy), Nyiragongo (D.R. Congo); ash from Etna (Italy), Copahue (Argentina), San Miguel (El Salvador). Among with plume and rain samples, several leaves of plants from volcanic areas were collected for biomonitoring investigations: Etna, Vulcano and Stromboli (Italy), Nyiragongo (D.R. Congo), Nisyros (Greece), Gorely (Kamchatka), Turrialba (Costarica), Masaya (Nicaragua), Soufriere (Guadalupe); for comparison plant samples were collected also from an industrial area (Augusta, Italy) and a rural forest (Ficuzza, Italy). Samples of soils were also collected from Nisyros (Greece) to better understand the soil-plant distribution.

From a literature review, there is a scarcity of data available about Tellurium abundances in the environment, expecialy for volcanic areas. This fact can be ascribed to the scarce use of this element in the past. During the last decades, the use of Te increased considerably due to its importance for electronics and solar photovoltaic manufacturing. Moreover, the recent natural disaster of Fukushima in March 2011 drew attention to the environmental impact of isotope Tellurium-132, produced after the nuclear power plant failure. As consequence, a lot of new studies are focused on Te behaviour in the environment. Regarding Te plume concentrations and fluxes from active volcanoes, only few estimations were reported in previous studies. Sixty-five plume samples were collected and analysed thus significantly increasing the existing worldwide dataset. The concentrations of Te detected range from <0.003 to 0.15 µg/m^3, significantly higher than the background level.

The atmospheric depositions are the most important way to transfer the elements from the atmosphere to the ground and consequently to all the terrestrial environments (soils, groundwater, plants, animals and humans). Nowadays very few data are available about Te abundances in atmospheric deposition and no data in volcanic environments. The data here reported are the first results of the concentrations of Te in rainwater collected close to active volcanoes. The samples of rainwater samples (bulk deposition) representative of the bulk deposition, were collected from three different volcanoes (Etna, Vulcano and Nyiragongo). A total of 98 rainwater samples were analysed for the major and minor constituents including Te, so creating a complete and unique dataset. The results show clearly higher Te contents close to the crater with values up to 3.20 µg/l with respect to far away background values below 0.04 µg/l, suggesting a volcanogenic origin. In particular, the concentrations of Te, among with other volatile metals e.g. As, Bi, Cs, Cu, Cd, Tl, Pb, are inversely correlated with pH values. This trend confirms that the volcanic emissions can significantly impact the chemical composition of atmospheric deposition. In the same way it influences the geochemical cycle of Te, causing a major accumulation into the soil-plants system. Interesting results were obtained by chemical analysis of Te contents in ash leachates. As well as for rainwaters, no data of volcanic ashes leachates are reported in the literature. For this study we

analysed the fresh ashes ejected from: Copahue (Argentina) emitted in December 2012, after 12 years of inactivity; Etna (Italy), collected during 20 paroxysmal events occurred in 2011 and 2012; San Miguel (El Salvador) erupted in December 2013. The samples, when possible, were divided in the different grain size, otherwise the bulk grain size was studied. The results highlight the rapid dissolution of Te from the ash surface indicating high mobility of this element among with other known mobile metals. Te is probably carried out during the volcanic explosion forming hydro-soluble salts with the main acid volatile species (SO_2, HCl, HF), $Te(SO_4)_2$, $TeCl_4$ and TeF_4 but also in elemental form. As expected, the experiments showed that the Te concentrations increase with decreasing grain size, due to the increase of specific surface of the ash. This process, including Te dissolution, have important implications on atmospheric deposition chemistry: when the smaller particles are injected into the atmosphere they can be transported for long distance from the source-point, participating in the cloud processing and affecting sequentially the chemistry of the rain, plants and soils in the surrounding of active volcanoes.

The plants commonly contain low contents of Te with variable range. The highest concentration of Te is reported in onion and garlic (up to 300 µg/g) and the characteristic garlic odour is caused by vapours of dimethyl telluride. In the last frame of this study, leaves of 11 species were collected and analysed from 9 different volcanic areas; for comparison samples from an industrial area (Augusta) and a rural area (Ficuzza) were also investigated. The same species but in different volcanoes are featuring the same range, while plants that bioaccumulate more Te are *Senecio sp.*, mosses and lichens with values up to 0.575 µg/g. At Nisyros island (Greece), concentrations of Te in two indigenous plants (*Cistus s*p. and *Erica sp*.) were compared with those in the soils. For this study, the soil samples were taken in the Lakki Plain caldera inside and outside the main fumarolic areas. Also in this case, the data show the influence of volcanic emissions on Te concentrations, recording the highest values within the active fumarolic areas. Anyway, in general the concentrations inside the caldera (0.056 – 0.746 µg/g) are higher than the local background (0.004 µg/g). Comparing the soil with the plants, the values of Te in plants tend to grow with the increase of this element in soils. The plants, particularly *Cistus*, tend to take up more Te near the active fumarolic areas. The results showed very high enrichments of Te in volcanic emissions comparable with other volatile elements like selenium, arsenic, thallium and bismuth.

Concluding, the results of this study increase our knowledge about abundances and distribution of Te in volcanic areas, providing a great amount of unpublished data regarding Te, among with many others major and trace elements, in different matrices. We highlighted the prevailing volcanogenic origin of Te and the potential impact of this toxic metalloid on the environment. The results also suggest a primary transport of Te in the volatile phase, probably in gaseous form (as also suggested by recent studies) and/or as soluble salts (halides and/or sulfates) adsorbed on the surface of volcanic particles and ashes. Comparison between different volcanic systems, Etna and Nyiragongo with persistent passive degassing from one side and Nisyros without a volcanic plume, suggest a bioaccumulation of Te in vegetation both from soils and directly from the atmosphere, confirming the high geochemical mobility of this element in volcanic emissions. New flux estimations confirm the relevance of this element in the total volatile output from active volcanoes. The first estimates of volcanic flux of tellurium from Etna range from 0.26 to 12.3 tons per year, confirming that this volcano is one of the biggest point sources to the atmosphere also for this element. The new dataset, among with previous data, allowed to extrapolate a Global Volcanogenic Flux of Te (GVF-Te) through the Te/SO_2 ratios and the global budget of SO_2 from active volcanoes taken from literature. The total output estimated range from 15.3 to 316 ton/a with a median value of 98, coherently with the estimation obtained from previous authors. Moreover, this value is significantly high if compared with the global production of Te (about 500 ton/a in 2010) by human industrial activities.

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Sommario

Introduction

Tellurium is a metalloid that since its discovery, occurred in the 1782, arose little interest to the scientific community but in the last twenty years the commercial interest for this element is changed, due to its growing use in semiconductor technologies. For example CdTe is used in solar cell batteries, in semiconductor and laser techniques and Bi_2Te_3 and Sb_2Te_3 are used in thermogenerators.

The chemical properties of Tellurium are similar to sulphur and selenium but its activity is less marked and in general the compounds formed are less stable than their analogues of sulphur and selenium. Hydrogen telluride is an unstable gas and a colourless gas, the odour of which is notably different from that of its selenium and sulphur analogues, being less pronounced and faintly recalling that of arseniuretted hydrogen. The gas is poisonous; a bubble inhaled is sufficient to cause a severe attack of vertigo.

The halogen elements are related with good combination with tellurium. Tellurium Hexafluoride, TeF_6, appears to be more stable than Tellurium Tetrafluoride. The gas has an unpleasant odour, recalling ozone and tellurium hydride.

Tellurium Dichloride, $TeCl_2$, is the first product of the regulated action of chlorine on Tellurium, but it is difficult to prevent further conversion into the tetrachloride. The bivalent Tellurium is not stable and the dichloride in the solid state tends to undergo self-oxidation and reduction, forming a solid solution of the element in the tetrachloride. The dichloride is stable only in the gaseous condition or in solution when in equilibrium with its decomposition products. Tellurium tetrachloride is a colourless crystalline solid. Tellurium burns in air with the formation of the Tellurium Dioxide, TeO_2 and it is very sparingly soluble in water.

Tellurium is recovered in many minerals like telluride together with sulfides and selenides; Tellurium, having two common oxidation states, (IV) and (VI), can be partially oxidized to oxyanions (tellurite, TeO_3^{2-}, and tellurate, TeO_4^{2-}, or in the oxide form, TeO_2) (Greenwood, 1994). Instead, the Tellurium exists in the native state in two forms: crystal (bright silvery color with metallic sheen) and amorphous (from dark gray to brown) (Jović, 1999). It has eight natural stable isotopes with atomic weight between 120 and 130. In natural waters, the tellurium (IV), in the form of tellurite ($HTeO_3^-$) ion, is probably the main species (Ferguson, 1990).

It is a peculiar element because it presents a higher cosmic abundance than the other elements with atomic mass exceeding 40, but in contrast is also one of the rarest elements on earth. The background levels of tellurium in the crust vary from a few ppb to hundreds of ppm, in relation to the lithology in which it is contained.

Tellurium appears to enter less readily than selenium and sulphur into the composition of organic compounds, it is a toxic element and occurs in large quantities in plants and primary consumers, including humans, 700 μg/g (Cohen, 1984; Emsley, 1999). It is highly poisonous for mammals and it may cause inhibition of growth, fall-off and paralysis. This suggests that once deposited, this element is very reactive and potentially harmful but, despite the large use in industry, the scientific knowledge about the potential impact of this element on the environment is limited and few previous authors reported result of tellurium concentrations in volcanic area.

In order to better understand the geochemical behavior of this element, considering the scarcity of available data in litterature, the main focus of the study is to create the first dataset of Tellurium abundances in different geochemical sinks (plume, rainwaters, ash, soils and plants) of active volcanic environments. To achieve this main aim the specific objectives are: to define specific protocol for sampling and analysis of tellurium; to create the first dataset about the concentrations of tellurium in different matrices in volcanic environments; to better constrain and understand the geochemical cycle of tellurium in volcanic environments (formation, transport, storage and speciation).

1. State of the art

Tellurium, atomic number 52, is a metalloid and a chalcophile element, according to the Goldschmidt classification. It belongs to the group 16 of the Periodic Table of the Elements along with oxygen, sulfur, selenium and polonium.

In 1782 this element was discovered by Franz –Joseph von Reichenstein, who extracted the new metalloid from an ore of gold, sixteen years later (1798) Martin Heinrich Klaproth named it like the goddess of the "Earth", ***Tellus***.

Tellurium can be found in its elemental form in nature, but is most often found in ores such as sylvanite ($AgAuTe_4$), calaverite ($AuTe_2$) and krennerite ($AuTe_2$). It is also present in coal (Moscoso-Perez *et al*., 2004a, b; Matusiewicz and Krawczyk, 2007).

Since 2000 the tellurium demand has increased significantly, due to its growing use in electronics (Kavlak & Graedel, 2013) (Fig. 1).

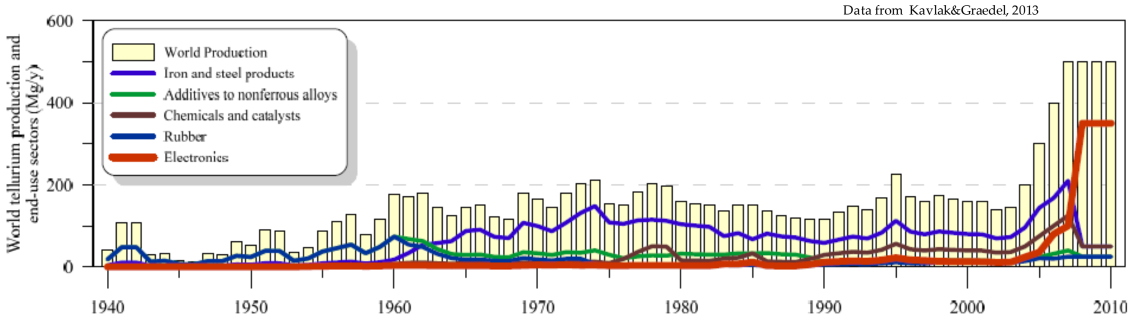

Figure 1: World production and use of Tellurium from 1940 to 2010. Data from Kavlak&Gradel, 2013

Tellurium is increasingly used in solar photovoltaics where it is combined with cadmium (CdTe) to form the active layer of cadmium–telluride thin-films. While the use of CdTe is promising for climate change mitigation potential, there are concerns regarding Tellurium availability and whether it might constitute an obstacle to large-scale deployment of CdTe (Kavlak & Graedel, 2013).

In addition to CdTe thin-films, tellurium is used in optical data storage systems (Welnic and Wuttig, 2008), thermoelectric cooling devices in which an electric current causes heat transfer between the two ends of the thermo element and therefore enables cooling on one side, as a metallurgical additive in steels alloys to improve machining characteristics and in copper alloys to improve machinability without reducing conductivity in lead alloys to improve resistance to vibration and fatigue, in cast iron to help control the chill depth, and in malleable iron as a carbide stabilizer (US Geological Survey, 2016).

Other uses include various chemicals, as pigments in glass and ceramics, catalysts for synthetic fiber production, and rubber compounding agents. Rubber compounding was once a large tellurium use, where it was used as a vulcanizing agent to reduce curing time of rubber and increase its resistance to heat and abrasion (Hoffmann *et al*., 2011).

Global consumption estimates for the end use of tellurium are as follows: solar, 40%; thermoelectric power generation, 30%; metallurgy, 15%; rubber applications, 5%; and other, 10% (US Geological Survey, 2016).

Tellurium is obtained from minerals mined for their other constituents. Approximately 90% of tellurium is recovered as a byproduct of copper mining, more specifically from the anode slimes formed during the electrolytic refining of copper (Roskill Information Services, 1982). In electrolytic copper refining, as copper accumulates at the cathode of the electrolytic cell impurities such as tellurium, selenium, silver, gold, and platinum group metals settle in the anode slimes at the bottom of the tank house (Kavlak & Graedel, 2013).

The remaining amount is extracted as a byproduct of lead, gold, nickel, platinum, and zinc mining (US Geological Survey, 2016). Tellurium production may occur in the country where the host metal is refined, or the refinery byproduct may be exported for tellurium recovery elsewhere. Tellurium production began in the United States in 1918 (Roskill Information Services, 1991), in the Soviet Union in 1924 and in Canada in 1934. Today, United States, Russia, Canada, Japan, Peru, Sweden and various other countries are known to produce refined tellurium. World production of tellurium in 2015 is estimated at 400 tons (US Geological Survey, 2016).

For traditional metallurgical and chemical uses, there was little or no old scrap from which to extract secondary tellurium because these uses of tellurium are highly dispersive or dissipative (US Geological Survey, 2016).

Tellurium is one of the most abundant heavy elements in the cosmos (Zemann and Leutwein, 1978), between the elements having an atomic number >40. But it is rare in the earth’s crust, where its abundance is estimated to be only 1-5 µg/kg, according to several sources (e.g. Bowen, 1979; Emsley, 1992; Kabata-Pendias and Pendias, 2000), it is one of the least abundant elements in the lithosphere. This is probably due to the fact that Tellurium readily forms metal hydrides and most of the element was lost to space during the Earth's formation (Jovic, 1999).

The geochemistry of Tellurium is still poorly known, but it is often compared to that of selenium because tellurium can also exist in the same oxidation states as selenium (-II, 0, IV, VI) and it is mainly found as Te (IV) and Te (VI) in various chemical systems (Brookins, 1988) but in anoxic environments it usually occurs in sulfide ores, replacing S^{2-} (Pohl, 2011).

In oxic solutions Tellurium can form anions of oxic acids, where XO_2 or XO_3 are the oxidized solid form; it is frequently found in iron oxides (Schirmer *et al*., 2014).

Hein *et al*. (2003) conducted a study about the ferromanganese crusts, the results had shown an extreme enrichment of Tellurium over the Earth's crust and seawater, caused by a surface oxidation process of Te (IV) to Te (VI) on the Fe–Mn oxide surfaces, indeed marine sediments and ferromanganese nodules show high concentrations in Tellurium. Coal and sulfide cores are slightly enriched in Tellurium compared to bulk silicate earth. Furthermore this element does not fit into the crystal lattices of the typical ultramafic minerals (olivine, pyroxene, plagioclase and oxides) for this reason these rocks have the lowest concentrations in Tellurium (Schirmer *et al*., 2014).

The Tellurium minerals, generally combined with silver, gold, copper, lead, iron and bismuth, are rare in nature. More than 50 tellurium minerals are known mostly in the form of telluride minerals. The tellurides occur in primary hypogene deposits. Secondary Tellurium minerals are relatively rare due to the stability of the native element and many tellurides in the weathering environment. The tellurium is mobile ($HTeO^{3-}$) in zones of high oxidation potential and acid leaching, gossan zones (Lueth, 2016).

Tellurium is found in deposits of other minerals of magmatic origin containing sulphides and is exhaled by active volcanoes and hydrothermal systems.

Active volcanoes have a fundamental role in the transport of volatile elements between the Earth's interior and its surface, being, through the volcanic emissions, a source for many chemicals, such as SO_2, H_2S, HCl, HF, CO_2, H_2O, metals and trace elements (Fulignatti *et al*., 2006). This is confirmed by incrustations and sublimates present surrounding high temperature fumarolic vents (Symonds *et al*. 1987; Symonds 1992;

Kavalieris 1994; Korzhinsky *et al*. 1994; Fulignati and Sbrana 1998; Taran *et al*. 1995, 2000), by the sublimates collected in silica tubes placed in fumaroles (Le Guern 1988; Bernard *et al*. 1990; Garavelli *et al*. 1997; Cheynet *et al*. 2000; Zelenski and Bortnikova 2005, Zelenski *et al*., 2013), and from the bioindicator investigation of lichens and mosses (Grasso *et al*. 1999; Varrica *et al*. 2000, Calabrese *et al*., 2015; Calabrese & D'Alessandro, 2015).

Zelensky *et al*., (2013) conducted a study about trace elements in the gas emission of Erta Ale deposited in the sublimates on the silica tube walls inserted into vent with high temperature (1084°C), after approximately 50 h of exposure. The temperature distribution along the silica tube with sublimates and main phases of sublimates is show in the figure 2. Volatile Te was deposited mainly in the cold end of the tube, this is evidence of the fact that the tellurium persists in the gaseous phase, indeed only the most volatile trace elements (As, Sb, Se, Te, and Hg) passed through the tube in significant amounts.

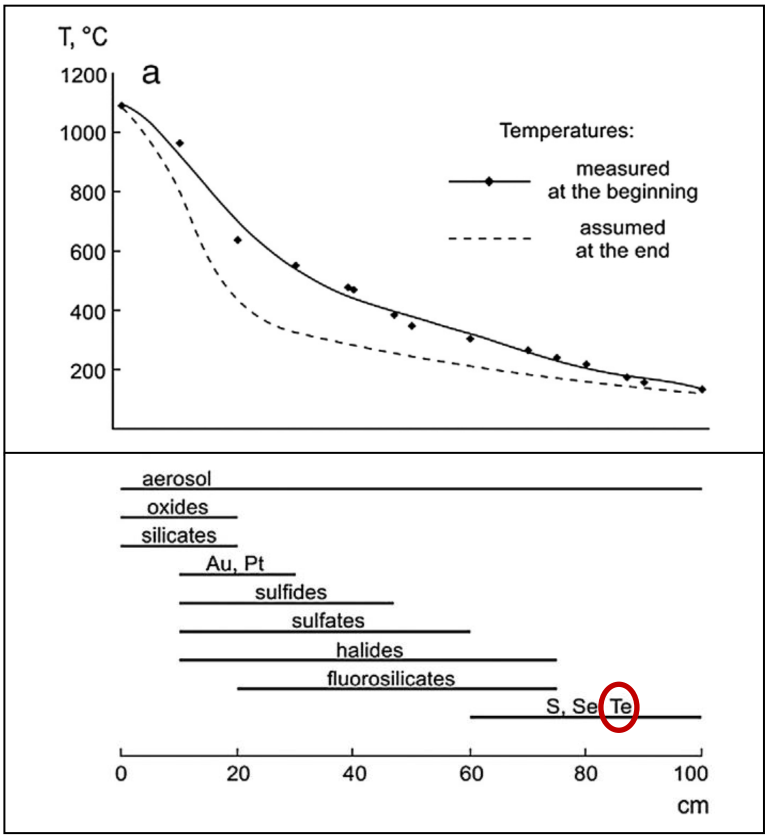

Figure 2: Temperature distribution along the tube with sublimates of the gas emission of Erta Ale (Etiopia) and main phases of sublimates where the tellurium deposited is mainly in the cold end of the tube (from Zelensky *et al*., 2013.

On the island of Vulcano the presence of native tellurium has long been known, in 1898 Cossa identified this element in samples taken inside the crater of La Fossa. After a century the presence of the native Tellurium was confirmed by Fulignatti & Sbrana (1998) that found it in silicified rocks within the crateric fumarolic field of the La Fossa volcano, near high-temperature fumaroles (250–300°C). The Tellurium is present as rounded granules, the size of a few micrometers, associated mostly to amorphous silica (Campostrini *et al*., 2011).

In this Island the chemical composition of altered rocks associated with sublimate deposition indicate the presence of a significant concentration of Tellurium up to 75 ppm (Fulignatti & Sbrana, 1998).

In generally, in the literature, very few studies reported concentrations of Tellurium in natural waters, soils, sediments and airborne particles, probably because of its very low natural abundance.

The concentrations of tellurium in natural waters reported from previous studies vary from few ng/l to tenths of µg/l but higher concentrations were found in proximity of anthropogenic sources. The concentrations of tellurium, indicated in the literature, are higher in rivers and lakes than in the open oceans, that reported up to 0.002 µg/l (e.g. An and Zhang, 1983; Chiou and Manuel, 1988; Yoon *et al*., 1990; Dave and Pitre, 1991; Fujino *et al*., 1997; Lee and Edmond, 1985; Najafi *et al*., 2010) and inland waters (e.g. Chung *et al*., 1984; Yoon *et al*., 1990; Najafi *et al*., 2010).

In rainwater and snow the concentrations of tellurium indicated are from 0.002 and 0.025 µg/l (Andreae, 1984; Yoon *et al*., 1990; Belzilea & Chen, 2015).

In soil and sediments the values for total tellurium is in general from less than one to a few µg/g depending on locations and sources of contamination. Jovic (1999) reported that the natural abundances of this elements in the soils varies from 0.5 to 37 µg/g; Reimann and Caritat (1998) estimated the world average Tellurium concentration in soil as 0.006 µg/g –dry weight; more recently, the world average Tellurium concentration in soil was estimated in 0.027 µg/g (Ba *et al*., 2010) as reported in Yang *et al*., 2013, 2014.

Tellurium concentrations in aerosols and air particulate matter, reported in the literature, are usually lower than 1 ng/m^3 (Belzilea & Chen, 2015).

The Tellurium concentrantions in plants depends on the species analysed, on the level of Tellurium in the soil and in the surrounding environment (Yang *et al*., 2013).

According to the chemical characteristics of Tellurium in soil, it will not be highly bioavailable to plants, in fact Tellurium has high mobility in soil and its chemical forms are TeO_3^{2-} and TeO_4^{2}, but these chemical forms have affinities to Fe(III) (Harada and Takahashi, 2008, Yang *et al*., 2014).

Regarding the plants, the data of Tellurium reported in literature are generally in the range 0.013–6 μg/g (D'Ulivo, 1997) and 0,013-0,35 μg/g (Kabata-Pendias, 2011) for plants with concentration up to about 300 μg/g in garlic and onions (Kabata-Pendias, 2011); seleniferous plants are able to accumulate Tellurium up to the level of 1 μg/g (Yang *et al*., 2014); concentrtions <0.001 μg/g have been measured in wheat and barley (Eriksson, 2001), from 0.018 to 0.033 μg/g in Japanese herbaceous plants (Asami *et al*., 1999) and from 0.0001 to 0.0038 μg/g in different samples of vegetables (potatoes, carrots, radishes, lettuce) (Yang *et al*., 2013).

There is no known biological role for tellurium but despite its very low abundance in the earth's lithosphere it is the fourth most abundant trace element after Fe, Zn and Rb in the human body (Cohen, 1984) with values up to 770 μg/g, reported from Hein *et al*., 2003. It is a toxic element, teratogenic, and tellurite, Te (IV) is considered to be more toxic than tellurate, Te (VI) (Basnayake *et al*., 2001; Chasteen and Bentley, 2003). The exposition of Tellurium can cause the "*tellurium breath*", with an odor similar to garlic, suggesting a methylation reaction to dimethyl telluride. This suggests that this element is very reactive and potentially harmful but the scientific knowledge about the potential impact of this element on the environment is limited.

2. Study areas

The volcanic areas, sampled in this work, are different for location and geodynamical setting. In figure 3 (modified from Aiuppa, 2015), the chemical composition of the main gases released by some of the volcanoes investigated in this research is shown evidencing a considerable intervolcano variability. The gases can be released either in large quantities during large-scale volcanic eruptions or as persistent and passive release from quiescent or mildly erupting volcanoes (Aiuppa, 2015). The major components of volcanic gases are represented by H_2O, CO_2, SO_2 and H_2S. The volcanic gases released by arc volcanoes are richer in H_2O than the within-plate/rift volcanoes; the water in volcanic gases depends from two processes, the mantle-inherited hydrous composition of source magmas (Wallace, 2005) and the extensive hydrothermal interactions within the crust (Giggenbach, 1996).

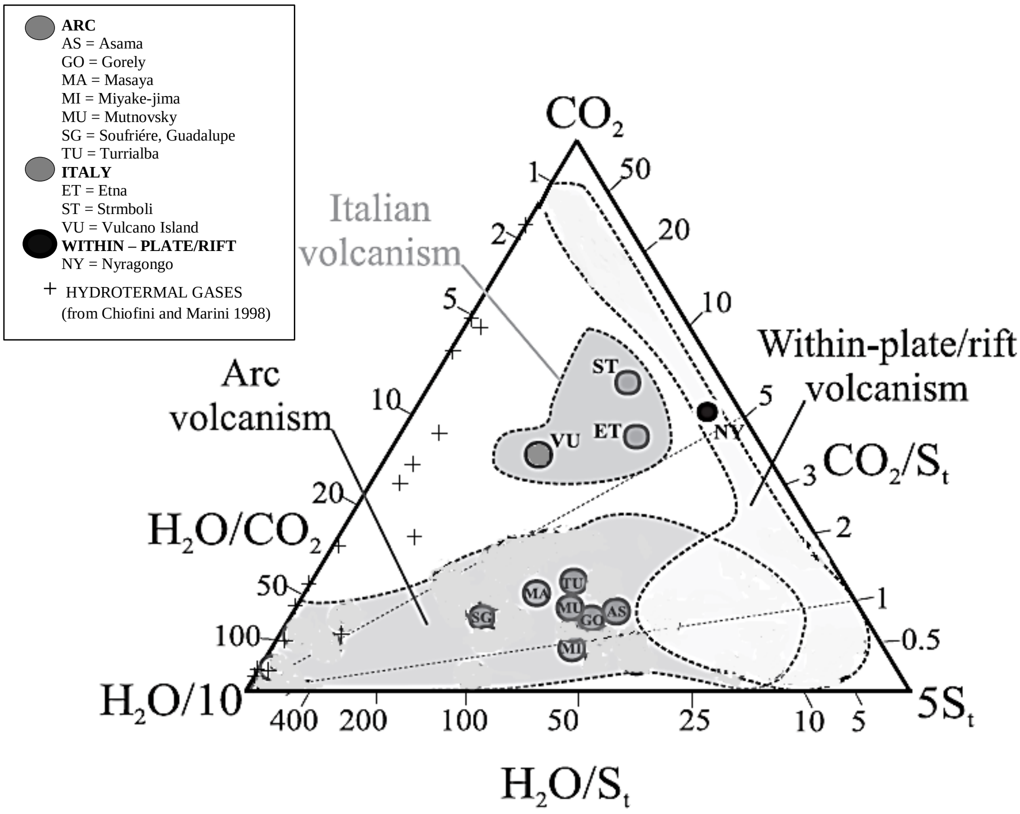

Figure 3: The graph shows the H_2O–CO_2–St (i.e. SO_2 + H_2S) gas compositions for some of volcanoes investigated in this research (modified from Aiuppa, 2015).

In this study we are presenting the results of different matrix samples investigated and collected from various volcanoes of the world (Fig. 4). In particular, we collected samples of:

a) volcanic aerosol from: Etna and Vulcano (Italy); Turrialba (Costarica); Myake-jima, Asama and Aso (Japan); Mutnovsky and Gorely (Kamchatka, Russian Federation); Copahue (Argentina); Nyamuragira and Nyiragongo (D.R. Congo);

b) atmospheric depositions from: Etna and Vulcano (Italy); Nyiragongo (D.R. Congo);

c) ash from Etna (Italy); Copahue (Argentina); San Miguel (El Salvador);

d) soils from: Nisyros (Greece);

e) plants from i) volcanic (Etna, Vulcano and Stromboli (Italy); Nyiragongo (D.R. Congo); Nisyros (Greece); Gorely (Kamchatka, Russian Federation); Turrialba (Costarica); Masaya (Nicaragua); Soufriere (Guadalupe)), ii) industrial (Augusta, Italy) and iii) rural (Ficuzza, Italy) areas.

Figure 4: The world map indicates the areas (yellow circles) sampled for this study.

The characteristics of some volcanoes sampled during this research are reported in the following paragraphs.

2.1. Etna

Mount Etna, in eastern Sicily, is one of the most active and most intensely monitored volcanoes of the planet (Bonaccorso *et al.,* 2004). It is the biggest volcano in Europe. Etna is a large 0.6 Ma old stratovolcano built upon tensional faults cutting a ≈20 km thick continental crust (Chester *et al.,* 1985), and formed after the break-up of the African plate margin during its collision with the European continental block since the Upper Miocene (Barberi *et al.,* 1974). The edifice consists of a lower shield unit overlain by a stratovolcano (Chester *et al.*, 1985). The shield complex rests discordantly on Miocene flysch to the NW and argillaceous Pleistocene sediments to the SE.

Etna’s present-day volcanic activity consists of persistent passive degassing at the summit craters and from the upper flanks as diffuse soil emanations (Allard *et al.,* 1991; Allard 1997), occasionally interrupted by lava emissions associated with paroxysmal eruptions (Bonaccorso *et al.,* 2004) (Fig. 5). These emissions result from degassing of alkali basalt-hawaiite magma which rises from a shallow mantle diapir (D’Alessandro *et al.,* 1997; Hirn *et al.,* 1997). This persistent activity makes Mt. Etna one of the most interesting volcanoes in the world. It is known as one of the largest global contributors of magmatic gases such as CO_2, SO_2, and halogens (Allard *et al.,* 1991; Allard, 1997; Bruno *et al.*, 1996; Caltabiano *et al.,* 2004; Aiuppa *et al.,* 2005).

Continuous degassing occurs mainly from the four summit craters of the volcano (Voragine, Bocca Nuova, North-East Crater and South-East Crater), while temporary emissions take place during flank eruptions, from fractures and lateral vents.

It has been proposed that the contribution of Mt. Etna to the annual global volcanic budget accounts for about 16% and 19% during active periods for heavy and alkali metals, respectively, and only for 2% and 4% in quiescent periods (Gauthier *and* Le Cloarec, 1998). The chemical composition of Etnean groundwaters has also been extensively investigated in the past (Aiuppa *et al.,* 2000, 2003b; Brusca *et al.,* 2001). The surface of Etna’s edifice lacks a real hydrographic network and waters mostly tend to seep and feed the underground circulation, the run-off coefficient being only 5%, and evapo-transpiration about 20% (Ferrara, 1975). The importance of the effective infiltration is highlighted by high outflows at the springs along the perimeter of the volcano, at the contact with the underlying impermeable sedimentary rocks especially along the coastline, where considerable amounts of water are discharged into the sea (Ogniben, 1966; Ferrara, 1975).

Figure 5: Panoramic view of south east crater during small ash emission.

2.2. Vulcano

Vulcano is an island in the south of Italy located in the Quaternary Aeolian Island Arc. La Fossa is the most recent crater in the middle of the island and it is a volcano-tectonic pull-apart structure (Ventura, 1994). La Fossa cone, formed in the last 6000 years, has passively degassing activity since the last eruption (1888-1890) through a high-temperature fumarolic field (up to 700°C) located at the northern side of La Fossa crater (Fulignatti *et al.,* 2006).

The main fumarolic species are the H_2O and CO_2 but also the acid gases (SO_2, H_2S, HCl and HF) are present in high concentrations, this characteristic indicates that the fumarolic vents are dominated by the magmatic component (Bolognesi and D’Amore 1993; Chiodini *et al*. 1993, 1995; Capasso *et al*. 1997).

SO_2 and H_2S govern the redox state of high-temperature fumarolic gases of the La Fossa volcano (Chiodini *et al.*, 1993). The fumarolic area is identified by high-sulfidation hydrothermal alteration system (Fulignati *et al*. 1998).

The fumaroles of La Fossa crater are powered by the mixture of magmatic fluids and hydrothermal fluid of marine origin that is completely vaporized in the high temperature zones of the volcanic conduit (Campostrini *et al.*, 2011).

In addition the fumaroles of La Fossa crater introduce into the surficial environment variable concentrations of numerous metallic and trace elements (mainly Pb and Bi, but also Tl, As, Se and Zn) (Fulignatti *et al.*, 2006).

2.3. Nisyros

Nisyros is an island of the South Aegean Active Volcanic arc in Greece. It is an active stratovolcano, mainly consisting of Quaternary volcanic rocks and alternations of lava flows, pyroclastic deposits and lava domes. The island covers an area of 47 Km^2 and forms a truncated cone with a base diameter of 8 km and a 4 km wide central caldera (Vougioukalakis, 1993).

The northern part of the caldera is named Lakki Plain and the southern Ramos Plain. The faults of the island have a prevailing radial pattern. There are 8 major fault zones, 157 minor faults and 105 structures (Caliro *et al*, 2004; Tibaldi *et al.*, 2008; Nomikou, 2013). No historical magmatic activity is known on Nisyros and the most recent activity was of hydrothermal character (Marini *et al.* 1993). Fumarolic emissions are located in the southern Lakki Plain and on the southeastern flank of the Lofos dome both within the caldera. Hydrothermal eruptions formed a series of hydrothermal explosion craters whose ages decrease from southeast to northwest. The last phreatic eruptions took place in 1871–1873 and 1887 partially destroying the small Lofos dome. Two deep explorative geothermal wells drilled in the Lakki plain revealed the existence of two distinct hydrothermal aquifers. The shallowest at about 500 m depth has temperatures around 150 °C while the deeper one (> 1500 m) reaches temperatures up to 340 °C (Brombach *et al.*, 2003). The fumarolic field is affected by fracturing along the main NW- and NE-trending active fault systems (Papadopoulos *et al.* 1998). All the fumaroles have temperatures close to the boiling point of water (96 – 100 °C). Their main chemical components are H_2O followed by CO_2 and H_2S, while N_2, H_2, CH_4, CO, Ar, and He are at relatively low concentrations (Chiodini *et al*, 1993, 2002; Brombach *et al*, 2001, 2003).

2.4. Nyiragongo and Nyamulagira

Nyiragongo (3469 m a.s.l.) and Nyamulagira (3058 m a.s.l.) volcanoes are located in the west rift of the East African Rift System, being a classic example of ongoing continental rifting where mafic, alkalic and ultrabasic magmatism is produced. They form part of Virunga Volcanic chain in the Democratic Republic of the Congo, north of the city of Goma.

The Nyiragongo has the summit crater of around 1.3 km in diameter and its lava has low SiO_2 content and, therefore, low viscosity. Its products are characterized by strongly alkaline and silica-undersaturated leucite, melilite and nepheline basanitic lavas (Platz *et al*., 2004).

Nyiragongo lavas are also geochemically distinct from the other volcanoes of the Virunga volcanic province in the western rift of the East African Rift system (Chakrabarti et al. 2009). Chakrabarti et al. (2009) argued that the highly sodic and potassic compositions of the Nyiragongo lavas cannot be explained by subduction-introduced fluids, instead requiring partial melting of a source with pristine mineralogy, possibly in the deep lower mantle. They also observed that the trace-element composition of these lavas precludes any continental crustal contamination and suggests sublithospheric and subasthenospheric origin.

Even if Nyamuragira is located only 15 km to the north of Nyiragongo its composition is very different and less extreme. Nyamulagira is well known for the release of large quantities of sulfur dioxide (SO_2) during its frequent effusive eruptions (Tedesco *et al.*, 2007), for example Campion (2014) reported that the cumulative SO_2 production by the 17 eruptions that occurred since 1980 to 2014 amounts to around 30 Tg, for this reasons it is considered to be one of the most effusive volcanoes worldwide (Chakrabarti *et al.*, 2009).

2.5. Copahue

Copahue (2997 m a.s.l.) is an active stratovolcano with an elliptical base, on the border between Argentina and Chile in the Andes Mountains. It is located on the southwestern rim of a volcano-tectonic depression called Caldera de Caviahue (Agusto *et al.*, 2013) and has a unique concave-down shape, resembling a Hawaiian shield volcano (Varekamp *et al.*, 2006).

A small glacier, residual of glaciation in the volcano summit during the Pleistocene time, supplies meltwater to the hyper-acidic lake (pH<1) in the eastern summit crater that is surrounded by walls of phreatic debris. The active cone consists of surge and near-vent fallout deposits, whereas the broad base consists of debris avalanches, lahars, and lava flows (Varekamp *et al.*, 2001).

Two acid hot springs (60-80 °C) are located on the eastern flank (Mangue, 1978; Martini *et al*., 1997; Varekamp *et al*., 2001, 2004; Caselli *et al*., 2005; Varekamp *et al*., 2009; Agusto, 2011) and form the upper Agrio river (pH 2–3), that flows into a glacial lake, Lake Caviahue, (pH~3) (Tamburello *et al*., 2015).

Copahue activity has been reported since the eighteenth century. Most eruptions were phreatic, with rare phreato-magmatic and sulfur pyroclastic emissions (Delpino and Bermúdez, 1993).

Hydrothermal manifestations in the northeast of the volcano (Mas *et al*., 1996; Mas *et al*., 2000; Agusto *et al*., 2013) originate from meteoric water and volcanic acid gases that boil in hydrothermal reservoir with estimated temperatures of around 250-300 °C (Ouimette, 2000; Varekamp *et al*., 2004; Agusto *et al*., 2013; Tamburello *et al*., 2015).

3. Materials and Methods

The determination of this element in most samples has presented some complication from analytical point of view, due to the low concentration of Tellurium in the environment.

The most commonly analytical techniques used to measure tellurium in natural samples presents in the literature are the following (Tab. 1): UV-visible spectrophotometry, instrumental neutron activation analysis (INAA), graphite furnace atomic absorption spectrometry (GFAAS), quartz tube atomic absorption spectrometry (QTAAS), voltammetry, hydride generation atomic fluorescence spectrometry (HG – AFS), inductively coupled plasma source atomic absorption spectrometry (ICP – AES), inductively coupled plasma mass spectrometry (ICP – MS) and sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS), Isotope Dilution Hydride Generation-Inductively Coupled Plasma-Mass Spectrometry (ID-HG-ICP-MS) (D'Ulivo,1997; El-Shahawi *et al.*, 2013; Filella, 2013; Belzilea & Chen, 2015).

Table 1: Comparison of the analytical methods in different reports (modified by Yang *et al.*, 2013)

Sample	**Measurement**	**LOD (ng/g)**	**References**
Soil and river sediment	Quadrupole ICP-MS	Not reported Te isotope unknown	Ivanova *et al.*, 2001
Rock	ID – HG – MC – ICP - MS	< 1 (^{125}Te and ^{126}Te)	Konig *et al.*, 2012
Silicate rock and soil	ICP - MS	0.5 (^{126}Te), 0.8 (^{128}Te)	Hu *et al.*, 2006
Basalt rock	ID – HG – ICP - MS	0.003 (^{125}Te and ^{126}Te)	Forrest *et al.*, 2009
Stream sediment and rock	HG – ICP - MS	1 (^{128}Te and ^{130}Te)	Hall & Pelchat, 1997
Silicate materials	ID – ORC – ICP - QMS	0.1 (^{125}Te), 0.07 (^{126}Te)	Makishima & Nakamura, 2009
Geological materials (rock, soil, deposit etc)	GFAAS	0.2	Terashima, 2001
Stream sediment, coal fly ash and garlic	Flame atomic absorption spectrometry	0.9 ng/ml	Matusiewicz & Krawczyk, 2007
Soil	SF – ICP - MS	0.17 (^{126}Te)	Yang *et al.*, 2013
Plant	SF – ICP - MS	0.02 (^{126}Te)	Yang *et al.*, 2013

For the present work each type of sample was collected and analyzed with specific techniques according to the treated matrix using the best suited analytical technique for the determination of tellurium.

3.1. Sampling methods

Trace elements are generally transported in volcanic plume as sub-micron sized particles. The plume was sampled at crater rims to avoid excessive dilution of the plume by using common filtration techniques for aerosols. Sampling was performed by pumping plume air (a mixture of gases and aerosol) in downwind direction at a rate of 4–18 L/min, for a period variable from one hour to few hours, through untreated 47-mm filter discs (Sartorius - polytetrafluoroethylene (PTFE) filter discs, pore size 0.45 μm placed inside a polycarbonate filter holder (NILU Filter Holder System, Fig. 6). This allowed solid and liquid particles to be trapped on the filter surface for successive analyses. Meteorological conditions at the summit craters of the volcanoes are extremely variable, mainly for wind speed and direction that affect the plume dilution by atmospheric air during the sampling. All the samples were collected during days that optimal weather conditions occurred, mainly in dry summer periods, following some criteria (Calabrese *et al*. 2011): no excessive humidity and no rain that could damage the filter, wind speed and direction suitable to perform the sampling in downwind sites with respect to the plume and sufficient sampling-time to accumulate enough particulate onto the filters. However, it was not always possible to find the appropriate weather conditions and many of the collected filters were discarded (e.g. too low amount of TSP or wet filters after the sampling due to high humidity).

Atmospheric SO_2 concentration was simultaneously determined by collecting the plume air through three base-treated filters in series previously impregnated with a solution 1 N NaOH (Aiuppa *et al*. 2002; Wittmer *et al*. 2014).

After the sampling, the filters were sealed in plastic bags and stored in the refrigerator until the analysis. The filters are weighed before and after the exposure to volcanic plume.

The atmospheric deposition was sampled with rain gauge collector. The collectors were installed on the down-wind at different distances from the main volcanic vents, from within the crater (Vulcano Island) or on the rim of the crater (Nyiragongo and Etna) up to distances of tens of km. To define the local atmospheric background, some collectors were installed in a site up-wind, in an area poorly affected by volcanic emissions.

Figure 6: Common filtration techniques for aerosols.

The samples were taken after a time period the allowed the collection of a volume of water sufficient for all analyses which varied, depending on the rainfall intensity of the area, from 1 to 15 days. The design and installation of the collectors conformed to EMEP (European Monitoring and Evaluation Programme) site requirements for precipitation gauges. The rain gauges used were bulk collectors which remained open during the whole sampling period, thus receiving both wet and dry deposition (Figs. 7-8). They were composed of a funnel and a polypropylene (PP) bottle. The funnel (Büchner type, Ø 240 mm) can be separated in two pieces for easy and total cleaning. A sheet of filter paper (DP-400–240 – basis weight: 80±3 g m^{-2}; thickness: 0.180–0.190 mm; retention of particles: 35–40 lm) was put inside the funnel, and a HDPE disc was inserted between the filter paper and the perforated Büchner plate to avoid clogging of the holes. The filter-system (perforated plate, HDPE disc and filter paper) excluded a prolonged interaction between sampled rainwater and coarse particulate, and minimized evaporation. All the equipments were washed with a 2% nitric acid (Merck Suprapur) solution, and then rinsed several times with de-ionized (MilliQ) water, dried under hood, packed in double clean plastic bags, and zipped until exposure in the field. Disposable plastic gloves were used whenever working with samples and sampling equipment. At the end of the sampling period, the sampling bottle was capped and transported in the laboratory for analysis.

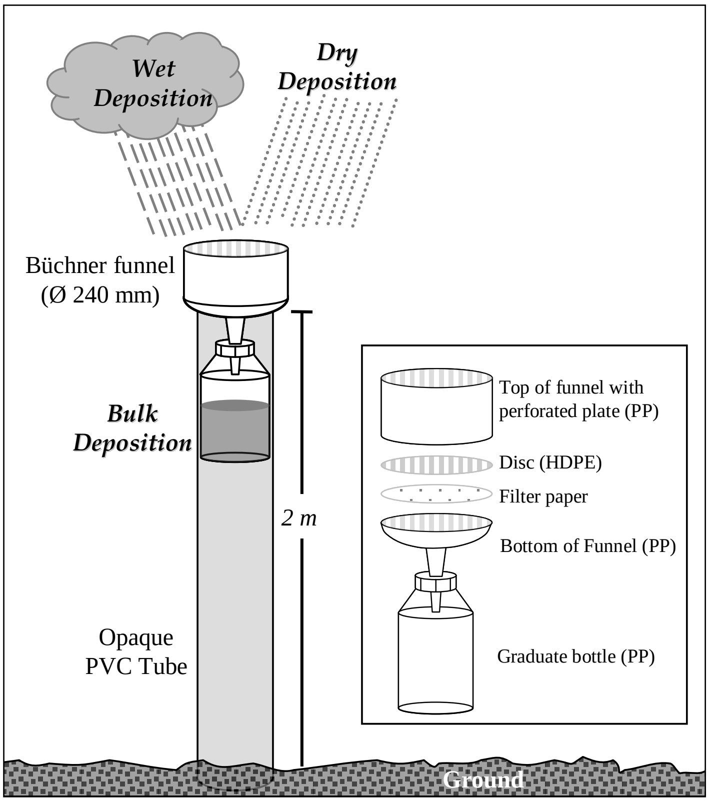

Figure 7: Scheme of rain gauges for bulk deposition sampling; in the inset shows the filter-system.

Figure 8: Collectors installed for the bulk deposition sampling.

The Volcanic ash samples were taken immediately after the eruptive activity. It was collected a sample for each paroxysmal event, except for the ashes erupted from San Miguel (El Salvador), in this case two samples were taken, on the crater rim and in the valley.

The samples, waiting to be analysed, were kept in tightly sealed plastic bags so as to avoid external contamination. Some of the samples were sieved through standard sieves to measure the distribution of the grain size, while leaching experiments were performed later on each grain size class.

Leaves of vegetation and soils were also collected in the volcanic areas, the sampling occurred at different distances from the active volcanic vents and some samples were collected outside the volcanic area as local background. The soils, meaning the first centimeter of topsoil, were collected at Nysiros near the plants (Fig. 9).

At each volcanic system at least one plant species was chosen and collected on the widest possible area around the volcano. At the end many different plant species were sampled and only rarely one species was sampled in more than one volcanic system. When possible, one endemic species and one general species were chosen. At each sampling site, a composite sample was obtained from plants growing in an area of about 25 to 100 m^2 depending on the species. For trees branches from different sides of the tree and from at least three plants were collected. The branches were air-dried; the leaves or needles were subsequently hand-picked and further dried in an oven at 40 °C for about two days. The pine needles were separated into years of growth. For small plant species leaves were hand-picked directly in the field and subsequently oven-dried at 40 °C in the laboratory.

Also in this case the sampling and storage of the samples were carried out avoiding contaminations.

A separate description is made for the use of moss bags as bioindicators through their accumulation of trace elements. The mosses used were a mixture of Sphagnum species (*Sphagnum fuscum* and *Sphagnum tenellum*), picked in a rural forest close to Gothenburg (Sweden).

Figure 9: Sampling of soil and plants

The moss bags, covered and uncovered and positioned on a stake about a meter from the ground, were left in different parts of Nisyros (Greece) for 10 days and Nyiragongo (D.R. Congo) for 3 or 35 days (Figs. 10-11).

Before exposure the mosses have undergone a pre-treatment: they were rinsed several times with deionized water and dried at room temperature in a fume hood. Finally 2g of prepared moss was packed in the containers were made from a nylon net (2 mm mesh size).

Figure 10: The moss bags used as bioindicator

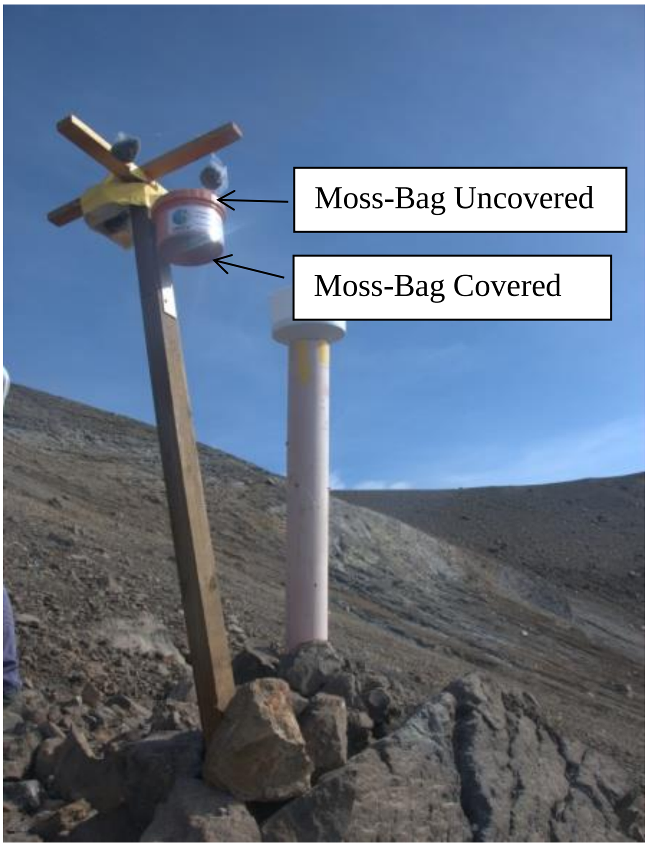

Figure 11: The figure shows how the convered and uncovered moss-bags have been positioned.

3.2. Methods of Analysis

3.2.1. Analyses of Volcanic Aerosol

The particles trapped on filters, inside a Teflon vessel, were totally dissolved in a mixture of strong acids (HNO_3, HF, $HClO_4$ – 3:1:1) by a microwave oven. Subsamples of the filters collected with the high volume air sampler were leached with 50ml of milliQ water (>18.2MΩ) for 4 h, constantly stirring to dissolve all the soluble part of the collected particulate. The mineralized solutions and the leachates were analysed for both major elements with ICP-OES (Jobin Yvon Ultima2) and trace elements, including Tellurium, with ICP-MS by using an Agilent 7500ce instrument. The absolute concentrations were corrected for filters blanks and normalized to the sampled volume ($\mu g/m^3$).

3.2.2. Analyses of Atmospheric bulk deposition

The collected water samples were split into sub-samples. One unfiltered aliquot was immediately taken for the determination of pH and conductivity (ISO 10523; ISO 7888), and a sub-sample was stored for silica determination. Subsequently, three aliquots were filtered using cellulose acetate filter with 0.45 μm pore size (Sartorius, Minisart®), to remove any solid material and to stabilise the solution for the subsequent analysis. One filtered aliquot for major anions (F^-, SO_4^{2-}, Cl^-, NO_3^-) were stored, and the sub-samples to be used for the determination of major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and trace elements were acidified by the addition of 100 µl of HNO_3 (Ultrapure, MERK) to each 50 ml of sample. The samples were stored dark and refrigerated (4°C) until analysis.

3.2.3. Analyses of ash leachates

The soluble fraction in the ash is calculated in the bulk e/o in the different grain sizes. During the leaching procedures, aliquots of 1 g of ash were eluted in 25 ml of deionised water for 2 hours with constant agitation, following the method proposed by Witham *et al.* (2005). The supernatant was subsequently centrifuged at 3500 rpm for 15 min, and filtered through 0.45 μm filters (Sartorius, Minisart®). A part of solvent (15 ml), acidified with 100 µl HNO_3, Ultrapure MERK, was used to determine the concentrations of trace metals (including tellurium), obtained by ICP- MS, an other aliquot was analysed by ion chromatography (IC) for major Cations and Anions. The samples were stored dark and refrigerated (4°C) until analysis.

3.2.4. Analyses of Soil Samples

All soil samples were dried at a temperature of about 40 °C. An aliquots of samples (500 mg) were used to determinate the soluble fraction with deionised water (50 ml), see ashes above for the procedure and analyses, and the pH was determined. Other aliquots were powdered in an agate mortar, a part the powder (0.25g), using HNO_3 +

HCl (2:1), closed microwave digestion, were extracted in order to determine the near-total composition. All the solutions were analysed, after appropriate diluition, by inductively plasma spectrometry (ICP-MS).

3.2.5. Analyses of Vegetation Samples

The leaves samples, including the mosses tissues, were dried and were completely powdered by planetary ball mills, agate jars and disposable gloves were used to avoid metal contamination. An aliquot of the powder was dried at 40 °C for 24 h, and about 250 mg of each homogenized sample were mineralized for 60 min by Closed Vessel Acid Digestion in a microwave oven (CEM MARS Xpress) using Teflon vessels with 3 mL concentrated HNO_3 (ultrapure grade 65%), 2 mL H_2O_2 (ultrapure 39%) and 5 mL milliQ-water. Control samples were added to each batch of samples as follows: at least four certificate reference materials (CRM), three replicates of one random sample and one method blank (acid solution without any powder). Digestates were further diluted with milliQwater up to a total volume of 50 mL and analyzed by ICP-MS (Agilent 7500-ce) and ICP-OES (Jobin Yvon Ultima2). Method blank values were subtracted from the raw concentrations of all samples.

3.3. Tellurium determination by ICP - MS

All the samples, after the leaching to evaluate the soluble fraction and/or the mineralization for tellurium bulk composition, were analysed by inductively coupled plasma mass spectrometry (ICP-MS).

The analysis of this element showed different problems caused by its low concentrations.

The first problem is that the Tellurium has a high first ionization potential (9.009 eV), so it has a lower sensitivity compared to sensitivities of other elements having low first ionization energy (Fig. 12).

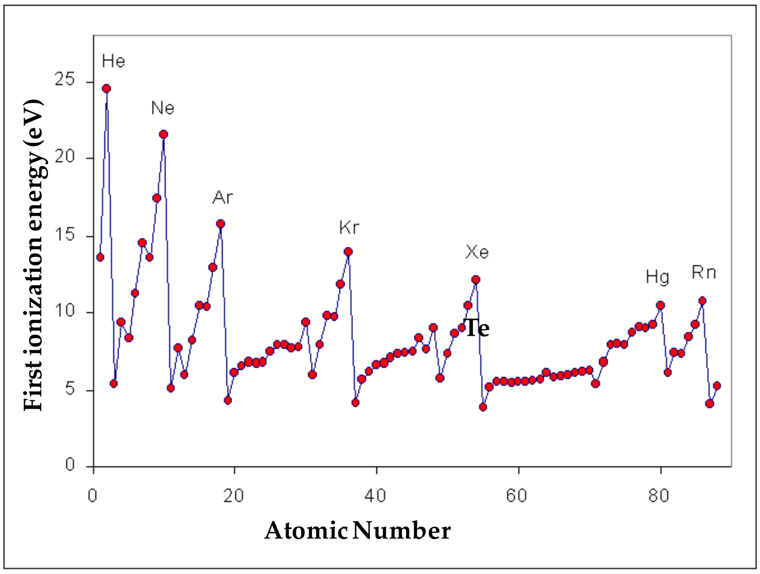

Figure 12: The diagram shows the First ionization energy respect the Atomic Number of the elements.

The second problem is the Isotopes Interference that did not permit the use of Tellurium isotopes with higher abundance for the analysis. Tellurium has eight stable isotopes, namely: ^{120}Te (0.09 %), ^{122}Te (2.55 %), ^{123}Te (0.89 %), ^{124}Te (4.74 %), ^{125}Te (7.07 %), ^{126}Te (18.84 %), ^{128}Te (31.74 %), and ^{130}Te (34.08 %).

The table 2, that reported the data of Yang *et al*., 2013, highlights that the two Tellurium isotopes with the highest abundance (> 31 %), ^{128}Te and ^{130}Te, have serious isobaric interferences from ^{128}Xe (1.92 %), ^{130}Xe (4.08 %) and ^{130}Ba (0.106 %). It has been reported that background signal intensities at m/z 128 and 130 caused by the impurities of ^{128}Xe and ^{130}Xe in ultra-pure argon gas are significantly high, seriously deteriorating the determination of nanogram levels of Tellurium using ICP-MS (Yang *et al*., 2013).

Although the extent of interferences decreased with the increase of Tellurium concentration, the Xe interferences can still be observed even at a concentration of 1 µg/l. Thus, ^{128}Te and ^{130}Te were excluded for further investigation. The use of ^{120}Te, ^{122}Te, ^{123}Te and ^{124}Te is hampered by their low abundance (0.09 % - 4.74 %) and isobaric interferences from Sn, Sb and Xe. These six Tellurium isotopes (^{120}Te, ^{122}Te, ^{123}Te, ^{124}Te, ^{128}Te and ^{130}Te) are thus unsuitable for trace level Tellurium analysis by ICP-MS. The two remaining isotopes, ^{125}Te and ^{126}Te have a sufficiently high abundance (7.07 % and 18.84 %, respectively). In addition, ^{125}Te has no isobaric interference, and the isobaric interference from ^{126}Xe is not significant for ^{126}Te due to the low abundance of ^{126}Xe (0.09 %).

Table 2: Isobaric interferences of Tellurium isotopes (modified by Yang *et al.*, 2013)

Isotopes	Abundance (%)	Interference	Abundance (%)
^{120}Te	0.09	^{120}Sn	32.58
^{122}Te	2.55	^{122}Sn	4.63
^{123}Te	0.89	^{123}Sb	42.79
^{124}Te	4.74	^{124}Sn, ^{124}Xe	5.79, 0.09
^{125}Te	7.07		
^{126}Te	18.84	^{126}Xe	0.09
^{128}Te	31.74	^{128}Xe	1.92
^{130}Te	34.08	^{130}Xe, ^{130}Ba	4.08, 0.106

The third problem is the Polyatomic Interference: the major polyatomic interferences are from the Ar-associated interferences, such as ^{87}Sr^{38}Ar^{+}, ^{87}Rb^{38}Ar^{+}, ^{89}Y^{36}Ar^{+}, and ^{85}Rb^{40}Ar^{+} for ^{125}Te analysis, and ^{88}Sr^{38}Ar^{+}, ^{86}Sr^{40}Ar^{+}, ^{90}Zr^{36}Ar^{+}, and ^{86}Kr^{40}Ar^{+} for ^{126}Te analysis. The m/z of these Ar-associated polyatomic interferences is slightly smaller than the m/z of ^{125}Te and ^{126}Te. The table 3 (Yang *et al.*, 2013) reported the major polyatomic interferences on ^{125}Te (*m/z* 124.90444) and ^{126}Te (*m/z* 125.90331) analyses.

Table 3: Polyatomic interferences of Tellurium 125 and 126 (modified by Yang *et al.*, 2013)

Potential interferences for ^{125}Te	**Mass**	**Abundance of former isotope**	**Abundance of latter isotope**	**Resolution m/Δm**
^{87}Sr^{38}Ar	124.87162	7.0015	0.0632	3806
^{87}Rb^{38}Ar	124.87191	27.8346	0.0632	3840
^{89}Y^{36}Ar	124.87341	100.0000	0.3365	4025
^{85}Rb^{40}Ar	124.87418	72.1654	99.6003	4128
^{109}Ag^{16}O	124.89966	48.1608	99.7628	26131
^{107}Ag^{18}O	124.90426	51.8392	0.2000	693914
Potential interferences for ^{126}Te				
^{88}Sr^{38}Ar	125.86835	82.5845	0.0632	3601
^{86}Sr^{40}Ar	125.86165	9.8566	99.6003	3022
^{90}Zr^{36}Ar	125.87226	51.4520	0.3365	4055
^{86}Kr^{40}Ar	125.87299	17.29835	99.6003	4152
^{109}Ag^{17}O	125.90388	48.1608	0.0372	220883

All the samples collected for this thesis were analysed for both ^{125}Te and ^{126}Te isotopes which, although less abundant, should be subject to less isobaric and polyatomic interferences. From various tests on different matrices a good correlation between the two isotopes (Fig. 13) supporting the fact that no significant isobaric and polyatomic interference affects the analyses. Due to the fact that ^{125}Te tends to be slightly overestimated, especially at low concentrations, tthe results of the most abundant ^{126}Te have been chosen (Fig. 13). The limit of quantification for undiluted low salinity water samples has been 10 ng/l.

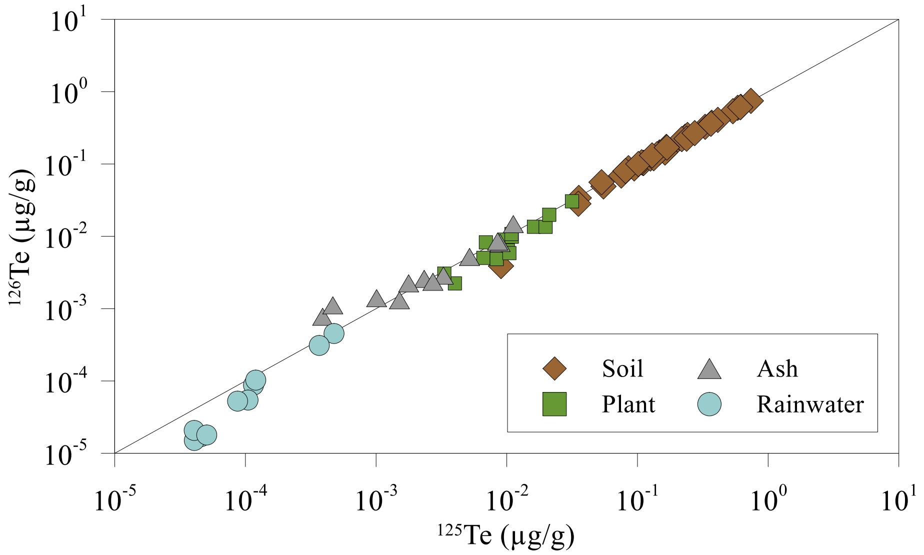

Figura 13: Correlation between ^{125}Te and ^{126}Te in samples of soil, plant, ash and rainwater.

The validation of measurements is usually done checking the recovery of the element analysing certified reference materials (CRM). Unfortunately we did not have any CRM for which tellurium concentrations were certified. For the analyses of plants and soils, 6 CRM (3 for soils and 3 for plants) were used finding good agreements (within ±15%) for almost all certified elements. These results indicate a good quality of the whole sample preparation procedure at least for the certified elements. Three of the CRM were determined also for Te in previous studies and were found on GEOREM database (http://georem.mpch-mainz.gwdg.de/). The results of the present analyses of the CRM gave low concentration values for Tellurium (0.0075 to 0.021 µg/g). For two of them (GBW7603 and 7604) the results are very different (20-46%) from that found on GEOREM. These data are taken from a paper written in Chinese (Li Yan-xiang *et al.*,

2010) so it was impossible to compare the analytical methods. For one other (GBW7605) the values obtained in the present study range from 0.0088 to 0.0115 µg/g (4 replies) which is 68-88% of the value reported by Rodushkin *et al.* (2008). The small negative difference could be due to the fact that Rodushkin *et al.* (2008) used a mixture of acids with HF for the mineralization of their samples and CRMs which is more effective in the dissolution of some mineral phase with respect to the mixture used in this study and analysis were performed with ICP-SFMS that is more sensitive with respect to ICP-QMS.

4. Results

4.1. Volcanic Aerosol

Aerosol is defined as a suspension of fine solid or liquid particles in a gas (Mather *et al.*, 2003).

The volatile elements that are released by volcanic degassing, during and between eruptions, take part in the major geochemical cycles involving the lithosphere, hydrosphere, atmosphere and biosphere (Holland, 1984; Arthur, 2000) and contribute to atmospheric chemistry by increasing the amount of reactive and greenhouse gases and aerosols.

The volcanic degassing occurs through a plume, being a mixture of particles and gas emitted by volcanoes directly by the magma, or by fumaroles that are the main expression of the presence of hydrothermal systems.

The most abundant volcanic gases are water vapor followed by carbon dioxide, sulfur dioxide, hydrogen sulfide, hydrogen chloride and hydrogen but also in many trace elements including alkali, alkali-earth, transition and heavy metals (Zoller *et al.*, 1974).

Magma evolution then partitions volatiles between the crust and the atmosphere/hydrosphere via degassing and eruption and the trace elements are degassed as halides, sulphates, sulphides and/or metals, and are usually in the aerosol phase of the airborne plume (Gemmell, 1987; Symonds *et al.*, 1987; LeGuern, 1988; Hinkley, 1991; Symonds *et al.*, 1994; Moune *et al.*, 2010).

Volcanic degassing depends on the degree to which gas–melt separation proceeds and the gas leaves the magma, indeed it begins with the expulsion or exsolution of volatiles from the melt and formation of gas bubbles. The expansion of bubbles of gas accompanying decompression of magmas conditions the over-pressuring of magmatic systems, in their dynamics and in eruption style. The state of the system conditions the partitioning of volatiles into the vapor phase (Oppenheimer, 2003):

- if the degassing is closed the exsolved vapor, does not leave the melt;
- if the degassing is open the separated gas phase produced at each stage in the magma body, is expelled into country rock (possibly through a hydrothermal system) or directly, via the magmatic plumbing system, to the atmosphere.

Volcanic emissions are considered one of the major natural sources of several trace elements, including Tellurium, into the atmosphere. Nevertheless, estimates of global volcanic fluxes, both for major and trace elements vary widely. These uncertainties depend on the large variability in the emission of the different volcanoes, and on their changing stage of activity (eruptive or non-eruptive periods). Mather *et al.*, (2003) confirmed the difficulty to provide accurate estimates of the global volcanogenic budget of trace elements injected into the atmosphere.

4.1.1. Volcanic Aerosol Results

In this study 70 samples of volcanic plume and fumaroles were collected by using filtration techniques. They were sampled at the summit vents of 11 differents volcanoes: Etna and Vulcano (Italy); Turrialba (Costarica); Myake-jima, Asama and Aso (Japan); Mutnovsky and Gorely (Kamchatka, Russian Federation); Copahue (Argentina); Nyamuragira and Nyiragongo (D.R. Congo). Thus the existing worldwide database regarding the concentration of Tellurium in volcanic plume has increased significantly.

The concentrations of Tellurium detected vary from <0.003 to 0.15 µg/m^3 (Fig. 14). The values of concentrations present a wide-ranging variability due to many factors: the differents distances of the sampling points from the active vents; the variable meteorological conditions, such as the direction and intensity of the wind and the relative humidity, which both influence the degree of dilution of the plume; the different stage of volcanic activity, which may condition the output rates of trace species, and the relative contribution from erosive and gas-to-particle conversion processes; heterogeneity between the active vents in different volcanoes but also in the same volcano. For these reasons the data are not directly comparable, for example the highest concentrations of Tellurium were found at Mount Etna, an open conduit volcano, on the rim of the Bocca Nuova Crater (BNC), 0.15 µg/m^3, and at Mutnovsky, 0.14 µg/m^3, where the sampling occurred within a fumarolic field with temperatures around 700°C. Instead the value reported at Gorely is low because the sample was collected about a 1 km far from the rim. Nevertheless all the obtained values are one/two order of magnitude greater than the atmospheric background (<0.001 µg/m^3) indicated from Belzilea & Chen (2015).

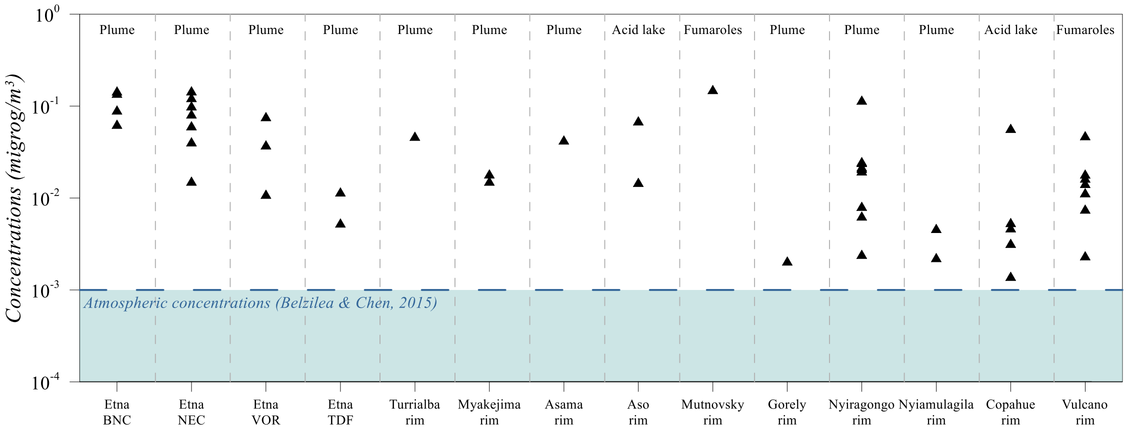

Figure 14: The diagram reports the data obtained for this study regarding the concentrations of Tellurium (µg/m^3) measured during the emission of different volcanoes.

To better understand the plume composition, Tellurium concentrations of Etna, Nyiragongo and Vulcano are here presented among with all the major and trace elements investigated (Figs. 15, 16 and 17). In the plume of Nyiragongo and Nyamulagira (Fig. 16) the most abundant metals are Na, Si and K, the same is for the Etna (Fig. 15) with the addition of Mg, Ca, Al, Fe and Ti. These elements constituite about 98% of the total particulate abundance and they are the main constituents of basaltic rocks, so reflecting the magma composition. Their abundances on filters indicate the presence of small ash fragments in the plume, which derive from rock fragments eroded from the vent walls, and juvenile fragments of the magma, including glass and silicate minerals (Gauthier *and* Le Cloarec, 1998; Aiuppa *et al.*, 2003a; Mather *et al.*, 2003). Being Vulcano island a high-temperature hydrothermal system volcano, without an open conduit, these elements, representative of the silicatic particles contribution, show lower relative concentrations with respect to the other three open conduit volcanoes (Fig. 17).

Minor and trace elements account for about 2% of the total particles budget. The relative abundances of Tellurium is around 0.01% of the total.

Basing on the vapor-phase transport of the elements in the plume system, they can be divided into volatile (e.g. Te but also Se, Cd, Tl, Sb, As, Cu) and non-volatile (e.g. U, Th, Cs, La, Rb, Ba) elements. The non-volatile are lithophile elements with a refractory behaviour because of their strong affinity for the silicate melt, even at low-pressure and high-temperature. In contrast, volatile elements are thought to be extensively partitioned into the gas phase during high-temperature magmatic degassing, likely because of their strong affinity with the degassed S and halogens (Aiuppa *et al.*, 2003a). Therefore Tellurium, being a volatile element, tends to be concentrated and enriched into the aerosol phase (respect to the parental magma) and in all three volcanoes it presents a lower variability (around one order of magnitude) with respect to the other elements.

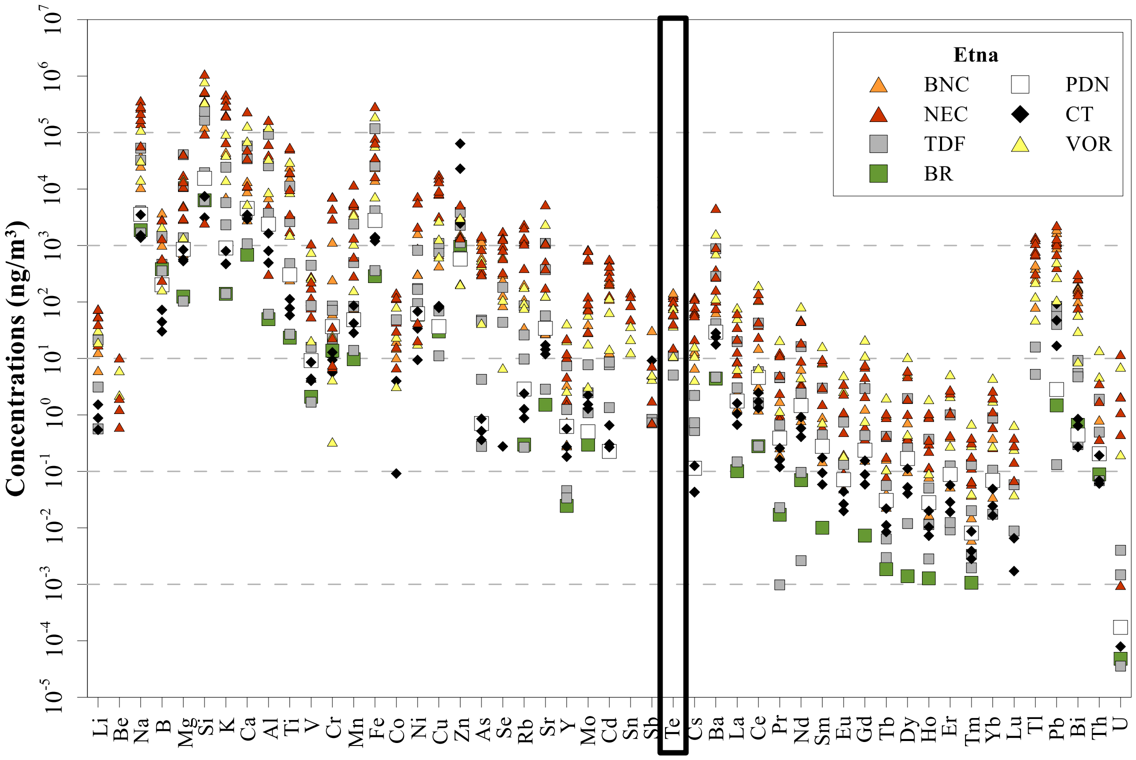

Figure 15: Diagram shows the volcanic aerosol concentrations for Etna volcano. Tellurium is indicated with the rectangle. In the legend BNC is Bocca Nuova Crater, NEC is North East Crater, TDF is Torre del Filosofo (≈1,25 km from the craters), BR is Bosco Ragabo(≈8.7 km from the craters), PDN is Pizzi de Neri(≈2.5 km from the craters), CT is Catania city, VOR is Voragine Crater. Br, PDN and CT were all below the quantification limit for Te (<0.003 μg/m^3).

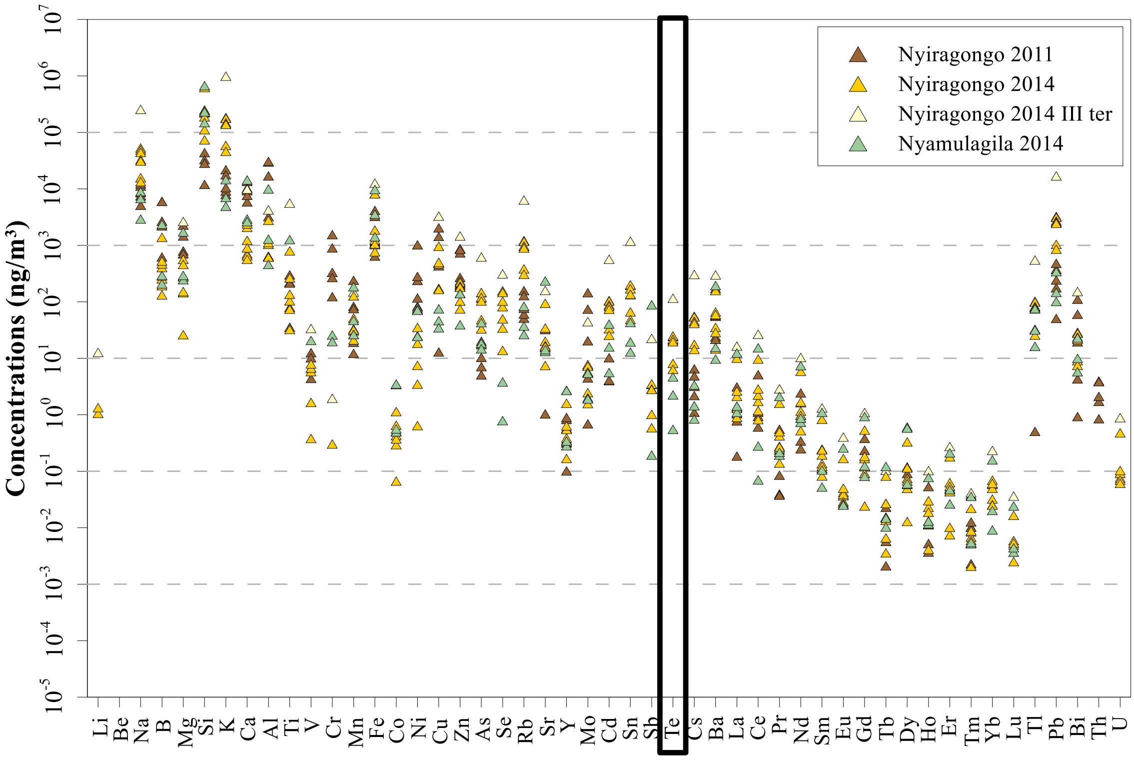

Figura 16: Diagram shows the aerosols concentrations in Nyiragongo and Nyamulagira plume, collected during the fieldtrips on the 2011 and 2014. Nyiragongo III ter indicates a particular sample collected very close to the lava lake surface, less than 0.1 km.

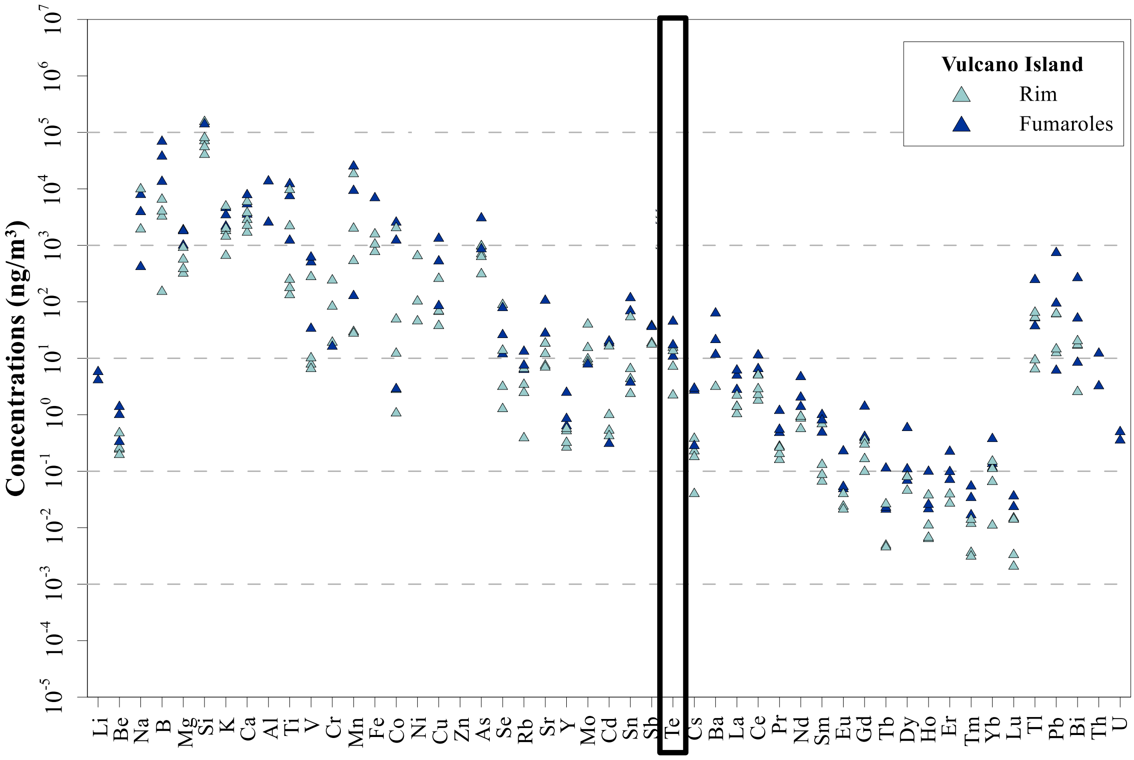

Figura 17: Diagram shows the volcanic emissions concentrations within the fumarolic field and somewhat further away on the rim of la Fossa crater at Vulcano Island.

In the binary plot of figure 18, Tellurium is correlated with other volatile elements (Tl, Pb, Rb, Cu). Together with the new results, data from previous studies, reported in the table 4, are plotted. Taking Etna as a case study, the concentrations of tellurium measured in the proximity of the craters, Bocca Nuova Crater (BNC) and North East Crater (NEC), are higher than samples taken at a greater distance from the craters, Torre del Filosofo (TDF), but although varying in absolute values, they show generally good linear correlations.

Table 4: Concentrations of Tellurium indicated in previous studies.

Site	Concentration of Tellurium (μg/m^3)	References
Atmospheric background	< 0.001	Belzilea & Chen, 2015
Etna (Italy)	0.001 – 0.089	Aiuppa *et al.*, 2003
Kilauea (USA)	0.001 – 0.134	Mather *et al.*, 2012
Masaya (Nicaragua)	0.11 – 0.19	Moune *et al.*, 2010
Stromboli (Italy)	0.005 – 0.02	Allard et al., 2000

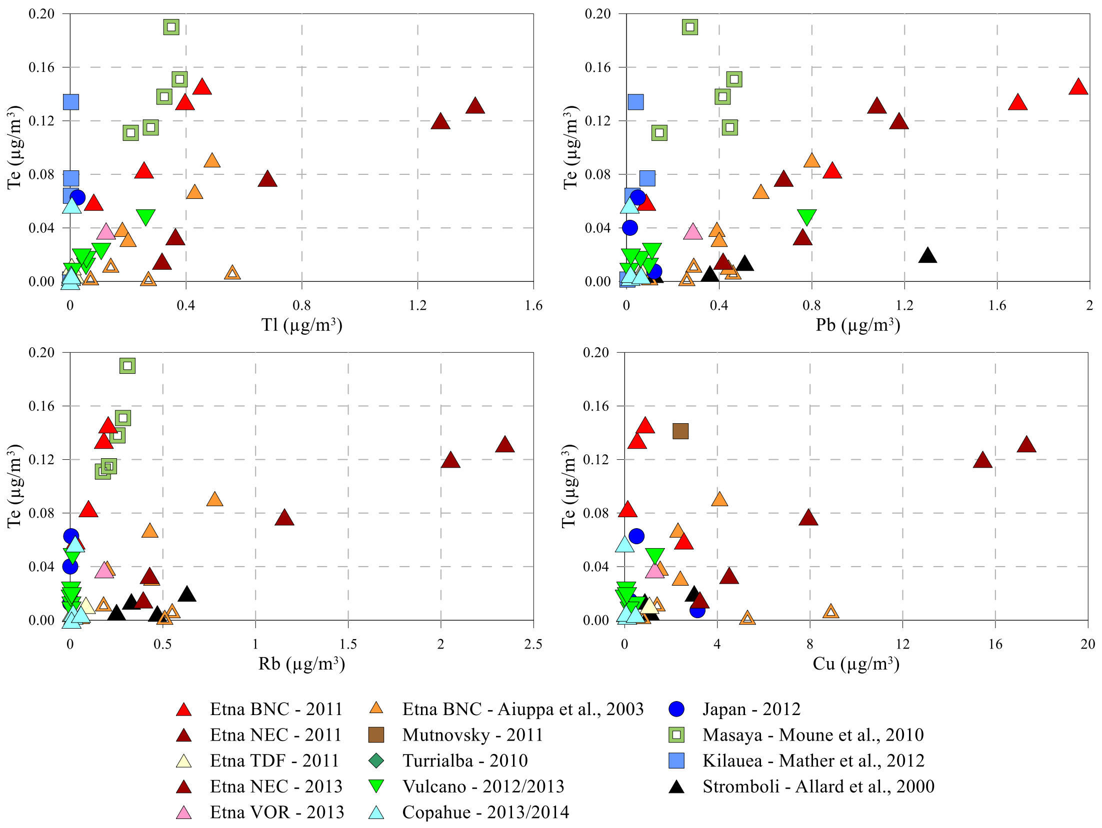

Figure 18: Linear Correlation of concentrations of Tellurium with other elements in volcanic aerosol in different volcanos. Together with the results of this study, data from literature are plotted (see legend).

4.2. Atmospheric deposition

4.2.1. Atmospheric Deposition - Rain

The atmosphere is a thin layer of gases surrounding our planet that protects and assures the life on Earth. Gases and particles in the atmosphere fall on the surface via Atmospheric Deposition that consists in: Wet Deposition, the flux of dissolved components from the atmosphere (rain, snow, hail, fog); Dry Deposition, the flux of gases and particles falling down from the atmosphere in the absence of precipitation, it also includes the fallout of particles and mineral dusts (Al, Si, Ti), sea salts (Na, Cl), organic particles (pollen and spores), soot including vegetation fires (C, As, Cr, Cu, Pb, V, Zn), industrial smog (ammonium sulphate and nitrate). Through the Dry deposition the atmospheric gases interact with any kind of surface (rocks, soil, leafs, water bodies, etc). The sum of wet and dry deposition is called Bulk Deposition, which is the total flux of dissolved components from the atmosphere in open field with precipitations, combined with dry removal of particle and gas to the ground.

The atmosphere is an oxidizing environment and many important reactions occur in water droplets of cloud and rain; enormous quantities of airborne compounds, such as organic substances, Fe(II), SO_2, and nitrogen oxides, are oxidized by oxidants, such as oxygen, OH- radicals, H_2O_2, and Fe (III) dissolved in water droplets. Moreover, the atmosphere is an important conveyer belt for many pollutants, sensitive to natural and/or anthropogenic disturbances (e.g. big volcanic eruptions, industrial emissions, etc.) because it represents a smaller reservoir with respect to lithosphere and hydrosphere.

The atmospheric water plays a very important role in the water cycle considering that the average residence time of water vapour in the atmosphere is about 11 days (Berner *and* Berner, 1996). This rapid turnover is very important for the removal of atmospheric pollutants that are washed out by rain.

The composition of rain reflects the acid-base titration that occurs in the atmosphere; the water phase promotes oxidation reactions, such as the oxidation of SO_2 to H_2SO_4.

Aerosol particles, which generally consist of $(NH_4)_2SO_4$ and NH_4NO_3, can form the nuclei for the condensation of liquid water; particle diameters range from 0.01 µm up to a few hundred micrometers. Water droplets (10 - 50 µm in diameter) condense on aerosols particles and can dissolve gases such as CO_2, SO_2, and HCl, which contribute to the acidity of the droplet, and NH_3 that neutralizes mineral acids and buffers the solution phase. When the droplets become big enough, about 1 mm, they can fall as raindrops. In conclusion, it is possible to distinguish two different mechanisms of chemical enrichment of wet deposition from the atmosphere: rainout wich refers to in-cloud scavenging and washout to below-cloud scavenging by falling rain or snow.

Atmospheric deposition processes (wet and dry) provide the pathways through which volcanic volatiles emitted into the atmosphere return to the ground. In fact, acid gases and trace metals, once redeposited on the ground, can be fixed in the soil or taken up by plants, and can have both harmful and beneficial effects (Baxter *et al.,* 1982; Delmelle *et al.,* 2002). The detrimental effects are generally either mediated through acidification of soils (Parnell, 1986; Parnell *and* Burke, 1990; Delmelle *et al.,* 2002; Floor *et al.,* 2008) or by direct fumigation of vegetation (Johnson *and* Parnell, 1986; Stoiber *et al.,* 1987; Notcutt & Davies, 1989; Varrica *et al.,* 2000; Delmelle *et al.,* 2002; Bellomo *et al.,* 2007; Watt *et al.,* 2007; Martin *et al.,* 2009). Nevertheless volcanic activity has been shown to have also a fertilizing effect on the environment (Frogner *et al.,* 2001, 2006). Finally, volcanogenic output may enter into the hydrological cycle and contaminate aquifers (Aiuppa *et al.,* 2000, 2003b; Brusca *et al.,* 2001; Flaathen *et al.,* 2007).

4.2.1.2 Atmospheric Deposition – Rain Results

This study reports the first data regarding the tellurium concentrations in rainwater in volcanic areas. The samples of rain were collected at three different volcanoes: Vulcano Island (Italy), Mount Etna (Italy) and Nyiragongo (D.R. Congo) (Tab. 5). In total the samples of rain collected and analysed have been approximately 100.

At Vulcano Island the rain was collected between April and June 2012 at three different points: within the crater in the fumarolic field and on the rim of “la Fossa” and at the volcanological observatory “Marcello Carapezza” of the INGV, more distant from volcanic emissions and close to the sea (Fig. 19).

Table 5: Information about the rainwater sampling sites

Site	ID	Volcano	Coordinates UTM			Altitude	Distance from Craters	Period	Number of samples	Expos.
			Zone			m (a.s.l)	Km			
Torre del Filosofo	TDF	Mount Etna (Italy)	33 S	4176659	500009	2905	1,25	2006 2007	7	down-wind
Citelli	CIT	Mount Etna (Italy)	33 S	4180074	504769	1750	5,54	2006 2007	4	down-wind
Casa del Vescovo	CDV	Mount Etna (Italy)	33 S	4172356	502202	1705	6,49	2006 2007	1	down-wind
Intraleo	INT	Mount Etna (Italy)	33 S	4175104	492873	1510	7,30	2006 2007	3	up-wind
Zafferana	ZAF	Mount Etna (Italy)	33 S	4173454	508202	862	9,86	2006 2007	1	down-wind
Crater of "La Fossa"	Crater	Vulcano Island (Italy)	33 S	4250840	496630	273	0,10	2012	3	down-wind
Rim of "La Fossa"	Rim	Vulcano Island (Italy)	33 S	4250707	496872	319	0,50	2012	3	down-wind
“Marcello Carapezza” Center	INGV	Vulcano Island (Italy)	33 S	4252094	495816	18	3,00	2012	3	up-wind
Rim west direction	Rim	Nyiragongo (D.R. Congo)	35 M	749706	9831499	3425	0,30	2011 2014	8	down-wind
Rim est direction	Rim base	Nyiragongo (D.R. Congo)	35 M	750384	9830975	3416	0,50	2014	7	up-wind
Rusayo	Rusayo	Nyiragongo (D.R. Congo)	35 M	741189	9824066	1667	10,00	2014	14	down-wind
Bulengo	Bulengo	Nyiragongo (D.R. Congo)	35 M	735761	9821214	1569	16,00	2014	9	down-wind
Kingi	Kingi	Nyiragongo (D.R. Congo)	35 M	728788	9835096	1821	23,00	2014	12	down-wind
Kibumba	Kibumba	Nyiragongo (D.R. Congo)	35 M	759353	9833619	2016	9,50	2014	24	up-wind
Goma	Goma	Nyiragongo (D.R. Congo)	35 M	747781	9813923	1533	17,40	2014	4	up-wind

Due to field logistic problems, only one sample of rain was taken at the summit crater of Nyiragongo (D.R. Congo) in December 2011. The second field trip, held from October to December 2014, a network of 7 pluviometers were installed on the crater rim and on the lower flank of the volcano at different distances from the crater.

The sampling sites at the rim were two: one positioned at the base camp, less affected by the plume, and one on the rim in the west direction with respect to the base camp

The other sites were close to the villages positioned down-wind, Rusayo, Bulengo and Kingi, marked by red triangles in figure 20 and the villages positioned up-wind, Kibumba, and the city of Goma (blue triangles in the figure) in which therefore the interaction with volcanic gases should be minimal or very rare.

Figure 19: Map of Vulcano Island (Italy). The triangules indicate the points where the collectors were positioned: within the crater and on the rim of “la Fossa” (down – wind) and at the volcanological observatory “Marcello Carapezza” of the INGV (up-wind).

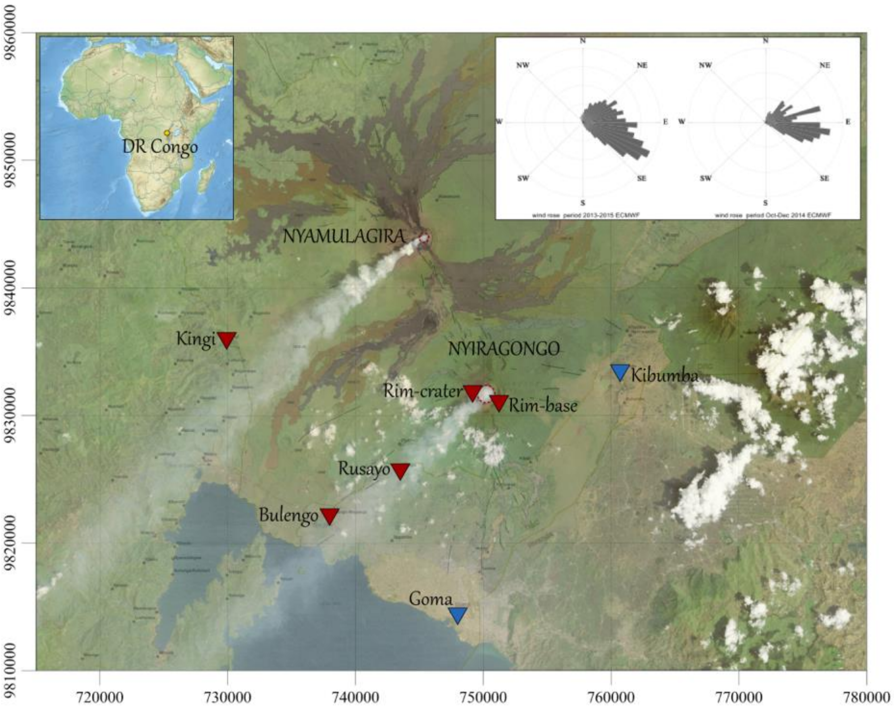

Figure 20: Map of Nyiragongo (D.R. Congo). The red Triangules indicate the sampling point in down – wind, while the blue triangules report the position of the collector in up – wind with respect to the summit craters.

Atmospheric deposition was monitored at Mt. Etna for about 2 years, in 2006 and 2007. The sampling sites of Mt. Etna were collected at five rain gauges at various altitudes around the summit: Torre del Filosofo (TDF), Citelli (CIT), Casa del Vescovo (CDV), and Zafferana (ZAF) are on the eastern flank, down-wind with respect to the summit craters, in the prevailing plume direction; Intraleo (INT), the up-wind site, defined the local atmospheric background, being on the western flank, in a rural area insignificantly affected by volcanic or anthropogenic emissions. A small selection of these samples was chosen to determine tellurium concentrations (Fig. 21).

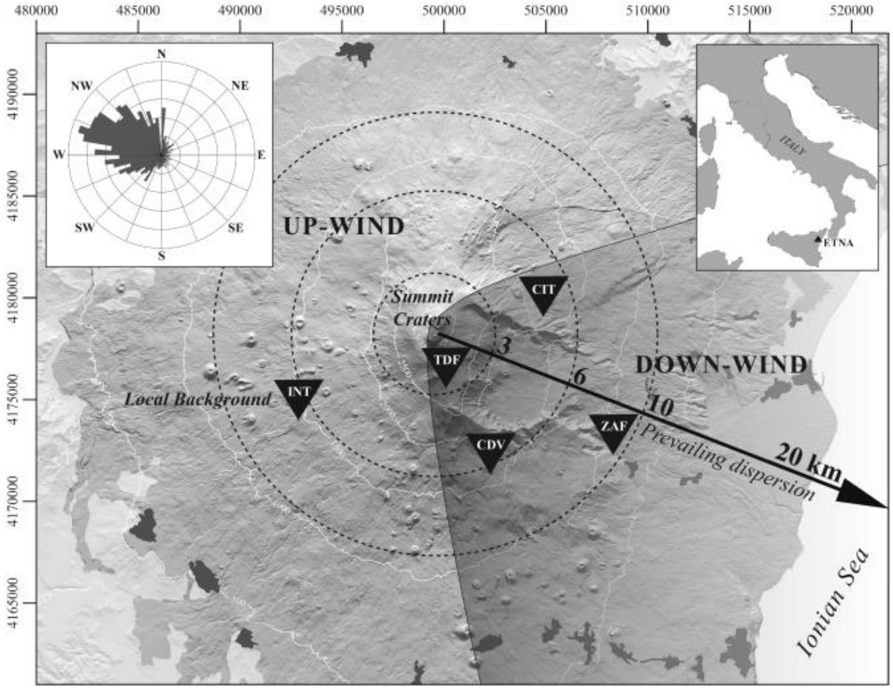

Figure 21: Map is subdivided in sectors basing on the axis of plume-dispersion (corresponding to the main direction of the blowing winds). Sectors are subdivided in down-wind and up-wind with respect to the summit craters. The upper-right inset shows the geographical position of Mt. Etna; the upper-left inset shows the wind rose referring to the altitude of the summit for the period 2006–2007 (data from Birgi station). Map from Calabrese *et al*., 2011.

The diagram 22 shows the chemical compositions of the rain samples collected in the examined volcanoes. A great variation in the concentrations of each chemical element is apparent, which in many cases exceeds 3 orders of magnitude. Generally, samples collected from Etna are showing the most elevated concentrations for the majority of the elements. However, it should be also taken into consideration that both Etna and Nyiragongo are among the greatest open conduit volcanic emitters worldwide whereas Vulcano is a closed conduit volcano in which the emissions come from the fumarolic activity of the summit crateric area.

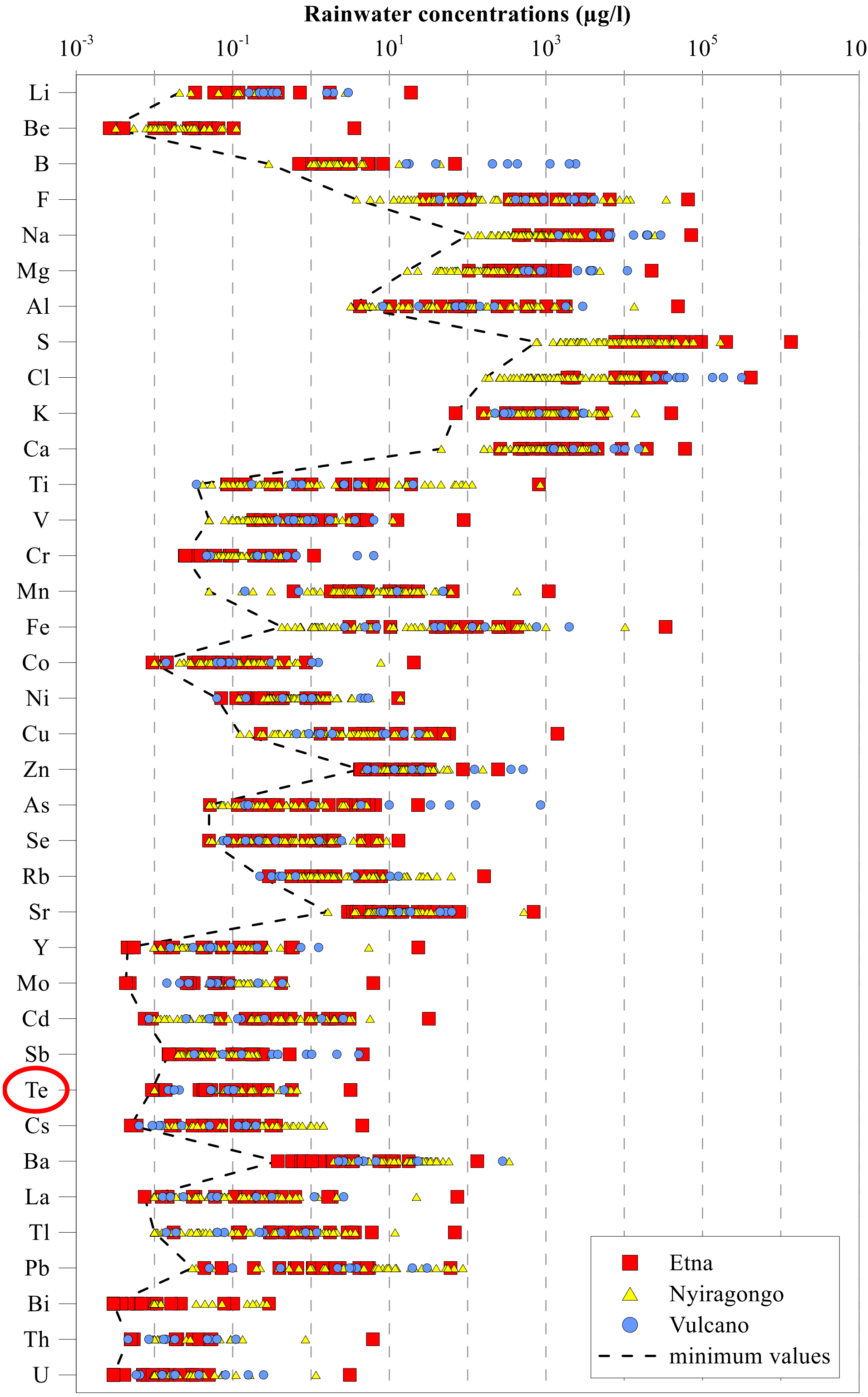

Figure 22: Diagram with the concentrations of the rain components collected at Mount Etna (Italy), Nyiragongo (D.R. Congo) and Island of Vulcano (Italy). Tellurium is evidenced by a red circle.

The Na- Cl graph (Fig. 23) shows a good correlation between the two parameters. The Sodium originates either from the marine spray or from the mineralogical phase of silicates (plagioclases), whereas the chloride is attributed to two sorces, either the marine spray or the volcanic plume (chloride, as HCl, is among the volatiles found in greatest quantities in volcanic emissions). Samples taken from background sites show a Na-Cl ratio very close to that of seawater indicating a main contribution from marine spray (Fig. 23). Such contribution is evident also at Nyiragongo despite its great distance from the sea evidencing how sea spray can travel very long distances. On the contrary the samples collected close to the volcanic vents and in the downwind direction display a chloride excess deriving from the HCl of the volcanic emissions (Fig. 24a) Such pattern is typical of all elements or compounds of prevailingly volcanic origin as for example H^+ (Fig. 24b), SO_4 (Fig. 24c) or F (not shown). On the contrary, compound like NO_3 of prevailing anthropogenic origin do not show any decreasing pattern with the distance from the vents (Fig. 24d).

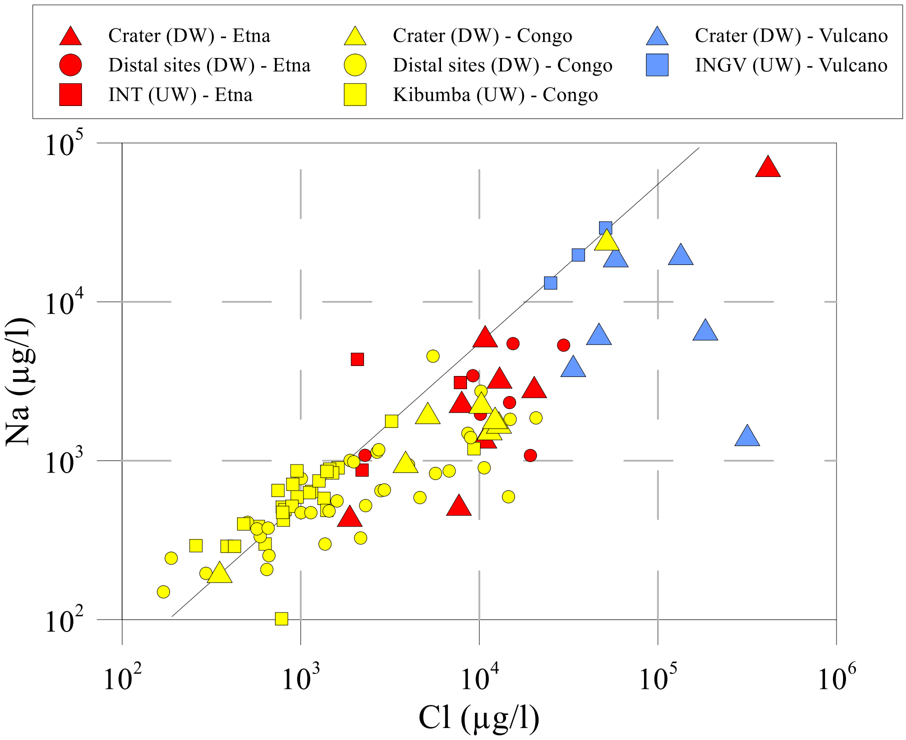

Figura 23: Correlation of Sodium and Chloride in the samples of rainwater, the line represents the sea water Na-Cl ratio.

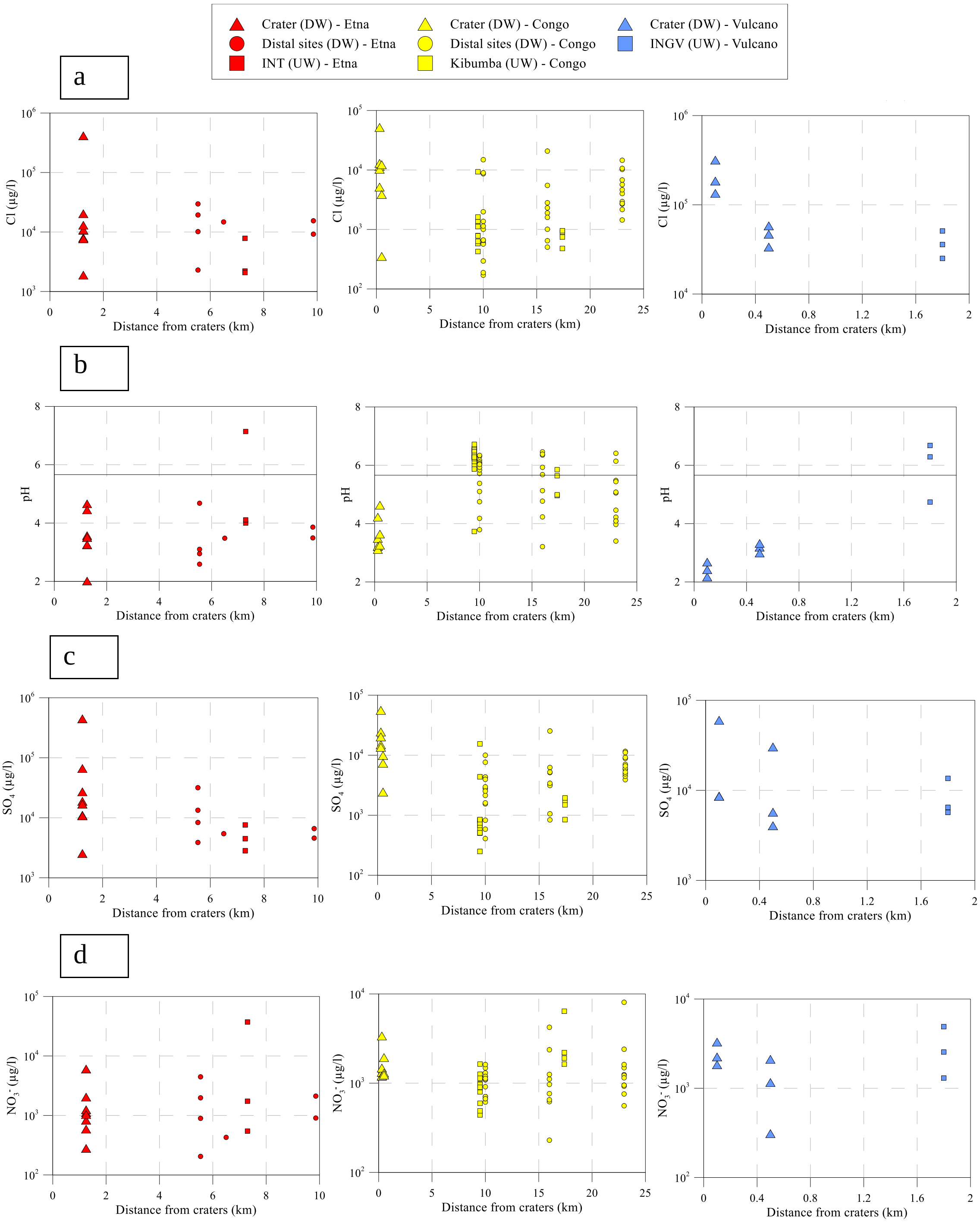

Figure 24: a) The three diagrams, one for each volcano, Etna (red symbols) , Nyiragongo (yellow symbols) and Vulcano (blue symbol), show that the highest concentrations of Chlorine are close to the volcanic vents (the triangle); b) The Diagrams pH-distance describe an increase of pH with increasing distance from the vents; c) The sulphates tend to increase close the volcanoes; d) Diagrams of the nitrates concentrations vs. the distance from the craters show no increasing nor decreasing trend.

The pH of the rain in the active volcanic areas is mainly controlled by the contribution of the strong acids emitted by the summit craters, both in passive degassing emissions and in paroxysmal phases (Etna and Nyiragongo), or from the persistent fumarolic activity (Vulcano). On the other hand, the neutralization process is controlled by heterogenic reactions on solid phases mainly silicates deriving from pyroclastic material. This material may interact with meteoric water either directly during paroxysmal phases (Etna and Nyiragongo) or to the uplift of the material deposited in the flanks of the volcanoes by strong winds. The influence of the acidic contribution can be well noticed in all the samples collected close to the crateric area (Etna, Nyiragongo and Vulcano) (Figs. 24b – 25) that show the lowest pH values. Whereas the buffer and dilution effects on pH are noticed in the samples that were collected far from the summit craters. The pluviometers on the flanks of Nyiragongo are more affected from the neutralization effect, showing values of pH between 6 and 7.

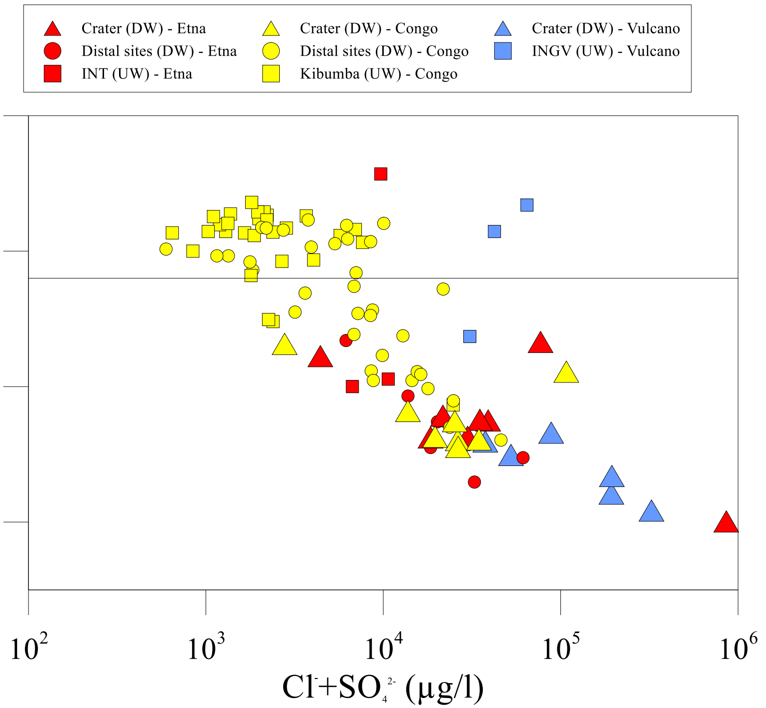

Figure 25: The diagram reports the correlations of pH vs. $Cl+SO_4^{2-}$.

The concentrations of Tellurium in the three sampling points show a great variability ranging from < 0.01 to 3.20 µg/l (Figs. 26a-b). Belzilea & Chen (2015) in a previous study reported a range of 0.002-0.025 µg/l for rainwater background. In general, the results show clearly higher Tellurium contents close to the craters with values up to 3.20

µg/l with respect to far away background values from below 0.01 µg/l to 0.04 µg/l (Fig. 26b), suggesting a mainly volcanogenic origin.

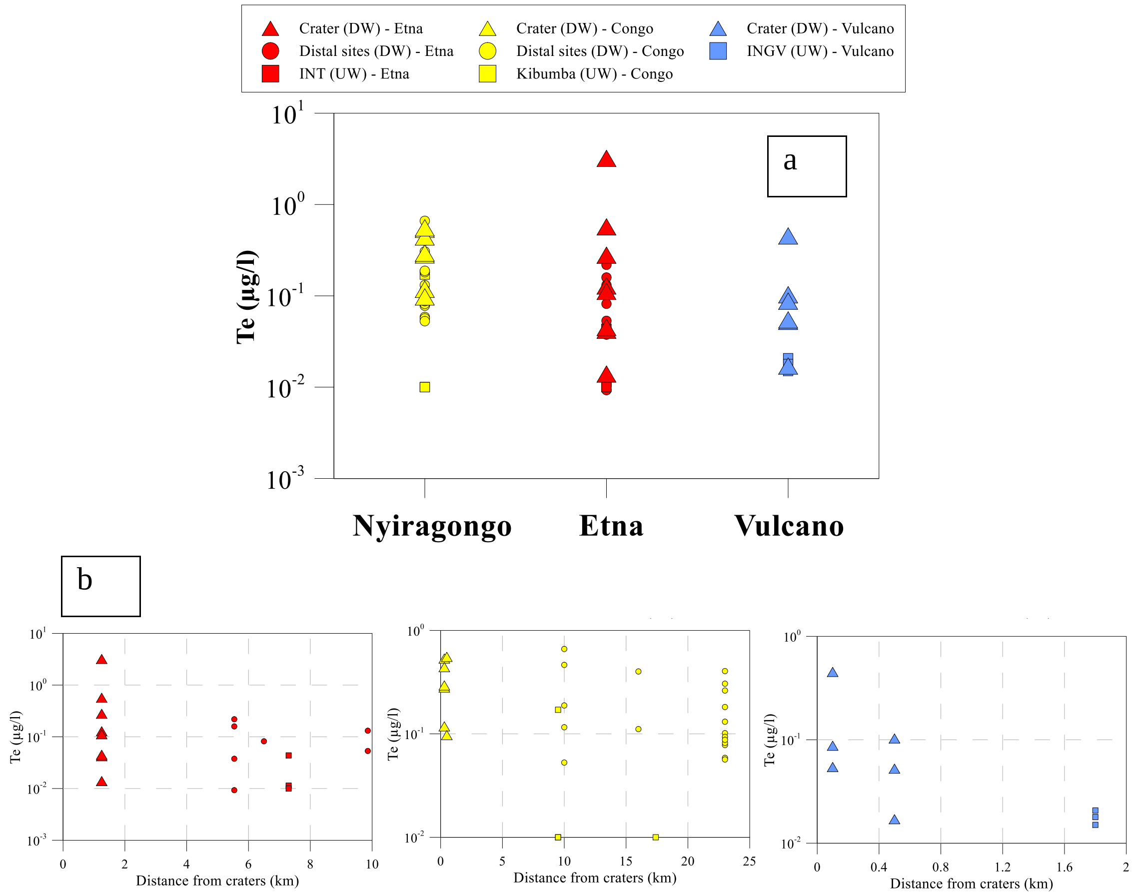

Figure 26: The concentrations of Tellurium in the samples of rainwater collected at Nyiragongo, Etna and Vulcano (a) that show a variability due to the distance of the pluviometers respect to the craters (b).

The contribution of the volcanic emissions on rainwater can be described by the following three graphs (Fig. 27). The degassing process of the plumes of Etna and Nyiragongo and of the fumaroles of Vulcano emits in the atmosphere great quantities of Sulfur, Chlorine and Fluorine in the form of acidic gases. The most obvious effect is noticed when the pH and the three major constituents are compared. The lowest values of the pH correspond to the highest concentrations noticed for the Chlorine, Fluorine Deposition and Sulfate in the rain samples (inverse correlation).

Tellurium has a positive correlation with the three main constituents of the acidic volcanic plume (Fig. 27), which is particularly evident in the pluviometers close to the emission points (red, blue and yellow triangles). However, at cases (see Tellurium and Chlorine), the ratio can vary in the different examined volcanic systems (eg. an increase of Chlorine in Vulcano is noticed, where there is a remarkable component of marine aerosol).

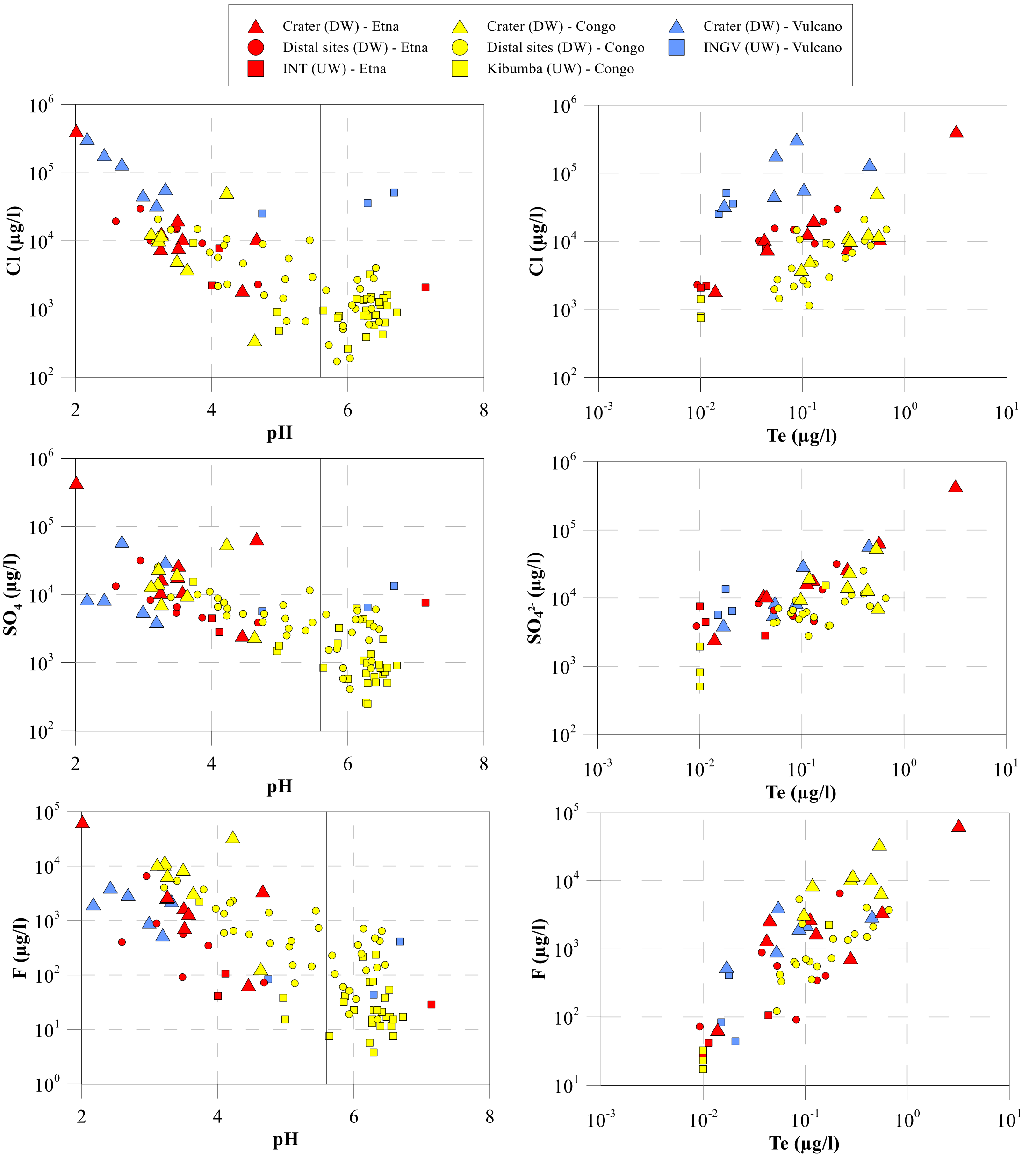

Figura 27: The diagrams in the right show the decrease of pH in the rain with the increase of three main acidic constituents in the volcanic plume (Chlorine, Fluorine and sulphate), the Tellurium reports a positive correlation with these components (diagrams in the left.) further underscoring its mainly volcanogenic origin.

The concentrations of Te, among with other volatile elements (e.g. As, Bi, Cs, Cu, Cd, Tl, Pb) are inversely correlated with pH values. This testifies for a common origin from volcanic emissions. Many of the above mentioned volatile elements show therefore a good positive correlation (Fig. 28).

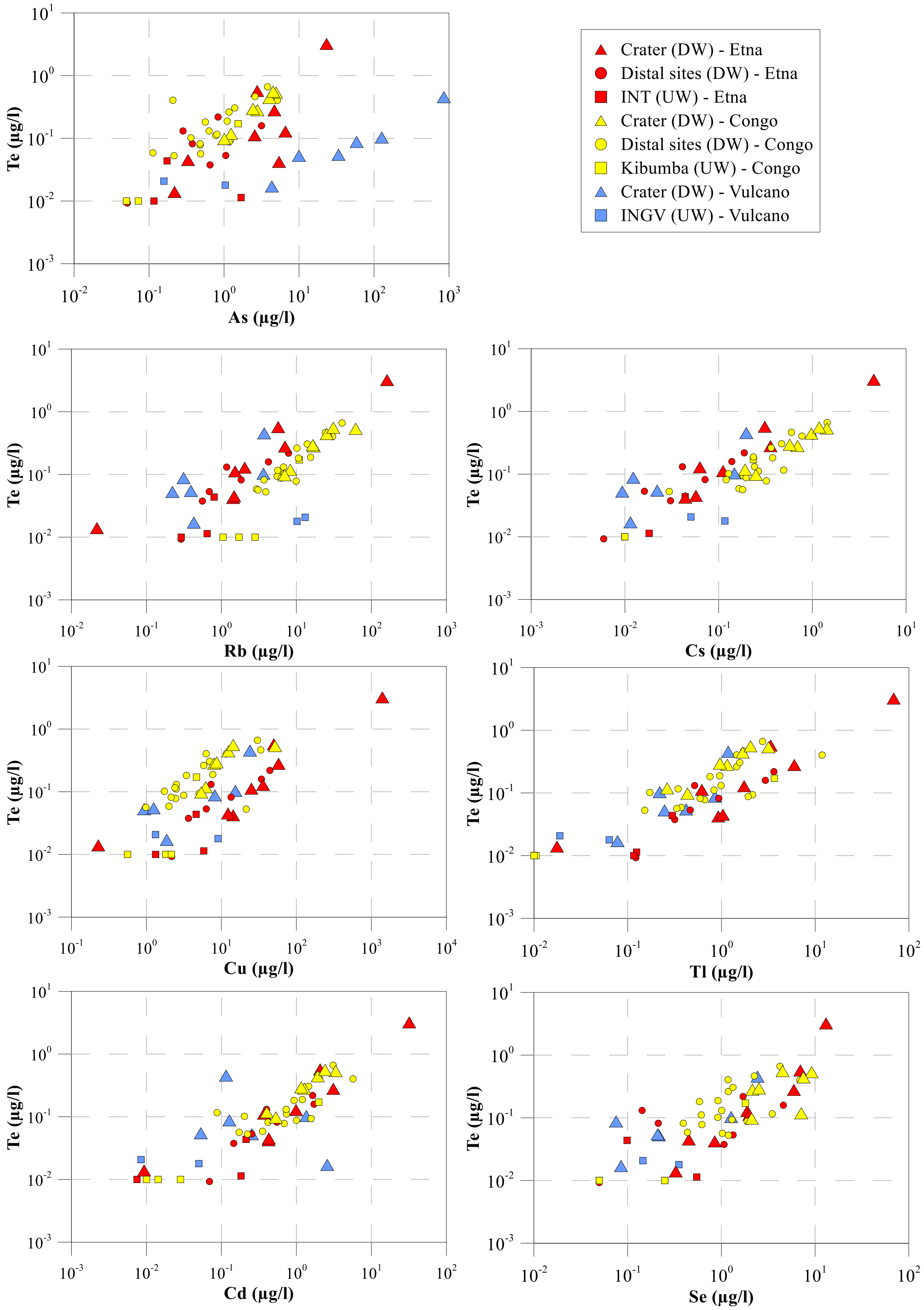

Figure 28: Correlation of Tellurium with others volatile elements in rainwater samples.

As previously seen with the major acidic gas species also for some volatile elements clear differences can be recognised between the different volcanic systems. For example at Vulcano a higher As/Te ratio with respect to the other volcanic systems can be recognised while Mt. Etna displays a higher Cu/Te ratio. Previous studies indeed revealed As enrichment at Vulcano (Arndt et al., 2016) and Cu enrichmet at Mt. Etna (Calabrese et al., 2011). These differences can be justified by differences in the geologic conditions of the studied volcanic systems (magmatic composition, presence of hydrothermal systems, etc.).

4.2.2. Volcanic ash and its contribution to atmospheric deposition

Volcanic ash is formed by fragmentation processes of the magma and the surrounding rock material of the volcanic vent (Langmann, 2013).

The interaction between ash, gases and aerosols is one of the important process that occurs within eruption plumes, indeed the volcanic ashes can be a sinks for various volcanic and atmospheric chemical species and sources for others (Delmelle *et al*, 2007).

Volcanic ash is released into the free troposphere and/or the stratosphere and interacts with the atmospheric, terrestrial and oceanic systems. The volcanic ash is transported by the prevailing winds until it is removed from the atmosphere by gravitational settling and wet deposition (Langmann, 2013). Its deposition brings also adsorbed materials that can be dispersed into the environment and is potentially hazardous for vegetation, livestock and people. The rate of their dispersal depends on the affinity of the materials to the ash, the nature of the surface of the ash, the substrate on which the ash is deposited and the presence of water. In addition, the volatile concentrations in the ash leachates can change according to eruption parameters and sample location (Witham *et al*., 2005). The chemical composition of the volcanic ash is mainly determined by the magma from which it is generated and each magma has different melting points, viscosities, and typical volatile contents and this can change during the same eruption.

Óskarsson in the 1980 developed the idea that within eruption plumes variable scavenging of volatiles occurs in three temperature-dependent zones (Fig. 29): the “salt formation zone” where sulphate and halide salt aerosols are formed at near magmatic temperatures and adsorbed onto ash particles; the “surface adsorption zone” where halogen gases react directly with the surface of ash at some what lower temperatures (∼700 °C); and the “condensation zone” characterized by the formation of sulphuric and halogen acids at temperatures below 338 °C, which will also be adsorbed onto ash particles (Delmelle *et al*, 2007).

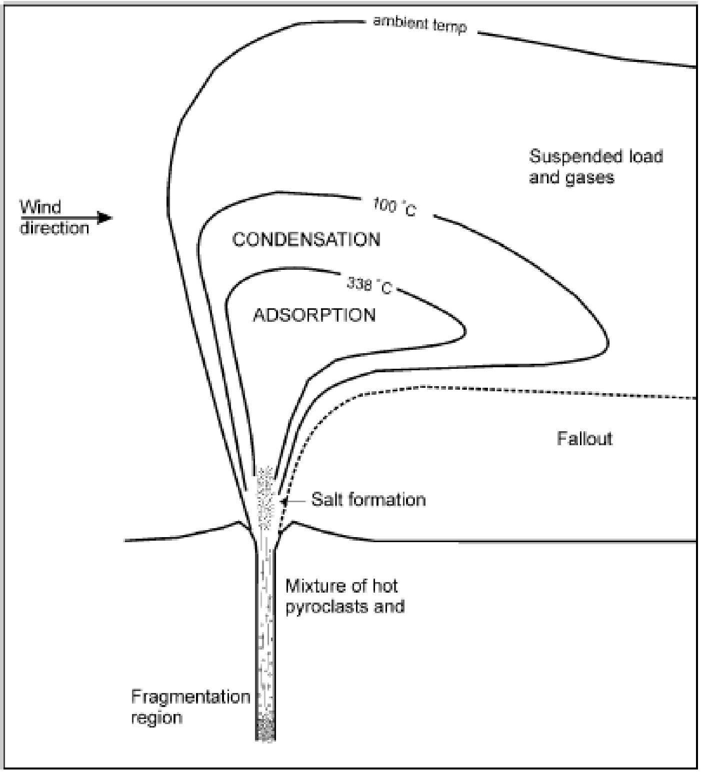

Figura 29: Source Witham *et al*., 2005 (modified after Oskarson, 1980) The figure depicts a Plinian eruption column with three hypothetical temperature-dependent zones

4.2.2.1 Volcanic Ash Results

In this study the fresh ashes ejected from Etna (Italy), Copahue volcano (Argentina) and San Miguel (El Salvador) were analysed. The samples, for all three volcanoes, were collected immediately after the eruptions. The event of Copahue occurred in December 2012, after 12 years of inactivity. Etna ashes samples were collected during 20 paroxysmal events occurred during the years, 2011 and 2012. San Miguel erupted in December 2013, after 11 years of inactivity.

The samples, when possible, were divided in the different grain sizes, otherwise the bulk sample was analysed (Fig. 30).

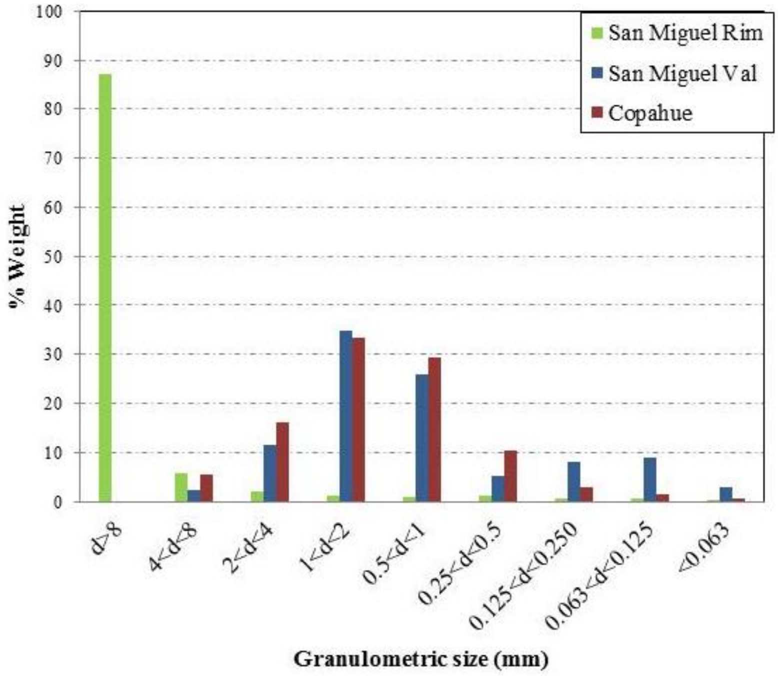

Figure 30: The histogram reports the different weight percent in the granulometric size in the ash of San Miguel, rim and valley (Val), and Copahue.

The concentrations measured in the ash leaching solutions range from <0.0003 to 0.015 µg/g. All the samples collected in Etna gave values of Tellurium below the quantification limit (Fig. 31). Taking in account the same granulometric size, almost all the components, including Tellurium, presented higher concentrations in the ashes collected at Copahue.

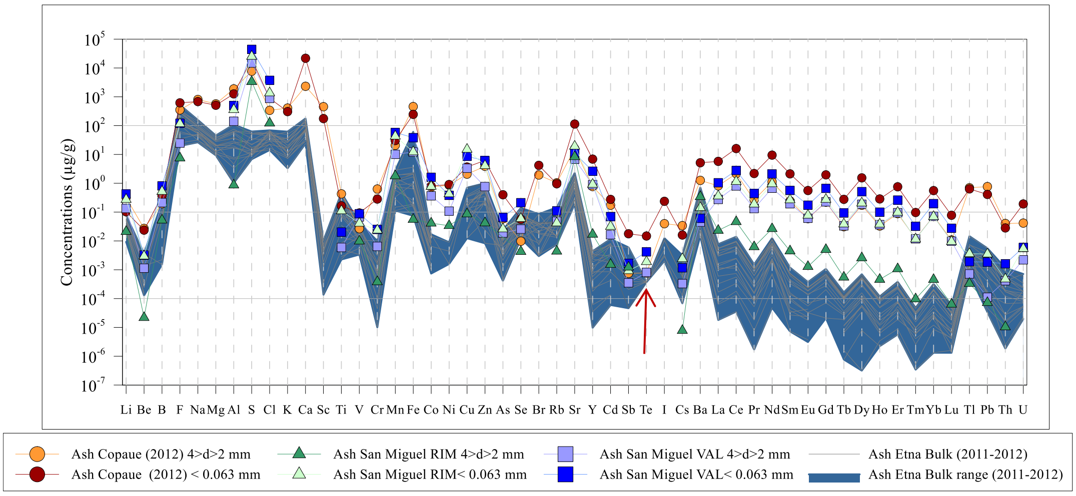

Figure 31: Diagram with the concentrations of the leached ashes. The samples were collected at Mount Etna (Italy), Copahue (Argentina) and San Miguel (El Salvador). The red arrow indicates the Tellurium concentrations.

The results highlight the rapid dissolution of Tellurium from the ash surface indicating high mobility of this element among with other known mobile metals. Tellurium is probably carried out during the volcanic explosion forming hydro-soluble salts with the main acid volatile species (SO_2, HCl, HF), $Te(SO_4)_2$, $TeCl_4$ and TeF_4.

Also in this case Tellurium presents a good correlation with the others volatile elements, Antimony and Arsenic (Fig. 32). As expected, the concentrations of Tellurium increase with decreasing grain size of the ashes leached because of the greater specific surface area (Fig. 32). This process has important implications on atmospheric deposition chemistry: when the smaller particles are ejected into the atmosphere they can be transported for longer distance from the source-point, participating in the cloud processing and affecting sequentially the chemistry of the rain, plants and soils in the surroundings of active volcanoes.

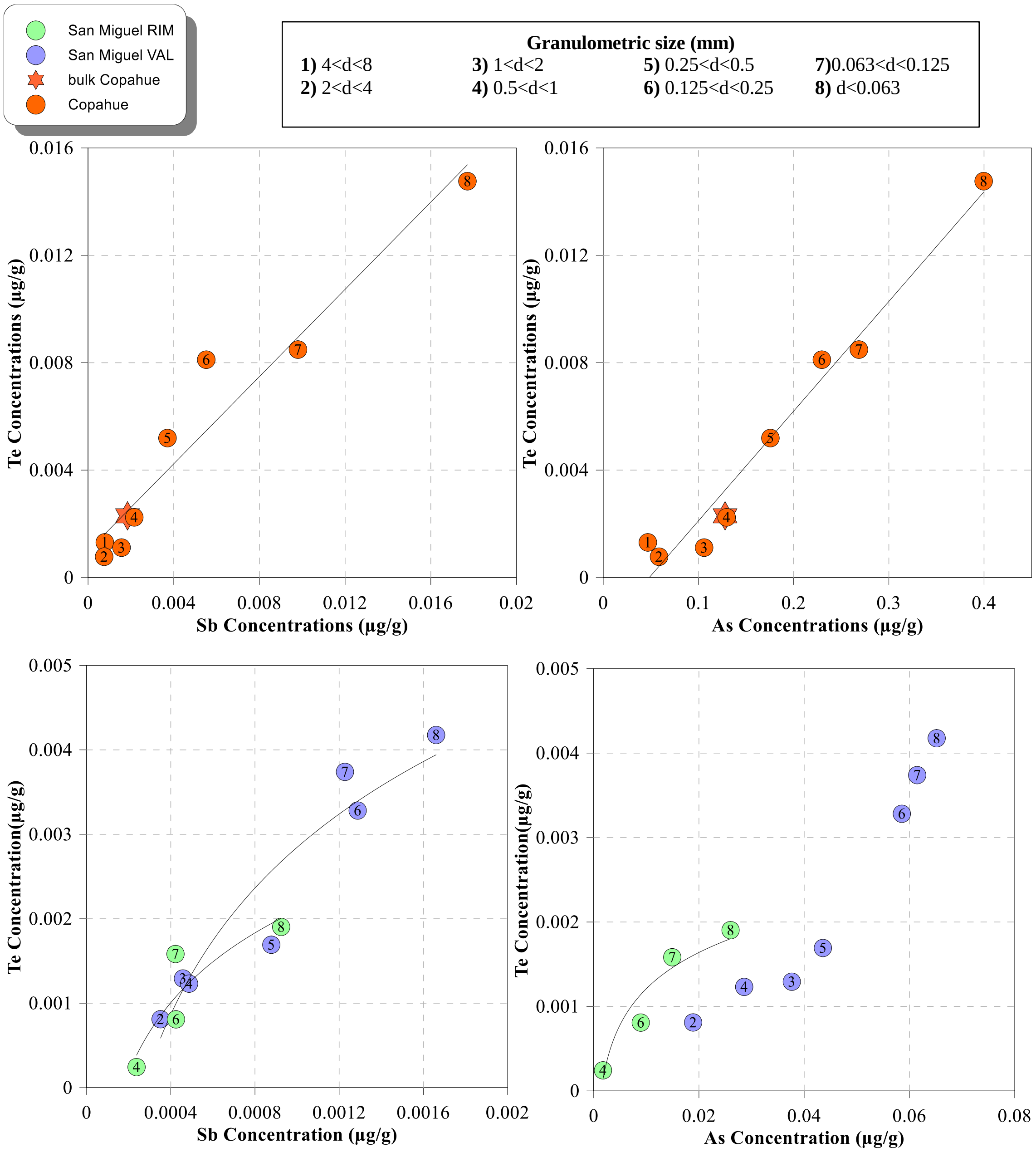

Figure 32: The diagrams reported the correlation of Tellurium with others volatiles elements (Sb and As) in the volcanic ashes from Copahue and San Miguel. The numbers inside the circle rapresent the different granulometric sizes.

4.3 Soil and Plants

The plants need macronutrients (carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium and sulfur) and micronutrients (chlorine, iron, boron, manganese, zinc, copper, molybdenum and nickel) for their optimal growth and most of these elements are provided by the soil.

The soils represent the mass of inorganic and organic material, also containing gas and water, which develops in the upper part of the crust following the alteration by chemical and physical weathering of the rocks and biological action by microorganisms and vegetable cover. It is the interface between the lithosphere, the biosphere and the atmosphere (Amundson, 2003).

The inorganic constituents of the soils are mostly silicates, oxides and hydroxides of iron, aluminum, manganese, etc.

By degradation processes of plant residues (leaves, fruits, dry branches or whole plants), dead animals and from living or dead microorganism derives, instead, the organic fraction of soil. The organic compounds may remain unchanged for long periods (non-humic compounds) or run into deep and rapid transformations of their original chemical structure (humic compounds or humus).

The morphological, mineralogical, soil chemical and physical properties depend on the bedrock and environmental factors; in the case of volcanic environments, the soil, its constituents and its pH are the product of chemical alterations due to dry volcanic gas aerosol and ash depositions and the wet atmospheric depositions, determining a higher or lower availability of nutrients in plants. In the same way the pH of the soil affects the absorption of nutrients by plants. Along with nutrients, the deposition of volcanic emissions may also comprise toxic or undesirable elements and compounds.

The plants can be used for the biomonitoring that may be defined as the use of organisms to obtain information on certain characteristics of the atmosphere, as long as they qualitatively (bioindicators) and quantitatively (bioaccumulators) reflect their ambient conditions. The exposed bioindicators are subjected to variation of the physiology, the morphology and spatial distribution, while the bioaccumulators accumulate in their tissue without necessarily show external visible changes. Various bioaccumulators have been used in trace element air monitoring, such as mosses, lichens, ferns, grass, treebark and tree rings, leaves and conifer needles. This technique relays on the fact that airborne elements and compounds can be delivered also directly from the atmosphere and absorbed by the aerial part of the plants (leaves, needles, bark). In the case of mosses and lichens this pathway is almost the only one the absorption from the soil being severely limited by the absence of roots.

The biomonitoring is passive when the organisms found in the area of study are used as biomonitors, instead it is active if the organisms are transplanted for this reason in the study area and analysed after a known period of exposition.

4.3.2 Passive Biomonitoring: Plant Results

Previous studies showed that the plants commonly contain low concentrations of Tellurium with variable range, according to the plant species, the availibility of this element in the soil and the environment of growth. For example it was observed that in some mining districts the vegetables, like the soil, have higher contents of Tellurium. The highest concentration of Tellurium is found in onion and garlic, up to 300 µg/g, and the garlic odour is caused by vapours of dimethyltelluride (Kabata-Pendias, 2011).

For this study, the passive biomonitoring has been done at 9 different volcanic areas through the collection of leaves belonging to the following 9 different species: *Cistus sp.* (Vulcano Island, Stromboli and Nisyros); *Erica sp.*(Nysiros); *Amaranthus sp.* (Nyiragongo); *Senecio sp.* (Nyiragongo and Etna); *Rumex aethnensis* (Etna); *Salix sp.* (Gorely); Fern (Masaya and Soufriere); and samples of Mosses (Gorely) and Lichens (Turrialba). For comparison some plants from an industrial area (Augusta), *Olea sp.* and *Pinus sp.*, and a rural area (Ficuzza), *Pinus sp.*, were also investigated.

Generally the concentrations of Tellurium in the plants sampled for this study vary from < 0.0005 to 0.575 µg/g. The same species but in different volcanoes feature similar ranges (Fig. 33), while plants that bioaccumulate more tellurium are Senecio sp., mosses and lichens with values up to 0.575 µg/g. Comparing the concentrations of Tellurium with the distance it is deduced that the values of this element tend to decrease with the increase of the distance from volcano, thus confirming the contribution of the volcanoes to the accumulation of Tellurium in plants (Fig. 34).

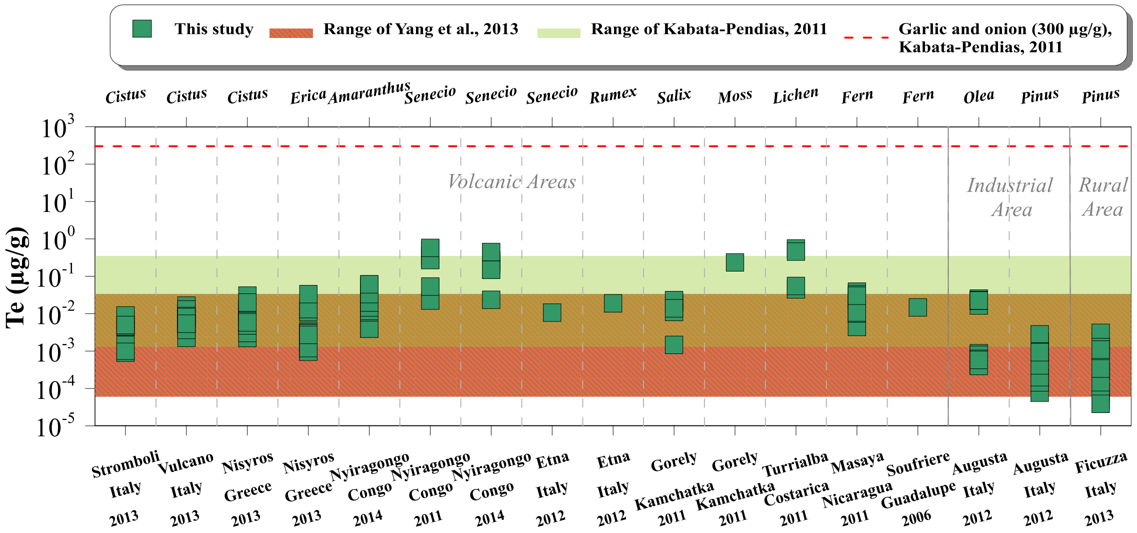

Figure 33: The diagram represents with the green square the concentrations of Tellurium in different plants, 11 species in 9 volcanic areas, an industrial area and a rural area, collected and analysed for this study. The coloured bands indicate the range of previous studies and the dotted line reports the greater concentrations of tellurium in plants that were been found in garlic and onion (see the legend above).

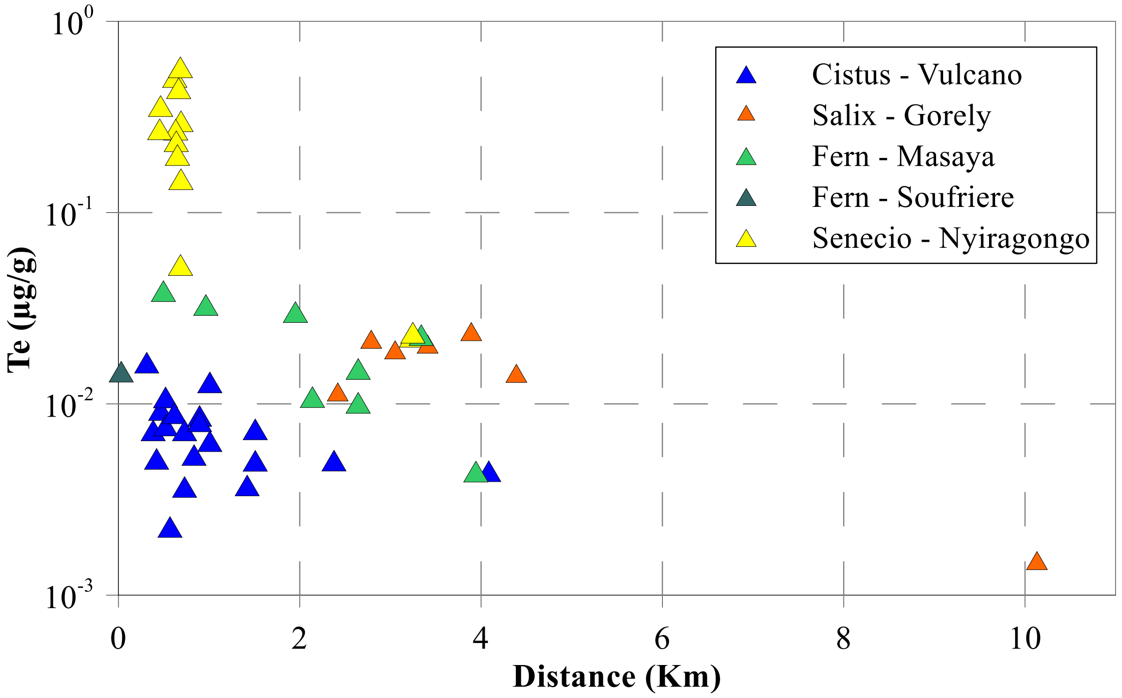

Figure 34: The diagram reports the concentration of Tellurium *versus* the distance from the volcanic vents. The values of Tellurium tend to decrease with the distance.

Also in this case the tellurium shows a good correlation with the other volatile elements, as it is possible to see in the binary diagrams with Selenium and Bismuth (Fig. 35), where, considering the same species, the concentrations have a linear correlation.

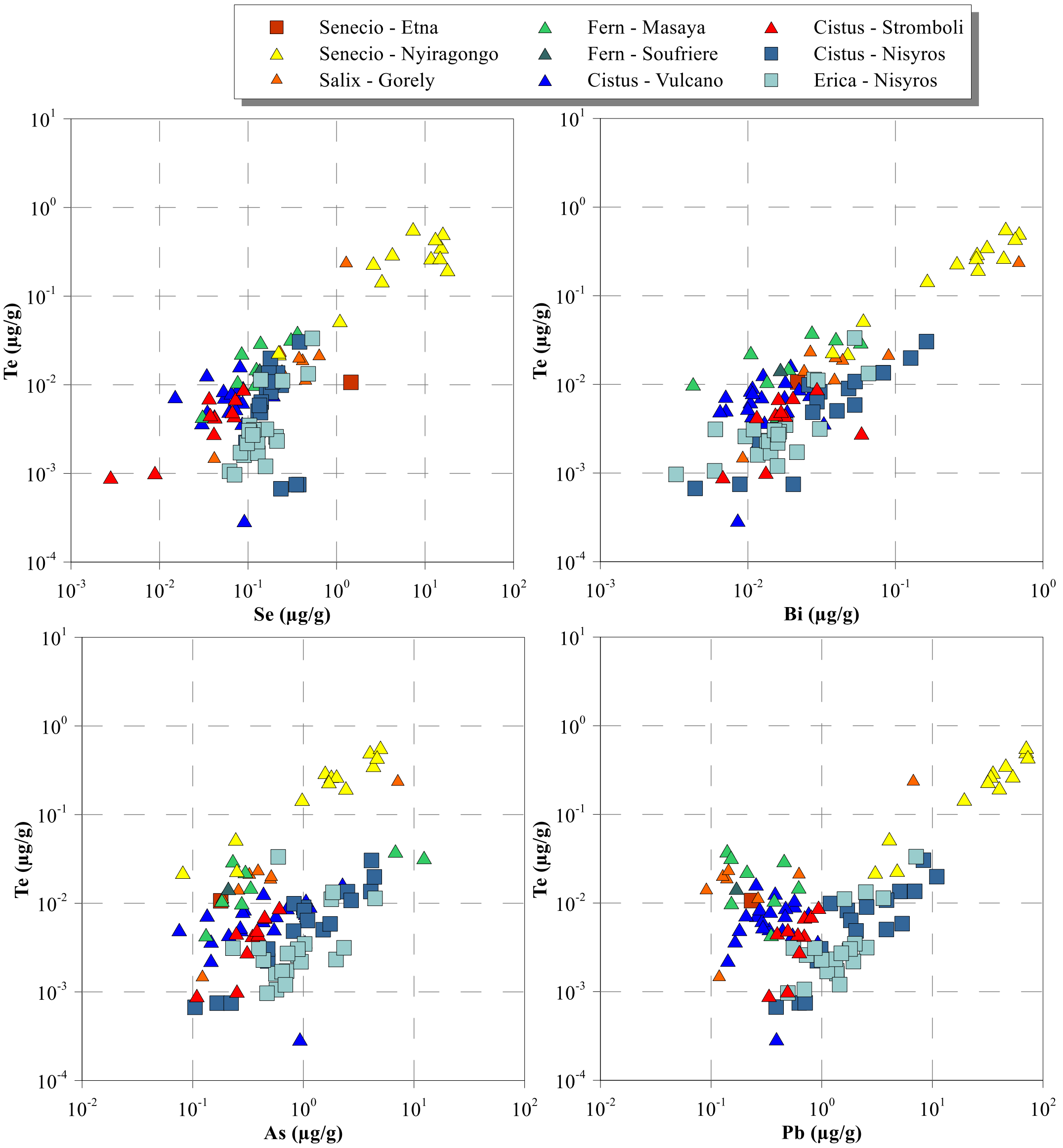

Figure 35: The binary diagrams show the Tellurium versus volatiles elements with a good linear correlation.

4.3.3 Soil Results – Nisyros, a case of study

Regarding the Tellurium in the soils, also in this case, there are scarce data in the literature. For this study the soils from the Island of Nisyros (Greece) have been collected and analyzed. Samples were taken in the caldera, Lakki Plain, inside and outside the four craters.

The data show the influence of volcanic emissions on Tellurium concentrations, recording the highest values within the craters, particularly at Stephanos, 0.746 µg/g (Fig. 36). Anyway, in general the concentrations inside the caldera are higher than the local background (0.004 µg/g).

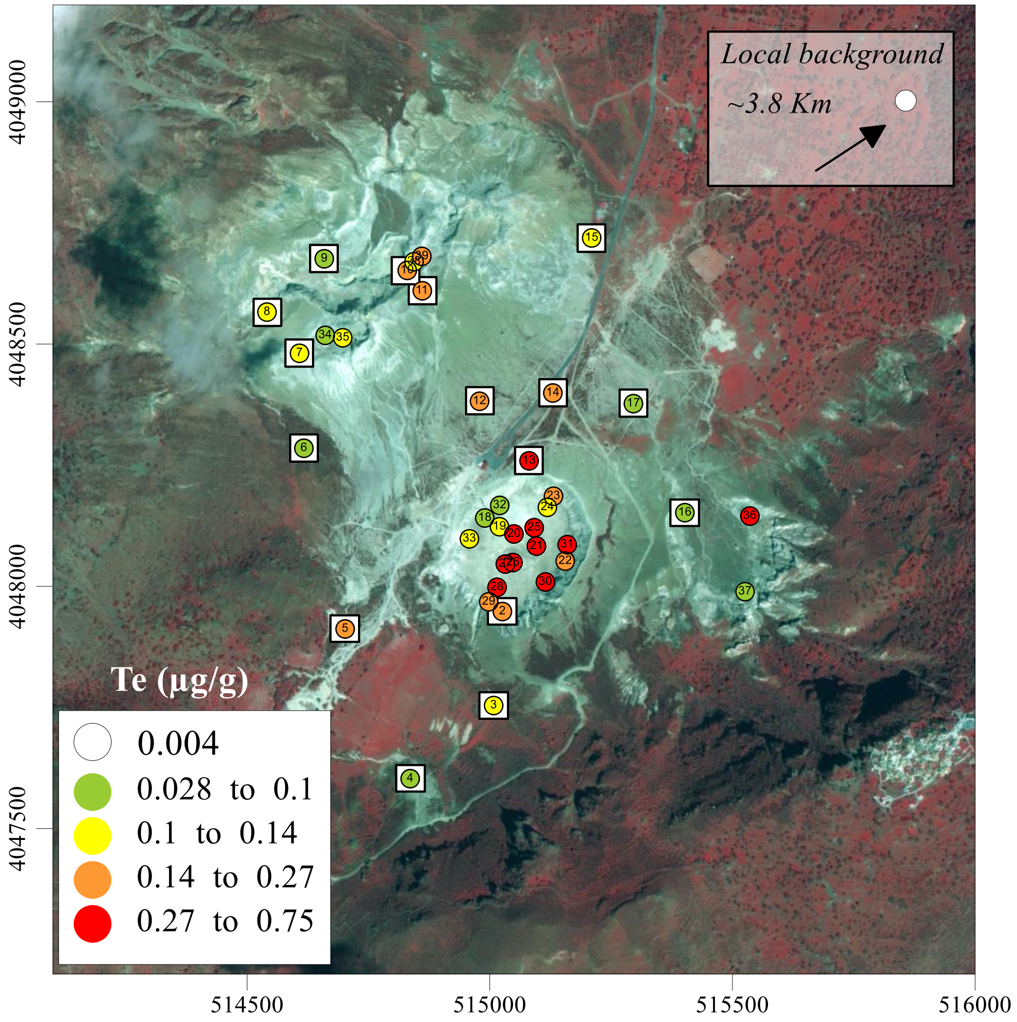

Figure 36: Map of Nisyos, the circles indicate the point of soils sampling, the circles inside the square are the points from 1 to 17 where also plants have been collected.

The concentrations of Tellurium in leaves of two indigenous plants (*Cistus sp.* and *Erica sp.)* collected at Nisyros were compared with the corresponding concentrations in the soils collected around the respective plant samples. The values of Tellurium in the leaves tend to grow with the increase of this element in soils (Figs. 37-38). The plants, particularly *Cistus*, tend to take up more Tellurium close to the active fumarolic areas. This suggests a bioaccumulation of tellurium from the soil but also from the atmosphere.

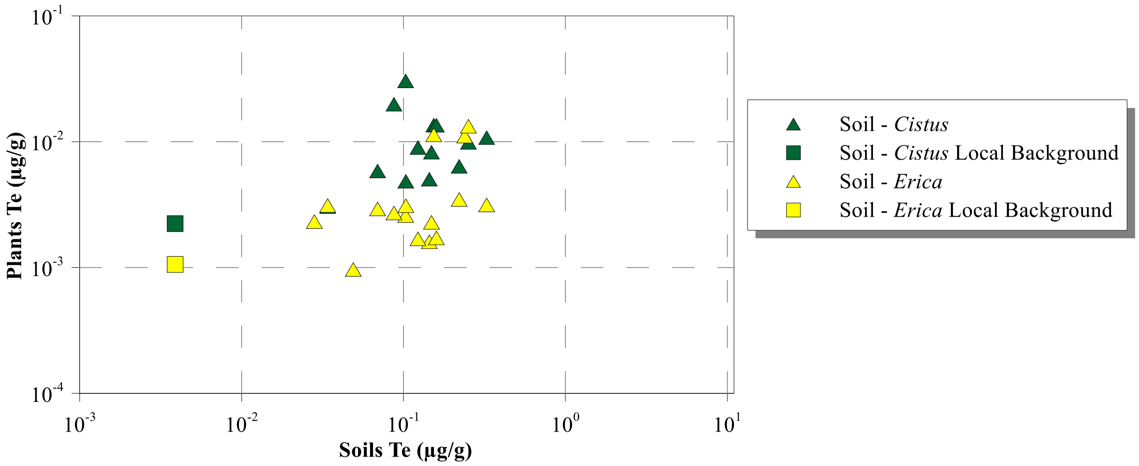

Figure 37: Diagram shows the concentrations of Tellurium in plants and respective soils.

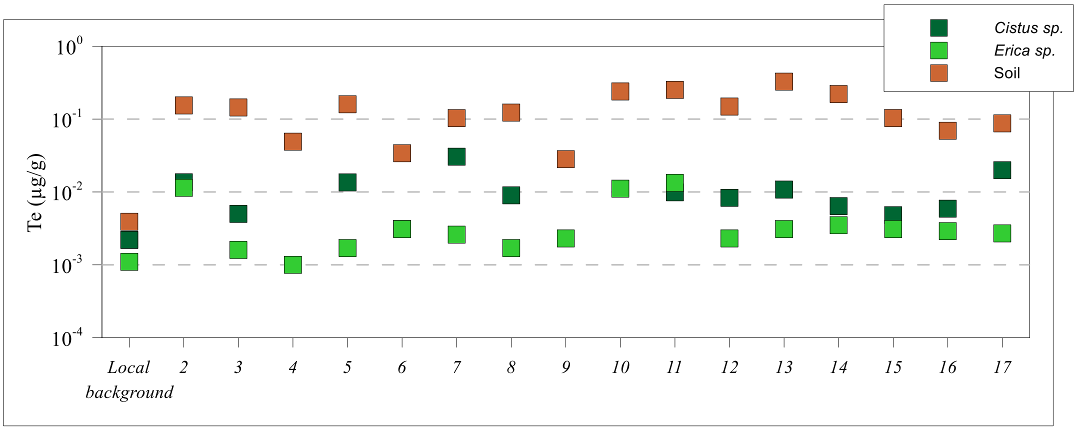

Figura 38: Concentrations of Tellurium in soil and plants (*Cistus* and *Erica*), values are generally greater than the local background and the concentrations in the plants are positively correlated with that of the soils.

As for other analysed media, Tellurium shows at Nisyros a good correlation with other volatile elements also in soils and plants. The figure 39 shows as an example the correlation of Tellururium with Selenium.

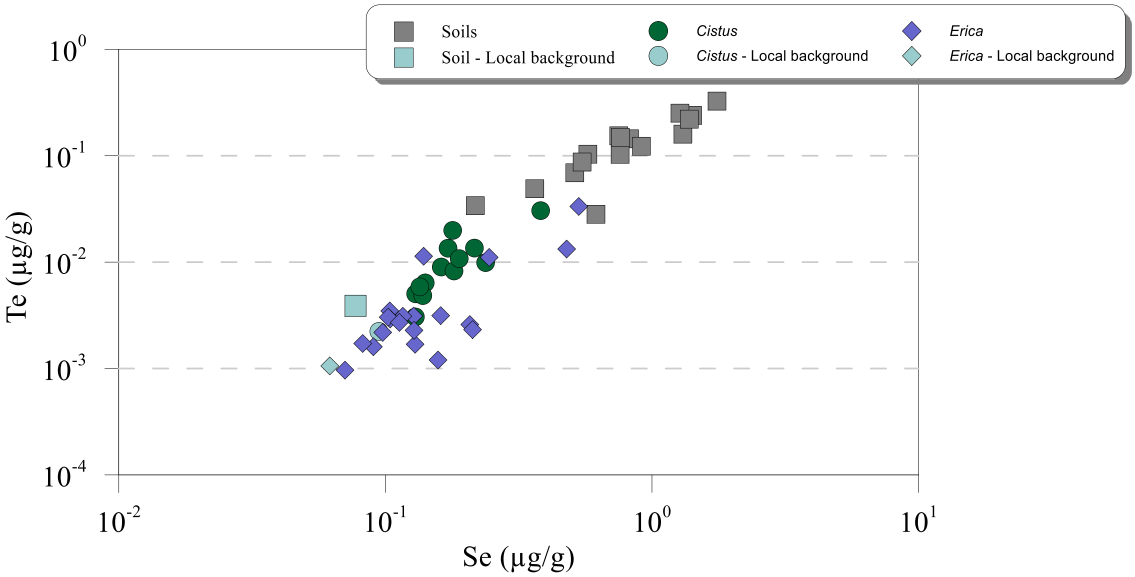

Figure 39: The concentrations reported in the binary diagram Te vs. Se shows a good positive correlation both in soils and plants.

4.3.4 Active Biomonitoring: Moss Bag Results

The moss-bags technique has been extensively used for active biomonitoring in the past 40 years as an efficient technique to study atmospheric pollutants, but in the last years the moss bags have been successfully applied also in volcanic environments (Arndt et al., 2014; Calabrese *et al.* 2015; Calabrese & D'Alessandro, 2015).

In this study the moss-bags have been used to study Tellurium and other trace element's emissions from two volcanic areas: Nyiragongo (D.R. Congo) and Nisyros (Greece).

On the 2014 six moss-bags, covered and uncovered, were positioned at Nyiragongo (Fig. 40) but with different times of exposition. Four moss–bags situated on the rim of volcano were exposed to volcanic emissions for three days, while other two, at greater distance from the rim, at Rusayo and Kingi, were exposed for 35 days.

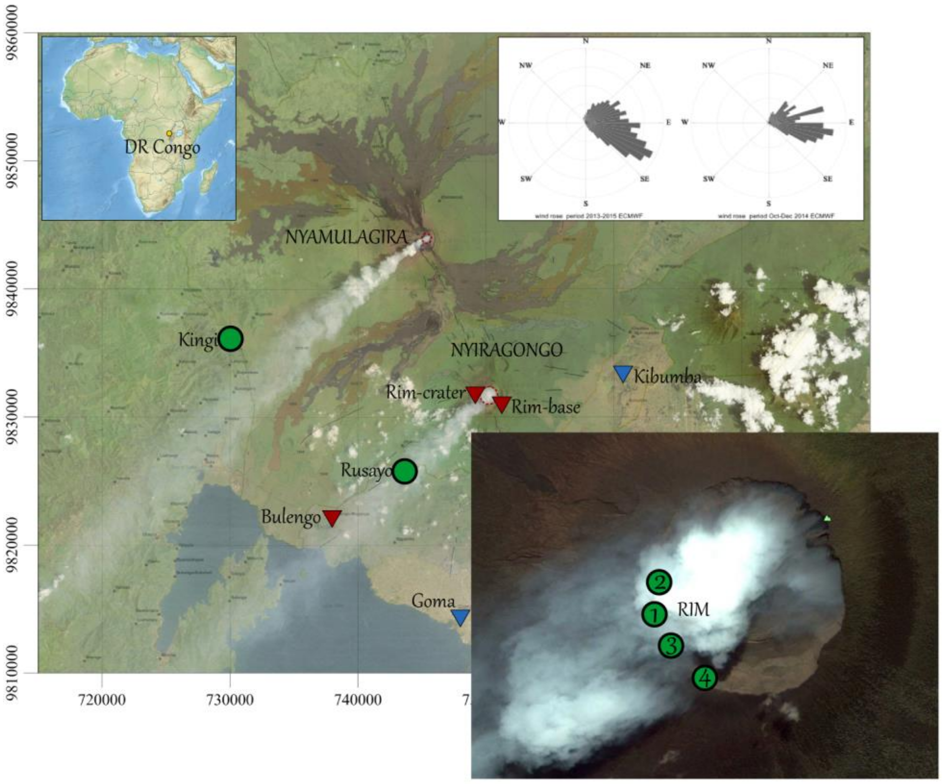

Figure 40: Map of Nyiragongo (D.R. Congo) with the green circles that indicate the sampling sites where the moss-bags were positioned, the circles with the numbers were on the rim.

Moreover, 16 uncovered moss-bags were exposed at the island of Nisyros for ten days on 2013. In the map (Fig. 41) only the points inside the Lakki Caldera are indicated and the point, Belvedere, was positioned on the caldera rim at greater distance (2,5 km). In this map the concentration ranges of Tellurium are reported. The values are highest inside the hydrothermal explosion craters, Phlegeton, Andreas and Stephanos, where the main fumarolic areas are found and decrease progressively moving away from the main vents. The lowest value of concentration for this element was found at Belvedere point (Fig. 41).

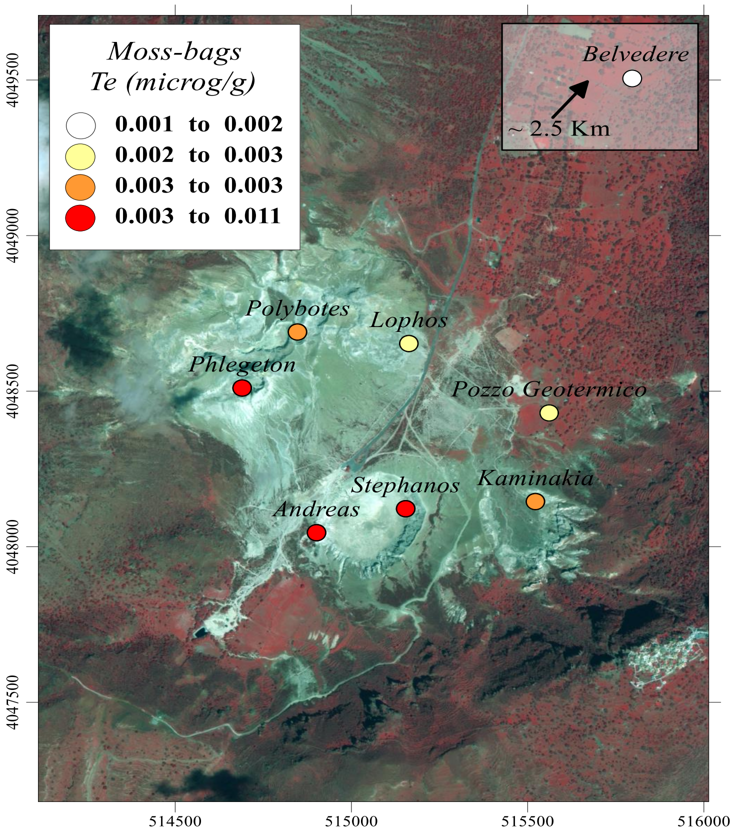

Figure 41: Map of Volcanic area at Nisyros (Greece), the circles with differents colour indicate the points of some moss-bags positioned in the island and the ranges of concentration of Tellurium.

Considering all two volcanoes, in the moss-bags the concentrations of Tellurium range from 0.001 µg/g, measured in the unexposed mosses and at the point Belvedere, at Nisyros, far from the main vents of the island, up to 0.111 µg/g in the uncovered moss-bag at Nyiragongo on the rim, the point 1 in the map (Fig. 40), confirming the enrichment of this element from the volcanoes through emissions and/or deposition. In all the samples the uncovered moss-bags show values of Tellurium greater than the corresponding covered ones (Fig. 42). Comparing it with some of the others elements it is possible to see that Tellurium tends to increase its concentrations especially close to the emission vents and, in all two volcanoes, the values of Tellurium have ranges that are greater with respect to other elements. In particular, this enrichment is more accentuated at Nisyros where the others elements in the moss-bags seem not be influenced from the fumarolic emissions possibly due to the too short exposition time (Fig.42).

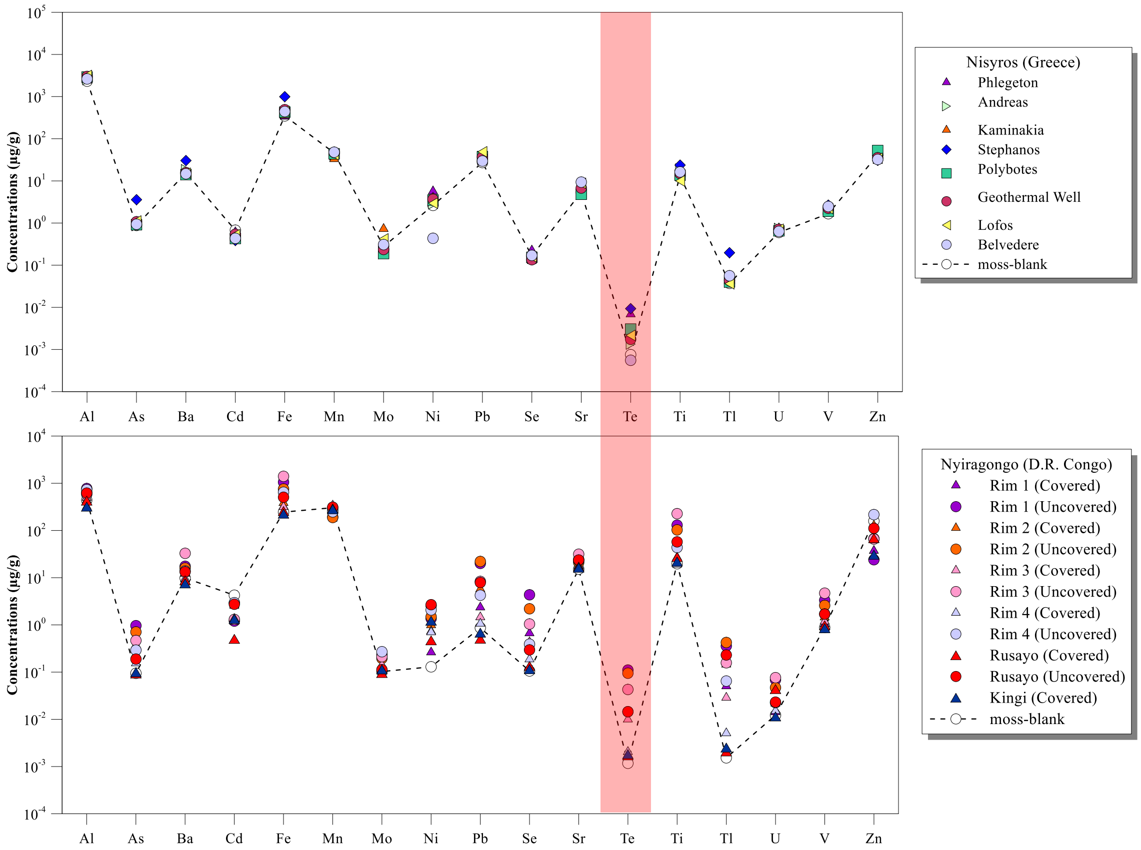

Figure 42: The two diagrams show the concentration of some elemments measured in the moss-bags in Nisyros (Greece) and Nyiragongo (D.R. Congo). The red band indicates the concentratons of Tellurium.

5. Discussion

The results of this study contribute to increase significantly our knowledge about tellurium distribution in volcanic areas. The table 5 shows the different matrices and the numbers of samples analysed, the range obtained in this study were compared with the range of previuos studies.

Table 5: Comparation between the ranges of this study and previous studies.

Matrices investigated	**Number of samples**	**Range of this study**	**Range in literature**	**References**
Volcanic plume	65	<0.003-0.151 µg/m^3	0.001-0.19 µg/m^3	Aiuppa *et al.*, 2003; Mather *et al.*, 2012; Moune *et al.*, 2010; Allard et al., 2000
Rainwater	98	<0.01-3.2 µg/l	0.002-0.025 µg/l (Rainwater background)	Belzilea & Chen, 2015
Volcanic ash	23	<0.0003-0.015 µg/g	No data	
Plants Passive biomonitoring	200	<0.0005-0.575 µg/g	0.013-0.35 µg/g	Kabata-Pendias, 2011 and reference there in
Moss Bags Active biomonitoring	19	0.001-0.111 µg/g	No data	
Soil	22	0.004-0.746 µg/g	<0.02-0.81 µg/g 0.027 µg/g (world average)	Fulignatti *et al.*, 2006 Yang *et al.*, 2014

Regarding the estimates of Tellurium in volcanic emissions (concentrations and fluxes), the volcanic areas studied have been 11 and the concentrations of Tellurium were calculated for the first time in 10 of these. All the values, including the data of literature, are greater than the atmospheric background levels (<0.001 µg/m^3 - from Belzilea & Chen 2015), indicating the prevailing volcanogenic origin of Te.

Volcanic emissions are dispesed in the atmosphere, influencing the composition of rainwater. Atmospheric depositions are the most important way to transfer the elements from the atmosphere to the ground and consequently to all the terrestrial environments (soils, groundwater, plants, animals and humans). Nowadays very few data are available about Te abundances in atmospheric deposition and no data in volcanic environments. The data here reported are the first results of the concentrations of Te in rainwater collected close to active volcanoes; results showed very high concentrations of Te in rainwater with respect to the background values reported by Belzilea & Chen (2015) (Tab. 5). As well as for rainwaters, no data about Tellurium in volcanic ashes are reported in the literature. During the paroxysmal event the ejected ash interacts with the atmosphere and is subjected to leaching processes during its travel through the atmosphere affecting the composition of rainwater and, after its deposition, also that of the soil and plants. Also for the plants (active and passive biomonitoring) the concentrations of Tellurium are the first results obtained in volcanic area. Regarding the soil in volcanic area, one previous study reported data of Tellurium (Fulignatti *et al.*, 2006) and the range reported are the same of this study (Tab. 5).

5.1. The volatility of Tellurium

The volatility of an element or compound is not a univocally defined concept but roughly we can state that highly volatile elements or compounds have a higher tendency to be partitioned in the vapour or gaseous phase.

From the chemical-physical point of view, volatility is defined as the tendency of a substance (liquid or solid) to vaporize into an evacuated space and can be measured through the substance's vapour pressure with which it is directly related. At a given temperature, a substance with higher vapour pressure vaporizes more readily than a substance with a lower vapour pressure. Figure 43 shows that elemental Tellurium is among the native elements, solid or liquid at ambient temperature, with relatively high vapour pressure. The measured values are similar to other metals and metalloids considered highly volatile at magmatic temperatures like Cd, As and Se (Honig and Kramer, 1969).

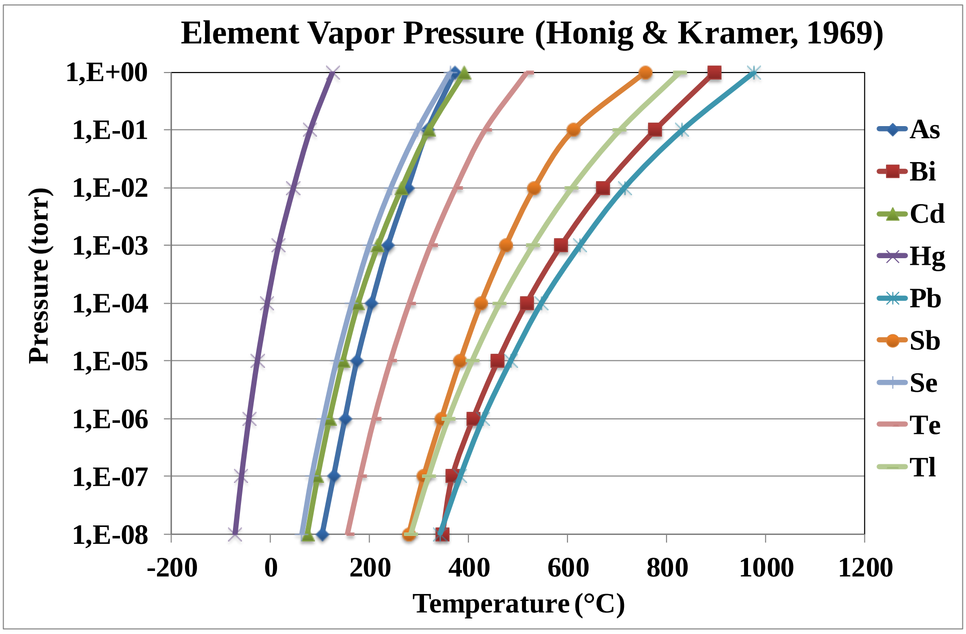

Figure 43: The diagram correlates the ambient temperature with vapour pressure, the curves indicate the behaviour of elements more volatiles.

Another way to characterize the “volatility” of an element takes in account the boiling point (or sublimation point) of the native elements. On this basis Haynes (2010) proposed this sequence of the relative anhydrous volatility of the elements of geochemical and economic interest: Hg>As>Se>Te>Tl»Sb>Pb>Ag>Cu>Au. Again Tellurium is among the most volatile elements.

In natural conditions native elements are very rare and the elements are incorporated in various mineral phases which are more or less stable in the range of conditions found at active volcanic systems. In addition, the element’s partitioning into the vapour phase can be significantly enhanced by complexing with sulfur, water, and halides in the vapour (Zajacz *et al.*, 2010).

Furthermore, degassing conditions can be very different from one volcanic system to another. For example, at open-conduit volcanoes gas-rich magmatic fluids are released at magmatic temperatures directly from molten lava to the atmosphere. Such fluids are very different from high temperature hydrothermal fluids where the composition is dominated by solubility-driven exchanges between hot water and rocks. Hydrothermal fluids will additionally be influenced by pressure and temperature changes on their way to the surface up to their emission point to the atmosphere. The result of thermodynamic and kinetic controls on the composition of these gases as they exit a volcano can vary greatly in space and time (Saunders and Brueseke 2012).

To have an idea of the “volatility” of an element in such wide range of chemical and physical conditions some empirical indicators have been adopted as for example the emanation coefficient (Rubin, 1997) or the enrichment factor (Mather, 2015). Both parameters cannot be directly compared between different volcanic systems but rather give a relative scale of “volatility” for the examined elements. Some examples of volatility orders are given for different volcanic systems:

- Kudryavy volcano (Russian Federation) - Bi>Cd≈Se≈Te>Pb>As>Tl≈Zn>Rb≈Sb>Cu
- Hekla volcano (Iceland) - Cd>Te≈Tl>Bi≈Cu≈Pb>Zn≈Sb>Rb (As and Se not included)
- Kilauea (U.S.A.) - Se≈Te>Cd≈Bi>Tl>As≈Pb≈Sb≈Zn>Cu≈Rb

In this examples Tellurium is compared to other elements that are considered volatile and is mostly found in the highest part of the ranking notwithstanding the fact that volcanic systems in different state of activity are considered. At the time of the sampling Kudriyavy volcano was a closed conduit volcano with intense high temperature (up to 950°C) fumarolic activity (Taran *et al.*, 1995), Hekla volcano was erupting (Moune *et al.*, 2006) and Kilauea an open conduit volcano in passive degassing state (Mather *et al.*, 2012).

A strong impact on the high volatility of Tellurium derives from the fact that this element can form a lot of compounds that are in the gaseous phase a relatively low or even ambient temperature in a wide range of redox conditions and chemical compositions.

For example at the very low redox conditions ($fO_2 < 10^{-25}$) of hydrothermal systems Grundler *et al.* (2013) calculated a partitioning coefficient (K_d = Te concentration in vapour/Te concentration in liquid) up to $>10^5$ in favour of the vapour at 300°C. Cooke and McPhail (2001) calculated sub-ppt concentrations of Te in 300 °C epithermal-type waters, and suggested that the high volatility of reduced Te species (e.g., $H_2Te(g)$; $Te_2(g)$) is responsible for the enrichment of Te in fumarolic emissions of up to about 0.1 ppm.

At higher redox conditions Tellurium oxidize to TeO_2 which is also volatile at high temperature. But its volatility is significantly enhanced in the presence of steam (water vapour), because of the formation of $TeO_2{\bullet}xH_2O(g)$ species (Glemser *et al.*, 1964, 1965). The stoichiometry of the volatile Te species is dependent on the vapour pressure: at low steam pressure (≤ 1 bar, 450–700 °C), $TeO(OH)_2(g)$ is present whereas at higher pressures (3 to 455 bar, 418 °C and 470 °C), $Te(OH)_4(g)$ is the main Te-bearing species (Glemser *et al.*, 1964, 1965). The latter species could be one of the main species that could be emitted directly from the magma during passive degassing or eruptive phases. But in these conditions the presence of high contents of halogens in magmas will lead to the formation of Te-halide compounds. These are all in the gaseous phase at magmatic temperatures and some of them are gaseous also at ambient temperature although all are highly instable at atmospheric oxygen concentrations. On the basis of the high positive correlation between Te and F Moune et al. (2006) hypothesized that Te, during the eruption of Hekla volcano (Iceland) in 2000, was transported prevailingly as fluorides (TeF_4 or TeF_6) and in minor quantities as chlorides.

5.2. The enrichment factors

To disentangle the contributions from ash/silicate versus volatilisation and thus assess the volatility of trace metals from magmas several methodologies have been used including: (i) emanation coefficients (εx), (ii) enrichment factors (EFs) and (iii) weight ash fraction (WAF) (Mather, 2015).

Here we used the EFs to comprehend the behaviour of Te and its relation respect to the other investigated elements.

The (EF) is a useful tool to highlight the degree of enrichment or depletion of a given element in a geochemical medium compared to the relative abundance of the same element in a reference material (rm) (Goldberg, 1972; Chester *and* Stoner, 1973; Zoller *et al.*, 1974, Peirson *et al.*, 1974; Duce *et al.*, 1975; Rahn, 1976; Buat-Ménard *and* Chesselet, 1979).

The enrichment factors can be calculated as shown by Chester *and* Stoner (1973) or Zoller *et al.* (1974):

$$\mathbf{EF = (Cx/Cr)_{sample} / (Cx/Cr)_{rm}}$$

where $\mathbf{(Cx/Cr)_{sample}}$ is the concentrations ratio of an element (x) normalized to a reference element (r) in the sample, and $\mathbf{(Cx/Cr)_{rm}}$ is the corresponding ratio observed in a reference material (rm) generally the average crustal composition (Mason and Moore, 1982).

In the case of volcanic aerosol for each element the Enrichment Factor (EF) was calculated referring to the continental crust compositions (Wedepohl, 1995) and the reference element used was magnesium, as recently used by several authors (e.g. Calabrese et al., 2011; Zelenski et al., 2014; Gauthier et al., 2016). Tellurium is enriched in volcanic emissions similarly and sometimes even more than other volatile elements of volcanogenic origin. This is clearly visibile in the figures 44-45-46 where the EFs of the three volcanic systems are represented.

Notwithstanding the fact that Tellurium is one of the less abundant elements of the terrestrial crust, in the emissions of the three volcanoes it is one of the most enriched elements, further underscoring its extreme volatility in this environment.
In all three volcanoes, Tellurium is the most enriched element and shows EFs>1000.
Among the elements with EF>10, considering the median values of the calculated EFs, the most enriched in order are:

- Te>Se>Tl>Bi≈Cd>As>B≈Sb≈Zn≈Cu for Mount Etna;
- Te>Se≈Cd>Bi>Tl≈Pb>As≈B≈Sn>Cu for Nyiragongo;
- Te>Sb>B>As>Bi>Se>Tl>Cd>Sn≈Cu for Vulcano Island.

Mount Etna and Nyiragongo, both with open conduit, show a similar order of enrichment, while Vulcano Island a close conduit volcano with significant hydrothermal contribution shows a different order.

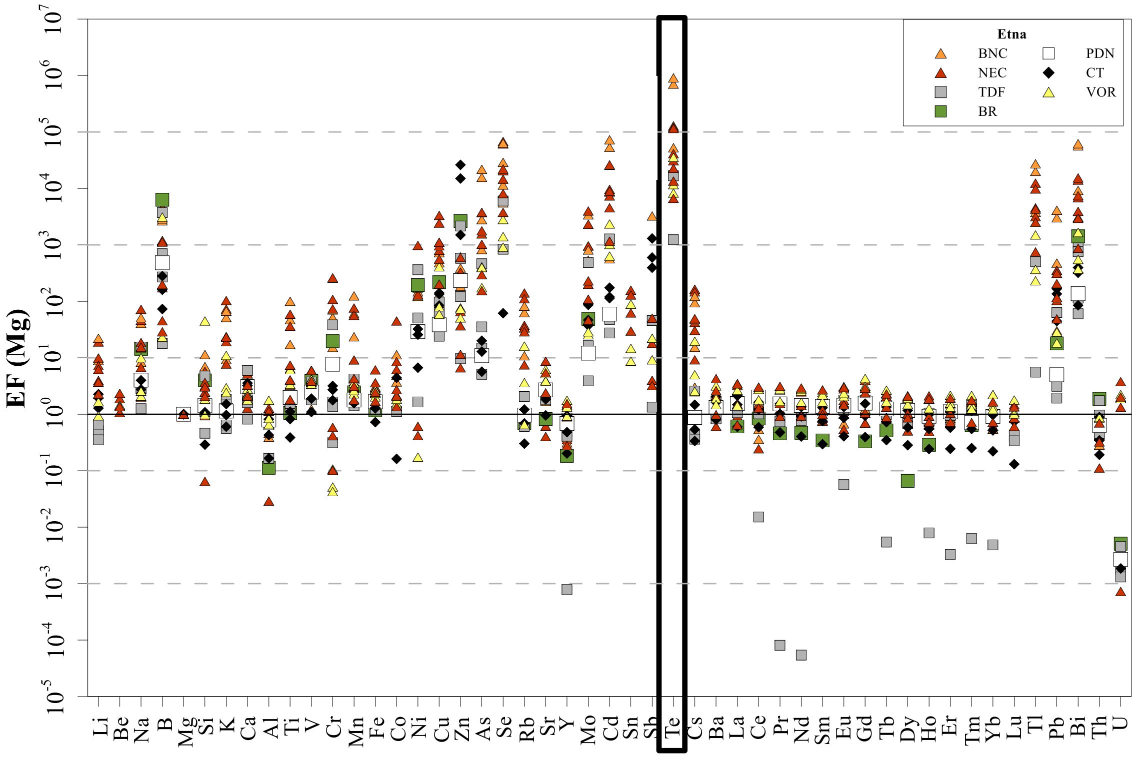

Figura 44: Diagram shows the EF(Mg) in volcanic emissions at Mount Etna with respect to the continental crust. Tellurium is evidenced by the rectangle.

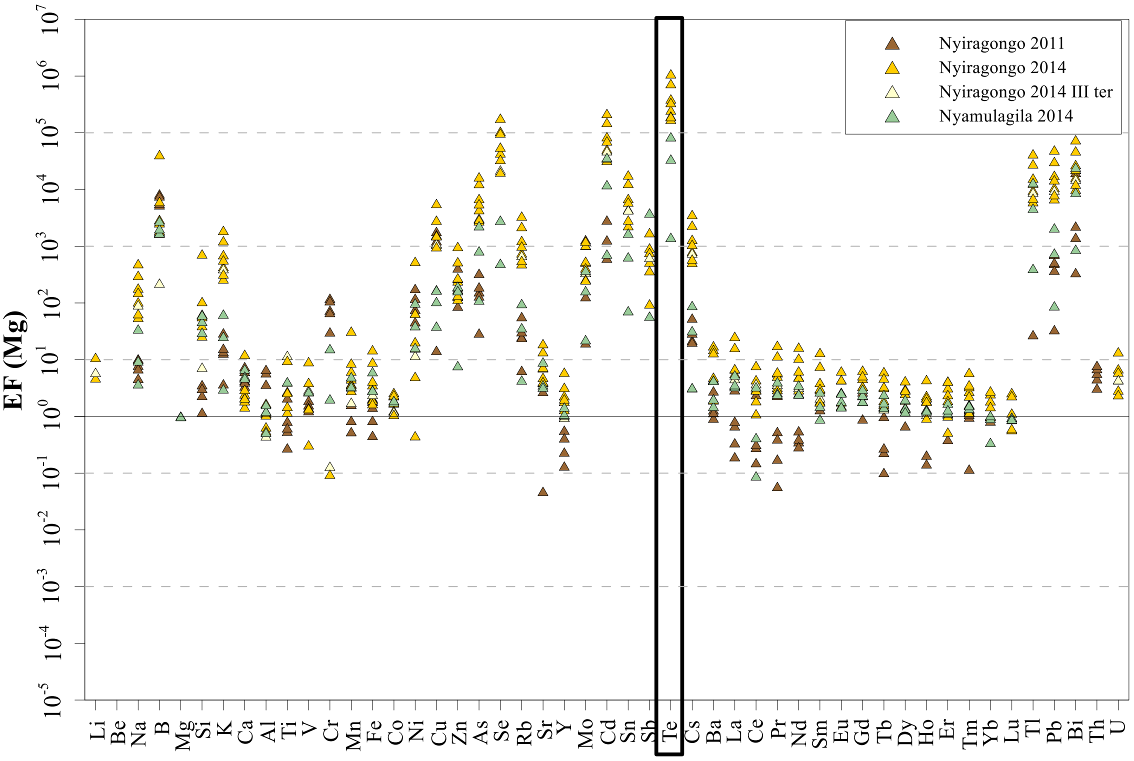

Figura 45: Diagram shows the EF(Mg) in volcanic emissions at Nyiragongo with respect to the continental crust. Tellurium is evidenced by the rectangle.

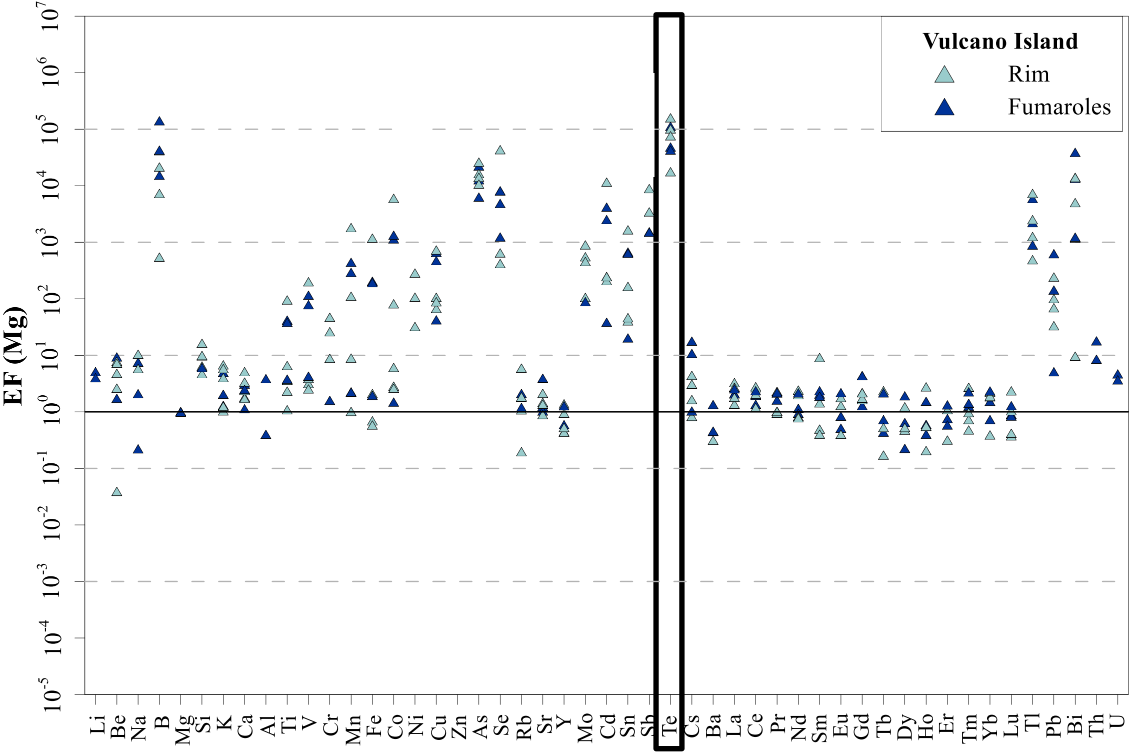

Figura 46: Diagram shows the EF(Mg) in volcanic emissions at Vulcano with respect to the continental crust. Tellurium is evidenced by the rectangle.

Also for bulk deposition enrichment factors have been calculated with respect to the mean crustal composition and Mg as normalizing element. Notwithstanding its sometimes very low concentrations (Fig. 22) also in bulk deposition Te shows high enrichment factors comparable or sometimes even higher than typical volcanogenic volatile elements like S, Cl, F, As and Se (Fig. 47).

Also in this case, excluding the major species, Tellurium is the most enriched element in Mount Etna and Nyiragongo, instead boron is the first element in order of enrichment at Vulcano Island probably due to the influence of hydrothermal system, although Tellurium is still one of the most enrichment elements.

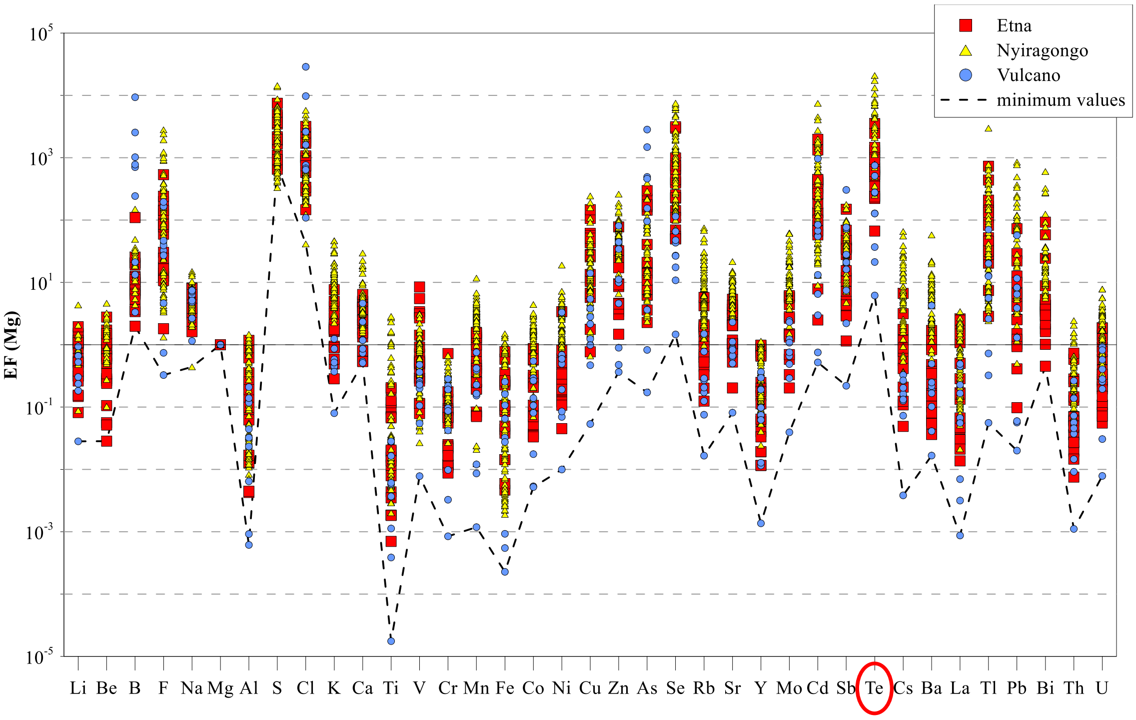

Figure 47: Diagram with the EFs of the rain components collected at Mount Etna (Italy), Nyiragongo (D.R. Congo) and Island of Vulcano (Italy). Tellurium is evidenced with a rectangle.

The Enrichment Factor (EF) refered to the continental crust compositions (Wedepohl, 1995) and magnesium as the reference element was calculated also in the moss-bags. In this case, in general, the mosses are enriched in tellurium in comparison to the continental crust, see the blanks, but the enrichment is greater in the uncovered moss-bags (Fig.48). Tellurium is always among the most enriched elements with respect to the unexposed moss (moss-blank). In the case of Nisyros it results the only element, besides sulphur, that is significantly enriched with respect to moss-blank (Fig. 48).

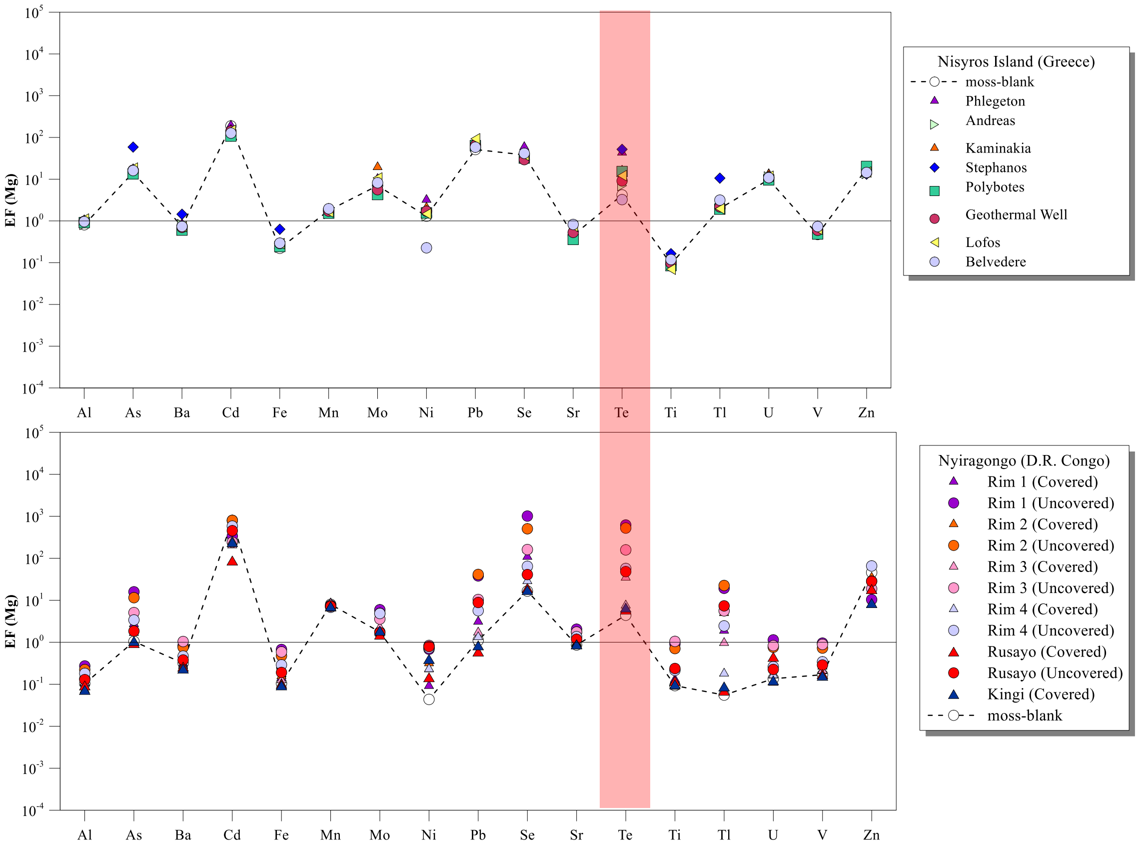

Figure 48: The two diagrams show the EFs of the three volcanic systems in the moss-bags and the blanks

The enrichment factor (EF) was calculated also for the soils of Nisyros, referring to the values of the local background. Also in this case the reference element used was the Magnesium. The figure 49 shows the diagram of the EFs of Tellurium, Selenium and Sulphur. Tellurium is more enriched than Selenium and its enrichment increases when the pH decreases. The variation of pH is due to the oxidation of H_2S, in fact the Sulphur is particularly enrichment at low values of pH (Fig. 49). Lower pH values testify for higher fumarolic gas fluxes through the soil correlated to enhanced enrichments of Tellurium, Selenium and Sulphur which probably rise up from the hydrothermal system in their most reduced form following the gaseous phase (H_2Te, H_2Se and H_2S). These gases are subsequently oxidised both within the shallowest part of the soil and in the atmosphere.

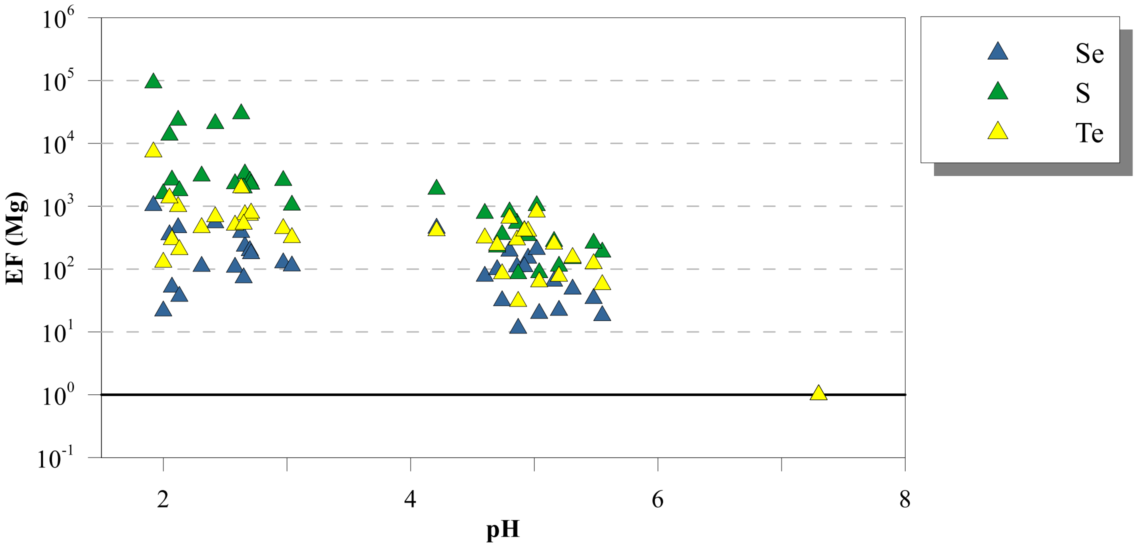

Figura 49: EF (Mg) calculated for Tellurium, Sulphur, and Selenium in the soil compared with the pH of the soils. The soil collected in the local background is the reference for EF calculation.

If we calculate the enrichment factor of Tellurium with respect to the corresponding soil on which the plant, *Cistus sp.* and *Erica sp.* collected at Nisyros, was growing and always Mg as normalizing element it can be evidenced that the element is always depleted except in the background samples (Fig. 50). Comparing the calculated EFs with the measured soil pH evidences a positive relation with the most depleted samples showing the lowest pH. Such pattern probably reflects a lower Te absorption by the roots of the plant with respect to Mg. This should depend from different mobility of the two elements in the soil at different pH values. Indeed Mg is almost exclusively present as Mg^{2+} ion in the whole range of measured pH values while Te is in the form of H_2TeO_3(aq) in the range 2.4 – 6.3 and as $HTeO_3^-$ between 6.3 and 8.7 (McPhail, 1995). The different speciation strongly affects the aqueous solubility of Te which shows its minimum value at pH 4 and an increase of solubility of nearly two orders of magnitude between pH 5 and 7 (Grundler et al., 2013). Although this cannot be simply transferred to more complex soil environment, where interactions with soil components such as organic matter, Fe and Al oxi-hydroxides, clay minerals may play an important role, but may justify a lower uptake of Te with respect to Mg in the soils with lower pH values.

In all cases Tellurium, in soil and plants, is enriched with respect to the continental crust and it is evident that the enrichment of this element increases with the decrease of pH in all matrices (Fig. 51).

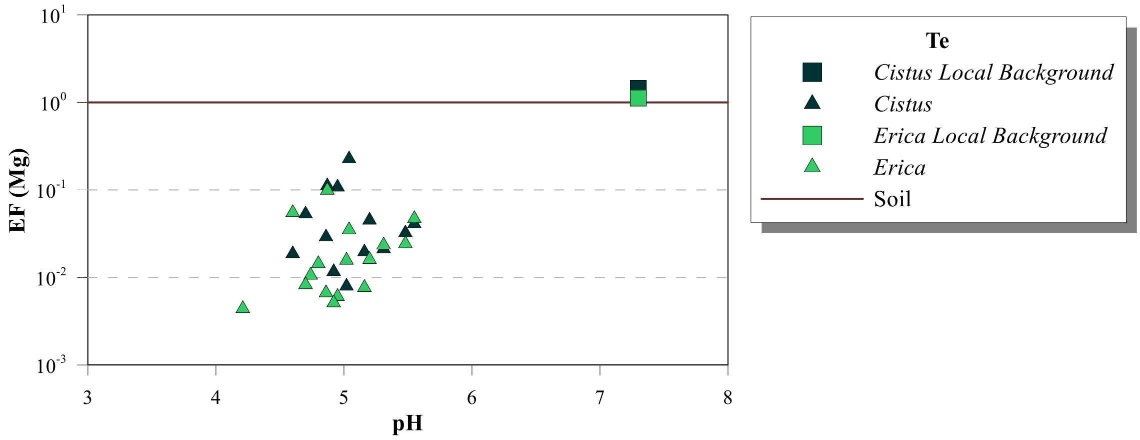

Figure 50: EF (Mg) calculated for Tellurium in plants (*Cistus sp.* and *Erica sp.*) compared with the pH of the soils at Nisyros. The soils collected in each point together to the plants are the reference for EF calculation.

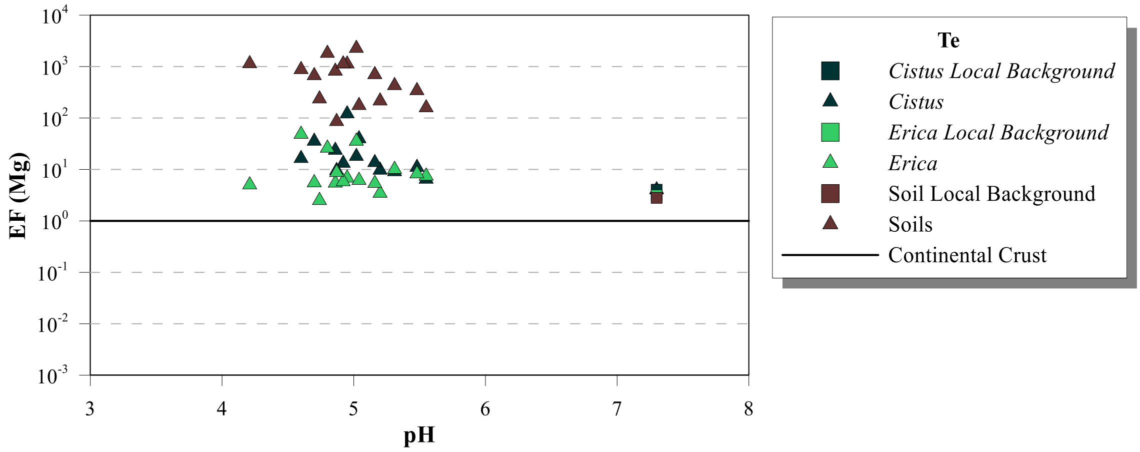

Figure 51: EF (Mg) calculated for Tellurium in soil and plants (*Cistus sp.* and *Erica sp.*) compared with the pH of the soils at Nisyros. The continental crust is the reference for EF calculation.

5.3. Volcanic global budget of Tellurium

5.3.1. Literature review on Tellurium in volcanic emission

In the literature only few estimations regarding Tellurium plume concentrations and fluxes from active volcanoes were reported. The figure 52 shows all estimations of Tellurium fluxes in volcanic environment presented in the previous studies, the highest estimations of Tellurium fluxes in volcanic environment are given by Hinkley and coworkers (1999) with 22 ton/year released from Kilauea (Hawaii, USA), while for Erta Ale (Ethiopia) only 0.2 ton/year were reported (Zelensky *et al.*, 2013). The fluxes of volatile elements, including Tellurium, vary with time also in the same volcano. In the same work of Hinkley *et al.* indicated above a maximum value for the global estimate of tellurium of 270 tons/year is reported, confirming the fact that the volcanic emissions provide an important contribution of this element to the atmosphere (Fig. 53).

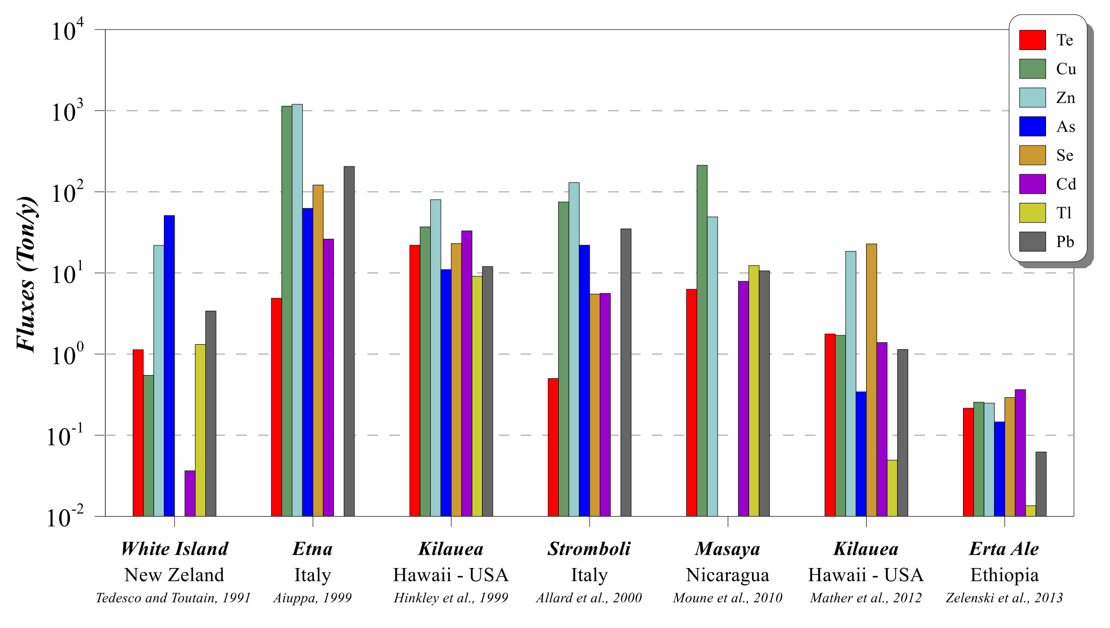

Figura 52: The diagram shows the fluxes to the atmosphere of some elements, including Tellurium (the red bars), reported in the literature for different volcanoes.

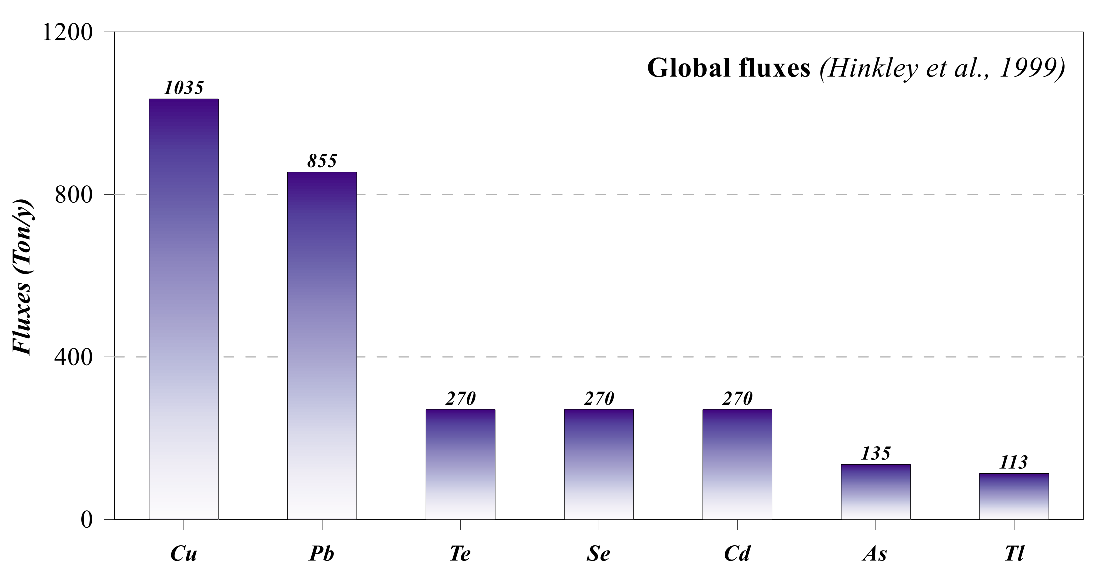

Figure 53: The grapic reports the global estimate of some volcanogenic trace elements, including Tellurium, indicated in the work of Hinkley and coworkers (1999).

5.3.2. New estimations

Basing on the measured concentrations of Tellurium in atmospheric particulate it was possible to estimate the fluxes of this element. Generally, the approach used to estimate the fluxes of volcanogenic metals consist in scaling the metal/sulphur ratio of volcanic emissions, by the sulphur fluxes (Oppenheimer, 2003). In this study, the fluxes of tellurium are calculated by the following expression:

$$\Phi_{Me} = (|Me|/|SO_2|)\,\Phi_{SO2}$$

where Φ_{Me} is the metal flux, $|Me|/|SO_2|$ is the metal-to-sulphur dioxide mass ratios, and Φ_{SO2} is the flux of sulphur dioxide. The SO_2 fluxes were taken from literature or communicated from other research groups and were obtained by using remote sensing techniques, for example: Correlation Spectrometry (COSPEC), Differential Optical Absorption Spectroscopy (DOAS), UV – Camera.

In order to obtain the fluxes, the Tellurium/sulphur dioxide ratios were calculated. The data range from 10^{-8} to $5 \cdot 10^{-5}$, considering that samples of various volcanoes with different activity status have been analysed. From this ratios the fluxes of Tellurium were estimated and there is a general agreement between fluxes estimated in this work and previous assessments (Fig. 54).

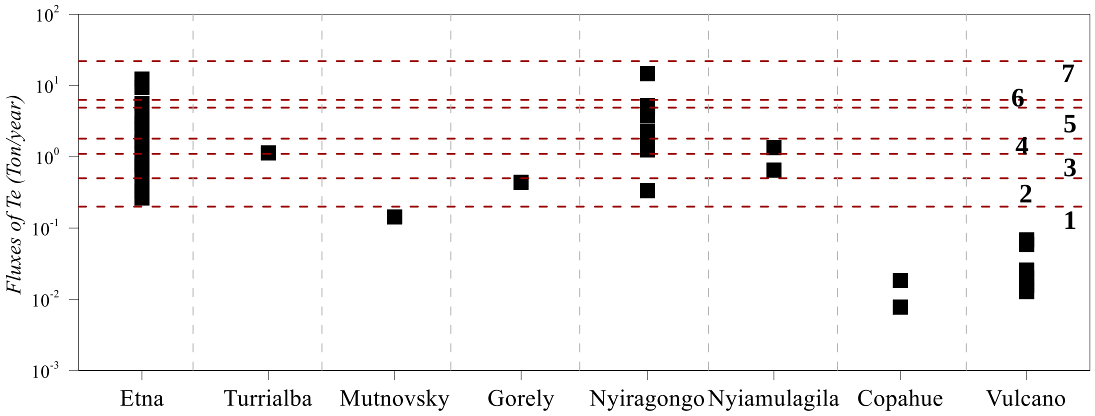

Figure 54: The diagram presents the fluxes of Tellurium calculated in this study. Excepting Copahue (acid lake) and Vulcano (fumarole), the values are in agreement with the previous works, indicated with the red dotted line, the key of numbers is: 1) Erta Ale - Zelenski *et al.*, 2013; 2) Stromboli - Allard *et al.*, 2000; 3) White Island – Tedesco & Toutain, 1991; 4) Kilauea – Mather et al., 2012; 5) Etna – Aiuppa, 1999; 6) Masaya – Moune *et al.*, 2010; 7) Kilauea – Hinhley *et al.*, 1999.

Taking into account old and new data a global Volcanic flux of Tellurium (GVFTe) was extrapolated considering the Te/SO_2 ratios obtained in the present and previous studies and the global volcanic SO_2 flux estimations taken from literature (Fig. 56). As seen in the figure 55 the global range of Te/SO_2 is large but most of the values fall in the narrower range from 1.02×10^{-6} to 7.9×10^{-6} (interquartile range) which was considered for calculation. For the global flux of SO_2 we took in account the range 15 – 40 Mton/year, considering the minimum and maximum estimations of the most recent works (Graf *et al.* 1997; Halmer *et al.*, 2002; Fig. 56). Thus the global Volcanic flux of Tellurium should range from a minimum of 15.3 to a maximum of 316 ton/year. Considering the median value from the considered Te/SO_2 ratios and the average value of Halmers and coworkers global SO_2 flux estimation, our best estimation of the global volcanic Tellurium flux results in 98 ton/year. This value is not so different from the only previous value of Hinkley and coworkers that estimated an upper limit of 270 ton/year and thus confirming the relevance of this element in the total volatile output from active volcanoes.

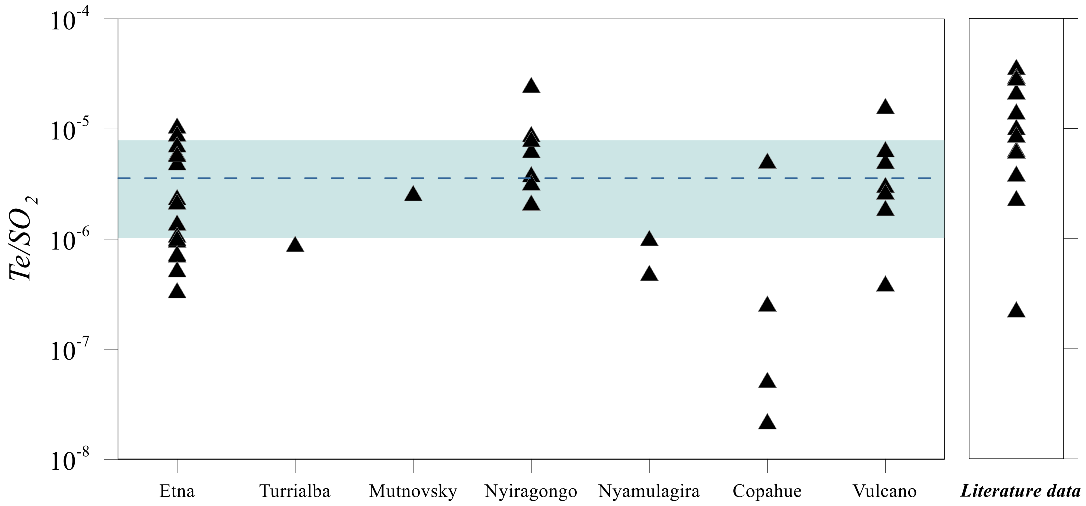

Figure 55: The diagram shows the Ratio Te/SO_2 calculated with data from previeus and this study.

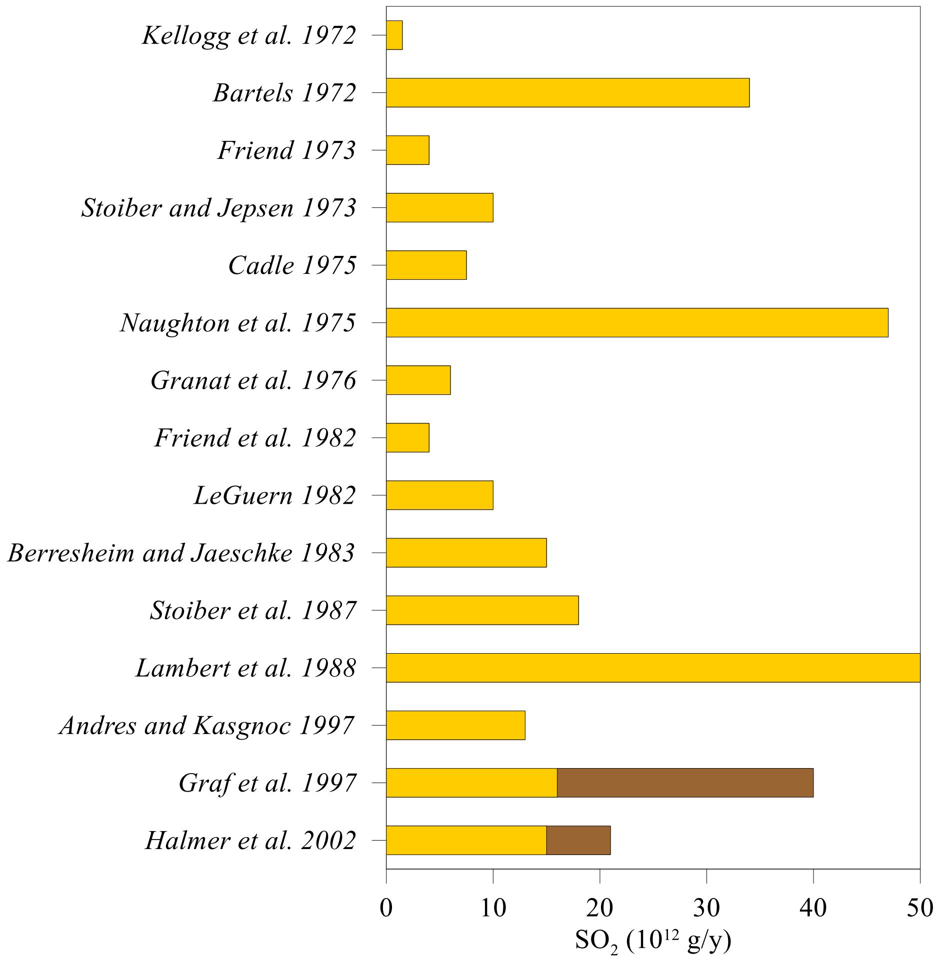

Figure 56: Annual global volcanic SO_2 emission fluxes into the atmosphere by different authors. For the last two estimations the brown area represents the most probable range.

5.4. Impact on human health and the environment

From previous studies we know that the toxicity of Tellurium is similar to Arsenic and Selenium. Tellurite, Te (IV), is a little more toxic than selenite or arsenite, and instead tellurate, Te (VI), is little less toxic than selenite and arsenate (Taylor, 1999 - Tab. 6). The less oxidated species are more toxic in all three elements.

In volcanic areas, the concentrations of Tellurium in plume emission are lower, sometimes orders of magnitude, than the concentrations of Arsenic and Selenium, as reported in the results of this study. Furthermore also other elements with similar toxicity as for example Pb and Sb display similar or higher concentrations, while less toxic compounds like SO_2, H_2S, HCl or HF are emitted in quantities that are many orders of magnitude higher than Te. Consequently, the tellurium contribution to toxic burden of volcanic plume emissions can be considered minor and the effects of tellurium on humans due to inhalation in volcanic areas can be regarded as negligible. Nevertheless, the high Tellurium enrichment factors calculated for bulk deposition, soil and plants in volcanic areas testify for a clear impact of volcanic emissions on the environment close to volcanic areas. But also for plants and animals despite its much higher than background levels, in volcanic areas this element doesn't seem show effect of toxicity.

Table 6: Table modified from Taylor (1997)

Minimum Fatal Doses Associated with Te, Se and As Compounds		
Sodium tellurite	Na_2TeO_3	2.25-2.50 mg Te/kg
Sodium tellurate	Na_2TeO_4	20.0-30.0 mg Te/kg
Sodium selenite	Na_2SeO_3	3.25-3.50 mg Se/kg
Sodium selenate	Na_2SeO_4	5.25-5.75 mg Se/kg
Sodium arsenite	Na_2HAsO_3	4.25-4.75 mg As/kg
Sodium arsenate	Na_2HAsO_4	14.0-18.0 mg As/kg

In the figure 57 is reported the global production of Tellurium from 1940 to 2010. The trend shows the considerable increase of the production during the last years, due to the development of industrial use of this element, from 12.5 ton/year in 1946 to 500 ton/year in the last years (Kavlak & Graedel, 2013). Comparing this data with the GVFTe estimated in this study (Fig. 57), it is evident that the impact of Tellurium on the environment by human industrial activities is greater respect to the past; however, the effects of end-use are almost unknown.

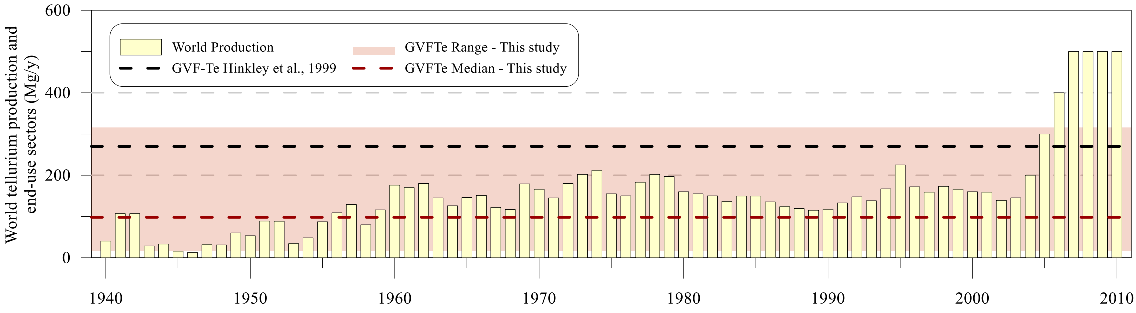

Figure 57: World Tellurium production (data from Kavlak & Graedel, 2013) comparison with GVFTe.

Conclusions

Tellurium is one of the most abundant elements in the Universe among the elements with atomic number over 40, but in contrast is also one of the rarest elements on earth, considering that background levels of tellurium in the crust vary from a few ppb to hundreds of ppm, in relation to the different kind of rocks. In the last years the commercial importance of tellurium has considerably increased because of its wide use in solar cells and electronic devices. Despite such large use, scientific knowledge about volcanogenic tellurium is very poor. Only few reports are available about tellurium concentrations in volcanic plumes and more generally in volcanic areas.

In order to better understand the geochemical behaviour of this element in volcanic systems, considering the scarcity of available data in literature, a dataset of Tellurium abundances in different geochemical matrices (volcanic plumes, rainwaters, ashes, volcanic soils and plants) has been created.

The main results of this work regard the study of mobility of tellurium in active volcanic environments. Coupling all the obtained data it was possible to trace the path of this metalloid starting from the emission sources that are both volcanic gases and in some cases volcanic soluble salts adsorbed on ashes, until its dispersion path through the atmosphere, and the deposition processes to the soils and accumulation in the vegetation.

The results of the volcanic gas emissions (plume, fumaroles, ash leachates) from some active volcanoes, Etna, Vulcano, Turrialba, Miyakejima, Aso, Asama and Mutnovsky, suggest a primary transport of Tellurium in the volatile phase, mainly during passive degassing in gaseous form and as soluble salts mainly as halides adsorbed on the surface of volcanic particles and ashes during explosive activity. Volcanic ashes emitted during explosive events on Etna and Copahue volcanoes (analyzed for tellurium bulk composition and after leaching experiments to evaluate the soluble fraction of tellurium), shows, as expected, an increase with decreasing grain size of the ashes because of the greater specific surface area. This means that when the smaller particles are ejected into the atmosphere they can be transported for longer distance from the source-point, participating to the cloud processing and affecting sequentially the chemistry of the rain, plants and soils in the surroundings of the emission area. The high Tellurium enrichment factors comparable and sometimes even higher than typical volcanogenic volatile elements like S, Cl, F, As and Se calculated for the rainwaters (bulk deposition), for the soils and plants in volcanic areas testify a clear impact of tellurium on the environment close to the active volcanic areas. Soils and leaves of vegetation sampled close to active volcanic vents (Etna, Vulcano, Nisyros, Nyiragongo, Turrialba, Gorely and Masaya) and investigated for tellurium contents show higher concentrations suggesting a bioaccumulation process of tellurium.

On the base of the new data obtained on many active worldwide volcanoes an estimation of the global volcanic flux of Tellurium (GVFTe) has been made. The best estimation of the global volcanic Tellurium flux results in 98 ton/year, confirming the relevance of this element in the total volatile output from active volcanoes (previous study of Hinkey *et al.*, 1999 estimated an upper limit of 270 ton/year). Moreover these new data show very high enrichments of tellurium in volcanic emissions comparing with other volatile elements like mercury, arsenic, thallium and bismuth suggesting a primary transport in the volatile phase, probably directly in gaseous form.

Concluding the results of this study with a great amount of unpublished data on the different matrices analyzed increase our knowledge about the abundances and the distribution of tellurium in volcanic active areas and improves our knowledge about the mechanisms of transport, deposition and bioaccumulation of this extraordinary element.

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