University of São Paulo
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Soil-to-plant transfer of heavy metals and an assessment of human health risks in vegetable-producing areas of São Paulo state

Sabrina Novaes dos Santos-Araujo

Thesis presented to obtain the degree of Doctor in Science.Area: Soils and Plant Nutrition

Piracicaba
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Sabrina Novaes dos Santos-Araujo
Agronomist

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Adviser:
Prof. Dr. **LUÍS REYNALDO FERRACCIÚ ALLEONI**

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CONTENT

RESUMO

Transferência solo-planta de metais pesados e avaliação de risco à saúde humana em áreas olerícolas do estado de São Paulo

Uma das principais vias de exposição de elementos potencialmente tóxicos (EPT) para a maioria da população é por meio da ingestão de alimentos, mas poucos são os estudos relacionados às concentrações de EPTs em solos e em vegetais de regiões tropicais úmidas, sobretudo no Brasil. O índice mais comumente utilizado para estimar o acúmulo de EPTs em vegetais e a subsequente exposição humana pelo consumo de vegetais é o fator de bioconcentração (BCF), que é a razão entre a concentração de metais em partes comestíveis de hortaliças e da concentração total do metal no solo. Porém, o BCF não descreve adequadamente a transferência solo-planta de metais. Assim, a utilização de relações envolvendo os principais atributos dos solos que influenciam a disponibilidade dos EPTs às plantas pode explicar com mais detalhe as relações solo-planta. O estado de São Paulo é o maior mercado consumidor, além de ser o maior e mais diversificado produtor olerícola no Brasil. Assim, são necessárias pesquisas referentes às concentrações de metais pesados em solos e hortaliças, para avaliação da qualidade dos mesmos em relação aos limites estabelecidos pela legislação. Os objetivos neste trabalho foram: (i) caracterizar e avaliar as relações solo-planta entre as concentrações de Cd, Cu, Ni, Pb e Zn em solos e olerícolas de folhas e raiz no estado de São Paulo, tendo em vista os limites estabelecidos pela legislação; (ii) desenvolver modelos empíricos para poder derivar adequados limites críticos do solo e fornecer uma avaliação de risco precisa para regiões tropicais; (iii) desenvolver propostas para melhorar os limites críticos baseados na saúde humana para Cd, Cu, Ni, Pb e Zn em solos de São Paulo, utilizando relações solo-planta adequadas para as condições tropicais. Com exceção do Cd, houve correlação positiva entre os teores pseudototais e biodisponíveis dos EPTs. Os teores de Cd e de Pb nas plantas, por outro lado, não correlacionaram significativamente com nenhuma das variáveis estudadas. Os modelos de florestas aleatórias e árvores foram bons preditores de resultados gerados a partir de um modelo de regressão e forneceram informações úteis sobre quais covariáveis foram importantes para previsão apenas para o teor de Zn na planta. A aplicação de modelos de transferência solo-planta proposto neste estudo tiveram bom desempenho e foram úteis para oito das dez combinações (cinco metais contra duas espécies). O conjunto de resultados de SP pode ser combinado com o da Holanda usando o modelo em que se incluem pH, teor de carbono orgânico - CO e teor de argila para Cd em alface e para Ni e Zn na alface e na cenoura. O modelo foi mais eficiente com os conjunto de resultados combinados para Cu, Pb, Zn, em alface e para Cd e Cu na cenoura. A abordagem não foi eficiente para Ni e para Pb em cenoura, com resultados incoerentes para os conjuntos de resultados combindados ou separados, para os quatro modelos testados.

Palavras-chave: Contaminação do solo; Padrão de qualidade do solo; Solos tropicais; Saúde humana; Metais pesados; Propriedades do solo

ABSTRACT

Soil-to-plant transfer of heavy metals and an assessment of human health risks in vegetable-producing areas of São Paulo state

While contaminated food products are known to be a leading source of exposure to potentially toxic elements (PTEs), for the general population, few studies have been carried out to examine PTEs levels in soils and plants in wet tropical regions such as Brazil. While the most commonly used index for estimating PTEs accumulation in vegetables and the subsequent exposure to humans who eat them is the bioconcentration factor (BCF) - the ratio between the concentration of metals in the edible portions of produce and their total concentration in soils - the BCF does not provide an adequate description of soil-to-plant metal transfers. A better understanding of such transfers requires information about the soil attributes that influence the availability of PTEs to plants. The state of São Paulo (SP) is the largest consumer of vegetables in Brazil, as well as the largest and most diversified producer. Studies are therefore needed on PTEs concentrations in soils and vegetables, in order to assess their quality under guidelines established by Brazilian legislation. It is likewise crucial to establish critical limits of these elements in soils, via models that assess risks to human health, based on data that reflect current conditions in the soils of São Paulo. The objectives in this study were: (i) to characterize and to evaluate the relations between the concentrations of Cd, Cu, Ni, Pb and Zn in soils and in vegetables from the "Green Belt" of the state of São Paulo, Brazil, taking the limits established by legislation into account; (ii) to develop empiric models to derive appropriate soil screening values and to provide an accurate risk assessment for tropical regions; (iii) to develop proposals for improved human health-based screening values for Cd, Cu, Ni, Pb and Zn in São Paulo soils, using soil – vegetable relations. With the exception of Cd, there was a positive correlation between pseudototais and bioavailable contents of PTEs. Cd and Pb content in plants, moreover, not significantly correlated with any of the variables studied. All models of random forests and trees were good predictors of results generated from a regression model and provided useful information about which covariates were important to forecast only for the zinc concentration in the plant. The soil-plant transfer models proposed in this study had a good performance and are useful for eight of the ten combinations (five metals versus two species). SP data combined with NL data for Cd in lettuce and for Ni and Zn in lettuce and in carrot when pH, organic carbon - OC and clay contents were included in the model. Including such soil properties results in improved relations between PTEs concentrations in soils and in vegetables to derive appropriate screening values for SP State. The model in which pH, OC and clay contents were included gave the most useful results with SP and NL data set combined for Cu, Pb, Zn in lettuce and for Cd and Cu in carrot. Our setup did not work for Ni and for Pb in carrot because the data models gave an inconsistent result and the combination of datasets did not or insufficiently improve the results.

Keywords: Soil contamination; Soil quality standard; Tropical soils; Human health; Heavy metals; Soil properties

1 INTRODUCTION

Excessive levels of heavy metals, also called trace elements or potentially toxic elements (PTE’s) in soils can inhibit plant growth, modify plant communities (BAKER et al., 1994) and have adverse effects on soil microorganisms (VALSECCHI et al., 1995). PTEs are also responsible for negative impacts on ecosystems and various forms of life, especially human beings.

The transport of toxic metals in soils depends on two primary factors: the mobility and the availability of these chemical species. While only a small portion of metals in soils is subject to mobilization, it is enough to generate environmental concerns, due to the metals movement to the water table and assimilation in the food chain.

Absorption by plants is one of the leading mechanisms by which PTEs enter the food chain (ANTONIOUS; KOCHHAR, 2009). Because these elements accumulate in both edible and inedible plant parts at high enough concentrations to pose a risk to animal and human health. Therefore, monitoring both the quality of soils and the quality of the water used in agriculture is essential. In plants, PTEs accumulation varies among species and varieties, and between different parts of the plant. Cereals, grains, vegetables, and tuberous vegetables tend to accumulate lower concentrations of metals than fast-growing leafy plants such as lettuce (SIMEONI et al., 1984).

In Brazil, the area cultivated with vegetables and also vegetable consumption is high. The state of São Paulo (SP) is the largest producer and the largest consumer of vegetables in Brazil. In 2011, 53 species of vegetables were cultivated in 86 thousand hectares of agricultural lands, producing 4 million tons, according to the Brazilian Institute of Agricultural Economics (IEA). The production is concentrated near the state capital (São Paulo city), in the so-called SP “green belt”, which extends along the slopes of the Serra do Mar and the Serra da Mantiqueira and is home to farms that supply vegetables, fruits, fungi, and flowers to the São Paulo General Warehousing and Centers Company (CEAGESP) and large supermarket chains in Rio de Janeiro, Curitiba, and elsewhere.

The relationship between PTEs concentrations in edible plant parts and total concentrations in soils is known as the bioconcentration factor (BCF). The higher the BCF, the greater the accumulation of metals in living organisms. The index is is easy to be used (ALONSO et al, 2003; SIPTER et al, 2008; MURRAY; THOMPSON; MACFIE, 2009) and is commonly used to estimate the accumulation of PTEs in crop plants and the exposure to humans who eat them (SWARTJES et al., 2007).

In the case of vegetables, BCF is estimated separately for roots and for leaves. BCF is not, however, appropriate for describing soil-to-plant pollutant transfer, because soils vary widely in their attributes (VRIES et al, 2007; RÖMKENS et al., 2009a, 2009b). As a result, two soils that have identical concentrations of PTEs and are cultivated with the same plant species but have different soil attributes (e.g., different levels of pH, clay, or organic matter - OM) are likely to show different values of BCF. The most useful soil attributes for assessing soil-to-plant metal transfer are OM, Fe and Al oxides, cation exchange capacity (CEC), pH, ionic strength, specific surface area, and mineralogical composition (GRAY et al., 1998).

In recent years researchers have developed various empirical models to describe soil-plant relationships for PTEs. Romkens et al. (2009) derived empirical soil-plant relationships for Cd and observed that soil pH and CEC were the principal drivers of the transfer of this metal to plants. Melo et al. (2011) obtained significant soil-plant relationships in leafy vegetables and roots for Cd, and included pH and the total metal content of soils as variables, using published data from tropical and temperate regions. Rodrigues et al. (2012) studied a model for soil-plant-animal transfer and observed that soil pH and organic carbon content (OC) affected levels of Cd, Cu, and Zn in forage. Contents of Al oxides were also correlated to Pb contents in soil.

As Melo et al. (2011) observed for Cd, the great majority of researchers to date have focused on soils and plants of temperate regions, and thus are not representative of wet tropical conditions in Brazil. The lack of studies in tropical regions and in Brazil itself means that temperate-based results are often used to obtain critical limits for tropical soils, as has been the case in São Paulo state (CETESB, 2001). Extrapolating temperate results to wet tropical regions is unsatisfactory because of the broad differences between temperate and tropical regions in soil attributes, plant behavior, and climate (MCLAUGHLIN et al., 2000; RIEUWERTS, 2007).

Deriving critical concentrations of PTEs in soils, also known as soil quality standards, is necessary so that environmental agencies can establish criteria to determine acceptable levels of soil pollution, based on risk analysis. The United States and Holland were the first countries to establish such criteria, in 1989 and 1990, respectively (SWARTJES et al., 2007).

Assessing the risk of a given pollutant requires taking into account factors such as the maximum exposure dosage per live weight of organism and the toxic effects of the element under study, following the basic premise that contamination of soils or groundwater is unacceptable if the risk to public health exceeds the Maximum Tolerable Risk (SWARTJES et al., 2007). Because risk analysis studies and the variables that determine the risks associated with soil pollution are complex, computer models of risk analysis are being developed.

Models that are parameterized with field measurements but that ignore the various sources of exposure can over- or underestimate risks to human health (NIEUWENHUIJSEN et al., 2006). For that reason, assessing exposure in specific cases offers greater precision. The Dutch Method, for example, uses the CSOIL mathematical model developed by the National Institute for Public Health and the Environment (RIVM) to simulate the risks to a population exposed to a given pollutant in soils or groundwater via various sources of human exposure (VROM, 1994). The Dutch criteria reflect the multiple functions of soils, incorporating risks to both human health and the environment. One of the advantages of the mathematical model is that it allows changes to the basic variables of the model, thereby facilitating the adaptation to local conditions at a given study site. The CSOIL model calculates the concentration of the pollutant in all phases, based on the law of equilibrium and on scientific knowledge of the physical and chemical properties of pollutants and their coefficients of distribution (BERG, 1994).

In Brazil risk assessments are a relatively recent tool for complementing impact assessments of soil and water pollution, and even for making decisions regarding potential remediation measures. São Paulo was the first Brazilian state to adopt a table establishing limits of metals in soils, under different exposure scenarios (CASARINI et al., 2001). Those values have since been adopted at the national level (CONAMA, 2009) and are slated to be updated every five years.

The objectives in conducting this study were:

- To characterize and evaluate the soils-plant relations between the concentrations of cadmium, copper, lead, nickel, and zinc in soils and in vegetables areas in the state of São Paulo, Brazil, considering the limits established by legislation.

- To develop empiric models to derive appropriate soil screening values and provide an accurate risk assessment for tropical regions in SP. For this, improved relations between the concentrations of cadmium, copper, lead, nickel, and zinc in soils and vegetables from tropical and not tropical regions were assessed.

- To develop proposals for improving human health-based screening values for Cd, Cu, Ni, Pb and Zn in SP soils, using improved soil – vegetable relations.

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2 CONCENTRATIONS OF POTENTIALLY TOXIC ELEMENTS IN SOILS AND VEGETABLES FROM THE MACROREGION OF SÃO PAULO, BRAZIL: AVAILABILITY FOR PLANT UPTAKE

Abstract

The occurrence and accumulation of heavy metals or so called potentially toxic elements (PTEs) in soils and plants have driven long-standing concerns about the adverse effects such metals have on the environment and on human health. Furthermore, contaminated food products are known to be a leading source of exposure to PTEs for the general population. It is crucial to accurately assess the concentrations of metals in crops and the bioavailable contents of these elements in the soil. The state of São Paulo is the largest consumer market of horticultural products in Brazil with production focused essentially on urban and industrial areas, which greatly increases the degree of exposure to contaminants, cultivated soils and vegetables there. The objective of the authors in this study was to characterize the soil-plant relationships between concentrations of Cd, Cu, Ni, Pb and Zn cultivated in soil and in vegetable growing areas in the state of São Paulo, Brazil. To accomplish this, we collected 200 soil (0-20 cm) and plant samples, from 25 species in the production areas. With the exception of Cd, there was a positive correlation between pseudototals (USEPA 3051a) and the bioavailable contents (extracted with DTPA) of PTEs. However, the Cd and Pb content in plants was not significantly correlated with any of the variables studied. All random forest and tree models proved to be good predictors of results generated from a regression model and provided useful information including covariates that were important for specifically forecasting zinc concentration in plants.

Keywords: Soil contamination; Metals; Principal component analysis; Prediction models; Permitted limits

2.1 Introduction

Potentially toxic elements (PTEs), including heavy metals, are usually found in low concentrations in soils and rocks. Concern about the presence and accumulation of these PTEs in soil and plants has been constant, due to the adverse effects can cause to on the environment and human health. One of the main exposure routes of PTEs for most of the population is the intake of food (RÖMKENS et al., 2009a; AJMONE-MARSANE E BIASIOLI, 2010). Because of this it is crucial to assess accurately the concentrations of metals in crops and the bioavailable concentrations of these elements in the soil (RODRIGUES et al., 2010).

Studies relating to PTE concentrations in soils and plants in humid tropical regions are scarce, especially in Brazil. Based on risk assessment models to human health, Melo et al. (2011) established the critical limits of Cd in soils in the state of São Paulo, Brazil, under different exposure scenarios. For this, results from humid temperate and tropical regions were used.

However, no data were available in Brazil due to the lack of this type of study being carried out in this country.

The availability of PTEs to plants depends mainly on redox processes and adsorption and/or complexing of these elements in the reactive surfaces of the soil colloids (SAUVÉ et al, 2000; RIEUWERTS et al., 2006; RODRIGUES et al., 2010). Each of these processes is controlled largely by the pH and the contents of organic matter, clay and Fe, Al and Mn oxides (RÖMKENS et al, 2009; RODRIGUES et al , 2010). Thus, relationships involving these soil attributes can help in the evaluation of soil-plant relationships, especially if they involve research results from field conditions.

In addition to soil properties, interactions with the rhizosphere of plants also influence the absorption of EPTs by plants. However, studies that describe these interactions are scarce due to the complexity of the processes involved in as much the soil-root interface, as in the regulation and internal translocation of contaminants by the tissues (STERCKEMAN et al., 2005; KALIS et al., 2007).

Forecasting studies using the random forest and tree models are relatively new to environmental investigations into the environment. The random forest model consists of a set of random classifications and regression trees (BREIMAN, 2001). Numerous trees generated within the algorithm are aggregated to give a single forecast. Its use in simulation studies and comparative analysis is on the increase, as it is the most accurate method when compared to other methods of forecasting and the classification of important variables (CUTLER et al., 2007; LAWLER et al., 2006; PRASAD et al., 2006). So far, these studies have been applied to remote sensing (GISLASON et al. 2006; LAWRENCE et al. 2006), ecology (PETERS et al., 2008; PRASAD et al., 2006) and genetics (WU et al., 2009).

The state of São Paulo is the largest consumer market of horticultural products in Brazil, accounting for 22% of total production (EMBRAPA VEGETABLES, 2009). The area under cultivation with over 50 species of vegetables, is around 145,000 hectares, producing about 4 million tons, according to the Brazilian Agricultural Economics Institute (IEA). Production is concentrated near the capital, in the so-called green belt of the state of São Paulo, and supplies the metropolitan region of São Paulo, which has over 20 million inhabitants (IBGE, 2013). This region is made up of mostly urban and industrial zones, which greatly increases the degree of exposure to contaminants in the soil and vegetables grown there.

The authors’ goal in this study was to characterize the soil-plant relationships between the concentrations of Cd, Cu, Ni, Pb and Zn in the soil and grown leaves and root vegetable crops in the state of São Paulo, Brazil, in keeping with the limits established by Brazilian legislation.

2.2 Material and Methods

2.2.1. Sampling collection

Samples were collected from a number of areas in the state of São Paulo with significant vegetable crop production (Figure 1). Sampling was initially concentrated in the area known as the "Green Belt", comprising a 120 km (approximately) band circling the state capital and covers 73 municipalities around the city of São Paulo (CAMARGO, 2008). This is a horti-fruit-fungi-flori production area under the management of farmers who supply the major population centers in Brazil, such as São Paulo, Rio de Janeiro and Curitiba. 53 producing properties of vegetable crops were visited in 19 cities where samples were harvested (Figure 1). These rural farms were chosen because they are the main producers of vegetables in the state of São Paulo and also because of production seasonality.

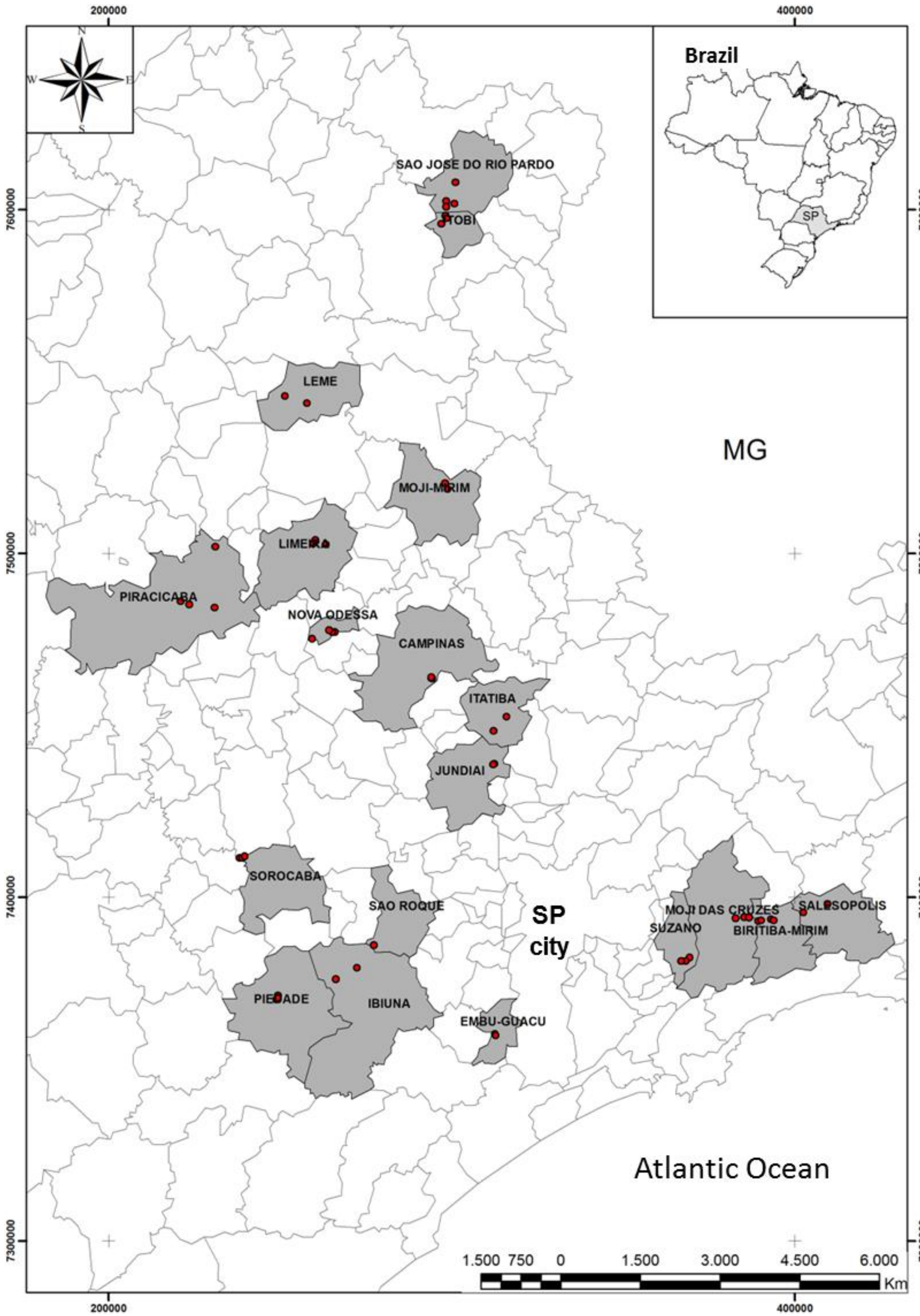

Figure 1 - Location of sampling areas of soils and vegetables in the state of São Paulo - Brazil

Were collected 200 composite samples of soil and plants, 25 species (Table 1) in the production areas.

Table 1 – Species of vegetables collected

Vegetables	Family Botany	Scientific name	Group classification	N° of samples	Total
Chard	Amaranthaceae	*Beta vulgaris var. cicla*	Leaves	3	
Watercress	Brássica	*Nasturtium officinale R. Br.*	Leaves	2	
Lettuce	Asterácea	*Lactuca sativa var. crispa*	Leaves	36	
Purple Lettuce	Asterácea	*Lactuca sativa L.*	Leaves	3	
Chicory	Asterácea	*Cichorium intybus*	Leaves	38	
Chive	Liliácea	*Allium fistulosum. L.*	Leaves	11	
Coriander	Apiácea	*Coriandrum sativum*	Leaves	8	
Cabbage	Brássica	*Brassica oleracea, grupo Acephala*	Leaves	21	159
Endro Dill	Apiácea	*Anethum graveolens*	Leaves	1	
Spinach	Aizoácea	*Tetragonia tetragonoides*	Leaves	8	
Mint	Lamiáceas	*Mentha spicata*	Leaves	1	
Basil	Lamiáceas	*Ocimum Basilicum L.*	Leaves	1	
Cole	Brássica	*Brassica oleracea, grupo Capitata*	Leaves	11	
Rocket	Brássica	*Eruca sativa*	Leaves	9	
Parsley	Apiácea	*Petroselin crispan*	Leaves	6	
Beet	Quenopodiácea	*Beta vulgaris L.*	Root	5	
Carrot	Apiácea	*Daucus carota*	Root	14	
Turnip	Brássica	*Brassica rapa L.*	Root	1	26
Radish	Brássica	*Raphanus sativus*	Root	1	
Leek	Aliácea	*Allium porrum*	Root	1	
Onion	Liliácea	*Allium cepa*	Root/bulb	4	
Broccoli	Brássica	*Brassica oleracea, Grupo Italica*	Flower	4	
Sprouting Broccoli	Brássica	*Brassica oleracea, Grupo Italica*	Flower	4	15
Cauliflower	Brássica	*Brassica oleracea, Grupo Botrytis*	Flower	7	

To identify the soil-plant relationships, soil and plants the samples were collected in a paired manner, i.e., a stainless steel auger used for soil collection was introduced up to 20 cm deep in the exact location where the plant sampling had been carried out (soil in contact with the roots of plants collected) (Figure 2). Fifteen sub-samples were collected to form one composite sample. The material was homogenized, and a portion of approximately 500 g was transferred to plastic bags.

Figure 2 – Soil and plant sampling in the city of Suzano – SP

Only the edible parts of plants were collected, including in the collection at least ten units per farmland, to obtain a homogeneous sample from each species selected for each area sampled. The samples were immediately placed in plastic bags and later kept under refrigeration (10° C).

The criteria of Swartjes et al. (2007) were used for sampling the plants: (i) preference of selection being given to edible plants; (ii) frequency of occurrence in the vegetable garden; (iii) samples representative of consumer buying patterns of vegetables grown; and (iv) affinity for the accumulation of contaminants. Also, when possible, a questionnaire was put to farmers, in order to obtain information related to the history of the area, soil type, fertilization, type of sowing, harvest time and the type of vegetables grown during the year, application of pesticides, proximity to potential pollution sources etc., resulting in an aggregate of information that assisted in the characterization of samples.

2.2.2. Pre-treatment of samples

Soil samples were dried in the shade and then sieved (2 mm) in order to obtain air dried soil (ADS). The vegetable crops were washed in running water to remove impurities and transferred for drying to an oven at 60° C. After being dried, the samples were ground in a stainless steel mil (Figure 3).

Figure 3 – Steps of drying, washing, grinding and packaging of soil and plants

2.2.3. Extraction procedures and chemical analysis of soils and plants

The plant material was digested in a microwave oven, as described by Araujo et al. (2002), and the concentrations of Cd, Cu, Ni, Pb and Zn in the plant extracts were determined using optical emission spectrometry (ICP-OES). The pseudototal contents of PTEs in the soil samples were extracted with concentrated acid in a microwave oven, with temperature control and pressure in accordance with EPA method 3051a (1:3 HCl: HNO3, v/v) (USEPA, 1998), and methods considered available to the plants were extracted with diethylenetriaminepentaacetic acid – DTPA (ABREU et al., 2001), which is considered standard for the state of São Paulo. Cd, Cu, Ni, Pb and Zn content in the soil samples were determined by ICP-OES.

Although the extraction method prescribed by EPA 3051a does not ensure complete dissolution of the samples, it was the method of choice recommended by the Environmental Sanitation Technology Company of São Paulo - Cetesb (2001) and the National Environmental Council - CONAMA (2009) for this type of analysis to facilitate comparison of results with bibliographical references. Reference materials in the form of NIST SRM certificate 2709a and San Joaquin soil were used to attest the quality of the analysis, with a satisfactory recovery rate of PTEs content (between 71 and 92%).

The granulometric fractions were obtained by the hydrometer method (GEE; OR, 2002). Chemical analyses selected for the assessment of soil fertility are described in Anderson and Ingram (1992). Organic carbon content was determined after dry combustion in a LECO CN-2000 elemental analyzer. "Free" oxide content (well crystallized) of Fe and Al were also identified by extraction using sodium dithionite-citrate-bicarbonate (MEHRA; JACKSON, 1960) as were the content of poorly crystallized oxides of Fe, Al and Mn by extraction using oxalic acid and ammonium oxalate (LOEPPERT; INSKEEP, 1996).

2.2.4. Statistical analysis

The analytical results were evaluated by descriptive analysis and Pearson correlation analysis ($p < 0.05$) using the statistical program SPSS 19.0 for Windows. Principal component analysis (PCA) was carried out on a data matrix composed of 16 variables (physical and chemical soil properties and pseudototal levels of PTEs) and 200 soil samples, having established two main components, using the Statistica7.0 software program (STATSOFT, 2005). In this analysis, the "PTE" variables were used as active variables and the “physical and chemical properties of the soil" variables as supporting or explanatory variables. All data were normalized because of the non-normality in the variables (for derivation of the soil-plant relationship, the total concentration of EPTs soil, pH,% clay and total organic carbon were used in the percentile ranging from 5 to 95).

For predictive analysis and classification of predictor variables in terms of force relative to the response, we used the Windows R 3.0 program (R DEVELOPMENT CORE TEAM, 2008). The random forest programs rpart and rpart.plot (LIAW; WIENER, 2002) were also used, based on two types of statistical forecasting model, random forest and tree, in which the predictor variables (covariates) are the pseudototal and available contents of Cd, Cu, Ni, Pb and Zn in the soil and the physical and chemical properties of the soil, while the dependent variable (the variable to be predicted) is the concentration of metals in the plant. This analysis was divided into three parts: (i) a set of data from the input data was created, (ii) the data set was prepared for predictive analysis, and (iii) analyses were carried out based on the random forest and tree models.

2.3. Results and discussion

2.3.1. Soil characteristics

Most of the samples consisted of slightly acidic soils with a pH ranging from 3 to 7 (mildly-acidic to neutral) and with an average of 5 (Table 2). These values are similar to those found in horticultural soils in the state of São Paulo, which ranged from 5.1 to 7.7 (VALARINI et al., 2011). The samples had 100-677 g kg^{-1} of clay, with an average of 384 g kg^{-1},with a high sand content of between 153 to 805 g kg^{-1} and, in general, contained average silt, averaging 156 g kg^{-1}. The range of texture varied from sandy to heavy clay, with a predominance of clay soils. These soils are preferred by farmers engaged in horticultural activities; however, it is this class of soil that has greater potential for retaining contaminants compared to soils of average sandy texture.

Carbon content varied greatly, ranging from 5.7 to 232.5 g kg^{-1}, with an average of 25.4 g kg^{-1}. The retention of metals in the soil is very much influenced by clay and organic matter (RÖMKENS et al, 2009; RODRIGUES et al., 2010). The effective CEC (CECe), which expresses the effective capacity of the soil to retain cations close to the value of its natural pH, was on average 80 mmol kg^{-1}. Base saturation (V%) ranged between average and high values (18-97%). Al content and Al saturation (m%) were very low on average. Crystalline iron oxide contents (FeDCB) also varied greatly (0.3 to 81 g kg^{-1}).

Table 2 – Descriptive analysis of physical-chemical properties of soil samples (n=200)

Variables	Mean	Mín.	Máx.	Median	Std. Deviation
pH H_2O	5.9	3.6	7.5	5.9	0.7
pH 0.01 M $CaCl_2$	5.7	3.8	7.2	5.8	0.6
P (mg kg^{-1})	483.7	72.7	1877.1	441.2	265.3
		--------------**$mmol_c$ kg^{-1}**--------------			
K	4.7	0.7	12.5	4.4	2.2
Ca	59.8	2.5	361.8	50.6	45.9
Mg	15.7	1.4	51.3	14.5	8.2
Al	0.5	0.0	8.4	0.0	1.2
H+Al	23.3	9.0	84.0	20.0	14.2
SB	80.3	8.1	424.1	69.8	51.7
CEC_t	103.6	25.1	441.1	94.4	49.6
CEC_e	80.8	8.1	424.1	71.1	51.6
		--------------**%**--------------			
V	74	1	97	74	17
m	1	<1	29	<1	3
		--------------**g kg^{-1}**--------------			
OC	25	6	232	18	26
Sand	460	153	805	444	137
Silt	156	20	488	150	79
Clay	385	100	678	377	132
$Fe_2O_{3\ DCB}$	7	<1	82	2	12
$Al_2O_{3\ DCB}$	12	<1	27	12	5
$Fe_2O_{3\ OXA}$	1	<1	28	<1	4
$Mn_2O_{3\ OXA}$	<1	<1	5	<1	<1
$Al_2O_{3\ OXA}$	5	<1	53	<1	10

DCB – sodium dithionite-citrate-bicarbonate , OXA – oxalic acid and ammonium oxalate, OC – Organic carbon, CECt - Cation exchange capacity total, CECe - Cation exchange capacity effective

In general, the samples were representative soils that had high chemical quality, something that is expected in vegetable crop cultivation, since periodically acidic correctives, mineral and organic fertilizers are added to the soil. However, at the same time this can facilitate the incursion of contaminants, including PTEs. A parameter that deserves mention here is the bioavailable P levels, which had a range from 72 to 1.877 mg kg^{-1} with an average of 484 mg kg^{-1}. P concentrations up to 120 mg kg^{-1} are considered high and sufficient to achieve high yields in vegetables (RAIJ et al., 2011). However, excessive concentrations, can lead to Zn deficiency problems in sensitive crops (ALLOWAY, 2008).

2.3.2. Pseudototal and available content of Cd, Cu, Ni, Pb and Zn in soil

There was great variability in the Cd, Cu, Ni, Pb and Zn content in the soil (Figure 4). The results are comply with the legal standard of acceptable limits of PTEs in soils for the state of Sao Paulo (the guideline values of quality prevention and intervention), according to Cetesb (CETESB, 2005). The Prevention Value (PV) indicates possible harmful changes to the quality of the soil and is administered in a preventive way, and, where levels are excessive in the soil, to monitor impacts already sustained. The Intervention Value (IV) indicates the contamination limit above which there are potential risks, be they direct or indirect, to human health and, where excessive, the area will be placed under investigation to identify the need for intervention action (CETESB, 2014).

The Cd content varied from 0 to 2 mg kg^{-1}, with an average of 0.12 mg kg^{-1}, where most of the samples had levels below or equal to the reference value set by the Cetesb guideline values table for the state of São Paulo. Cu, Pb and Zn had significant heterogeneous levels, averaging 33 mg kg^{-1}, 22 mg kg^{-1} and 166 mg kg^{-1}, respectively. These metals were at levels above the PV in some areas, as well as Ni, which averaged 8 mg kg^{-1}. Cu, Pb and Zn had at least one sample with a level in excess of the agricultural IV as prescribed by law for the state of São Paulo. This shows the need for further studies in these areas, in which remediation actions may be required.

Fernandes et al. (2007) found average levels of Cd, Cu, Ni, Pb and Zn of 6, 13, 24, 5 and 42 mg kg^{-1}, respectively, in vegetable crop soils from the state of Minas Gerais (MG), Brazil. The soil in the state of Sao Paulo had average concentrations of Cu, Pb and Zn higher than in MG, but lower than the values observed in horticultural soils in Hungary (SZOLNOKI S.; FARSANG A., 2013), except for Zn. This relatively large variation and differences that are significant between the average concentration values are typical of soils impacted by anthropogenic contamination both on a local and a regional scale (RODRIGUES et al., 2013; MADRID et al., 2007).

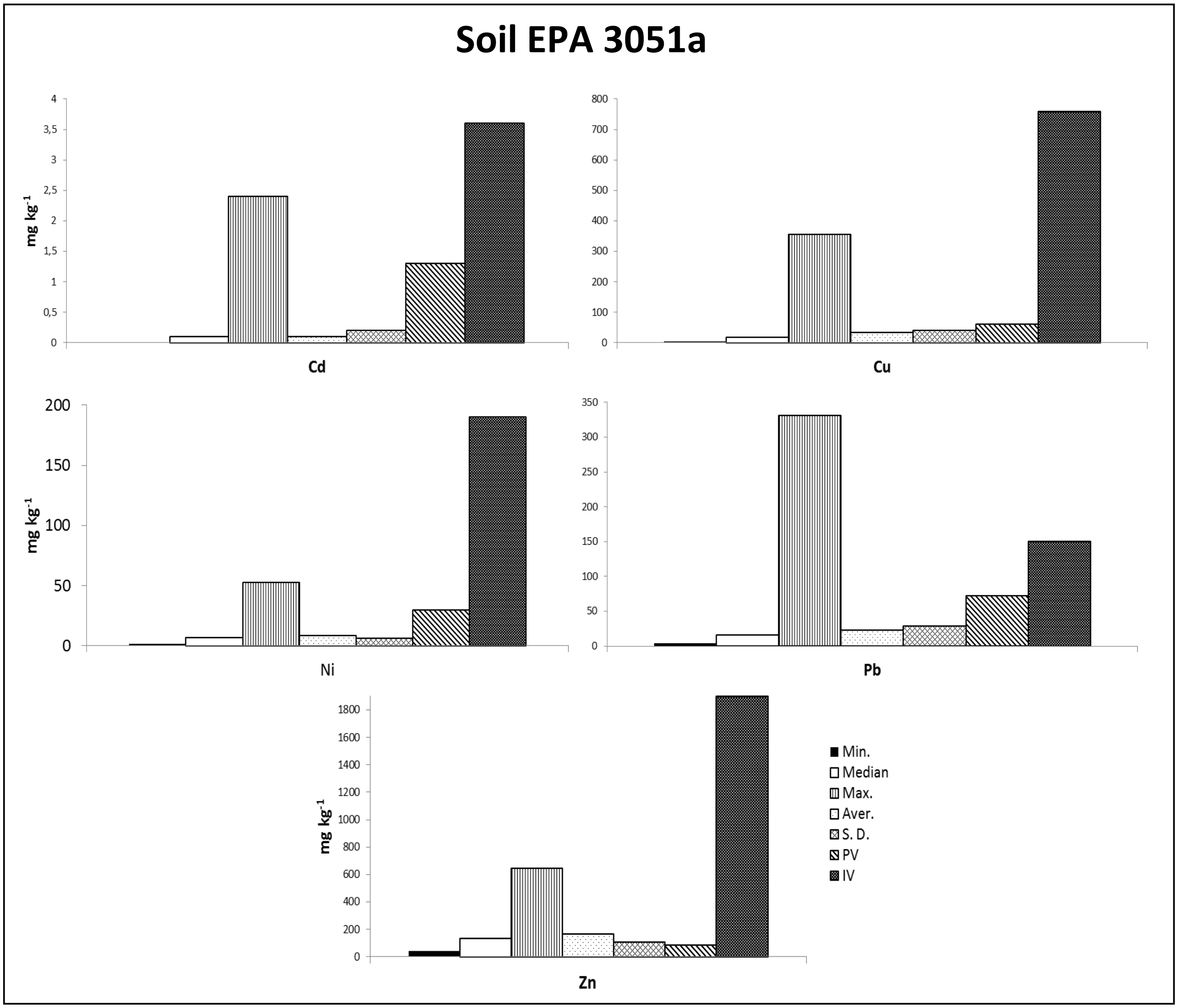

Figure 4 – Pseudototal contents (EPA 3051a) of metals in the soil samples (*IV – Investigation value established for soil and groundwater in the state of São Paulo (rural exposure scenario; **PV – Prevention value established for soil and groundwater in the state of São Paulo).

The pseudototal levels of PTEs varied widely between vegetable samples (Figure 5). Cd concentrations, in general, were very low or null, except for hardwood species classified as aromatic herbs (endrodil, mint and basil). The level of Cu in parsley, endive, lettuce and cabbage was elevated; significant levels of Ni were found in onion, lettuce and beets, of Pb in spinach, parsley and lettuce, and of Zn in spinach, endrodil, mint, chicory and basil. However, the levels, when averaged out, were below the PV for soil established by Cetesb.

Soils under cultivation of lettuce showed the highest levels of Cu, Ni and Pb. This is worrying as this plant species is accumulating metals in relatively high concentrations because of absorption by the roots and efficient subsequent redeployment to the shoot (PEIJNENBURG et al., 2000). In the state of São Paulo, Brazil, lettuce is one of the most produced and consumed of all the leafy vegetables (MELO et al., 2011).

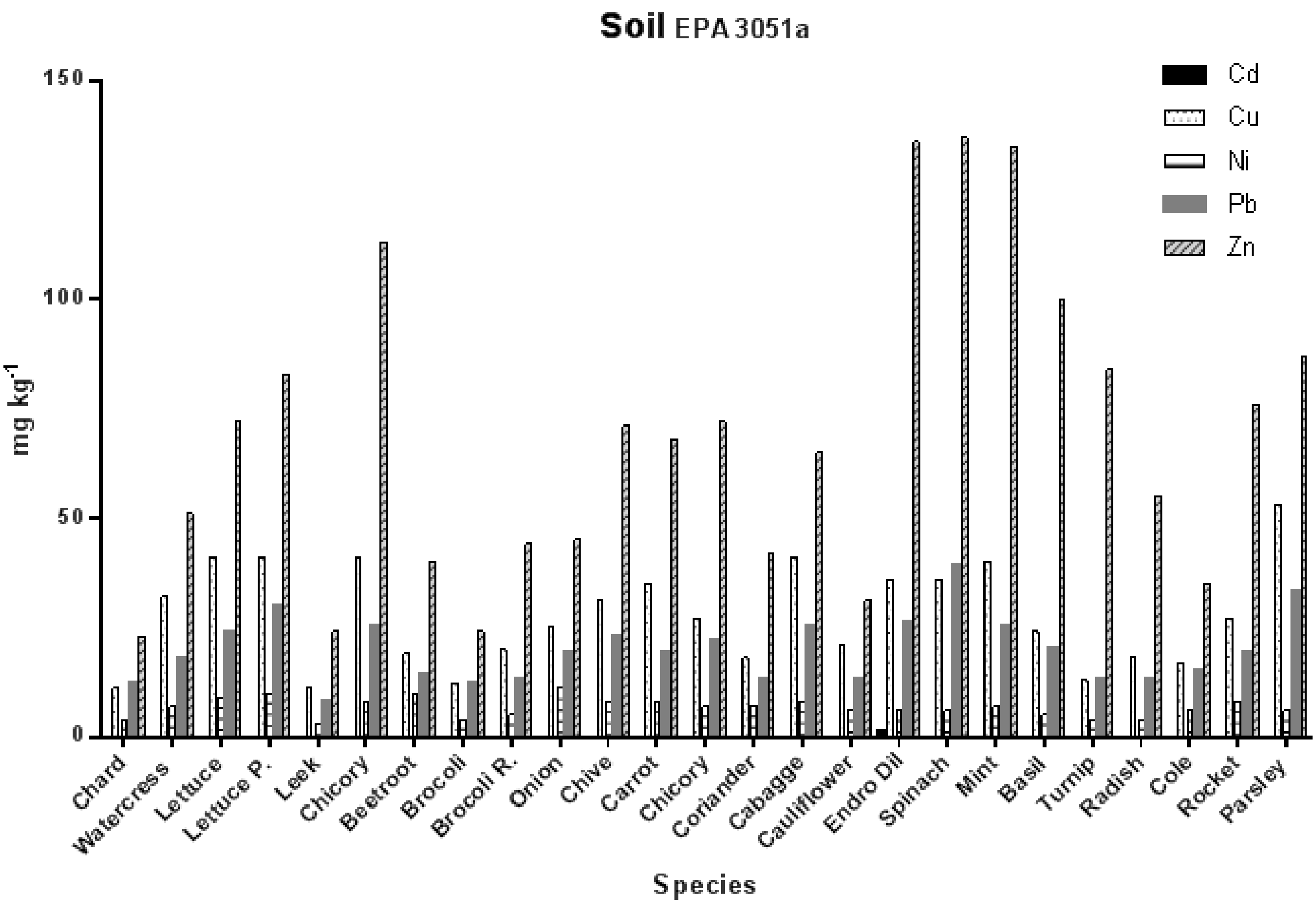

Figure 5 – Means of pseudototal contents (EPA 3051a) of potentially toxic elements in soil by species

The bioavailable levels of PTEs were extracted with DTPA. This extractor is among the most commonly used for assessing the bioavailability of cationic micronutrients in soil samples, as well as for predicting the absorption of metals such as Cd, Cr, Ni and Pb in soils enriched with these metals (ABREU et al., 2001). In general, the SP bioavailable levels in soils were low (Table 3). Cd presented content levels very close to the prevention limits established by Cetesb at certain parts on the samples. Cu also had levels above the PV at a number of points, but with low average levels, as well as Pb and Zn. These results are similar to those presented by Fernandes et al. (2007), who found negligible amounts of bioavailable levels of Cd and Ni, with availability rates near zero in soils from the state of Minas Gerais. Fernandes et al. (2007) found higher bioavailable values for Cu, Pb and Zn. Rodrigues et al. (2013) also reported low levels of Cd, Cu, Pb and Zn in Portugal.

Table 3 – Descriptive analysis of the bioavailable contents available (DTPA) of potentially toxic elements in the soil samples (mg kg^{-1})

	Cd	**Cu**	**Ni**	**Pb**	**Zn**
(n = 200)					
Minimum	<L.D	0.41	0.02	0.30	0.49
Maximum	1.28	125.4	2.15	16.15	52.14
Median	0.03	2.98	0.15	0.96	6.15
Mean	0.04	6.21	0.24	1.59	10.48
Std. Deviation	0.01	1.02	0.02	0.13	0.79

<L.D = limit detection

2.3.3. Total concentration of Cd, Cu, Ni, Pb and Zn in plant

The minimum and maximum concentrations of PTEs in vegetables (in mg kg^{-1} dry matter) were 0.0 to 2.7 for Cd; 2.4 to 16.9 for Cu; 0.1 to 2.5 for Ni; 0.0 to 20.2 for Pb, and 39.6 to 1072.5 for Zn to (Table 4). PTE concentrations in the edible parts of vegetables were compared to the critical limits established by the Brazilian Health Surveillance Agency (ANVISA, 1965). According to ANVISA, the critical limits for Cd, Cu, Ni, Pb and Zn are 1; 30; 5; 0.5 and 50 mg kg^{-1}, respectively. Cd, Pb and Zn had concentrations above the critical limits in some spots. For Pb and Zn, 40% and 99%, respectively, of the samples were above the allowable limit. These results are in line with the contents of the pseudototal PTEs in the samples, which were also higher than the other elements studied and some points on the samples above the ceiling set by law. Brazilian law does not impose critical limits for vegetable crops grown for human consumption.

Guerra et al. (2012) found Cd concentrations ranging from 0.01 to 0.18 mg kg^{-1}, of Ni between 0.01 and 0.74 mg kg^{-1} and Pb between 0.02 and 2.50 mg kg^{-1} in the edible parts of plants collected in the state of São Paulo and observed that Cd and Ni concentrations did not exceed the permissible limits established by ANVISA. But in the case of Pb, 45% of the samples did exceed the allowed limit. Yang et al. (2007) also showed similar results for Pb in studies of PTEs in vegetable edible parts grown in China, where some points on the samples were above Chinese health standards for edible vegetables (National Bureau of Standards of China, 2011). This limit is more restrictive in China (0.2 mg kg^{-1}) than in Brazil.

Cd, Ni,and Pb tend to accumulate in the leaves of plants, not only due to their broad leaf area and high rates of perspiration, but also for the high rate of growth of these plants (ITANNA et al., 2002). However, in this study, no difference in a specific class of vegetables was found when samples of Pb and Zn exceeding the permissible limit were separated into groups.

Table 4 – Descriptive analysis of potentially toxic elements contents of plant samples (mg kg^{-1})

	Cd	**Cu**	**Ni**	**Pb**	**Zn**
(n = 200)					
Minimum	<L.D	2.4	0.1	<L.D	39.3
Maximum	2.7	16.9	2.5	20.2	1072.5
Mean	0.2	7.2	0.3	0.9	168.3
Median	0.1	7.0	0.3	0.1	133.6
Std. Deviation	0.1	2.6	0.2	2.1	116.4
ANVISA limits	1.0	30.0	5.0	0.5	50.0

<L.D = limit detection

2.3.4. Pearson correlations

Despite the low levels of bioavailable PTEs in the samples studied, except for Cd, there was, in general, a significant correlation between pseudototal levels and bioavailable elements, with positive and high coefficients ranging from 0.77 (NiEPA with CdDTPA) to 0.97 (CuEPA with PbDTPA) (Table 5).

There were no significant correlations for contents of Cd and Pb in plants for any of the variables studied. A high content of contaminants in the soil is not always associated with a high content in vegetables (CHOPIN; ALLOWAY, 2007; CHARY et al., 2007). The soil type, the solubility of PTEs therein, the metal distribution in the tissues of the plant and characteristics of the specific plant species interfere with this relationship (INTAWONGSE et al., 2006).

The pH correlated positively with Cu, Ni and Zn in soils with relatively high coefficients (r = 0.6 to 0.7) for both methods of extraction. The CECe was positively correlated with the C content (r = 0.9) and the content of Fe, Al and Mn oxides. The clay, sand and silt content correlated with the low-form content of EPTs and oxides in its various forms, with the exception of clay, with high coefficient rates.

Table 5 – Matrix of Pearson correlation with significant values (p < 0.05) highlighted in bold, between pseudototal contents (EPA 3051a) and bioavailable (DTPA) contents of potentially toxic elements (PTEs) in soil and concentrations of PTEs in plants and soil attributes

Variá.	pH_{H2O}	CEC_e	Fe_2O_{3D}	Al_2O_{3D}	Fe_2O_{3OX}	Mn_2O_{3OX}	Al_2O_{3OX}	OC	Clay	Silt.	Sand	Cd_{EPA}	Cu_{EPA}	Ni_{EPA}	Pb_{EPA}	Zn_{EPA}	Cd_{DTPA}	Cu_{DTPA}	Ni_{DTPA}	Pb_{DTPA}	Zn_{DTPA}	Cd_P	Cu_P	Ni_P	Pb_P	Zn_P
pH_{H2O}	1																									
CEC_e	**0.719**	1																								
Fe_2O_{3D}	**0.673**	**0.954**	1																							
Al_2O_D	**0.718**	**1**	**0.954**	1																						
Fe_2O_{3OX}	**0.719**	**1**	**0.954**	**1**	1																					
Mn_2O_{3OX}	**0.719**	**1**	**0.954**	**1**	**1**	1																				
Al_2O_{3OX}	**0.7**	**0.984**	**0.938**	**0.983**	**0.984**	**0.984**	1																			
OC	**0.7**	**0.984**	**0.938**	**0.983**	**0.984**	**0.984**	**1**	1																		
Clay	**0.388**	**0.504**	**0.473**	**0.502**	**0.504**	**0.504**	**0.508**	**0.508**	1																	
Silt	**0.69**	**0.978**	**0.932**	**0.978**	**0.978**	**0.978**	**0.961**	**0.961**	**0.486**	1																
Sand.	**0.715**	**0.987**	**0.943**	**0.987**	**0.987**	**0.987**	**0.972**	**0.972**	**0.491**	**0.966**	1															
Cd_{EPA}	0.081	-0.011	-0.035	-0.013	-0.011	-0.011	-0.025	-0.025	0.076	-0.03	-0.012	1														
Cu_{EPA}	**0.719**	**0.967**	**0.922**	**0.967**	**0.967**	**0.967**	**0.951**	**0.951**	**0.484**	**0.944**	**0.956**	0.043	1													
Ni_{EPA}	**0.719**	**0.967**	**0.922**	**0.966**	**0.967**	**0.967**	**0.95**	**0.95**	**0.482**	**0.944**	**0.947**	0.007	**0.933**	1												
Pb_{EPA}	**0.703**	**0.96**	**0.915**	**0.959**	**0.96**	**0.96**	**0.944**	**0.944**	**0.505**	**0.938**	**0.948**	-0.016	**0.927**	**0.941**	1											
Zn_{EPA}	**0.693**	**0.929**	**0.885**	**0.929**	**0.929**	**0.929**	**0.913**	**0.913**	**0.479**	**0.906**	**0.918**	-0.03	**0.896**	**0.932**	**0.89**	1										
Cd_{DTPA}	**0.635**	**0.81**	**0.763**	**0.809**	**0.81**	**0.81**	**0.791**	**0.791**	**0.445**	**0.794**	**0.806**	0.03	**0.781**	**0.77**	**0.803**	**0.774**	1									
Cu_{DTPA}	**0.712**	**0.971**	**0.925**	**0.971**	**0.971**	**0.971**	**0.955**	**0.955**	**0.496**	**0.948**	**0.959**	0.045	**0.937**	**0.937**	**0.931**	**0.9**	**0.804**	1								
Ni_{DTPA}	**0.69**	**0.938**	**0.892**	**0.937**	**0.938**	**0.938**	**0.921**	**0.921**	**0.489**	**0.918**	**0.927**	0.004	**0.92**	**0.903**	**0.897**	**0.866**	**0.756**	**0.91**	1							
Pb_{DTPA}	**0.747**	**0.99**	**0.944**	**0.989**	**0.99**	**0.99**	**0.973**	**0.973**	**0.496**	**0.967**	**0.977**	-0.008	**0.97**	**0.956**	**0.951**	**0.919**	**0.795**	**0.96**	**0.926**	1						
Zn_{DTPA}	**0.679**	**0.964**	**0.918**	**0.963**	**0.964**	**0.964**	**0.948**	**0.948**	**0.505**	**0.941**	**0.952**	0.005	**0.931**	**0.93**	**0.924**	**0.893**	**0.817**	**0.935**	**0.901**	**0.953**	1					
Cd_P	-0.022	-0.036	-0.041	-0.038	-0.036	-0.036	-0.006	-0.006	0.04	-0.039	-0.031	0.077	0.016	-0.057	-0.025	-0.005	0.005	-0.051	-0.006	-0.039	-0.056	1				
Cu_P	**0.613**	**0.902**	**0.859**	**0.902**	**0.902**	**0.902**	**0.939**	**0.939**	**0.476**	**0.88**	**0.893**	-0.054	**0.869**	**0.869**	**0.863**	**0.834**	**0.72**	**0.873**	**0.838**	**0.892**	**0.866**	-0.008	1			
Ni_P	**0.413**	**0.492**	**0.5**	**0.493**	**0.492**	**0.492**	**0.471**	**0.471**	**0.278**	**0.517**	**0.499**	0.099	**0.504**	**0.49**	**0.503**	**0.438**	**0.419**	**0.482**	**0.464**	**0.486**	**0.489**	-0.012	**0.471**	1		
Pb_P	0.087	0.126	0.098	0.131	0.126	0.126	0.109	0.109	0.032	0.138	0.112	**-0.154**	0.129	0.102	0.122	0.118	0.032	0.088	0.086	0.144	0.116	0.247	0.119	0.007	1	
Zn_P	**0.736**	**0.97**	**0.924**	**0.969**	**0.97**	**0.97**	**0.953**	**0.953**	**0.502**	**0.947**	**0.958**	0.033	**0.936**	**0.936**	**0.929**	**0.899**	**0.831**	**0.94**	**0.906**	**0.959**	**0.933**	-0.044	**0.871**	**0.483**	0.104	1

The oxides of Fe, Al and Mn, were in general, variables that were significantly correlated with high levels of coefficients with all the PTEs. Alloway (1990) and Fontes; Weed (1991) cited the importance of Fe oxides and PTEs mobility controllers in moist tropical soils. The oxides have different capacities for adsorbing metal ions. In one type of oxide, the ability to adsorb cations varies with their degree of crystallization, and this is a function of the weathering process to make changes in crystal shapes, the surface area and the chemical properties of the surface oxide (YU et al., 1997). In general, poorly crystallized substances have a large specific surface area and capacity for high adsorption of metals. In contrast, the activity of well crystallized substances is comparatively lower (YU et al., 1997).

Despite their rare occurrence in soils, Mn oxides and hydroxides are efficient adsorbents of heavy metals because of their small size and high specific surface (McKENZIE, 1979). As Fe oxides, manganese oxides are very stable, i.e. exhibit low solubility (STUMM; MORGAN, 1996), they have high reactivity on the surface and precipitate as tiny amorphous or poorly crystallized crystals (FORTIN et al., 1993; TESSIER et al., 1996).

2.3.5. Principal component analysis (PCA)

Two main components were established, which explained 95% of the total variability (Table 6). The variability of the results was explained 75% by principal component 1 (PC1) and 20% by principal component 2 (PC2) (Figure 6). With the exception of Cd, all eigenvectors were very close and correlated, highlighting the Ni content in relation to CP1, which had a positive eigenvector, followed by Pb, Cu and Zn, respectively and out of all the attributes the CECe stands out, followed by Al oxides, Fe and Mn, carbon, pH and in last place the clay. However, in general, all the physical and chemical parameters had great influence on variation in the components, which can be seen in the vicinity of the vectors on the graph, thus making it difficult to see the components.

In PC2, the Cd eigenvector was positive, the only change being in the correlation axis. Thus, it was observed that the chemical and physical properties of the soil were of great importance and had a direct relationship with the pseudototal concentrations of Cu, Ni, Pb and Zn in soils, especially CECe. Brazilian law, through the establishment of default values of soil quality or guideline values for the prevention of soil contamination (CONAMA, 2009), uses the same parameters, since it uses the criterion that the natural concentration of PTEs can be estimated through its correlation with a number of physical and chemical properties of soil that influence the micro-environmental conditions and are determinants of the adsorption of metals (CETESB, 2005).

Table 6 – Results of principal components analysis

n	Eigenvectors	Total variance (%)	Cumulative eigenvectors	Cumulative (%)
1	**3.759**	**75**	**3.759**	**75**
2	**1.003**	**20**	**4.763**	**95**
3	0.117	3	4.880	98
4	0.073	1	4.953	99
5	0.047	1	5.000	100

Variable	Factor 1[(1)]	Factor 2[(1)]
Cd_{EPA}	-0.002	-1.000
Cu_{EPA}	-0.969	-0.045
Ni_{EPA}	-0.981	-0.005
Pb_{EPA}	-0.969	0.018
Zn_{EPA}	-0.959	0.035
$*pH_{H2O}$	-0.731	-0.080
$*CTC_e$	-0.986	0.012
Fe_2O_{3DCB}	-0.940	0.035
Al_2O_{3DCB}	-0.986	0.014
Fe_2O_{3OXA}	-0.986	0.012
Mn_2O_{3OXA}	-0.986	0.012
Al_2O_{3OXA}	-0.969	0.025
C	-0.969	0.025
CLAY	-0.503	-0.075
SILT	-0.963	0.031
SAND	-0.972	0.013

[(1)] Factors ≥ | 0.70 | are significant (Manly, 1994).

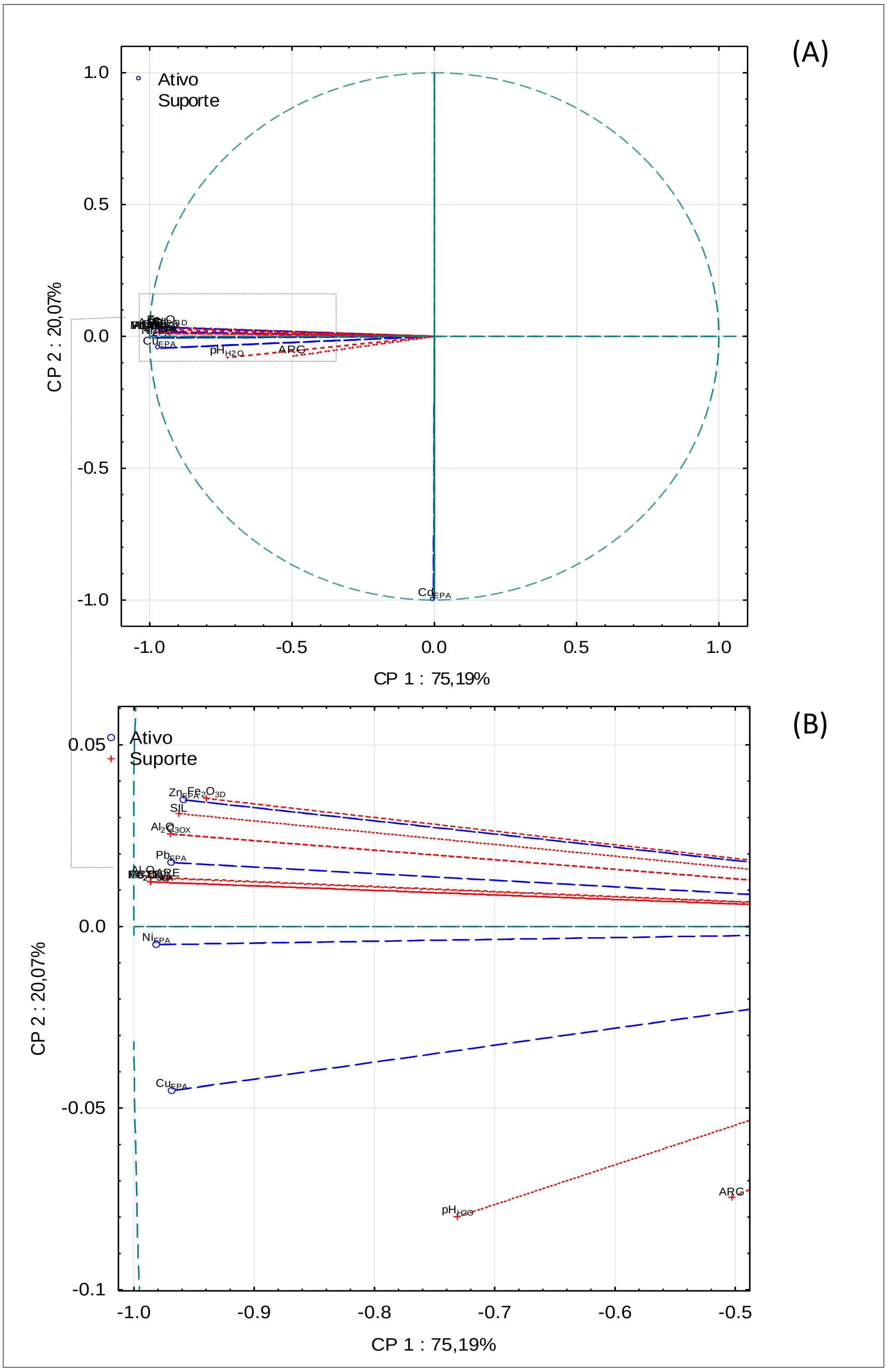

Figure 6 – (A) Principal components analysis of the variables related to chemical and physical characteristics and concentrations of potentially toxic elements in soils of SP, (B) zoom of the overlapping the axis for better visualization of the components

2.3.6. Predictive Analysis

It was possible to obtain good predictions for Zn from the random forest model. However, the proportion of variance explained for Cd, Cu, Ni and Pb was practically nil. This finding can be explained by the low Cd, Cu, Ni and Pb content in soil in relation to noise measurements (a common phenomenon dubbed "low signal to noise ratio"). However, the parameters used to quantify the quality of forecasts, mean absolute error (MAE: the higher or closer to 1, the better the quality of the forecast) and the proportion of variance explained for Zn were 0.79 and 22.95, respectively, proving that it was possible to obtain good quality forecasts of Zn concentrations in the plant from the studied predictor variables studied (Figure 7A).

A random forest model also allows for a classification of covariates in terms of their relative importance in determining forecasts. The random forest software (HASTIE et al., 2009) used in this study calculates the importance of measures ("variable importance") for each covariate. Figure 7B shows an "importance chart" in which the covariates are sorted in descending order of importance (from top to bottom) in terms of percentage reduction in forecast error of Zn levels absorbed by the plant.

In the ranking of importance of covariates for the prediction of Zn concentrations in plants (Figure 7B), CECe stood out as an excellent predictor, followed by pseudototal Zn concentrations in the soil and to a lesser degree, the pH, the contents of pseudototal Cu in the soil, the bioavailable concentrations of Cu in the soil, the carbon and the bioavailable Zn content in the soil in descending order of importance. The CEC is closely linked to the concentrations of exchangeable ions present in the soil solution and the exchange sites in the colloidal system interfaces. A high CEC provides high metal retention in the soil. However, the CEC is an indirect variable, because its effect is the result of the action of many variables on the soil such as pH and carbon content that are the chemical variables next appearing in the ranking of importance.

The second best variable for predicting Zn in the plants was the pseudototal content and not the Zn in the soils. This result corroborates the opinion of several researchers who advocate the use of pseudototal levels for assessing soil contamination PTEs, even though appropriate extractors have not yet been selected that are capable of being compared as identifiers of the bioavailable levels for the plants (ALVES et al., 1999). Other important variables are the pH, and the concentrations of Cu and carbon in the soil. Barber (1995) and Rhoton (2000) report the interaction between these variables, namely that Cu and Zn are biologically essential elements, with an enzymatic role in low concentrations, but can cause damage to health if ingested in high concentration.

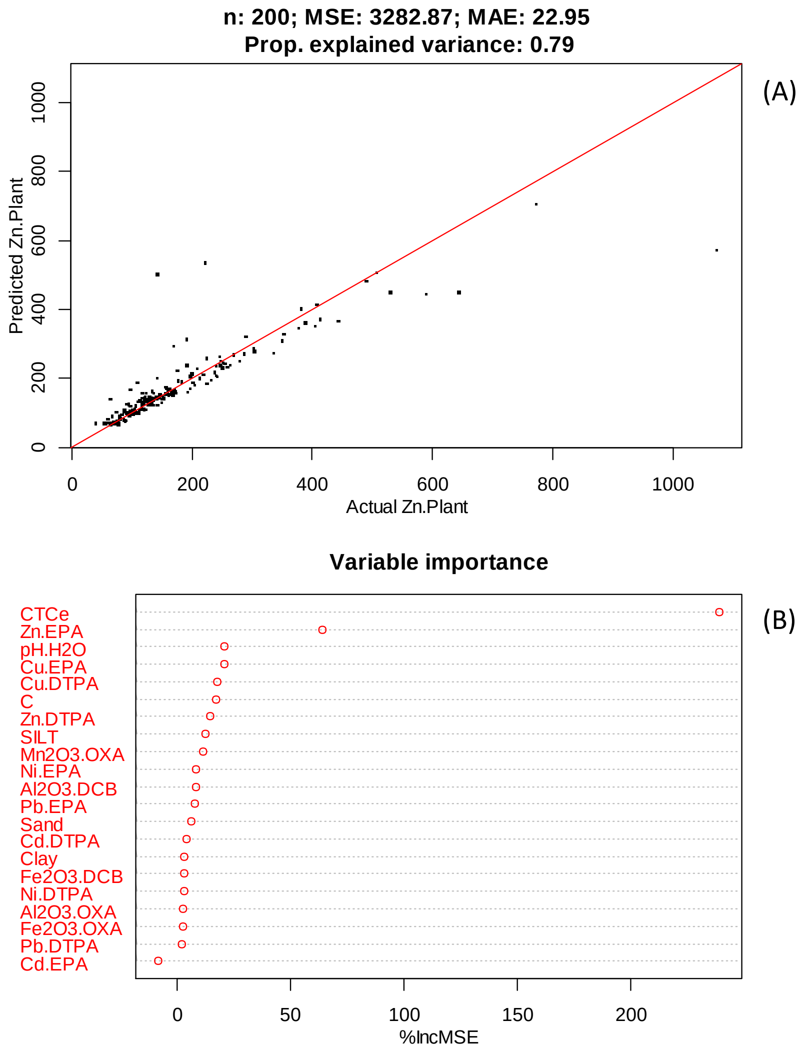

Figure 7 – Results of the prediction of zinc using the model of random forests: (A) scatter plot comparing the actual values (horizontal axis) and the predicted values of Zn in plant in mg kg^{-1}; (B) ranking of covariates in terms of their relative importance

Figure 8C is represented by a tree model. This model is, in essence, a covariate space partition in "compartments", whereby each compartment corresponds to a particular combination of permissible values for the covariates. Each compartment has just a single value that serves to allocate forecasts of the elements that fit (BREIMAN, 2011). The forecasts in the random forest model are often better quality than in the tree model. However, the disadvantage of forests is that they do not illustrate the effect of the covariates on the response variable, in contrast to what can be derived from a tree (BREIMAN, 2011) Thus, the two models are complementary and because of this, were employed together in this study.

Figure 8A compares the Zn forecasted values in the plant with the actual figures and shows the estimates of the MAE and a proportion of the explained variance, which are 40.34 and 0.63, respectively, showing a worse performance than the random forest model. Figure 6B shows the estimates and the confidence levels of possible error relating to the tree as a function of a "parameter complexity - cp", which corresponds to the tree size (number of divisions and terminal nodes) and which in our study should not pass six, the level indicated by the horizontal dotted line (after this level there is no gain in tree growth).

The rpart software used for constructing the tree employs a cross validation method ("cross-validation") to determine the size a tree must have, as tree size is measured in terms of a relative decrease in measurement error, and that beyond a certain size, larger trees reduce the forecasting error (LIAW; WIENER, 2002). Thus, trees made up of four to six terminal compartments were large enough to achieve the best possible prediction level, which produce errors that tend to be minimal (Figure 8B).

The forecasts relating to the six terminal compartments consisted of averages based on 73, 58, 19, 9, 24 and 17 observations (making 200 observations in total) (Figure 8C). The forecasts obtained would have greater instability if the tree grew a little more, based on an average of about five observations. The predicted value of Zn in the plant was 457 mg kg^{-1} when the the CECe was greater than or equal to 442 mmol kg^{-1} or more (Figure 6C). Otherwise, the branch on the left of the tree should be observed from which the forecast of the value of the CECe and subsequently the pseudototal values of Zn (ZnEPA) and Al oxides (Al_20_{3DCB}) in the soil, so as to determine which terminal chambers ("terminal nodes") are suitable for a forecast, which in this case were 91, 140, 146 or 231 mg kg^{-1} of Zn concentration in the plants.

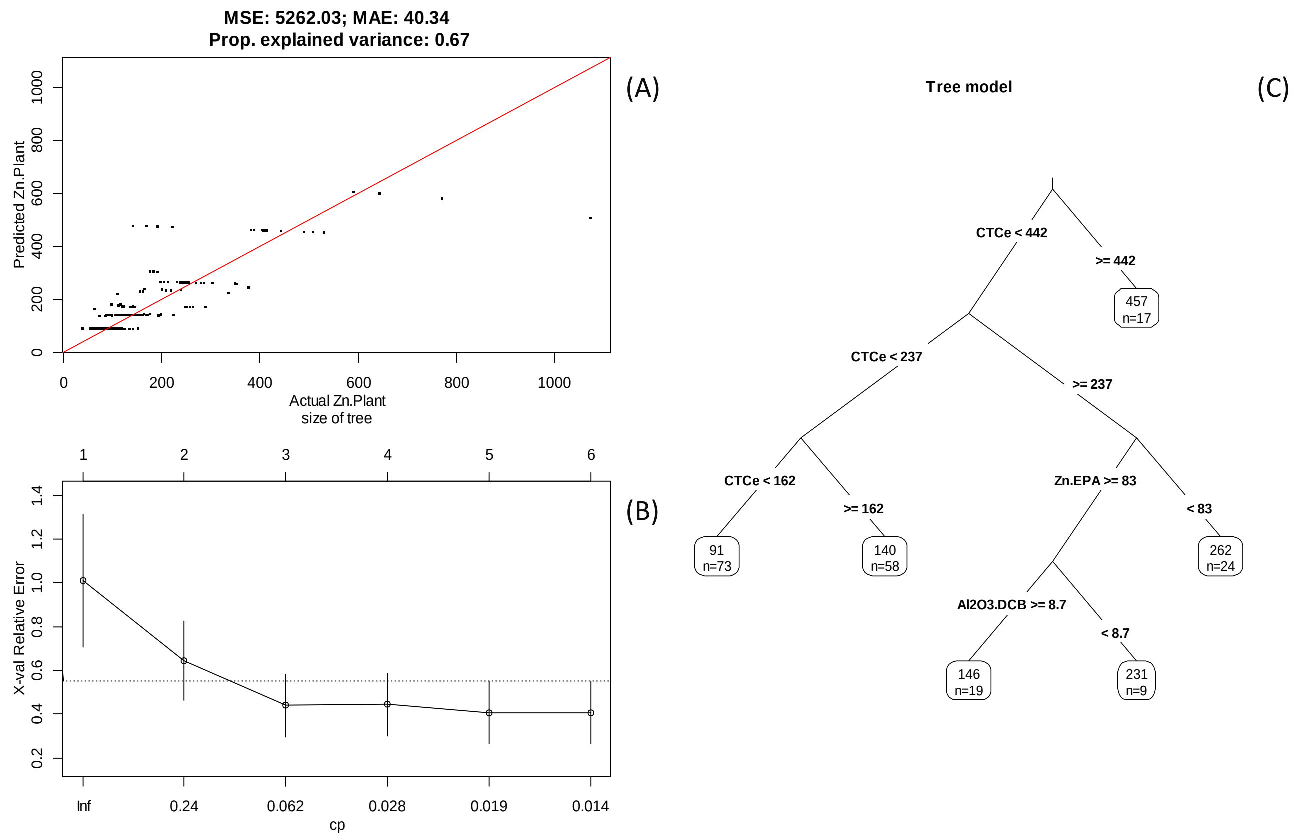

Figure 8 – Results of the prediction of zinc using the trees model: (A) scatter plot comparing the actual values (horizontal axis) and the predicted values of Zn in plant in mg kg^{-1}; (B) estimates and confidence intervals of the relative error; (C) Regression Tree

2.4. Conclusions

- The concentrations of Cu, Pb and Zn were higher than the PV. For only one sample the values were larger than the IV.
- With the exception of Cd, there was a positive correlation between bioavailable and pseudototal contents of the PTEs, indicating a high affinity of the geochemistry of the elements and their occurrence in the environment
- The soil vegetables analyzed, all concentrations were lower than PV.
- Cd and Pb content in plants had no significant correlation with any of the variables studied. The random forest and tree models were good predictors of results generated from a regression model and they provided useful information about which covariates were important for forecasting only the Zn concentration in the plants. The most important covariates for predicting Zn content in plants were the effective CEC, pseudototal content of Zn in the soil, pH, the pseudototal concentration of Cu in the soil,

the available content of Cu in the soil and the carbon content, in a descending order of importance.

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3 RELATIONS BETWEEN CONCENTRATIONS OF CADMIUM, COPPER, LEAD, NICKEL, AND ZINC IN SOILS AND VEGETABLES, FOR SÃO PAULO STATE, BRAZIL

Abstract

Vegetable consumption is considered as a major exposure pathway of heavy metals or so called potentially toxic elements (PTEs) for the general population. Soil screening values based on total concentrations in the soil which do not account for the availability of metals have been conventionally used to assess risks. The ratio between the concentration of PTEs in edible parts of plants and the total concentration in the soil is called bioconcentration factor (BCF). This is a widely used index to estimate the accumulation of metals in vegetables. However, a generic BCF is not appropriate to describe the accumulation of metals in plants accurately. A substantial variation among BCF values due to differences in soil factors and different plant types can be expected. In Brazil, there is a lack of combined soil-plant data and information on the uptake and accumulation of PTEs in plants. As a consequence, no appropriate plant–soil relations are available to include in risk assessments or for the derivation of soil screening values. The objective of the authors was to develop empirical soil-plant models for cadmium, copper, lead, nickel, and zinc, to be able to derive appropriate soil screening values and to enable a more accurate risk assessment for tropical regions such as São Paulo (SP) - Brazil. To accomplish this, we collected 200 soil (0-20 cm) and plant samples, from 25 species in the production areas to compose SP data set. However, to derive the soil screening values, it is necessary to use a BCF valid in the expected range of the screening values, since the BCF varies with concentration and low soil concentrations of metals found in samples of SP. Therewith, was included other data set, covering additional concentrations of these metals in soils and plants, the Netherland (NL) data set. The impact of combining the SP and NL datasets has to be investigated. The application of soil-plant transference models derived in this study has potential, i.e showed a good performance for 8 of the 10 combinations (five metals versus two vegetables).This offers improved possibilities for the derivation of appropriate screening values for SP State, Brazil. For Cd in lettuce and for Ni and Zn in lettuce and in carrot, it was shown that the SP data can be combined with the NL data using equation 4 (including pH, OC content and clay content). For Cu, Pb, Zn in lettuce and for Cd and Cu in carrot, also model 4 (including pH, OC content and clay content) gave the most useful results, with SP and NL data sets combined. For 2 cases (Ni and Pb in carrot) application of the models gave an inconsistent result and the combination of datasets did not or insufficiently improve the results.

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

3.1 Introduction

3.1.1 Scope

Metals may cause adverse effects to the environment, animals and human health. As metals do accumulate in the edible parts of plants, exposure through vegetable consumption is an exposure pathway often considered as a major pathway (ROMKENS et al, 2009;

RODRIGUES et al, 2012). For this reason there has been much attention on the development of tools to characterize the pathways relating soil contamination and plant uptake. However, there are only few studies which focus on the relationships between the concentrations of metals in soils and plants in humid tropical regions, especially in Brazil.

Soil screening values based on total concentrations in the soil which do not account for the availability of metals have been conventionally used to assess risks (DE VRIES et al., 2008; RODRIGUES et al., 2012). The ratio between the concentration of PTEs in edible parts of plants and the total concentration in the soil is called bioconcentration factor (BCF). This is a widely used index to estimate the accumulation of metals in vegetables (SWARTJES et al., 2007), mainly because simple application (ALONSO et al, 2003; SIPTER et al, 2008, MURRAY; THOMPSON; MACFIE, 2009). However, a generic bioconcentration factor (BCF) is not appropriate to describe the accumulation of metals in plants accurately (DE VRIES et al., 2007; RÖMKENS et al., 2009a, 2009b; RODRIGUES et al., 2012). A substantial variation among BCF values due to differences in soil factors and different plant types can be expected. Mechanistic models, however, with the potential of predicting accumulated plant concentrations for an array of PTEs, have not yet been developed, let alone validated under field conditions (SWARTJES, 2011).

To evaluate the transfer of metals from soil to plant the most important soil factors are: metal concentration in soil, organic matter content, content of oxides of Fe and Al, the cation exchange capacity, pH, ionic strength of the solution, the specific surface area and mineralogy (PÉREZ et al, 1997; GRAY et al., 1998; MEURER, 2004).

In more recent years, empirical models such as the Freundlich-type models, i.e. an exponential relationship between the concentration of metals in the plant versus the concentration in soils, and including the soil properties, have been used by several researchers. Römkens et al. (2009), for example, derived such empirical soil-plant relationships for Cd and observed that pH and cation exchange capacity (CEC) of the soil were the variables that had the greatest influence on the transfer of cadmium into the plants. Melo et al. (2011) found significant soil-plant relationships for leafy vegetables and roots for Cd and included total metal concentration in soil and the pH as variables. For this purpose, Melo et al. (2011) used data measured in tropical and temperate regions. However, the vast majority of studies considers a limited number of metals and specific soil properties, thus, studies that contribute to a wider range of results capable to compose a dataset in order to increase the applicability of these models is important.

In Brazil, there is a lack of combined soil-plant data and information on the uptake and accumulation of PTEs in plants. As a consequence, no appropriate plant–soil relations are available to include in risk assessments or for the derivation of soil screening values.

3.1.2 Purpose

The objective of the authors was to develop empirical soil-plant models for cadmium, copper, lead, nickel, and zinc, to be able to derive appropriate soil screening values and to enable a more accurate risk assessment for tropical regions such as São Paulo - Brazil.

3.2 Materials and methods

3.2.1 Selection of areas, collection and analysis of samples

In total, 200 soil samples (0-20 cm depth) and 200 corresponding plant samples were collected, of 25 species, in 53 vegetable crop producing areas, covering 19 cities in the state of São Paulo, chosen because they cover the main production of vegetables in the State of São Paulo and also due to the seasonality of production. The sampling sites were in rural, urban and industrial areas, in an attempt to obtain samples with a wide range of contamination levels in soil for the various metals studied. Sampling was concentrated in the area called "Green Belt" zone, which is located within roughly 120 km of the city of São Paulo and includes 73 surrounding townships (CAMARGO, 2008).

In the laboratory, plant samples were washed in running water to remove impurities and transferred to drying oven at 60 °C. Subsequently, the samples were grounded in a stainless steel mill and packed in plastic bottles. The soil samples were dried and subsequently sieved (2 mm mesh).

Plant material was digested using a microwave oven (Mars Xpress, CEM Corporation), as described by Araújo et al. (2002), and concentrations of Cd, Cu, Ni, Pb, and Zn in the plant extracts were determined using optical emission spectrometry (ICP-OES). Total concentrations of PTEs in the soil samples were extracted with concentrated acid in a microwave oven, under controlled temperature and pressure, following the EPA 3051a method (1:3 $HCl:HNO^3$, v/v) (USEPA, 1998). Cd, Cu, Ni, Pb, and Zn contents of the soil samples were determined via ICP-OES. Certified reference materials NIST SRM 2709th and San Joaquin soil were used to attest the quality of the analysis. Recovery rates of PTEs were of satisfactory levels (between 71 and 92%). Soil samples were subjected to routine chemical and fertility tests (ANDERSON; INGRAM, 1992). Organic carbon was determined following dry combustion in a LECO CN-2000 elemental analyzer. A more detailed description of the sampling sites, sample collection and pre-treatment procedures has been provided by chapter 2.

3.2.2 Additional soil and plant data

To increase the number of data for derivation of appropriate soil-plant relations, existing data sets (soil concentrations and corresponding plant concentrations) of Cd, Cu, Ni, Pb and Zn have been evaluated. These dataset are the RIVM dataset and Alterra dataset (VERSLUIJS; OTTE, 2001); the combination of these datasets will be indicated in this study as the Netherlands dataset (NL). 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 2 the characteristics of the two datasets used in this study have been summarized. The Intervention Values for São Paulo State are mentioned because the goal is to estimate BCF values valid in the same concentration range as the Intervention Values. The state of Sao Paulo distinguishes three exposure scenario where vegetables are supposed to be grown: rural (agricultural), urban (residential) and industrial.

Table 1 –Range in soil concentration for two datasets (São Paulo and Netherland) and Intervention Values for the state of São Paulo related to three scenarios (rural, urban and industrial)

	SP dataset						**Netherlands dataset**						**Intervention Values for SP State (Cetesb, 2014)**		
Soil Conc. Metal	**Min.**	**Median**	**Max.**	**Aver.**	**S. D.**	**n**	**Min.**	**Median**	**Max.**	**Aver.**	**S. D.**	**n**	**Rural**	**Urban**	**Indust.**
			mg kg^{-1}						mg kg^{-1}					mg kg^{-1}	
Cd	<L.D	0.1	2.4	0.1	0.2	200	<L.D	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	10000
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	10000

<L.D = limit detection, S.D. = standard deviation, n = number of observations

3.2.3 Development soil-plant relations

3.2.3.1 How to overcome the limitation in view of data from tropical areas?

To derive the soil screening values, valid for tropical conditions, in São Paulo - Brazil, it is necessary to use a BCF valid in the expected range of the screening values, since the BCF varies with concentration. Although the screening values are unknown at forehand, the current screening values for the State of São Paulo might be a good estimate. The low concentrations of metals found in soil samples of SP are not appropriate for the derivation of soil screening values (Table 1). An option to be considered is the inclusion of other data sets, covering additional concentrations of these metals in soils and in plants, especially in the higher concentration range. The lack of data of soil – plant for tropical conditions similar to the conditions in São Paulo in bibliographic references, however, hampers this intention. A remaining option was to include an additional data set from a different region and different climatic conditions, e.g., a dataset that was derived in the Netherlands, widely used in other studies involving soil-plant relations. This data set was also used to develop screening values in the Netherlands.

The impact of combining the SP and Netherlands datasets has to be investigated in terms of representation of tropical conditions prevailing in São Paulo and appropriate concentration range in soil regarding the derivation of screening values for the three exposure scenario. To this purpose, the following methods were used: a visual interpretation, the development and comparison of empirical soil – plant relations and statistical analyses. The combined results from the three assessment is used to conclude on the ideal dataset (multiple lines of evidence) (Figure 1).

For the derivation of soil screening values the groups of leafy and root vegetables were distinguished, because these groups of plants have different plant uptake characteristics, resulting in different soil – plant relations. To be able to investigate the impact of combining the SP and Netherlands datasets, this study focusses on one species of each vegetable group, i.e., lettuce (leafy vegetables) and carrots (root vegetables). Doing so, difference in uptake characteristics between vegetables within one vegetable group are eliminated as confounding factor. The two species were chosen for representativeness for the vegetable group and larger number of samples.

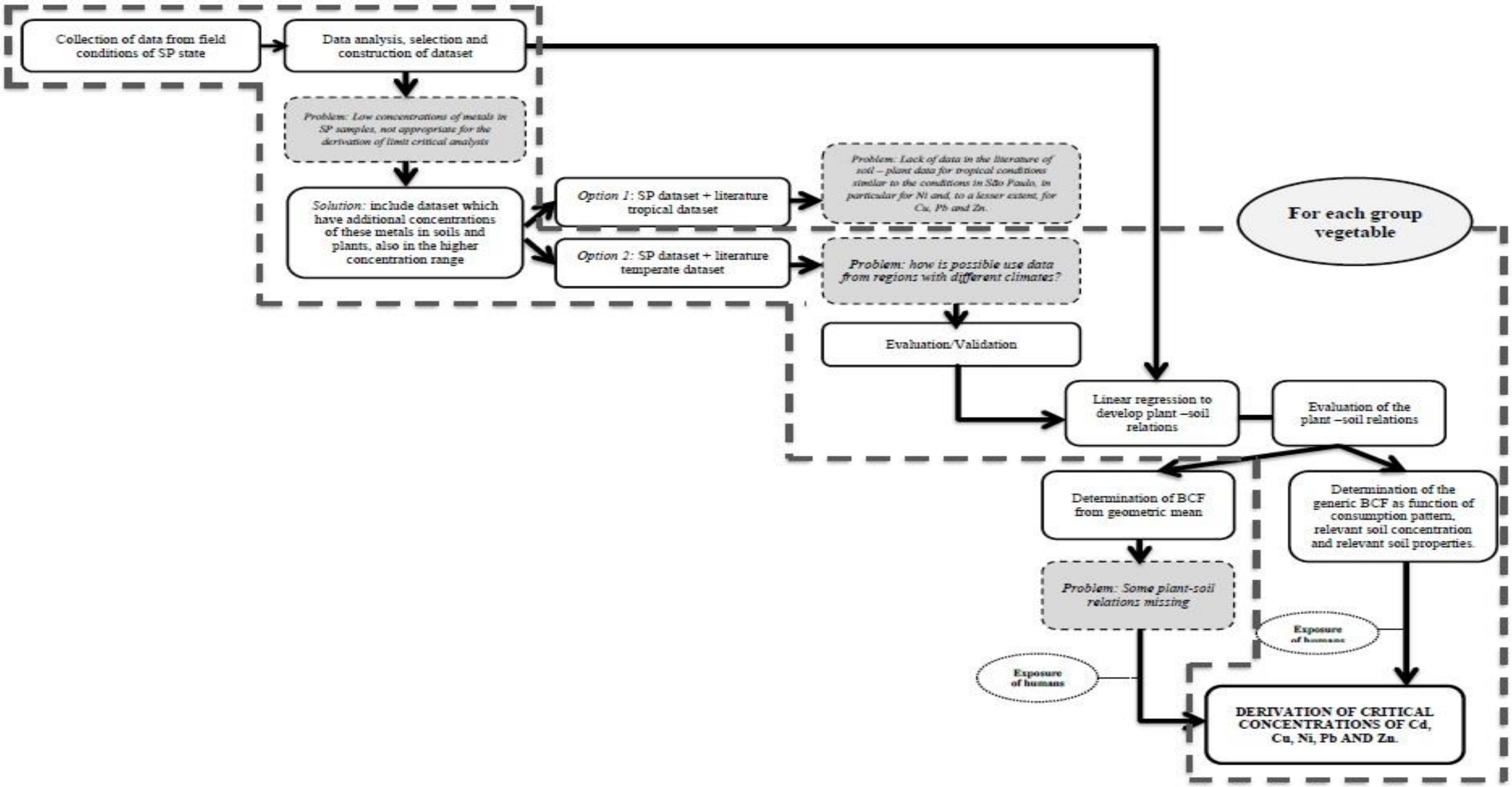

Figure 1 – Overview of model described in section 3.3.1

3.2.3.2 Visual interpretation

Graphs were made with the objective to provide insight into the plant concentrations as a function of soil concentrations. For this relation an exponential curve is expected, characterized by a less than (linear) proportional metal concentration in plants with increasing metal concentration in soil. Subsequently, it is possible to visually judge whether the data from the different data sets could be compatible, i.e. fit within the same exponential relationship. In this respect, possible differences in uptake behavior between the São Paulo dataset (SP) and the temperate datasets (NL) are registered.

3.2.3.3 Model development

In this study, several regression models were applied to predict the accumulated concentration in vegetables as a function of the total soil concentration and the soil properties, using multiple linear regression analysis (SPOSITO, 1980; VERSLUIJS; OTTE, 2001).

For each vegetable, the following equations were derived:

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

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

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

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

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 KCl = -log H^+ soil, %Clay = clay content of the soil (%), %OC = organic carbon content of the soil (%) and a, b, c, d and e are empirical regression parameters.

These models were developed on the basis of the São Paulo datasets and the Netherlands datasets separately and, when justifiable (section 2.3.4), for the combined dataset. The validity of the soil-plant models described above for these data sets was evaluated.

When for a specific combination of metal and vegetable no statistically significant soil-plant relation could be derived, a constant BCF was derived as a fallback through a statistical interpretation of measured BCF values for this combination of soil and vegetable (more details in section 3.2.3.5).

3.2.3.4 Statistics

For descriptive statistics and for statistical analysis of data the SPSS 16.0 software package for Windows was used. Except for pH, all data were log transformed (Log10) due to the occurrence of non-normality in the variable distributions. The plant - soil relations were evaluated for statistical correctness using an F-test (one-sided exceeding probability, $\alpha = 0.05$) and significance ($p<0.05$) (VERSLUIJS; 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 on the percentage of explained variance. The relative contribution of the different variables was assessed by comparing the average explained variance (details in section 3.2.3.5). 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 data sets (São Paulo and the Netherlands).

3.2.3.5 Evaluation of the accuracy of tests and soil-plant models using SP and NL data sets

The tests applied to assess the usefulness of the soil-plant models, focused on two main questions: (A) does the data fit within the model? and (B) can the results of the soil-plant models be improved by the combination of data from the two available datasets (from São Paulo and The Netherlands), in spite of the different conditions (climate, soils, genotypes of plants, agricultural practice). The following tests were passed for each available combination of vegetable and metal (Figure 2):

(A) the test on the accuracy of the model was based on the standard error of the model (significant when less than or equal to 0.5, which is the order of the experimental standard error of the concentration in the plant). The significance of the model relations was based on the coefficient of determination (r^2 in 5% probability with F-test for n data points). The model results were used only when tests were passed.

(B) comparison of the average explained variance for the combined dataset with the explained variance for the separate datasets (São Paulo and the Netherlands). This comparison gives an indication of the predictive power of the separate and combined datasets and to decide whether the combination of SP data set and the Netherlands dataset is useful.

To assess the importance of the effects of the available soil parameters to explain the data, the tests A and B are performed for the models (1)- (4) (see 3.2.3.3), with three possible outcomes and consequences:

(1) When **(A)** is positive and **(B)** indicates a higher explained variance for the combined dataset: use the combined date set and the model with the highest explained variance.

(2) When **(A)** is positive and **(B)** does not indicate a higher explained variance for the combined dataset: use the dataset for SP or for the Netherlands, the choice based on highest n or best standard error of the estimate se(y).

(3) When **(A)** is negative (independent of outcome of **(B)**): skip modelling efforts and follow a statistical approach using averages or percentiles of the measured BCF values. To consider the usually large difference in BCF results for low and high concentrations, the data is stratified in relation to the concentration in soil, when possible, i.e. when a sufficient number of data is available (preferably groups of minimal 30 data points).

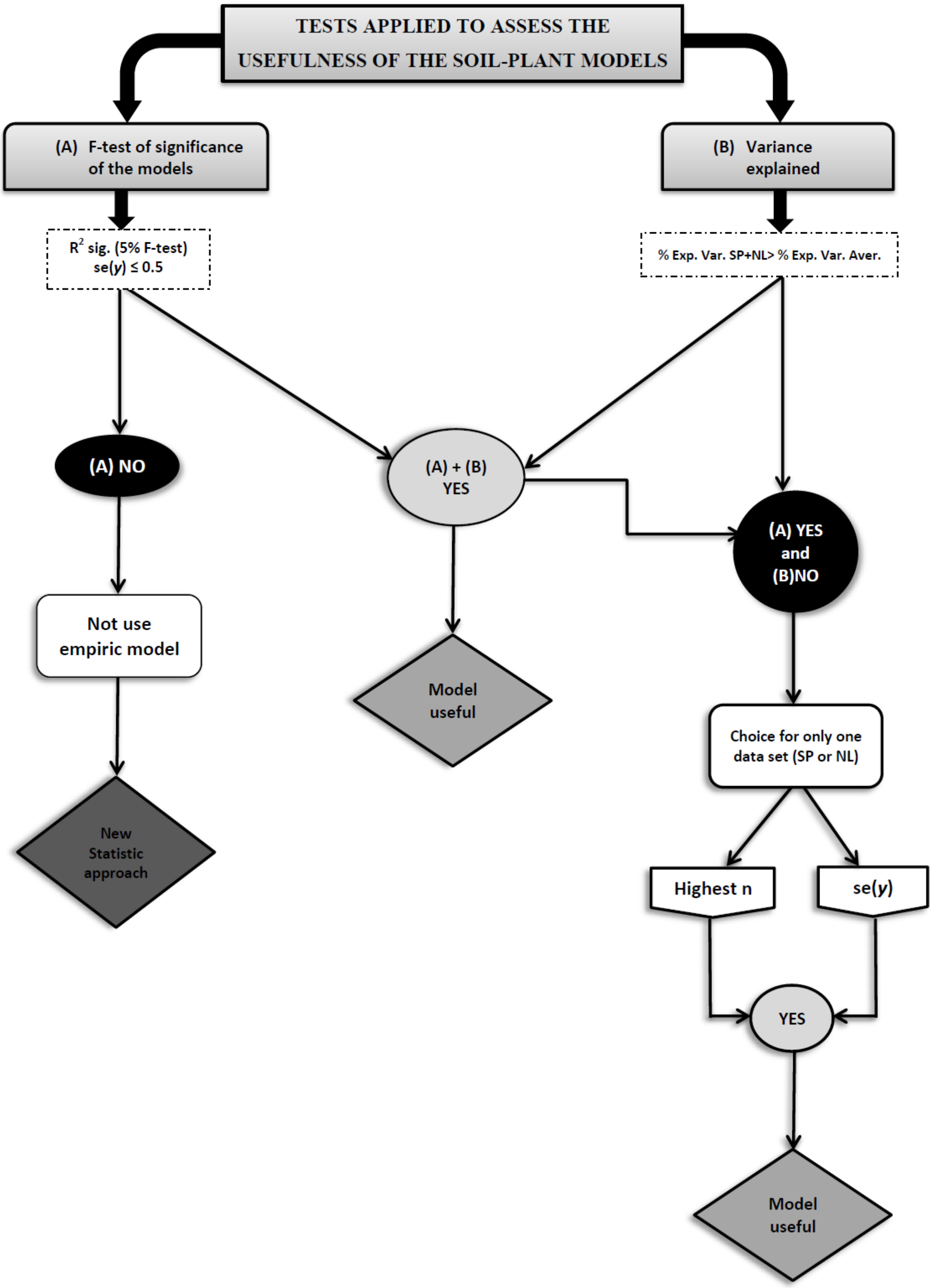

Figure 2 – Schematization of the steps described in section 3.2.3.5, choice statistical

3.3 Results and discussion

3.3.1 Descriptive analysis

The SP data set collected in the field has Cd concentrations in soil ranging from 0 to 2 mg kg^{-1}, with a mean of 0.12 mg kg^{-1}. Mean Ni, Cu, Pb and Zn levels are 8 mg kg^{-1}, 32 mg kg^{-1}, 22 mg kg^{-1} and 166 mg kg^{-1}, respectively. The results show that the mean concentrations of metals in soils are below the Intervention Values prescribed by law for the state of São Paulo (Table 1). Therefore, as explained in sections 3.2 and 3.4, we consider the use of an additional dataset, with higher concentrations of metals in soil.

The Netherlands dataset (the additional dataset) shows mean concentrations of Cd, Cu, Ni, Pb and Zn of 1.3, 40.4, 24.3, 93.5 and 489 mg kg^{-1}, respectively. The decision to include soils from different climatic and geological zones opens the possibility to extend the applicability of this study in research to assess environmental risks, for example. As leaves and roots generally have significant differences in plant uptake we distinguish between these groups. To eliminate the confounding factor 'impact from different vegetables on uptake' it was decided to evaluate one representative species of each vegetable group, i.e. lettuce (leafy vegetables) and carrots (root vegetables).

Table 2 summarizes the distribution characteristics (considering physical–chemical properties of the studied soils, soil and plant concentrations for each metal and for lettuce and carrots) of the overall data set and the separate SP and NL data sets.

For the overall dataset, the soil pH ranges from acidic to neutral, i.e. from 3.6 to 8.4 for lettuce and 4.4 to 8.4 for carrot, where the outliers for acid pH are in the SP data set and the for alkaline pH are in the NL data set. For both vegetables, the average pH values between metals ranges from 5.6 to 6.6. The pH range is 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 (tropical and temperate) are demonstrably different (RIEUWERTS, 2007). The pH values, however, can be comparable in tropical and temperate agricultural soils, since soil management practices aim at ideal soil properties for agricultural production.

Values for soil organic carbon, as well as pH values listed above, show a large variation in both datasets, ranging from 1 to 40% for lettuce and 1 and 37% for carrot. It is worth mentioning that the retention of metals in soil is greatly influenced by soil organic matter and clay (RÖMKENS et al, 2009; RODRIGUES et al, 2010a). The clay content of the soils were different between the data sets (SP - 3 to 36% for lettuce and 2 to 45% for carrot; NL - 12 to 15% lettuce and 10 to 12% carrot) and within the data set of SP (3-45%), which showed that the soil texture ranges from sandy to clayey, with predominantly clay soils preferred by farmers with horticultural activities.

The difference between the data sets presented here (tropical and temperate data set) has also been reported by other authors (e.g., MELO et al., 2011). 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 yields a low cation exchange capacity (FONTES; ALLEONI, 2006). In other words, the dominant mechanism of retention of metals is different between different geographical regions (NAIDU et al. 1998).

The soil concentrations show a wide range in both data sets. The NL data set has substantially higher concentrations, for all metals and both vegetables studied, with the exception of Cu in lettuce. However, when comparing the average concentrations in the soil, Cu also has a lower average in the SP data set than in the NL data set (SP - 34.8 and NL- 39.4 Cu, in mg kg^{-1}) as well as other metals. This relatively large variation as well as significant differences between the average concentrations are 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 is higher for lettuce, which is representing the leaf vegetable group, for both data sets.

Average concentrations of metals in vegetables collected in the field in SP (mg kg^{-1}) were: for lettuce, 0.2 for Cd; 7.4 for Cu; 0.4 for Ni; 1.1 to 76.2 for Pb and Zn and for carrot, 0.1 for Cd; 6.7 for Cu; 0.3 for Ni; 0.3 to 48.2 for Pb and Zn. Metal concentrations in lettuce have slightly higher average concentrations than carrots, for all metals. Itanna et al. (2002) stated that Cd, Ni and Pb tend to accumulate in leave crops, due not only to their area of broadleaf, but also to the high transpiration rate.

According to the Brazilian National Agency of Sanitary Surveillance (ANVISA, 1965), the allowable limits for Cd, Cu, Ni, Pb and Zn in edible parts of vegetables are 1.0; 30.0; 5.0; 0.5 and 50.0 mg kg^{-1}, respectively. Pb and Zn show concentrations in lettuce and carrots in the SP dataset at concentrations above these allowable limits, with exceedances of the 40% and 99% of the collected samples, respectively. Guerra et al. (2012) found Cd concentrations in edible parts of plants collected in the state of São Paulo ranging from 0.01 to 0.18 mg kg^{-1}, from Ni 0.01 to 0.74 mg kg^{-1} and of the Pb between 0.02 to 2.50 mg kg^{-1} and observed that the concentrations of Cd and Ni did not exceed the permissible limits established by ANVISA. But for Pb, 45% of samples from this study exceeded the allowable limit.

3.3.2 Evaluation of datasets for development soil-plant relations

3.3.2.1 Visual interpretation

Graphs of the lettuce and carrot concentrations as a function of soil concentration of the datasets SP and NL for all metals studied can be seen in Figure 3.This figure shows in all cases a wide range of concentrations in vegetables. This happens in the SP data set and also between the two data set (RIVM and Alterra), both from temperate regions, however, from different areas which combined form the NL dataset. This can be partly explained by a variation in the soil properties not shown in the figure, but is also inherent due to differences in micro-climate, crop varieties, etcera. Moreover, it is technically difficult to exactly sample soil material that corresponds to the metals taken up in the vegetables.

In general, even with such variation, the relationship between the soil and vegetables follows a similar pattern for the NL and SP data sets (Figure 3). Despite the large variation for Cd in lettuce, the cloud of data points tends to an exponential curve, characterized by a less than linear proportional concentrations of metals in plants with increased metal concentrations in soil. Note that the SP data is found in the low soil concentration range while the NL soil concentrations vary from low to high. Visually, the datasets could be considered as belonging to the same exponential curve. For Cd in carrot, however, an exponential curve is hardly imaginable. The connection and partial overlap may hold, but the two data sets are in different concentration ranges and there are few data points from the SP data set.

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

			SP + Netherlands data set							SP data set							Netherlands data set							n
	Cd		Min.	5 Perc.	Median	95 Perc.	Max.	Average	Stand. D.	Min.	5 Perc.	Median	95 Perc.	Max.	Average	Stand. D.	Min.	5 Perc.	Median	95 Perc.	Max.	Average	Stand. D.	
Lettuce		Csoil	0.1	0.0	0.6	3.5	12.6	1.2	4.2	0.1	0.1	0.1	0.5	2.4	0.1	0.2	0.1	0.2	0.7	4.0	12.6	1.4	4.6	SP + Holland = 293 SP = 36 Holland = 257
		pH	3.9	5.1	6.5	7.5	8.4	6.4	0.8	3.9	4.7	5.8	6.8	7.3	5.8	0.6	4.7	5.3	6.8	7.5	8.4	6.6	0.7	
		%OC	0.7	1.6	3.9	12.8	40.1	5.4	4.4	1.0	1.6	3.2	13.2	40.1	4.7	5.0	0.7	1.6	4.1	12.8	36.1	5.5	4.3	
		%Clay	0.5	3.0	17.0	47.7	67.8	20.3	13.2	10.0	15.1	37.6	57.7	67.8	36.5	13.3	0.5	2.2	16.0	30.0	49.0	15.3	8.3	
		Cveg	0.1	0.0	0.6	2.6	11.3	0.9	1.0	0.1	0.1	0.1	0.8	1.7	0.2	0.3	0.1	0.2	0.8	2.8	11.3	1.1	1.1	
	Cu																							
		Csoil	3.3	6.4	27.0	87.5	356.0	37.4	36.8	3.3	4.8	18.1	98.6	356.0	34.8	43.8	6.0	12.6	30.4	85.5	217.0	39.4	30.4	SP + Holland = 177 SP = 39 Holland = 138
		pH	3.9	4.8	6.1	7.1	8.4	6.1	0.7	3.9	4.7	5.8	6.8	7.3	5.8	0.6	4.7	5.2	6.4	7.2	8.4	6.3	0.7	
		%OC	0.6	1.0	2.2	6.6	23.3	2.9	2.3	0.6	0.9	1.9	7.7	23.3	2.7	2.9	0.7	1.0	2.8	6.1	8.4	3.0	1.7	
		%Clay	0.3	0.5	2.2	12.0	35.6	4.2	4.9	0.3	0.5	1.8	9.9	35.6	3.5	4.4	12.0	*	12.0	*	16.3	12.6	1.6	
		Cveg	1.6	3.0	7.9	14.1	47.8	8.2	3.9	2.5	2.8	7.5	11.6	17.0	7.4	2.6	1.6	3.2	8.3	14.8	47.8	8.8	4.5	
	Ni																							
		Csoil	1.6	2.6	9.8	28.1	46.3	12.4	9.2	1.6	2.4	6.7	19.4	30.7	8.1	5.5	12.4	13.2	20.5	45.2	46.3	22.2	8.2	SP + Holland = 101 SP = 39 Holland = 62
		pH	3.9	4.7	6.0	6.8	7.3	6.0	0.6	3.9	4.7	5.8	6.8	7.3	5.8	0.6	5.6	5.6	6.4	6.8	6.8	6.4	0.4	
		%OC	1.0	1.7	3.7	12.7	40.1	5.1	4.5	1.0	1.6	3.2	13.2	40.1	4.7	5.0	2.9	2.9	5.4	12.2	14.4	5.9	3.0	
		%Clay	10.0	12.0	35.2	57.7	67.8	34.5	14.4	10.0	15.1	37.6	57.7	67.8	36.5	13.3	12.0	*	12.0	*	16.3	12.6	1.5	
		Cveg	0.1	0.1	0.4	2.3	10.2	0.6	0.9	0.1	0.1	0.3	0.9	2.5	0.4	0.3	0.2	0.3	0.8	3.7	10.2	1.2	1.5	
	Pb																							
		Csoil	3.6	11.5	49.1	265.7	548.0	86.8	88.0	3.6	6.7	16.0	65.8	331.4	23.7	31.5	3.8	15.0	57.0	265.7	548.0	95.4	89.7	SP + Holland = 574 SP = 39 Holland = 535
		pH	3.8	4.9	6.8	7.6	7.7	6.6	0.9	3.9	4.7	5.8	6.8	7.3	5.8	0.6	3.8	5.0	6.9	7.6	7.7	6.7	0.9	
		%OC	0.7	1.3	3.6	14.4	40.1	5.4	4.9	1.0	1.6	3.2	13.2	40.1	4.7	5.0	0.7	1.3	3.7	14.4	28.3	5.5	4.8	
		%Clay	0.5	1.0	17.0	40.1	67.8	18.3	12.2	10.0	15.1	37.6	57.7	67.8	36.5	13.3	0.5	1.0	16.0	35.9	39.7	15.8	9.6	
		Cveg	-0.3	0.1	1.1	5.2	57.9	1.8	2.8	0.1	0.1	0.2	4.0	20.2	1.1	2.3	0.3	0.2	1.2	5.3	57.9	1.9	2.9	
	Zn																							
		Csoil	39.6	69.8	184.5	1041.5	1650.0	333.8	343.4	39.6	65.0	141.3	413.3	643.3	174.8	110.2	42.0	78.3	320.0	1469.1	1650.0	454.2	405.8	SP + Holland = 177 SP = 39 Holland = 138
		pH	3.6	4.7	6.1	7.1	8.4	6.0	0.8	3.6	4.4	5.5	6.6	7.2	5.5	0.7	4.7	5.2	6.4	7.2	8.4	6.3	0.7	
		%OC	0.5	1.0	2.8	8.5	29.9	3.6	3.4	0.5	1.0	2.9	13.3	29.9	4.4	4.6	0.7	1.0	2.8	6.1	8.4	3.0	1.7	
		%Clay	4.0	6.6	13.4	41.0	64.3	17.1	10.7	4.0	6.5	14.1	41.3	64.3	17.5	11.0	12.0	*	12.0	*	16.3	12.3	1.2	
		Cveg	8.7	20.1	75.0	220.0	513.4	88.5	66.1	8.7	16.8	49.8	228.9	513.4	76.2	79.5	19.0	29.7	88.1	202.2	353.0	97.8	52.0	
Carrot	Cd																							
		Csoil	0.1	0.0	0.4	3.2	62.0	1.0	3.1	0.1	0.1	0.0	0.7	1.0	0.1	0.2	0.1	0.1	0.4	3.2	62.0	1.0	3.2	SP + Holland = 240 SP = 5 Holland = 235
		pH	4.4	5.1	6.8	7.5	8.4	6.5	0.8	4.9	4.9	5.6	6.7	6.8	5.8	0.6	4.4	5.1	6.8	7.5	8.4	6.6	0.8	
		%OC	0.2	0.9	3.2	10.6	12.8	3.9	2.9	1.5	1.5	2.2	11.3	12.0	3.2	2.4	0.2	0.9	3.3	10.7	12.8	4.0	3.0	
		%Clay	0.5	1.0	11.2	35.4	65.3	12.9	11.9	27.6	27.6	45.2	64.4	65.3	45.3	10.3	0.5	1.0	9.0	26.4	30.6	10.7	8.4	
		Cveg	0.1	0.1	0.3	1.5	29.5	0.5	1.5	0.1	0.1	0.1	0.3	0.3	0.1	0.1	0.1	0.1	0.3	1.5	29.5	0.5	1.5	
	Cu																							
		Csoil	6.1	9.9	26.3	108.0	92.0	24.9	21.8	7.4	7.6	17.7	55.3	57.6	22.8	13.9	9.0	12.0	29.7	200.7	217.0	43.9	45.2	SP + Holland = 34 SP = 5 Holland = 29
		pH	4.9	5.0	6.3	8.1	8.4	6.4	5.9	4.9	4.9	5.6	6.7	6.8	5.8	0.6	4.7	5.3	6.4	8.1	8.4	6.4	0.8	
		%OC	0.9	0.8	1.9	5.9	37.5	3.5	6.6	0.9	0.9	1.3	6.6	7.0	1.9	1.4	0.6	0.7	2.3	5.8	5.9	2.6	1.5	
		%Clay	0.7	0.8	3.2	12.0	5.8	2.3	1.4	0.7	0.8	1.8	5.5	5.8	2.3	1.4	12.0	*	12.0	*	12.0	12.0	0.0	
		Cveg	2.5	2.6	4.8	11.1	356.0	20.8	62.9	2.5	2.9	6.6	12.2	12.4	6.7	2.5	2.3	2.5	4.0	8.8	11.3	4.7	1.9	
	Ni																							
		Csoil	2.7	2.6	7.4	26.6	117.7	20.7	22.7	2.7	2.9	6.3	42.1	52.8	9.5	10.2	13.9	13.9	21.7	117.7	117.7	27.6	25.4	SP + Holland = 26 SP = 5 Holland = 21
		pH	4.9	4.7	5.9	6.8	6.8	6.2	0.6	4.9	4.9	5.6	6.7	6.8	5.8	0.6	5.6	5.6	6.4	6.8	6.8	6.4	0.4	
		%OC	1.5	1.6	3.3	12.1	13.3	4.8	3.0	1.5	1.5	2.2	11.3	12.0	3.2	2.4	2.9	2.9	4.9	12.7	13.3	5.7	2.9	
		%Clay	12.0	12.0	37.6	57.7	65.3	35.4	17.7	27.6	27.6	45.2	64.4	65.3	45.3	10.3	12.0	*	12.0	*	12.0	12.0	0.0	
		Cveg	0.1	0.1	0.3	1.2	7.1	0.7	1.1	0.1	0.1	0.3	0.8	0.8	0.3	0.2	0.2	0.2	0.5	3.1	7.1	1.0	1.3	
	Pb																							
		Csoil	1.8	10.2	51.0	265.7	461.0	83.8	91.5	8.6	8.6	14.9	25.7	26.3	15.6	4.7	1.8	9.2	48.3	254.3	461.0	88.1	92.7	SP + Holland = 273 SP = 5 Holland = 268
		pH	3.9	4.8	6.9	7.6	7.7	6.3	0.9	4.9	4.9	5.6	6.7	6.8	5.8	0.6	3.9	4.9	6.5	7.5	7.7	6.4	0.9	
		%OC	0.2	1.2	4.0	17.4	22.1	5.3	5.3	1.5	1.5	2.2	11.3	12.0	3.2	2.4	0.2	0.8	3.1	18.8	22.1	5.4	5.4	
		%Clay	0.1	1.0	17.1	43.5	65.3	12.3	11.9	27.6	27.6	45.2	64.4	65.3	45.3	10.3	0.1	1.0	10.3	22.2	31.5	10.2	8.3	
		Cveg	-0.4	0.1	0.7	4.6	4.5	0.6	0.5	0.1	0.1	0.1	3.6	4.5	0.3	0.9	0.4	0.1	0.5	1.6	3.8	0.6	0.5	
	Zn																							
		Csoil	40.0	49.2	139.1	1650.0	2035.0	457.6	594.1	53.8	55.1	100.5	252.1	279.3	114.2	51.3	40.0	47.3	286.5	2035.0	2035.0	623.0	662.7	SP + Holland = 34 SP =5 Holland = 29
		pH	4.7	4.8	6.2	7.4	8.4	6.1	0.7	4.7	4.8	5.5	6.5	6.6	5.6	0.6	4.7	5.2	6.3	8.1	8.4	6.3	0.7	
		%OC	0.6	0.8	2.3	5.9	9.2	2.7	1.6	1.2	1.2	2.3	8.1	9.2	2.8	1.7	0.6	0.7	2.3	5.9	5.9	2.6	1.6	
		%Clay	5.4	5.6	12.0	22.9	27.9	11.5	4.6	5.4	5.5	10.1	25.2	27.9	11.4	5.1	12.0	*	12.0	*	12.0	12.0	0.0	
		Cveg	17.0	20.3	39.1	97.6	158.5	45.5	24.4	20.3	20.6	39.8	138.7	158.5	48.2	29.4	17.0	18.8	36.3	87.6	102.2	44.2	21.7	

n = number of the samples

This same difficulty of deduce the soil-plant uptake from those graphs are observed for the other metals in carrot, especially for Cu and Ni, where the uncertainties, (roughly) visible as the vertical variations, are dominant over the variation with the soil concentrations. It remains to be seen if this can be ascribed to the variation in the other soil parameters. For Ni, the NL dataset has significant higher plant concentrations as the SP dataset. This is also the case for lettuce and may possibly originate from a difference in the methods of chemical analyses or interference with a soil parameter in this method(s).

The concentrations of Cu, Ni, Pb and Zn in lettuce also have as main feature the wide variation in accumulated concentrations in vegetables at similar concentrations in soil between the data sets, and within the same data set. With the exception of Ni, it is possible to observe an overlap of data clouds formed by the data of the different data sets. Moreover, at higher concentrations of metals in the soil, a mild increase of the accumulated concentrations in vegetables is observed.

To evaluate the soil-plant relationships, it is important to note a few other soil factors may be responsible for the concentration of PTEs 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, while total soil concentrations, soil pH, soil organic matter and clay content in soil are measured (XIAN, 1989). To be able to derive screening values appropriate for a specific tropical region, i.e. São Paulo State - Brazil, the inclusion of such factors is crucial to improve the relations between the concentrations of cadmium, copper, lead, nickel, and zinc in soils and in vegetables.

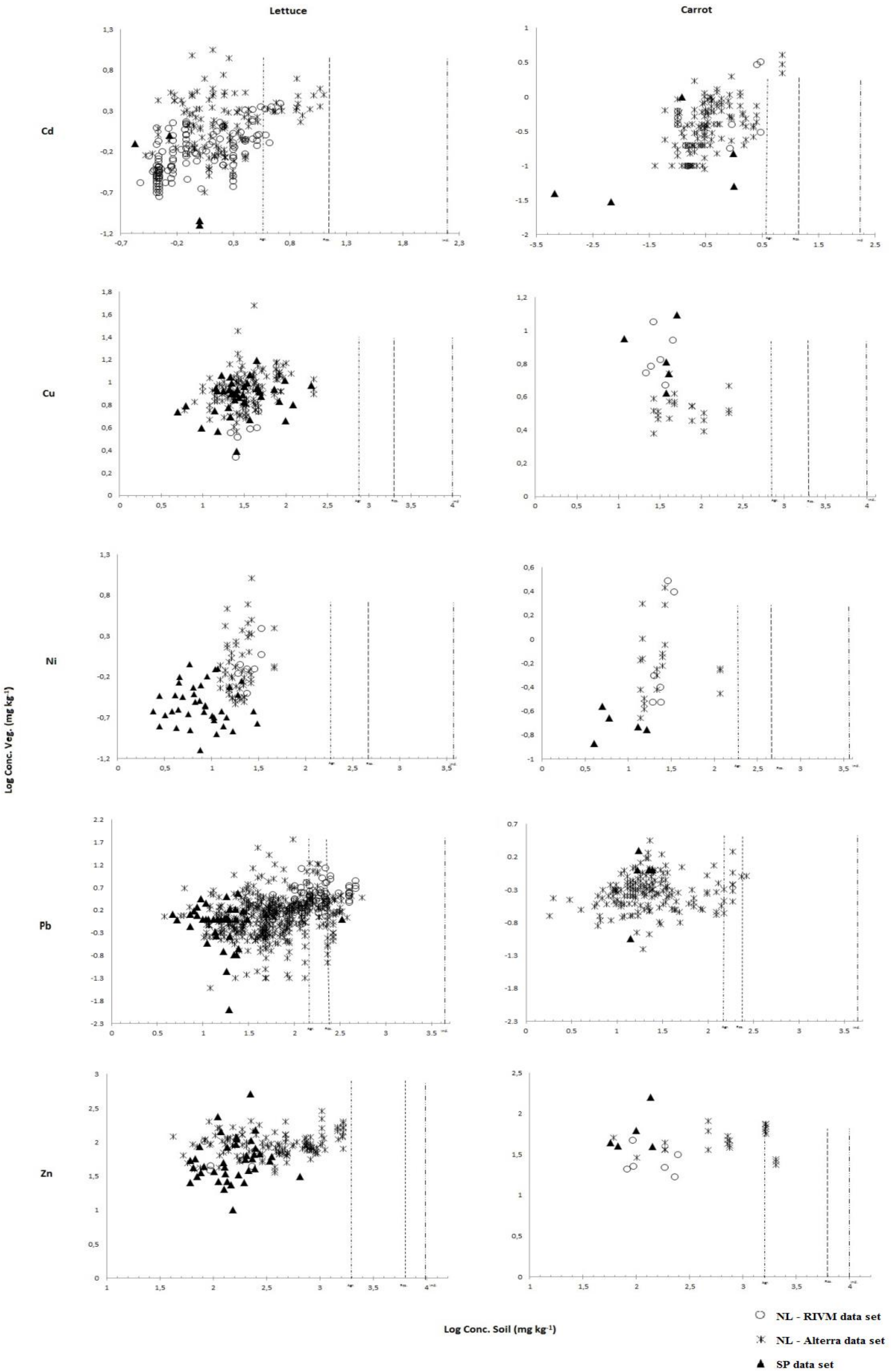

Figure 3 – Scatterplots of the vegetable concentration as a function of soil concentration for metals of the two datasets (SP and NL); the vertical lines represent the Intervention Values for the rural, urban and industrial exposure scenario, respectively, envisaged in the legislation of the state of São Paulo, Brazil

3.3.2.2 Evaluation soil-plant models

In the following text the possibilities for using Equations 1 to 4 (section 3.2.3.5)), for all ten combinations of metal (Cd, Cu, Ni, Pb and Zn) and vegetable (lettuce and carrot) is 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, $\alpha = 0.05$).

Concentrations of Cd in lettuce and carrot could be explained quite well. Significant soil–plant correlations were found in all models studied, with r^2 values between equations ranging from 0.35 to 0.47 and from 0.33 to 0.45, respectively. Equation 4 (for Cd) had the highest r^2 (0.47 and 0.45 for lettuce and carrot, respectively) and lowest standard error (se(y) 0.32 e 0.29, for lettuce and carrot, respectively).

For the Cu/lettuce combination, the r^2 were low for all equations. However, only equation 4 showed no significant correlation and again showed the best result with r^2 of the 0.15 and se(y) of the 0.16. For the Cu/carrot combination, only equation 4 was significant with r^2 0.52 and se(y) 0.13, showing that the clay content was an influential variable in relation to the other parameters.

For Ni and Pb in lettuce, all equations were significant, but for Pb in lettuce r^2 is low, ranging from 0.07 to 0.1. For carrot, no significant soil-plant equations were found for the two metals, that is, the predictive power of these equations was nil, precluding the use for the calculation of BCFs and, hence, for the derivation of the screening values.

In case of Zn in lettuce and carrot, equations 1 and 2 were not significant, showing that for Zn the pH does not contribute to the improvement of the prediction of the concentration in these vegetables. For lettuce and carrot equation 4 was the best with r^2 equals 0.35 and 0.71, respectively and se(y) of 0.12 and 0.19, respectively.

These first results about the significance of the soil-plant models or equations of regression are indicative to show which of the models tested has a good 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 is compared with that of the separate datasets (SP and NL; table 4).

Generally the explained variance is expected to increase with increase of the number of explaining parameters and this holds in all cases. For some combinations of metal and vegetable the improvement is marginal and in other cases the addition of a specific parameter significantly improves the equation. For Cd in lettuce the pH was the variable that contributed most to this increase. The average explained variance for the separate datasets are combined into a weighted average which ranges from 12 to 35% between the equations. These results were compared with the average of the explained variance for the combined dataset, which had an explained variance from 34.7 to 47.1% between equations. The explained variance of the combination is higher than the average explained variance of the separate datasets for all four equations. This indicates that the hypothesis that the data sets combined is useful for the prediction of the concentration of lettuce in Cd. The same behavior was observed for Ni in lettuce and carrot in with the explained variance for the data sets combined (equation 4) is of the 37 and 22%, respectively.

For Cd in carrot, the observation is different. The average explained variance of the separate data sets (29 - 47%) was slightly higher than the explained variance of the combined data set (33 - 45%). It shows that the two datasets differ inherently, probably due to climatic influences. Regions with different climates have different water regimes, temperature and evaporation rates. The same behavior as seen for Cd in carrot was observed for Cu in carrot, for Pb in lettuce and carrot and for Zn in lettuce, with the average explained variance for separate data set 71, 12, 18 and 50% greater that the explained variance of the combined data set, which was 52, 10, 35 and 7% respectively.

Table 3 – Regression coefficients of the soil-plant relations for Cd, Cu, Ni, Pb and Zn (dataset combined), according to Eq. (1,2,3 and 4) for lettuce and carrots

		Lettuce									Carrot								
Metal	**Model**	**a Const.**	**b Csoil**	**c pH**	**d %OC**	**e %clay**	**R^2**	**F**	***se* (Y-*est*)**	**n**	**a Const.**	**b Csoil**	**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	369	-0.19	0.46	*	*	*	0.33	119.29	0.31	238
	2	1.1	0.44	-0.18	*	*	0.42	131.37	0.33	368	0.89	0.42	-0.17	*	*	0.45	96.94	0.29	237
	3	1.35	0.48	-0.18	-0.28	*	0.44	97.61	0.33	367	0.9	0.42	-0.17	-0.01	*	0.45	64.37	0.29	236
	4	1.11	0.39	-0.14	-0.22	-0.14	0.47	81.38	0.32	366	0.92	0.43	-0.18	-0.01	0.04	0.45	48.44	0.29	235
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	176	0.63	-0.28	0.07	*	*	**0.25***	5.92	0.16	35
	3	0.61	0.17	0.01	-0.01	*	0.14	6.51	0.16	175	0.61	-0.27	0.08	-0.03	*	**0.25***	3.85	0.16	34
	4	0.57	0.21	0.01	-0.04	-0.08	0.15	5.79	0.16	174	1.05	-0.06	-0.07	0.07	0.36	0.52	8.99	0.13	33
Ni	**1**	-1.02	0.67	*	*	*	0.24	31.39	0.34	99	-0.8	0.4	*	*	*	**0.13***	4.47	0.34	30
	2	-0.85	0.71	-0.03	*	*	0.24	15.69	0.34	98	0.05	0.5	-0.15	*	*	**0.15***	2.58	0.34	29
	3	-0.86	0.72	-0.03	-0.03	*	0.24	10.37	0.34	97	0.13	0.51	-0.16	-0.1	*	**0.15***	1.7	0.35	28
	4	-0.13	0.43	-0.05	-0.25	-0.25	0.4	14.21	0.31	96	-0.24	0.21	0.01	-0.41	-0.21	**0.22***	1.94	0.34	27
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	556	-0.28	0.09	-0.03	*	*	**0.03***	2.64	0.26	170
	3	-0.06	0.26	-0.06	0.11	*	0.09	18.36	0.42	555	-0.24	0.15	-0.04	-0.17	*	**0.04***	2.61	0.26	169
	4	-0.11	0.29	-0.04	0.11	-0.12	0.1	15.37	0.42	554	-0.39	0.22	-0.03	-0.14	-0.13	**0.08***	3.55	0.26	168
Zn	**1**	1.45	0.19	*	*	*	**0.10***	20.38	0.22	175	1.46	0.07	*	*	*	**0.03***	1.05	0.2	32
	2	1.5	0.19	-0.01	*	*	**0.11***	10.25	0.22	174	2.28	0.08	-0.13	*	*	**0.27***	5.75	0.18	31
	3	1.65	0.11	-0.02	0.24	*	0.15	10.38	0.22	173	2.29	-0.09	-0.11	0.64	*	0.68	21.71	0.12	30
	4	2.3	-0.05	-0.07	0.44	-0.24	0.35	23.04	0.19	172	2.29	0.21	0.06	-0.74	-0.13	0.71	17.79	0.12	29

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

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***	**Explained Variance**			**df**			**(weighted) average**	**Test***
		SP+NL	**NL**	**SP**	**SP+NL**	**NL**	**SP**			**SP+NL**	**NL**	**SP**	**SP+NL**	**NL**	**SP**		
		----------------	%	----------------				%		----------------	%	----------------				%	
Cd	**Equat. 1**	34.7	13.5	3.2	369	330	37	12	TRUE	33.4	29.4	2.1	238	233	3	29	TRUE
	Equat. 2	41.7	31.8	11.0	368	329	36	30	TRUE	45.0	46.1	10.2	237	232	2	46	FALSE
	Equat. 3	44.4	37.3	11.2	367	328	35	35	TRUE	45.0	46.1	98.7	236	231	1	46	FALSE
	Equat. 4	47.1	37.8	11.2	366	327	34	35	TRUE	45.2	47.4	100.0	235	230	1	47	FALSE
Cu	**Equat. 1**	10.0	9.4	6.0	177	135	37	9	TRUE	16.1	10.4	1.9	36	25	3	10	TRUE
	Equat. 2	10.0	9.8	8.5	176	134	36	9	TRUE	25.3	42.4	49.1	35	24	2	43	FALSE
	Equat. 3	10.0	13.3	10.1	175	133	35	13	FALSE	25.4	51.1	59.8	34	23	1	51	FALSE
	Equat. 4	11.8	14.9	10.1	174	132	35	14	FALSE	52.1	71.5	59.8	33	22	1	71	FALSE
Ni	**Equat. 1**	24.1	6.9	0.1	99	60	37	4	TRUE	13,0	0.8	0.6	30	25	3	1	TRUE
	Equat. 2	24.2	6.9	21.8	98	59	36	13	TRUE	15.1	1.7	69.0	29	24	2	7	TRUE
	Equat. 3	24.3	7.2	24.8	97	58	35	14	TRUE	15.4	3.6	69.1	28	23	1	6	TRUE
	Equat. 4	37.2	7.4	27.0	96	57	34	15	TRUE	22.3	7.1	100.0	27	22	1	7	TRUE
Pb	**Equat. 1**	6.9	8.9	1.1	557	540	37	8	FALSE	2.2	2.4	33.5	171	166	3	3	FALSE
	Equat. 2	8.5	10.9	5.6	556	539	36	11	FALSE	3,0	3.8	92.8	170	165	2	5	FALSE
	Equat. 3	9.0	11.6	5.8	555	538	35	11	FALSE	4.4	7.0	94.2	169	164	1	8	FALSE
	Equat. 4	10.0	12.6	6.2	554	537	34	12	FALSE	7.8	17.5	100.0	168	163	1	18	FALSE
Zn	**Equat. 1**	10.4	5.7	2.8	175	136	37	5	TRUE	3.2	15.2	24.9	32	27	3	16	FALSE
	Equat. 2	10.5	34.3	30.6	174	135	36	33	FALSE	27.1	42.8	88.4	31	26	2	46	FALSE
	Equat. 3	15.3	35.5	100.0	173	134	35	49	FALSE	68.5	64.5	100.0	30	25	1	66	TRUE
	Equat. 4	34.9	36.3	100.0	172	133	35	50	FALSE	71.0	66.0	100.0	29	24	1	67	TRUE

***** %Exp. Var. SP+NL > % Ave. Exp. Var. for separated dataset (reported in section 2.3.4 **(B)**), **df** - degree of freedom

Cu in lettuce showed higher explained variance of the combined data set than the average of the explained variance for separate data sets, only in case of equations 1 and 2. However, the percentage explained was very low and there was an increase with addition of the pH (10%). For Zn in carrot the combined data set can be used only for equations 3 and 4, with 71% of explained variance for equation 4, with OC content and clay being the variables with major influence.

With the evaluation of the results presented above and following the proposal in section 3.4.4, the best model was selected. To this purpose the following choices were investigated: the use of the combined or a separate data set; type of model (Equation 1 to 4), or the use of a numerical interpretation of measured BCF values. See table 5.

Table 5 – Selection of data following the procedure described in section 3.4.4 and observing the results of tables 3 and 4

Metal	Lettuce	Carrot
Cd	**X**	**O**
Cu	**O**	**O**
Ni	**X**	**-**
Pb	**O**	**-**
Zn	**O**	**X**

X Combined dataset **O Separate dataset** **- Statistic approach**

For Cd in lettuce and for Ni and Zn in lettuce and in carrot, we chose to use the combined data sets and equation 4, which includes the largest number of soil properties (pH, OC and clay) with the highest r^2 and a higher explained variance compared with other equations. For Cd and Cu in carrot and Cu, Pb and Zn in lettuce, the criterion (B) has not been met (section 3.4.4), excluding the possibility of using the combined data sets. Here still remains the use of one of the separate data sets. Ideally the data set of SP is chosen because it coincides with the conditions of SP. However, 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, increasing the standard error and the noise of the data set for statistical analysis. Therefore, we decided to select the NL data set (equation 4), which despite of the to have impact of the soil variables influencing the soil-plant uptake possibly different of the impact in the SP data set, has considerably more samples with representative concentrations of these metal in soil and plants valid in the expected range of the screening values. This is a significant contribution to make the use of predictive models for the transfer of metals from soil to plant possible, incorporating the effect of important factors such as: (total) metal concentration in soil, pH, organic matter content and clay content.

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 6.

Table 6 – 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)***	**n**
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

∗∗ and ∗ Significant coefficients at p <0 .01 and at $p < 0.05$, respectively; *se* (Y-*est*) = standard error of the estimate; n = number of observations.

Based on the selected coefficients for Cd in lettuce, the OC content had the highest impact on the concentration in vegetables compared with 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 has been demonstrated to be a significant soil property to predict Cd uptake. However, for Cd in lettuce 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 data sets (NL and SP), which have similarities regarding Cd uptake, but increase the variability due to the individual 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 availability. This was also observed in other studies reporting that organic matter have 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 high molecular organic matter and clay on bioavailability and, hence, on plant uptake. This phenomenon, however, may be due to the fact that the dataset used to derive these model includes samples with unknown clay content, making it difficult to assess the effective role of this soil property in the availability of soil contaminants.

For Cu in carrot and Ni and Pb in lettuce, the OC content and clay contents had an impact in reducing the availability for plant uptake and clay was the largest contributor to this. For Zn in carrot, the regression coefficient was not significant for pH, and the OC had the greatest impact in reducing the availability of Zn for plant uptake.

In general, the performance of the soil-plant transfer model selected (as indicated by the r^2 and the standard error values) was quite good, for both crops included here, except for Cu (r^2 0.15) and Zn (r^2 0.13) in lettuce. The poor quality of the respective models is also due to the fact that the range of levels in soil was relatively narrow, which hampers the clear evaluation of the impact of soil quality standards on metals levels in vegetables.

For Ni and Pb in carrot, for which none of the equations derived from the SP, NL or NL+SP data sets, were significant. Therefore, we chose to use a statistical approach using measured BCF values. These conclusion can be explained by several factors, i.e., the range of soil types was extensive, with different origin and mineralogy, land management materials, which results in a large amount of noise in the data sets 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, and for Ni in carrot, the data was stratified in three groups, also of 30 data points. Usually, the uncertainty of this approach is high, but for Ni, the BCF values at low and high concentrations are extremely different, show to large uncertainty, so this BCF value was disregarded (see in figure 4).

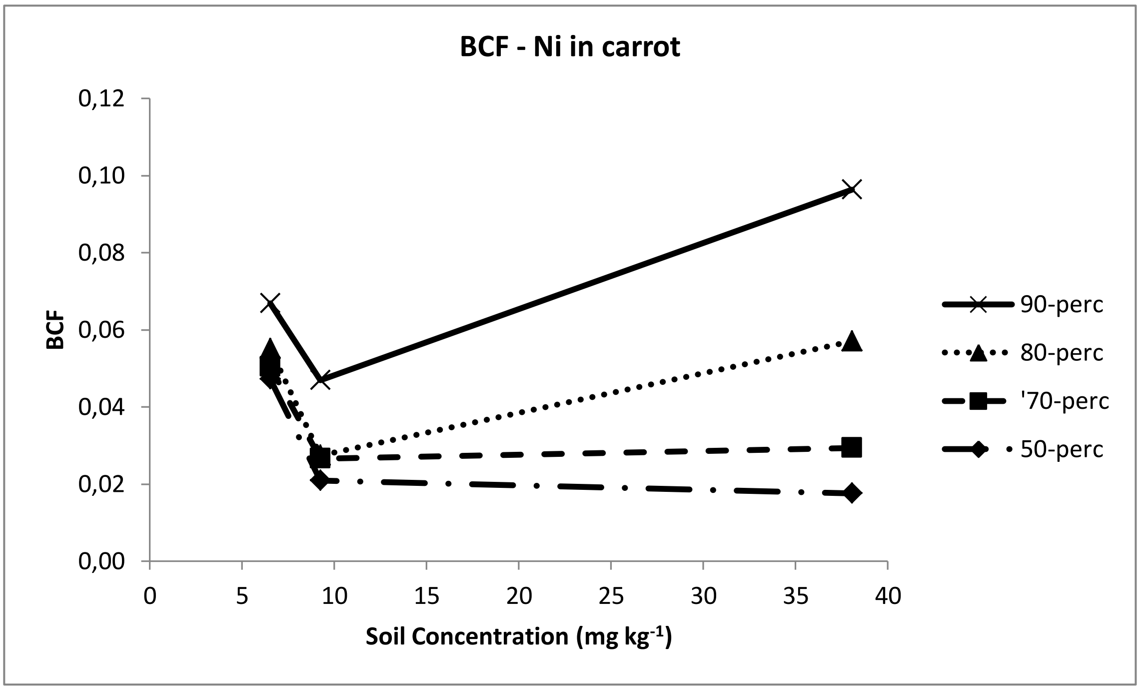

Figure 4 – BCF of Ni-concentrations in carrot, stratified for the concentration range

For elements such as Cd and Pb, which are particularly important elements by its pollution potential, the models performance can be improved in the future, in order of increase research that creates appropriate data sets representing a wider range in 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 total metal content, this paper provides relevant improvements for soil-plant relationships previously derived for Brazilian soils (MELO et al., 2011). This study shows that, aside from plant specific properties, pH and OC content but also clay influence the uptake in vegetables. This means that conctant bioconcentration factors are not suitable to assess the transfer of metals such as Cd, Cu, Ni, Pb and Zn from soil to feed and food crops.

3.3.2.3 BCF values

BCF values for Cd, Cu, Ni, Pb and Zn for different exposure scenario (rural, urban and industrial) and different pH values (5.0 - 6.0), obtained from the soil-plant relations selected, are shown in Table 7. Mean values and different percentiles are given. The BCF values currently used as basis for the Intervention Values in SP (CETESB model) and in the

Netherlands (CSOIL model) are also given in this table. The values of BCFs in both models are based on Versluijs and Otte (2001), divided into groups of roots and leavy vegetables, based on data obtained from soil and vegetables grown in temperate zones.

Table 7 – BCF values for Cd, Cu, Ni, Pb and Zn for different exposure scenario (rural, urban and industrial) and different pH values (5.0 – 6.0), obtained from the soil-plant relations selected, for means and different percentile, and BCF values currently used as basis for the Intervention Values in SP and in the Netherlands, 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
	P 50	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	0.370*		0.159*		0.370*		0.159*		0.370*		0.159*	
	CSOIL	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
	P 50	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	0.100*		0.100*		0.100*		0.100*		0.100*		0.100*	
	CSOIL	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	-	
	P 50	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	0.100*		0.070*		0.100*		0.070*		0.100*		0.070*	
	CSOIL	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*
	P 50	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	0.003*		0.001*		0.003*		0.001*		0.003*		0.001*	
	CSOIL	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
	P 50	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	0.400*		0.100*		0.400*		0.100*		0.400*		0.100*	
	CSOIL	0.359*		0.031*		0.359*		0.031*		0.359*		0.031*	

***Constant BCF**

Some countries have derived soil quality standards for metals as a function of pH in their legislations (DEFRA e EA 2002; Ministry for the Environment 2010). From table 7, it can be concluded the pH does not have a high contribution to the BCF values for metals, except for Cd. For Cd BCF are higher at pH 5.0 than pH 6.0 for lettuce and carrot and both exposure scenario. Among the soil properties, pH is the most important in controlling Cd availability and uptake by vegetables (ANDERSON; CHRISTENSEN, 1988; PEIJNENBURG et al., 2000;. MCBRIDE, 2002; GOLIA et al., 2008). Cd also shows higher BCF values and higher uptake in lettuce and in carrot, comparable with others metals studies, which shows that vegetables this species can be classified as hyperaccumulators of Cd, such also reported in previous studies (ZHENG et al., 2007; RAMIREZ-ANDREOTTA et al., 2013).Cd, Cu and Pb uptake in lettuce and carrots are in the same order of magnitude, with the exception of Zn, where the plant uptake is higher in lettuce than in carrot.

Differences between exposure scenario are observed. BCFs for Industrial exposure scenario are three or four times lower than BCFs for urban exposure scenario and for rural exposure scenario two times higher than BCFs in urban exposure scenario, for all metals. The same behavior is observed in BCFs exhibited by their different percentiles. BCF values from different percentiles of the frequency distribution calculated from the regression models results is due to the high level of uncertainty analyses. In a similar study, Versluijs et al. (2001), reported that correlations coefficients of the derived soil-plant relationships are generally low.

Gibbons (2003), says for comparison with based in health criteria, which the standards are often based on average exposures, interest is typically in comparison of the true mean concentration to the regulatory standard. Since the true mean concentration is never known with certainty, statistical confidence intervals for the mean are typically used to incorporate uncertainty in the true mean of the concentration distribution.

The 50 and 70 percentiles of the BCFs presented here are more conservative values, while the 80 and 90 percentiles are more permissive (higher BCF leading to lower screening values for the same human risk/uptake level). The uncertainty increases in the order 50-70-80-90 percentile, which can make the 80-90 percentiles highly uncertain for a small body of data, with a high risk of overestimating (compared with a larger body of data). Also, when the results of the 80 and 90 percentiles are based upon an assumption of independence between the concentration in soil and plant uptake, an additional risk of overestimating occurs, because it is known that BCF values most often decrease when soil concentrations increase (DUDKA; MILLER, 1999; SAMSOE-PETERSEN et al., 2002; GAW et al., 2008). The high BCF values which are more frequent for the 80-90 percentiles are generally valid for the lower soil concentration regions, while the screening values for which they should apply are in the higher soil concentration regions.

However, this approach is important in order to present options of the choice for the bodies environmental monitoring, assisting in decision-making, since the derivation of soil quality standards includes both scientific knowledge and policy decisions (SWARTJES et al., 2007).

Finally, we propose new BCFs values for three different exposure scenario, for pH 5.0 and 6.0, for Cd, Cu, Ni, Pb and Zn in lettuce and for Cd, Cu, Pb and Zn in carrot, presented as mean values and their respective percentiles, compared to only one BCF value for each group of vegetables (leaf and root) used currently the basis for the Intervention Values in SP (model CETESB). The application of soil-plant models and the BCFs proposed in this study has potential and are useful to derive national soil quality criteria. However, this methodological approach includes differences between climatic conditions and soil types and this need to be carefully considered.

3.4 Conclusions

- The application of soil-plant transference models derived in this study had a good performance for eight of the ten combinations (five metals x two vegetables).This offers improved possibilities for the derivation of appropriate screening values for the São Paulo State, Brazil.
- SP data can be combined with the NL data using model 4 (including pH, OC content and clay content) for Cd in lettuce and for Ni and Zn in lettuce and in carrot.
- Model 4 (including pH, OC content and clay content) gave the most useful results when SP and NL data sets were combined for Cu, Pb, Zn in lettuce and for Cd and Cu in carrot.
- For two cases (Ni and Pb in carrot) the use of the models gave an inconsistent result, and the combination of datasets did not (or insufficiently) improve the results. For these cases, BCF values were derived from measured BCFs, as a fallback, by the statistical interpretation of the measured BCF values.

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4 DEVELOPMENT OF SCREENING VALUES OF POTENTIALLY TOXIC ELEMENTS OF SOILS FOR VEGETABLE PRODUCING AREAS OF SÃO PAULO STATE, BRAZIL

Abstract

Contamination of the soil by potentially toxic elements (PTEs) occurs as a result of a variety of human activities, and the health of people living nearby or consuming foods from contaminated sites may be seriously damaged. Contaminated food products are one of the leading sources of exposure to PTEs for the majority of the human population. Thus, it is crucial to establish criteria whereby the risks posed by soil and water pollution to human health can be assessed. The maximum acceptable levels of PTEs in soils cultivated with food crops, such as the screening values of PTEs in soils, also called soil quality standards, are defined as the value that indicates the limit of contamination above which there is potential risk of deleterious effects on human health. The objective of the authors was to determine soil screening values (SSV) for Cd, Cu, Ni, Pb and Zn in the state of São Paulo, Brazil, based on the potential threat to human health, using soil–vegetable relationships. A data set on Cd, Cu, Ni, Pb and Zn concentration in soils and in edible vegetables was used to derive soil–plant relationships, and then SSVs were calculated based on human exposure parameters. The SSVs determined were appropriate for Cd, Cu, Pb and Zn, but were inconsistent for Ni. They evaluated the exposure pathways only, as adapted to conditions in São Paulo, and showed which have high potential for increasing the soil screening values appropriate to the local conditions in Sao Paulo. The soil screening values proposed for all PTEs were different from current soil screening values for the state of São Paulo (CETESB values) and also the least restrictive. The 70 percentile (intermediate value) was the most suitable option for adoption for soil screening values for the local conditions in Sao Paulo.

Keywords: Vegetable consumption; Metals; Soil quality standard; Human exposure; Risk assessment

4.1. Introduction

Contamination of soil by potentially toxic elements (PTEs) is a consequence of human activities, and the health of people may be seriously damaged through either living in the vicinity or through consuming foods from contaminated sites (HELLSTRÖM et al., 2007; LIU et al., 2013). The concentrations of PTEs in cultivated crops increase in line with the contamination level, and crops grown in contaminated soils can contain PTEs concentrations that do not comply with foodstuff regulations (KHAN et al., 2008a; GAW et al., 2008; DOUAY et al., 2013).

Contaminated food products are one of the leading sources of exposure to heavy metals for the majority of the human population (RÖMKENS et al., 2009a; AJMONE-

MARSANE E BIASIOLI, 2010). Consequently, it is crucial to establish criteria against which the risks to human health posed by soil and water pollution can be assessed.

Key criteria requiring definition are maximum acceptable levels of PTEs in soils cultivated with food crops, such as the screening values of PTEs in soil, also called soil quality standards, which can be defined as a value that indicates the limit of contamination above which there potential risk of deleterious effects on human health (CETESB, 2001).

The United States and the Netherlands were the first countries to establish such criteria, in 1989 and 1990, respectively (SWARTJES et al., 2007). The Dutch methodology on contaminated sites' risk assessment includes the CSOIL exposure model, developed by the National Institute of Public Health and Environment of the Netherlands (RIVM). This model simulates the exposure of individuals to contaminated soil and groundwater, by various exposure pathways (BRAND et al., 2007) and considers three important elements: (i) contaminant distribution over the soil phases; (ii) contaminant transfer from (the different phases of) the soil to contact media; and (iii) direct and indirect exposure to humans (SWARTJES et al., 2012).

Studies using risk assessment tools for soil and water pollution in Brazil are relatively new. São Paulo (SP) was the first Brazilian state to adopt risk-based limits of metals in soils and to develop soil screening values, under different exposure scenarios (CASARINI et al., 2001). A methodology similar to the CSOIL exposure model was initially used by the environmental company in SP (Cetesb), Brazil, for the development of soil screening values, called Intervention Values (CETESB, 2001). More recently, in May 2013, this model was updated and incorporated new substances and the toxicological and physicochemical parameters of the November 2012 version of the Risk Screening Levels spreadsheet- RSLs of the "Superfund" program from the United States environmental protection agency – USEPA. In this model, the input parameters are standardized, and it is not possible to make modifications in the exposure parameter in the version available. These values have also been used at the national level in Brazil (CONAMA, 2009) and are slated to be updated every five years.

Additionally, for the derivation of soil quality standards, an exposure scenario should be defined to describe the appropriate conditions a specific critical concentration in the soil, and is thus a combination of both scientific knowledge and policy decisions (SWARTJES et al., 2007). Countries differ in their specific criteria for defining different usage scenarios and exposure scenario. The state of São Paulo is regulated by State Decree No. 32,955 of 07/02/1991; the industrial, residential and agricultural areas of maximum protection exposure scenario, which are differentiated by length of residence, by the probability of soil ingestion and by the magnitude of vegetable production. In the update of May 2013, a new exposure scenario related to civil construction workers was also included.

With regard to the contribution to total human exposure the major exposure routes are exposure through soil ingestion (lower in adults than in children), crop consumption and inhalation of indoor air. Other pathways also considered are the inhalation of soil particles and dermal uptake via soil material.

In this study, specific attention was given to the exposure pathway through vegetable consumption, since this is the dominant exposure pathway for metals. Most researchers use a constant BCF (Bioconcentration Factor), i.e. the ratio of a metal's concentration in the edible parts of a vegetable to its total concentration in soil (SWARTJES et al., 2007). However, this index does not provide an adequate description of soil-plant transfer of metals, because of the difference in the characteristics of the soils (DE VRIES et al., 2007; RÖMKENS et al., 2009a, 2009b) and the plant uptake characteristics (ZHENG et al., 2008).

A more advanced understanding of soil-plant relationships requires taking into consideration the principal soil attributes that influence the availability of PTEs to plants, e.g., pH, clay, organic matter (OM) and oxides' content (RÖMKENS et al., 2009; RODRIGUES et al., 2010a). However, due to the complexity of the subject, mechanistic models capable of predicting levels of PTEs in plants have not yet been developed or validated under field conditions (SWARTJES, 2011). Thus, researchers have proposed empirical models as a first approach to describe the soil-plant transfers of metals, using data collected under field conditions. However, in wet tropical regions such as Brazil, studies with plant-soil relationships are lacking.

4.1.1. Purpose

The objective of the authors was to develop proposals for soil screening values for Cd, Cu, Ni, Pb and Zn in São Paulo, based on levels that jeopardize human health, using improved soil–vegetable relationships.

4.2. Material and Methods

4.2.1. Model construction

The dataset were grouped into two categories of vegetables: leafy and root (including tubers). The crop BCFs were calculated using the non-linear model, according to Krauss et al.

(2002), De Vries et al. (2007) and Kalis et al. (2007), for Cd, Cu, Pb and Zn, in lettuce and carrot, with the exception of Ni and Pb in carrot. It was decided to use a constant BCF derived from a statistical interpretation of measured BCF values for all individual combinations of soil and plant, as described in section 4.2.1.2. Subsequently, the screening values of PTEs in soils were determined based on the CSOIL exposure model (BRAND; OTTE; LIJZEN, 2007), 2010 version.

4.2.1.1. Exposure model

In order to improve human health-based screening values for Cd, Cu, Ni, Pb and Zn in São Paulo soils, the CSOIL exposure model (BRAND; OTTE; LIJZEN, 2007) was used which considers all the routes and toxicological reference doses for each metal (metal mass per body weight per day) (BAARS et. al., 2001) - Table 1. However, some input parameters have been adapted to SP, so that the model simulations are closer to the actual conditions, and these parameters are presented in Table 2.

Table 1 – Toxicological reference dose for each metal used in CETESB (2014) and in C-SOIL models

Metal RfDo	CETESB	C-SOIL
	--------mg kg^{-1}-day--------	
Cd	0.001	0.0005
Cu	0.04	0.14
Ni	0.02	0.05
Pb	0.0036	0.0036
Zn	0.3	0.5

For risk analysis, two scenarios were established as patterns of exposure: (i) rural (agricultural areas, traditionally used for growing vegetables) and (ii) urban (predominantly residential areas), taking into account the levels of vegetable consumption under each scenario. Specific BCF values for a particular soil pH (5.0 and 6.0), exposure scenario and averages or percentiles of the soil concentration measured were determined through an iterative process, in which the starting soil metal concentration and the resulting critical soil metal concentration converge to values closer than 1% (MINISTRY FOR THE ENVIRONMENT, 2010; MELO et al., 2011). Consumption rates of vegetables will come from the Brazilian Institute of Geography and Statistics for the state of São Paulo, Brazil (IBGE, 2010), also used in the CETESB spreadsheet. The SPSS 10.0 for Windows program was used for the descriptive analyzes and statistical data analysis.

Table 2 – Parameters from CSOIL model and parameters adapted for conditions in São Paulo to use in the CSOIL model

Specific Soil Data	**Value SP**	**Value NL**	**unit**
Soil temperature	298	283	K
Volume fraction air in soil	0.281	0.200	-
Volume fraction water in soil	0.179	0.30	-
Volume fraction solids in soil	0.540	0.50	-
Organic carbon fraction	0.0116	0.0116	-
Clay content	25	25	%
pH	5.0 and 6.0	6.0	-
Dry bulk density	1.3	-	kg dm^{-3}
Dataset			
Water solubility	3,00 x 10^{3}	3,00 x 10^{3}	mg dm^{-3}
Partition coefficient metals	Cd 2.23 x 10^{2}; Cu 8.13 x 10^{2}; Ni 1.18 x 10^{2}; Pb 2.13 x 10^{3}; Zn 1.38 x 10^{2}	Cd 2.50 x 10^{2}; Cu 2.12 x 10^{2}; Ni 2.00 x 10^{2}; Pb 3.60 x 10^{3}; Zn 2.60 x 10^{2}	dm^{3} kg^{-1}
Bioconcentration factor	dependent on the calculation as described in Material and methods	Cd 0.367 and 0.073; Cu 0.297 and 0.156; Ni 0.056 and 0.014; Pb 0.044 and 0.002; Zn 0.359 and 0.031 for rural and urban scenarios	-
Fraction of contaminated vegetables	Scenario: rural - 0.33, urban - 0.04 and industrial - 0.02	Scenario: rural - 0.50, urban - 0.10 and industrial - 0.00	-

Model Parameter Values									
	Rural scenario				**Urban scenario**				
	Children SP	**Children NL**	**Adults SP**	**Adults NL**	**Children SP**	**Children NL**	**Adults SP**	**Adults NL**	
Body weight	15	15	63	70	15	15	70	70	kg
Daily intake soil (year average)	2.00 x 10^{-4}	1.00 x 10^{-4}	1.00 x 10^{-4}	5.00 x 10^{-5}	2.00 x 10^{-4}	1.00 x 10^{-4}	1.00 x 10^{-4}	5.00 x 10^{-5}	kg d^{-1}
Consumption of leafy vegetables	8 x 10^{-3}	2.7 x 10^{-2}	1.6 x 10^{-2}	9.3 x 10^{-2}	7 x 10^{-3}	4.8 x 10^{-2}	1.3 x 10^{-2}	1.1 x 10^{-1}	kg d^{-1}
Consumption of root/tuber vegetables	1.9 x 10^{-2}	2.8 x 10^{-2}	3.8 x 10^{-2}	5.6 x 10^{-2}	1.6 x 10^{-2}	1.9 x 10^{-2}	3.1 x 10^{-2}	3.8 x 10^{-2}	kg d^{-1}
Inhalated soil particles	3.13 x 10^{-7}	3.13 x 10^{-7}	8.33 x 10^{-7}	8.33 x 10^{-7}	3.13 x 10^{-7}	3.13 x 10^{-7}	8.33 x 10^{-7}	8.33 x 10^{-7}	kg d^{-1}
Body surface	0.48	0.95	1.04	1.80	0.48	0.95	1.04	1.80	m^{2}

(-) Dimensionless

4.2.1.2. Plant-soil relations

In Chapter 3, the development of soil-plant relations have been described in details, here summarized below.

Study sites, collection and analysis of samples

Samples were collected from 19 cities in the state of São Paulo, from the area called the "Green Belt" zone, which is located within roughly 120 km of the city of São Paulo and includes 73 surrounding townships (CAMARGO, 2008a). The sampling included rural and urban areas as well as properties near industrial areas, selected in an attempt to obtain samples with a wide range of contamination levels for the various metals studied. A total of 200 soil samples (0-20 cm depth) and 200 corresponding vegetables samples (25 species) were collected.

Plant and soil material was digested in a microwave oven (Mars Xpress, CEM Corporation), using methods described by Araújo et al. (2002) and USEPA (1998) (method EPA 3051a), respectively. Concentrations of Cd, Cu, Ni, Pb, and Zn in the plant and soil extracts, were determined using optical emission spectrometry (ICP-OES). Certified reference materials NIST SRM 2709th and San Joaquin soil were used to attest to the quality of the soil analysis, with recovery rates of PTEs at satisfactory levels (between 71 and 92%). The description of the methods for the determination of pH, organic carbon (OC), granulometric fractions of the soil was given in Chapter 3, as well as more details about the description of the sampling sites, sample collection and pre-treatment procedures.

Development soil-plant relations

The basis for the soil-plant relationships are two datasets, i.e. the measured dataset from São Paulo – SP, and the Netherlands – NL data set (measured in moderate regions in the world) (Chapter 3). The additional data set was used with the aim of increasing the number of data points for evaluation of appropriate soil and plant relationships, because it is necessary to have concentrations of these metals in soil and plants that are sufficiently representative to define the soil screening values, relating to the appropriate soil concentration range since, in low concentrations, plant uptake rates are assumed to be too high to represent unacceptable human health risks. Low concentrations of metals were found in SP samples and were not appropriate for deriving soil screening values, although the viability of using these combined data sets from different climatic and geological zones and the real implications for each metal is evaluated in Chapter 3.

Several models were developed which predict the accumulated concentration in vegetables as a function of the total soil concentration and the soil properties (pH, organic carbon - OC and clay), using multiple linear regression analysis (SPOSITO, 1980; VERSLUIJS; OTTE, 2001). In this study, the model used (out of four proposed models) was the one that stood out as most appropriate and with the least degree of uncertainty for predicting the accumulated concentration in vegetables as a function of total soil concentration for the conditions in SP.

This decision was based on the evaluation of the accuracy of tests and soil-plant models for assessing the suitability of soil for vegetable cropping with two data sets. Two points were observed: (i) standard error of the model (significant when less than or equal to 0.5, which is the order of the experimental standard error of the concentration in the plant). The significance of the model relations was based on the coefficient of determination (r^2 significant in 5% probability with F-test for n data points); and (ii) comparison of the average explained variance for the combined dataset with the explained variance for the separate datasets (São Paulo and the Netherlands). More details in Chapter 3.

For each vegetable, the following equation chosen was derived as follows:

$$\text{Log}\,[C_{Veg}] = a + b \log [Csoil] + c\, pHsoil + d \log [\%OC] + e \log [\%clay] \quad \text{(Equat.1)}$$

Where, C_{Veg} = metal concentration in the edible part of the vegetable (mg dry weight kg^{-1}), Csoil = total metal concentration in the soil in (mg kg^{-1}), pH KCl = -log H+ soil, %Clay = clay content of the soil (%), %OC = organic carbon content of the soil (%) and a, b, c, d and e are the empirical parameters.

4.3. Results and discussion

4.3.1. Soil and plant characterization

Table 3 summarizes characteristics of the range of the pH, %OC, % clay and soil and plant concentration for two datasets (SP and The Netherlands), for leaf and root group vegetable and intervention values for the state of São Paulo (CETESB, 2013) related to three scenarios (rural, urban and industrial).

Table 3 – Range of the pH, %OC, % clay and soil and plant concentration for two datasets (SP and The Netherlands), for leaf and root group vegetable and intervention values for the state of São Paulo (CETESB, 2013) related to three scenarios (rural, urban and industrial)

			SP data set						Netherlands data set						Intervention values for SP State		
Metal	**Group**		**Min.**	**Median**	**Max.**	**Aver.**	**S. D.**	**n**	**Min.**	**Median**	**Max.**	**Aver.**	**S. D.**	**n**	**Rural**	**Urban**	**Indust.**
				mg kg^{-1}						mg kg^{-1}						mg kg^{-1}	
		Csoil	<L.D	0.07	2.35	0.13	0.23		0.02	0.70	118.00	1.41	4.61				
		pH	3.86	5.77	7.26	5.75	0.63		4.69	6.80	8.40	6.60	0.69				
	Leaf	%OC	0.98	3.23	40.08	4.71	4.95	159	0.70	4.07	36.10	5.54	4.27	723			
		%Clay	10.03	37.61	67.77	36.54	13.26		0.51	16.00	49.00	15.33	8.31				
Cd		Cveg	<L.D	0.10	1.73	0.19	0.26		0.01	0.78	11.25	1.07	1.07		3.6	14	160
		Csoil	<L.D	0.01	0.98	0.07	0.19		0.02	0.41	62.00	1.02	3.15				
		pH	4.92	5.62	6.79	5.79	0.60		4.40	6.80	8.40	6.56	0.79				
	Root	%OC	1.53	2.22	11.95	3.22	2.43	26	0.23	3.30	12.79	3.95	2.95	452			
		%Clay	27.58	45.23	65.26	45.30	10.31		0.50	9.00	30.60	10.71	8.41				
		Cveg	<L.D	0.05	0.28	0.07	0.08		0.05	0.27	29.50	0.53	1.50				
		Csoil	3.31	18.11	356.00	34.75	43.77		6.00	30.35	217.00	39.41	30.42				
		pH	3.86	5.77	7.26	5.75	0.63		4.69	6.38	8.40	6.32	0.69				
	Leaf	%OC	0.57	1.88	23.30	2.74	2.88	159	0.67	2.78	8.37	2.98	1.66	210			
		%Clay	0.33	1.81	35.60	3.48	4.38		12.00	12.00	16.30	12.61	1.56				
Cu		Cveg	2.45	7.49	16.97	7.40	2.61		1.60	8.30	47.83	8.80	4.50		760	2,100	10,000
		Csoil	7.39	17.74	57.61	22.77	13.90		9.00	29.68	217.00	43.93	45.20				
		pH	4.92	5.62	6.79	5.79	0.60		4.74	6.36	8.40	6.40	0.80				
	Root	%OC	0.89	1.29	6.95	1.87	1.42	26	0.61	2.31	5.93	2.57	1.46	62			
		%Clay	0.74	1.77	5.76	2.28	1.39		12.00	12.00	12.00	12.00	0.00				
		Cveg	2.47	6.55	12.39	6.69	2.48		2.34	4.04	11.30	4.67	1.93				
		Csoil	1.64	6.65	30.73	8.06	5.53		12.40	20.50	46.25	22.23	8.22				
		pH	3.86	5.77	7.26	5.75	0.63		5.57	6.39	6.81	6.39	0.36				
	Leaf	%OC	0.98	3.23	40.08	4.71	4.95	159	2.91	5.38	14.40	5.94	2.99	70			
		%Clay	10.03	37.61	67.77	36.54	13.26		12.00	12.00	16.30	12.57	1.51				
Ni		Cveg	0.07	0.28	2.49	0.37	0.29		0.20	0.76	10.21	1.21	1.45		190	480	3,800
		Csoil	2.74	6.25	52.83	9.47	10.17		13.85	21.65	117.65	27.56	25.38				
		pH	4.92	5.62	6.79	5.79	0.60		5.57	6.39	6.80	6.37	0.39				
	Root	%OC	1.53	2.22	11.95	3.22	2.43	26	2.91	4.92	13.30	5.69	2.91	43			
		%Clay	27.58	45.23	65.26	45.30	10.31		12.00	12.00	12.00	12.00	0.00				
		Cveg	0.13	0.30	0.83	0.34	0.20		0.19	0.50	7.11	0.96	1.27				
		Csoil	3.63	16.02	331.42	23.69	31.45		3.80	57.00	548.00	95.43	89.70				
		pH	3.86	5.77	7.26	5.75	0.63		3.83	6.94	7.69	6.67	0.85				
	Leaf	%OC	0.98	3.23	40.08	4.71	4.95	159	0.67	3.69	28.30	5.53	4.83	723			
		%Clay	10.03	37.61	67.77	36.54	13.26		0.51	16.00	39.73	15.75	9.64				
Pb		Cveg	<L.D	0.23	20.20	1.06	2.32		<L.D	1.20	57.88	1.86	2.89		150	240	4,400
		Csoil	8.58	14.91	26.31	15.64	4.67		1.80	48.27	461.00	88.08	92.65				
		pH	4.92	5.62	6.79	5.79	0.60		3.86	6.48	7.70	6.38	0.89				
	Root	%OC	1.53	2.22	11.95	3.22	2.43	26	0.23	3.05	22.05	5.38	5.37	452			
		%Clay	27.58	45.23	65.26	45.30	10.31		0.51	10.25	31.52	10.23	8.33				
		Cveg	<L.D	0.27	4.47	0.31	0.94		<L.D	0.50	3.79	0.63	0.48				
		Csoil	39.63	141.25	643.25	174.78	110.23		42.00	320.00	1,650.0	454.23	405.81				
		pH	3.61	5.53	7.16	5.53	0.70		4.69	6.38	8.40	6.32	0.69				
	Leaf	%OC	0.51	2.89	29.85	4.43	4.62	159	0.67	2.78	8.37	2.98	1.66	210			
		%Clay	3.96	14.13	64.33	17.48	11.02		12.00	12.00	16.30	12.33	1.19				
Zn		Cveg	8.73	49.75	513.42	76.16	79.50		19.00	88.12	353.00	97.83	51.99		1,900	7,000	10,000
		Csoil	53.81	100.50	279.34	114.21	51.26		40.00	286.50	2,035.0	622.97	662.66				
		pH	4.74	5.53	6.56	5.63	0.59		4.74	6.32	8.40	6.29	0.71				
	Root	%OC	1.18	2.31	9.21	2.80	1.71	26	0.61	2.27	5.93	2.57	1.55	54			
		%Clay	5.38	10.05	27.93	11.42	5.13		12.00	12.00	12.00	12.00	0.00				
		Cveg	20.27	39.75	158.46	48.24	29.39		17.00	36.25	102.20	44.17	21.73				

<L.D = limit detection, S.D. = standard deviation, n = number of observations

The additional dataset (The Netherlands dataset) increased the number of valid observations for all PTEs studied and also for lettuce and carrot, with the exception of Ni in lettuce (SP - 159 data points; NL - 70 data points). This can improve the quality of the statistical analysis, especially, for Cd and Pb in lettuce, where the number of valid observations changed from 159 (SP data set) to 723 (NL data set). Swartjes et al. (2007) reported that it is possible, although not necessarily so, that the noise in the data sets will subside when the volume of the data set increases, by adding other data sets.

The characteristic common to both data sets is the wide range of soil and plant concentrations. These relatively sizeable variations as well as the significant differences between average concentrations are typical of soils as affected by local or regional anthropogenic contamination (RODRIGUES et al., 2013; MADRID et al., 2007). Nevertheless, the NL data set has substantially higher concentrations for all PTEs and both group of vegetables studied when compared with the SP data set, with maximum values of soil concentration more compatible with the Intervention Values described by SP laws, also presented in Table 3. That just does not apply to Cu soil concentration in lettuce that has means of 44 and 39 mg kg^{-1}, for SP and NL data sets, respectively.

Metal concentrations in leaves have higher average concentrations than roots, for all PTEs studied. Although depending on the metal, the difference in plant uptake between the two groups of vegetables was not significant enough, as e.g. for Ni. Many authors showed differences regarding the absorption and accumulation of PTEs which can vary highly depending on the vegetable type (ALEXANDER; ALLOWAY; DOURADO, 2006) or even between cultivars or genotypes of the same vegetable (McLAUGHLIN et al., 1994; ALEXANDER; ALLOWAY; DOURADO, 2006; ZHENG et al., 2008).

The pH of all soil samples ranged from 3.6 to 7.3 for the SP data set and 3.8 to 8.4 for the NL data set, from acidic to neutral, but the acid outliers are in the SP data set (average values pH 5) and the basic outliers in the NL data set (average values pH 6). In tropical and temperate agricultural soils, this behavior was expected, since soil management practices aim at producing soil properties that are ideal for agricultural production.

The organic carbon as well as pH had a wide variation between data points, but not between data sets, from 1 to 40% for the SP data set and from 1 to 36% for the NL data set. Nevertheless, clay content in the soils was different between the data sets (SP - 3 to 67% for lettuce and 1 to 65% for carrot; NL - 1 to 49% for lettuce and 1 to 31% for carrot). As well as for the lettuce and carrot species (reported and discussed in chapter 3) the leaf and root group had textural classes ranging from sandy to clayey, and predominantly clay soils as preferred by farmers involved in horticultural activities.

4.3.2. Coefficients of the soil-plant relations and BCFs

The coefficients of the soil–plant relations obtained by linear regression (equation 1), from the selected datasets, following the rules described in section 4.2.1. for Cd, Cu, Pb and Zn in the leaf group and for Ni in leaf group vegetables are shown in Table 4. Further discussion can be found in Chapter 3, where all the soil-plant relations for the conditions in São Paulo were established for lettuce and carrot specie of vegetables and are here extrapolated to the leaf and root vegetable group.

The soil-plant transfer model selected had a significant coefficient of determination (r^2 significant at 5% probability by F-test for n data points), with values ranging between 0.2 to 0.7. The significance order of metals for leaf was Zn > Ni > Cd > Cu = Pb, while it was Zn > Cu > Cd for root and standard error of the models also significant (when less than or equal to 0.5) ranging from 0.1 to 0.4.

Table 4 – Coefficients of the soil–plant relationships determined by multiple linear regressions from the selected dataset

Metal	**Vegetable type**	**Soil-plant relationship**	R^2	***se (Y-est)***	**n**
Cd	Leaf	Log [Cd veg] = 0.34 + 0.30^{**}log [Cd soil] − 0.14^{**} pH soil − 0.26^{*} log [OC] − 0.03^{**} log [Clay]	0.30	0.43	877
	Root	Log [Cd veg] = 1.16 + 0.48^{**} log [Cd soil] − 0.20^{**} pH soil − 0.36^{**} log [OC] − 0.11^{**} log [Clay]	0.35	0.33	447
Cu	Leaf	Log [Cu veg] = 0.82 + 0.30^{*} log [Cu soil] − 0.06^{*} pH soil + 0.04^{**} log [OC] + 0.09^{**} log [Clay]	0.20	0.19	205
	Root	Log [Cu veg] = 0.96 + 0.00 log [Cu soil] − 0.05^{*} pH soil − 0.18 log [OC] − 0.30^{**} log [Clay]	0.52	0.11	57
Ni	Leaf	Log [Ni veg] = 0.52 + 0.36^{**} log [Ni soil] − 0.14^{**} pH soil − 0.18^{**} log [OC] − 0.27^{**} log [Clay]	0.40	0.28	224
Pb	Leaf	Log [Pb veg] = − 0.37 + 0.36^{**} log [Pb soil] − 0.03^{*} pH soil − 0.25^{**} log [OC] − 0.16^{**} log [Clay]	0.20	0.41	1154
Zn	Leaf	Log [Zn veg] = 2.51 + 0.29^{*} log [Zn soil] − 0.20^{**} pH soil − 0.05^{**} log [OC] − 0.07^{**} log [Clay]	0.41	0.18	205
	Root	Log [Zn veg] = 1.92 + 0.12^{**} log [Zn soil] − 0.05^{**} pH soil − 0.82^{**} log [OC] − 0.10^{**} log [Clay]	0.71	0.12	75

** and * Significant coefficients at $p < 0.01$ and at $p < 0.05$, respectively; *se* (Y-*est*) = standard error of the estimate; n = number of observations.

BCF values currently used in CETESB and the CSOIL model are also shown. These values are based on geometric means. The values of BCFs in both models are based on

Versluijs and Otte (2001), divided into groups of roots and leaves, whose values were obtained from soil and vegetables grown in The Netherlands.

For Cd in leaf, the range of BCF values was 0.17-2.20 at pH 5.0 and 0.16-1.60 at pH 6.0, while the literature values have been found between 0.24 and 9.70, respectively (XU et al., 2013). The wide variation suggested BCF results with significant uncertainties. It is important to point out which soil physical and chemical properties and the type and specie of grown vegetables contribute to this wide variation in BCF values. However, this wide variation in BCF values can be a function of the different methodology used in the calculation of values; for example, average BCF values range between the 5th and 95th percentile can be used, and many studies are based on a limited number of samples.

The pH did not contribute to changing the BCF values for metals except for Cd, which had higher mean values for BCF at pH 5.0 than at pH 6.0, for leaf and root and for both exposure scenario, although some countries have derived soil quality standards for metals as a function of pH in their legislations (DEFRA; EA, 2002; MINISTRY FOR THE ENVIRONMENT, 2010). For Cd, the mean values as well as the BCF percentile value are high (above 1) in rural exposure scenario, which shows that many kinds of vegetables can be classified as hyperaccumulators of this metal. The results of the previous studies showing that the uptake of Cd is higher in vegetables were also consistent (LIU et al., 2005; INTAWONGSE; DEAN, 2006; ZHENG et al., 2007; GAW et al., 2008; KHAN et al., 2008b; WANG et al., 2012; WATERLOT et al., 2013; XU et al., 2013). Cd, Cu and Pb uptake in leaf and root vegetables are in the same order of magnitude, with the exception of the Zn, where the plant uptake is higher for root groups. These results are consistent with the results of previous studies (ZHENG et al., 2007; RAMIREZ-ANDREOTTA et al., 2013).

Table 5 – BCFs results for metals Cd, Cu, Pb and Zn for different scenarios (rural and urban) and different pH (5.0 – 6.0), obtained from the soil-plant relationships selected, determined by multiple linear regressions and BCFs used currently for Cetesb and C-SOIL, based on geometric means

		BCF's							
		Rural				Urban			
		Leaf		Root		Leaf		Root	
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**
Cd	**Mean**	1.128	1.040	1.610	1.063	0.820	0.632	1.499	1.410
	P 50	1.573	1.210	2.039	1.520	1.288	1.102	2.244	2.010
	P70	1.956	1.321	2.488	1.730	1.496	1.372	2.576	2.320
	P80	2.019	1.401	2.544	2.020	1.608	1.501	2.756	2.511
	P90	2.223	1.591	2.721	2.136	1.787	1.654	3.043	2.791
	CETESB	0.370*		0.159*		0.370*		0.159*	
	C-SOIL	0.367*		0.073*		0.367*		0.073*	
Cu	**Mean**	0.139	0.130	0.095	0.087	0.055	0.051	0.002	0.002
	P 50	0.290	0.279	0.188	0.184	0.179	0.171	0.087	0.083
	P70	0.339	0.332	0.225	0.222	0.240	0.230	0.115	0.108
	P80	0.401	0.370	0.261	0.247	0.282	0.263	0.134	0.127
	P90	0.463	0.433	0.292	0.289	0.338	0.327	0.160	0.160
	CETESB	0.100*		0.100*		0.100*		0.100*	
	C-SOIL	0.297*		0.156*		0.297*		0.156*	
Pb	**Mean**	0.073	0.066	0.010*	0.010*	0.047	0.047	0.010*	0.010*
	P 50	0.129	0.123	0.007*	0.007*	0.101	0.093	0.007*	0.007*
	P70	0.150	0.141	0.011*	0.011*	0.129	0.122	0.011*	0.011*
	P80	0.162	0.153	0.012*	0.012*	0.143	0.136	0.012*	0.012*
	P90	0.179	0.170	0.017*	0.017*	0.170	0.156	0.017*	0.017*
	CETESB	0.003*		0.001*		0.003*		0.001*	
	C-SOIL	0.044*		0.002*		0.044*		0.002*	
Zn	**Mean**	0.831	0.800	0.256	0.216	0.505	0.404	0.085	0.083
	P 50	1.249	1.000	0.500	0.469	1.130	0.960	0.325	0.310
	P70	1.430	1.210	0.760	0.620	1.202	1.188	0.423	0.405
	P80	1.521	1.331	0.810	0.741	1.367	1.318	0.491	0.456
	P90	1.601	1.460	0.850	0.792	1.591	1.505	0.572	0.533
	CETESB	0.400*		0.100*		0.400*		0.100*	
	C-SOIL	0.359*		0.031*		0.359*		0.031*	

*** Constant BCF**

For the leaf and root groups and for all metals, in general, mean BCF values were overall higher than the generic factors (Cetesb and CSOIL), suggesting that the generic values tend to generally overestimate the uptake in leaf and root vegetables (Table 5). Mean or median values are generally recommended to be used as generic BCF values by national environmental protection agencies. Despite the fact that many researchers recommend developing site-specific BCFs, general uptake factors may not be provided in cases where information is limited or lacking, thus resulting in a high level of uncertain analyzes, and these are often used in exposure assessments in practice.

Our study had a high level of uncertainty. Consequently, we introduced BCFs extracted from different percentiles of the frequency distribution calculated from the regression models in order to improve the BCF results. However, choosing the most appropriate percentile (50, 70, 80 or 90) for defining soil quality standards is a decision best left to environmental protection agencies, since this decision is guided by a combination of not only scientific knowledge but also policy decisions (SWARTJES et al., 2007).

4.3.3. Proposals for screening values

The contribution of the exposure pathways to total exposure for the CSOIL model under different exposure scenario is in Table 6. The same table, also shows the contribution of the exposure pathways to total exposure for the CSOIL model “adapted” for the conditions in São Paulo and after the contribution of the toxicological reference dose (RfDo), the so-called “Adapted + RfDo”. Then, before presenting the proposals for screening values for the conditions in São Paulo, including the impact of the BCFs values obtained from the soil-plant relationships for Cd, Cu, Pb and Zn, it is important to evaluate only the impact of the contribution of exposure pathways and also of the toxicological reference dose in the CSOIL model.

In the CSOIL model, the Serious Concentration Risk (SCR) to human health (mg kg^{-1}), which is the maximum soil concentration of an inorganic chemical substance that can cause harm to human health may vary with the increase or decrease in some exposure parameters of the model. In Table 6, it is observed that introducing soil intake or consumption from one's own garden as parameters will cause greater variation in the SCR.

Table 6 – Contribution of the exposure pathways to total exposure

		Scenarios							
		Rural				Urban			
	Metal	SRC* human	Soil intake	Inhalation of soil particles	Vegetable Consumption	SRC* human	Soil intake	Inhalation of soil particles	Consumption from own garden
		mg kg^{-1}	------------------ % ------------------			mg kg^{-1}	------------------ % ------------------		
CSOIL	**Cd**	3.4	0.8	0.0	99.2	44.2	10.8	0.1	89.1
	Cu	1,001.0	0.9	0.0	99.1	8,295.6	9.8	0.1	90.1
	Pb	211.5	5.3	0.1	94.6	1,897.7	47.8	0.5	51.7
	Zn	3,684.7	0.9	0.0	99.1	51,033.1	12.5	0.1	87.4
CSOIL Adapted to SP	**Cd**	58.4	30.3	0.1	69.6	166.5	81.6	0.3	18.1
	Cu	9,151.7	23.7	0.1	76.2	18,469.6	76.1	0.3	23.6
	Pb	1,508.0	80.4	0.4	19.2	1,931.8	97.2	0.5	2.2
	Zn	71,814.5	37.3	0.1	62.6	175,018.8	85.7	0.3	13.9
CSOIL Adapted to SP + RfDo	**Cd**	116.8	30.3	0.1	69.6	333.1	81.6	0.3	18.1
	Cu	3,285.2	23.7	0.1	76.2	8,972.3	76.1	0.3	23.6
	Pb	1,508.0	80.4	0.4	19.2	1,931.8	97.2	0.5	2.2
	Zn	4,3088.7	37.3	0.1	62.6	105,011.3	85.7	0.3	13.9

*SRC – *Serious Concentration Risk*

The need for using consistent data in the exposure of the affected population and in the effects of contaminants in this population or other indicator organisms are fundamental points if good results from studies of risk assessment are to be obtained. These data usually differ in different scenarios in terms of use, occupation of land and exposure pathways.

The percentage contribution of the "soil intake" parameter in the CSOIL model is higher in urban as compared to rural exposure scenario. The same behavior was observed when the exposure parameters were adapted for the conditions in São Paulo. The percentage contribution of this parameter, however, increased when compared with values obtained from the non-adapted CSOIL model, in all exposure scenario. The result of this change was the increase in SCR values, for all metals, under both rural and urban exposure scenario. This difference occurred because the parameter "vegetable consumption", unlike the "soil intake", makes the highest percentage contribution to the CSOIL model without adaptation and to the CSOIL model adapted to conditions in São Paulo, for all metals, for both exposure scenario. The "inhalation of soil particles" parameter had a very small contribution, not in excess of 1%.

It was expected that SCR values obtained in the CSOIL model (exposure parameters for temperate regions) were different from the SCR values obtained in the CSOIL model adapted to all the metals studied. However, the impact of these differences was extremely high. For Cd, for example, the SCR value in the CSOIL model was 3.4 mg kg^{-1} and for the adapted CSOIL model this value increased to 58.4 mg kg^{-1}, in rural exposure scenario. This is due mainly to changes in the values of the consumption fraction of vegetables, which in São Paulo ranged from 2 to 33% only among exposure scenario, according to the Brazilian Institute of Geography and Statistics - IBGE (2010), also used in CETESB spreadsheets. The CSOIL model is based on the rate of consumption fraction from the Netherlands, which reaches 100% under urban exposure scenario (SWARTJES et al., 2007). The greater the rate of consumption of vegetables, the lower the SCR values. Melo et al. (2011) observed the same behavior for Cd.

In addition to the parameter fraction of vegetable consumption, the relevant exposure parameters that have been modified are: the "Body weight", only for rural exposure scenario, the "Consumption of leaf and root / tuber vegetables" in kg d^{-1}, "Inhalated soil particles" also in kg d^{-1} and the "Body surface" in m^2. Values were described in Table 2.

Finally, the SCR values for metals increased or remained the same, as was the case of Pb, when the adjustments to the toxicological reference dose (RfDo) with modifications, related to exposure parameters for the conditions in São Paulo in the CSOIL model were added. The variation in SCR values in this case was directly proportional to the variation in RfDo.

Based on the results shown in Table 6, we can conclude that evaluating only the exposure parameters adapted to the conditions of São Paulo, not including the improved BCFs from empiric relations soil-plant, will impose a heavy burden on increasing the soil screening values for São Paulo as compared to the values established for soil screening values for The Netherlands. In other words, the soil screening values established for the conditions in Sao Paulo will be less restrictive than the soil screening values established for The Netherlands as calculated by the CSOIL model, regardless of the different soil-plant relationships.

The proposals for the soil screening values of the Cd, Cu, Pb and Zn under different exposure scenario, pH and percentiles and setting of data, using improved soil – vegetable relationships are in Figure 2. The screening values were not proposed for Ni as the soil-plant relationship was not improved due to lack of consistent data.

The soil screening values proposed for all PTEs were different from the current soil screening values for the State of São Paulo. The improved BCfs had an important role in increasing the soil screening values, i.e., the least restrictive values for the conditions in São Paulo. In both exposure scenario and the pH evaluated, soil screening values were relatively high as compared to the values established for The Netherlands, from the CSOIL model, as well as when compared to the values established in the legislation for the state of São Paulo, from the CETESB spreadsheet.

According to Swartjes et al. (2013), a risk assessment with regard to the protection of human health should be simple when possible (conservative) and more complex when necessary (when realistic). In order to do this, we chose to include exposure scenario, pH and the percentiles by proposals of soil screening values of the Cd, Cu, Pb and Zn, thereby presenting options for the environmental protection agencies in case of complex risk assessments in which the PTE contents are high. However, the variable pH (5.0 and 6.0) alone had a significant effect and should only be considered for Cd and Zn PTEs, for the two exposure scenario, rural and urban. Because Sao Paulo is located in a humid tropical region, in which several soils are acidic or can be easily acidified, the proposed soil screening values for Cd and Zn at pH 5.0 seem to be more appropriate than at pH 6.0.

The soil screening values' mean and percentiles should be considered for all metals and for all exposure scenario. However, uncertainty increases in the order 50-70-80-90 percentile, which can make the 80-90 percentiles highly uncertain for a small body of data, with a high risk of overestimating (compared to a larger body of data). On the other hand, the soil screening values' means and 50 percentile are more permissive. Thus, an intermediate value (70 percentile) seems to be a better choice for the soil screening values for the conditions in Sao Paulo.

Thus for Cd, the proposed soil screening value for the conditions in Sao Paulo could be 10.7 and 82.2 mg kg^{-1} at pH 5.0 or 13.1 and 91.1 mg kg^{-1} at pH 6.0 for the rural and urban exposure scenario, respectively. Therefore, it is assumed that vegetables can be grown and consumed, in the aforementioned proportion, without unacceptable risks to humans when these Cd concentrations in soils are not exceeded (MELO et al., 2011). These values are much higher than the current Cd soil screening values for the state of São Paulo, which are 3.6 and 14.0 mg kg^{-1} for the same aforementioned exposure scenario (CETESB, 2013). However, current Cd soil screening values for the state of São Paulo were derived using information from the exposure routes adapted to the conditions in Sao Paulo, but using BCFs under temperate regions conditions.

Others studies conducted in tropical regions also showed Cd soil screening values lower than Cd soil screening values proposed for the state of São Paulo. New Zealand, for example, has Cd soil screening values of 0.5 and 1.4 mg kg^{-1} for pH 5.0 and 6.0, respectively, for both rural and urban exposure scenario. However, the rate of consumption of vegetables is considered to be 50% (Ministry for the Environment, 2010), much higher than the vegetable consumption rate considered in Brazil, and the conditions in São Paulo. However, as the proportionate consumption of vegetables increases in São Paulo, the soil screening values will become more restrictive. The same was observed in the other PTEs studied, which presented soil screening values of 6760.2 and 60024.2 mg kg^{-1} at pH 5.0 and 8432.0 and 63013.9 mg kg^{-1} at pH 6.0, for Zn; 2555.7 and 9347.2 mg kg^{-1} at pH 5.0, for Cu; 986.6 and 1828.7 mg kg^{-1} at pH 5.0, for Pb; all for rural and urban exposure scenario, respectively.

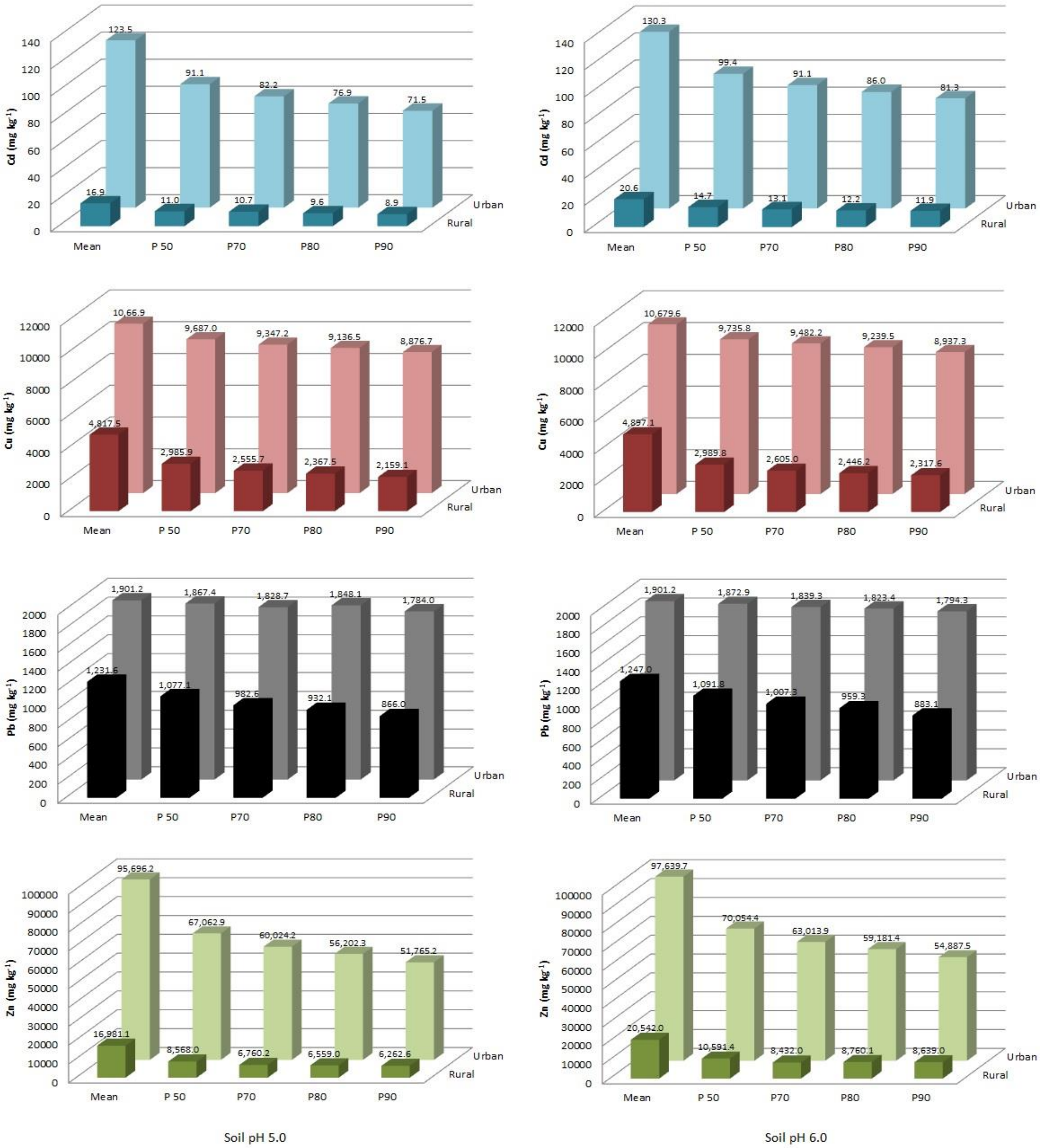

Figure 2 – Screening values of the Cd, Cu, Pb and Zn under different exposure exposure scenario, pH and percentiles and setting of data

4.4. Conclusions

- The soil screening values appropriate for the São Paulo conditions were adequate for Cd, Cu, Pb and Zn. The same was not observed for Ni because of the inconsistent results and because the combination of datasets did not (insufficiently) improve the results.
- The soil screening values proposed for all PTEs were less restrictive than the soil screening values for the State of São Paulo (Cetesb values).
- The 70 percentile (intermediate values) was the most suitable option to be adopted as soil screening values for São Paulo conditions.

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5 FINAL REMARKS

Despite the research on risk assessments in Brazil and São Paulo are relatively new, advances have been made in recent years to obtain the soil screening values of heavy metals. We emphasized the importance of the Environmental Sanitation Technology Company – Cetesb, with its pioneering work for SP soils in the generation of an official document of great importance, the "Securities Establishment Report for guiding soil and groundwater in the state of São Paulo ". This document was the precursor to Resolution # 420/2009 of the National Environmental Council - Conama. On the other hand, more studies are still needed in order to improve the risk assessment in the state of São Paulo, and the main focus should be the measurement of the accumulation of PTEs in different vegetables species and harvest times in areas subjected to sources of pollution, so that consistent soil-plant relationships for these areas could be developed. With a more consistent data set, the next step should be focused on local measurements of different exposure pathways, especially the rate of consumption of vegetables, which is still low in Brazil and in SP when compared to temperate countries, for example.

Environmental agencies and public and private research institutions should work togheter in order to carry out studies to generate more detailed results regarding risk assessment models.

The high uncertainty was causewd by the the heterogeinity of the results. For Ni in carrot, for example, the uncertainty was extremely large and the resulting BCF was rejected.

The species is also another important point in this type of study, because different species may absorb different amounts of metals. We collected 25 species of vegetables, including leaf and root groups. Among all species, lettuce, stood out as an accumulator of PTEs, and it is an easy species to be collected as it is produced on a large scale in all cities. However, attention should be given the species classified as spices which are bioaccumulators species.

The total and the available contents of PTEs in the soils of SP in general were low. Some areas, however, need a little more research, because the levels of PTEs were above the value of prevention or investigation.

The BCF and the soil screening values proposed for all PTEs were less restrictive than the soil screening values for the State of São Paulo (Cetesb values). However, the values proposed by

Cetesb are valid for the entire state of São Paulo, and this study included only part of the state. Then, although we proposed much less restrictive values than those derived by Cetesb, that does not mean that the legislation is being very strict, because other areas not included in this study within the state of São Paulo may contain higher PTEs values, justifying more restrictive screening values.