Impact of grass cover on the magnetic susceptibility measurements for assessing metal contamination in urban topsoil

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A R T I C L E   I N F O

Keywords:
- Magnetic susceptibility
- Soil metal contamination
- Grass cover
- In situ MS
- Environmental magnetism

A B S T R A C T

In recent decades, magnetic susceptibility monitoring has developed as a useful technique in environmental pollution studies, particularly metal contamination of soil. This study provides the first ever examination of the effects of grass cover on magnetic susceptibility (MS) measurements of underlying urban soils. Magnetic measurements were taken in situ to determine the effects on $\kappa$ (volume magnetic susceptibility) when the grass layer was present ($\kappa_{\text{grass}}$) and after the grass layer was trimmed down to the root ($\kappa_{\text{no grass}}$). Height of grass was recorded in situ at each grid point. Soil samples (n=185) were collected and measurements of mass specific magnetic susceptibility ($\chi$) performed in the laboratory and frequency dependence ($\chi_f$) calculated. Metal concentrations (Pb, Cu, Zn and Fe) in the soil samples were determined and a gradiometry survey carried out in situ on a section of the study area. Significant correlations were found between each of the MS measurements and the metal content of the soil at the $p < 0.01$ level. Spatial distribution maps were created using Inverse Distance Weighting (IDW) and Local Indicators of Spatial Association (LISA) to identify common patterns. $\kappa_{\text{grass}}$ (ranged from 1.67 to 301.00 $\times 10^{-5}$ SI) and $\kappa_{\text{no grass}}$ (ranged from 2.08 to 530.67 $\times 10^{-5}$ SI) measured in situ are highly correlated ($r=0.966$, n=194, $p < 0.01$). The volume susceptibility datasets in the presence and absence of grass coverage share a similar spatial distribution pattern. This study re-evaluates in situ monitoring techniques and the results suggest that the removal of grass coverage prior to obtaining in situ $\kappa$ measurements of urban soil is unnecessary. This layer does not impede the MS sensor from accurately measuring elevated $\kappa$ in soils, and therefore $\kappa$ measurements recorded with grass cover present can be reliably used to identify areas of urban soil metal contamination.

1. Introduction

Metal contaminants are a useful indicator of environmental pollution in urban soils. The assessment of magnetic susceptibility of soils has become an established reliable and efficient proxy for metal contamination. The magnetic susceptibility of soils mainly depends on ferromagnetic mineral content which are a result of natural and anthropogenic processes. Natural processes can include weathering of rocks (Kapička et al., 2008) or occur during pedogenic processes which can be mediated by microorganisms (D’Emilio et al., 2007). Magnetic particles occurring in industrial and urban dusts have an anthropogenic source and are referred to as technogenic magnetic particles (TMPs). These iron minerals are formed as a result of technological processes at very high temperatures which are released into the atmosphere (Hanesch and Scholger, 2002; Magiera et al., 2011).

Fossil-fuel burning power plants are a significant source of airborne TMPs (Hanesch and Scholger, 2002; Evans and Heller, 2003). Combustion of coal causes the release of sulfur gas and formation of spherical iron particles which can oxidize to form magnetite (Fe$_3$O$_4$) (Flanders, 1999; Hanesch and Scholger, 2002), pyrrhotite (Fe-S$_2$) and other minerals can also form which are rarely found in the natural environment (technogenic ferrites) (Łukasik et al., 2015). In the event where natural processes are not a significant contributing factor in the magnetization of soil, magnetic susceptibility has emerged as an alternative technique for monitoring environmental metal pollution (Chianese et al., 2006). Particulates resulting from anthropogenic emissions may integrate potentially toxic elements (PTEs) into their structure. Magnetic particles TMPs can act as a host of metals and...
contaminants by either incorporating metals into the crystalline structure during combustion, or PTEs may adhere onto their exterior after formation (Chaparro et al., 2006; Kapićka et al., 2008).

Magnetic parameters are widely applied in many fields including archaeology and environmental science. The application of magnetic studies to environmental features of archaeology was first established in the 1950's which concerned the magnetic susceptibility of soils. Le Borgne observed enhanced magnetism in topsoils in comparison to the underlying bedrock (Evans and Heller, 2003). Initially, magnetic susceptibility was used to investigate magnetic enhancement of soils relating to fire which could be a result of natural or human activity or pedogenic processes (Dalan, 2008). More modern applications include the locating, mapping and interpretation of earthworks and also as part of the excavation process, carrying out magnetic susceptibility surveys on walls and floors at the microscale to add an additional layer of data to an excavation (Dalan, 2008). Environmental magnetism involves relating magnetic properties of mineral assemblages to the environmental conditions that govern them (Liu et al., 2012). The technique has been developed over the past thirty years and the range of applications of magnetic susceptibility conveyed by many (i.e. Thompson and Oldfield, 1986; Verosub and Roberts, 1995; Maher and Thompson, 1999; Evans and Heller, 2003; Gibson and George, 2013).

The use of magnetic parameters as a proxy for environmental metal contamination in urban environments is established (Canbay et al., 2010; El Baghdadi et al., 2012; Girault et al., 2016; Golden et al., 2015; Liu and Bai, 2006; Morton-Bermea et al., 2009; Yang et al., 2012; Zhang et al., 2012; Zhu et al., 2012). Environmental magnetic methods have been extensively used to examine the extent and causes of anthropogenic contamination, providing a simple, rapid, non-intrusive and feasible tool in the identification of metal pollutants (Chianese et al., 2006; Zhang et al., 2012).

Magnetic susceptibility can be measured in the laboratory as mass specific magnetic susceptibility (\(\chi\)) and in situ as volume magnetic susceptibility (\(\kappa\)) and is a quick and economical technique compared to traditional chemical methods of analysis for soil geochemistry (Jordanova et al., 2003; Soodan et al., 2014).

Volume magnetic susceptibility has been applied as a proxy for metal contamination in many environmental samples such as sediments (Canbay et al., 2010), leaves (Gautam et al., 2005), tree bark (Kletetschka et al., 2003), mosses (Fabian et al., 2011), lichens (Salo et al., 2012), fly ash (Kapićka et al., 1999; Zawadzki et al., 2010) and soils (Bityukova et al., 1999; Hoffmann et al., 1999; Boyko et al., 2004; Schmidt et al., 2005; Canbay et al., 2010). The capability of \(\kappa\) to provide instant measurements make it possible to determine relative pollution impacts directly in the field (Jordanova et al., 2003). The main limitation of this technique in relation to environmental studies is the depth of analysis. In situ magnetic susceptibility studies are limited to the upper topsoil horizon as significant MS properties may lie below this horizon.

MS mapping has developed as an important technique in soil analyses and monitoring of temporal changes in environmental studies (Dau et al., 2010, 2012, 2013, 2014; Petrovský and Ellwood, 1999; Hanesch et al., 2007). Many studies have incorporated the use of \(\kappa\) to assist in soil metal pollution mapping studies particularly in urban soils (Wang and Qin, 2005; Fišalová et al., 2006; Lu et al., 2007). Urban soils occur within populated areas and provide many ecosystem services, natural resources and recreational amenities for communities globally and are considered vulnerable to metal contamination from industrial and domestic sources. Some studies have explored the impact of a vegetative layer on magnetic susceptibility in varying soil environments including a former mining site (Schmidt et al., 2005), a laboratory setting (D’Emilio et al., 2007) and a forest floor (Zawadzki et al., 2010). However, the effects of a vegetative layer on magnetic susceptibility measurements in urban soils remains unknown.

The main aim of this paper was to identify for the first time whether magnetic susceptibility (\(\chi\)) of underlying urban soils. The study area is a well-established metal contamination hotspot and hence ideal to test this hypothesis. In addition, field-based magnetic susceptibility measurements were evaluated as a proxy for metal contamination in soil by comparing spatial distribution maps of \(\kappa\) and metals. Laboratory-based magnetic susceptibility (\(\chi\)) and a magnetic gradient survey on a section of the study area was carried out to assess the field-based \(\kappa\) measurements obtained. Percentage frequency dependence (\(\chi_{FD}\)) was also calculated to identify the possible locations of anthropogenic magnetic minerals. The findings will potentially impact methodological approaches in environmental soil science.

2. Materials and methods

2.1. Study area and vegetation cover

The study site is located in an urban park of approximately 20 acres of former swampy seaside wetland known as South Park in the Claddagh region (O’Dowd, 1993 as cited in Carr et al., 2008) of Galway City (53° 15' 56 N, – 9° 03' 10 E), Ireland (Fig. 1). In the past, the site has been considered a metal contamination hotspot (due to its use as an unregulated waste deposit site) prior to its current use as a green space amenity. A first attempt at reclaiming the flood prone region into a recreational site occurred at the beginning of the twentieth century with the development of a half-mile track around the perimeters of the area (Galway Advertiser, 2008). Much of the track layout is used as a pedestrian walkway/ bicycle path surrounding the green area. This was not a successful undertaking and it was soon after this that the site was used as a municipal landfill. The landfill was potentially in use for twenty to thirty years until 1931, a grant was provided to develop part of the site into a number of playing pitches. Development occurred gradually until the early 1950's when the area was fully converted into a municipal park (Galway Advertiser, 2008). It is not known whether its use as a municipal dump continued during this development phase. Colloquially, it is claimed that the removal of deposited materials such as glass and tin from the topsoil was required post-development of the playing pitches (Galway Advertiser, 2008). A previous study conducted at the site revealed very high levels of As, Pb and Cu present in the soils. In the past, a fertilizer plant was situated adjacent to the park and the type of pollution identified was similar to the industrial waste originating from a fertilizer plant processing pyrite ores (U.S. EPA 1997 as cited in Carr et al., 2008).

While the main soil type in the region is brown earths, the surface soils in South Park were imported, which were used to cover the rubbish when the sportsground was built. There were no natural grass coverage significantly affects volume magnetic susceptibility (\(\kappa\)) of urban soils. The study area is a well-established metal contamination hotspot and hence ideal to test this hypothesis. In addition, field-based magnetic susceptibility measurements were evaluated as a proxy for metal contamination in soil by comparing spatial distribution maps of \(\kappa\) and metals. Laboratory-based magnetic susceptibility (\(\chi\)) and a magnetic gradient survey on a section of the study area was carried out to assess the field-based \(\kappa\) measurements obtained. Percentage frequency dependence (\(\chi_{FD}\)) was also calculated to identify the possible locations of anthropogenic magnetic minerals. The findings will potentially impact methodological approaches in environmental soil science.

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horizons in the soils and the thickness of the imported soil varied across the study area, e.g. the west and north parts were relatively poorly covered.

The study site (Fig. 2) is comprised of the widespread cultivation of the grass species *Lolium*-mix, predominately *Lolium perenne* L., also known as Ryegrass, Ray Grass or Eavers. This versatile species is commonly found in agricultural settings; in improved or reseeded neutral grassland, livestock grazing pasture and fodder (Beddows, 1967); as a turfgrass species used in domestic gardens, parks, recreational amenities, commercial landscapes and other green belts (Bandaranayake et al., 2003) and on disturbed or waste ground (Averis, 2013). *Lolium perenne* is tolerable to grazing and environmental contamination (Cockerham et al., 1990) and as a result is commercially important globally, with widespread uses in urban and amenity spaces (e.g. football pitches, roadsides and waste places).

2.2. Sampling grid

A systematic 20×20 m² sampling grid was employed in the collection of 185 soil samples and two datasets of 185 corresponding \(\kappa\) measurements: 1) \(\kappa^{\text{grass}}\) – measured with the grass layer present and 2) \(\kappa^{\text{no grass}}\) – measured after the grass layer was trimmed down to the root. The locations of a selection of sampling points were altered due to obstructions present in the field e.g. gravelled areas, tarmacked pavements or water-logged areas. A portable global positioning system (GPS) Trimble GeoExplorer® was used to locate and record sampling point coordinates.

2.3. Soil collection, preparation and analysis

At each point on the sampling grid, three soil samples were collected using a plastic scoop at a depth of \(-0\text{–}10\) cm within \(1\text{ m}^2\) area of the sampling point. The soils samples were combined to form one composite sample and stored in polythene bags. Special attention was paid to ensure the soil samples were removed from the same points as the \(\kappa\) sub-measurements. Soil samples were air-dried at \(-20\) °C, before being gently disaggregated using a mortar and pestle and sieved using a 2 mm stainless steel sieve.

A portable X-ray fluorescence analyser, Innov-X Alpha Series 6500 (PXRF, ©Innov-X Systems, Inc.) was used to analyse the metal content of the soil samples. PXRF is a non-destructive method of examining possible contaminated sites which can perform accurate quantitative analysis over a whole host of elements including Ba, Hg, Cd, As, Cr, Pb, Mn, Sr, Cu, K, Co, Ti, Fe and Zn (Soodan et al., 2014). XRF measurement uncertainties are within a specified relative standard deviation of the measurement, which are as follows: Cu (± 4), Fe (± 286), Pb (± 13) and Zn (± 9). The XRF was operated for 120 s per sample to generate data for elements lead (Pb), copper (Cu), zinc (Zn) and iron (Fe). The limits of detection are relatively low ranging from \(-10\) ppm (Innov-X Systems Inc, 2013). Tangible limits are dependent upon the sample type and matrix (Innov-X Systems Inc, 2013).

2.4. Volume magnetic susceptibility (\(\kappa\))

Volume magnetic susceptibility measurements were obtained using a Bartington MS2 meter (©Bartington Instruments Ltd.) in situ with a MS2D search loop. The field penetration depth of the MS2D sensor used is approximately 10 cm. The majority of the susceptibility signal, approximately 95%, comes from the upper 8 cm in the shape of a toroid with an integrated volume of approximately 0.0043 m³ (Lecoanet et al., 1999). Values of volume magnetic susceptibility (\(\kappa\)) are dimensionless and expressed as \(10^{-5}\) SI units (Zawadzki et al., 2015).
Volume magnetic susceptibility was measured in two phases within a 1 m² sampling location. Firstly, three sub-measurements were recorded with the grass layer present. The approximate length of grass coverage was noted to determine whether the presence of this layer had a significant impact on the magnetic measurements obtained. The length of grass was recorded by removing blades of grass from the sampling locations and measuring them. Measurements were rounded to the nearest cm. Lastly, the grass layers were trimmed to the root from each of the three previously measured locations and a secondary κ of the bare soils beneath were recorded. Three sub-measurements were taken at each location because high variability can occur between field measurements even at close distances (Lees et al., 1999). The mean of two air measurements (taken before and after) was subtracted from each surface measurement. The mean of the three surface measurements is then used as the representative measurement for each location.

2.5. Mass specific magnetic susceptibility (χ)

The mass specific magnetic susceptibility of the homogenized soil samples was measured using a Bartington MS2 meter with a dual-frequency MS2B sensor in the laboratory. Samples were measured at the low frequency range (0.46 kHz) expressed as χ₀ and at the high frequency range (4.6 kHz) expressed as χ₆. Frequency dependence is the difference between the two frequencies and is expressed in %. Percentage frequency dependence (χ₆/₀%) was calculated to detect the presence of ultrafine (< 0.03 µm) superparamagnetic ferrimagnetic minerals (Dearing, 1999). Samples were measured in compact 10 cm³ plastic cylinders. In order for true comparisons to be made between magnetic susceptibility measurements, mass specific magnetic susceptibility values were converted to volume magnetic susceptibility in accordance with the methodology applied by Dearing (1999) which states that χ(10⁻⁶ m³ kg⁻¹) can be calculated by dividing κ by sample mass and then dividing by 10. Therefore the following formula was used to calculate χ₆/₀:

(χ₆/₀*10) × sample mass = κ₆/₀

2.6. Fluxgate gradiometry survey

Measurements of magnetic gradient were taken using a Bartington 601 fluxgate gradiometer. These instruments feature two sets of two fluxgate sensors placed vertically above one another, separated by 1 m and measure the vertical component of the Earth’s magnetic field (Gaffney and Gater, 2003). Measurements were taken at regular 0.5 m intervals along a series of parallel transects positioned 1 m apart within 8 grid panels measuring 20 m × 20 m. Measurements were taken facing north along each transect. The survey grid design was based on the technique employed by Fenwick (2004).

2.7. Quality control

To evaluate the precision of the chemical analysis by PXRF, the determination of the studied elements was performed using the soil certified reference materials (CRMs) San Joaquin (SRM 2709a), Montana I (SRM 2710a) and Montana II (SRM 2711a) from the National Institute of Standards and Technology, USA (NIST). These CRMs have been established for use in technique development, technique validation and routine quality assurance in the analysis of major, minor and trace element concentrations of soils (Mackey et al., 2010). PXRF exhibited particularly good analytical accuracy for Cu and Zn (Table 1).

The field sensor calibration was performed prior to carrying out the survey. Every time the meter was switched on, after an appropriate amount of time (approx. 10 min) a test point was measured ~10 times to check the measurement consistency. Variance was < ±3%. To maintain the accuracy of field-based κ measurements, air measurements were taken in between surface measurements to allow for any drift in the measurement sequence to be identified. The meter was ‘zeroed’ if air measurements fell outside the ± 0.5 × 10⁻⁵ tolerance level applied.

The MS2B sensor is calibrated electronically, to ensure the validity of the χ₆/₀ values obtained, a calibration standard was used to check the stability of the measurement (Dearing, 1999). The calibration sample has a value of 3062 × 10⁻⁵ SI units. Every 10 samples, the calibration sample measurement was repeated. If a drift in air measurements was detected, samples were removed from the sensor, the meter was zeroed and the measurement repeated. The soil samples were compressed into each container to capacity and weights ranged from 8.48 to 14.55 g.

2.8. Spatial analysis of metals and magnetic susceptibility

Inverse Distance Weighting (IDW) was applied for the interpolation of elemental and magnetic data. Spatial interpolation maps (Fig. 3) were prepared using the extension Geostatistical Analyst within ArcGIS® ArcMap™ v.10.2 (©2013 ESRI). This method is based on the assumption that the value of a particular variable at a location which has not been sampled is the weighted average of known values of that variable within its vicinity. Weights are inversely associated with the distances between the unknown value point location and determined value point locations. The inverse distance weight is dependent on a constant, known as a power parameter. Points closer to the unknown value point can have much more influence over the determined value based on the power parameter (Lu and Wong, 2008). In the current study, a power parameter of 2 was applied to the elemental and magnetic data during geostatistical analysis. Maps produced using a power parameter of 2 attribute more weight to samples closer to the unknown value. This results in a much more abrupt surface which highlights the complexity of the metal concentrations and the magnetic susceptibility signature present.

Local indicators of spatial association (LISA) (Anselin, 1995) maps of metals Pb, Cu, Zn and Fe and magnetic measurements κ and χ₆/₀% (see Fig. 3) were created to identify statistically significant spatial clusters including high value areas (‘high-high’) and low value areas (‘low-low’) within the urban park. Spatial outliers are also featured, these are denoted as ‘high-low’ and ‘low-high’ on the LISA maps representing statistically significant outliers of high and low values in comparison to surrounding data values. Prior to LISA analysis, each of the datasets were transformed to an approximate normal distribution using a natural logarithm transformation (ln). The weight function used was based on K-nearest neighbours (8 neighbours) (Golden et al., 2015).

**Table 1**

<table>
<thead>
<tr>
<th>CRM</th>
<th>Measured</th>
<th>Certified</th>
<th>Recovery (%)</th>
<th>Recovery (%)</th>
<th>Recovery (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2709a</td>
<td>33.9 ± 0.5</td>
<td>33.60 ± 700</td>
<td>17.3 ± 0.1</td>
<td>103 ± 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>San Joaquin</td>
<td>31 ± 6</td>
<td>32.87 ± 296</td>
<td>13 ± 3</td>
<td>97 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montana I</td>
<td>3518 ± 46</td>
<td>50.53 ± 497</td>
<td>5564 ± 58</td>
<td>4412 ± 51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2710a</td>
<td>3420 ± 50</td>
<td>43.20 ± 800</td>
<td>5520 ± 30</td>
<td>4180 ± 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montana I</td>
<td>118 ± 8</td>
<td>25.75 ± 244</td>
<td>1402 ± 18</td>
<td>374 ± 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2711a</td>
<td>140 ± 2</td>
<td>28.20 ± 400</td>
<td>1400 ± 10</td>
<td>414 ± 11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montana II</td>
<td>118 ± 8</td>
<td>25.75 ± 244</td>
<td>1402 ± 18</td>
<td>374 ± 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2711a</td>
<td>84.29%</td>
<td>91.32%</td>
<td>100.14%</td>
<td>90.34%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.9. Principal Component Analysis (PCA)

Principal Component Analysis is a technique used for data reduction (Boruvka et al., 2005; Manta et al., 2002). The data must be correlated in order for PCA to be employed. Standardization is applied when variables are measured at different scales or in circumstances where some variables may have much larger variance than others and dominate the first principal component (Miller and Miller, 2005). This

Fig. 3. Total concentration distributions and local Moran’s I maps of volume magnetic susceptibility – $k^{\text{grass}}$ and $k^{\text{no grass}}$ ($10^{-5}$ SI), mass specific magnetic susceptibility – $k^{\text{lab}}$ ($10^{-5}$ SI), percentage frequency dependence – $\chi_{fd}$% and metal concentrations – Cu, Fe, Pb and Zn (mg kg$^{-1}$).
Fig. 3. (continued)
is avoided by making all variables carry equal weight. PCA is employed in the current study to aid in the interpretation of interrelations between metals and magnetic susceptibility in the contaminated urban topsoils.

2.10. Data transformation

Due to the heterogenic nature of geochemistry, a Kolmogorov-Smirnov test of normality was applied to the metal and magnetic susceptibility datasets. A Kolmogorov-Smirnov test is based on the maximum deviation of the observed value series from the theoretical model (Webster and Oliver, 2007). Each of the magnetic susceptibility sampled populations (with the exception of $X_{Fe}$%) were non-normally distributed at the significance level of $p < 0.01$. A natural logarithmic transformation (ln) was performed in an attempt to transform the measured values to a new scale on which the distributions are closer to normality.

2.11. Integrated Pollution Index (IPI)

The degree of metal contamination at the site was also demonstrated by the calculation of an accumulation factor (Integrated Pollution Index (IPI)) (Jung, 2001 as cited in Morton-Bermea et al., 2009) in relation to background regional values (Zhang, 2006) for quantitative purposes. Integrated pollution index (IPI) refers to the mean value of all Pollution Indices (PI) of all the metals being investigated (Morton-Bermea et al., 2009). PI are commonly used to discriminate metal contamination and evaluate the degree of environmental pollution present at a site (Dong et al., 2014). An IPI was calculated for the soil samples defined as:

$$IPI = \frac{(\text{PI}_{\text{Cu}}) + (\text{PI}_{\text{Fe}}) + (\text{PI}_{\text{Pb}}) + (\text{PI}_{\text{Zn}}))}{4}$$

where $\text{PI}_{i}$ = (Concentration$_{i}/\text{Background median}_{i}$), $i$ = metal.

2.12. Data analysis and statistics

Data management was carried out in Microsoft® Excel 2010. Statistical analysis was performed using SPSS 21 (IBM®SPSS® Statistics). Hotspot analysis was applied to the data using GeoDa™1.4.6. (Anselin et al., 2006) and spatial analysis was carried out within a Geographical Information System (ESRI® ArcGIS® ArcMap™ 10.2) using ArcGIS World Imagery basemap service. Mass specific magnetic susceptibility measurements were determined using Multisus v2.44 software.

3. Results and discussion

3.1. Effects of grass coverage on magnetic susceptibility ($\kappa$)

A strong linear relationship is shown (Fig. 4) between $\kappa_{\text{grass}}$, $\kappa_{\text{no grass}}$ and $\kappa_{\text{lab}}$. The two $\kappa$(ln) datasets exhibited a strong positive pearson's correlation coefficient of $r^2=0.966$, n=185, $p < 0.01$. In general, $\kappa_{\text{grass}}$ obtained initially, prior to the grass layer being disturbed, are lower than $\kappa_{\text{no grass}}$. This is because the sensitivity of the sensor for magnetic susceptibility measurements diminishes exponentially with distance from material (Lecoanet et al., 1999). The MS2D search loop is affected by material up to ~14 cm from the sensor. For example, a layer of vegetation 0.5 cm in depth can possibly reduce the MS2D measurement to 75% of the expected value compared to if the sensor was directly placed on the soil surface (Dearing, 1999). The gap between the sensor and the soil surface is a contributing factor in relation to grass height effects. This gap was at least 1.5 cm from the sensor to the soil surface for grasses < 10 cm and 1.5–2 cm for grasses > 10–15 cm.

In this study, a substantial amount of magnetic susceptibility data was obtained in the field. The length of grass blades were also recorded at each sampling point. The grass heights ranged from 2 to 15 cm. A possible negative relationship between grass height and the difference in $\kappa$ values was explored and a Spearman’s Rho correlation revealed a weak significant $r^2$ value between these parameters ($r^2=0.253$ $p < 0.05$) (see Supplementary materials for graph depicting grass blade lengths at the sub-measurement locations a1, b1, and c3 versus mean % difference in field-based $X$ measurement). The mean % $X$ measurement error in relation to grass coverage height was calculated (Please see Fig. 5). Where $\kappa_{\text{no grass}}$ was considered as the true $\kappa$ magnetic susceptibility measurement for each sampling point, $\kappa_{\text{grass}}$ measurements were treated as a recovery percentage and the (%) $X$ measurement error determined using the following calculation: 100 – ($\kappa_{\text{grass}}$ – $\kappa_{\text{lab}}$)/$\kappa_{\text{no grass}}$ x 100). This graph demonstrates a trend in the data and infers an inverse relationship between grass coverage height and $\kappa$. Error bars are included to depict the level of variance within each of the three grass height groups. 

![Fig. 4. Relationships between three log-transformed magnetic susceptibility measurements: field-based volume magnetic susceptibility (10$^{-5}$ SI) taken with and without grass coverage ($\kappa_{\text{grass}}$(ln) and $\kappa_{\text{no grass}}$(ln), respectively) and volume magnetic susceptibility of soil samples ($\kappa_{\text{lab}}$(ln)).](image-url)
of conformity in experimental protocols for magnetic susceptibility represented as volume magnetic susceptibility of soil samples $\kappa^{lab}$ (10^{-5} SI) and frequency dependence (%) of soil samples. Volume magnetic susceptibility measurement uncertainties are within a standard deviation of the measurements, which are as follows: $\kappa^{lab}$ (± 0.37), $\delta\kappa$ (± 1.8) and $\kappa$ (± 0.3).

### Table 2

Summary of volume magnetic susceptibility (10^{-5} SI) taken in the field, mass specific magnetic susceptibility represented as volume magnetic susceptibility of soil samples $\kappa^{vol}$ (10^{-5} SI) and frequency dependence (%) of soil samples. Volume magnetic susceptibility measurement uncertainties are within a standard deviation of the measurements, which are as follows: $\kappa^{vol}$ (± 0.37), $\delta\kappa$ (± 1.8) and $\kappa$ (± 0.3).

<table>
<thead>
<tr>
<th>Soil</th>
<th>$\kappa^{lab}$</th>
<th>$\gamma$%</th>
<th>$\kappa^{vol}$</th>
<th>$\kappa$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>2091</td>
<td>-1.46</td>
<td>1.7</td>
<td>2.1</td>
</tr>
<tr>
<td>25th</td>
<td>4328</td>
<td>2.87</td>
<td>21.8</td>
<td>27.5</td>
</tr>
<tr>
<td>med</td>
<td>9022</td>
<td>3.84</td>
<td>37.7</td>
<td>53.3</td>
</tr>
<tr>
<td>75th</td>
<td>18,764</td>
<td>4.70</td>
<td>74.8</td>
<td>105.3</td>
</tr>
<tr>
<td>max</td>
<td>85,684</td>
<td>7.97</td>
<td>301.0</td>
<td>530.7</td>
</tr>
<tr>
<td>S.D.</td>
<td>12,290</td>
<td>1.51</td>
<td>50.8</td>
<td>73.8</td>
</tr>
</tbody>
</table>

< 5 cm) and group 2 (6–10 cm) in comparison to group 3 (> 10–15 cm). This is related to site specific conditions at the study area. The study site is a well-maintained urban park. Grass is mowed on a regularly basis resulting in a low average blade height of 6 cm at the sampled points. This demonstrates that grass height has the potential to effect measurements but not in the present study where maintained grass dominates the study area.

Based on these results, it is not possible to create a model to identify approximate (%) $\kappa$ measurement error at varying grass heights. The level of variance across the grass height groups mean the results are not robust enough to back calculate to create a model. The (%) difference calculated in this study can be used as an indicator for other urban soil studies carrying out $\chi$ surveys where grass coverage maybe a factor.

It is possible that where very high grasses are present in e.g. wastelands or roadsides that grass height may affect $\kappa$ measurement obtained. But due to the small number of sample points with grass blade height > 10 cm (n=3), it does not affect the predictive power in the current study.

### Four magnetic susceptibility datasets

Two volume magnetic susceptibility (for each of the volume magnetic susceptibility were obtained in this study and the descriptive statistics are summarized in Table 2. The measurements revealed elevated and varied levels of magnetic particulates present in these urban soils. Shape parameters of each of the volume magnetic susceptibility datasets demonstrate a strong positive correlation between $\kappa^{lab}(ln)$ and $\kappa^{vol}(ln)$ r²=0.752 and $\kappa^{vol} graso\kappa^{vol}(ln)$ r²=0.756, n=185, p < 0.01.

A small number of studies have recognised and addressed the issue of inhomogeneity (D’Emilio et al., 2007). As part of the MAGPROX team, Schibler et al. (2002) evaluated the data reproducibility of soil, covered by vegetation and after the vegetation was removed was also examined. Based on the distribution shapes of each dataset, the removal of the vegetation layer during field surveys was considered necessary due to its inhomogeneity (D’Emilio et al., 2007).

In regards to urban soils, the results of this study suggest it is not necessary to remove the grass prior to obtaining magnetic susceptibility measurements in the field. Although vegetation can cause reduced contact with the soil surface, the shape and penetration range of the instrument sensor (to a depth of 10 cm) allow for the detections of anthropogenic particles present in deeper horizons. Lower value, diamagnetic minerals in the upper organic layers may dilute the measurement slightly but not detrimentally particularly when greater levels of particles are present. The main argument in favour of removing the vegetation layer is that most anthropogenic contaminants accumulate at a depth of 3–7 cm (Zawadzki et al., 2010) but this may be pathway specific, e.g. atmospheric deposition versus landfill leachate. Furthermore, a vegetative cover, including Lolium perrenne prevents the spreading of metal-associated particles via wind erosion or water and reduces the mobility of metals through root secretion and precipitation processes (Yangromsveld et al., 1995). Vegetative stabilization also enhances the biological and chemical properties of the contaminated soil by boosting nutrients, biological activities, organic matter content and cation exchange capability (Norland and Veith, 1995; Arienzo et al., 2004).

Thick upper organic layers may significantly influence the measured $\kappa$ due to limitations of the penetration range, e.g. 50% of the magnetic susceptibility measurement comes from the top 1.5 cm (Lecanuet et al., 1999). Unlike urban soils, undisturbed soils are likely to be allowed to develop over time naturally and accumulate anthropogenic particles via atmospheric deposition. Urban soils are transient as urban environments are constantly modified, leading to a more complicated contamination sources and pathways.

### 3.2 Metals

The anthropogenic influence at the park is evident in the Pb, Cu and Zn concentrations (see Supplementary materials) as a result of previous municipal and industrial waste disposal activities. However, there is a much smaller PI for Fe between the park soil samples and median regional background values (Zhang, 2006). The maximum pollution indices are 84.5 for Cu, 116.43 for Pb and 56.12 for Zn. Concentrations of Fe did not differ much from background levels and this is reflected in a PI of 1.25. This may be because Fe content in topsoil is largely related to the parent rock (Morton-Bermea et al., 2009). Based on the metal concentration PIs we can speculate that the soils of this urban park remain heavily contaminated with Pb as the largest contributor. The park has a complex history of contamination and remediation activities and this leads to a diverse genetic origin. Pearson correlation values between Pb(In) and Cu(In) r²=0.931, Pb(In) and Zn(In) r²=0.941 and Cu(In) and Zn(In) r²=0.962, n=185, p < 0.01 show a strong positive linear correlation suggesting the same contamination source, resulting from industrial waste. There is also a positive correlation between Fe(In) and Pb(In) r²=0.841, Fe(In) and Cu(In) r²=0.883 and Fe(In) and Zn(In) r²=0.863, n=185, p < 0.01 but it is slightly lower. These soils subjected to high levels of contamination with elevated concentrations of Pb, Cu and Zn show slightly lower Fe content and this may be due to Fe being associated with low levels of anthropogenic influence (Morton-Bermea et al., 2009).
3.3. Spatial distribution of metals and magnetic susceptibility

Elevated levels of magnetic susceptibility can be found throughout this urban amenity signifying the strong presence of magnetic particles in these soils. The contents of metals Cu, Pb and Zn in the surveyed samples exhibit a considerable enhancement compared to regional background values. Total lead concentrations ranged from 28 to 6753 mg kg\(^{-1}\). Copper concentrations were found to vary from 15 to 2281.50 mg kg\(^{-1}\) and zinc ranged from 56 to 4770 mg kg\(^{-1}\). In the north east corner, soils are reddish in colour indicating the presence of industrial waste. Historically, a fertilizer plant was situated adjacent to the park. It processed pyrite ores. There are some high value outliers of Cu, Zn and particularly Pb in this area. In particular, a ‘high-high’ value cluster of Fe, \(\chi_{\text{grass}}\), \(\chi_{\text{lab}}\) and Fe are a feature of this area which coincides with a ‘high-high’ value cluster of \(\chi_{\text{per}}\). High \(\chi_{\text{lab}}\) and Fe are associated with natural processes. Reddish soils can also be found in the central west region of the sports ground, covering the main football pitch where patches of bare soil are visible particularly around goal posts (Carr et al., 2008). The magnetic susceptibility sensor was also capable of detecting these sections of the park as the most highly contaminated. The northern and western sections are the most heavily contaminated. The northern and western sections are the most highly contaminated. The northern and western sections are the most highly contaminated.

A Pearson’s correlation was performed, after necessary data transformations between magnetic susceptibility datasets \(\chi_{\text{grass}}\), \(\chi_{\text{lab}}\), \(\chi_{\text{grass}}\) and \(\chi_{\text{lab}}\) (Gibson and George, 2013). A spatial distribution map of the surveyed sub-section of the study area can be seen in Fig. 5. It is possible to identify magnetic anomalies in the lower half of the surveyed region visible as white spots. The closer to the surface the more defined the body of the anomaly appears. The appearance of these anomalies suggest the presence of large metallic objects approximately 1–1.5 m below the surface. A comparison to the results obtained in this survey can be made with field- and laboratory-based \(\chi\) measurements and Fe content of soils samples taken in this section of the park (see Fig. 6). Each of these parameter maps featured elevated measurements in the same locale as the gradiometry survey. This infers that the enhanced magnetic measurements recorded in this area are related to anthropogenic waste as proposed and not naturally occurring.

3.4. Comparison between \(\chi\) and gradiometry surveys

A single magnetic reading cannot determine the exact depth or source of magnetic anomalies in soils. However, with a magnetometer in gradiometer mode acquiring two simultaneous readings from two sensors located at different heights it is possible to estimate the depth of magnetic anomalies based on their associated measurements (Gibson and George, 2013). A spatial distribution map of the surveyed sub-section of the study area can be seen in Fig. 5. It is possible to identify magnetic anomalies in the lower half of the surveyed region visible as white spots. The closer to the surface the more defined the body of the anomaly appears. The appearance of these anomalies suggest the presence of large metallic objects approximately 1–1.5 m below the surface. A comparison to the results obtained in this survey can be made with field- and laboratory-based \(\chi\) measurements and Fe content of soils samples taken in this section of the park (see Fig. 6). Each of these parameter maps featured elevated measurements in the same locale as the gradiometry survey. This infers that the enhanced magnetic measurements recorded in this area are related to anthropogenic waste as proposed and not naturally occurring.

3.5. Relationship between metals and \(\chi\)

A Pearson’s correlation was performed, after necessary data transformations between magnetic susceptibility datasets \(\chi_{\text{grass}}\), \(\chi_{\text{lab}}\), \(\chi_{\text{grass}}\) and \(\chi_{\text{lab}}\) (Gibson and George, 2013). A spatial distribution map of the surveyed sub-section of the study area can be seen in Fig. 5. It is possible to identify magnetic anomalies in the lower half of the surveyed region visible as white spots. The closer to the surface the more defined the body of the anomaly appears. The appearance of these anomalies suggest the presence of large metallic objects approximately 1–1.5 m below the surface. A comparison to the results obtained in this survey can be made with field- and laboratory-based \(\chi\) measurements and Fe content of soils samples taken in this section of the park (see Fig. 6). Each of these parameter maps featured elevated measurements in the same locale as the gradiometry survey. This infers that the enhanced magnetic measurements recorded in this area are related to anthropogenic waste as proposed and not naturally occurring.

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Vegetation Cover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaplňka et al. (1997, p. 392)</td>
<td>Not stated. (\text{&quot;Attention was paid to keep constant conditions at the measurement sites (regarding e.g. vegetation cover)&quot;} )</td>
</tr>
<tr>
<td>Lecoanet et al. (1999)</td>
<td>Not stated. Measurements taken at graduated distances from ground.</td>
</tr>
<tr>
<td>Schibler et al. (2002, p. 47)</td>
<td>Vegetation. (\text{&quot;The preferred measurement surface is covered well in litter. No surface preparation is allowed, except for removing high grass or branches.&quot;} )</td>
</tr>
<tr>
<td>Schmidt et al. (2005)</td>
<td>Grass/Grass removed.</td>
</tr>
<tr>
<td>D’Emilio et al. (2007)</td>
<td>Grass/Grass removed.</td>
</tr>
<tr>
<td>Magiera and Zawadzki (2007, p. 21)</td>
<td>Vegetation. Measurements were taken without any surface preparation, except for cutting of high grass or removal of twigs.</td>
</tr>
<tr>
<td>Zawadzki et al. (2007, p. 115)</td>
<td>Vegetation. Measurements were taken without any surface preparation, except for cutting of high grass or removal of twigs.</td>
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<tr>
<td>Kaplňka et al. (2008)</td>
<td>Grass</td>
</tr>
<tr>
<td>D’Emilio et al. (2010)</td>
<td>Grass removed</td>
</tr>
<tr>
<td>Zawadzki et al. (2010)</td>
<td>Vegetation/Without vegetation layer (referred to as organic layer (OL))</td>
</tr>
<tr>
<td>D’Emilio et al. (2012)</td>
<td>Grass removed</td>
</tr>
<tr>
<td>Lukasik et al. (2015)</td>
<td>Surface measured using an MS2D Bartington loop.</td>
</tr>
<tr>
<td>Grison et al. (2016)</td>
<td>The soil surface volume magnetic susceptibility was measured.</td>
</tr>
</tbody>
</table>

Table 3
Summary of literature that used a MS2D sensor with the objective of obtaining magnetic susceptibility measurements in soil studies.
magnetic susceptibility datasets and the (In)metals (Fig. 7). It is evident that the magnetic signal is increased for soils affected by anthropogenic waste (Fig. 8).

3.6. Principal Component Analysis (PCA)

A Principal Component Analysis (PCA) was applied to the metal and magnetic susceptibility datasets. Prior to carrying out PCA, the variables were standardised as they were on different measurement scales. Based on the eigenvalues and scree plot results, two principal components (Factor I and Factor II) were selected. The obtained Factors were rotated using varimax which allows an easier interpretation of factor loadings (Boruvka et al., 2005; Manta et al., 2002). The resulting rotated Factor loadings and Communalities can be found in Supp. Mats. The cumulative variance % explained by Factor I and Factor II is > 90%.

A projection of the components is illustrated in Supplementary materials. All three magnetic susceptibility measurements are positively loaded close to the second axis. $\kappa_{\text{grass}}$ and $\kappa_{\text{no grass}}$ are particularly close reiterating the similarity between the before and after in situ magnetic susceptibility measurement of the topsoil. Factor I is dominated by Cu, Fe, Pb and Zn. Based on the history of the site, the spatial distributions and Pearson correlations of these metals, they are interpreted as having an anthropogenic origin. The concentrations of Cu, Pb and Zn are tightly clustered close to the first axis and indicate they are of the same anthropogenic origin in the topsoil sampled. The position of Fe close to this clustering is understandable as Fe is heavily associated with the anthropogenic metals but also naturally occurring in soil. Laboratory-based $\kappa_{\text{lab}}$ features in between both clusters but is more closely associated with Factor II. Based on previous interpretations of the relationships of $\kappa_{\text{lab}}$ and the other soil parameters the reason for this positioning may be related to this technique being a more sensitive measure of the field-based MS measurements and because the measurements were made on the same homogenized soil samples as were used to obtain the metal concentrations. The results of the PCA were also plotted on two maps (see Fig. 8) which correspond well with the spatial distribution maps of magnetic susceptibility and metal concentrations. Factor I which was dominated by the metal variables (Cu, Fe, Pb and Zn mg kg$^{-1}$) closely resembles the distributions of metals which feature elevated concentrations expanding the length of the western section and dominating the northeast corner. Factor II primary elevated values are spread across the northern section and down the western pitch, a pattern mirrored by the volume magnetic susceptibility distribution maps.

4. Conclusions and recommendations

This study rea...
Overall, magnetic surveying is a more cost effective alternative to geochemical surveying and can be used for large scale campaigns investigating potentially contaminated soils with anthropogenic particulates.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envres.2017.02.032.

References


