RESEARCH ARTICLE

Environmental risk of trace elements in P-containing fertilizers marketed in Brazil

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Abstract

The input of trace elements (TEs) into agricultural soils from phosphate fertilizers may compromise the sustainability of agroecosystems and pose a risk to human health. We evaluated 53 sources of P marketed in Brazil in regard to As, Cd, Cr, Hg, and Pb concentrations in order to assess the risks associated with their application to soils. Based on the concentrations of TEs and the consumption of different sources, we estimated the amounts of TEs added annually to agricultural soils. As, Cr, Pb, and Hg concentrations did not exceed those found in fertilizers sold in other regions of the world. Phosphate rocks had Cd concentrations that were twice as high as any other source. The potential risk of Cd affecting soil quality is at least nine times higher than that of the other TEs assessed. Due to high consumption, monoammonium phosphates and single superphosphates are the main sources of TEs to Brazilian soils. In general, TEs in P-containing fertilizers sold in Brazil did not pose a high human health risk in a medium time frame. Nevertheless, intensive application of fertilizers with high concentrations of TEs requires monitoring of the TE accumulation in soils to ensure the sustainability of agroecosystems.

Keywords: Rock phosphate, agricultural soils, heavy metals, cadmium, arsenic

1. Introduction

Currently, Brazil has 69.2 million hectares of cultivated land and is one of the leading food producers in the world (IBGE, 2012; MAPA, 2016). As a result of such intensive agriculture, Brazil is the world's fourth largest fertilizer consumer after China, India, and the USA (IFA, 2016). In 2015, the estimated consumption of fertilizers was nearly 30 million tonnes, of which 38% is related to phosphate fertilizers alone (IPNI, 2016).

Although fertilizer use is essential for meeting the crop demand for nutrients exported from soil, fertilizers can contain trace elements (TEs) that are inadvertently added to the soil (Kratz *et al.*, 2016). The amount of TEs transferred to the soil in a single application of fertilizer is very low or negligible. However, repeated applications of fertilizers with relatively high contents of TEs can lead to significant accumulation (Jiao *et al.*, 2012).

Therefore, elements such as As, Cd, Cr, Hg, and Pb can affect soil quality and pose a risk to human and animal health through food chain contamination (Hosseinpur and Motaghian, 2015).

Trace elements are present in fertilizers as a result of the composition of raw materials used in their manufacture. Phosphate rocks and industrial/animal wastes are among the main sources of TEs in agricultural soils (Gonçalves Jr *et al*., 2014; Seshadri *et al*., 2015). The concentration of TEs in nitrogen and potassium fertilizers is usually very low, and hence, their application does not imply a significant accumulation of TEs (McBride and Spiers, 2001). On the other hand, the prolonged use of P-containing fertilizers is a major source of TEs in soils, particularly Cd (Jiao *et al*., 2012). For instance, soils cultivated with sugarcane and fertilized for a long period with phosphate fertilizers accumulated Cd levels above the allowable limit according to Brazilian legislation (Silva *et al*., 2016). Estimates of the annual input of TEs in soil via phosphate fertilizers range from 22.0 to 299.0; 24.0 to 30.0; 319.0 to 1626.0; 0.1 to 17.0; and 10.0 to 777.0 tonnes for As, Cd, Cr, Hg, and Pb, respectively (Luo *et al*., 2009;).

Due to the risk associated with the presence of TEs in fertilizers, several countries have limited the concentrations of these elements in marketable products (Gonçalves Jr *et al*., 2014; Jiao *et al*., 2012; Kratz *et al*., 2016). In Brazil, Normative Instruction No. 27/2006 of the Ministry of Agriculture, Livestock and Supply (MAPA) established maximum allowable concentrations of TEs in fertilizers (MAPA, 2006). However, few studies have evaluated the concentration and risk of As,

Cd, Cr, Hg, and Pb in P-containing fertilizers used in Brazil. Cadmium is the most studied element, especially in phosphate rocks (Freitas *et al*., 2009). There is also a scarcity of data on the supply of TEs via fertilizers in Brazilian soils since a plethora of mineral and organic sources are used.

Human and animal health risks associated with TEs in fertilizers need to be evaluated carefully (Hartley *et al*., 2013). As the concentrations of TEs vary markedly with the raw materials available in each region or country, the production of local and regional data is essential. In this scenario, we aimed to assess the concentrations of As, Cd, Cr, Hg, and Pb in P-containing fertilizers marketed in Brazil in order to estimate the accumulation of TEs in agricultural soils through phosphorus fertilizer use. In addition, we estimated both the total amount (kg year^{-1}) and the rate (g ha^{-1} year^{-1}) of TEs applied to soils with aims to calculate the number of mineral fertilizer applications needed to reach the limit of TEs in agricultural soils established by Brazilian legislation (MAPA, 2006).

2. Materials and Methods

2.1. Selection, preparation, and analysis of trace elements in fertilizers

We analyzed 53 P-containing fertilizers sold in Brazil and obtained from the National Agricultural Laboratory (LANAGRO-PE) of MAPA (Table 1). The samples were dried at 60 °C, pulverized in an agate mortar, and passed through a 0.30-mm mesh stainless steel sieve.

Table 1. Description of the phosphate fertilizers evaluated in this study

Product	Number of samples	(%) P_2O_5[a]	Consumption (1,000 t)[b]
Rock phosphate (RP)	5	24	184.09
Monoammonium phosphate (MAP)	6	50	3558.41
Simple superphosphate (SSP)	23	18	5336.79
Multi-nutrient fertilizers (NPK)	12	13	*nd*
Organo-mineral + rock phosphate (OM+RP)	6	26	1519.27

(a) average value of samples certified by manufacturers; (b) Brazilian consumption in 2015 (ANDA, 2015); *nd* not available.

1.000 gram of the various fertilizer powder samples was digested by adding 9 mL HNO3 + 3 mL HCl in a microwave oven at 175 ^{o}C for 4 minutes and 30 seconds (USEPA, 1998). This method provides similar results to the official method currently in use in Brazil (MAPA, 2006), and it is preferred due to the lower cost of acids, shorter digestion time, and higher reproducibility (Silva *et al*., 2014). All analyses were performed in duplicate.

For quality control, we also analyzed blank samples and a multi-element fertilizer (SRM 695) with certified TE concentrations (National Institute of Standards and Technology, USA). The recoveries of TEs obtained from the certified sample were 97, 100, 72, 90, and 73% for As, Cd, Cr, Hg, and Pb, respectively. Cd, Cr, and Pb concentrations were determined by optical emission spectrometry (ICP-OES) (Perkin-Elmer/ICP-OES 8000), while As and Hg concentrations were measured by hydride generation atomic absorption spectroscopy (HGAAS) (Perkin-Elmer/AA 800).

2.2. Inputs of trace elements to soils via fertilizers

Equation 1 was used to estimate the total annual inputs (tonne year^{-1}) of TEs in soil via P-containing fertilizers. Other inputs and losses of TEs in agricultural soils such as atmospheric deposition, crop uptake or leaching were not included in this calculation.

$$TA_i = \sum_j (Q_j \times C_{ij}) \times 10^{-6} \quad (1)$$

Where TA_i is the total amount of the TE (i) added each year (tonne year^{-1}) from P-containing fertilizers (j), Q_j is the amount of fertilizer (tonne) currently consumed in Brazil, and C_{ij} is the TE concentration in the fertilizer (mg kg^{-1}). The rate of application (g ha^{-1} year^{-1}) was estimated with equation 2:

$$TA_{ij} = \left[\left(\frac{\overline{D}}{FP_j} \right) \times C_{ij} \right] \times 10^{-3} \quad (2)$$

Where TA_{ij} is the amount of TE (i) added annually per unit area through fertilizer (j) (g ha^{-1}), D is the average recommended dose for the main crops grown in Brazil (140 kg ha^{-1} P_2O_5) (CFSEMG, 1999; IPA, 2008), and FP_j is the fraction of P_2O_5 in fertilizers (0.18, 0.24, 0.26 and 0.50 for SSP, RP, OM+RP and MAP, respectively) (dimensionless).

We also estimated the number of applications needed to increase the TE natural background of the soil surface layer (0–0.2 m) up to the permissible limit for agricultural soils established by Brazilian legislation (CONAMA, 2009). The estimate was applied only to fertilizers with high addition of TEs:

$$NA_j = \frac{2.6 \times 10^3 \times AL_i}{TA_{ij}} \quad (3)$$

Where NA_j is the number of fertilizer (j) applications required to increase the TE concentration (i) in the topsoil up to the allowable limit (AL) (mg kg^{-1}), and 2.6 x 10^3 is the unity conversion factor g ha^{-1} to mg kg^{-1} of the parameter TA_{ij}, taking into account the depth of 0.2 m and the soil density of 1300 kg m^{-3} (Ferreira, 2010) for the calculation of the soil mass in 1 hectare.

2.3. Statistical analyses

Descriptive statistics of the dataset were obtained by calculating the mean, median, standard deviation and amplitude. The data with a normal distribution assumption were verified by the Shapiro-Wilk test ($p > 0.05$). Data without a normal distribution were normalized through logarithmic transformation.

Hierarchical cluster analysis (AH) was applied to group different types of P-containing fertilizers. AH was carried out using Ward's algorithm with the Euclidean distance as a binding measure and the dissimilarity between the products was assessed as a function of the TE concentration. Statistical analyses were performed using STATISTICA software (version 10.0).

3. Results

3.1. Trace element concentrations in P-fertilizers

The mean concentration of TEs in fertilizers had the following descending order: Cr (67.9) > Pb (19.2) > Cd (9.4) > As (6.6) >> Hg (0.1). The highest values found for As, Cd, Hg, and Cr were approximately 7 times higher than their respective median values, and the Pb concentration was 17 times higher than the median Pb value (Table 2). The distributions of As and Pb concentrations in the fertilizers had a similar trend, with over 65% of the data lying in the ranges of 0.5 to 4.2 and 0.3 to 14.7 mg kg^{-1}, respectively. More than 80% of the Cd and Cr concentrations were <17.2 mg kg^{-1} and <148.1 mg kg^{-1}, respectively. On the other hand, Hg showed low variability with a high percentage of samples near the mean concentration.

Table 2. Descriptive statistics of the trace elements content in fertilizers containing P sold in Brazil

Trace elements	Minimum	Maximum	Mean	Median	± SD	SW-*p*
	---------------------------------- (mg kg^{-1}) ----------------------------------					
As	0.54	26.72	6.55	3.41	7.23	<0.001
Cd	0.40	40.03	9.39	6.05	10.08	<0.001
Cr	10.72	341.75	67.82	51.67	77.31	<0.001
Hg	0.06	0.54	0.14	0.11	0.09	<0.001
Pb	0.35	102.46	19.18	6.03	27.64	<0.001

SD standard deviation; *SW-p p*-value of the Shapiro-Wilk normality test.

Three groups of fertilizers regarding TE concentration were distinguished by hierarchical cluster analysis (Figure 1). In the group of high concentrations, the organic-mineral fertilizers were the main representatives, with 83% of the evaluated organic-mineral fertilizers presenting high concentrations of trace elements. Mixed fertilizers have phosphorus sources with the highest number of cases (58%) in the group with low concentrations of trace elements. This is due to the fact that sources of N and K present very low concentration of metals (Luo *et al.*, 2009), which causes a dilution effect.
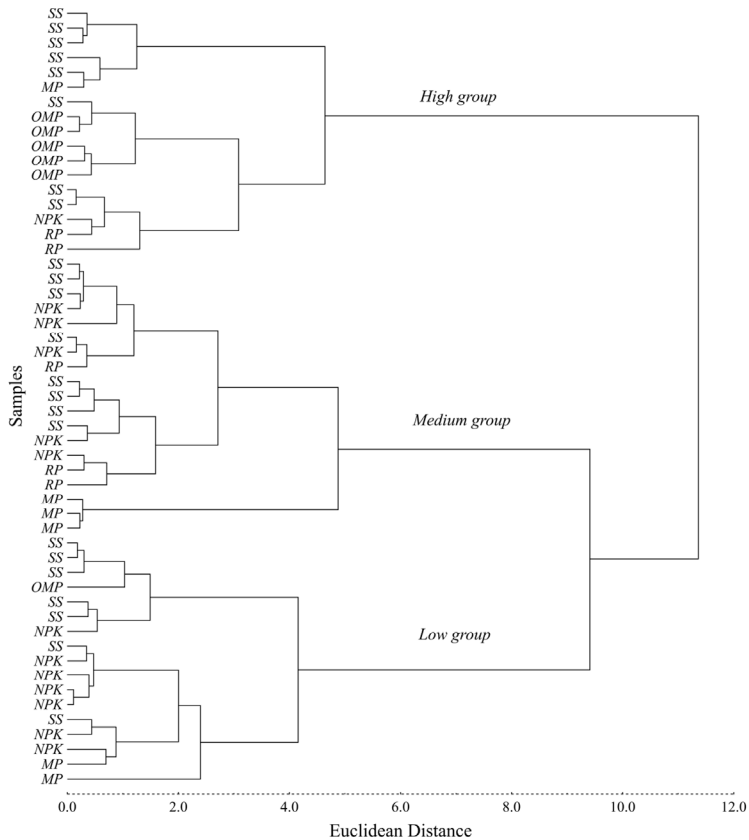

Figure 1. Hierarchical clustering of phosphate fertilizers as the contents metals using as criterion the concentrations of As, Cd, Cr, Hg and Pb in products. *SS* simple superphosphate, *NPK* multi-nutrient fertilizers, *RP* rock phosphate, *OMP* organo-mineral + rock phosphate and *MP* monoammonium phosphate.

The mean concentrations of As, Hg, and Pb were higher in organic-mineral fertilizers, while monoammonium phosphate (MAP) and phosphate rock (PR) presented the highest concentrations of Cr and Cd, respectively (Figure 2). The mean concentration of Pb in organic-mineral + phosphate rock (OM + PR) was 8 times higher than other sources (Figure 2e).
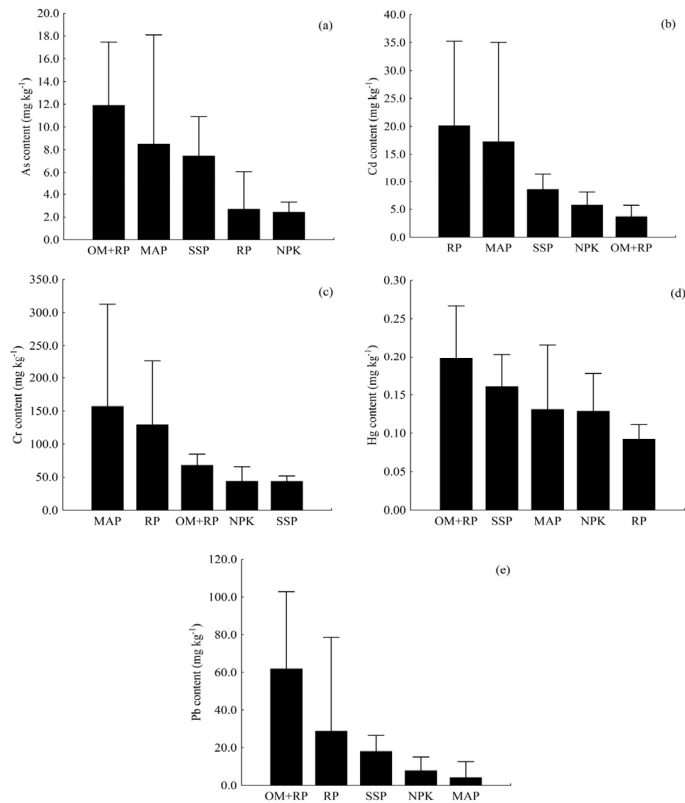
Figure 2. Average contents (standard deviation) of As(a), Cd(b), Cr(c), Hg(d) and Pb(e) in different types of P containing fertilizers marketed in Brazil. RP phosphate rock, *SSP* simple superphosphate, *MAP* monoammonium phosphate and *OMP+RP* organo-mineral + rock phosphate.

Phosphate rocks presented mean Cd concentrations two times higher than those of other fertilizers except for MAP (Figure 2b). A similar concentration of Cd was found in phosphate rocks of sedimentary origin marketed in Germany (Kratz *et al.*, 2016), while the Cd content observed in this study was 4 times higher than in phosphate rocks of igneous origin (Campos *et al.*, 2005).

3.2. Addition of trace elements in soil via fertilizers

The average addition rates (g ha^{-1} year^{-1}) for the TEs were 4.0 (As), 6.3 (Cd), 47.3 (Cr), 0.08 (Hg), and 16.3 (Pb). The average addition rates for all elements in our study exceed the average additions of European countries, which were 20.7, 1.0, 1.6 and 2.3 g ha^{-1} yr^{-1} for Cr, Pb, Cd and As, respectively (Nziguheba and Smolders, 2008).

We estimated that phosphate rock adds larger amounts of Cd and Cr than other fertilizers containing P, while the use of organic-mineral fertilizers contributes greatly to the input of As and Pb to the soil. Hg additions ranged from 0.04 (MAP) to 0.12 g ha^{-1} yr^{-1} (SSP) (Table 3). The biggest sources of TE are those with the highest levels in their composition except for Cr (Figure 2). Because the MAP samples are more enriched for P$_2$O$_5$ than phosphate rock, the amount of MAP needed to achieve the recommended dose is lower than that for phosphate rock.

Table 3. Mean values (± standard deviation) of per unit area additions (g ha^{-1} year^{-1}) of trace elements in agricultural soils via phosphate fertilizers marketed in Brazil

	SSP	MAP	RP	OM+RP
Cr	33.7 (±3.1)	43.9 (±17.8)	75.3 (±20.3)	36.5 (±3.5)
Pb	14.0 (±3.2)	1.1 (±1.0)	16.8 (±10.5)	33.3 (±8.6)
Cd	6.6 (±1.1)	4.8 (±2.0)	11.7 (±3.2)	2.0 (±0.4)
As	5.8 (±1.3)	2.4 (±1.1)	1.6 (±0.7)	6.4 (±1.2)
Hg	0.12 (±0.02)	0.04 (±0.01)	0.05 (±0.01)	0.11 (±0.01)

RP phosphate rock, SSP simple superphosphate, MAP monoammonium phosphate and OMP+RP organo-mineral + rock phosphate.

Based on the Brazilian consumption and concentrations of TEs in fertilizers, we estimated that Cr and Pb represent the largest total additions to soil, 915.8 and 209.9 t year^{-1}, respectively (Table 4). Minor addition was observed for Hg (1.72 t year^{-1}). The sources that incorporate more TEs in soils are SSP and MAP, which are the sources of P most consumed in Brazil (Table 1). Estimates made with fertilizer composition of TEs indicated that SSP and MAP together provide more than 90% of Cd, 86% of Cr, and 79% of As. Organic-mineral fertilizers represented the main input of Pb to soils (45%).

Table 4. Mean values (±standard deviation) of total additions (tonne year^{-1}) of trace elements in agricultural soils via phosphate fertilizers marketed in Brazil

	SSP	MAP	RP	OM+RP	Total
Cr	231.3 (±21.4)	557.7 (±226.7)	23.8 (±6.4)	103.0 (±24.5)	915.8
Pb	96.0 (±22.2)	14.6 (±12.4)	5.3(±3.3)	94.0 (±59.3)	209.9
Cd	45.6 (±7.5)	61.3 (±25.9)	3.7 (±1.0)	5.6 (±2.9)	116.2
As	39.7 (±8.9)	30.2(±14.0)	0.5 (±0.2)	18.1 (±8.1)	88.5
Hg	0.9 (±0.1)	0.5 (±0.1)	0.02 (±0.00)	0.3 (±0.1)	1.72

RP phosphate rock, *SSP* simple superphosphate, *MAP* monoammonium phosphate and *OMP+RP* organo-mineral + rock phosphate.

In order to assess whether the levels of TEs in fertilizers exceed the maximum permitted concentrations, the values of the metals are based on the percentage points of P_2O_5 established by Brazilian legislation (MAPA, 2006). This practice is also adopted in California (USA) (AAPFCO, 2015) (Figure 3). Unlike other countries that regulate only Cd in phosphate fertilizers (CCR, 2007), Brazilian law regulates the concentrations (mg kg^{-1} %$P_2O_5$$^{-1}$) of As, Cd, Cr, Hg, and Pb.
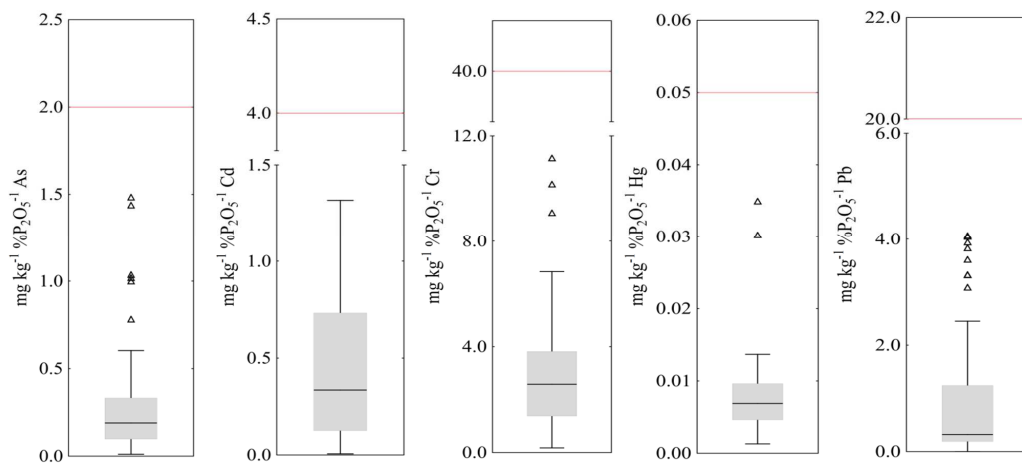

Figure 3. As, Cd, Cr, Hg and Pb concentrations per % of P_2O_5 in fertilizer containing P sold in Brazil. The dashed red line shows the permissible limits of heavy metals in phosphate fertilizers in accordance with Brazilian legislation (MAPA, 2006).

The ascending order of maximum permissible concentrations is Hg <<< Cd < As << Pb < Cr. Cd had the highest variability in phosphate fertilizers, with concentrations of 0.33, 0.73 and 1.31 mg kg^{-1} %$P_2O_5$$^{-1}$ for the median, 75th percentile and maximum values, respectively. Arsenic and Pb had the highest numbers of anomalous values. SSP samples showed the highest ratio of As/P_2O_5, while the highest values of Pb/P_2O_5 were observed for OM + PR and SSP samples.

The increases in the concentrations of TEs in soil (mg kg^{-1}) had the following order: Cr > Pb > Cd > As > Hg. The Cr and Pb concentrations were an order of magnitude higher than those of other trace elements. The increase of Hg through the richest fertilizer (OM + PR) was negligible, and the estimated number of applications was > 12,000 (Table 5).

Table 5. Number of applications of fertilizers containing P needed to increase the concentrations of metals in the soil to the permissible limit

	Source	P_2O_5 soluble (%)	Concentration[a] (mg kg^{-1})	Increase per application[b] (mg kg^{-1})	Number de applications
As	OM+RP	26	15.0	0.002	6097
Cd	RP	24	1.3	0.005	288
Cr	RP	24	75.0	0.029	2591
Hg	OM+RP	26	0.5	<0.001	12082
Pb	OM+RP	26	72.0	0.013	5621

(a) Permissible limit in soil (CONAMA, 2009); (b) based on the application of 140 kg ha^{-1} of P_2O_5 incorporated 0.2 m depth in soils with bulk density of 1300 kg m^{-3}, *OM +RP* organo-mineral + rock phosphate, *RP* rock phosphate

4. Discussion

The As concentration found in p-containing fertilizers marketed in Brazil was the lowest among data from other parts of the world (Table 6). Cr and Pb had high mean concentrations, but the Cr concentration of the fertilizers marketed in the European Union is the largest in the literature, as is the Pb concentration in China. The average concentration of Cd in Brazil, Chile, and Argentina is similar to or higher than those reported for Europe and China. The concentration of Cd in the USA is the highest among the selected countries. Although there is a scarcity of studies on Hg in fertilizers, Hg concentrations found in phosphate fertilizers used in China amount to 0.8 mg kg^{-1}, which is 6 times higher than in Brazil (Luo *et al.*, 2009).

Table 6. Average content (mg kg^{-1}) of As, Cd, Cr, Hg and Pb in phosphate fertilizers marketed in Brazil and in other parts of the world

Site	As	Cd	Cr	Hg	Pb	Reference
China	13.5	2.6	*na*	0.9	30.0	Luo *et al.*, 2009
USA (California)	10.5	53.0	*na*	*na*	*na*	CDFA, 1997
Europe	7.6	7.4	89.5	*na*	2.9	Nziguheba and Smolders, 2008
Argentina	*na*	10.1	29.7	*na*	12.2	Carnelo *et al.*, 1997
Chile	15.1	12.3	*na*	*na*	10.4	Molina *et al.*, 2009
Brazil	6.6	9.4	67.8	0.1	19.2	Present study

na not available; *CDFA* California Department of Food and Agriculture.

Among the fertilizers we analyzed, high TE values in the OM + PR can be explained by the use of peat as the main organic matrix for the production of organic-mineral fertilizers in Brazil (Junek *et al.*, 2014). Peat is organic sediment formed by the decomposition of plant residues in wet and acidic conditions. Studies have shown that peat soils close to urban and industrial areas can be enriched by TEs through atmospheric deposition (Shuttleworth *et al.*, 2014); in addition, the metal complexation capacity of organic matter makes peat an important Pb scavenger (Farmer *et al.*, 2005; Hosseinpur and Motaghian, 2015). There have been no studies in Brazil that quantify the levels of TEs in the peat used for organic-mineral fertilizers; however, data from the international literature have shown that high concentrations of trace elements, especially Pb, can be found in peat (Mighall *et al.*, 2002).

Phosphate rocks are well known for carrying Cd to soils. Cadmium concentrations are generally higher in phosphate rocks of sedimentary origin than those of igneous origin (Kratz *et al.*, 2016). The phosphate deposits in Brazil are predominantly igneous, but a significant amount of this fertilizer is imported from Morocco, Russia, China, Israel, and the US, which have mainly sedimentary reserves (IFA, 2016); the high Cd concentrations reported here are probably due to these imported levels.

The higher input of trace elements via fertilizers in Brazilian soils as compared to Europe is mainly due to the average rate of P applied to the soil. In Brazil, the average recommendation of P_2O_5 is 140 kg ha^{-1}, whereas 43 kg ha^{-1} is the average rate in European countries. The higher demand for P in Brazilian agriculture as compared to other countries is owing to the high concentration of Fe and Al oxides in Brazilian soils that adsorb P through a specific adsorption mechanism (fixation) making it unavailable to plants (Fontes and Weed 1996). We did not find data on the addition of Hg via fertilizers for European conditions.

When comparing the levels of metals in fertilizers with maximum concentrations allowed by Brazilian law, it was found that the P sources evaluated meet the legislative guidelines and are therefore considered safe. The potential risk for soil sustainability resulting from additions of As, Cr, and Pb via phosphate fertilizers are for a medium to long-term time frame. If the estimated additions of Cd are kept high, the concentration in the soil may exceed the allowable limit after 288 applications.

5. Conclusions

In general, TEs in P-containing fertilizers sold in Brazil did not pose a high human health risk in a medium timeframe. Nevertheless, intensive application of fertilizers with high concentrations of TEs requires monitoring of the TE accumulation in soils to ensure the environmental sustainability of agro-ecosystems. The contents of all evaluated metals were below the maximum found in other regions of the world. Organic-mineral fertilizers are an important source of As, Hg, and Pb. Monoammonium phosphate and single superphosphates presented higher additions for As, Cd, and Pb in soils of Brazil. Phosphate rocks pose the main potential risk for soil quality owing to the high Cd concentration. Mixed fertilizers had low potential for increasing the concentration of TEs in soils.

Acknowledgement

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