

## BARIUM AND LEAD LEVELS IN SITES FOR DISPOSAL OF OIL WELL WASTE<sup>1</sup>

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**ABSTRACT** – Indiscriminate disposal of waste from the oil industry has led to contamination of soils and water sources and toxic effects in the biota. Thus, this study aimed to assess barium (Ba) and lead (Pb) spatial variability in disposal sites for oil well drilling and prospecting wastes. The soil in the study area is classified as Red Latosol, and the area is located in Santa Maria do Oeste, Paraná State (Brazil). Barium and Pb spatial variabilities were determined using a 76-point sampling grid. The levels of metals were determined in soil samples collected at each sampling point, at the depth ranges of 0.0-0.3, 0.3-0.6, 0.6-0.9 and 0.9-1.2 m. Data were mapped using geostatistical interpolators for spatial dependence determination, modeling and validation of semivariograms, and respective interpolation. Thirty Ba and Pb high concentration samples were selected for leaching and solubilization assays. As semivariogram analysis showed spatial dependence, mapping by ordinary kriging was performed for both metals. The high levels found for both metals arose from well drilling activities, as no direct relationship was found between such levels with geology and genesis of the local rock. The concentrations of the metals were higher than the research values considering the Agricultural / AP-Max scenario, therefore, the study area was characterized as class 4 (contaminated). Although these metals have low solubility, i.e. low contamination risk to subsurface waters, they may pose contamination risks to water bodies by means of soil runoff.

**Keywords:** Geostatistics. Heavy metal. Soil contamination.

## BÁRIO E CHUMBO EM ÁREAS DE DISPOSIÇÃO DE RESÍDUOS DE POÇOS DE PETRÓLEO

**RESUMO** – A disposição indiscriminada de resíduos da indústria petrolífera levam a contaminação dos solos e mananciais, afetando toda a biota. O objetivo do trabalho foi avaliar a variabilidade espacial dos teores de bário e chumbo em área de disposição de resíduos de perfuração de poços de petróleo. O Latossolo estudado encontra-se no município de Santa Maria do Oeste, no estado do Paraná-Brasil. Para a determinação da variabilidade espacial dos metais criou-se uma grade de amostragem com 76 pontos. Em cada ponto, foram coletadas amostras de solo nas profundidades: 0-0.3, 0.3-0.6, 0.6-0.9 e 0.9-1.2 m para a determinação dos teores de bário e chumbo. A geração dos mapas de bário e chumbo foi realizada através de interpoladores geostatísticos com determinação da dependência espacial, modelagem e validação de semivariogramas experimentais e sua interpolação. Selecionou-se 30 amostras com concentrações de bário e chumbo mais elevadas para realização de ensaios de lixiviação e solubilização. Na análise do semivariograma verificou-se dependência espacial, permitindo a confecção de mapas por krigagem para os dois metais. Os elevados teores encontrados foram decorrentes das atividades associadas à perfuração de poços, visto que, não foi encontrado correspondência direta com a geologia das rochas locais e a gênese. As concentrações dos metais foram superiores aos valores de investigação considerando o cenário Agrícola/AP-Máx, caracterizando a área sujeita a “Investigação”, pertencendo a Classe 4, área contaminada. Apesar desses metais possuírem baixa solubilidade, demonstrando baixo risco de contaminação de águas subsuperficiais, podem apresentar risco de contaminação de corpos d’água por meio do carreamento desse solo.

**Palavras-chave:** Geoestatística. Metal pesado. Contaminação de solo.

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## INTRODUCTION

Oil industry produces a large range of wastes that, when indiscriminately disposed, can contaminate soils and groundwater and impact biota (BUSINELLI et al., 2009). One of the wastes produced by onshore well drilling operations is gravel, which is disposed in high amounts and has potentially toxic substances. This basically consists of a mixture of fragmented rocks and drilling fluids (BAUDER et al., 2005).

In general, drilling fluids contain hydrocarbons, sodium, and heavy metals such as barium (Ba) and lead (Pb) (BAKKE; KLUNGSØYR; SANNI, 2013; ANDRADE et al., 2014; FREITAS et al., 2015). Among the main components, barite (BaSO<sub>4</sub>) adds large amounts of Ba to the waste produced (LIMA et al., 2012; MAGALHÃES et al., 2014a). Moreover, oil- and water-based fluids may contain diesel oil in their compositions (SANTOS, 2012), adding metals such as Pb to the oil well drilling waste.

Recent studies have shown phytotoxicity risks and groundwater contamination caused by Ba from barite are very low, except under extreme reduction conditions (Eh < - 250 mV). Under this condition, increased solubility and consequently increased mobility and bioavailability of Ba have been observed (LIMA et al., 2012; MAGALHÃES et al., 2014a; MAGALHÃES et al., 2014b; SAMPAIO JUNIOR et al., 2015). Although the risks of groundwater contamination by Pb are also low, continued disposal of oil well drilling residues into the soil for prolonged periods of time can result in contamination thereof. Andrade et al. (2014) verified that after 20 years of waste disposal into a typical dystrophic Red Latosol, it presented 350.4 mg kg<sup>-1</sup> Pb in its composition.

Among the numerous soil-polluting contaminants, heavy metals are especially dangerous

due to high toxicity, environmental persistence, and food-chain bioaccumulation (ESMAEILI et al., 2014). Even in small amounts, contamination by heavy metals can cause environmental and public health problems (ONG et al., 2013; ESMAEILI et al., 2014; GHERASIM; MIKULASEK, 2014).

Studies on concentrations and spatial distribution of heavy metals in the soil are extremely important to identify the location and extent of the polluted area. In this sense, geostatistics has been used as a tool in studies of spatial variability of heavy metals in contaminated soils (CARVALHO; SILVEIRA; VIEIRA, 2002). Through this technique, the most relevant areas, in terms of contamination and remediation needs, can be identified, enabling more targeted actions and minimizing costs (AMARAL SOBRINHO et al., 2018).

Based on the above, this study aimed to evaluate Ba and Pb solubility in disposal sites for oil well drilling and prospecting wastes and to determine the spatial variability of their pseudo-total contents in contaminated soils. In brief, the purpose was to characterize Ba and Pb spatial variability and analyze the behavior of such metals in the environment.

## MATERIAL E MÉTODOS

### Study area and sampling

The study was carried out in a disposal site for oil well drilling and prospecting wastes. The area is located in Santa Maria do Oeste, Paraná State - Brazil (24° 56' 20" S, 51° 51' 46" W). The local soil was previously characterized according to Donagemma et al. (2011) and classified by Santos et al. (2013) as typical dystrophic Red Latosol, moderate A, and wavy relief. Table 1 describes the soil physical and chemical features.

**Table 1.** Soil chemical and particle-size characterizations (Red Latosol).

Layers Symbol	Depth m	pH (H <sub>2</sub> O)	Ca <sup>2+</sup>	Mg <sup>2+</sup>	H+Al	Al <sup>3+</sup>	S	T	V	P	K	C	Sand	Silt	Clay
			-----cmol <sub>c</sub> dm <sup>-1</sup> -----				-----%-----			mg kg <sup>-1</sup>		-----g kg <sup>-1</sup> -----			
Ap	0–0.1	5.2	4.9	0.6	7.6	0.0	5.8	13.4	43	1	10.6	25.4	141	302	557
BA	0.1–0.2	5.2	3.6	0.6	8.9	0.9	4.4	13.3	33	1	5.5	19.2	107	280	613
Bw <sub>1</sub>	0.2–0.3	5.0	1.6	1.3	8.9	1.6	3.0	11.9	25	1	2.7	11.4	136	198	666
Bw <sub>2</sub>	0.3–0.6	5.0	2.1	0.2	8.9	1.9	2.4	11.3	21	1	1.2	8.9	79	151	770
Bw <sub>3</sub>	0.6–1.0	5.1	1.5	0.8	7.9	1.7	2.4	10.3	23	0	1.2	10.0	70	141	789
Bw <sub>4</sub>	1.0–1.5	5.2	2.0	0.4	5.0	0.4	2.5	7.5	33	0	0.8	5.4	106	174	720
Bw <sub>5</sub>	-1.6+	5.6	1.6	2.0	4.6	0.0	3.6	8.2	44	1	0.8	6.0	83	195	722

pH in water (1:2.5); Ca and Mg, H+Al extracted in 1000 Mol m<sup>-3</sup> KCl; Al extracted in 1000 Mol m<sup>-3</sup> calcium acetate at pH 7.0; P and K extracted with North Carolina solution; C extracted with potassium dichromate – Walkley – Black. (DONAGEMMA et al., 2011).

Waste from oil well drilling and prospecting was deposited in the studied soil over 20 years ago. It is composed of fragmented rock mixed with well drilling fluid (removed during well drilling). In the area, there is also deposition of sediments from upstream soil erosion by surface runoff.

A geostatistical model was used to measure spatial variability of barium (Ba) and lead (Pb) in the area. To this end, a 15-m soil sampling grid was created, with 76 sampling points. Each point was georeferenced at each grid vertex using a topographic global positioning system (GPS) with post-processing differential correction (DGPS - Trimble Pro XT model). The UTM coordinate system was used (fuse 22 and horizontal datum SAD 69). To further improve the accuracy, a differential correction was used, with sub-meter accuracy (average location error equal to 0.6 m). At each point, soil samples were collected from the following depth layers: 0.0-0.3, 0.3-0.6, 0.6-0.9, and 0.9-1.2 m. Each sampling trench was dug using a backhoe loader, and soil samples were collected by hand.

### Chemical analyses

All samples were analyzed for pseudo-total levels of Ba and Pb by EPA 3051 (USEPA, 1994). Thirty of the samples with the highest pseudo-total concentrations were selected for analysis by NBR 10004 (ABNT, 2004a). Leaching and solubilization tests were carried out following NBR 10005 (ABNT, 2004b) and NBR 10006 (ABNT, 2004c) standards, respectively.

For leaching assay, a 100-g sample was sieved through a 0.0095-m mesh sieve and added with 11.4-mL extractant solution of glacial acetic acid in 2-L deionized water (pH = 4.93). This solution was stirred at 30 rpm and 25 ° C for 18 h, using a flask of inert material (borosilicate glass). Then it was filtered through 0.6- to 0.8- $\mu\text{m}$  fiberglass filter to obtain the leachate for analysis. Additionally, a 250-g sample was sieved through a 0.0095-m mesh sieve and added with deionized water in a 1,500-mL flask, then stirred at low speed for 5 min. The flask was covered by a PVC film and left to rest for 7 days at 25 °C. After, the solution was filtered through a 0.45- $\mu\text{m}$  membrane, and solubilized extract was analyzed.

Concentrations of Ba and Pb in soil extracts were determined by plasma emission spectrometry (ICP-OES) (Perkin Elmer, OPTIMA 3000 model). The method detection limit (DL) was calculated as the blank mean plus three times the standard deviation of the blank of all analyses (10 replications). The DLs for Ba and Pb were 0.036 and 0.25 mg kg<sup>-1</sup>, respectively. The QLs (quantification limits) for Ba and Pb were 0.36 and 0.5 mg kg<sup>-1</sup>, respectively. The methods were validated by certified reference material: NIST SRM 2709a (San Joaquin Soil) with Ba content of 979 $\pm$ 28 mg kg<sup>-1</sup>

(95 % of recovery) and Pb content of 17.3 mg kg<sup>-1</sup> (92% recovery). The results of certified reference materials were within the confidence limits stated by NIST.

### Barium and lead spatial variability

Ordinary kriging geostatistical interpolation was used to create Ba and Pb concentration isoline maps. After spatial dependence was identified and measured, maps were produced with precision and without trends. Isovalue maps were then generated using the following procedures: 1) descriptive statistical analysis, 2) spatial dependence determination (variography), 3) semi-variogram modeling and validation, and 5) interpolation. All the steps were performed by GEOESTAT software (VIEIRA et al., 1983).

The models fitted to the semivariograms were validated by nugget effect ( $C_0$ ), range (a), sill ( $C_0+C_1$ ), spatial dependence index  $\frac{C_0}{C_0+C_1}$ , and  $R^2$  values, which are often used to evaluate interpolation performance.

## RESULTS AND DISCUSSION

### Descriptive analysis of soil levels of barium and lead

The overall sample mean for Ba level was 732.15 mg kg<sup>-1</sup> (Table 2), the maximum was 10,557.00 mg kg<sup>-1</sup> and the minimum was below 0.036 mg kg<sup>-1</sup> (undetected). As standard values have not been established yet for Paraná State, we used the reference values in resolution n° 420 of the Brazilian Council for the Environment - CONAMA (BRASIL, 2009). At all depth layers, Ba contents were higher than the limit in the most restrictive scenario (Agricultural/AP-Max), which is 300 mg kg<sup>-1</sup>. The Ba contents were about 30 times higher than the limit for agricultural areas. Barium concentrations were even higher than the limit for industrial areas, which is 750 mg kg<sup>-1</sup>. According to Magalhães et al. (2014b) and Freitas et al. (2015), Ba concentration in areas contaminated by oil well drilling residues is increased due to waste disposal near the wells. It is worth mentioning that Ba has no direct relationship with the genesis of local rocks or respective mineralization, as seen in local geochemical surveys (LICHT; BITTENCOURT, 2013). In the soils of northern Paraná State, natural levels of Ba fluctuate within a range between 38.5 to 63 mg kg<sup>-1</sup> (PAVELHAO, 2015). In the coastal plain of the state, the levels are even lower (< 0.17 mg kg<sup>-1</sup>) (BUSCHLE, 2013). That said, the abnormal levels found in this study may result from oil well drilling waste incorporation.

**Table 2.** Mean, minimum, and maximum contents of barium and lead in soil samples.

	Depth (m)			
	0-0.3	0.3-0.6	0.6-0.9	0.9-1.2
	Metals			
	Barium (mg kg <sup>-1</sup> )			
Mean	983.31	814.06	550.03	581.18
Maximum	8928.16	10557.00	6256.60	6716.21
Minimum	16.54	15.86	<0.036	<0.036
	Lead (mg kg <sup>-1</sup> )			
Mean	38.61	24.60	12.36	14.75
Maximum	602.49	314.41	218.59	165.65
Minimum	<0.25	<0.25	<0.25	<0.25

The overall sample mean for the Pb level was 22.58 mg kg<sup>-1</sup>, the maximum was 602.49 mg kg<sup>-1</sup>, and the minimum was below 0.25 mg kg<sup>-1</sup> (undetected). The maximum values at the depth layers of 0.0-0.3, 0.3-0.6, 0.6-0.9 and 0.9-1.2 m were 602.49, 314.41, 218.59, and 165.65 mg kg<sup>-1</sup>, respectively, while the minimum value was below 0.25 mg kg<sup>-1</sup> (undetected) at all four depth layers (Table 2). In one of the sampling points, the Pb contents were also higher than the limit in the most restrictive scenario (Agricultural/AP-Max), which is 180 mg kg<sup>-1</sup>. Moreover, in the three upper layers, the maximum values reached were higher than the reference values established by CONAMA (BRASIL, 2009). In the 0.0-0.3 m depth interval, the maximum content was about three times higher than the references. Therefore, the area is not only contaminated by Ba but also by Pb up to a depth of

0.9 m. When considering maximum allowable Pb contents for farmland of other countries, the values found in the study area are also above the standards of the European Union (50-300 mg kg<sup>-1</sup>) and the United States (150 mg kg<sup>-1</sup>) (MCGRATH et al., 1994).

#### Spatial variability in depth of barium and lead

For Ba, the Gaussian model showed determination coefficient values (R<sup>2</sup>) equal to or above 0.80, at the four depth layers (Table 3). However, for Pb, the 0.0-0.3 and 0.6-0.9 m depth layers showed a more erratic behavior when using the Gaussian model, with R<sup>2</sup> values much lower than those observed for Ba at these depths. At the 0.3-0.6 m and 0.9-1.2 m depth layers, the spherical model presented better fit, with higher R<sup>2</sup> values.

**Table 3.** Parameters of the models adjusted to the experimental semivariograms

Attribute	Model	C <sub>0</sub>	C <sub>1</sub>	Level	Co/Co+C1	Range (m)	R <sup>2</sup>
Ba 0-0.3 m	Gaussian	0.19	0.34	0.53	0.36	63.8	0.80
Ba 0.3-0.6 m	Gaussian	0.10	0.43	0.53	0.19	53.2	0.85
Ba 0.6- 0.9 m	Gaussian	0.10	0.39	0.49	0.20	59.5	0.84
Ba 0.9-1.2 m	Gaussian	0.10	0.40	0.50	0.20	50.0	0.85
Pb 0-0.3 m	Gaussian	0.35	0.24	0.59	0.59	59.7	0.54
Pb 0.3-0.6 m	Spherical	0.23	0.22	0.45	0.51	57.3	0.56
Pb 0.6-0.9 m	Gaussian	0.19	0.11	0.30	0.63	75.2	0.60
Pb 0.9-1.2 m	Spherical	0.09	0.23	0.32	0.28	59.4	0.84

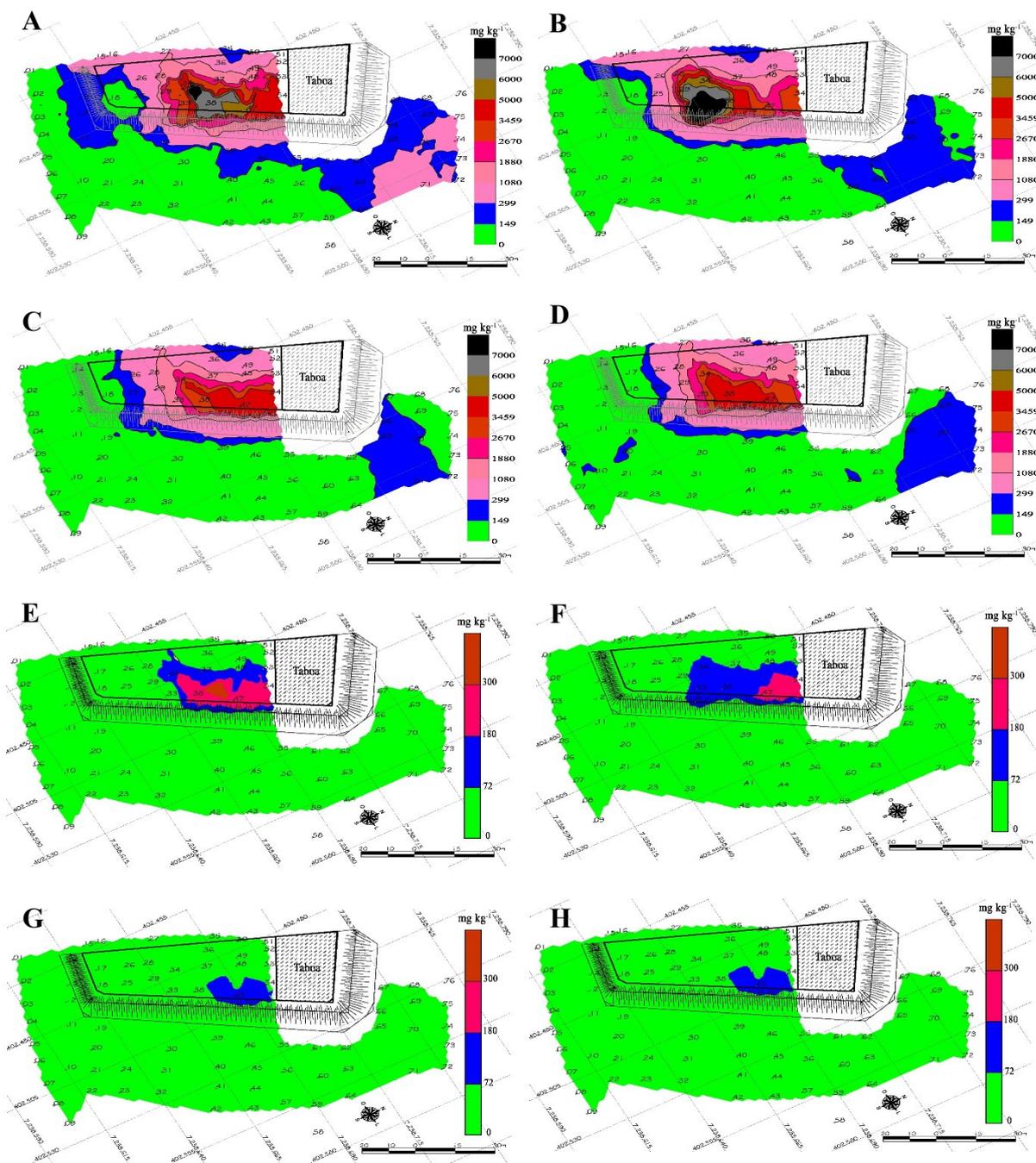
Comparing each parameter for Ba in the different depth layers, a total agreement was observed, that is, according to depth and metal type the parameters had a good fit. This is because Co (nugget effect) varied from 0.10 to 0.19 (Table 3), R<sup>2</sup> was greater than 0.8, and range above 50 m. Amaral Sobrinho et al. (2018) found similar Gaussian model fit results to Ba distribution data, which were also collected in waste disposal areas for oil well drilling and prospecting. Accordingly, a 15 x 15-m grid was suitable for the range values found. However, for Pb, the nugget effect (Co) and R<sup>2</sup> values with the best fit were found only at the 0.9-1.2 m depth layer; yet, the range values were suitable with a good autocorrelation for all depth layers. These values of

range highlight that the Pb had a spatial variability pattern other than random (GUEDES et al., 2012). The mean R<sup>2</sup> values at the depths 0-0.3, 0.3-0.6, and 0.6-0.9 m do not necessarily denote that data interpolation was lower at these layers. This is because R<sup>2</sup> refers only to model fit for all semivariance points. What matters, however, for geostatistical interpolation is the model fitting to the semivariance points within the range limit.

Spatial dependence of Ba and Pb contents was identified by means of geostatistical treatment; hence, geostatistical interpolators could be used to generate spatial variability maps for the four soil layers (0.0-0.3, 0.3-0.6, 0.6-0.9, and 0.9-1.2 m) (Figure 1). The green areas correspond to classes 1

and 2 (BRASIL, 2009), which have concentrations up to the limit value for prevention, for Ba ( $0$  and  $150 \text{ mg kg}^{-1}$ ) and for Pb (between  $0$  and  $72 \text{ mg kg}^{-1}$ ). The blue area comprises class 3, in which concentrations were above the prevention limits and below investigation limits, for Ba (between  $150\text{-}300 \text{ mg kg}^{-1}$ ) and for Pb ( $73\text{-}180 \text{ mg kg}^{-1}$ ). Shades from pink to black were classified as class 4. In the case of Ba, other hues were added due to a large range of values. Also for Ba, the sum of the percentages of

areas classified as class 3 and class 4 reaches more than 50% of the total at all depth layers. For Pb, classes 1 and 2 represent over 90% of the area, and most of the contamination is within the first  $0.6 \text{ m}$  depth and around the waste disposal dike. This indicates that more than 50% of the area has Ba concentrations that disturb soil main functions and pose direct or indirect risks to human health (BRASIL, 2009).



**Figure 1.** Spatial variability of barium (A, B, C, and D) and lead (E, F, G, and H) at the depth layers of  $0\text{-}0.3$ ,  $0.3\text{-}0.6$ ,  $0.6\text{-}0.9$  and  $0.9\text{-}1.2 \text{ m}$ , respectively.

**Leaching and solubilization tests**

Thirty samples with higher pseudo-total concentrations of Ba and Pb were selected. All these samples had concentrations of both elements below the limit for leaching test according to NBR-10005

(ABNT, 2004b), 70 mg L<sup>-1</sup> for Ba and 1.00 mg L<sup>-1</sup> for Pb. Likewise, the contents of all samples were below the limit for solubilization test according to NBR-10006 (ABNT, 2004c), 0.7 mg L<sup>-1</sup> for Ba and 0.01 mg L<sup>-1</sup> for Pb (Table 4).

**Table 4.** Leached and solubilized contents of barium and lead in soil samples from well drilling waste disposal area.

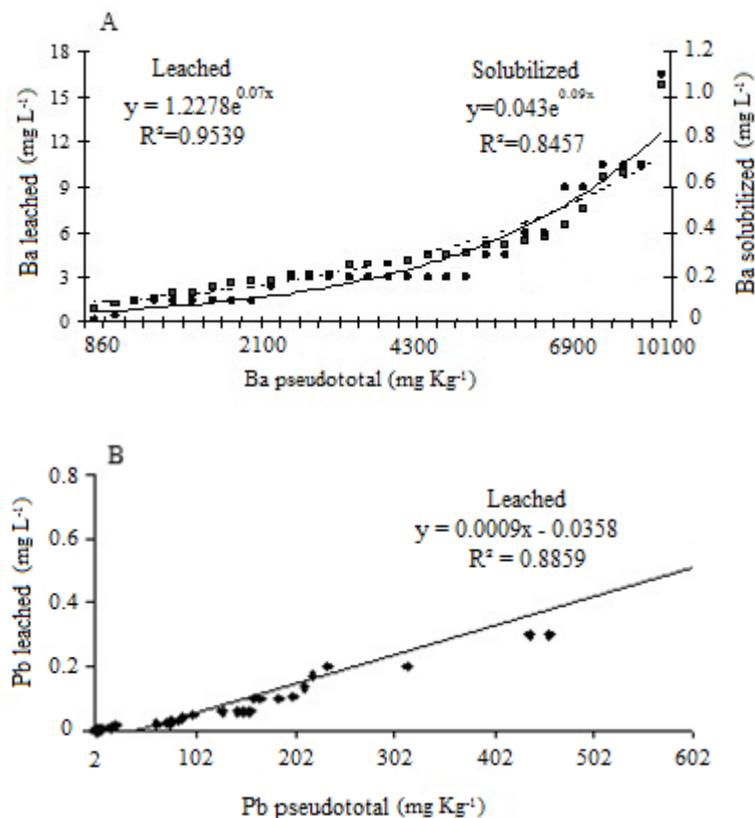
Sample	Depth (m)	Georeference		Barium			Lead		
				Total	Leach	Solub	Total	Leach	Solub
		L	N	mg kg <sup>-1</sup>	mg L <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg L <sup>-1</sup>	mg kg <sup>-1</sup>
15	0.3-0.6	402451	7238648	859.3	7.60	0.162	nd	0.011	nd
16	0.3-0.6	402452	7238653	938.9	5.54	0.118	1.6	nd	nd
27	0.9-1.2	402461	7238671	872.6	3.91	0.313	1.9	nd	nd
28	0-0.3	402470	7238664	5484.6	15.82	0.012	199.1	0.133	nd
28	0.9-1.2	402470	7238664	1477.0	1.95	0.102	4.1	nd	nd
29	0.3-0.6	402477	7238662	8585.0	10.79	0.666	210.1	0.096	nd
33	0-0.3	402485	7238666	8928.2	9.73	0.650	75.6	0.030	nd
33	0.9-1.2	402485	7238666	3396.6	2.15	0.144	20.6	0.004	nd
34	0-0.3	402477	7238671	7108.9	5.77	0.399	456.9	0.260	nd
34	0.9-1.2	402477	7238671	6716.2	3.10	0.216	72.3	0.055	nd
37	0-0.3	402486	7238682	7711.9	6.64	1.137	602.5	0.660	nd
37	0.9-1.2	402486	7238682	3713.5	4.54	0.178	83.9	0.137	nd
38	0-0.3	402490	7238675	5122.9	5.23	0.348	142.5	0.061	nd
38	0.3-0.6	402490	7238675	10557.0	5.18	0.687	159.5	0.103	nd
38	0.9-1.2	402490	7238675	4091.5	2.63	0.166	78.0	0.013	nd
47	0-0.3	402499	7238687	5459.6	3.81	0.580	314.9	0.226	nd
47	0.9-1.2	402499	7238687	6469.1	4.10	0.223	165.6	0.059	nd
48	0-0.3	402487	7238694	6894.3	3.97	0.586	437.2	0.168	nd
48	0.3-0.6	402487	7238694	1806.8	2.26	0.234	233.5	0.340	nd
48	0.6-0.9	402487	7238694	3107.7	0.88	0.155	218.6	0.190	nd
48	0.9-1.2	402487	7238694	2484.8	3.15	0.112	149.3	0.137	nd
52	0-0.3	402486	7238707	5100.4	10.52	0.164	98.4	0.027	nd
52	0-0.3	402492	7238703	3961.1	4.48	0.244	128.9	0.036	nd
53	0.9-1.2	402492	7238703	4296.8	1.45	0.283	88.7	0.030	nd
54	0-0.3	402499	7238700	3726.7	1.70	0.101	185.0	0.019	nd
54	0.6-0.9	402499	7238700	5591.1	2.82	0.200	62.3	0.064	nd
54	0.9-1.2	402499	7238700	1348.0	1.28	0.032	156.9	0.054	nd
70	0-0.3	402544	7238736	2076.1	3.12	0.100	8.2	0.021	nd
74	0-0.3	402549	7238749	1507.4	4.71	0.214	6.7	nd	nd
75	0-0.3	402540	7238754	875.8	2.74	0.145	16.6	nd	nd

Leach - leached; Solub – solubilized; nd – not detected.

The low solubility of barite-derived Ba has already been reported in studies on soils with varying organic matter, iron, calcium, and sulfur contents (CAPPUYNS, 2017) and soil from A horizon of a Red-Yellow Latosol (MAGALHÃES et al., 2011; LIMA et al., 2012; MAGALHÃES et al., 2014a). This low solubility is due to the high pH and redox potential (Eh), resulting in its slow release to the soil. Barium tends to remain in poorly soluble forms (NOGUEIROL; ALLEONI, 2013) with sulfate ion, which makes it more associated with sediment contamination than with water (DAVIDSON et al., 2005). Barium soluble fraction only increases under

extreme reduction conditions (Eh < -250 mV), hence increasing its mobility and bioavailability (LIMA et al., 2012; MAGALHÃES et al., 2014a; MAGALHÃES et al., 2014b; SAMPAIO JUNIOR et al., 2015).

Pseudo-total concentrations of Ba and Pb to reach the maximum limit for leaching and solubilization assays were estimated using data from Table 4. This way, regression curves could be plotted (Figure 2), finding R<sup>2</sup> values equal to 0.85, 0.95, and 0.89 for Ba solute, Ba leachate, and Pb leachate, respectively.



**Figure 2.** Regression analysis for contents of barium (leached and solubilized) (A) and lead (leached) (B) as a function of total contents in the soil.

The regression curve equation shows that Ba pseudo-total concentrations above 61,000 mg kg<sup>-1</sup> are able to reach the upper limit for leaching (70 mg L<sup>-1</sup>). This is 6 times the value of the most concentrated sample (10,557.00 mg kg<sup>-1</sup>), for both leaching and solubilization analysis. On the other hand, for Pb, the concentrations should be above 1,071.33 mg kg<sup>-1</sup> to reach the limit for leaching (1 mg L<sup>-1</sup>). This is about 1.8 times the value of the most concentrated sample (602.50 mg kg<sup>-1</sup>), according to the maximum limits defined in NBR-10004 (ABNT, 2004a).

## CONCLUSIONS

The study area is contaminated by barium and lead according to the current legislation.

In all samples, lead and barium concentrations were below the limit for leaching analysis defined in NBR-10005 standard (ABNT, 2004b) and also below the limit for solubilization analysis (ABNT, 2004c).

Although barium and lead showed high pseudo-total concentrations in soils where oil well drilling wastes were disposed, leading to investigation values higher than the most restrictive scenario (Agricultural/AP-Max), defined by CONAMA's resolution n° 420 (BRASIL, 2009), both metals showed low solubility. Thus, under

proper removal and disposal conditions, the soil has a low risk of contaminating subsurface water through leaching; however, water bodies can be contaminated by soil runoff.

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