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Soil–plant transfer models for metals to improve soil screening value guidelines valid for São Paulo, Brazil

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Abstract In Brazil, there is a lack of combined soil–plant data attempting to explain the influence of specific climate, soil conditions, and crop management on heavy metal uptake and accumulation by plants. As a consequence, soil–plant relationships to be used in risk assessments or for derivation of soil screening values are not available. Our objective in this study was to develop empirical soil–plant models for Cd, Cu, Pb, Ni, and Zn, in order to derive appropriate soil screening values representative of humid tropical regions such as the state of São Paulo (SP), Brazil. Soil and plant samples from 25 vegetable species in the production areas of SP were collected. The concentrations of metals found in these soil samples were relatively low. Therefore, data from temperate regions were included in our study. The soil–plant relations derived had a good performance for SP conditions for 8 out of 10 combinations of metal and vegetable species. The bioconcentration factor (BCF) values for Cd, Cu, Ni, Pb, and Zn in lettuce and for Cd, Cu, Pb, and Zn in carrot were determined under three exposure scenarios at pH 5 and 6. The application of soil–plant models and the BCFs proposed in this study can be an important tool to derive national soil quality criteria. However, this methodological approach includes data assessed under different climatic conditions and soil types and need to be carefully considered.

Keywords Tropical soils · Bioconcentration factor · Soil pollution · Plant uptake · Empirical Freundlich-type models

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Introduction

Metals can cause adverse effects to the environment, animals, and human health. As metals do accumulate in the edible parts of plants, vegetable consumption is a human exposure pathway often considered in soil risk assessments (Römkens et al., 2009; Rodrigues et al.

2012). There is a growing interest in the development of models to quantify the link between soil contamination and resulting contaminant levels in edible crops in order to calculate the actual intake via consumption. However, most studies regarding soil–plant transfer models were done in non-tropical regions, and few studies have focused on the relationships between the concentrations of metals in soils and plants in humid tropical regions, especially in Brazil.

In this country, studies using risk assessment as a complementary procedure to determine the impacts of soil and water contamination on human health are scarce. However, individual efforts were achieved in this direction by some states. For example, Casarini et al. (2001) derived soil intervention values for soil quality protection in the state of São Paulo, using the CSOIL model, and Finotti (1997) evaluated the applicability of mathematical models within the context of risk-based corrective action (RBCA) applied for groundwater and soil contamination due to gasoline and ethanol spills in the state of Santa Catarina. However, the estimation of risks to the human health through variables that characterize the physical environment and the human contact to soil and to soil-related media specifically focused on Brazilian conditions is lacking.

To derive soil quality standards (also known as "soil screening values"), it is important to obtain the concentration of contaminants in both soil and vegetables. It is also necessary to include the soil properties in soil–plant relationships, because soil processes such as redox potential, adsorption, and/or formation of metal complexes with the reactive surfaces of soil colloids influence the availability of metals for plant uptake (Sauvé et al. 2000; Rieuwerts, 2007; Rodrigues et al., 2010). These processes are controlled largely by the pH and the soil content of organic matter, clay, and Fe, Al, and Mn oxides (Römkens et al., 2009; Rodrigues et al., 2010). Thus, relationships featuring these soil attributes can assist in the evaluation of soil–plant relationships, mainly if they incorporate research results obtained under field conditions (Swartjes et al. 2007; Santos-Araujo and Alleoni 2016).

The ratio between the concentration of metals in edible parts of plants and the total concentration in the soil is called the bioconcentration factor (BCF). Due to its inherent simplicity and applicability, BCF has been widely used to estimate the accumulation of metals in vegetables (Alonso et al. 2003; Sipter et al. 2008; Swartjes et al. 2007; Murray et al. 2009). However, using constant soil and plant concentrations for calculating a specific metal BCF may not describe the accumulation of metals in plants accurately because of the high variation in soil properties (De Vries et al. 2007; Römkens et al., 2009, Rodrigues et al. 2012). On the other hand, mechanistic models that predict accumulated plant concentrations for an array of heavy metals have not yet been developed sufficiently, let alone validated under field conditions (Swartjes 2011).

To overcome the limitation of the simple BCF approach, and to account for the impact of soil properties on the uptake of metals by plants, empirical models have been explored to predict contaminant levels in plants, such as the Freundlich-type model, which describes the concentration of metals in the plant versus the concentration in soils through an exponential relationship. However, the majority of studies has considered a limited number of metals and soil properties. Römkens et al. (2009) derived empirical soil–plant relationships for Cd in rice (*Oryza sativa*) plants and observed that pH and CEC of the soil were the variables that had the greatest influence on the transfer of cadmium into the plants. Melo et al. (2011) derived significant soil–plant relationships for Cd in leaf vegetables and roots using total metal concentration in soil and pH as explanatory variables. For this purpose, Melo et al. (2011) used data measured in tropical and temperate regions. In Brazil, there is a lack of combined soil–plant data attempting to explain the influence of specific climate, soil conditions, and crop management practices on heavy metal uptake and accumulation by plants. As a consequence, soil–plant relationships to be used in risk assessments or for derivation of soil screening values are not available.

In this study, soil–plant transfer empirical models for cadmium, copper, lead, nickel, and zinc were developed to be used for both risk assessment and derivation of soil screening values in humid tropical regions, such as in the state of São Paulo, Brazil. Therefore, we tested two hypotheses: (i) metal soil–plant transfer models, including soil properties such as pH, and organic carbon and clay contents offer more realistic screening values for the state of São Paulo, Brazil; (ii) results of the soil–plant transfer empirical models can be improved by the combination of data from the two available datasets (from SP and a dataset from temperate regions), in spite of the different conditions (climate, soils, genotypes of plants, agricultural management).

Materials and methods

Selection of sites, collection, and analysis of samples

The sampling sites were selected in rural, urban, and industrial areas, in an attempt to obtain samples with a wide range of contamination levels in soils for the various metals studied. Sampling was concentrated in the "Green Belt" zone, which is an area located within roughly 120 km of the city of São Paulo, including 73 surrounding townships (Camargo et al., 2008). In total, 200 composite soil samples (0–20-cm depth) and 200 corresponding plant samples (plant pairs) of 25 species were collected. The sampling campaign covered 53 vegetable crop-producing sites, located in 19 cities in the state of São Paulo, thus representing the main vegetable production areas of SP (Fig. 1). Soil samples were taken in the immediate vicinity of the root crop samples.

In the laboratory, plant samples were washed with running water to remove impurities. Plant samples were only washed with tap water to simulate vegetable preparation for human consumption. Washed plant material was dried at 60 °C for 48 h, milled in a stainless steel mill, and packed in plastic bottles before storing at 25 °C. The soil samples were air dried until constant weight and subsequently sieved (2-mm mesh). Digestion of the ground and dried plant biomass (250 mg) was microwave-assisted (Mars Xpress, CEM Corporation) by using 2 ml of H_2O_2 and 2 ml of HNO_3 in closed vessels (waiting approximately 30 min when using H_2O_2, to avoid overpression inside the vessels), as described by Araújo et al. (2002). The heating program was performed in four steps: (i) 80 °C in 3 min, (ii) 150 °C in 5 min, (iii) 180 °C in 10 min and stay resting for 5 min, and (iv) 25 °C in 8 min. Temperature and pressure sensors were used in all digestions. After digestion, samples and blank solutions were filtered and transferred to 25-ml volumetric flasks, and the volume was made up with water.

Pseudototal concentrations of metals in the soil samples were extracted according to the EPA 3051a method using a 1:3 HCl/HNO_3, *v*/*v* extraction methods (USEPA 1998), as recommended by the Environmental Agency of São Paulo State (Cetesb) and National Environment Council (Conama). Weighed 0.5 g of soil was transferred to Teflon tube in triplicate; then, 9 ± 0.1 ml of concentrated HNO_3 (65% PA) and 3 ± 0.1 ml of HCl (37% PA) were added. The tubes were kept in a semi-closed pre-digestion system for approximately 12 h in order to allow the gases to escape and eliminate the danger of reactions. The tubes were taken to microwave oven for digestion at 175 ± 5 °C for 10 min. After extraction, soil samples were filtered and transferred to 25-ml volumetric flasks, and the volume was filled with ultrapure water (Milli-Q). The extracts were diluted five times for further determination by inductively coupled plasma optical emission spectroscopy (ICP-OES). A certified reference material by the National Institute of Standards and Technology (NIST), SEM 2709 (San Joaquin soil) was used for quality control. Recovery rates of PTEs, around 92%, were considered satisfactory. Concentrations of Cd, Cu, Ni, Pb, and Zn in the plant and soil extracts were determined by ICP-OES.

Soil samples were subjected to routine chemical and fertility tests (pH and granulometric analysis) (Anderson and Ingram 1993). The organic carbon (OC) content was determined following dry combustion in a LECO CN-2000 elemental analyzer.

Development of soil–plant transfer empirical models

It is necessary to use a BCF valid in the expected range of the soil screening values (Table 1) to derive the soil screening values representative of humid tropical conditions and to avoid extensive extrapolations (Swartjes et al. 2007). The low soil concentrations of metals found in SP samples were not appropriate for the derivation of soil screening values (Table 1). An option is to include other datasets, covering greater concentration range of these metals in soils and plants, especially in the higher concentration range. A remaining alternative was to include the dataset obtained in the Netherlands (NL), widely used in studies involving soil–plant relations or also used to develop screening values in this country.

The impact of combining the São Paulo (SP) and Netherland (NL) datasets for the derivation of soil screening values in terms of representation of humid tropical conditions prevailing in São Paulo and appropriate soil concentration range was investigated. To this purpose, the following methods were used (multiple lines of evidence; Fig. 2): (i) provisional visual interpretation, (ii) development and comparison of empirical soil–plant relations, and (iii) statistical analyses. The combined result from the three assessments was used to conclude on the ideal dataset, described in detail in the following sections.

Leaf and root vegetables were considered separately for the derivation of soil screening values, because these

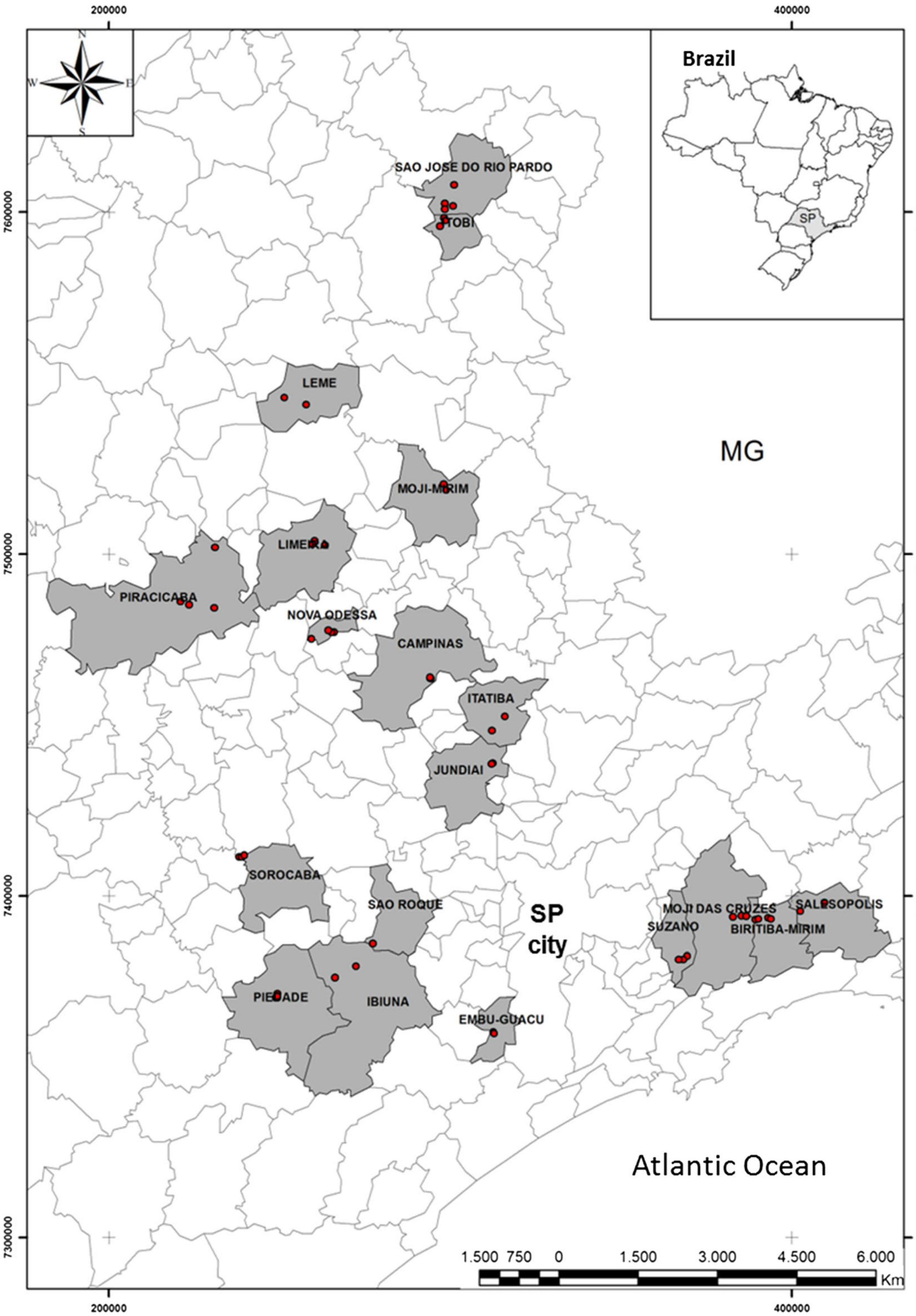

Fig. 1 Location of sampling areas of soils and vegetables in the state of São Paulo, Brazil (Santos-Araujo and Alleoni 2016)

main groups of vegetables have different plant uptake characteristics (Dudka and Miller 1999), resulting in different soil–plant relations. To be able to investigate the impact of combining the SP and NL datasets, this

Table 1 Range in soil concentration for two datasets (SP and NL) and intervention values for the state of São Paulo related to three scenarios (rural, urban, and industrial)

SP dataset							NL dataset						Intervention values for SP state (Cetesb 2014)		
Soil conc. metal	Min.	Median	Max.	Aver.	SD	*n*	Min.	Median	Max.	Aver.	SD	*n*	Agric.	Resid.	Indust.
	mg kg^{-1}						mg kg^{-1}						mg kg^{-1}		
Cd	< LD	0.1	2.4	0.1	0.2	200	< LD	0.6	12.6	1.3	4.1	1175	3.6	14	160
Cu	3.3	18.1	356.0	33.1	41.1	200	6.0	30.4	217.0	40.4	34.3	272	760	2100	10,000
Ni	1.6	6.5	52.8	8.3	6.4	200	12.4	21.2	117.7	24.3	17.0	113	190	480	3800
Pb	3.6	16.0	331.4	22.6	29.3	200	1.8	48.2	548.0	93.5	90.5	1175	150	240	4400
Zn	39.6	134.1	643.3	166.3	106.0	200	40.0	312.0	2035.0	488.8	473.3	264	1900	7000	10,000

< *LD* limit of detection, *SD* standard deviation, *n* number of observations

study selected one species of each vegetable group, i.e., lettuce *Lactuca sativa* (leaf vegetables) and carrots *Daucus carota* (root vegetables), which are considered representative for the vegetable group and because of the large number of paired soil and plant concentrations available.

Additional plant and soil data

To increase the number of data for derivation of appropriate soil–plant relations, existing datasets (soil concentrations and corresponding plant concentrations) of Cd, Cu, Ni, Pb, and Zn have been evaluated. RIVM

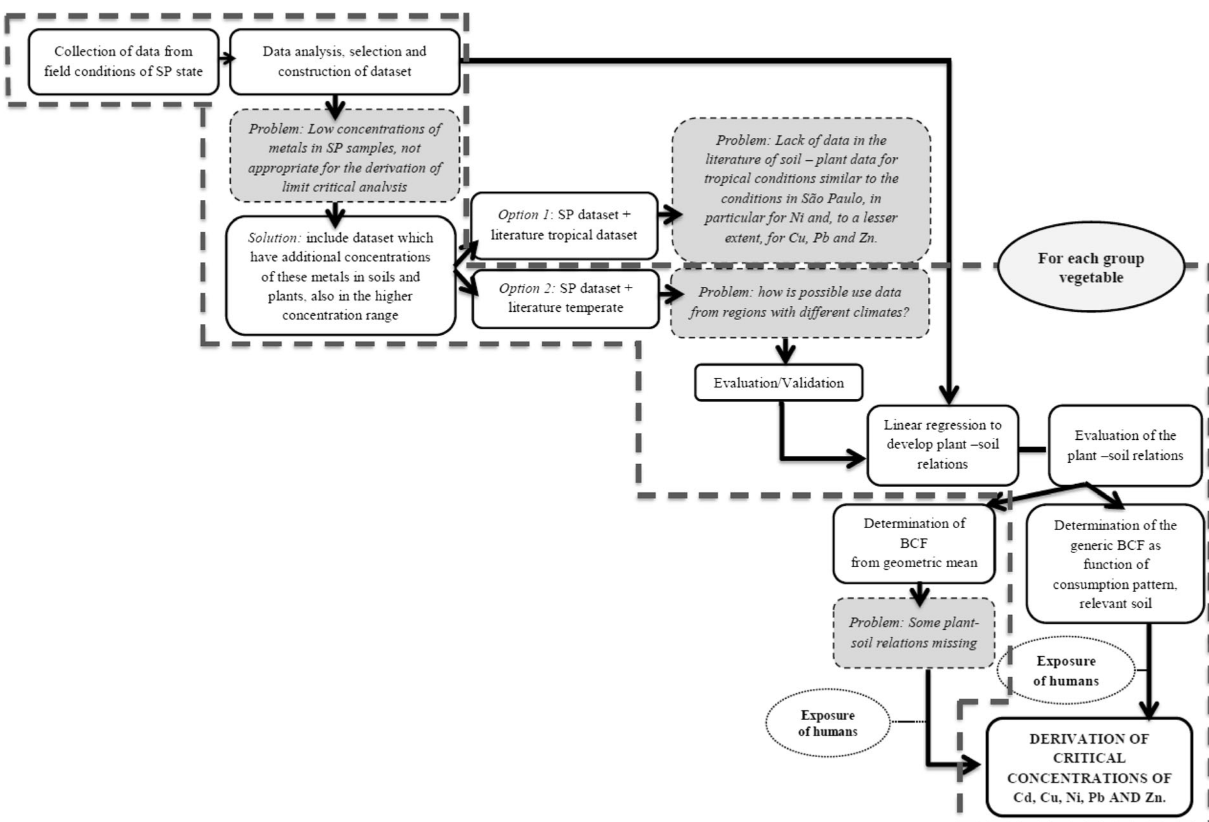

Fig. 2 Overview of model described in "Descriptive analysis" section

(National Institute of the Public Health and the Environment) and Alterra (Wageningen University and Research Center) datasets (Versluijs and Otte 2001) were thus combined to form the NL dataset. The RIVM dataset includes data from Dudka et al. (1996), Logan et al. (1997), Krebs et al. (1998), Mellum et al. (1998), van der Torn et al. (1994), and Wiersma et al. (1986), all measured in temperate regions of the world. In Table 1, the total content of metals in soils from the two datasets used in this study has been summarized. For comparison purposes, the São Paulo state intervention values for three land uses were also included.

Graphs with data from different datasets were made to show the response of plants to an increase in soil concentrations. In this respect, possible differences in uptake behavior between the "tropical" SP and the "temperate" NL datasets can be recognized as well as variations related to different soil properties.

Mathematical model development

In this study, multiple linear regression analysis was used to test several regression models to predict the accumulated vegetable concentration as a function of total soil concentrations and soil properties (Sposito 1980; Versluijs and Otte 2001).

Soil properties were selected as variables for the models according to the following criteria: (i) degree of importance in the evaluation of the transfer of soil–plant metals and (ii) availability in the database. Several authors report correlations between clay content, soil organic matter, pH, and total metal content in soils (Valadares 1975; Souza et al. 1996; Pérez et al. 1997; Alleoni et al., 2009; Römkens et al. 2009a; Rodrigues et al. 2012).

For each vegetable, the following equations were derived:

$$\text{Log}\left[C_{\text{Veg}}\right] = a + b\ \log\left[C_{soil}\right] \quad (1)$$

$$\text{Log}\left[C_{\text{Veg}}\right] = a + b\ \log\left[C_{soil}\right] + c\ \text{pH}_{\text{soi}} \quad (2)$$

$$\text{Log}\left[C_{\text{Veg}}\right] = a + b\ \log\left[C_{soil}\right] + c\ \text{pH}_{soil} + d\ \log\left[\%\text{OC}\right] \quad (3)$$

$$\text{Log}\left[C_{\text{Veg}}\right] = a + b\ \log\left[C_{soil}\right] + c\ \text{pH}_{soil} + d\ \log\left[\%\text{OC}\right] + e\ \log\left[\%clay\right] \quad (4)$$

where C_{Veg} = metal concentration in the edible part of the vegetable (mg kg^{-1}), C_{soil} = total metal concentration in the soil in (mg kg^{-1}), pH_{soil} = pH measured in 1 M KCl, %clay = clay content of the soil (%), %OC = organic carbon content of the soil (%), and *a*, *b*, *c*, *d*, and *e* are empirical regression parameters. All concentrations used were on dry weight basis, unless stated otherwise.

The models were computed on the basis of the SP datasets and NL datasets separately and, when justifiable, for the combined dataset. The usefulness of the soil–plant models described above for these datasets was evaluated. When no statistically significant soil–plant relation could be derived for a specific combination of metal and vegetable, a BCF based on geometric means was derived and used as a fallback.

Statistics

The SPSS 16.0 software package for Windows was used for descriptive statistics and for statistical analysis of data. Except for pH, all data were log transformed (log10) due to the occurrence of non-normality in the variable distributions. The soil–plant relations were statistically evaluated using an *F* test (one-sided exceeding probability, $\alpha = 0.05$) and significance ($p < 0.05$) (Versluijs and Otte 2001). The stepping method criteria using a probability of *F* of 0.05 for entry and 0.10 for removal was applied for linear regression. The relevance of inclusion of each variable (pH, %OC, %clay) into the model was determined on the basis of the percentage of explained variance. The relative contribution of the different variables was assessed by comparing the average explained variance. The relevance of combining the datasets was assessed by comparing the average explained variance of the combined dataset with the average explained variance of the separate datasets (SP and NL).

The criteria applied to assess the usefulness of the soil–plant models relate to the questions: (i) do the data fit within the model?, (ii) which of the models is the best in terms of predictive power and minimum of data needed?—in other words: which soil properties contribute most to explain variations in the available data, (iii) does the addition of a new parameter results in improvement on the percentage of explained variance?, and (iv) can the results of the soil–plant models be improved by the combination of data from the two available datasets (SP an NL), in spite of their different origins and conditions (climate, soils, plant genotypes, agricultural management)?

The following tests were applied for each available combination of vegetable and metal (Fig. 3): (A) the test on the accuracy of the model relations, based on the standard error of the model (significant when less than or equal to 0.5, on a log scale). The significance of the fitted regression for *n* data points was assessed through the *F* test (at 0.05 significance level) and the coefficient of determination (r^2). (B) Comparison of the average explained variance for the combined dataset with the explained variance for the separate datasets (SP and the NL). This comparison gives an indication of the predictive power of the separate and combined datasets and to decide whether the combination of SP dataset and NL dataset is allowed.

To assess the importance of the effects of the available soil properties to explain the data, tests A and B are performed for the models (1) to (4), with three possible outcomes and consequences:

1. When (A) is passed and (B) indicates a higher explained variance for the combined dataset, the combined dataset and the model with the highest explained variance were used.
2. When (A) is passed and (B) does not indicate a higher explained variance for the combined dataset, the dataset for SP or for NL was used, the choice based on the highest *n* or the best standard error of the estimate se(*y*).
3. When (A) is not passed [independent of outcome of (B)], skip modeling efforts. In this case, it was applied a new statistical approach using averages or percentiles of the measured BCF values. The data was stratified in relation to the concentration in soil where possible, i.e., when a sufficient number of data is available (preferably groups of minimal 30 data points), considering the usually large difference in BCF values between low and high soil concentrations.

Results and discussion

Descriptive analysis

In general, SP soil samples presented high fertility because acidity correctives and mineral and organic fertilizers are periodically added to the soil for vegetable crop cultivation. The samples had the following characteristics: 5.7 to 232.5 g kg^{-1} of carbon content, with an average of 25.4 g kg^{-1}; average 80 mmol$_c$ kg^{-1} of effective CEC (CECe); base saturation (V%) ranged between average and high values (18–97%); Al content and Al saturation (m%) very low on average; crystalline iron oxide contents (Fe_{DCB}) varying greatly (0.3 to 81 g kg^{-1}); pH ranging from 3 to 7 (mildly acidic to neutral) with an average of 5; 100–677 g kg^{-1} of clay with an average of 384 g kg^{-1}; and a high sand content ranging between 153 and 805 g kg^{-1} with an average silt content of 156 g kg^{-1} (more discussions in Santos-Araujo and Alleoni 2016).

The mean concentrations of metals in soils of SP were below the intervention values, as prescribed by São Paulo state law (Table 2). Thus, the NL additional dataset was used so as to expand the range of metal concentrations in soils (as explained in "Development of soil–plant transfer empirical models" section). This dataset had mean concentrations of 1.3 mg kg^{-1} of Cd, 40.4 mg kg^{-1} of Cu, 24.3 mg kg^{-1} of Ni, 93.5 mg kg^{-1} of Pb, and 489 mg kg^{-1} of Zn. Table 2 summarizes the distribution characteristics (considering soil physical and chemical properties as well as soil and plant metal concentrations) for the overall dataset and for the separate SP and NL datasets.

It is important to note that, for vegetables, the BCF (plant to soil metal concentration ratio) used for derivation of soil screening values is estimated individually for roots and leaves due to the importance that each of these fractions can represent for human consumption. However, even within leaf and root group vegetables, there may be different plant uptake characteristics, due to genetic variability of the plant species (Dudka and Miller 1999). Some plant species accumulate large amounts of metals, thus being extremely tolerant to a certain contaminant in the soil and others not so much (SWARTJES et al. 2007). Some species of plants can regulate the bioavailability of the metals in the soil (Murray et al. 2009) and reduce the bioavailability of the element in the root zone, which consequently decreases soil–plant relationships (De Vries et al., 2007). The introduction of datasets with different plant species and, thus, with a diverse capacity of metal assimilation can reduce the predictive capacity of the models tested. Luis et al. (2014) concluded that the concentration of macronutrients, micronutrients, and metals (Cd and Pb) in sweet potatoes is influenced by tuber variety, soil type, and agricultural production area. To be able to

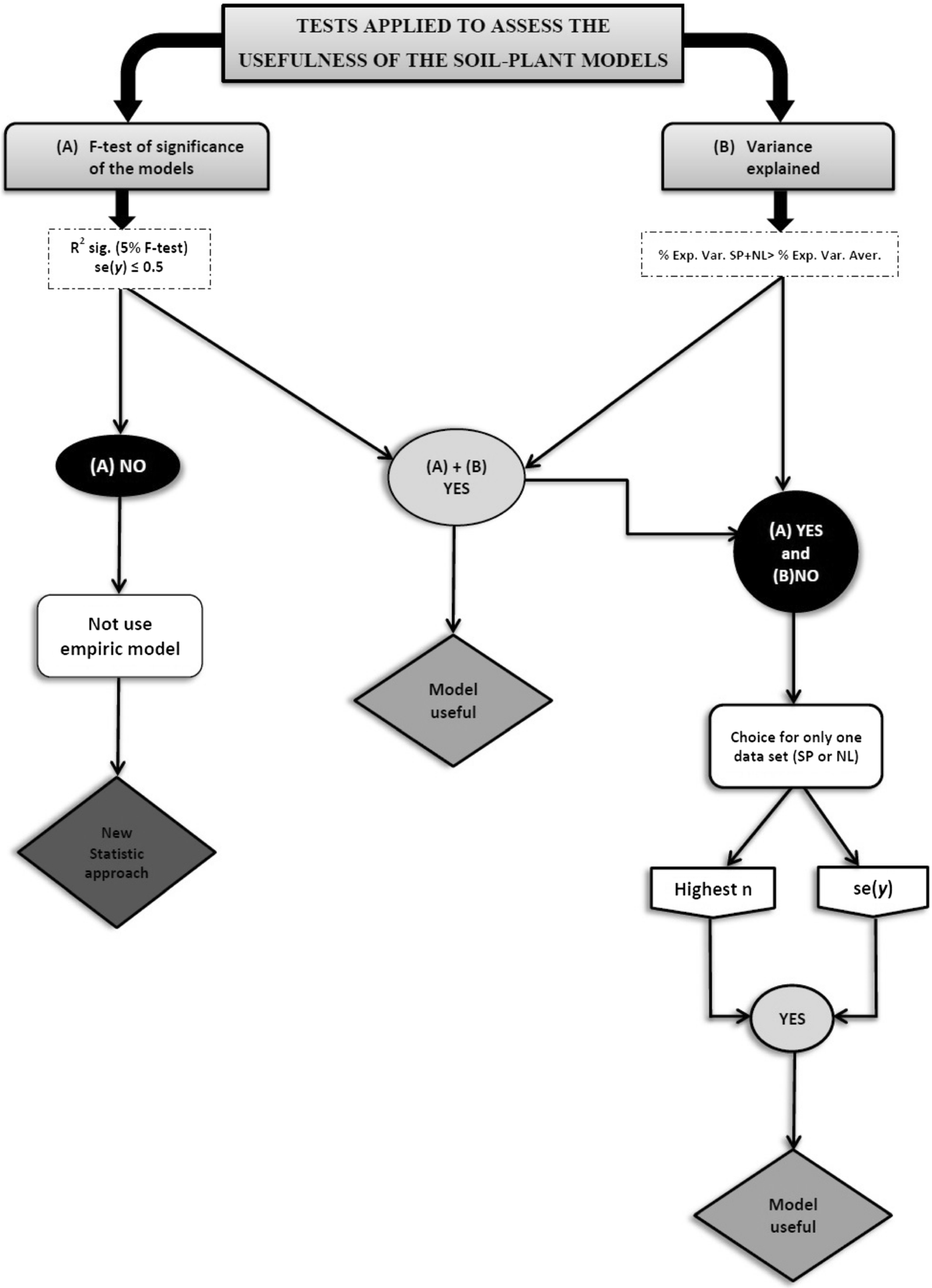

Fig. 3 Schematization of the steps described in "Selection of sites, collection, and analysis of samples" section, choice statistical

investigate the impact of combining SP and NL datasets and because of the large number of paired soil and plant concentrations available, we selected one species of each vegetable group, i.e., lettuce *Lactuca sativa* (leaf vegetables) and carrots *Daucus carota* (root vegetables).

Table 2 Characteristics of the overall dataset (soil and plant concentrations in mg kg^{-1}) for SP and NL datasets for Cd, Cu, Ni, Pb, and Zn

Species	Metal	Parameters	SP + NL dataset Min.	5 Perc.	Median	95 Perc.	Max.	Mean	SD	SP dataset Min.	5 Perc.	Median	95 Perc.
Lettuce	Cd												
		C_{soil}	< LD	0.0	0.6	3.5	12.6	1.2	4.2	< LD	0.1	0.1	0.5
		pH	3.9	5.1	6.5	7.5	8.4	6.4	0.8	3.9	4.7	5.8	6.8
		%OC	0.7	1.6	3.9	12.8	40.1	5.4	4.4	1.0	1.6	3.2	13.2
		%Clay	0.5	3.0	17.0	47.7	67.8	20.3	13.2	10.0	15.1	37.6	57.7
		C_{Veg}	0.1	0.1	0.6	2.6	11.3	0.9	1.0	0.1	0.1	0.1	0.8
	Cu												
		C_{soil}	3.3	6.4	27.0	87.5	356.0	37.4	36.8	3.3	4.8	18.1	98.6
		pH	3.9	4.8	6.1	7.1	8.4	6.1	0.7	3.9	4.7	5.8	6.8
		%OC	0.6	1.0	2.2	6.6	23.3	2.9	2.3	1.0	1.6	3.2	13.2
		%Clay	0.3	0.5	2.2	12.0	35.6	4.2	4.9	10.0	15.1	37.6	57.7
		C_{Veg}	1.6	3.0	7.9	14.1	47.8	8.2	3.9	2.5	2.8	7.5	11.6
	Ni												
		C_{soil}	1.6	2.6	9.8	28.1	46.3	12.4	9.2	1.6	2.4	6.7	19.4
		pH	3.9	4.7	6.0	6.8	7.3	6.0	0.6	3.9	4.7	5.8	6.8
		%OC	1.0	1.7	3.7	12.7	40.1	5.1	4.5	1.0	1.6	3.2	13.2
		%Clay	10.0	12.0	35.2	57.7	67.8	34.5	14.4	10.0	15.1	37.6	57.7
		C_{Veg}	0.1	0.1	0.4	2.3	10.2	0.6	0.9	0.1	0.1	0.3	0.9
	Pb												
		C_{soil}	3.6	11.5	49.1	265.7	548.0	86.8	88.0	3.6	6.7	16.0	65.8
		pH	3.8	4.9	6.8	7.6	7.7	6.6	0.9	3.9	4.7	5.8	6.8
		%OC	0.7	1.3	3.6	14.4	40.1	5.4	4.9	1.0	1.6	3.2	13.2
		%Clay	0.5	1.0	17.0	40.1	67.8	18.3	12.2	10.0	15.1	37.6	57.7
		C_{Veg}	< LD	0.1	1.1	5.2	57.9	1.8	2.8	0.1	0.1	0.2	4.0
	Zn												
		C_{soil}	39.6	69.8	184.5	1041.5	1650.0	333.8	343.4	39.6	65.0	141.3	413.3
		pH	3.6	4.7	6.1	7.1	8.4	6.0	0.8	3.6	4.4	5.5	6.6
		%OC	0.5	1.0	2.8	8.5	29.9	3.6	3.4	1.0	1.6	3.2	13.2
		%Clay	4.0	6.6	13.4	41.0	64.3	17.1	10.7	10.0	15.1	37.6	57.7
		C_{Veg}	8.7	20.1	75.0	220.0	513.4	88.5	66.1	8.7	16.8	49.8	228.9
	Cd												
		C_{soil}	< LD	0.0	0.4	3.2	62.0	1.0	3.1	< LD	0.1	0.0	0.7
		pH	4.4	5.1	6.8	7.5	8.4	6.5	0.8	4.9	4.9	5.6	6.7
		%OC	0.2	0.9	3.2	10.6	12.8	3.9	2.9	1.5	1.5	2.2	11.3
		%Clay	0.5	1.0	11.2	35.4	65.3	12.9	11.9	27.6	27.6	45.2	64.4
		C_{Veg}	0.1	0.1	0.3	1.5	29.5	0.5	1.5	0.1	0.1	0.1	0.3
Carrot	Cu												

Table 2 (continued)

Species	Metal	Parameters	SP + NL dataset Min.	5 Perc.	Median	95 Perc.	Max.	Mean	SD	SP dataset Min.	5 Perc.	Median	95 Perc.
		C_{soil}	6.1	9.9	26.3	108.0	92.0	24.9	21.8	7.4	7.6	17.7	55.3
		pH	4.9	5.0	6.3	8.1	8.4	6.4	5.9	4.9	4.9	5.6	6.7
		%OC	0.9	0.8	1.9	5.9	37.5	3.5	6.6	0.9	0.9	1.3	6.6
		%Clay	0.7	0.8	3.2	12.0	5.8	2.3	1.4	0.7	0.8	1.8	5.5
		C_{Veg}	2.5	2.6	4.8	11.1	356.0	20.8	62.9	2.5	2.9	6.6	12.2
	Ni												
		C_{soil}	2.7	2.6	7.4	26.6	117.7	20.7	22.7	2.7	2.9	6.3	42.1
		pH	4.9	4.7	5.9	6.8	6.8	6.2	0.6	4.9	4.9	5.6	6.7
		%OC	1.5	1.6	3.3	12.1	13.3	4.8	3.0	1.5	1.5	2.2	11.3
		%Clay	12.0	12.0	37.6	57.7	65.3	35.4	17.7	27.6	27.6	45.2	64.4
		C_{Veg}	0.1	0.1	0.3	1.2	7.1	0.7	1.1	0.1	0.1	0.3	0.8
	Pb												
		C_{soil}	1.8	10.2	51.0	265.7	461.0	83.8	91.5	8.6	8.6	14.9	25.7
		pH	3.9	4.8	6.9	7.6	7.7	6.3	0.9	4.9	4.9	5.6	6.7
		%OC	0.2	1.2	4.0	17.4	22.1	5.3	5.3	1.5	1.5	2.2	11.3
		%Clay	0.1	1.0	17.1	43.5	65.3	12.3	11.9	27.6	27.6	45.2	64.4
		C_{Veg}	< LD	0.1	0.7	4.6	4.5	0.6	0.5	0.1	0.1	0.1	3.6
	Zn												
		C_{soil}	40.0	49.2	139.1	1650.0	2035.0	457.6	594.1	53.8	55.1	100.5	252.1
		pH	4.7	4.8	6.2	7.4	8.4	6.1	0.7	4.7	4.8	5.5	6.5
		%OC	0.6	0.8	2.3	5.9	9.2	2.7	1.6	1.2	1.2	2.3	8.1
		%Clay	5.4	5.6	12.0	22.9	27.9	11.5	4.6	5.4	5.5	10.1	25.2
		C_{Veg}	17.0	20.3	39.1	97.6	158.5	45.5	24.4	20.3	20.6	39.8	138.7

Species	Metal	SP dataset Max.	Mean	SD	NL dataset Min.	5 Perc.	Median	95 Perc.	Max.	Mean	SD	*n*
Lettuce	Cd											
		2.4	0.1	0.2	< LD	0.2	0.7	4.0	12.6	1.3	4.6	SP + Holland = 293
		7.3	5.8	0.6	4.7	5.3	6.8	7.5	8.4	6.6	0.7	SP = 36 Holland = 257
		40.1	4.7	5.0	0.7	1.6	4.1	12.8	36.1	5.5	4.3	
		67.8	36.5	13.3	0.5	2.2	16.0	30.0	49.0	15.3	8.3	
		1.7	0.2	0.3	0.1	0.2	0.8	2.8	11.3	1.1	1.1	
	Cu											
		356.0	34.8	43.8	6.0	12.6	30.4	85.5	217.0	39.4	30.4	SP + Holland = 177

Table 2 (continued)

Species	Metal	SP dataset			NL dataset							
		Max.	Mean	SD	Min.	5 Perc.	Median	95 Perc.	Max.	Mean	SD	*n*
		7.3	5.8	0.6	4.7	5.2	6.4	7.2	8.4	6.3	0.7	SP = 39 Holland = 138
		40.1	4.7	5.0	0.7	1.0	2.8	6.1	8.4	3.0	1.7	
		67.8	36.5	13.3	12.0	*	12.0	*	16.3	12.6	1.6	
		17.0	7.4	2.6	1.6	3.2	8.3	14.8	47.8	8.8	4.5	
	Ni											
		30.7	8.1	5.5	12.4	13.2	20.5	45.2	46.3	22.2	8.2	SP + Holland = 101
		7.3	5.8	0.6	5.6	5.6	6.4	6.8	6.8	6.4	0.4	SP = 39 Holland = 62
		40.1	4.7	5.0	2.9	2.9	5.4	12.2	14.4	5.9	3.0	
		67.8	36.5	13.3	12.0	*	12.0	*	16.3	12.6	1.5	
		2.5	0.4	0.3	0.2	0.3	0.8	3.7	10.2	1.2	1.5	
	Pb											
		331.4	23.7	31.5	3.8	15.0	57.0	265.7	548.0	95.4	89.7	SP + Holland = 574
		7.3	5.8	0.6	3.8	5.0	6.9	7.6	7.7	6.7	0.9	SP = 39 Holland = 535
		40.1	4.7	5.0	0.7	1.3	3.7	14.4	28.3	5.5	4.8	
		67.8	36.5	13.3	0.5	1.0	16.0	35.9	39.7	15.8	9.6	
		20.2	1.1	2.3	0.3	0.2	1.2	5.3	57.9	1.9	2.9	
	Zn											
		643.3	174.8	110.2	42.0	78.3	320.0	1469.1	1650.0	454.2	405.8	SP + Holland = 177
		7.2	5.5	0.7	4.7	5.2	6.4	7.2	8.4	6.3	0.7	SP = 39 Holland = 138
		40.1	4.7	5.0	0.7	1.0	2.8	6.1	8.4	3.0	1.7	
		67.8	36.5	13.3	12.0	*	12.0	*	16.3	12.3	1.2	
		513.4	76.2	79.5	19.0	29.7	88.1	202.2	353.0	97.8	52.0	
	Cd											
		1.0	0.1	0.2	< LD	0.1	0.4	3.2	62.0	1.0	3.2	SP + Holland = 240
		6.8	5.8	0.6	4.4	5.1	6.8	7.5	8.4	6.6	0.8	SP = 5 Holland = 235
		12.0	3.2	2.4	0.2	0.9	3.3	10.7	12.8	4.0	3.0	
		65.3	45.3	10.3	0.5	1.0	9.0	26.4	30.6	10.7	8.4	
		0.3	0.1	0.1	0.1	0.1	0.3	1.5	29.5	0.5	1.5	
Carrot	Cu											
		57.6	22.8	13.9	9.0	12.0	29.7	200.7	217.0	43.9	45.2	SP + Holland = 34
		6.8	5.8	0.6	4.7	5.3	6.4	8.1	8.4	6.4	0.8	SP = 5 Holland = 29
		7.0	1.9	1.4	0.6	0.7	2.3	5.8	5.9	2.6	1.5	

Table 2 (continued)

Species	Metal	SP dataset			NL dataset							
		Max.	Mean	SD	Min.	5 Perc.	Median	95 Perc.	Max.	Mean	SD	*n*
		5.8	2.3	1.4	12.0	*	12.0	*	12.0	12.0	0.0	
		12.4	6.7	2.5	2.3	2.5	4.0	8.8	11.3	4.7	1.9	
	Ni											
		52.8	9.5	10.2	13.9	13.9	21.7	117.7	117.7	27.6	25.4	SP + Holland = 26
		6.8	5.8	0.6	5.6	5.6	6.4	6.8	6.8	6.4	0.4	SP = 5 Holland = 21
		12.0	3.2	2.4	2.9	2.9	4.9	12.7	13.3	5.7	2.9	
		65.3	45.3	10.3	12.0	*	12.0	*	12.0	12.0	0.0	
		0.8	0.3	0.2	0.2	0.2	0.5	3.1	7.1	1.0	1.3	
	Pb											
		26.3	15.6	4.7	1.8	9.2	48.3	254.3	461.0	88.1	92.7	SP + Holland = 273
		6.8	5.8	0.6	3.9	4.9	6.5	7.5	7.7	6.4	0.9	SP = 5 Holland = 268
		12.0	3.2	2.4	0.2	0.8	3.1	18.8	22.1	5.4	5.4	
		65.3	45.3	10.3	0.1	1.0	10.3	22.2	31.5	10.2	8.3	
		4.5	0.3	0.9	0.4	0.1	0.5	1.6	3.8	0.6	0.5	
	Zn											
		279.3	114.2	51.3	40.0	47.3	286.5	2035.0	2035.0	623.0	662.7	SP + Holland = 34
		6.6	5.6	0.6	4.7	5.2	6.3	8.1	8.4	6.3	0.7	SP = 5 Holland = 29
		9.2	2.8	1.7	0.6	0.7	2.3	5.9	5.9	2.6	1.6	
		27.9	11.4	5.1	12.0	*	12.0	*	12.0	12.0	0.0	
		158.5	48.2	29.4	17.0	18.8	36.3	87.6	102.2	44.2	21.7	

SD standard deviation, *n* number of observations, *OC* organic carbon, C_{soil} concentration of metal in soil, C_{Veg} concentration of metal in plant, < *LD* limit of detection

For the overall dataset, the soil pH ranged from 3.6 to 8.4 for lettuce and from 4.4 to 8.4 for carrot. The outliers for acidic conditions were observed in the SP dataset whose metals in the soil solution were, possibly, in the form of insoluble precipitates (Mclaughlin 2002), therefore not available for plant absorption while alkaline conditions were found in the NL dataset. This large pH variation may reflect a large variation of the soil metal content, since pH is one of the soil characteristics that has important influence on the dynamics of metals of soil. Cu and Ni, for example, complex more strongly and in greater proportion with organic substances, so its greater mobility occurs only at pH close to 3 (Islam et al. 2000). Zn, on the other hand, increases its mobility under high oxidation conditions in acidic medium. In a neutral, alkaline, and reducing environment, Zn has little mobility. Its main barriers are pH, adsorption by clays, Fe–Mn oxides, and organic matter (Reimann and Caritat 1998). For both vegetables, the average pH values between metals ranged from 5.6 to 6.6.

Most horticultural species develop well at pH values ranging from 6.0 to 6.5. However, these values are relative, especially regarding soil type, organic matter content, and species considered. The pH range was comparable to the range reported by Valarini et al. (2011) for other horticultural soils of São Paulo and by Reis et al. (2009) for European agricultural soils. In general, natural soils of different climatic regions are demonstrably different (Rieuwerts 2007). The pH values, however, can be comparable for humid tropical and temperate agricultural soils, since soil management practices aim at ideal soil properties for agricultural production everywhere in the world.

Values for soil OC content had a large variation in both datasets, ranging from 1 to 40% for lettuce and from 1 to 37% for carrot. High levels of OC were expected because areas cultivated with vegetables generally have a high amount of soil organic matter (SOM). Furthermore, these crops require a considerable supply of nutrients, and SOM provides significant effects on the physical, chemical, and biological properties of the soil. The availability of metals in soils is greatly influenced by soil organic matter and clay contents (Römkens et al. 2009; Rodrigues et al. 2010a). The soil texture ranged from sandy to clayey, with predominantly clayey soils which are preferred by farmers with horticultural activities. The clay content of the soils varied between the datasets (SP—3 to 36% for lettuce and 2 to 45% for carrot; NL—12 to 15% for lettuce and 10 to 12% for carrot). Many tropical soils are highly weathered, and normally, their clay fraction is dominated by 1:1 layer silicates (mainly kaolinite) and iron and aluminum oxyhydroxides, which results in a low cation exchange capacity (Fontes and Alleoni 2006).

The concentrations of the metals ranged widely in both datasets. The NL dataset had substantially higher soil concentrations for all metals and both vegetables studied, with the exception of Cu in lettuce. However, when comparing the average soil concentration, Cu also had a lower average in the SP dataset than in the NL dataset (SP—34.8 and NL—39.4 mg kg^{-1}). This relatively large variation as well as differences between the average concentrations is typical of soils affected by local or regional anthropogenic contamination (Rodrigues et al. 2013; Madrid et al. 2007).

The additional NL dataset introduced a substantial increase in the number of observations for lettuce (293 for Cd, 177 for Cu, 101 for Ni, 574 for Pb, and 177 for Zn) and for carrot (240 for Cd, 34 for Cu, 26 for Ni, 273 for Pb, and 34 for Zn). The number of observations was higher for lettuce, representing the leaf vegetable group for both datasets.

According to the Brazilian National Agency of Sanitary Surveillance (ANVISA 2013b), the allowable limits in edible parts of vegetables are 1.0 mg kg^{-1} for Cd, 30.0 mg kg^{-1} for Cu, 5.0 mg kg^{-1} for Ni, 0.5 mg kg^{-1} for Pb, and 50.0 mg kg^{-1} for Zn (dry weight). Pb and Zn had concentrations in the SP dataset above these limits for lettuce and carrots, with exceedances in 40 and 99% of the collected samples, respectively. As this gives reason for concern, we checked it on another available data source. Guerra et al. (2012) found metal concentrations in edible plant samples collected in the state of São Paulo ranging from 0.01 to 0.18 mg kg^{-1} for Cd, 0.01 to 0.74 mg kg^{-1} for Ni, and 0.02 to 2.50 mg kg^{-1} for Pb and observed that Cd and Ni concentrations did not exceed the permissible limits established by Anvisa. But for Pb, 45% of samples from this study exceeded the allowable limit, which is comparable with the 40% exceedance for Pb that we found.

Evaluation of datasets for development of soil–plant transfer empirical models

Visual interpretation

Graphs of the lettuce and carrot metal concentrations as a function of soil concentration for the SP and NL datasets can be seen in Fig. 4. A wide range of concentrations in vegetables for a specific soil concentration was observed in all cases (Fig. 4). This variation occurred in the SP dataset and in the two other temperate datasets (RIVM and Alterra). The data in the NL datasets, however, were obtained in different areas.

The relationship between the soil and vegetables followed a similar pattern for the NL and SP datasets (Fig. 4). Despite the large variation for Cd in lettuce, the cloud of data points tended to an exponential curve, characterized by a less than linear increase of the concentrations of metals in plants with increased metal concentrations in soil. The SP data were within the low soil concentration range, and the NL soil concentrations varied from low to high. The variation in vegetable concentrations can be largely explained by the variation in soil properties. Cd, like other metals, may participate in ion exchange reactions on the surface of negatively charged clay minerals, but not in acid soils, where the reaction is reversible. Its adsorption often implies pH and may become irreversible. It can also precipitate as insoluble compounds and form of complexes or chelates by the interaction with organic matter (Azevedo and Chasin 2003). For Cd in carrot, however, identification of an exponentially shaped curve was hardly possible. The connection and partial overlap between the datasets may hold, but the two datasets are in different concentration ranges, and there were few data points from the SP dataset.

The difficulty in evaluating the similarities and differences in the soil–plant metal relationships can be observed specially for Cu and Ni in carrot, where uncertainties, (roughly) visible as vertical variations, are dominant over variations in Cu and Ni soil concentrations. The combination of the NL and SP datasets makes this effect even stronger. It remains to be seen if this can be ascribed mainly to the variation in the other soil properties. For Ni, the NL dataset had higher plant concentrations than the SP dataset. This is also the case for lettuce and may possibly originate from different soil properties (which we will check below), but it also may be due to climatic conditions, the methods employed for chemical analyses, etc.

The concentrations of Cu, Ni, Pb, and Zn in lettuce also have the wide variation in accumulated concentrations in vegetables at similar soil concentrations between the datasets as well as within the same dataset as main features. An overlap of data clouds formed by the data of the different datasets was observed, with the exception of Ni. Moreover, the accumulated concentrations in vegetables appear to increase as a function of soil metal concentrations at the higher range. This was important in this study because if the variation in concentrations in plants at a given metal concentration in soil is equal or larger than the range in metal concentrations in plants across the metal concentration in soil, this would mean that there is no functional relationship between concentrations in soil and plant.

Fig. 4 Scatterplots of the vegetable concentration as a function of soil concentration for metals of the two datasets (SP and NL). The vertical lines represent the intervention values for the rural, urban, and industrial exposure scenario, respectively, envisaged in the legislation of the state of São Paulo, Brazil

A few other factors may be responsible for the concentration of metals in plants, apart from their levels in the soil. Some of such factors may be the specific form in which the metal exists in the pore water, or even the genetic variability of the plant, while an effect of climatic conditions is also possible. On the basis of the visual inspection, we can conclude that some of the data of SP and NL overlap and connect and that differences between the climate zones are less detectable due to intrinsic variations in the measurements. In spite of the handicap of using data from different climate zones, a number of conclusions could be drawn, and the limitations of the results regarding the pursued certainties will be discussed.

Evaluation of soil–plant transfer empirical models

Equations 1 to 4 ("Development of soil–plant transfer empirical models" section), for all 10 combinations of metal (Cd, Cu, Ni, Pb, and Zn) and vegetable (lettuce and carrot), are evaluated. Regression coefficients of the soil–plant relationships are presented in Table 3, and the significance of the models was investigated on the basis of an F test (one-sided exceeding probability, $\alpha = 0.05$).

Significant soil–plant correlations were found for Cd in lettuce and carrot in all models studied, but the goodness of fit as indicated by the coefficient of determination (r^2) was limited, ranging from 0.35 to 0.47 in lettuce and from 0.33 to 0.45 in carrot. In a similar study, Versluijs and Otte, 2001reported that correlation coefficients of the derived soil–plant relationships are generally low. Equation 4 (for Cd) had the highest r^2 (0.47 for lettuce and 0.45 for carrot) and the lowest standard error (se(y) 0.32 for lettuce and 0.29 for carrot). For

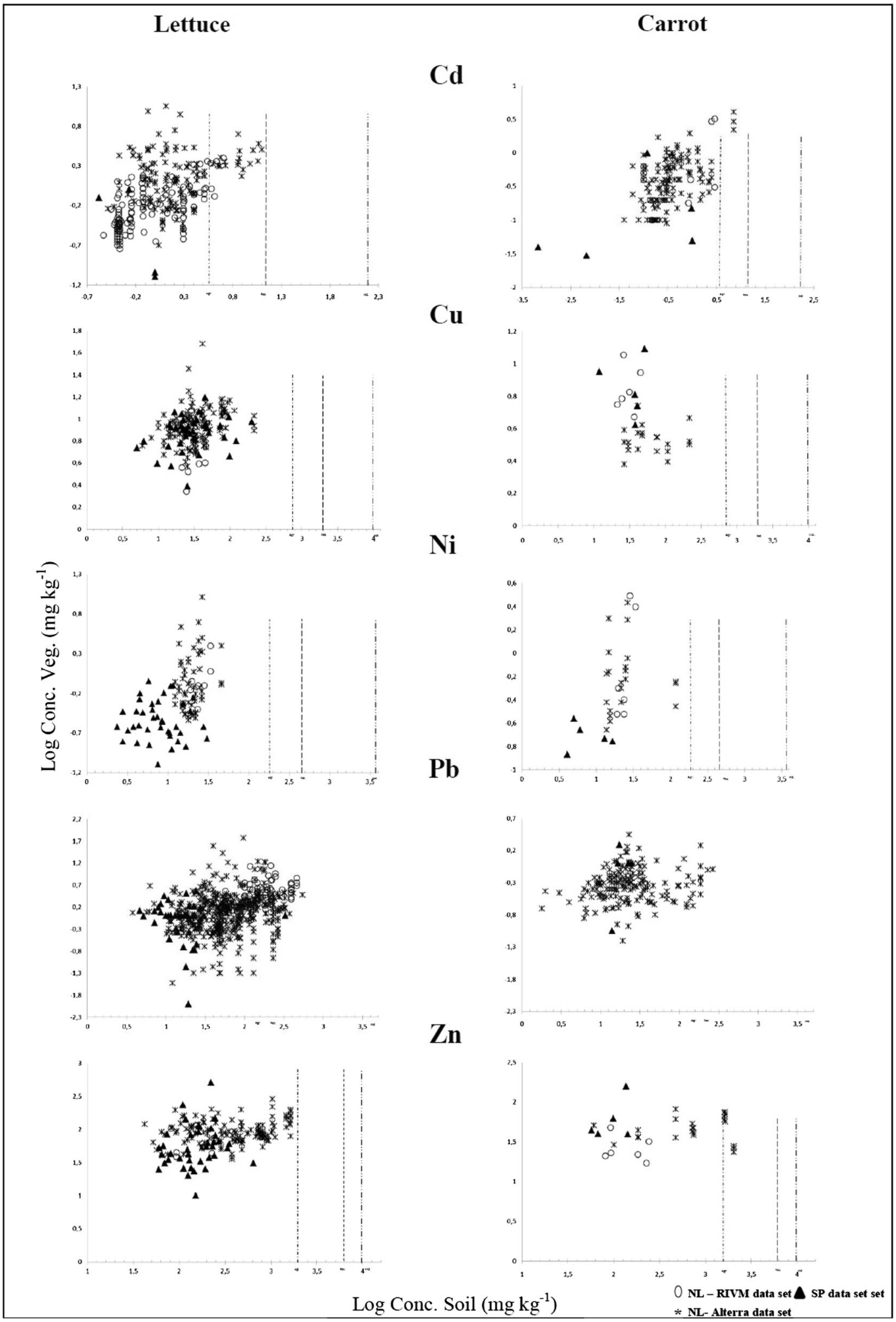
Lettuce
Carrot
Cd
Cu
Ni
Pb
Zn
Log Conc. Veg. (mg kg-1)
Log Conc. Soil (mg kg-1)
NL – RIVM data set
SP data set set
NL- Alterra data set

Table 3 Regression coefficients of the soil–plant relations for Cd, Cu, Ni, Pb, and Zn (dataset combined), according to Eqs. 1–4 for lettuce and carrots

	Lettuce										Carrot								
Metal	Model	a Const.	b C_{soil}	c pH	d %OC	e %Clay	r^2	F	*se* (*Y-est*)	*n*	a Const.	b C_{soil}	c pH	d %OC	e %Clay	r^2	F	*se* (*Y-est*)	*n*
Cd	1	− 0.06	0.39	*	*	*	0.35	196.04	0.35	293	− 0.19	0.46	*	*	*	0.33	119.29	0.31	238
	2	1.1	0.44	− 0.18	*	*	0.42	131.37	0.33		0.89	0.42	− 0.17	*	*	0.45	96.94	0.29	
	3	1.35	0.48	− 0.18	− 0.28	*	0.44	97.61	0.33		0.9	0.42	− 0.17	− 0.01	*	0.45	64.37	0.29	
	4	1.11	0.39	− 0.14	− 0.22	− 0.14	0.47	81.38	0.32		0.92	0.43	− 0.18	− 0.01	0.04	0.45	48.44	0.29	
Cu	1	0.65	0.17	*	*	*	*0.10**	19.59	0.16	177	1.01	− 0.23	*	*	*	*0.16**	6.89	0.16	36
	2	0.62	0.17	0.01	*	*	0.12	9.82	0.16		0.63	− 0.28	0.07	*	*	*0.25**	5.92	0.16	
	3	0.61	0.17	0.01	− 0.01	*	0.14	6.51	0.16		0.61	− 0.27	0.08	− 0.03	*	*0.25**	3.85	0.16	
	4	0.57	0.21	0.01	− 0.04	− 0.08	0.15	5.79	0.16		1.05	− 0.06	− 0.07	0.07	0.36	0.52	8.99	0.13	
Ni	1	− 1.02	0.67	*	*	*	0.24	31.39	0.34	101	− 0.8	0.4	*	*	*	*0.13**	4.47	0.34	30
	2	− 0.85	0.71	− 0.03	*	*	0.24	15.69	0.34		0.05	0.5	− 0.15	*	*	*0.15**	2.58	0.34	
	3	− 0.86	0.72	− 0.03	− 0.03	*	0.24	10.37	0.34		0.13	0.51	− 0.16	− 0.1	*	*0.15**	1.7	0.35	
	4	− 0.13	0.43	− 0.05	− 0.25	− 0.25	0.4	14.21	0.31		− 0.24	0.21	0.01	− 0.41	− 0.21	*0.22**	1.94	0.34	
Pb	1	− 0.41	0.28	*	*	*	0.07	41.52	0.43	557	− 0.48	0.1	*	*	*	*0.02**	3.78	0.27	171
	2	− 0.02	0.31	− 0.07	*	*	0.08	25.8	0.42		− 0.28	0.09	− 0.03	*	*	*0.03**	2.64	0.26	
	3	− 0.06	0.26	− 0.06	0.11	*	0.09	18.36	0.42		− 0.24	0.15	− 0.04	− 0.17	*	*0.04**	2.61	0.26	
	4	− 0.11	0.29	− 0.04	0.11	− 0.12	0.1	15.37	0.42		− 0.39	0.22	− 0.03	− 0.14	− 0.13	*0.08**	3.55	0.26	
Zn	1	1.45	0.19	*	*	*	*0.10**	20.38	0.22	177	1.46	0.07	*	*	*	*0.03**	1.05	0.2	32
	2	1.5	0.19	− 0.01	*	*	*0.11**	10.25	0.22		2.28	0.08	− 0.13	*	*	*0.27**	5.75	0.18	
	3	1.65	0.11	− 0.02	0.24	*	0.15	10.38	0.22		2.29	− 0.09	− 0.11	0.64	*	0.68	21.71	0.12	
	4	2.3	− 0.05	− 0.07	0.44	− 0.24	0.35	23.04	0.19		2.29	0.21	0.06	− 0.74	− 0.13	0.71	17.79	0.12	

se (Y-est) standard error of the estimate

*Not significant for F test ($p > 0.05$)

the Cu/lettuce combination, the r^2 was very low for all equations. For the Cu/carrot combination, only Eq. 4 was significant with r^2 of 0.52 and se(y) of 0.13, showing that the clay content was an influential variable in relation to the other parameters. Soil texture affects metal availability to vegetables as finer textured soils (clays) have a greater cation exchange capacity (CEC) and hence a greater ability to retain cationic metals (higher coefficient of distribution—Kd) compared to sandy soils. Given the same total metal concentration in soil, clay-rich soils will produce crops with lower (cationic) metal concentrations.

For Ni and Pb in lettuce, all equations were significant, but for Pb in lettuce, the r^2 was low, ranging from 0.07 to 0.1. Pb uptake from soil is biased from lead uptake from the air, since Pb values were low in soil but high in crops, thus resulting in low r^2 values. For carrot, no significant soil–plant equations were found for the two metals, that is, the predictive power of the equations for carrot was nil, precluding the use of BCFs for the derivation of the screening values. In the case of Zn in lettuce and carrot, Eqs. 1 and 2 were not significant. For lettuce and carrot, Eq. 4 gave the best r^2 of 0.35 and 0.71, respectively, and $se(y)$ of 0.12 and 0.19, respectively.

This significance of the soil–plant models or equations of regression indicated which of the tested models had the ability to predict the accumulated concentration in vegetables as a function of the total soil concentration and the soil properties. With the purpose to evaluate if the combination of the SP and the NL datasets is useful, the average explained variance of the combined dataset was compared with that of the separate datasets (SP and NL; Table 4).

Generally, the explained variance is expected to increase with the increase of the number of explaining parameters, and this holds in all cases. For some combinations of metal and vegetable, the improvement is marginal, whereas in other cases, the addition of a specific parameter significantly improves the equation. The explained variance of the combined dataset was higher than the average explained variance of the separate datasets for all four equations. This indicates the hypothesis that the combination of datasets was useful for the prediction of the concentration of lettuce in Cd. The same behavior was observed for Ni in lettuce in which the explained variance for the combined datasets (Eq. 4) was 37%. For the other cases, the combination of datasets was not always successful.

For Cd in carrot, the observation was slightly different. The average explained variance of the separate datasets (29–47%) was slightly higher than the explained variance of the combined dataset (33–45%). However, since the variances are in the same order of magnitude, the combination of datasets could be beneficial compared to using the SP dataset alone. On closer view, this does not always give a substantial improvement. For Cu in carrot, for Pb in lettuce and carrot, and for Zn in lettuce, it was observed that the average explained variance for the separate datasets (71, 12, 18, and 50%, respectively) was clearly higher that the explained variance of the combined dataset (52, 10, 7, and 35%, respectively). The two datasets cannot be combined because they differ inherently, probably due to different water regimes, temperatures, and evaporation rates.

Cu in lettuce had a higher explained variance for the combined dataset than the average of the explained variance for the separate datasets, only in the case of Eqs. 1 and 2. However, the percentage explained was very low, and there was an improvement with the addition of pH (10%). For Zn in carrot, the combined dataset can be used only for Eqs. 3 and 4, with 71% of explained variance for Eq. 4, with OC content and clay being the variables with major influence.

The best model was selected with the evaluation of the results presented. To this purpose, the following choices were investigated: (i) the use of the combined or a separate dataset, (ii) the type of model (Eqs. 1 to 4), or (iii) the use of a numerical interpretation of measured BCF values (Supplementary material 1).

We chose to use the combined datasets and Eq. 4 for Cd in lettuce and for Ni and Zn in lettuce and in carrot, which includes the largest number of soil properties (pH, OC content, and clay content) with the highest r^2 and a higher explained variance compared with other equations. The criterion (B) ("Development of soil–plant transfer empirical models" section) has not been met for Cd and Cu in carrot and Cu, Pb, and Zn in lettuce, thus excluding the possibility of using the combined datasets. Here still remains the use of one of the separate datasets. Ideally, the SP dataset should be chosen because it coincides with the conditions of SP. While for each case the models were significant, the SP dataset contains a relatively small number of valid samples (values above of the detection limit), including many outliers, therefore increasing the standard error and the noise of the dataset (variations in the data, due to explaining parameters not considered in the model, were

Table 4 Percentage of the explained variance for Cd, Cu, Ni, Pb, and Zn, for lettuce and carrots

		Lettuce								Carrot							
Metal	Model	Explained variance			df			(Weighted) average	Test[a]	Explained variance			df			(Weighted) average	Test[a]
		SP + NL	NL	SP	SP + NL	NL	SP	%		SP + NL	NL	SP	SP + NL	NL	SP	%	
		%								%							
Cd	Eq. 1	34.7	13.5	3.2	369	330	37	12	True	33.4	29.4	2.1	238	233	3	29	True
	Eq. 2	41.7	31.8	11.0	368	329	36	30	True	45.0	46.1	10.2	237	232	2	46	False
	Eq. 3	44.4	37.3	11.2	367	328	35	35	True	45.0	46.1	98.7	236	231	1	46	False
	Eq. 4	47.1	37.8	11.2	366	327	34	35	True	45.2	47.4	100.0	235	230	1	47	False
Cu	Eq. 1	10.0	9.4	6.0	177	135	37	9	True	16.1	10.4	1.9	36	25	3	10	True
	Eq. 2	10.0	9.8	8.5	176	134	36	9	True	25.3	42.4	49.1	35	24	2	43	False
	Eq. 3	10.0	13.3	10.1	175	133	35	13	False	25.4	51.1	59.8	34	23	1	51	False
	Eq. 4	11.8	14.9	10.1	174	132	35	14	False	52.1	71.5	59.8	33	22	1	71	False
Ni	Eq. 1	24.1	6.9	0.1	99	60	37	4	True	13.0	0.8	0.6	30	25	3	1	True
	Eq. 2	24.2	6.9	21.8	98	59	36	13	True	15.1	1.7	69.0	29	24	2	7	True
	Eq. 3	24.3	7.2	24.8	97	58	35	14	True	15.4	3.6	69.1	28	23	1	6	True
	Eq. 4	37.2	7.4	27.0	96	57	34	15	True	22.3	7.1	100.0	27	22	1	7	True
Pb	Eq. 1	6.9	8.9	1.1	557	540	37	8	False	2.2	2.4	33.5	171	166	3	3	False
	Eq. 2	8.5	10.9	5.6	556	539	36	11	False	3.0	3.8	92.8	170	165	2	5	False
	Eq. 3	9.0	11.6	5.8	555	538	35	11	False	4.4	7.0	94.2	169	164	1	8	False
	Eq. 4	10.0	12.6	6.2	554	537	34	12	False	7.8	17.5	100.0	168	163	1	18	False
Zn	Eq. 1	10.4	5.7	2.8	175	136	37	5	True	3.2	15.2	24.9	32	27	3	16	False
	Eq. 2	10.5	34.3	30.6	174	135	36	33	False	27.1	42.8	88.4	31	26	2	46	False
	Eq. 3	15.3	35.5	100.0	173	134	35	49	False	68.5	64.5	100.0	30	25	1	66	True
	Eq. 4	34.9	36.3	100.0	172	133	35	50	False	71.0	66.0	100.0	29	24	1	67	True

df degree of freedom

[a] %Exp. var. SP + NL > %ave. exp. var. for separated dataset (reported in section 2.3.4 (B))

considered here as noise) for statistical analysis. Therefore, we decided to select the NL dataset (Eq. 4), which has considerably more samples with representative concentrations of these metals in soil and plants valid in the expected range of the screening values. In other words, we preferred a larger number of data in the relevant concentration range over a limited number of data measured under representative soil, vegetable, and climatic conditions. The coefficients of the soil–plant relationships determined by multiple linear regressions from the selected datasets for each metal and both vegetables are shown in Table 5.

Based on the selected coefficients for Cd in lettuce, the OC content had the highest impact on the concentration in vegetables as compared to the clay content. For Cd uptake in carrot, however, the OC coefficient was not significant. Efroymson et al. (2001), McBride (2002), Li et al. (2003), Adams et al. (2004), Römkens et al. (2009), and Melo et al. (2011) have shown that Cd uptake by different vegetables can be predicted by taking into account soil properties, and all of them included pH as a predictor. In this study, in agreement with former findings, pH was a significant soil property to predict Cd uptake. For Cd in lettuce, however, the OC content had greater impact than the pH.

The heterogeneous distribution of Cd in the soil increases the variability in plant uptake (Millis et al. 2004). Contrary to other studies, we have investigated two different datasets (NL and SP), which have similarities regarding Cd uptake, but greater variability because of individual plant uptake characteristics. Nevertheless, the soil–plant relationships were significant. Empirical models selected for Cu and Zn in lettuce also expressed the role of OC in the retention of the metals by the soil solid phase, thereby reducing the plant availability. This was also observed in other studies reporting that organic matter has a dominant role in the partitioning of metals in soils (Groenenberg et al. 2010). For the clay content, the sign of the regression coefficients was positive, contrary to what was expected. This positive relation cannot be explained with general knowledge on the influence of clay on availability and, hence, on plant uptake. For Cu in carrot and Ni and Pb in lettuce, the OC and clay contents had a greater impact in reducing the availability for plant uptake (clay content had the highest impact only for Cu in carrot and Pb in lettuce). For Zn in carrot, the regression coefficient was not significant for pH, and the OC content had the greatest impact in reducing the availability of Zn for plant uptake.

In general, the performance of the selected soil–plant transfer models (as indicated by the r^2 and the standard error values) was quite good, for both crops, except for Cu (r^2 0.15) and Pb (r^2 0.13) in lettuce. The poor quality

Table 5 Coefficients of the soil–plant relations determined by multiple linear regressions from the selected dataset

Metal	Vegetable type	Soil–plant relationship	r^2	*se* (*Y*-est)	Number
Cd	Lettuce	Log [Cd veg] = 1.11 + 0.39∗∗ log [Cd soil] − 0.14∗∗ pH soil − 0.22∗∗ log [OC] − 0.14∗∗ log [clay]	0.50	0.32	366
	Carrot	Log [Cd veg] = 0.90 + 0.41∗ log [Cd soil] − 0.18∗ pH soil + 0.04 log [OC] + 0.11∗ log [clay]	0.50	0.27	230
Cu	Lettuce	Log [Cu veg] = 0.72 + 0.33∗ log [Cu soil] − 0.04∗ pH soil − 0.15∗∗ log [OC] + 0.11∗∗ log [clay]	0.15	0.15	132
	Carrot	Log [Cu veg] = 0.67 + 0.04∗∗ log [Cu soil] − 0.04∗∗ pH soil − 0.28∗∗ log [OC] − 0.34∗ log [clay]	0.72	0.09	22
Ni	Lettuce	Log [Ni veg] = − 0.13 + 0.43∗ log [Ni soil] − 0.05∗ pH soil − 0.25∗∗ log [OC] − 0.25∗ log [clay]	0.40	0.31	96
Pb	Lettuce	Log [Pb veg] = − 0.20 + 0.36∗ log [Pb soil] − 0.04∗∗ pH soil − 0.12∗ log [OC] − 0.15∗ log [clay]	0.13	0.42	537
Zn	Lettuce	Log [Zn veg] = 2.36 + 0.28∗ log [Zn soil] − 0.17∗ pH soil − 0.13∗∗ log [OC] + 0.09∗∗ log [clay]	0.36	0.14	133
	Carrot	Log [Zn veg] = 2.29 + 0.21∗∗ log [Zn soil] + 0.06 pH soil − 0.74∗∗ log [OC] − 0.13∗ log [clay]	0.71	0.12	29

se (*Y-est*) standard error of the estimate

∗∗Significant coefficients at $p < 0.01$

∗Significant coefficients at $p < 0.05$

Table 6 BCF values for Cd, Cu, Ni, Pb, and Zn for different exposure scenarios (rural, urban, and industrial, each with set values for clay and OC content) and different pH values (5.0–6.0), obtained from the soil–plant relations selected, compared with the BCF values currently used as basis for the intervention values in SP and NL, based on geometric means

		BCF											
		Rural				Urban				Industrial			
		Lettuce		Carrot		Lettuce		Carrot		Lettuce		Carrot	
Metal	UCL	pH 5.0	pH 6.0	pH 5.0	pH 6.0	pH 5.0	pH 6.0	pH 5.0	pH 6.0	pH 5.0	pH 6.0	pH 5.0	pH 6.0
Cd	Mean	0.653	0.473	0.652	0.427	0.286	0.207	0.291	0.191	0.065	0.047	0.068	0.045
	P50	1.326	1.012	1.266	0.864	0.604	0.461	0.598	0.409	0.147	0.113	0.156	0.107
	P70	1.687	1.302	1.595	1.099	0.774	0.597	0.763	0.525	0.191	0.148	0.203	0.140
	P80	1.932	1.498	1.818	1.258	0.890	0.690	0.874	0.605	0.221	0.171	0.235	0.162
	P90	2.295	1.789	2.148	1.494	1.061	0.826	1.039	0.722	0.266	0.207	0.282	0.196
	Cetesb[a]	0.370		0.159		0.370		0.159		0.370		0.159	
	CSOIL[b]	0.367		0.073		0.367		0.073		0.367		0.073	
Cu	Mean	0.007	0.007	0.011	0.011	0.003	0.003	0.004	0.004	0.001	0.001	0.001	0.001
	P50	0.024	0.023	0.070	0.161	0.009	0.009	0.027	0.062	0.002	0.002	0.006	0.014
	P70	0.032	0.032	0.102	0.105	0.013	0.013	0.039	0.040	0.003	0.003	0.009	0.009
	P80	0.038	0.038	0.124	0.128	0.016	0.015	0.047	0.049	0.004	0.004	0.011	0.011
	P90	0.047	0.046	0.155	0.161	0.019	0.019	0.060	0.062	0.005	0.005	0.014	0.014
	Cetesb[a]	0.100		0.100		0.100		0.100		0.100		0.100	
	CSsoil[b]	0.297		0.156		0.297		0.156		0.297		0.156	
Ni	Mean	0.008	0.007	–		0.005	0.004	–		0.002	0.001	–	
	P50	0.090	0.220	–		0.061	0.150	–		0.026	0.064	–	
	P70	0.135	0.142	–		0.091	0.096	–		0.039	0.041	–	
	P80	0.164	0.173	–		0.112	0.118	–		0.047	0.050	–	
	P90	0.209	0.220	–		0.142	0.150	–		0.060	0.064	–	
	Cetesb[a]	0.100		0.070		0.100		0.070		0.100		0.070	
	CSOIL[b]	0.056		0.0145		0.056		0.0145		0.056		0.0145	
Pb	Mean	0.012	0.011	0.010	0.010	0.009	0.008	0.010	0.010	0.001	0.001	0.010	0.010
	P50	0.033	0.032	0.007	0.007	0.025	0.024	0.007	0.007	0.004	0.004	0.007	0.007
	P70	0.044	0.043	0.011	0.011	0.033	0.032	0.011	0.011	0.006	0.006	0.011	0.011
	P80	0.051	0.050	0.012	0.012	0.039	0.038	0.012	0.012	0.007	0.007	0.012	0.012
	P90	0.062	0.061	0.017	0.017	0.047	0.047	0.017	0.017	0.009	0.009	0.017	0.017
	Cetesb[a]	0.003		0.001		0.003		0.001		0.003		0.001	
	CSOIL[b]	0.044		0.002		0.044		0.002		0.044		0.002	
Zn	Mean	0.173	0.118	0.012	0.011	0.068	0.046	0.003	0.002	0.052	0.036	0.002	0.001
	P50	0.504	0.359	0.137	0.318	0.212	0.151	0.034	0.079	0.167	0.119	0.023	0.054
	P70	0.682	0.488	0.205	0.204	0.289	0.207	0.051	0.051	0.229	0.164	0.035	0.035
	P80	0.802	0.576	0.250	0.250	0.342	0.245	0.062	0.062	0.271	0.194	0.043	0.042
	P90	0.980	0.706	0.317	0.318	0.419	0.302	0.079	0.079	0.332	0.239	0.054	0.054
	Cetesb[a]	0.400		0.100		0.400		0.100		0.400		0.100	
	CSOIL[b]	0.359		0.031		0.359		0.031		0.359		0.031	

The indicated means and *x*-percentile upper values relate to the variation in experimental data (where *x*% is the probability that a value found may exceed the given BCF value). Higher certainties however result in lower screening values

[a] BCF values currently used as basis for the intervention values in SP for Environmental Agency of São Paulo State (Cetesb mathematical model)

[b] BCF values currently used as basis for the intervention values in the Netherlands (CSOIL mathematical model)

of the abovementioned models may be due to the fact that the range of levels in soil was relatively narrow, which hampers the clear evaluation of the impact of soil screening values on metal levels in vegetables (not clear). None of the equations derived from the SP, NL, or NL + SP datasets were significant for Ni and Pb in carrot. Therefore, we chose a statistical approach using measured BCF values. This conclusion can be explained by several factors, i.e., the range of soil types was extensive with different origins and mineralogy and distinct land management practices, which results in a large amount of noise in the datasets that may influence the predictive ability of the models (Römkens et al. 2004).

With the purpose to account for the usually large difference in BCF values between low and high soil concentrations, the data was stratified according to soil concentrations. For Pb in carrot, the data was stratified in six groups of 30 data points, whereas for Ni in carrot, the data was stratified in three groups, also of 30 data points. By using this approach, the BCF values for Ni were extremely different at low and high concentrations, indicating a high uncertainty. Therefore, this BCF value was disregarded (Supplementary material 2).

For Cd and Pb, which are particularly important elements by their impact on human health, the model performance can be improved in the future, by additional research that creates appropriate datasets representing a wider range of soil properties and contaminant levels in São Paulo state and Brazil in general. By taking into account soil properties and a more refined concept of chemical availability rather than using the pseudototal metal content, this study provides relevant improvements when compared to soil–plant relationships previously derived for Brazilian soils (Melo et al. 2011). Aside from plant-specific properties, pH and OC content, but also clay content, influenced metal uptake in vegetables. This means that BCFs derivated from a constant relation between concentration in soil and plant are not suitable to assess the transfer of metals such as Cd, Cu, Ni, Pb, and Zn.

BCF values

BCF values for Cd, Cu, Ni, Pb, and Zn from rural, urban, and industrial land uses, which differ in soil properties and soil metal concentration, were obtained from the soil–plant relationships selected, as shown in Table 6. The BCF values were calculated for two different pH values (5 and 6) to demonstrate their influence as well as the soil metal content on this index. These pH values were chosen because they are compatible to most rural or urban soils at the state of São Paulo, Brazil. Mean values and different percentiles are also given. The BCF values used to derive the intervention values in the São Paulo state (Cetesb model) and in the Netherlands (CSOIL model) are also shown. The BCF values in both models are based on Otte et al. (2001), who distinguished leaf and root vegetables, based on data obtained from soil and vegetables grown in temperate zones.

Some countries have derived soil screening values for metals as a function of pH in their legislations (DEFRA and Environment Agency 2002). In this study, the pH did not have a high contribution to the BCF values for metals, except for Cd. For this metal, BCF values were higher at pH 5 than pH 6 for lettuce and carrot for both land uses (Table 6). Among the soil properties, pH is the most important in controlling Cd availability and uptake by vegetables (Anderson, 1988; Peijnenburg et al. 2000; Mcbride 2002; Golia et al. 2008). Cd, Cu, and Pb BCFs in lettuce and carrots were in the same order of magnitude, with the exception of Zn, for which the BCF was higher in lettuce than in carrot.

Differences between exposure scenarios were observed. BCFs for the industrial exposure scenario were three to four times lower than BCFs for urban exposure scenario, and BCFs for rural exposure scenario were two times higher than BCFs in urban exposure scenario, for all metals. The same behavior was observed in BCFs exhibited by their different percentiles.

The 70, 80, and 90 percentiles of the BCFs, which are more conservative, not only give more protection but also lead to more false positives and a higher remediation load (higher BCF leading to lower screening values for the same maximum human risk/uptake level). The balance between protection level and level of protection imposed is a policy issue. The 80 and 90 percentiles of the BCF may be overestimated since BCF values most often decrease when soil concentrations increase, and thus, these BCFs incline to be based upon an assumption of independence between the concentration in soil and plant uptake (Dudka and Miller 1999; Samsoe-Petersen et al. 2002; Gaw et al. 2008). This is an additional reason to make a choice for less strict percentile values and to accept the inevitably connected lower certainty to avoid possible higher risks than anticipated. Percentile 80 and

90 are more conservative values and are therefore safer as precaution for soil metal concentrations linked to contamination. However, this approach is important in order to present options for environmental monitoring companies assisting in the decision-making, since the derivation of soil screening values includes both scientific knowledge and policy decisions (Swartjes et al. 2007).

Finally, we propose new BCF values for three exposure scenarios at pH 5 and 6, for Cd, Cu, Ni, Pb, and Zn in lettuce and for Cd, Cu, Pb, and Zn in carrot, which were presented as mean values and their respective percentiles. This compares to only one BCF value for each group of vegetables (leaf and root) used currently as the basis for the intervention values in SP (model Cetesb). The application of soil–plant models and the BCFs proposed in this study are useful to derive national soil quality criteria. However, this methodological approach includes data assessed under different climatic conditions and soil types, and this needs to be carefully considered.

Conclusions

- The application of soil–plant transfer models derived in this study had an acceptable performance for 8 out of the 10 combinations (five metals × two vegetable groups). This offers improved possibilities for the derivation of more appropriate screening values for the state of São Paulo, Brazil.
- SP data can be combined with the NL data using a model including pH, OC, and clay content for Cd and Ni in lettuce (representing the leaf vegetable group) and for Zn in carrot (representing the root group); the best models resulted when SP and NL datasets were combined for Cu, Pb, and Zn in lettuce and for Cd and Cu in carrot.
- For two cases (Ni and Pb in carrot), the use of the models was inconsistent, and the combination of datasets did not (or insufficiently) improve the results. For these cases, representative BCF values were derived from measured individual BCFs.
- It is recommended to collect more appropriate data by measuring combined soil and vegetable data in Brazil (or in other tropical regions) in areas subjected to sources of pollution, so that consistent soil–plant relationships for these areas could be developed.

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