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Comissão 3.5 - Poluição, remediação do solo e recuperação de áreas degradadas

TRANSFER OF CADMIUM AND BARIUM FROM SOIL TO CROPS GROWN IN TROPICAL SOILS[1]

Leônidas Carrijo Azevedo Melo[2], Evandro Barbosa da Silva[3] & Luís Reynaldo Ferracciú Alleoni[4]

SUMMARY

Phytotoxicity and transfer of potentially toxic elements, such as cadmium (Cd) or barium (Ba), depend on the availability of these elements in soils and on the plant species exposed to them. With this study, we aimed to evaluate the effect of Cd and Ba application rates on yields of pea (*Pisum sativum* L.), sorghum (*Sorghum bicolor* L.), soybean (*Glycine max* L.), and maize (*Zea mays* L.) grown under greenhouse conditions in an Oxisol and an Entisol with contrasting physical and chemical properties, and to correlate the amount taken up by plants with extractants commonly used in routine soil analysis, along with transfer coefficients (Bioconcentration Factor and Transfer Factor) in different parts of the plants. Plants were harvested at flowering stage and measured for yield and Cd or Ba concentrations in leaves, stems, and roots. The amount of Cd accumulated in the plants was satisfactorily evaluated by both DTPA and Mehlich-3 (M-3). Mehlich-3 did not relate to Ba accumulated in plants, suggesting it should not be used to predict Ba availability. The transfer coefficients were specific to soils and plants and are therefore not recommended for direct use in risk assessment models without taking soil properties and group of plants into account.

Index terms: soil pollution, transfer factor, bioconcentration factor.

RESUMO: *TRANSFERÊNCIA DE CÁDMIO E BÁRIO EM PLANTAS CULTIVADAS EM SOLOS TROPICAIS*

*Fitotoxicidade e transferência de elementos potencialmente tóxicos como o cádmio (Cd) ou bário (Ba) dependem da disponibilidade desses elementos nos solos e das espécies de plantas expostas a esses. Objetivaram-se, neste trabalho, avaliar o efeito de doses de Cd e Ba na produção de ervilha (*Pisum sativum L.*), sorgo (*Sorghum bicolor L.*), soja (*Glycine max L.*) e*

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*milho (*Zea mays *L.), cultivados em casa de vegetação num Latossolo Vermelho distrófico e num Neossolo Quartzarênico com atributos físicos e químicos contrastantes; e correlacionar a quantidade absorvida pelas plantas com extratores comumente utilizados na análise de solo, além dos coeficientes de transferência (fator de bioconcentração e fator de transferência) de diferentes partes das plantas. As plantas foram colhidas na fase de floração e medidas a produtividade e as concentrações de Cd ou Ba em folhas, caules e raízes. O Cd foi avaliado satisfatoriamente tanto pelo DTPA quanto pelo Mehlich-3 (M-3), em relação à quantidade de Cd acumulado nas plantas. O M-3 não se relacionou com Ba acumulado nas plantas, sugerindo que ele não deve ser usado para prever a disponibilidade de Ba. Os coeficientes de transferência foram específicos para solos e plantas e, portanto, não são recomendados para uso direto em modelos de avaliação de risco, sem considerar as características do solo e do grupo de plantas.*

Termos de indexação: poluição do solo, fator de transferência, fator de bioconcentração.

INTRODUCTION

Human activities have been increasing environmental pollution for decades. Soils and water are two natural resources severely affected by these activities. Areas contaminated with potentially toxic elements have steadily grown around the world, especially in developing countries (Li et al., 2009). In this context, research on phytotoxicity and the transfer of metals to soils and plants provides useful information on metal bioaccumulation in crops and helps define limits for contaminants in soils.

Cadmium (Cd) is of special concern among metals because it can be mobile in soils, toxic to plants and animals at very low concentrations (Das et al., 1997), and easily taken up by plants. These qualities are heightened in acidic soils because soil pH is indirectly correlated with Cd solubility and consequently with its availability for uptake (McBride et al., 1997). Plants are thus the main entry route of Cd into the food chain. The most common symptoms of Cd toxicity are stunted growth, wilting, and leaf chlorosis (Manciulea & Ramsey, 2006). A major problem of Cd as compared to other metal pollutants is that it may pose risks to human health at plant tissue concentrations below the phytotoxic level (Peijnenburg et al., 2000). Researchers have demonstrated its toxic effects on plants (Aery & Rana, 2003; Hasan et al., 2007). In a recent study, Guerra et al. (2012) found that Cd did not exceed the critical limit (1.0 mg kg^{-1}, fresh weight) for human consumption in a set of vegetables samples collected at a distribution center in the city of São Paulo, Brazil.

Barium (Ba), however, has been little studied in soils and plants, although Chaudhry et al. (1977), Llugany et al. (2000), Suwa et al. (2008) and Monteiro et al. (2011) report phytotoxicity when large amounts accumulate in plants. The chemical species of this element are highly influential on its availability in potentially "contaminated" soils, especially when the source of contamination is barite ($BaSO_4$), or there is sulfate present in the soils (Ippolito & Barbarick, 2006; Menzie et al., 2008). Barium guideline values have been defined by Brazilian environmental legislation (Conama, 2009), but more studies are needed under wet tropical conditions, especially regarding Ba availability in soils for plant uptake. The Brazilian government established the "prevention" values of 150 and 1.3 mg kg^{-1} for Ba and for Cd, respectively. These values were defined based on phytotoxicity, and environmental agencies monitor actions to identify sources of pollution when such values are exceeded, in order to prevent soils from becoming contaminated (Conama, 2009).

Total soil concentrations of metals are commonly used to evaluate soil quality standards, although their usefulness in predicting soil-to-plant transfer is often questioned since the bioavailability of metals in soils varies greatly due to physical and chemical soil properties (Wang et al., 2006). Single chemical extractants are frequently used to assess metal availability for plant uptake, and such procedures are commonly used in laboratories.

The bioconcentration factor (BCF) is an index that measures the relationship between metal concentrations in plants and in soils. It is widely used to calculate human exposure to metals through vegetable consumption (Swartjes, 2011) and also to evaluate phytoremediation efficiency by plants (Ghosh & Singh, 2005).

In this study, we aimed to evaluate the effect of the addition of Cd and Ba on the yield of four crops grown in two soils with contrasting physicochemical properties. The relationships of the amounts taken up and pseudo-total and available metal contents in the soils were also evaluated.

MATERIAL AND METHODS

Soil sampling, characterization, and acidity correction

Samples from the topsoil layer (0-0.2 m) of two soils [a Typic Quartzipsamment (Entisol) and a Typic Hapludox (Oxisol)] under native forest and with contrasting physical and chemical properties were collected in Piracicaba, São Paulo, Brazil (22º 42' S; 47º 38' W). Soil material was air-dried and sieved

(< 4mm) to remove thick roots. After homogenization, a sub-sample of each soil was taken and sieved (< 2 mm) for analysis. Soil pH was measured in 0.01 mol L^{-1} $CaCl_2$ solution (1:2.5, soil:solution ratio on a volume basis). C and N contents were determined in a CNS automatic analyzer, while the background concentrations of Cd and Ba were extracted using aqua regia ($HCl:HNO_3$, 3:1, v/v) (McGrath & Cunliffe, 1985) in powdered samples (< 0.15 mm) and then determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Soil physical fractionation (sand > 53 µm; 53 µm ≥ silt ≥ 2 µm; clay < 2 µm) was performed by using the densimeter method (Gee & Or, 2002). Oxide contents were extracted with a 9 mol L^{-1} sulfuric acid solution.

Soil acidity was corrected to raise base saturation to 50 %. Dolomitic lime (34 % CaO and 16 % MgO) was added to the Oxisol and Entisol at 14.8 and 3.5 g per pot, respectively. Soils were incubated in 4.0 dm^3 plastic pots for 30 days, and moisture maintained at ±70 % of maximum water retention capacity (MWRC). Each pot was filled with 4.0 dm^3 of Oxisol (bulk density = 0.95 kg dm^{-3}) or Entisol (bulk density = 1.25 kg dm^{-3}). After one month of incubation, pH (0.01 mol L^{-1} $CaCl_2$) reached and stabilized at 5.2±0.1 and 5.0±0.1 in the Oxisol and Entisol, respectively.

Experiments with crops

To evaluate the toxic effects and accumulation of metals in plants, 0.65, 1.3, 2.6, 5.2, and 10.4 mg kg^{-1} of Cd and 75, 150, 300, and 600 mg kg^{-1} of Ba were added separately to the soils by using nitrate salts. These concentrations represent 0.5, 1, 2, 4, and 8 times the prevention value of Cd and 0.5, 1, 2, and 4 times the prevention value of Ba in soils, according to the environmental legislation of the State of São Paulo. A control treatment (no metal added) was also included. After one week of incubation, a sub-sample of each pot was taken and air-dried for analysis.

The following levels of nutrients were added to the soils: P (200 mg kg^{-1} as $Ca(H_2PO_4)_2$), K (200 mg kg^{-1} as KCl), S (20 mg kg^{-1} as K_2SO_4), Mn (10 mg kg^{-1} as $MnSO_4.H_2O$), Zn (10 mg kg^{-1} as $ZnSO_4.7H_2O$), B (5 mg kg^{-1} as H_3BO_3), Cu (10 mg kg^{-1} as $CuSO_4.5H_2O$), and Mo (1 mg kg^{-1} as $(NH4)_6Mo_7O_{24}(4H_2O)$. After nutrient addition, the soil of each pot was homogenized and wetted to reach ± 70 % of MWRC. For all species, five seeds were sown in each pot and, after emergence, seedlings thinned to two plants per pot within five days. Subsequently, 50 mg kg^{-1} of N as NH_4NO_3 p.a. were added weekly in the first three weeks, discounting the NO_3^--N added with the metals in each treatment. From April to June 2008, pea (*Pisum sativum* L.) and sorghum (*Sorghum bicolor* L.) were grown until the flowering stage (53 and 68 days, respectively). Plants were harvested and separated into leaves, stem, and roots. After that, the four replicates of each treatment were mixed, homogenized, air-dried, and stored. In January 2009, the same soil material was again placed into pots for crop succession, which means the soil used to grow sorghum was used to grow soybean, while the soil used to grow pea was used to grow maize. Again, a sub-sample of each pot was collected for posterior analysis. The mean value of 0.01 mol L^{-1} $CaCl_2$ pH was 4.9±0.1 and 4.8±0.2 for the Oxisol and for the Entisol, respectively. Soils were wetted to reach ±70 % of the MWRC, and 150 mg kg^{-1} of N (applied as described for the 1st experiment), 200 mg kg^{-1} of P, 200 mg kg^{-1} of K, and 20 mg kg^{-1} of S were added. Soybean (*Glycine max* L.) and maize (*Zea mays* L.) were then grown until the flowering stage (45 and 55 days, respectively), at which point they were harvested and separated into leaves, stem, and roots.

Leaves and stems were rinsed in distilled water to remove possible contaminants. Roots were separated from the soil with a 2-mm sieve, washed thoroughly in a 1-mm sieve, and rinsed with distilled water. All plant material was oven dried (60 °C) until reaching constant weight. After dry weight (DW) was recorded, the plant material was ground (< 1 mm) in a Willey grinder and stored in plastic bags.

Analysis of soil and plant samples

Pseudo-total concentrations of Cd and Ba in soil samples were obtained through the aqua regia method (3:1 mixture of hydrochloric acid and nitric acid, respectively), as described in McGrath & Cunliffe (1985). The soil digests were filtered and diluted to 50 mL with ultrapure filtered water. Contents of available Cd and Ba were determined after extraction with DTPA (diethylenetriamine pentaacetic acid). Briefly, 20 g of soil were shaken for 2 h with 40 mL of a solution containing 0.005 mol L^{-1} DTPA, 0.01 mol L^{-1} $CaCl_2$, and 0.1 mol L^{-1} TEA (triethanolamine) buffered at pH 7.3 (Lindsay & Norvell, 1978). In addition, 2.5 g of soil were shaken for 10 min with 25 mL of Mehlich-3 solution (M-3): 0.2 mol L^{-1} CH_3COOH + 0.25 mol L^{-1} NH_4NO_3 + 0.013 mol L^{-1} HNO_3 + 0.015 mol L^{-1} NH_4F + 0.001 mol L^{-1} EDTA (Mehlich, 1984). In both cases, the extracts were filtered. These extractants were used for testing because the procedures are simple and commonly used (in the case of DTPA) to evaluate micronutrients and contaminants in soils of the State of São Paulo. All filter papers used for analysis were quantitative, with pore size of 3 µm (Nalgon®, REF: 3552).

Samples of pea and sorghum (1st experiment) were digested on a block by using nitric-perchloric acid. In 65 mL digestion tubes, 0.5 g of plant material was weighed, 8 mL of HNO_3 was added, and the mixture was left overnight. On the block the temperature was increased slowly to 120 °C. After a volume reduction to ±4 mL and cooling, 1 mL of $HClO_4$ was added, and the temperature increased to 180 °C until acid evaporation to ±1 mL. The final volume was then brought to 25 mL with deionized water. Samples of soybean and maize (2nd experiment) were digested by using a microwave oven following Araujo et al. (2002). Briefly, 0.25 g of plant sample was weighed and placed in vessels, and 2 mL of H_2O_2 were added and left to react for 1 h. After that, 2 mL of HNO_3 were added and left to react another hour, followed by the addition of 5 mL of deionized water. Then the vessels were closed and placed in the microwave oven. In soil and plant extracts, Cd concentrations were determined by flame atomic adsorption spectrometry (FAAS), and when the concentration was below the detection limit, a graphite furnace (GF-AAS) was used. Barium was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Quality analysis control

In all digestion procedures, blank reagents and a certified sample of Montana Soil II (NIST-SRM 2711) or Tomato Leaves (NIST - SRM 1573a) were included with each 20 samples. In addition, all glassware was cleaned in an acidic solution and rinsed in deionized water prior to use. Mean percentages for recovery of Cd and Ba in the reference soil material, using the aqua regia extraction, were 96 and 29 %, respectively. These recovery levels are in accordance with the leachable concentrations using EPA 3050B or similar methods according to the National Institute of Standards and Technology - NIST.

Bioconcentration factor and transfer factor

To compare the accumulation and transfer of metals in the different plant parts and soils, two indices were calculated according to the procedure described by Li et al. (2009). The bioconcentration factor (BCF) and the transfer factor (TF) were calculated according to equations 1 and 2:

$$BCF = [\text{M stem or M leaves or M root}]/[\text{M soil}] \quad (1)$$

$$TF = [\text{M shoot}]/[\text{M root}] \quad (2)$$

where [M shoot] is the metal concentration in the above ground portion of the plant (stem and leaf tissues), [M soil] is the metal concentration in the soil (determined by aqua regia method), and [M root] is the metal concentration in roots. All concentrations were expressed on a dry weight basis, unless stated otherwise.

The metal quantity in each plant part was obtained by the metal concentration multiplied by dry matter yield. Therefore, metal accumulation in the plant was calculated as the sum of metal quantities in root, stem, and leaves.

Data analysis

The experimental design consisted of randomized blocks, with four replicates. The concentrations of metals (obtained by different extractors) were considered the factor of study. Therefore, each plant species grown in each soil was evaluated separately. Analysis of variance (one-way ANOVA) was performed to verify the effect of Cd or Ba concentrations (extracted by aqua regia) on dry matter yield for each soil and crop. Regression analyses were performed to assess the relationship between the amount of metals extracted by aqua regia and the other extraction procedures (M-3 and DTPA), and the relationship between the concentration of metals in plant parts and the pseudo-total soil Cd or Ba concentration (aqua regia extraction) or the amount of available Cd or Ba by DTPA or M-3 extraction.

RESULTS AND DISCUSSION

Relationships among extractants for pseudo-total and available Cd and Ba contents

Both soils were acidic under natural conditions, but differed in other properties (Table 1). The higher total C, clay, and Fe and Al oxide contents yielded a higher cation exchange capacity (CEC) in the Oxisol than in the Entisol. Both soils exhibited naturally low levels of Cd and Ba. Thus, the primary source of soil pollution was the additional application of Cd or Ba. Data on these soils characteristics are published elsewhere (Melo et al., 2011).

Table 1. Soil properties under natural conditions and soil pH after liming

Property	Oxisol	Entisol
pH 0.01 mol L^{-1} $CaCl_2$	3.5±0.1(1)	3.6±0.1
pH 0.01 mol L^{-1} $CaCl_2$(2)	5.2±0.1	5.0±0.1
pH 0.01 mol L^{-1} $CaCl_2$(3)	4.9±0.1	4.8±0.2
Total C (g kg^{-1})	32±1.0	8.0±0.4
Total N (g kg^{-1})	2.9±0.07	0.7±0.01
Sand (g kg^{-1})	260	811
Silt (g kg^{-1})	108	129
Clay (g kg^{-1})	632	60
Fe_2O_3 (g kg^{-1})	76	5
Al_2O_3 (g kg^{-1})	211	26
WRC at 0 MPa (%)(4)	60	46
WRC at 0.01 MPa (%)	31	9
CEC ($mmol_c$ kg^{-1})(5)	188±11	41±1.0
Ca ($mmol_c$ kg^{-1})	9.0±0.4	5.3±0.6
Mg ($mmol_c$ kg^{-1})	4.9±0.1	1.0±0.1
K ($mmol_c$ kg^{-1})	1.8±0.03	0.4±0.0
Pseudo-total Cd (mg kg^{-1})	0.30±0.02	0.01±0.01
Pseudo-total Ba (mg kg^{-1})	32±3.6	3.5±0.4

(1) Mean (n = 3) ± standard deviation; (2) Soil pH after lime addition and incubation; (3) Soil pH in the second crop; (4) WRC: Water Retention Capacity; (5) CEC: Cation Exchange Capacity was calculated as the sum of cations (Ca^{2+}, Mg^{2+}, K^+ - extracted by a ionic resin) plus H+Al, estimated at pH 7.5 with 1.78 mol L^{-1} SMP solution. Source: Adapted from Melo et al. (2011).

There was a significant ($p<0.05$) linear regression for Cd between the aqua regia extraction and the M-3 and DTPA extractions for both soils (Figure 1a,c). Cadmium availability, as measured by M-3 and DTPA, was slightly higher in the sandy Entisol (low sorption capacity) than in the clayey Oxisol. The M-3 procedure extracted more Cd than DTPA, as illustrated by the slope of the regressions. The variation in soil properties was narrow, though the relationship found in this study was high. Therefore, extrapolation of these results to a wider range of soil properties is not recommended.

Menzies et al. (2007) found weak relationships (always $R^2 \leq 0.50$) of phytoavailability in a range of monocotyledons for five trace metals, including Cd. Menzies et al. (2007) argued that this lack of relationship may have been due to differences in soil organic matter content, soil pH, the amount, source, and form of the metal contaminant, and also the "age" of the contaminant. In this study, the relatively high proportion between pseudo-total and available Cd can be explained by the absence of an aging process. Although the specific adsorption may be the predominant mechanism of Cd retention in soils (Moreira & Alleoni, 2010), the short time of contact with the soil, as well as the soil acidity (pH around 5.0) may have contributed to the high availability of Cd in this study. Therefore, the availability of metals would be expected to be lower under field conditions with other sources of soil contamination.

The high Cd availability found in this study also explains the slight difference in the amount extracted by DTPA and by M-3. Usually, this difference is higher, due to the different extraction mechanisms between DTPA (complexing reagent) and M-3 (acid extractant + complexing reagent), as reported by Sims et al. (1991). Those authors found that DTPA was able to remove approximately 11 % of the total soil metal for Cd, Zn, and Ni, while Mehlich solutions (M-1 and M-3) extracted up to 32 % of the total soil metal content.

An exponential relationship was observed between Ba contents extracted by aqua regia and by M-3 in the Oxisol. No significant relationship, however, was found for these extractants in the Entisol (Figure 1b). DTPA exhibited a linear regression with aqua regia in the Oxisol, but extracted only about 3 % of the pseudo-total contents of Ba (Figure 1d). Conversely, DTPA had a weak exponential regression with aqua regia extraction for Ba in the Entisol, especially when pseudo-total Ba concentration increased.

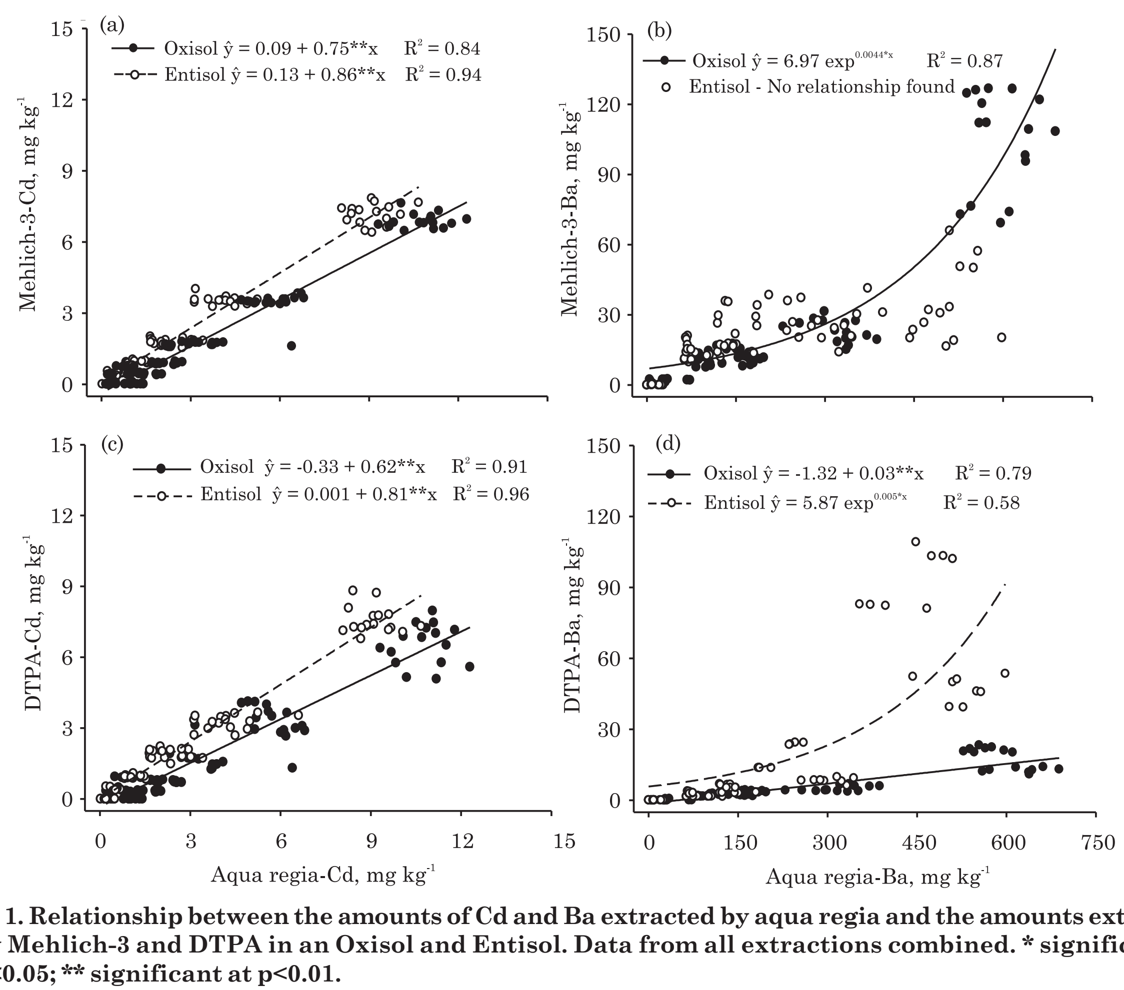

Figure 1. Relationship between the amounts of Cd and Ba extracted by aqua regia and the amounts extracted by Mehlich-3 and DTPA in an Oxisol and Entisol. Data from all extractions combined. * significant at $p<0.05$; ** significant at $p<0.01$.

One reason for the low or absent relationship found for Ba and these extractants (especially in the Entisol) may be due to a precipitation reaction between Ba and sulfate [extractable by 0.01 mol L^{-1} $Ca(H_2PO_4)_2$] since it declined linearly in both soils as the Ba concentration increased (Figure 2). In fact, few researchers have studied available Ba as measured by similar extractants. Ippolito & Barbarick (2006) observed a reduction in Ba availability as measured by DTPA combined with ammonium bicarbonate (AB-DTPA) in biosolid-amended soils, despite the increase in total soil Ba. Ippolito & Barbarick (2006) found that Ba was precipitated with S, possibly as $BaSO_4$. The much higher Ba sorption capacity of the Oxisol as compared to the Entisol caused a reduction in the Ba availability extracted by DTPA (Figure 1d). Soil retention of Ba is controlled by electrostatic forces, specific adsorption onto metal oxides, solid precipitates and, to a limited extent, by soil organic matter (Kresse et al., 2000).

Phytotoxicity and crop yield

Visual symptoms of toxicity (chlorosis) were observed in soybean plants at the two highest concentrations of Cd (5.2 and 10.4 mg kg^{-1}) in both soils studied. Plants also exhibited necrosis at the highest concentration of Cd. Soybean dry matter yield in both soils showed a linear decrease with increasing Cd concentrations and, in the Oxisol, it was up to 90 % lower at the highest concentration than in the control (Figure 3a,b). In contrast, dry matter yield in maize showed a quadratic trend in both soils with increasing soil Cd concentrations, though the relationship in the Entisol was low (R^2 = 0.55) (Figure 3a,b). The apparent increase in dry matter of maize and soybean (Oxisol - 0.65 mg kg^{-1}) under low Cd concentrations can be attributed to a kind of stimulatory effect. Several reasons have been proposed to explain this phenomenon, including an increase in stomatal opening (and, consequently, enhanced gas exchange); an increase in amino acid metabolism and enhanced concentrations of lignin or derived compounds; and increased root biomass production (Costa & Morel, 1994). Other authors have also reported an increase in dry matter production under low Cd concentrations in lettuce (Costa & Morel, 1994), sorghum (Pinto et al., 2004), and pea (Wani et al., 2008). Sorghum and pea were not affected by Cd in either soil (Figure 3a,b).

Barium treatments in the Oxisol only affected pea (Figure 3c), which suggests that that crop had the most sensitive response to the element. In the Entisol, however, all plants (except maize) were slightly affected and showed declining dry matter production with increased Ba concentration (Figure 2d). This result reflects the higher availability (lower sorption capacity) of Ba in this soil, such that plants cultivated in it are more exposed to the toxic effects of the metal. Visual symptoms of chlorosis were only observed in soybean and pea.

These differences in tolerance/sensitivity among plant species can be attributed to differences between C3 (soybean and pea) and C4 (maize and sorghum) photosynthetic systems. The abundance of phosphoenolpyruvate carboxylase (PEPC) in C4 plants alleviates the toxic effects of heavy metals, because it favors the production of oxaloacetic acid, which is then converted to acidic malate by the action of NAD-dependent malate dehydrogenase enzyme (NAD-MDH EC 1.1.1.37). This NAD-MDH enzyme acts as a detoxifying agent as it also catalyzes the formation of stable compounds of malate and metals (Srivastava et al., 2012).

Plant metal accumulation and transfer coefficients

The relationships of pseudo-total (extracted with aqua regia) or available (extracted with either DTPA or M-3) Cd or Ba contents in soils and their accumulation in plants are presented in figures 4 and 5, in order to evaluate the capacity of these solutions

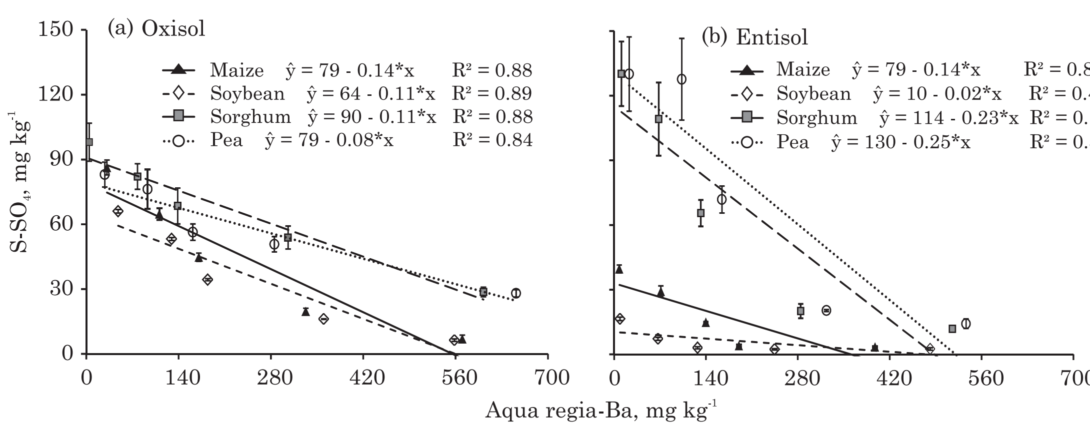

Figure 2. Effect of barium (Ba) concentration in the soil on sulfur (S) availability. Points are mean values (n = 4) and error bars are ± the standard deviation. Only significant (p<0.05) linear regressions are shown.

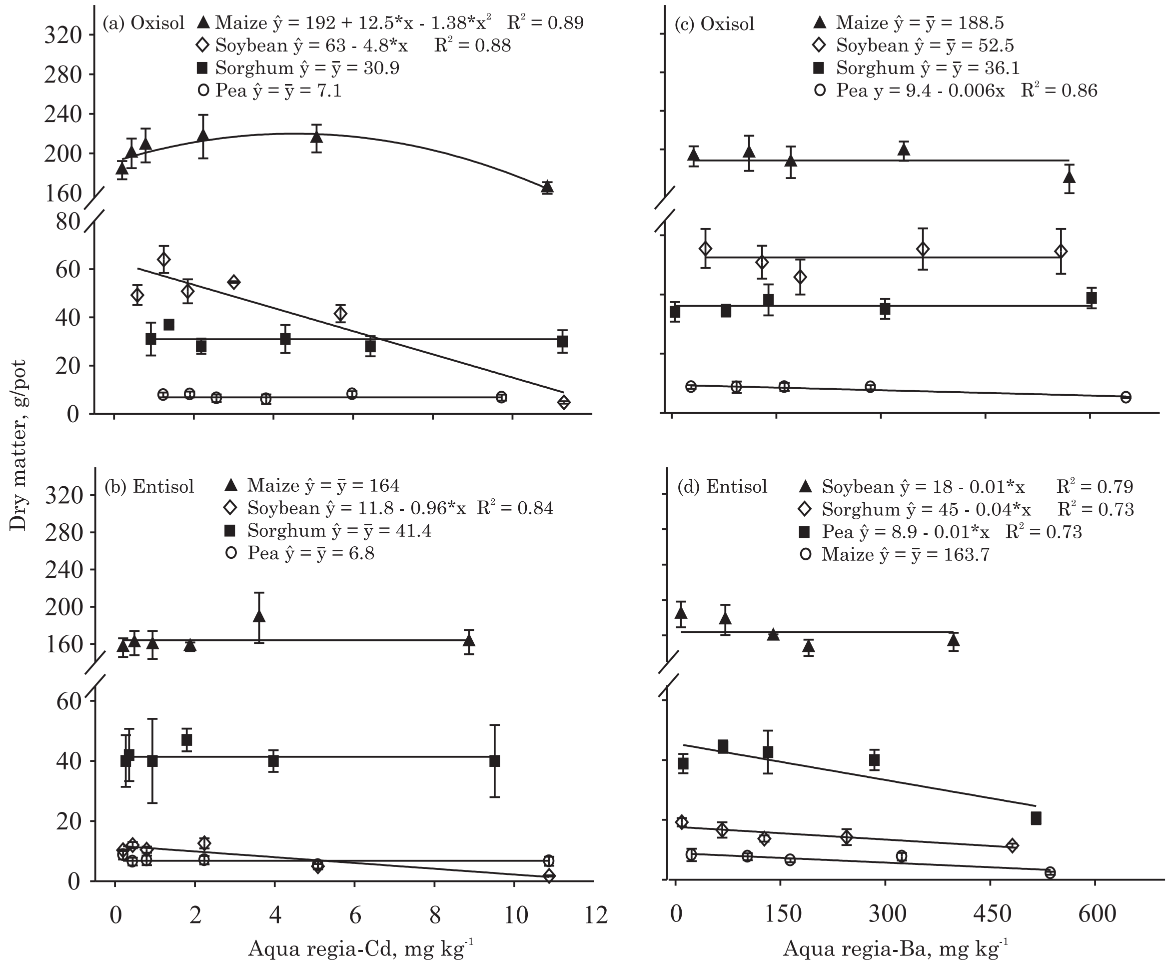

Figure 3. Effect of Cd and Ba concentrations in an Oxisol and Entisol on the dry matter yield of maize, soybean, sorghum, and pea. Points are mean values (n = 4) and error bars are ± the standard deviation. Only significant (p<0.05) regressions (linear or quadratic) are shown; for non-significant regressions, only the average is presented.

to extract contents of the elements well correlated to the contents of the metals in the plants. The pattern of Cd accumulation was plant species-specific and also dependent on soil type (Figure 4). Most relationships between Cd or Ba accumulation in plants and available or pseudo-total soil concentrations were high ($R^2 > 0.95$). Pea showed a linear relationship with available Cd (regardless of whether it was extracted by DTPA or M-3) and pseudo-total Cd (extracted with aqua regia) in soils. In many cases, for the other species, Cd accumulation reached a maximum accumulation, as observed by the quadratic regressions.

Sorghum had a linear correlation with either available (DTPA extraction) or pseudo-total Cd (aqua regia extraction) in the Oxisol (Figure 4a,c). In contrast, maize had a linear correlation with available Cd (DTPA or M-3 extraction) in the Entisol (Figure 4d,e). Cadmium accumulation was about twice as high in the Entisol (Figure 4d,e,f) as in the Oxisol (Figure 4a,b,c). In the case of Ba, all regressions in the Oxisol had a linear trend (Figure 5a,b,c). The regression was either linear or quadratic in the Entisol, depending on the plant or the extractor (Figure 5d,e,f). The M-3 extraction for Ba showed no relationship with maize and soybean (Figure 5e). Merlino (2013) also did not observe correlation between Ba extracted by Mehlich-3 and dry matter production for sorghum, regardless of the source of Ba ($BaCl_2$ or $BaSO_4$) contamination in an Oxisol (Latossolo Vermelho).

Sukkariyah et al. (2005) noted that quadratic responses can be related to both soil and plant variables. For example, exclusion of trace metals by plant mechanisms limits transport from root to shoot, and saturation of the carrier system may also contribute to decreasing the uptake of metal loadings. In this study, a reduction in Cd accumulation was observed in soybean at the highest soil concentrations and was related to the great reduction in dry matter in the species.

The Bioconcentration factor (BCF) indicates the ability of a plant to take up a metal from the soil (Li et al., 2009). Non-hyperaccumulator species (such as those of the present study) have a BCF lower than 1, as found for Cd by Ghosh & Singh (2005), which means the contents of Cd in the plants are lower than in the respective soil contents. For Cd, BCF values were greater than 1.0 in almost all crops and plant parts (leaves, stems, and roots), and in both soils (Table 2), indicating that this metal is easily taken up by plants. As expected, in all plants and soils, BCF in roots was higher than in leaves or stems (except for sorghum in the Oxisol), and was also higher in the Entisol than in the Oxisol.

The BCF in leaves was higher than the BCF in stems for maize and soybean in both soils. Conversely, BCF in stems was higher than in leaves for sorghum and pea, except for pea in the Oxisol, which had the same BCF value. In the case of Ba, in general, the following trend was observed: BCF in roots > BCF in stems > BCF in leaves. In addition, most BCF values were less than 1.0, especially in the Oxisol, indicating a more limited soil-to-plant transfer of this metal compared to Cd. In the case of TF, both Cd and Ba values were less than 1.0, with the exception of the TF of Cd for sorghum in the Oxisol. These results suggest that roots may regulate the transport of Cd to shoots.

Perriguey et al. (2008) suggested that a "floodgate" in the root/stem junction regulates Cd transfer from

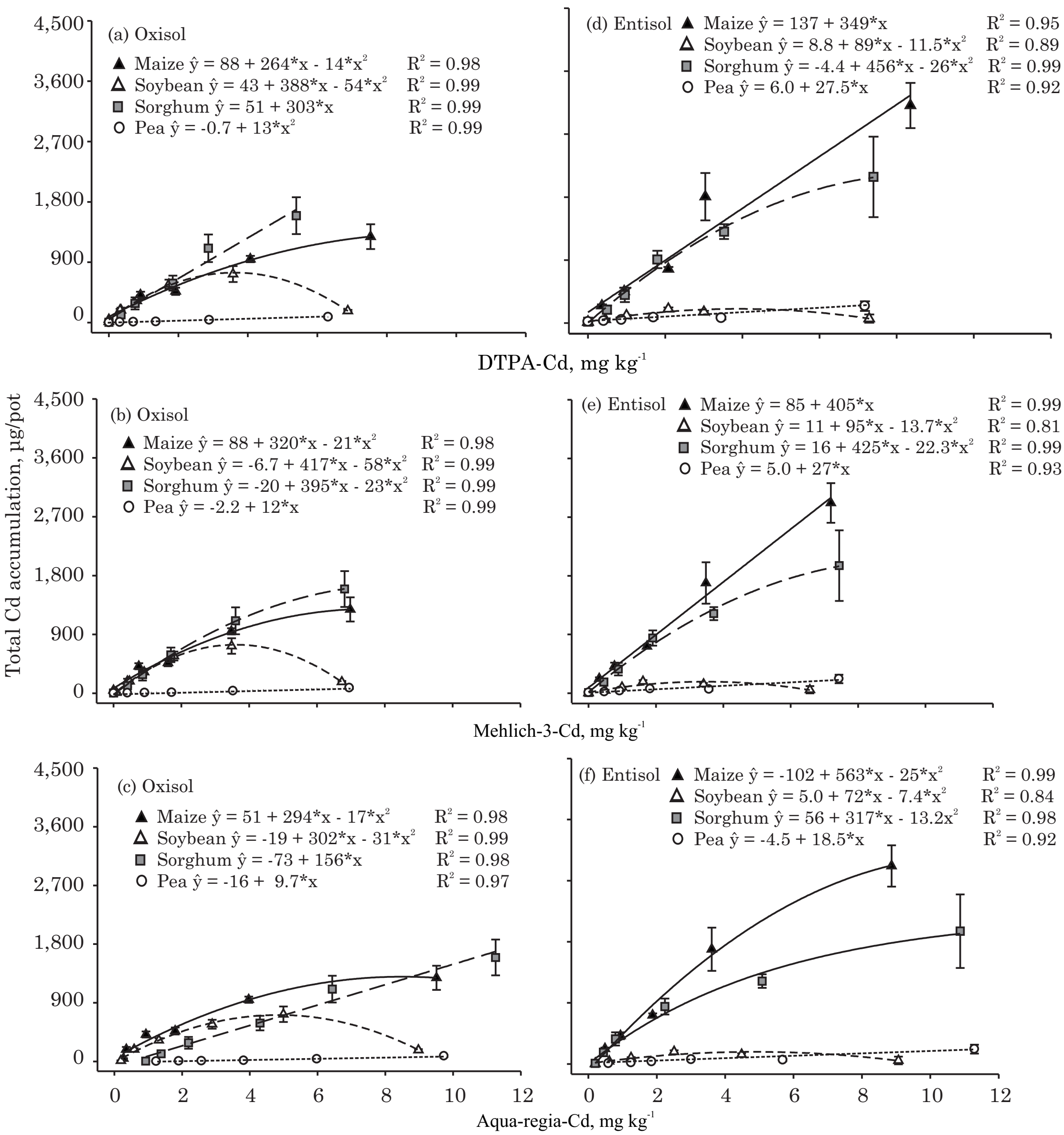

Figure 4. Relationships between Cd in an Oxisol as extracted by DTPA (a), Mehlich-3 (b), and Aqua regia (c) and in an Entisol by the same extractants (d, e, and f) and total Cd accumulation in four cultivated plant species. Points are mean values (n = 4) and error bars are ± the standard deviation. The Cd accumulation in each plant part was obtained by the concentration of Cd multiplied by dry matter yield.

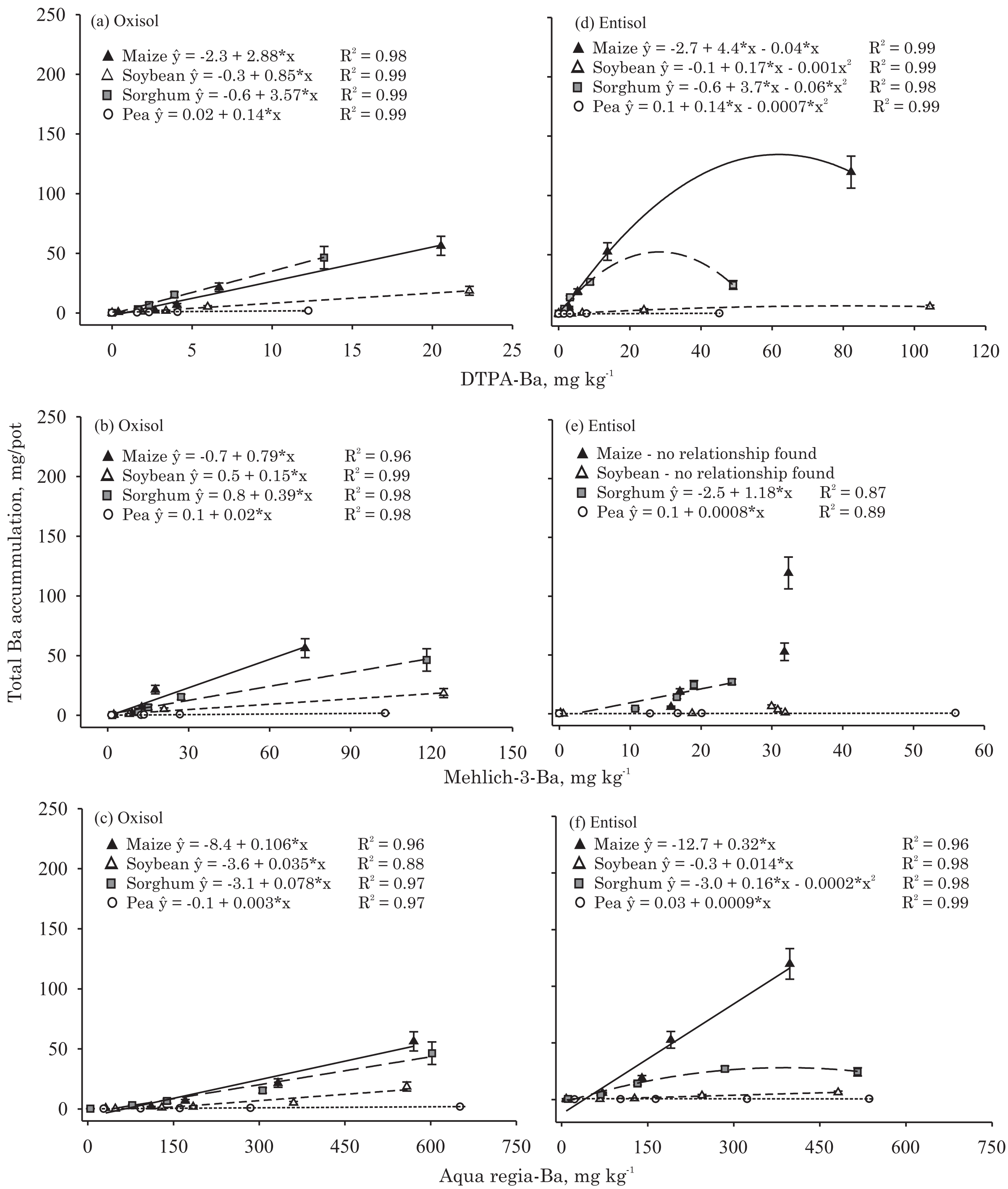

Figure 5. Relationships between Aqua regia-Ba in an Oxisol as extracted by DTPA (a), Mehlich-3 (b), and Aqua regia (c) and in an Entisol by the same extractants (d, e, and f) and total Ba accumulation in four cultivated plant species. Points are mean values (n = 4) and error bars are ± the standard deviation. The Cd accumulation in each plant part was obtained by the concentration of Cd multiplied by dry matter yield.

roots to shoots. Also, our results showed that BCF varied greatly and was strongly specific, depending on plant type, plant part, and soil type. Li et al. (2009) cultivated maize combined with several intercrops and found BCF values in shoots (stems + leaves) ranging from 0.4 to 2.1, and TF values ranging from 0.04 to 0.74, which reinforce that this index is very site/system-specific.

Table 2. Bioconcentration factors (BCF) and transfer factors (TF) of cadmium (Cd) and barium (Ba) in crops grown in two soils contaminated with these elements

Soil	BCF_{Leaf}	BCF_{Stem}	BCF_{root}	TF
		Cd treatment		
		Maize		
Oxisol	1.04	0.78	9.59	0.15
Entisol	2.26	1.23	7.46	0.23
		Soybean		
Oxisol	3.47	1.72	4.24	0.94
Entisol	5.09	4.44	5.63	0.94
		Sorghum		
Oxisol	3.28	4.72	2.70	1.50
Entisol	3.95	9.65	13.43	0.58
		Pea		
Oxisol	0.37	0.37	2.37	0.20
Entisol	0.48	5.17	14.12	0.59
		Ba treatment		
		Maize		
Oxisol	0.32	0.22	0.45	0.73
Entisol	0.88	1.08	2.64	0.43
		Soybean		
Oxisol	0.20	0.31	0.39	0.64
Entisol	0.42	0.77	1.74	0.57
		Sorghum		
Oxisol	0.94	1.41	2.74	0.51
Entisol	1.38	1.26	4.46	0.61
		Pea		
Oxisol	0.21	0.24	0.67	0.38
Entisol	0.23	0.09	0.59	0.45

BCF: metal concentration in the plant/metal concentration in the soil; TF: metal concentration in the shoots/metal concentration in the roots.

CONCLUSIONS

1. DTPA and Mehlich-3 are able to evaluate available Cd in soils. For Ba, DTPA is more able than Mehlich-3 to evaluate availability.

2. The bioconcentration factor is higher in roots than in shoots for both Cd and Ba.

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