Full Length Research Paper

Investigation of the relation between heavy metal contamination of soil and its magnetic susceptibility

Mücella Canbay
Kocaeli University, Engineering Faculty, Department of Geophysics, 41300 İzmit-Kocaeli, Türkiye.
E-mail: mucella@kocaeli.edu.tr.

Accepted 1 April, 2010

This study aims to reveal the extent of industrial pollution in the soil in the province of Kocaeli, Turkey. In order to determine the environmental damages caused by İzmit Waste Treatment, Incineration Recycling Corporation (İzaydaşı) which has been operating since 1996, the magnetic sensitivity method has been used to detect the heavy metal concentrations in an area of 1 km². The sampling from the region is carried out periodically to observe the trends in pollution with time and to project predictions for the future. The soil profiles of 30 cm deep samples taken from 13 sampling stations at different coordinates that were suspected to be contaminated with heavy metals are investigated by Magnetic Susceptibility (MS) measurements both on site and in the laboratory. The value of magnetic susceptibility is observed to vary between $12 \times 10^{-5}$ and $84 \times 10^{-5}$ SI in the upper layers of the soil samples in on-site measurements. On the other hand, the mass-specific magnetic susceptibility of the samples changes between $2.10^{-5}$ and $202.10^{-5}$ SI in the laboratory measurements. The geochemical analysis is carried out and the heavy metal content consisting of Pb, Cu, Zn, Co, Cd and Ni is determined using the atomic absorption spectrometry method. Additionally, the correlation coefficient is determined from the comparison of magnetic susceptibility with the heavy metal concentrations.

Key words: Magnetic susceptibility, soil contamination, geochemical analysis.

INTRODUCTION

Magnetic properties of different types of soil display different aspects of soil mineralogy. The minerals that are present in soil are either natural (through lithogenesis, pedogenesis) or of anthropogenic origin (industrial residues). The magnetic mineral content of the soil can be expressed in very broad terms by its magnetic susceptibility (Thompson and Oldfield, 1986). Magnetic susceptibility is a measure of iron-bearing components in a material and it can be used to identify the type of the material on which the test is conducted as well as the amount of the iron-bearing minerals that the material contains. The determination of magnetic susceptibility can be a useful, sensitive and fast method which provides an important parameter used in mineralogy and granulometry. In recent years, this method is widely adopted for its use in agriculture. Moreover, the techniques that employ the magnetic properties of soil have been widely applied by the environmental scientists and have been remarkably successful determinants in pollution research. Many anthropogenic emissions contain fine particles of highly magnetic nature that cause heavy metal contamination in the soil of industrially active regions.

Many studies are available in literature where the heavy metal contamination and industrial activities causing soil, air or water pollution were investigated (Le Borgne 1955, 1960; Vadiunina et al., 1972; Tite et al., 1975; Mullins et al., 1973, 1977). In addition, magnetic susceptibility was shown to be a highly useful indicator of industrial pollution, gas emission into air due to traffic and other atmospheric pollutants (Thompson et al., 1986; Hay et al., 1997; Strzyszcz et al., 1998; Durza, 1999; Hoffmann et al., 1999; Kapicka et al., 1997, 1999, 2003; Lecointe et al., 1999, 2001; Knab et al., 2001; Hanesch et al., 2002, 2003, 2005; Lu et al., 2007). Several studies show that the reconstruction of a soil and sediment magnetic susceptibility map of the landscape proves useful in estimating the extent of anthropogenic pollution (Schibler et al., 2002; Hanesch and Scholger 2002; Hanesch et al., 2003). In environmental magnetism studies, the relationship between the heavy metal content, magnetic, lithological and pedological properties
of soil were investigated comprehensively by magnetic measurements to provide a measure of heavy metal contamination. (Hanesch et al., 2001; Jordanova et al., 2004; Schmidt et al., 2005). The direct correlation between the magnetic susceptibility of contaminated soils and the presence of hydrocarbons as well as certain heavy metals such as Pb and Zn has been previously confirmed (Morris et al., 1995).

Arhan (1997) reported that the constructions and industrial operations in the region cause soil pollution, resulting in the contamination of surface and underground water reserves. Yılmaz (1999) determined the Cd, Cu, Fe, Mn, Ni, Pb and Zn concentrations from 20 soil samples from heavily industrialized regions around Kocaeli and Sakarya and 10 soil samples outside of this region. The results of the analyses showed that the concentration levels in the industrial area were higher than the average values of the quantity over the earth (surface). Okay et al. (1996, 1998 and 2001) concluded from their studies that Izmit Bay was the most polluted region in Turkey, during the past 25 years and they had also carried out a study to show the damages of Tüpraş Refinery fire in 17 August 1999 on sea water, sea sediments and the ecosystem in general. Tolun et al. (2001) conducted a study concerning the effects of growing population and industry on heavy metal concentrations of sea sediments and concluded that the limiting values were exceeded specifically for Cd, Hg and As. Yaşar et al. (2001) investigated the extent of sea pollution in Izmit Bay by making geochemical analysis of surface sediments and the results of the analyses of 41 elements determined in 24 samples showed a significant increase in the total organic carbon and sulfur contents and heavy metal concentrations. Yılmaz et al. (2003) and Özkul (2003) conducted geochemical analysis of soil samples collected from rural, urban and industrial regions of the same area and determined the heavy metal concentration. Canbay et al. (2006 and 2008), Canbay (2006, 2008 and 2009) reported the results of the pollution analyses and the magnetic susceptibility studies carried out in the region.

The aim of this paper is to determine the relationship between the magnetic susceptibility and heavy metal contamination in the Kocaeli area. In this study, the traditional geochemical methods were complemented by the magnetic susceptibility measurements resulting in a more comprehensive study of the extent of soil contamination in the region. However, the relationship between the magnetic susceptibility and heavy metals content in the particular region remains inclusive due to the lack of more systematic information.

**MATERIALS AND METHODS**

**Geological and geophysical properties of the study area**

The ground survey of İzmit Regular Domestic and Industrial Solid Waste Storage Area was carried out by the Underground Research Unit of Kocaeli University. In order to investigate the underground structure of the Dangerous Waste Material Storage Area, the seismic and electrical (resistivity) studies were carried out. Additionally, soil samples from 2 and 6 m depths were taken from two different locations in the area using underground mechanical drilling and the samples were analyzed in the Soil Mechanics Laboratory of the Geotechnical Science Discipline in Sakarya University. In the locations of interest, six seismic refraction profiles and two resistivity profiles were recorded. In the seismic study, the data was recorded such that the geophones were kept within 3 m intervals and they were investigated following the necessary adjustments. 150 m spacing was used in the resistivity study. The study designated a soil layer of 80 cm thickness, containing limestone particles, around the dangerous waste material storage area. Below this layer, a layer of clay stone possessing a seismic speed property of 600 - 750 m/sec and a resistivity of 130 ohm/m was identified. The thickness of this layer was approximately found as 4 m. The permeability coefficient of the samples taken from this layer were determined to be 7.03 × 10⁻⁹ cm/sec. Below this layer, up to a depth of 100 m, the soil was found to be strong and salty with the following properties: the seismic speed of 2000 m/sec and a resistivity of 160 ohm/m.

The permeability coefficient in the upper levels (at 6 m depth) of this layer was determined to be 7.03 × 10⁻⁶ cm/sec and this coefficient was expected to decrease in the deeper levels due to the increase in pressure and the compactness which was also confirmed by the seismic reflection studies that have been carried out on that area. The permeability of the compressed clay stones was determined as 7.28 × 10⁻¹⁰ m/sec in the Geotechnical Laboratory in the Istanbul Technical University (www.izaydas.com). The determined permeability coefficient is more than sufficient to meet the permeability criteria (K = 1 × 10⁻⁹ m/sec) required by the regulation regarding the dangerous waste storage areas in Article 30 of the Official Gazette dated August 27th 1995, no 22387.

**Sampling**

In order to determine the environmental effects of the İzmit Wastes Treatment, Incineration and Recycling Inc. Co, known as Izaydaş on the area, 13 radial samples were taken from the surrounding area at 1 km intervals, placing the facility at the center, as far as practicable depending on the topography and the physical conditions of the area (Figure 1). Some sampling stations (Mc 10, 11 and 12) were selected close to the industrial locations (around the neighborhood of Hyundai Car Factory, Cement-Sand processing facility of Alıkahya Municipality and Yıldız Chipboard Factory). The geographical locations of the sampling stations were re-identified via GPS at each sampling. The samples were taken vertically at 5 - 10 - 15 cm deep down in the soil layer in the 13 stations adding up to a total of 39 samples at a time. Magnetic susceptibility instrument, registered trademark of Bartington, was used in the application of method. Following the measurement of magnetic susceptibility in laboratory, the heavy metal (Pb, Cu, Zn, Co, Cd and Ni) contents and concentrations of the samples were determined using 6001 model Atomic Absorption Spectrometer of Shimadzu. The MS distributions were mapped using the Surfer 8.0 software. The magnetic susceptibility measurements were carried out both in the field and in the laboratory and the mass-specific magnetic susceptibility values measured in laboratory and the determined heavy metal contents and concentrations are collected in Table 1. Table 2 provides information on the average heavy metal concentrations in the earth's crust, world average values for soil and the Turkish regulations for soil. Linear correlations have been made to establish the relationship between the magnetic susceptibility and the heavy metal concentrations in the topsoil. For this purpose, Microsoft Excel 2007 SP3 software was used (Figures 2, 3 and 4).
Susceptibility measurements

The on-site surface volume magnetic susceptibility measurements were performed using SM-20 and MS-2 Bartington loop sensors with a diameter of 185 mm at the stations. The soil cores were collected at 13 stations at 1 cm intervals, from a penetration depth of 30 cm (with a Humax SH 300 sampler) with the help of plastic tubes and then mixed to form a composite sample for further chemical analysis. To avoid errors in measurement, each data point was recorded three to four times to ensure the reproducibility of the results. The volume susceptibility was measured and mass-specific susceptibility was computed.

Soil chemical analysis

The chemical analyses of the dried and sieved soil samples were performed by the Popular and Fast Growing Forest Trees Research Institute of the Ministry of Environment and Forestry in Turkey. The heavy metal content of the samples was determined using an Atomic Absorption Spectrophotometer (Shimadzu model AA-6601F Shimatsu Ltd., Australia).

Sample preparation for the analysis of heavy metal content

1.0 ± 0.09 g soil samples were weighed and placed in platinum or porcelain crucibles. In the ash furnace, the temperature was gradually increased to 900°C. The samples were then left to cool in the furnace and then taken into 100 ml beakers, in which 10 ml HNO₃ and 30 ml HCl (both acids should be concentrated, 'king water') were added. The mixture was dried by evaporating the liquid mixture in a fume cupboard and then 5 ml of concentrated HCl was added to the mixture after which it was dried by evaporating the mixture. The remaining mixture was dissolved in a small amount of HCl just enough to dissolve the samples. The volume was finally brought up to 250 ml with HCl solution (5%).

RESULTS AND DISCUSSION

Sampling station sites and the heavy metal concentrations

The sampling stations were so selected that they provide a representative subset of the diversity in various rural and urban activities in the area of study. Among the sampling stations in the study area, Mc8 and Mc13 are located in the rural parts, Mc1 and Mc2 allow sample collection from sparsely settled areas, Mc9, Mc10, Mc11 and Mc12 represent the locations with densely populated settlement areas and Mc4, Mc5, Mc6 and Mc7 represent the locations in close proximity to İzaydaş. In addition to
Table 1. Average Heavy metal concentrations for Pb, Cu, Zn, Co, Cd, Ni and the on-site and in the magnetic susceptibility (MS) measurements for each sampling station

<table>
<thead>
<tr>
<th>Sampling stations</th>
<th>Average heavy metal concentrations</th>
<th>topsoil MS field measurements $\times 10^5$ (SI)</th>
<th>mass-specific MS laboratory measurements $\times 10^5$ (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mc 1</td>
<td>133.20 58.70 41.60 5.60 0.06 3.50 16.5</td>
<td>125.4</td>
<td></td>
</tr>
<tr>
<td>Mc 2</td>
<td>31.60 307.10 70.00 28.10 0.05 15.20 13.9</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>Mc 3</td>
<td>35.10 54.70 83.40 16.80 0.06 3.20 16.8</td>
<td>85.9</td>
<td></td>
</tr>
<tr>
<td>Mc 4</td>
<td>28.60 66.90 80.30 16.00 0.05 4.10 84.8</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>Mc 5</td>
<td>37.50 81.70 78.70 25.20 0.08 6.60 67.9</td>
<td>90.7</td>
<td></td>
</tr>
<tr>
<td>Mc 6</td>
<td>50.40 164.60 77.00 39.20 0.08 17.80 54.9</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>Mc 7</td>
<td>41.60 64.40 43.70 16.10 0.05 4.00 37.4</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td>Mc 8</td>
<td>72.20 76.80 75.00 25.00 0.07 6.90 15.7</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>Mc 9</td>
<td>66.30 47.30 55.50 15.90 0.07 3.70 12.3</td>
<td>80.6</td>
<td></td>
</tr>
<tr>
<td>Mc 10</td>
<td>99.90 36.60 25.40 24.20 0.06 4.90 17.8</td>
<td>202.9</td>
<td></td>
</tr>
<tr>
<td>Mc 11</td>
<td>87.50 38.30 41.50 26.00 0.05 4.50 15.4</td>
<td>41.7</td>
<td></td>
</tr>
<tr>
<td>Mc 12</td>
<td>105.20 47.80 69.50 38.50 0.07 3.60 15.8</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>Mc 13</td>
<td>157.70 35.50 23.10 36.20 0.08 3.60 14.2</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Reference heavy metal concentrations acquired from the literature (mg/kg).

<table>
<thead>
<tr>
<th>Reference value for heavy metal concentrations</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average for the Earth crust</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>68</td>
<td>99</td>
<td>13</td>
<td>76</td>
</tr>
<tr>
<td>Average for the Earth soil</td>
<td>0.06</td>
<td>8</td>
<td>100</td>
<td>30</td>
<td>40</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Average for the Turkish soil</td>
<td>1.00</td>
<td>20</td>
<td>100</td>
<td>50</td>
<td>30</td>
<td>50</td>
<td>150</td>
</tr>
</tbody>
</table>

being located in densely populated urban areas, Mc10, Mc11 and Mc12 stations were also selected due to their immediacy to some industrial activities including Hyundai Car Factory, Cement-Sand processing facility of Alikahya Municipality and Yildiz Chipboard Factory (Figure 1). One must be careful about the choice of samples as accuracy of the measured values depends on the samples taken for analyses. For the present study, only 15 samples out of 39 taken from 13 stations at three different depths were chosen for magnetic and geochemical analysis and the correlation analysis has been done on the results obtained.

The highest heavy metal concentrations analyzed from the samples taken from various locations are Pb, Cu and occasionally Zn. This observation was particularly noticeable in the first 15 cm of depth in the soil. The heavy metal causing the largest soil contamination, taken from the sampling station closest to Izaydaş (eg. Mc6) is Cu (concentration = 164.6 mg/kg) which is also the case for Mc8, where the Cu concentration with 76.8 mg/kg. The other heavy metals sampled from the same station were also identified to contain higher amounts than the acceptable limits. Rural areas, have been found to have high Pb content in the soil, the highest recorded amongst all 13 stations (157.7 mg/kg). The soil of the sparsely settled areas (Mc1 and Mc2), far away from Izaydaş, was also noted to have high Pb, Cu and Zn content.

Correlation between the magnetic susceptibility and heavy metal concentrations in the area

The magnetic susceptibility of the soil at the sampling stations, where the samples for the determination of the heavy metal contents were collected, was measured both on-site and on the samples that have been brought for laboratory measurements. Magnetic susceptibility values were observed to lie between $12.30 \times 10^5$ SI and $84.80 \times 10^5$ SI for the top-soil and between $202.90 \times 10^5$ and $2.30 \times 10^5$ SI for the mass specific magnetic measurements. The on-site measurements were detected to be considerably different from the laboratory measurements. Repeating the measurements and taking replicate samples could not make the discrepancies vanish although it helped to exclude the very extreme measurements taken from the same station although the higher values were always measured to be high as samples...
Figure 2. Linear correlation between the magnetic susceptibility values measured on-site and the magnetic susceptibility measured in the laboratory.

Figure 3. Scatter plots of mass-specific susceptibility versus concentration of heavy metal contents.

from deeper parts of the soil were taken. The correlation between the magnetic susceptibility values measured on site and in the laboratory still rendered low with a low correlation coefficient (Figures 2, 3 and 4). Moreover, as was shown on the same figures by the error bars representing the average of the absolute deviations of the data points. The points plotted in the graph are seen as too scattered. Although this approach uses a variety of situation has not changed. All three types of soil frequently encountered in the area, especially the limestone composing the upper layer (top 80 cm) under investigation were known to have very low susceptibility values of their own. Given this fact, especially Pb and Cu were observed to exceed their corresponding values generally observed in the top soil. Therefore, the susceptibility in the top soil might depend more on the
soil-forming factors than on the parent materials. Some metals detected (Pb, Cu and Zn) in the fly ashes and the soil samples suggest that the fly ashes could be the main source of heavy metal contamination and also of magnetic susceptibility in topsoil. The correlation between the magnetic susceptibility and the heavy metal concentrations has also been carried out. The correlation between the geochemically determined average heavy metal concentrations taken from the sampling stations and the magnetic susceptibility values is poor, at some sampling stations, while it is quite high for some other stations, specifically for Pb (Mc1, Mc9 and Mc10). At some stations, contrary to low correlation expectations (Mc1, Mc2, Mc5Mc10 and Mc13), a good correlation between susceptibility and heavy metal content was observed. Poor correlations between magnetic susceptibility and heavy metal concentrations to some extent have been reported in literature previously (Charlesworth and Lees, 1997, 2001; Chaparro et al., 2004; Schmidt et al., 2005). As a general rule, it can be deduced that when the magnetic susceptibility and the heavy metal concentrations are both high, the source is most likely to be anthropogenic. Conversely, when magnetic susceptibilities are high but heavy metal concentrations are low, the source is most likely a natural one, indicating the presence of geogenical anomalies. The transportation of heavy metal plume away from the source in several ways and the atmospheric, geological, anthropogenic effects might have resulted in the poor correlation in this study. The linear correlation method might have been insufficient to account for several various effects simultaneously, leading to poorer correlations between the two observables.

**Conclusion**

The enrichment of soil with Pb, Cu, Zn, Ni and Co as well as other metals may be caused by the emissions from the vehicles and the waste products of various industries (heavy machine manufacture, petrochemical plants, coal-burning power plants, metallurgical power plants) as well as the long distance transportation from remote sources.
of emissions. Soil in rural areas are generally found to contain relatively lower levels of average metal concentrations and the anthropogenic impact of the metals is generally not as significant as in the soils of industrial and urban areas. The anthropogenic emission sources of heavy metals in the study area, especially for the soil of urban and industrial locations, are the atmospheric emissions, domestic and industrial waste disposal. This is caused not only by the various industries located there, but also by the heavy traffic and the high population density in the area. The correlation between the susceptibility of heavy metals in the sample and the standard values shows that the dominant sources of pollution in İzmit are industrial activities, population density, heavy traffic and wind direction (E-SE) of the region.

ACKNOWLEDGEMENTS

The author is grateful to the researchers in the Poplar and Fast Growing Forest Trees Research Institute of Ministry of Environment and Forestry for the chemical content analyses and to A. Aydin from the Department of Geophysics in the Faculty of Engineering, in Pamukkale University, Turkey for valuable discussions on the study.

REFERENCES

Canbay M (2009). Heavy Metal Contamination of Soils with magnetic susceptibility method in Kocaeli (Turkey) and Comparison of in Situ Field Measurements of Soil Magnetic Susceptibility with Laboratory Data (Poster Presentation). International Earthquake Symposium Kocaeli,Turkey.
Canbay M, Gider D, Alpaslan N (2008). Comparison of in Situ Field Measurements of Soil Magnetic Susceptibility with Laboratory Data, the 18th International Geophysical Congress and Exhibition of Turkey.
Okay OS, Tolun L, Telli-Karakoç F, Tüfekçi V, Tüfekçi H, Morkoç E

Özkul C (2003). A preliminary investigation into industrial impacts on heavy metal concentrations in the topsoil around Izmit (Kocaeli) (in Turkish), master of science, Kocaeli.


