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Impact of chemical elements released by the volcanic eruption of La Palma (Canary Islands, Spain) on banana agriculture and European consumers

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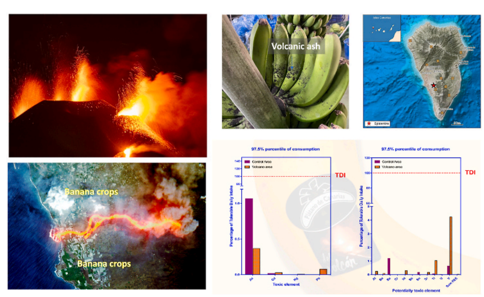
HIGHLIGHTS

- Volcano bananas contain more molybdenum, capable of providing 35% of the RDI.
- Washing the bunch can remove most of the toxic elements deposited on the bananas.
- Concentrations of Mo, Co, Pb, Fe, Al, Ti, V, and REE were increased in the flesh of volcano bananas.
- The banana skin accumulates much higher concentrations of toxic elements than the flesh.
- In the worst-case scenario, they would provide less than 5% of the tolerable daily intakes of toxic elements.

GRAPHICAL ABSTRACT



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ABSTRACT

The recent volcanic eruption on the island of La Palma has aroused the concern of banana producers and consumers, given that in its area of influence there are thousands of hectares of banana plantations with an annual production of about 100 million kilos for export. Since volcanoes are one of the main natural sources of heavy metal contamination, we sampled bananas from the affected area and determined the concentrations of 50 elements (Ag, Al, As, Au, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, Ho, In, La, Lu, Mn, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pm, Pr, Pt, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, Y, Yb and Zn). The levels of 36 elements were elevated but the washing implemented after the eruption can remove a good part. After the washout, bananas have elevated levels of Fe, Al, Ti, V, Ba, Pb, most of the rare earth elements, Mo, and Co. In all cases, except Mo, the elevation is much higher in the peel than in the flesh. In the case of Mo, the elevation in

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banana flesh would translate into a higher nutritional intake of this trace element, which could represent up to 35% of the daily nutritional requirements. Exposure to toxic or potentially toxic elements, does not represent a health risk, since would not exceed 5% of the tolerable daily intake, even in the worst-case scenario.

1. Introduction

Volcanism is one of the most powerful geological manifestations and reflects the dynamic activity of the earth's interior and the movements of the earth's crust (Fabricio Neta et al., 2018). During a volcanic eruption, generally of short duration, huge quantities of pyroclastic material, ashes, and gases are emitted and projected to great distances (Ruggieri et al., 2010) which causes important and lasting changes in the environment (Pérez-Hernández et al., 2021). In volcanic regions, pyroclastic materials have formed soils with unique physical, chemical, and mineralogical properties (Amaral et al., 2007; Ruggieri et al., 2010), and are generally rich in trace elements and plant nutrients, but also toxic or potentially harmful elements and minerals (Alonso Gonzalez et al., 2021; Franco-Fuentes et al., 2021; Marques et al., 2019). In fact, volcanic eruptions have been described as one of the main non-anthropogenic sources of contamination by toxic elements, which are either released in gaseous form during the eruption itself, and disseminated in the atmosphere and oceans (Ermolin et al., 2018; Rubin, 1997), or from the release to the ground from pyroclastic material or ashes (Fabricio Neta et al., 2018). Several studies indicate that leachable elements from this material easily enter the biological cycle, and that this, in the long term, enriches the soil by adding nutrients such as Ca, Mg, K, Na, P, Si and S (Anda and Suparto, 2016). However, in the short term, this potential transfer of bioavailable elements may have toxicological implications for the environment and for the food safety of crops exposed to this influence (Rodriguez-Espinosa et al., 2015; Wardell et al., 2008), which is of concern to producers and consumers.

The Canary Islands are a Spanish volcanic archipelago located in the Atlantic Ocean about 100 km off the coast of Western Sahara. It is located on the African Tectonic Plate, and regular volcanic eruptions occur there (Becerril et al., 2013; García-Cervigón et al., 2019). The last one started last September 19 in the Cumbre Vieja ridge, on the island of La Palma, and is still ongoing. So far, lava has covered an area of 1000 ha, and volcanic ash is distributed throughout the island of La Palma, having even reached the neighboring islands of Tenerife and El Hierro. The eruption has severely affected the main economic engine of this island, the production of bananas for export, with losses so far estimated at 100 million euros. Banana peel has proven to be an efficient absorbent of metallic elements (Bediako et al., 2019; Memon et al., 2009; Rashid et al., 2010), to the point that it has been used for bioremediation of contaminated sites (Bediako et al., 2019; Memon et al., 2009). This effect is particularly important in the case of some toxic elements associated with volcanic eruptions, such as arsenic (Tabassum et al., 2019), lead (Afolabi et al., 2021) and other heavy metals and toxic elements (Massimi et al., 2018), including rare earths (Gasnier et al., 2010). Thus, there could be reasonable doubt that bananas exposed to these large amounts of ash could present any food safety issues. Beyond a purely local problem, it should be noted that more than 95% of the banana production of the island of La Palma is destined for export (which amounted to more than 150,000 tons in 2021), so these bananas are consumed mostly throughout Spain and a small part in other European countries, reaching a potential population of about 50 million consumers.

In this study, bananas recently harvested in the area most affected by the volcanic ash were sampled, as well as bananas from the same area, but sampled before the volcanic eruption and, therefore, free from its influence. Fifty essential, toxic, and potentially toxic elements have been quantitatively determined, both in the peel and in the flesh of the bananas, and an estimate has been made of the intake of these elements and their food safety for consumers.

2. Material and methods

2.1. Sampling

In this investigation, banana samples were taken in two processing plants. These facilities receive the production from the region most affected by the volcanic ash rain, which has been constant since the time of the eruption. The sampling was performed on the 40th day of the eruptive process. During the volcanic eruption, the protocol established by the agricultural cooperatives in the region consists of blowing with pressurized air on the farm itself to remove as much of the ash as possible (Fig. 1A) and avoid damage to the bananas due to friction during transport (Fig. 1B). Eight samples were taken at this point. Once at the processing plant, the banana bunch is immersed in a tank with water prepared for this purpose, which sprays jets of water at moderate pressure in a first wash to remove much of the ash still adhering. After the banana hands were separated, they were subjected to the usual process of washing on a belt or mat and application of the post-harvest treatment (Fig. 1C), and at this point other 12 samples were taken. As a control, 6 samples from the same area were used, which had been taken in the week prior to the volcanic eruption as part of the usual protocol for self-control of pesticide residues prior to export, which is routinely performed in the Environmental Analysis Department of the Technological Institute of the Canary Islands, and where they remained frozen, as required by protocol in case it is necessary to perform counter-analysis. In other words, a total of 26 samples were processed (about 60 kg of bananas): 6 controls, 8 samples of bananas before the additional washing (implemented due to the volcanic eruption), and 12 samples of bananas ready for consumption. Each sample consisted of 2 hands of bananas taken from different points of the bunch (one from the top and one from the bottom of the bunch), with a total weight of approximately 2 kg each. The samples were taken to the laboratory on the same day of collection and processed for analysis the following day. Banana skins and flesh were processed separately, except for the study of the effect of washing, where whole bananas were processed, as is required for the analysis of pesticide residues.

2.2. Standards and elements

The concentration levels of 50 elements in banana skins and flesh or in whole banana homogenates, as appropriate, were determined. The list of elements analyzed included the essential elements as well as the traditional toxic elements. In addition, we included a set of other elements, of proven or potential toxicity. According to the latest edition of the list of priority pollutants developed by the Agency for Toxic Substances and Disease Registry (ATSDR), there are up to 18 elements whose effects on human and environmental health should be monitored (ATSDR, 2019; Cabrera-Rodríguez et al., 2018) based on a combination of their frequency, toxicity, and potential for human exposure. It should be noted that this list includes several essential elements, indicating that although these are homeostatically regulated, overexposure to some may pose a threat to human health. All of these elements were included in the study. In addition, there are a number of other elements that have not been classified as toxic or priority pollutants and to which human exposure has been irrelevant in the past because their presence in the earth's crust is limited or extremely unlikely. These are the rare earth elements (REE) and other minority elements (ME), to which only living beings and crops grown near the places with the highest concentrations of these elements would be exposed under natural conditions. Different rock types (phonolites, trachytes, rhyolites and syenites) have been identified in the Canary Islands, all of them of magmatic origin, which contain an enrichment of REE and other ME in relation to the average of the Earth's crust (Menéndez et al., 2019; Neumann et al., 2004). They have recently been identified as emerging pollutants, not so much because of natural pollution, but because of their extensive and increasing by the technological industry (Hussain and Mumtaz, 2014; Tansel, 2017), the medical industry and zootechnics. The potential health effects of human exposure to these "emerging" contaminants began to concern the scientific community, as animal studies and human occupational exposure data suggest specific bioaccumulation of REE and ME in tissues (Pagano et al., 2015b). In this case, not because of their technological applications, but because of natural contamination in the context of a volcanic eruption, we considered it interesting to include this group of elements in the study.

The complete list of elements comprises: Ag (silver); Al (aluminum); As (arsenic); Au (gold); Ba (barium); Be (beryllium); Bi (bismuth); Cd (cadmium); Ce (cerium); Co (cobalt); Cr (chromium); Cu (copper); Dy (dysprosium); Er (erbium); Eu (europium); Fe (iron); Ga (gallium); Gd (gadolinium); Hg (mercury); Ho (holmium); In (indium); La (lanthanum); Lu (lutetium); Mn (manganese); Mo (molybdenum); Nb (niobium); Nd (neodymium); Ni (nickel); Os (osmium); Pb (lead); Pd (palladium); Pm (promethium); Pr (praseodymium); Pt (platinum); Sb (antimony); Sc (scandium); Se (selenium); Sm (samarium); Sn (tin); Sr (strontium); Ta (tantalum); Tb (terbium); Th (thorium); Ti (titanium); Tl (thallium); Tm (thulium); U (uranium); Y (yttrium); Yb (ytterbium); and Zn (zinc). Pure standards for all elements were purchased in acid solution (5% HNO3, 100 mg/L, CPA Chem, Stara Zagora, Bulgaria).

2.3. Analytical procedure

Six fingers (bananas) were taken from each of the two hands forming each sample. The peels were separated from the flesh and homogenized separately in a domestic food processor with ceramic blades. For the study of the effect of washing, another 3 bananas from each hand were processed, without separating the skin. Duplicate digestions of each of the subsamples were performed, and from each digestion 3 independent analyses were performed, so that each result represents the median value of 6 independent measurements. Acid digestion of the homogenized samples was performed with the aid of a microwave digester (Ethos Up, Milestone SRL, Italy). For this purpose, 1 g of homogenate was weighed into the digestion vessels and 50 μL of the internal standard solution (Sc (scandium), Ge (germanium), Rh (rhodium) and Ir (iridium) at a stock concentration of 20 mg/mL each), and 2.5 mL of concentrated HNO_3 (65%) and 7.5 mL of Mili-Q water were added to each sample. The digester was programmed in three stages at 1800W of power: 1) 5 min at 100 °C; 2) 5 min at 150 °C; and 3) 15 min at 200 °C. After cooling, the complete digests were transferred to conical bottom polypropylene tubes and diluted to 15 mL with Mili-Q water. Finally, an aliquot of each sample was taken for analysis. Reagent blanks were prepared similarly to the samples, and every tenth sample was included in the analytical batch. For instrumental analyses, we employed an Agilent 7900 ICP-MS (Agilent Technologies, Tokyo, Japan) equipped with standard nickel cones and a crossflow nebulizer with a make-up gas port (× 400 nebulizer, Savillex Corporation, MN, USA) for all measurements. All data were acquired and processed with Agilent MassHunter data analysis software (version 4.2). Daily, the ICP-MS was optimized using a tuning solution consisting of a mixture of Cs (cesium), Co (cobalt), Li (lithium), Mg (magnesium), Tl (thallium) and Y (yttrium) (Agilent Technologies, Palo Alto, CA, USA). The entire procedure was validated prior to use in the sample analyses. To avoid isobaric interferences, in the development of our analyses the atomic mass of highest abundance is always selected, so that, for the elements included in the study, the isotopes are totally different from each other, avoiding that the mass of one element can interfere in the quantification of the rest. In addition, the 4th generation Octopolar Reaction System (ORS4) was operated in helium mode (He_2) to reduce polyatomic interferences, improving detection limits for most elements, and completely ruling out the need for mathematical correction of interferences (Agilent, 2014). Two standard curves (5-point, 300 ng/mL-0.005 ng/mL) were developed to avoid inter-element interferences: (1) one using a commercial multi-element mixture (CPAchem, 100 mg/L, 5% HNO_3) containing all essential elements and major heavy metals and (2) another multi-element mixture custom-made in our laboratory from individual elements (CPAchem) containing REE and TE. Linear calibration curves were found for all elements (regression coefficients ≥0.995). To avoid the memory effect associated with Hg, a cleaning solution composed of 2.0% HNO_3 and 0.5% HCl was introduced between the samples.

The entire/complete procedure was validated prior to its use in the analyses of samples. The quality parameters including linearity (correlation coefficient, R^2), limits of detection and quantification, precision (coefficient of variance, CV%), and accuracy. Furthermore, the methods were also validated through participation in accredited laboratory proficiency test (inter laboratories calibrations) organized by the German External Quality Assessment Scheme for Analyses in Biological Materials (G-EQUAS).

Recoveries obtained ranged from 82 to 115% for all the elements. Instrumental LODs and LOQs were calculated as the concentration of the element that produced a signal that was three and ten times higher than that of the averaged blanks, respectively. The sample LOQs were calculated by multiplying the instrumental LOQ by the dilution factor suffered by the sample during the digestion procedure (1:10 v:v) (Supplementary Table 2). The accuracy and precision was assessed performing recovery studies using alkaline solution fortified at three different levels of concentration. In general, the calculated relative standard deviations (RSD) were lower than 8%. However, for some elements (Ti, Cr, Cu, Ni, Se, Fe, Ba, Zn, Sm), the RSD raised to 15–16% at the at the lowest level of fortification. On the other hand, the precision was improved at the highest level of concentration studies, as it was lower than 5% for all elements.

Fig. 1. (A) Hand of bananas in the bunch with volcanic ash still adhering after on-farm blowing. **(B)** Damage caused by volcanic ash rubbing during transport to the processing plant. **(C)** Banana washing belt, where the remaining ash and dirt is removed, and post-harvest treatment is applied.

2.4. Estimates of the dietary intake of the elements, evaluation of the nutritional contribution of essential elements and the health risk of toxic elements

For the estimation of the intake of elements, the total consumption of bananas by the Spanish (Suarez et al., 2016), and the European population (highest consumption values reported (EFSA, 2021)) were considered. The case of the Canary Islands, where the consumption of bananas is the highest in Europe (Serra Majem et al., 2000), was also studied. The banana intakes at the 50th and 97.5th percentile (g/day) were multiplied by the element concentrations in the edible part of the banana (median values expressed in ng/g fresh weight) according to the results obtained in this study. For the estimation of the risk-benefit ratio, the estimated daily intake (EDI) values of elements for each scenario (average and high consumers) were compared with the reference values. As dietary reference values (in the case of essential elements, DRVs), the population reference intake (PRI) values reported by the European Food Safety Authority (EFSA) were used (López-Sobaler et al., 2019; Lupiañez-Barbero et al., 2018). According to the European standard, the PRI is the equivalent of the Recommended Dietary Allowances (RDA) in the United States, i.e., the level of daily dietary intake of a nutrient that is considered sufficient to meet the needs of 97.5% of healthy individuals in each life stage and sex group. Where EFSA has not reported the RDA, the adequate intake (AI) has been used as the reference value. The AI is the amount established as somewhat less than adequate for all members of the population group. On the other hand, as toxic reference values (TRVs), the EPA non-carcinogenic EPA tolerable daily intake (TDI) values (EPA, 2021) were used. There are some elements, such as Pr, Th or Ti, for which no TRV has been established, so they have been excluded from the risk analysis. An official TDI has also not been established for REE and other MEs included in this investigation. However, some authors have proposed an allowable daily intake of 61 μg/kg body weight for rare earth oxides (Zhuang et al., 2017), obtained from human health studies in REE mining areas and experimental results in animals. We have used this value as TDI for these elements, which have therefore been considered as a group for risk analysis.

2.5. Statistical analysis

All statistical analyses were performed with GraphPad Prism v9.3 software (GraphPad Software, CA, USA). The distribution of the variables included in this study was evaluated using the Kolmogorov-Smirnov test. The concentration of most of the elements in bananas did not follow a normal distribution, so the results are expressed in terms of median and interquartile range (25^{th} percentile - 75^{th} percentile). For this same reason, we employed nonparametric tests to test for statistical differences between groups, as these evaluate the median rather than the mean, which is appropriate given the relatively high number of undetected values in some elements (specially REE and ME). Homogeneity of variance (homoscedasticity) was previously tested using Levene's test. The Kruskal-Wallis and Mann-Whitney U tests were used as nonparametric tests for overall and pairwise comparisons, respectively. However, as an additional check, pairwise comparisons were also performed using Student's t-test after logarithmic transformation of the data. A P value of less than 0.05 (two-tailed) was considered statistically significant. Data below the LOQ but above the LOD were assigned a random value between these two limits. Data below the LOD were considered undetected.

3. Results and discussion

3.1. Effect of banana washout

Since the eruption began, it is estimated that the volcano has expelled an average of 150,000 cubic meters of ash per day. This enormous amount of pyroclastic material affects an area of about 3500 ha, 51% of which (about 1800 ha) is occupied by banana plantations (ISTAC, 2009), with an annual production of about 100 million kg. A week after the eruption began, banana cooperatives implemented a series of protective measures for the harvest, such as the use of micro-perforated plastic covers for banana bunches on the farms or blowing the bunches with machinery just before cutting (ASPROCAN, 2021). As an additional measure, some processing plants have adopted the immersion of the bunches in specially prepared water tanks, where they are subjected to medium-pressure water jets to mechanically wash off the ash, prior to the normal washing of banana hands to remove dust and debris. For this study, samples of bananas were taken before (n = 8) and after washing (n = 12) to test the efficacy of washing in removing possible contamination by elements of magmatic origin. Fig. 2 shows the results of this analysis. As can be seen, washing produced a significant reduction of 37 of the 50 elements analyzed (74%). There are some very striking cases such as Ti, a very low abundant element in the fruit, but which shows very high concentrations in the unwashed bananas (median = 4689.3 ng/g) and which after washing was reduced by 96.8% (median = 146.7 ng/g) (Fig. 1C). Equally striking were the cases of Al and Fe, both at very high concentrations in the unwashed bananas (medians of 22069.8 and 17018.5 ng/g, respectively), and which after washing were reduced by 88% (median = 2613.4 ng/g) and 83% (median = 2890 ng/g), respectively. Other cases of very striking reduction are those of As and Pb (Fig. 1B), V (Fig. 1C), and the totality of detected rare earth elements (Fig. 1E). Clearly, in all these cases, the high or relatively high concentrations of elements in the unwashed bananas are due to volcanic ash deposits. In the case of Ti, Al, and Fe, it has been frequently described that volcanic ash is very rich in these elements (Gislason et al., 2011; Ovalle et al., 2018). It has been also described that nanoparticle of volcanic ash have a role in the transport of toxic elements, such as Ni, Zn, Cd, Ag, Sn, Se, Hg, Tl, Pb, and Bi on a global scale. The concentration of these elements in ash nanoparticles can be 100 to 500 times more concentrated than in the bulk volcanic material (lavas and pyroclasts) (Ermolin et al., 2018). However, the composition can vary greatly from region to region (Aullón Alcaine et al., 2020). Early data obtained by scientists from the magma of La Palma volcano indicate that it contains large amounts of tephrite (IGME-CSIC, 2021; IGN, 2005), a silica-based mineral containing Ca, Na, Fe, Mn, Li, Mg, Cr, Al, and Ti, as main components (Klügel et al., 2000). The magmatic material also contains basanite, as it is usual in the eruption of the Canary Islands, which is rich in heavy metals (Nuez Pestana et al., 2001). In view of these results, the rest of the work was carried out with washed bananas.

3.2. Nutritional evaluation of banana consumption (essential elements)

We first analyzed the essential element content of ready-to-eat bananas, using samples prior to eruption (n = 6) and those collected specifically for this work (n = 12). Skins and flesh were analyzed separately (Table 1). In the skins we only found significant differences in Zn and Se, both with higher levels in the skins of ash-affected bananas than in the controls. As we already commented, it has been described that pyroclastic material can contain significant concentrations of metals, including Zn and Se, particularly associated with nanoparticles thereof, which travel long distances (Ermolin et al., 2018). Significant differences were also found in banana flesh, but in this case for Mn, Mo, and Co, which were higher in post-volcanic eruption bananas. This results in an increase in the nutritional contribution of these three elements (Fig. 3), being very significant in the case of Mo. In average consumers of bananas, this fruit provides about 11% of the daily nutritional requirements of this element, while in bananas harvested after the volcanic eruption this contribution would be almost 18%. These contributions would be more than double in European consumers in the 97.5th percentile, and almost five times higher in Canary Island consumers in this percentile, reaching around 85% of the dietary reference value in these consumers (data not shown in the figure). Molybdenum is a structural constituent of molybdopterin, which is essential for the

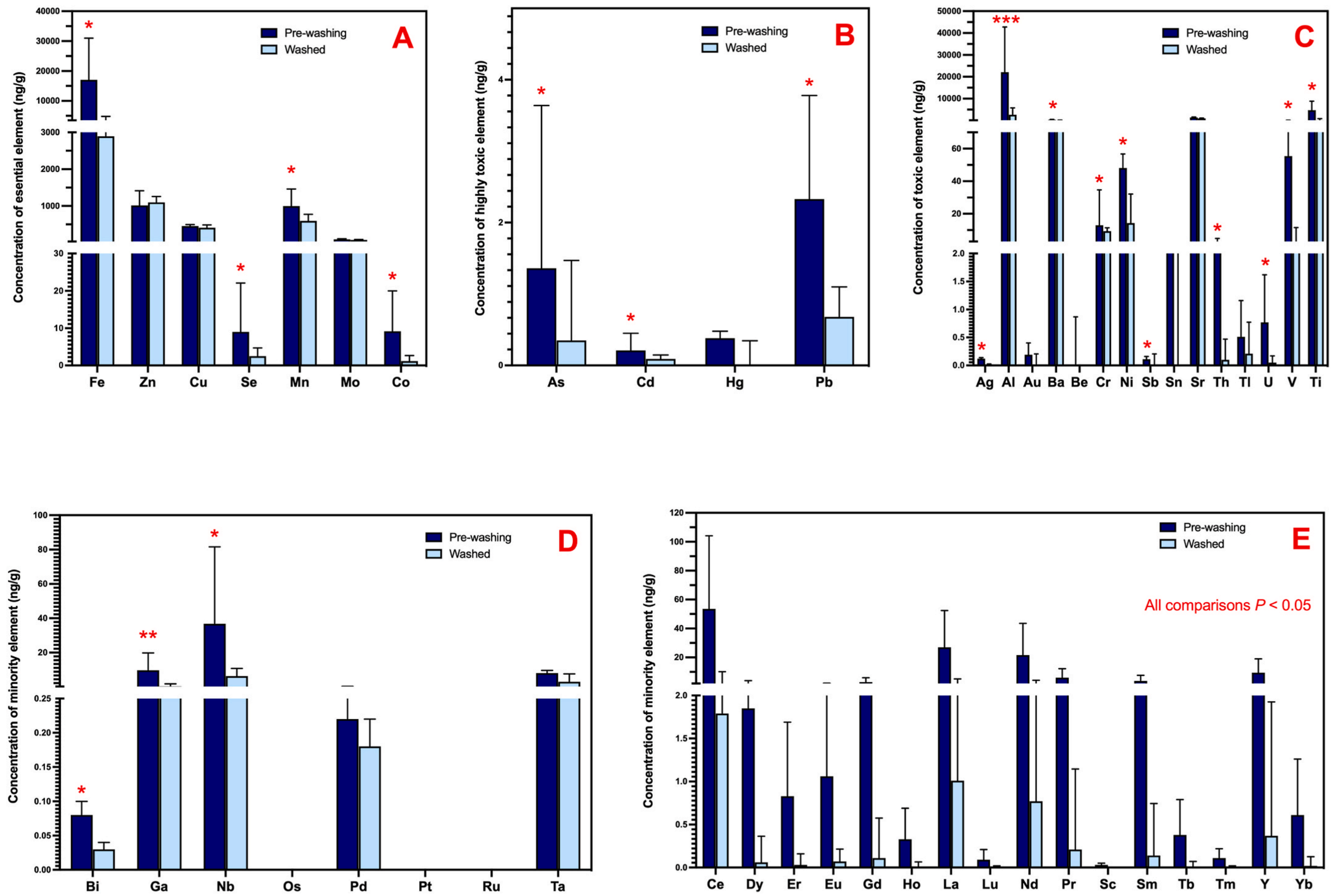

Fig. 2. Comparison of the element content of banana homogenate from the volcano area before and after the washing protocol implemented to remove the ash deposited on the bananas. **(A)** Essential elements, **(B)** very toxic elements, **(C)** other toxic or potentially toxic elements, **(D)** minority elements, **(E)** rare earth elements. *P < 0.05; **P < 0.01; ***P < 0.001.

Table 1
Concentrations of essential elements in bananas from the Canary Islands. Sampled during the eruption of the Volcano La Palma in 2021. Results are expressed in ng/g as median and interquartile range (P25–P75).

	PEEL							FLESH						
	CONTROL AREA			VOLCANO AREA			P	CONTROL AREA			VOLCANO AREA			P
	Median	P25	P75	Median	P25	P75		Median	P25	P75	Median	P25	P75	
Fe	3027.0	1922.0	3559.0	5724.0	2461.0	3559.0	n.s.	3354.0	2312.0	2312.0	3167.0	2822.0	4203.0	n.s.
Zn	829.8	458.3	1521.0	1271.0 *	1046.0	1521.0	0.0182	1425.0	1261.0	1261.0	1216.0	798.2	1428.0	n.s.
Cu	252.6	186.0	276.4	170.7	133.5	276.4	n.s.	666.3	589.5	589.5	591.7	469.4	664.9	n.s.
Se	1.4	1.2	3.7	4.6 *	2.3	3.7	0.0432	0.9	0.7	0.7	2.6	0.4	4.0	n.s.
Mn	1113.0	967.5	1251.0	1014.0	674.4	1251.0	n.s.	720.8 *	630.1	630.1	504.5	436.1	598.3	0.0245
Mo	41.3	33.4	44.2	38.3	32.4	44.2	n.s.	76.0	71.8	71.8	111.3 *	87.1	143.2	0.0415
Co	1.5	0.7	2.4	3.0	1.5	2.4	n.s.	1.5	0.4	0.4	1.7 *	1.1	2.6	0.0312

functioning of sulfite oxidase, xanthine oxidase, aldehyde oxidase and the mitochondrial amidoxime reducing component (mARC). These enzymes metabolize sulfur-containing amino acids and heterocyclic compounds, such as purines and pyrimidines, as well as detoxifying numerous toxicants (Beedham, 2008). Bananas are the fruit with the highest levels of this element in the diet (US Institute of Medicine, 2001). Our results indicate that Mo concentrations are significantly higher in the flesh than in the skin, especially in bananas from the volcano area. This would indicate that Mo is absorbed by the root system of the banana tree and does not reach the fruit by simple atmospheric deposition (Fig. 4).

Also in the Canarian consumers, who eat up to 420 g/day of bananas (97.5th percentile) (Serra Majem et al., 2000), the bananas under the influence of the volcano would provide them with almost 15% of the nutritional requirements of Co, although in this case the difference with the pre-eruption bananas is minimal. The contributions of the rest of the essential elements to the total daily requirements are not very important through the consumption of bananas, whether they are the regular bananas or the bananas from the volcano area. Even in the case of iron, and despite the high levels detected in the complete homogenates, the nutritional contribution would not exceed 1% of the daily requirements in intensive banana consumers.

3.3. Risk assessment of banana consumption (As, Cd, Hg, and Pb)

One of the major concerns since the onset of the volcanic eruption

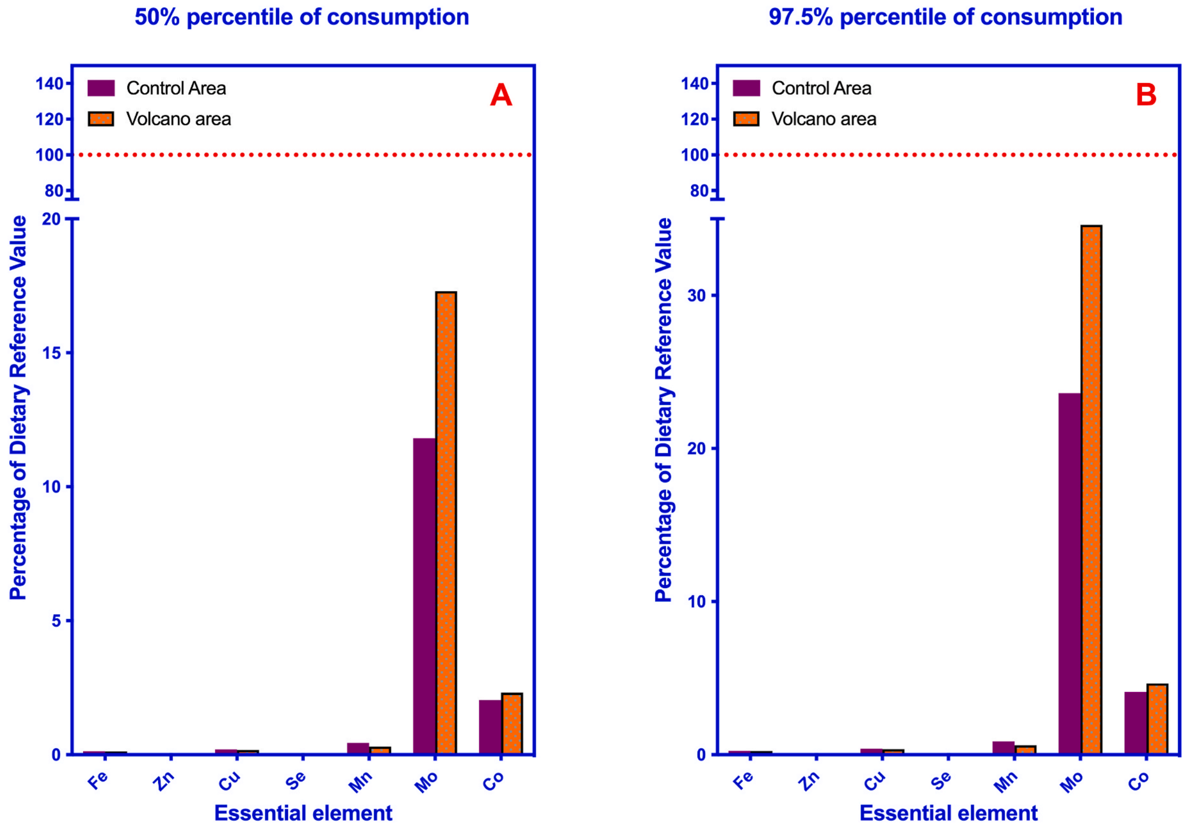

Fig. 3. Bar graph showing the percentage of dietary reference values (DRV) of essential elements provided by the consumption of bananas grown under normal conditions and under the influence of ash and gases from the volcanic eruption of La Palma 2021. **(A)** Average consumption (50th percentile); **(B)** high consumption (97.5th percentile). The red dotted line indicates 100% of the RDV of each element. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

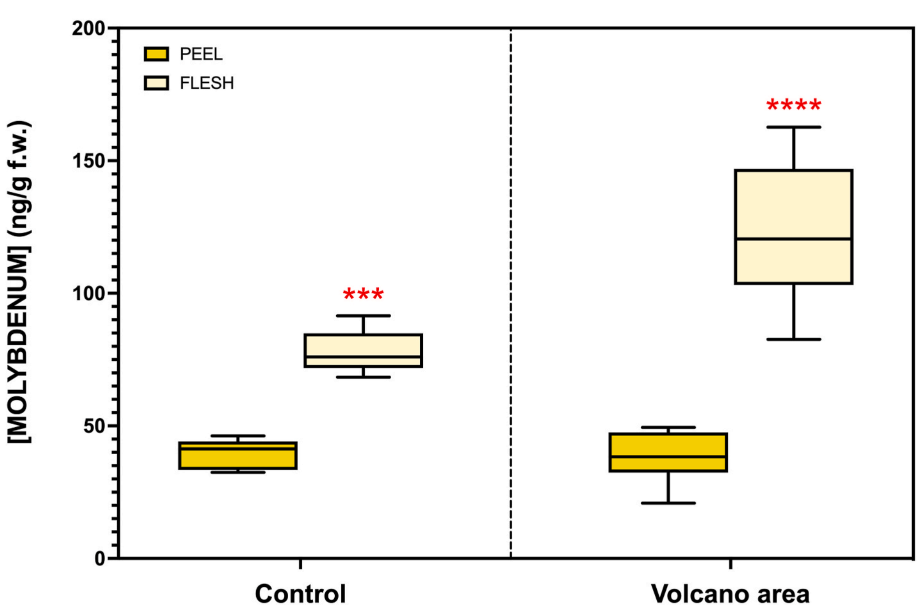

Fig. 4. Box-and-whisker plot showing statistical comparison of molybdenum levels in the peel and flesh of bananas grown under normal conditions and under the influence of ash and gases from the La Palma 2021 volcanic eruption. The line inside the box represents the median, the bottom and top of the box are the first and third quartiles of the distribution, and the lines extending vertically from the boxes indicate the variability outside the upper and lower quartiles. ***$P < 0.001$; ****$P < 0.0001$.

has been the possibility of crops becoming contaminated with highly toxic heavy metals, as there is abundant literature indicating that volcanoes are the main source of natural (non-anthropogenic) contamination by these elements (Juncos et al., 2016; Wygel et al., 2019). Thus, in certain volcanic regions, health problems in inhabitants have been described, mainly respiratory, due to inhalation of gases and particles, but also associated with exposure to toxic elements (Tepanosyan et al., 2021). Although in many studies, fortunately it is concluded that there is no risk for the associated with exposure (Schiavo et al., 2020; Shruti et al., 2018), in other studies worrying associations have been found, such as for example the increase in the incidence of thyroid cancer in the inhabitants, related to the increase of cadmium, mercury and other potentially toxic elements (Mn, V, Tl, U, Pd) as a consequence of repeated volcanic eruptions of Mount Etna (Malandrino et al., 2016).

Table 2 shows the results of the analysis of the 4 most studied elements worldwide by virtue of their high toxicity and potential risk. First, As is a recurrent and highly volatile component of volcanic gases (Symonds et al., 1992), and a highly mobile element of tephrites (Ruggieri et al., 2012), and its levels are frequently increased in volcanic regions (Queirolo et al., 2000; Tepanosyan et al., 2021). However, according to our results, As levels are not affected by the volcanic eruption of La Palma. In fact, the levels detected in bananas not subjected to the influence of the volcano, although very low, are significantly higher than in the controls in the series sampled (Table 2). In both cases, these concentrations would translate into a very low intake of As, which would barely reach 1% of the TDI in intensive banana consumers (Fig. 5).

In the case of cadmium, there are also numerous scientific publications reporting higher levels of this metal in soils and inhabitants of volcanic regions (Andaloro et al., 2012; Di Marzio et al., 2020; Ermolin et al., 2018; Queirolo et al., 2000; Vargas-Solano et al., 2019). This is not the case of the banana fruits sampled for this study, which presented extremely low levels of this metal, both in the control zone and in those subjected to the influence of the volcano (Table 2). A slight increase in Cd concentration was detected in the banana skins from the problem zone, but this did not translate into an increase in the flesh. According to our estimation, the contribution of Cd through banana consumption would only mean 0.01% and 0.02% of the TDI in average and heavy banana consumers, respectively (Fig. 5).

The global mercury flux from volcanic eruptions is estimated at 57 t/year, while the flux from degassing activities is 37.6 t/year, which would represent only 0.8% of the annual mercury release to the environment (Nriagu and Becker, 2003). However, at the regional level it may indeed have relevance on exposure of humans and animals, either via inhalation or through food and water consumption (Guédron et al., 2019). Again, we did not detect any variation in Hg levels in the sampled bananas (Table 2). In fact, levels are extremely low, undetectable in most samples, and this translates into virtually zero exposure of the consumers (Fig. 5).

In our study, Pb is the only highly toxic element that appears significantly increased in both skin and flesh of bananas from the problem area (Table 2). Even so, these concentrations would translate into only a small increase in consumer exposure, amounting to 0.8% of the TDI in consumers at the 97.5th percentile (Fig. 5). We also observed that lead concentrations in the skin were significantly higher than those in the flesh of bananas (about 2.5 times higher) (Table 2). Numerous studies have evaluated the performance of banana peel as a very effective biosorbent for elements, because it contains high quantities of cellulose, which possesses functional groups able to bind metals (Fabre et al., 2020), so it is likely that, in the case of the La Palma volcano, the ashes, gases and nanoparticles of magmatic material have low concentrations of As, Cd and Hg, but moderate concentrations of Pb, that can be adsorbed by the banana skin.

3.4. Risk assessment of banana consumption (other toxic and potentially toxic elements)

In this work we also analyzed a good number of elements, all of them related to a greater or lesser extent with the magmatic material and posing degrees of toxicity (Table 3). One of the most striking results is that of Al, an element classically associated with volcanic ash. Although the magmatic material from this eruption consists largely of tephrite, which is an aluminum-poor rock, it also contains basanite, which has large amounts of Fe, Al, and Ti (Gordeychik et al., 2018). Al appeared at 9- and 15-times higher concentrations in the skin and flesh respectively of bananas from the volcano area with respect to the controls. Something as striking as this, although of much less toxicological significance as it is an inert metal, occurred with Ti, which appeared 21- and 12-times more concentrated in the skins and flesh of bananas from the volcano area than in those from the control area.

We also found significant increases for V, and for the rare earth elements considered as a group (sum of the 16 elements), and significant for 13 of the 16 individual elements within this group (data not shown). These results are also logical, since both V and REE have been described as relatively abundant in the composition of volcanic ash in different regions of the world (Aullón Alcaine et al., 2020; Orecchio et al., 2016; Ruggieri et al., 2012) and also from the Canary Islands (Menéndez et al., 2019; Padrón Armas et al., 2020). Another element that resulted more concentrated in bananas from the volcano area was barium, although in this case only in the banana skins and not in the flesh (Table 3). This buffering effect of banana skin is probably related to the already mentioned metal and element adsorption capacity of this material, which makes it a good alternative for the preparation of biochar and makes it very useful for the bio-remediation of contaminated sites (Negroiu et al., 2021; Zhou et al., 2017). In fact, in bananas from the volcano area we checked the concentration capacity of toxic elements in the skin, in which significantly higher concentrations were reached than in the flesh in all cases (Fig. 6). Unfortunately, we cannot know whether this concentration of elements in the skin is responsible for the increased concentrations of toxic elements in the banana flesh compared to the control area, or whether this increase is due to the elements having been absorbed by the root system of the banana plants. It will be necessary to conduct a study once the volcano's emission activity ceases, and bananas that have spent their entire growth cycle in banana plantations grown in soils now rich in volcanic ash.

In any case, these higher levels do not translate into a real risk for the consumer. As shown in Fig. 7, with the consumption of bananas grown under normal conditions, exposure to all these elements is practically negligible. With the consumption of bananas from the volcano area, the exposure increases, but is of little relevance in terms of health. Exposure in the most unfavorable case, which would be the exposure to V in consumers of the 97.5th percentile, would only represent 4.5% of the TDI.

4. Conclusions

The volcanic eruption of La Palma in 2021 has raised the levels of most of the elements studied in bananas grown on farms in the affected

Table 2
Concentrations of highly toxic elements in bananas from the Canary Islands. Sampled during the eruption of the Volcano La Palma in 2021. Results are expressed in ng/g as median and interquartile range (P25–P75).

	PEEL							FLESH						
	CONTROL AREA			VOLCANO AREA				CONTROL AREA			VOLCANO AREA			
	Median	P25	P75	Median	P25	P75	P	Median	P25	P75	Median	P25	P75	P
As	0.9	0.8	1.2	0.9	0.2	1.2	n.s.	1.4 *	1.2	1.2	0.5	0.2	1.3	0.0320
Cd	0.1	0.1	0.1	0.2 *	0.1	0.1	0.0193	0.1	0.1	0.1	0.1	0.1	0.2	n.s.
Hg	0.0	0.0	0.2	0.0	0.0	0.2	n.s.	0.0	0.0	0.0	0.0	0.0	0.4	n.s.
Pb	1.0	0.8	1.3	3.8 *	1.0	1.3	0.0324	0.0	0.0	0.0	1.4 *	0.5	1.0	0.0296

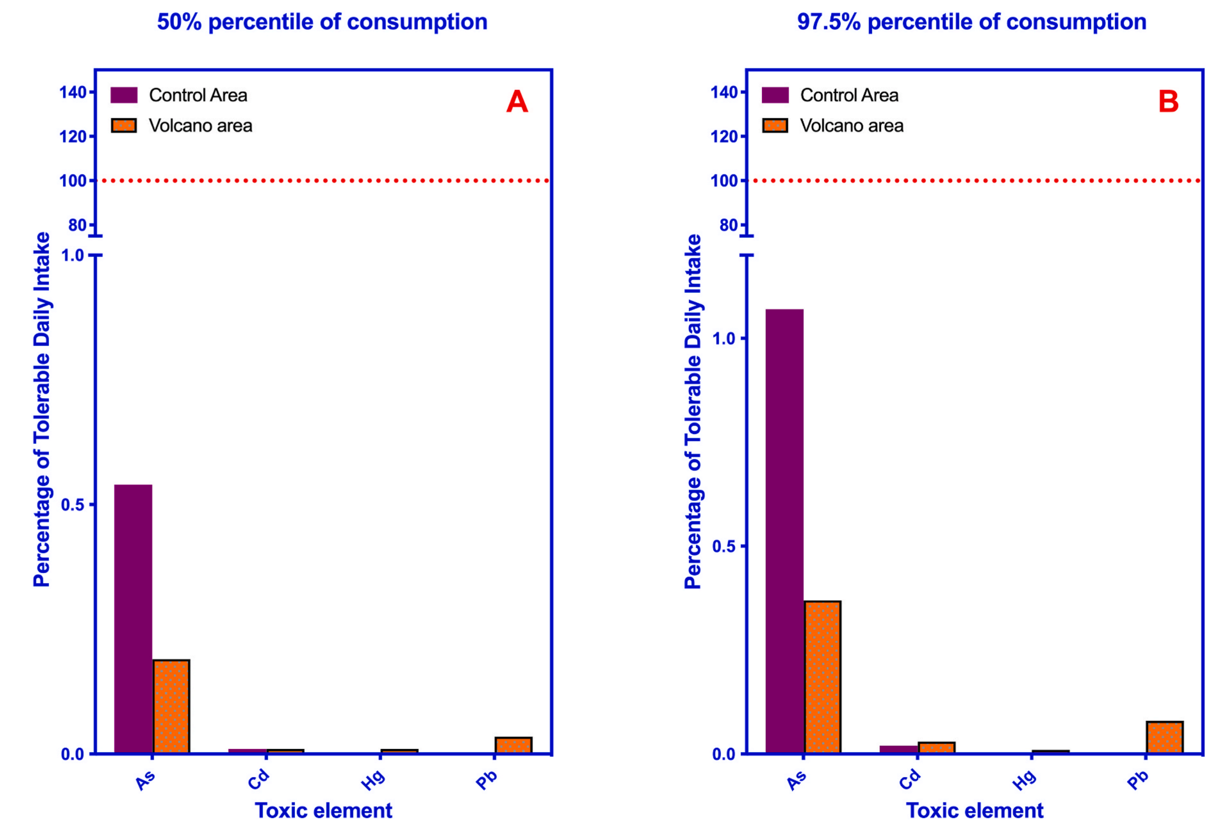

Fig. 5. Bar graph showing the percentage of the tolerable daily intake (TDI) of highly toxic elements provided by the consumption of bananas grown under normal conditions and under the influence of ash and gases from the volcanic eruption of La Palma 2021. **(A)** Average consumption (50th percentile); **(B)** high consumption (97.5th percentile). The red dotted line indicates 100% of the TDI of each element. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Concentrations of other toxic and potentially toxic elements in bananas from the Canary Islands. Sampled during the eruption of the Volcano La Palma in 2021. Results are expressed in ng/g as median and interquartile range (P25–P75).

	PEEL							FLESH						
	CONTROL AREA			VOLCANO AREA				CONTROL AREA			VOLCANO AREA			
	Median	P25	P75	Median	P25	P75	P	Median	P25	P75	Median	P25	P75	P
Ag	0 × .0	0.0	0.0	0.0	0.0	0.0	n.s.	0.0	0.0	0.0	0.0	0.0	0.0	n.s.
Al	810.5	673.2	920.9	7355.0 **	3996.0	920.9	0.0069	79.7	0.0	0.0	1120.0 ***	519.5	2415.0	0.0004
Au	0.0	0.0	0.2	0.0	0.0	0.2	n.s.	0.0	0.0	0.0	0.0	0.0	0.2	n.s.
Ba	104.3	76.7	208.7	216.9 *	130.5	208.7	0.0412	43.9	38.0	38.0	87.3	61.3	112.9	n.s.
Be	0.0	0.0	0.1	0.0	0.0	0.1	n.s.	0.0	0.0	0.0	0.0	0.0	0.0	n.s.
Cr	23.5	12.2	75.6	18.3	11.0	75.6	n.s.	29.0	3.4	3.4	4.4	3.3	10.0	n.s.
Ni	40.9	14.4	101.2	18.5	17.6	101.2	n.s.	61.5	19.6	19.6	27.5	18.6	44.6	n.s.
Sb	0.1	0.0	0.3	0.1	0.0	0.3	n.s.	0.1	0.1	0.1	0.0	0.0	0.1	n.s.
Sn	1.3	0.0	2.8	2.2	0.4	2.8	n.s.	0.0	0.0	0.0	0.0	0.0	2.5	n.s.
Sr	1748.0	1012.0	2210.0	1558.0	1114.0	2210.0	n.s.	487.3	407.7	407.7	494.8	430.1	555.5	n.s.
Th	0.1	0.1	0.1	0.7 *	0.2	0.1	0.0101	0.0	0.0	0.0	0.1 *	0.0	0.3	0.0007
Tl	0.2	0.0	0.4	0.4	0.2	0.4	n.s.	0.3	0.0	0.0	0.3	0.2	0.8	n.s.
U	0.1	0.1	0.1	0.2	0.1	0.1	n.s.	0.0	0.0	0.0	0.0	0.0	0.1	n.s.
V	2.0	1.4	2.7	18.8 *	4.4	2.7	0.0071	0.5	0.2	0.2	2.8 *	0.8	6.8	0.0135
Ti	66.8	52.0	73.9	1400.0 *	265.6	73.9	0.0031	18.5	14.1	14.1	229.3 ***	71.1	496.9	0.0002
Sum REE	16.2	9.5	36.1	61.4 *	33.3	36.1	0.0023	5.7	3.6	3.6	14.2 *	8.5	31.7	0.0182
Sum ME	0.4	0.2	0.5	0.3	0.2	0.5	n.s.	0.1	0.1	0.1	0.1	0.0	0.2	n.s.

area. It appears that this increase is mainly due to the deposition of ash and nanoparticles of magmatic material on the surface of the bananas, since much of this contamination disappears with the washing that takes place in the processing plants. Even after washing, there is a significant increase in the concentration of some elements of clear magmatic origin, such as Fe, Al, Ti, V, Ba, Pb, most of the rare earth elements, Mo, and Co. In practically all cases, except for Mo, the elevation is much higher in the peel than in the edible part of the banana. In the case of Mo, the concentration is higher in the banana flesh, and this would translate into a higher nutritional intake of this trace element, which could represent up to 35% of the daily nutritional requirement. Exposure to toxic or potentially toxic elements, even in the worst-case scenario, is not very relevant, and would not exceed 5% of the tolerable daily intake of any of them.

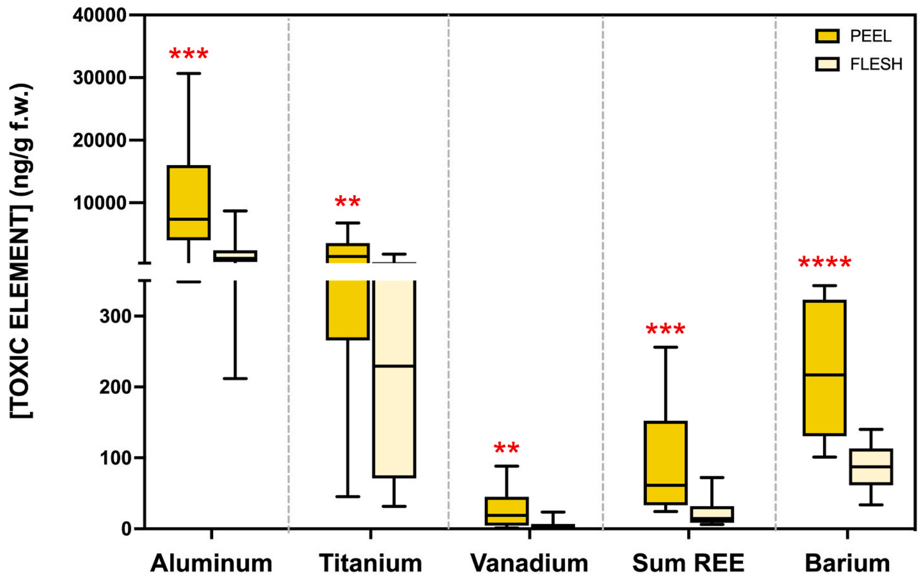

Fig. 6. Box-and-whisker plot showing statistical comparison of several potentially toxic elements in the peel and flesh of bananas grown under the influence of ash and gases from the La Palma 2021 volcanic eruption. The line inside the box represents the median, the bottom and top of the box are the first and third quartiles of the distribution, and the lines extending vertically from the boxes indicate the variability outside the upper and lower quartiles. ***P < 0.001; ****P < 0.0001.

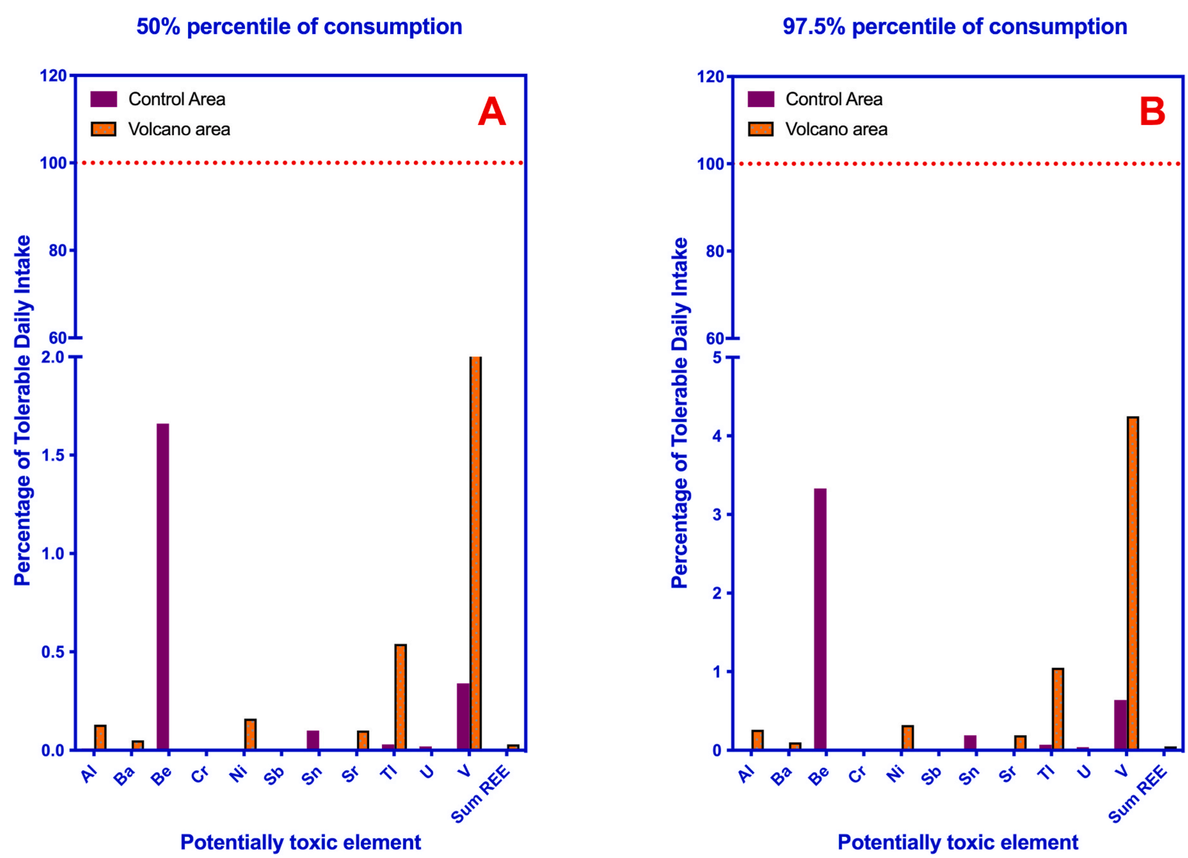

Fig. 7. Bar graph showing the percentage of the tolerable daily intake (TDI) of potentially toxic elements provided by the consumption of bananas grown under normal conditions and under the influence of ash and gases from the volcanic eruption of La Palma 2021. **(A)** Average consumption (50^{th} percentile); **(B)** high consumption (97.5^{th} percentile). The red dotted line indicates 100% of the TDI of each element. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.133508.

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