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Heavy Metals in P Fertilizers Marketed in Brazil: Is This a Concern in Our Agroecosystems?

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Abstract

Fertilizers are key for sustainable use of land and for intensification of crop production, especially in tropical agroecosystems, which have soil fertility constraints that hamper agricultural production on weathered soils. Heavy metals (HM) occur in fertilizers in low concentrations, as contaminants. Yet, some HM are plant nutrients and are intentionally included in fertilizer formulations. Exposure to high levels of HM (nutrient or not) could pose a health risk to humans. This risk may be estimated by collecting data on HM content in soils and plants (e.g., edible parts) in the field, as well as thru modeling. This work presents information concerning HM contents - with a focus on cadmium - in Brazilian fertilizers and agroecosystems - including agricultural products -, aiming to contribute to a better definition of safe limits of HM in phosphate fertilizers, soils, and food. These limits are key not only for food safety purposes, but also for assuring fair trade. In addition, we demonstrate the usefulness of a tool - the software EtraceProDB -, for easy calculation of risk-based concentrations (RBC) of HM in inorganic fertilizers post application, which suggest safe limits for agricultural use. The purpose of this software is to calculate values of HM concentrations in inorganic fertilizers that may, flexibly, be used by regulators to protect human and soil health. The results obtained indicate that HM do not cause harm to human health when considering post application of phosphate fertilizers in Brazil. Also, a survey of HM contents in Brazilian food and food products evidenced the safety of agricultural crops with respect to their contents of As, Cd, and Pb. Our findings concerning RBC and analyses of HM in mixed fertilizers, as well as current information published in Brazil suggest that HM contents - Cd inclusive - in major agroecosystems as well as the HM limits currently established for P fertilizers by the Brazilian legislation are safe in terms of health risk assessment. Considering the great importance of Brazil as a global food provider, such results are relevant to show that fertilizer use in Brazilian agriculture is done in such a way as to guarantee the production of healthy crops as well as adequate food quality criteria.

Keywords: Food Security; Food Safety; Trace Elements; Sustainable Tropical Agriculture; Brazil

1. Introduction

Intensification of crop production systems and yield increases are clearly important in securing an adequate food supply while avoiding the need of additional land clearing, and the role of fertilizers in this is undeniable. Trace elements (hereafter called heavy metals - HM - for simplicity) occur naturally in agroecosystems and in source materials used to manufacture fertilizers and HM loads to agricultural soils by fertilizers - mineral or organic - are of concern due to their potential risk for the environment and food security. In some agricultural systems, the input of HM to soil by the application of fertilizers and other agricultural inputs may be greater than the outputs due to plant absorption and leaching, and therefore, the continued use of these products can result in the accumulation of HM in soils [1]. However, a significant increase of the HM content in soil by fertilizer application may take decades [2,3]. Phosphate fertilizers can be a source of HM to agricultural soils, such as arsenic (As), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), uranium (U), telurium (Tl), and, especially, cadmium (Cd) [4,5,6]. The contamination of agricultural soils with Cd is expected to increase in the future, due

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to the prolonged application of Cd-containing P fertilizers [7]. Heavy metal concentrations in phosphate rocks vary greatly depending on the type and source of the mineral [8], yet it is important to stress that, once phosphate rock reserves are depleted, it is likely that phosphate rocks with higher concentrations of HM will increasingly be used [9].

Brazil is a worldwide leader when it comes to the "4Fs" (food, feed, fuel, and fiber), i.e., the country is a global player in the production of food, renewable energy, and fibers [10]. Agriculture is an activity of great importance for Brazil, since it provides not only food security, but also jobs, income, and well being for many Brazilians. Furthermore, the share of agricultural products in Brazil's trade balance with the world has been growing steadily over the last two decades, culminating in a contribution of ~ 43% in total value of the country's exports in 2018 [11]. Yet, a drawback related to the balance of payments of the Brazilian agricultural sector is our heavy dependence on fertilizer imports. In fact, this is a very challenging scenario not only for Brazil, but also for most tropical agroecosystems [12]. Brazil imports about 75% of its needs of fertilizer products in general, with a lower external dependence (~60%) for phosphate and a higher (~95%) for potassium fertilizers [13]. This is relevant, given the peculiarities of tropical soils, which have low fertility and require frequent build-up and maintenance fertilization practices for sustainable production [14]. Assuring a good quality of such fertilizers no only in terms of nutrient content but also concerning contaminants (e.g., heavy metals) is, therefore, a major issue for the sustainability of Brazilian agriculture.

In Brazil, laboratory analyses of fertilizers and quality control procedures made by the Ministry of Agriculture, Livestock and Supply (MAPA) until 2006 neither included the evaluation of potentially toxic HM in inorganic fertilizers, nor discussed their tolerable limits. Currently, the Brazilian legislation in force through the normative instruction 27/2006 already provides maximum concentrations of As, Cd, Cr, Hg, and Pb in fertilizer to be produced, imported or sold [15]. Such normative has similarities with those proposed in several countries - namely the US legislation - yet it is less restrictive than the EU legislation concerning Cd in P fertilizers [16;17].

An estimate of risk-based concentrations (RBC) of heavy metals provided by an industry-commissioned study (The Fertilizer Institute) [18] has shown that HM levels in commercial inorganic fertilizers are safe for consumers of farm products in the United States. The methodology for calculating RBC in the aforementioned study was a back-calculation of health risks and is standard for a screening level risk evaluation. Based on that, and in order to assess health risks of selected HM in fertilizers post application in Brazil, Guilherme and Marchi [19] and Guilherme et al. [20] have calculated RBC for P-carrying fertilizers by using a software package - EtraceProDB - developed exclusively for estimating RBC for HM in inorganic fertilizers. The software uses the same methodology proposed to develop the RBC in the US study [18] and calculates risk-based concentrations of twelve HM in several exposition scenarios. EtraceProDB presents a pre-loaded database designed for a generic scenario of fertilizers use in Brazil, yet it can be easily modified in order to help legislative decision making processes in specific regions of Brazil and elsewhere.

The worldwide concern about the presence of HM in fertilizers is related to the possibility of such elements being transferred to the food chain. In fact, food ingestion of HM is a relevant exposure route to humans [21] and, depending on the amount of HM that is ingested, they can cause serious health problems as skin lesions, cancer, cardiovascular diseases (e.g., for As contamination) [22], neurological function loss (e.g., for Pb contamination) [23], as well as stomach irritation and kidney diseases (e.g., for Cd contamination) [24].

Given that fertilizers are a potential source for HM loads to the environment, knowing their concentration in fertilizers as well as in agroecosystems is relevant to provide information that is key for assuring not only food security, but also soil quality, especially in areas of intensive agriculture, as in Brazil. In this context, this document assessed the concentrations of three HM of great environmental relevance - As, Cd, and Pb - in 36 mixed fertilizers, with a focus on P-carrying fertilizers commonly marketed in Brazil, which is important due to the significant consumption of phosphorus in Brazilian agriculture, as well as because of the fact that Brazil is one of the greatest food exporters worldwide. Results of such HM analyses are contrasted with risk-based concentrations as well as with limits set by the current Brazilian legislation governing HM contents in P fertilizers. Lastly, we also evaluated the levels of HM in Brazilian food products, through a database compilation of available literature. By evaluating the concentrations of As, Cd, and Pb in fertilizers, agroecosystems, and food products, we will be able to assess not only if they could pose a threat to human health or to the environment, but also if HM concentrations in exported food and food products are such as to avoid non-tariff barriers to trade.

2. Materials and Methods

2.1 Fertilizer analysis

The analyzes were performed at the Environmental Geochemistry Laboratory located in the Department of Soil Science of Federal University of Lavras, with fertilizer samples provided by the quality control program of the Brazilian Ministry of Agriculture, Livestock and Supply (MAPA). In total, we analyzed 36 mixed fertilizers produced by different companies with different sources of phosphate rocks and presenting various amounts of nitrogen, phosphorus, potassium, calcium, and sulfur (table 1).

Table 1: Identification (ID) and composition of fertilizers in terms of available N, P, K, Ca, and S (%N, %P_2O_5, %K_2O, %Ca, and %S).

ID	N:P:K	Ca	S	ID	N:P:K	Ca	S
1	4:12:8	10	5	19	6:24:12	6	6
2	4:12:8	-	4	20	10:20:10	3	9
3	6:10:8	-	4	21	6:24:16	4	5
4	4:14:8	12	10	22	7:18:18	4	6
5	4:14:8	14	12	23	8:28:16	2	4
6	10:10:10	9	5	24	2:18:18	6	6
7	4:14:8	12	7	25	4:24:12	9	6
8	3:17:6	13	10	26	0:20:10	13	7
9	4:14:8	10	10	27	4:24:12	9	6
10	4:14:8	11	10	28	4:24:10	10	7
11	4:14:8	12	11	29	5:36:0	9	5
12	4:14:8	11	11	30	17:44:0	-	-
13	2:16:8	15	12	31	12:60:0	-	-
14	4:14:8	10	7	32	10:30:10	2	6
15	0:18:18	12	6	33	1:32:0	12	6
16	6:15:15	8	10	34	19:0:3	-	23
17	4:14:8	14	10	35	15:6:0	5	18
18	2:20:20	8	4	36	12:5:0	2	12

The fertilizers samples were prepared and analyzed in triplicate following a rigid quality assurance/quality control (QA/QC) program to ensure accurate and reliable analytical data. The fertilizer samples were first ground to pass through a 2-mm sieve and then microwave-digested according to the United States Environmental Protection Agency (USEPA) Method 3051A [25], using a CEM1 Mars-5 microwave system (Matthews, NC, USA). An aliquot of a 0.5 g sample was combined with 10 mL HNO_3 in Teflon1 PTFE vessels and digested for 10 min in the microwave at a pressure of 0.76 MPa. The HNO_3 used was of high purity – Sigma-Aldrich (St Louis, MO, USA), and was distilled prior to use in the digestions. Standard reference materials - SRM (BCR® 032 Natural Moroccan Phosphate Rock and Trace elements in Multi-Nutrient Fertilizer NIST® SRM® 695) were used to substantiate the accuracy of the analytical results obtained. Blank and certified reference samples were analyzed along with every batch of digestion. The concentrations of HM in the digested solutions were determined by graphite-furnace atomic absorption spectrometry (GF-AAS, Perkin–Elmer AAnalyst™800 - Waltham, MA, USA). Statistical analyses of the data were performed using variance analysis (ANOVA) at 5% probability level to test significant differences between HM levels in all fertilizers. The normality of replicate data on HM concentrations was examined by Shapiro-Wilk's W test. In addition to measuring HM contents, this study attempted to verify the existence of a relationship between amounts of P_2O_5 and the HM contained in the fertilizers. For that, the samples were divided into different classes of P_2O_5 content (0-10%; 11-15%; 16-20%; > 20% of P_2O_5). When significant differences were detected ($P < 0.05$), comparisons of means were made between all P_2O_5 classes using Tukey's test.

2.2. Risk-based calculations

The EtraceProDB software was used to assess health risks of the evaluated HM for a real scenario of fertilizers use in Brazil, as described in Guilherme and Marchi [19] and Guilherme et al. [20]. The software is available for download at: http://ainfo.cnptia.embrapa.br/digital/bitstream/item/70630/1/ETraceProDB.exe. Manuals and input data for managing the software are available in English (https://ainfo.cnptia.embrapa.br/digital/bitstream/item/77800/1/doc-300.pdf), Spanish (http://ainfo.cnptia.embrapa.br/digital/bitstream/item/77789/1/doc-291.pdf), and Portuguese (http://ainfo.cnptia.embrapa.br/digital/bitstream/item/77787/1/doc-290.pdf). Parameters such as body weight, ingestion rates (crops), lifetime, application rates, soil accumulation factors, and plant uptake factors were adopted from the scientific literature. Specific data for the Brazilian population was extracted from IBGE [26;27], Couto [28] and Casarini et al. [29]. Data on inorganic fertilizers were provided by the Brazilian industry as well as literature studies. Plant uptake factor for Cu, Pb, Ni, Zn, and Hg were compiled from published studies developed in Brazil. Other parameters, considered non-specific for the Brazilian population, were derived from the US study, according to TFI [18].

The risk-based concentration equation was developed using standard USEPA risk practices and exposure parameters [30]. The standard equation to calculate risk combines 3 factors: estimated intake from exposure, toxicity of the element of interest, and concentration of the trace element in the media of concern (i.e., fertilizer or product). In a back-calculation risk-based approach, the equation is arranged to solve for the RBC using an estimate of potential exposure, toxicity, and an acceptable risk level.

Risk-based concentrations (RBC) are normalized to represent a 1 percent fraction of nutrient (FON) content. These RBC are called unit RBC. Unit RBC can easily be adjusted to represent a particular product with a certain percent nutrient content. The concentrations of the HM (sometimes also called *metal of potential concern, MOPC*) in products must be in the same units as the RBC for a direct comparison. Values of RBC and HM contents in fertilizer products are normally reported in most analyses as mg HM kg^{-1} of product (i.e., parts per million or ppm). However, before proceeding with the comparison, HM concentrations in fertilizers must be adjusted to the same fraction of nutrients (FON) used in the RBC (1%). Heavy metal concentrations in fertilizer products are adjusted by dividing their content by the P_2O_5 percent concentration, for phosphate fertilizers. Such normalization was done with As, Cd, and Pb concentrations measured in the aforementioned 36 mixed fertilizers in order to evaluate the risks associated with their post application.

2.3 Food data analysis

An archive firstly comprising 41 studies published in the scientific literature was created to assess HM contents in edible parts of agricultural products marketed/produced in Brazil, through a search performed in several scientific databases, as *Web of Science* and *Scopus*. As a first requirement, the study should contain HM contents (As, Cd, and/or Pb) in edible parts of food crops and should be conducted with Brazilian products. A second requirement was the use of information concerning samples collected from field conditions or at the market, since experiments under controlled conditions (e.g., greenhouse) do not express the real circumstances of HM transfer from soils to plants, especially to edible parts. Finally, a third condition required that the articles should contain sufficient information for allowing replicable results as well as information about quality assurance/quality control (QA/QC) protocols that could demonstrate the reliability of the data.

The information on HM contents in edible parts collected from studies attending the previous requirements was then compared with the maximum permissible levels (MPL) of each element (As, Cd, and Pb) in the Brazilian legislation [31], as well as with those limits defined by Codex Alimentarius [32] and the European Commission [33]. These MPL are expressed in fresh weight, while most of the results are expressed in dry weight. In view of that, all MPL and data were converted to dry weight, using the following conversion equation:

$$HM_{DW} = \frac{HM_{FW}\ x\ 100}{100 - U\%}$$

where: HM_{DW} is the HM level in dry weight (μg kg^{-1}); HM_{FW} is HM level in fresh weight (μg kg^{-1}); and U% is the percentage of water of each crop [34-36].

3. Results and Discussion

3.1 Heavy metal contents in fertilizers marketed in Brazil

The mean concentrations of As, Cd, and Pb of repeated analyses (n = 5) of the SRM are presented in table 2. The mean recoveries in the certified samples show a reliable analytical data accuracy for the USEPA 3051A methodology [25] used for analyzing As, Cd, and Pb in P fertilizers, especially for detecting Cd.

Table 2: Certified value, determined concentration and recovery of As, Cd, and Pb on certified fertilizer materials.

Element	SRM	Certified value (mg kg^{-1})	Determined concentration* (mg kg^{-1})	Mean recovery (%)
As	BCR®032	9.5 ± 0.5	6.8 ± 0.6	72
Cd	BCR®032	20.8 ± 0.7	20.3 ± 0.9	98
Pb	SRM695	273 ± 17	237.5 ± 15	87

*Average of 5 measurements of standard reference material (SRM) samples

Using the Shapiro-Wilk's W test, we found that the distribution of the concentration of As, Cd, and Pb in fertilizers was not normal. The concentrations ranged from: 0.3 to 7.5 mg kg^{-1}, for As; 1.3 to 19.6 mg kg^{-1}, for Cd; and, 3.8 to 103.3 mg kg^{-1} for Pb. Mean concentrations for As, Cd, and Pb were 1.9, 3.9, and 30.4 mg kg^{-1}, respectively (table 3). It is noteworthy that all P-carrying fertilizers evaluated in this study presented HM concentrations well below the maximum admissible levels accepted by the Brazilian legislation.

Table 3: Concentrations of As, Cd and Pb in mixed fertilizers marketed in Brazil and maximum limits set for the Brazilian legislation

ID	As	Cd	Pb
	--	mg kg^{-1}	--
1	1.6 ± 0.4	3.0 ± 1.1	30.0 ± 5.9
2	0.3 ±0.1	1.3 ± 0.5	77.2 ± 7.9
3	0.8 ± 0.2	2.7 ± 0.4	45.6 ± 7.5
4	2.4 ± 0.7	3.0 ± 0.6	23.5 ± 3.7
5	2.0 ± 0.5	2.7 ± 0.7	27.6 ± 4.7
6	0.3 ±0.1	1.4 ± 0.4	43.3 ± 7.6
7	0.4 ± 0.1	2.3 ± 0.5	38.2 ± 7.4
8	4.7 ± 0.8	10.4 ± 2.1	103.3 ± 10.8
9	2.6 ± 0.3	2.4 ± 0.7	32.2 ± 4.3
10	1.4 ± 0.4	3.1 ± 0.9	38.6 ± 2.7
11	1.2 ± 0.3	3.4 ± 0.8	35.6 ± 4.5
12	1.8 ± 0.2	2.9 ± 0.9	42.1 ± 5.7
13	2.3 ± 0.9	6.1 ± 1.8	34.6 ± 3.4
14	1.0 ± 0.4	2.9 ± 0.5	29.6 ± 3.6
15	1.1 ± 0.2	4.0 ± 0.9	23.4 ± 4.3
16	2.8 ± 0.9	8.9 ± 1.9	16.1 ± 3.2
17	3.7 ± 1.1	7.0 ± 1.8	22.2 ± 3.1
18	3.1 ± 0.9	2.7 ± 0.7	19.4 ± 2.9
19	2.5 ± 0.6	4.2 ± 0.7	45.1 ± 3.9
20	3.3 ± 0.8	5.4 ± 0.9	12.7 ± 1.7
21	4.2 ± 1.2	4.3 ± 0.8	13.0 ± 2.1
22	0.3 ±0.1	2.9 ± 0.9	41.8 ± 7.8
23	1.7 ± 0.5	3.6 ± 1.1	15.0 ± 3.2
24	0.7 ± 0.3	3.1 ± 1.2	27.6 ± 4.7
25	7.5 ± 1.7	19.6 ± 2.9	28.8 ± 5.8
26	0.8 ± 0.2	1.5 ± 0.4	30.1 ± 6.4
27	0.7 ± 0.2	2.3 ± 0.5	19.9 ± 3.2
28	1.0 ± 0.3	2.7 ± 0.4	26.4 ± 5.4
29	3.5 ± 0.9	2.5 ± 0.6	28.3 ± 3.2
30	4.4 ± 0.9	2.5 ± 0.7	6.5 ± 2.3
31	2.2 ± 0.2	6.6 ± 0.9	3.8 ± 1.2
32	0.5 ±0.2	0.9 ± 0.2	9.4 ± 2.1
33	0.5 ±0.1	2.4 ± 0.5	28.1 ± 8.4
34	1.2 ± 0.4	1.6 ± 0.5	13.4 ± 3.2
35	2.4 ± 0.6	2.9 ± 0.6	22.2 ± 5.8
36	0.5 ± 0.2	3.6 ± 0.8	38.0 ± 4.5
Range	0.2 – 7.5	1.3 – 19.6	3.8 – 103.3
Mean	1.9	3.9	30.4
Limit - Brazilian legislation	**250**	**57**	**1000**

Values are the means ± standard deviation (SD) (n = 3). Limits of the Brazilian legislation expressed in mg of As, Cd, Pb per 1 kg of fertilizer dry mass [15].

Considering the highest and lowest concentrations of HM found in the present study and bearing in mind the average consumption of fertilizers (~35.5 million tons) and the cultivated area in Brazil (~75.4 million ha) in 2018, it is estimated that As, Cd, and Pb inputs in Brazilian soils via fertilizers could range from 0.094 to 3.525, 0.611 to 9.212, and 1.786 to 48.551 g ha^{-1} yr^{-1}, respectively. Reported mean inputs of As, Cd, and Pb in soils from England and Wales through phosphate fertilizers application were 1.1, 1.6 and 0.5 g ha^{-1} yr^{-1}, respectively [37]. In Europe, Cd inputs in soils via application of phosphate fertilizers ranged from 0.3 to 8.9 g ha^{-1} yr^{-1} [38], whereas the acceptable limit for Cd input in soils of Canada and in the State of Washington (USA) due to the application of P fertilizers is 0.0889 kg Cd ha^{-1} yr^{-1} [8;16].

The contents of As, Cd and Pb found in the fertilizers studied here are in agreement with data reported by Nziguheba and Smolders [39], who observed similar contents analyzing 196 phosphate fertilizers (including NPK blends, phosphate rock samples and processed phosphates such as MAP, DAP, and TSP) from twelve European countries. These authors found Cd contents ranging from 0.7 to 42 mg kg^{-1}, and an average content of 7.4 mg kg^{-1}. For As and Pb, the authors found average contents of 7.6 and 2.9 mg kg^{-1}. In different Chinese fertilizers, including major P-carrying fertilizers, i.e., monoammonium phosphate (MAP), diammonium phosphate (DAP), and triple superphosphate (TSP), this average concentrations of HM were 13.5, 2.6, and 30 mg kg^{-1}, for As, Cd, and Pb, respectively [40].

In general, the As average content found for the studied Brazilian fertilizers was lower than that reported in studies published in Europe and China; for Cd, the average was lower than that found in Europe, but higher than values reported in China [40]. Finally, for Pb, the mean of 30.4 mg kg^{-1} found in the present study is similar to that found in China (30 mg kg^{-1}), and higher than that evaluated in Europe [39].

To investigate whether or not P-carrying raw materials would be a major source of HM to fertilizers, we assessed correlations between the percentage of P_2O_5 with the contents of As, Cd, and Pb in phosphate fertilizers. For that, we sorted the evaluated fertilizers into four different groups according to their percentage of P_2O_5: 0-10%, 11-15%, 16-20%, and >20% P_2O_5 (figure 1). For As, the mean levels were 1.1, 1.4, 1.9, and 0.4 mg kg^{-1}, respectively for classes 0-10%, 11-15%, 16-20%, and >20% of P_2O_5 (figure 1A), and a positive correlation was only found for the first three P_2O_5 classes. Apparently, the high-grade P fertilizers, which are formulated mostly with MAP, have smaller As contents because less As remains in the phosphoric acid that is used as a raw material for producing MAP, as well as DAP (this last fertilizer is rarely marketed in Brazil). For Cd contents, a positive correlation with P_2O_5 content was observed over all classes of P_2O_5 (figure 1B). A similar result was reported by Nziguheba and Smolders [39], who observed the same trend of increasing contents of Cd with an increase of P_2O_5 in fertilizers. On the other hand, a negative correlation between Pb contents and P_2O_5 levels was observed (figure 1C). In the class with 0-10% of P_2O_5, the mean Pb level was 33.6 mg kg^{-1}, and continuously decreased to 23.26 mg kg^{-1} in the highest class (>20% P_2O_5). This indicates an apparent competition between Cd and Pb for calcium sites in hydroxyapatite (phosphate rock).

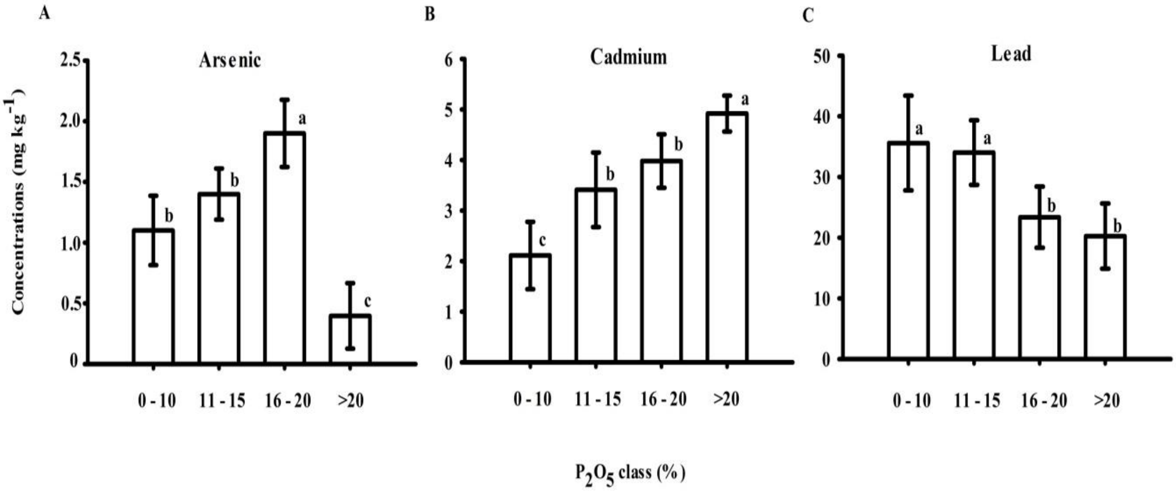

Fig.1. Concentration (means ± standard deviation) of arsenic (A), cadmium (B), and lead (C) in P-carrying fertilizers (n = 36) marketed in Brazil, separated by classes of P_2O_5 content.

3.1. Risk-based analysis

Estimates of RBC normalized to represent a 1 percent fraction of P_2O_5 calculated for selected HM considering two scenarios of P fertilizers use in Brazil, as described in Guilherme and Marchi [19] and Guilherme et al. [20], are shown in table 4, along with RBC data reported for USA, in the TFI study [18]. Limits accepted by the Brazilian legislation [15], also based on a 1 percent fraction of P_2O_5, are similarly presented in table 4 for comparison.

When RBC for selected HM are calculated for different exposure scenarios and considering both adults and children, the lowest RBC is always used for comparisons with HM concentrations reported in different studies and databases. This comparison provides the most protective estimate of health risks. If the concentration of the HM in the fertilizer is smaller than the RBC, there is no health risk. In contrast, if the concentration of the HM in the fertilizer exceeds the RBC estimated for a specific scenario, further evaluation is justified. In the first study conducted by Guilherme and Marchi [19] for the Brazilian scenario, in 2007, there was only one fertilizer sample evaluated at that time exceeding the RBC for Cd in P-containing fertilizers (n = 111). The abovementioned study also suggested that the limits established for selected HM in phosphate fertilizers by the Brazilian Normative Instruction N° 27 released in 2006 were safe in terms of health risk assessment.

Considering data on HM present in the previously mentioned mixed fertilizers (table 3), a comparison of normalized HM results to represent a 1 percent fraction of P_2O_5 (table 5) with unit risk-based concentrations (table 4) revealed that all P-carrying fertilizers analyzed in this study are safe in terms of health risks. Moreover, they are also safe taking into consideration the admissible levels (expressed as mg HM kg^{-1}/% P_2O_5) accepted by the Brazilian legislation [15].

Table 4: Unit risk-based concentrations (mg HM kg^{-1}/% P_2O_5) considering different scenarios in Brazil and in the USA and limits imposed by the current Brazilian legislation concerning acceptable levels of selected HM in P fertilizers.

Scenario	As, carcinogenic	Cd	Cr	Co	Cu	Pb	Hg	Mo	Ni	Se	V	Zn
	Adult	---------- Child ----------										
Brazil - Guilherme and Marchi [19]	2.9	5.8	81470	6389	165	85	0.6	216	435	582	10064	388
Brazil - Guilherme et al. [20]	2.9	1.8	91602	6105	132	110	0.1	216	579	31	10064	350
USA - TFI [18]	4.5	23	34000	3100	280	73	0.9	42	350	120	2200	1200
Brazilian legislation [15]*	**2**	**4**	**40**	**-**	**-**	**20**	**0.05**	**-**	**-**	**-**	**-**	**-**

* Limits of the Brazilian legislation expressed in mg of As, Cd, Pb per 1 kg of fertilizer dry mass are presented in table 3.

Table 5: Average concentrations of As, Cd, and Pb per 1% of P_2O_5 in mixed fertilizers marketed in Brazil

ID	As	Cd	Pb
	---------- mg kg^{-1} ----------		
1	0.13	0.25	2.50
2	0.03	0.11	6.43
3	0.08	0.27	4.56
4	0.17	0.21	1.68
5	0.14	0.19	1.97
6	0.03	0.14	4.33
7	0.03	0.16	2.73
8	0.28	0.61	6.08
9	0.19	0.17	2.30
10	0.10	0.22	2.76
11	0.09	0.24	2.54
12	0.13	0.21	3.01
13	0.14	0.38	2.16
14	0.07	0.21	2.11
15	0.06	0.22	1.30
16	0.19	0.59	1.07
17	0.26	0.50	1.59
18	0.16	0.14	0.97
19	0.10	0.18	1.88
20	0.17	0.27	0.64
21	0.18	0.18	0.54
22	0.02	0.16	2.32
23	0.06	0.13	0.54
24	0.04	0.17	1.53
25	0.31	0.82	1.20
26	0.04	0.08	1.51
27	0.03	0.10	0.83
28	0.04	0.11	1.10
29	0.10	0.07	0.79
30	0.10	0.06	0.15
31	0.04	0.11	0.06
32	0.02	0.03	0.31
33	0.02	0.08	0.88
34*	0.00	0.00	0.00
35	0.40	0.48	3.70
36	0.10	0.72	7.60

* Fertilizer formula without P - 19:0:3 + (22.8 S)

A update of the pre-loaded database of the EtraceProDB software designed for a generic scenario of fertilizers use in Brazil was made in 2012 by Guilherme et al. [20] and the new RBC calculated for the same HM revealed that, except for Cd, which had its suggested limit lowered to 1.8 mg kg^{-1}/% P_2O_5 (compared with the current limit of 4 mg kg^{-1}/% P_2O_5 imposed by the Brazilian legislation), for all other HM, the limits currently established for selected HM in phosphate fertilizers by the Brazilian Normative Instruction N° 27 are safe in terms of health risk assessment. The largest discrepancy between the new calculated RBC for the Brazilian scenario and the limits of the Brazilian legislation (NI 27) for phosphate fertilizers occurs for Cr, where the estimated RBC for Cr_{III} is about 2,000 times greater than the NI 27 limit (which makes no distinction between Cr_{III} - less toxic - and Cr_{VI}, more toxic). For Pb and Hg, the estimated RBC values in the Brazilian scenario are 5.4 and 2 times higher than the NI 27 limits. Finally, in the case of As, the RBC in table 4 is 1.45 times higher than the limit set by the Brazilian legislation.

If the new limit for Cd proposed by Guilherme et al. [20] is used (i.e., 1.8 mg Cd kg^{-1}/% P_2O_5) and considering the maximum Cd admissible level accepted by the Brazilian legislation per 1 kg of fertilizer dry mass (57 mg of Cd kg^{-1} - see table 3), a P-carrying fertilizer marketed in Brazil would exceed the imposed maximum limit for Cd only if its P_2O_5 content is > 31.7%. This is very unlikely to happen if we take into consideration that the average fertilizer formulation in Brazil contains ~14 to 15% P_2O_5.

Data previously reported by Guilherme and Marchi [19] and Guilherme at al. [20] as well as the current information concerning HM concentrations in mixed phosphate fertilizers marketed in Brazil are in accordance with results of a recent study of Silva et al. [41]. These authors have analyzed 53 P-containing fertilizer samples marketed in Brazil and found also that heavy metals present in P-containing fertilizers sold in Brazil did not pose a high human health risk in a medium time frame.

3.2. Heavy metals in edible parts of food crops from Brazil

Information assessing contents of HM in Brazilian agricultural products are essential not to for guaranteeing food security, but also to avoid non-tariff barriers, yet few studies have addressed this issue in Brazil due to the lack of data of adequate detail and reliability.

Our first survey of food data analyses comprised 41 studies, from which 37% were written in Portuguese, i.e., with limited access for the international scientific community. Moreover, 46% of the abovementioned studies did not present any data on QA/QC protocols and a few others did not show clear information on sample preparation for assuring replicable results, which makes them less reliable. These studies were not considered in our analysis. As a result, our discussion concerning HM contents in edible parts of Brazilian agricultural food was restricted to 15 studies reporting contents of As, Cd, and/or Pb, in corn, wheat, rice, soybeans, common beans, potato, cassava, carrots, onion, garlic, lettuce, cabbage, cauliflower, pumpkin, tomato, apple, banana, orange, pineapple, and coffee.

A major part of the available data comprised analyzes of HM from products purchased in the market and very few studies have related HM contents in edible parts to their levels in the soil. Corguinha et al. [42;43] observed that soil HM contents may increase after the continuous application of P fertilizers in some tropical agroecosystems, yet the reported HM levels in the soil were well below the maximum permissible levels for agricultural soils (As: 15-20; Cd: 1-5; Pb: 20-300 mg kg^{-1}) [21]. Furthermore, no correlation was observed between P contents and HM levels in the soil or in the edible parts of rice, wheat, corn, soybeans, and potatoes [42,43].

Arsenic, Cd, and Pb contents in edible parts of Brazilian food crops, as well as maximum permissible levels based on dry weight of the edible parts (MPL_{DW}) for these HM as established by the Brazilian legislation - ANVISA [31], *Codex Alimentarius* [32], and European Commission [33] are presented in table 6. Rice was the crop that presented the highest amount of studies, especially, concerning As. This crop is a staple food in Brazil and other countries and have greater ability to accumulate As than other cereals, mainly as inorganic As, the most toxic chemical form [48].

Among the available crops, some studies showed higher As content than MPL in rice grains [48;49;51;53;54]. Kato et al. [49] reported that 19% of the evaluated rice samples presented total As levels higher than the ANVISA limits [31], noting also that the observed As levels were higher for rice plants grown under flooded conditions. In fact, higher mobilization of soil As has been reported in rice paddy fields under flooded conditions, when compared with nonflooded ones, which may lead to increased As accumulation [57]. Despite of the high total rice As contents reported in the study of Kato et al. [49], these authors have showed that the levels of inorganic forms As were in accordance with the legislation.

Table 6 – Arsenic, cadmium, and lead contents in edible parts of agricultural products from Brazil and maximum permissible levels[§]

Crop	U %	Sampling Conditions	Range or Mean Value			Maximum Permissible Level			Reference
			As	Cd	Pb	As	Cd	Pb	
			μg kg^{-1}			μg kg^{-1}			
						a - *b* - **c** *			
					CEREALS				
Corn	**13**					345 - *N/A* - **N/A**	115 - *115* - **115**	230 - *230* - **230**	
Grain									
		Field	42 - 51	< DL - 51	< DL - 110				[42]
		Field	4.2 - 10.5	0.52 - 1.76	2.8 - 195.6				[44]
Flour									
		Market	-	0.7 - 1.0	< 0.09 - 20				[45]
		Market	-	< 0.02	-				[46]
Wheat	**13**					230 - *N/A* - **N/A**	230 - *230* - **230**	230 - *230* - **230**	
Grain									
		Field	11 - 25	< DL - 83	< DL - 92				[42]
Flour									
		Market	-	1.0 - 20	< 0.02 - 16				[45]
		Market	-	< 0.02	-				[46]
Pasta									
		Market		4.6 - 13	**< 0.003 - 489**				[45]
		Market	45	-	-				[47]
		Market	42 - 48	-	-				[48]
Rice	**13**					345 - 402 *(230)*[#]- **N/A**	460 - *460* - **230**	230 - *230* - **230**	
Grain									

		Field	< DL	17 - 50	< DL				[42]
		Field	**< DL - 630**	2.9 - 44	-				[49]
		Field	190 - 340	< DL	-				[50]
		Market	-	0.4 - 54	<0.002 - 90				[45]
		Market	212	-	-				[47]
		Market	**59 - 782**	-	-				[48]
		Market	**< 38 - 660**	< 12 - 420	< 30 - 127				[51]
		Market	68 - 249	7 - 23	-				[52]
		Market	**109 - 428**	-	-				[53]
		Market	**5.2 - 419**	-	-				[54]
		Market	-	< 2	< 40				[55]
LEGUMES									
Soybeans	**15**					118 - *N/A* - **N/A**	235 - *118* - **235**	235- *118*- **235**	
Grain									
		Field	51 - 79	10 - 38	90 - 114				[42,43]
Common Beans	**14**					116 - *N/A* - **N/A**	116 - *116* - **233**	233 - *116* - **233**	
Grain									
		Market	-	< 0.05 - 9.0	< 0.02 - 0.04				[45]
		Market	50	-	-				[47]
		Market	5 - 223	-	-				[48]
ROOT, BULB AND TUBERS VEGETABLES									
Potato	**83**					1177 - *N/A* - **N/A**	588 - *588* - **588**	588 - *588* - **588**	
Tuber									
		Field	46 - 67	14 - 43	< DL				[42,43]
		Market	-	2.2 - 10	< 0.008 - 10				[45]
		Market	53	-	-				[47]

		Market	53 - 59	-	-				[48]
Cassava	**62**					526 - *N/A* - **N/A**	263 - *263* - **263**	263 - *263* - **263**	
Tuber									
		Market	-	3.0 - 5.0	< 0.004 - 170				[45]
Flour									
		Market	-	1.2 - 2.3	**279 - 502**				[45]
		Market	-	< 0.02	-				[46]
Carrot	**90**					2000 - *N/A* - **N/A**	1000 - *1000* - **1000**	1000 - *1000* - **1000**	
Roots									
		Market	-	0.6 - 7	0.2 - 72				[45]
		Market	70	-	-				[47]
		Market	42 - 67	-	-				[48]
Onion	**89**					909 - *N/A* - **N/A**	455 - *455*- **455**	909 - *909* - **909**	
Bulbs									
		Market	-	1.1 - 7.0	< 0.003 - 1.0				[45]
Garlic	**68**					313 - *N/A* - **N/A**	156 - *156* - **156**	313 - *313* - **313**	
Bulbs									
		Market	41	-	-				[47]
		Market	25 - 63	-	-				[48]
					VEGETABLES				
Lettuce	**95**					6000 - *N/A* - **N/A**	4000 - *4000* - **4000**	6000 - *6000* - **6000**	
Leaves									
		Field	-	< DL	< DL				[56]

		Market	-	2.4 - 9.7	17 - 75				[45]
		Market	340	-	-				[47]
		Market	100 - 443	-	-				[48]
Cabbage	**93**					4286 - *N/A* - **N/A**	2857 - *714* - **714**	4286 - *1428* - **4286**	
Leaves									
		Market	-	1.9 - 6.6	< 0.003 - 53				[45]
		Market	86	-	-				[47]
		Market	57 - 129	-	-				[48]
Cauliflower	**95**					6000 - *N/A* - **N/A**	1000 - *1000* - **1000**	6000 - *2000* - **6000**	
Flower									
		Market	-	1.0 - 3.0	3.0 - 19				[45]
Pumpkin	**93**					1428 - *N/A* - **N/A**	714 - *714* - **714**	1428 - *714* - **1428**	
Fruit									
		Market	-	0.4 - 6.9	< 0.006 - 16				[45]
Tomato	**94**					1667 - *N/A* - **N/A**	833 - *833* - **833**	1667 - *833*- **1667**	
Fruit									
		Market	-	1.3 - 4.4	< 0.002 - 13				[45]
		Market	83	-	-				[47]
		Market	50 - 133	-	-				[48]
						FRUITS			
Apple	**84**					1875 - *N/A* - **N/A**	313 - *N/A* - **313**	625 - *625* - **625**	
		Market	-	< 0.008 - 9.2	0.02 - 27				[45]
Banana	**71**					1034 - *N/A* - **N/A**	172 - *N/A* - **172**	345 - *345* - **345**	
		Market	-	< 0.02 - 0.03	< 0.01 - 6.0				[45]

Orange	**87**					2308 - *N/A* - **N/A**	385 - *N/A* - **385**	769 - *769* - **769**	
		Market	-	< 0.03 - 0.3	9.0 - 44				[45]
Pineapple	**86**					2143 - *N/A* - **N/A**	357 - *N/A* - **357**	714 - *714* - **714**	
		Market	-	0.02	0.01				[45]
					BEVERAGES				
Coffee	**4**					208 - *N/A* - **N/A**	104 - *N/A*- **N/A**	520 - *N/A* - **N/A**	
Grain									
		Market	-	5 - 19	230 - 308				[45]
		Market	49	-	-				[47]
		Market	38 - 76						[48]

§ Whenever informed as fresh weight, values were adjusted to dry weight, including those of the permissible levels;
* a - *b* – **c**: MPL_{DW} in: a ANVISA ; *b Codex Alimentarius;* **c European Commission**;
\# husked grains (polished grains).

Ciminelli et al. [48] and Matavelli et al. [51] observed that only one of the total evaluated samples presented high As content (i.e., > MPL), and Segura et al. [54] reported two samples with higher As. Samples of these studies were purchased from markets, which does not allow tracing the region of production and if the soil in the area has high contents of As or not. The samples with high As level in Matavelli´s [51] and Segura´s [54] studies were brown rice samples, which tends to present higher amounts of As than white (polished) rice, since greater part of As is concentrated in the rice bran. Milling process can be a good alternative to alleviate rice grains As contamination. This information (brown or polished rice) is not available in Ciminelli´s study [48].

Contrary to what was observed for As, the contents of Cd and Pb in edible parts and food products presented in Table 6 where all below MPL, except for Pb values found in pasta and cassava flour [45], which may be related to the manufacturing process. Cadmium inputs to agricultural soils have been associated with the addition of phosphate fertilizers for crop intensification [7], which is especially relevant in tropical soils. Chen et al. [58] reported that the application of P over 100 years could increase Cd content by 3 times, making this HM later available for plant absorption. However, the fact that Cd concentrations reported in Brazilian food is in accordance with the MPL and do not pose risk to human health is noteworthy, even with the high records of P fertilizers application in Brazilian soils [14;16].

Lastly, it is true that the number of studies analyzing HM contents in fertilizers, soils, and crops is still incipient in Brazil, especially those carried out with a rigid QA/QC protocol that could guarantee data reliability. Nevertheless, taking into consideration the historical and successful records of sustainable and resilient soil management in low-fertility soils and the fact that Brazil is being able to export its agricultural products worldwide, namely in the last two decades, it is very unlikely that these HM will represent a threat to human health or to the environment in Brazilian agroecosystems.

4. Conclusions

Our results indicate that inputs of As, Cd, and Pb in Brazilian agroecosystems via addition of P-carrying fertilizers vary considerably due to the great variability observed for the contents of these heavy metals (HM) in P fertilizers marketed in Brazil. Concentrations of Cd were positively correlated whereas those of Pb where negatively correlated with P contents in mixed fertilizers.

None of the mixed fertilizers showed As, Cd, and Pb total concentrations exceeding the limits of the Brazilian legislation or the ones estimated as safe based on health risk assessments. Moreover, the results obtained from studies assessing risk-based concentrations (RBC) of HM in P fertilizers used in Brazil indicate that HM do not cause harm to human health when considering the current scenario of post application of P fertilizers in Brazil. They also suggest that the limits currently established by the Brazilian legislation are safe in terms of health risks. Finally, a survey of HM analyzes in edible parts of Brazilian agricultural food and food products evidenced the safety of such products with respect to their contents of As, Cd, and Pb.

Considering the growing importance of Brazil as a global food provider, our findings are relevant to show that fertilizer use in Brazilian agriculture is done in such a way as to guarantee the production of healthy crops as well as adequate food quality criteria. These results are also economically relevant, since they show that the concentration of these elements in Brazilian fertilizers and agroecosystems are safe, thus avoiding non-tariff barriers to trade of Brazilian agricultural products.

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