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Magnetic susceptibility and heavy metal contamination in agricultural soil of Tadla plain

Mohamed El Baghdadi [a,*], Khalid Jakani [a], Ahmed Barakat [a], Yahya Bay [b]
[a] *Laboratoire Géoressources et Environnement, Université Sultan My Slimane, Faculté des Sciences et Techniques, B.P. 523 Béni Mellal 23000, Morocco.*
[b] *Institut National de la Recherche agronomique, Afourer, Morocco.*
* *Corresponding author. Department of Earth Sciences, Faculté des Sciences et Techniques, P.O. Box 523, 23030 Beni-Mellal, Morocco. Tel.: +212 523 485 112. Fax: +212 523 485 201. E-mail address:* mohaelbaghdadi@gmail.com mbagdadi@fstbm.ac.ma

Abstract
Excessive accumulation of heavy metals in agricultural soils may not only result in environmental contamination, but elevated heavy metal uptake by crops may also affect food quality and safety. This study is conducted in two agricultural topsoil parcels according to the road emission proximity. Magnetic susceptibility is highly recorded in parcel 1 near the road compared to the values recorded in parcel 2 far away from road exhausts.
Heavy metals show high values in parcel 1 near the road and are correlated positively with the magnetic susceptibility. The enrichment of Pb, Cd, Cu, Fe and Zn in parcel 1 soils was strongly influenced by anthropogenic activities, and Pb accumulated in fine particles was mainly derived from past vehicular emissions. According to the PLI values, studied areas do not shows highly pollution factors for Cd, Cu, Zn and Cr. But the high PLI value of lead in both parcels is signifying high pollution degree.
Keywords: Magnetic susceptibility, heavy metal, pollution, road exhaust, Agricultural soil, Beni Mellal.

1. Introduction
Magnetic minerals present in soils may be either inherited from the parent rocks (lithogenic origin), form during pedogenesis (pedogenic origin) or may stem from anthropogenic activities (secondary ferromagnetic materials). In the case of minor contributions of the first two sources to the magnetic properties of soils, susceptibility measurements become very important for monitoring environmental pollution (Magiera et al. 2006; Jordanova et al., 2006; Petrovsky et al., 2001; Petrovsky et al., 2004). Some recent studies have successfully applied soil χ mapping as a tool for preliminary pollution monitoring (Hoffmann et al., 1999; Boyko et al., 2004), mapping areas polluted by industrial emissions (Heller et al., 1998; Hay et al., 1997; Duan et al., 2009) and detecting roadside pollution by automotive exhausts (El Baghdadi et al., 2011; Bucko et al., 2011; Wang and Qin, 2005, 2006; Lu et al. 2007).
This paper presents research results concerning magnetic susceptibility of agricultural topsoil in INRA station far from the urban activities to compare effect of proximity to the road emission. The correlations between soil magnetic susceptibility and heavy metal contents are made. On this basis, magnetic and chemical properties are discussed in order to highlight environmental implications.

2. Materials and methods
2.1 Study area
The study area is located at 19 km to the southwest of Beni Mellal (32°15'34" and 6°32'10") in the station of INRA (Institut National de la Recherche Agronomique) (Fig. 1). Situated in Tadla plain with altitude about 446 m, this area is characterized by semi-arid climate with averaged annual temperature of 26 °C and annual rainfall of 400 mm. The wind direction is east to northeast. The geology of the region is presented by the Mesozoic limestone with travertine and Mio-pliocene alluvial fan conglomerates. Geologic control of magnetic signal is very low (20-40 × 10^{-5} SI).
The study area is reserved to experimental tests of main crop in the region. The main soils are Calcic to Argilic Spodsols, Ultisols, Vertisols, Randzinas brown calcareous soil showing high increase of lime at depth horizons

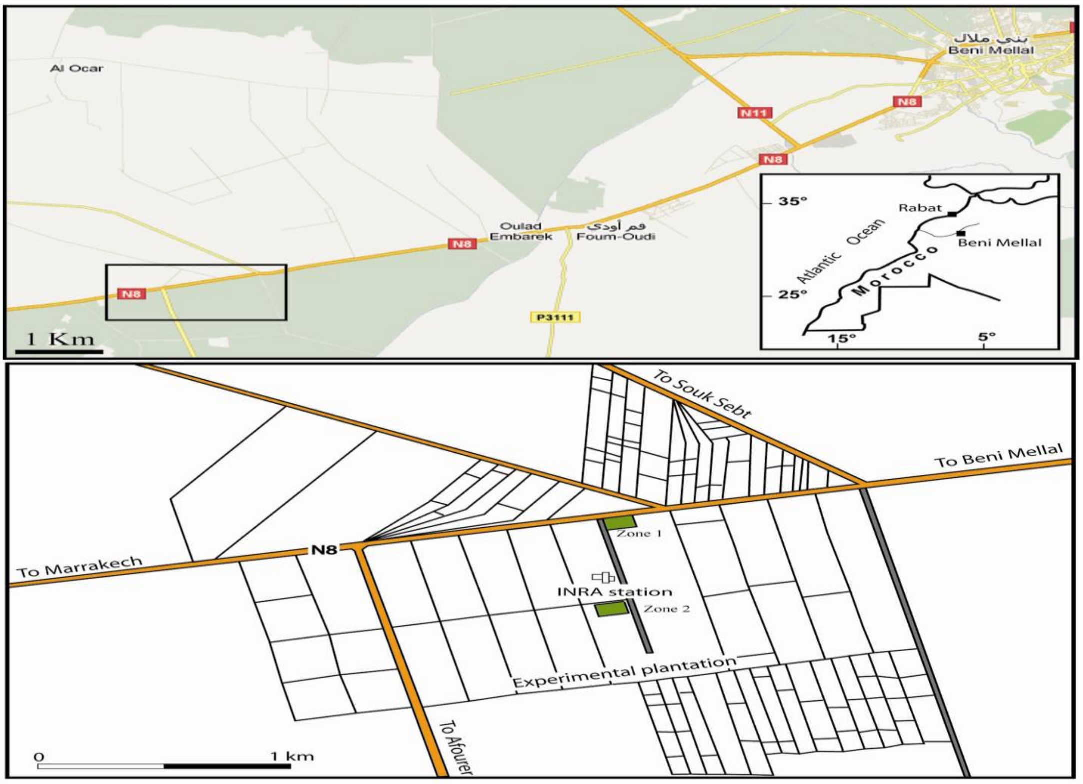

Figure 1: Location maps showing the study area and sampling stations.

2.2 Magnetic susceptibility measurement

In situ measurements of volume magnetic susceptibility κ were made in a grid of 50 x 50 m^2 using pocket GF Magnetic susceptibility meter SM20 making access to 90% of measuring signal e.g., concentration of ferrimagnetic material in the top 20 mm of the land surface with operating frequency of 10 kHz and sensitivity of 1×10^{-6} SI units. In order to check reproducibility and to avoid measurement errors, each measurement represents the mean of five readings magnetic susceptibility (MS).

2.3 Heavy Metal analysis

The collected soil samples were ground in a mechanical agate grinder until fine particles (<200 μm) were obtained. The prepared soil samples were analyzed for their heavy metal concentrations using acid digestion method (Li and Thornton, 1993). About 0.250 g of the soil samples were weighed and placed into Pyrex test tubes. Concentrated nitric acid (4.0 ml) and 1.0 ml concentrated perchloric acid were added. The mixtures were heated in an aluminum block until complete dryness. After the test tubes were cool, 5% (0.8M) nitric acid was added and heated at 60°C for 1 h with occasional mixing. Upon cooling, the mixtures were decanted into polyethylene tubes and centrifuged at 3500 rpm for 10 min. Heavy metal concentrations of the solutions were measured using Inductively Coupled Plasma (ICP–AES).

3. Results and discussion

3.1 Soil magnetic susceptibility spatial distribution

Magnetic sceptibility values are about 121 x 10^{-5} SI, ranging from 31 to 198 x 10^{-5} SI in parcel 1 and about 53 x 10^{-5} SI, ranging from 25 to 89 x 10^{-5} SI in parcel 2. Parcel 1 shows enhancement of magnetic susceptibility compared to the parcel 2 far away to the road. The highest values of topsoil susceptibility are recorded in parcel 1 varied by two to three orders of magnitude compared to the values recorded in parcel 2. For comparison with value found in Beni Mellal urban topsoil (600×10^{-5} SI) (El Baghdadi et al., 2011), the mean value in agricultural topsoil is lower.

In order to highlight the trend of MS versus distance on the road side, histogram distribution of magnetic susceptibility was given in Figure 2. In parcel 1, magnetic susceptibility show inhomogeneous repartition with two peaks at 0-5 m and 40-45 m from the road with standard deviation ~ 48×10^{-5} SI. In parcel 2, magnetic distribution is slightly homogeneous with a standard deviation about 15×10^{-5} SI.

The relatively high magnetic susceptibility values suggested that the soil was enriched with ferrimagnetic grains probably as a consequence of road gasoline emissions. In parcel 2, Lower susceptibility values were found and distributed widely in all prospected surface topsoil. In respect to the same physical characteristic of soil in both sites and remoteness to the road edge, lower magnetic susceptibility values in parcel 2 reveal no affected soil by road emission dust.

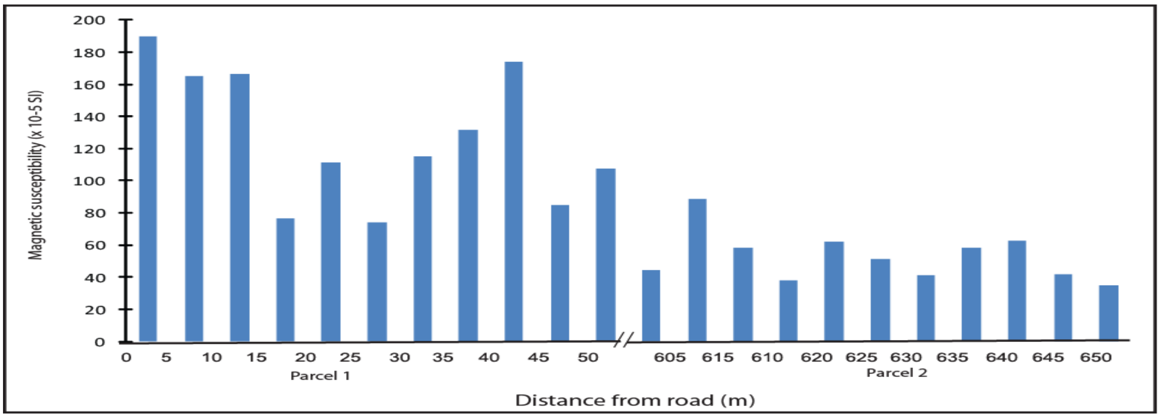

Figure 2: Histogram plot showing magnetic susceptibility variation versus distance from road and automotive exhausts

3.2 *Soil magnetic susceptibility vertical distribution*

The vertical variation of magnetic susceptibility in soil profile is shown in Figure 3. The magnetic susceptibility values of the soils from parcel 2, representing the lower level of soil magnetic susceptibility, ranged from 69 to 18 × 10^{-5} SI throughout the profile. Low enhancement of magnetic susceptibility (89 × 10^{-5} SI) at the upper horizon (0–10 cm) could be reported to pedogenic processes in this area. Profiles from parcel 1 show increased magnetic susceptibility (135-190 × 10^{-5} SI) in its surface horizons (0–10 cm) and steeply decreased from upper horizon to 20–50 cm horizon, thus suggesting the contribution of ferrimagnetic minerals of anthropogenic origin.

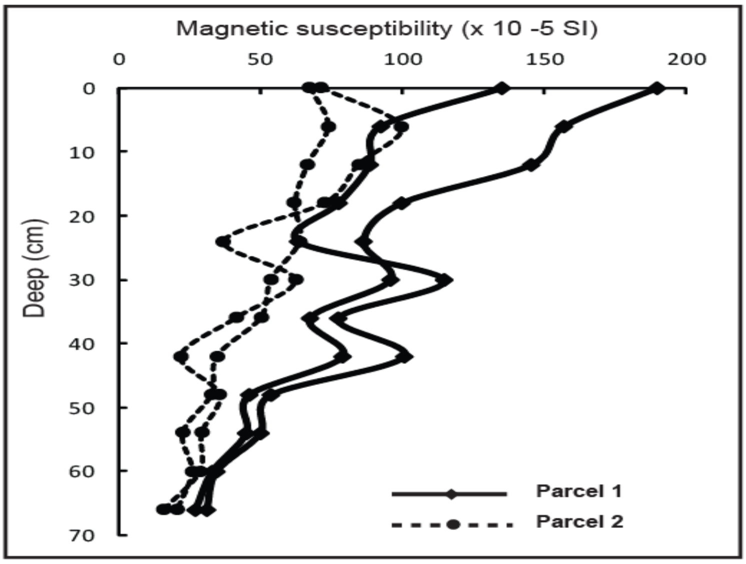

Figure 3: . Magnetic susceptibility variation along vertical profiles of representative soils from Parcel (1) and parcel (2) in agricultural soil far from urban activities.

3.3 *Heavy metal content*

In parcel 1, the mean Cd, Cu, Pb, Zn and Cr contents of soils were 0.428, 27.82, 127.24, 103.4 and 63.99 mg kg^{-1} respectively. The mean Fe content is about 2.13%. In parcel 2, the mean of Cd, Cu, Pb, Zn and Cr contents of soils were respectively 0.345, 20.90, 72.14, 33.90 and 46.32 mg kg^{-1}. The mean Fe content is about 1.70%. In general, Pb and Zn concentrations in parcel 1 topsoils significantly exceed five times and two times respectively the worldwide average for soils (Pb: 26 mg kg^{-1}, Zn: 74 mg kg^{-1}; Li, 2000; Callender, 2005). Cd, Cu and Cr concentrations are very little beyond the worldwide soil average (Callender, 2005). All measured heavy metal shows low contents in parcel 2 compared to their contents in parcel 1 near the roadside. The results indicate that soils near road paved ridge have elevated metal concentrations.

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3.4 Correlation between magnetic susceptibility and heavy metal content

Linear correlation coefficients between magnetic susceptibility and concentrations of chemical elements, as well as the regression equations of statistically significant correlation pairs, are listed in Table 1.

The correlation coefficients were calculated for all points as a single group and not for each parcel. According to correlation analysis of soil samples, all heavy metal analyzed show strong positive correlations with magnetic susceptibility (Fig. 4).

Cd, Pb and Zr have high correlation coefficients (0.83, 0.87 and 0.83 respectively) followed by Cr, Cu and Fe with high moderate coefficients (0.72, 0.63, and 0.60 respectively) with magnetic susceptibility.

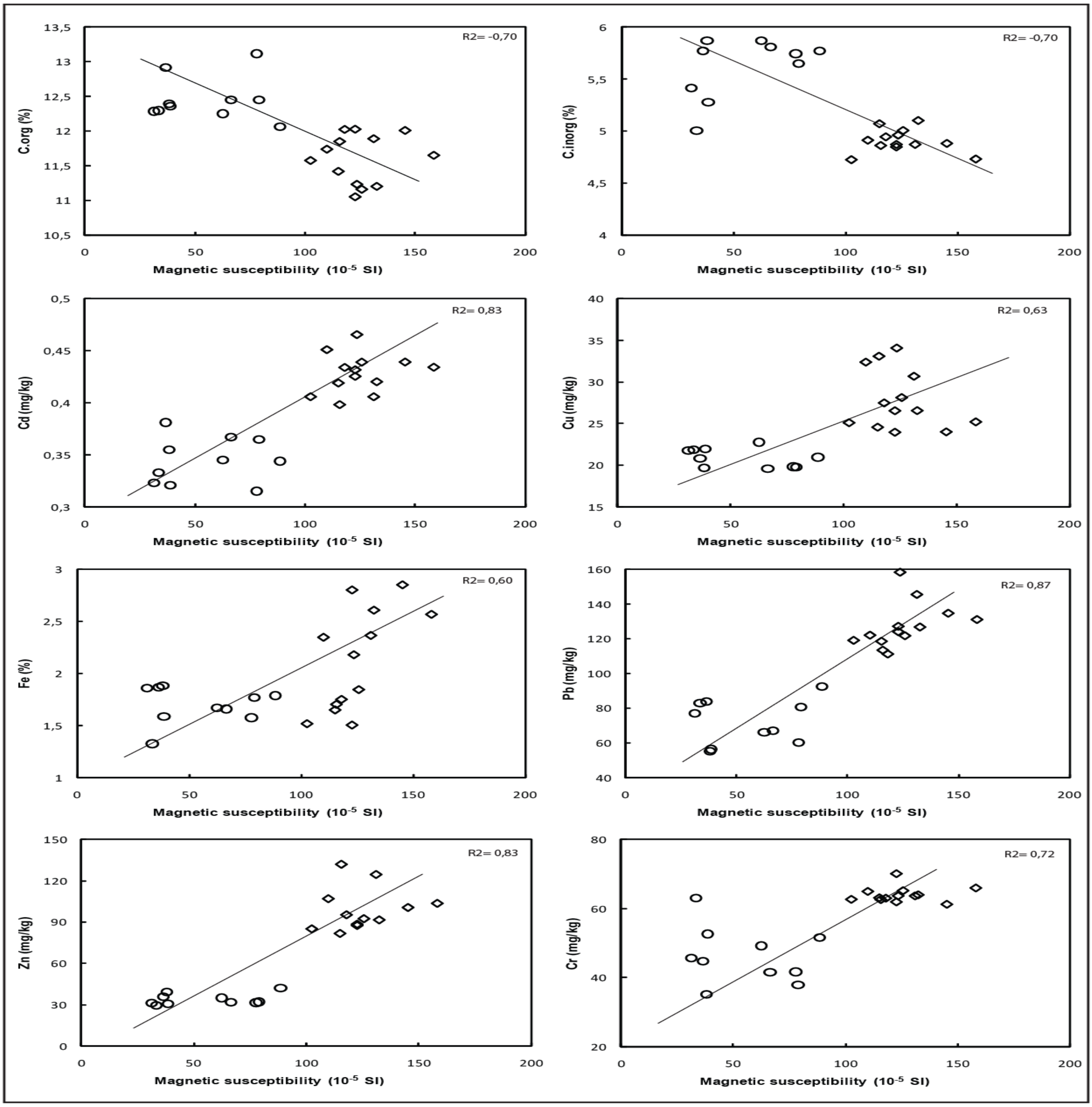

Figure 4: Scatter plots of the concentration of organic and inorganic carbon, Cd, Cu, Fe, Pb, Zn and Cr and magnetic susceptibility for agricultural topsoil samples.

Table 1 : Pearson correlation matrix for magnetic susceptibility κ MS and heavy metals concentrations in soils

	Cd	Cu	Fe%	Pb	Zn	Cr	κ MS (10^{-5} SI)
Cd	1	0,73	0,57	0,89	0,86	0,72	0,83
Cu		1	0,38	0,78	0,92	0,74	0,63
Fe%			1	0,58	0,51	0,40	0,60
Pb				1	0,92	0,83	0,87
Zn					1	0,76	0,83
Cr						1	0,72
κ MS (10^{-5} SI)							1

3.4 Heavy metal pollution assessment

Figure 5 shows calculated PLI (Tomllinson et al., 1980) of five heavy metals in studied areas. In parcel 1 Cd, Pb and Zn PLI values are greater than 1 but Cu and Cr have lower values. In parcel 2, only Pb shows PLI higher than 1. It is found that the lead shows very high values of PLI in both stations. This increase in parcel 2 far from road influence can be attributed to equipment such as tractors and others machine that are used in farming work. Cd, Cu, Zn and Cr show values of PLI very close to 1. This means that the soil of both parcels is not very contaminated by these metals but highly polluted by lead.

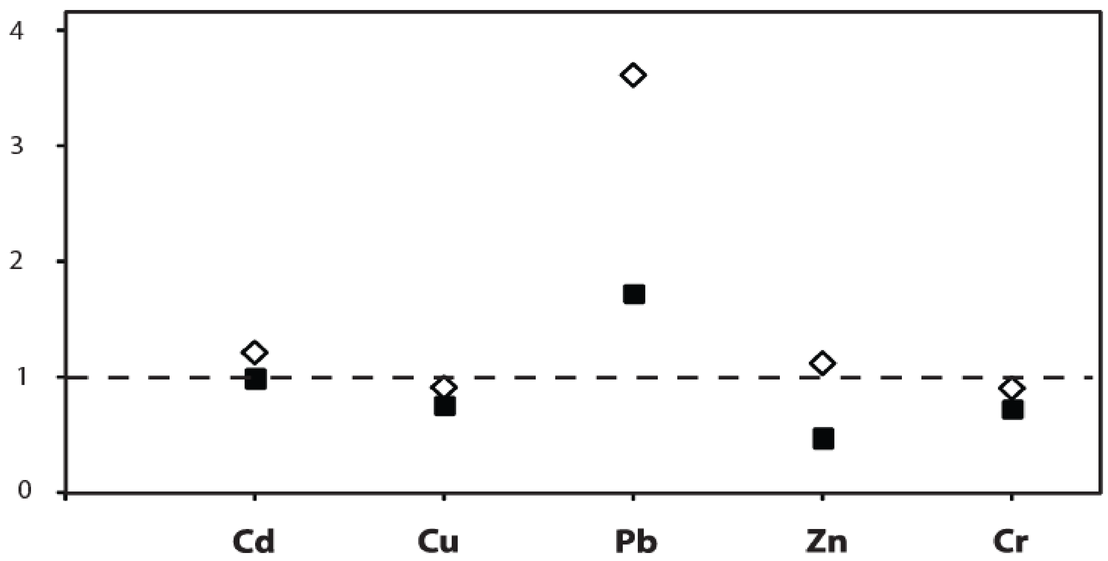

Figure 5: Comparison of the Tomlinson Pollution Load Index (PLI) of analyzed heavy metal concentration (Cd, Cu, Pb, Zn and Cr) in the topsoils in parcel 1 (light diamond) and parcel 2 (dark square).

3.5 Scanning electron microscopy

Scanning electron microscopy of magnetic extracts in parcel 1 revealed the presence of typical spherules consisting mainly of iron and iron oxides (Kapićka et al., 2003). Typical example, with the spherule diameter of about 5 µm with the corresponding spectra is shown in Fig. 6a. In parcel 2, there are no spherules which indicate the action of automotive exhausts but Pb is found sometimes as sulfured spots with some content of Fe and Co (Fig. 6b). Major magnetic particles extracted in this parcel are mostly angular (octahedral form), probably titano-magnetite (Fig. 6c), resulting from pedogenic processes.

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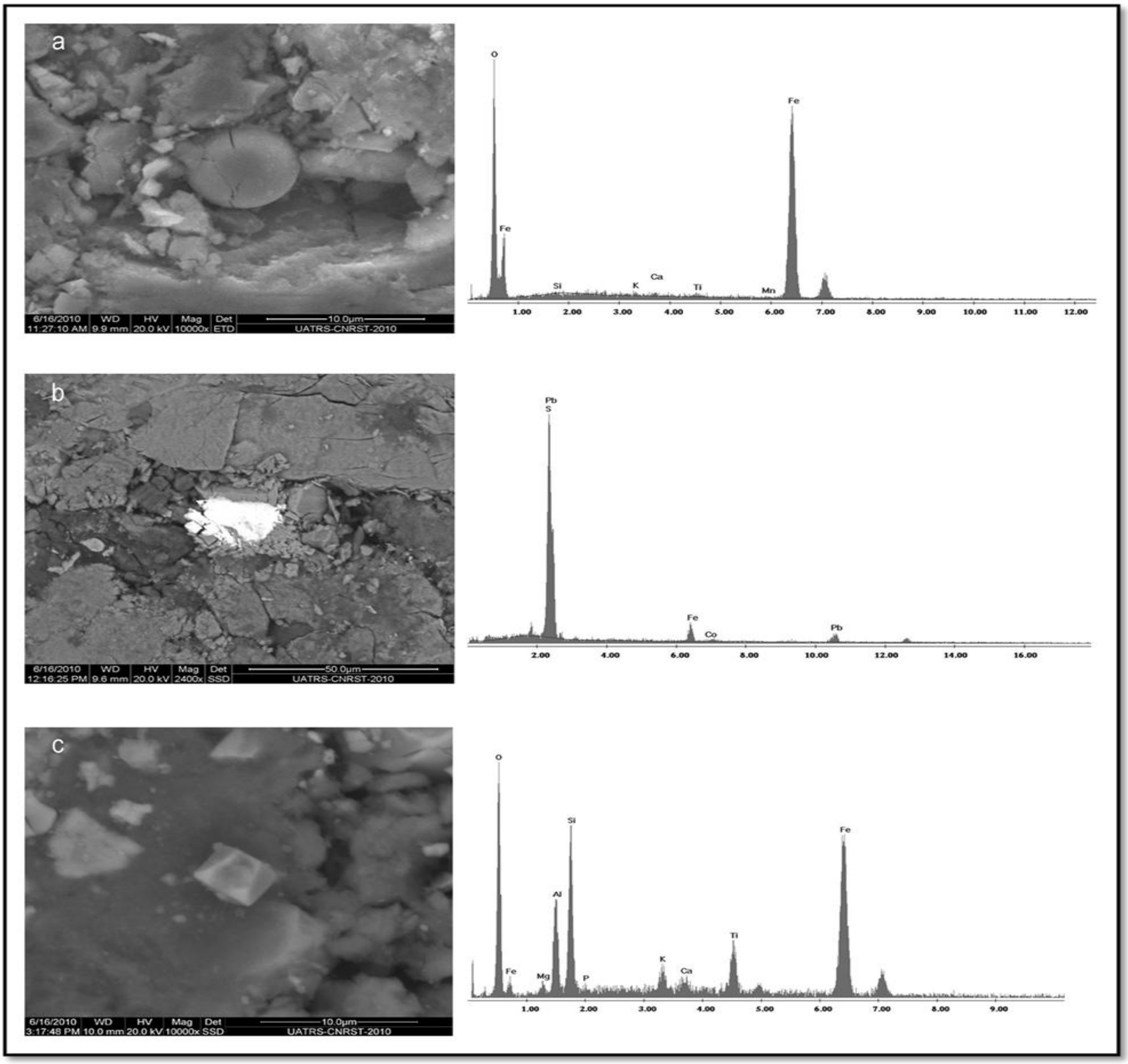

Figure 6 : Scanning electron micrograph (SEM) with corresponding energy spectra of extracted magnetic fractions in parcel (1) with spherule form (a) and in parcel (2) showing Pb spots (b) and titano-magnetite octahedron associated with silicates (c).

Conclusion

The magnetic susceptibility in INRA parcels shows different horizontal and vertical profiles according to the proximity to the road. The highest values of topsoil susceptibility are recorded in parcel 1 varied by two to three orders of magnitude compared to the values recorded in parcel 2 far away from road exhausts.

Heavy metals show high values in parcel 1 near the road and are correlated positively with the magnetic susceptibility. Common presence of some heavy metals from the traffic emissions also accounts for the stronger correlations between the magnetic susceptibility and these metals in the urban topsoil. The enrichment of Pb, Cd, Cu, Fe and Zn in parcel 1 soils was strongly influenced by anthropogenic activities, and Pb accumulated in fine particles was mainly derived from past vehicular emissions. According to the PLI values, studied areas do not shows highly pollution factors for Cd, Cu, Zn and Cr. But the high PLI value of lead in both parcels is signifying high pollution degree.

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