

Characterization and phytoavailability evaluation of micronutrients and contaminants in some Brazilian phosphate fertilizers

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Brazilian fertilizer legislation considers the total concentration of micronutrients as being the guarantee of their presence in fertilizers. This fact allows the use industrial by-products as micronutrient source for fertilizers, which brings the risk of the presence of high amounts of toxic elements that may lead to soil contamination. The purpose of this study was to determine the micronutrient and contaminant contents in six Brazilian commercial phosphate fertilizers and to evaluate the phytoavailability of elements from soils treated with these fertilizers. Instrumental neutron activation analysis (INAA) followed by gamma-ray spectrometry was the analytical method used to determine the contents of the elements. As, Cd, Co, Cr, Fe, Mo, Na, Sb and Zn were detected in fertilizers. Concentrations in vegetal tissue were not modified by the treatments, except for Cd, which was increased due to fertilizers application.

Introduction

Phytoavailability of micronutrients and inorganic contaminants from mineral fertilizers has been the object of many studies, in the last decades. Brazilian fertilizer legislation considers the total concentration of micronutrients as being the guarantee of their presence in fertilizers.¹ This fact allows the use industrial by-products as micronutrient source for fertilizers, which brings the risk of the presence of high amounts of inorganic contaminants that may lead to soil contamination, affecting harvest and the quality of the agricultural products.

B, Cl, Co, Cu, Fe, Mn, Mo, Ni and Zn are considered as micronutrients for the plants and microorganisms. However, they are toxic at high concentration in the soil solution. The elements As, Cd, Hg and Pb are considered toxic for the domestic animals.² Uptake of these elements by plants consumed directly or indirectly by humans can be one avenue of entry to food chain.

Micronutrients and contaminants contained in the fertilizer, when added to the soil, suffer several reactions which can make them available for plants.^{3,4} In order to uptake these elements, plants make use of the following mechanisms of tolerance: (a) selective absorption of ions; (b) membrane permeability reduction or other differences; (c) immobilization of ions in the roots, foliages and seeds; (d) deposition of insoluble compounds; (e) alterations in the metabolic equilibrium; (f) substitution of a toxic element in a physiological enzyme for another element; (g) elimination of ions through the excretion by roots.⁵ Contaminant absorption capacity is differential among the various plant organs. In general, the root is the main organ for inorganic element entrance and accumulation, being the process influenced by root density and radicular volume.⁶

In view of this, the objectives of this study were to determine the micronutrient and contaminant content in six Brazilian commercial phosphate fertilizers and to evaluate the phytoavailability of the following elements: As, Cd, Co, Cr, Fe, Mo, Na, Sb and Zn for rice plants that were cultivated in two different types of soils treated with fertilizers. Instrumental neutron activation analysis (INAA) followed by gamma-ray spectrometry was the analytical method used to determine the contents of the elements.⁷

Experimental

Treatment of fertilizer samples and installation of the experiment for phytoavailability evaluation

Samples of six commercial phosphate fertilizers of different manufactures (Fertilizers: 14, 15, 16, 19, 23 and 31), with N, P, K, Ca, S, Mg and micronutrients were ground in an agate mortar until passed through a 0.84 mm sieve (ABNT No. 20).

To assess the microelemental phytoavailability, rice plants (*Oryza sativa* IAC 201 cultivar) were grown in pots containing 1 dm³ of soil. The trial was performed at the green house of Centro de Energia Nuclear na Agricultura-USP, Piracicaba, SP, Brazil.

The Typic Quartzipsamment (TQ) and Typic Oxisols (TO) had been the soils used in this study. The soils were treated with a mixture of CaCO₃ and MgCO₃ (4:1) to increase the saturation basis to 50%, then they were incubated for 30 days under 60% moisture content. After this treatment, the soil was dried, crushed and homogenized. Samples of 1.0 dm³ were placed into plastic bags and packed in pots.

Control treatment was constituted by addition of N, P, K and S in the following rates: 100, 200, 150 and

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100 mg·dm⁻³, respectively, and B, Cu, Fe, Mn, Mo and Zn in the following rates: 4, 4, 20, 20, 0.4 and 6 mg·dm⁻³. The treatments with commercial fertilizers were added to the pots in rates equivalent to the contained nutrients in the control treatment. After fertilization, soil samples were incubated for one week and ten rice seeds were sown in each pot. One week after germination the plants were thinned to five plants per pot. The experiment was carried out in a green house with ventilation and humidification system and, the statistic design was completely randomized, with 7 treatments, two soils and 3 replications.

Aboveground part of the each plant was collected at 60 days after of germination, oven dried, weighed and ground in agate mortar for elemental analysis by INAA.

For irradiation, aliquots of fertilizers (40 mg) and plant samples (200 mg) were transferred to polyethylene bags, which had been cleaned by leaching with a diluted HNO₃ (1:5) and purified water.

Preparation of standards

Certified standard solutions (Spex Certiprep) of As, Cd, Co, Cr, Fe, Mo, Na, Sb and Zn were used to prepare the standards. Aliquots (50–100 µL) were pipetted on small sheets of analytical filter paper (Whatman No. 42) for irradiation. After drying, these filter papers were placed into polyethylene bags.

Irradiation and counting

Irradiations were carried out at the IEA-R1 nuclear research reactor, in a thermal neutron flux of 3·10¹² n·cm⁻²·s⁻¹. Sample and standards (As, Cd, Co, Cr, Fe, Mo, Na, Sb and Zn) were irradiated together in an aluminum container for 5 hours. The ⁷⁶As, ¹¹⁵Cd, ⁹⁹Mo, ²⁴Na and ¹²²Sb were measured after 3 days of decay time, while ⁶⁰Co, ⁵¹Cr, ⁵⁹Fe, and ⁶⁵Zn were measured after, at least, 10 days of decay time.

The equipment used to measure the gamma-radiation was a Canberra Model GX2020 hyperpure Ge detector, coupled to a Model 1510 Integrated Signal Processor and MCA System 100, both from Canberra. The detector used had a resolution (FWHM) of 0.9 keV for 122 keV gamma-rays of ⁵⁷Co and 1.9 keV for 1332 keV gamma-ray of ⁶⁰Co.

Analyses of reference materials NIST 1515 Apple Leaves and IAEA Soil-7 were also carried out simultaneously and, the results obtained were within the range of certified values.

Results and discussion

Elemental concentrations determined in fertilizers are shown in Table 1. Each value is the result of one determination, followed by its uncertainty evaluated

using the error from statistical counting. The fertilizers are complex matrices, so photopeaks of elements present at in low concentrations can be masked by high gamma-ray activities. This interference problem occurred in the analysis of cadmium, an important contaminant that remains with phosphorus fertilizers, during manufacture, from phosphate rock ores. For this reason cadmium was determined in fertilizers by inductively coupled plasma – optical emission spectrometry (ICP-OES). The concentrations of the elements varied among the fertilizers (Table 1), due to their different origins and production processes. The knowledge of the total concentrations of the elements in the fertilizers is not indications that the plants will uptake these elements.

In Tables 2 and 3 are shown the elemental concentrations found of rice plants cultivated in two types of soil treated with distinct phosphate fertilizers. As, Cd, Co, Cr and Sb (Table 2) found in rice plant have tendency to be toxic for animals and/or plants.² Fe, K, Mo, Na and Zn (Table 3) are considered nutrient elements. Each result, presented in Tables 2 and 3, is the arithmetic mean of three pots, as the experimental design. Coefficient of variation values of these results varied from 3 up to 50% in the case of some elements. This coefficient represents the uncertainty of the analytical method and the elemental concentration variation observed within each treatment. The effect was presumably on account of the biological variations of the element uptake and the soil composition variations among the different pots. Variance analysis was applied to the values of Tables 2 and 3, using Tukey test,⁸ $p < 0.05$, to verify if there is a difference among element concentrations obtained in rice plant, as affected by fertilizers. Statistical *t*-test,⁸ $p < 0.05$, was also applied to verify the effect of soil type: Typic Quartzipsamment and Typic Oxisols in the element uptake by vegetal tissue.

Cadmium was determined in the plants by INAA. The results in Table 2 show that cadmium concentrations in rice plants were significantly influenced by application of phosphate fertilizers containing Cd, since this element was not detected in the control plant. Cadmium contained in phosphate fertilizers is somewhat available to plants although the pH of the soil also affects Cd uptake by the plants.^{4,9} This fact also occurred for the antimony in lesser ratio on Typic Quartzipsamment.

The element As for fertilizers 14 and 16, Co for fertilizers 16 and 19, Cr for fertilizer 31 and Sb for all the fertilizers presented concentrations of these elements above the plant control in the TQ soil (Table 2). These referred elements in the fertilizers can contain As, Co, Cr and Sb in soluble forms which the plants have capacity to absorb. In the TO soil the same happened with Co for the fertilizer 15 and Cr for the fertilizers 14, 23 and 31.

Table 1. Elemental concentrations in fertilizers determined by INAA

Element	Fertilizer					
	14	15	16	19	23	31
As, mg.kg ⁻¹	44 ± 1	58 ± 2	50 ± 1	2.5 ± 0.3	3.1 ± 0.3	5.8 ± 0.7
Co, mg.kg ⁻¹	12.4 ± 0.4	39 ± 1	13.3 ± 0.4	0.33 ± 0.06	0.42 ± 0.05	34 ± 1
Cr, mg.kg ⁻¹	69 ± 4	52 ± 3	82 ± 5	246 ± 17	245 ± 17	992 ± 74
Fe, %	1.3 ± 0.1	0.96 ± 0.06	1.46 ± 0.09	0.19 ± 0.13	0.15 ± 0.01	6.4 ± 0.4
Mo, mg.kg ⁻¹	90 ± 22	210 ± 29	83 ± 25	68 ± 8	135 ± 12	83 ± 34
Na, mg.kg ⁻¹	4588 ± 15	4722 ± 17	3450 ± 12	8399 ± 12	8777 ± 36	1424 ± 6
Sb, mg.kg ⁻¹	17 ± 1	19 ± 1	<LD	<LD	0.7 ± 0.2	23 ± 1
Zn, mg.kg ⁻¹	4334 ± 183	8294 ± 100	4737 ± 200	438 ± 28	504 ± 32	758 ± 44
Cd,* mg.kg ⁻¹	70	240	80	59	146	61

LD: Limit of detection.

* Cadmium was determined by inductively coupled plasma – optical emission spectrometry, ICP-OES.

Table 2. Mean values of As, Cd, Co, Cr, and Sb concentrations in rice plants, cultivated in Typic Quartzipsamment (TQ) and Typic Oxisols (TO) soils

Treatment	As, µg.kg ⁻¹		Cd, µg.kg ⁻¹		Co, µg.kg ⁻¹		Cr, µg.kg ⁻¹		Sb, µg.kg ⁻¹	
	TQ	TO	TQ	TO	TQ	TO	TQ	TO	TQ	TO
Fertilizer 14	141 aA	64 aB	1063 aA	4227 bB	41 aA	27 aA	299 aA	637 aB	11a	<LD
Fertilizer 15	116 abA	65 aB	<LD	2967 b	41 aA	48 aA	304 aA	552 aB	14 a	<LD
Fertilizer 16	154 aA	93 aB	4888 bA	7073 cA	61 aA	33 aA	297 aA	484 aB	15 aA	7 aB
Fertilizer 19	64 bA	111 aB	<LD	477 ab	71 aA	25 abA	329 aA	535 aB	22 aA	12 aA
Fertilizer 23	73 bA	124 aA	1598 aA	764 abB	40 aA	27 aA	326 aA	669 aB	56 aA	8 aB
Fertilizer 31	71 bA	41 aA	1743 ab	<LD	49 aA	20 abA	466 aA	629 aB	15 aA	9 aA
Control:	100 abA	120 aA	<LD	<LD	46 aA	30 aA	348 aA	563 aB	<LD	13 a

Mean values followed by the same small letter in vertical indicate no difference by Tukey test ($p < 0.05$).For each element, mean values followed by the same capital letter in horizontal indicate no difference by t -test ($p < 0.05$).

LD: Limit of detection.

Table 3. Mean values of Fe, Mo, Na and Zn concentrations in rice plants, cultivated in Typic Quartzipsamment (TQ) and Typic Oxisols (TO) soils

Treatment	Fe, mg.kg ⁻¹		Mo, mg.kg ⁻¹		Na, mg.kg ⁻¹		Zn, mg.kg ⁻¹	
	TQ	TO	TQ	TO	TQ	TO	TQ	TO
Fertilizer 14	91 aA	104 aA	34 aA	22 aA	131 aA	140 aA	172 aA	197 bA
Fertilizer 15	73 aA	122 aB	15 bA	8 bB	150 aA	444 bB	240 aA	220 bA
Fertilizer 16	100 aA	99 aA	9 bA	6 bA	94 bA	117 aA	183 aA	180 bA
Fertilizer 19	82 aA	107 aA	19 bdA	7 bB	78 bA	163 aB	113 abA	199 bB
Fertilizer 23	92 aA	115 aA	22 bdA	9 abB	50 bdA	141 aB	128 abA	152 bA
Fertilizer 31	115 aA	106 aA	57 cA	26 aB	46 bdA	101 acB	106 abA	70 abA
Control:	100 aA	112 aA	25 adA	15 abA	23 cdA	112 aB	180 aA	135 bB

Mean values followed by the same small letter in vertical indicate no difference by Tukey test ($p < 0.05$).For each element, mean values followed by the same capital letter in horizontal indicate no difference by t -test ($p < 0.05$).

Analysis of the data presented in Table 3 shows that, in most cases, the elemental concentrations in rice plants were not significantly modified, excepting in case of sodium (fertilizer 15). Some significant differences that were observed between element uptaken by vegetal tissue of the plant cultivated in TQ and TO soils may be explained by the quantity of element available in soil solution. This availability is the result of processes such as precipitation, dissolution, formation of complexes with organic and inorganic compounds.⁵ Studies with successive cultivations and with new applications of fertilizers are necessities for a more precise evaluation on the contamination of agricultural soils for fertilizers.

Conclusions

As, Cd, Co, Cr, Fe, Mo, Na, Sb and Zn were detected in fertilizers. Cd in vegetal tissue was increased due to fertilizers application.

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