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Deposition of potentially toxic metals in the soil from surrounding cement plants in a karst area of Southeastern Brazil

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Abstract

Cement factories are the main sources of environmental pollutants among the different industrial activities, including soil contamination by potentially toxic metals and the Karst region of Southeastern Brazil is known for the implementation of large cement producing facilities. This study aims to evaluate whether there is an increase in the concentration of PTM in the soil surrounding the cement plants and to estimate their harmfulness to both local human population and environment. In total, 18 soil samples were collected from the surroundings of three cement plants as well as four soil samples from areas outside the influence of cement plants and concentration of the following potentially toxic metals (PTM) were estimated: Cd, Pb, Co, Cu, Cr, Mn, Ni, and Zn. The results revealed that all PTM concentrations from cement plant surroundings were significantly higher than PTM concentrations from control areas and no PTM concentrations from CPS or CA soil samples exceeded national and global contamination thresholds. However, Igeo Index indicated low level soil contamination by Pb, Cu and Cr and high levels for Co. We could not verify significant Non-carcinogenic risk to health for any soil sample, but carcinogenic risk analysis revealed different levels of carcinogenic risk among the sampled locations, for both adults and children. Our results indicate that exclusively evaluating the concentration of potentially toxic metals is not enough to verify the potential harmful effects of cement production for the surrounding population. Here we evidence that additional indices, based on both contamination indices and health risk assessments, should be considered for better evaluation of the impacts of cement production activity.

Keywords: heavy metals, soil, cement, environmental risk, pollution

Introduction

Soils are remarkable systems, constituted of an extraordinarily diverse range of mineral and organic components, organized and interactive in particular ways that result in the delivery of the range of ecosystem services, contributing to basic human needs such as food, water, and air supply (Keesstra et al. 2016, Wall et al. 2012). Soil ecosystem services depend on soil properties and their interactions, and are mostly influenced by its use and management (Adhikari and Hartemink 2016). The intensification and expansion of human activities has increased the pressure on land resources and led to soil degradation (Levin et al., 2017). One of the main concerns regarding the impact of human activities in soil systems are soil contamination events by potentially toxic metals (PTM), since they poses alarming threats to agricultural productivity, food safety, and human health (Naila et al. 2019). Potentially toxic metals (PTM) – the most widespread term for heavy metals – are those with high density (> 5g cm^{-3}), compared to other elements and atomic number greater than 20. These metals are resistant to degradation and can accumulate in the components in which they manifest their toxicity (Yadav et al. 2019).

Unlike organic pollutants, PTM cannot be biodegraded and, mainly due to their cumulative power in living organisms, posing risks to health and to the environment (Karimi et al. 2020, Tsezos 2009). Moreover, PTM can remain in the soil for long periods, depending on soil retention capacity and physical-chemical properties (El Sherbiny et al. 2019, Kabata-Pendias and Mukherjee 2007). Soil contamination by PTM is usually the result of anthropogenic activities related to urbanization, including automotive exhaust pipe, and industrialization (Qasemi et al. 2018, Li and Feng 2012). Cement plants are one of the most common sources of PTM pollution by gas emissions and production of cement powder (Jafari et al. 2019).

The cement industry has a high polluting potential at all stages of production (Yadegarnia et al. 2019). The levels and characteristics of pollutant emissions depend on the technological and operational characteristics of the industrial process, especially rotary kiln furnaces, the chemical and mineralogical composition of raw materials, the chemical composition of the fuels used; the operational speed of kiln furnaces, and the efficiency of the emission control systems of installed pollutants (Chen et al. 2015). The primary pollutants emitted in the cement manufacturing process are particulate matter, carbon dioxide, sulfur oxides, and nitrogen oxides (Bermudez et al. 2010). According to the U.S. environmental agency, cement manufacturing plants are among the largest sources of hazardous pollutant emissions, including PTM (Ogunkunle and Fatoba 2014, USEPA 2013, Yahaya et al. 2013). Significant parts of these pollutants

66 are deposited in the soil, including the burning of fuels for the kiln furnaces, generating fine dust particles
67 that are deposited in the soil (Mandal and Voutchkov 2011). This dust contains PTM that are deposited in
68 the soil and cause serious environmental and health impacts since it is not biodegraded, accumulating
69 (Ogunkunle and Fatoba 2013).

70 About 2-3% of the Brazilian territory is formed by karst environments, structured in 19 karst
71 regions (Travassos, 2019). These regions are characterized by vast areas of sedimentary carbonate rocks,
72 with limestone, dolomite rock, and marbles being the most common components. Due to calcareous
73 composition, these regions in Brazil are commonly used for limestone exploitation for use in agriculture,
74 but also as an input in the manufacturing process of Portland cement, in which it is common to install this
75 type of facility in the karstic regions of Brazil (Travassos, 2019). This study was carried out in an area
76 located at the Southern portion of one of the largest Brazilian karst regions (called Grupo Bambuí), at
77 Southeastern Brazil. This area represents a mosaic of environments characterized by areas used for
78 agricultural production, limestone mining, small urban settlements, and presence of cement plants (IBGE
79 2010).

80 Here, we hypothesized that cement production in the study area leads to the deposition of PTM in
81 its surroundings and that these events of increasing in PTM concentrations can be potentially harmful to
82 vicinal human population of the cement plants. Thus, our main goal is to evaluate whether there is an
83 increase in the concentration of PTM in the soil surrounding the cement plants and to estimate their
84 harmfulness to both local human population and environment, applying worldwide used indices. This
85 investigation also aims to provide evidence that conventional strategies for estimating of soil contamination
86 by cement production plants adopted by local regulatory agencies are not sufficient to estimate the risks of
87 PTM soil contamination to human health.

88 ## Materials and methods

89

90 *Sampling and quantification of potentially toxic metals in the soil*

91

92 The study area comprises the Southern portion of the widest karstic region in Brazil, called Grupo
93 Bambuí, located in the Southeast region of Brazil (Figure 1). In this area, soil samples were collected from
94 the surroundings of three Portland Cement plants (named CPS1, CPS2 and CPS3) and also soil samples in
95 two agricultural production areas located outside the influence of cement production plants (10 km far from

CPSs) taken as control areas (CA). Six sampling points were selected around each cement production plant (CPS), in which each point presented a plant distance of less than 500 meters (a circular scheme). In each control area, two sampling points were selected. The samples were collected in a single round, performed in May 2020 (dry season). In each sampling point, approximately 2000 g of surface soil was collected with depth between 0 and 15 cm, following procedures described in Pacchioni et al. (2014).

Concentration of the following potentially toxic metals (PTM) were estimated in soil samples: Cd, Pb, Co, Cu, Cr, Mn, Ni, and Zn. The quantification of heavy metals was performed following the methodology of air-acetylene flame atomic absorption spectrometry proposed by USEPA 3050B (USEPA, 1998a) and USEPA 3051A (USEPA, 1998b). All quantifications were performed by a laboratory facility certified by local regulatory agencies (Oceanus-Hidroquímica Laboratory, certification code: UN015590/55.11.10).

Analysis of potentially toxic metals concentrations in the soil

Soil PTM contamination analyses were performed using the following internationally recognized indices: Enrichment Factor (EF) and Geoaccumulation Index (Igeo). In addition to the indexes, raw data about PTM concentration were also included to compare them with previous studies and also to compare with soil PTM contamination limits established in both Brazilian (CONAMA No. 420/09, BRASIL 2009) and local (COPAM No. 166/11, MINAS GERAIS 2011) laws.

The Enrichment Factor (EF) was used to evaluate the degree of enrichment of PTM in soil. EF is used to assess the level of human impact, by differentiation anthropogenic source from natural sources of PTM (Barbieri 2016). The EF value near to unity indicates natural origin, those less than unity suggests possible mobilization/depletion of metal, while EF value greater than unity recommends that the element is of anthropogenic origin (Yadav et al. 2019). EF index was calculated by equation as follows, where *Ci* is the concentration of individual elements in soil (mg/kg); C_{Ref} is the concentration of reference element for normalization (mg/kg). In this study, used Fe as reference element, so that Fe concentration was determined for all soil samples to perform EF calculations.

$$EF = (C_i/C_{Ref})_{soil} /(C_i/C_{Ref})_{background}$$

The Geoaccumulation Index (Igeo) was calculated to estimate the degree of soil pollution by a given PTM, comparing observed PTM concentration with its reference concentration, proposed by Muller

(1969). Also, Igeo index was ranked in seven classes of soil pollution, described in Mohammadi et al. (2020). Igeo was calculated by equation as follows, where *Ci* is the PTM concentration in soil samples, and *Bi* is the background concentration of these elements. Background values (Bi) used in this study were based on reference values proposed for carbonate sedimentary rocks by Turekian and Wedepohl (1961) and they were presented in Table S1.

$$I_{geo} = \log_2 \left(\frac{Ci}{1{,}5.Bi}\right)$$

We performed non-paired Wilcoxon tests to compare PTM concentration as well as adopted contamination indices (EF and Igeo) between the CPS and CA soil samples, using R statistical program (R version 3.3.2).

Health risk assessment

In this study, non-carcinogenic health risks assessments (NCR) for CPS vicinal human populations by soil PTM contamination was estimated using USEPA health risk methods for oral, dermal, and contact pathways (USEPA 2013). First, the Average Daily Dose (ADD) in milligrams per kilogram per day values of PTM through oral, dermal, and inhalation pathways was calculated using the following equations. References parameters for both adult and children exposure were presented in Table 1.

$$ADD_{ing} = C \times \frac{IngR \times EF \times ED \times CF}{BW \times AT}$$

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT}$$

$$ADD_{derm} = C \times \frac{SA \times SL \times ABS \times EF \times ED \times EF}{BW \times AT}$$

As a second step, ADDs were used to calculate the Hazard Quotient (HQ) by dividing the daily exposure doses (ADD_{ing}, ADD_{inh}, and ADD_{derm}) for each PTM with its corresponding reference doses (RfD) (mg kg^{-1} day^{-1}). Adopted RfDs and calculated ADDs values for the eight PTM were presented in Table S2 and Table S3, respectively. Then, to estimate the non-carcinogenic risks of PTM for humans (NCR), we calculated the Hazard Index (HI) which corresponds to the sum of HQ indices: NCR = HI = ∑HQi. HI <1 indicates that there are no significant risks of non-cancerous effect, and HI>1 indicates a chance that non-carcinogenic effects may occur, with a probability that it tends to increase as HI value increases (Wang et al. 2020).

The carcinogenic risks to humans (CR) was estimated as described by Yadav et al. (2019), which CR corresponds to the average daily doses (∑ADD) multiplied by respective slope fator (SF). A slope factor is an upper bound probability of an individual developing cancer as a result of a lifetime exposure to an agent by ingestion or inhalation. Adopted Slope Factors for the eight PTM were presented in Table S2. When $CR < 10^{-6}$, no cancer risk exists. When $10^{-6}<CR<10^{-4}$, the risk is within the acceptable range. When $CRN>10^{-4}$, human tolerance is exceeded.

Results

Our first approach in this study was to compare PTM concentrations estimated for CPS and CA soil samples. The results of these comparative analyses revealed that all PTM concentrations from CPS were significantly higher than PTM concentrations from CA areas (Figure 2). Moreover, when we compared PTM concentrations between the three CPS (CPS1, CPS2 and CPS3), we could not verify significant differences in PTM concentrations between the three CPS, except for Cr element, in which soil samples from CPS3 presented values higher than CPS1 and CPS2 (Table S4).

Here, we also compared PTM concentrations from CPS soil samples with soil contamination thresholds established by local (COPAM No. 16/11, MINAS GERAIS, 2011), national (CONAMA No. 420/09, BRAZIL, 2009) and global (WHO, 1993) recommendations. The results revealed that several CPS soil samples exceeded local PTM contamination threshold for Co and Pb. However, no PTM concentrations from CPS or CA soil samples exceeded national and global contamination thresholds (Table S1). In addition, when we compared PTM concentrations estimated from CPS or CA soil samples with PTM concentration values reported for PTM soil contamination events worldwide by previous studies, we could observe that the levels of PTM concentration in CPS or CA soil samples were lower than those described in reported PTM soil contamination events (Table 2).

The results of our PTM enrichment analyses, estimated by the EF Index, revealed that the soil enrichment by PTM was superior in CPS areas when compared with control areas (CA) for all studied PTM (Table 3). However, we could verify high enrichment level only for Co element in CPS soil samples (EF > 5), with a single sampling point showing a very high level of enrichment (EF > 20). Similarly, our Igeo analysis of soil contamination by PTM revealed that the levels of soil contamination in CPS soil samples were higher when compared with CA samples, for all PTM (Figure 3). Considering the mean values of Igeo Index, we did not verify significant contamination by Mn, Ni and Zn in both CPS and CA soil samples.

184 Low level soil contamination were verified for Pb, Cu and Cr elements. However, Igeo Index for Co
185 element showed varying degrees of contamination between soil samples, ranging from moderate to extreme
186 level of soil contamination (Figure 3).

187 Our non-carcinogenic health risk (NCR) analyzes, estimated by Hazard Quotient (HQs) and
188 Hazard Index (HI) calculations, revealed that for all sampled locations (CPS1, CPS2, CPS3 and CA), we
189 could not verify significant risk to health (HI > 1), for all studied PTM. Still, similar NCR results were
190 verified for both adults and children estimates. On the other hand, carcinogenic risk analysis (CR) revealed
191 different levels of carcinogenic risk (CR) among the sampled locations (CPS1, CPS2, CPS3 and CA), for
192 both adults and children (Table 5). In addition, the five PTMs, which was possible to perform the CR
193 analysis (Cd, Pb, Co, Cr and Ni), also presented distinct levels of CR among the sampled locations where
194 soil were accessed (Table 5).

195 **Discussion**

196

197 Several studies reporting events of soil enrichment contamination by PTM in Brazilian territory
198 have been published recently: Brito et al. (2020) also estimated PTM concentration in soils from areas
199 under agricultural exploration and natural Cerrado vegetation, but in Northeast region; Silva et al. (2016)
200 verified and differentiated the sources of emission of PTMs in soils used for sugarcane cultivation in
201 Northeast region;, Smidt et al. (2011) identified potential sources of pollution by PTMs in soils highly
202 influenced by a phosphorus fertilizer factory. However, this is the first study performed in Brazil focused
203 on estimating potential soil PTM contamination caused by cement plants operation and their potential health
204 risks to local human population. Some studies have already been published relating concerning events of
205 soil contamination by PTM and the anthropic activity of cement production in some regions of the world,
206 reporting events of PTM soil contamination more severe than those observed in this study (Table 2),
207 probably related to the fact that these previous studies have been performed in countries whose laws about
208 gas emissions as well as soil contamination by PTM are less restrictive than in Brazil (El-Sherbiny et al.
209 2019; Kolo et al. 2018, Ogunkunle and Fatoba, 2014, Mandal and Voutchkov, 2011; Al-Khashman and
210 Shawabkeh, 2006). On the other hand, when considering studies on PTM contamination events in general,
211 China is the country where most of these studies have been reported, indicating that soils from areas of
212 intense urban and industrial activity are severely contaminated by PTM, creating alarming risks to the

environment and the health of local populations (Han et al. 2021, Ma et al. 2020, Han et al. 2020, Jin et al. 2019, Yadav et al. 2019).

In this study we hypothesized that PTM concentration around the cement plants would be higher than in control areas, which was in accordance with our findings, even at moderate levels when compared with other similar studies (El-Sherbiny et al. 2019; Kolo et al. 2018, Ogunkunle and Fatoba, 2014, Mandal and Voutchkov, 2011; Al-Khashman and Shawabkeh, 2006) and also with the concentration thresholds of PTM recommended by local (COPAM No. 16/11, MINAS GERAIS, 2011) and national (CONAMA No. 420/09, BRAZIL, 2009) regulatory laws as well WHO recommendations (WHO, 1993). On the other hand, when we accessed the status of PTM contamination not by PTM concentration solely, but by applying contamination (Igeo) and enrichment (EF) indices, these parameters could indicate that some PTM contamination presented above the "negligible status", attributing environmental concerns to soil contamination in cement plant surroundings which are operating in the study area. Thus, we consider that our results constitute strong evidences of the need to incorporate the contamination and enrichment indices (Igeo and EF) not only in instruments of risk assessment to the environmental contamination by local environmental agencies, but also as a tool for monitoring programs of PTM pollution to be incorporated in Environmental Management Systems of cement industries.

PTMs can be introduced in soil environment by natural routes, such as volcanic activities and weathering of rocks, or by anthropogenic disturbances (Antoniadis et al. 2019, Weissmannová and Pavlovský, 2017). The entry of PTMs into the ecosystem via the food chain can collapse the ecosystem since they: affect the biodegradability of organic pollutants and magnifying their toxic effects; change soil properties such as pH and porosity; and can disrupt the taxonomic and functional structure of biological communities that maintain part of the ecosystem services provided by the soil (Okereafor et al. 2020, Abdu et al. 2017, Giller et al. 2009). In addition to interfering in the ecosystem, PTMs also directly influence people's health, causing inhibition of enzymatic activities, altering protein synthesis, nucleic acid functions and changes in membrane permeability, cause lipid peroxidation, dehydration of sulfhydryl proteins, along with other effects (Fu and Xi 2020, Briffa et al. 2020).

In our Igeo results, we found moderate to extreme soil contamination by Cobalt, since observed concentrations of this metal were higher the reference values defined for sedimentary carbonatic rocks which form the geological context of the study area (Turekian and Wedepohl 1961). Natural occurrence of Cobalt is highly concentrated in mafic rocks as well in black shales, commonly forming minerals with S,

As and Se, such as cobaltite, smaltite, linneite and arsenosulfide. In soils, high level of Co were found in loamy (Cambisols) and in organic (Histosols) soils (Kabata-Pendias, 2010). Events of soil contamination by Cobalt has been associated with mining and smelting activity, fertilizer use, and sewage sludge spreading (Hamilton 2000) and this study represents the first record of soil contamination by Cobalt in studies focused on soils from cement plant surroundings. Although Cobalt is considered a plant micronutrient (component of several enzymes and co-enzymes), it has been shown to affect growth and metabolism of plants, depending on the concentration and status of cobalt in rhizosphere and soil (Palit et al. 1994). In addition to harmful effects on plants, soil contamination events by Cobalt are also associated with disturbances in the soil microbiota (Shaheen et al. 2016, Zaborowska et al. 2016, Gál et al. 2008). Cobalt contamination has direct interactions with human health, with skin and respiratory issues (Leyssens et al. 2017). Cobalt has been noted to have a high affinity to the sulphydryl group, thus causing inhibition of crucial enzymes (Simonsen et al. 2012). Moreover, has also been linked to carcinogenic effects, possibly related to the evidence that Cobalt interfere in process of DNA repair and can cause direct induction of DNA-protein crosslinking DNA damage and sister-chromatid, as well evidences of cobalt-mediated free radicals formation (Valko et al. 2005). Here, we also verified low levels of soil contamination by Lead, Copper and Chromium in soil samples from cement plant surroundings. Small particles of inorganic Lead can be absorbed through the respiratory and gastrointestinal tract and chronic exposure to lead contributes to alterations in hormonal and neuronal systems, toxicity in renal cells and affect the hematopoietic system (Briffa et al. 2020). Chromium which is not absorbed through the lungs, may then enter the gastrointestinal tract, primarily absorbed in the jejunum. Toxicity mechanism and carcinogenicity of chromium is a complex process, including higher redox potential, free radicals production and DNA lesions (Dayan and Paine 2001). Oral intake of Copper may cause hepatic and kidney disease, including Wilson's disease, related to copper accumulation in organs instead of being excreted by bile (Harris and Gitlin 1996). In addition to the harmful effects of these PTMs on human health, there are strong evidences that events of soil contamination by these three MTPs are related to disturbances of the soil ecosystem which is related to deterioration of soil quality (Gong et al. 2021, Song et al. 2021, Tang et al. 2019, Lin et al. 2019, Fajardo et al. 2019, Giller et al. 1998, Kandeler et al. 1996).

Our Carcinogenetic Risks (CR) estimates showed significant carcinogenic risks for children related to soil contamination by Chromium and Cobalt in all sampled locations, with the exception of two sampling points in CPS2 and CPS3. Considering the estimated CR for adults, risks for Chromium were

also detected, the other PTMs (Co, Pb, Ni and Cd) presented low or nonsignificant risks (Qing et al., 2015). Similar results were also observed in previous studies performed in China Wan et al. (2016) and Mao et al. (2019). Other studies related significant carcinogenic risks related to soil contamination by Cd, Ni and Zn (Mohammadi et al. 2020, Karimi et al. 2020, Yadav et al 2019). Our results raised the need for constant monitoring of the levels of PTMs in the soil from cement plant surroundings, using both NCR and CR indices of health risk for local human populations. These indices proved to be more sensitive to conventional metrics recommended by local and national environmental laws (CONAMA, 420/09, COPAM, 166/11). Thus, we consider that our results constitute strong evidences of the need to incorporate the contamination and enrichment indices (Igeo and EF) as well as Health Risk Assessments (NCR and CR indices) not only in instruments of risk assessment to the environmental contamination by local environmental agencies, but also as a tool for monitoring programs of PTM pollution to be incorporated in Environmental Management Systems of cement industries.

Conclusion

In this study, we hypothesized that cement production at karstic areas from Southeast Brazil could be related to soil PTM contamination at cement plant surroundings and that these events could be potentially harmful to vicinal human population. Our findings revealed that all PTM concentrations from Cement Plant Surroundings were significantly higher than PTM concentrations from Control areas. Moreover, although the soil contamination events seen in this study can be considered mild when compared to other similar studies, health risk assessments revealed there are concerning carcinogenic risks by the local human population due to long-term exposure to PTM found in soil of the surrounding the cement plants.

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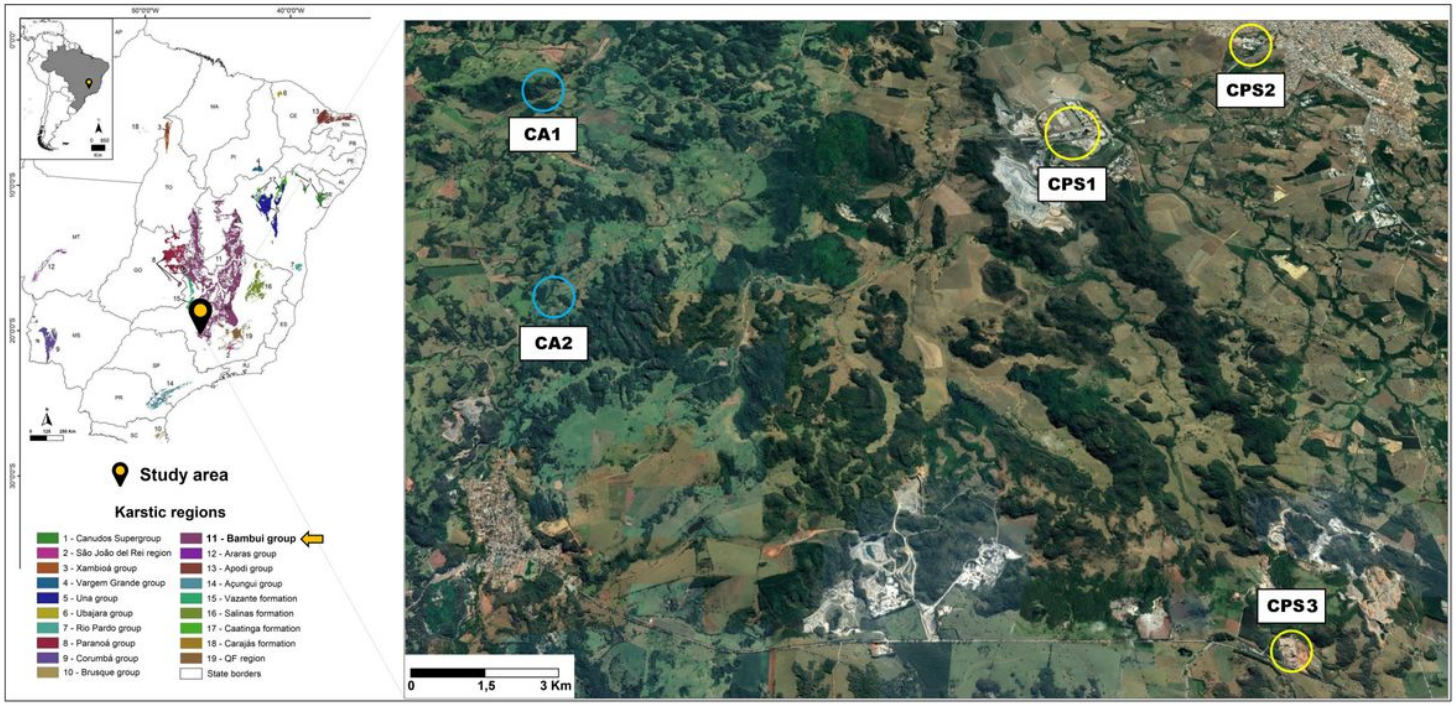
Figure captions

Figure 1: Google Map of study area (on the right) comprising the Southern part of the karst region, located in the Southeast region of Brazil (on the left). Blue and Yellow circles represents control and cement plant surroundings sampling sites, respectively.

Figure 2: Boxplot of PTM concentrations by sampled environments: Cement Plant Surroundings (CPS) and Control (CA). Wilcoxon tests p-values (CPS vs. CA) were described on the on the lower right corner.

Figure 3: Boxplot of Geoaccumulation Index (Igeo Index) for each accessed PTM, by sampled environments: Cement Plant Surroundings (CPS) and Control (CA). Wilcoxon tests p-values (CPS vs. CA) were described at the bottom.

Figures



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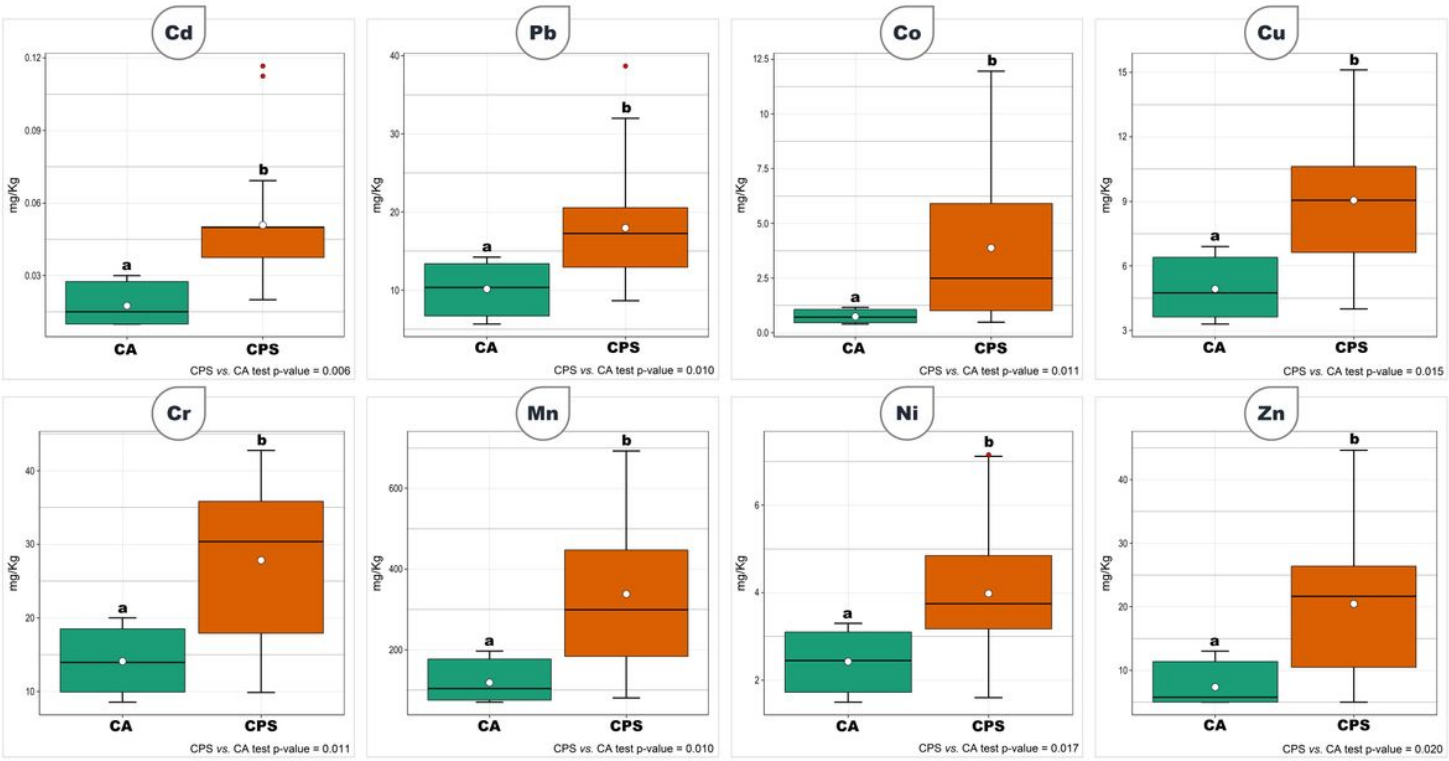

Figure 2

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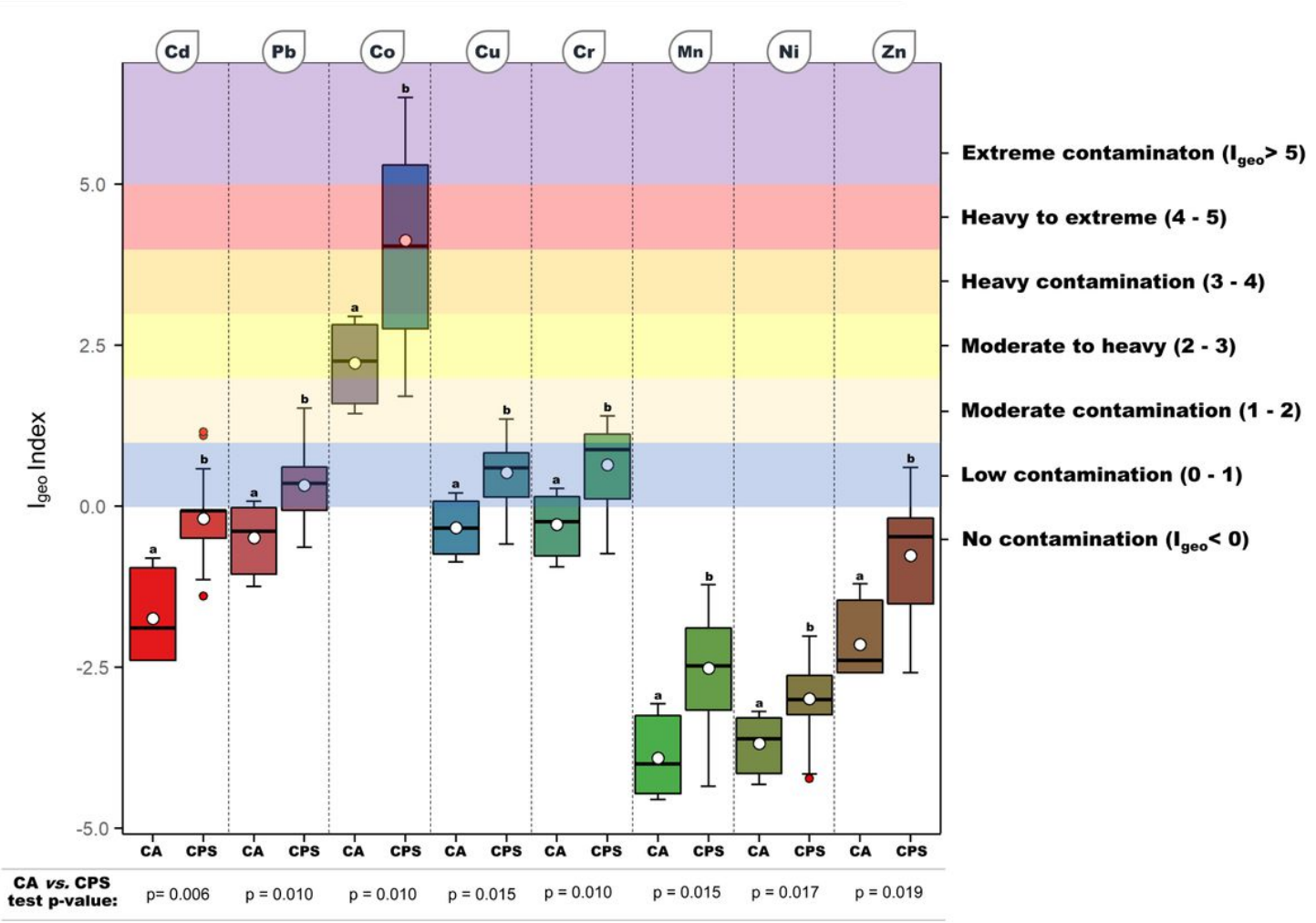

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Boxplot of Geoaccumulation Index (Igeo Index) for each accessed PTM, by sampled environments: Cement Plant Surroundings (CPS) and Control (CA). Wilcoxon tests p-values (CPS vs. CA) were described at the bottom.

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