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# Distribution of potentially harmful elements in soils around a large coal-fired power plant

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**Abstract** An understanding of the spatial distribution and contribution of a power plant to local soil contamination is important for the planning of soil use and prioritizing remedial actions for public safety. Consequently, the aim of this study was to map the spatial distribution of potentially hazardous elements (PHEs; Cu, Pb, Zn, Ni, Cr, Fe, Mn, Cd, As, and Se) in soils around a large (796 MW) coal-fired power plant in Brazil. For the purpose, 33 soil samples were collected in the area within a radius of approximately 17.5 km from the plant and subsequently analyzed for PHEs. The frequency and direction of winds were also obtained from a meteorological station in the region.

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The sampling area was divided into four quadrants (northwest: N-NW; northeast: N-NE; southeast: S-SE; southwest: S-SW), and there were significant negative correlations between the distance and the concentrations of Se in the S-SE quadrant and As in the S-SW and S-SE quadrants. There were positive correlations between distance from the plant and the concentration of Mn in the N-NE quadrant and the concentration of Cd in the S-SW quadrant. The dominant direction of the winds was N-NE. The indexes used in this study showed low-to-moderate enrichment factor, but detailed analysis of the dominant quadrant of the winds showed a correlation with higher concentrations in the soils closer to the power plant for at least seven of the PHEs analyzed, especially with regard to As. Therefore, we conclude that the distribution of the metalloid As can be used as a marker of the spatial

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distribution of contamination from the thermoelectric plant, but the dynamics of the other elements suggests that the presence of other sources of contamination may also compromise the quality of local soils.

**Keywords** Metals · Arsenic · Soil contamination · Coal region

#### Introduction

Burning of coal in coal-fired power plants is a potentially polluting activity capable of releasing high concentrations of ash and toxic elements into the environment (Rodriguez-Iruretagoiena et al. 2015). Among these elements are metals and metalloids such as arsenic and selenium, but the concentrations of these elements in ashes depend on the composition of the coal used in the power plants (Goodarzi 2006; Tang et al. 2012). Several studies report environmental contamination by substances released due to coal burning (Agrawal et al. 2010; Zhang et al. 2018a), and these increase the risk to human health (Masto et al. 2019). Negative health impacts on the population living near these plants or involved in coal-related activities (Pinto et al. 2017; Da Silva Júnior et al. 2017) have been observed.

Despite this, developing countries have encouraged the policy of using coal for power generation based on increased demand for energy and the controversial economic benefits generated at local and national levels (Barrows et al. 2018; Masih 2018; World Coal Association 2018). Global coal stocks are expected to last for at least another 150 years; Brazil ranks 10th in terms of global coal reserves. The study region (Candiota mine) contains almost 40% of Brazilian coal, which is mainly used in a thermoelectric power plant with an energy potential of 796 MW (ANEEL 2008).

Candiota coal is classified as sub-bituminous (Côrrea da Silva 1993), with a high mineral content (almost 50% ash), including heavy metals and fluoride, which produces acidic emissions. According to Teixeira (2008), 54 chemical elements were found in Candiota coal, with the exception of Sb, Se, and Sc. The elements present in highest concentrations were Ta, Cs, Gd, Dy, Yb, Er, and Rb. The concentration of Mn was twice as high as that of other Brazilian coal samples (Swaine 1990; Swaine and Goodarzi 1995). The elements with the lowest concentrations include Cu, Mo, Se, and Zn (Pires et al. 2002a, b). Kalkreuth et al. (2006) identified the presence of Se in carbon samples in this area (average concentration of 9.5 ppm).

Coal burning in a coal-fired power plant releases volatile compounds. Thus, coal ash, being the combustion by-product of coal, should closely resemble it in composition (Roisenberg et al. 2016). The composition of coal ash depends on several factors related to the concentration and geochemical distribution of the elements in coal, as well as to the processes of burning and control measures of pollutants used (Pires et al. 2002a). There may be some difference element composition and concentration in the ashes and the coal because of the latter having a high mineral content and low burning efficiency (Pires et al. 2002a). In Candiota, the same trace elements found in the coal were found in the fly and bottom ashes (Pires and Querol 2004). The major elements of coal and coal ash were two trace elements, Ga and Ge, and Al and Si, respectively (Roisenberg et al. 2016).

Fly ash is composed of glassy aluminum–silicate matrix, mullite, quartz, and magnetite (Pires and Querol 2004). Most of the finer particles are not captured by the electrostatic precipitator and are emitted into the atmosphere. Pires et al. (2001) reported high ash content in the region of this study, and Silva et al. (1999) reported significant concentrations of trace elements (Mn, Zn, Cu, Pb, Hg, Cr, Cd, and Ni). In addition, there are reports of SO<sub>2</sub> emissions, sometimes exceeding the permitted emission standards. Bottom ash has a similar composition, but with a higher magnetite content (Pires and Querol 2004).

Although the use of coal is reducing worldwide, this energy source will certainly accompany us in the next decades. Consequently, it is important to understand the spatial distribution of contaminants released due to coal burning. This information can be useful for land use planning, management of contaminated areas, and provision of public policies for focal groups.

The aim of the present study was to map the spatial distribution of PHEs, including Cu, Pb, Zn, Ni, Cr, Fe, Mn, Cd, As, and Se in soils around a large coal-fired power plant in Brazil, highlighting the contamination

indexes and the association between proximity to the power plant and concentration of PHE.

#### Materials and methods

#### Study area

The study was carried out around a coal-fired power plant located in Candiota, in the extreme south of Brazil  $(54^{\circ}10'58''/53^{\circ}18'35'')$  west,  $31^{\circ}17'35''/31^{\circ}02'41''$  south). Being the largest coal-fired power plant in the country, it has a maximum installed capacity of 796 MW, but currently operates at a capacity of 446 MW,

#### Soil sample collection

In total, 33 samples of superficial soil (0–10 cm) were collected in Candiota and surrounding cities (Pinheiro Machado, Pedras Altas, and Hulha Negra) (Fig. 1), between 0.4 and 17.5 km away from the center of power plant, in all directions. Soils were selected after determining their structural integrity and considering only soils with no apparent physical disturbances. The collections were made in forest areas, close to the face

of forests facing the emission source, avoiding roads, crops, and other activities or uses that could move the soil and change its structure.

Sample preparation and analytical methods

Soil samples were dried at 40 °C and subsequently disaggregated and pulverized, followed by acid extraction in a microwave oven (USEPA 2007). Elemental composition of the acid extract was determined using F-AAS in a GBC model 932 AA. Arsenic was analyzed using a PerkinElmer AAS800 with a Zeeman graphite furnace. All analyses were performed in triplicate, with RSD < 7%, demonstrating good reproducibility of the results. In order to control the analytical precision, parallel samples were analyzed by the National Research Council of Canada (Marine Sediment Reference Materials for Trace Metals and other Constituents (MESS-3 and PACS-2). A certified reference material analyzed generally showed good recovery of the reference value, within a range of  $\pm$  5%.



Fig. 1 Study area in extreme south of Brazil and sampling location map

Analysis of spatial distribution of PHEs in soil

The sampling area was divided into four quadrants with a thermoelectric plant as the central point: N-NW (quadrant 1), N-NE (quadrant 2), S-SW (quadrant 3), and S-SE (quadrant 4) (Fig. 1). Quadrant 1 had 9 points (ranging from 0.8 to 14.8 km distance from the power plant), quadrant 2 had 13 points (ranging from 0.4 to 13.6 km), quadrant 3 had 8 points (ranging from 1.7 to 17.5 km), and quadrant 4 had 6 points (6.8–15.4 km). To evaluate the influence of the plant on the concentrations of chemical elements, a Pearson correlation analysis was performed for each quadrant. Of those elements with significant (positive or negative) correlation, simple linear regression analysis was performed to generate a model of an estimation of concentrations at the site. The frequency and distribution of winds in the region were recorded by a local weather station.

Finally, in order to evaluate the relationship between concentrations of the metals and distance to the center of the coal-fired power plant, a factor analysis with varimax rotation of principal axes factors was undertaken.

# Measures to quantify contamination

To better estimate the degree of pollution of the region, the following were calculated: enrichment factor (EF), geo-accumulation index ( $I_{geo}$ ), contamination factor (CF), and pollution load index (PI). All equations and categories were based on Ćujić et al. (2016) and are briefly described in the following sections.

# Enrichment factor (EF)

To estimate the extent of contamination in relation to the background levels for each element, an enrichment factor for each element  $(EF_x)$  was calculated based on the following equation:

$$\mathrm{EF}_{x} = \left(\frac{M_{x}}{\mathrm{Fe}_{\mathrm{area}}}\right) / \left(\frac{M_{\mathrm{back}}}{\mathrm{Fe}_{\mathrm{back}}}\right)$$

where  $M_x$  is the concentration of a given element, Fe<sub>area</sub> is the concentration of iron in the region, and  $M_{\text{back}}$  and Fe<sub>back</sub> refer to the background values of the region. These background values were determined from analysis of soils within a protected area in the region made in our laboratory (Cu, Pb, Zn, Fe, Mg, As, and Cd) or extracted from de Quadros et al. (2016) (Ni and Cr). A Se enrichment factor was not estimated because there is no background value for this element in the study region. Categories of contamination were based on Ćujić et al. (2016), where EF < 2 indicates deficiency to minimal enrichment, EF = 2–5: moderate enrichment, EF = 5–20: significant enrichment, EF = 20–40: very high enrichment, and EF > 40: extremely high enrichment.

Geo-accumulation index  $(I_{geo})$ 

The geo-accumulation index was obtained from the following equation:

$$I_{\text{geo}} = \log 2\left(\frac{[M_x]}{k[M_{\text{back}}]}\right)$$

where k = 1.5 is a correction factor to correct differences between background values due to lithospheric variations. The  $I_{geo}$  values were categorized into seven classes as described in Ćujić et al. (2016).  $I_{geo} < 0$ , Class 0 (practically uncontaminated);  $0 < I_{geo} < 1$ , Class 1 (uncontaminated to moderately contaminated);  $1 < I_{geo} < 2$ , Class 2 (moderately contaminated);  $2 < I_{geo} < 3$ , Class 3 (moderately to heavily contaminated);  $3 < I_{geo} < 4$ , Class 4 (heavily contaminated);  $4 < I_{geo} < 5$ , Class 5 (heavily to extremely contaminated);  $I_{geo} > 5$ , Class 6 (extremely contaminated).

# Contamination factor (CF)

The contamination factor (CF) is the ratio of the concentration of the element in the area to its background value, following the equation:

$$CF = \frac{M_x}{M_{back}}$$

Pollution load index (PI)

The pollution load index (PI) was calculated using the following equation:

$$\mathrm{PI} = \sum_{i=1}^{n} (\mathrm{CF})$$



Fig. 2 Winds direction and intensity in the study area

where n is the number of elements analyzed. This index provides comparative information between the samples analyzed and the regional background values. The region was considered polluted when PI exceeds 1.

#### Results

The dominant wind direction was N-NE and prevailing winds were of low intensity (Fig. 2). The concentration of PHEs of each quadrant and total area of study are presented in Table 1, while the spatial distribution based on the map of isolines is represented in Fig. 3. The mean ratio of each element (i.e., the mean values determined in the present study and the regional background) ranged from 0.48 to 3.5. The lowest ratio was for As, while Cr and Mn presented concentrations more than 3 times higher than the regional background (Table 1). All analyzed elements had concentrations lower than Brazilian legal limits.

There was no difference in the mean concentration of the chemical elements between quadrants, with the exception of Mn, which showed a difference between the concentration in quadrant 3 and quadrant 4 (p = 0.04). The highest concentrations of the analyzed elements did not coincide with the prevailing direction of winds, except for Fe, which had a slight increase in the concentration in the quadrant 3 (the dominant direction of winds).

The maps of isolines showed that As and Fe had higher concentrations around the power plant. In addition to the area surrounding the power plant, Cr exhibited high concentrations at some points in quadrant 2 and Zn in quadrants 1 and 3. The elements Cd and Pb exhibited higher concentrations in quadrant 1, Cu in quadrant 3, Se in quadrants 1 and 4, Ni in quadrant 2, and Mn in quadrants 2, 3, and 4 (Fig. 3).

There were significant correlations between PHEs concentration and distance to the plant in quadrants 2, 3, and 4. Significant positive correlation between

Table 1 Potentially harmful elements concentration (mg  $\mathrm{Kg}^{-1}$ ) in each quadrant and total area of study, background, and Brazilian legal limits values

		Cu	Pb	Ni	Zn	Cr	Fe	Mn	As	Cd	Se
Q 1	Mean	9.6	10.5	7.5	42.9	11.2	15830.4	467.0	1.7	56.2	393.4
N-NW	SD	2.7	3.9	3.2	14.4	5.1	5120.5	139.8	0.5	25.9	90.3
Q 2	Mean	11.0	12.7	9.2	59.1	14.3	15804.7	446.4	3.0	67.5	431.7
N-NE	SD	4.9	10.6	5.7	28.2	8.0	6825.8	180.9	1.0	60.3	96.5
Q 3	Mean	11.1	9.7	7.6	42.6	12.3	17214.6	424.0	2.7	59.8	411.8
S-SW	SD	2.4	2.8	2.1	8.7	2.6	3762.7	156.5	2.0	31.5	114.0
Q 4	Mean	11.5	9.6	10.0	52.8	12.5	14477.7	680.0	2.0	78.9	289.6
S-SE	SD	5.8	4.9	8.9	13.6	7.8	5280.3	182.8	0.7	28.1	66.2
Total area	Mean	10.8	11.0	8.4	50.3	12.8	15903.3	485.5	2.4	64.8	394.0
	SD	4.0	7.0	5.2	20.5	6.3	5434.0	182.6	1.3	42.1	103.7
	CV (%)	35.9	65.8	60.1	36.5	45.8	34.2	37.2	55.3	61.7	26.4
Background		4.4	7.6	5.0	32.0	4.0	11263.0	137.0	5.1	36.0	_
Legal limits		60	72	30	300	75	-	-	15	1300	-

SD standard deviation, CV (%) coefficient of variation



Fig. 3 Spatial distribution of potentially harmful elements in soil samples based on isolines maps

distance and concentration of Mn (in quadrant 2) and Cd (in quadrant 3) and significant negative correlation for As (in quadrants 3 and 4) and Se (in quadrant 4) (Table 2) were observed. Linear regression analysis

showed significance for As in the quadrant 3 and Mn in quadrant 2 (Table 3).

Results of the factor analysis are presented graphically in Fig. 4. The analysis resulted in four



Fig. 3 continued

 Table 2 Correlation index between plant distance and potentially harmful elements concentrations

	Correlation	Cu	Pb	Ni	Zn	Cr	Fe	Mn	As	Cd	Se
Q 1	r	_	_	_	_	_	_	_	_	_	-
N-NW	p value	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05
Q 2	r	_	_	_	_	-	-	0.63	-	-	_
N-NE	p value	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	0.04	> 0.05	> 0.05	> 0.05
Q 3	r	_	_	_	_	-	-	-	- 0.73	0.77	_
S-SW	p value	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	0.01	0.006	> 0.05
Q 4	r	_	_	_	_	-	-	-	- 0.79	_	- 0.74
S-SE	p value	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	0.01	> 0.05	0.02

Bold values mean values r with statistical significance (p < 0.05)

significant principal components explaining, respectively, 31.8, 17.8, 13.1, and 10.5% of total variance. Factor 1 was positively correlated with Cu, Ni, and Cr. Pb and Cd, in turn, were related to Factor 2, and As (positively) and distance (negatively) were related to Factor 3. Finally, Mn was positively correlated with

Element/ quadrant	$r^2$	Curve equation	p value
Arsenic Q3	0.748	$y = -\ 0.0003x + 5.4067$	0.005
Cadmium Q3	0.453	y = 0.0037x + 26.861	0.067
Manganese Q2	0.381	y = 0.026x + 344.27	0.025
Arsenic Q4	0.391	y = -0.0001x + 3.245	0.184
Selenium Q4	0.075	y = -0.0048x + 343.03	0.600

 
 Table 3 Linear regression analysis between plant distance and potentially harmful elements concentrations

Factor 4, while Se was negatively correlated. These data are plotted for the two main factors, element concentration and distance from the power plant (Fig. 4), and show that elements such as Cu, Ni, Cr, Fe, and Zn had similar behavior in the soil samples of the study region. The behaviors of both Mn and Cd differed from the remaining elements, and their concentrations were strongly correlated with distance to the power plant. Metalloids Se and As were inversely associated with distance to the power plant, and these results corroborate those shown in Fig. 3 (notably for Mn, Cd, As, and Se).

Because quadrant 3 captures the dominant wind direction, we plotted the detailed spatial distribution per point for each PHEs (Fig. 5) in this quadrant. The concentrations of Cu and Pb decreased up to a distance of 10 km, followed by a significant increase, and a further decrease up to 17.5 km. The concentrations of Ni, Zn, Cr, Fe, and Se decreased up to 5 km followed by an expressive increase and a subsequent decline. This distance (5 km) coincided with the distance between the power plant and the coal mining area (Fig. 6). The concentration of As decreased with increasing distance from the power plant, while Cr had the opposite behavior with low concentrations close to the power plant and a gradual increase in concentrations as distance increased. In contrast, Mn exhibited no pattern in quadrant 3.

Contamination indexes are given in Table 4. The enrichment factors for Cu, Pb, Ni, Zn, Fe As, and Cd in all quadrants and in the study region were classified as deficient or minimally enriched. Cr (in quadrants 2, 3, and 4 and in the region) and Mn (in quadrants 1, 2, 3, 4 and in the study region) had an enrichment factor considered moderately enriched. It was not possible to



**Fig. 4** Factorial analysis between PHEs and distance in coal region



Fig. 5 Potentially harmful elements concentration in soil of the Quadrant 3 considering the distance to coal-fired power plant



1 - coal-fired power plant; 2 - open-cast coal mine.

Fig. 6 Distance between the coal-fired power plant and open-cast coal mine. 1-coal-fired power plant; 2-open-cast coal mine

establish any of the indexes for Se because there are no background records of this element in the region.

The  $I_{geo}$  of Cu, Pb, Ni, Zn, Fe, As, and Cd in all quadrants or in the total area was always below 0 or at most 1 mg kg<sup>-1</sup>, while Cr and Mn had  $I_{geo}$  ranging from 0.9 to 1.7 mg kg<sup>-1</sup>. These results classify the soils of the region as Class 0, 1, or 2 ranging from uncontaminated to moderately contaminated. CF

varied from 0.3 mg kg<sup>-1</sup> (As in quadrant 2) to 5.0 mg kg<sup>-1</sup> (Mn in quadrant 4), while PI was between 1 mg kg<sup>-1</sup> and 2 mg kg<sup>-1</sup> for all quadrants and equal to 1.7 mg kg<sup>-1</sup> in the total study area.

Table 4 Enrichment factor (EF), geo-accumulation index  $(I_{geo})$ , contamination factor (CF), pollution load index (PI) of soil potentially harmful elements concentrations (mg Kg<sup>-1</sup>), considering each quadrant and total area of study

		Cu	Pb	Ni	Zn	Cr	Fe	Mn	As	Cd	Se	PI
Q1	EF	1.6	1.0	1.0	0.9	2.0	1.0	2.4	0.2	1.11	-	-
	$I_{\text{geo}}$	0.5	- 0.1	- 0.1	- 0.7	0.9	- 0.1	1.2	- 2.2	0.1	-	_
	CF	2.2	1.4	1.4	1.3	2.8	1.4	3.4	0.3	1.6	-	1.5
Q2	EF	1.8	1.2	1.3	1.3	2.5	1.0	2.3	0.4	1.3	-	_
	$I_{\text{geo}}$	0.8	0.2	0.3	0.3	1.3	- 0.1	1.1	- 1.3	0.3	-	_
	CF	2.5	1.7	1.8	1.9	3.6	1.4	3.3	0.6	1.9	-	1.9
Q3	EF	1.7	0.8	1.0	0.9	2.0	1.0	2.0	0.4	1.1	-	_
	$I_{\text{geo}}$	0.8	- 0.2	0.0	- 0.2	1.0	0.0	1.0	- 1.5	0.2	-	-
	CF	2.5	1.3	1.5	1.3	3.1	1.5	3.1	0.5	1.7	-	1.6
Q4	EF	2.0	1.0	1.6	1.3	2.4	1.0	3.9	0.3	1.7	-	-
	$I_{\text{geo}}$	0.8	- 0.3	0.4	0.1	1.1	- 0.2	1.7	- 2.0	0.6	-	-
	CF	2.6	1.3	2.0	1.7	3.1	1.3	5.0	0.4	2.1	-	1.8
Total area	EF	1.7	1.0	1.2	1.1	2.3	1.3	2.5	0.3	1.3	-	-
	$I_{\text{geo}}$	0.7	- 0.1	0.2	0.1	1.1	- 0.1	1.2	- 1.7	0.3	-	_
	CF	2.5	1.4	1.7	1.6	3.2	1.4	3.5	0.5	1.8	-	1.7

# Discussion

This study investigated the spatial distribution of PHEs within a 17.5-km radius of a large coal-fired power plant in the extreme south of Brazil. Although the concentrations of Cr and Mn were 3-5 times above background levels of the region, the indexes used to quantify the contamination revealed that the area has a low degree of contamination. In addition, no element exceeded the legally defined acceptable levels established for Brazilian soils (CONAMA 2009).

Chemical analysis in each quadrant revealed that the mean concentration of the analyzed elements (with the exception of Fe, which has a slightly larger concentration) was not higher in the dominant quadrant for wind direction (quadrant 3), in contrast to other studies (Li and Feng 2010; Agrawal et al. 2010; Dragovic et al. 2013; Ćujić et al. 2016). Statistically, there was only a difference between the concentration of Mn, which was higher in the quadrant 4 than in the quadrant 3.

Correlations and multivariate analysis of PHEs concentration and distance from the power plant were only significant for Mn and Cd (positive) and As and Se (negative). The regression analysis showed significance associations between Mn and As concentrations and distance from the power plant. These results contrast with numerous other studies that show an association between the concentration of elements and Environ Geochem Health (2019) 41:2131-2143

proximity to the power plant (Ćujić et al. 2016; Stafilov et al. 2018; Tanić et al. 2018). This difference seems to be due to other sources of pollution in the region, which contributed to the increases in concentrations of the elements. A gradual decrease in the concentration of several elements (up to 10 km for Cu and Pb and up to 5 km for Ni, Zn, Fe, and Se), but a further increase in concentration coinciding with the presence of the coal mine (contamination source) that is 5 km away from the power plant, and also in the dominant direction of the region's winds, was apparent (Fig. 5).

The contribution of the coal mine to soil contamination seems important for these elements, but mainly for Cd. Cd concentrations were low close to the power plant but increased after passing through the coal mine. In addition, the concentrations of Cd appear to be increasing in the region, since the present study showed concentrations of this element at least 2 times higher than 25 years ago in the same region  $(13-31 \ \mu g \ kg^{-1}; Morsch \ et \ al. \ 1993).$ 

Differences in dispersion and deposition of elements are common in areas of coal mining (Stalikas et al. 1997). These differences arise because of variations in the concentrations of PHEs in atmospheric particulate materials of different sizes (Zhang et al. 2018b), and it is commonly observed that the influence of power plants extends more than 5 km (Tanić et al. 2018).

Manganese did not exhibit any well-defined pattern of distribution in the dominant quadrant of the winds; the study of Tanić et al. (2018) also showed similar results. In contrast, As appears to be the element most related to the contribution of the power plant, as its levels gradually decreased as distance to the plant increased and it was little affected by the coal mine. The distinct behaviors of these two elements in relation to the other PHEs were confirmed by the multivariate analysis.

Nanos et al. (2015), studying the effect of scale size on the correlation between heavy metals and arsenic in an area with four thermoelectric power plants in Greece, observed no major sources of soil contamination in the region, but concluded that As in soil was related to the deposition of fly ash from the thermoelectric plants. In Macedonia, Stafilov et al. (2018) came to a similar conclusion, observing a trend of discrete anthropogenic local enrichment. Their study also showed that although the concentration of As and Pb was low, deposition in the soil of these elements was due to the deposition of fly ashes of the power plant.

The element As is found in higher concentrations in the finer particulate matter emitted by power plants (Guo et al. 2004). In addition, the high volatility of As facilitates long-distance atmospheric transport, but before this occurs it is subject to enrichment within the plume immediately above the source of pollution (Reddy et al. 2005). This influence may exceed 5 km distance from the emission source (Keegan et al. 2006).

The indexes used to quantify the degree of contamination (FE,  $I_{geo}$ , and CF) revealed low/moderate impact of these PHEs in contamination of the region, with higher degrees of enrichment for Mn and Cr. Stalikas et al. (1997) in a study in the region of a coal-fired power plant in Greece showed that the elements with the highest degree of enrichment in the area were Cr, Ni and Mn. The average  $I_{geo}$  of the PHEs was below 0.2, ranging from -2.2 (As) to 1.73 (Mn), and studies in regions of other thermoelectric plants in the world also showed uncontaminated-to-moderately contaminated soils (Zhai et al. 2009; Bhuiyan et al. 2010; Chandrasekaran et al. 2015; Ćujić et al. 2016), while some studies revealed higher rates of contamination (Mandal and Sengupta 2006; Li et al. 2014).

Another parameter used to measure anthropogenic activity was the coefficient of variation of the samples

(CV%) (Lu et al. 2013). Based on this parameter, we ordered the elements in decreasing order of CV %: Pb > Cd > Ni > As > Cr > Mn > Zn > Cu > Fe > Se. Although not an accurate measurement of anthropogenic activity, large variation among samples from the same region may indicate the contribution of anthropogenic sources.

The number of points investigated in the present study allowed a preliminary evaluation of the distribution of PHEs in the study area, revealing an interesting scenario in the dominant quadrant of winds. The study region needs to be further investigated, especially in two respects: a more systematic study in the dominant quadrant of the direction of winds that determine, with greater precision, the distribution of PHEs and the contribution of the power plant and a study that examines the importance of other point sources of contamination, such as coal mines and industries in the region.

# Conclusions

The concentration of the PHEs (Cu, Pb, Zn, Ni, Cr, Fe, Mn, Cd, As, and Se) did not exceed Brazilian legal limits for soil. Within the dominant quadrant of local winds, their concentrations were highest closest to the plant, but their concentrations were not higher than those of soils sampled elsewhere in the region. Therefore, there was little apparent contribution of the power plant to the concentrations of these PHEs in the region. Nevertheless, we consider that information concerning the spatial distribution of the contamination by these elements should be considered by managers for the purpose of land use planning in the region. Additional studies should be undertaken to identify the origin of the hot spots observed for some elements outside the dominant direction of the winds, including natural geochemical origins or other sources of pollution.

#### References

Agrawal, P., Mittal, A., Prakash, R., Kumar, M., Singh, T. B., & Tripathi, S. K. (2010). Assessment of contamination of soil due to heavy metals around coal fired thermal power plants at Singrauli region of India. *Bulletin of Environmental Contamination and Toxicology*, 85(2), 219–223.

- ANEEL Agência nacional de energia elétrica. (2008). Atlas de Energia Elétrica no Brasil. http://www.aneel.gov.br. Accessed 31 May 2018.
- Barrows, G., Garg, T., & Jha, A. (2018). The economic benefits versus environmental costs of India's coal-fired power plants. https://doi.org/10.2139/ssrn.3281904.
- Bhuiyan, M. A. H., Parvez, L., Islam, M. A., Dampare, S. B., & Suzuki, S. (2010). Heavy metal pollution of coal mineaffected agricultural soils in the northern part of Bangladesh. *Journal of Hazardous Materials*, 173, 384–392.
- Chandrasekaran, A., Ravisankar, R., Harikrishnan, N., Satapathy, K. K., Prasad, M. V. R., & Kanagasabapathy, K. V. (2015). Multivariate statistical analysis of heavy metal concentration in soils of Yelagiri Hills, Tamilnadu, India— Spectroscopical approach. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 137, 589–600.
- CONAMA—Conselho Nacional do Meio Ambiente. (2009). Resolução no 420, de 28 de dezembro de 2009. "Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas.", Diário Oficial [da República Federativa do Brasil], Brasília, DF, n° 249, de 30/12/2009 (pp. 81–84).
- Corrêia da Silva, Z. (1993). Candiota coalfield: A world class Brazilian coal deposit. *International Journal of Coal Geology*, 23(1–4), 103–116.
- Čujić, M., Dragović, S., Đorđević, M., Dragović, R., & Gajić, B. (2016). Environmental assessment of heavy metals around the largest coal fired power plant in Serbia. *CATENA*, 139, 44–52.
- da Silva Júnior, F. M. R., Tavella, R. A., Fernandes, C. L. F., Soares, M. C. F., de Almeida, K. A., Garcia, E. M., et al. (2017). Genotoxicity in Brazilian coal miners and its associated factors. *Human & Experimental Toxicology*. https://doi.org/10.1177/0960327117745692.
- de Quadros, P. D., Zhalnina, K., Davis-Richardson, A. G., Drew, J. C., Menezes, F. B., Flávio, A. D. O., & Triplett, E. W. (2016). Coal mining practices reduce the microbial biomass, richness and diversity of soil. *Applied Soil Ecology*, 98, 195–203.
- Dragović, S., Ćujić, M., Slavković-Beškoski, L., Gajić, B., Bajat, B., Kilibarda, M., et al. (2013). Trace element distribution in surface soils from a coal burning power production area: A case study from the largest power plant site in Serbia. *CATENA*, 104, 288–296.
- Goodarzi, F. (2006). Characteristics and composition of fly ash from Canadian coal-fired power plants. *Fuel*, 85(10–11), 1418–1427.
- Guo, X., Zheng, C. G., & Xu, M. H. (2004). Characterization of arsenic emissions from a coal-fired power plant. *Energy & Fuels*, 18(6), 1822–1826.
- Kalkreuth, W., Holz, M., Kern, M., Machado, G., Mexias, A., Silva, M. B., et al. (2006). Petrology and chemistry of Permian coals from the Paraná Basin: 1. Santa Terezinha, Leão-Butiá and Candiota Coalfields, Rio Grande do Sul. Brazil. International Journal of Coal Geology, 68(1–2), 79–116.
- Keegan, T., Farago, M., Thornton, I., Hong, B., Colvile, R., Pesch, B., et al. (2006). Dispersion of As and selected heavy metals around a coal-burning power station in

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central Slovakia. *Science of the Total Environment*, 358(1–3), 61–71.

- Li, X., & Feng, L. (2010). Spatial distribution of hazardous elements in urban topsoils surrounding Xi'an industrial areas,(NW, China): Controlling factors and contamination assessments. *Journal of Hazardous Materials*, 174(1–3), 662–669.
- Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., & Huang, L. (2014). A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. *Science of the Total Environment*, 468–469, 843–853.
- Lu, X., Liu, W., Zhao, C., & Chen, C. (2013). Environmental assessment of heavy metal and natural radioactivity in soil around a coal-fired power plant in China. *Journal of Radioanalytical and Nuclear Chemistry*, 295, 1845–1854.
- Mandal, A., & Sengupta, D. (2006). An assessment of soil contamination due to heavy metals around a coal-fired thermal power plant in India. *Environmental Geology*, 51(3), 409–420.
- Masih, A. (2018). Thar Coalfield: Sustainable Development and an Open Sesame to the Energy Security of Pakistan. *Journal of Physics: Conference Series*, 989(1), 012004.
- Masto, R. E., Singh, M. K., Rout, T. K., Kumar, A., Kumar, S., George, J., Selvi, V.A., Dutta P., Triphati, R.C. & Srivastava, N. K. (2019). Health risks from PAHs and potentially toxic elements in street dust of a coal mining area in India. *Environmental Geochemistry and Health*. https://doi.org/ 10.1007/s10653-019-00250-5.
- Morsch, V. M., Menegotto, E., & Martins, A. F. (1993). Cádmio em solos e sedimentos das regiões carboenergéticas de Candiota e de Charqueadas. *Geochimica Brasiliensis*, 7(1), 35–42.
- Nanos, N., Grigoratos, T., Martín, J. A. R., & Samara, C. (2015). Scale-dependent correlations between soil heavy metals and As around four coal-fired power plants of northern Greece. *Stochastic Environmental Research and Risk Assessment*, 29(6), 1531–1543.
- Pinto, E. A. D. S., Garcia, E. M., de Almeida, K. A., Fernandes, C. F. L., Tavella, R. A., Soares, M. C. F., et al. (2017). Genotoxicity in adult residents in mineral coal region—A cross-sectional study. *Environmental Science and Pollution Research*, 24(20), 16806–16814.
- Pires, M., & Querol, X. (2004). Characterization of Candiota (South Brazil) coal and combustion byproducts. *International Journal of Coal Geology*, 60, 57–72.
- Pires, M., Querol, X., & Teixeira, E. C. (2001). Caracterização do carvão de Candiota e de suas cinzas. *Geochimica Brasiliensis*, 15(1/2), 113–130.
- Pires, M., Fiedler, H., & Teixeira, E.C. (2002a). Distribuição geoquimica de elementos traço no carvão: Modelamento e aspectos ambientais. In E. C. Teixeira & M. Pires (Eds.), *Carvão e Meio ambiente* (p. 450) FEPAM/PUCRS/UFSC.
- Pires, M., Teixeira, E.C., & Querol, X. (2002b). Testes de lixiviação e extração sequencial em sistemas aberto e fechado das cinzas leves do carvão de Candiota—RS, em preparação.
- Reddy, M. S., Basha, S., Joshi, H., & Jha, B. (2005). Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion. *Journal of Hazardous Materials*, 123(1–3), 242–249.

- Rodriguez-Iruretagoiena, A., de Vallejuelo, S. F. O., Gredilla, A., Ramos, C. G., Oliveira, M. L., Arana, G., et al. (2015).
  Fate of hazardous elements in agricultural soils surrounding a coal power plant complex from Santa Catarina (Brazil). Science of the Total Environment, 508, 374–382.
- Roisenberg, C., Loubet, M., Formoso, M. L., Berger, G., Munoz, M., & Dan, N. (2016). Tracing the origin and evolution of geochemical characteristics of waters from the Candiota coal Mine Area (Southern Brazil): Part I. *Mine Water and the Environment*, 35, 29–43.
- Silva, N. I., Calarge, L. M., Chies, F., Mallmann, J. E., & Zwonok, O. (1999). Caracterização de cinzas volantes para aproveitamento cerâmico. *Cerâmica*, 45(296), 184–187.
- Stafilov, T., Šajn, R., Arapčeska, M., Kungulovski, I., & Alijagić, J. (2018). Geochemical properties of topsoil around the coal mine and thermoelectric power plant. *Journal of Environmental Science and Health, Part A*, 53(9), 1–16.
- Stalikas, C. D., Chaidou, C. I., & Pilidis, G. A. (1997). Enrichment of PAHs and heavy metals in soils in the vicinity of the lignite-fired power plants of West Macedonia (Greece). *Science of the Total Environment*, 204(2), 135–146.
- Swaine, D. J. (1990). *Trace elements in coal* (p. 278). London: Butterworths.
- Swaine, D. J., & Goodarzi, F. (1995). Environmental aspects of trace elements in coal (p. 312). Netherlands: Kluwer Academic Ž. Publishers.
- Tang, Q., Liu, G., Yan, Z., & Sun, R. (2012). Distribution and fate of environmentally sensitive elements (arsenic, mercury, stibium and selenium) in coal-fired power plants at Huainan, Anhui, China. *Fuel*, 95, 334–339.

- Tanić, M. N., Ćujić, M. R., Gajić, B. A., Daković, M. Z., & Dragović, S. D. (2018). Content of the potentially harmful elements in soil around the major coal-fired power plant in Serbia: Relation to soil characteristics, evaluation of spatial distribution and source apportionment. *Environmental Earth Sciences*, 77(1), 28.
- Teixeira, E. C., Migliavacca, D., Pereira Filho, S., Machado, A. G. M., & Dallarosa, J. B. (2008). Study of wet precipitation and its chemical composition in South of Brasil. *Anais da Academia Brasileira de Ciências*, 80(2), 381–395.
- World Coal Association. (2018). https://www.worldcoal.org. Accessed 01 June 2018.
- Zhai, M., Totolo, O., Modisi, M. P., Finkelman, R. B., Kelesitse, S. M., & Menyatso, M. (2009). Heavy metal distribution in soils near Palapye, Botswana: An evaluation of the environmental impact of coal mining and combustion on soils in a semi-arid region. *Environmental Geochemistry and Health*, 31(6), 759.
- Zhang, K., Chai, F., Zheng, Z., Yang, Q., Zhong, X., Fomba, K. W., et al. (2018a). Size distribution and source of heavy metals in particulate matter on the lead and zinc smelting affected area. *Journal of Environmental Sciences*, 71, 188–196.
- Zhang, K., Qiang, C., & Liu, J. (2018b). Spatial distribution characteristics of heavy metals in the soil of coal chemical industrial areas. *Journal of Soils and Sediments*, 18(5), 2044–2052.

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