



## BACKGROUND VALUES FOR CHEMICAL ELEMENTS IN SEDIMENTS OF THE GUALAXO DO NORTE RIVER BASIN, MG, BRAZIL

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### ABSTRACT

The aim of this study was to establish local background values for Fe, As, Pb, Mn, Ba, Zn and Ni using sediments from cutbanks and alluvial terraces of the Gualaxo do Norte River basin, Minas Gerais State, Brazil. A total of 16 stratigraphic sections were surveyed along the basin and 120 samples were analyzed. To establish background values we took into account mineralogical and grain-size analyses, faciologic interpretations, geochemical evaluations (by means of *aqua regia* partial digestion and ICP-OES readings), and the application of statistical techniques (boxplot representations, iterative  $2\sigma$  technique, cumulative frequency curve and calculated distribution function). The results reveal relatively high background values for As, Pb, Mn, Ba, Zn and Ni (respectively 64.2; 43.8; 1636.0; 141.4; 65.3 and 39.0 mg.kg<sup>-1</sup>). The concentrations of these elements are possibly related to the local geology, being the concentrations higher than these values linked to mining activity in the study region, in special gold mining. On the other hand, the background values established for Fe is lower than the values identified in the majority of the sections analyzed. The background value established for Fe corresponds to a concentration of 8.2%. However, concentrations higher than 48% were identified in the study area. There is a strong evidence of Fe enrichment due to mining at the head of the basin. In conclusion, we can say that the proposed values are important parameters for local environmental/territorial management and may help alerting public managers of the necessity of remediation of certain sites, where anomalous toxic element concentrations are identified.

**Keywords:** environmental contamination, heavy metals, reference values, environmental geochemistry and iron mining

### RESUMO

**Valores de *background* para elementos químicos em sedimentos da bacia do rio Gualaxo do Norte, MG, Brasil.** Este estudo teve como objetivo estabelecer valores de *background* locais para os elementos

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Fe, As, Pb, Mn, Ba, Zn e Ni, utilizando sedimentos de *cutbanks* e terraços aluviais da bacia do rio Guaxo do Norte, MG, Brasil. Um total de 16 perfis estratigráficos foi levantado ao longo da bacia e 120 amostras foram analisadas. No estabelecimento dos valores de *background* consideraram-se análises mineralógicas, granulométricas, interpretações faciológicas, avaliações geoquímicas (por digestão parcial com água régia e leitura via ICP-OES) e aplicação de técnicas estatísticas (representações *boxplot*, técnica iterativa  $2\sigma$ , curva de frequência acumulada e a função de distribuição calculada). Os resultados evidenciam valores de *background* relativamente elevados para os elementos As, Pb, Mn, Ba, Zn e Ni cujas concentrações possivelmente estão relacionadas com a geologia local, estando as concentrações superiores a esses valores ligadas a atividades de exploração mineral, especialmente a aurífera. Para o Fe o valor de *background* estabelecido é inferior aos valores identificados na maioria dos perfis analisados. O valor de *background* estabelecido para o Fe correspondeu a uma concentração de 8,2%. No entanto, concentrações superiores a 48% foram identificadas na área de estudo. Nesses casos, há forte evidência de enriquecimento do elemento pela mineração do elemento na cabeceira da bacia hidrográfica investigada. Em conclusão, pode-se dizer que os valores propostos são importantes para a gestão ambiental/territorial local, servindo de subsídios para a confecção de guias de alerta aos gestores públicos com relação à necessidade de remediação de locais onde são identificadas concentrações anômalas de elementos tóxicos.

**Palavras-chave:** contaminação ambiental, metais pesados, valores de referência, geoquímica ambiental e mineração de ferro

## INTRODUCTION

Gałuszka (2007) highlighted the need in recent environmental studies to establish of background values for chemical elements and organic compounds in biotic and abiotic systems. Interference of natural distributions and alterations caused by anthropogenic activities is an important issue, with important implications in geological, toxicological and biologic studies. This is especially important when dealing with geochemical analyses of toxic elements.

As discussed in Reimann and Garret (2005), there is no clear definition for the term geochemical background. However, many authors, including Matschullat *et al.* (2000), Reimann *et al.* (2005) and Gałuszka (2007), define geochemical background as a reference to distinguish natural concentrations of a certain element from the concentrations affected by anthropogenic activities, considering temporal and spatial variables of the area under investigation. For these authors, the establishment of geochemical background values for certain elements is crucial, because it enables the separation of geogenic contributions to a certain environment (*i.e.*, waters, soils, sediments, plants) from those of anthropogenic origin. Once these values are established, it is possible, for example, to elaborate geochemical maps focusing on the geoenvironment. These maps are considered important tools to territorial management and can be turned into alert guides to public managers, warning them on the necessity of remediation of sites where anomalous concentrations of toxic elements are identified.

There are a large number of methodologies to establish geochemical background values, which are recurrent in several studies (Matschullat *et al.*, 2000; Reimann *et al.*, 2005; Gałuszka, 2006; Mrvić *et al.*, 2011; Zhang *et al.*, 2011). Among the methods that are usually used in studies involving the determination of the background of chemical elements, direct (geochemical) and indirect (statistical) methods stand out.

The geochemical method is based on the analysis of samples known to be free of anthropic inter-

ference (Crommentuijn, *et al.* 2000; Baize and Sterckeman, 2001; Horckmans *et al.*, 2005). Background values are determined using mean metal concentration values obtained for an area or sedimentary deposit that has not undergone anthropogenic interference. The indirect method, also named statistical method, demands the specific knowledge of exploration methods for which the relationship cost/surveyed area is preferably low. The intrinsic characteristic of such method is the use of finite statistical samples, which constitute the whole or part of a population represented by samples effectively collected and from which the required quantitative data are obtained (Frizzo *et al.*, 2007). By means of procedures or statistical techniques performed by appropriate softwares, the data set relative to different chemical elements is analyzed and from this analysis it is possible to interpret the data and make considerations and inferences on the sampled population and consequently on the study area. Among the statistical methods, the following have been widely applied: the iterative  $2\sigma$  technique, the cumulative frequency curve in linear scale, boxplot representations, histograms, among others (Teng *et al.*, 2009; Costa *et al.*, 2010; Peh *et al.*, 2010; Mrvić *et al.*, 2011; Zglobicki *et al.*, 2011; Mrvić *et al.*, 2012).

However, difficulties are encountered when trying to establish a system comprehensive enough to encompass reference patterns for heavy metals, in order to evaluate areas suspected to be contaminated. Such difficulties result from the lack of systematic studies and mainly of particularities intrinsic of each study area. In Brazil, a few studies have been developed with the objective of understanding and/or differentiating the influence of geogenic and anthropic contributions in the dynamics of contaminating elements. Despite some studies exist that put in evidence the presence of heavy metals in fluvial sediments (Lewin and Macklin, 1987; Taylor and Lewin, 1996; Brewer and Taylor, 1997; Eleutério, 1997; Costa, 2001; Costa *et al.*, 2010), studies that aim at establishing reference patterns for such elements are scarce, in particular when the objects of study are deposits formed at different times, such as recent and older sediments (cutbanks and alluvial terraces, respectively). The establishment of geochemical background values taking into account not only the chemical element concentrations, but also geologic, facilogic and mineralogic characteristics, has not been very much practiced. In Brazil pioneer studies applying this approach were carried out only by Costa (2007) and Costa *et al.* (2010).

In this context, this work aims at establishing local geochemical background values for Fe, As, Pb, Mn, Ba, Zn and Ni, using sediments from cutbanks and alluvial terraces of the Gualaxo do Norte River basin, Minas Gerais, Brazil. The anthropic activity in the Gualaxo do Norte River area is intense, particularly iron ore and gold mining, the latter having been practiced in the last 300 years. We hope that this study can contribute for the elaboration of environmental and public health political plans, which can minimize the impacts caused by mining activities in the study region.

## MATERIAL AND METHODS

Samples from eight cutbanks and eight alluvial terraces located along the Gualaxo do Norte River basin were collected. The head is northeast of Ouro Preto and northwest of Mariana (Fig. 1). The basin crosses several units of the Quadrilátero Ferrífero, which is considered one of the largest and well-known areas for mineral deposits of the world, and one of the most important mining regions of Brazil (Deschamps *et al.*, 2002; Roeser and Roeser, 2010). The Gualaxo do Norte River spring is situated in the domain of the Minas Supergroup supracrustal rocks, *i.e.* quartzites, itabirites and phyllites, whereas its

medium and lower courses run through the Santa Bárbara, Acaiaca and Mantiqueira Metamorphic Complexes, and also the Rio das Velhas Supergroup schists and quartzites (Costa, 2001).

At the locations where cutbank and alluvial terrace deposits were identified (Figure 1) sections were drawn documenting the facies, similarly to the method adopted by Costa *et al.* (2010). Sediment samples from all strata were collected for grain-size, mineralogical and geochemical analyses, totaling 120 samples. To determine chemical element concentrations, fractions of grain-size less than 63  $\mu\text{m}$  were partially digested with aqua regia, following Rauret *et al.* (1999) and Shiowatana *et al.* (2001) recommendations. The analyses were carried out at the Environmental Geochemistry Laboratory (Degeo/UFOP), by means of atomic emission spectrometry (ICP-OES – Spectro, model Ciros CCD).

For  $\text{C}^{14}$  dating, samples of carbonaceous material found in some stratigraphic sections were collected.  $\text{C}^{14}$  dating was performed by the Radiocarbon Laboratory of the University of Waikato of New Zealand (equipped with an Accelerator Mass Spectrometer). It is worth mentioning that the geochronologic data thus obtained helped correlate the anomalous chemical element concentration levels with the deposition age, making the understanding of the relationship between these values and mining activities in the study area possible.

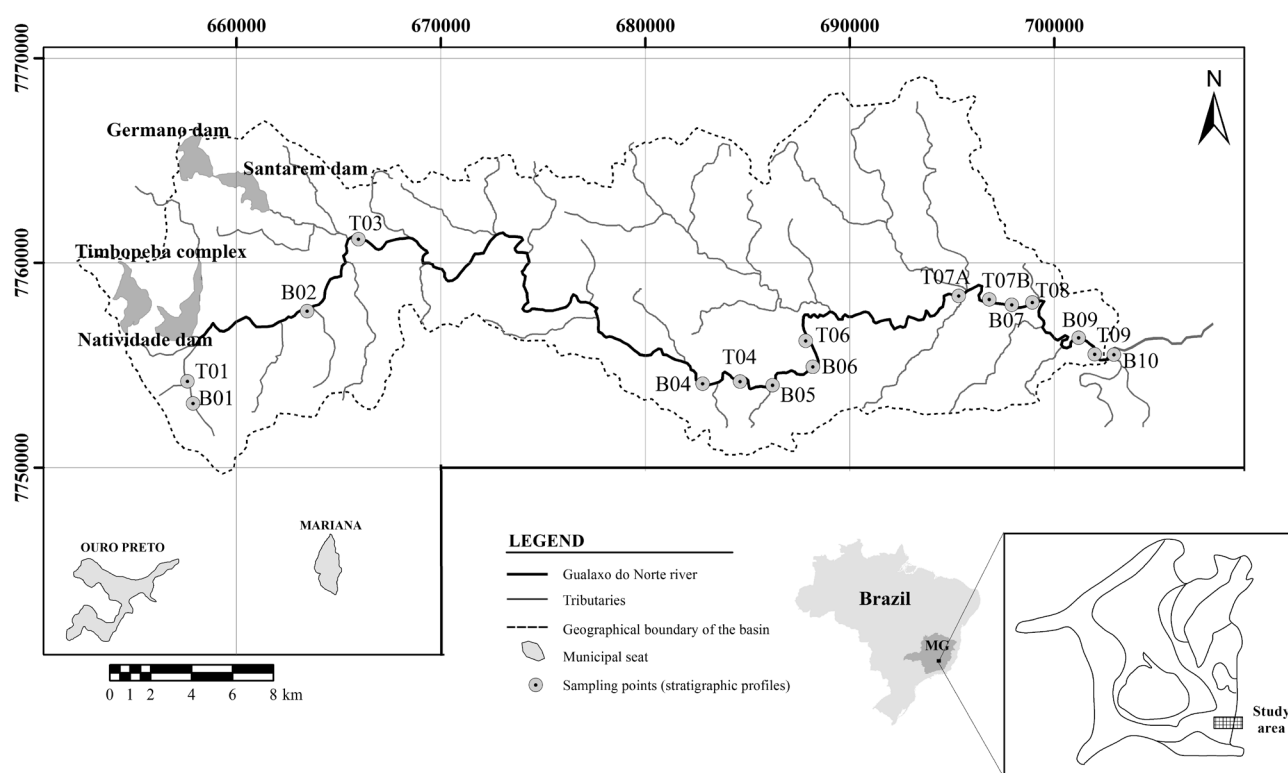


Figure 1. Geographic location of the Gualaxo do Norte River basin, Minas Gerais, Brazil, and sampled points.

It is important to stress that all the analyses were useful in the recognition of anthropogenic influence in chemical element concentrations. Efforts were made to eliminate biases that could cause overestimation of the results obtained. Samples from sediments that were known to have been affected by anthropogenic activities were analyzed separately from those with no evidence of anthropogenic metal enrichment. Prior to the application of the specific techniques for the determination of background values, the original data consisting of chemical element concentrations were treated by means of a descriptive exploratory analysis. This step was necessary in order to check the statistical and mathematical properties of the data,

as recommended by Burrough *et al.* (1996). In the present study the following descriptive exploratory techniques were adopted: tests for normality (Anderson-Darling, Lilliefors, Kolmogorov-Smirnov), mean, median, standard deviation, maximum, minimum, dispersion graphs, histograms, parametric and non-parametric tests for mean comparison, among others. All these techniques helped identifying trends, discrepant points, distribution types, choose the analysis to be applied and characterize variability.

Specific techniques were chosen for the determination of local geochemical background values. Because many techniques can be used in geochemical background studies and because all of them have advantages and disadvantages, more than one statistical technique was applied in this work, such as: boxplot representations, iterative  $2\sigma$  technique, cumulative frequency curve and the calculated distribution function. The use of some of these techniques can be observed in the following studies: Panno *et al.* (2006), Díez *et al.* (2007), Micó *et al.* (2007), Galán *et al.* (2008), Pérez-Sirvent *et al.* (2009), Teng *et al.* (2009), Costa *et al.* (2010), Nakić *et al.* (2010), Peh *et al.* (2010), Guillén *et al.* (2011), Mrvić *et al.* (2011) and Zglobicki *et al.* (2011).

The results obtained from the application of different techniques were analyzed and the background values were established from the arithmetic mean of the values obtained by each technique. Such decision was based on the method adopted in Zglobicki *et al.* (2011). It is stressed out that the statistical techniques adopted in this work are similar to those adopted by Zglobicki *et al.* (2011). Four statistical techniques were used to establish the background values, namely: boxplot representations (Tukey 1977), cumulative frequency curves (Lepeltier, 1969; Matschullat *et al.*, 2000), iterative  $2\sigma$  technique (Erhardt *et al.*, 1998; Matschullat *et al.*, 2000) and calculated distribution function (Matschullat *et al.*, 2000). A detailed description of the statistical techniques used is given below, followed by the results obtained for Fe, As, Pb, Mn, Ba, Zn and Ni.

## Statistical Methods

### *Boxplot representations*

The method proposed by Tukey (1977) was adopted to define background values by means of boxplot representations. Initially, ranges were determined by delimiting the interquartile (IQ) range augmented 1.5 times. From the range thus obtained the background value was considered as the upper limit given by  $[UL=Q3+1/2(1.5IQ-IQ)]$ , where UL = upper limit and Q3 = upper quartile. The Minitab® software was used to draw the boxplot representations.

### *Cumulative frequency curves*

The establishment of background values for the chemical elements chosen was also carried out using an approximation of the Lepeltier (1969) statistical method, which is the cumulative frequency curves in linear scale, as also proposed by Matschullat *et al.* (2000). In a general way, the original data are plotted in a spreadsheet and the curves are drawn by a statistics software (in this case, Minitab®). For the analysis of the curves and subsequent establishment of background values, the procedure proposed by Costa *et al.* (2007) was taken as a basis, which helps to evaluate variations in the data populations by means of inflexion points in the curves. The following cases occurred in the present study:

1. Two inflection points: This clearly indicates the existence of three distinct data populations. In this case, a range is defined from the lower to the upper inflection points. This range represents the most homogeneous data of the whole data set and the background value is defined as the upper limit of this range.
2. Multiple inflection points: The presence of several populations is observed in this case. Their characteristics may have been influenced by natural or anthropogenic factors. The establishment of background values must take into consideration the homogeneity of the data within each defined population. In other words, the background population will be that most representative of the whole data set and the background value will be the upper limit of such population.
3. Iterative  $2\sigma$  technique: According to Erhardt *et al.* (1998) and Matschullat *et al.* (2000), the iterative  $2\sigma$  technique [ $\text{mean} \pm 2\sigma$ ] is mainly used to define background values because it approximates the original data set to a normal distribution. In practice, the technique consists in the calculation of the mean and the standard deviation ( $\sigma$ ) of the data set. After that, all the values outside the range [ $\text{mean} \pm 2\sigma$ ] are excluded. Such procedure is repeated until all the values of the remaining data set are constrained to the range [ $\text{mean} \pm 2\sigma$ ] (Matschullat *et al.*, 2000). This range is then considered the background range for the analyzed element and the background value is the upper limit of this range.

To apply this technique the freeware Visual Basic macro entitled VB *Background*<sup>®</sup> (MS Excel) and developed by Nakić *et al.* (2007) was used. According to these authors, VB *Background*<sup>®</sup>, as it incorporates algorithms of the iterative  $2\sigma$  technique, allows the automated treatment of the geochemical data, making the generation of background values for chemical parameters possible. At the same time, the macro generates a graphic representation that helps the interpretation of the data.

### ***Calculated distribution function***

The calculated distribution function, as described by Matschullat *et al.* (2000), aims at defining the upper limit of natural concentrations. The use of such technique is recommended when anthropogenic activities tend to cause enrichments in the natural systems, causing positive anomalies shown in a distribution function as a positive asymmetry of a normal curve (Nakić *et al.*, 2007). The lowest values must therefore be free of anthropic influence (Matschullat *et al.*, 2000). For the application of this technique the macro VB *Background*<sup>®</sup> was also used.

Algorithms based on the calculated distribution function are used to calculate the median of the original data set and all the values above the median are eliminated. Then, VB *Background*<sup>®</sup> “mirrors” all the remaining values against the calculated median value, according to: [“mirrored” value = median – value of each datum + median] (Nakić *et al.*, 2007). The macro calculates the mean and the standard deviation for the prepared data and the range [ $\text{mean} \pm 2\sigma$ ]. After calculating [ $\text{mean} \pm 2\sigma$ ], all the values outside the calculated range are excluded. Next, the macro calculates the accumulated normal distribution for the new mean and the standard deviation. Finally, the macro generates a graph showing a histogram (for the original data and the background range), as well as the cumulative frequency curve for the original data and background and the normal distribution curve.

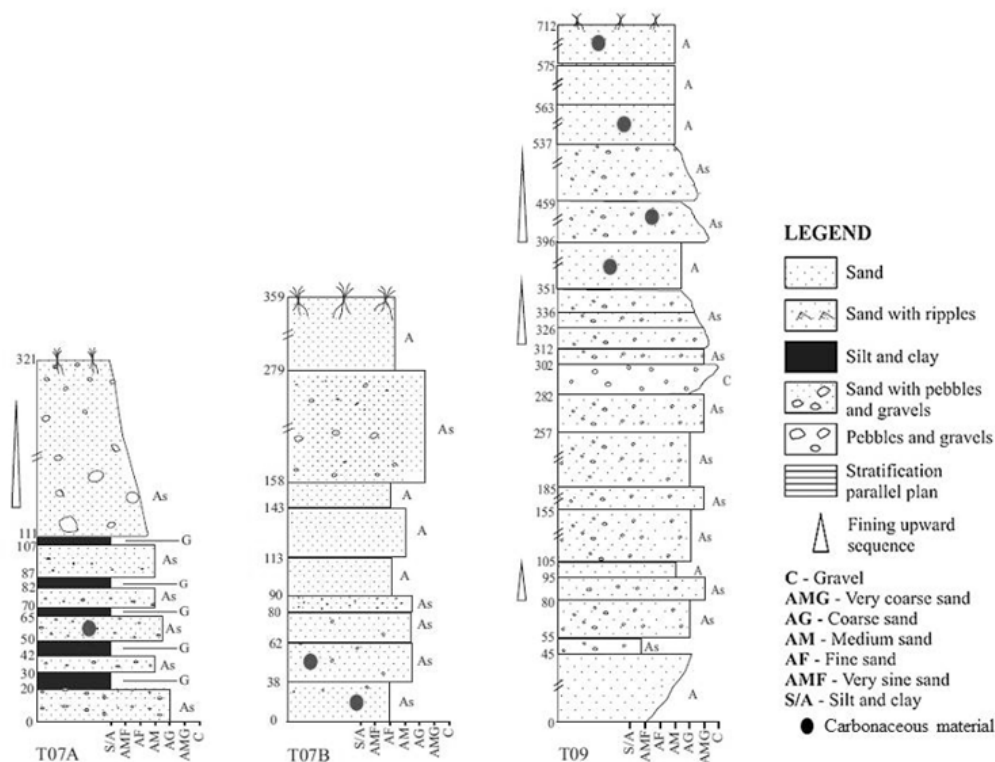
It is worth mentioning that both the iterative  $2\sigma$  technique and the calculated distribution function

have the advantage of not requiring that the combined (processed) total data follow normal or log-normal distribution, and can be applied to a relatively small data set ( $n > 30$ ) (Nakić *et al.*, 2007). Besides, both techniques calculate the normal range of background values with 95% confidence. The macro VB *Background*<sup>®</sup> supplies the  $T$  and critical  $T$  ( $T_{crit}$ ) values from the Lilliefors (1969) normality test, which is an adaptation of the Kolmogorov-Smirnov procedure. The application of such techniques is considered valid only when  $T$  is lower than  $T_{crit}$ . If  $T$  is higher than  $T_{crit}$ , the number of anomalous samples is larger or equal to the number of background samples, which means that the background values are overestimated.

For some elements the statistical techniques were applied to the whole data set with no distinction between those coming from the cutbanks or from alluvial terraces, whereas for others, the data were analyzed separately.

### RESULTS AND DISCUSSION

Regarding Fe, samples unaffected by anthropogenic interference were chosen. Mining upstream the Gualaxo do Norte River basin causes increase in Fe concentrations in sediments. The samples were collected in the T07A, T07B and T09 terraces for which  $C^{14}$  dating of carbonaceous material revealed ages older than 80 years (Figure 2). This age is previous to the installation of iron ore mining activities, which started approximately 40 years ago in the basin.



Samples	Sample 1 (T07A)	Sample 2 (T07B)	Sample 3 (T09)
Results from dating	105 ± 30 BP	131 ± 0.5 BP	81 ± 30 BP

Figure 2. Alluvial terraces used to establish the background range for Fe and the results of  $C^{14}$  dating of carbonaceous materials.

Once the samples to be analyzed were chosen, the statistical techniques to determine the background range were applied, excepting the cumulative frequency curve. Such technique was discarded since it is not recommended for a sample sets with  $n < 50$  (Matschullat *et al.*, 2000). The values obtained for Fe and other elements are presented in Table 1.

Table 1. Background ranges established for the elements studied in this work.

Statistical Techniques	Elements (mg/kg <sup>-1</sup> , except Fe)						
	Fe (%)	As	Pb	Mn	Ba	Zn	Ni
<i>Boxplot</i>	9.1	-	-	-	-	68.2	38.6
Cumulative frequency curve	-	61.3	44.3	-	-	61.2	41.4
2 $\sigma$ iterative technique	7.3	56.5	43.3	1400.0	129.0	62.2	35.9
Calculated distribution function	8.3	74.8	-	1872.0	153.8	69.7	40.1
<b>Average of the background values obtained</b>	<b>8.2</b>	<b>64.2</b>	<b>43.8</b>	<b>1636.0</b>	<b>141.4</b>	<b>65.3</b>	<b>39.0</b>

Note: (-) technique not applicable to the analyzed data set.

Fe concentrations up to 8.2% can be associated with supracrustal rocks from the Rio das Velhas and Minas supergroups, which are enriched in Fe oxides. In the specific case of the study area, there are evidences that an increase of iron in fluvial sediments is related to iron ore mining activities located upstream. Leakage from Fe oxide-rich tailings causes Fe enrichment in sediments along the basin's main water course. Higher Fe concentrations were detected in the bank sediments of the main river (>20%), when compared to the Fe concentrations in the sediments of its tributaries (<12%) (data not discussed in this article). Visual observation reveals the deposition of dark, fine sediments rich in Fe oxides along the basin's main river and not along its tributaries.

The establishment of background values for As was based on three statistical techniques: cumulative frequency curve, iterative 2 $\sigma$  technique and calculated distribution function, applied to the whole sample set (no distinction between cutbanks and terraces). The boxplot representation was not used because, according to Reimann *et al.* (2005), it is more informative when the number of outliers is less than 10%. In our case, the number of anomalous samples represented 13.6% of the total analyzed for As, thus making the use of this technique less usefull.

It is necessary mentioning that all samples of all sections were used for the establishment of the background value for As, as no geochronological data were available to justify selection of samples. Samples older than the historical gold mining activities were not identified, although As concentrations in the alluvial terraces T07A, T07B, T08 and T09 were not directly or indirectly related to anthropogenic activities (Table 1).

The relatively high As concentrations (up to 64.2 mg.kg<sup>-1</sup>) (Table 1) can be linked to natural As enrichment, possibly originated from the presence of sulfides, sulfoarsenides and arsenides such as arsenopyrite, which is common in the study area. Besides, As can also be associated with the crystalline structures of primary minerals, silicates or aluminates, constituting an inert or residual fraction of the sediments. However, it is important to stress out that anomalous As concentrations were identified, and could be related to historical gold mining activities. In this case, As sulfide-enriched tailings would be



made available from source areas associated with gold mineralization and enriched in deposition areas downstream.

The anomalous As concentrations were identified in facies characterized by the presence of stratigraphically disordered gravels and boulders, where predominant minerals are quartz, magnetite, hematite, feldspar, gibbsite, kyanite and tourmaline. These facies are interpreted as canals with direct or indirect interference of mining activities such as digging or dredging. The excellent sorting of coarse grains observed in these facies is not expected from natural processes operating in fluvial systems. Such sorting resulted from rudimentary techniques such as the use of transversal dikes to break the water course, which forced the dredged sediments to deposit, washing the heavier sediment in the pans or carpets. Moreover, such sorting can also result from rudimentary mining by means of picking, where gravel is also separated. In the study region bombs were intensely used to remove fine sediments and force canal deviations.

As for arsenic, the establishment of background values for Pb was based on the cumulative frequency curve and iterative  $2\sigma$  techniques, using all the analyzed samples (cutbanks and terraces). The boxplot representation, in this case, was not used, since the number of outlier values corresponded to 24% of the data set, making the use of this technique less useful (Reimann *et al.*, 2005). The calculated distribution function technique was discarded due to  $T$  being higher than  $T_{crit}$ . The background values are presented in table 1.

Pb concentrations up to  $43.8 \text{ mg.kg}^{-1}$  can be of natural origin, specifically related to the host rocks (Rio das Velhas Supergroup) of gold mineralization, associated with sulfide veins. On the other hand, it is possible that the concentrations higher than this value are related to human activities causing Pb enrichment in fluvial sediments. The observation of high Pb concentrations in all samples (median of  $81.1 \text{ mg.kg}^{-1}$ ) collected in sections located in the head of the basin (B01, B02, T01 and T02) corroborates the hypothesis of Pb enrichment due to gold and iron ore mining. Both As and Pb occur naturally in the rocks hosting the gold mineralization, associated with sulfide veins exposed when the mines are open for gold extraction. Besides, Pb can also be associated with galena (PbS), which occurs in deposits associated with Fe. The strong correlation between Fe and Pb ( $\rho=0.97$ ) seen in section T01, for example, attests for this hypothesis (Table 2). In section T03, the strong positive Fe-Pb correlation and the weak correlation with other elements (Table 3) show a pattern similar to the observed in terrace T01. In addition, Pb can be associated with Fe and Mn oxides-hydroxides that envelope clay particles, as indicated by the strong correlation between Al and Pb concentrations ( $\rho>0.85$ ) (the clay particles present aluminosilicatic composition).

Table 2. Spearman correlation matrix for the concentrations of some trace elements identified in section T01.

	<b>Ba</b>	<b>Be</b>	<b>Co</b>	<b>Mn</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Ba</b>	1						
<b>Be</b>	0.994	1					
<b>Co</b>	0.619	0.611	1				
<b>Mn</b>	0.905	0.922	0.81	1			
<b>Pb</b>	-0.683	-0.705	-0.168	-0.539	1		
<b>Zn</b>	0.952	0.934	0.762	0.905	-0.455	1	
<b>Fe</b>	-0.762	-0.79	-0.262	-0.667	0.97	-0.545	1

Table 3. Spearman correlation matrix for the concentrations of some trace elements identified in section T03.

	<b>Ba</b>	<b>Be</b>	<b>Co</b>	<b>Mn</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Ba</b>	1						
<b>Be</b>	0.741	1					
<b>Co</b>	0.327	0.68	1				
<b>Mn</b>	0.786	0.815	0.218	1			
<b>Pb</b>	0.071	-0.185	-0.327	0.286	1		
<b>Zn</b>	0.786	0.445	-0.054	0.75	0.571	1	
<b>Fe</b>	0.214	-0.111	-0.436	0.429	0.964	0.679	1

For Mn, background values were proposed from samples collected in terraces T07A, T07B and T09. The choice of these terraces is justified by the fact that they are older than the Miguel Congo manganese mine exploitation (intensely mined in the 1980's), localized in the upper Gualaxo do Norte River basin. The data were analyzed via the iterative  $2\sigma$  technique and the calculated distribution function. The boxplot representation was discarded, once anomalous values represented more than 12% of the total data set related to the alluvial terraces, making the use of this technique impossible. The frequency curve was discarded because the number of samples analyzed was less than 50.

It is considered as local background value for Mn the concentration of  $1,636 \text{ mg.kg}^{-1}$ . It is important to stress out that Mn concentrations are usually high in the study area and are mainly associated with Fe occurrences, being such elements siderophile or lithophile. The Mn exploitation in the Miguel Congo mine corroborates to the hypothesis that high Mn concentrations are natural in the basin. However, it is worth mentioning that concentrations higher than the established background value can be directly linked with anthropic activities, which can mobilize Mn to the environment during and after mining operations. The median Mn concentration for the samples from the stratigraphic sections of the basin's upper course was  $12,180 \text{ mg.kg}^{-1}$ , whereas in the sections located farther from the head the median was  $1,040 \text{ mg.kg}^{-1}$ . A concentration higher than  $26,000 \text{ mg.kg}^{-1}$  was found in the upper stratum of cutbank B01 (set 30-38 cm), located in the basin's upper course.

As for Mn, background values for Ba were obtained using the samples from terraces T07A, T07B and T09, once they are older than the Mn mining in Miguel Congo. In the sections of this part of the basin (T01, T03, B01 and B02) a strong correlation was observed between Ba and Mn ( $p > 0.81$ ). Such correlation could justify the availability of both elements in the sediments as a consequence of mining. High Ba concentrations were observed in all points sampled in the basin's upper course, as shown by Costa (2001), when investigating canal and flood plain sediments. The author attested high Ba concentrations (from  $458.0$  to  $655.0 \text{ mg.kg}^{-1}$ ) in all points sampled in the upper course of the Gualaxo do Norte river basin. Besides, Cabral *et al.* (2002) report the existence of Mn minerals with important Ba contents in the Quadrilátero Ferrífero, which corroborates to the hypothesis of a common origin for these elements. The data were treated applying the following statistical techniques: iterative  $2\sigma$  and calculated distribution function. The boxplot representation and cumulative frequency curve were discarded for the same reasons presented for Mn. The proposed background values are given in table 1.

Ba concentrations up to  $141.4 \text{ mg.kg}^{-1}$  may be linked to the natural presence of the element, which

complexes with clays (kaolinite and montmorillonite) and Fe or Mn oxides-hydroxides. However, concentrations higher than this value seem to be related to gold occurrences, as mining plays an equally important role in increasing Ba in sediments (Table 1).

The establishment of background values for Zn was made by means of the four statistical techniques mentioned before and using the whole sample set. The use of all samples is justified because Zn concentrations in the cutbanks and alluvial terraces do not show statistically significant differences ( $p = 0.29$ ) according to the Mann-Whitney test. The background value established for Zn is  $65.3 \text{ mg.kg}^{-1}$ . Concentrations up to this value can be associated with the occurrence of sulfide-bearing rocks containing chalcopyrite and galena. On the other hand, concentrations above the established background value could be explained by enrichment caused by anthropogenic activities, especially gold mining, which also mobilizes the element to fluvial sediments. According to Rodrigues-Filho and Maddock (1997), in gold mining areas during ore beneficiation, dense elements such as Zn can be concentrated, causing the contamination of waters and sediments.

Also for Ni, the background values were established applying the four techniques previously described and using all samples analyzed. The background value established for Ni is  $39 \text{ mg.kg}^{-1}$ . Ni is a siderophile element, found in more than 80 minerals, relatively high concentrations occurring in ferromagnesian minerals and sulfides, which are common in the study area.

To determine and distinguish the geogenic or anthropogenic origins of the concentrations of chemical elements in the ecosystem is of relevant importance, once they can attest actions in favor of environmental conservation and remediation, in cases of contamination or contamination potential. In this sense, studies that aim at proposing background values are necessary to decision making directed to the environmental issues. Not knowing them may cause under- or overestimation of the significance of contamination levels in a certain area (Hursthouse, 2001).

However, these same studies present peculiarities that many times lead to polemic and hard criticism. Such peculiarities are mainly related to the diversity of methods that can be used in the establishment of background values (and that vary from researcher to researcher) and the scarcity of studies, which many times make the comparison of results reported in the few existing works difficult or even impossible. As discussed by Poletto and Merten (2008), this difficulty increases due to the impossibility of a universalization of proposed values, because they are exclusive to a study area. Significantly high values can be obtained for a certain area and not for another, simply because of mineralogic/geologic differences in each of them, fact that makes it not meaning reliable to use data produced in other regions or countries.

When it comes to fluvial sediments, the lack of local, regional or national studies for the establishment of background values is even more important, due to the recognition that the majority of the few existing works establish background values for soil and water. In Brazil there is not a specific legislation that deals with toxic element or organic contaminant levels for the protection of the aquatic life that is valid throughout the Brazilian territory or at least in some states. Only one pioneer work named *QualiSed*, developed by researchers of the São Carlos Federal University (UFSCar), Campinas Statal University (Unicamp) and the São Paulo State Environmental Sanitary Technology Company (CETESB), is cited here. *QualiSed* aimed at collecting preliminary data for the Guide Values for Sediment Quality (VGQS) for metals and xenobiotic organic compounds (Mozeto, 2003). The data set gathered in this study formed

the basis for the project named Integrated and Hierarchic Evaluation of the Sediment Quality (AIHQs), in which VGQS in use in Canada and USA were employed as guides to certain actions (physical, chemical, biologic and ecotoxicologic analyses) taken at the different steps of the decision tree.

Despite *QualiSed*, there are no regulated and validated VGQS by Brazilian official environmental agencies. The legal instrument that is close to this “*regulation and validation*” is the #344 resolution of the National Environment Council (CONAMA). Such resolution was created aiming at establishing general guidelines and minimal procedures for the evaluation of the material to be dredged and the managing of it disposal (CONAMA, 2004). In the resolution two levels or limits for the material to be dredged are fixed: *level I*, which refers to a threshold below which low probability of adverse effects to the biota are expected, and *level II*, which refers to a threshold above which a probable adverse effect to the biota is expected. However, due to the lack of Brazilian studies that could support the proposal of national threshold values and the fact that this resolution is exclusively based on international recommendations, such as Canadian and North American, such resolution is faulty and in many cases the suggested VGQS do not reflect the Brazilian reality.

Internationally some studies have proposed VGQS, which in practice are scientific tools that synthesize information on the relationships between pollutant concentrations in sediments and any adverse effect resulting from the exposure to contaminants. Such studies have been conducted by several federal, state or provincial agencies, moreover in North America for fresh water and coastal and marine ecosystems. As reviewed by Silvério (2003), several VGQS can be found in the literature for metals in aquatic sediments: i) partition equilibrium (VGQS of the volatilizable sulfides by acidification and interstitial waters) (Ankley, 1996); ii) SEL (*severe effect level*) and LEL (*lowest effect level*) (Persaud *et al.*, 1993); iii) ERL (*effect range-low*) and ERM (*effect range-median*) (Long and Morgan, 1991); iv) TEL (*threshold effect level*) and PEL (*probable effect level*) (Smith *et al.*, 1996); v) AET (*apparent effect threshold*) (Alden and Rule, 1992); vi) TEC (*threshold effect concentration*) and PEC (*probable effect concentration*) (MacDonald, 2000), and vii) LRM (*linear regression model*) (Field *et al.*, 1999).

The VGQS proposed by the legislation of Canada (CCME, 2001), North America (USEPA, 2003) and Brazil (CONAMA, 2004) are presented in Chart 1 together with the background values proposed by Crommentuijn *et al.* (2000) (used by the Dutch government) and those proposed by Costa (2007), which are values obtained for the Ribeirão do Carmo basin, also in the Quadrilátero Ferrífero, using flood plain and alluvial terrace sediments. This last study is closest to our study region. As can be seen in Chart 1, there is a large variation regarding the values proposed by the different studies when compared to local background ranges proposed here. These differences specifically reflect the distinct natural or anthropized characteristics of the study areas, for which the values were proposed. Therefore, the comparison of the background ranges proposed here in relation to the values established by other studies is limited or inadequate to enable a classification of the concentrations obtained in this study.

Chart 1. Background values proposed for varied studies and those proposed in this work.

Reference	Elements (mg.kg <sup>-1</sup> )						
	As	Fe <sup>1</sup>	Pb	Ba	Mn	Zn	Ni
<b>Crommentuijn <i>et al.</i> (2000)</b>							
Negligible concentration (CN)	31.0	-	132.0	157.0	-	145.0	35.0
Maximum permitted concentration (CMP)	190.0	-	4800.0	300.0	-	620.0	44.0
Background concentration (CB)	29.0	-	85.0	155.0	-	140.0	35.0
<b>Canadian legislation (CCME, 2001)</b>							
TEL	5.9	-	35.0	-	-	123.0	18.0
PEL	17.0	-	91.3	-	-	315.0	35.9
<b>North-American legislation (EPA, 2004)</b>							
TEL	-	-	30.2	-	-	-	124.0
PEL	-	-	112.0	-	-	-	271.0
<b>Brazilian legislation (CONAMA, 2004)<sup>2</sup></b>							
Level 1	5.9	-	35.0	-	-	123.0	18.0
Level 2	17.0	-	91.3	-	-	315.0	35.9
<b>Costa <i>et al.</i> (2007)</b>							
Geochemical method <sup>3</sup>	2.0 (10.0)	-	-	25.0 (130.0)	218.0 (1911.0)	68.0 (513.0)	18.0 (104.0)
Statistical method <sup>3</sup>							
Ribeirão do Carmo Basin	35.3 (810.0)	-	-	18.5 (-)	189.8 (5800.0)	124.0 (-)	53.1 (-)
Clayey facies	10.2 (241.4)	-	-	18.1 (196.1)	189.7 (-)	118.9 (-)	12.0 (50.1)
Gravelly facies	229.3 (705.0)	-	-	51.9 (655.0)	398.1 (1694.6)	39.0 (124.0)	104.4 (-)
<b>The present study</b>							
	4.4–74.8	3.0–9.1	27.5–44.3	0–153.8	0–1872.0	28.7–69.7	11.9–41.4

<sup>1</sup>Values in percentage.

<sup>2</sup>The guiding values adopted by CONAMA (2004) are based on the *Canadian Council of Ministers of the Environment* (CCME, 2001); Long *et al.* (1995) and the *Florida Department of Environmental Protection* (FDEP, 1994).

<sup>3</sup>The numbers indicate the average and the maximum value (in brackets) of the obtained concentrations. (-): values not established or not found in the literature.

Arsenic is good example of the limitation and difficulty in comparing these data. The background value proposed here for As encompasses values that can represent adverse effects to the biota (>17 mg.kg<sup>-1</sup>), both by the Canadian and Brazilian legislations, once it is 64.2 mg.kg<sup>-1</sup>. Concentrations up to this value are considered basal and naturally present in the study area. The concentrations higher than “PEL” and “Level 2” and that are directly related to the geologic characteristics of the region where the Gualaxo river basin is installed. As already commented, the natural As enrichment can be related to the rocks hosting the gold mineralization, which are associated with sulfide veins exposed when the mines are open for gold extraction. On the other hand, in relation to the Background Concentration (CB) proposed by Crommentuijn *et al.* (2000) (29 mg.kg<sup>-1</sup>), this refers to approximately half of the value proposed in the present study. According to the authors, all the values proposed represent the percentile 90 of non-polluted

areas, which suggests that As enrichment in the study regions are natural. The difference basically consists of the fact that whereas concentrations larger than  $29 \text{ mg.kg}^{-1}$  are considered abnormal by Crommentuijn *et al.* (2000), in the present study concentrations up to  $64.2 \text{ mg.kg}^{-1}$  may not be related to human activities.

It is possible to compare, even with caution, studies developed in areas of similar geological characteristics. For example, high As concentrations observed by Costa (2007) in gravelly samples were also observed in the present study. Costa (2007) and our study, present similar characteristics and have been developed in neighboring regions, differences are perceived, which once again attests the difficulty in comparing results. Another example is given by As concentrations in the clayey facies. The present study evidenced higher As concentrations when compared to Costa (2007). A mean concentration of  $276.1 \text{ mg.kg}^{-1}$  (27 times higher) and median of  $238 \text{ mg.kg}^{-1}$  were obtained for clayey sediments. Besides, whereas the maximum concentration obtained by Costa (2007) in such sediment was  $241.2 \text{ mg.kg}^{-1}$ , we obtained a maximum concentration of  $570 \text{ mg.kg}^{-1}$ .

In light of the exposed above, the development of local or regional background studies, especially when it comes to sediment contamination, are necessary and important. From a practical viewpoint, the results here presented are an alert for the authorities responsible for environmental managing, moreover when there is evidence, even if natural, of high concentrations of highly toxic elements such as arsenic, which indicate potential risk to human health.

## CONCLUSIONS

The proposed background values are coherent with the local geologic characteristics, which must be taken into account both by environmental agencies (for pro-environmental decision making) and the academic community, in face of the necessity of continuing studies (in other areas) using the approach presented here. In order to propose background values, it is important to know the geology of the study area, so that biases, which can cause over or underestimation of the proposed values, are eliminated. Finally, the choice of the method to be used must be related not only to the geologic knowledge of the area, but also to the distinct deposition sites chosen for sampling. It is important to identify whether the sample was taken from old (possibly free of anthropogenic interference) or recent environments, in which anthropic activities can directly or indirectly affect the concentration of certain elements.

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## REFERENCES

- ANKLEY, G. T. *et al.* 1996. Technical basis and proposal for deriving sediment quality criteria for metals. **Environmental Toxicology and Chemistry**, **15**(1):2056-2066.
- BAIZE, D.; STERCKEMAN, T. 2001. Of the necessity of knowledge of the natural pedogeochemical background content in the evaluation of the contamination of soils by trace elements. **Science of the Total Environment**, **264**(1-2):127-139.
- BREWER, P.; TAYLOR, M. P. 1997. The spatial distribution of heavy metal contaminated sediment across terraced floodplains. **Catena**, **30**(2-3):229-249.
- BURROUGH, P. A.; VAREKAMP, C.; SKIDMORE, A. K. 1996. Using Public Domain Geostatistical and GIS Software for Spatial Interpolation. **Photogrammetric Engineering & Remote Sensing**, **62**(7):845-854.
- CCME, Canadian Council of Ministers of the Environment. 1999. **Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0, User's manual**. In: Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment, Winnipeg.
- CONAMA, Conselho Nacional de Meio Ambiente. 2004. **Resolução nº 344 de 25 de março de 2004**: Estabelece as diretrizes gerais e os procedimentos mínimos para a avaliação do material a ser dragado em águas jurisdicionais brasileiras. Available in: <<http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=445>>. Accessed: 02 Jan. 2013.
- COSTA, A. T. 2001. **Geoquímica das águas e dos sedimentos da Bacia do Rio Gualaxo do Norte, leste – sudeste do Quadrilátero Ferrífero (MG): estudo de uma área afetada por atividade de extração mineral**. Dissertação (Mestrado em Ciências Naturais) - Universidade Federal de Ouro Preto, 187p.
- COSTA, A. T. 2007. **Registro histórico de contaminação por metais pesados, associados à exploração aurífera no alto e médio curso da bacia do ribeirão do Carmo, QF: um estudo de sedimentos de planícies de inundação e terraços aluviais**. Tese (Doutorado em Ciências Naturais) - Universidade Federal de Ouro Preto, 190p.
- COSTA, A. T. *et al.* 2010. Análise estratigráfica e distribuição do arsênio em depósitos sedimentares quaternários da porção sudeste do Quadrilátero Ferrífero, bacia do Ribeirão do Carmo, MG. **REM: Revista da Escola de Minas**, **63**(4):703-714.
- CROMMENTUIJN, T. *et al.* 2000. Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations. **Journal of Environmental Management**, **60**(2):121-143.
- DESCHAMPS, E. *et al.* 2002. Soil and Sediment Geochemistry of the Iron Quadrangle, Brazil: The Case of Arsenic. **Journal of Soils & Sediments**, **2**(4):216-222.
- DÍEZ, M. *et al.* 2007. Background arsenic concentrations in Southeastern Spanish soils. **Science of Total Environment**, **378**(1-2):5-12.
- ELEUTÉRIO L. 1997. **Diagnóstico da situação ambiental da cabeceira da bacia do rio Doce, MG, no âmbito das contaminações por metais pesados em sedimentos de fundo**. Tese (Doutorado em Ciências Naturais) - Universidade Federal de Ouro Preto, 150p.

- ERHARDT, W.; HÖPKER, K. A.; FISCHER, I. 1998. Verfahren zur Bewertung von immissionsbedingten Stoffanreicherungen in standardisierten Graskulturen. **Umweltchem Okotox**, **8**(4):237–240.
- FIELD, L. J.; MACDONALD, D. D.; NORTON, S. B. 1999. Evaluating sediment chemistry and toxicity data using logistic regression modeling. **Environmental Toxicology and Chemistry**, **18**(6):1311-1322.
- FRIZZO, S. J.; LICHT, O. A. B. 2007. Estatística uni e bivariadas aplicadas à prospecção geoquímica. In: O. A. B. Licht, C. S. B. de-Mello, C. R. da-Silva (Eds.). **Prospecção geoquímica de depósitos minerais metálicos, não-metálicos, óleo e gás**. Rio de Janeiro: Sociedade Brasileira de Geoquímica e Serviço Geológico do Brasil, 788p.
- GALÁN, E. *et al.* 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South–West Spain. **Journal of Geochemical Exploration**, **98**(3):89-106.
- GALUSZKA, A. 2007. A review of geochemical background concepts and an example using data from Poland. **Environmental Geology**, **52**(5):861-870.
- GALUSZKA, A. 2006. Methods of determining geochemical background in environmental studies. Problems of landscape ecology. **Polish association of landscape ecology - Warsaw**, **16**(1):507-519.
- GUILLÉN, M. T. *et al.* 2011. Environmental geochemical mapping of Huelva municipality soils (SW Spain) as a tool to determine background and baseline values. **Journal of Geochemical Exploration**, **109**(1-3):59-69.
- HORCKMANS, L. *et al.* 2005. Local background concentrations of trace elements in soils: a case study in the Grand Duchy of Luxemburg. **Catena**, **59**(3):279-304.
- LEPELTIER, C. 1969. A simplified statistical treatment of geochemical data by graphical representation. **Economy Geology**, **64**(5):538-550.
- LEWIN, J.; MACKLIN, M. G. 1987. Metal mining and floodplain sedimentation in Britain. In: V. Gardiner (Ed.). **International Geomorphology 1986: Proceedings of the First International Conference on Geomorphology**. Part 1. Chichester: John Wiley and Sons, p. 1009-1027.
- LILLIEFORS, H. W. 1969. On the Kolmogorov–Smirnov test for the exponential distribution with mean unknown. **Journal of the American Statistical Association**, **64**(325):387-389.
- LONG, E. R.; MORGAN, L. G. 1991. **The potential for biological effects of sediment – sorbed contaminants tested in the National Status and Trends Program**. NOAA Technical memorandum NOS OMA 52. 2. ed. Seattle, Washington: NOAA, 229p.
- MACDONALD, D. D.; INGERSOLL, C. G.; BERGER, T. A. 2000. Development and evaluation of consensus - based sediment quality guidelines for freshwater ecosystems. **Archives of Environmental Contamination and Toxicology**, **39**(1):20-31.
- MATSCHULLAT, J.; OTTENSTEIN, R.; REIMANN, C. 2000. Geochemical background - can we calculate it? **Environmental Geology**, **39**(9):990-1000.
- MICÓ, C. *et al.* 2007. Baseline values for heavy metals in agricultural soils in an European Mediterranean region. **The Science of the Total Environment**, **378**(1-2):13-17.
- MOZETO, A. A. 2003. **Bases técnico-científicas para o desenvolvimento de critérios de qualidade de**



- sedimentos (CQS):** experimentos de campo e laboratório. Unpublished final report, Qualised Project - Process. n. 98/12177-0.
- MRVIĆ, V. V. *et al.* 2012. Background limit of Zn and Hg in soils of Eastern Serbia. **Journal of Agricultural Science**, **55**(2):157-163.
- MRVIĆ, V. *et al.* 2011. Methods for assessment of background limit of Ni and Cr in soils of eastern Serbia. **Ratarstvo i povrtarstvo**, **48**(1):189-194.
- NAKIĆ, Z.; POSAVEC, K.; BACĀANI, A. 2007. A Visual Basic Spreadsheet Macro for Geochemical Background Analysis. **Ground Water**, **45**(5):642-647.
- NAKIĆ, Z.; POSAVEC, K.; PARLOV, J. 2010. Model-based objective methods for the estimation of groundwater geochemical background. **Aquamundi**, **1**(1):65-72.
- PANNO, S. V. *et al.* 2006. Estimating Background and Threshold Nitrate Concentrations Using Probability Graphs. **Ground Water**, **44**(5):697-709.
- PEH, Z.; MIKO, S.; HASAN, O. 2010. Geochemical background in soils: a linear process domain? An example from Istria (Croatia). **Environmental Earth Sciences**, **59**(6):1367-1383.
- PÉREZ-SIRVENT, C. *et al.* 2009. Geochemical background levels of zinc, cadmium and mercury in anthropically influenced soils located in a semi-arid zone (SE, Spain). **Geoderma**, **148**(3-4): 307-317.
- PERSAUD, D.; JAAGUMAGI, J.; HAYTON, A. 1993. **Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario**. Toronto: Ministry of Environment and Energy, PIBS, 24p.
- POLETO, C.; MERTEN, G. H. 2008. Elementos traço em sedimentos urbanos e sua avaliação por Guidelines. **Holos Environment**, **8**(2):100-118.
- RAURET, G. *et al.* 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. **Journal of Environmental Monitoring**, **1**(1):57-61.
- REIMANN, C.; FILZMOSE, P.; GARRETT, R. G. 2005. Background and threshold: critical comparison of methods of determination. **The Science of the Total Environment**, **346**(1-3):1-16.
- REIMANN, C.; GARRETT, R. G. 2005. Geochemical background - concept and reality. **The Science of the Total Environment**, **350**(1-3):12-27.
- RODRIGUES-FILHO, S.; MADDOCK, J. E. L. 1997. Mercury Pollution in Two Gold Mining Areas of the Brazilian Amazon. **Journal of Geochemical Exploration**, **58**(1):231-240.
- ROESER, H. M. P.; ROESER, P. A. 2010. O Quadrilátero Ferrífero - MG, Brasil: aspectos sobre sua história, seus recursos minerais e problemas ambientais relacionados. **Revista Geonomos**, **18**(1):33-37.
- SHIOWATANA, J. *et al.* 2001. A novel continuous-flow sequential extraction procedure for metal speciation in solids. **Journal of Environmental Quality**, **30**(4):1195-1205.
- SILVÉRIO, P. F. 2003. **Bases técnico-científicas para a derivação de valores guia de qualidade de sedimentos para metais:** experimentos de campo e laboratório. Tese (Doutorado em Ciências da Engenharia Ambiental) - Escola de Engenharia de São Carlos, Universidade de São Paulo, 145p.

SMITH, S. L. *et al.* 1996. A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. **Journal of Great Lakes Research**, **22**(3):624-638.

TAYLOR, M. P.; LEWIN, J. 1996. River behaviour and Holocene alluvial: The river Severn at Welshpool, mid-Wales, U.K. **Earth Surface Processes and Landforms**, **21**(1):77-91.

TENG, Y. *et al.* 2009. Geochemical baseline of trace elements in the sediment in Dexing area, South China. **Environmental Geology**, **57**(7):1649-1660.

TUKEY, J. W. 1977. **Exploratory data analysis**. Massachusetts: Addison-Wesley, 83p.

USEPA, United States Environmental Protection Agency. Region 5, RCRA. 2003. **Ecological Screening Levels**, 2003. Available in: <<http://www.epa.gov/RCRIS-Region-5/ca/edql.htm>>. Accessed: 23 Apr. 2010.

ZGLOBICKI, W. *et al.* 2011. Geochemical and statistical approach to evaluate background concentrations of Cd, Cu, Pb and Zn (case study: Eastern Poland). **Environmental Earth Sciences**, **62**(2):347-355.

ZHANG, Q. *et al.* 2011. Comparison of Sequential Chemical Extraction Procedure and DGT Technique to Measure Effective Arsenic in Sediment of Lake Taihu, China. **Journal of Agro-Environmental Science**, **30**(7):1398-1403.