Proceedings of the 7th International Symposium on Recent Advance in Exploration Geophysics in Kyoto (RAEG2003)
Kyoto University, January 2003

Environmental Magnetic Study of Surface Soil/Sediment in Northern Tunisia – Field Screening for Potentially Toxic Elements Contamination -

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Abstract: Field Magnetic susceptibility measurement has been carried out for various soil/sediment in northeastern Tunisia, Mediterranean coast of North Africa, where industrial /urban zones have been rapidly expanded in late 20th century. The variation of magnetic susceptibility is compared with the environmental geochemical data, the concentration of potentially toxic elements (PTEs) possibly derived from anthropogenic activities. There is a correlation between the magnetic susceptibility and the concentration of PTEs, As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, where remarkable anomaly could be observed in and around Tunis industrial/urban zone. The result of principal component analysis (PCA) also showed that some of elements, As, Cu, P, and Se, significantly correspond to magnetic susceptibility value. It suggests us the magnetic susceptibility measurement is applicable for a low-cost and quick field screening of soil/sediment contamination by PTEs.

Keywords: Magnetic susceptibility, Environmental pollution, Heavy metals, PTEs, PCA

1. Introduction

Potentially toxic elements (PTEs; Alloway, 1995) such as heavy metals and metalloids naturally occur in rocks sediments, soils, and groundwater, but their anthropogenic derivatives have drastically increased since the industrialization during the 20th century. Contamination of such substances has caused significant pollution reducing environmental quality and affecting human health. In order to plan effective protection measures, quick mapping and detecting soil/sediment pollution have become increasingly important.

Magnetic susceptibility measurement is a simple, rapid, and non-destructive technique that can be applied on soil/sediment samples. It has been expected that magnetic measurement is applicable for assessing anthropogenic pollution, especially heavy metal pollution (Oldfield et al., 1978; Beckwith et al., 1986; Locke and Bertine, 1986; Tompson and Oldfield, 1986; Verosub and Roberts, 1995; Georgeaud et al., 1997; Durža, 1999; Hoffmann et al., 1999; Petrovský and Ellwood, 1999; Yoshida et al., 1999; Magiera and Strzyszcz, 2000) and sedimentary environment analysis (Karbassi and Shankar, 1994). These previous works indicate a possible correlation between magnetic susceptibility and concentration of toxic heavy metals.

In natural soils and sediments, ferromagnetic (or ferrimagnetic) minerals, magnetite (β-Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (a-Fe_2O_3), goethite (a-FeOOH), pyrrhotite (Fe_7S_8), and greigite (Fe_3S_4), account for the increase of values of magnetic susceptibility. The major carrier of magnetic susceptibility in most soils and sediments are the magnetite and maghemite, which is understood that the pedogenic environment affects these Fe oxide minerals in soil (Singer and Fine, 1989). Some non-ferromagnetic heavy metals also account for the increase of values of magnetic susceptibility as a consequence of the effect of humic, fulvic, and non-specific organic compounds in the soil (Durža, 1999). On the other hand, values of magnetic susceptibility is inversely correlated with leaching concentration (solubility) of heavy metals due to relative enrichment of adsorbing minerals and/or a presence of metal scavenger (Yoshida et al., 1999; Yoshida et al., 2002a,b).

In this paper, we report the result of magnetic susceptibility measurement and magnetic mineralogy of soil/sediments in northeastern Tunisia where large industrial and urban zones have been rapidly expanded. The magnetic susceptibility variation is statistically compared with the results of environmental geochemistry of the soil/sediment.

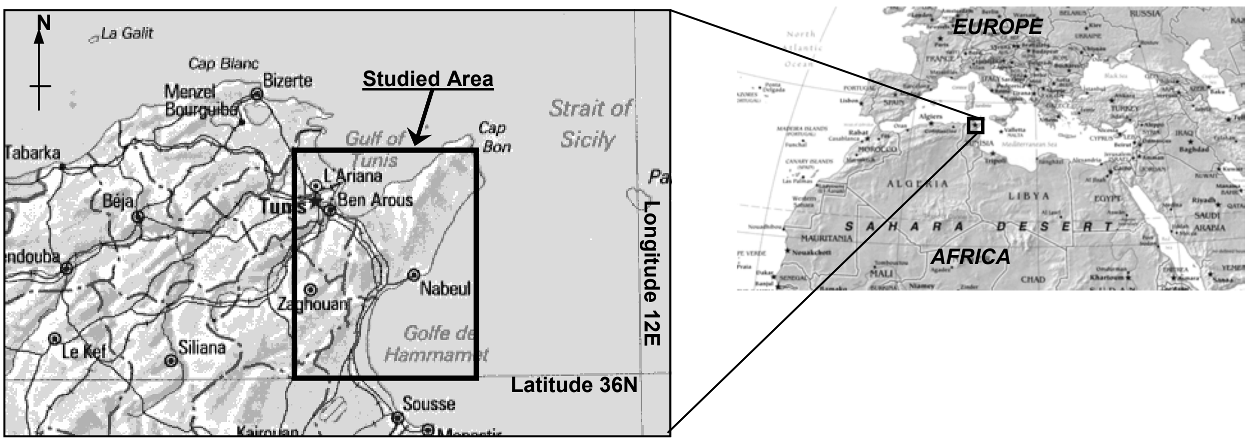


Figure 1: Studied area (the base map images are compiled from the maps in www.lib.utexas.edu/maps/tunisia.html)

2. Samples and Method

2.1 Sampling

A total of 148 samples were collected from natural soil, agricultural soil, urban soil, natural sediments, and waste-related artificial deposits distributed in northern Tunisia (Figure 1). The sampling was made based on longitude 7.5' (approx. 13.8 km) x latitude 7.5' (approx.11.1 km) grid defined on 1/200,000 topographic map in advance. Each sampling site was identified using GPS. Detailed information on the sampling sites was reported by Yoshida et al. (2002a,c).

2.2 Magnetic Measurement

Magnetic susceptibility measurement was done using a field magnetic susceptibility meter, model SM20 (ZH Instruments), where the operation frequency is 10 kHz with the sensitivity of 10^{-6} (SI). All the measurements have been performed at the field exposures directly attaching the sensor coil onto a flat surface at sampled site. Five-time readings were averaged and used for the interpretation. The drift of each reading is corrected by air, the zero adjustments, before and after the reading. In order to determine magnetic mineralogy of the sample, Isothermal Remanent Magnetization (IRM) acquisition experiment was attempted for selected two samples. The IRM acquisition experiment was performed under a 50Hz pulse magnetizer, where applied field was progressively increased up to 3mT at room temperature and then 3T IRM (SIRM) was demagnetized by back-field application. The IRM in each magnetization step was measured with a spinner magnetometer.

2.3 Chemical Analysis

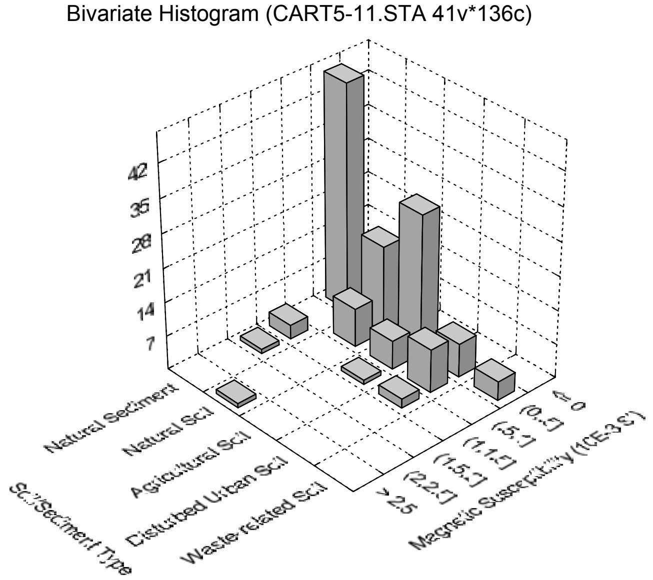
Collected samples are dried at room temperature and sieved by 1.0mm mesh. A 15.0 g sample split of the same sample was digested in 90 mL aqua regia ($HCl-HNO_3-H_2O$) at 95℃ for one hour. The solution is diluted to 300 mL with water. Analysis was made by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS). Total 37 elements were measured: B, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Mo, Ag, Cd, Sb, Te, Ba, La, W, Au, Hg, Tl, Pb, Bi, Th, and U. The upper detection limit for Ag, Au, Hg, W, Se, Te, Tl, and Ga is 100 ppm, that for Mo, Co, Cd, Sb, Bi, Th, U, and B is 2 %, and that for Cu, Pb, Zn, Ni, Mn, As, V, La, and Cr is 10 %. The aqua regia digestion of sediments extracts only a fraction of the major elements because silicates are not completely dissolved with this method. Owing to this limitation, results are total to near total for trace and base metals and possibly partial for rock-forming elements such as Na, Mg, Al, K, Ca, Mn, and Fe. However, environmentally concerned components like heavy metals or PTEs not bound to silicates are expected to be efficiently dissolved (Ure, 1995; Giusti, 2001).

3. Results

3.1 Magnetic Susceptibility Variation and Magnetic Mineralogy

The magnetic susceptibility of natural soil/sediment in the area varies widely from 10^{-5} to 10^{-2} (SI system), while the magnetic susceptibility of most soil/sediment ranges from 1.0 - 5.0 x 10^{-4}. The population of susceptibility value depends on soil/sediment type (Figure 2). The peak population of urban soil appears larger magnetic susceptibility values than that of other types. The samples showing very large susceptibility were obtained from the sites near solid waste landfill sites (Tunis Port, Ariana, and Sejoumi) that probably contain ferromagnetic materials of anthropogenic origin.

The result of IRM acquisition experiment for selected two sediment samples showing relatively larger magnetic susceptibility values is given in Figure 3. According to the IRM vs. applied field plots (the first phase experiment), it is obvious that the samples show near-saturation of IRM before applying 300 mT field, which means the main magnetic carrier of these samples is magnetite (β-Fe_3O_4) and/or maghemite (γ-Fe_2O_3). However, under higher applied fields (>300 mT, max 3 T), the IRM still increases gradually. It indicates magnetically trace but negligible presence of high saturation minerals such as hematite (α-Fe_2O_3) and goethite (α-FeOOH).



←**Figure 2**: Bivariate histogram of magnetic susceptibility values observed in the area.

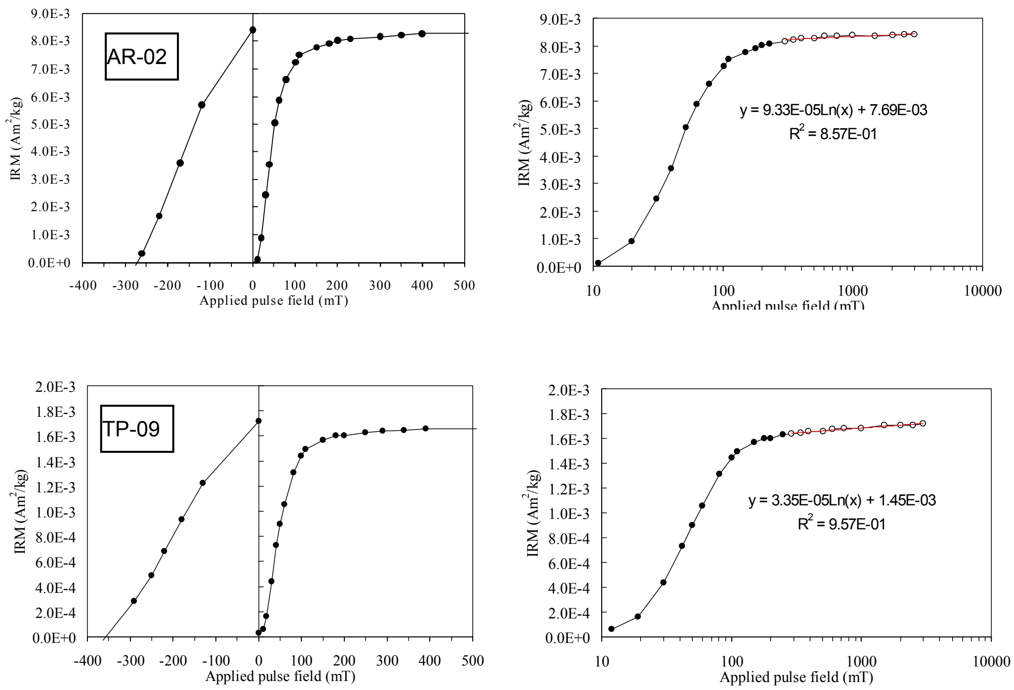


Figure 3: IRM acquisition curve (right graph) and back-field demagnetization curves (left side of left graph) for two samples (AR-02 and TP-09).

3.2 Environmental Geochemistry

The result of chemical analysis using aqua regia extraction method is summarized as a Box & Whisker Plot for each element concentration (Figure 4). It is remarkable that the standard deviation range is relatively larger for Se, Ti, Te, Ba, Mg, and K, and the standard error range is larger for three heavy metals, Zn, Cd, and Pb.

The characterization of spatial distribution of PTEs in the area is briefly summarized in Table 1 based on Yoshida et al. (2002c). According to the spatial distribution pattern of each element concentration, we estimated the background value for each element. The background values are mostly within normal level in comparing with the international background values (NOAA, 1999), but that of As, Ni, and Sb shows rather higher values, which may be a characteristic feature of this area. The spatial distribution of PTEs indicates that high anomaly of PTEs concentration in soil/sediment often appears in Tunis urban/industrial zone and its south, the agricultural zone between Tunis and Zaghouan. These areas are probably much contaminated by human activities; urbanization, industries, waste disposal and so on. Comparing the concentration level of each anomaly with the international standards (NOAA, 1999), the concentration of seven PTEs, As, Cd, Cu, Hg, Pb, Sb, and Zn, indicates abnormal high values that exceed the environmental quality standards, which is potentially hazardous.

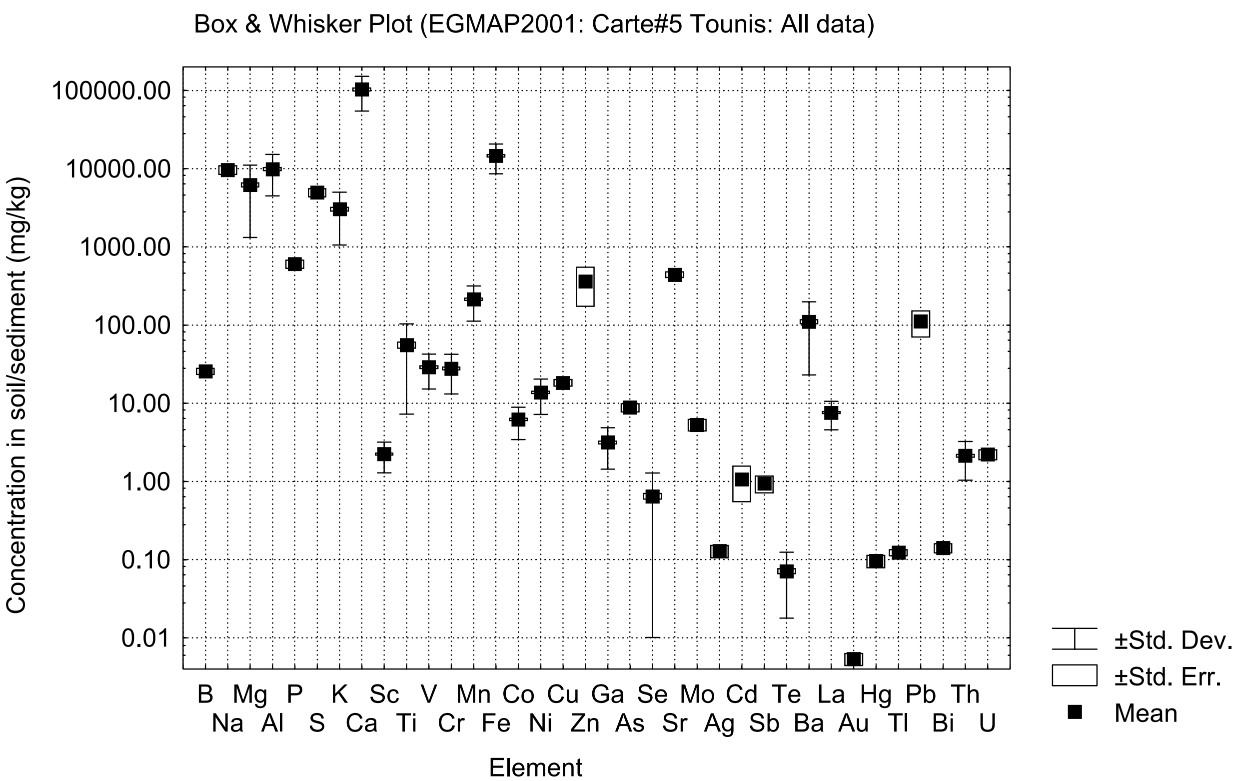


Figure 4: Box & Whisker Plot for the distribution of element concentration in soil/sediment samples.
Std. Dev.: Standard Deviation, Std. Err.: Standard Error

Table 1: Summary of the soil/sediment contamination screening (after Yoshida et al., 2002c)

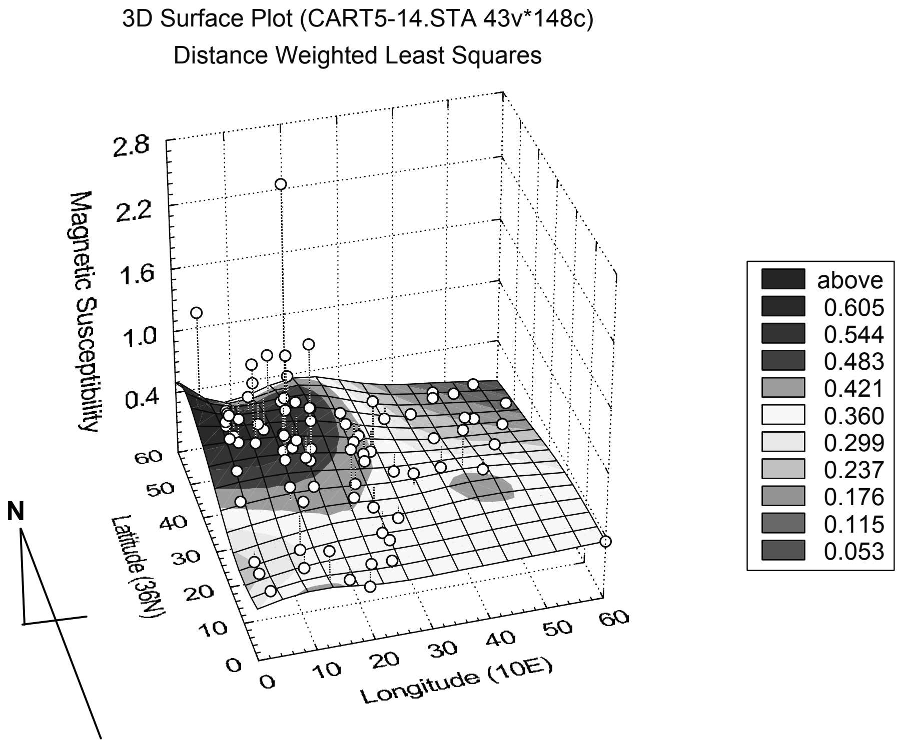
PTEs	Background* unit: mg/kg	Anomaly	Possible polluters
As	<7.7 (high)	Agricultural zone between Tunis and Zaghouan	Natural, Agriculture, Urban, Waste
B	<6.6 (normal)	Lake Tunis to Carthage; agricultural zone between Hammamet and Zaghouan	Natural, Waste
Cd	<0.15 (normal)	Tunis urban zone and its south	Urban, Waste, Agreiculture
Co	<6.1 (low)	Tunis urban zone to the agricultural zone between Tunis and Zaghouan	Natural, Urban, Waste
Cr	<17.1 (high)	Tunis urban zone to the agricultural zone between Tunis and Zaghouan	Urban, Industrial, Waste
Cu	<19.4 (normal)	Tunis urban zone, especially Lake Tunis	Urban, Industrial, Waste
Hg	<0.055 (normal)	Agricultural zone between Tunis and Zaghouan	Natural, Waste, Agricultural
Mo	<0.55 (low)	Rades Industrial Zone	Industrial (Fuel burning?)
Ni	<11.1 (high)	Tunis urban zone to the agricultural zone between Tunis and Zaghouan	Urban, Waste, Industrial
Pb	<17.9 (normal)	Tunis urban zone	Urban, Industrial, Waste
Sb	<0.4 (high)	Agricultural zone between Grombalia and Nabeul	Natural (?), Waste, Industrial (?)
Se	<0.12 (normal)	Coastal zone between Tunis and Hammam-Lif	Urban, Waste, Natural
Zn	<26.4 (normal)	Tunis urban zone and its surroundings	Urban, Waste, Industrial

* (   ) gives the comparison with international background values (NOAA, 1999).

3.3 Correlation between Magnetic Susceptibility and Geochemistry

The variation of magnetic susceptibility in the area is graphically illustrated in a 3D surface diagram, Figure 5 (upper diagram). There is a distinct positive anomaly of magnetic susceptibility in the northwestern part of the area, Tunis urban/industrial zone and its surroundings. Similar anomaly pattern can be observed in the concentration variation of various PTEs, As, Cd, Co, Cr, Cu, Ni, Pb, and Zn (Table 1); for example, the variation of Cu concentration is graphically displayed in Figure 6 (lower diagram). Such correlation has been known in other areas; Georgeaud et al. (1997) reported a correlation of magnetic susceptibility with Zn, Cd, and Cr, and weaker correlation with Cu, Ni, Pb, and Fe, among the sediments distributed in polluted catchments. Probably these PTEs have been enriched in and around the urban/industrial area caused by intensified human activities, industrial emission, waste disposal, and so on. At the same time the materials like magnetite and maghemite (iron oxide minerals), which enhance magnetic susceptibility, also enriched in the area.

The result of PCA indicates that magnetic susceptibility value is statistically well correlated with the concentration of four elements, As, Cu, P, and Ti (Figure 6).



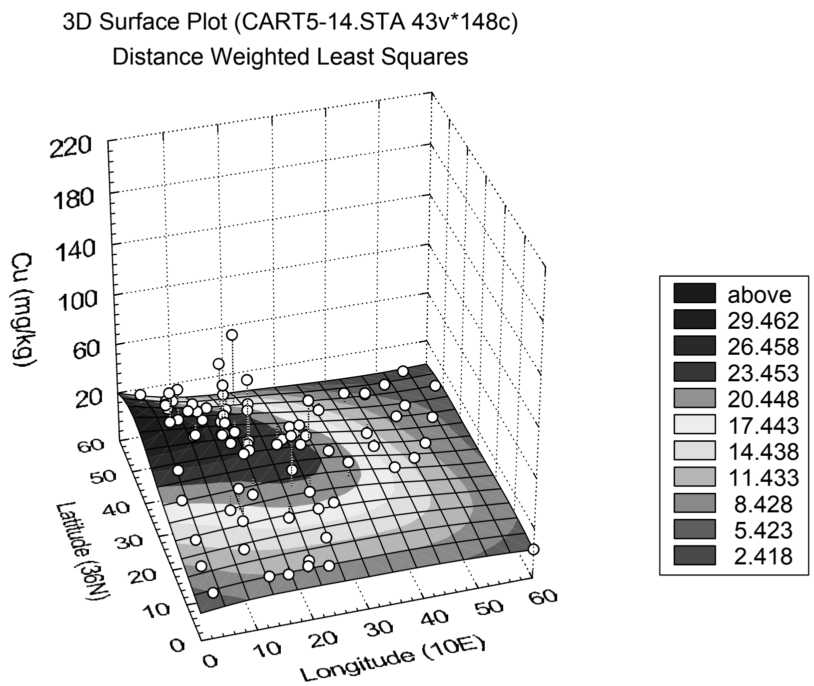
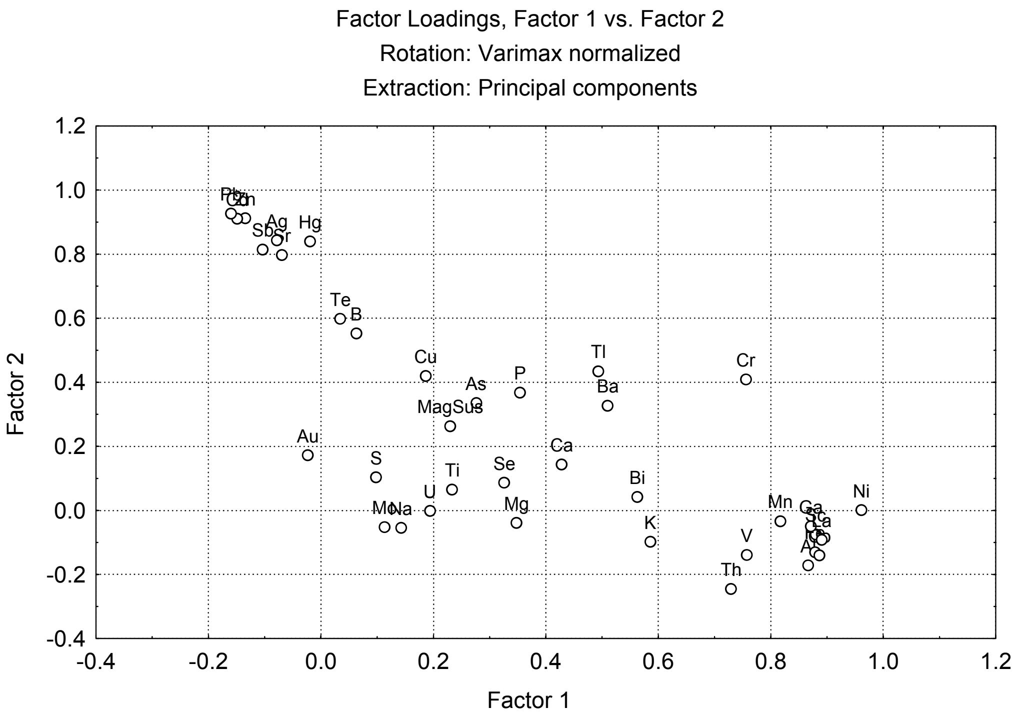


Figure 5: Spatial variation of magnetic susceptibility value (upper diagram) and Cu concentration (lower diagram) in the area. In the northwestern (upper left) part, Tunis urban/industrial zone and its surroundings, both magnetic susceptibility and Cu show strong positive anomaly. The geographic position of the outer grid is shown in Figure 1.



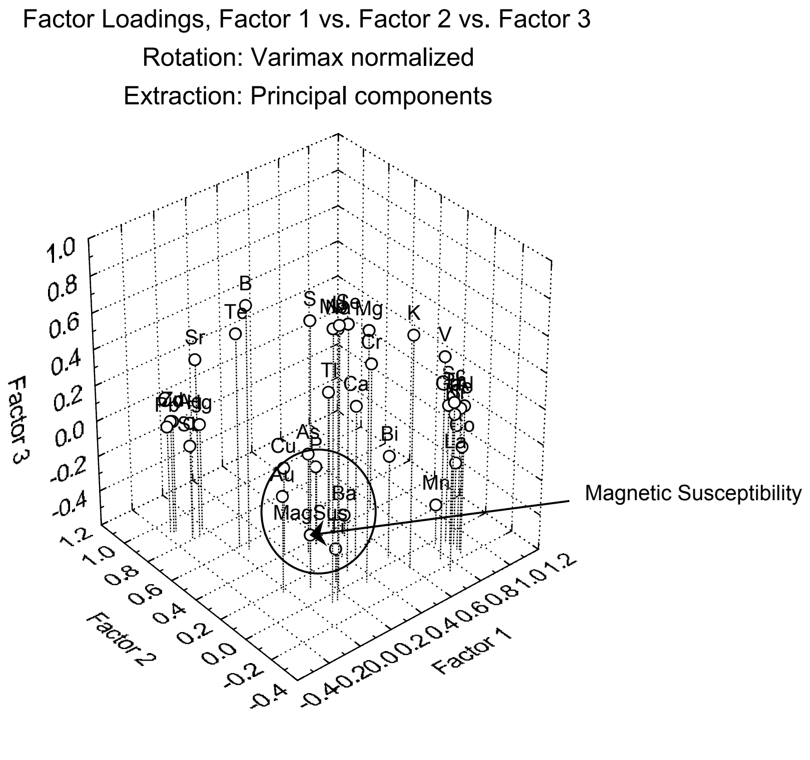


Figure 6: Results of Principal Component Analysis (PCA) for magnetic susceptibility and chemical data. 2D plot for Factors 1-2 (upper diagram) and 3D plot for Factors 1-2-3 (lower diagram)

4. Conclusions

(1) The variation of soil/sediment magnetic susceptibility can be correlated with that of the PTEs concentration, such as As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, where the positive anomaly of susceptibility corresponds to highly contaminated zone.
(2) The result of PCA indicates that magnetic susceptibility value is statistically well correlated with the concentration of four elements, As, Cu, P, and Ti.
(3) Field measurement of magnetic susceptibility can be applicable for field screening of soil/sediment contamination by PTEs.

Acknowledgements

We thank to Ahmed Ghrabi of INRST, Mounier Ferchichi of ANPE, and Ali M'hiri of INAT, for their valuable suggestions. We also thank to Fethia Ayari, Helmi Hamdi, Ibrahim Nasser, and Maher Chebil of INRST for their supports in laboratory and field works. We are indebted to Zheng Zhong, Department of Geoscience, Sogo Kaihatsu Co., Ltd., Tokyo, for assisting the IRM experiments. This collaborative research work is one of the outcomes of the INRST-JICA technical cooperation project in 2000-2002.

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