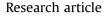
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## Biomagnetic monitoring of heavy metals contamination in deposited atmospheric dust, a case study from Isfahan, Iran





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### ABSTRACT

Tree leaves are considered as one of the best biogenic dust collectors due to their ability to trap and retain particulate matter on their surfaces. In this study, the magnetic susceptibility (MS) and the concentration of selected heavy metals of plane tree (Platanus orientalis L) leaves and deposited atmospheric dust, sampled by an indirect and a direct method, respectively, were determined to investigate the relationships between leaf magnetic parameters and the concentration of heavy metals in deposited atmospheric dust. The objective was to develop a biomagnetic method as an alternative to the common ones used for determining atmospheric heavy metal contaminations. Plane tree leaves were monthly sampled on the 19th of May to November, 2012  $(T_1-T_7)$ , for seven months from 21 different sites in the city of Isfahan, central Iran. Deposited atmospheric dust samples were also collected using flat glass surfaces from the same sites on the same dates, except for  $T_1$ . MS ( $\chi_{If}$ ,  $\chi_{hf}$ ) values in washed (WL) and unwashed leaves (UL) as well as Cu, Fe, Mn, Ni, Pb, and Zn concentrations in UL and deposited atmospheric dust samples were determined. The results showed that the MS content with a biogenic source was low with almost no significant change during the sampling period, while an increasing trend was observed in the MS content of UL samples due to the deposition of heavy metals and magnetic particles on leaf surfaces throughout the plant growth. The latter type of MS content could be reduced through washing off by rain. Most heavy metals examined, as well as the Tomlinson pollution load index (PLI) in UL, showed statistically significant correlations with MS values. The correlation between heavy metals content in atmospheric dust deposited on glass surfaces and leaf MS values was significant for Cu, Fe, Pb, and Zn. Moreover, the similarity observed between the spatial distribution maps of leaf MS and deposited atmospheric dust PLI provided convincing evidence regarding the suitability of the biomagnetic approach as a relatively rapid and inexpensive method for identifying highly polluted urban areas with selected heavy metals, especially those subjected to anthropogenic and other traffic related sources.

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#### 1. Introduction

Atmospheric dust is known as the major factor influencing atmospheric environmental quality (Ren et al., 2004). Heavy metals in atmospheric dust have been reported to be one of the most harmful pollutants in the atmospheric environment. It has also been found that prolonged exposure to non-degradable heavy metals adsorbed onto atmospheric dust can be a serious potential public health threat (Pope, 2000; Saldiva et al., 2002; Shi et al., 2011).

\* Corresponding author. E-mail address: hkhademi@cc.iut.ac.ir (H. Khademi). Although a wide variety of devices are commonly employed for air pollution assessment (Rai, 2013), studies of atmospheric contamination have been frequently hampered by the high cost of instrumental monitoring methods and the difficulties experienced with extensive spatial and temporal sampling (Anicic et al., 2011). For such reasons, air quality is not usually investigated at a high spatial resolution. To tackle these problems, some efforts have been made to use the relatively cheap and user-friendly bio-indicators in order to probe air pollutants at a high spatial resolution (Moreno et al., 2003; Kardel et al., 2010).

Biological monitors are known as organisms providing quantitative information on some aspects of the environment, such as atmospheric pollutant load. Tree leaves, such as conifer needles and evergreen and deciduous tree leaves, can serve as efficient passive pollution collectors. This is because they can provide a large surface area for particle deposition, thereby allowing for a large number of samples to be tested (Sant'Ovaia et al., 2012). Due to their wide distribution in urban areas and their ease of sampling, tree leaves can be utilized to investigate spatial and temporal patterns of various pollutants in atmospheric dust (Urbat et al., 2004; Davila et al., 2006).

The study of various magnetic parameters in recent decades has led to the development of environmental magnetic methods that can be regarded as quick, economical, non-destructive, sensitive, and efficient tools (Evans and Heller, 2003). Such methods have been found to be successful for characterizing and quantifying heavy metal contamination in various environments including atmosphere (Salo et al., 2012).

It has been established that magnetic particles are associated with atmospheric dust (Triantafyllou, 2003). It has been shown that many anthropogenic effects on the environment can be simultaneous with considerable emissions of ferrimagnetic constituents (Yang et al., 2011). The magnetic minerals in the atmosphere are mostly originated from combustion products or taken from vehicle brake systems and asphalt (Gautam et al., 2005). In addition to human induced emissions, natural sources such as rocks and sediments may also contribute to the release of magnetic minerals into the atmosphere (Maher et al., 2008; Rai, 2011). Exhaust gases and dust particles which are released from anthropogenic processes are known to contain ferrimagnetic particles, particularly iron oxides such as maghemite or magnetite, and heavy metals. As they have the same origin, significant correlations between such magnetic parameters as magnetic susceptibility or saturation isothermal remanent magnetic (SIRM) and concentrations of such heavy metals as Pb, Zn, Cu, and Cd have been reported (Gautam et al., 2005; Maher et al., 2008; Bućko et al., 2010; Yang et al., 2011; Zhang et al., 2012). Therefore, it seems plausible to assume that magnetic properties can be employed as a good substitute for routine time-consuming, and mostly very expensive geochemical approaches to identify and trace airborne particulate pollutants and ferromagnetic minerals in the environment (Muxworthy et al., 2001; Lu et al., 2008). Biomagnetism can serve as a great proxy for atmospheric pollution levels based on the analysis of plant samples including tree leaves (Lu et al., 2008; Hansard et al., 2011), needles (Lehndorff et al., 2006), and lichens and mosses (Salo et al., 2012; Chaparro et al., 2013; Salo and Makinen, 2014).

Different factors have been reported to control the amount of dust accumulation on the leaves as well as the magnetic susceptibility in plants. They include tree species (evergreen or deciduous) (Moreno et al., 2003), height and areal coverage of leaves (Gautam et al., 2005), leaf characteristics such as texture, leaf rugosity and specific surface area (Moreno et al., 2003; Kardel et al., 2011), duration of plant exposure to pollution (Moreno et al., 2003), the degree of pollution (Gautam et al., 2005) and atmospheric and meteorological processes including the number and intensity of precipitation events and intensity and direction of wind (Gautam et al., 2005; Kardel et al., 2011).

The results of some early studies have shown that biomagnetic approach is a quantitative technique that can be employed for identifying the concentrations of PM<sub>10</sub> and suspended particulate matter (McIntosh et al., 2007; Mitchell and Maher, 2009; Mitchell et al., 2010; Hansard et al., 2011; Rai and Chutia, 2014). Many studies have been carried out on the relationship between leaf magnetic properties and concentrations of some toxic metals such as lead, zinc and iron in the leaf samples (Urbat et al., 2004; Gautam et al., 2005; Davila et al., 2006; Lu et al., 2008; Maher et al., 2008; Rai and Chutia, 2015). No investigation has yet been performed to evaluate the relationship between leaf magnetic susceptibility and heavy metal concentrations in deposited atmospheric dust

sampled via a direct sampling method. Research work by Rai et al. (2014) appears to be the only investigation which reported the relationship between Fe content in  $PM_{10}$  fraction of atmospheric dust and leaf magnetic signals. These investigators did not examine other fractions of atmospheric deposits and neither did they study other heavy metals other than Fe. This paper seems to be the first report which focuses on the relationship between the geochemistry of directly sampled deposited atmospheric dust and the magnetic characteristics of a bioindicator.

The main objectives of this investigation were: 1) to evaluate the effectiveness of plane tree leaves as collectors of anthropogenic magnetic particulates; 2) to determine temporal variations of magnetic susceptibility and heavy metal contamination in plant leaves as well as their relationships; and 3) to examine the correlation between heavy metal concentrations in deposited atmospheric dust and magnetic susceptibility in plant leaves. The expected result was to develop a biomagnetic method as a qualitative indicator of areas with larger deposition of heavy metals.

#### 2. Materials and methods

#### 2.1. Study area

The City of Isfahan, which is located in the central part of Iran  $(51^{\circ} 39^{''}40' E, 32^{\circ} 38^{''}30' N)$ , was chosen as the study area. This city has an area of 482  $\text{km}^2$  and a population of 1,796,967 making it the third most populated city in Iran. The main sources of air pollution in Isfahan are heavy traffic, handling a total number of 24,324 registered public transports in 2012 (Isfahan Governor's Office, 2013), and many different kinds of industries, making it the second largest industrial zone in Iran. A large steel mill, the biggest steel plant in the country, a petrochemical plant, and an oil refinery, along with many major and minor plants, are all located in and around this city. The desert lands on the eastern and northern stretches of the city, along with their dry climate with hot summer, seem to be the main reasons for dust events occurring during the year. In this study, 21 sites well distributed across the city were chosen for collecting deposited atmospheric dust and plane tree leaves samples (Fig. 1).

#### 2.2. Leaf and deposited atmospheric dust sampling

Leaves were monthly collected from plane trees (Platanus orientalis L., Platanaceae) common in the area from the beginning to the end of the seasonal vegetation cycle (T<sub>1</sub>: 19th May, T<sub>2</sub>: 19th June, T<sub>3</sub>: 19th July, T<sub>4</sub>: 19th Aug., T<sub>5</sub>: 19th Sept., T<sub>6</sub>: 19th Oct., and T<sub>7</sub>: 19th Nov., 2012). Platanus orientalis L. is a deciduous species bearing broad and five-lobed leaves. Young leaves have fine hairs lost as the leaves mature, though some may be retained on the lower leaf surface (McIntosh et al., 2007). Trees of approximately the same age were chosen to reduce the age variation among the tree samples. The leaves were cut off from about 2 to 2.5 m height by means of stainless steel scissors. At each sampling site, 15-20 well developed leaves were randomly taken from different sides of the tree and immediately put in a paper envelope so that they would be carried to the laboratory. It must be mentioned here that a moderate rainfall event occurred after T<sub>2</sub> and a heavy one after T<sub>6</sub> sampling events, showing the possibility of washing leaf surfaces.

Deposited atmospheric dust samples were collected at the end of 30-day periods over 6 months. They were collected at the leaf sampling times, except for May19th, 2012 (T<sub>1</sub>), using a dry flat surface with an area of 1 m<sup>2</sup> (Menendez et al., 2007; Hojati et al., 2012). Each collection tray consisted of a glass surface (100 × 100 cm) covered with a PVC net (2 mm mesh openings) on the top of the glass tray, thereby forming a rough area capable of

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