ROCK-MAGNETIC AND SCANNING ELECTRON MICROSCOPY STUDIES ON LEAVES, SOILS AND URBAN DUSTS FROM MONTEVIDEO AND PIRIAPOLIS (URUGUAY)

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Abstract

Montevideo as well as any Latin-American capital city is confronted to air pollution and human health problems. However, the limited number of monitoring stations does not allow the production of high-resolution pollution maps. In order to contribute to the air pollution monitoring and to better characterize health pollutants in Montevideo, the present study was done on tree leaves, soils and urban dusts coming from different parts of the town using magnetic properties and SEM (Scanning Electron Microscopy) observations. Magnetic analyses consist in the study of mass-specific magnetic susceptibility (χ) and its frequency-dependence (χ_{fd} (%)), hysteresis loops, IRM (isothermal remanent acquisition), FORC (first-order reversal curves) diagrams and thermomagnetic curves at high temperature. In order to carry out a comparative study and to check the sensitivity of magnetic methods for environmental purposes, the same kind of investigation was performed on leaves, soils and urban dusts in Piriapolis, a small coastal city of less than 10 000 people.

Resumen

Montevideo, como cualquier capital de América Latina se enfrenta a la contaminación del aire y los problemas para la salud humana que esto conlleva. Sin embargo, el número limitado de estaciones de monitoreo no permite la producción de mapas de contaminación de alta resolución. Con el fin de contribuir a la vigilancia de la contaminación del aire y para caracterizar mejor los contaminantes en la ciudad de Montevideo, se llevó a cabo un estudio de propiedades magnéticas en hojas de árboles, suelos urbanos y polvos procedentes de diferentes partes de la ciudad. Así también se efectuaron análisis de SEM (Scanning Electron Microscopy). El análisis magnético consistió en el estudio de la susceptibilidad magnética (χ) por unidad de masa de y su dependencia con la frecuencia (χfd (%), ciclos de histéresis, adquisición de IRM, diagramas y curvas FORC termomagnéticas a altas temperaturas. Para llevar a cabo un estudio comparativo y comprobar la sensibilidad de los métodos magnéticos aplicados al monitoreo ambiental, se realizó el mismo tipo de estudio - hojas, suelos y polvo urbano- en Piriápolis, una pequeña ciudad costera con menos de 10 000 habitantes.

Introduction

Vehicular motors, industries and domestic heating systems emit particles in the air similar to PTS and PM10 (less than 10 microns) which are definitively harmful for human health (Zhao *et al.*, 2006). In order to better characterize health pollutants and their spatial repartition in urban areas, surveys combining chemical analyses and magnetic properties of urban dusts and tree leaves are performed during last decades different areas of world. The high content of the magnetic minerals in urban PM perfectly justifies the use of magnetic techniques to assess the urban PM (Gautam *et al.*, 2005). In this work we report a rock-magnetic and SEM study on tree leaves, soils and urban dusts coming from different places in two towns in Uruguay - Montevideo and Piriapolis. Our goal is to complete the geochemical results obtained by the monitoring stations in terms of type of magnetic minerals associated to the air pollutants. The study of tree leaves, soils and urban dusts are performed to obtain the additional information about the air pollutants and their dynamics.

Study areas and sampling

We focused this study on two towns of different size in Uruguay: Montevideo, the capital of the country, which has more than one million inhabitants, and Piriapolis, a smaller coastal city of less than 10 000 people situated at about 105 km east of the national capital.

In Montevideo city outcrops the homonymous Formation (Paleoproterozoic) and comprises amphibolites, paragneisses and micaschists generally covered by Libertad Formation (Pleistocene loess and reworked loess, clay and silt) and Holocene coast sands (Preciozzi, 1993; Oyhantçabal *et al.*, 2007; Sánchez Bettucci and Oyhantçabal, 2008; Sánchez Bettucci *et al.*, 2010). Based on the contents of clay and biological activity, is a soil that retains metals as oxides, hydroxides and other forms associated with organic matter. In Montevideo, air pollution is most likely due to emissions by vehicular motors and, during the winter, by domestic heating systems. The industrial activity is low, although a few miles to the NW of the town is located an oil refinery (ANCAP). The sulfur dioxide (SO_2) in Montevideo is caused almost exclusively by the industrial sector while the PM10 is generated mainly in the residential sector (IAM, 2009).

The Piriapolis city is located in Neoproterozoic basement, particularly outcrops an association of intrusive, volcanic and sedimentary rocks named Sierra de Las Animas Complex (Sanchez Bettucci *et al.,* 2009, 2010). Like in Montevideo, air pollution in Piriapolis is principally due to emissions by vehicular motors and domestic heating systems in winter.

The method of sampling was the same in the two towns and samples were taken in different type of places depending on the degree of air pollution (near roads more or less big, avenues, residential places, gardens, parks…). 17 sites were sampled for Montevideo, 10 for Piriapolis. Tree leaves were sampled from Fraxinus americana which is native to eastern North America. Fraxinus americana tree leaves were collected within a distance from 1.5 to 3m from the road and sampling when the leaves had a month and a half on average growth. As all samples have been collected in a limited area under the same living conditions (1.5 m high, distance to the avenue, car circulation and meteorological factors), the differences due to problems of reproducibility are minimized. Soils and urban dusts were always sampled with a non magnetic instrument and as close as possible from sampled tree leaves. A volume of about 100 cm^3 was taken for soils, and urban dusts were systematically sampled on a surface of $1m^2$ on the nearest road or on the corresponding pavement.

Methods

Tree leaves, soils and urban dusts samples were studied using both magnetic properties and SEM observations. Before laboratory analyses, they were all dried in air, and soils and dusts were sieved in order to remove grains bigger than 2 mm.

Low-field mass-specific magnetic susceptibility at room temperature was performed with a Bartington MS2B dual-frequency susceptibility probe working at frequencies of 465 Hz (= χ_{lf}) and 4650 Hz (= χ_{hf}). The percentage frequency dependent susceptibility, $\chi_{fd}(\%)$, defined as $[(\chi_{lf} - \chi_{hf})/ \chi_{lf}]\times 100$ and giving information about the quantity in ferrimagnetic grains characterized by near superparamagnetic (SP)-single domain (SD) size (≈ 10-20 nm) grains (Dearing *et al.*, 1996, 1999), was determined from these measurements for the soils and dusts samples only, this parameter being not calculable for tree leaves because of too low values. Low-field high-temperature magnetic susceptibility versus temperature measurements (*K-T* curves) were performed in air using a Bartington susceptibility bridge (MS2WFP) equipped with a furnace (MS2WF). Soils and dusts samples were heated up from room temperature to 550-700°C (essentially to 650°C) at a heating rate of 10°C/min and then cooled at the same rate (Figure 1). In order to estimate the domain state and to have an idea about the magnetic particle size, we performed hysteresis, isothermal remanent magnetization (IRM) and first-order reversal curve (FORC) measurements on soils and dusts samples using an Alternating Force Magnetometer « Micromag » apparatus in fields up to 0.5T. Saturation magnetization (J_s), saturation remanence (J_{rs}), and coercivity (H_c) were determined after correction for the dia/paramagnetic contribution identified from the slope at high fields. The coercivity of remanence (H_{cr}) was determined by applying progressively increasing backfield after saturation. A progressive acquisition of IRM curves was obtained too until 700 mT using a IM-10 Impulse Magnetizer, the remanence being measured by a JR6 spinner magnetometer. A progressive backfield was applied until 300 mT in order to calculate the parameter S = - IRM_{-300mT}/SIRM which gives the relative proportion of soft magnetic minerals compared to hard ones. For the FORC diagrams, which give the distribution of magnetostatic interaction fields versus the distribution of particle microcoercivities, an averaging time of 100 ms was used and 100 minor loops for each FORC diagram were measured. The smoothing factor was all the time set at 5.

SEM observations were performed using a JEOL JSM-6400Scanning Microscope. High resolution observations and punctual chemical analyses were made on tree leaves, soils and dusts representative samples.

Results

The results indicate that the magnetic properties are always two or three times bigger (depending on the parameter) for samples coming from Montevideo than for those coming from Piriapolis. For both, Montevideo and Piriapolis, dusts show bigger magnetic susceptibility but lower frequency-dependence than soils, these latter containing at least 10% of SP grains (Dearing *et al.*, 1996, 1999) (Figure 3). Fraxinus Americana leaves studied both in Montevideo and Piriapolis show good results too, samples near busy road intersections having always higher magnetic concentration than those sampled near parcs, which confirms that vehicular motors are the principal origin of air pollution in these towns. Globally magnetic studies point to magnetite or Ti-poor titanomagnetite grains which are five times more present in the dusts than in the soils (Figure 1). IRM curves clearly confirm the presence of ferrimagnetic phases in tree leaves with a saturation reached at low field (200-300 mT) (Figure 2), this saturation being a little bit more difficult for soils and dusts which traduces the presence of both some high-coercivities magnetic minerals like (titano)hematite and low-coercivities minerals like (titano-)magnetite, these latter being dominants. Hysteresis experiments indicate that globally soils are richer in fine SP particles than dusts which seem to contain much more multidomain (MD) magnetic particles (Day, 1977; Dunlop, 2002a and 2002b). However dusts of Piriapolis are closer to soils of both Montevideo and Piriapolis which all show magnetite grains between 4 and 8 µm (Thompson and Oldfield, 1986), whereas some dusts of Montevideo show magnetite grains two times bigger. SEM observations confirm these results, particularly on tree leaves where it was possible to observe on samples near busy roads Fe-rich near-spherical (~1 µm in diameter, which we observed too on dusts coming directly from a car muffler) and bigger agglomerate particles (~10 µm) generally containing S, Al, Ca, K and sometimes Ti (Figure 3) (Mitchell and Maher, 2009). Despite of technical difficulties in observation, soils and dusts show the presence of larger (~10-30 µm) and more angular, silica-rich particles containing generally iron and elements like Ca, S, K and occasionally Cr (Lu *et al.*, 2008). More agglomerate particles between 10 and 100 µm containing iron were found in dusts than in soils.

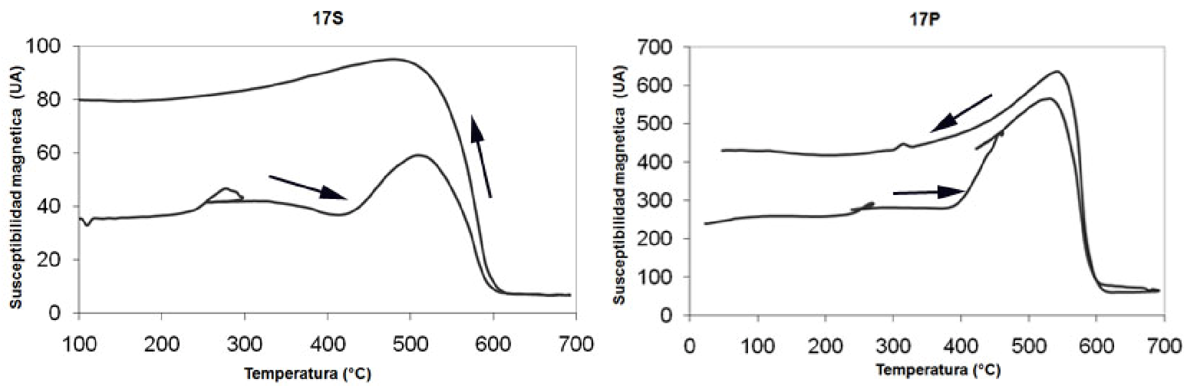

Figure 1: *magnetic susceptibility versus temperature (K-T) curves obtained in air for a soil sample and its corresponding dust sample taken in Montevideo near a road (site 17). Heating and cooling curves are indicated by arrows.The magnetic susceptibility is given in arbitrary units (AU).*

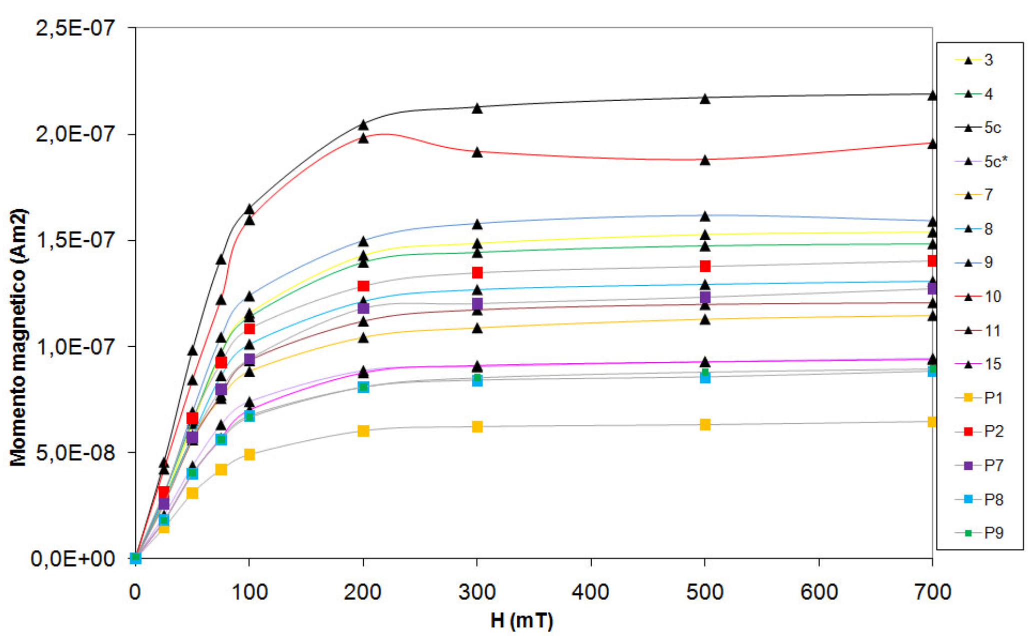

Figure 2: *IRM acquisition curves obtained for tree leaves from Montevideo (black triangles) and Piriapolis (coloured squares) sampled in various places.*

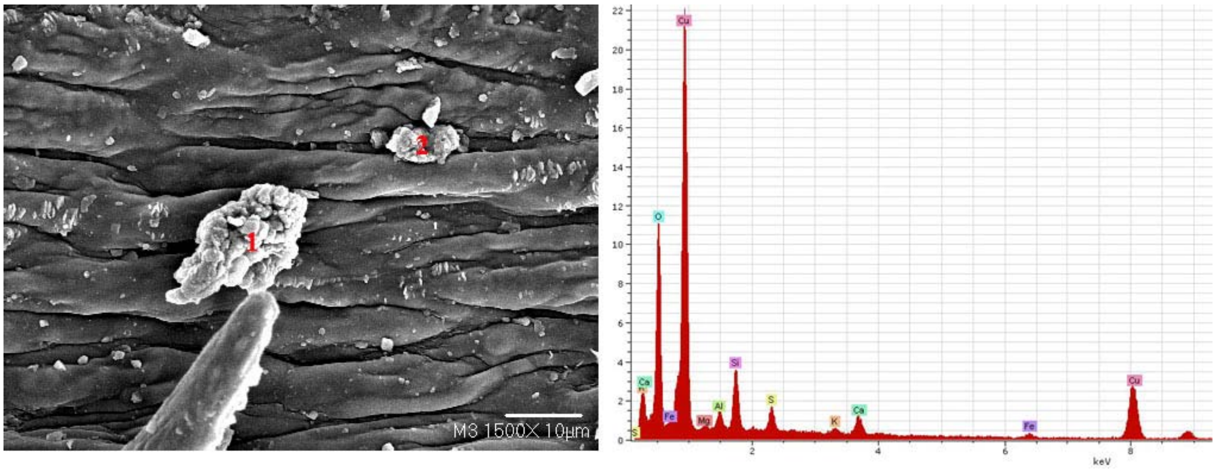

Figure 3*: Scanning electron microscopy image (at the left) of clustered, spherical particulatescoming from leaves sampled on a site situated near 3 roads in Montevideo. At the right is showing the corresponding chemical analysis for the point 1. The elements present are Fe, S, K, Ca, Al, Mg and Si . They are the same as for the point 2.*

Conclusion

The correlation between magnetic properties, location of the samples and heavy metal concentration makes it possible to use the magnetic techniques as a non-destructive and time-efficient tool for bio-monitoring of the air pollution in urban areas. Magnetic properties studies and SEM observations allowed to better characterize magnetic minerals associated to air pollution in Montevideo and Piriapolis and to rapidly revealing the polluted areas and their degree of pollution. Despite of high complexity, soil and urban dust samples may bring important complementary information to those obtained from tree leaves. In particular, the issues related to the history of air pollution of the studied urban areas.

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