Theme 1. Dealing with contamination of soil, groundwater and sediment

**PAPER OF A POSTER PRESENTATION – 4975**

# FATE OF HAZARDOUS ELEMENTS IN SOILS SURROUNDING A COAL-FIRED POWER PLANT COMPLEX

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**Abstract.** A study was carried out in the vicinity of a Portuguese coal-fired power plant in order to determine the extent and degree of soils contamination that may be related to the dispersion of the atmospheric emissions from the this coal-fired power plant. Metals and soluble ions concentrations have been determined both in-situ and in soil samples collected at sites potentially affected by the stacks' emissions. The analysis of trace elements was performed by means of X-ray fluorescence. The concentrations of twenty trace elements were determined: As, Ba, Ca, Co, Cu, Fe, Hg, K, Mn, Mo, Ni, Pb, Rb, S, Sb, Se, Sr, Ti, Zn, Zr, even though very few measurements were obtained for some of these elements in some specific areas around the power plant. The spatial distribution obtained by kriging in combination with the analysis of the data by Principal Component Analysis (PCA) showed three important situations in what concerns to metal concentration in soils and according to soil uses and geographic localization: the power plant (peak concentrations in the immediate area around the stacks), in the prevailing wind direction (from N-NW to E-SE and SE-S) and the area comprised between 6 and 20 km from the power plant (mostly agricultural and pasture areas). Considering that soil's concentration for the studied elements may had its origin in the past atmospheric emissions from the coal-fired power plant and were accumulated in surface soils over the past decades, the height of the stacks and the dispersion by seasonal winds, could explain the observed enrichment of some elements in the area between the 6 and 20 km. However, some of the typical heavy metals associated with coal combustion emissions such as Cd, Cr, Hg and Ni were not significantly registered in the area under study and this may suggest the contribution from other industrial plants present in the region.

Keywords: Soils, element contamination, coal power plant, spatial interpolation

## 1. Introduction

Many hazardous air pollutants are associated with emissions from coal-fired power plants. Coal is composed mainly by organic material with inorganic material as minor constituent. Organically coal consists primarily of carbon, hydrogen and oxygen and with lesser quantities of sulphur and nitrogen. The inorganic constituents include minerals and trace elements such as As, B, Be, Cd, Cl, Cr, Co, Cu, F, Hg, Mn, Mo, Ni, Pb, Se, V, and various acid gases.

Following coal combustion, some trace elements become concentrated in ash and may be released to the environment either through leachate from ash disposal dams or in the gas or particulate phase in flue gas. Flue-gas emissions from coal burning are characteristically enriched in nanoparticles, toxic and greenhouse gases, volatile organic compounds and volatile inorganic species, including As, B, Cd, Hg, Se, organometallic compounds, and other gas components (Hower et al., 2013; Ribeiro et al., 2010). The solid products of coal burning include fly ash, bottom ash and boiler slag, which may be enriched in several trace elements. In what concerns to metals and metalloids, atmospheric emissions and leaching of solid combustion by-products during their disposal or sedimentation, are the main pathways to soils of the surrounding area.

Soils around a coal power plant are enriched in Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti and Zn (Klein and Russell, 1973) and in Mo, As, Mn, Pb, Be, and V (Mandal and Segupta, 2006). Bityukova et al., (2000) observed that the levels of As, Cr, Mn and V were more than three times higher and the levels of Pb and Zn were more than five times higher than the background levels for industrial polluted soils resulting from fossil fuel combustion. Dragović et al., (2008) observed an enrichment of Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn in soils surrounding a coal-fired power plant in Serbia and Keegan et al., (2006) observed an increase of As in soils around a coal-burning power station in Slovakia. Thus, soil at sites in the surrounding area of a coal-fired power plants potentially present higher concentrations in various pollutants depending upon the power plant technology (filtration systems), coal characteristics, and climatic variations, including humidity and rainfall. These factors change over time mostly due to the technology development and due to the different types of coal used as fuel.

A study was carried out in the vicinity of a Portuguese coal-fired power plant in order to determine the extent and degree of soils contamination that may be related to the dispersion of the atmospheric emissions from the plant's stacks. Metals and soluble ions have been determined both in situ and in soil samples collected at sites potentially affected by these atmospheric emissions. At the same time, dust collectors were set in these sites to study the flux deposition of the particle matter and establish a relation between the deposition flux and soil contamination patterns. The variation of the concentration pattern with the distance to the emitting source was also analyzed as well as the influence of local meteorological parameters in the concentration pattern. To achieve this, spatial distribution obtained by kriging in combination with the analysis of the data by Principal Component Analysis (PCA) were used.

## 2. Materials and methods

### *2.1 Study area*

The present study was conducted in the vicinity of a coal-fired power plant located in the southwest coastline of Portugal, 6 km south-east from the town of Sines. This power plant is located in an important industrial center with others heavy industrial plants, including a petrochemical complex, a refinery and a resins plant. The power plant has been operational since 1986 with two stacks of 225 m height and it is fuelled by bituminous coal. It has a coal storage capacity over than 1 million tons in 4 active piles with 150 000 tons each and in one passive pile with 700 000 tons (Dinis et al., 2012; 2013; 2014).

Data on this emission source is reported in the European database "European Pollutant Release and Transfer Register" for the period between 2007 and 2012 (Table 1) (E-PRTR, 2015).

Table 1: Pollutant releases to air from Sines coal-fired power plant (extracted from E-PRTR, 2015)

| **Releases to air** | **2007** | **2008** | **2009** | **2010** | **2011** | **2012** |
|---|---|---|---|---|---|---|
| Arsenic and compounds | 40.0 kg | 31.0 kg | 33.0 kg | - | 27.2 kg | 34 kg |
| Chromium and compounds | 127 kg | - | - | - | - | - |
| Mercury and compounds | 107 kg | 209 kg | 95.0 kg | 54.7 kg | 76.6 kg | 98.2 kg |
| Nickel and compounds | 126 kg | 271 kg | 341 kg | 254 kg | 305 kg | 336 kg |
| Zinc and compounds | - | 265 kg | 349 kg | 220 kg | 290 kg | 354 kg |
| Particulate matter ($PM_{10}$) | 587 ton | 394 ton | 130 ton | 99.7 ton | 286 ton | 178 kg |

Despite the efficiency of the stacks' filtration system has been improved over the years and reduced significantly the amount of particulate matter released, the atmospheric emissions from this power plant still present a high fluctuation in what concerns to the amount of trace metals released into the environment. Therefore, the potential increase in soil metals concentration remains due to both past and present fugitive emissions.

The historical (10 years) meteorological data referring to the study area indicates that the prevailing wind direction is from the sector N-NW. The sampling periods were performed during March/April and September/October 2011 and the prevailing wind direction during these periods were from N-NW and from N-NE, respectively (Dinis et al., 2012).

### *2.2 Sampling and analysis*

The design of the sampling area was based on the influence of the stacks emissions considering the potential effect on soils contamination up to a distance of 20 km from the coal plant. The sampling area was defined by two concentric circles with a radius of 6 and 20 km centered in the plant stacks. The spatial heterogeneity and the deposition flux of dust fallout were assessed in both areas.

A total of 50 samplings sites, represented in Figure 1, were defined in the area under study: 13 sampling sites within the 6 km circle, with urban and sub-urban characteristics, and 37 sampling sites within the 6-20 km circle, mainly rural. The sampling sites were selected according to the influence from the height of the stacks, the distance to residential areas, the use of soil and accessibility to the sites. Sampling procedure was carried out in two different periods, representing dry or rainy atmospheric conditions (Dinis et al., 2013; 2014).

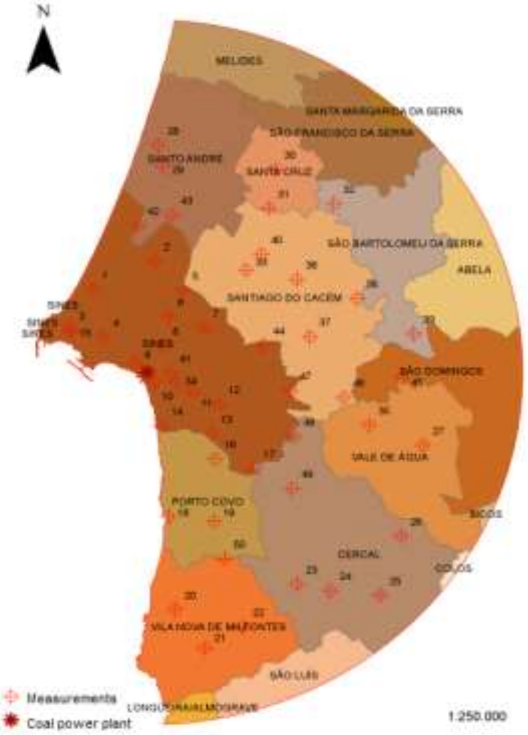

Figure 1: Study area and sampling sites around the coal-fired power plant (source: Dinis et al., 2013, 2014).

The analysis of trace elements concentration in soil was performed by means of X-ray fluorescence (XRF) with a field portable equipment. Two measurements were done in-situ and repeated in the laboratory with soil samples collected in the upper 5 cm of soil at each sampling site.

The element concentration detected in surface soils were compared with soil quality guidelines according to soil use: agricultural, residential, commercial and industrial (Dinis et al., 2012; CCME, 2011).

## 3. Results and discussion

The elemental analysis of the soil samples collected in the study area measured the concentration of the following trace elements: As, Ba, Ca, Co, Cu, Fe, Hg, K, Mn, Mo, Ni, Pb, Rb, S, Sb, Se, Sr, Ti, Zn, Zr, even though very few measurements were obtained for some of these elements in some specific areas around the power plant. Mercury was identified only in 16 measurements, nickel in 11 measurements, selenium in 8 measurements and antimony in 6 measurements. The results presented in this study refers to two sampling campaigns, Nº 2 (SC2) and Nº 3 (SC3), carried out between March/April and between September/October 2011. The average values and the statistical description of the obtained results from both sampling campaigns are presented in Table 2 and Table 3. The number of cases for each detected element is also presented (N) showing the variation in abundance of several elements in the study area.

Table 2: Statistical summary of trace element concentrations measured in the SC2 (mg/kg)

| Element | Average | Median | S.D. | Skewness | Max. | Min. | N |
|---|---|---|---|---|---|---|---|
| As | 71.22 | 70 | 13.28 | 0.31 | 101 | 52 | 41 |
| Ba | 1679 | 1679 | 195.16 | - | 1817 | 1541 | 2 |
| Co | 330.75 | 252 | 183.52 | 1.87 | 603 | 216 | 4 |
| Cu | 41.33 | 39 | 12.42 | 0.75 | 61 | 29 | 6 |
| Fe | 17839.85 | 10066 | 17631.61 | 1.49 | 74805 | 829 | 41 |
| Hg | 12 | 12 | - | - | 12 | 12 | 1 |
| Mn | 517 | 280 | 658.05 | 2.82 | 3392 | 59 | 36 |
| Mo | 11 | 9 | 3.46 | 1.73 | 15 | 9 | 3 |
| Ni | - | - | - | - | - | - | - |
| Pb | 23.61 | 18 | 25.84 | 5.08 | 162 | 8 | 33 |
| Rb | 55.39 | 52 | 31.06 | 0.69 | 138 | 10 | 41 |
| Sb | - | - | - | - | - | - | - |
| Se | - | - | - | - | - | - | - |
| Sr | 71.49 | 51 | 78.23 | 2.68 | 386 | 10 | 41 |
| Ti | 3143.06 | 2738 | 1728.07 | 0.25 | 6468 | 647 | 35 |
| Zn | 52.51 | 38 | 61.34 | 3.48 | 351 | 9 | 37 |
| Zr | 112.1 | 107 | 71.13 | 0.45 | 259 | 16 | 41 |

Table 3: Statistical summary of trace element concentrations measured in the SC3 (mg/kg)

| Element | Average | Median | S.D. | Skewness | Max. | Min. | N |
|---|---|---|---|---|---|---|---|
| As | 69.51 | 63 | 19.79 | 0.72 | 122 | 35 | 42 |
| Ba | 1001 | 1001 | 209.3 | - | 1149 | 853 | 3 |
| Co | 320.89 | 276 | 116.26 | 0.68 | 495 | 187 | 5 |
| Cu | 72.75 | 46 | 74.24 | 2.57 | 252 | 31 | 5 |
| Fe | 17606.27 | 9440 | 19296.29 | 1.53 | 89231 | 782 | 42 |
| Hg | 14 | - | - | - | - | - | 1 |
| Mn | 558.45 | 389 | 585.95 | 2.09 | 3091 | 49 | 34 |
| Mo | 18.42 | 15 | 9.26 | 2.25 | 51 | 9 | 14 |
| Ni | - | - | - | - | - | - | - |
| Pb | 29.58 | 19.5 | 41.27 | 5.81 | 300 | 10 | 31 |
| Rb | 49.72 | 42 | 35.31 | 0.87 | 152 | 3 | 42 |
| Sb | 82 | 82 | - | - | 82 | 82 | 1 |
| Se | 4 | 4 | - | - | 4 | 4 | 1 |
| Sr | 78.69 | 48.50 | 85.01 | 2.59 | 506 | 5 | 41 |
| Ti | 4141.67 | 3214 | 4105.6 | 3.78 | 27900 | 625 | 35 |
| Zn | 93 | 41. | 310.21 | 8.24 | 2676 | 10 | 37 |
| Zr | 99.85 | 75 | 77.72 | 1.04 | 304 | 10 | 41 |

Some of the selected elements were detected in very few sampling points: Ba, Co, Cu, Hg and Mo in addition to Ni for sampling campaign Nº 3. Elements content in soils were compared with reference levels according to soil use: agricultural, residential commercial or industrial. The Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health were used for comparison with the selected elements (CCME, 2011).

The concentration values obtained for As and Co are above the respective guideline level for all types of soil use while Cu concentration is below the guideline level only for commercial and industrial soil use and Pb and Sn concentrations are below the respective guideline level for all types of soil use. Barium, mercury and molybdenum concentrations exceed the respective guideline levels for agriculture and residential soils. Nevertheless, it should be pointed out that some of these elements were detected in very few sampling sites and are not statiscally representative.

The same variation pattern was observed in the second sampling campaign: Pb, Zn and Cu concentrations are below the guidelines limits and As and Co concentrations are above the guidelines levels for all types of soil use. Barium, Hg and Mo concentration values are above the respective guidelines levels for agricultural and residential soil use.

On average, the concentration values are very similar for both sampling campaigns with the exceptions of Hg, Sb and Se, which were detected only in one of the two presented sampling campaigns and of Ba, Cu and Zn, which concentrations present a fluctuation from SC2 to SC3. The concentrations of the selected elements within the 0-6 km area and within the 6-20 km area are presented in Table 4.

Table 4: Average values and statistical description of measurements for selected elements from SC2 and SC3.

| | **Sampling Campaign Nº 2** | | | | | **Sampling Campaign Nº 3** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Average** | **± σ** | **Max.** | **Min.** | **N** | **Average** | **± σ** | **Max.** | **Min.** | **N** |
| Area within the 6 km circle | | | | | | | | | | |
| As | 68.67 | 13.61 | 101 | 53 | 12 | 67.04 | 19.04 | 122 | 48 | 12 |
| Ba | 1817 | - | 1817 | 1817 | 1 | - | - | - | - | - |
| Co | - | - | - | - | - | 365.5 | 183.14 | 495 | 236 | 1 |
| Cu | 35.5 | 9.19 | 42 | 29 | 2 | 37 | - | 37 | 37 | 1 |
| Fe | 14682.75 | 20980.5 | 74805 | 1847 | 12 | 14797.71 | 19747.92 | 81125 | 782 | 12 |
| Mn | 294.56 | 296.42 | 926 | 67 | 9 | 415.11 | 373.75 | 1270 | 49 | 10 |
| Mo | 9 | - | 9 | 9 | 1 | 16.89 | 5.9 | 26 | 9 | 6 |
| Pb | 17.67 | 8.06 | 35 | 8 | 9 | 22.5 | 9.44 | 40 | 11 | 7 |
| Rb | 56.58 | 28.13 | 123 | 18 | 12 | 41.92 | 29.49 | 120 | 4 | 12 |
| Sb | - | - | - | - | - | 82 | - | 82 | 82 | 1 |
| Se | - | - | - | - | - | 4 | - | 4 | 4 | 1 |
| Sr | 92.42 | 94.64 | 299 | 20 | 12 | 100.45 | 87.46 | 293 | 5 | 11 |
| Ti | 2719.89 | 1720.69 | 6468 | 1081 | 9 | 5430.81 | 6955.99 | 27900 | 643 | 9 |
| Zn | 34.11 | 28.02 | 83 | 9 | 9 | 62.79 | 53.34 | 182 | 11 | 10 |
| Zr | 102.5 | 70.62 | 229 | 29 | 12 | 79.17 | 52.72 | 215 | 16 | 12 |
| Area within the 6 and 20 km circles | | | | | | | | | | |
| As | 72.28 | 13.24 | 95 | 52 | 29 | 70.54 | 20.17 | 113 | 35 | 29 |
| Ba | 1541 | - | 1541 | 1541 | 1 | 1001 | 209.3 | 1149 | 853 | 2 |
| Co | 330.75 | 183.52 | 603 | 216 | 4 | 308.14 | 107.6 | 495 | 187 | 4 |
| Cu | 44.25 | 13.96 | 61 | 30 | 4 | 77.86 | 78.66 | 252 | 31 | 4 |
| Fe | 19146.24 | 16283.04 | 60366 | 829 | 29 | 18788.82 | 19155.93 | 89231 | 804 | 29 |
| Hg | 12 | - | 12 | 12 | 1 | - | - | - | - | - |
| Mn | 591.81 | 730.03 | 3392 | 59 | 27 | 617.65 | 648.2 | 3091 | 71 | 24 |
| Mo | 12 | 4.24 | 15 | 9 | 2 | 19.33 | 10.89 | 51 | 9 | 8 |
| Pb | 25.83 | 29.79 | 162 | 9 | 24 | 32.18 | 47.85 | 300 | 10 | 23 |
| Rb | 54.9 | 32.66 | 138 | 10 | 29 | 53 | 37.23 | 152 | 3 | 29 |
| Sr | 62.83 | 70.42 | 386 | 10 | 29 | 70.14 | 83.26 | 506 | 5 | 28 |
| Ti | 3289.54 | 1739.83 | 5954 | 647 | 26 | 3650.57 | 2199.12 | 9506 | 625 | 21 |
| Zn | 58.43 | 68.08 | 351 | 9 | 28 | 103.63 | 359.61 | 2676 | 10 | 28 |
| Zr | 116.07 | 72.20 | 259 | 16 | 29 | 108.56 | 85.01 | 304 | 10 | 29 |

For both sampling campaigns, the obtained concentrations are higher in the outer sampling area (6-20 km) with the exception of Ba, Rb and Sr for SC2 and Co, Sr and Ti for SC3.

Some of the typical heavy metals associated with coal combustion emissions such as Cd, Cr, Hg and Ni were not detected in the sampling area or at least in a significant number of cases. This may result from the limitations of the field XRF, in particular high soil moisture, metals interference (Fe tends to absorb Cu X-rays, whereas Cr levels will be enhanced in the presence of Fe), lack of sensitivity due to peak overlapping (high detection limits demanding more field measurement time, e.g., Cd and Hg are not detected easily by XRF because of their detection limit) (Hunter, 2011).

The dispersion of the atmospheric emissions from industrial processes and consequently the deposition on soils is mainly influenced by wind parameters, rainfall, resuspension of dust from earth's surface, intensified agricultural activities, road traffic and other sources of emissions that may be present. In cases where none of these factors is present, the intensity of particles deposition and consequently the concentration on soil should decrease with the distance to the main source of pollution.

The element concentrations were interpolated to unsampled sites by ordinary kriging. Iso-concentration maps have been made for some elements with the interpolated data from both sampling campaigns. The distribution profiles are presented in Figure 3 and Figure 4.

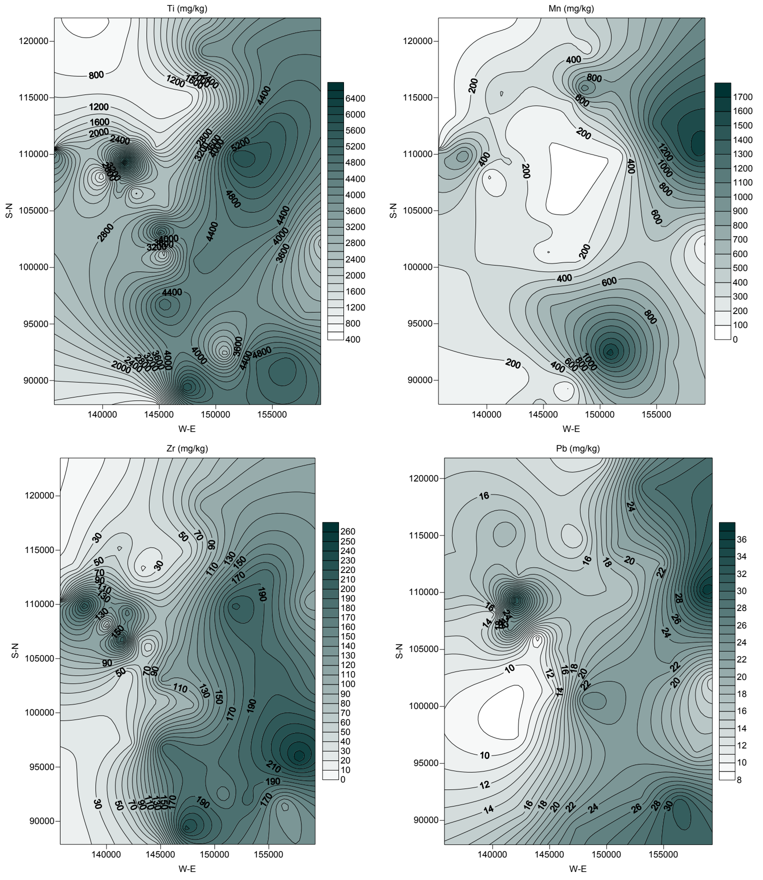

Figure 3: Iso-concentrations maps for Ti, Mn, Zr and Pb (data from SC2).

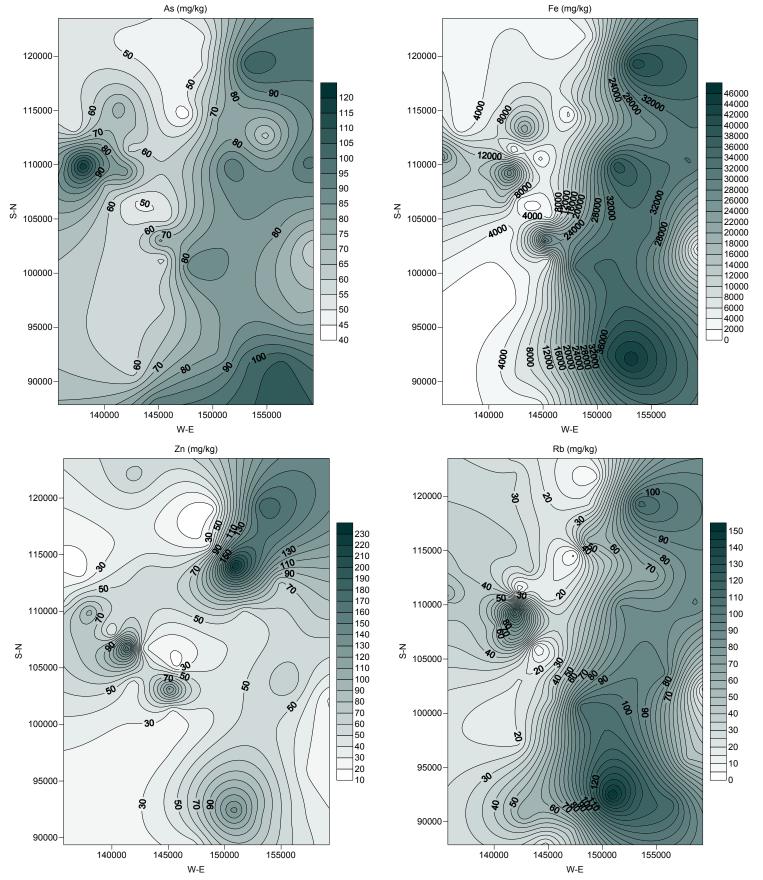

Figure 4: Iso-concentrations maps for As, Fe, Zn and Rb (data from SC3).

The iso-concentration maps for the selected trace elements showed a pattern concentration described by either marked element enrichment for distances between the 6 and 20 km in the NE-E and E-SE sectors and peak concentrations in the immediate area around the stacks. The stacks are locate at approximately 141000 m (x) and 107600 (y). The distribution of the selected elements as well as other elements in surface soil seems to follow a similar pattern observable in both sampling campaigns. Nevertheless, no regular trends could be observed for elemental concentration and distance from the power plant.

During both sampling campaigns the prevailing wind directions were from N-NW and N-NE and this trend was confirmed with data from a 10 years period of meteorological observations. This could explain at some extent the metals concentration pattern in soils. However, peak concentrations in other wind directions rather than the prevalent one, suggest the contribution from others sources. An important feature in atmospheric emissions is the influence of stack height in the dispersion and deposition patterns: about 25% of emitted particles from a 40 m stack fell within 5 km and 34% within 10 km (Keegan et al., 2006). It should be pointed out the presence of the coal storage in the immediate area around the stacks and the peak concentrations in the immediate vicinity of the power plant is likely to be predominately from local fugitive sources in the form of windblown ash and dust.

The results from the application of the principal component analysis (PCA) showed that there four significant principal components: 1) As, Ti, Zr, Rb and Mn; 2) Pb; 3) As and 4) Pb and Zn. In general, for these sets of significant association, the highest concentration values were observed near the power plant (S8, S9, S12, S14), in the SE direction (S16, S17, S23, S24) and in the NE direction (S7, S32, S33).

The spatial distribution obtained by kriging in combination with the analysis of the data by principal component analysis showed three important situations in the study area according to soil uses, wind direction and geographic localization: the power plant (peak concentrations in the immediate area around the stacks), in the prevailing wind direction (from N-NW to E-SE and SE-S) and the area comprised between 6 and 20 km from the power plant (mostly agricultural and pasture areas). These findings overlap with the pattern of the particulate matter flux deposition registered in the study area. Also, soil's concentration pattern was observed for most of the detected elements in some repetitive areas in all sampling campaigns, which explains the correlation found between some elements. Soil concentration and deposition flux correlation made also possible the identification of common sources of contamination to the area under study (Dinis et al., 2011; Dinis et al., 2012).

## 4. Conclusions

A study was carried out in the vicinity of a Portuguese coal-fired power plant in order to determine the extent and degree of soils contamination related to the atmospheric emissions from this industrial facility. The concentration of trace elements have been determined both in-situ and in top soil samples, collected at sites potentially affected by power plant operations. The obtained results were above of the international soil quality guidelines for some of the identified elements. On average, the concentrations of several elements measured in soil, such as As, Ba, Co, Hg, Mo, Ni and Se, are above the soil quality guidelines for agricultural and residential soils. Nevertheless, with the exception of As and Mo very few measurements were obtained for these elements.

The concentrations were used to evaluate the spatial distribution obtained by kriging in combination with the analysis of the data by principal component analysis (PCA). A similar spatial pattern was observed for both sampling campaigns: on average the concentration is higher within the outer area (6 - 20 km). High concentrations were measured in the NE, E and SE directions, influenced by the wind parameters and the height of the stacks, which are expected to have transported the atmospheric emissions for relatively long distances from the source. The peak concentrations measured in soils around the stacks could not have fallen from the plume vertically and may be directly related with the coal storage near the stacks, in addition to fugitive emissions from ground-level areas enriched in these elements by other means.

Considering that soil's concentration for the measured trace elements had its origin in the past emissions from the power plant' s stacks and were accumulated in surface soils over the past decades, the height of the stacks and the dispersion by seasonal winds, could explain the observed enrichment of some elements within the 6 - 20 km area. However, some of the typical heavy metals associated with coal combustion emissions such as Cd, Cr, Hg and Ni were not significantly registered in the area under study and this may suggest the contribution from other sources related to coal combustion or to the power plant, in addition to others industrial plants present in the region (Dinis et al., 2011).

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