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OCCURRENCE OF COPPER, CADMIUM, ZINC, AND LEAD IN THE SOILS IN AREAS ADJACENT TO THE BR-010

OCORRÊNCIA DE COBRE, CÁDMIO, ZINCO E CHUMBO NOS SOLOS EM ÁREAS ADJACENTES À BR-010

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ABSTRACT

The concentration of the reference points presented between the government limits is to evaluate the adjacent points. They were produced as combined metals and organic matter, pH in KCl, cation exchange capacity, and bioavailable. Soils have a low content of organic matter and pH at all points indicated as characteristic of medium to organic nature and, in general, inorganic characteristics. The highest CTC observed were in points 3 and 5. As the values of metals must be considered polluting, they show that the control of pollutant emissions is carried out by motor vehicles. Therefore, actions to mitigate environmental damage are important to avoid remote monitoring investigated and avoid serious environmental damage.

KEYWORDS: Soil contamination; Potentially Toxic Metals; Road traffic

RESUMO

O objetivo do presente trabalho é avaliar a concentração de metais potencialmente tóxicos nos solos em pontos adjacentes à rodovia BR-010 no trecho entre Governador Edison Lobão-MA e Imperatriz-MA e determinar o nível de contaminação dos solos em questão. Foram realizadas as análises de matéria orgânica, pH em água e KCl, capacidade de troca catiônica e metais biodisponíveis. Os solos apresentaram baixo percentual de matéria orgânica e o pH em todos os pontos indicou caráter de acidez média a fraca e, em geral, características inorgânicas. Os maiores valores de CTC observados foram nos pontos 3 e 5. As concentrações de metais biodisponíveis mostram que o controle das emissões de poluentes por veículos automotores deve ser realizado. Portanto, o monitoramento e as ações para mitigar os efeitos do tráfego de veículos são importantes para evitar a contaminação no trecho investigado e evitar sérios danos ambientais.

PALAVRAS-CHAVE: Contaminação do solo; Metais Potencialmente Tóxicos; Trânsito

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INTRODUCTION

Although they occur naturally in soils, potentially toxic metals (MPTs) are the main mineral pollutants resulting from road traffic, whose main source is vehicle exhaust gases, tire and brake wear, friction elements of brake and clutch systems, oil and particulate spillage from road paving (ZHANG *et al.*, 2013; GILL *et al.*, 2014; KLUGE; WERKENTHIN; WESSOLEK, 2014).

When present in high concentrations, MPTs pose health hazards, adversely affecting the nervous, cardiovascular, renal, and reproductive systems (WHO, 2000). Metals are also found in road dust that receives these pollutants from vehicular emissions, road pavement particles, industrial activities, and as a result of the weathering reactions of minerals in soils and rocks (GUNAWARDANA *et al.*, 2012; SAEEDI *et al.*, 2012).

Dust deposited on lanes can pollute the air, soil, and water bodies adjacent to highways. For Duong and Lee (2011), the smaller the size of the particles that make up the dust, the higher the metal content, and dimensions below 63 µm are the most harmful to the respiratory system of men and animals (SAEEDI *et al.*, 2012; SOLTANI *et al.*, 2015).

Metals are deposited on the asphalt and/or by the action of wind and/or rain, are conducted to soils close to highways, lanes, and avenues that can be absorbed by plant roots, releasing potentially toxic metals into soils as well as many toxic organic compounds, there are accumulations in the upper layers of soils.

Thus, the occurrence of potentially toxic metals in soils close to highways is essential for estimating the impact of traffic activities on the environment. This work aimed to evaluate the concentration of metals in soils along the BR-010 highway between Governador Edison Lobão-MA and Imperatriz-MA and to relate possible contamination with road traffic activities.

MATERIALS AND METHODS

The framework of the study area BR-010 or Rodovia Bernardo Sayão is a federal highway, with a length of 1,959, 6 km. Its starting point is in the state of Distrito Federal, in the city of Brasília, and the end in the state of Pará in the city of Belém, passing through the following states: Maranhão, Tocantins, and Goiás. The stretch of BR-010 between Imperatriz-MA and Governador Edison Lobão-MA in the last four years the flow of vehicles that travel between these cities has been growing (Figura 1).

Figure 1 - Location map of the investigated area and sampling points.

Sources: Araújo, 2020

This increase is due to the emergence of new residential complexes and because it is a transport route for eucalyptus logs for the Suzano Papel e Celulose industry. With this reality, it is believed that this study area has become a potential for potentially toxic metal emissions on the side of the road.

METHODS

Soil sampling

Soil samples were collected with a stainless-steel auger in a soil layer of 0.10 m and 0.20 m, taking three simple samples, at a distance of 1 to 5 m from the highway at six sampling points. After collection, soil samples were identified and placed in plastic bags and transported to the laboratory under refrigeration. The simple samples were homogenized, resulting in a composite sample of 1 kg for each collection point along the highway.

To estimate the natural content of metals, soil samples were collected (reference) under native vegetation (free or with minimal anthropogenic interference) for all lithologies identified along the investigated stretch.

Preparation and treatment of soil samples

The soil samples were transferred to a plastic tray and air-dried in the Chemistry laboratory. After drying, the samples were decompressed and ground in a porcelain grain; then, they were fractionated using 0.35 mm sieves. The fractionated material was placed in a dark-colored polyethylene bottle and submitted to refrigeration until the moment of analysis.

CHEMICAL ATTRIBUTES OF SOILS

Determination of pH in H_2O and KCl

The samples of air-dried soils, passed through a 0.35 mm sieve and homogenized, were submitted to pH analysis in water and KCl 1 mol L-1. Potentiometrically determined in suspension, using 10.0 grams in each sample, 25 mL of water and soil were added (ratio 1:2.5) and stirred for 40 minutes. After stirring the suspension was left to stand for 1h. For the pH in KCl 1 mol L -1, the same relationship between soils and water was used to determine the pH in water and the same agitation/rest time was maintained. Then, the pH measurements were made in the samples according to Raij *et al.*, (2001). Analyzes were performed in triplicate.

Estimate of soil loads (ΔpH and PCZ)

Estimates of soil loads were determined from pH values in water and 0.1 mol L-1 KCl (MEKARAU; UEHARA, 1972) and PCZ according to the equation proposed by Keng and Uehara (1974) from equations 1 and 2 respectively.

$\Delta pH = pH_{KCl} - pH_{H2O}$ (Equation 1)
$PCZ = 2pH_{KCl} - pH_{H2O}$ (Equation 2)

Determination of percentage of organic matter and organic carbon.

In porcelain crucibles previously calcined at 550° C and checked. The dry soil samples sieved at 0.35 mm were subjected to calcination for 4 hours in a muffle furnace at 550º C. After the calcination time, the crucible was cooled in a desiccator. The difference between the initial sample weight and the weight after calcination obtained the organic matter percentage. The organic carbon content was obtained by dividing the result of organic matter by 1.724. This factor is used because it is assumed that, in the average composition of the humus, carbon participates with 58% (EMBRAPA, 2006). Analyzes were performed in triplicate.

Determination of cation exchange capacity

To determine the total exchangeable cations, CTC, 2.50 g of the samples were weighed, adding 25 ml of the 1.00 mol L^{-1} acetic acid solution. Then, the suspension was shaken for 1 h in an incubator with an orbital shake, and subsequently, the pH of both the acetic acid solution and the suspension containing the sample was determined according to the method used by Cotta *et al.* (2006). The determinations were made in three repetitions. The CTC was determined according to the equation below:

CTC (cmolc kg^{-1}) = [pH1 -pH2] x Kctc
Where:
pH 1 = pH of the suspension containing the sample;
pH 2 = pH of acetic acid solution;
Kc = sum of the cation charges present in the soil CTC.

DETERMINATION OF METALLIC SPECIES

Determination of potentially bioavailable metals (MPB)

The method used in this work for the determination of MPT in the bioavailable fraction of soils is the one proposed by De Paula and Mozeto (2001). Approximately 1g of the dry soils was transferred to an Erlenmeyer flask, 25mL of 0.1 mol L^{-1} HCl was added and the mixture was stirred for 2 hours on a table with an orbital shaker. Once the extraction time was completed, the suspension was left to rest for a period necessary for decanting the solid material, and then filtered on a quantitative filter paper. The filtrate was collected in a polyethylene bottle and kept under refrigeration until the determination of metals. A blank control of the extracting solutions was performed during the extraction processes for each sample set analyzed on the same day. Analyzes were performed in triplicate.

RESULTS

The values of the chemical variables found in the analysis of samples collected along the BR-010 Highway in the soils on the margins of the BR-010 stretches between Governador Edison Lobão-MA and Imperatriz-MA are shown in Table 1.

Table 1 - Values of chemical variables with means ± standard deviation (n=3).

S. P	OM (%)	pH_{H2O}	pH_{KCl}	ΔpH	CEC
P1	4,63 ± 0,12	6,76 ± $0,12^{a}$	4,85 ± $0,09^{b}$	– 1,91	2,94
P2	5,46 ± 0,01	6,42 ± $0,03^{a}$	4,47 ± $0,12^{bc}$	– 1,95	2,52
P3	8,64 ± 0,16	6,37 ± $0,13^{a}$	5,58 ± $0,21^{a}$	– 0,79	4,79
P4	2,69 ± 0,2	6,07 ± $,66^{ab}$	4,54 ± $0,20^{bc}$	– 1,53	3,01
P5	7,14 ± 0,04	5,33 ± $0,17^{b}$	3,56 ± $0,21^{d}$	– 1,77	1,79
P6	4,08 ± 0,09	6,06 ± $,05^{ab}$	4,28 ± $0,06^{c}$	– 1,78	2,5

S.P = Sample points; OM = Organic matter; pH_{H2O}= pH in water; pH_{KCl} = pH in sodium chloride; CEC = Cation Exchange Capacity; PCZ = Zero charge point; - Different letters indicate significant differences between sampling points in the same column p<0,05.

Figures 2.1 to 2.4 indicated that the bioavailable MPTs concentrations generally differ significantly ($p < 0.05$) between the sample points, except zinc (Fig 2.4), the figures indicate that point 5 was where the highest occurred. enrichment of the investigated species and that Zn was the metallic species with the highest concentration.

Figure 2.1 - Values of bioavailable cadmium concentrations at different sampling points. Values are means ± standard deviation. Different letters indicate significant differences between sampling points, $p < 0.05$.

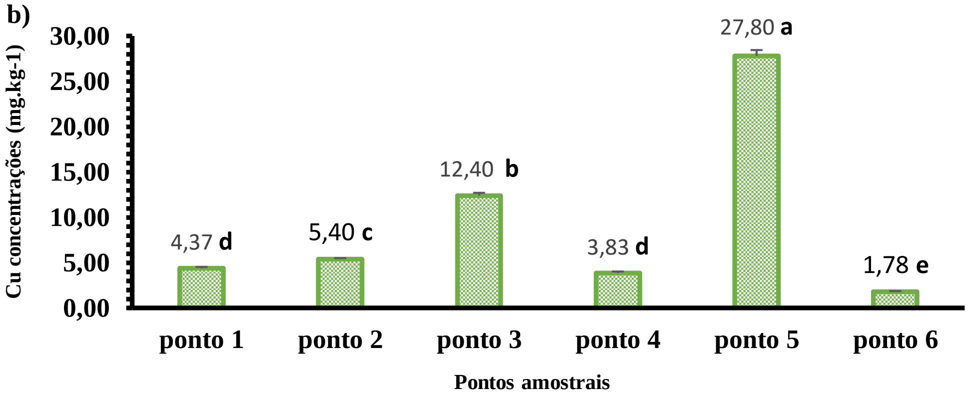

Figure 2.2 - Values of bioavailable copper concentrations at different sampling points. Values are means ± standard deviation. Different letters indicate significant differences between sampling points, $p < 0.05$.

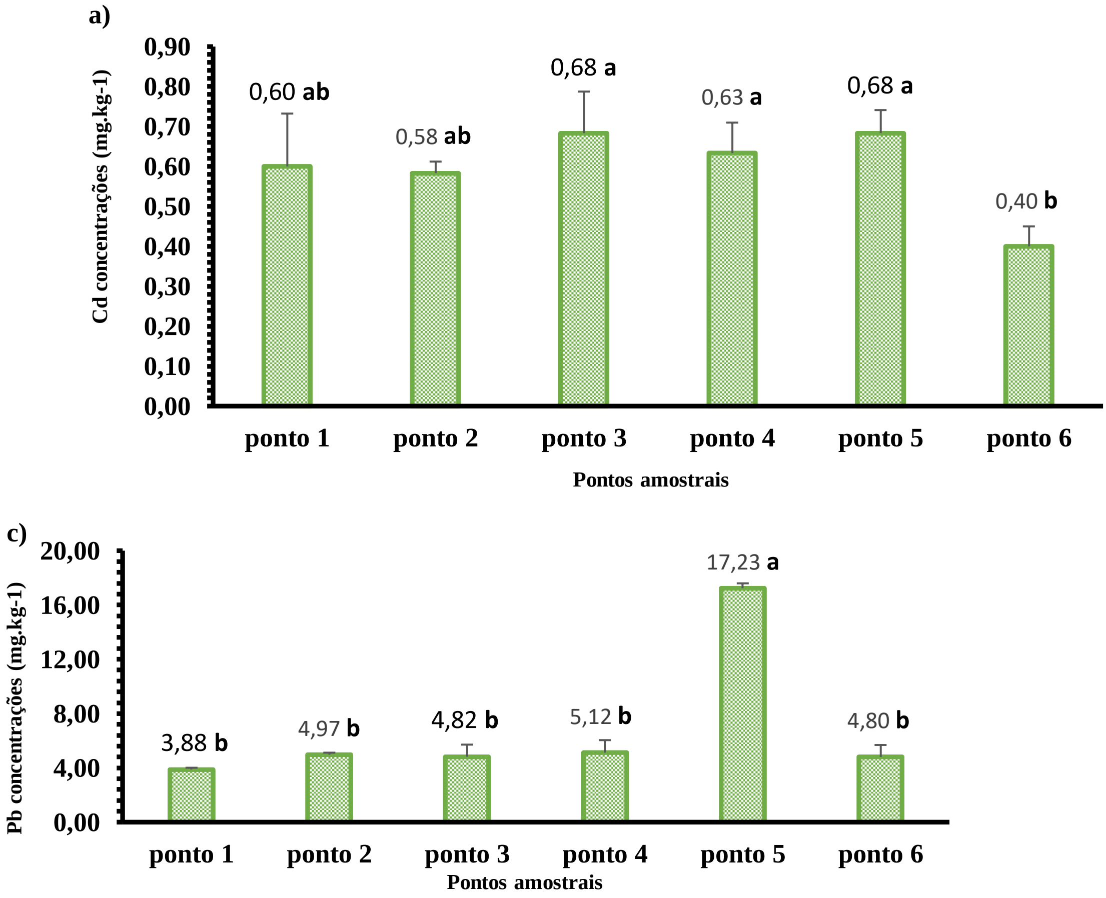

Figure 2.3 - Values of bioavailable lead concentrations at different sampling points. Values are means ± standard deviation. Different letters indicate significant differences between sampling points, $p<0.05$.

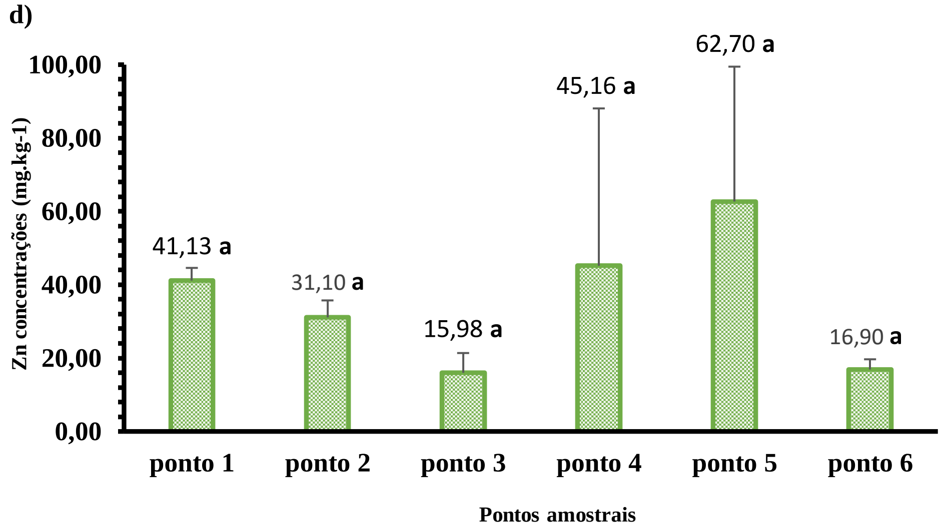

Figure 2.4 - Values of bioavailable zinc concentrations at different sampling points. Values are means ± standard deviation. Different letters indicate significant differences between sampling points, $p < 0.05$.

DISCUSSIONS

The chemical variables are shown in Table 1, all these variables, together or separately, contribute to the investigated metallic species adsorbed on the colloidal particles that constitute the investigated soils, becoming mobile, and consequently bioavailable to soil and plant biota. Organic matter originates from dead substances in soils that come from animal and plant waste in different stages of decomposition. It plays an important role in the soil, improving its physical and chemical conditions and adding important physicochemical properties, such as its ability to exchange cations and pH (EMBRAPA, 2010).

The organic matter contents ranged from 2.69 to 8.64%, the highest contents occurred at sampling point 3 with 8.64% (86.4 g k^{-1}) considered high and the other values considered low (EMBRAPA, 2018).

Regarding the active acidity (pH_{H2O}) (Tab. 1), it is observed that the mean values of pH_{H2O} ranged from medium acidity (5.1-6.0) to weak acidity (6.1-6.9) according to the proposed classification by Cordeiro *et al.* (2018). The values obtained for the pH at all sampling points favor the availability, solubility, and possible leaching of potentially toxic metals (MPTs) (AWOUKUMMI *et al.*, 2015).

The pH values in water were higher than the values obtained for the pH in KCl (Tab. 1), this can be attributed to the fact that not always when measured in water, the pH value may only have the total acidity, due to the protons and aluminum forms attached to the exchange complex, which also contribute to the acidity. Generally, the exchangeable acidity resulting from fixed protons in ion-exchange complexes are likely to shift after the exchange of neutral salts (KCl).

Negative values of ΔpH (Tab. 1) indicate that soils presented a negative net charge. When ΔpH is negative, there is a predominance of negative charges, and in these cases, the soil retains more cations than anions. When ΔpH is positive, positive charges predominate and the soil retains more anions than cations.

Soils can contain a balance of positive, negative, or zero electrical charges. When the balance is null, its name is PCZ, at this point the values of positive and negative charges are equal. According to EMBRAPA (2017) if the soil pH is higher than the PCZ, the

The soil will be negatively charged on the surface of the particles, thus presenting cation exchange capacity (CTC) that is, cation adsorption capacity. If the pH is lower than PCZ, the soil will have a positive charge and will have an anion exchange capacity (CTA), thus the adsorption of anions.

The CTC of soil represents the number of positive ions (cations) that the soil is capable of retaining under certain conditions, exchangeable for equivalent stoichiometric amounts of other cations (ions of the same sign) it is a function of the intensity of negative charges that manifest themselves in the colloids.

Therefore, CTC represents the grading of the release capacity of ions and/or of various nutrients, following the interpretation class of effective CTC proposed by Prezotti and Guarconi (2013) where 2.5 comic dm3 is considered low, and between 2 .5 – 6.0 mol dm^3 are evaluated as a medium, and values greater than 6.0 comic dm^3 are considered high, points 1, 2, 4 and 6 were defined as low CTC, with mean 1.81; 1.09;1.38;1.41 mol dm3, while points 3 and 5 were classified with an average CTC content of 3.81 and 2.53 mol dm^3.

Bioavailability is the measure of the number of certain contaminants present in the soil that can be absorbed or metabolized by man or other ecological receptors, or that are available to interact with biological systems, which depends largely on metal speciation, factors physicochemical, environmental, and biological (ISO 11074, 2004).

According to the graphs, it can be seen that the metallic species with the highest bioavailability at all points investigated was Zn and Cd was the metallic species with the lowest bioavailability. The higher concentration for Zn can be explained by the pH values varied from 5.33 to 6.76, which favors the adsorption of this metal on the surface of colloidal soil particles (ALEXANDRE *et al.*, 2012), influencing the mobility of Zn in soils, according to Mukhopaddhyay *et al.* (2018), comments that at pH above 6 its mobility is significantly reduced.

The lowest concentration observed for Cd is that Cd tends to remain in the less available form under competitive conditions with other metallic species, remaining specifically adsorbed on organic matter and silicate minerals and oxides. Zapusek and Lestan (2009) suggest that the concomitant presence of other metals in high concentrations in soil samples may, over time, lead to a decrease in adsorption and an increase in the mobility of certain metals, particularly Cd, which explains be the Cd metallic species with the lowest concentration.

The following decreasing order of availability was found at points 1, 2, 3, and 5: Zn > Cu > Pb > Cd, whereas for points 4 and 6 it was found: Zn > Pb > Cu > Cd. on the soil surface at points 4 and 6 is believed to be associated with organic matter in the form of complex chelates and other constituents (oxides, carbonates, clay, silt, etc.). soil, which interferes with the uptake or absorption of Pb by plants (ADRAINO, 1986), which justifies the lower concentration of Pb about Cu at points 4 and 6. According to Belluta *et al.* (2018), among metallic soil species, Pb is the least mobile, although its sorption is lower than that of Cu.

CONCLUSION

The soil samples from BR-010 in the stretch between Imperatriz-MA and Governador Edison Lobão-MA showed characteristics of medium to weak acidity and, in general, inorganic characteristics. And with good adsorption capacity of MPTs on colloidal particles on the soil surface. The presence of Cd, Cu, Pb, and Zn was verified in all sampled points.

The high concentration of this metallic species at point P5 requires a study to identify the main contaminating sources, given that at this point, in addition to being located between the two roadsides of BR-010, it is also located close to the road, in front of a gas station, truck mechanic workshops, high motive dealership, and heavy traffic.

Comparing the concentration of bioavailable metals with the concentrations found in the preserved area, it is possible to infer the contribution of anthropogenic sources such as flow of motor vehicles, combustion of motor vehicles, tire wear, and gas station in the distribution of the concentration of investigated metallic species in the investigated stretch of BR-010.

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