EFFECTS OF PHOSPHORUS ADDITIONS ON LEAD AND MERCURIUM BIOAVAILABILITIES IN A CONTAMINATED SOIL

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ABSTRACT

The soils enriched with elements potentially toxic (EPT) have limited use for agricultural purposes. In this case, the corresponding site should be isolated and then procedures for decontamination or stabilization of EPT in the soils must be applied. The objective of this study was to evaluate the influence of adding different rates of phosphate on the bioavailability of mercury (Hg) and lead (Pb) in a contaminated soil, using lettuce grown on this soil. For this, different phosphorus rates were used to control bioavailability of Hg and Pb, in lettuce plants. The element concentrations were analyzed by instrumental neutron activation analysis (INAA), and the results were compared to control treatment to verify the reduction of absorption of Hg and Pb. The Hg concentration in shoots decreased with the application of 250 mg kg^{-1} of P and Pb with the application of 250 to 1000 mg kg^{-1} of P. The accumulation of Hg and Pb in shoots of lettuce increased as a function of P demonstrating the inefficiency of application of P in the absorption of these elements.

Keywords: contamination, lettuce, imobilization

EFEITO DA ADIÇÃO DE FÓSFORO SOBRE A BIODISPONIBILIDADE DE CHUMBO E MERCÚRIO EM SOLO CONTAMINADO

RESUMO

Os solos enriquecidos com elementos potencialmente tóxicos (EPT) têm seu uso limitado para fins agrícolas. Neste caso, o local deve ser isolado e, em seguida, os procedimentos para a descontaminação ou estabilização dos EPT nos solos devem ser aplicados. O objetivo deste estudo foi avaliar a influência da adição de fósforo sobre a biodisponibilidade de mercúrio (Hg) e chumbo (Pb), em solo contaminado, cultivando alface neste solo. Para isso, diferentes taxas de fósforo foram usadas para controlar a biodisponibilidade de Hg e Pb, em plantas de alface. As concentrações dos elementos foram analisados por análise instrumental por ativação de neutrônica (INAA), e os resultados foram comparados para controlar o tratamento para verificar a redução de absorção de Hg e Pb. A concentração de Hg na parte aérea diminuiu com a aplicação de 250 mg kg^{-1} de P e Pb com a aplicação de 250 a 1000 mg kg^{-1} de P. O acúmulo de Hg e Pb na parte aérea da alface aumentou em função de P demonstrando a ineficiência da aplicação de P na absorção desses elementos.

Palavras-chave: contaminação, alface, imobilização

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INTRODUCTION

In most cases, the concentration of microelements and toxic elements found in soil does not pose a risk to the environment. However, in recent decades the mining, industrial process, the use of agricultural inputs such as fertilizers, limestone, pesticides has greatly contributed to the enrichment of inorganic elements in areas close to events (ALLOWAY, 1995; SILVA et al., 2007).

Cadmium, lead, mercury and arsenic, classified as elements potentially toxic (EPT) are a huge problem for the public health. When they are present in the soil may persist due to their long life-time in soils, and could be readily available for plants, especially in acid soils, and being transferred to the human food chain. (KPONBLEKOU & TABATABAI, 1994; CAMELO, 1997). Thus, soils enriched with EPT have limited use for agricultural purposes. In this case, the corresponding site should be isolated and then procedures for decontamination or stabilization of EPT in the soils must be applied (TREVIZAM et al., 2010).

The addition of chemicals to contaminated soil is one of the practices used for immobilization of EPT through reducing the solubility and bioavailability of these elements, due to the complex formation and/or precipitation (MCGOWEN, 2001). Phosphates, limestone, Fe or Mn oxides, organic materials and zeolites are the chemicals used for the reduction and bioavailability.

It is known that Pb phosphates are very stable forms of Pb in the environment. From the reaction of lead with soluble phosphate (P) various pyromorphite minerals insoluble are formed, thus immobilizing Pb in soil and in consequence reducing its absorption by plants (BOLAN et al., 2003; ZWONITZER et al., 2003).

The uptake of Hg by lettuce, under the conditions of this study, was evaluated because of Hg to be an important EPT, although not known very stable compounds Hg phosphate. Despite the presence of Hg in the soil, there is evidence that almost no Hg from the soil is taken up into the shoots. Experiments carried out in some plant species using culture solutions has shown that 95 to 99% of Hg has remained in the root (LINDQVIST et. al, 1991).

The objective of this study was to evaluate the influence of adding different doses of phosphate on the bioavailabilities of Hg and Pb in a contaminated soil, using lettuce grown on this soil.

MATERIAL AND METHODS

Soil sampling and treatment for the experiment

The soil was collected from a site of 22.000 m^2, located in Piracicaba, SP-Brazil. This site is under receivership of the Companhia de Tecnologia e Saneamento Ambiental (CETESB) because it has high level of contamination by potentially toxic elements.

A sample of 50 kg soil was collected for this study in an area of 2 x 3 m from 0-20 cm depth, passed through 4 mm mesh sieve and then homogenized. Subsamples of 2 kg soil were transferred to pots where plants were sown. A 1 kg subsample soil was taken for chemical and physical characterizations (pH; available P, Ca, Mg and K; total acidity and organic matter) (RAIJ et al, 2001). In the Table 1 show the chemical attributes of soil.

Installation of the experiment with lettuce

To assess the effect of phosphorus in reducing and the availability of EPT in soil, lettuce plants (*Lactuca sativa* L.) were grown in pots containing 2 kg of soil. The trial was performed at the green house with ventilation and humidification system at the CENA.

The experimental design was a randomized block, with 6 treatments (rates of phosphorus): 0, 250, 500, 1000, 2000 and 4000 mg kg^{-1} of P, with 3 replicates of each treatment, totaling 18 pots. The P source used was $Ca(H_2PO_4)_2$.

The soils of the pots, after receiving the P fertilizer, were incubated for 15 days under 60% moisture content. At the end of the incubation period six seedlings of lettuce were transplanted in each pot. After 7 days, the plants were thinned to two plants per pot. Soil moisture was maintained at 70% by daily watering with deionized water. As additional fertilizer, nitrogen was applied as ammonium nitrate at rates of 100 mg N per pot in four applications. Ten days after transplanting, 0.2 mg of boron as boric acid and 0.25 mg of molybdenum in the form of ammonium molybdate were applied in all pots.

The lettuce leaves were collected at 70 days after transplanting, rinsed with deionized water, oven dried (at 65ºC), weighed and ground in agate mortar for quantification of Hg and Pb.

Analytical method used

The quantification of Hg was performed with cold vapour atomic absorption spectroscopy (CV AAS, Perkin Elmer® FIMS), where it was used stannous chloride as reducing agent. Eletrothermal atomic absorption spectroscopy (ET AAS, Perkin Elmer® Analyst 800 spectrometer with Zeeman background correction) was employed to quantify Pb.

Aliquots of about 40 mg for lettuce and 200 mg for Mixed Polish Herbs (INCT-MPH-2), a certified reference materials (SRM) were digested with 4 ml of concentrated HNO_3 (Merck®) and left standing for a period of 8 h, after 1 ml of 30% H_2O_2 was added. The flasks were stirred and left again for about 15 h. To finalize the sample digestion, the closed flasks were placed in an aluminum block at 90°C, for 3 h. The reference material was analyzed to control the analytical results.

For the construction of calibration curves were used solutions whose concentrations ranged from 0.5 to 2.5 µg/L in the case of Hg, and from 5 to 25 µg/L for Pb. During the analysis and construction of calibration curves, the following parameters were kept fixed, 1.) Hg: injection volume in 500 µL, flow charger (HCl P.A. 3% v/v – Merck) in 10 mL min^{-1}, flow reducer in 6 mL min^{-1} and flow of argon (carrier gas) in 50 mL min^{-1}; 2.) Pb: wave-length in 283.3 nm, slit in 0.7 nm, current lamp in 440 mA, volume of sample injection in 20 µL and injection volume of the chemical modifier in 10 µL.

RESULTS AND DISCUSSION

The results obtained for Hg and Pb in Mixed Polish Herbs (INCT-MPH-2) are shown in Table 2. The agreement between the values of Hg and Pb concentrations obtained and certified, around 12%, for Mixed Polish Herbs showed that the analytical procedure was appropriate to determine these elements in lettuce.

Regarding the development of lettuce in the contaminated soil, especially in relation to adverse soil characteristics (Table 1). The lettuce presented increase of dry matter production of shoots when treatments are compared to the control treatment, at doses between 250-2000 mg kg^{-1} of P, demonstrating that the addition of P does not compromise their development.

The increased production of dry matter demonstrates that possibly occurred a decrease the toxic effect of Hg and Pb, however its greatest development may result in greater absorption of these elements occurred. The lettuce crop is used as an indicator of the availability of heavy metals in contaminated soils and thus entry into the food chain (BASTA et al., 2001; MACHADO et al., 2008).

The Hg concentration in the shoots of lettuce (Figure 1) ranged 17-168 μg kg^{-1}. The values found are above 6.9 μg kg^{-1} encountered by STERTZ et al. (2005) in lettuce collected in production fields.

The objective of immobilize of Hg with the application of phosphorus in the soil was only observed with the application of 250 mg kg^{-1} P, where there was a reduction of 15.3% compared to the control treatment. In this sense the application of high rates above 250 mg kg^{-1}, promoted an increase in dry matter production of shoots and consequently greater absorption of Hg.

ZHAO & WANG (2010) verified the availability of Hg contained in calcium superphosphate (5.1 mg kg-1) to maize. The authors concluded that the fertilizer may decrease the toxicity of Hg in maize, inhibiting Hg uptake and translocation from the root to the shoots of culture.

The Hg concentration in lettuce shoots may be related to their greater binding to cell walls of roots or its smallest transport through the flow of transpiration in plants (DU et al., 2005). This peculiarity of the Hg may significantly influence the results obtained in this study.

When the development of lettuce associated with Hg concentration in shoots it was verified that the accumulation of Hg in shoots increased with the addition of P to the soil, and this increase of 530% compared to the control treatment (Figure 1). The increased accumulation of Hg demonstrates the inefficiency of P on the absorption of Hg, verified by the accumulation of Hg in shoots of lettuce.

The Pb concentrations in the shoots of lettuce ranged 1069-5501 μg kg^{-1} (Figure 2). P addition to soil promoted a reduction of Pb in the shoots of lettuce at 250-1000 mg kg^{-1} rates of P.

BASTA et al. (2001) working with lettuce, the phosphate rock used to mitigate the absorption by lettuce, however found an increase of Pb content in shoots of lettuce in soil containing 397 mg kg^{-1}, and other soil containing 2450 mg kg^{-1} of Pb presented in lettuce at the same concentration of the control treatment. The authors reported that by presenting concentration below 6 mg kg^{-1} in lettuce resulted in difficulties to determine the element.

The Pb concentrations in the shoots of lettuce can be quite different depending on the cropping system and the type of soil that is contaminated or not. COSTA et al. (2001) found maximum concentration of 4.95 mg kg^{-1} in three varieties of lettuce grown with urban waste compost and COSTA et al. (1994), applying organic compost, found concentration of 6.33 mg kg^{-1} dry matter of lettuce leaves. SANTOS et al. (1998) found concentrations ranging from 6.53 to 23.48 mg kg^{-1} in ten cultivars of lettuce grown with urban waste compost. AGBENIN et al. (2009) found in Nigeria Pb concentration in lettuce from 0.65 to 4.8 mg kg^{-1} on fresh weight.

The accumulation of Pb in the shoots of lettuce increased as a function of P applied to the soil (Figure 3). The increased accumulation of P in the shoots of lettuce demonstrates the inefficiency of application of P in reducing the availability of Pb in the soil, especially when compared to the control treatment.

In relation the addition of P in soils contaminated was verified the reduction of 51.9% of Pb in *Brassica oleracea* L. var. acephala and in 65.5% in *Brassica campetris* L. var. communis (ZHU et al., 2004), from 32.6 to 57.9% in *Sorghum bicolour* L. (CHEN et al., 2007) and in *Sorghum vulgare* L. Moench and *Beta vulgaris* L. Koch (Hettiarachchi & Pierzynski 2002). Although these studies verify the effectiveness of the reduced availability of Pb to crops, in none of these work has verified the accumulation of Pb, which is of fundamental importance since this parameter takes into account the development of culture.

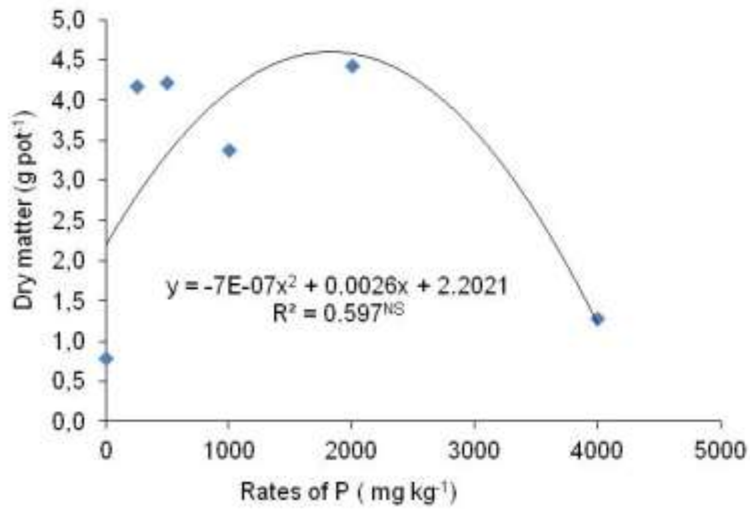
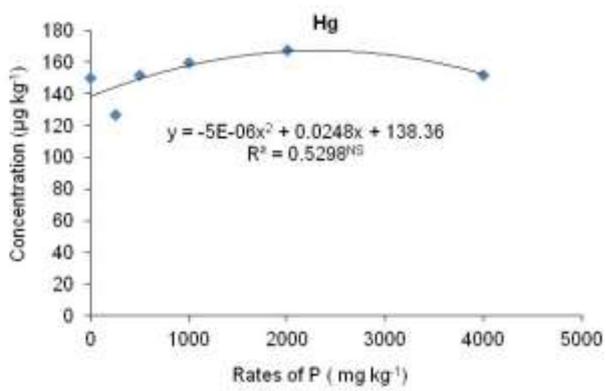


FIGURE 1 – Dry Matter of lettuce in function of rates of phosphorus



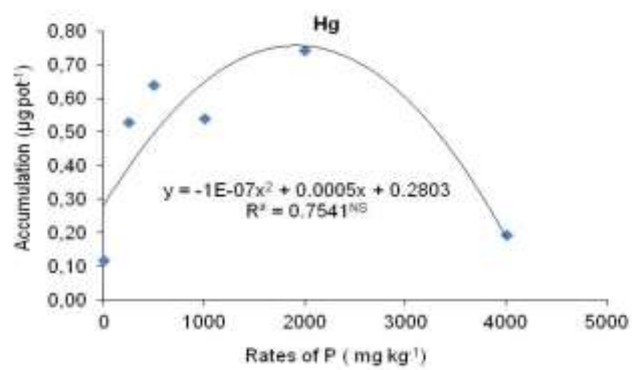


FIGURE 2 – Mercury concentration and accumulation in lettuce

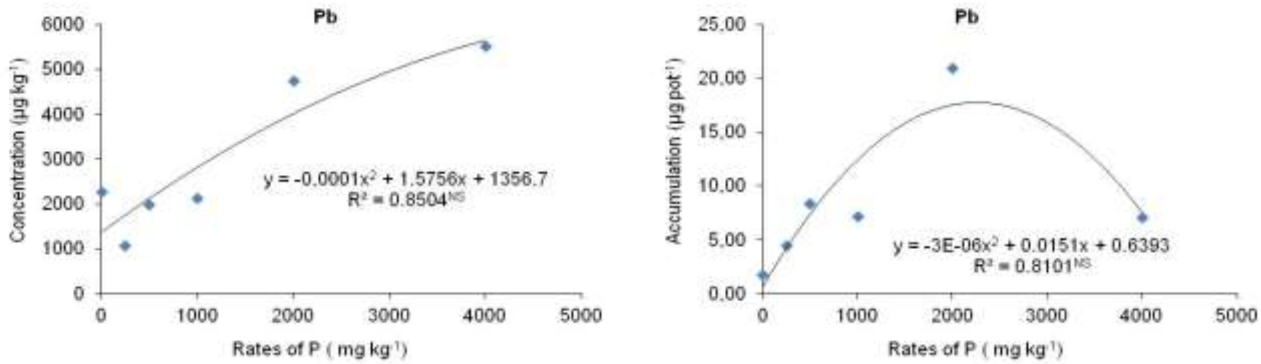


FIGURE 3 – Lead concentration and accumulation in lettuce

TABLE 1 - Chemical characteristics of soil used in the experiment

Characteristics	Solo
pH ($CaCl_2$)	7.06
Organic Matter (g dm^{-3})	28
Phosphorus (mg dm^{-3})	75
Potassium ($mmol_c$ dm^{-3})	7.0
Calcium ($mmol_c$ dm^{-3})	400
Magnesium ($mmol_c$ dm^{-3})	92.0
H + Al ($mmol_c$ dm^{-3})	9.0
Sum of bases ($mmol_c$ dm^{-3})	499
CTC ($mmol_c$ dm^{-3})	508
V (%)	98
Mercury $_{total}$ (µg kg^{-1})	204±52
Lead $_{total}$ (µg kg^{-1})	891±151
Sand (g kg^{-1})	650
Silt (g kg^{-1})	80
Clay (g kg^{-1})	270
Texture	medium clay

Table 2. Hg and Pb Concentrations obtained for Mixed Polish Herbs

Element	Obtained	Certified*
Hg (µg kg^{-1})	19.7 ± 1.4	17.6 ± 1.6
Pb (mg kg^{-1})	2.44 ± 0.22	2.16 ± 0.23

*Certified values with uncertainties reported by the producer

CONCLUSIONS

The Hg concentration in shoots of lettuce decreased with the application of 250 mg kg^{-1} of P and Pb with the application of 250 to 1000 mg kg^{-1} of P. The accumulation of Hg and Pb in shoots of lettuce increased as a function of P, demonstrating the inefficiency of application of P in the absorption of these elements.

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