STUDY OF PM EMISSION FROM A COKE FACTORY USING ENVIRONMENTAL MAGNETISM AND COMPLEMENTARY METHODS

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Abstract

The coke production can lead to adverse consequences for the human health and the environment. The particulate matter (PM) emission comprises particles with a variety of grain size, morphology and composition.
As first approach, the dispersion of PM was studied using a simple atmospheric dispersion model (Gaussian Models) according to the emission conditions. Then, taking into account the prevalent wind direction, 16 sites in the study area were sampled (soil samples) and studied *in-situ* (magnetic susceptibility measurement, κ_{is}).
Chemical and magnetic mineralogy results show high concentration of Vanadium and Nickel and strong predominance of ferrimagnetic mineralogy. On the other hand, the spatial distribution of these variables shows agreement with Gaussian models of dispersion.

Resumen

El coke es el residuo sólido que se produce por destilación del carbón en ausencia de oxígeno. La producción de coke puede generar consecuencias adversas sobre la población y el medio ambiente en general expuesto a las emisiones atmosféricas. El material particulado (MP) emitido comprende una amplia variedad de tamaños de granos, morfología y composición.
En una primera aproximación, la dispersión del MP fue estudiada utilizando un modelo de dispersión atmosférico simple (Modelo Gaussiano) acorde a condiciones aproximadas de emisión. Luego, teniendo en cuenta las direcciones más frecuentes de los vientos, 16 puntos geográficos en el área de estudio fueron elegidos. En estos, se tomaron muestras de suelo y se midió la susceptibilidad magnética *in situ* (κ_{is}).
Estudios químicos y de mineralogía magnética muestran alta concentración de Vanadio-Níkel y una fuerte predominancia de minerales magnéticos del tipo ferrimagnéticos. Por otro lado, la distribución espacial de estas variables muestra concordancia con los resultados del modelo Gaussiano de dispersión.

Introduction

Coke is a solid residue produced by distillation of coal in the absence of oxygen (coking). The particulate matter (PM) emission comprises particles with a variety of grain size, morphology and composition. In the PM detached we could found a wide range of trace elements such as As, B, Br, Cr, Cu, Fe, Hg, Mo, Ni, Pb, Ti, V, Zn between others. Some of these heavy metals are characteristics of the process in mention (e.g. Ni and V), helping to identify the affected area for the pollution source.

Magnetic mineralogy studies have been successfully developed in recent years, starting with the investigation of sediments in the 1980s (Thompson and Oldfield, 1986). Ferrimagnetic iron oxide particles (mainly magnetite and maghemite) in fly ashes, originating during high-temperature combustion of fossil fuels, are potentially the most significant source of anthropogenic ferrimagnetic found in the upper soil horizons e.g. Flanders (1994). Several authors have examined the effectiveness of this method to study different environmental impacts and they have obtained positive results

(Kapicka et al. 1999, Chaparro et al. 2006a, 2006b). Magnetic parameters allow us to estimate the extension of the area affected by pollutants. On the other hand, the heavy metals and their relative concentration need to be determined by other methods.
Several studies have shown that a close relation exists between the distribution of magnetic particles and the distribution of heavy metals around industrial sites. For example, Strzyszcz (1993) and Heller et al. (1998) studied magnetic parameters of soils and the association with heavy metals content.

The aim of this study was to examine in detail urban topsoil from the city of Tandil (37° 17' 22" S; 59° 11' 47" W, Argentina) using magnetic mineralogy. In addition, links between concentrations of anthropogenic magnetic particles and concentrations of V, Ni, Cr and Zn were analyzed. Magnetic and non-magnetic studies in soils from the influence area of a small coke factory (PM emission) are reported. As a first approach, the dispersion of PM was studied using a simple atmospheric dispersion model (Gaussian Model) according to the emission conditions.

Methods

Sampling and in situ κ_{is} measurements were done in several sites (Fig. 1). Sites were chosen regarding the prevalent wind directions, the potentially affected population and the proximity from other pollutants sources. Several in situ readings at each site were done and then averaged. Thirty six soil samples (at 2 cm and 20 cm depth) were collected for measurements in the laboratory. At each sampling point, soil samples were collected by a stainless steel trowel and stored in a plastic bag. In the laboratory, each sample was sieved through a 2-mm steel mesh.

Figure 1: The study area

At the laboratory of IFAS (Argentina): Magnetic susceptibility (χ), Anhysteretic Remanent Magnetization (ARM) and Isothermal Remanent Magnetization (IRM) were measured. They are magnetic concentration-dependent parameters. Combining magnetic parameters graphically is very useful for assessing magnetic mineralogy. For example, SIRM/ χ vs H_{CR} plot can be used to identify magnetic mineralogy (Peters et al. 2003).

The King's plot (anhysteretic susceptibility κ_{ARM} versus κ, King et al. 1982) was used to identify dominant size of the magnetic minerals. On the other hand, the κ_{ARM}/κ-ratio (Dunlop et.al., 1997) was also used to analyze the presence of fine magnetite (<0.1µm).
From backfield IRM studies, the S-ratio is a dimensionless parameter that indicates content of ferrimagnetic (e.g.: magnetite, titanomagnetite or maghemite) versus antiferromagnetic materials (e.g.: hematite or goethite). Values close to +1 correspond to the predominance of ferrimagnetic material; on the contrary, values close to -1 correspond to antiferromagnetic materials.

Trace elements (V, Ni, Cr and Zn) in soil samples were determined using LIBS technique (laser induced breakdown spectroscopy, Diaz Pace, 2002). Laser pulse (Nd:YAG, 100 mJ, temporal delay at 6 µs, temporal width of 2 µs) is focused into sample surface. Little plasma (dielectric breakdown) is generated, which is analyzed by spectroscopy. This technique is able to both quantify and identify trace elements (a few ppm), the method is high sensitive; very low cost and fast. For quantitative calibration, 7 soil samples were measured by ICP-OES (Method US-EPA/600/R-94/111), and then for each element, calibration curves were done (i.e. concentration by ICP-OES vs. LIBS signal).

The spatial continuity of magnetic and chemical variables was investigated using the Moran's Index (MI) (Crassie, 1993). It is a measure of spatial autocorrelation, how related the values of a variable are based on the locations where they were measured. In the absence of spatial autocorrelation I has expected value: $E[I]= -1/(n-1)$. Values $I > E[I]$ indicate positive autocorrelation and values $I < E[I]$ negative autocorrelation.

The relationship between magnetic and chemical variables was studied using multivariate statistical techniques. There are several measures of correlation to express the relationship between two or more variables (Johnson, et.al 1992). Simple correlation analysis estimates the extent to which two variables are related; multiple correlation analysis estimates the relationship between a variable and a set of variables. Principal component analysis (PCA) was computed to found a new variable set (Principal Component) not correlated, reducing the initial number of variables to facilitate the data interpretation. On the other hand, canonical analysis (CCA) allows the investigation of the relationship between two sets of several variables. In CCA, a data set concerning several variables is considered and grouped into two sets. The use of CCA is appropriated when the study of structure of covariance matrix between two sets of variables is the main analysis aim. Specifically, CCA estimates the correlation among a set of variables Xi and another Yi.

Results

Air pollution model SCREEN3 (USEPA, 1992) predicts two very different outputs according to atmospheric conditions. The Figure 2 shows the results. There are strong influences of the stability class over the PM distribution. For unstable classes (A and B), the well-marked peaks concentration are closer to the factory (about 1000 m) and then decreases quickly. On the contrary, the peaks for stable class (C and D) are not well defined; in this condition the peaks are about between 2000-2500 m from factory, and the concentration beyond these peaks would become about constant.
The Fig. 3 shows the distribution of concentration of heavy metals from the pollution source. Vanadium, Chrome and Nickel have a similar behavior, showing a strong decrease of concentration from the factory to 800-1000 m. The concentration increases about 2000 m, and decreases for farthest zones (>2000 m). This general behavior could be explained as following: large particles that are not reached by Gaussian Model (>>20 µm) fall out closer to the source. On the other hand, at about 2000 m, small particles (<20 µm) deposited as Gaussian Model predicts for wind velocities (close to annual mean condition) and atmospheric stability (unstable conditions).

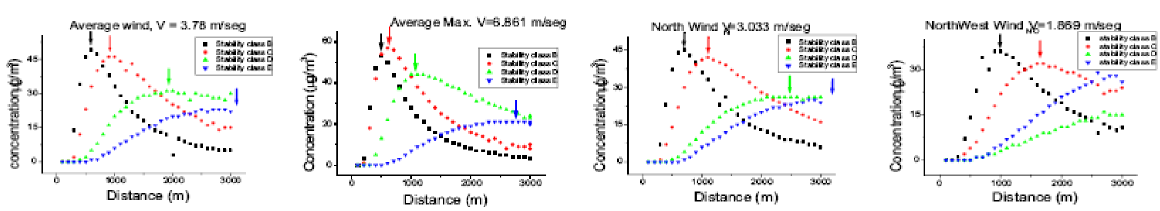

Figure 2: Pollutant distribution predicted by Gaussian Model

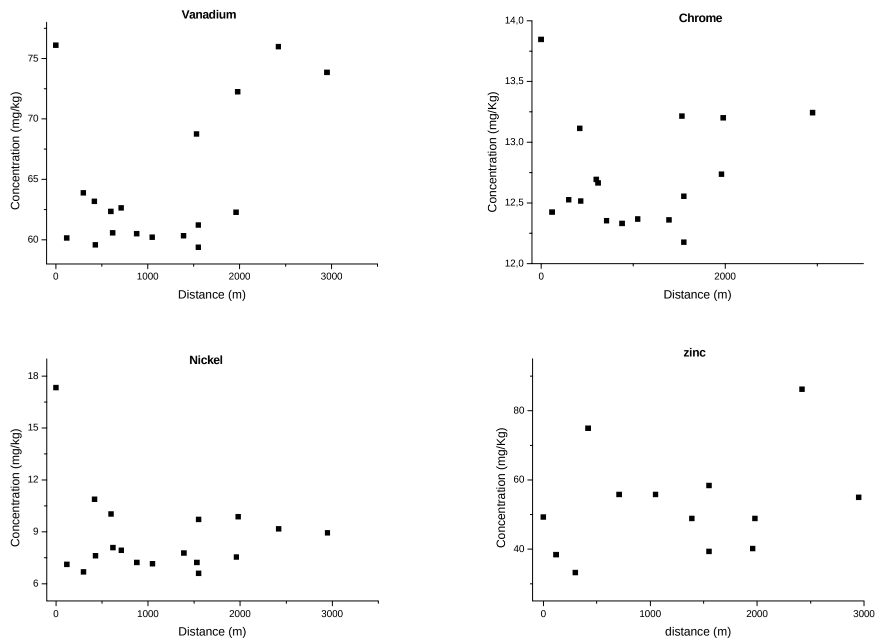

Figure 3: Concentration of heavy metals from the pollution source

Magnetic concentration versus distance (from the source) is shown in Figures 4. The trends are similar to heavy metal distribution for all parameters. It shows a decrease from peaks at about 400 m to 1000 m. In 1700-2000 m region, values increase and finally decrease. As appreciated from figures, these distributions are in agreement whit the PM distribution (modeled).

Spatial continuity analysis was carried out with the aim of find out if these spatial trends have statistically significant. Then, Moran's Index was achieved for each one of them. In all case, these spatial trends (Figures 3 and 4) are non-statistically significant (*p-values> 0.1* was achieved for all variables, *n*=17). However, some results suggest that increasing the numbers of point samples (*n*) the spatial auto-correlation may be improved.

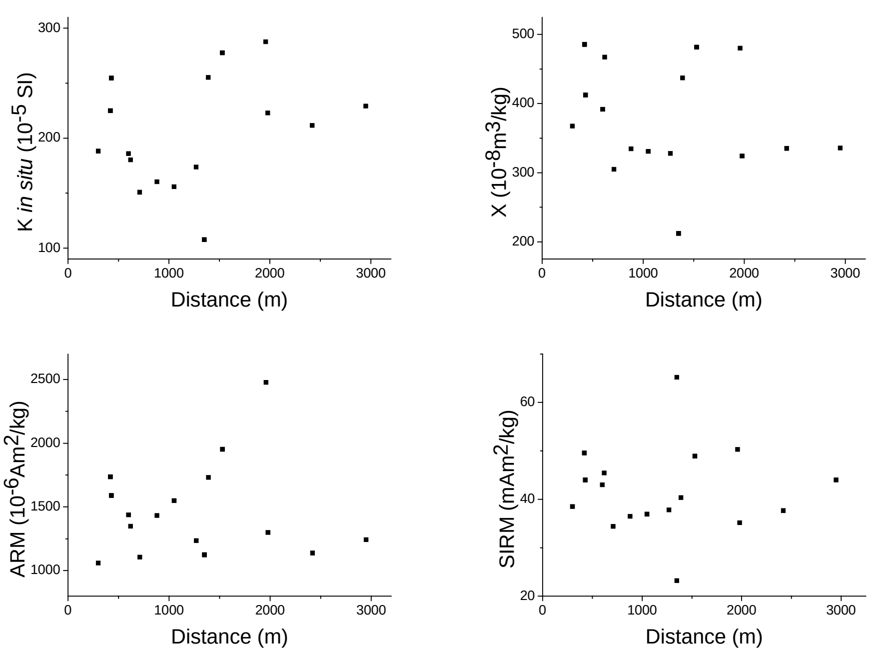

Figure 4: Magnetic concentration versus distance from source

Magnetic characterization of carriers, magnetomineralogy and magnetic grain size, was analyzed from IRM curves, κ_{FD} %, S-ratios, Hcr, SIRM/χ and κ_{ARM}/κ-ratio. The integrated analysis revealed the predominance of fine and ultra-fine (<0.1-0.2 μm) ferrimagnetic minerals in all samples, being magnetite the main magnetic carrier.

The statistical multivariate analysis was made from matrix of correlation between all measured variables. This analysis did not show significant correlation between heavy metals and magnetic variables. The PCA analysis (Fig. 5) shows two main variable set (these factor explain 67% of the total variance). The first group is comprised of heavy metals (CP1), and the second one concentration-related magnetic parameters (CP2). In this study, all measured heavy metals have a similar statistical behavior, as the variable sets in group CP2.

For CCA analysis, four sets of variables were considered. A first analysis between Chemical Group (V, Ni, Cr and Zinc, **CG**) and Magnetic Group (all measured magnetic parameters, MG) was carried out. The canonical correlation R=0.9215 was non-statistically significant (p=0.1941). Then, a new study dividing the set **MG** was also tried, set MG was divided into two groups in order to investigate the relevance of variables contributing to the relationship; one group concerning concentration-dependent magnetic parameters (set **MGC**: χ, ARM and SIRM) and the other one concerning feature-dependent magnetic parameters (set **MGP**: κ_{ARM}, S-ratio, H_{CR}, κ_{ARM}/κ-ratio, κ_{FD} %). This new analysis revealed different canonical R=0.8025 (non-statistically significant, *p=0.3846*) for sets **CG** and **MGC**, and R=0.8564 (statistically significant, *p=0.0784*) for sets **CG** and **MGP**. These results showed better correlation for the group feature-dependent parameters.

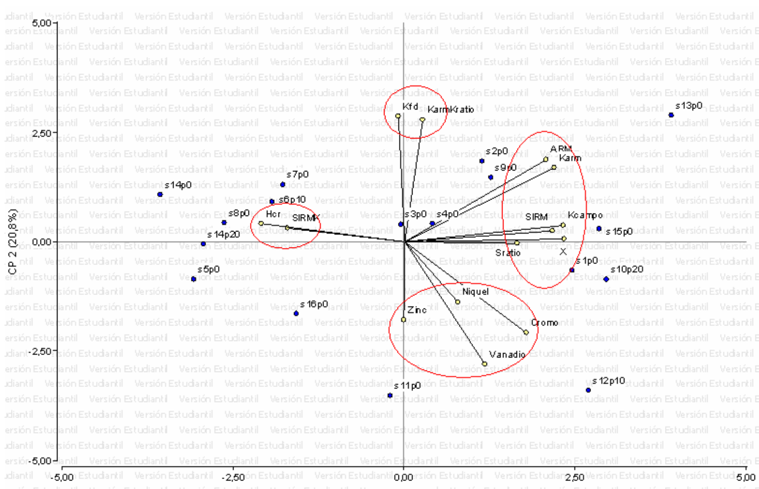

Figure 5: Biplot produced by PCA

Conclusion

Coke production is identified as a very important factor of air and soils pollution. Several dangerous heavy metals to population health have been found in the PM detached from this process.

Similar spatial trends between PM concentrations (modeled), trace metals (V, Ni and Cr) and magnetic parameters (κ_{is}, χ and SIRM) were found, also all variables have showed highest values around 1500-2000 m from the source. Although auto-correlation test for these spatial distribution have no statistically significant results, they could be improved increasing the number of soil sites.

Magnetic characterization of carriers shows that the magnetic response is strong dominated for the presence of submicron (<0.2 μm) magnetite. Moreover, according to the results on unpolluted site in Tandil, a balance between ferrimagnetic and antiferromagnetic minerals is observed in natural sites.

From multivariate statistical methods, it was found that: i) the 16 studied variables can be reduced to only 2 new variable sets. These new variables CP1 and CP2 explain 67% of the total variance. ii) The CCA analysis confirms the existence of a linear relationship between magnetic feature-dependent parameters (**MGP**) and chemical variables (**CG**).

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