Observing Urban Soil Pollution Using Magnetic Susceptibility

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ABSTRACT: Pollution of urban soils dramatically reduces life and environmental quality. The most common pollutants are heavy metals and organic contaminants like polycyclic aromatic hydrocarbons and polychlorinated biphenyl. Main source of these pollutants is fossil fuels which are pervasive in urban and/or industrialized areas. Identifying type and intensity of the pollution is essential to prepare an effective hazard mitigation plan. The study has been focused on the determining the distribution of pollutants in Denizli city center. The magnetic susceptibility measurements and chemical analysis are performed at several locations. The low frequency magnetic values are differing significantly over the study area. They are concentrated at the northern and southeastern parts of the study area. The spatial distribution of the PLI proved that the industrial area showed very high anomalous. They mainly come from magnetic particle sources in the area. Scattering patterns of Fe, Pb, Cu, Cr and Ni are compatible with the susceptibility maps and the topography. The highest concentration of Ni, Cr, Pb and Cu oxides elements are observed near the major roads and close to the industrial enterprises in the northern part of the city. High correlations are documented between low frequency magnetic susceptibility and Fe, Si, Pb and Cr. The method can effectively be employed for monitoring the urban soil pollution.

Key words: Heavy metals, Magnetic susceptibility, Pollution, Denizli

INTRODUCTION

Pollution of urban soils dramatically reduces life and environmental quality. The most common pollutants are heavy metals and organic contaminants like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCB) (Wcislo, 1998; Hoffmann et al., 1999). Main source of these pollutants is fossil fuels which are pervasive in urban and/or industrialized areas. Identifying type and intensity of the pollution is essential to prepare an effective hazard mitigation plan.

Generally chemical methods, need a bulky effort, are engaged for monitoring the soil contamination. Many anthropogenic emissions are of fine particles and they are highly magnetic (Bityukova et al., 1999). The studies indicate a correlation between magnetic susceptibility and atmospheric contaminants and they can provide information at low cost and in shorter time (Morris et al., 1995; Hanesch and Scholger, 2002; El-Hasan and Lataifeh, 2013; Jordanova et al., 2013; Ayoubi et al., 2014; Wang, 2014). Magnetic susceptibility shows the amount of the iron-bearing minerals in the material and identifies the type of material and it can be used as an indicator of pollution level. The magnetic properties depend on the grain

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
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<tbody>
<tr>
<td>χ</td>
<td>Mass Magnetic Susceptibility</td>
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<tr>
<td>χlf</td>
<td>Low Frequency Magnetic Susceptibility</td>
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<tr>
<td>χhf</td>
<td>High Frequency Magnetic Susceptibility</td>
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<td>PLI</td>
<td>Tomlinson Pollution Load Index</td>
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<tr>
<td>χfd%</td>
<td>Frequency Dependent Magnetic Susceptibility</td>
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<tr>
<td>CFHMk</td>
<td>Multiplication of the Concentration Factors</td>
</tr>
<tr>
<td>CHM</td>
<td>Concentration Ratio of Each Heavy Metal</td>
</tr>
<tr>
<td>amv</td>
<td>The Mean Values</td>
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size, concentration and type of the magnetic minerals in the soil. Ferromagnetic minerals like magnetite have the strongest magnetic characteristics. Paramagnetic and diamagnetic minerals have low positive and low negative susceptibilities, respectively. Clay and sandstone typically display higher values while carbonate rocks are characterized by low susceptibility values (Bityukova et al., 1999). Many studies are available about the magnetic susceptibility measurements for evaluating the degree of heavy metal pollution of soils near roads and industrial areas (Ward et al., 1975; Wheeler and Rolfe, 1979; Sihole et al., 1993; Flanders, 1994; Scholger, 1997; Canbay et al., 2010; Hanesch and Scholger, 2005; Hanesch et al., 2003). It is highly effective for detecting industrial, traffic and other atmospheric pollutants (Francek, 1992; Kapicka et al., 1999; Hoffmann et al., 1999; Strzyszcz and Magiera, 1998; Shu et al., 2000; Petrovsky et al., 2000; Lu et al., 2007; Hanesch and Scholger, 2005). Magnetic susceptibility is employed not only for determining the presence of hydrocarbons and certain heavy metals such as Pb, Zn, Cr, etc. (Hanesch and Scholger, 2002; Moreno et al., 2003) but also for estimating anthropogenic pollution of the soils and sediments in urban areas (Hanesch and Scholger, 2002; Jordanova et al., 2003). Low frequency magnetic susceptibility is more effective for monitoring the pollution levels. The systematic monitoring is essential in urban areas because of the fluctuations of the anthropogenic factors.

This study is focuses on determining the pollution levels in the soils originated from exhaust gases and chimney fumes in Denizli municipal area (Turkey) using magnetic susceptibility technique. The magnetic susceptibility and heavy metal contamination of the collected samples are correlated. We established links between enhanced concentrations of anthropogenic magnetic particles and Pb, Cu, Ni and Cr (PLI The Tomlinson Pollution Load Index). The collected soil samples were also analyzed by atomic absorption spectrometer. This study is a sample of a fast and simple method for analyzing polluted areas based on the magnetic susceptibility measurements. It is suitable for a systematic pollution monitoring of extensive areas at low costs and in less time.

MATERIALS & METHODS

Denizli, called capital of textile and travertine, is a very crowded inner city in Aegean Region, Turkey. Climatic conditions in Denizli are usually hot, whereas higher regions have more severe weather conditions. Summers are hot with scarce rainfalls while winters are rainy and occasionally cold. Average annual temperature is 18°C. It was one of the most polluted cities and it was originated mainly from anthropogenic activity. The city center has a population of 555,000 due to 2012 census. In last two decades, there is a dramatic economic development in the city, as a result of economical developments, their traffic increased fifteen times from 1995 to now. To determine the distribution of the heavy metal concentration, the exhaust gases and the chimney fumes are potential sources in the city. The magnetic susceptibility measurements were carried on at 251 locations (Fig. 1). The 241 samples were collected for the chemical analysis in the laboratory. The susceptibility maps based on the topsoil measurements were compiled with a randomly ranged distance density by using Surfer software.

The studied area involves different types of soils. The study area is covered mainly by carbonated sandy soils. The urban soils are originated from carbonate rocks located at the south of the city. The samples were collected from the depth between 0-20 cm an area of 17 km². Each sample is roughly 0.5 kg from about 10x10 cm area. The sample locations were close to the buildings and roads in the open field.

To investigate magnetic features of the road surface samples, low frequency magnetic susceptibility (χlf) and high frequency magnetic susceptibility (χhf) measurements were carried out in the laboratory using dual-frequency MS meter MS2, Bartington Instruments Ltd. Frequency dependent magnetic susceptibility was defined as:

$$\chi_{fd}(\%) = \left[\frac{\chi_{hf} - \chi_{lf}}{\chi_{lf}}\right] \times 100$$ (1)

The low and high frequency magnetic susceptibility values were measured at 0.47 and 4.7 kHz, respectively. Collected samples of each data points were measured 3-4 times to check reproducibility and to avoid measurement errors. The errors of mass magnetic susceptibility measurement were smaller than 2%, using repeat-measurements. PLI is chemical product concentration and can be used as an index. The PLI normalizes the data by employing the proportions acquired by dividing each concentration by a baseline concentration for each chemical, that is, by the lowest concentration of each chemical (Angulo, 1996). A linear correlation between mass magnetic susceptibility and PLI was originally presented by Angulo (1996). The PLI was used to show how much a sample exceeds the contents of heavy metal background of the natural environments (Chan et al., 2001). The PLI, a result of the contribution of several heavy metals, is defined as the root of the multiplication of the concentration factors (CF_HMk);

$$PLI = \frac{1}{\sqrt{n}} \prod_{k=1}^{n} CF_{HMk}$$ (2)
RESULTS & DISCUSSION

The low and high frequency magnetic susceptibility data are illustrated in Figs 2 and 3 respectively. The low frequency magnetic values differ significantly over the study area. It appears that they are concentrated at the northern and southeastern parts of the study area (Fig. 2). The first involves many industrial facilities (like mill, machine-building, metal-manufacturing industry and small vehicle repairing shops etc.) and while the latter has only few. In the anomalous zones, the mass magnetic susceptibility increases up to 850x10^{-8} m^3 kg^{-1}. The northern part has also the lowest altitude (Fig. 6a). The level of low frequency magnetic susceptibility lessens in western and central part of the study area (10-100x10^{-8} m^3 kg^{-1}) where has less or none activities cause contamination. Two local anomalies of low frequency magnetic susceptibility are observed at the southeast part of the urban Denizli (450-800 x10^{-8} m^3 kg^{-1}). The distribution of the high frequency magnetic susceptibility data are compatible with the low frequency records (Fig. 3) and have the same cause-effect relation.

The frequency-dependent susceptibility has a relation with paramagnetic component and it was examined in the study (Fig. 4). The frequency-dependent susceptibility values of the samples range from 3% to 13% with a mean value of 8% (Dearing et al., 1996). It is fairly low and indicates that the magnetic properties of the samples are predominantly contributed by the coarse multidomain grains, rather than by the super paramagnetic particles (Kapicka, 1999). Dearing’s frequency-dependent susceptibility model was predicted two types of magnetic clusters in the samples. The frequency-dependent susceptibility is dominated by coarse multi domain grains if it is lower than 2% (Jordanova, 2003). It is called intermediate group when the data are placed between 2% and 6%. These values correspond to a mixture of multi domain and stable single domain. Other samples placed at the western part of the area were evaluated to be dominated by the frequency-dependent grains ($\chi_{fd}$%>6%). Hence the ferromagnetic grains are present in high concentration.

The spatial distribution of the PLI was measured and the data are given in Fig. 5 and not surprisingly the industrial area show very high values. These values demonstrate that there are many magnetic particle
sources of this area. In the light of the PLI data and the composition of the tested samples it can be concluded that were mainly controlled by technogenic factors.

For comparing the results, the distribution of Fe, Pb, Cu, Cr and Ni values for the surface samples examined and they are illustrated the Fig. 6. It is because the contamination is closely related with altitude it is also illustrated. The topography of the area decreases toward the northeast (Fig. 6a). Spatial distribution of Fe, Pb, Cu, Cr and Ni (Fig. 6b to 6f) is congruent with the low and high frequency magnetic susceptibility scattering. The heavy metal contour maps are also compatible with the susceptibility maps and the topography. The areas with lower altitude show higher pollutants. The heavy metal pollution in the soils of north of the area is six times higher than the unpolluted parts. Especially Cu, Pb and Zn is strongly connected with industrial and exhaust gases contamination of soils. The highest concentration of Ni, Cr, Pb and Cu
oxides elements were seen near the major roads and close to the industrial enterprises in the northern part of the city. Pb concentrations are varying from 4 mg/kg up to 26 mg/kg, which are very high like others. The results of the Na\textsubscript{2}O, MgO, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Cr\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, NiO, CuO and PbO concentrations of the tested samples are given in Table 1. Al\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, NiO and PbO values are fluctuating in a very wide range. Low frequency magnetic susceptibility data are also correlated with Fe, Si, Pb and Cr (Fig. 7). Pb has the highest correlation coefficient while Si has the lowest. Fe and Cr correlations are also high with R=0.85. Kim et al. (2010) proposed that there was a weak correlation between the magnetic susceptibility and Cu; it is because of its paramagnetic feature. Si has inverse correlation as expected. It is because of its paramagnetic and diamagnetic characteristics. In other words, it has strong but inverse correlation coefficient due to low magnetic susceptibility.
Fig. 6. Altitude map (a) and distribution of Fe (b), Pb (c), Cu (d), Cr (e) and Ni (f)

Table 1. Chemical analysis results of the tested samples

<table>
<thead>
<tr>
<th></th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>NiO</th>
<th>CuO</th>
<th>PbO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>0.2</td>
<td>2.2</td>
<td>3.9</td>
<td>11.4</td>
<td>432.9</td>
<td>3.4</td>
<td>2.53</td>
<td>28.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Max</td>
<td>0.5</td>
<td>4.8</td>
<td>10.4</td>
<td>26.1</td>
<td>1481.6</td>
<td>6.3</td>
<td>1019.0</td>
<td>53.0</td>
<td>26.3</td>
</tr>
<tr>
<td>Mean</td>
<td>0.34</td>
<td>3.14</td>
<td>6.35</td>
<td>17.15</td>
<td>777.22</td>
<td>4.53</td>
<td>493.11</td>
<td>36.06</td>
<td>15.33</td>
</tr>
</tbody>
</table>
CONCLUSION

The study has been focused on the determining the distribution of pollutants in Denizli city center. The magnetic susceptibility measurements and chemical analysis were performed at several locations. The area involves different types of soils, mainly the carbonated sandy soils. The tested samples were collected from the depth between 0-20 cm and each of them is roughly 0.5 kg from about 10x10 cm area. The sample locations were close to the buildings and roads in the open field. The low frequency magnetic values were differed significantly over the study area. It appeared that they are concentrated at the northern and southeastern parts of the study area. The mass magnetic susceptibility should be around $40-80 \times 10^{-6} \text{m}^3\text{kg}^{-1}$ in ordinary unpolluted such soils. In the anomalous zones, the mass magnetic susceptibility increased up to $850 \times 10^{-6} \text{m}^3\text{kg}^{-1}$. The distribution of the high frequency magnetic susceptibility data were compatible with the low frequency records and had the same cause-effect relation. The spatial distribution of the PLI proved that the industrial area showed very high values. These values demonstrated that there are many magnetic particle sources of this area. In the light of these data and the composition of the tested samples it can be concluded that were mainly controlled by technogenic factors. Spatial distribution of Fe, Pb, Cu, Cr and Ni was congruent with the low and high frequency magnetic susceptibility scattering. The heavy metal distributions were also compatible with the susceptibility maps and the topography. The areas with lower altitude showed higher pollutants. The heavy metal pollution in the soils of north of the area was six times higher than the unpolluted parts. The highest concentration of Ni, Cr, Pb and Cu oxides elements were observed near the major roads and close to the industrial enterprises in the northern part of the city. Pb concentrations were varying from 4 mg/kg up to 26 mg/kg, which are very high like others. Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, NiO and PbO values were fluctuating in a very wide range. Low frequency magnetic susceptibility data were also correlated with Fe, Si, Pb and Cr. Pb had the highest correlation coefficient while Si had the lowest. Si has inverse and lower correlation than the others. The method can effectively be employed for monitoring the urban soil pollution.

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