Chemical and magnetic analyses on tree bark as an effective tool for biomonitoring: A case study in Lisbon (Portugal)

Daniele Brignole[1], Giuliana Drava[1*], Vincenzo Minganti[1], Paolo Giordani[1], Roeland Samson[2], Joana Vieira[3], Pedro Pinho[3,4], and Cristina Branquinho[3]

[1]Department of Pharmacy, University of Genova, Viale Cembrano 4, Genova, Italy

[2]Department of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, Antwerpen, Belgium

[3]Centre for Ecology, Evolution and Environmental Changes, Faculdade de Ciências, Universidade de Lisboa, Campo Grande C2, Lisboa, Portugal

[4]Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

[*]Corresponding author: drava@difar.unige.it (*Giuliana Drava*)

ABSTRACT

Tree bark has proven to be a reliable tool for biomonitoring deposition of metals from the atmosphere. The aim of the present study was to test if bark magnetic properties can be used as a proxy of the overall metal loads of a tree bark, meaning that this approach can be used to discriminate different effects of pollution on different types of urban site. In this study, the concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, V and Zn were measured by ICP-OES in bark samples of *Jacaranda mimosifolia*, collected along roads and in urban green spaces in the city of Lisbon (Portugal). Magnetic analyses were also performed on the same bark samples, measuring Isothermal Remanent Magnetization (IRM), Saturation Isothermal Remanent Magnetization

(SIRM) and Magnetic Susceptibility (χ). The results confirmed that magnetic analyses can be used as a proxy of the overall load of trace elements in tree bark, and could be used to distinguish different types of urban sites regarding atmospheric pollution. Together with trace element analyses, magnetic analyses could thus be used as a tool to provide high-resolution data on urban air quality and to follow up the success of mitigation actions aiming at decreasing the pollutant load in urban environments.

KEYWORDS: Air quality; Atmospheric pollutants; *Jacaranda mimosifolia*; Metals; Trace elements.

1. Introduction

Air quality is a crucial factor for human health (Kelly and Fussell, 2015; WHO, 2013); air pollutants (e.g. particulate matter, trace elements, nitrogen oxides, sulphur oxides) have been associated to an increased risk of lung cancer mortality (Chen et al., 2016b; Pope et al., 2002; Raaschou-Nielsen et al., 2016), to the outbreak of cardiovascular and pulmonary diseases (Chen et al., 2016a) and to several other pathologies (Davidson et al., 2005; Jung et al., 2015; Ribeiro et al., 2014). Thus, an effective air quality monitoring process is a key point to be aware of the spatial and temporal patterns of contaminants. This can allow relating the concentrations of pollutants with the possible effects on human health, with the aim of planning and implementing regulatory policies to reduce emissions, as well as tracking the emission decrease (Nowak et al, 2015; WHO, 2017).

In the past decades, many studies on pollutants (Jarup, 2003; Nriagu, 1979; Pacyna and Pacyna, 2001; Schwarze et al., 2006) have been focused on trace elements which may represent a serious health threat even at low concentrations (Tørseth et al., 2012). However, despite the relevance of the European policy for air pollution reduction, only few monitoring stations are currently monitoring metals throughout the continent (EEA, 2016). This lack of monitoring data affects the reliability of high-resolution models of air pollution, which are needed both to define the real population exposed and to plan mitigation strategies. Additionally, urban areas are not homogeneous and may considerably differ from sites where air quality monitoring stations are located. Factors such as microclimatic conditions (e.g. local winds), the presence or absence of green spaces and particular situations such as a stop light in uphill roads might interfere with the air quality in small distances (Llop et al., 2012). Therefore, in order to obtain information with high spatial resolution, other tools to monitor atmospheric pollutants are needed. Biomonitors of air pollution (e.g. lichens, tree bark and leaves) are reliable tools for assessing the effects of pollution on the biotic component of ecosystems, providing complementary information with respect to traditional chemical-physical monitoring (Nimis et al., 2002) and have the potential to deliver data with high spatial resolution.

Among indicators, tree bark has been extensively used to assess air pollution (Cucu-Man and Steinnes, 2013; Drava et al., 2016; El-Hasan et al., 2002; Minganti et al., 2016) because of its ability to accumulate atmospheric trace elements during many years, both through wet and dry deposition. Although the mechanisms of metal accumulation in the bark are not yet fully understood, the uptake of pollutants from the roots can be considered negligible (Catinon et al., 2008, 2011). Consequently, tree bark reflects the concentration of pollutants in the atmosphere, even though it does not allow relating the accumulation of trace elements to a defined period of time (Drava et al., 2017).

Depending on physical and chemical processes acting in the atmosphere, metals emitted from pollution sources may be accumulated under different forms that may influence the magnetic fingerprint of living organisms. This characteristic has led to an increasing application of different magnetic techniques, i.e. Isothermal Remanent Magnetization (IRM), Saturation Isothermal Remanent Magnetization (SIRM), Magnetic Susceptibility (χ), for biomonitoring purposes. Magnetic measurements are usually applied to leaves (Hofman et al., 2014; Kardel et al., 2012; Maher et al., 2008; Matzka and Maher, 1999; Szonyi et al., 2008), dust (Qiao et al., 2013; Sipos et al., 2014; Zhang et al., 2012), soil samples (Lourenco et al., 2012; Lu and Bai, 2006) or mosses and lichens (Salo et al., 2012; Salo and Makinen, 2014; Vukovic et al., 2015), but there are very few data in the literature about the application of these techniques to tree bark samples (Kletetschka et al., 2003) and they do not relate the data with measured metal concentrations.

As a novel approach, in this study we compared the element concentrations in tree bark with the results obtained by magnetic techniques. The aims of this study were: i) to test whether magnetic intensity in tree bark is a good proxy of the overall metal loads of the bark; ii) to test whether the two methods can discriminate among the trees located in different types of urban site (green spaces, small roads and large roads).

For achieving these goals the concentrations of selected trace elements (As, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, V and Zn) were measured in bark samples of *Jacaranda mimosifolia* collected from trees in different areas of the city of Lisbon (Portugal). The choice of the trace elements was made according to: i) the possible impact on human health; ii) the sensitivity of the analytical method and iii) the possibility to have good reproducibility and accuracy. On the same samples SIRM, IRM and χ were performed to characterize their magnetic properties. The choice of the sampling sites took into consideration the absence of industrial activities directly influencing the central area of the city.

2. Materials and methods

2.1. Sampling

Sampling was carried out in Lisbon, the capital city of Portugal. Lisbon metropolitan area has a population of 2.8 million people and is located in the estuary of river Tagus. It has a typical Subtropical-Mediterranean climate according to Köppen climate classification, with hot dry season and a mild wet season. The annual average temperature is 17.4 °C and the total annual precipitation 705.8 mm (averages from 1981 to 2010, IPMA).

Bark samples were collected in January and February 2016 from trees of *Jacaranda mimosifolia* in 34 sites. The tree species was chosen according to: i) the widespread presence in the urban area; ii) the roughness of the trunk, assuming that more rugose trunk can trap more dust/pollutants than smooth bark surface.

After a preliminary investigation of the distribution of *Jacaranda* trees in the survey area, a number of sites were selected where the species occurred and, among these, 34 sites were chosen on the basis of a stratified random sampling. Lacking information from an adequate number of monitoring stations or from other possible descriptors of atmospheric pollution, a proxy variable for traffic intensity was used. Therefore, sites were categorized according to their land-use (Llop et al., 2017) into: i) large roads (two or more lanes); ii) small roads (one lane); and iii) green spaces (presence of green areas/urban parks even if very small). For each site, the closest 3 trees were selected (except for two sites, where only two trees were available).

A small portion of tree bark (approximately 30 cm^2) was removed at a height between 1.5 and 2.0 meters all around the tree circumference, using a stainless-steel knife. The bark samples collected were put in a plastic bag and taken to the laboratory, where they were freeze-dried and homogenized in 25 mL Teflon grinding jars using a MM 400 Mixer Mill (Retsch, Germany).

2.2. *Trace element analysis*

About 0.10–0.15 g of the samples were mineralized using 5 mL of 65% (m/m) nitric acid (for trace metal analysis from Scharlau, Spain) in closed Teflon PFA vessels heated in a microwave digestion system MDS 2000 (CEM Corporation, U.S.A.). After cooling, the solutions were transferred into 25 mL volumetric flasks and diluted to volume using ultra-pure (>18 MOhm cm) water (Elgastat UHQ, Elga Ltd., U.K.). All glassware used was washed with 3 M nitric acid and rinsed with ultra-pure water.

The concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, V and Zn were measured by atomic emission spectrometry with an inductively coupled plasma source (ICP-OES) using an iCAP™ 7000 Series (Thermo Scientific, U.K.). Axial plasma view was used for a better sensitivity. All concentrations are reported on a dry weight (d.w.) basis.

Calibration was carried out with aqueous standard solutions in 3 M nitric acid, using Be at 1 μg mL^{-1} as an internal standard. For each run (10 samples), two blanks were analyzed in order to control any possible contamination.

The accuracy was assessed by analyzing a certified reference material (CRM), the CRM 482 (Lichen), certified by the European Commission – Joint Research Centre – Institute for Reference Materials and Measurements (IRMM). The results of the quality control process are reported in Table 1.

2.3. Magnetic Analyses

On the same bark samples used for trace element determination, magnetic analyses were also carried out. About 0.85–0.9 g d.w. of the powder obtained from the milling process was wrapped in a layer of cling film; to avoid any influence on the magnetic analysis, the same amount of cling film was taken for the wrapping process of each sample. The samples were then put in a 10 cm^3 sampling pot and analyzed for Magnetic Susceptibility (χ), both at low frequency (χ_{LF}) and at high frequency (χ_{HF}), Isothermal Remanent Magnetization (IRM at 0.05T and 0.2T) and Saturation Isothermal Remanent Magnetization (SIRM at 1T). All the values obtained from magnetic analyses were normalized for sampling pot volume and for sample dry mass.

Magnetic Susceptibility was measured using a MS2 Magnetic Susceptibility System (Bartington Instruments Ltd., U.K.) with a MS2B type dual frequency sensor, with a resolution of 2×10^{-6} SI. The frequencies used by the MS2B sensor were 0.465 kHz (χ_{LF}) and 4.65 kHz (χ_{HF}) ± 1%. Before measuring the samples, the instrument was calibrated for both frequencies with a sample containing a small ferrite bead. Considering that the values for the samples were under the critical value for discriminating weak samples from strong ones, the correction for air drift fluctuations was applied to all the measurements and calculations in order to remove the background drift (Dearing, 1994).

The Frequency Dependence Susceptibility was then calculated as:

$$\chi_{fd} = [(\chi_{LF} - \chi_{HF}) / \chi_{LF}] \times 100$$

For the IRM and SIRM measurements, each sample was magnetized using a Pulsemag DS4 magnetizer (Molspin Ltd., U.K.) at the selected intensities (0.05T, 0.2T and 1T) and immediately read in a triple-shielded, annular fluxgate, Minispin magnetometer (Molspin Ltd, U.K.). The instrument was calibrated for each intensity with a rock specimen provided with the instrument; each sample was measured twice and, to avoid errors, the instrument was recalibrated every ten measurements.

2.4. Statistical analysis

The data of trace element concentrations and magnetic intensities for the 98 samples were correlated using Pearson correlation, applying the Bonferroni correction to the calculation of *p* values; on the same data-set, hierarchical cluster analysis (Pearson correlation coefficient as dissimilarity measure, single linkage as clustering algorithm) was used to visualize the groups of correlated variables.

Principal Component Analysis (PCA) was performed on the median values of trace element concentrations and magnetic intensities for the 34 sites. Furthermore, on the scores of the PCA, ANOVA analysis was run to study the possibility of a significant distinction in land use (large roads, small roads and green spaces). The software Systat for Windows Version 13 (Systat Software Inc., U.S.A.) was used for statistical analyses and graphs.

3. Results

Descriptive statistics of the data of trace element concentrations and magnetic intensities per land-use are reported in Table 2. The Pearson correlation analysis between chemical and magnetic variables showed that Co, Cu, Fe and Zn were highly correlated with all the magnetic variables ($r > 0.7$, $p < 0.001$); As, Cd, Mn, Ni, P were less correlated ($0.68 > r > 0.48$, $p < 0.001$); only Pb and V showed low correlation with all the magnetic parameters ($r < 0.48$); furthermore, V showed nonsignificant correlation with magnetic susceptibility measurement. Among magnetic variables, χ_{fd} showed no significant correlation with element concentrations.

The results obtained from cluster analysis showed the magnetic parameters grouped together and highly correlated (Figure 1); a good similarity was also found between the group of the magnetic variables and the cluster including Cu, Fe and Cd.

3.1. Magnetic Analysis

Figure 2 shows the SIRM profile for the median values of the selected intensities according to land use. Large roads have a higher SIRM profile if compared to small roads and green spaces. Instead, small roads showed a slightly lower profile than green spaces; thus, it is possible to distinguish between different types of urban land use. Magnetic susceptibility follows a similar pattern, with the values for large roads clearly higher than small roads and green spaces; while for small roads were obtained lower values if compared to green spaces. On the other hand, χ_{fd} showed lower percentage values for large and small roads if compared to green spaces.

3.2. Principal Component Analysis

The median data of elemental concentrations and magnetic intensities for 34 sites were submitted to PCA. The first two components explained 78.6% of the total variance (Figure 3). The first component (66.1% of the total variance) was associated with a gradient of increasing elemental concentrations and increasing magnetic intensities. Only χ_{fd} was not correlated with the trace element concentrations and the magnetic intensities. The second component (12.5% of the total variance) seemed to be associated to an inverse relationship between the concentration of some elements and the magnetic intensities.

3.3. ANOVA

The scores of PC1 and PC2 were submitted to ANOVA analysis to test whether the two components of the PCA were able to discriminate between trees located in different types of urban sites. Figure 4 shows the results of the ANOVA analysis: significant differences (p=0.004) were obtained only for PC1. To formally test the results obtained, a post-hoc test (Tukey test) was performed. Considering PC1, a significant difference was found between green spaces and large roads (p=0.039) and between small roads and large roads (p=0.006).

4. Discussion

4.1. Magnetic analyses in tree bark as a proxy of metal loads in urban areas

The analysis of tree bark samples can provide useful information on the concentrations of trace elements in the atmosphere (Cucu-Man and Steinnes, 2013). In our study a good correlation between the magnetic parameters and trace element concentrations was obtained, thus it is possible to hypothesize the existence of a causal relation between magnetic particles and trace elements. Except for Fe, which is directly related to magnetic properties, several authors (El Baghdadi et al., 2012; Lu and Bai, 2006) reported that the causal relation could be due to trace element incorporation onto the surface or in the lattice structure of pre-present magnetic particles. In agreement with this assumption, in the present study, the major traffic-related elements (e.g. Cu, Fe, Ni, and Zn) were significantly correlated with magnetic parameters. This finding is in line with the results obtained by Lu et al. (2005) in the magnetic analyses of automobile particulate emission. Lead, no more emitted by vehicles exhaust since 2001, showed a low correlation with all the magnetic variables, in contrast with what found by Lu and Bai (2006) and by Maher et al. (2008). This low correlation could be due to the different structure of the sampling area, to a reduced resuspension from roads and/or to a low grade of incorporation in the structure of magnetic particles.

Apart from the main traffic related elements, the other trace elements (As, Cd, Co, Mn and P) were positively correlated with the magnetic parameters, probably due to their good correlation with Fe, and between each other, suggesting a common emission source, related to traffic or domestic emissions. Arsenic is usually associated with coke production (Drava et al., 2016), but this activity is not present in the sampled area. However, the concentrations observed were comparable to those found near an industrial site (Drava et al., 2016); in that case, data were measured on a different tree species, but having similar bark texture characteristics.

Cadmium has been associated to diesel engines and the wearing of the brake (Tanner et al., 2008) while several other authors founded a correlation between Cd and traffic levels (Khan et al., 2011; McKenzie et al., 2009). Since no other evident source is identifiable in the area studied, Cd in Lisbon is likely traffic related.

Cobalt and Mn have been respectively associated with vehicular emission and corrosion of automobile parts (El-Hasan et al., 2002), thus these are probably, as for Cd, the main sources of emission.

Unfortunately, the lack of articles in literature, reporting a correlation between magnetic parameters and element concentrations in tree bark, does not allow any direct comparison with the results obtained in this study. Overall, the results suggested that higher values of magnetic variables were associated with higher element concentrations, especially those related to higher automobile emissions.

4.2. Large roads can be effectively distinguished from green spaces and small roads

Lacking large sources of industrial emissions, large roads in Lisbon are likely the main source of particle pollution. In fact, large roads showed different magnetic fingerprint and chemical composition, if compared to green areas and to small roads (Figure 4). This could be mainly related to the high traffic volume that can increase the amount of vehicle exhaust emission leading to an increased level of elements emitted to the atmosphere. On the other hand, the presence of green spaces seems to reduce the dust effect created by roads (Gautam et al., 2005; Santos et al., 2017), leading to a lower trace element concentration in the inner part of the green space itself and subsequently to a lower magnetic fingerprint (Kardel et al., 2012). Except for large roads, which exhibit higher magnetic profile, related to higher levels of trace elements, we found that small roads can have a lower magnetic profile and lower concentrations of trace elements if compared to green spaces. This could be probably related to the dimensions of the green space considered; the smaller the site, the bigger the similarity with the roads nearby. Such an outcome could help in planning new green spaces, especially in those streets characterized by high traffic/pollution levels, considering that the presence of green areas could actively reduce the dust effect at respirable height (Gautam et al., 2005), with a positive impact in reducing dust particles emitted by large and polluted roads/areas.

This study has pointed out that the combination of magnetic and chemical analyses provides a powerful tool to distinguish the different effects of atmospheric pollution on different types of urban site.

5. Conclusions

Air quality monitoring studies, especially in big cities, require a high spatial resolution for a better understanding of the distribution and possible effects of pollutants; in fact, only a high sampling density takes into account the possible presence of different local situations related to wind, resuspension, road directions (uphill, downhill) and several other factors. The use of biomonitors, e.g. tree bark, can help to achieve such resolution by allowing the collection of a large number of samples.

This study has pointed out that magnetic analyses can be effectively applied on tree bark samples for biomonitoring purposes, since they are a good proxy of different metal loads. Moreover, the combination of magnetic and chemical analyses provided a powerful tool in order to distinguish the different effects of atmospheric pollution on different types of urban site.

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Table 1. Quality assurance. The results obtained for the Certified Reference Material CRM 482 (European Commission – Joint Research Centre – Institute for Reference Materials and Measurements, IRMM), expressed as μg g^{-1} d.w., are compared with the certified or reference concentrations. The values found are reported as mean ± standard deviation (n = 7).

Element	Certified μg g^{-1} d.w.	Found μg g^{-1} d.w.
As	0.85±0.07	0.98±0.12
Cd	0.56±0.02	0.58±0.03
Co[a]	0.32±0.03	0.36±0.02
Cu	7.03±0.19	7.00±0.22
Fe[a]	804±160	748±40
Mn[a]	33.0±0.5	29.5±0.6
Ni	2.47±0.07	2.47±0.08
P	690±10	703±26
Pb	40.9±1.4	39.8±1.6
V[a]	3.74±0.61	3.73±0.18
Zn	100.6±2.2	101.1±3.9

[a] No certified data available and the reference concentrations are reported.

Table 2. Descriptive statistics (median, mean ± standard deviation and min-max range) of trace element concentrations and magnetic parameters based on land use for 34 sampling sites.

LAND USE	STAT	As $\mu g\ g^{-1}$ d.w.	Cd $\mu g\ g^{-1}$ d.w.	Co $\mu g\ g^{-1}$ d.w.	Cu $\mu g\ g^{-1}$ d.w.	Fe $\mu g\ g^{-1}$ d.w.	Mn $\mu g\ g^{-1}$ d.w.	Ni $\mu g\ g^{-1}$ d.w.	P $\mu g\ g^{-1}$ d.w.
LARGE ROADS	Median	1.11	0.20	1.31	57.70	1517	28.5	3.88	534
N = 16	Mean ± S.D.	1.21 ± 0.55	0.3 ± 0.32	1.20 ± 0.44	75.96 ± 55.8	1844 ± 1295	30.3 ± 11.1	4.05 ± 2.68	583 ± 207
	Range	0.40-2.75	0.09-1.39	0.42-2.18	26.6-254.28	301-5290	12.5-49.9	1.10-11.89	372-1233
SMALL ROADS	Median	0.72	0.09	0.80	31.05	643	29.8	1.68	519
N = 9	Mean ± S.D.	0.73 ± 0.20	0.09 ± 0.04	0.86 ± 0.34	31.58 ± 6.44	651 ± 340	26.5 ± 10.9	1.76 ± 0.64	535 ± 96
	Range	0.40-1.01	0.05-0.18	0.42-1.44	20.68-42.49	269-1290	11.3-43.2	0.80-2.70	369-687
GREEN SPACES	Median	1.03	0.15	0.85	40.18	863	24.9	1.81	432
N = 9	Mean ± S.D.	1.09 ± 0.29	0.19 ± 0.15	0.89 ± 0.26	40.98 ± 21.22	789 ± 393	26. ± 10.0	2.59 ± 1.67	462 ± 96
	Range	0.72-1.59	0.06-0.54	0.48-1.28	12.82-87.08	223-1464	12.8-44.4	0.89-5.98	303-609

LAND USE	STAT	Pb $\mu g\ g^{-1}$ d.w.	V $\mu g\ g^{-1}$ d.w.	Zn $\mu g\ g^{-1}$ d.w.	IRM 0.05T $10^{-4} A\ m^2 kg^{-1}$	IRM 0.2T $10^{-4} A\ m^2 kg^{-1}$	SIRM $10^{-4} A\ m^2 kg^{-1}$	χ $10^{-8} m^3\ kg^{-1}$	χ_{fd} %
LARGE ROADS	Median	25.3	4.36	115.4	10.94	23.82	25.25	31.46	3.14
N = 16	Mean ± S.D.	60.5 ± 64.1	4.89 ± 2.77	114.9 ± 52.6	12.24 ± 7.69	26.91 ± 16.96	28.42 ± 17.87	33.03 ± 20.42	6.82 ± 8.82
	Range	3.4-185.4	1.23-12.27	42.5-237.7	1.02-27.45	2.48-54.52	2.62-58.23	3.2-75.28	-1.19-27.5
SMALL ROADS	Median	7.0	2.23	30.7	3.59	8.01	8.45	6.62	3.64
N = 9	Mean± S.D.	10.6 ± 10.6	2.62 ± 1.04	37.3 ± 22.7	4.70 ± 2.96	9.64 ± 5.54	9.99 ± 5.86	10.15 ± 6.63	19.08 ± 48.78
	Range	1.3-32.7	1.14-4.66	15.8-89.0	1.1-8.33	2.52-17.25	2.68-17.97	2.68-20.61	-6.9-147.27
GREEN SPACES	Median	16.3	3.07	72.1	5.27	11.24	11.77	11.17	14.25
N = 9	Mean ± S.D.	20.5 ± 17.2	4.02 ± 2.55	79.2 ± 42.7	4.89 ± 2.58	10.39 ± 5.42	10.99 ± 5.72	9.51 ± 4.92	16.81 ± 15.27
	Range	2.7-57.2	1.77-9.78	29.2-178.6	1.19-9.41	2.79-19.87	2.99-20.96	2.82-14.98	-2.13-44.4

Figure captions

Figure 1. Dendrogram of magnetic intensities and trace element concentrations, Pearson correlation coefficient as dissimilarity measure and single linkage as agglomeration method, n= 98.

Figure 2. SIRM profiles for land use classification.

Figure 3. Results of Principal Component Analysis. Loading plot (left) of trace element concentrations and magnetic intensities; score plot (right) of the samples.

Figure 4. Box plot of the scores on the first Principal Component (PC1) from PCA on magnetic intensities and element concentrations according to land use classification.

Figure 1
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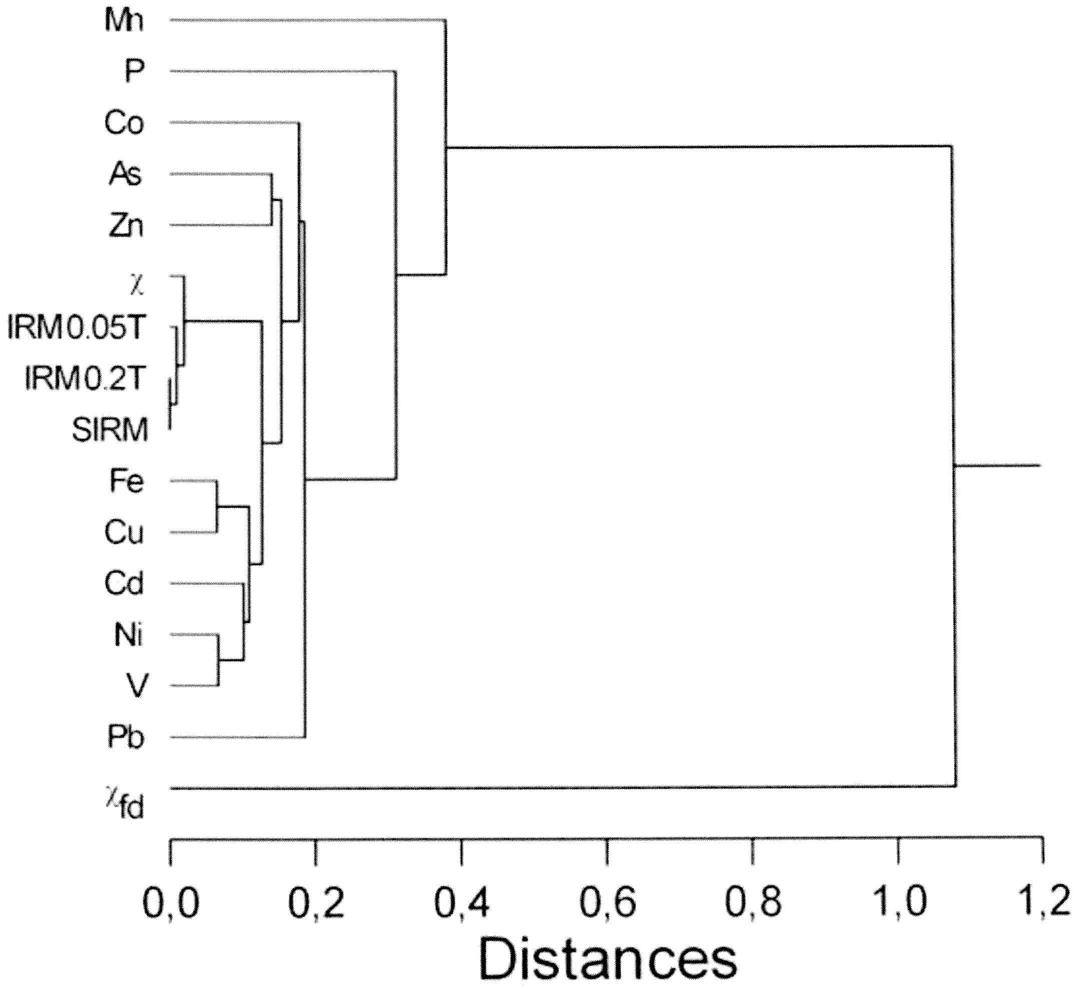

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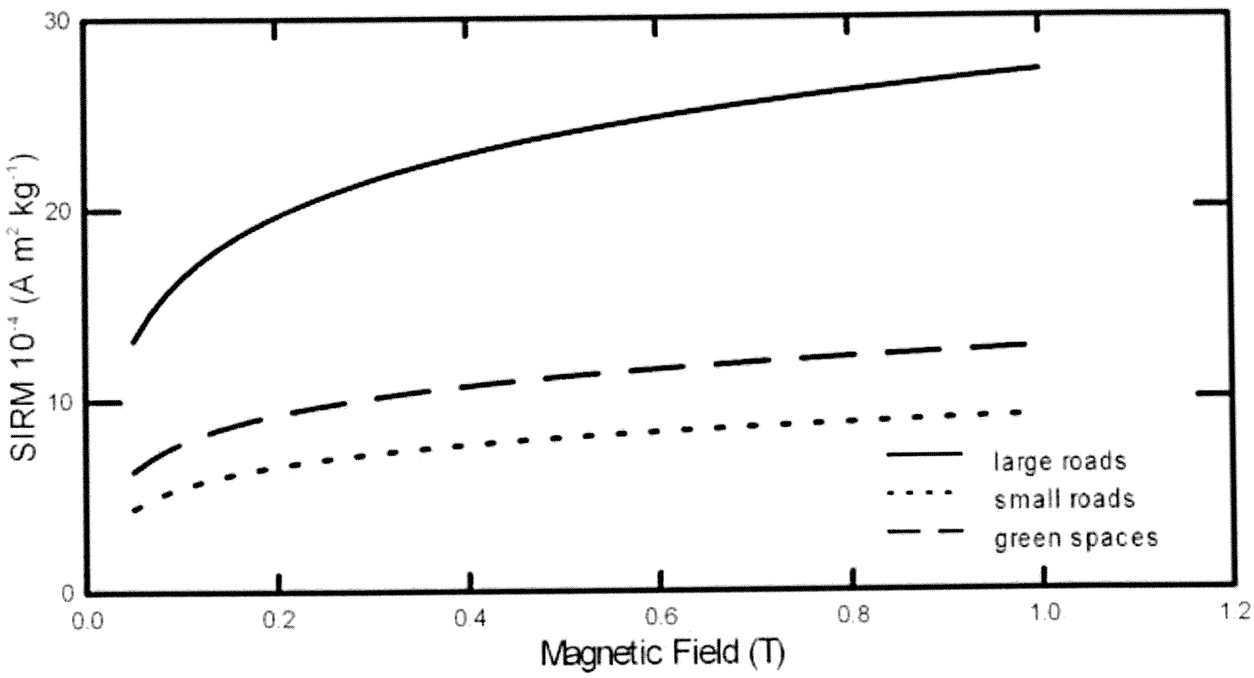

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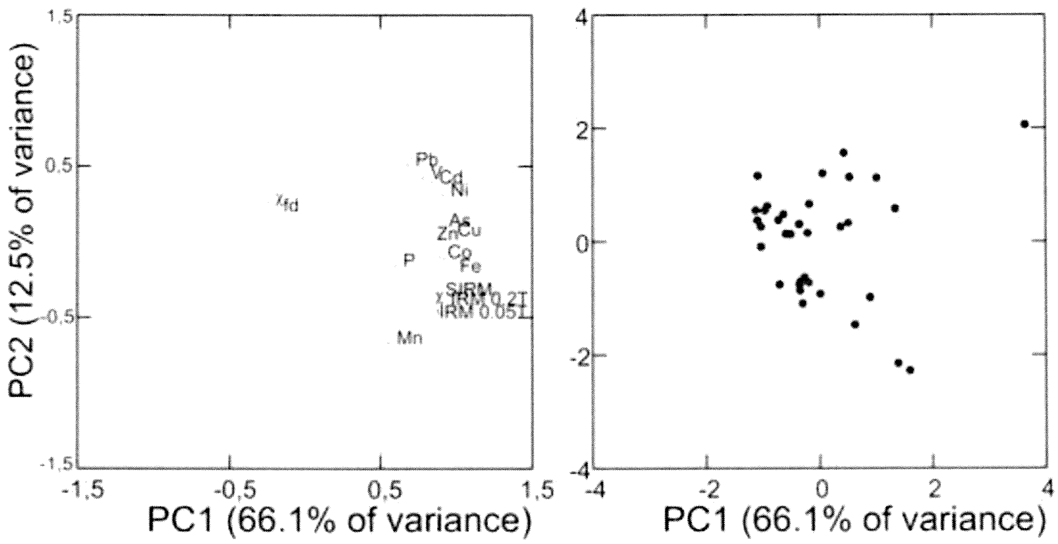

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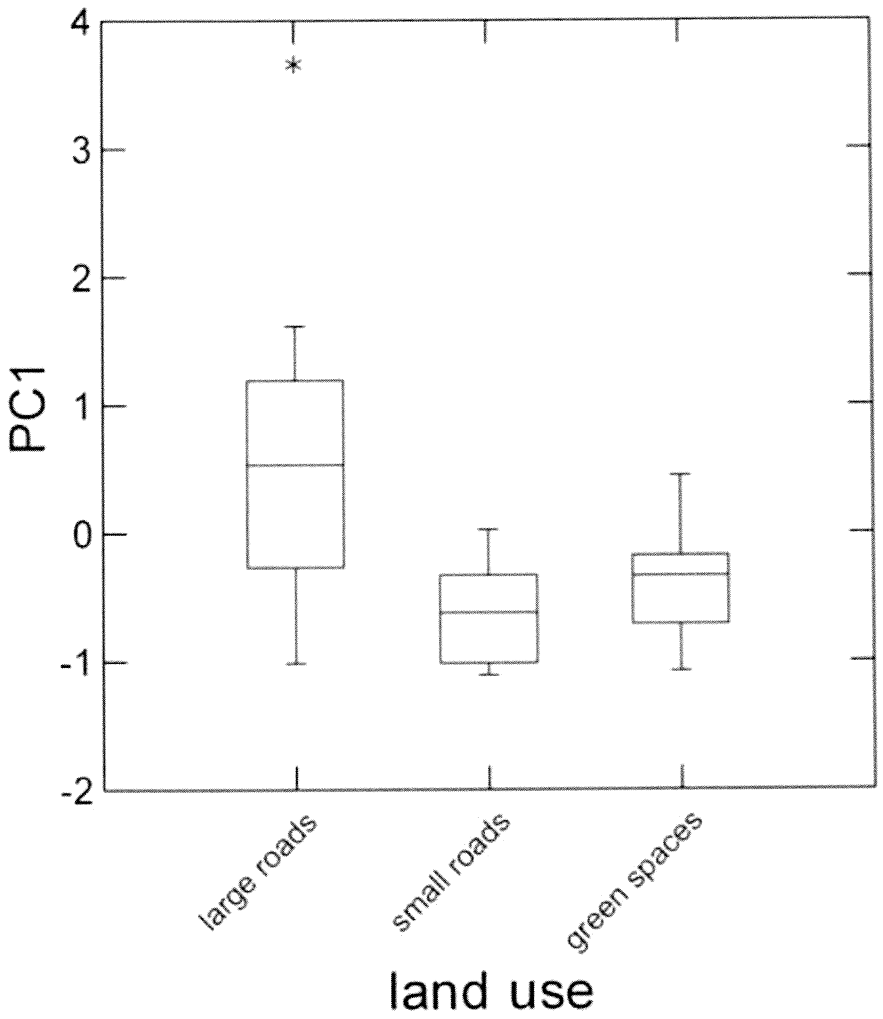

Graphical Abstract