Chapter

Trace Elements in Volcanic Environments and Human Health Effects

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Abstract

Trace elements play an essential role in the normal metabolism and physiological functions of living beings. The distribution and concentration of trace elements in the environment results from both anthropogenic and natural origins; this chapter will focus on volcanism as one of the major natural sources of trace elements. In volcanic areas, the emissions and deposits of volcanogenic elements are key factors for geochemical mobility of trace elements and their distribution in the environment and, their effects on animals and human health. Volcanic areas have been associated with increased incidence of several diseases, such as fluorosis or even some types of cancer, leveraging the studies on the potential of this natural phenomenon as a promoter of diseases. As the Azores Archipelago is a volcanic area, with several manifestations of active volcanism, this region presents itself as an ideal study scenario for a multidisciplinary approach on environmental health problems, such as the exposure to toxic and/or deficient levels of trace elements. This chapter will present an integrated approach, describing the occurrence, the monitoring of trace elements and their characterization, the biological role in human body, and the human biomonitoring and health risk assessment, using case studies as examples.

Keywords: human health, biomonitoring, risk assessment, volcanism, trace elements

1. Introduction

Quality of life is based on an intricate relationship of various factors that include having sufficient nutrition, adequate accommodation and environment, social and psychological fulfillment, and health. Not neglecting the importance of these factors, environment stands out as it plays a crucial role in people's physical, mental, and social well-being.

Given the link between environment and health, as environmental chemicals affect not only the surroundings but also the quality of food and water, there has been a growing concern in the scientific community in the last decades, and consequently an increase in studies characterizing the environmental availability of elements, particularly in the soil. These recent studies have added substantial knowledge regarding elemental availability in soils, particularly for the biogeochemistry of trace elements [1]. The assessment of the concentrations of trace elements in soil is very important not only for environmental purposes, such as quantifying the contamination level, but also to help solve problems associated with elemental toxicity or deficiency in humans and plants.

Trace elements (TEs) are dietary minerals present in living tissues in small amounts; some of them are known to be nutritionally essential, playing a vital role in the normal metabolism and physiological functions of animals and humans [2]. The TEs' essentiality for the human body has been a matter of discussion throughout time and the term "trace elements" has never been clearly defined, being used both in geochemistry and biological sciences for chemical elements that occur in the Earth's crust in amounts less than 0.1% (1000 mg/kg) [1]. Despite their "low" content in the human body, TEs are components of a complex physiological system involved in the regulation of vital functions at all stages of development of the living organism [3].

Throughout time, limited attempts have been made for classifying trace elements. In 1973, WHO [4] classified 19 trace elements into three groups: (i) essential elements: zinc, copper, selenium, chromium, cobalt, iodine, manganese, and molybdenum; (ii) probably essential elements; and (iii) potentially toxic elements. Shortly after, Frieden [5] considered 29 types of elements present in the human body and classified them into five groups:

i. Group I: basic components of macromolecules such as carbohydrates, proteins, and lipids. Examples include carbon, hydrogen, oxygen, and nitrogen;

ii. Group II: nutritionally important minerals also referred to as principal or macroelements. The daily requirement of these macroelements for an adult person is above 100 mg/day. Examples include sodium, potassium, chloride, calcium, phosphorus, magnesium, and sulfur;

iii. Group III: essential trace elements. The trace elements are also called minor elements. An element is considered a trace element when its requirement per day is below 100 mg/day. The deficiency of these elements is rare but may prove fatal. Examples include copper, iron, zinc, chromium, cobalt, iodine, molybdenum, and selenium;

iv. Group IV: additional trace elements. Their role is yet unclear and they may be essential. Examples include cadmium, nickel, silica, tin, vanadium, and aluminum. This group may be equivalent to probably essential trace elements in the WHO classification;

v. Group V: these metals are not essential and their functions are not known. They may produce toxicity in excess amounts. Examples include gold, mercury, and lead. This group is equivalent to potentially toxic elements defined in the WHO classification.

More recently, Frieden [6] proposed a biological classification of trace elements based on their amount in tissues: (i) essential trace elements: boron, cobalt, copper, iodine, iron, manganese, molybdenum, and zinc; (ii) probably essential trace elements: chromium, fluorine, nickel, selenium, and vanadium; and (iii) physically promoter trace elements: bromine, lithium, silicon, tin, and titanium.

As TEs play a significant role in the regulation of many important adaptive mechanisms, including the functioning of all vital systems of the organism, the balance of each element in an optimum range of concentrations is fundamental. The chronic deficiency of essential TEs can, therefore, result in metabolic disturbances and distinct clinical and morphological changes; on the other hand, we must

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not disregard that all TEs can be toxic if consumed at high levels for long periods, disturbing the normal function of vital systems.

2. Trace elements in soil

The main advances in trace element research have been made in soil sciences since soils are considered the most important environmental compartment functioning as a sink for TEs [7–9]. Trace elements are usually distributed over different soil compartments and their retention will depend on several soil characteristics, as well as the parent rock material.

The main soil characteristics include pH, cation exchange capacity (CEC), particle size distribution, electrical conductivity, and organic matter content [10, 11]. These soil properties can promote the accumulation of TEs in soils or their depletion. The most adequate pH for the maximum TE availability is within 6.0–8.0; however, some TEs such as manganese, iron, boron, copper, and zinc are more available to plants when the soil is acidic (pH between 4.5 and 6.5), which contributes to manganese and boron toxicities in plants growing on acidifying soils [12].

The CEC is also a very important soil property as it can influence the soil structure stability, nutrient availability, soil pH, and the soil reaction to fertilizers and other ameliorants [13]. For example, negatively charged sites increase the CEC, holding H^+, Ca^{2+}, Mg^{2+}, Na^+, and NH^{4+}, while the positively charged sites increase the retention of OH^-, SO_4^-, NO_3^-, and PO_4^- [14]. All these soil properties, either combined or isolated, can promote the accumulation or the leakage of TEs in soils.

The parent rock material also assumes high importance in TE availability; when parent materials have high trace element concentrations, the resulting soils also have high or even higher TE concentrations, particularly when the former also result from anthropogenic activities, such as agriculture [15].

Considering that specific soil characteristics can affect the TE availability, the use of universal background concentrations is inadequate, as it may not reflect the "normal" values for specific regions. In this way, each country should determine the background levels for each region with different geological substrates and establish normative values for environmental legislation based on these studies, avoiding misinterpretation of abnormally low or high TE contents [16].

2.1 Measurement of trace element levels in soils

The soil background concentrations/levels will depend on the mineralogical composition of the parent rock material and on the weathering processes that have led to its formation, the granulometry fractions, and the organic matter content [17–19]. These background measurements, which represent natural concentrations in unpolluted pristine soils, are very difficult to assess because they require a soil free of contamination. Given this difficulty, the measurement usually applied is the geochemical baseline concentration that represents an expected range of element concentrations around medium normal sample mean [20]. Although the TE baseline concentration levels in the soil may differ between countries and/or geographical regions, their assessment has been recognized as the only means to establish reliable worldwide elemental concentrations in natural materials [21, 22].

The measurement of TE in soils requires well-planned sampling strategies to achieve accurate data. There are several defined protocols for soil sampling and many digestion techniques to optimize the TE quantification [23]. The conventional methods are based on a regular soil sampling design, with soil sample collection at a depth of 0–20 cm and subsequent chemical analysis of the sampled soils in the laboratory, followed by geostatistical interpolation of the data to obtain the spatial distributions of soil heavy metal content. For the assessment of TE in agricultural areas, the protocol of geochemical mapping of agricultural soils and grazing land of Europe (GEMAS) is the most used as the aim of the project is to provide harmonized geochemical data of arable land and of land under permanent grass cover at the continental European scale. The application of this protocol for meadows requires that all samples will be taken as rather large (2–2.5 kg) composite samples from one extensive field; the minimum size of field should be about 25 × 50 m [24]. The sampling stage is critical and it must take into account what we want to measure and the geological attributes of the site. Also, in order to avoid cross-contamination in the sampling of TEs, metal tools should not be used in the field or in the lab. The sample preparation and storage in the lab often require that the soil samples are air-dried and sieved to less than 2 mm [25]. Afterward, the total TE contents or the extractable fraction can be determined.

Given that the application of these methods has some disadvantages, since they are time-consuming and costly and cannot provide accurate estimates of soil heavy metal content over large areas, new approaches such as remote sensing are starting to be widely used as they can rapidly lead to spatially explicit estimates of soil heavy metal content and monitor their dynamics at a regional scale with low cost [26]. By capturing electromagnetic radiation reflected from the target, remote sensing can be used in the detection of heavy metals in soil and vegetation [27]. However, soil's properties cannot be easily assessed using hyperspectral sensing so the monitoring heavy metal contamination in soils has not been assessed comprehensively and it needs further studies [28].

The assessment of the total concentration of trace elements is required to: (i) determine the background (natural) TE levels in the soil; (ii) assess the total metal content; and (iii) evaluate if there has been TE accumulation over time [29, 30]. To assess the total concentration of TE, soils need to be digested to break down the primary silicate structures of the more resistant quartz and feldspar soil minerals and release the TE into solution. The most common types of digestion are carried with concentrated nitric acid and hydrogen peroxide or with a mixture of *aqua regia* concentrated nitric and hydrochloric acids.

Finally, the elemental concentrations of the digest solutions can be determined by spectroscopic methods, such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), or by plasma mass spectrometry (ICP-MS) [31]. ICP-OES and ICP-MS have more advantages when compared with the AAS, as they allow one to obtain numerous data from running the sample just once and have very low detection limits [32]. While ICP-OES is based on the measurement of excited atoms and ions at the wavelength characteristic for the specific element being measured, ICP-MS measures an atom's mass by mass spectrometry (MS). These distinct approaches result in different lower detection limits; the lower detection limit in ICP-OES is in parts per billion (ppb) while in ICP-MS can be extended to parts per trillion (ppt) [33]. On the study of trace elements in environmental samples, ICP-OES is more commonly used since it may be applied for samples with high total dissolved solids or suspended solids and is, therefore, more robust for analyzing groundwater, wastewater, soil, and solid waste. It is therefore, usually used to measure contaminants for environmental safety assessment and elements with a higher regulatory limit [31]; if the trace elements in study have very low regulatory limits, ICP-MS is adequate for quantification.

2.2 Sources of trace elements

Trace elements can enter the soil by natural or anthropogenic sources [34], and their behavior and fate in soils differ according to their source and species.

The most important anthropogenic sources of trace elements for soils include mining and metallurgical activities, commercial fertilizers, biosolids, irrigation water, coal combustion residues, and auto emissions [34, 35]. Mining and metallurgical activities are recognized as the most important producers of waste and environmental pollution; the metalliferous mines, processing plants, and smelters generate huge amounts of mine tailings that can be transported mainly in the form of wastewater and airborne dust particles [36–38]. Using fertilizers in intensive agriculture can increase the TEs in the soil given that fertilizers contain trace amounts of several elements [15]. Sewage sludges and effluents also contain variable amounts of trace elements of various nature and various anthropogenic origins, although they can be an interesting way to enrich the soil with organic matter [39]. The direct use of sewage sludge can lead to heavy metal phytotoxicity problems due to the lack of stability of organic matter that could be obtained through an appropriate composting process. The TEs also enter the soil trough the water used for irrigation or even by the atmospheric deposition from industrial and urban combustion emissions. The TEs can travel long distances in either gaseous form or in particle phase before deposition; therefore, the contaminated zones can extend up to a great distance from the contamination site. This is easily observed with the automobile exhaust emissions that contaminate not only the roadside soils but, depending on the location, traffic intensity and predominant wind conditions (direction and frequency); the contamination can be observed in soils hundred meters apart from the road [40].

There are also several natural sources (and processes) that contribute to TEs' deposition in soils. The main natural source is the soil parent material as the weathering of rocks and mineral deposits produces metals in dust, sediments, groundwaters, and surface waters [17]. Forest fires with the release of metal and mineral particulate matter in ash, gas, and aerosols or even sea spray with metals in the water droplets can also contribute to the deposition of TEs in soils, not only in the vicinity of their sources but also in areas far away. Another natural factor of major importance is geological activities; they are rather volcanic activities, earthquakes, landslides, debris flows, etc. all of which introduce major and trace elements into the environment [41]. The concentration of metallic TEs is the most affected by volcanic activity [42], resulting in high baseline concentrations of some metals in volcanic soils [15, 43].

The excess of metals in soils may affect the surrounding ecology and human health as these elements are non-biodegradable and therefore environmentally persistent [44]. While some of these trace elements are essential for plant growth and development, the monitoring of TE baseline values in soils is fundamental since at elevated levels they can become toxic. The toxicity of TEs will depend on the dose, exposure pathway, and duration of exposure [45, 46]. Regarding the bioavailability of TE in soils, the context is much wider as it includes chemical availability to a variety of biota [47]. Even with no universal definition, it is assumed that for the study of the environmental risk assessment of TEs in soils, the bioavailability assessment should include their soluble and solid-phase-associated labile fractions. Although the dissolution-desorption, transport, and uptake are very complex processes, the Committee on Bioavailability of Contaminants in Soils and Sediments [48] considered that bioavailability is the fraction of the total concentration of contaminants present in soil (solid and solution phases) which is potentially available for plant uptake or absorption by soil-dwelling organisms.

Considering that the excess of TEs in soil due to volcanic activity cannot be controlled, and that TE ingestion, inhalation, or dermal contact can cause damage to several human systems, the monitoring and baseline determination of TEs in volcanic environments assume particular importance for the inhabitants of these areas.

2.3 Trace elements in volcanic soils

There are several hazards that result from a volcanic eruption; the most immediate and threatening hazards are pyroclastic falls, pyroclastic density currents, lava (flows and domes), lahars and flooding, debris avalanches, and volcanic gases. Nevertheless, volcanic emissions also occur in the post-eruptive phase and in quiescent volcanoes, continuing to affect the ecosystem and consequently human health.

Volcanic regions step-up important scenarios for the study of TEs in soils because: (i) they are densely inhabited in some areas of the Earth and (ii) due to the physicochemical properties, volcanic soils retain TEs, acting as a reservoir and affecting agriculture [15].

2.4 Human health effects

The concern regarding the health effects of environmental exposure to TEs from natural sources has driven the development of tools and methods for assessing the impact of emissions in water, soil, and air. Biological monitoring or biomonitoring is the most commonly applied method to measure human exposure to xenobiotics [49]. There are several studies worldwide that establish the association between concentrations of TE in volcanic soils and its effects on human health.

One of the most well-detailed health problem associated with volcanic activity is fluorosis, which results in high fluoride (F) concentrations in groundwater. The problem was first recognized in Japan and was called "Aso volcano disease" [50], but during the course of the year, high fluoride concentrations (greater than the WHO guideline value of 1.5 mg/l) were also found in Africa, where the crater lakes of western Uganda often have high F concentrations (e.g.4.5 mg/l F in Lake Kikorongo) [51]. High concentrations of F were also found in eastern Turkey, near the Tendurek Volcano, where the natural waters contained fluoride levels between 2.5 and 12.5 ppm [52], and in oceanic islands, such as Tenerife Island (Canary-Spain) [53] and São Miguel Island (Azores-Portugal) [54–56].

Another health problem that has been proven to be strongly associated with the exposure to volcanic environments is thyroid cancer, in particular papillary thyroid cancer (PTC). In 2009, Pellegriti et al. [57] in a register-based epidemiologic study showed that the residents of Catania, a province in the vicinity of Mt. Etna, presented a higher incidence of papillary thyroid cancer than elsewhere in Sicily. More recently, these results were reinforced in the study conducted by Malandrino et al. [58]. In this study, the authors evaluated the environmental pollution and biocontamination in a volcanic area of Sicily and compared the data with the thyroid cancer epidemiology data obtained from the Sicilian Regional Registry for Thyroid Cancer. Their results indicated that the residents in Mt. Etna volcanic area had significantly higher levels of several TEs in their urine when compared to the control area [Cd (×2.1), Hg (×2.6), Mn (×3.0), Pa (×9.0), Th (×2.0), V (×8.0)] and that thyroid cancer incidence was 18.5 and 9.6 per 105 inhabitants in the volcanic and the control areas, respectively; the observed thyroid cancer incidence was exclusively from the papillary histotype.

Besides these, that pose as the most studied TE and linkages to human health effects, there are several other health issues that have an increased risk due to environmental exposure. In Sicily, Italy, various soil types developed from different parent materials were analyzed to compare heavy metal distribution under different geopedological conditions, evidencing that the former depended on the parent rocks [59]. In Turkey, an association was established between the volcanic soil and the high prevalence of upper gastrointestinal cancer rates in the Van region as the fruit and vegetable samples produced in those soils contained potentially carcinogenic levels of heavy metals [60]. More recently, Rodriguez-Espinosa and co-authors [61] analyzed the elemental composition of 25 soils and ash samples after the eruptions of the Popocatépetl Volcano in México, observing that the concentrations of TEs such as Zn, Pb, Ni, Hg, Cr, Cd, Cu, and As were significantly higher than those observed in older samples from eruptions in 1997, suggesting that the naturally highly volatile and mobile metals leach into nearby freshwater sources. In the Azorean volcanic islands, there are also some studies focusing in the concentrations of TEs in soils [15, 62] and its effects on local organisms [39, 63, 64] and human health [50, 53], the latter being particularly focused on fluoride [65–67].

In 2016, Linhares and co-authors [65] verified that there are areas in São Miguel Island-Azores that even with modern water treatment systems present fluoride concentrations slightly above the WHO recommendations [68]. Considering that the main sources of human exposure to fluoride are diet, especially through the ingestion of water and, that in volcanic regions fluoride is continuously released into the environment, these authors developed a biomonitoring study to investigate the feasibility of urine and nail clippings as biomarkers of exposure. Nail clippings revealed to be a more reliable biomarker of chronic exposure to fluoride than urine for populations of different age classes (children vs. adults), with a positive correlation between the fluoride daily intake and fluoride content in nail clippings in children ($r_s = 0.475$; $p < 0.001$), and in adults ($r_s = 0.495$, $p < 0.001$). More recently, Linhares et al. [66] assessed the risk of skeletal fluorosis from environmental exposure to fluoride in hydrothermal areas, using wild mice (*Mus musculus*) as bioindicator species. *Mus musculus* were collected in Furnas village (a village located inside the caldera of Furnas volcano), an area where volcanic activity is marked by active fumarolic fields, hot and cold CO_2-rich springs, and soil diffuse degassing phenomena [69, 70]. The results demonstrated that mice from Furnas village had higher concentrations of fluoride in bones when compared with mice from an area without volcanic activity (616.5 ± 129.3 mg F/g vs. 253.8 ± 10.5 mg F/g, respectively), reinforcing that chronic exposure to fluoride may lead to the development of not only dental fluorosis but also of skeletal fluorosis.

3. Azores as a volcanic scenario

The Azores archipelago is located in the North Atlantic Ocean, in the triple junction of the North American, African, and Eurasian plates [71–73]. The archipelago is formed by nine islands of volcanic origin that represent the emerged part of the Azores Plateau, a thick and irregular area of the oceanic crust roughly limited by the 2000-m bathymetric curve [74]. As a result of the Azores archipelago's location on an active plate boundary, frequent seismic and volcanic activity occurs, including volcanic eruptions and secondary manifestations of volcanism, such as hydrothermal vents and soil degassing processes.

São Miguel, the largest island of the archipelago, is formed by five active volcanic systems, including three central active volcanoes (Sete Cidades, Fogo and Furnas), separated by two fissure systems (Picos and Congro), and two extinct volcanic systems (Povoação and Nordeste) [75, 76].

Since the volcanic activity on the island contributes to a distinct soil elemental profile, resulting in a higher baseline for elements, the study of the baseline levels of TE is fundamental. When bioavailable to plants, animals, and humans, TEs can cause several diseases due to their elevated concentrations in soils. In addition, the high concentrations of some TEs in soils can inhibit the bioavailability of other elements, promoting the deficiency in elements that can be essential for plants, animals, and human health.

Considering that in this island, volcanic activity is usually in a quiescent phase, it presents itself as an ideal study scenario for an approach on environmental health problems, such as the exposure to toxic levels of TE and/or their deficiency.

3.1 Distribution of TEs in São Miguel island soils

In São Miguel island, with five active volcanic systems, all the soils have TE inputs resulting from the volcanic activity along the island. Nevertheless, in an island where the main income is agriculture, with the production of dairy, meat, and horticulture, little is known about the TE profile in these young volcanic soils.

In 2006, Amaral et al. [62] undertook a study to determine some baseline levels of trace elements in soils with different ages from active (Furnas; S. Miguel Island) and inactive volcanic sites (Santa Maria Island) of the Azores archipelago. These authors observed that, except for SiO_2, Na_2O, K_2O, and Zn, the concentrations of major and trace elements were higher in Santa Maria soils. The authors point that these differences may be related to the higher capability of Santa Maria soils to retain the elements, given that these soils are richer in fine grain size particles, to retain those elements. In the study by Amaral et al. [63], using the earthworm *Lumbricus terrestris* as a model, the authors found that even though the volcanic site showed lower levels for most of the analyzed metals, the earthworms presented higher concentrations of the same TEs than those from the site without volcanic activity. These earthworms, with higher levels of trace metals, responded to this environment with higher bioavailability of TEs with a reduction of the thickness of the chloragogenous tissue and intestinal epithelium [63]. The higher bioavailability of TEs in these soils can be explained by the lower pH and clay content, as the authors suggested. Later on, a higher risk for uptake of potentially toxic metals in the active volcanic area was observed by Amaral et al. [77] when studying the scalp hair of men living in Furnas and in Santa Maria Island. The authors found that the scalp hair of men from Furnas had higher concentrations of Cd (96.9 ppb), Cu (16.2 ppm), Pb (3417.6 ppb), Rb (216.3 ppb), and Zn (242.8 ppm) when compared with men living in Santa Maria Island.

More recently, Parelho et al. [15] collected and analyzed soil samples from the farms of the main producers of vegetables in São Miguel island; these farms were located in the Picos Fissural Volcanic System, in the western half of the island. Results revealed that the TE background values fitted in the average values for European volcanic soils. However, this work showed that in addition to agricultural input there are elements of volcanogenic origin and that these specific soils tend to accumulate some trace metals due to their physicochemical properties.

Although these studies gather some information regarding the TE profile in the island volcanic soils, they were limited to areas of island without active volcanism and, therefore, TE contents may be even higher in the soils from where active manifestations of volcanism occur. Lately, there have been some studies that focused on the distribution of several TEs in all the volcanic complexes of São Miguel Island, evidencing a depletion of some TEs in the soils, such as iodine [55] and cobalt [78] and elevated concentrations of others, such as manganese [78].

3.2 Iodine

Iodine is a vital micronutrient required at all stages of life, with the fetal stage and early childhood being the most critical phases of requirement [79]. The connection between geological materials and TE deficiency is well documented for iodine since an inadequate intake of iodine results in disease conditions collectively known as Iodine Deficiency Disorders (IDD) [80]. The iodine overload is less common, but can cause thyrotoxicosis as hyperthyroidism, chronic thyroiditis, Hashimoto's thyroiditis, and even may increase the risk of thyroid gland cancer [81–83].

Since the 1980s, the existence of health problems associated with iodine deficiency has been acknowledged. In 1986, Oliveira et al. [84] made a survey for endemic goiter on the island of São Miguel-Azores and observed that the median iodine intake ranged from 10 to 49 mg iodine/g creatinine, with a goiter prevalence usually greater than 20%. Later on, the studies by Limbert et al. [85, 86] established that urinary iodine deficiency was not only observed in children, but also in pregnant women. The most noteworthy fact of these studies was that the deficient iodine intake was not the same in all the islands of the Azores, with a positive highlight for the population of the island of Santa Maria, with mild deficiencies in iodine intake and, a negative one for the population of São Miguel, with severe deficiencies in iodine intake.

Since it is recognized that the ocean is the main reservoir of iodine and that the Azorean islands have geographical and climatic features that are clearly oceanic, Linhares et al. [55] investigated the environmental availability of iodine and bioavailability to human populations, especially in children at school age. This study reinforced the observations obtained in the previous studies [84, 86], revealing a deficient intake of iodine in the resident population of São Miguel Island, but it went further in the establishment of the causes. In this study, Linhares and the coauthors observed that the environmental availability of iodine was different in the soils from both islands, being significantly higher in the soils of Santa Maria than in São Miguel (58.12 ppm ± 40.94 vs. 14.53 ppm ± 11.79, respectively). The volcanic activity of São Miguel island; the islands' geomorphology; and consequently climate characteristics, such as orography and rainfall, are the main causes for the lower content of iodine in its soils. It must also be taken into account that the iodine soil content results from the complex dynamic balance of three processes: incorporation from the atmosphere, fixation, and volatilization. Soil characteristics, such as soil organic and inorganic components and the clay fraction, can affect iodine fixation. Higher concentrations of the organic and inorganic components and a higher clay content, as observed in Santa Maria island, provide a strong fixation of iodine in the soil, reducing the volatilization; therefore, in more mature volcanic soils (like those from Santa Maria) higher deposits of iodine are expected.

The outcome of this last study reinforces the risk of iodine deficiency in São Miguel Island, emphasizing the necessity of introducing an iodine supplementation program in the population of this island, to overcome the low environmental availability of this halogen and its continued vigilance by periodic urinary iodine surveys.

3.3 Cobalt

Cobalt is usually found in the environment combined with other elements such as oxygen, sulfur, and arsenic. Small amounts of these chemical compounds can be found in rocks, soil, plants, and animals. The concentrations of cobalt in soil range from about 1 to 40 ppm and the amount of cobalt in the air is less than 2 ng/m^3. This specific TE has some notorious differences when compared with the remaining TEs; whereas the other elements are required in ionic form and are then converted into their metabolically active species, the body requires Co in a preformed compound, vitamin B_{12}. The ability to synthesize vitamin B_{12} is only found in some bacteria, algae, and in some ruminants. Grazing cattle can synthesize vitamin B_{12} in the rumen, but in humans the main source of vitamin B_{12} is animal-related foods.

There are reports of health problems related to B12 deficiency, such as pernicious anemia and nerve damage [87, 88], and even psychical disorders, like impaired memory, irritability, depression, dementia, and psychosis [89].

Like iodine, cobalt deficiency has been long ago identified in São Miguel Island, particularly in grazing ruminants [90, 91]. However, it has been a subject of more interest only a few years ago, when Pinto [92] verified that approximately 40% of the dairy cattle in his study had deficient Co intake. These findings are extremely important for volcanic regions like the Azores, where livestock industries, such as dairy cattle farms, rely mostly on pasture grazing, where cattle are raised outdoors with an almost 100% natural diet of grass available in pastures.

To better understand the distribution of Co and its baseline levels on the island of São Miguel, Linhares et al. [78] collected soil samples from grazing sites through the island and observed a distinct pattern in the distribution. The highest concentrations of Co in soils were observed in the volcanic regions of Nordeste and Picos. These differences are related to the volcanic bedrock characteristics of the island; the Co content in the parental volcanic rocks is higher (20–58 mg/kg Co) in the low-silica rocks of Nordeste and Picos when compared to the high-silica rocks of the other volcanic regions. The differences within the volcanic regions of the island lie in the pedogenesis of parental volcanic materials; distinct geochemical compositions related to different degrees of magmatic evolution at depth result in different types of magma: (i) low-silica magmas (basalts and trachybasalts) as in Nordeste and Picos volcanic regions, that have high concentrations of iron, magnesium, chromium, nickel, and cobalt and; (ii) high-silica magmas (trachytes and rhyolites), such as Sete Cidades, Fogo/ Congro, and Povoação, that have low concentrations of these elements [93–95]. Linked to this, the existence of other TEs in the soils can also restrict the Co availability, as it happens with manganese (Mn) when present in high concentrations in the soils of São Miguel Island.

The study by Linhares et al. [78] revealed that the soils' volcanic origin (related to the parent rocks) and soil-forming processes affect the Co availability and, therefore, it is expected that severe Co deficiency can occur in most animals, especially the ones grazing in areas such as Furnas/Congro and Povoação.

The human dietary cobalt deficiency is unusual in individuals that consume animal-related food, fish, nuts, leafy green vegetables, such as broccoli and spinach, and cereals, including oats, since these are good food sources of cobalt [96].

In São Miguel Island, the lack of Co in soil assumes particular importance as the basis of the population feeding relies on locally produced agricultural products, and on meat and dairy products from grazing ruminants that are mainly fed with the available pasture grass in the grazing sites. Therefore, it is expected that, as observed in the ruminants, there might be some defined populated areas where the residents will have a deficient intake of Co and consequently may be more prone to develop several health problems associated with the lack of Co availability.

3.4 Manganese

Manganese (Mn) is a bioelement that has a cofactor function in the enzymatic processes [97]. It takes part in the functioning of antioxidant, musculoskeletal, immune, and reproductive systems and in detoxification processes [98]; nevertheless, excessive quantities of Mn cause toxic effects, especially in the central nervous system resulting in neurological diseases [99]. Manganese is ubiquitous in the environment, and human exposure arises from both natural and anthropogenic activities.

The Mn concentrations in soils strongly depend on the parent rock composition; the Mn contents in rocks can go from 174 mg/kg in sandstones to 1300 mg/kg in basalts, with an overall mean of 733 mg/kg Mn in the upper continental crust [100]. The Mn oxides in soils have very high sorption ability and they can accumulate ions from the soil solution; these oxides have a strong affinity for Co ions, which can reduce Co availability to plants.

The human exposure to Mn occurs mainly by ingestion; this TE is naturally present in a wide variety of foods, including whole grains, clams, oysters, mussels, nuts, soybeans and other legumes, rice, leafy vegetables, coffee, tea, and many spices [101, 102]. Manganese is absorbed in the small intestine and, after absorption, some Mn remains free, but most of it is bound to transferrin, albumin, and plasma alpha-2-macroglobulin. Mn deficiency is very rarely observed in humans but cases of Mn toxicity have been reported. Mn toxicity can be related to the dietary Mn intake and to chronic environmental exposure in welding and mining sites, as the inhalation of Mn dust can be toxic [103]. Mn toxicity affects the central nervous system and can cause tremors, muscle spasms, tinnitus, and hearing loss [101, 102]. Mn toxicity can also cause "manganism," a neurodegenerative disease with symptoms that resemble Parkinson's disease [104] and "Machado Joseph Disease (MJD)," a progressive spinocerebellar ataxic disorder [105].

In the Azores, there are few studies focusing on Mn availability and its effects. The existing studies focus on the assessment of Mn concentration in hydrothermal vents, as tracer of hydrothermal activity intimately related to mid-ocean ridge processes [106] and the Mn bioaccumulation in marine species, such as *Cystoseira abies-marina* [107]. Regarding the assessment of Mn in soils, the most recent studies are orientated to vineyard soils in the islands of Terceira, Graciosa, and Pico. Lima et al. [108] revealed that the Mn concentration in the soils of cultivated vines was 692.5 mg/kg in Pico, 1023.8 mg/Kg in Terceira, and 2041.6 mg/kg in Graciosa, evidencing significant differences between these islands.

More recently, in a survey to access cobalt concentration in volcanic soils to predict the risk of cobalt deficiency [78], the concentration of Mn was also determined as it can affect Co bioavailability. These authors verified an uneven distribution of Mn in the defined volcanic regions of the island; the highest Mn concentrations were observed in Nordeste and Picos (1782.50 mg/kg ± 108.98 and 1461.11 mg/kg ± 63.93, respectively), while the lowest concentrations were observed in the soils of Povoação and Furnas/ Congro (874.88 mg/kg ± 78.52 and 746.25 mg/kg ± 209.07, respectively). As observed for Co, the Mn concentration in soil is strongly associated with their content in the parental volcanic rocks. Therefore, low-silica magmas (basalts) of Nordeste and Picos have higher contents of Mn when compared to Furnas/ Congro and Povoação parent volcanic rocks formed by high-silica magmas (trachytes).

The most noteworthy aspect of the Mn concentration in the volcanic soils of São Miguel island is that all the volcanic regions have concentrations above the estimated background mean of the European soils (524 mg/kg) [24] and that in most grazing sites the measured concentrations were higher than 900 mg/kg (upper limit threshold) [Linhares et al. (unpublished data)]. Considering that high concentrations of Mn can be associated with the Machado Joseph disease [105, 108], this scenario undertakes a singular meaning in the Azorean context. There are two major ancestral origins: (1) a worldwide-spread haplotype, TTACAC or the Joseph lineage, and (2) a more recent one, GTGGCA or the Machado lineage, seen mostly in Portuguese people [109, 110], being associated with families with MJD from the Portuguese Azorean islands of Flores and São Miguel (respectively, the birthplace of the Joseph and the Machado kindreds). Nowadays, the Azorean group remains the most important cluster of this disease, with 32 extended MJD families with origins in Flores, S. Miguel, Terceira, and Graciosa islands [111]. In Flores Island, the prevalence of the disease has been decreasing through the years but MJD still reaches its highest worldwide value (1:239), constituting a public health problem [112].

In 2004, Purdey [105] established a common abnormal hallmark of high manganese (Mn)/low magnesium (Mg) status and suggested that this aberrant mineral ratio inactivates the Mn/Mg catalyzed endonuclease-1 enzyme. The high Mn/low Mg rate observed in all volcanic regions of São Miguel Island reinforces the need for further studies in these elements as they are intimately related to MJD.

These studies evidence that the Azores archipelago presents itself as an ideal scenario for the study of TE availability and possible health effects. However, the total TE concentration in soil is a relatively weak measure of their bioavailability. Given that the bioavailability depends on specific soil characteristics, such as organic matter content and pH, similar concentrations of TEs in different soils may not have the same bioavailability.

The assessment of TE bioavailability is fundamental, as the bioavailable fraction of trace elements is the fraction most likely to harm plants and animals. Consequently, the impact of TEs on soil and the surrounding environment cannot be predicted by measuring the total concentration of elements *per se*, since only the soluble and mobile fraction has the potential to leach or to be taken up by plants and enter the food chain [113]. Future studies should consider the assessment of the bioavailable part of the TEs in volcanic environments, to define remediation strategies in order to prevent health problems associated with TE depletion or excessive intake.

4. Conclusions

The assessment of the concentrations of TE in the soil is very important, not only for environmental purposes but also to help solve problems associated with human health and plant toxicity. Trace elements' profiles in soil result essentially from the weathering of geologic parent materials since their concentrations are directly linked to the parent material based on their immobile nature.

Given the volcanic origin of the Azorean soils, the natural enrichment of some elements, such as manganese, and an uneven and reduced distribution of others, such as cobalt and iodine, can contribute to the development of health problems in plants, animals, and humans. Due to the natural enrichment of some chemical elements in volcanic soils, resulting from the volcanic activity, which cannot be controlled, a very tight control of the possible sources of anthropogenic contamination is crucial to prevent the occurrence of toxic levels that prejudice plants, animals, and human's health. Regardless of substantial progress in the study of soil TEs, the application of critical exposure concentrations and the associated health risks are yet scarce and not fully clarified. Although the data obtained for the Azorean soils pinpoints to possible toxicity of manganese and deficiency of cobalt in some areas, more thorough studies, such as the ones developed for iodine, are required. Only with further information, focusing primarily on the bioavailability and bioaccessibility of the trace elements, it will be possible to adequately predict the health risks of exposure to soil TEs, which is particularly relevant in the areas where the environmental risk is greater, such as the volcanic environments.

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