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# Assessment of the Environmental Risk of a Floodplain Contaminated by Metals Based on Different Indices and Environmental Classification Factors, Minas Gerais, Brazil

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## Abstract

The geochemical characterization, of an industrial area in Minas Gerais State, Brazil, revealed presence of high levels of potentially toxic metals, higher than the values admitted. The use of three environmental classification indices enabled the comparison of data with the adopted classifications for each index, having identified cadmium, lead and zinc as the main contaminants. The construction of interpolation maps allowed the visualization of the e contaminants evolution throughout the area. It was possible to identify places where natural mitigation processes can be used end produce a comprehensive remediation proposal in places identified as requiring a more complex intervention.

**Keywords:** geochemical characterization, potentially toxic metals, environmental classification indices, interpolation maps, environmental remediation

## Introduction

Metals contamination in soils is very common, and is mostly associated with the deposition of contaminated toxic compounds from anthropic activities (Raymond 2011). Knowledge of metals mobility in the environment is essential for a rigorous assessment of the potential geochemical risks associated with these elements and, it consists of an important tool to control and monitor environmental pollution. The study of the chemical forms and the occurrence of a chemical element allows it to estimate its mobility, bioavailability and ecotoxicity in the environment (Lu 2003, Davidson 2004, Cappuyns 2007). The *Aqua Regia* digestion method for solid samples is a simple approach to determinate mobile phases, based on bi-acid dissolution of the fractions with greater facility to be transferred to the environment and resulting, as residual fraction, silicate minerals geologically stable and therefore neither influencing the chemical conditions of the environment nor the assimilation by biota (Pinho 2013, Pinho 2018). The study area is highly contaminated by toxic metals, including zinc (Zn), nickel (Ni), cadmium (Cd), copper (Co), chromium (Cr), and lead (Pb) and arsenic (As). This contamination is mainly associated to the presence and operation of a local industrial unit. One of the objectives of this work is the elaboration of an environmental remediation proposal, while considering the results obtained from the geochemical characterization and the evaluation of those elements contents according to three environmental classification indices. The investigation and identification of alternative techniques for the remediation and/or recovery of contaminated areas, at low cost and with viable execution times, are currently of high importance (USEPA 2008, Pinho 2018). In this study the proposed solution for the recovery of this area should be applied taking into account the intrinsic and unique chemical and climatic conditions. As a good example of remediation technologies, we can mention the use of innovative reactive materials to fill permeable reactive barriers (PRB's) or bioremediation techniques (Carvalho 2008, Pinho 2018). The success or failure of a technology depends on the contaminations control on the source, and its applicability depends not only on the nature of the contaminants, but also on the intrinsic characteristics of the geological materials (Pinho 2018).

## Overview of the Study Area

The study area, with an area of approximately 3 km$^2$, is located in the Brazilian State of Minas Gerais, in the municipality of Três Marias. It is embedded in the hydrographic basin of São Francisco River, limited at North and South by two small water ways, the Consciência and the Barreiro Grande creek, geographically located next to the river's bank (Fig. 1) (Pinho 2018, Pinho 2019). Geologically, this area is part of the Três Marias Formation, belonging to the Bambuí Group, which is as lithostratigraphic unit belonging to the São Francisco Group and constitutes a Neoproterozoic sedimentary cover of the São Francisco Craton. This formation is mainly composed of detrital sedimentary rocks consisting of micaceous and clayey siltstones with calcareous matrix, arkoses, ferruginous shales and metamorphosed limestones (Alkimim 2001) in Ribeiro (2010).

## Methodology

The study area was divided into three areas (A1, A2 and A3) where samples were collected, trying to guarantee the representativeness of the sedimentary materials. Sampling also took place in an area located upstream and outside of the influence of the industrial activity (A0), representing the geochemical background (Pinho 2018). In the alluvial plain and in the margins of Consciência creek, samples were collected with a manual auger mainly at three depths (0 to 20 cm, 20 to 40 cm and 40 to 60 cm), aiming to have an in-depth knowledge of the levels of contaminants and also the chemical forms in which elements occur. In the stream bed of the waterway samples were collected with a manual Shipeck dredge and for deeper sampling (60 to 80 cm and 80 to 100 cm) a Kajak drilling corer was used and samples were divided into 20cm-thick layers. Sampling was followed by immediate readings of Eh and pH values, using a portable multi-parameter Consort, C5020 model probe (SP10T model for pH, SP50X model for redox potential) and samples were preserved at about 4 °C (from the time of collection) until the transportation to the laboratory. In the laboratory, previously grounder samples through an agate mill, the contamination degree was determined by the *Aqua Regia* digestion with subsequent quantification by ICP-OES (Perkin-Elmer, Optima 8300) following USEPA 2007. Data was compared with the legislated accepted values, that consider two levels of danger: Level 1, which corresponds to the threshold below which no harmful effects are expected on aquatic life

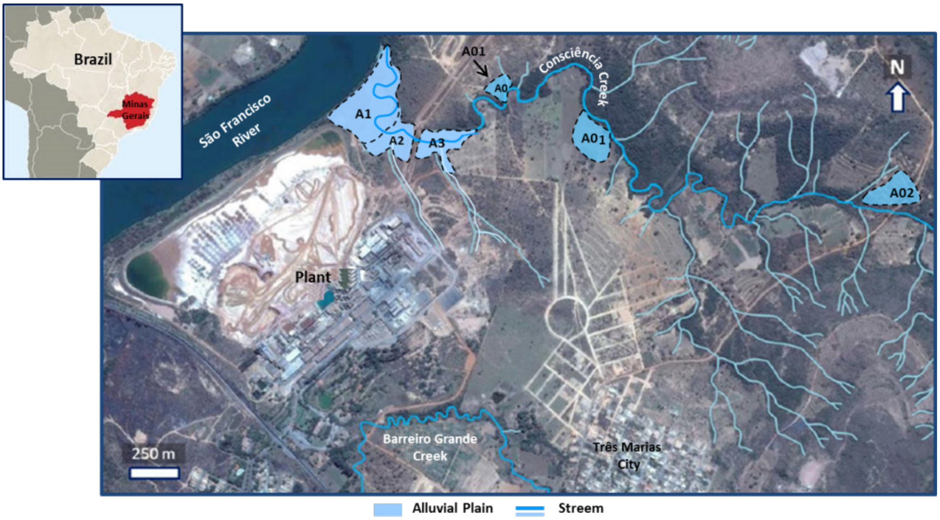


*Figure 1 Overview of the study area.*

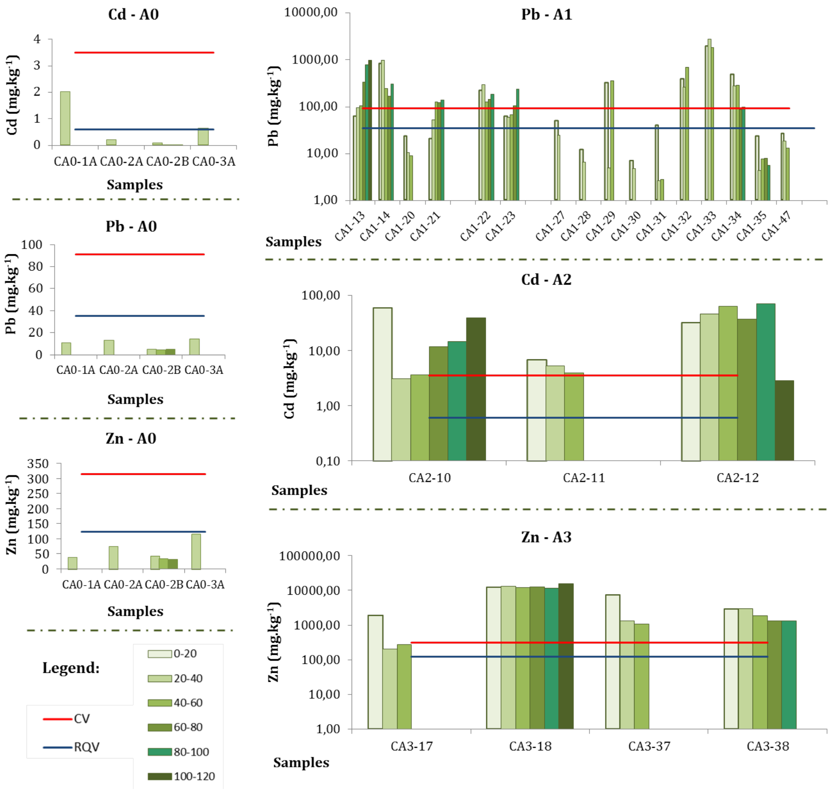


*Figure 2* *Content obtained by aqua regia in depth.*

(equivalent to the Reference Quality Values – RQV) and Level 2, which corresponds to the threshold above which harmful effects to biota are expected (equivalent to the Critical Value – CV) (CONAMA 2012). From this comparative study, three environmental classification indices were calculated in order to identify the extent of local contamination: (1) the Enrichment Factor (EF), according to the definition proposed by Lee (1997) (in Nude 2011, Pinho 2013, Martins 2014, Pinho 2018), compares the contents of each element in the samples of the contaminated areas to the corresponding contents in the background area (area A0). (2) the Index of Geochemical Load (IGL) allows the calculation, based on a local reference, of the enrichment for a given element in a given sample (Pendias, 2001, Nude 2011, Trindade 2012, Martins 2014, Pinho 2018), (3) the Contamination Factor (CF), determines the pollution index of a given element from its comparison with the content obtained in area A0, taken as a reference value (Nude 2011, Martins 2014).

## Results and Discussion

The geochemical characterization of the samples identified Cd, Pb and Zn as the contaminants with greater expressiveness in the area. The comparison between these levels and the legislated accepted values for RQV and CV, according to CONAMA 2012 (CV in mg.kg$^{-1}$ Cd: 3.5; Pb 91.3; Zn: 315 and RQV in mg.kg$^{-1}$ Cd: 0.6; Pb: 35; Zn: 123), allowed to evaluate their dangerousness in the environment for each area (A1, A2, A3). In the background area A0, as expected, non-compliances under the admitted legal levels were found for most elements. However occasional records of Cd levels above RQV were observed, which may be due to natural enrichment or generated from the wind transport of particles from adjacent areas (Figure 2). Bothe areas A1 and A2 have very high levels for all of these elements, above the RQV and CV, graphically represented by Pb and by Cd, respectively for A1 and A2 (Figure 2). In area Ae Cd has high levels throughout the sampling profile, with higher levels in the intermediate depth layers (20-40, 40-60 and 60-80 cm) (Figure 2). Concerning area A3, Zn, depicted as an example in the graph of Figure 2, also has levels higher than RQV and CV in all the analysed samples, there is an increase in depth, of the levels of all elements in all the samples collected in the three areas, mainly in the rainy season.

In general, in the sediments of the alluvial plains (areas A2 and A3) and in those deposited on the creek margins (area A1), mostly above water level throughout the year, metal distribution in depth is seasonal, with preferred accumulation on the surface during the dry period, and on deeper layers after the rainy season. This pattern may be due to an increase of the stream flow, with consequent increase of interstitial water circulating through the sediments, dragging the most runoff, but rather as variably soluble salts in surficial porewater and groundwater.

The Enrichment Factors (EF) was calculated using Fe as the standard element, since it did not represent a contaminant fin the area because it is very abundant in the local geology. The results were classified according to the adapted classification of Nude (2011) (in Pinho 2013, Martins 2014, Pinho 2018), which assumes five classes: (1) Min. Enr – Minimum Enrichment; (2) Mod. Enr. – Moderate Enrichment; (3) SE – Significant Enrichment; (4) VHE – Very High Enrichment; (5) EHE – Extremely High Enrichment. The elements Cd, Pb and Zn were identified as those that presented factors of VHE and EHE in all the areas. In relation to As, SE is verified for areas A1 and A3, highlighting in area A2 the classification from SE to EHE. For Cu and Mn, Mod. Enr. to SE in areas A1 and A3, and VHE in area A2, may be related to occasional contamination and to the regional geology rich in Fe-Mn oxides. The Figure 3a) gives an overview of the identified enrichments, where the occurrence of VHE to EHE is verified in all the areas, especially in areas A1 and A2 whose most samples belong to these more enriched classes mainly for Cd, Pb and Zn. The lowest enrichments (Min. Enr., Mod. Enr., SE) of the remaining elements (As, Co, Cr, Cu, Mn and Ni) mostly occur in samples belonging to areas A1 and A3. The Index of Geochemical Load (IGL) was classified according to seven categories, taking into account the concentrations obtained in mg.kg$^{-1}$: (1) Uncontaminated (UN): <0; (2) Uncontaminated to Moderately Contaminated (UN-MC): 0–1; (3) Moderately Contaminated (MC): 1–2; (4) Moderately Contaminated to Highly Contaminated (MC-HC): 2–3; (5) Highly Contaminated (HC): 3–4; (6) Highly to Extremely Contaminated (HC-EC): 4–5; (7) Extremely Contaminated (EC): >5 (Nude 2011, Trindade 2012, Martins 2014, Pinho 2018). Similar to the results obtained for EF, there were also high IGL values for the main contaminants in the area (Cd, Pb and Zn). For these three more problematic metals, IGL was classified as MC-HC, HC, HC-EC and EC for all the areas. In less contaminated classes (UN-MC and MC) and in a few samples in UN, Pb was classified in the areas A1 and A2 (Figure 3b). IGL values for Fe and Mn

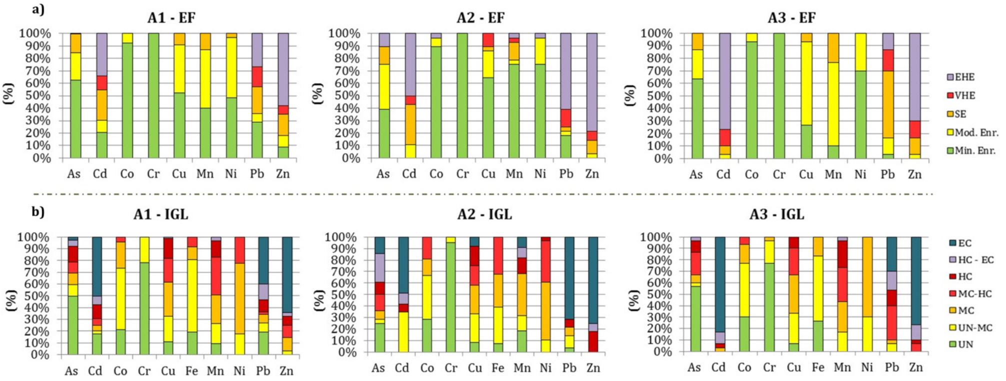


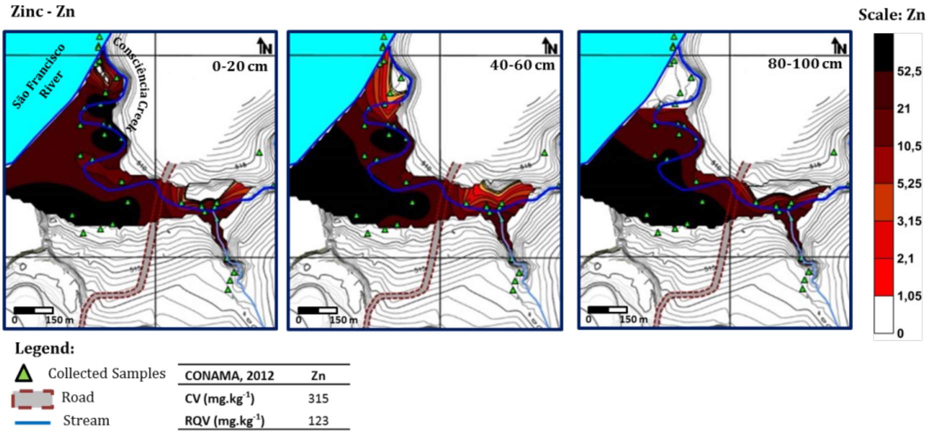
*Figure 3* *Classification the levels obtained through the EF and IGL indices.*

range between UN and HC in the three areas with area A2 presenting classifications of EC and HC-EC only for Mn. According to this indices classification, lower contamination was found in Co, Cr, Cu and Ni, ranging, in all the areas, between UN and MC-HC. Only in the A2 area only for Cu, IGL was classified as HC and EC. Thus, the occurrence of IGL with elements in the classes belonging to the most contaminated levels is verified for all the areas, with less representation in areas A1. The Contamination Factor (CF) classifies metals abundances into four categories in mg.kg$^{-1}$: (1) Low level of contamination (LLC): <1; (2) Moderate level of contamination (MLC): 1–3; (3) Considerable level of contamination (CLC): 3–6; (4) High level of contamination (HLC): >6 (Nude 2011, Martins 2014, Pinho 2018). CF, like EF and IGL, identified Cd, Pb and Zn as the most contaminating elements with most samples classified with high levels of contamination (HLC). Only for As in area A1, and for Mn in all the areas sediments have considerable level of contamination (CLC). The remaining elements, with significantly lower levels compared to the critical levels (Cu, Co, Fe and Ni) area classified as MLC.

Spatial distribution maps of the concentrations of acid-extractable fractions of metals have been constructed in order of obtaining an over view of the dispersion of the most relevant elements throughout the area and in depth. The classes used have been adapted according to the limits considered for each element by CONAMA (2012). The software, based on the kriging method, was SURFER12. Figure 4 shows the maps built for Zn. This element has a heterogeneous distribution in either for sediments collected closer to the waterway or at those located further away, but always with values higher than the critical ones (CV; CONAMA 2012). Although concentrations are mostly above the CVs, there is a decrease in sediments accumulated at the margins of Consciência creek and near the mouth with São Francisco River, visible at 40-60 cm in depth. This decrease may be due a result of the natural attenuation caused by the diluting effect the rainwater, the stream and the river.

## Conclusion

The geochemical characterization of sediments deposited in a floodplain on a in the margins and bed of a narrow waterway near an industrial unit identified Cd, Pb and Zn as elements with higher environmental hazard, as their contents are much higher than the CV proposed by current environmental standards. The quality parameters attained from the application of three selected indices proved to be very similar to each other, also indicating these three metals as the main contaminants. However, making a comparison between the three, EF and IGL show as greater agreement. CF is the index that allows the simplest identification of the main contaminants in the area, although it also depends directly on the reference values. The use of any of these indices and



| CONAMA, 2012 | Zn |
|---|---|
| CV (mg.kg$^{-1}$) | 315 |
| RQV (mg.kg$^{-1}$) | 123 |

***Figure 4** Spatial distribution of the levels obtained for Zn in the study area.*

the analysis of their results was carried out bearing in mind all the interferences to which they are subject, without any disadvantages for anyone, which is why they were used together in order to allow a more reliable characterization. The spatial and depth distribution of the contents of these elements allowed a visualization of the contaminants evolution throughout the whole area, with the subsequent identification of zones of possible natural attenuation. The proposal of an appropriate remediation methodology for this area will have to be based on in situ techniques, with preferential application in the dry season, in order to minimize the effects of dispersion of contaminants by dissolution, In the alluvial area, the capping technique to increase its infiltration capacity, followed by the construction of a Permeable Reactive Barrier with a "funnel and gate" configuration and impermeable lateral areas, is suggested as the most appropriate in order to guarantee its greater effectiveness.

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