Combination of magnetic parameters: an efficient way to discriminate soil-contamination sources (south France)

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"Capsule": Biplots combining magnetic parameters allow identification of different pollutant emission sources.

Abstract

Biplots combining magnetic parameters allow to identification and differentiation different pollutant emission sources. A major problem in soil pollution is the characterization of the relative contributions of different anthropogenic particles sources. This paper demonstrates the efficiency of magnetic techniques to provide identification and differentiation of contaminating emission sources. About 100 soil samples were collected across a mixed agricultural and industrial area (Crau plain/Berre-Fos basin) in southern France. Nine soil profiles were realized. They are aligned along a transect, from the Mediterranean coast to the north. Measurements of initial magnetic susceptibility (\(K_i\)) and remanent magnetization (ARM, IRM) have been carried out at room temperature. Several ratios of magnetic parameters were calculated and tested. Bivariate analyses allow to characterize different pollution sources and graphic results suggest three dominant contributions originated from road traffic, airport and steel industry. Moreover, magnetic grain-size discrimination between surface-soil samples and bottom-soil samples is obtained. An increase of hard magnetic components from topsoil towards the bottom of the profiles is evidenced.

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1. Introduction

Many recent works on atmospheric dusts and soils close to industrial area pointed out a relationship between materials enhanced in heavy metals and magnetic properties (Lecoanet et al., 1999; Georgeaud et al., 1997; Durza, 1999; Strzyszcz et al., 1996; Strzyszcz, 1993). Particular studies reveal the possibility to identify various source-types of industrial pollution only by using simple magnetic parameters. In fact, biplots combining different magnetic parameters are an useful, efficient and qualitative graphical technique. They allow to obtain a fast and easy discrimination without expensive chemical analyses.

For example, through a study focused on two potential sources, power station fly-ashes and motor vehicle emissions, Hunt et al. (1984) found distinctive magnetic contrasts in the dust fallout. The distinction was based on comparing the differences between magnetically soft and hard fractions, characterized by measuring isothermal remanent magnetization (IRM) at \(-20\) mT and \(-200\) mT (back-field IRM), and then normalizing to saturation values (IRM\_\text{20mT}/SIRM and IRM\_\text{200mT}/SIRM). Furthermore, coercivities of SIRM and IRM\_\text{100mT}/SIRM ratios were used to discriminate between ferrimagnetic and imperfect antiferromagnetic minerals present in their samples. The vehicular emissions were dominated by ferrimagnetic particles, while the fly-ash samples exhibited magnetically harder behavior, the result of being contaminated by hematite.

Beckwith et al. (1986) were also able to identify pollution sources from urban sediment samples. This work, complementary to previous results (Beckwith et al.,...
1984), confirmed high linear relationship between IRM\textsubscript{20mT}/IRM\textsubscript{300mT} and magnetic susceptibility, delimiting specific sample populations with different origins.

Recently, Lecoanet et al. (2001) studied salt-marsh soils contaminated by iron industry emissions. In this case, authors showed that magnetic methods reflect not only the concentration of ferrimagnetic minerals but also their grain size, thus enabling discrimination of metallurgical dusts and fine pedogenic particles created in-situ. Moreover, their results suggest that pollution is not the only source and that pedogenesis also plays a role.

The present study attempts to show which combinations of magnetic parameters are suitable to characterize soil samples containing mixtures of anthropogenic magnetic mineral fallout in Crau plain/Berre-Fos basin (road traffic, airport, iron and steel industry). Several magnetic parameters were calculated and tested. Bivariate analyses (biplots), combining the most efficient pairs of magnetic parameters acquired at room temperature (SIRM versus \(\chi\), \(\text{IRM}_{200mT}/\text{SIRM}\) ratio versus \(\text{IRM}_{20mT}/\text{SIRM}\) ratio and \(\text{ARM}_{40mT}/\text{SARM}\) ratio versus \(\chi\)) were used to identify magnetic minerals in soils and to determine possible contamination sources.

2. Materials and methods

2.1. Area description

The soils of Crau plain are made with Alps conglomerate deposits inside silts. Vegetation is a typical Mediterranean steppe. Main agricultural activities are ovine breeding, vegetable and fruit farming. But this area (approximately 500 km\(^2\)) is also the main road connecting Italy and Spain, with the A54 highway and many expressways, the military airport of Istres, railways for the servicing of Fos industrial complex. Many different industrial activities are in full expansion since the development of Fos-Berre harbor complex in the 1970s: refineries and oil complexes, chemical and iron industries, cement plant and others (Fig. 1). Meteorological conditions are dominated by north-westerly wind.

2.2. Soil sampling

Across the study area, nine soil profiles of 30 cm depth were realized during April–May 1999, indexed R, S, T, U, V, W, X, Y and AA (Fig. 1):

- Profile R is the north head of the transect. This site is supposed to be sufficiently isolated in order to provide the natural soil-background signal of the area investigated;
- Profiles S and T are made on both sides of expressways (site T is very close to A54 highway, about 5 m from road side);
- Profiles Y, X and V are located in Crau plain, and are not supposed to record specific anthropogenic contamination;
- Profile W is realized next to the runways of the military airport;
- Profile U is made on the side of crossroads;
- And profile AA is the south extremity of the transect. It is located inside the iron and steel industry.

In order to avoid any contamination, soil samples were collected from bottom to surface, and put in situ into 8 cm\(^3\) plastic cubes. Samples (90 in number) were stored in a cool place until analysis.

2.3. Magnetic measurements

The susceptibility meter used was the Kappabridge KLY-2 at CEREGE. Magnetic susceptibility is expressed in specific mass unit (\(\chi\), m\(^3\)/kg). Anhysteretic remanent magnetization (ARM) was acquired during A.C. demagnetization with amplitude decreasing from maximum of 100 mT to zero, around a steady field of 0.1 mT, using a Schönsstedt demagnetizer (Schönsstedt Instrument Company, USA). The ARM acquired at 100 mT is referred to as the saturation anhysteretic remanent magnetization (SARM).

Isothermal remanent magnetization (IRM) was acquired by placing samples in increasing magnetic fields at room temperature using a pulse magnetizer MMPM9 (Magnetic Measurements Ltd., GB). The IRM acquired at 2800 mT is referred to as the saturation isothermal remanent magnetization (SIRM). D.C. demagnetization was carried out using the same field increments as during acquisition, but with the field oriented against SIRM.

All remanent magnetization measurements were performed along the axial direction using a 2G Enterprises DC-SQUID cryogenic magnetometer housed at the magnetically shielded room of CEREGE.

3. Results and discussions

Magnetic susceptibility (\(\chi\)), anhysteretic remanent magnetization (ARM) and the isothermal remanent magnetization used here (IRM) are all concentration parameters. In most samples, \(\chi\) is proportional to the concentration of ferrimagnetic oxides (magnetite and maghemite). However, the measured susceptibility of weakly ferrimagnetic samples, in which water, carbon, calcium carbonate or silica are abundant, will be reduced by diamagnetism. Also, where ferrimagnetic concentrations are low in iron-rich samples, anti-ferrimagnetism and/or paramagnetism will contribute significantly to the magnetic susceptibility. Moreover, ARM and IRM values are more highly affected by
magnetic grain-size variations and by anti-ferromagnetic component (e.g. hematite, goethite) than is susceptibility (Walden et al., 1999).

Magnetic susceptibility values range from 0.29 to $1.46 \times 10^{-6}$ m$^3$/kg (Fig. 2). A great association is obtained between SIRM and $\chi$ (correlation coefficient $R^2 = 0.83$). The content of anthropogenic ferrimagnetic minerals decreases towards the bottom left corner of the diagram. Samples in the lower part of the diagram and shifted to the left of the diagonal (sites R, S and T) are characterized by low SIRM and moderate susceptibility. Their characteristics are probably due to dominant paramagnetic mineral content. Moreover, SIRM and magnetic susceptibility values at the natural-soil background site (R) are higher than those observed at contaminated sites of the road traffic group (S and T). Post-depositional weathering and/or formation of magnetic phases by pedogenic processes (Zheng et al., 1991; Zhou et al., 1990) could be an explanation for these higher values.

Data, which are displaced in the upper part to the right of the main group (site AA), indicate soil samples with considerable contributions from coarse ferrimagnetic grains, with an anthropogenic origin supported coming from steelworks’ emissions. These results can be interpreted as a mixture between natural magnetic background soil (site R) and highly magnetic contaminated soil (site AA).

The value of SIRM/$\chi$ ratio is used commonly to determine the grain size of magnetic particles over several microns in diameter. Data plotted along the diagonal of the diagram SIRM = $f(\chi)$ correspond to a mean value of 6.4 kA m$^{-1}$ (Fig. 2). According to Thompson and Oldfield (1986), it should be characteristic for a magnetite grain size of approximately 5 μm, and according to Sandgren and Thompson (1990) for mean grain size of about 8 μm. But, it is obvious that soil samples are made of a mixture of magnetic and non-magnetic minerals. Then it is not really realistic to conclude so precisely.

The ratio of IRM$_{200mT}$/SIRM enables to distinguish a ferrimagnetic component from an anti-ferromagnetic component. Ratio values close to $-1$ indicate the presence of ferrimagnetic mineral component for which saturation is obtained at a field of $-200$ mT. Ratio values close to zero mean soil samples are weakly magnetic and saturation is not reached at a field of $-200$ mT. Concerning the ratio of IRM$_{20mT}$/SIRM, reasoning is similar. But in this case, due to the weak field applied ($-20$ mT), ratio values close to 1 indicate the strong dominance of ferri-, indeed even ferromagnetic minerals in soil samples.
Fig. 3 plots IRM_{20mT}/SIRM versus IRM_{200mT}/SIRM for the various sets of soil samples. Results are similar to those obtained by Hunt et al. (1984) with atmospheric particulate samples. The range of variation in the lower reverse field ratio is rather small (0.183 < IRM_{20mT}/SIRM < 0.370) and does not clearly differentiate the sample set. However, additional information is obtained with arrows indicating bottom-surface trends along soil profiles. In fact, this kind of combination reveals a systematic trend for each profile corresponding to an increase of the IRM_{20mT}/SIRM ratio from bottom-soil samples to topsoil samples. The high reverse field ratio discriminates between the sample sets rather effectively (−0.595 < IRM_{200mT}/SIRM < −0.936).

Thus, mineralogy of samples collected close to the iron industry (AA), crossroads (U), airport (W) and Crau plain (V, X, Y) is dominated by ferrimagnetism for which saturation is obtained at −200 mT field.

Rendzine soil samples (site R) provides a weak magnetic signal. This feature could be due to a low ferrimagnetic mineral concentration and/or a hard magnetic component related to the presence of anti-ferromagnetic hematite.

The ARM_{40mT}/SARM ratio is used to determine the grain-size magnetite variability of the sample set. Fine grains are characterized by values close to 1 (a high per-
percentage of magnetization remains after the demagnetization at an alternating field of 40 mT). In contrast, coarse multi-domain grains are characterized with ratio values close to zero (only a low percentage of magnetization).

All soil samples show low \( \text{ARM}_{40} / \text{SARM} \) ratio values (<0.20). However, different trends appear (arrows indicate bottom-surface trends along soil profiles) and each site can be identified (Fig. 4):

- Samples of profiles W, V, U, Y, X and R place successively along a straight line whose slope reveals a magnetic dilution. Surface samples of site R have the lowest susceptibility values.
- Steelworks' signal displays an opposite trend. Samples are located aside, in the right part of the diagram. They exhibit a clear enhancement of magnetic minerals in topsoil with a decrease of magnetic grain size. According to the values of \( \text{ARM}_{40} / \text{SARM} \), bottom samples of profile AA have the same grain size characteristics than bottom samples coming from site W (close to airport), whereas characteristics of surface sample are comparable to profile R.
- An increase of susceptibility with depth is observed for airport (W) profile and rendzine (R) profile, while Crau plain group (V, X, Y) and road traffic group (S and T) are characterized by relatively constant values of magnetic susceptibility. The distribution/concentration of magnetic minerals in W and R soil profiles could be partly due to pedogenic processes.
- Three distinct groups are identified for traffic signal (S, T and U). Values of \( \text{ARM}_{40} / \text{SARM} \) ratios are similar for each of them (~0.15), while magnetic susceptibility of sites S and T is lower than susceptibility of samples collected close to crossroads (site U). In fact, samples of profile U are located among samples coming from Crau plain. This shift can be easily attributed to the steelworks’ influence.
- Three different groups are identified for the soil samples collected from Crau plain (V, X, Y). Magnetic mineral concentration is constant along these three soil profiles.
- Finally, for all profiles, even if values of \( \text{ARM}_{40} / \text{SARM} \) ratio are low (characteristic of the soil samples with coarse grains), there is an increase of grain sizes with depth.

4. Conclusions

The results of our investigation confirm that magnetic measurements can provide a basis for discrimination and identification of different soil-contamination sources. The range of normalized parameters used here varies according to the magnetic mineral and grain size assemblages present. Using these parameters alone, it is difficult to make quantitative estimates of the proportion of different magnetic mineral phases present in samples. With a combination of magnetic parameters, it is nevertheless possible to differentiate between sample sets and to identify contaminating sources. Using bivariate analyses, size-discrimination between surface-soil samples and bottom-soil samples is obtained. An increase of hard magnetic components from topsoil towards the bottom of the profiles is exhibited.

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![Fig. 4. ARM\text{40}/SARM ratio versus magnetic susceptibility (\( \chi \), 10\(^{-6}\) m\(^3\)/kg). Arrows indicate bottom-surface trends along soil profiles.](image-url)
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