Rock-magnetic properties of topsoils and urban dust from Morelia (>800,000 inhabitants), Mexico: Implications for anthropogenic pollution monitoring in Mexico’s medium size cities

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Received: January 10, 2012; accepted: January 15, 2013; published on line: March 22, 2013

Resumen

En el presente trabajo, investigamos la correlación entre algunos parámetros magnéticos y el nivel de contaminación por metales pesados en suelos urbanos de la ciudad de Morelia, en el occidente de México. El estudio magnético fue llevado a cabo en 98 muestras urbanas provenientes de diferentes tipos de uso de suelo. La mayoría de las muestras contienen minerales ferrimagnéticos como responsables de la magnetización, pertenecientes probablemente a las soluciones sólidas de las titanomagnetitas/titanomaghemitas. Esto es inferido a partir de las mediciones de susceptibilidad en función de la temperatura y de los experimentos de magnetización remanente isotérmica (MRI). Estas mediciones indican además, que la mayoría de las muestras se saturan casi completamente antes de los 300 mT. Adicionalmente, los valores S-200 (S-200 = IRM -200/SIRM, donde IRM -200 = magnetización a campo inverso de 200 mT después de la saturación magnética) se encuentran entre 0.7 y 1.0, característicos de minerales de baja coercividad magnética. Las curvas promedio de magnetización remanente isotérmica de saturación (SIRM) pueden ser usadas como un indicador del nivel de contaminación, ya que estas curvas muestran diferentes valores de saturación de acuerdo al nivel de contaminación por metales pesados: Cu, Ni, Cr y Sr. Estas asociaciones de (titano)magnetitas con metales pesados fueron observadas bajo el Microscopio Electrónico de Barrido, revelando algunos agregados complejos en lugar de las esferulas detectadas comúnmente.

Palabras clave: ambientemetría, magnetismo de rocas, metales pesados, contaminación urbana, agregados magnéticos.

Abstract

In this work, we investigate the correlation between some magnetic parameters and the level of contamination by heavy metals in urban soils from Morelia city, western Mexico. The magnetic study was carried out on 98 urban soils samples belonging to distinct land uses. Most of analyzed samples contain ferrimagnetic minerals as the responsible for magnetization, most probably corresponding to the titanomagnetites/titanomaghemites solid solutions. This is inferred from the susceptibility vs. temperature measurements and the isothermal remanent magnetization (IRM) experiments. These measurements also indicate that most of samples are almost completely saturated before 300 mT. Additionally, the S-200 values (S -200 = IRM -200/SIRM, where IRM -200 = Back-field of 200 mT after magnetic saturation) are between 0.7 and 1.0, characteristic of low coercivity magnetic minerals. The averaged saturation isothermal remanent magnetization (SIRM) curves can be used as an indicator of pollution level, as these curves show different saturation values according to the level of contamination by heavy metals: Cu, Ni, Cr and Sr. These associations of (titano)magnetite with heavy metals were observed by Scanning Electron Microscope revealing some complex aggregates rather than commonly detected spherules.

Key words: environmetrics, rock-magnetism, heavy metals, urban pollution, magnetite aggregate.

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**Introduction**

Urban areas represent potential sources of magnetic pollution due to human activities: vehicle usage, industrial activity, and emissions from burning of fossil fuel, domestic and industrial. Other source includes power stations and metallurgic works (Chaparro et al., 2002; Goluchowska, 2001; Hullet et al., 1980; Hunt, 1986; Kapička et al., 1999; Kim et al., 2007; Kukier et al., 2003; Petrovský and Elwood, 1999; Strzyszcz et al., 1996; Sutherland, 2003; Thompson and Oldfield, 1986; Vassilev, 1992). Among these activities, the vehicles are used throughout the entire city, representing a source of widespread and growing pollution.

The magnetic particles derived by vehicular combustion are due to Fe impurities in fuel (Abdul-Razzaq and Gautam, 2001) as well as wear and friction of engine components. The fine magnetic particles (< 10 mm: PM10) represent a greater danger when they are inhaled because they are easily absorbed into the human body, causing serious health problems such as cardiovascular diseases and respiratory illnesses (Becher et al., 1998; Gómez et al., 2002; Kim et al., 2003; Muxworthy et al., 2001). Additionally, the ultrafine particles (<0.1 mm, PM0.1) are proven to have worse health effects than fine particles (<2.5 mm, PM2.5) (Harrison and Yin, 2000; Lu et al., 2008; Wichmann and Peters, 2000). Furthermore, these particles can lodge in their structures other toxic metals like Pb, Zn, Ba, Cd and Cr (Harrison and Jones, 1995; Maher et al., 2006; Muxworthy et al., 2003) probably due to the affinity of Fe oxides with trace metals (Gautam et al., 2005; Hunt et al., 1984; Lu et al., 2007; Ma and Rao, 1997; Meena et al., 2011). In particular, Pb, Cu and Zn and ferromagnetic minerals are commonly associated with industrial activity and traffic pollution (Beckwith et al., 1986; Hanesch and Scholger, 2002; Li et al., 2001; Lu et al., 2005).

Therefore, the concentration of magnetic minerals may reflect not only magnetogenic pollutants but the content of toxic metals in urban soils and other environmental samples (Bityukova et al., 1999; Magiera et al., 2006, Maher et al., 2008). The magnetic method has been developed to provide a fast and inexpensive alternative for monitoring anthropogenic pollution.

Several studies have reported a good correlation between magnetic susceptibility and the heavy metal content (Bityukova et al., 1999; Desenfant et al., 2004; Đurža, 1999; Fialova et al., 2006; Hanesch and Scholger, 2002; Hoffmann et al., 1999; Lecoanet et al., 2003; Muxworthy et al., 2003; Petrovský et al., 2000). These studies are generally site specific and correlations are linked to evidence of fly ash, pollution products from traffic and metallurgic plants.

In most of cases, it is very difficult to interpret the result because of soil composition and other factors which can have an influence on this magnetic property (Ruiping and Cioppa, 2006) such as biological activity in soils and the diamagnetic mineral content. A good correlation has been reported between the saturation isothermal remanent magnetization (SIRM) and heavy metals content in urban dust (Maher et al., 2008; Mitchell and Maher, 2009).

This study reports the results of magnetic measurements obtained for 98 samples of soils and urban dusts from Morelia, Mexico. The objective is to correlate the magnetic properties with heavy metal content, and to establish a relative level of pollution in each point referred to a natural background. In our case, this reference is a natural reserve located in the southeast of the city. We show that SIRM has a strong correlation with the metal content, for soil samples as well as urban dust, showing the different degrees of pollution according to the IRM acquisition curves. The magnetic particles have been identified through SEM observations under spherical shapes and irregular aggregates of < 2 mm.

**Methods**

**Description of the city**

Morelia is situated on a valley in northeast of the state of Michoacan in central part of Mexico, at an altitude of 1900 m.

Morelia is the most populated city on the state of Michoacan and the twentieth of the whole country. The metropolitan area has 806822 inhabitants (INEGI, 2010). 597511 of them are concentrated in Morelia. The main economic activity includes services, among them financial, real estate and tourism, followed by the construction industry, manufacturing industry and ultimately the primary sector activities.

Morelia city has an average temperature of 17.5 ° C, and annual precipitation of 773.5 mm, with a subhumid climate. The prevailing winds come from southwest and northwest; the intensity varies 2.0 to 14.5 km / h in July and August.

The rock basement of the city is composed of rhyolite (commonly known as “cantera”), as well as unconsolidated volcanic materials, which is called “tepetate”. The principal soils groups, in agreement with World Reference Base for Soil Resources are Luvisols, Andosols, Vertisols, Acrisols and Leptosols. The municipality has 69,750 ha of land, of which 20,082 are cultivated...
(rainfed and irrigated), 36,964 ha are used for grassland, and 12,234 ha of forests. The rest is unproductive land (Oyama et al., 2011).

The industrial zone of Morelia covers 354 ha, and houses 180 enterprises. However, only 30% of them are manufacturing companies. The rest of them are warehouses and distribution centers. The industry is focused in production of: comestible oil, meal, plastic, resins, paper and other cellulose products; there is also the foundry and manufacture of electrical and hydraulic turbine generators. This city is then characterized by vehicular fuel combustion as the principal source of pollution, additionally to few local pollution sources.

**Sampling**

We collected a total of 98 topsoil samples (Figure 1) within the urban area based on use of land, according to Bautista et al. (2011): Housing (24), Equipment (16), Industrial (8), Mixed (28), Green areas (6), Ecological Reserves (5), Urban dusts (11). Equipment refers to areas occupied by institutions providing public services. Mixed refers to areas intended to commercial activities as well as housing and equipment. All samples were georeferenced using a GPS. Samples were taken in triplicate in each point, then the three samples were mixed to obtain only one homogeneous sample. We collected the first five centimeters of superficial soil by using PVC (polyvinyl-chloride) cores and then kept in PVC packages. The urban dust samples were collected by brushing 1 m² of previously delimited surface of asphalt.

The samples were air-dried and sieved through a 2-mm sieve. In order to proceed with magnetic measurements, soil material was placed into standard plastic cubes (11 cm³).

**Magnetic measurements**

All magnetic measurements were carried out in the LIMNA facilities, National University of Mexico Campus Morelia. We used the Bartington MS2B susceptibility meter to measure the susceptibility (k) at high and low frequency (k₉ at 4700 Hz, kₕ at 470 Hz). From these k values, mass specific susceptibility cₜ was calculated. The thermomagnetic curves (k-T curves) were obtained by heating under air one sample from each site, from room temperature up to about 700°C, followed by cooling at the rate of 20°C/min. The T_c was calculated by differentiation on the heating curve.

![Figure 1. Map of Morelia, showing the localization of sampling sites.](image-url)
Frequency-dependent susceptibility $\chi_{df} [%] = 100(\chi_0 - \chi_0)/\chi_0$, is used to determine the possible presence of superparamagnetic (SP) grains in the magnetic fraction (Dearing et al., 1996; Evans and Heller, 2003). At higher frequencies of applied magnetic field, a portion of the small SP grains is unable to follow the field changes and will no longer contribute to the susceptibility. Isothermal remanent magnetization (IRM) was acquired by placing samples in increasing magnetic fields at room temperature using a pulse magnetizer ASC IM-10. The IRM acquired at 700 mT is referred to as the saturation isothermal remanent magnetization (SIRM). Following the acquisition of SIRM, the back-field magnetization at 200 mT after magnetic saturation was obtained (IRM$_{200}$). Then, we calculated the $S_{200}$ ratio ($S_{200} = \text{IRM}_{200}/\text{SIRM}$) to determine the proportion of low coercivity magnetic minerals. All remanent magnetizations were measured using an AGICO JR6 spinner magnetometer.

The observations under the Scanning Electron Microscope (SEM) were made on selected samples using a SEM/FRG ZEISS Ultra 55 scanning electron microscope, and the concentration of heavy metals was determined with the help of Noran System 7 EDS detector at SEM laboratory in the Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie, Paris, France.

**Chemical analyses**

The powdered soils were pressed into pellets 1 cm wide, without any chemical treatment or binders; and put in a plastic sample holder covered with a mylar film. ED-XRF analyses were performed with a Jordan Valley EX-6600 spectrometer, equipped with a Si(Li) detector with a 20 mm$^2$ active area and 140 eV resolution at 5.9 keV and operated at a maximum of 54 kV and 4800 mA. Trace elements were acquired in air atmosphere using a changeable secondary target. Typical measurement time was 300 s. Each measurement was repeated five times in order to obtain the average concentration. Quantitative calculation was made through a fundamental parameter method. The experimental parameters were obtained by calibration of the whole system by means of geological standard reference materials (Lozano and Bernal, 2005).

**Geostatistical analysis**

We constructed a georeferenced data matrix based on SIRM values, and subsequently performed a geostatistical analysis by kriging interpolation (Isaaks and Srivastava, 1989; Webster and Oliver, 1990) using the Gamma Design Software (GS+, 2006). The maps were edited with ArcGIS 9 software (ESRI, 2004). The extreme data were put as points. We used the UTM projection, zone 14, horizontal datum ellipsoid and the World Geodetic System 84 (WGS84).

**Main results and discussion**

The thermomagnetic curves corresponding to each group of use of soil are plotted on Figure 2.

The samples from the ecological reserve (Figure 2e) show a reversible behavior. We see a first decay at about 350°C and the second one at 500°C, indicating the probable presence of two magnetic phases, maghemite and Ti-poor Ti-magnetite. No magnetic enhancement was noticed in this group of samples. For the rest of the samples, we observe a non reversible behavior and we notice a transformation during heating: the sample from equipment areas (Figure 2a) shows a continuous decay, starting at 300°C to 500°C, due to a variable composition within the series of Ti-magnetite; the calculated $T_c$ is 507 °C. In contrast, samples from housing areas and “mixed sites” (Figure 2b and 2c), show a $T_c$ of 578°C indicating the presence of an almost pure magnetite. Samples of these three types of land use show different degrees of magnetic enhancement; this may be explained by the conversion of ferric oxides (such as ferrhydrite) to maghemite or magnetite in the presence of soil organic matter (Hanesch et al., 2006).

The heating curve of the sample coming from industrial area (Figure 2d) shows two weak inflection points at ~330°C and 570 °C. The first one indicates the probable presence of maghemite (or pyrrhotite) while the second one indicates the presence of magnetite (Jordanova et al., 2004; Kapicˇka et al., 2001; Petrovsky and Kapicˇka, 2006). The magnetic phase is probably an impure magnetite because the $T_c$ is slightly lower than 580°C (Dunlop and Özdemir, 1997).

The heating curve of urban dust (Figure 2f) shows a Hopkinson peak, judging by the gradual increase of susceptibility up to 460 °C and subsequent decrease down to 560 °C. This peak has been previously observed in k-T curves from polluted samples (Aguilar et al., 2011; Jelenska et al., 2004; Ruiping and Cioppa, 2006).

Figure 3 shows the average IRM acquisition curves by type of land use. These curves were obtained by using the OriginPro Software. There is a clear difference between the un-polluted areas and the rest of samples: the SIRM value for urban dust is much higher than for the other samples. This parameter has been used as an indicator of the degree of pollution for urban dust (Mitchel and Maher, 2009, Yang et al. 2010), and river sediments (Chaparro et al., 2011). Some studies have found that remanence parameters are more robust tracers of magnetic particles derived from...
Figure 2. Thermomagnetic curves of samples from: a) Equipment, b) Housing, c) Mixed areas, d) Industrial area, e) Ecological reserve and f) Urban dust.
anthropogenic sources than susceptibility alone (Chaparro et al., 2003; Georgeaud et al., 1997; Yang et al., 2007). The IRM acquisition curves show a rapid saturation below 300 mT indicating that the magnetic minerals are dominated by low coercivity ferrimagnetic minerals.

Additionally, the $S_{200}$ values range between 0.7 and 1.0 for the majority of samples confirming the presence of low coercivity magnetic minerals—a ferrimagnetic phase—(Figure 4). In most of environmental studies, authors evaluate $S_{\text{ratio}}$ by choosing an opposing DC field of 300 mT. In present work, we evaluate $S_{200}$ to detect small differences in coercivity; the $S_{300}$ is too close to 1.0 for the majority of samples of our case. Values of $S_{200}$ lower than 0.7 mean that magnetic carriers are Ti rich Ti-magnetite.
The $\chi_{\text{rd}}$% parameter (Figure 5) places the majority of samples between 2 and 10%, while some abnormal values (above 10%) are observed for some samples. The abnormal values (one sample from industry and one from green areas) are probably due to fertilizers or pesticides (Ruiping and Cioppa, 2006) because the majority of samples from ecological reserves, show values less than 5% high points to low biological activity. Values above 8% are due to high levels of SP grains (Dearing et al., 1996) in soils magnetically enhanced by secondary magnetite/maghemite due to pedogenic processes. The values of urban dusts from Morelia are placed in a range from 0 to 7%, which indicates that the magnetic fraction is not dominated by SP grains (Maher 1988). For urban dust an average of 2% has been reported for several cities (Aguilar et al., 2011; Blundell et al., 2009; Kapicka et al. 2000; Lu & Bai, 2006; Shan and Lu 2005; Xie et al., 2001; Yang et al., 2007). We assume that urban dust has a contribution from soils due to wind, which explains the values which are up to 7%.

We plot the relationship between SIRM and content of heavy metals (HM) (Figure 6). We observed a good correlation ($R^2 = 0.62$) between SIRM and the sum of contents of Sr, Cu, Ni and Cu. Lower values correspond to samples from ecological reserves and parks while the higher ones correspond to samples from urban dust and industrial area. In contrast, we observed a very weak correlation between Pb and Zn levels with both $\chi_{\text{rd}}$ and IRM parameters ($R^2 < 0.1$). Yang et al. (2010) have reported an association of Cu and Ni with Fe, coming from vehicles emissions (PSD/MD grains) in road dusts. The linear correlation between trace metal and magnetic remanence in polluted areas is probably due to bounding tendency of Fe–Mn oxides with trace metals (Ma and Rao, 1997).

An important number of studies have indicated that soil type should be taken into account to discriminate the pollution signals using magnetic methods (Fialova et al., 2006; Hanesch and Scholger, 2005; Jordanova et al., 2008; Magiera et al., 2006; Ruiping and Cioppa, 2006). However, in our particular case, it is possible to obtain a very strong correlation between SIRM values and the pollution level, with no influence from the soil type. In the study area, the good correlation observed between Cu, Ni, Cr and Sr and magnetite, not only in urban dust but also in soils makes it possible to use SIRM measurements as a tool for mapping soils and urban dusts pollutions. According to Figure 7, the areas with the highest values of SIRM are in the west and southeast of the city. Ranges of SIRM values were defined in this study, as high (> 56), medium (28-56) and low (0.1-28). The degree of pollution detected does not appear to be conditioned by the prevailing winds, since they should affect more the east and the center of the city.

The urban dust and soil samples have been observed under the scanning electronic microscope (SEM). In all cases, we identified an association between magnetite and heavy metals. In figure 8a we showed a soil sample from a

![Figure 5. $\%\chi_{\text{rd}}$ as a function of susceptibility.](image-url)
“mixed area” in which we can observe particles of magnetite with a spherical shape (center) and as irregular shaped aggregates (<1 mm). The punctual analysis (arrow) indicates mostly Fe associated with S and heavy metals as Cr, Ni and Cu. This association is probably produced from the abrasion or corrosion of the vehicle engine since these metals are used in making parts of automotive pieces (Kim et al., 2007; Maher et al., 2008). In figure 8b we show the results for an urban dust sample. We identified the irregular magnetic aggregates, composed mostly of pure...
magnetite associated with S, Zn, Cr, Cu and Pb. The anthropogenic magnetic particles are usually dominated by magnetite (Kapička et al., 2001; Muxworthy et al., 2001) and this magnetic mineral has been identified as a combustion-derived component of vehicle exhaust materials (Abdul-Razzaq and Gautam, 2001) with spherical shapes and as aggregates (Maher et al., 2008; Moreno et al., 2003; Shilton et al., 2003). In fact, vehicle fuel combustion is the major source for Fe and Pb pollutants, rather than resuspension of roadside dust or from tyre, brake or other vehicle wear (Maher et al., 2008).

Figure 8. SEM observations and EDS analyses, showing the pure Fe associated to Ni, Cr and Cu (a) and magnetite, Mt, associated with heavy metals (b).
Conclusions

The urban, presumably unpolluted soils from Morelia (ecological reserves) contain maghemite and Ti-poor titanomagnetite as magnetic carriers. An impure magnetite was identified in the polluted samples, which almost exclusively comes from the vehicle combustion according to SEM observations performed on samples of soil and urban dust. These observations allowed us to identify spherical and irregular aggregates of ~1 mm, containing magnetite associated with S and heavy metals like Zn, Cr, Cu and Pb. We also identified irregular aggregates in which almost pure Fe is associated with Cr, Ni and Cu; this kind of particles probably comes from abrasion or corrosion of the vehicle engine and it is less common than previously described cases. A strong correlation between SIRM and the sum of the contents of Ni, Cr, Cu and Sr, was found. This correlation can be used as a proxy to determine different degrees of pollution by heavy metals in urban dust as well in urban soils.

Acknowledgements

This work was supported by the Universidad Nacional Autónoma de México through the projects CONACYT 118971 and PAPIIT IN 223110. The authors would like to thank Thomas Ihl for the map design and Ma. Carmen Delgado for the geostatistic analysis. We also thank Hector Franco and Francisco Bautista Delgado for sampling and to MSc D. Aguilar for the ED-XRF technical assistance. Dr. Avto Goguitchaichvili acknowledges the Conacyt and UNAM-PASPA sabatical program fellowships.

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