Photosynthetic parameters and growth of rice, lettuce, sunflower and tomato in an Entisol as affected by soil acidity and bioaccumulation of Ba, Cd, Cu, Ni and Zn

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Abstract

The bioaccumulation of trace elements (TEs) in crops consumed by humans can lead to a lower food production due to photosynthetic damages and several diseases in humans, but decreasing soil acidity could mitigate these problems by decreasing TEs bioavailability. Thus, we evaluate the effect of increasing soil base saturation (BS%) on photosynthesis, growth and bioaccumulation of barium (Ba), cadmium (Cd), copper (Cu), nickel (Ni) or zinc (Zn) in lettuce (*Lactuca sativa* L.), rice (*Oryza sativa* L.), sunflower (*Helianthus annuus* L.) and tomato (*Solanum lycopersicum* L.) grown in sandy Entisol. The crops were grown in uncontaminated or contaminated Entisol, under two BS% ratios: 30% for all crops or 50% for rice and 70% for lettuce, sunflower and tomato. The photosynthesis-related parameters varied depending on the metal and crop, but in general, increasing BS% did not attenuate photosynthetic damages induced by Ba, Cd, Cu, Ni and Zn in the crops. There was no strong correlation between the photosynthetic parameters measured and biomass production, which suggest us that the suppression on biomass induced by Ba, Cd, Cu, Ni or Zn is related to other metabolic disorders besides the impairment on CO₂ assimilation or chlorophyll synthesis in the crops assayed, with exception of Ni and Zn in lettuce. In conclusion, increasing BS% was not consistent in decreasing Ba, Cd, Cu, Ni and Zn accumulation in the edible parts of lettuce, rice, sunflower and tomato grown in the sandy soil, which probably is related to the low capacity of this soil in control TEs bioavailability.

Introduction

Trace elements (TEs) are minor components of the solid soil phase, but they play an important role in soil fertility, soil contamination and food production (Gupta et al. 2019). Although soil composition is diverse, elements such as barium (Ba), cadmium (Cd), copper (Cu), nickel (Ni) and zinc (Zn) are commonly present in low concentrations (Kabata-Pendias 2011). In the State of São Paulo - Brazil, concentrations of 54.1, 0.1, 24.2, 36.0 and 21.8 mg kg⁻¹ have been reported for Ba, Cd, Cu, Ni and Zn, respectively, in unpolluted soils (Cardoso-Silva et al. 2016; Nogueira et al. 2018). However, the increasing soil contamination with these elements through anthropogenic activities, like mining, have become a global issue and environmental threat because these TEs can be accumulated in plant tissues and enter into food chain (Jolly et al. 2013).

Crops such as lettuce (*Lactuca sativa* L.), rice (*Oryza sativa* L.), sunflower (*Helianthus annuus* L.) and tomato (*Solanum lycopersicum* L.) are between the most consumed food in the world, and these crops can accumulate TEs in their edible parts in concentrations enough to cause clinical problems to humans (Piotto et al. 2018; Gupta et al. 2019; Lavres et al. 2011, 2019). Nervous, cardiovascular, renal, and neurological impairment as well as bone diseases caused by TEs have been reported in humans (Tchounwou et al. 2012; Petrosino et al. 2018). In this sense, the employment of strategies that mitigate TEs uptake by crops is quite important to decrease their intake.

Plants can take up only bioavailable TEs from the soil, and this process depends on uptake mechanisms, physicochemical properties of the soil and chemical speciation of the metals and metalloids in the soils (Gupta et al. 2019). Thus, agricultural practices that influence TEs' bioavailability often have an impact on their accumulation in plants. Lime is often used to correct soil acidity and allow an adequate crops' development (Raij et al. 1996). Higher pH tends to increase sorption and decrease the bioavailability and mobility of most TEs in tropical soils (Rieuwerts 2007). Macedo et al. (2020) evaluated the effect of two base saturation (BS ratios of 50 and 70%) on sunflower and soybean growth in an Alfisol and observed that Ni bioavailability was lower and the biomass production was higher at soil base saturation of 70% compared to 50%. Although TEs such as Cu, Ni and Zn are essential (micronutrients) at low concentrations for plant growth (Hänsch and Mendel 2009), they also can cause toxic effects on plant growth at high concentrations, as well as Ba and Cd that are non-essential for plants.

Physiological effects of TEs toxicity in plants include reductions on biomass, changes on photosynthetic efficiency and transpiration (Gupta et al. 2019). Changes on chlorophyll synthesis and starch accumulation have been reported also in plants exposed to many TEs (Moya et al. 1993; Piotto et al. 2018; Lavres et al. 2019). In this sense, a lower TEs uptake and translocation is desirable to avoid photosynthetic damages and to decrease TEs intake by humans.

The differences observed in TEs' accumulation among crops depends on the TEs' bioavailability, efficiency of a plant species in accumulating TEs into its tissues from the soil, TEs' translocation from roots to shoot and further from leaves and stems to fruits or grains (Antoniadis et al. 2017). Li et al. (2019) measured, through bioconcentration factor (BCF) and translocation factor (TF), Cd transfer from soils to rice plants in China, and reported that Cd translocation to the grains of rice plants grown in soils that presented higher pH values (which correspond to higher base saturation) was lower. According to Li et al. (2019), soil properties were highly relevant for Cd accumulation in rice plants.

Increasing soil base saturation through liming is an important strategy to decrease TEs bioavailability in soils presenting low organic carbon (OC) and clay contents, and low cationic exchange capacity (CEC), such as sandy soils (Rieuwerts 2007). To the best of our

knowledge there is no available information on TEs transfer from soil to edible parts of crops grow in Entisols. Thus, our aims with this study were to evaluate: i) the effect of base saturation on changes induced by TEs on chlorophyll concentration, leaf CO₂ assimilation, stomatal conductance, intracellular CO₂ concentration and transpiration, and growth of lettuce, rice, sunflower and tomato grown in Ba, Cd, Cu, Ni or Zn-contaminated Entisol; and ii) the uptake and root-to-shoot translocation of Ba, Cd, Cu, Ni and Zn and in the crops.

Material And Methods

Soil characterization

The soil (Typic Quartzipsamment) used in this study was collected from the upper layer (0.0-0.2 m depth), apart from litter, in São Pedro, state of São Paulo, Brazil (22°32' S; 47°54' W). Soil characteristics were determined on air-dried soil sieved with a 2-mm mesh (Table 1), following the procedures described by Nelson and Sommer (1982) to determine OC content, after digestion with K₂Cr₂O₇ and H₂SO₄. Exchangeable aluminum (Al³⁺) was extracted with 1 mol L⁻¹ KCl and determined by titration with 0.025 mol L⁻¹ NaOH (Raij et al. 2001). The pH was determined firstly in 0.01 mol L⁻¹ CaCl₂ and then in SMP solution to estimate the potential acidity (H+Al) (Raij et al. 2001). The available concentrations of Ca, Mg, K and P were extracted with ionic exchange resin (Raij et al. 1986).

From these results we calculated then the sum of bases (SB), total cationic exchange capacity (CEC₇), base saturation (BS%), and Al³⁺ saturation (m%) (EMBRAPA 1997). The pseudo-total Ba, Cd, Cu, Ni, and Zn concentrations were determined using the method 3051A (digestion in a closed microwave oven system with concentrated HNO₃ and HCl (3:1) proposed by United States Environmental Protection Agency - USEPA (USEPA 2007). Granulometric fractions (sand, silt and clay) were obtained by the hydrometer method (Gee and Bauder 2002).

Plant material and experimental design

To assay the effect of base saturation on plant growth and Ba, Cd, Cu, Ni and Zn uptake by crops ingested by humans, plants of lettuce (cv. Amanda), rice (cv. IAC-202), sunflower (cv. Aguará 4), and tomato (cv. Santa Clara VF 5600) were grown in greenhouse conditions in unpolluted (control treatment) or polluted Entisol, under two base saturation (30% for all crops or 50% for rice and 70% for lettuce, sunflower and tomato). The original base saturation of the Entisol (Table 1) was increased to 30% for all crops or to 50% for rice and 70% for lettuce, sunflower and tomato (optimum recommended to growth the crops assayed), following the recommendations for Brazil (Raij et al. 1996). The Entisol was polluted individually with Ba (120 mg kg⁻¹), Cd (1.3 mg kg⁻¹), Cu (60 mg kg⁻¹), Ni (30 mg kg⁻¹) or Zn (86 mg kg⁻¹ Zn). These concentrations correspond to the prevention levels established by The Environmental Agency of São Paulo State - CETESB, in Brazil (CETESB 2014). According to CETESB (2014), prevention level is the concentration of the substance (*e.g.*, TEs) above which harmful changes to soil and groundwater quality can occur. The pots used to grow the crops were distributed in completely randomized design with three replicates per condition.

Soil treatment, growth conditions, plant harvesting and sampling

After collection, drying and soil characterization, the base saturation of the Entisol was increased to the desirable values (30% for all crops or 50% for rice and 70% for lettuce, sunflower and tomato) by using MgCO₃ and CaCO₃. Then, 6 kg of soil for lettuce and rice and 10 kg of soil for sunflower and tomato were arranged in plastic pots that received deionized water until the soil reach 95% of their maximum water holding capacity.

The soil was incubated in this condition for 21 days, at maximum temperature of 31 °C. After this incubation period, Ba, Cd, Cu, Ni or Zn solutions were added in the following concentrations: 120 mg Ba kg⁻¹ [Ba(NO₃)₂], 1.3 mg Cd kg⁻¹ [Cd(NO₃)₂.4H₂O], 60 mg Cu kg⁻¹ [Cu(NO₃)₂.3H₂O], 30 mg Ni kg⁻¹ [Ni(NO₃)₂.6H₂O] and 86 mg Zn kg⁻¹ [Zn(NO₃)₂.6H₂O]. Variations on N supply were corrected by using NH₄NO₃, including the unpolluted Entisol (control treatment), and then, the soil was incubated again for seven days at 95% of their maximum water holding capacity.

After soil incubation, lettuce and tomato seedlings germinated in vermiculite were transferred to their pots at 29 and 34 days after sowing, respectively, whilst rice and sunflower were sown directly in the pots. One plant of sunflower and tomato was kept per pot after thinning, whilst three plants of lettuce and five plants of rice were kept per pot. Soil moisture content was maintained at a constant level (70% of the maximum water holding capacity) during the study, with deionized water.

The basic fertilization was performed applying 90 mg N kg⁻¹, 200 mg P kg⁻¹, 50 mg K kg⁻¹, 23.2 mg S kg⁻¹, 1 mg B kg⁻¹, 5 mg Cl kg⁻¹, 1 mg Cu kg⁻¹, 5 mg Mn kg⁻¹ and 3 mg Zn kg⁻¹ (Cu and Zn were not applied in the Cu and Zn-polluted soils), following the recommendations of Raij et

al. (1996). Fifteen days after lettuce, sunflower and tomato sowing, and 20 days after rice sowing, 50 mg K kg⁻¹ and 20.5 mg S kg⁻¹ were applied on the top. A new fertilization on the top with 50 mg N kg⁻¹ and 50 mg K kg⁻¹ was performed at 48 days after rice, sunflower and tomato sowing (Raij et al. 1996).

To control the caterpillar pest known as "cabbage looper" (*Trichoplusia ni*) that was found in the leaves of all crops during the study, 28.2 mL ha⁻¹ of thiamethoxam and 21.2 mL ha⁻¹ of lambda-cyhalothrin were applied after the first top fertilization. It was also necessary to control the powdery mildew (*Microsphaera diffusa*) in rice and sunflower plants, which was done through two applications of 250 g ha⁻¹ of carbendazim in their leaves (the first application occurred after the first top fertilization, and the second application was performed after the second top fertilization).

Plants of lettuce were harvested at 42 days after transplanting (end of vegetative phase), while rice was harvested at 98 days after sowing (phenological reproductive stage R8), sunflower was harvested at 82 days after sowing (phenological reproductive stage R9), and tomato was harvested at 68 days after transplanting (after the harvesting of mature fruits). Plants were harvested and separated into roots, shoot and fruits or grains (except for lettuce that was separated only into roots and shoot). The plant material collected was dried in a forced ventilation oven at 45 °C until reach constant weight to determine the biomass production. The soil collected at the end of the study was sieved (2-mm mesh) and dried in a forced ventilation oven at 45 °C to determine the pseudo-total Ba, Cd, Cu, Ni and Zn concentrations.

Determination of the pseudo-total Ba, Cd, Cu, Ni and Zn concentrations in the Entisol

Pseudo-total concentrations were determined in triplicate after a microwave-assisted (Model TC plus labstation, Milestone, Sorisole, Italy) according to the USEPA 3051A method (USEPA, 2007). Extracts were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7000 SERIES, Thermo Fisher Scientific, Waltham, USA). Blank reagent samples and standard reference material (SRM 2709a - San Joaquin soil) were used during digestion for quality control.

Determination of Ba, Cd, Cu, Ni and Zn concentrations and contents in the plant material

After drying in an oven at 45 °C until reach constant weight, the plant material was ground in a Wiley type mill (Model 4, Thomas Scientific, Swedesboro, USA) and digested in a microwave (Model TC plus labstation, Milestone) oven using a mixture of HNO₃ + H₂O₂, following the USEPA 3051A method (USEPA 2007) for TEs determination by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7000 SERIES, Thermo Fisher Scientific).

Blank reagent samples were used in the digestion for quality control. Standard reference material (SRM1515 - apple leaves) was also used to assure the accuracy and precision of the analytical methods. Then, from the TEs concentrations we calculated the TEs content by multiplying the TE concentration in the tissue (roots, shoot and grains or fruits) by the dry weight of the respective tissue. Subsequently, the TE content in each tissue was added, resulting in the total TE content (roots + shoot + grains or fruits).

Calculation of BCF and TF for Ba, Cd, Cu, Ni and Zn

The transfer of TEs in the crops tissues was evaluated by two indicators (Antoniadis et al. 2017): i) the bioconcentration factor (BCF), which indicates the efficiency of a plant species in accumulating a TE into its tissues from the soil (Eq. 1), and ii) the translocation factor (TF), which indicates the plant capacity to translocate TEs from roots to aboveground parts (Eq. 2):

$$BCF = [TE_{crop}] / [TE_{soil}] \quad (1)$$

where: [TE_{crop}] (mg kg⁻¹ DW) is the TE concentration in the roots, shoot and grains or fruits of the plants, and [TE_{soil}] (mg kg⁻¹ soil) is the pseudo-total TE concentration in the soil.

$$TF = [TE_{shoot}] / [TE_{roots}] \quad (2)$$

where: [TE_{shoot}] (mg kg⁻¹ DW) is the TE concentration in the shoot (stem + leaves + grains or fruits), and [TE_{roots}] (mg kg⁻¹ DW) is the TE concentration in the roots.

Determination of the photosynthetic parameters in the crops assayed

Leaf area was determined in a leaf area integrator model LI 3100 (Li-Cor Inc., Lincoln, USA) in the moment of the plant harvest. Chlorophyll concentration was measured during the vegetative phase (at 17 and 18 days after lettuce and tomato transplanting, respectively, and at 14 days after rice and sunflower emergence) by a Chlorophyll Meter SPAD-502 (Soil-Plant Analysis Dev., Section, Minolta Camera Co., Osaka,

Japan). Chlorophyll concentrations as well as the following photosynthetic parameters were measured in the first fully expanded leaf of lettuce and rice, and in the second pair of leaves from above to the top of sunflower and tomato.

Photosynthetic parameters [leaf CO₂ assimilation (*A*), stomatal conductance (*g_s*), intracellular CO₂ concentration (*C_i*) and transpiration (*E*)] were measured using infrared gas analyzer (Li-6400, Li-cor Inc.) before the plant harvest. The parameters were measured at air CO₂ concentration of 350 μmol mol⁻¹ with photosynthetic photon flux density of 1000 μmol m⁻² s⁻¹ for lettuce and rice and 2000 μmol m⁻² s⁻¹ for sunflower. All measurements were performed following the recommendations of Long and Bernacchi (2003). These photosynthetic measurements described (except for chlorophyll concentration) were not performed in tomato plants due to the beginning of the leaf senescence process in the moment of the plant harvest.

Statistical analyses

Both normality and homoscedasticity were checked. Then, all data were submitted to analysis of variance (F test) and post-hoc Tukey test ($P \leq 0.05$) through the Statistical Analysis System v. 9.2 (SAS Institute 2008). The graphs were constructed and plotted with SigmaPlot v. 10.0 (Systat Software Inc., San Jose, CA, USA). Results were expressed as mean ± standard error of the mean.

Results

Effect of base saturation on pseudo-total Ba, Cd, Cu, Ni and Zn concentrations in the Entisol

In general, there was no effect of soil base saturation on pseudo-total Ba, Cd, Cu, Ni and Zn concentrations in the polluted Entisol, with few exceptions (Fig. 1). The pseudo-total Ba concentration in the Entisol cultivated with lettuce was 20% lower at base saturation of 70% compared to 30% (Fig. 1A). The increase on base saturation resulted also in a reduction of 28% in the pseudo-total Cu concentration in the Entisol cultivated with rice (Fig. 1C). On the other hand, there was an increase of 13 and 14% on the pseudo-total Cd concentration in the Entisol cultivated with rice and sunflower, respectively, when the soil base saturation was augmented (Fig. 1B).

The same occurred for the pseudo-total Zn concentration that was 55 and 23% higher in the Entisol cultivated with rice and sunflower, respectively, at the highest soil base saturation (Fig. 1E). However, in general, Ba, Cd, Cu, Ni and Zn bioavailability decreased due to the increase on soil base saturation (results not shown). Details about the TEs bioavailability can be found in Pinto and Alleoni (2018).

Effect of soil base saturation and Ba, Cd, Cu, Ni and Zn exposure on biomass and photosynthesis

Lettuce plants had higher shoot biomass when grown at base saturation of 70%, regardless of TEs exposure (Fig. 2B). However, there was no effect of soil base saturation on root biomass, except for lettuce plants grown on Cu-polluted Entisol that presented higher root biomass at soil base saturation of 70% (Fig. 2C). Lettuce plants grown at base saturation of 30% were more susceptible to Cu, Ni and Zn toxicity, but the increase on soil base saturation to 70% decreased the toxicity Cu-induced compared to the other TEs (Figs. 2B-C).

There was a positive effect of increasing soil base saturation on rice grains' production only for plants exposed to Cd or Zn (Fig. 2D). Meanwhile, rice growth and grains' production were more compromised by the toxicity Cu-induced compared to the other TEs (Figs. 2D-F). In general, sunflower plants grown at soil base saturation of 70% presented higher grains production (Fig. 2G), shoot (Fig. 2H) and root biomass (Fig. 2I) compared to plants grown at base saturation of 30%. Sunflower was more susceptible to toxicity induced by Ni and Zn compared to the other TEs, especially when the plants were grown at the lowest base saturation (Figs. 2G-I).

There was no effect of base saturation on tomato fruits production, with exception for plants exposed to Ni that had higher fruits' production at base saturation of 70% (Fig. 2J). On the other hand, shoot and root biomass of tomato plants exposed to all TEs was higher at soil base saturation of 70% (Figs. 2K-L). Tomato plants were more susceptible to Ni-induced toxicity, followed by Cd, Cu and Zn, especially when grown at BS of 30% (Figs. 2J-L).

Besides to biomass decrease, TEs can induce several damages to photosynthesis-related parameters of plants. Lettuce was more susceptible to inhibition Cu-induced on leaf area and transpiration when grown at base saturation of 30% compared to 70% (Table 2). However, Cd, Ni and Zn exposure decreased much more chlorophyll concentration of lettuce compared to Cu, regardless of base saturation. The leaf CO₂ assimilation and stomatal conductance in lettuce was compromised specially by Ni and Zn, regardless of base saturation.

In general, there was no effect of base saturation on photosynthetic parameters measured in rice, as well as there was no great changes induced by the different TEs on leaf area, chlorophyll concentration, stomatal conductance, intracellular CO₂ concentration and transpiration of rice grown at base saturation of 50% (Table 2). Nevertheless, there was inhibition Ni-induced on leaf CO₂ assimilation of rice grown at base saturation of 50%. There was increase on chlorophyll concentration and transpiration induced by the higher soil base

saturation in sunflower exposed to Zn, which was also observed for leaf CO₂ assimilation, stomatal conductance, intracellular CO₂ concentration and transpiration of sunflower exposed to Ba. Despite the biomass of sunflower had been decreased by Ni and Zn (Figs. 2G-I), these TEs did not induce severe photosynthetic damages, which suggest us that Ni and Zn toxicity in sunflower is related with other processes. Chlorophyll concentration in tomato was not affected by base saturation or TEs exposure.

Effect of base saturation on uptake and transfer of Ba, Cd, Cu, Ni and Zn to edible parts of crops

The concentrations of the TEs in the edible parts of lettuce, rice, sunflower and tomato grown on unpolluted Entisol remained below of the maximum permitted levels by International Organizations, regardless of base saturation (data not shown). The Food and Agriculture Organization of the United Nations (FAO) for the World Health Organization (WHO) have established threshold values of 0.2 mg kg⁻¹ DW for Cd, 40 mg kg⁻¹ DW for Cu and 60 mg kg⁻¹ DW for Zn (FAO and WHO 2011). In the case of Ba and Ni, nor FAO and WHO have established threshold values, but the Environmental Protection Agency's Integrated Risk Information System (EPA-IRIS) has established 0.3 mg kg⁻¹ DW for Ba and Ni (EPA-IRIS 1987a,b). Thus, from this point, our focusing was directed to understand the effect of base saturation on uptake and translocation of Ba, Cd, Cu, Ni and Zn in the crops grown in the polluted Entisol (Figs. 3 and 4). Barium, Cd and Ni concentrations recorded in the edible parts of all crops grown on polluted Entisol exceeded the maximum permitted levels described (Figs. 3A-B, 3E-F and 3M-N). Only lettuce grown on Cu-polluted Entisol at base saturation of 30% exceeded the maximum permitted levels for Cu in its edible part (Figs. 3I-J). Zinc concentration in the edible parts of lettuce and sunflower grown on Zn-polluted Entisol also exceeded the maximum permitted levels for Zn (FAO and WHO 2011), regardless of base saturation (Figs. 3Q-R).

Although lettuce had presented shoot's Cu concentration below of the maximum permitted levels for Cu when grown in the Cu-polluted Entisol at base soil saturation of 70%, there was no significant effect of base saturation on Ba, Cd, Cu, Ni and Zn concentrations in its shoot or roots (Figs. 3A-C, 3E-G, 3I-K, 3M-O and 3Q-S). There was also no effect of base saturation on Ba, Cd, Cu and Ni concentrations in the grains, shoot or roots of rice plants (Figs. 3A-C, 3E-G, 3I-K and 3M-O). However, Zn concentrations in the grains and roots of rice were lower at base saturation of 50% compared to 30% (Figs. 3Q and 3S).

In general, sunflower tissues had higher Ba concentrations and lower Zn concentrations when this plant was grown at the highest base saturation (Figs. 3B-C and 3Q-R). There was no effect of soil base saturation on Cd, Cu and Ni concentrations in the grains, shoot or roots of sunflower plants (Figs. 3E-G, 3I-K and 3Q-S). Tomato plants grown at base saturation of 70% presented lower Ba and Zn concentrations in its roots (Figs. 3C and 3S). Meanwhile, there was no effect of soil base saturation on Cd, Cu and Ni concentrations in the fruits, shoot or roots of tomato (Figs. 3E-G, 3I-K and 3Q-S).

Sunflower plants presented higher Ba (Fig. 3A), Cd (Fig. 3E), Cu (Fig. 3I), Ni (Fig. 3M) and Zn (Fig. 3Q) concentrations in their grains compared to rice grains and tomato fruits, when the plants were grown at the highest base saturation. On the other hand, lettuce had higher Ni (Fig. 3N) and Zn (Fig. 3R) concentrations in its leaves compared to the other crops grown at the highest base saturation.

Higher TEs concentrations were found in the roots for all crops, followed by shoot and grains or fruits, respectively (Fig. 3). There was no effect of base saturation on Cd (Fig. 3H), Cu (Fig. 3L) and Ni (Fig. 3P) contents. However, sunflower and rice presented higher Ba content (Fig. 3D), whilst lettuce, sunflower and tomato presented higher Zn content (Fig. 3T) at the highest soil base saturation compared to 30%, which can be attributed to the higher biomass production at the highest soil base saturation. Taking the TEs contents (Figs. 3D, 3H, 3L, 3P and 3T) into account, the crops assayed absorbed TEs from the polluted Entisol in the following order: lettuce, Ba = Zn > Cu = Ni > Cd; rice, Zn > Ba > Ni > Cu > Cd; sunflower, Ba > Zn > Cu > Ni > Cd; and tomato, Ba = Zn > Ni > Cu > Cd.

The higher TEs concentrations observed in the roots compared to shoot and grains or fruits (Fig. 3) were directly associated with the BCF and TF values recorded in this study (Fig. 4). All crops presented higher BCF in the roots, followed by shoot and grains or fruits, respectively (Figs. 4A-C, 4E-G, 4I-K, 4M-O and 4Q-S). There was effect of base saturation on BCF and TF values only in few cases. Lettuce plants grown at soil base saturation of 70% presented lower BCF for Cd and Ni in its shoot compared to soil base saturation of 30% (Figs. 4F and 4N). The lower Ni BCF in the shoot was close related to the lower Ni TF observed in lettuce grown at base saturation of 70% (Fig. 4P).

Increasing soil base saturation to grow rice resulted in lower Zn BCF in the whole plant (Figs. 4Q-S) in relation to base saturation of 30%, but oppositely there was an increase on Zn TF (Fig. 4T). Sunflower plants grown at the highest base saturation had lower Cd BCF in their shoots (Fig. 4F) and Zn BCF in their shoots and roots (Figs. 4R-S) in relation to plants grown at the lowest base saturation. In the same way, increasing soil base saturation resulted in lower TEs BCF in tomato. There was lower Ba BCF in the roots (Fig. 4C) and lower Ni BCF in the fruits and shoot (Figs. 4M-N) of tomato plants grown at base saturation of 70%.

Cadmium can easily reach edible parts of the crops assayed compared to the other TEs (Figs. 4A-C, 4E-G, 4I-K, 4M-O and 4Q-S). There was a strong restriction on Ba and Cu long distance-translocation from roots to edible parts of all crops (Figs. 4A-C and 4I-K), which was

evidencing by the low Ba and Cu TFs (Figs. 4D and 4L). In general, lettuce, sunflower and tomato presented lower capacity to restrict Ba, Cd, Cu, Ni and Zn concentration in their tissues than rice (Fig. 4).

There was not a clear relationship between BCF and TF values (Fig. 4), which indicates that besides TEs bioavailability, mechanisms involved on TEs uptake and translocation affected TEs concentration in the edible parts of the crops assayed. Comparatively, sunflower and tomato plants had higher Cd and lower Zn translocation, respectively, in relation to lettuce and rice (Figs. 4H and 4T). Tomato presented high capacity for Ni translocation, as well as lettuce (Fig. 4P). In summary, our results suggest that increasing base saturation tends to decrease TEs BCF, but this process strongly depends on physiological mechanisms of the crops involved on TEs uptake and translocation.

Discussion

There is a great variation among plant species and genotypes concerning their ability to take up and accumulate TEs (Jolly et al. 2013; Gupta et al. 2019; Li et al. 2019). This ability depends in a first moment on the TEs bioavailability, and then, on the physiological mechanisms involved on TEs uptake and translocation (Antoniadis et al. 2017). In this sense, agricultural practices that influence TEs bioavailability (*e.g.*, increase soil base saturation) often shape their accumulation in plants (Macedo et al. 2020). There was no effect of base saturation on pseudo-total Ba, Cd, Cu, Ni and Zn concentrations in the contaminated Entisol, with few exceptions (Fig. 1). This result occurred because the effect of the higher pH and CEC resulting from the increasing base saturation often affects only the chemical distribution of the TEs into soluble, readily exchangeable, complexed with organic matter or hydrous oxides forms (Rieuwerts 2007). Therefore, normally there is no effect of pH and CEC on the pseudo-total TEs concentration. On the other hand, increasing base saturation decreased Ba, Cd, Cu, Ni and Zn bioavailability in the Entisol (Pinto and Alleoni 2018), *i.e.*, there was a reduction on TEs fractions that can be absorbed and involved in the plant cell metabolism. Similar results were pointed out in other studies, in which that Ba, Cd, Cu, Ni and Zn bioavailability and toxicity on different plant species decreased after increasing base saturation by liming (Guo et al. 2013; Han et al. 2013; Myrvang et al. 2016a; Cioccio et al. 2017).

When present at high concentrations in plant tissues, Ba, Cd, Cu, Ni and Zn inhibit plant growth and decrease photosynthetic activity (Moya et al. 1993; Gupta et al. 2019; Lavres et al. 2019). In our study, the biomass production of lettuce exposed to Cu, Ni and Zn was strongly lower than the control (Figs. 2B-C), which also happened with the leaf CO₂ assimilation and stomatal conductance of lettuce plants exposed to Ni and Zn, especially at soil base saturation of 30% (Table 2). Possibly, the lower biomass observed in lettuce exposed to Ni and Zn is related to inhibitory effect of Ni and Zn in the activities of enzymes involved on photosynthetic carbon reduction cycle (Moya et al. 1993; Benzarti et al. 2008), and with changes on abscisic acid (ABA) synthesis that caused stomatal closure (Rucińska-Sobkowiak 2016). Rauser and Dumbroff (1981) reported that bean (*Phaseolus vulgaris* L.) exposed to Ni and Zn presented increased ABA concentrations that led to stomatal closure, lower transpiration, and water stress. On the other hand, the suppression Cu-induced on biomass of lettuce (Figs. 2B-C), as well as in rice (Figs. 2D-F), was not related to chlorophyll concentration and leaf CO₂ assimilation (Table 2), suggesting that the toxicity Cu-induced in these plants was not directly related to these photosynthetic processes. As a redox-active element, Cu can directly cause reactive oxygen species formation and induces lipid peroxidation of membranes and protein oxidation, leading to growth inhibition (Adrees et al. 2015), as reported for lettuce (Trujillo-Reyes et al. 2014) and rice (Da Costa et al. 2020).

Similarly to lettuce, sunflower was more susceptible to toxicity induced by Ni and Zn compared to the others TEs, especially when the plants were grown at soil base saturation of 30% (Figs. 2G-I). However, differently from lettuce, Ni and Zn did not induce great changes on photosynthetic parameters measured in sunflower (Table 2). Despite Ni and Zn can decrease photosynthetic activity of plants, these TEs also can induce other metabolic disorders that compromise the biomass production, such as oxidative stress (Akladios and Mohamed 2017; Shahbaz et al. 2018).

Oxidative stress has often been discussed as a primary effect of TEs exposure in plants (Clemens 2006). Shahbaz et al. (2018) assessed the toxicity Ni-induced in sunflower grown in a Ni-polluted soil (77 mg Ni kg⁻¹) and reported that the oxidative stress Ni-induced strongly decreased the plant biomass. Shahbaz et al. (2018) also described that the use of biochar was essential to decrease Ni bioavailability and increase the biomass production of sunflower. In our study, we observed that increasing soil base saturation was essential to decrease Ni bioavailability, allowing the survival of sunflower grown on Ni-polluted Entisol (Figs. 2G-I). Similar results were reported by Macedo et al. (2020) in an Alfisol. Sunflower grown on Zn-polluted soil also had higher biomass at base saturation of 70% (Figs. 2G-I), probably due to a lower Zn concentration in its shoot and grains (Figs. 3Q-R). Excess Zn may inactivate enzymes that mitigate oxidative stress, such as superoxide dismutase (EC 1.15.1.1), catalase (EC 1.11.1.6) and ascorbate peroxidase (EC 1.11.1.11) (Akladios and Mohamed 2017).

It is probable that oxidative stress or water stress or both had been the main cause for the lower root biomass of tomato grown on Cd, Cu, Ni or Zn-polluted Entisol at base saturation of 30% (Fig. 2L). Metals often decrease elongation of the primary roots, impair secondary growth, increase roots dieback or reduce root hair by inducing oxidative stress, which exert deleterious effects on root-absorbing area and water

uptake (Rucińska-Sobkowiak 2016; Ahmad et al. 2018). Despite Cd, Cu, Ni and Zn had decreased root biomass of tomato, only Ni exposure decreased fruits production compared to control in tomato plants grown at base saturation of 30% (Fig. 2J). Probably, this result is related to the high Ni concentration observed in the tomato fruits compared to the other TEs concentrations (Figs. 3A, 3E, 3I, 3M and 3Q).

The interval between levels of sufficiency and toxicity of Ni for plants is very short since this TE is required in low concentrations (Macedo et al. 2016, 2020). High Ni concentrations in tomato fruits can be a problem not only for plants but also for the human health (Correia et al. 2018). Nickel concentration recorded in the edible parts of the crops grown in the Ni-polluted Entisol in our study were above of the maximum permitted level (EPA-IRIS 1987b), which means that the intake of these crops by humans could lead to health problems (Petrosino et al. 2018).

As occurred with Ni, the concentrations of Ba and Cd in the edible parts of the crops assayed exceeded the maximum levels permitted by EPA-IRIS (1987a), and FAO and WHO (2011), respectively, when the plants were grown in the Entisol spiked with TEs concentrations corresponding to the prevention levels proposed by CETESB (2014). According to CETESB (2014), harmful changes to soil and groundwater quality can occur in soils presenting TEs concentrations corresponding to the prevention levels, but direct and indirect potential risks to the human health are expected only in soils presenting TEs concentrations equal or above the intervention levels for agricultural areas. Therefore, the prevention levels established by CETESB (2014) for Ba, Cd and Ni possibly should be revised for soils presenting low OC and clay contents, and low CEC such as Entisol (Rieuwerts 2007), because Ba, Cd and Ni concentrations recorded in the edible parts of the crops assayed in our study (Figs. 3A-B, 3E-F and 3M-N) were potentially dangerous to human health (Tchounwou et al. 2012; Petrosino et al. 2018), regardless of soil base saturation.

Entisol presents lower capacity to control TEs bioavailability compared to clayey soils presenting highest OC content and CEC, which favor TEs accumulation (Melo et al. 2014). This fact is clear if we consider that we spiked the Entisol with TEs in the order Ba > Zn > Cu > Ni > Cd (considering their concentration), and the crops assayed accumulated TEs in the following order: lettuce, Ba = Zn > Cu = Ni > Cd; rice, Zn > Ba > Ni > Cu > Cd; sunflower, Ba > Zn > Cu > Ni > Cd; and tomato, Ba = Zn > Ni > Cu > Cd (Figs. 3D, 3H, 3L, 3P and 3T). Maybe for its characteristics, increasing base saturation in Entisol was not so effective to reduce Ba, Cd, Cu, Ni and Zn accumulation in lettuce, rice, sunflower and tomato (Figs. 3 and 4) when compared to other soils (Han et al. 2013; Cioccio et al. 2017; Li et al. 2019; Macedo et al. 2020).

The effect of increasing base saturation on TEs accumulation varied depending on metals and plants (Figs. 3 and 4) because TEs accumulation in the edible parts of the crops do not depend only on their bioavailability, but also on mechanisms involved on TEs uptake and translocation of each plant species (Antoniadis et al. 2017). To exemplify, lettuce grown at base saturation of 30% exceeded the maximum levels for Cu and Zn proposed by FAO and WHO (2011) (Figs. 3J and 3R), differently from rice and tomato. Sunflower also exceeded the maximum level for Zn proposed by FAO and WHO (2011) (Fig. 3Q).

As reported in other studies (Singh et al. 2010; Pereira et al. 2011; Melo et al. 2014; Gupta et al. 2019), Ba, Cd, Cu, Ni and Zn tissues' concentrations and BCFs for lettuce, rice, sunflower and tomato tissues followed the order: roots > shoot > grains or fruits (Figs. 3 and 4). Roots are normally the first structure of the plant in contact with TEs, and they present mechanisms to avoid excessive metals translocation, with exception of hyperaccumulators (Antoniadis et al. 2017; Gupta et al. 2019). Meng et al. (2019) reported that Cd was more accumulated in the roots than shoot in leafy vegetables due to the higher synthesis of phytochelatins [PCs, (γ -Glu-Cys) $_n$ -Gly, with $n = 2-11$] in the roots. Phytochelatins act on Cd²⁺ chelation and its transport from the cytosol to the vacuole (Clemens 2006). Kendziorek et al. (2016) suggested us that Cd and Zn distribution among roots and shoot was related to expression of the gene *HMA4* (involved on metals efflux) in tomato roots. TEs translocation from roots to shoot mainly depends on the rate of trapping in compartments of root cells, the mobility within the root symplast and across barriers such as endodermis, loading into the xylem, and upward mobility in the xylem (Clemens and Ma 2016). Therefore, physiological mechanisms control TEs translocation from roots to shoot, although there is still a great influence of highest TEs bioavailability on their shoot accumulation due to the higher TEs uptake in this scenario. To exemplify, Melo et al. (2014) mentioned that there was a positive correlation of Ba and Cd bioavailability with Ba BCF_{roots}, Ba BCF_{shoot}, Cd BCF_{roots} and Cd BCF_{shoot} in different crops, but there was no correlation of TEs bioavailability with Ba TF and Cd TF.

Increasing soil base saturation (lower TEs bioavailability) decreased the Cd BCF_{shoot} in lettuce and sunflower, Ni BCF_{shoot} in lettuce and tomato, and Zn BCF_{shoot} in rice and sunflower grown in a polluted Entisol. Interestingly, there was no effect of soil base saturation on Ba and Cu BCF_{shoot} or Ba and Cu BCF_{grains or fruits} in the crops assayed in our study (Figs. 4A-C, 4E-G, 4I-K, 4M-O and 4Q-S). Myrvang et al. (2016b) evaluated the effect of liming on Ba transfer from soil to shoot of different crops and observed that there was a great variation on Ba BCF_{shoot}, regardless of Ba bioavailability, which was attributed to physiological differences between the plant species.

Trace elements accumulation in leaves (or shoot) depends on physiological factors such as TEs loading from xylem and the availability of metal-binding molecules (Clemens and Ma 2016), as observed in rice exposed to Cu (Ando et al. 2013). Furthermore, entering into the

shoots, some TEs such as Cu can be accumulated in the epidermis, which serves as an effective mechanism for their detoxification by decreasing metal influx into mesophyll (Seregin and Kozhevnikova 2020; van der Ent et al. 2020). These processes restrict TEs redistribution to grains and fruits (Seregin and Kozhevnikova 2020), and probably occurred in our study for Ba and Cu, because there was a strong restriction on Ba and Cu translocation from roots to edible parts of all crops compared to the other TEs (Fig. 4). Nevertheless, Hladun et al. (2015) stated that Cu presented high mobility inside radish (*Raphanus sativus* L.). This finding reinforces that there is a great variation among plant species and genotypes concerning their ability to take up and accumulate TEs (Jolly et al. 2013; Gupta et al. 2019; Li et al. 2019).

Cadmium easily reached edible parts of the crops assayed compared to the other TEs, differently from the results observed for Ba and Cu (Figs. 4A-C, 4E-G, 4I-K, 4M-O and 4Q-S). Hladun et al. (2015) also mentioned that Cd presented high mobility inside radish. Meanwhile, Riesen and Feller (2005) described that Ni and Zn presented higher mobility inside wheat (*Triticum aestivum* L.) than Cd, and suggested that this result is associated with the plant capacity to transfer metals from xylem to phloem. However, this transfer process is unknown for the most TEs and crops, with exception for some TEs in rice (Clemens and Ma 2016; Seregin and Kozhevnikova 2020).

In our study, in general, lettuce, sunflower and tomato had lower capacity to restrict Ba, Cd, Cu, Ni and Zn uptake and translocation than rice, even when rice grown in Entisol at a lower soil base saturation (50% vs. 70%) - Figs. 4A-C, 4E-G, 4I-K, 4M-O and 4Q-S. Probably this result is related to an efficient control of TEs distribution to shoot from the nodes of rice, which is a hub for metals distribution in graminaceous (Yamaji and Ma 2014). The distribution of TEs among leaves and grains in rice depends on phloem loading, the efficiency of xylem-to-phloem transfer, the rates of various symplast-to-apoplast and apoplast-to-symplast transport processes, and the availability of storage sites (Clemens and Ma 2016). Several types of metal-binding compounds including nicotianamine and PCs were reported to be relevant for TEs transport in the phloem of crops destined to human feed (Gupta et al. 2019). These compounds can affect TEs translocation to grains or fruits since the roots, as observed in rice and tomato (Morishita et al. 1983). However, although there are studies evaluating TEs accumulation in plants, most processes involved on TEs translocation are still poorly known or unknown for the most plant species consumed by humans (Seregin and Kozhevnikova 2020).

Conclusions

In general, increasing soil base saturation did not attenuate photosynthetic changes induced by Ba, Cd, Cu, Ni and Zn in the crops cultivated in the Entisol, since this agricultural practice was not so effective in reducing these TEs bioaccumulation.

The photosynthetic changes observed in the crops assayed varied depending on the metal and plant species. There was no a strong correlation between the photosynthetic parameters measured and biomass production, which suggest us that the suppression on biomass induced by Ba, Cd, Cu, Ni or Zn is related to other metabolic disorders besides the impairment on CO₂ assimilation or chlorophyll synthesis in the crops assayed, with exception of Ni and Zn in lettuce. Increasing soil base saturation was not consistent in decreasing Ba, Cd, Cu, Ni and Zn accumulation in the edible parts of lettuce, rice, sunflower and tomato grown in the Entisol, which probably was related to the low capacity of this soil in control TEs bioavailability due to its low organic carbon and clay contents and low cation exchange capacity.

Barium, Cd, Cu, Ni and Zn bioaccumulation in the edible parts of the crops was affected by TEs bioavailability, which means that other agricultural practices maybe can be more efficient than increasing soil base saturation to avoid the bioaccumulation of TEs into edible parts of crops grown in Entisol. There was a great variation on Ba, Cd, Cu, Ni and Zn translocation, which is associated to physiological mechanisms of each crop, but this process is still poorly known or unknown.

Declarations

Author contributions

FHSR wrote and revised the manuscript; JL performed the analysis; FAP performed the experiment and data collection; LRFA supervised the study and obtained financial support. All authors read and approved the final manuscript.

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Compliance with ethical standards

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Tables

Table 1 Descriptive analysis of some chemical and physical properties of the Entisol used in this study

pH 0.01 mol L ⁻¹ CaCl ₂	4.2	Al (mmol _c kg ⁻¹)	5
		H+Al (mmol _c kg ⁻¹)	21
P (mg dm ⁻³)	6		
		SB (mmol _c kg ⁻¹)	3.3
K (mmol _c kg ⁻¹)	0.3	CEC _{7.0} (mmol _c kg ⁻¹)	24.3
Ca (mmol _c kg ⁻¹)	2		
Mg (mmol _c kg ⁻¹)	1	BS (%)	13
		m (%)	60
Ba (mg kg⁻¹)	3.6		
Cd (mg kg⁻¹)	0.8	OC (g kg ⁻¹)	5
Cu (mg kg⁻¹)	15.2	Sand (g kg ⁻¹)	906
Ni (mg kg⁻¹)	2.2	Silt (g kg ⁻¹)	31
Zn (mg kg⁻¹)	14.5	Clay (g kg ⁻¹)	63

SB: sum of bases; CEC_{7.0}: Cation Exchange Capacity at pH 7.0; BS: Base saturation; m: saturation by aluminum; OC - Organic Carbon.

Table 2 Leaf area, chlorophyll concentration, leaf CO₂ assimilation - *A*, stomatal conductance - *g_s*, intracellular CO₂ concentration - *C_i* and transpiration - *E* of lettuce, rice, sunflower, and tomato grown in unpolluted (control treatment) or Ba, Cd, Cu, Ni or Zn-polluted Entisol under two base saturation (BS%)

Parameters	Leaf area (cm ² /pot)		Chlorophyll (SPAD units)		A (μmol CO ₂ m ⁻² s ⁻¹)		g _s (mol H ₂ O m ⁻² s ⁻¹)		C _i (μmol CO ₂ mol ⁻¹)		E (mmol m ⁻² s ⁻¹)	
Lettuce	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%
Control	853 ± 60 Aa	1032 ± 100 Aa	14.9 ± 1.9 Aab	13.2 ± 1.1 Aab	14.26 ± 2.06 Aa	10.98 ± 0.22 Aab	0.91 ± 0.05 Aa	0.33 ± 0.09 Bab	353 ± 5 Aa	307 ± 10 Aa	11.27 ± 0.78 Aa	6.06 ± 1.19 Ba
Ba	1032 ± 99 Aa	1142 ± 233 Aa	14.8 ± 0.7 Aab	13.3 ± 0.9 Aab	8.11 ± 0.50 Aab	9.26 ± 0.12 Aabc	0.30 ± 0.05 Abc	0.09 ± 0.02 Bbc	337 ± 11 Aa	261 ± 16 Ba	5.15 ± 0.40 Ab	2.23 ± 0.57 Bb
Cd	971 ± 91 Aa	1106 ± 152 Aa	12.4 ± 0.6 Abc	11.6 ± 0.6 Ab	14.44 ± 3.94 Aa	12.25 ± 2.25 Aa	0.56 ± 0.14 Ab	0.05 ± 0.00 Bc	335 ± 8 Aa	256 ± 52 Ba	8.76 ± 1.22 Aa	1.36 ± 0.19 Bb
Cu	300 ± 38 Bb	1285 ± 147 Aa	16.4 ± 1.5 Aa	15.0 ± 1.1 Aa	12.89 ± 2.96 Aa	11.09 ± 3.54 Aa	0.22 ± 0.05 Acd	0.36 ± 0.04 Aa	279 ± 2 Aa	282 ± 35 Aa	1.46 ± 0.64 Bc	6.42 ± 0.58 Aa
Ni	188 ± 21 Bb	500 ± 29 Ab	11.7 ± 1.9 Ac	12.0 ± 0.0 Ab	0.52 ± 0.11 Ab	2.23 ± 0.35 Ac	0.03 ± 0.00 Ad	0.03 ± 0.00 Ac	355 ± 6 Aa	288 ± 33 Aa	0.81 ± 0.10 Ac	0.77 ± 0.17 Ab
Zn	196 ± 29 Ab	206 ± 39 Ab	12.4 ± 0.7 Abc	11.0 ± 1.2 Ab	1.34 ± 0.39 Ab	2.47 ± 0.50 Abc	0.03 ± 0.00 Acd	0.02 ± 0.00 Ac	289 ± 36 Aa	234 ± 26 Aa	1.69 ± 0.86 Ac	0.64 ± 0.03 Ab
Rice	30%	50%	30%	50%	30%	50%	30%	50%	30%	50%	30%	50%
Control	2861 ± 142 Aab	3134 ± 58 Aa	36.7 ± 0.3 Aa	34.7 ± 1.3 Aa	11.88 ± 1.85 Aa	12.22 ± 2.59 Aab	0.06 ± 0.00 Ad	0.11 ± 0.02 Aa	158 ± 73 Ab	188 ± 6 Aa	1.40 ± 0.02 Ac	2.42 ± 0.46 Ab
Ba	3328 ± 136 Aa	3114 ± 63 Aa	36.5 ± 0.6 Aa	36.0 ± 0.7 Aa	14.21 ± 1.12 Aa	16.18 ± 0.86 Aa	0.27 ± 0.01 Aa	0.20 ± 0.05 Aa	277 ± 6 Aa	253 ± 26 Aa	4.92 ± 0.36 Aa	3.89 ± 0.89 Aab
Cd	2994 ± 73 Aa	3479 ± 25 Aa	36.5 ± 0.2 Aa	35.5 ± 0.6 Aa	12.51 ± 1.05 Ba	15.69 ± 0.34 Aa	0.15 ± 0.01 Abcd	0.17 ± 0.00 Aa	234 ± 23 Aab	259 ± 25 Aa	3.22 ± 0.24 Aabc	4.42 ± 1.01 Aa
Cu	2159 ± 449 b	*	31.7 ± 2.8 a	*	15.44 ± 1.57 a	*	0.21 ± 0.03 abc	*	233 ± 28 ab	*	4.09 ± 0.61 ab	*
Ni	2704 ± 119 Aab	3061 ± 33 Aa	32.9 ± 1.3 Aa	30.6 ± 2.3 Aa	11.05 ± 0.94 Aa	8.56 ± 0.42 Ab	0.11 ± 0.01 Acd	0.18 ± 0.03 Aa	211 ± 22 Aab	264 ± 27 Aa	2.56 ± 0.20 Abc	3.49 ± 0.42 Aab
Zn	3359 ± 255 Aa	3173 ± 238 Aa	35.2 ± 0.6 Aa	34.0 ± 0.9 Aa	13.82 ± 0.65 Aa	12.36 ± 0.66 Aab	0.22 ± 0.03 Aab	0.18 ± 0.03 Aa	252 ± 27 Aab	249 ± 33 Aa	4.29 ± 0.47 Aab	3.57 ± 0.47 Aab
Sunflower	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%
Control	3213 ± 459 Aa	3816 ± 405 Aab	31.2 ± 0.5 Aa	31.5 ± 0.4 Aa	17.89 ± 1.19 Aab	23.17 ± 2.18 Aa	0.15 ± 0.00 Bb	1.13 ± 0.13 Aa	170 ± 10 Ba	322 ± 20 Aa	3.94 ± 0.00 Bbc	10.39 ± 0.01 Aa
Ba	2948 ±	3990 ±	34.0 ±	31.5 ±	11.58 ±	25.20 ±	0.13 ±	0.94 ±	213 ±	295 ±	3.00 ±	10.27 ±

	515 Aa	284 Aa	0.1 Aa	0.7 Aa	0.77 Bb	3.44 Aa	0.06 Bb	0.06 Aa	43 Ba	15 Aab	1.15 Bc	0.21 Aa
Cd	2096 ± 573 Bab	4188 ± 366 Aa	30.3 ± 1.8 Aab	30.5 ± 1.0 Aa	20.39 ± 4.86 Aab	21.94 ± 3.95 Aa	0.35 ± 0.20 Aab	0.70 ± 0.18 Aab	208 ± 44 Aa	285 ± 24 Aab	5.52 ± 1.95 Aab	8.82 ± 1.12 Aa
Cu	2345 ± 7 Aa	2085 ± 337 Aab	31.7 ± 6.5 Aa	35.4 ± 0.5 Aa	28.68 ± 2.51 Aa	23.22 ± 6.02 Aa	0.83 ± 0.08 Aa	0.11 ± 0.00 Bb	279 ± 12 Aa	214 ± 28 Aab	9.86 ± 0.37 Aa	3.00 ± 0.00 Bb
Ni	*	1757 ± 335 b	*	33.9 ± 0.9 a	*	27.10 ± 5.53 a	*	0.54 ± 0.23 ab	*	202 ± 26 b	*	6.93 ± 1.94 ab
Zn	1879 ± 197 Ab	3314 ± 120 Aab	21.2 ± 1.2 Bb	28.0 ± 0.5 Aa	27.15 ± 0.01 Aab	25.89 ± 2.93 Aa	0.38 ± 0.04 Aab	0.62 ± 0.21 Aab	196 ± 14 Aa	238 ± 56 Aab	4.23 ± 1.11 Bbc	8.25 ± 1.96 Aa
Tomato	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%
Control	-	-	39.8 ± 2.9 Aa	42.5 ± 0.7 Aa	-	-	-	-	-	-	-	-
Ba	-	-	39.7 ± 1.7 Aa	40.9 ± 1.6 Aa	-	-	-	-	-	-	-	-
Cd	-	-	38.4 ± 4.0 Aa	36.5 ± 1.5 Aa	-	-	-	-	-	-	-	-
Cu	-	-	45.5 ± 4.2 Aa	43.4 ± 3.6 Aa	-	-	-	-	-	-	-	-
Ni	-	-	49.3 ± 2.2 Aa	45.8 ± 1.2 Aa	-	-	-	-	-	-	-	-
Zn	-	-	37.3 ± 6.0 Aa	42.8 ± 0.6 Aa	-	-	-	-	-	-	-	-

Means followed by distinct upper case letters indicate difference between base saturation within each condition (Control = unpolluted, or Ba, Cd, Cu, Ni or Zn-polluted Entisol) for each crop, and distinct lower case letters indicate difference between each condition (Control = unpolluted, or Ba, Cd, Cu, Ni or Zn-polluted Entisol) within each base saturation for each crop (Tukey test, $P \leq 0.05$). Asterisks (*) indicate treatment lost due to plant death

Figures

Figure 1

Pseudo-total concentrations of Ba (A), Cd (B), Cu (C), Ni (D) and Zn in unpolluted (control treatment) or Ba, Cd, Cu, Ni or Zn-polluted Entisol cultivated with lettuce, rice, sunflower or tomato under two soil base saturation (BS%). Distinct upper case letters indicate difference between base saturation within each crop for each condition (unpolluted or polluted Entisol) and distinct lower case letters indicate difference between unpolluted or polluted Entisol within each base saturation for each crop (Tukey test, $P \leq 0.05$). The dash line (in red) indicates the trace elements concentrations corresponding to the prevention levels established by The São Paulo State Environmental Agency - CETESB, in Brazil (CETESB 2014)

Figure 2

Fruits or grains biomass (A, D, G and J), shoot biomass (B, E, H and K) and root biomass (C, F, I and L) of lettuce (A-C), rice (D-F), sunflower (G-I), and tomato (J-L) grown in unpolluted (control treatment) or Ba, Cd, Cu, Ni or Zn-polluted Entisol under two soil base saturation (BS%). Distinct upper case letters indicate difference between base saturation within each condition (Ctr. - unpolluted or Ba, Cd, Cu, Ni or Zn-polluted Entisol) for each crop and distinct lower case letters indicate difference between each condition (Ctr. - unpolluted or Ba, Cd, Cu, Ni or Zn-polluted Entisol) within each base saturation for each crop (Tukey test, $P \leq 0.05$). Asterisks (*) indicate treatment lost due to plant death

Figure 3

Concentrations of Ba (A-C), Cd (E-G), Cu (I-K), Ni (M-O) and Zn (Q-S) in fruits or grains (A, E, I, M and Q), shoot (B, F, J, N and R) and roots (C, G, K, O and S) and total content of Ba (D), Cd (H), Cu (L), Ni (P) and Zn (T) in lettuce, rice, sunflower and tomato grown on Ba, Cd, Cu, Ni or Zn-polluted Entisol under two soil base saturation (BS%). Distinct upper case letters indicate difference between base saturation within each crop for each trace element and distinct lower case letters indicate difference between each trace element within each base saturation for each crop (Tukey test, $P \leq 0.05$). Asterisks (*) indicate treatment lost due to plant death. ND = non-detected

Figure 4

Bioconcentration factor (BCF) for Ba (A-C), Cd (E-G), Cu (I-K), Ni (M-O) and Zn (Q-S) in fruits or grains (A, E, I, M and Q), shoot (B, F, J, N and R) and roots (C, G, K, O and S) and translocation factor (TF) for Ba (D), Cd (H), Cu (L), Ni (P) and Zn (T) in lettuce, rice, sunflower and tomato grown on Ba, Cd, Cu, Ni or Zn-polluted Entisol under two soil base saturation (BS%). Distinct upper case letters indicate difference between base saturation within each crop for each trace element and distinct lower case letters indicate difference between each trace element within each base saturation for each crop (Tukey test, $P \leq 0.05$). Asterisks (*) indicate treatment lost due to plant death. ND = non-determined