

**FRANCISCO DE SOUSA LIMA**

**BIOCONCENTRAÇÃO DE CHUMBO E ZINCO EM PARTES COMESTÍVEIS  
DE HORTALIÇAS CULTIVADAS EM SOLOS CONTAMINADOS**

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Tese apresentada à Universidade Federal Rural de Pernambuco, como parte das exigências do Programa de Pós-graduação em Ciência do Solo, para obtenção do título de Doctor Scientiae.

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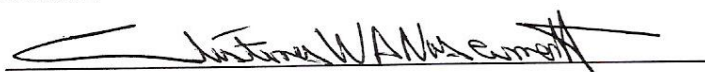
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Tese intitulada por **“BIOCONCENTRAÇÃO DE CHUMBO E ZINCO EM PARTES COMESTÍVEIS DE HORTALIÇAS CULTIVADAS EM SOLOS CONTAMINADOS”**, apresentada ao Programa de Pós-graduação em Ciência do Solo da Universidade federal Rural do Pernambuco, como exigência para obtenção do título de Doutor, e aprovada em 11 de fevereiro de 2010.



**Profº Dr. Clístenes Williams Araújo do Nascimento (UFRPE)**

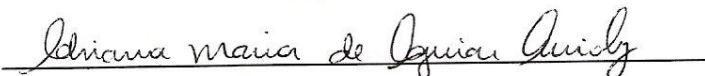
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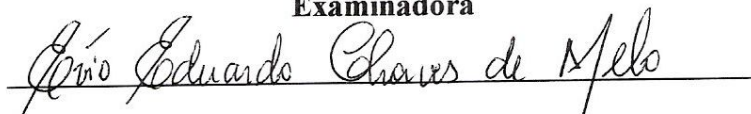
**Profº Dr. Mateus Rosas Ribeiro Filho (UFRPE)**

**Examinador**



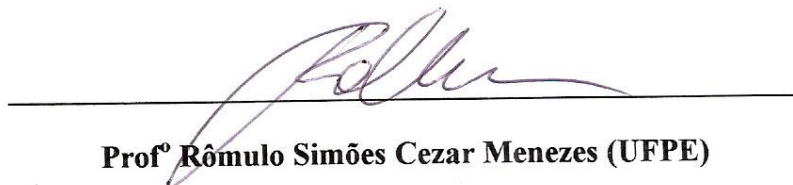
**Dra Adriana Maria de Aguiar Accioly (EMBRAPA)**

**Examinadora**



**Profº Évio Eduardo Chaves de Melo (UFPB)**

**Examinador**



**Profº Rômulo Simões Cezar Menezes (UFPE)**

**Examinador**

## **COMITÊ DE ORIENTAÇÃO**

---

**Profº Dr. Clístenes Williams Araújo do Nascimento (UFRPE)**  
**(Orientador)**

---

**Profº Dr. Mateus Rosas Ribeiro Filho (UFRPE)**  
**(Co-orientador)**

---

**Dra Adriana Maria de Aguiar Accioly (EMBRAPA)**  
**(Co- orientadora)**

A universidade deve ser um fator de mudanças para poder incluir as diferenças e não um ambiente preconceituoso que prejudica e reproduz as injustiças construídas e impostas pelas elites dominantes.

**Francisco de Sousa Lima**

“As lindas flores vindas do teu solo perfumam tuas belezas naturais. O teu vale esperançoso e tão fecundo, onde brotam os teus ricos arrozais, é o orgulho dos teus filhos que se ausentam, que te deixam, mas não te esquecem jamais”.

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“O desejo sincero e profundo do coração é sempre realizado; em minha própria vida tenho sempre verificado a certeza disto”.

**Mahatma Gandhi**

Às minhas queridas:

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Lara Araújo de Sousa Lima: filhinha de oito aninhos;

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Aos meus pais, por terem me proporcionado a vida e a coragem para lutar com  
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## RESUMO

LIMA, F.S. **Bioconcentração de chumbo e zinco em partes comestíveis de hortaliças cultivadas em solos contaminados**. 2010. 88f. Tese (Doutorado) – Departamento de Agronomia, Universidade Federal Rural de Pernambuco, Recife, 2010. Orientador: Clístenes Williams Araújo do Nascimento. Os metais pesados podem ser deletérios ou essenciais aos seres vivos. Entre os deletérios, o Pb tem destaque por ser extremamente tóxico para humanos. A intensificação das atividades industriais e agrícolas, devido ao aumento populacional nos últimos anos, tem contribuído à poluição dos solos agrícolas com Pb, podendo torná-los inadequados à produção de alimentos saudáveis. Com relação aos metais essenciais, o Zn tem causado preocupação, tendo em vista que a escassez deste elemento nos alimentos tem sido um dos maiores responsáveis pela desnutrição em grande parte da população do planeta. Para reduzir os efeitos da desnutrição, pesquisas estão sendo desenvolvidas através da estratégia de biofortificação de partes comestíveis de vegetais, visando a produção de alimentos saudáveis e com qualidade, que apresentem menor teor de contaminantes inorgânicos e maior concentração de micronutrientes essenciais. No entanto, no Brasil ainda são poucas as pesquisas que visam avaliar teores de metais deletérios e micronutrientes em alimentos vegetais e, nesse contexto, no presente trabalho foram desenvolvidos quatro experimentos tendo como objetivos avaliar: 1) teores e alocação de Pb por hortaliças cultivadas em solo contaminado com resíduos de reciclagem de baterias; 2) o efeito do Pb na concentração de nutrientes em olerícolas, bem como o potencial de transferência desse elemento de um solo contaminado por baterias automotivas para as partes comestíveis das hortaliças; 3) o efeito do Pb sobre a absorção de micronutrientes, distribuição do Pb entre as frações de um Espodossolo e a relação dessas frações com a disponibilidade do metal para hortaliças e 4) a transferência de Zn do solo para partes comestíveis de cenoura, couve manteiga e quiabeiro cultivadas em latossolo tratado com doses de zinco. Os resultados desses experimentos demonstraram que o teor de Pb determinado nas espécies obedeceu a ordem: cenoura > quiabo > tomate > berinjela > pimentão > couve-manteiga > repolho > beterraba, com alocação preferencialmente na raiz, seguida por caule, folha e parte comestível. A concentração de Pb transferida à parte comestível da cenoura foi superior ao limite de tolerância máximo estipulado na legislação. O Pb promoveu desbalanço nutricional nas plantas, sendo ainda observado que os macronutrientes concentraram-se, preferencialmente, nas folhas, enquanto que os

micronutrientes foram alocados nas raízes. Plantas de couve manteiga apresentaram maior potencial para concentrar Zn em sua parte comestível, comparativamente à cenoura e quiabeiro, sendo indicadas para utilização em programas de biofortificação.

**Palavras-chave:** metais pesados, biofortificação, extração seqüencial, hortaliças.

## **INTRODUÇÃO GERAL**

### **Contaminação de hortaliças por chumbo**

A poluição ambiental causada por metais pesados vem crescendo especialmente nas últimas décadas. A contaminação por metais é resultado, na maioria dos casos, das atividades antropogênicas relacionadas principalmente com a mineração, descarte de resíduos industriais, aplicação de lodo de esgoto, fertilizantes e pesticidas no solo (Freitas et al., 2009). Os metais lançados ao solo inicialmente são adsorvidos por meio de troca iônica ou interações eletrostáticas, forças de van der Waals ou ligações químicas estáveis (Linhares et al., 2009). No entanto, não havendo as interações estáveis com as partículas do solo, pode haver migração do elemento, culminando na contaminação da água e dos seres vivos.

Devido ao potencial tóxico e à elevada persistência no ambiente, o Pb tem despertado grande preocupação entre os metais pesados, sendo classificado como o segundo elemento mais perigoso no ambiente, conforme lista de prioridades da agência de proteção ambiental americana (ATSDR, 2009; Torri & Lavado, 2009). Embora o Pb ocorra naturalmente no solo em baixas concentrações, não causando problemas para a saúde da população, diversas atividades antropogênicas podem contribuir para o aumento do teor deste elemento acarretando na contaminação de solos cultivados (Melo et al., 2008; Gopal & Rizvi, 2008).

O elevado teor total do Pb no solo não indica necessariamente que o elemento esteja disponível ou móvel, podendo poluir o solo (Chen et al., 2009). O Pb é relativamente estável no solo (Maneck et al. 2006) devido principalmente a sua adsorção aos óxidos de Fe e Mn e à matéria orgânica, tornando-se pouco disponível (Liu et al., 2006). Neste contexto, o teor total do Pb não é um parâmetro adequado para indicar o potencial biodisponível de metais para os organismos vivos (Gupta & Sinha, 2006; Ortiz & Alcañiz, 2006; Li et al., 2007).

O potencial do Pb biodisponível pode variar conforme as características dos diferentes solos. A adsorção do Pb nas partículas do solo depende de várias reações e pode variar com as propriedades do elemento, características do solo e com o tempo de residência do metal no ambiente (Lu et al., 2005).

Técnicas de extração simples, através do EDTA, DTPA e  $\text{CaCl}_2$ , entre outros, e extração sequencial do Pb, tem sido implementadas visando avaliar o potencial do metal

biodisponível nos solos (Gupta & Sinha, 2006; Li et al., 2007). A extração sequencial pode ser muito útil para promover uma avaliação do risco do Pb no solo. A mesma é uma técnica de extração seletiva que, além de predizer o potencial do metal biodisponível, também pode predizer o potencial de mobilidade, lixiviação e poluição dos solos (Pueyo et al., 2003; Gupta & Sinha, 2006; Ishikawa et al., 2009). Entre os vários métodos utilizados, o método proposto por Shumam, (1985) é o mais indicado para os solos com pH relativamente ácido e que não apresentam carbonatos ou sulfetos na sua composição.

Os vegetais crescidos em ambiente contaminado podem absorver e acumular em quantidade excessiva o Pb potencialmente biodisponível, inclusive nas partes comestíveis (Nogueira et al., 2007; Lim et al., 2008), sem apresentar sintomas visíveis de toxidez ou mesmo redução na produção (Piechalak, et al., 2002; Hong et al., 2008), tornando-se motivo de grande preocupação devido à toxicidade desse metal para a saúde humana e dos animais (Wang et al., 2006).

O teor de Pb absorvido e acumulado nos tecidos das plantas é muito variável entre as espécies e variedades, e depende também das propriedades fisiológicas da cultura e de fatores ambientais como o pH, tamanho das partículas do solo, capacidade de troca de cátions, matéria orgânica e disponibilidade de nutrientes (Liu et al., 2005; Peris et al., 2007; Sharma et al., 2007). As hortaliças folhosas têm apresentado teores mais elevados de Pb, devido à sua grande área foliar, à elevada taxa de transpiração e ao rápido crescimento destas plantas (Itanna, 2002). Estes fatores tornam essas espécies mais perigosas caso sejam cultivadas em ambientes contaminados.

Embora a maior parte do Pb absorvido apresente-se preferencialmente retida nas raízes das plantas, este metal também pode ser transferido e alocado nas partes comestíveis (Silva et al., 2007; Lim et al., 2008). Quando a concentração do metal nas partes comestíveis excede os valores máximos considerados seguros para consumo humano (Codex Alimentarius, 2009; Muchuweti, et al., 2006), as plantas constituem importante rota de transferência do Pb do solo para os seres humanos.

Em humanos, o Pb não tem nenhuma função fisiológica no organismo e, ao ser absorvido, distribui-se pelo sangue e pode afetar diversos órgãos (Kede et al., 2008; Moreira & Neves, 2008), constituindo-se em ameaça à saúde da população, especialmente das crianças, por serem mais sensíveis. O Pb pode acumular-se nos diversos órgãos e sistemas dos seres humanos. Contudo, pessoas que têm contato

permanente com o Pb acumulam este metal em alguns componentes do organismo, tais como os ossos e a aorta, durante toda a vida (Moreira & Neves, 2008).

### **Biofortificação com zinco**

É pertinente ressaltar que existe um grupo de metais pesados com importantes funções vitais para os seres vivos. Entre estes, o Zn tem destaque no organismo humano, estando envolvido na síntese do material genético, na composição de enzimas, no crescimento e na diferenciação celular (Mayer et al. 2008). Contudo, este micronutriente tem sido objeto de muita preocupação, tendo em vista que grande parte da população mundial sofre por desnutrição, em virtude da baixa disponibilidade deste elemento nos solos e sua conseqüente escassez nos alimentos (Wu et al., 2007; Broadley et al., 2007).

A deficiência de Zn nos solos tornou-se cada vez mais acentuada, principalmente em áreas onde as novas variedades de alto rendimento foram introduzidas (Alloway, 2009). Plantas cultivadas em solos pobres apresentam baixa produtividade (Yang et al., 2007; Alloway, 2008) e concentram baixo teor de Zn em suas partes comestíveis, tornando-as inadequadas para uma alimentação saudável (White & Broadley, 2005). Contudo, a adequada nutrição vegetal com Zn contribui para o aumento da produção de biomassa (Wang et al., 2009) e pode proporcionar maior teor de Zn nos alimentos vegetais.

As estratégias convencionais de combate à desnutrição não tem sido eficazes, tendo em vista o alto custo deste procedimento e a baixa abrangência populacional (Yang et al., 2007). Diante deste contexto, a biofortificação de partes comestíveis de vegetais pode ser uma nova estratégia para minimizar o problema da deficiência de micronutrientes na dieta alimentar da população. A biofortificação das partes comestíveis de vegetais pode ser desenvolvida, efetivamente, por duas estratégias básicas: genética e agrônômica. A biofortificação genética envolve o melhoramento de plantas e desenvolve novas cultivares capazes de acumularem relativamente altas concentrações de Zn nas partes comestíveis (Cakmak, 2008).

Na biofortificação agrônômica, utilizam-se fertilizantes nos solos ou através de aplicações foliares e/ou sementes, como, por exemplo, o  $ZnSO_4$ , e o cultivo de plantas alimentícias visando aumentar as concentrações de Zn em suas partes comestíveis (Alloway, 2009). Segundo esse mesmo autor, esta estratégia também se aplica às



culturas cujos rendimentos não estão limitados pela deficiência de Zn, mas que apresentam baixo teor deste elemento nas suas partes comestíveis.

Outra importante estratégia de biofortificação vem sendo desenvolvida visando reduzir o teor de substâncias “antinutrientes” presentes nas partes comestíveis dos vegetais que impedem a absorção de Zn pelo organismo humano. Dentre as substâncias “antinutriente”, pode-se citar o ácido fítico, que é encontrado em sementes de legumes e grãos de cereais; fibras (celulose, hemicelulose, lignina, cutina, suberina etc.), encontrados em grãos de cereais como trigo, arroz, milho, aveia, cevada e centeio; taninos e polifenóis, encontrados em café, feijão e sorgo; ácido oxalacético presente em folhas de espinafre; hemoglobinas, encontradas em muitos legumes e no trigo; e metais pesados (Cd, Hg, Pb) presentes em vegetais folhosos e tuberosos contaminados (Graham et al., 2001; Ramírez-Cárdenas et al., 2008). Estas substâncias reduzem a absorção do Zn pelo organismo humano e contribuem para sua efetiva eliminação para o ambiente.

Através da biofortificação agronômica, respostas de plantas têm sido relatadas em vários países do mundo. Registros demonstram que os fertilizantes a base de Zn, utilizados nos campos de trigo na Austrália, Índia e Turquia, proporcionaram aumento dos teores desse metal nos grãos e proporcionando também aumento no rendimento da cultura, acarretando em grande benefício na economia destes países (Cakmak, 2004). Vários outros autores têm observado que o adequado fornecimento dos nutrientes no sistema solo-planta, através de práticas agronômicas, além de proporcionar melhor nutrição das plantas, aumenta o rendimento das culturas e o teor de Zn nas partes comestíveis, conseqüentemente melhorando a nutrição e a saúde humana (Broadley et al., 2007; Welch & Bouis, 2009), diminuindo o efeito da desnutrição e o risco de epidemias generalizadas. Segundo Hotz (2009) essa estratégia pode ser muito útil para fornecer o adequado suprimento de Zn, especialmente para a população rural, por ser muito afetada pela escassez desse elemento e, principalmente, por produzir os alimentos básicos em suas próprias localidades.

A biofortificação representa um método sustentável de prevenção da desnutrição em seres humanos, tendo em vista que os vegetais são fontes naturais de micronutrientes, como Zn, na dieta alimentar (Bosiacki & Tyksiński, 2009), principalmente nas regiões onde é mais difícil garantir que todos tenham acesso a dietas suplementadas com este elemento (Mayer et al., 2008; Alloway, 2009). Outro fator

muito importante e relevante da biofortificação, refere-se à não necessidade de processamento industrial prévio dos alimentos, tornando-os mais acessíveis a toda população (Hotz, 2009).

A identificação de espécies olerícolas com relevante contribuição na dieta da população e com maior potencial para absorver nutrientes e aumentar a densidade e biodisponibilidade de Zn nas partes comestíveis (Carvalho et al., 2006; Yang et al., 2007; Palmgren et al., 2008), pode orientar a seleção de hortaliças mais adequadas para uso em programas de combate à desnutrição humana.

Diante deste contexto e tendo em vista a efetiva importância da produção de alimentos vegetais com teores de micronutrientes normalmente mais elevados e cujo o teor de metais pesados deletérios não ultrapasse os limites permitidos pela legislação para consumo humano, esta pesquisa teve como objetivo avaliar a possibilidade de transferência de Pb e Zn para as partes comestíveis de olerícolas de diferentes grupos anatômicos e morfológicos cultivadas em solo contaminado.

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**CAPÍTULO I:**

**LEAD CONCENTRATION AND ALLOCATION IN VEGETABLE CROPS  
GROWN IN A SOIL CONTAMINATED BY BATTERY RESIDUES**

**(Revista Horticultura Brasileira)**



## **Lead concentration and allocation in vegetable crops grown in a soil contaminated by battery residues<sup>1</sup>**

Francisco de S Lima; Clístenes WA do Nascimento; Fernando BV da Silva; Vinícius GB de Carvalho; Mateus RR Filho

UFRPE – Dep<sup>to</sup> de Agronomia, Rua Dom Manuel de Medeiros s/n, Dois Irmãos, 50.171-900 Recife-PE, [clistenes@pq.cnpq.br](mailto:clistenes@pq.cnpq.br)

### **ABSTRACT**

Lead (Pb) is a metal that is very stable in soil and highly toxic to humans and animals. Exposure to Pb occurs via inhalation of particles from industry and soil, as well as household dust, water, and contaminated food. A greenhouse experiment was carried out to evaluate Pb contents and allocation in vegetable crops grown in soil contaminated by battery recycling wastes. The experiment was conducted in a randomized block design factorial 8x4, with four replicates. Four parts (root, stem, leaf and edible parts) of eight plant species (tomato, sweet pepper, beet, carrot, cabbage, green collards, eggplant, and okra) were studied. The results showed that carrot, green collards, beet, and okra were the most Pb tolerant species, while the others were very Pb-sensitive, since they did not complete their cycle. The decreasing order for Pb concentration in the root of crops was: carrot > okra > tomato and eggplant > sweet pepper > kale > cabbage. Taking into account Pb allocation in plants, the order was: root > stems > leaves > edible parts. Pb allocated in the edible parts may exceed o tolerable limit.

**Keywords:** Battery recycling, soil pollution, soil contamination, heavy metals.

## RESUMO

### **Teores e alocação de chumbo em hortaliças cultivadas em solo contaminado por resíduos de baterias**

O chumbo (Pb) é um elemento extremamente estável no solo e altamente tóxico para seres humanos e animais. A contaminação com chumbo geralmente ocorre pela exposição decorrente da inalação de partículas oriundas de indústrias ou do solo, ou ainda, pela ingestão de poeira doméstica, água e alimentos de origem animal e vegetal contaminados. O presente trabalho objetivou avaliar os teores e a alocação de Pb em hortaliças cultivadas em solo contaminado com resíduos de reciclagem de baterias. O experimento foi conduzido em casa de vegetação com delineamento experimental em blocos casualizados, no esquema fatorial 8x4, com 4 repetições. Os tratamentos consistiram de oito espécies de hortaliças (tomate, pimentão, beterraba, cenoura, repolho, couve manteiga, berinjela e quiabo) e quatro partes da planta (raiz, caule, folha e parte comestível). Os resultados mostraram que as espécies mais tolerantes ao Pb foram cenoura, couve-manteiga, beterraba e quiabo. As demais hortaliças foram consideradas muito sensíveis aos teores de Pb no solo, não completando inclusive seu ciclo biológico. A ordem decrescente de teores de Pb nas raízes das espécies foi: cenoura > quiabo > tomate e berinjela > pimentão > couve-manteiga > repolho. A alocação do Pb na planta, seguiu a ordem geral: raiz > caule > folha > parte comestível. O Pb alocado nas partes comestíveis pode exceder o limite de tolerância máximo estabelecido na legislação.

**Palavras-chave:** reciclagem de baterias, contaminação de solo, poluição do solo, metais pesados.

Heavy metals occur naturally in soils, and some of these, such as copper (Cu), zinc (Zn), and cobalt (Co), play an important role in the nutrition of plants and animals, while others, such as cadmium (Cd), lead (Pb), and arsenic (As), have deleterious effects on various components of the biosphere. Normally, these elements are present in the soil at concentrations or forms that do not pose a risk to the environment (Silva *et al.* 2007), but their levels can be altered by different anthropogenic routes.

Lead is an element that is extremely stable in soil and highly toxic to humans and animals (Reeder & Shapiro, 2003). The metal is classified as the second most dangerous

on the priority list of the U.S. Environmental Protection Agency (ATSDR, 2008). For this reason, Pb has evoked heightened concern due to its toxicity and high quantity in the environment, caused by its generalized utilization in various products (Segura-Muñoz *et al.* 2006). The exposure to this element can occur by inhalation of particulate material emitted by industrial processes or by re-suspension after deposition in the soil, or even, through the ingestion of household dust, water, and foods of animal and plant origin produced in locations close to pollutant sources (Okada *et al.* 2004).

Lead levels found in foods are greater in industrialized regions, especially those where the metal and its components are widely utilized. The concerns with lead effects on human health and the environment have led many countries to adopt laws restricting or prohibiting its utilization (Meyer *et al.* 1999). However, developing countries are not in the vanguard of controlling lead use (Olivero-Verbel *et al.* 2007). In view of the global scenario of lead utilization, it is estimated that the manufacture of batteries is responsible for about 70% of the lead consumed worldwide. The large worldwide growth in the automobile industry in the last decades (Paoliello & Chasin, 2001), as well as the expansion of the market for batteries, makes the use and recycling of batteries one of the principal forms of lead contamination in soils.

Lead can occur naturally in plants as a result of the uptake from soil. Lead forms and contents in vegetables vary greatly with the species and depend principally on the environmental conditions, because contaminated soils can induce lead accumulation by crops (Nan *et al.* 2002). Lead accumulation by vegetable crops grown in soils with abnormally elevated levels of the metal poses a risk to human health. Therefore, the capacity of these plants to accumulate lead and its presence in edible parts should be evaluated.

Thus, the aim of the present work was to determine lead contents and allocation in vegetables cultivated in soil contaminated with residues from the recycling of batteries.

## **MATERIAL and METHODS**

The soil used in the study was a haplic podzol with sandy texture, collected out of an area contaminated with lead (Pb), belonging to a company that recycles batteries. The soil was collected at the surface layer (0 – 20 cm), and was air-dried, broken up, homogenized, and sifted through a 2-mm mesh screen. Subsamples of the soil were

separated for chemical and physical characterization (EMBRAPA, 1997, 1999). The results were: pH in H<sub>2</sub>O = 3.89; P = 2.30 mg dm<sup>-3</sup>; Na<sup>+</sup> = 0.28 cmol<sub>c</sub> dm<sup>-3</sup>; K<sup>+</sup> = 0.05 cmol<sub>c</sub> dm<sup>-3</sup>; Ca<sup>+2</sup> = 4,6 cmol<sub>c</sub> dm<sup>-3</sup>; Mg<sup>+2</sup> = 0.90 cmol<sub>c</sub> dm<sup>-3</sup>; Al<sup>+3</sup> = 0.50 cmol<sub>c</sub> dm<sup>-3</sup>; H+Al = 3.30 cmol<sub>c</sub> dm<sup>-3</sup>; C.O. = 8.54 g kg<sup>-1</sup>; organic matter = 14.73 g kg<sup>-1</sup>; Pb = 413 mg kg<sup>-1</sup>; sand = 943 g kg<sup>-1</sup>; silt = 27 g kg<sup>-1</sup>; and clay = 30 g kg<sup>-1</sup>.

To determine the total Pb level, 10 ml of extracting solution (HCl:HNO<sub>3</sub>, in a proportion of 3:1) were added to 1 g of soil, and the mixture was allowed to stand in a beaker covered with a watch glass for 16 h, at room temperature. After this period, the samples were heated for 2 h (80°C), cooled, brought to 50 mL in a volumetric flask, and filtered (Pereira *et al.* 2007). After filtering, the extracts were transferred to PET-type flasks, labeled, and kept at 4°C in a refrigerator until read in an atomic absorption spectrophotometer.

The soil was incubated for 20 days with calcium carbonate and magnesium dioxide (3:1), to raise the pH to 6.5. Eight vegetable crops were studied: tomato (*Lycopersicon esculentum*), cultivar Rio Fuego; sweet pepper (*Capsicum annuum*), hybrid All Big; beet (*Beta vulgaris*), cultivar Itapuã 202; carrot (*Daucus carota*), cultivar Brasília; green collards (*Brassica oleracea* var. *acephala*), cultivar Georgia; cabbage (*Brassica oleracea* var. *capitata*), cultivar Coração-de-boi; eggplant (*Solanum melongena*), cultivar Embu; and okra (*Abelmoschus esculentus*), hybrid Dardo. Seedlings were produced in a greenhouse, in polystyrene foam trays, utilizing Vermicompost as substrate.

To set up the experiments, 5.5 kg of soil were transferred to a plastic pot and fertilized prior to sowing in accordance with Nascimento *et al.* (2006). Each pot corresponded to one experimental unit (plot). Twenty days after sowing, seedlings were transplanted to pots, and 15 days after, pots were thinned, leaving three plants per pot. During the study, the soil was kept at 80% of the maximum water retention, assessed by daily weighing and irrigation to replace the water lost by evapotranspiration. The experiments were carried out in a greenhouse, from January to April 2008, in blocks at random. Treatments corresponded to the eight vegetable crops, with four replications.

The plants were collected, separating roots, stems, leaves, and fruits. Plant parts were thoroughly washed with tap water and then with distilled water. The parts collected

were placed in paper bags and set in an oven at 65-70°C. The dry samples were weighed and then ground in a Wiley type mill. After, samples were submitted to nitroperchloric digestion (EMBRAPA, 1999) for assessing Pb levels in the extracts by atomic absorption spectrophotometry. Pb bioaccumulation rate in the plant, which represents the percentage of the element present in the dry biomass in relation to total content in the soil (Vyslouzilova *et al.* 2003), was calculated according the formula:

$$BR = \frac{Pb_{\text{plant}} \times B_{\text{plant}}}{Pb_{\text{soil}} \times W_{\text{soil}}} \times 100(\%), \text{ where}$$

$Pb_{\text{plant}}$  = concentration of Pb in the plant, obtained by the weighted average metal concentrations in plant organs ( $\text{mg kg}^{-1}$ );  $B_{\text{plant}}$  = total dry biomass collected (g);  $Pb_{\text{soil}}$  = concentration of total Pb in the soil ( $\text{mg kg}^{-1}$ );  $W_{\text{soil}}$  = total amount of soil in pot (g).

The translocation index (TI), in percentage, was calculated as the ratio between the amount of Pb accumulated in the aboveground part and the total amount in the whole plant (Abichequer & Bohnen, 1998). The experiment was conducted in randomized blocks design factorial 8 x 4. The treatments consisted of eight vegetable species (carrot, beet, tomato, sweet pepper, kale, cabbage, okra and eggplant) and four parts plants (root, stem, leaf and edible part), with four replications. Data regarding Pb contents in the various parts of the crops studied were submitted to analysis of variance and the means were compared by the Scott & Knott test at 5% probability.

## RESULTS and DISCUSSION

The highest Pb concentration in roots was found in carrots, while kale and cabbage showed the lowest level of Pb allocated in the root system (Table 1). Based on these results, carrots represent the crop with least biological restriction in absorbing Pb from the soil. The difference in the Pb concentration in roots between the plants analyzed was due to intrinsic characteristics of the crops. Similar results were observed by Al-Lahham *et al.* (2007), where two cultivars of tomato and their parts differed with respect to the capacity to accumulate heavy metals. This emphasizes the need for studies that indicate the differences in the preferential allocation of this metal in different crops and plant parts.

In examining the Pb concentration in the different plant parts, it is evident that the highest Pb level is found in the roots in all the crops studied. This finding corroborates the characteristic of Pb in concentration preferentially in the roots. This metal moves in the root through the apoplast, crossing the cortex, and accumulating close to the endodermis, which acts as a partial barrier in Pb translocation to the aboveground part. This may be one of the reasons for the greater accumulation of this metal in the roots in relation to the aboveground part (Verma & Dubey, 2003). The high Pb concentration in roots can also be related to the immobilization of this element by insoluble organic polymers present in the root tissue (Kahle, 1993).

There was no significant difference between the crops studied regarding the Pb content in stems, except for okra and kale which showed, respectively, the highest and lowest concentration. This result demonstrates that kale is the crop that, proportionally, restricts more the allocation of Pb in the stem.

The analysis of Pb level in leaves showed that okra had the highest concentration, followed by carrot and beet, while tomato, sweet pepper, kale, cabbage, and eggplant concentrated the lowest Pb amounts. In comparing the Pb concentration in kale leaves with percentage of moistness (90%), with the tolerable level of  $0.3 \text{ mg kg}^{-1}$  of fresh weight (Codex Alimentarius, 2008), it was found that the consumption of these leaves would pose a potential risk to human health.

On studying the edible parts of the vegetables, it is seen that beet has the highest level of Pb, followed by carrot, while kale and okra accumulated the lowest Pb amounts (Table 1). All these Pb contents in the edible parts are above the tolerance limits established by the Codex Alimentarius (2008): carrot, beet, and okra,  $0.1 \text{ mg kg}^{-1}$ ; and kale,  $0.3 \text{ mg kg}^{-1}$ . Similar results were obtained by Okada *et al.* (2004) who showed that the Pb level in the soil caused an increase in Pb contents in the edible parts of tuber vegetables. It is worth noting that (1) the allocation of Pb in the edible parts of plants represents a real risk to consumers, and (2) the analysis of the edible parts is definitely the most important to be carried out when human foods are taken into account.

Among the crops evaluated, carrot showed the highest bioaccumulation rate (1.29%). In carrots, little of the Pb absorbed was transferred to the aboveground part of the plant, thereby the remaining accumulated in the roots, as demonstrated by the low

translocation index (1.80%) (Figure 1). On the other hand, among the crops studied, beet showed the lowest bioaccumulation rate (0.02%) and highest translocation index (33.75%), being the crop that least restricts Pb to the root. Kale, cabbage and eggplant showed a behavior that was similar among the three, with a low bioaccumulation rate when compared to tomato, sweet pepper and okra.

In general, for all the crops studied, there was a very low bioaccumulation rate of the Pb present in the soil (ranging from 0.02 a 1.29%), due not only to the toxicity of this metal to the plants, but also to its inherent low solubility in the soil (Manecki *et al.* 2006). However, the highest translocation index observed for some crops (beet and cabbage) should be analyzed with caution due to the possibility of contamination of these vegetables.

Carrot, okra, beet, and kale, despite the uptake of Pb from the contaminated soil, completed the cycle without showing visible symptoms of phytotoxicity. It should be noted that the residue deposition in the soil, particularly discharges from the automobile battery industry, can result in metal bioconcentration in the plant before any phytotoxicity symptom become visible (CETESB, 2008). This represents a concern, since vegetables with considerable Pb contents can be inadvertently consumed.

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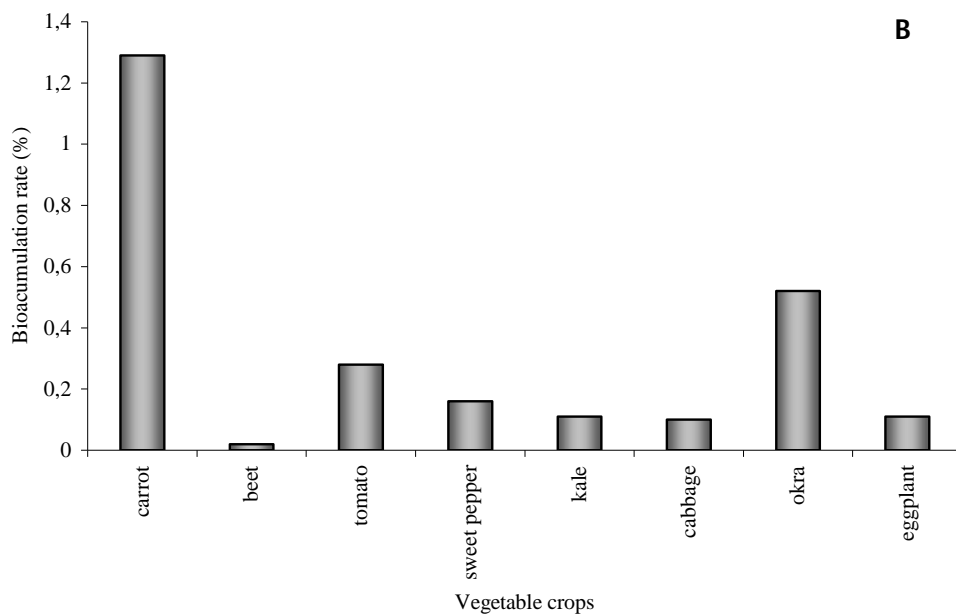
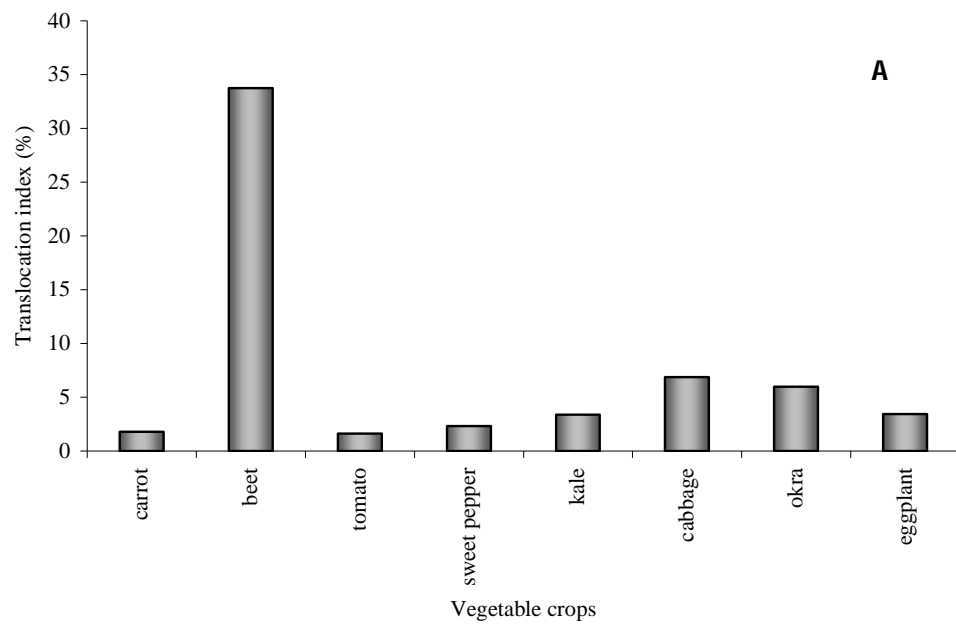
VYSLOUŽILOVÁ M; TLUSTOŠ P; SZÁKOVÁ J. 2003. Cadmium and zinc phytoextraction potential of seven clones of *Salix* spp. planted on heavy metal contaminated soils. *Plant Soil Environment* 49:542–547.

**Table 1.** Lead concentration in vegetable crops grown in Pb-contaminated soil (Concentração de chumbo nas hortaliças cultivadas em solo contaminado com Pb). Recife, UFRPE, 2009.

Crop	Pb Concentration (mg kg <sup>-1</sup> )			
	Root	Stem	Leaf	Edible part
Carrot	2.162.1 Aa	NA	25.4 Cb	54.6 Bb
Beet	MD	NA	40.3 Bb	108.3 Aa
Tomato	405.5 Ac	40.3 Bb	9.9 Cc	*
Sweet pepper	281.0 Ad	27.6 Bb	7.7 Cc	*
Kale	175.8 Ae	10.3 Bc	3.2Bc	3.2 Bc
Cabbage	152.5 Ae	23.3Bb	7.9Cc	*
Okra	757.2 Ab	133.5Ba	75.7Ca	5.2 Dc
Eggplant	389.4 Ac	37.9Bb	7.1Cc	*
CV (%)	11.95			

Means followed by the same capital letter in the row and small letter in the column do not differ significantly from each other, Scott & Knott test,  $P < 0.05$ . (Médias seguidas de mesma letra maiúscula nas colunas e minúscula nas linhas não diferem significativamente entre si, teste de Scott & Knott,  $P < 0,05$ ).

NA = not applicable (não se aplica); MD = missing data (dados não apresentados); \* species that did not complete production cycle (espécies que não completaram o ciclo de produção).



**Figure 1.** Translocation index (A) and bioaccumulation rate (B) of lead in vegetable crops grown in a contaminated soil. (Índice de translocação (A) e fator de bioacumulação (B) de chumbo em hortaliças cultivadas em solo contaminado). Recife, UFRPE, 2009.

**CAPÍTULO II:**

**LEAD AND NUTRIENT ALLOCATION IN VEGETABLES GROWN IN A SOIL  
FROM A BATTERY RECYCLING SITE**

**(Journal of Plant Nutrition and Soil Science)**

**Lead and nutrient allocation in vegetables grown in a soil from a battery recycling site**

Clístenes Williams Araújo do Nascimento

Federal Rural University of Pernambuco, Department of Agronomy, Av. Dom Manoel de Medeiros, s/n, Dois Irmãos, Recife PE, Brazil, 50171900. Tel: +55 81 33206236, E-mail: clistenes@depa.ufrpe.br

\* Total number of pages of work - 20

\* Total number of pictures of work - 1

\* Total number of tables of work - 4

# **Lead and nutrient allocation in vegetables grown in a soil from a battery recycling site<sup>1</sup>**

Francisco de Sousa Lima<sup>2</sup> and Clístenes Williams Araújo do Nascimento<sup>2</sup>

<sup>1</sup>Work of doctoral thesis of first author

<sup>2</sup>Federal Rural University of Pernambuco, Department of Agronomy, Av. Dom Manoel de Medeiros, s/n, Dois Irmãos, Recife PE, Brazil, 50171900.

## **Abstract**

The steady growth of the Brazilian automotive industry and the resulting development of the battery market, which represents a large proportion of the lead (Pb) consumed in the country, have made battery recycling one of the main sources of Pb soil contamination in Brazil. Plants cultivated in Pb contaminated soil can take up this metal, which not only affects their nutritional metabolism, but can also be transferred into the edible parts of plants and, therefore, impose threats to human health. The study was carried out to evaluate the concentration of Pb in edible parts of vegetables grown on a soil contaminated by battery recycling activities as well as the Pb effects on the concentration of nutrients in plants. The treatments consisted of two soil conditions (contaminated and non-contaminated), four plant species (lettuce, kale, carrot and okra) and four parts plants (root, stem, leaf and edible parts), with four replications. The results showed that regarding Pb concentrations observed in edible parts of vegetables grown in contaminated soil, only carrots presented Pb concentration above the acceptable threshold for human consumption. Among the vegetables evaluated, only the lettuce dry matter production was reduced due to the high concentration of Pb in soil. Lead altered the concentration of micronutrients in the evaluated plant parts, stimulating higher Fe, Mn, Zn and Cu concentrations in kale, carrots and okra cultivated in contaminated soil.

**Key words:** heavy metals / edible parts / nutrients uptake

## 1 Introduction

Heavy metals are naturally found in soils in low concentrations, as a result of weathering and other pedogenetic processes. However, such concentrations can be modified by biogeochemical processes and especially by anthropogenic effects (*Kede et al., 2008; Freitas et al., 2009*). Over recent decades, urban and industrial growths have caused considerable environmental contamination (*Gopal and Rizvi, 2008*). Among the main environmental contaminants, lead (Pb) poses an important threat, due to its high toxicity to human health (*Yadav et al., 2002; Wang et al., 2006; Kede et al., 2008*), and for this reason, it is regarded as the second most hazardous element on the EPA priority list (*ATSDR, 2009*).

Plants grown in contaminated soils can absorb and accumulate heavy metals (*Liu et al., 2006*), thereby resulting in photosynthesis inhibition, alterations in the plant structure and permeability of the membrane and disturbances in mineral nutrition (*Sarma et al., 2006*). Pb can decrease cation (K, Ca, Mg, Mn, Zn, Cu, Fe) and anion ( $\text{NO}_3^-$ ) absorption by the root system (*Sharma and Dubey, 2005*). Lead toxicity can also generate species reactive to oxygen, including peroxide radicals, hydrogen peroxide and hydroxyl radicals, which cause oxidative stress in plants (*Liu et al., 2009*). These oxygen-reactive species may rapidly attack nucleic acids, proteins, lipids and amino acids, generating various metabolic dysfunctions in plant (*Gopal and Rizvi, 2008*).

Pb accumulation in plants may differ among species or even varieties (*Peris et al., 2007*), and strongly depends on the species' physiological characteristics (*Liu et al., 2005*), as well as environmental factors such as pH, soil texture, cation exchange capacity, organic matter and nutrient availability (*Sharma et al., 2007*).

High Pb concentration in edible parts account for more than half of the number of people contaminated from consuming vegetables (*Nasreddine and Parent-Massin, 2002*). High concentrations of this metal in leafy vegetables are mainly due to their greater leaf area, elevated transpiration rate, and rapid plant growth (*Itanna, 2002*). Increased Pb concentrations in vegetable crops can be harmful to human beings (*Rattan et al., 2005*). Lead effects on children are associated with impaired cognitive development and intellectual performance. Adults suffer more from reproductive and renal problems, as well as higher blood pressure (*WHO, 1993*). In pregnant women, Pb

is easily transported to unborn babies through the placenta, and babies can be infected through breast feeding (Rabinowitz et al., 1985).

Some vegetable crops can grow naturally in contaminated soil, and absorb and accumulate Pb in great quantities in edible parts (Nogueira et al., 2007; Lim et al., 2008), without showing visible symptoms or reduction in production or growth (Hong et al., 2008). In such conditions, plants present Pb concentrations far above the thresholds considered safe for human consumption (Muchuweti, et al., 2006), thereby acting as a major route through which the element can be transferred from soil to humans.

The use of Pb-contaminated soil to grow vegetable crops is highly useful in studying the uptake potential of the element by different vegetable species. The greater the Pb transfer into edible parts, the greater the risk to consumers. This study aimed to evaluate the concentration of Pb in edible parts of vegetables grown on a soil contaminated by battery recycling activities as well as the Pb effects on the concentration of nutrients in plants.

## 2 Material and methods

The experiment was carried out in a greenhouse between May and July 2008 and used a soil collected near an automobile-battery recycling facility. The site is located in Rio Tinto, Paraíba state, Northeast Brazil (latitude 6°48'21.48''N and longitude 35°04'32.14'' O). Samples of the same soil type were also collected from a non-contaminated area to be used as a control. The soil samples were air-dried and sieved through a 2 mm-mesh sieve in order to perform the chemical and physical analysis (EMBRAPA, 1997; 1999) (Table 1). The total Pb concentration was obtained by *aqua regia* (HCl:HNO<sub>3</sub>, molar ratio 3:1). Soil acidity was corrected to a pH between 6.5 and 6.8 using calcium carbonate and magnesium oxide (3:1 molar ratio).

### Table 1

The four vegetables chosen for this study are among the most important ones in the typical Brazilian diet, and represent different edible parts (tubers, leaves and fruits). Seedlings of carrot (*Daucos carota*), kale (*Brassica oleracea* var. *acephala*), okra (*Abelmoschus esculentus*) and lettuce (*Lactuca sativa*) were grown in a greenhouse, in polystyrene trays, using vermicompost as substrate. To prepare the experiment, 5.5 kg



of soil was transferred into plastic pots, and held fertilization before transferring the seedlings (*Nascimento et al.*, 2006). Twenty days after sowing, the seedlings were transferred into the pots, and 15 days afterwards, they were thinned out, leaving four plants per pot. During the experiment, pots were irrigated daily with distilled water to maintain soils at approximately 80% of water retention capacity.

The experiment was conducted in randomized blocks design factorial 2 x 4 x 4. The treatments consisted of two soil conditions (contaminated and non-contaminated), four vegetable species (lettuce, kale, carrot and okra) and four parts plant (root, stem, leaf and edible parts), with four replications. The plants were separated into roots, stems, leaves and edible parts, and washed thoroughly in tap water and then in distilled water, to remove traces of nutrients and Pb ions from the surface (*Liu et al.*, 2009). The collected parts were weighed, put in paper bags and stored in a greenhouse at 65-70°C until they reached constant weight. The dried samples were weighed once more and ground in a Wiley cutting mill, and then submitted to a nitro-perchloric digestion (*EMBRAPA*, 1999) to establish concentrations of Ca, Mg, Fe, Mn, Zn, Cu and Pb by atomic absorption spectrophotometry; P by colorimetry; and K by flame photometry. The data obtained for dry matter, Pb content, and concentrations of macro and micronutrients in the various parts of the species under study were submitted to variance analysis and the measurements compared using the Scott-Knot test at 5% probability.

### **3 Results and discussion**

Pb significantly altered the production of dry matter of leaves and edible parts of plants grown in contaminated soil, with no apparent effect on root dry matter of any of the vegetable species studied (Table 2). A 14.55% reduction was observed in the dry matter production of leaves in the case of lettuce only. Okra plants showed greater production of dry matter in fruits when grown in Pb-contaminated soil. Taking into account the strong absorptive capacity of Pb by iron oxides, clay minerals and organic matter (*Bosso and Enzweiler*, 2008), these results of reduced phytotoxic effects of Pb in the soil studied indicate that the overall high concentration in soil do not necessarily imply high toxicity of plants.

## Table 2

Pb concentrations in edible parts of vegetables grown in contaminated soil ranged between 1.03 and 26.19 mg kg<sup>-1</sup> of dry matter, in the following order: carrot > okra > kale and lettuce (Figure 1). The carrot samples, despite having 20.15% of matter in their edible part when cultivated in contaminated soil (Table 2), are the species with the greatest potential to transfer Pb from the soil into the food chain given the high amounts of this metal. The edible part of kale cultivated in contaminated soil presented the highest dry weight in relation to the other plant parts. However, due to the low concentration of Pb, it represented the lowest accumulation of the element among the crops, as it is the species which transferred the lowest quantity of Pb from the soil to the plant (Figure 1). Kale concentrated only 1.03 mg kg<sup>-1</sup> of Pb in its edible part, and, all the same due to the high quantity of dry matter produced (Table 2), it not featured significant amounts of Pb extracted from the soil.

The high concentration of Pb in the edible part of carrot can be above the tolerable limits by legislation (*Codex alimentarius*, 2009), which if consumed may cause damage to human health. It is interesting to note that, even though the Pb concentrations were higher than those permitted for agricultural soils according to Brazilian regulations (*CONAMA*, 2009), the lettuce, kale and okra plants contained acceptable amounts of Pb in their edible parts. This indicates that Pb transfer to these parts is highly dependent on species.

## Figure 1

Pb reduced the concentration of Ca in parts plants of lettuce (Table 3). The presence of Pb generates antagonism in terms of calcium absorption, inhibiting this function due to the blocking of cationic channels through competitive transport (*Sharma and Dubey*, 2005; *Liu et al.*, 2009). On the other hand, the presence of Pb in the soil prompted increased Ca concentrations in kale and carrot roots. For the other vegetable parts, no significant effect of Pb on the concentration of this element was found. Pb can affect the natural processes of absorption and translocation of nutrients in plants grown in contaminated soil (*Sinha et al.*, 2006; *Gopal and Rizvi*, 2008), possibly by altering the selectivity of the plasma membrane (*Sarma et al.*, 2006), and thereby contributing, in some cases, to raising the concentration of certain nutrients in plants.

Pb increased the concentration of Mg in lettuce stems, kale leaves and carrot root grown in the contaminated soil (Table 3). However, it did not affect Mg concentration in

lettuce, carrot and okra leaves. *Díaz-Aquilar et al.*, (2001) also reported that Pb did not affect Mg concentrations in wheat leaves grown in soil with high lead concentration.

### Table 3

Pb caused significant increases in P concentrations in kale and carrot roots, although the concentration of this element was lower in kale and okra leaves (Table 3). Some authors (*Gopal and Rizvi*, 2008) have observed that the presence of Pb provokes synergism in P absorption in radish plants, due to the direct interference of this metal in the metabolism of P in the plant.

K concentrations in vegetable parts in contaminated and non-contaminated soil were altered by Pb (Table 3). It was only in the edible parts of carrots that no effects of Pb on K concentrations were observed. Pb promoted reduction in K concentrations in lettuce roots, although the opposite behavior was observed in other vegetable parts. The increase in K concentrations in plants parts may be related to the loss of selectivity in cellular membranes (*Sarma et al.*, 2006) provoked by Pb, favoring the passive uptake of K.

K concentrations in plant parts grown in contaminated soil varied from 13.58 to 55.51 mg kg<sup>-1</sup> (lettuce); 22.60 to 50.91 mg kg<sup>-1</sup> (kale); 15.95 to 36.72 mg kg<sup>-1</sup> (carrot) and 33.23 to 44.29 (okra) (Table 3). K was found to concentrate mainly in the leaves of the plants, except in the case of okra. The okra plants grown in contaminated soil contained greatest K concentrations in their stems, corresponding to 1.41-fold the amount found in the fruit, reflecting low transfer of this element to edible plant parts.

Pb increased Fe concentrations in roots of lettuce, kale, carrot and okra plants. On the other hand, concentrations of this element were 18% lower in the leaves of lettuce cultivated in contaminated soil (Table 4). Cabbage plants grown in Pb-contaminated soil have shown reduced concentrations of Fe in leaves (*Sinha et al.*, 2006). The Fe reduction in leaves results in loss of vitality and capacity to resist to stressful conditions (*Gebeelen et al.*, 2002). The increase in Fe concentrations in roots was also noted by *Gopal and Rizvi* (2008), when evaluating alterations in radish plants submitted to Pb excess. The increase in Fe concentrations in roots may be due to its higher flow due to loss of membrane selectivity caused by lead (*Sharma and Dubey*, 2005).

A high concentration of Mn was recorded in the roots and stems of plants grown in contaminated soil (Table 4). In contrast with the low concentration of Mn in lettuce leaves caused by Pb, kale and okra leaves grown in contaminated soil displayed greater

concentrations of this metal. Generally speaking, Mn concentrated mainly in leaves of plants. The effect of Pb in raising Mn concentrations was also reported by *Díaz-Aguilar et al.*, (2001) when evaluating the absorption of Mn in wheat plants parts.

#### **Table 4**

Although Pb prompted an increase in Zn concentrations in lettuce roots grown in contaminated soil, a 28.50% reduction was noted in the concentration of Zn in leaves (Table 4). The low concentration of Zn in leaves is related to the reduction in the stability of the plasma membrane, thus making plants less tolerant to stress (*Gebbelen et al.*, 2002).

As was observed in the case of lettuce, greater concentrations of Zn were observed in kale, carrot and okra roots grown in contaminated soil. The lettuce, kale and carrot plants grown in contaminated soil were found to have highest Zn concentrations in roots, whereas in okra plants the highest concentrations were found in leaves.

Pb caused high Cu concentrations in roots of lettuce, carrot and okra, but favored reductions in Cu concentration in kale roots (Table 4). In general, an imbalance in Cu allocation promoted by Pb was verified in plant parts, as was also reported by *Sharma and Dubey*, (2005). It was also found that, both in contaminated and non-contaminated soils, the highest and lowest Cu concentrations in plant parts were observed in roots and stems, respectively.

Pb also prompted a significant increase in the concentration of Cu in carrot roots, leaves and edible parts (Table 4). The increase in Cu concentrations in the parts plant may be due to its greater flow, due to the loss of membrane selectivity caused by Pb in the soil (*Sharma and Dubey*, 2005).

#### **4 Conclusion**

1. Regarding Pb concentrations observed in edible parts of vegetables grown in contaminated soil, only carrots presented Pb concentration above the acceptable threshold for human consumption.
2. Among the vegetables evaluated, only the lettuce dry matter production was reduced due to the high concentration of Pb in soil.

3. Lead altered the concentration of micronutrients in the evaluated plant parts, stimulating higher Fe, Mn, Zn and Cu concentrations in kale, carrots and okra cultivated in contaminated soil.

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**Table 1:** Chemical and physical characteristics of the Pb-contaminated and non-contaminated soil samples used for growing the vegetables.

Characteristic	Soil	
	Contaminated	Non-contaminated
pH (water - 1:2,5)	3.89	5.1
P (mg dm <sup>-3</sup> )	2.30	8.30
Na <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.28	0.31
K <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.05	0.10
Ca <sup>+2</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	4,6	4,4
Mg <sup>+2</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.90	2.90
Al <sup>+3</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.50	0.15
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	3.30	2.80
Pb (mg kg <sup>-1</sup> )	413.0	9.20
M.O (g kg <sup>-1</sup> )	14.73	26.9
Sand (g kg <sup>-1</sup> )	943.0	940.0
Silt (g kg <sup>-1</sup> )	27.0	27.0
Clay (g kg <sup>-1</sup> )	30.0	33.0

**Table 2:** Dry matter production ( $\text{g}^{-1}$  per pot) for vegetables grown in Pb-contaminated and non-contaminated soils.

Part	Soil	Lettuce		Kale		Carrot		Okra	
		C	NC	C	NC	C	NC	C	NC
Root		0.43Ac	1.01Ac	2.71Ac	2.02Ac	0.75Ac	0.54Ac	1.45Ac	1.55Ac
Stem		2.18Ab	3.70Ab	4.56Ab	4.54Ab	NA	NA	2.98Ab	4.11Ab
Leaf		9.45Ba	11.06Aa	14.28Aa	13.28Ba	14.82Aa	13.08Ba	6.67Aa	7.54Aa
Edible part		9.45Ba	11.06Aa	14.28Aa	13.28Ba	3.93Ab	2.51Ab	6.54Aa	3.86Bb
Total		12.07B	15.77A	22.25A	19.84B	19.51A	16.14B	17.64A	17.06A

C= contaminated soil; NC = non-contaminated soil; NA = non-applicable.

Means followed by the same letters are not significantly different by the Scott & Knott test at 5% probability. Capital letters compares plant parts, between a contaminated and a non-contaminated soil; small letters compares each plant part for each soil condition.

**Table 3:** Ca, Mg, P and K concentration in lettuce, kale, carrot and okra, grown in Pb-contaminated and non-contaminated soil.

Crop	Lettuce		Kale		Carrot		Okra		
	Soil	C	NC	C	NC	C	NC	C	NC
Ca (g kg <sup>-1</sup> )									
Root		9.09Bb	12.66Ab	13.55Ab	3.97Bb	15.41Aa	12.29Bb	13.27Ab	13.28Ab
Stem		5.80Bc	14.06Ab	3.74Ac	3.51Ab	NA	NA	14.29Ab	14.39Ab
Leaf		14.72Ba	18.77Aa	17.88Aa	17.31Aa	16.19Aa	16.40Aa	40.39Aa	42.02Aa
Edible plant		14.72Ba	18.77Aa	17.88Aa	17.31Aa	3.92Ab	3.75Ac	4.42Ac	4.46Ac
*CV (%)		12.03							
Mg (g kg <sup>-1</sup> )									
Root		33.52 Ab	35.92Ab	16.94Ab	15.96Ab	52.39Aa	39.70Ba	34.62Ac	34.93Ac
Stem		38.69Aa	17.89Bc	15.87Ab	15.80Ab	NA	NA	39.01Ab	38.50Ab
Leaf		41.27Aa	42.08Aa	39.10Aa	35.27Ba	34.35Ab	31.95Ab	53.48Aa	54.56Aa
Edible plant		41.27Aa	42.08Aa	39.10Aa	35.27Ba	18.48Bc	26.78Ac	29.10Ac	30.74Ad
*CV (%)		7.76							
P (g kg <sup>-1</sup> )									
Root		15.25Aa	13.83Aa	13.22Aa	8.36Bb	12.08Aa	9.54Ba	8.80Aa	9.21Aa
Stem		8.93Ab	8.33Ab	6.13Ac	6.40Ac	NA	NA	5.94Ab	6.06Ab
Leaf		7.63Ab	8.23Ab	11.60Bb	15.40Aa	7.52Ab	7.48Ab	8.25Ba	9.99Aa
Edible plant		7.63Ab	8.23Ab	11.60Bb	15.40Aa	6.73Ab	6.97Ab	6.28Ab	6.33Ab
*CV (%)		10.92							
K (g kg <sup>-1</sup> )									
Root		13.58Bc	22.10Ac	22.60Ab	17.80Bb	15.95Ac	6.90Bb	35.71Ab	28.91Ba
Stem		35.01Ab	30.72Bb	50.91Aa	31.13Ba	NA	NA	44.29Aa	29.05Ba
Leaf		55.51Aa	46.58Ba	50.19Aa	30.76Ba	36.72Aa	30.86Ba	33.23Ac	27.32Ba
Edible plant		55.51Aa	46.58Ba	50.19Aa	30.79Ba	28.00Ab	27.71Aa	31.37Ac	27.32Ba
*CV (%)		7.44							

C= contaminated soil; NC = non-contaminated soil; NA = non-applicable.

\*CV = Coefficient of Variation.

Means followed by the same letters are not significantly different by the Scott & Knott test at 5% probability. Capital letters in the line compare the same crop and the same plant part; small letters in the column compares parts of same crop for each soil condition.

**Table 4:** Concentration of Fe, Mn, Zn and Cu in lettuce, kale, carrot and okra grown in Pb-contaminated and non-contaminated soil.

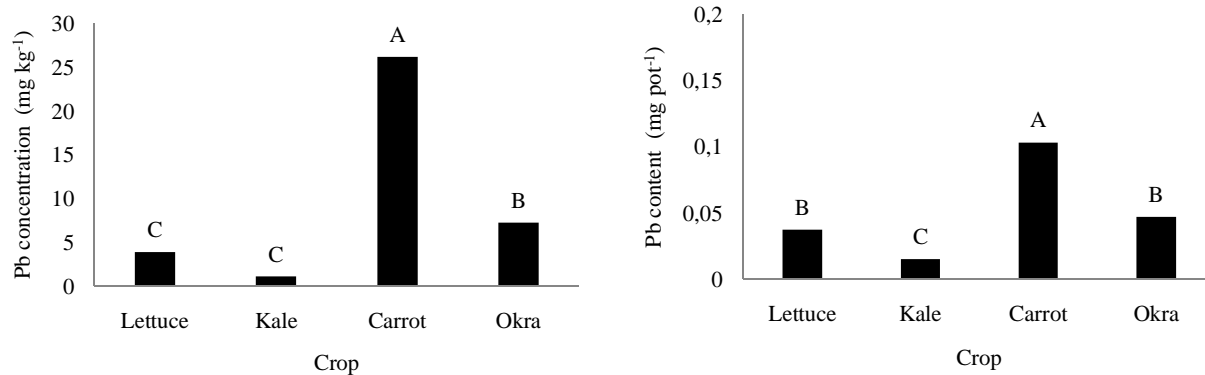
Crop	Lettuce		Kale		Carrot		Okra			
	Soil	C	NC	C	NC	C	NC	C	NC	
Fe (mg kg <sup>-1</sup> )										
Root		233.15Aa	189.60Ba	244.57Aa	149.93Ba	268.92Aa	149.31Ba	235.57Aa	133.70Ba	
Stem		43.11Ac	52.57Ac	21.01Ac	27.05Ac	NA	NA	26.20Ac	25.52Ad	
Leaf		136.41Bb	167.06Ab	83.89Ab	85.02Ab	71.51Ab	76.90Bb	74.88Ab	85.92Ab	
Edible part		136.41Bb	167.06Ab	83.89Ab	85.02Ab	48.51Ac	51.89Ac	36.34Ac	47.16Ac	
*CV (%)		10,05								
Mn (mg kg <sup>-1</sup> )										
Root		77.23Ab	35.89Bb	144.45Aa	16.28Bb	525.19Aa	128.98Ba	103.57Ab	40.46Bb	
Stem		30.73Ac	14.61Bc	13.95Ab	4.64Bc	NA	NA	39.90Ac	18.52Bc	
Leaf		126.49Ba	270.04Aa	142.12Aa	78.28Ba	182.51Ab	133.31Aa	260.83Aa	159.24Ba	
Edible part		126.49Ba	270.04Aa	142.12Aa	78.28Ba	42.38Ac	18.10Bb	40.88Ac	24.09Bc	
*CV (%)		7.16								
Zn (mg kg <sup>-1</sup> )										
Root		392.82Aa	188.92Bb	612.54Aa	227.17Bb	909.97Aa	253.03Ba	395.91Ab	255.01Ba	
Stem		236.81Ab	293.26Aa	263.36Ab	154.54Bc	NA	NA	226.44Ac	101.72Bc	
Leaf		227.70Bb	318.36Aa	617.88Aa	325.97Ba	178.73Ab	179.17Ab	486.81Aa	178.26Bb	
Edible part		227.70Bb	318.36Aa	617.88Aa	325.97Ba	171.16Ab	143.17Ab	164.08Ad	180.26Ab	
*CV (%)		14,12								
Cu (mg kg <sup>-1</sup> )										
Root		48.27Aa	22.54Ba	34.36Ba	38.30Aa	35.33Aa	18.59Ba	19.36Aa	7.71Ba	
Stem		9.96Ac	10.80Ac	14.49Ac	14.49Ab	NA	NA	5.89Ac	2.39Bb	
Leaf		13.48Ab	12.98Ab	19.27Ab	14.49Bb	8.88Ab	4.14Bb	8.63Ab	3.64Bb	
Edible part		13.48Ab	12.98Ab	19.27Ab	14.49Bb	8.13Ab	4.39Bb	6.14Ac	1.89Bb	
*CV (%)		9,60								

C= contaminated soil; NC = non contaminated soil; NA = non-applicable.

\*CV = Coefficient of Variation.

Means followed by the same letters are not significantly different by the Scott & Knott test at 5% probability.

Capital letters compare each plant part between a contaminated and a non-contaminated soil; and small letters compare each plant part for each soil condition.



**Figure 1:** Pb concentration (mg kg<sup>-1</sup>) and content (mg pot<sup>-1</sup>) in edible plant parts grown in contaminated soil. Means followed by the same letters are not significantly different by the Scott & Knott test at 5% probability.

**CAPÍTULO III:**

**BIOCONCENTRAÇÃO DE CHUMBO E MICRONUTRIENTES EM  
HORTALIÇAS CULTIVADAS EM SOLO CONTAMINADO <sup>(1)</sup>**

**(Revista Brasileira de Ciência do Solo)**

# BIOCONCENTRAÇÃO DE CHUMBO E MICRONUTRIENTES EM HORTALIÇAS CULTIVADAS EM SOLO CONTAMINADO <sup>(1)</sup>

Francisco de Sousa Lima<sup>(2)</sup>, Clístenes Williams Araújo do Nascimento<sup>(3)</sup> & Adriana  
Maria de Aguiar Accioly<sup>(4)</sup>

## RESUMO

A crescente poluição ambiental nas últimas décadas vem tornando os metais pesados uma ameaça constante aos seres vivos. Entre estes, o Pb é um dos mais importantes, tendo em vista a quantidade de áreas contaminadas e seus efeitos deletérios sobre a saúde humana. O objetivo deste estudo foi avaliar a produção de biomassa e absorção de micronutrientes por plantas olerícolas em um Espodossolo contaminado por chumbo. Adicionalmente, a distribuição de Pb entre as frações do solo e a relação dessas frações com a disponibilidade do Pb para hortaliças foi também estudado.

O experimento foi conduzido em blocos casualizados no esquema fatorial 5x3x4. Os tratamentos foram constituídos por 5 doses de Pb (0,0; 20; 50; 72 e 180 mg kg<sup>-1</sup> de solo), 3 espécies vegetais (quiabo, cenoura e couve-manteiga) e 4 partes das plantas (raiz, caule, folha e partes comestíveis). Esta última dose é equivalente ao Valor de Investigação para solos agrícolas (CONAMA, 2009). De acordo com os resultados, o Pb promoveu redução da matéria seca nas plantas de cenoura e quiabeiro, enquanto não influenciou a produção de biomassa da couve manteiga. O Pb afetou a concentração de micronutrientes nos órgãos das hortaliças, sendo observado na cenoura redução no teor de ferro enquanto na couve manteiga houve aumento do teor de Zn nas raízes. O Pb apresentou-se preferencialmente adsorvido à fração matéria orgânica. Plantas cultivadas em solo contaminado com a dose de investigação estabelecida pelo CONAMA, além de apresentarem desbalanço nutricional, podem tornar-se inadequadas ao consumo humano, devido ao elevado teor deste metal nas partes comestíveis.

Termos para indexação: Poluição de solo, contaminação de solo, metais pesados.

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<sup>2</sup> Doutorando do Programa de Pós-Graduação em Ciência do Solo do Departamento de Agronomia - UFRPE. R. Dom Manoel de Medeiros, s/n - Dois Irmãos, CEP 52171-900, Recife (PE). Bolsista da CAPES. e-mail: fsousalima@yahoo.com.br

<sup>3</sup> Professor Adjunto do Departamento de Agronomia da UFRPE, Área solos. R. Dom Manoel de Medeiros, s/n - Dois Irmãos, CEP 52171-900, Recife - PE. e-mail: clistenes@depa.ufrpe.br. Pesquisador do CNPq.

## **BIOCONCENTRATION OF LEAD AND MICRONUTRIENTS IN HORTICULTURAL CROPS GROWN ON A CONTAMINATED SOIL**

**SUMMARY:** The growing heavy metal environmental pollution poses a serious threat to human health. Lead is one of the main toxic metals regarding the abundance of contaminated areas and the deleterious effects on human health. The work was carried out to evaluate Pb effects on biomass and micronutrients uptake by horticultural crops as well as Pb distribution among soil fractions and Pb availability to plants. The treatments consisted of five doses of Pb (0.0; 20; 50; 72 and 180 mg kg<sup>-1</sup>), three species (carrots, kale and okra) and four parts plants (root, stem, leaf and edible parts), with four replications. The highest rate represents the Investigation Value for Pb in soil according to Brazilian Guidelines for contaminated soils (CONAMA, 2009). The results showed that Pb caused reduction on biomass yield for carrot and okra while kale had not influence of Pb on biomass. Pb affected the micronutrient concentration in plants parts. For instance, it was observed a decreasing Fe concentration in carrot whereas the Zn concentration in kale roots was increased. Lead in soil was mainly bound to organic matter fraction. Horticultural plants cultivated on soil contaminated presented not only nutritional disorders but also high levels of Pb in edible parts. This makes these crops inadequate to human consumption.

Index terms: Soil pollution, soil contamination, heavy metals.

### **INTRODUÇÃO**

Os metais pesados estão presentes nos solos como componentes naturais ou como resultado das atividades antropogênicas (Intawongse & Dean, 2006; Ruiz et al., 2009). O repetido uso de insumos em atividades agrícolas tais como fertilizantes, corretivos e lodo de esgoto têm, em alguns casos, elevado o teor de metais pesados no solo (Li et al., 2007; Melo et al., 2008). O crescimento urbano e industrial também tem causado contaminação ambiental (Gopal & Rizvi, 2008) e dentre as atividades que mais contribuem para a poluição do solo estão a indústria metalúrgica e a mineração (Gupta & Sinha, 2006).



O Pb tem destaque entre os metais pesados devido a sua ampla utilização e persistência no solo, sendo considerado um dos poluentes mais importantes (Chirenje et al., 2004; Cecchi et al., 2008). Este elemento, quando incorporado ao solo, pode afetar a cadeia alimentar, constituindo importante ameaça em virtude de sua alta toxicidade para seres humanos (Wang et al., 2006; Kede et al., 2008; Torri & Lavado, 2009).

As plantas restringem a translocação Pb à parte aérea, acumulando-o preferencialmente nas raízes, devido a proteção efetuada pela endoderme (Verma & Dubey, 2003). A retenção de Pb na raiz pode, também, ser atribuída a ligação do elemento às cargas negativas da parede celular presentes neste órgão da planta (Liu et al., 2009). Embora o vegetal restrinja o transporte do Pb à parte aérea, o elemento acumula-se nas diversas partes das plantas e sua fitotoxicidade pode afetar a atividade de enzimas e promover alterações hormonais (Sharma & Dubey, 2005; Teklic et al., 2008). O Pb também pode proporcionar inibição da fotossíntese, alterações na estrutura e permeabilidade da membrana celular e distúrbios na nutrição mineral das plantas (Nascimento et al., 1998; Sarma et al., 2006).

É pertinente ressaltar, contudo, que o elevado teor de Pb no solo não reflete o potencial de transferência desse elemento à cadeia alimentar, tendo em vista sua forte capacidade adsorptiva, principalmente a óxidos de Fe e argilominerías, o que ocasiona baixa mobilidade no solo (Chen et al., 2007; Bosso & Enzweiler, 2008). O teor total de Pb tem sido usado para avaliar o seu efeito na contaminação do solo (Chen et al., 2009). Entretanto, o teor total não indica os compartimentos do solo que o elemento se encontra nem a biodisponibilidade para organismos vivos (Gupta & Sinha, 2006; Ortiz & Alcañiz, 2006; Li et al., 2007), pois, dependendo da fração do solo, o Pb pode estar fortemente retido e não disponível em curto prazo (Lu et al., 2005; Bosso & Enzweiler, 2008).

O potencial de Pb biodisponível no solo tem sido avaliado através de extratores químicos, tais com EDTA e DTPA, ou através de fracionamento do solo (Gupta & Sinha, 2006; Li et al., 2007). O fracionamento é uma técnica de extração seletiva que define a proporção do metal associada a cada componente da fase sólida do solo e tem sido amplamente utilizada para avaliar a mobilidade de metais pesados (Peijnenburg & Páger, 2003; Guevara-Riba et al., 2004; Gupta & Sinha, 2006). O fracionamento permite prever o potencial do metal biodisponível, bem como o potencial de mobilidade, lixiviação e poluição dos solos (Pueyo et al., 2003; Gupta & Sinha, 2006;

Ishikawa et al., 2009). Nesta técnica, o solo é submetido a uma série de reagentes químicos de reatividade crescente, sendo que a fitodisponibilidade do Pb apresenta-se em ordem decrescente com relação às etapas da extração sequencial (Torri & Lavado, 2009). O teor de Pb disponível e adsorvido à fração trocável do solo indica alta mobilidade e biodisponibilidade imediata, enquanto as concentrações presentes nas frações matéria orgânica, óxidos de Mn e Fe amorfo e cristalino indicam que o metal está imobilizado, com menor risco de contaminação ambiental (Galindo et al., 2005; Lu et al., 2005; Andrade et al., 2007).

Neste contexto, o objetivo deste estudo foi: 1) avaliar o efeito do Pb sobre a produção de biomassa e a absorção de micronutrientes pelas plantas, 2) verificar se o teor de Pb no solo equivalente ao Valor de Investigação determinado pelo CONAMA (2009) para solos agrícolas é protetivo à saúde humana quanto ao teor de Pb em partes comestíveis; e, 3) avaliar a distribuição do Pb entre as frações de um Espodossolo, bem como a relação dessas frações com a disponibilidade do elemento para hortaliças.

## **MATERIAL E MÉTODOS**

O experimento foi desenvolvido em casa de vegetação, no período de janeiro a abril de 2009. Amostra de um ESPODOSSOLO DISTRÓFICO, textura arenosa, foi coletada na profundidade de 0 a 20 cm e, em seguida, seco ao ar, destorroado, homogeneizado e peneirado em malha de 2 mm. Após caracterização química e física (EMBRAPA, 1997; 1999) (Quadro 1), o solo foi incubado por 20 dias com carbonato de cálcio e dióxido de magnésio (3:1), visando elevar o pH para 6,5. Posteriormente, promoveu-se a incubação durante 30 dias com  $Pb(NO_3)_2$ , com concentrações ajustadas para 0,0; 20, 50; 72 e 180 mg de Pb por kg, sendo este último valor o nível de investigação indicado pela legislação brasileira (CONAMA, 2009) para solos agrícolas. Após a incubação, 6,0 kg de solo foram acondicionados em vasos plásticos, constituindo as unidades experimentais. Em cada vaso plástico, coletou-se amostra de solo para determinar o Pb disponível por EDTA e DTPA (Lindsay & Norvell, 1978; Lantmann & Meurer, 1982) e para o fracionamento do elemento.

O fracionamento de Pb nas amostras do solo foi efetuado pelo método de Shuman (1985), com exceção da fração óxido de ferro amorfo (Chao & Zhou, 1983), conforme descrito abaixo.

**Fração Trocável (Tr):** 5 g de TFSA e 20 ml de  $Mg(NO_3)_2$  1 mol L<sup>-1</sup> foram transferidos para tubo de centrífuga com capacidade para 50 mL. Após agitar por 2 horas, promoveu-se a centrifugação por 10 min e o extrato filtrado foi transferido para tubo de plástico. Adicionou-se 20 mL de água destilada ao tubo de centrífuga com a amostra de solo e ao agitar novamente por 3 min, centrifugar por 10 min e filtrar, os dois sobrenadantes foram combinados no mesmo frasco e, no extrato, foi realizada a análise do metal.

**Quadro 1.** Caracterização química e física do solo

<b>Característica</b>	<b>Valor</b>
pH (água – 1:2,5)	5,1
P (mg dm <sup>-3</sup> )	8,30
Na <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0,31
K <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0,10
Ca <sup>+2</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	4,40
Mg <sup>+2</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	2,90
Al <sup>+3</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0,15
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	2,80
Pb (mg kg <sup>-1</sup> )	16,50
C.O (g kg <sup>-1</sup> )	15,63
M.O (g kg <sup>-1</sup> )	27,0
Areia (g kg <sup>-1</sup> )	940,0
Silte (g kg <sup>-1</sup> )	27,0
Argila (g kg <sup>-1</sup> )	33,0

**Fração Matéria Orgânica (MO):** adicionou-se 10 mL de NaClO (hipoclorito de sódio) 5-6 dag L<sup>-1</sup>, com pH ajustado para 8,5, ao tubo de centrífuga contendo amostra de solo utilizada na etapa anterior, e promoveu-se o aquecendo em banho-maria a 100°C, durante 30 min, agitando ocasionalmente. Após o banho-maria, a amostra foi centrifugada por 10 min e o sobrenadante filtrado foi transferido para tubo plástico. Esse procedimento foi repetido por mais duas vezes e os três filtrados foram combinados em um único frasco. Após concluído o procedimento acima, efetuou-se a adição de 10 mL de água destilada à amostra de solo contida no tubo de centrífuga, e após agitar, centrifugar e filtrar, o extrato foi adicionado ao obtido das extrações anteriores.

**Fração Óxido de ferro amorfo (OxFeA):** 30 mL da solução composta por hidroxilamina cloridrato (NH<sub>2</sub>OH.HCl 0,25 mol L<sup>-1</sup> + HCl 0.25 mol L<sup>-1</sup>) com pH corrigido para 3,0 foram adicionados à amostra de solo no tubo de centrífuga, seguindo-se de agitação por 30 min a 180 rpm. A amostra foi centrifugada por 10 min a 1600

rpm, filtrada e transferida para frasco plástico. Adicionou-se 10 mL de água destilada à amostra contida no tubo de centrífuga e, após agitar por 3 min, centrifugar por 10 min e filtrar, o sobrenadante foi adicionado ao extrato obtido para leitura do chumbo.

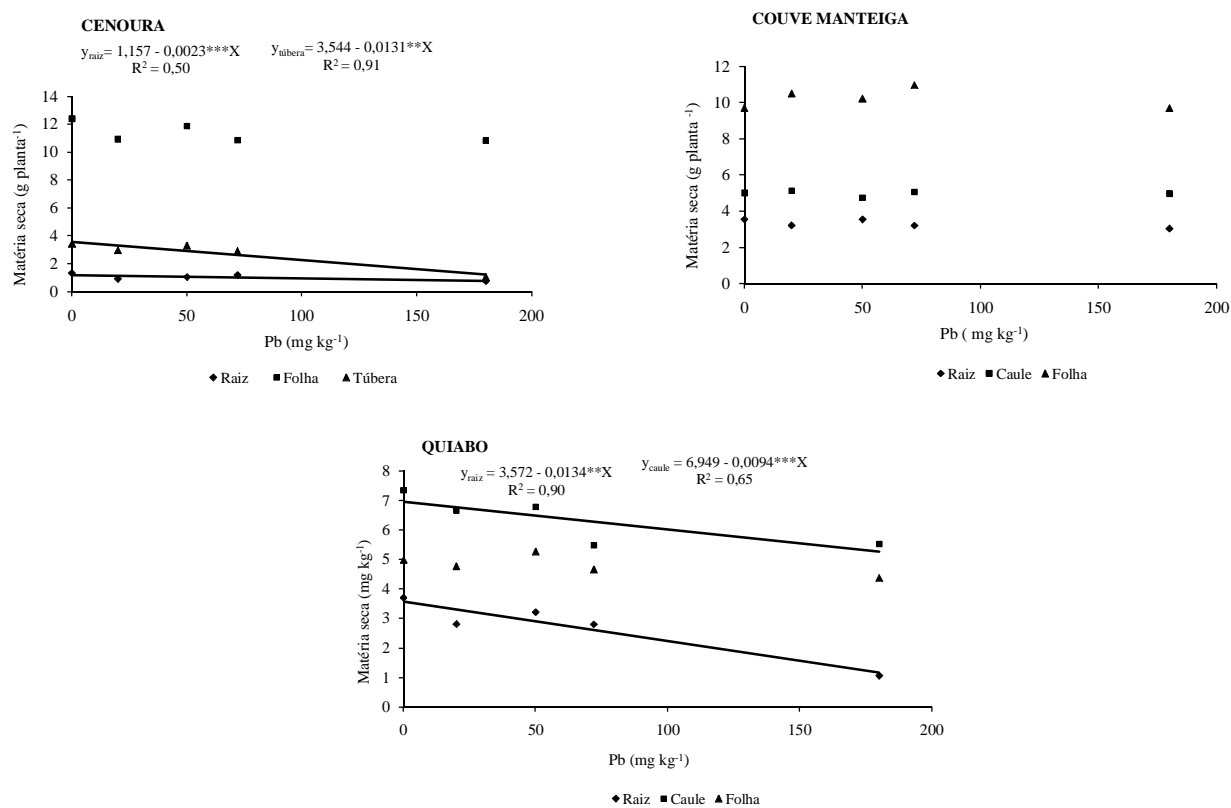
**Fração Óxido de ferro cristalino (OxFeC):** 30 mL da solução composta pela mistura de oxalato de amônio ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ )  $0,2 \text{ mol L}^{-1}$  + ácido oxálico ( $\text{H}_2\text{C}_2\text{O}_4$ )  $0,2 \text{ mol L}^{-1}$  + ácido ascórbico  $0,01 \text{ mol L}^{-1}$  e pH ajustado para 3,0 foram colocados em contato com a amostra de solo no tubo de centrífuga de 50 mL e aquecido por 30 minutos a  $100^\circ\text{C}$  em banho-maria. Em seguida, a amostra foi submetida à centrifugação por 10 min, sendo filtrada e o sobrenadante transferido para frasco plástico.

Para instalação do experimento, as mudas de cenoura (*Daucos carota*), couve manteiga (*Brassica oleracea* var. *acephala*) e quiabo (*Abelmoschus esculentus*), previamente produzidas em bandejas de isopor, foram transplantadas para vasos com solo previamente adubado (Nascimento et al., 2006), sendo utilizadas 04 mudas/vaso. Estas espécies foram escolhidas por representarem diferentes partes comestíveis (tubérculo, folha e fruto). Durante o ensaio, a umidade do solo foi mantida a 80% da capacidade máxima de retenção de água. Ao final do ciclo, raízes e parte aérea foram coletadas separadamente, lavadas em água de torneira e em seguida em água destilada. Após lavadas, as partes aérea e radicular foram, individualmente, acondicionadas em sacos de papel devidamente identificados e colocados em estufa com ventilação forçada, à temperatura entre  $65\text{-}70^\circ\text{C}$ , até atingirem peso constante. As amostras secas foram pesadas e trituradas em moinho tipo Wiley e em seguida submetidas à digestão nitroperclórica (EMBRAPA, 1999), sendo os teores de Pb, Fe, Zn, Mn e Ni quantificados por ICP-OES (Perkin Elmer Optima 7000 DV).

O experimento foi conduzido no delineamento experimental blocos casualizados em esquema fatorial  $5 \times 3 \times 4$ . Os tratamentos consistiram de 5 doses de Pb (0; 20; 50; 72 e  $180 \text{ mg kg}^{-1}$  de solo), 3 espécies de olerícolas (cenoura, couve manteiga e quiabo) e 4 partes da planta (raiz, caule, folha e parte comestível), com 4 repetições. Os dados obtidos foram submetidos à análise de variância (ANOVA) e a comparação de médias, análise de regressão e correlações foram realizadas através do SAS (2000).

## RESULTADOS E DISCUSSÃO

O Pb promoveu redução significativa na produção de matéria seca das raízes e partes comestíveis da cenoura (Figura 1). A redução da matéria seca pode ser atribuída à redução da respiração, alterações na fotossíntese e no metabolismo do nitrogênio causados pelo excesso de Pb na planta (Gopal & Rizvi, 2008; Merwe et al.,2009).



**Figura 1.** Produção de matéria seca (g vaso<sup>-1</sup>) nas partes de cenoura, couve manteiga e quiabo, em resposta às doses crescentes de Pb aplicado no solo

No quiabeiro, a produção de matéria seca das raízes e caule foi afetada, enquanto na couve manteiga não houve efeito negativo do Pb sobre a produção de biomassa em nenhum dos órgãos da planta. Isto demonstra que a couve manteiga é menos sensível aos efeitos adversos do Pb, o que corrobora que este metal afeta os vegetais de forma

diferenciada (Hussain et al., 2006). Estes resultados demonstraram ainda que, embora o Pb seja um metal fitotóxico, algumas espécies vegetais se desenvolvem em solos contaminados por este elemento sem apresentar redução no rendimento da matéria seca (Hong et al., 2008). O reduzido efeito da fitotoxidez do Pb pode ainda ser atribuído ao baixo teor disponível do metal, tendo em vista sua forte capacidade adsortiva com os componentes do solo (Bosso & Enzweiler, 2008). Portanto, alto teor de Pb no solo não está, necessariamente, relacionado com elevada toxidez aos vegetais.

Houve aumento significativo da concentração do Pb nas raízes das plantas avaliadas (Quadro 2), corroborando os resultados de Sinha et al. (2006) em plantas de repolho cultivadas sob altas doses de chumbo. A retenção de Pb nas raízes ocorre devido a formação de precipitados de carbonato de Pb ou através da ligação do elemento às cargas negativas presentes na parede celular (Sharma & Dubey, 2005). Contudo, com relação as plantas de cenoura e quiabeiro, o aumento do teor de Pb nas raízes pode ser atribuído à menor produção de matéria seca neste órgão, devido o aumento das doses do metal aplicado no solo (Figura 1).

**Quadro 2.** Equações de regressão para os teores de Pb nas partes das plantas de cenoura, couve manteiga e quiabo em resposta às doses crescentes do metal aplicadas no solo

Parte da planta	Equação de regressão	R <sup>2</sup>
<b>Cenoura</b>		
Raiz	$Y = 0,159 + 3,377^{***} X$	0,99
Folha	$Y = 7,593$	-
Túbera	$Y = 13,552 + 0,285^{**} X$	0,84
<b>Couve manteiga</b>		
Raiz	$Y = 0,571 + 0,925^{***} X$	0,99
Caule	$Y = 9,823 + 0,117^{**} X$	0,62
Folha	$Y = 10,518 + 0,070^{*} X$	0,74
<b>Quiabo</b>		
Raiz	$Y = 9,122 + 1,014^{***} X$	0,96
Caule	$Y = 13,006 + 0,358^{***} X$	0,89
Folha	$Y = 5,506 + 0,412^{*} X - 0,002^{*} X^2$	0,68

\* \*\* ° \*\*\* significativos a 5,1, e 0,1% respectivamente

O aumento do teor de Pb nas partes comestíveis da cenoura e couve manteiga, decorrente da aplicação de doses crescentes de Pb no solo, indica que esses vegetais podem absorver e concentrar elevados teores deste metal nestes órgãos. Contudo, com relação a parte comestível da cenoura, este aumento na concentração de Pb pode ser

atribuído à menor produção de biomassa neste órgão quando as plantas foram cultivadas no solo com 180 mg de Pb por kg de solo (Figura 1).

Constatou-se ainda que, quando as plantas foram cultivadas no solo contaminado com 180 mg kg<sup>-1</sup>, os teores deste metal na parte comestível da cenoura e couve manteiga (5,18 e 1,28 mg kg<sup>-1</sup> de peso fresco, respectivamente), superaram os limites considerados toleráveis pelo Codex Alimentarius (2009). Este nível de contaminação é considerado o limite de investigação para áreas agrícolas pelo Conama (2009) e, neste sentido, o solo não deve ser cultivado para a produção de alimentos, tendo em vista que o Pb poderá ser transferido às partes comestíveis dos vegetais, constituindo risco à população.

Nas folhas de quiabeiro, o teor de Pb apresentou comportamento quadrático, de modo que a partir da dose 103 mg de Pb por kg de solo, o metal possivelmente promoveu efeito fitotóxico e a planta restringiu o seu transporte para este órgão, ficando possivelmente retido pelas cargas negativas presentes nas paredes das células da raiz (Liu et al., 2009).

O Pb afetou significativamente a concentração de micronutrientes nos órgãos das hortaliças. Nas raízes da cenoura, observou-se redução no teor de Fe, enquanto as concentrações de Ni e Zn apresentam comportamento quadrático (Quadro 3). Nas folhas, verificou-se que os teores de Fe, Mn e Zn reduziram de forma linear, embora o teor de Ni não tenha sido afetado pelo Pb adicionado ao solo. Redução nos teores de Fe e Mn decorrente de doses crescentes de Pb também foi observada nas raízes e folhas de repolho (Sinha et al., 2006), possivelmente devido ao bloqueio da entrada destes elementos na planta (Sharma & Dubey, 2005). O Pb proporcionou aumento linear significativo nas concentrações de Ni e Zn nas túberas de cenoura. No entanto, o teor de Fe apresentou comportamento quadrático, enquanto a concentração de Mn não foi significativamente afetada pelo chumbo. O Pb pode alterar a seletividade da membrana plasmática nas células das raízes, afetando a absorção, o transporte e a alocação dos nutrientes nas partes das plantas, resultando no desbalanço nutricional (Sharma & Dubey, 2005).

Na couve manteiga, o Pb promoveu redução das concentrações de Fe, Mn e Ni nas folhas, embora tenha proporcionado aumento do teor de Zn neste órgão. Na raiz, o Pb não afetou os teores de Ni e Zn, contudo, proporcionou aumento na concentração de Fe, corroborando Gopal & Rizvi (2008) que também verificaram aumento na

concentração de Fe nas raízes das plantas de rabanete cultivadas sob doses crescentes de chumbo. Nas raízes de quiabeiro, o Pb promoveu redução do teor de Fe, não afetou a concentração de Mn, enquanto que os teores de Ni e Zn apresentaram comportamento quadrático. A redução do Fe nas raízes das plantas do quiabeiro pode ser devido ao bloqueio promovido pelo Pb limitando a entrada de cátions no sistema radicular das plantas (Sharma & Dubey, 2005). No caule, observou-se que o Pb reduziu o teor de Zn, entretanto não alterou as concentrações dos demais micronutrientes. O teor de Ni nas folhas de quiabeiro não foi afetado pelo Pb, embora tenha sido observada redução das concentrações de Fe, Mn e Zn neste órgão da planta.



**Quadro 3.** Equações de regressão para os teores de micronutrientes nas partes das plantas de cenoura, couve manteiga e quiabo em resposta às doses crescentes de Pb aplicado no solo

Nutriente	Parte da planta	Equação de regressão	R <sup>2</sup>
<b>Cenoura</b>			
Fe	Raiz	$Y = 165,889 - 0,1816^*X$	0,77
	Folha	$Y = 183,901 - 0,343^{***}X$	0,73
	Túbera	$Y = 123,985 + 6,193^{***}X - 0,025^{***}X^2$	0,86
Mn	Raiz	$Y = 645,229$	-
	Folha	$Y = 429,979 - 1,354^{***}X$	0,67
	Túbera	$Y = 126,293$	-
Ni	Raiz	$Y = 21,076 + 0,171^{***}X - 0,008^{***}X^2$	0,84
	Folha	$Y = 48,982$	-
	Túbera	$Y = 52,001 + 0,076^{***}X$	0,61
Zn	Raiz	$Y = 133,219 + 0,898^*X - 0,004^*X$	0,95
	Folha	$Y = 92,124 - 0,204^*X$	0,64
	Túbera	$Y = 103,755 + 0,172^*X$	0,59
<b>Couve manteiga</b>			
Fe	Raiz	$Y = 118,483 + 0,310^{**}X$	0,55
	Caule	$Y = 144,240$	-
	Folha	$Y = 207,768 - 0,539^{***}X$	0,62
Mn	Raiz	$Y = 141,605 + 1,187^*X - 0,006^*X$	0,81
	Caule	$Y = 61,212$	-
	Folha	$Y = 248,005 - 0,547^{***}X$	0,72
Ni	Raiz	$Y = 8,183$	-
	Caule	$Y = 49,005 + 0,003^*X - 0,001X^2$	0,55
	Folha	$Y = 48,955 - 0,001^*X$	0,91
Zn	Raiz	$Y = 81,099$	-
	Caule	$Y = 116,372$	-
	Folha	$Y = 138,223 + 0,358^{***}X$	0,83
<b>Quiabo</b>			
Fe	Raiz	$Y = 182,190 - 0,557^{***}X$	0,60
	Caule	$Y = 137,413$	-
	Folha	$Y = 182,012 - 0,440^{***}X$	0,67
Mn	Raiz	$Y = 120,451$	-
	Caule	$Y = 157,58$	-
	Folha	$Y = 603,913 - 2,964^{***}X$	0,73
Ni	Raiz	$Y = 10,814 + 0,242^{***}X - 0,001^{***}X^2$	0,80
	Caule	$Y = 49,283$	-
	Folha	$Y = 48,965$	-
Zn	Raiz	$Y = 68,544 + 0,662^{***}X - 0,004^{***}X^2$	0,57
	Caule	$Y = 131,568 - 0,172^{***}X$	0,62
	Folha	$Y = 101,046 - 0,298^{***}X$	0,65

\* \*\* ° \*\*\* significativos a 5,1, e 0,1% respectivamente

Estes resultados observados nas três espécies avaliadas, em relação ao teor dos elementos constatados nos órgãos das plantas, indicam que houve um desbalanço

nutricional nestas plantas, o que segundo Paivoke (2002) pode ser considerado um dos principais impactos do excesso de Pb sobre os vegetais.

As concentrações de Pb disponível, determinadas através dos extratores EDTA e DTPA, apresentaram correlação positiva e significativa com os teores do elemento na fração trocável e matéria orgânica (Quadro 4), indicando que o teor do metal determinado nestas frações do solo, também apresenta-se potencialmente biodisponível às plantas (Li et al., 2007).

**Quadro 4.** Coeficientes de correlação linear simples de Pearson entre os teores de Pb ( $\text{mg kg}^{-1}$ ) obtidos nas frações do solo: trocável (Tr), matéria orgânica (MO), óxido de ferro amorfo (OxFeA) e óxido de ferro cristalino (OxFeC) e Pb disponível extraído por EDTA e DTPA e os teores de Pb ( $\text{mg kg}^{-1}$ ) na raiz (R), parte aérea (PA) e parte comestível (PC) das hortaliças cultivadas em solo contaminado por chumbo

	Tr	MO	OxFeA	OxFeC	DTPA	EDTA
<b>EDTA</b>	0,69***	0,67***	ns	ns	-	-
<b>DTPA</b>	0,72***	0,73**	ns	ns	-	-
<b>R</b>	0,76***	0,64**	0,55**	0,49*	0,59**	0,48**
<b>PA</b>	0,61**	0,49*	0,45*	ns	0,57*	ns
<b>PC</b>	0,54*	0,51**	ns	ns	ns	ns

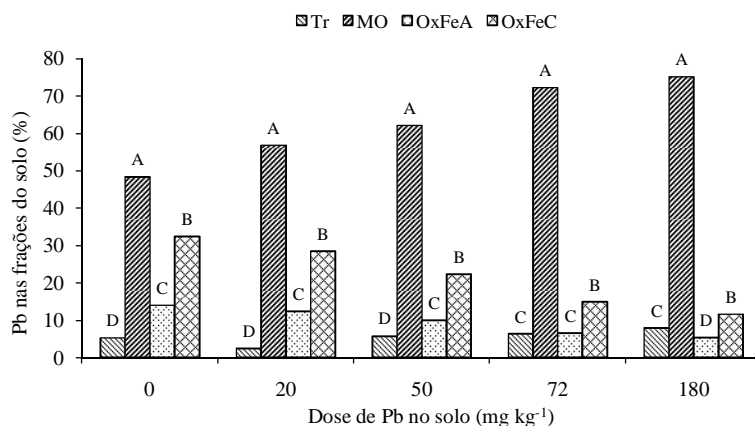
\*, \*\*, \*\*\* significativos a 5, 1 e 0,1%, respectivamente; ns = não significativo

Os maiores coeficientes de correlação observados entre os teores de Pb nas partes da planta e na fração trocável do solo, comparativamente à matéria orgânica, sugerem que o teor de Pb determinado nesta fração, devido estar adsorvido mais fracamente, é um bom indicativo do metal potencialmente disponível às plantas (Intawongse & Dean, 2006; Li et al., 2007).

O Pb retido nas frações óxido de ferro amorfo e cristalino, apresentou menores coeficientes de correlação com o teor de Pb nos órgãos das plantas, comparativamente às demais frações avaliadas, demonstrando que o metal adsorvido nestas frações do solo não está potencialmente disponível aos vegetais. A forte retenção do Pb nos óxidos de ferro, decorrente das intensas ligações químicas, faz com que este metal apresente-se pouco móvel no ambiente e, conseqüentemente, pouco disponível às plantas (Chen et al., 2007; Bosso & Enzweiler, 2008).

A distribuição do Pb nas frações do solo apresentou variações significativas (Figura 2). Observou-se predominância do Pb ligado à matéria orgânica, seguido da

fração óxido de ferro cristalino. A adição do Pb ao solo não aumentou a concentração do elemento na fração trocável, possivelmente em decorrência do baixo teor de argila (Quadro 1). A predominância do Pb adsorvido à fração matéria orgânica, pode estar associada a relativamente alta percentagem desta fração no solo (Quadro 1) ou decorre, ainda, da afinidade do metal por este compartimento do solo (Wang et al., 2004; Linhares et al., 2009). Esta distribuição de Pb corrobora os resultados observados por outros autores (Borges & Coutinho, 2004; Costa et al., 2007) ao promoverem o fracionamento seqüencial do Pb em solos.



**Figura 2.** Distribuição percentual de Pb (mg kg<sup>-1</sup>) nas frações do solo trocável (Tr), matéria orgânica (MO), óxido de ferro amorfo (OxFeA) e óxido de ferro cristalino (OxFeC) em função da aplicação de doses crescentes de Pb. Médias seguidas pela mesma letra maiúscula nas colunas, por dose de Pb, não diferem significativamente entre si pelo teste de Tukey, P < 0,05).

Embora o Pb tenha alta afinidade pelos óxidos de Fe (Bosso & Enzweiler, 2008; Silva & Vitti, 2008), a reduzida porcentagem do metal associada às frações óxido de Fe amorfo e cristalino, comparativamente à matéria orgânica, pode ser decorrente do baixo teor de argila presente no solo (Quadro 1).

É pertinente ressaltar que o Pb adsorvido à fração trocável e matéria orgânica pode ser potencialmente móvel no solo. As ligações eletrostáticas do Pb na fração trocável fazem com que o elemento seja facilmente biodisponível (Lu et al., 2005; Costa et al., 2007). Embora o Pb adsorva-se à matéria orgânica através de complexos metálicos mais estáveis que reduzem sua disponibilidade (Gupta & Sinha, 2006), o metal retido nesta fração do solo pode representar potencial risco ao ambiente, tendo em

vista que quando solúvel ou decomposta, a matéria orgânica pode liberar o elemento, contaminando solo, água e plantas (Torri & Lavado, 2009).

## CONCLUSÕES

1. O Valor de Intervenção indicado pelo CONAMA (2009) para solos agrícolas contaminados por Pb, realmente indica a necessidade de mitigação, pois plantas cultivadas nesta concentração de Pb apresentam alto teor do metal nas partes comestíveis.
2. O Pb afetou a absorção e a distribuição de micronutrientes nos diversos órgãos das hortaliças, causando desbalanço nutricional.
3. O teor do Pb verificado nas frações trocável e matéria orgânica foram bem correlacionados com os teores do metal na planta e podem predizer o potencial de biodisponibilidade do elemento no solo.

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**CAPÍTULO IV:**

**ZINC FERTILIZATION TO INCREASE THE CONCENTRATION OF  
MICRONUTRIENTS IN EDIBLE PARTS OF HORTICULTURAL CROPS**

**(Scientia Horticulturae)**

## **Zinc fertilization as an approach to increase the concentration of micronutrients in edible parts of horticultural crops**

Francisco de Sousa Lima<sup>a</sup>, Clistenes Williams Araujo do Nascimento<sup>a</sup>

<sup>a</sup> Federal Rural University of Pernambuco, Department of Agronomy, Av. Dom Manoel de Medeiros, s/n, Dois Irmãos, Recife PE, Brazil, 50171900. E-mail: clistenes@depa.ufrpe.br. Tel: +55 81 33206236

### **ABSTRACT**

Because nutrients consumed by human beings are derived from the soil-plant system, biofortification of the edible parts of horticultural crops can be a very useful technique for countering human malnutrition. The objective of this study is to evaluate the transfer of Zn from the soil to the edible parts of carrots, kale and okra in latosol treated with increasing doses of zinc. The experiment was conducted in a randomized block design with a 6x3x4 factorial scheme. The treatments consisted of six Zn doses (0, 50, 150, 300, 450 and 550 mg kg<sup>-1</sup> of soil), three plant species (carrot, kale and okra) and four parts plants (root, stem, leaf and edible parts), with four repetitions. The data were subjected to analysis of variance (ANOVA) and regression equations were fit between the Zn doses applied to the soil and the micronutrient content in the plants. The average contents of Zn, Fe, Mn and Cu observed in various organs of the plants were compared using the Scott-Knott test at 5% probability. It was found that with an increase in the content of Zn in the soil, the plant species, in general, presented a greater concentration of this element, showing that fertilization practices can increase the availability of Zn to plants. The kale plants exhibited a potential to concentrate Zn in their edible parts, indicating their suitability for use in biofortification programs. In contrast, the carrot and okra plants did not transfer Zn from the soil to their edible parts and, for this reason, are not suitable for use in biofortification programs with zinc.

**Keywords:** human malnutrition, zinc, horticultural plants

## 1. Introduction

Micronutrient deficiency is very common and affects more than half the world's population (Menkir, 2008; Mayer et al., 2008). A large part of the populations of Asia, Africa and Latin America continue to base their diets on cereals, which have low micronutrient contents, especially Fe and Zn (White and Broadley, 2005; Gao et al., 2007; Alloway, 2009). Zn deficiency affects more than 25% of the global population (Maret & Sandstead, 2006) and is fifth among the most important risk factors for human health in developing countries (Palmgren et al., 2008). The World Health Organization (WHO) estimates that 35% of children on the entire planet suffer from Zn deficiency (Yang et al., 2007).

Zn is essential for human beings (Broadley et al., 2007; Alloway, 2008) as it is active in more than two hundred enzymes, acting in the synthesis of genetic material, in cellular division, and in the synthesis and degradation of carbohydrates, lipids and proteins (Chairman, 2003). Zn deficiency in humans results in mental retardation, damage to the reproductive system, hair loss, diarrhea, loss of appetite, anemia and delayed wound healing (Chairman, 2003). In addition, Zn deficiency promotes other serious complications, such as immune system deficiencies, loss of learning ability and risk of generalized infections (Gibson, 2006; Prasad, 2007).

Numerous attempts to solve nutritional deficiencies in human beings have been promoted, principally through the supplementation of food products enriched with micronutrients. However, this strategy has not been adequate due to its elevated cost and low coverage (Yang et al., 2007). In Brazil, the policies for combating malnutrition are characterized by fragility in the coordination of the programs and by difficulties in distributing them to the poorest regions of the country, where the most vulnerable populations are found (Burlandy and Labra, 2007; Coutinho et al., 2008).

Zn deficiency in human nutrition is a consequence of its scarcity in food (Stein et al., 2007; Wu et al., 2007), which is associated with its low availability in a large part of cultivated soils (Cakmak, 2008; Fraige et al., 2007). Even though Zn is the twenty-third most abundant chemical element on the earth (Broadley et al., 2007), more than 90% of this element present in the soil is in an insoluble form. Therefore, it is unavailable to plants, which is the principal reason for its generalized deficiency in crops (Cakmak, 2008). In Brazil, deficiency of Zn in the soil is the most common among the

micronutrients, occurring principally in the sandy soils and latosols of the cerrado region (Fraige et al., 2007; Resende et al., 2008). Liming practices, which aim to correct the acidity of these naturally acidic soils, are frequent and further reduce the availability of Zn to plants, possibly by increasing the affinity of this element to the specific absorption sites in the soil (Cunha et al., 2008). Therefore, the plant species cultivated in these areas exhibit a low Zn content in their edible parts, thereby contributing to the malnutrition of the population, especially in rural populations that do not have access to fortified foods or foods that are naturally rich in Zn (Alloway, 2009).

Due to the fact that the nutrients consumed by human beings are derived from the soil-plant system, a new approach to solving the problem of micronutrient deficiency in the diet could be biofortification, with an emphasis on the selection of vegetable species with a greater potential to absorb nutrients in the soil and to increase the density and bioavailability of micronutrients in the edible parts (Yang et al., 2007; Palmgren et al., 2008; Alloway, 2009).

Biofortification represents the most desirable and sustainable method for preventing malnutrition in human beings, as vegetables are natural sources of micronutrients (Bosiacki and Tyksiński, 2009). This is especially true for rural populations, where it is more difficult to guarantee that everyone has access to diets supplemented with Zn (Mayer et al., 2008; Alloway, 2009). Adequate provision of nutrients in the soil-plant system through agronomic practices not only provides better nutrition for plants but also improves human nutrition and health (Broadley et al., 2007; Welch and Bouis, 2009).

In this sense, evaluation of the ability of horticultural plants to transfer Zn from the soil to their edible parts, in regards to the wide natural genetic variation among these plants and the important contribution of these plants to the diet of the Brazilian population (White and Broadley, 2005; Carvalho et al., 2006), is an essential step for biofortification programs. Therefore, the objective of this work is to evaluate Zn transfer from the soil to the edible parts of carrots, kale and okra in latosol treated with doses of Zn.

## 2. Materials and methods

The experiments were performed in a greenhouse from January to April 2009. Samples of typical Dystrophic Yellow Latosol were collected at a depth of 0 to 20 cm, then air-dried and sieved through a 2-mm mesh screen for later chemical and physical analysis (Table 1) in accordance with EMBRAPA (1997, 1999). Determination of available Zn content in the soil was performed by DTPA extraction (Lindsay and Norvell, 1978).

The three vegetables selected for the present study are among the most important in the Brazilian diet and represent three plant groups with different edible parts (tuber, leaf and fruit). The carrot (*Daucos carota*), kale (*Brassica oleracea* var. *Acephala*), and okra (*Abelmoschus esculentus*) seedlings were produced in a greenhouse, in Styrofoam trays, using vermicompost as a substrate. For the installation of the experiment, 6.0 kg of previously fertilized soil was transferred to plastic pots (Nascimento et al., 2006). The seedlings, were transferred to other pots, 20 days after germination and the pots were thinned out after 15 days, leaving only 4 plants per pot. During the experiment, the soils were kept at 80% of their maximum water retention capacity, mediated by daily weighing and watering to replace water lost through evaporation.

The plants were collected, and the roots, stems, leaves and edible parts were separated. Next, they were washed thoroughly with tap water and then in distilled water, to remove soil particles and impurities present on the surface of the plants. The collected parts were weighed, gathered in paper bags and placed in a stove to dry at 65-70°C until reaching a constant weight. The dry samples were weighed again, ground in a Wiley mill and then subjected to nitric-perchloric digestion (EMBRAPA, 1999) to determine the content of Zn, Fe, Mn and Cu by atomic absorption spectrophotometry.

The experiments were conducted in a randomized block design with a 6x3x4 factorial scheme. The treatments consisted of 6 doses of Zn (0, 50, 150, 300, 450 and 550 mg kg<sup>-1</sup> of soil), 3 plant species (carrot, kale and okra) and 4 parts plants (root, stem, leaf and edible parts), with 4 repetitions. The obtained data were subjected to analysis of variance (ANOVA), and regression equations were fit between the Zn doses applied to the soil and the micronutrient content in the plants. The average contents of Zn, Fe, Mn and Cu observed in diverse organs of the plants were compared with the Scott-Knott test at 5% probability.

### 3. Results and discussion

The Zn applied to the soil affected the concentrations of micronutrients in the evaluated plants (Table 2). The Zn and Cu contents in the carrot roots increased linearly, while a quadratic response was observed in relation to the Fe content, and no significant effect was observed for manganese. The linear increase of Zn and Cu observed in the carrot roots agrees with the observations of Nair et al. (2008), who evaluated the content of these elements in beet roots grown in solutions with different doses of these metals.

The linear increase in Cu content found in the carrot leaves can be associated with the high Zn content of the soil, which promoted a loss of cellular membrane selectivity (Sarma et al., 2006), resulting in greater absorption of Cu by the plants and a subsequent transfer to the leaves. However, the Zn and Mn content in the carrot leaves exhibited a quadratic response, while the Fe concentration was not significantly affected by the Zn content of the soil. The Mn content evaluated in the carrot tubers increased as a function of adding increasing doses of Zn to the soil, while the Zn, Fe and Cu concentrations were not influenced. The increase in Mn content of the edible part of the carrot (tuber) can make this food more nutritious, in view of the essentiality of this micronutrient for human beings (Kostava et al., 2008).

The absence of an increase in the Zn content in the carrot tubers indicates a low capacity to allocate this element in this organ (Yang et al., 2007) and, consequently, its low potential for use in biofortification programs aimed at Zn supplementation in the diet of a given population. The maximum Zn content in the carrot leaves was observed at a dose of 230 mg Zn kg<sup>-1</sup> of soil. This possibly indicates that, beginning at this concentration in the soil, a phytotoxic effect occurred with the consequent development of disturbances in the plant (Bosiacki and Tyksiński, 2009), inhibiting its absorption and allocation to the leaves.

With the increase of the Zn content in the soil, it was observed that all parts of the kale plants exhibited increased concentrations of this element. This indicates that this species absorbs and distributes Zn to all of its organs (Yang et al., 2007), indicating a high capacity for translocation of this element. A similar behavior was also verified in relation to Cu content in the kale roots and stems and for Mn in the kale leaves. In contrast, the Mn (root and stem), Fe (stem and leaf) and Cu (leaf) contents in the kale

plants were found to be unaffected by the application of increasing doses of Zn in the soil.

The Zn content encountered in the roots, stems and leaves of okra was significantly affected by the increasing doses of this element applied to the soil. A linear increase of Zn was found in the stems and leaves, whereas in the roots the content of this element presented a quadratic response with a maximum value of 2537.77 mg kg<sup>-1</sup> of dry material, observed at a dose of 150 mg kg<sup>-1</sup> Zn in the soil. A quadratic response was also observed for the Fe and Cu content in the okra roots. The reduction in concentration of these elements upon reaching the point of maximum concentration in the roots may be due to phytotoxicity caused by the high Zn content present in the soil (Alloway, 2009).

The Zn, Fe, Mn and Cu contents observed in the okra fruits were not affected by the use of increased doses of Zn in the soil. This demonstrates that Zn is not easily translocated from other organs to the fruit, suggesting that biofortification of okra fruits with Zn is not viable.

In general, with the increase of Zn content in the soil, it was found that the plant species exhibited a greater concentration of this element, showing that fertilization practices can increase the availability of Zn in the plants (Table 3). However, independent of the Zn dose applied to the soil, greater concentrations were observed preferentially in the plant roots, with low translocation to the aerial part of the plants. Zn is minimally translocated to the aerial part of the plants (Kabata-Pendias and Mukherjee, 2007) due to a natural impediment present in plant roots (Andrade et al., 2008). Retention of Zn in the root may be the result of the thickening of the endodermis and the Casparian strips, reducing translocation of this element, possibly to preserve the physiological processes in the aerial parts of the plants (Sharma and Dubey, 2005).

Increased Zn content in the Kale plants was observed in the roots, while the leaves concentrated intermediate values between 62.72 and 1801.05 mg kg<sup>-1</sup> of Zn in the dry material, as a function of the Zn doses. The kale presented great potential for transferring Zn from the soil to the leaves (edible part), demonstrating that its utilization in biofortification programs is feasible. However, biofortification programs should evaluate whether the Zn content allocated to the edible part of the plant adequately guarantees food safety, as ingestion of excessive quantities of Zn results in serious health problems (Scherz and Kirchof, 2006). In biofortification programs, it is also

necessary to evaluate the presence of “antinutrient” substances in the plants (Graham et al., 2001; Campos-Bowers and Wittenmyer, 2007). Since these substances inhibit the absorption of Zn by the organism, an increase of Zn concentration in the edible part may not be effective in increasing the bioavailable content in food.

The low allocation of Zn in the edible parts of the carrot (tuber) and okra (fruit) plants indicates that these species are not appropriate for use in biofortification programs with this particular element by means of agronomic practices through soil fertilization management (Alloway, 2009). However, more studies with these species should be performed with the aim of evaluating the capacity to accumulate other nutrients that are scarce in the population’s diet.

The distribution of Fe in carrot plants grown in soil with a natural concentration of Zn (dose of 0) did not significantly differ among the organs. However, it was observed that the plants grown in soil with the addition of Zn (50 to 300 mg kg<sup>-1</sup>) presented greater relative contents of Fe in the roots, supporting the natural variation of plants in relation to the preferential allocation of heavy metals in the roots (Smical et al., 2008).

In general, it was observed in all the vegetables that the Mn content is greatest in the leaves. According to Chandilyan et al. (2006), plants exhibit a greater concentration of Mn in the leaves than in the other organs. This may be due to its relative importance in photosynthesis and its high natural mobility in plants. The application of increasing doses of Zn to the soil resulted in an increase in the concentration of Mn in the carrot leaves, although it promoted a decrease in the content of this element in the edible part (tuber). Interference of Zn in the Mn content in the plant organs seems not to be a rule, and it seems to depend on the plant species, since the concentration of this element in the kale and okra plants was not affected.

The presence of Zn in the soil, independent of the applied dose, did not affect the Cu content in any of the evaluated plants. This demonstrates that the content of this element in the plants has little relation with the Zn content present in the soil.

As a consequence of the increasing doses of Zn in the soil, it was found that the largest percentage of this element was transferred to the leaves of kale, while the concentrations in the leaves of carrot and okra were not affected (Figure 1). These leafy vegetables presented greater potential for transferring Zn from the soil to their edible parts compared with other horticultural plants (Bosiacki and Tyksiński, 2009). These results demonstrate the differences among species in relation to the capacity to absorb



and concentrate Zn in tissues (Sinha et al., 2006; Yang et al., 2007). The low Zn content in the edible parts of the carrot (tuber root) indicates a reduced capacity of this species to accumulate Zn from the soil in this organ (Liu et al., 2006; Yang et al., 2007).

It was also confirmed that, as a function of the increasing doses of Zn applied to the soil, there was a reduction in the Fe content in the edible parts of carrot and okra. This is a consequence of competition among these metals (Alloway, 2008). In contrast, Zn increased the concentration of Mn in the edible parts of carrot and kale. This synergistic effect of Zn on Mn concentration in plants was also observed by Montezano et al., (2008) and may contribute to increasing the nutritive potential of plants by means of biofortification with Mn, an important micronutrient in the human diet.

Zn did not exert a significant effect on Cu concentrations observed in the edible parts of the plants, although Alloway, (2008) alleges that high Zn concentrations in the soil can reduce Cu availability due to competition for absorption sites on the roots, affecting absorption by the plant.

#### **4. Conclusion**

1. The kale plants exhibited the potential to concentrate Zn in their edible parts, indicating their usefulness for biofortification programs;
2. As a result of Zn application to the soil, an increase in Mn content was found in carrot tubers and there was a reduction of Fe in the okra fruits, affecting the nutritional balance of plant;
3. The carrot and okra plants did not transfer the Zn applied to the soil to their edible parts. For this reason, they are not appropriate for use in biofortification programs with zinc.

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**Table 1.** Chemical and textural characteristics of soil used in the experiment for the cultivation of vegetable crops.

Characteristics	Value
pH (water – 1:2.5)	6.26
P (mg dm <sup>-3</sup> )	19.0
Na <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.32
K <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.11
Ca <sup>+2</sup> +Mg <sup>+2</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	1.80
Mg <sup>+2</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	1.20
Al <sup>+3</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.0
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	3.51
C.O. g kg <sup>-1</sup>	8.52
M.O. g kg <sup>-1</sup>	14.65
Zn (mg kg <sup>-1</sup> )	2.8
Sand (g kg <sup>-1</sup> )	869.0
Lime (g kg <sup>-1</sup> )	13.0
Clay (g kg <sup>-1</sup> )	118.0

**Table 2.** Regression equations for the levels of micronutrients in plant parts of carrot, kale and okra in response to increasing doses of Zn in soil.

Nutrients	Parts of plants	Regression equations	R <sup>2</sup>
<b>CARROT</b>			
Zn	Root	$Y = 707.43 + 24.91***X$	0.89
	Leaf	$Y = 76.96 + 18.45***X - 0.04***X^2$	0.97
	Tuber	$Y = 65.70$	-
Fe	Root	$Y = 174.17 + 17.11***X - 0.05***X^2$	0.99
	Leaf	$Y = 194.26$	-
	Tuber	$Y = 266.76$	-
Mn	Root	$Y = 342.97$	-
	Leaf	$Y = 387.09 + 3.95***X - 0.011***X^2$	0.99
	Tuber	$Y = 80.09 + 0.46*X$	0.98
Cu	Root	$Y = 36.16 + 0.04*X$	0.88
	Leaf	$Y = 14.45 + 0.032*X$	0.94
	Tuber	$Y = 14.57$	-
<b>KALE</b>			
Zn	Root	$Y = 11.36 + 16.84***X$	0.99
	Stem	$Y = 17.83 + 2.38*X$	0.99
	Leaf	$Y = 95.07 + 5.62***X$	0.97
Fe	Root	$Y = 718.89 + 5.12***X - 0.12***X^2$	0.99
	Stem	$Y = 60.73$	-
	Leaf	$Y = 202.57$	-
Mn	Root	$Y = 77.16$	-
	Stem	$Y = 15.63$	-
	Leaf	$Y = 134.74 + 0.41*X$	0.95
Cu	Root	$Y = 38.49 + 0.069***X$	0.84
	Stem	$Y = 1.23 + 0.048*X$	0.85
	Leaf	$Y = 15.40$	-
<b>OKRA</b>			
Zn	Root	$Y = 35.47 + 26.33***X - 0.06***X^2$	0.98
	Stem	$Y = 26.22 + 2.94**X$	0.99
	Leaf	$Y = 69.10 + 23.17***X$	0.99
	Fruits	$Y = 28.72$	-
Fe	Root	$Y = 281.36 + 3.84***X - 0.01*X^2$	0.87
	Stem	$Y = 42.59$	-
	Leaf	$Y = 161.61$	-
	Fruits	$Y = 239.50$	-
Mn	Root	$Y = 35.70$	-
	Stem	$Y = 14.81$	-
	Leaf	$Y = 280.36 + 1.20***X$	0.98
	Fruits	$Y = 51.19$	-
Cu	Root	$Y = 30.36 + 0.18**X - 0.0006**X^2$	0.75
	Stem	$Y = 0.76 + 0.28***X - 0.0008***X^2$	0.79
	Leaf	$Y = 14.29$	-
	Fruits	$Y = 12.08$	-

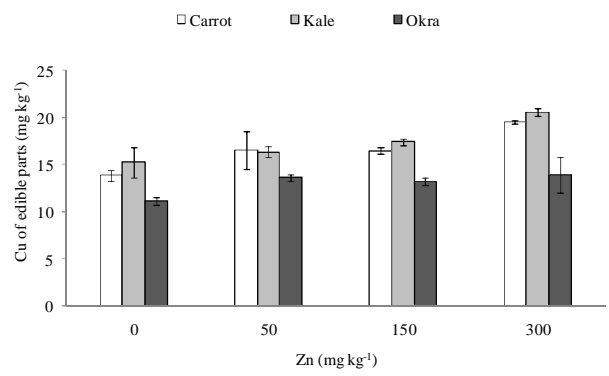
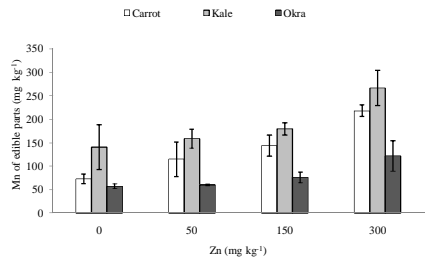
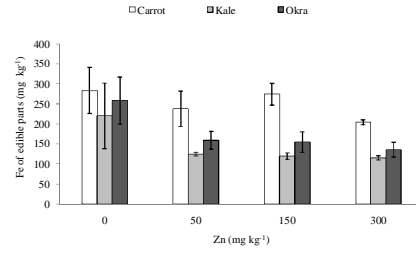
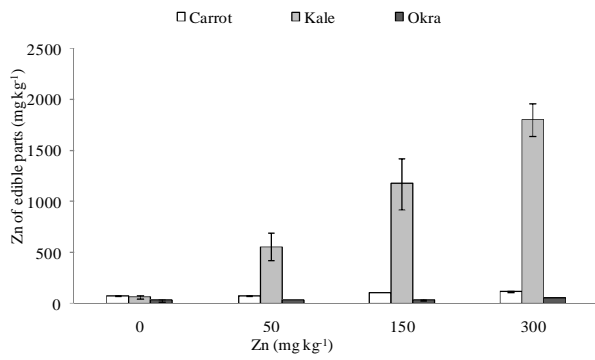
\* \*\* e \*\*\* significant at 5,1, e 0,1% respectively; NS = not significant

**Table 3.** Concentration of micronutrients in plants, carrots, kale and okra grown in soil with increasing doses of Zn.

Culture	Parts	Dose of Zn (mg kg <sup>-1</sup> )			
		0	50	150	300
		Zn (mg kg <sup>-1</sup> )			
Carrot	Root	420.60a	2419.22a	4600.40a	8024.37a
	Leaf	44.42b	523.62b	1879.82b	1703.90b
	Tuber	69.72b	72.85c	105.30c	113.40c
Kale	Root	77.87a	725.60a	2610.65a	5059.20a
	Stem	26.18a	149.87b	335.52c	747.90c
	Leaf	62.60a	553.72a	1174.17b	1801.05b
Okra	Root	55.40a	954.55a	2537.77a	1975.87a
	Stem	14.41a	188.67b	466.85b	908.75b
	Leaf	39.95a	1147.75a	2323.67a	2258.12a
	Fruits	28.72a	28.92c	33.00c	48.22c
CV (%)		16.58			
		Fe (mg kg <sup>-1</sup> )			
Carrot	Root	198.60a	859.35a	1626.97a	748.80a
	Leaf	192.37a	211.17b	227.82b	250.32b
	Tuber	283.57a	237.97b	274.40b	204.36b
Kale	Root	713.67a	949.95a	1172.02a	1016.70a
	Stem	63.36c	47.95c	44.67c	39.17c
	Leaf	220.05b	124.62b	119.65b	115.55b
Okra	Root	235.10a	533.40a	599.85a	595.47a
	Stem	41.48c	51.37c	53.47c	41.75c
	Leaf	160.40b	157.72b	145.65b	142.80b
	Fruits	258.52a	158.72b	154.75b	135.60b
CV(%)		17.46			
		Mn (mg kg <sup>-1</sup> )			
Carrot	Root	349.05a	349.15b	351.42b	388.52b
	Leaf	381.42a	566.82a	722.27a	566.72a
	Tuber	72.87b	114.70c	143.70c	218.06c
Kale	Root	82.50a	91.97a	139.40a	140.75b
	Stem	15.25b	16.90b	17.82b	28.37c
	Leaf	140.72a	158.52a	179.55a	266.77a
Okra	Root	30.60b	43.20b	59.55b	64.70c
	Stem	15.02b	19.45b	28.70b	37.92c
	Leaf	300.92a	311.47a	468.75a	643.20a
	Fruits	57.13b	60.00b	75.95b	121.83b
CV(%)		18.03			
		Cu (mg kg <sup>-1</sup> )			
Carrot	Root	36.75a	39.80a	39.82a	51.62a
	Leaf	14.20b	17.10b	17.90b	24.40b
	Tuber	13.85b	16.57b	16.47b	19.50b
Kale	Root	37.77a	39.35a	54.28a	56.38a
	Stem	2.78c	4.10c	4.52c	17.47b
	Leaf	15.22b	16.35b	17.40b	20.60b
Okra	Root	27.37a	43.40a	40.90a	29.68a
	Stem	2.81c	4.42c	25.10b	5.42c
	Leaf	13.25b	16.20b	16.62b	18.47b
	Fruits	11.07b	13.60b	13.15b	13.87b
CV(%)		14.86			

Means followed by the same letters in column do not differ significantly by test of Scott & Knott at 5% probability. Small letters compare the contents of the elements between the parts of each plant, by column.





**Figure 1.** Concentration of Zn, Fe, Mn and Cu in plants of carrot (tuber), cabbage (leaf) and okra (fruit) depending on the doses of Zn in the soil.