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Effects of metal pollutants on magnetic and chemical properties of soils and plant biomass: experimental studies in Environmental Magnetism

by

Birendra Sapkota

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Effects of metal pollutants on magnetic and chemical properties of soils and plant biomass: experimental studies in Environmental Magnetism

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DECLARATION OF CO-AUTHORSHIP/PREVIOUS PUBLICATION

This thesis includes three original papers that have been previously published/submitted for publication in peer reviewed journals, as follows:

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ABSTRACT

Understanding the interactions and effects of biotic and abiotic factors on magnetic parameter measurements used to assess levels of pollutants requires experimental analysis of potential individual parameters. Using magnetic and chemical measurements, three separate experimental studies were conducted in order to evaluate the separate and combined effects of soil composition, atmospheric exposure, and contaminant levels on soil magnetic susceptibility (MS) measurements, plant growth and metal uptake by plants. Experiment 1 examined the effects of incorporating an artificial Fe-rich contaminant into a synthetic soil on surficial soil magnetic properties and plant growth inside a greenhouse. Periodic measurements of surficial soil MS showed significant decreases in MS values in the three treatments (two levels of Fe-contamination and controls), with the greatest reduction in soils with the most contamination, and the least in controls. Three potential causes were suggested: Fe uptake by plants, magnetic minerals transformation, and downward migration of Fe-particles. Some arguments for the first two causes were discussed; however, the third possibility was separately evaluated in the second and third experiments. In the follow-up study (Experiment 2) conducted to examine the effects of ambient atmospheric pollution on magnetic and chemical properties of soils and plant biomass, the overall surficial soil MS was found to be significantly higher in synthetic soils exposed to a natural atmosphere in comparison to controls placed in a greenhouse. Root biomass samples taken from the exposed soils had much higher trace/heavy metal concentrations. Such increases in soil MS and bioavailability of metals in the exposed soils indicate that atmospheric pollution affected the soil and plants grown in there. Microscopic observations of Fe-rich particles from the post-harvest exposed soil revealed morphologies similar to Fe-containing particulates from power plants and transportation and related sources. Experiment 3 examined the vertical migration behavior of Fe-particles in natural soils, and contaminated soil cores showed magnetic enhancement at depths of 2 to 9 cm, with the Fe-rich particles at that depth having very similar morphologies to the contaminant (magnetite powder) used, suggesting that the contaminant migrated vertically downward in soil at a observable rate, most likely due to infiltration of rainwater.

Keywords: atmospheric pollution, magnetic mineral transformations, magnetic susceptibility, metal uptake, vertical migration

DEDICATION

To my parents, Mr. Punya Prasad Sapkota and Mrs. Uma Devi Sapkota; my spouse, Ambika Paudel, and our beloved son, Abiraj

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LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	analysis of variance
BMCT	Bonferroni multiple comparison test
EDS	energy-dispersive X-ray spectroscopy
H	external magnetic field
Hz	Hertz (per second)
ICP-OES	inductively coupled-plasma optical emission spectroscopy
K	volume magnetic susceptibility
LSD	least square distance
M	volume magnetization
MD	multi domain
MMVFTB	Magnetic Measurements variable field translation balance
MS	magnetic susceptibility
PSD	pseudo-single domain
SD	single domain
SEM	scanning electron microscopy
SP	superparamagnetic
XRD	X-ray diffraction
χ	mass specific magnetic susceptibility
$\chi_{FD}\%$	frequency dependence of susceptibility

CHAPTER 1

INTRODUCTION

1.1 Background and objectives

‘Environmental magnetism involves the application of rock and mineral magnetic techniques to situations in which the transport, deposition, or transformation of magnetic grains is influenced by environmental processes in the atmosphere, hydrosphere, and lithosphere’ (Verosub and Roberts 1995). The potential for addressing environmental problems with environmental magnetic techniques was first recognized in the early 1950s, when Le Borgne (1955) studied the enhancement of magnetic susceptibility (MS; the degree to which a material is magnetized when placed in an external magnetic field) in topsoil. The new field of environmental magnetism broadened significantly, however, with an increasing array of uses after the 1980s. In particular, environmental magnetic techniques have been used as a tool for detecting heavy (i.e., toxic) metal contamination caused by industrial emissions in soils and sediments, and for providing tracers of environmental conditions. Scope and applications of environmental magnetism have been provided in two seminal publications: Thompson and Oldfield (1986) and Evans and Heller (2003).

In recent years, environmental magnetism has been recognized as an interdisciplinary field, and its uses have expanded rapidly. A considerable number of studies have been conducted on mineral magnetic studies of soils (e.g., Maher 1986, Shi and Cioppa 2006), lake and marine sediments (e.g., Caitcheon 1993, Chan et al. 1998, Cioppa et al. 2010, Petrovsky et al. 1998, Shouyun et al. 2002) and atmospheric dust (e.g., Blaha et al. 2008, Gautam et al. 2004, Goddu et al. 2004, Hunt et al. 1984). Similarly, several studies have been performed to identify and delineate metal-contaminated sites and to determine the intensity of soil pollution on the basis of toxic metal content (e.g., Charlesworth and Lees 2001, Jordanova et al. 2008, Petrovsky et al. 2000, Sharma and Tripathi 2008). Some other studies related to biomonitoring of air quality (e.g., Jordanova et al. 2003, Kletetschka et al. 2003, Moreno et al. 2003, Urbat et al. 2004) have examined magnetic properties of plant parts (e.g., leaves, bark – considered as passive collectors) and organic contents to evaluate the degree of atmospheric pollution, and to determine the spatial and temporal distribution of atmospheric contamination in their studied areas. This wide range in applications illustrates the advantages of magnetic methods over conventional chemical methods, chiefly because they are rapid, simple, non-destructive and sensitive to low detection levels (Petrovsky and Ellwood 1999). Progress in the development of environmental magnetic techniques and sensitive instruments has made it easier to detect useful magnetic signals from environmental materials.

Although a wide range of magnetic studies dealing with atmospheric particulates and soil pollution have been conducted, monitoring of the effects of atmospheric pollution on soil magnetic properties and on plant biomass has not been performed so far. In addition, the dynamics and fate of the atmospheric particulates in soil has not been studied systematically using environmental magnetic techniques (Kapicka et al. 2011). This indicates a lack of sufficient knowledge in the degree of uncertainty about the extent to which environmental magnetic techniques would work in such cases. Therefore, this research was aimed at assessing the application of these techniques to monitor the effects of atmospheric metal pollutants (in particular Fe and correlated toxic metals) on the magnetic properties of synthetic soils, as well as how these pollutant particles are affected after deposition by physical, chemical and biological processes in soil.

Studies examining the effects of atmospheric pollution on soils have investigated the records from surface layers of soil and have found that anthropogenic particulate deposition has contributed significantly to the magnetic component of these surface soils (e.g., Boyko et al. 2004, Chapparo et al. 2010, Kapicka et al. 1999, Strzyszcz and Magiera 1996). Often in such studies, the concentrations of (ferri)magnetic particles and Cr, Mn, Co and Cd are found to correlate; and fine-grained ferromagnetic particles seem to have a correlation with Pb and Zn (Chapparo et al. 2010). All such studies have used magnetic parameters (e.g., bulk and mass-specific MS, temperature dependence of MS, magnetic permeability and coercivity) to determine the degree of soil pollution by considering it to be a function of the concentration of iron-bearing minerals and, through correlation, of the heavy metals. Similar magnetic parameters are also used in this research, in order to examine the effects of atmospheric pollutants on magnetic and chemical properties of soils and on plant biomass (shoots and roots), through three separate experimental studies:

Experiment 1 was conducted to examine the effects of artificial Fe-contaminant (magnetite powder) levels on the surficial magnetic properties of synthetic soils, as well as on shoot biomass and growth in a closed system (greenhouse). As Fe-containing particles are common both in soils contaminated with industrial effluents and as atmospheric particulates (Huliselan et al. 2010), as well as being detectable by magnetic techniques, such techniques were used in this biomonitoring study.

Phytoremediation studies, often conducted on metal-contaminated soils (e.g., Lai et al. 2008, Weiss et al. 2006) and mine tailing areas (e.g., Arreghini et al. 2006, Black 1995, Pulford et al. 2003), estimate the decrease in metal concentration in the contaminated soil and have become increasingly popular as an indirect method of treating shallow soils with low levels of contamination. This experimental study, in addition to examining the effects of Fe-contaminant levels on soil magnetic properties and on plant uptake, was also focused on assessing the usefulness of magnetic susceptibility measurements in quantifying the results of phytoremediation studies. The hypothesis that a considerable plant uptake of Fe and other commonly coexisting elements (such as, Ni, Cr, Co) would decrease soil MS, and that routine measurements of soil MS during the growth phase could be a good proxy for estimating the levels of soil pollution, was tested.

Experiment 2 was a follow-up study to Experiment 1, consisting of controls (inside a greenhouse) and exposed soil (placed in open air) and without added artificial Fe-contaminant, thus isolating the effects of atmospheric pollution on magnetic and chemical properties of soil and on root biomass. In addition, the magnetic and chemical characteristics of atmospheric particulates were examined and linked to their sources, as has been done in past studies (e.g., Bityukova et al. 1999, Hoffmann et al. 1999, Morris et al. 1995, Shu et al. 2001, Spassov et al. 2004). Vertical migration of Fe-containing particles due to watering and plant growth was also determined through MS profile measurements in potted soil from this experiment. These profile measurements were performed on the controls but not the exposed soil samples because the magnetic mineralogy, concentration and granulometry within the exposed samples could have been altered by the presence of, or the translocation of, Fe-containing atmospheric pollutants.

In the controls, increases in MS in soil below the surface could only be attributed to downward migration or chemical reactions during the growth period. Furthermore, comparisons were made between magnetic measurements (particularly soil MS) and element concentrations of trace/heavy metals in soils and plant biomass, through correlations. Such correlations between MS and concentrations of heavy metals in soils and atmosphere have been presented in some previous studies (Hay et al. 1997, Heller et al. 1998, Kapicka et al. 1999, Sagnotti et al. 2005).

While the growth experiments mainly focused on the effects of the Fe-contaminant on surficial magnetic properties of soils, Experiment 3 explored potential downward migration of the Fe-contaminant in natural soil. Some studies have shown that metal pollutants deposited on soils alter the chemical composition of these soils and further changes in soil chemical composition are due to uptake and storage of the metals by plants (e.g., Xian 1989) and/or translocation (migration) of metals in soil (Kapicka et al. 2011). As a consequence, these processes can affect the measures of soil pollution. Many authors have indicated a significant loss of metals from the topsoil, using either a mass balance approach (e.g., Ashworth and Alloway 2004, McBride et al. 1999) or in leaching experiments on soil columns (e.g., Gray et al. 2003, McLaren et al. 2004). Although a few studies have assessed the vertical extent of heavy metal contamination of soil by examining magnetic properties of soil cores in industrial areas (e.g., Blaha et al. 2008, Rosowiecka and Nawrocki 2010), monitoring of the migration behaviour of metal pollutants in soils using magnetic techniques has yet to be thoroughly tested. Therefore, this study was conducted in order to assess the migration of metal contaminants in soil and their subsequent effect on soil magnetic properties, as well as to monitor the surface pollution level.

Thus, within and between these three experiments, a number of potential variables are examined using both magnetic and chemical techniques: artificial contaminant level effects on surficial soils and shoot biomass in a controlled environment (Experiment 1); atmospheric exposure effects on surficial soils and root biomass in an open environment (Experiments 2, 3); pollutant distribution within the plants (Experiments 1, 2) and vertical migration of pollutants within artificial and natural soils (Experiments 2, 3).

1.2 Materials and methods

This section provides a brief description on the materials and methods used for each of these experimental studies (for overview see Fig. 1.7). The details are provided in their respective chapters.

1.2.1 Experiment 1: Effects of Fe-contaminant on magnetic and chemical properties of soil and plant biomass during growth

Three essential soil components – sand, topsoil and organic matter (all from Alltreat Farms®) – were used to construct a synthetic soil, and two soil mixtures were prepared from this starting material by changing the ratio of sand and topsoil, to represent some of the variability of soil mixtures found in nature. Two different levels of contaminant concentrations (low – 0.01 g/kg soil, and high – 0.05 g/kg of soil, details of level determination are in Chapter 2) were used to treat the soil to represent some variability in contaminant concentration in nature. These concentration levels are considered to represent the lower end of the Fe concentration range in urban soils determined in previous studies, such as Magiera et al. (2007) and Madrid et al. (2002). In order to examine the effect of contaminant levels in plants, Patio-hybrid tomato plants (http://www.stokeseeds.com) were grown in the synthetic soil inside a greenhouse located at the University of Windsor, Canada. In phytoremediation studies, plant species are usually selected based on their adaptability to climatic conditions, mineral nutrients present in the soil, and their ability to accumulate metals in higher concentration (hyperaccumalators) (Porebsca 1999). For this study, however, this plant species was used because it could easily be grown inside and outside of a greenhouse and has a relatively short growth cycle (approximately 3 months), but it is not a hyperaccumalator. Other species of tomato plants have been used previously for investigative purposes, i.e. investigations of iron uptake mechanisms, plant metabolic response to iron-deficiency stress, uptake of trace elements through time, and the effect of fly ash amendments in trace element uptake (Brown 1978, Brown and Jolley 1989, Jensen et al. 2004). The conditions imposed (such as growing containers, temperature, water and fertilizer supply, etc) on the growing plants from all three treatments (low and high contaminations, controls) (Fig1.1) were identical.

Fig. 1.1 Control and treated sample sets of Experiment 1 inside a greenhouse

Because the soil was synthetic, and the experiment was conducted in a greenhouse, the variables of atmospheric particulate contamination and unknown background levels of MS were eliminated. The effects of Fe-contaminant on plant height and shoot biomass, and on soil magnetic properties (particularly surficial soil MS) were measured *in situ* at four different growth stages (seedling, vegetative, reproductive and harvestable stages[1]).

The *in situ* magnetic measurements on the growth media (i.e., synthetic soils) were made using the Bartington MS2 system and a MS2F sensor. The MS2F (Fig.1.2) is a miniature sensor (35 mm diameter and 85 mm height, sensitivity is 10^{-5} SI in 1.0 range, similar to the MS2B sensor) with a depth of response of 10% at 6 mm from the end face and 4.5 mm from side wall (http://www.ascscientific.com). It is designed to measure

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[1] *Seedling* plants established, about 4 weeks of growth; *vegetative* until first flower opens, about 8 weeks of growth; *reproductive* until first fruiting occurs, about 10 weeks of growth; *harvestable* plant terminated after fully grown, about 12 weeks of growth (Sapkota et al. 2012)

smaller scale variations in MS than the larger (20 cm) search loop (MS2D sensor), and was suitable for this experimental study.

MS measurements were always made on relatively dry (i.e., non-saturated) soils to avoid the possible diamagnetic effects of water. Individual measurements were taken in five equally-spaced locations (3 in each location to ensure repeatability) in each container and averaged to give the MS reading per container at the time of measurement. Care was taken to apply uniform pressure on the probe throughout the measurements, to avoid possible MS variations due to pressure applied (Lecoanet et al. 1999).

Soil sampling was not carried out during the experimental period so as not to disturb the soil properties during plant growth. Therefore, after the plants were harvested, post-harvest bulk soils underwent laboratory magnetic and chemical measurements. Both volume (K) and mass-specific MS (χ) measurements of the soils (background, post-harvest bulk soils and their magnetic extracts) were performed in the lab, using a MS2B sensor. The MS2B (Fig.1.2) is a single sample, dual-frequency sensor, which is used to determine mass or volume susceptibility measurements of a sample. Although it can be operated at two different frequencies (4.65 Hz and 4.65 kHz) for the study of the frequency dependence of susceptibility (χ_{FD}%), the low frequency setting was selected for single frequency measurements, as is routine practice.

Fig. 1.2 (**a**) MS2 meter; (**b**) MS2B, and (**c**) MS2F sensors used for the study.

(Source: Paleomagnetics and Rock Magnetic Lab, University of Windsor).

In the laboratory measurement of soil MS, an AGICO KLY-3S Kappabridge (Fig1.3a) was used for identification of magnetic minerals and for comparing the degree of magnetic mineral transformations between the controls and the treated soils. The thermosusceptibility, temperature (T) variation of low-field magnetic susceptibility (K) of soil samples in the temperature range from ambient temperature to 700 °C, was measured using this system. The K−T curves generated from this measurement are strongly controlled both by magnetic mineralogy and grain size distributions (Liu et al. 2005), and characteristics of thermosusceptibility curves (and in particular Curie temperature) were used to identify the magnetic mineralogy in soil samples. Complementary information on the magnetic mineralogy and granulometry was determined through the measurement of magnetic properties using a MMVFTB (Magnetic Measurements variable field translation balance Fig1.3b). Magnetic Hysteresis, which is the lack of retraceability or reversibility of the magnetization curve, can be displayed for a specimen by plotting a graph of the magnetization (M) produced by a cyclic field (H). Paramagnetic and diamagnetic minerals do not exhibit hysteresis; instead they show a reversible linear relationship between the applied field and magnetization intensity. The parameters extracted from the hysteresis loop used to characterize the magnetic properties of samples were - the saturation magnetization (*Ms*); the remanence (M*r*); the coercivity (H*c*); and their ratios. The shape and characteristics of this loop were used to identify the magnetic mineral types (soft or hard) and also domain (magnetic 'grain') size.

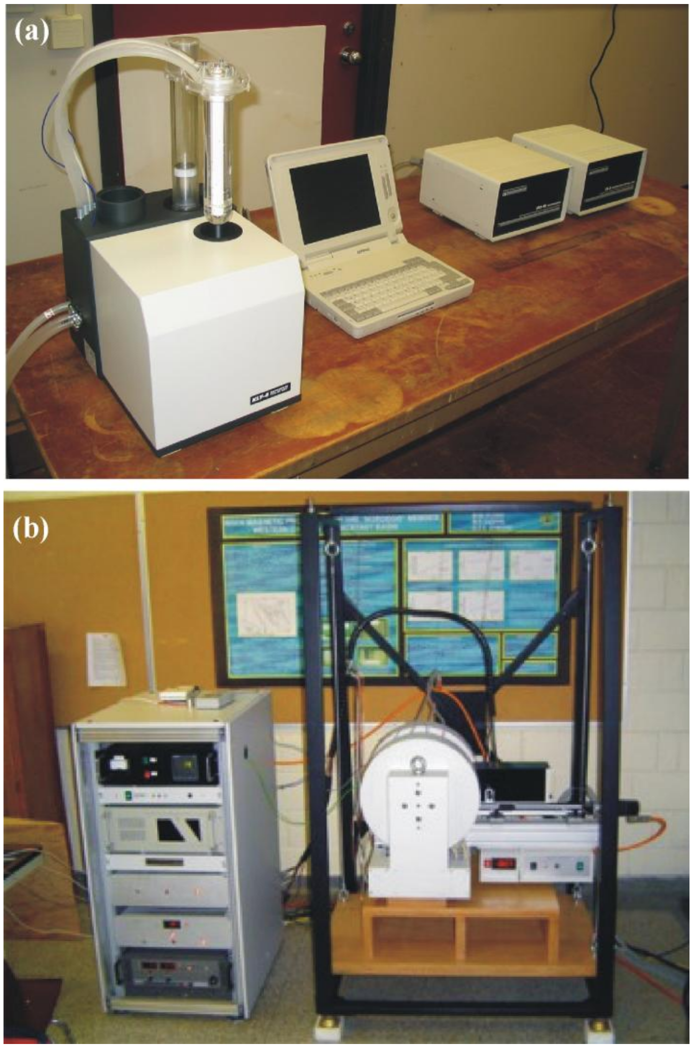

Fig.1.3 (**a**) AGICO-KLY3S, and (**b**) MMVFTB

(Source: Paleomagnetics and Rock Magnetic Lab, University of Windsor)

While rock magnetic measurements indicate the dominant magnetic carrier in a sample, identifying all the possible magnetic minerals in soil samples is more difficult, and the use of the powder X-ray diffraction (XRD) technique provides additional information through the identification of characteristic crystal structure. The observed X-ray diffractograms, by comparison with standard reference patterns and measurements, allow for identification of the material (Goldstein 2003; Fig. 1.4). In this experiment, the powder XRD performed at the University of Windsor was helpful in determining the mineral transformations during the plant growth period by comparing the dominant magnetic mineral types in soils before and after the growth. For such determinations, Match!® software and the Standard Diffraction Patterns were used, with the latter found to be more useful. Finally, ICP-OES (inductively-coupled plasma optical emission spectroscopy) was used to obtain concentrations of a number of elements present in the plant biomass and soils and to compare the differences in elemental uptake by plants from different treatments. Thus, the overall changes on magnetic and chemical properties of soils between their initial and post-harvest stages were evaluated using both magnetic and chemical measurements.

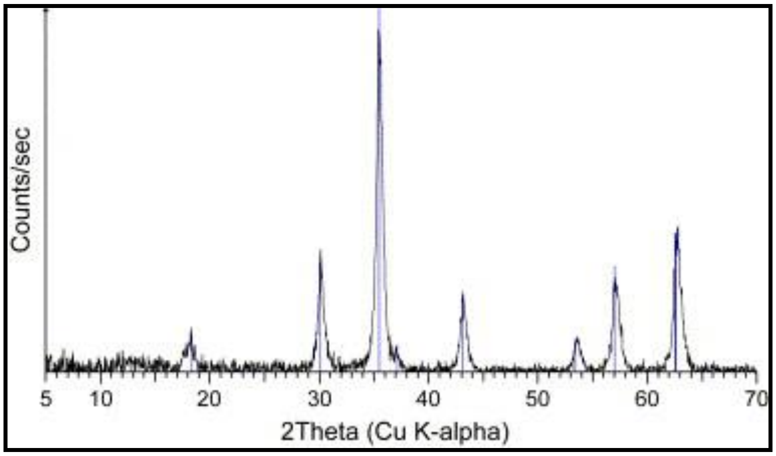

Fig. 1.4 X-ray powder diffractogram of magnetite, showing its primary characteristic diffraction peak at 35.4 degrees of 2theta (Legodi and Waal 2007).

1.2.2 Experiment 2: Detection of atmospherically-derived metal pollutants in soils and metal uptake in plants

Experiment 2 was conducted within a community garden, located on the University of Windsor Campus (Fig.1.5), following the methodology used in Experiment 1 to prepare the synthetic soils and to measure magnetic and chemical measurements during the growth of tomato plants, but eliminating the use of an artificial Fe-contaminant. The effects of atmospheric pollutants on magnetic and chemical properties of soils and the plant biomass were determined by comparing the properties of specimens grown within and outside a greenhouse on the property.

Fig.1.5 Control (inside greenhouse) and exposed (outside) soil sample sets of Experiment 2. HEPA air filters were placed in the vents to trap the majority of the atmospheric particulates while allowing air to pass through.

In addition to the magnetic and chemical measurements performed, as described in Section 1.2.1, ESEM (environmental scanning electron microscopy) equipped with EDS (energy-dispersive X-ray spectroscopy), located at the Great Lakes Institute for Environmental Research, University of Windsor, were used to identify the atmospheric pollutants collected in the exposed soil samples. While particle external morphology (size, shape) was examined under SEM, EDS was used to identify the major elements associated with the specimen, through its chemical composition. A spectrum of the energy versus relative counts of the detected X-rays was obtained and evaluated for determinations of the elements present in a soil sample (Fig.1.6).

Vertical migration of Fe-containing particles in potted soil was also examined in this experiment. The top 5 cm of the 8 cm deep longitudinal section of the container soil was used to construct MS profiles for control samples, by measuring the MS at 1 cm resolution using a MS2F sensor.

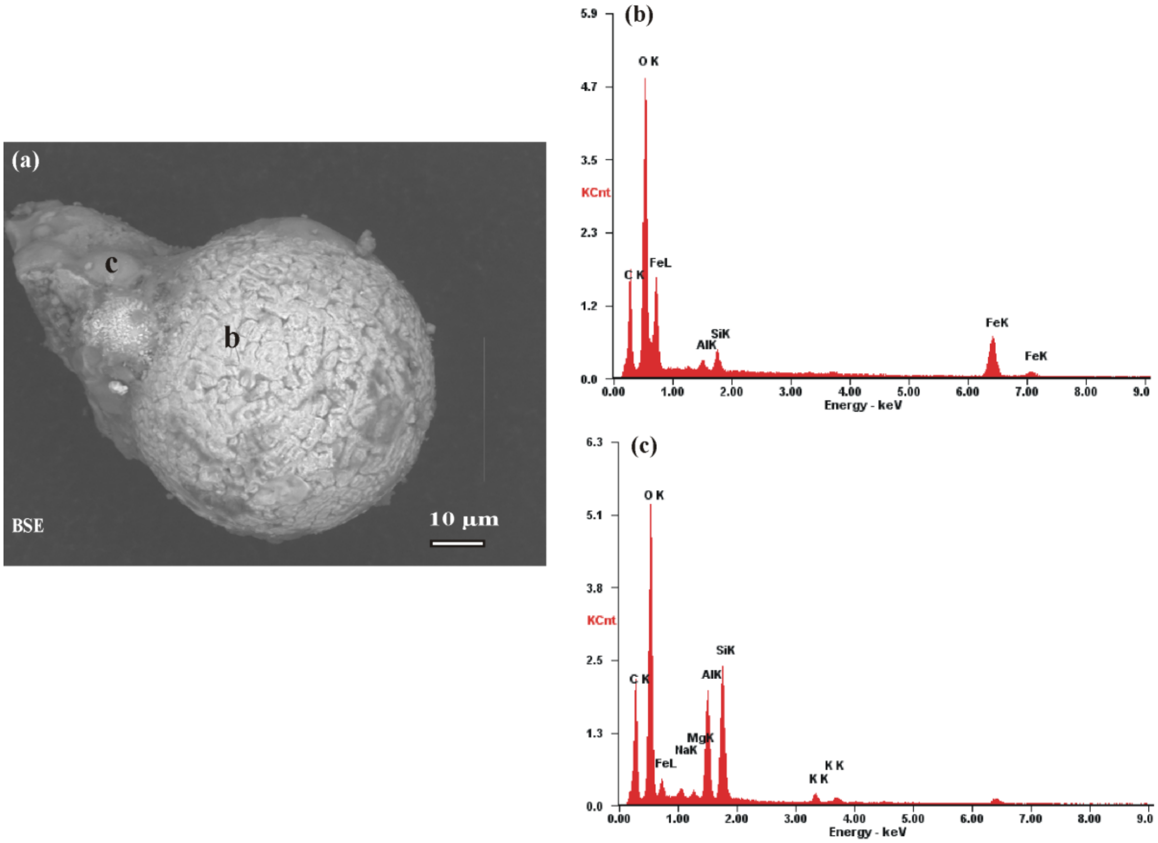

Fig.1.6 **(a)** Micrograph of a magnetic spherule, with both the bright areas (which are iron-rich, spectra **b**) and dark areas (which are most likely alumino-silicates, spectra **c**).

1.2.3 Experiment 3: Vertical migration of metal pollutants in soil

This experimental study was performed in a clay-rich glacial till near Belle River, Ontario. Fe-contaminant (magnetite-powder) was distributed (at a rate of 10g contaminant/tube) on the surface of vertically-inserted PVC test tubes (8” diameter and 16” length) and the surficial MS was monitored periodically for four months, using the MS2F sensor. As the Fe-containing particles infiltrate into the soil, it would be expected that the magnetic signal would decrease on the surface and the corresponding magnetic enhancement in soil layers resulting from the downward vertical migration could be traced by examining soil cores obtained from test tubes. Therefore, at the end of the experiment, soil cores were taken from the test tubes, and the MS of the individual soil layers at depths were measured using MS2B sensor, and the MS profiles obtained were compared to those from background (non-contaminated) soil. Susceptibility maxima were determined in each soil core, presumably corresponding to the maximum vertical migration of Fe particles in soil horizons during the experimental period in the given physicochemical conditions. SEM-EDS techniques were used to study the properties of soil sections with an enhanced magnetic signal, as determined from soil cores. In particular, the Fe-particles within the soils (obtained as magnetic extracts) were investigated to examine whether their morphology was similar to that of the contaminant used. Such similarity would then provide assurance that the magnetic enhancement in soil below the surface was due to vertical migration of the contaminant that had been distributed on the surface, but not due to the magnetite present *in situ*. Studies of this kind would help to enhance our understanding of the downward migration behavior of toxic metals in natural environments.

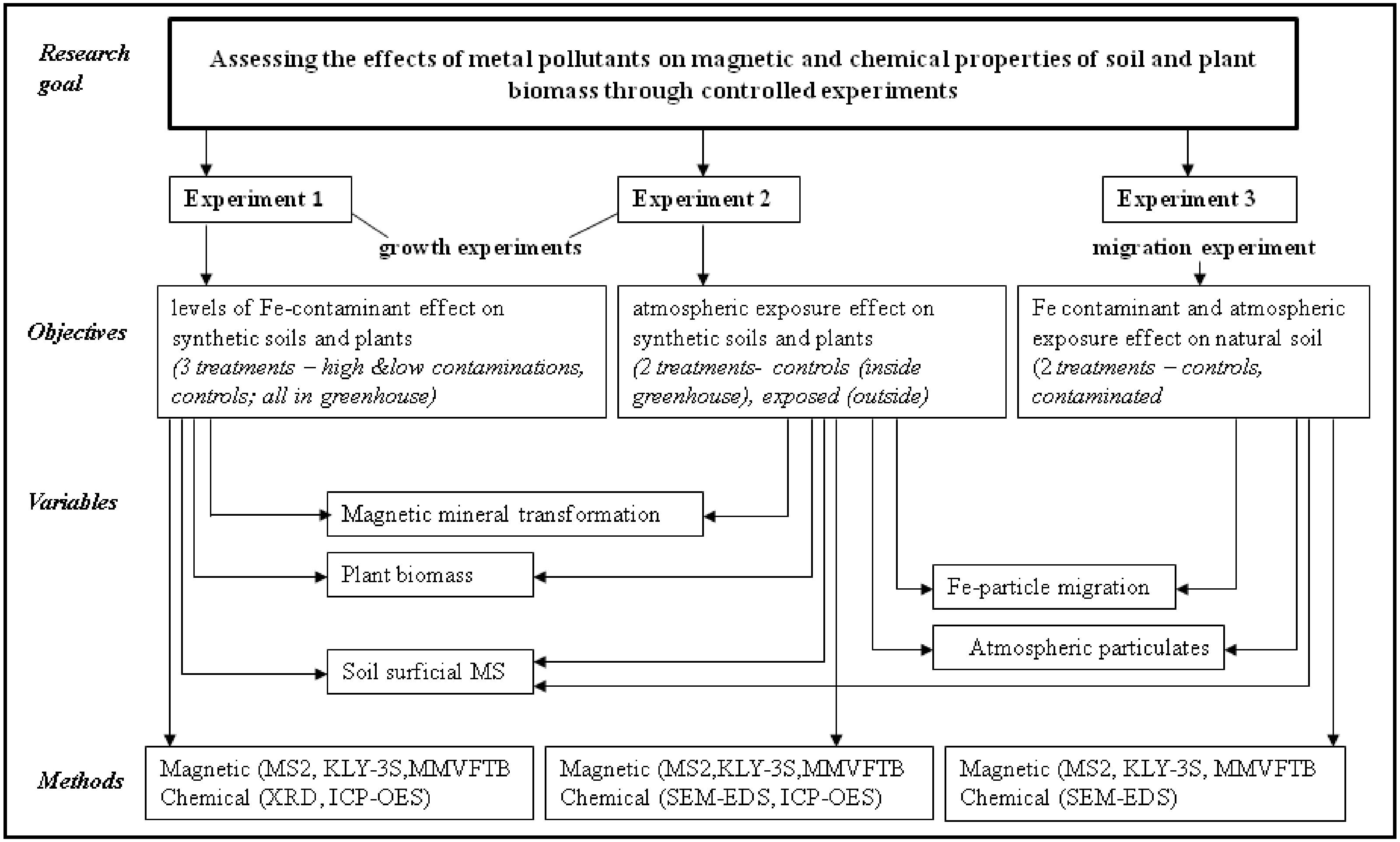

Fig. 1.7 Schematics showing an overview of the experimental studies conducted in this research

1.2.4 Data analysis

Statistical analysis of the experimental data (mean values of MS, plant morphology and chemical compositions of soils and plant biomass) were performed using the SPSS_ 12.0 and Excel (Microsoft Inc.) software packages. In Experiment 1, the differences in surficial MS values of background soils and those at plant harvestable stage in controls and treated samples were analyzed using one-way ANOVA. Similarly, the significance of the differences in plant height and dry biomass were also determined using this method. A null-hypothesis was not specifically set up and tested, rather, the MS, biometric and chemical data obtained were found to be different in their mean values between the treatments, therefore, these datasets were analyzed with ANOVA to test the significance of the differences. To further explore the effect of the parameters used (soil mixture vs. contamination levels), the Bonferroni Multiple Comparision Test (BMCT) was performed. BMCT is a measure of the significance of the parameters in causing change in the variables being investigated (Norusis 2000).

In Experiment 2, potential relationships between a single dependent variable (i.e., surficial MS) and two independent variables (i.e., treatment, soil mixture type) were assessed using a Linear Mixed Model, which used a confidence interval of 95% (p = 0.05), and statistical tests of pair-wise comparisons between soil mixture and treatment were made using a post-hoc Least Significant Difference technique (LSD). The LSD test is good for planned comparisons, and for determining whether the difference found between two treatments is due to the treatment or simply due to a random chance (Saville 1990). In addition, coefficient of determinations between the surficial soil MS and geochemical composition on some selected element concentrations (Fe, Ti, Mn) in plant biomass and bulk soils were calculated. Linear Mixed Model was also used in Experiment 3 to determine the significance of the differences in surficial MS values between the initial and post-test measurements from controls and treated tubes.

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CHAPTER 2

INVESTIGATION OF THE CHANGES IN MAGNETIC AND CHEMICAL PROPERTIES OF SOIL DURING PLANT GROWTH IN A CONTROLLED ENVIRONMENT

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2.1. Introduction

Magnetic measurements have been used as a proxy for measurement of toxic metal contamination in soils and sediments caused by industrial emissions (Sharma and Tripathi 2008). Many researchers have studied the magnetic properties of atmospheric pollutants (e.g., Goddu et al. 2004, Muxworthy et al. 2002, Spassov et al. 2004) and toxic metals in polluted soils (e.g., Charlesworth and Lees 2001, Gautam et al. 2005, Hanesch and Scholger 2002, Schmidt et al. 2005). Positive (moderate to strong) correlations between the results of magnetic measurements and chemical analysis of soils and sediments have been presented in some studies (e.g., Strzyszcz and Magiera 1998), and these show evidence that the concentration of magnetic minerals present in samples exposed to toxic elements derived from anthropogenic activities is related to the concentration of these toxic elements (Petrovsky et al. 1998).

In recent years, researchers have extended the application of magnetic methods in studying environmental pollution by integrating them with other disciplines of science, including biological applications, such as the biomonitoring of traffic air pollution using magnetic properties of tree leaves (e.g., Matzka and Maher 1999, Moreno et al. 2003), and civil/environmental engineering applications, such as studies of building facades to measure erosion rates and monitor urban atmospheric contamination (Monna et al. 2008). Porsch et al. (2010) showed that *in situ* magnetic susceptibility measurements were able to precisely detect magnetite transformation mediated by microbes (*S.oneidensis*) in the culture. This study examined the potential for using magnetic methods to monitor changes in soil magnetic properties (concentration of ferrimagnetic minerals and magnetic mineral transformations) during plant growth in metal-contaminated soil and the possible use of these changes as a proxy for monitoring toxic metal uptake by plants.

Metal-accumulating plant species, such as mustard and dandelion, have been shown to transport and concentrate metals from polluted soil into their harvestable parts, such as roots and above-ground shoots (e.g., Ebbs and Kochian 1998, Kovacs et al. 2005, Krolak 2003), in a process known as phytoextraction. Tomato plants have also been used to investigate iron uptake mechanisms, plant metabolic response to iron-deficiency stress, uptake of trace elements through time, and the effect of fly ash amendments in trace element uptake (Brown 1978, Brown and Jolley 1989, Jensen et al. 2004). Jensen et al. (2004) demonstrated that tomato plants increased their uptake of Cd, Co, and Mo as the fly ash content of soil was increased. In this experimental study, tomato (*Lycopersicon esculentum*) plants have been used to investigate the uptake of Fe and two other trace elements (Ni, Mn), which are often found in close association with Fe in material such as fly ash in previous studies (Hansen et al. 1981, Theis and Wirth 1977). In addition, morphological changes in the plants resulting from different levels of the synthetic Fe-contaminant (i.e., magnetite powder) have been studied. This paper presents an evaluation of the application of magnetic techniques, in conjunction with chemical analysis, for the detection of changes in soil magnetic properties and trace metal uptake by plants during their growth in a controlled environment. Such studies can be used to provide rapid, inexpensive information about the progress of phytoremediation in brownfield sites.

2.2. Materials and methods

2.2.1. Plant selection, growth media and treatments

A greenhouse experiment, in which tomato plants were grown in artificial soil mixtures, was carried out at the University of Windsor from May 2009 to August 2009. The patio hybrid (www.stokeseeds.com) variety of tomato plant was selected for the study because it has a relatively short life span (~ 12 weeks), is easily grown in containers, and is determinate (i.e., bears all fruits in a short time interval).

Growth media (i.e., synthetic soils) were prepared by mixing Alltreat Farms® play sand, sterilized natural topsoil, and manure (about one-fifth of the total mixture). From these starting materials, two types of soil mixtures were prepared, one with an equal amount of sand and clay (coded as S50), and the other with a sand to clay ratio of 1:4 (coded as S25), to provide some variability of soil types encountered in natural settings. These soil mixtures were treated with magnetite powder (quoted to be 98% pure, and milled to <5 µm by READE Advanced Materials®, USA) in order to simulate contamination by metals. Magnetite powder was used as a proxy for anthropogenic contamination, as it has been shown in literature to correlate well with anthropogenically-derived toxic materials. The magnetite concentrations used in the experiments were derived using Brake et al.'s (2004) study of fly ash amendments in soil for evaluating trace element uptake in plants. Six soil treatments were prepared from two types of soil mixtures: controls (without magnetite powder), low contaminations (0.01g of magnetite powder/kg of soil) and high contaminations (0.05g of magnetite powder/kg of soil); coded as CT, LCT and HCT, respectively. For LCT and HCT, the powder was spread on the surface of soil to simulate the accumulation of contaminants on the soil surface through atmospheric deposition, and was finally covered with a thin (approximately 1–2 mm) soil film of the same composition to prevent it from being blown or washed away from irrigation. Two contamination levels were used to compare the effect of magnetite powder at different concentrations on plant morphology and metal uptake, and on soil magnetic properties. For both soil mixtures, ten replicates of each treatment were prepared, totaling 60 samples.

Four seeds were sown in each container to ensure that the replicate plant requirement was met, even with a germination rate of 25%. The containers were irrigated daily, and fertilized bi-weekly with a chemical fertilizer (Greencare 20–20–20) dispensed in equal amounts in each container (190 mg/L).

2.2.2. Measurements

2.2.2.1. Morphological measurements

After emergence and establishment, the number of seedlings was reduced to one per container, selecting the best candidate (healthy) among those that germinated. Plant height was measured during four growth stages: seedling, vegetative, reproductive and harvestable[1] stages. A leaf color parameter, green color saturation (or spectral purity), was measured using a fibre optic spectrometer (USB400) in pre- and post- flowering stages of plant growth in order to measure the effect of the Fe amendment, if any, as a

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[1] *Seedling*- plants established, about 4 weeks of growth; *vegetative*- until first flower opens, about 8 weeks of growth; *reproductive*-until first fruiting occurs, about 10 weeks of growth; *harvestable*-plant terminated after fully grown, about 12 weeks of growth.

geochemical stressor to the spectral quality of visible light in the leaves. Measurements were made on leaf faces exposed directly to the light source. In each plant, five measurements were made on leaves that were randomly selected from the bottom of the plant to the apex, and a saturation value (ranging from 0 to 1) per plant was determined by averaging the readings. Chlorophyll concentration, which reflects green color saturation, has also been considered in studies as an indicator of nutritional stress (e.g., Curran et al. 1990).

The masses of the removed seedlings and the harvested plants were measured and calculated on a dry weight basis to determine the total amount of biomass generated. About 2/3 of the total number of plants were oven dried at 100 °C and their dry weight was measured. The dry weight of the remaining plants was estimated by a factor equal to the measured dry weight obtained from the balance of the plants. The conversion factor was calculated from dry weight/wet weight ratio and was found to be approximately 10%.

2.2.2.2. Magnetic measurements

Magnetic characterization of the initial soil mixtures (hereafter referred to as 'background soils', BG) and each component therein was performed by measuring mass-specific magnetic susceptibility (χ) and coercivity properties to determine the total magnetic fraction, and susceptibility dependence of temperature (χ–T) to determine magnetic phases. χ–T measurements were also performed for the contaminant, and a grain size analysis was performed using the Environmental Scanning Electron Microscope at the Great Lakes Institute for Environmental Research , Windsor.

Surficial MS measurements of the growth media (i.e., synthetic soil) were made periodically during plant growth under dry (i.e., non-saturated) soil surface conditions using a Bartington MS2 system and MS2F probe. MS measurements were taken at five locations in each container, one in each of the four corners and one in the centre, and averaged to give the MS reading per container at the time of measurement. To keep soil conditions undisturbed during the experiment, only the post-harvest soil samples underwent laboratory magnetic measurements. The post-harvest container soil was sieved using a 2 mm sieve size and then homogenized and sub-sampled. In order to prevent cross-contamination, the control and treated soils were sieved with different sieve sets. Once sub-sampled, in order to remove the diamagnetic effects of water, all soil samples were dried at room temperature for 24 hours and then stored in 6.8 cm^3 plastic pots for magnetic measurements in the Paleomagnetics and Rock Magnetics Laboratory at the University of Windsor. Room temperature magnetic measurements were obtained, which can discriminate samples rapidly and non-destructively (e.g., by magnetic concentration, mineralogy and grain size) (Maher 1998). A Magnetic Measurement variable field transition balance (MMVFTB) and a vibrating sample magnetometer (RTVSM; Institute for Rock Magnetism, University of Minnestota) were used to obtain hysteresis loops for soils (bulk and magnetic extracts), as well as for plant samples (maximum field 1 Tesla). The shape of the hysteresis loop provides information on the minerals contributing to the magnetic signature, where a flat, fat loop indicates high coercivity (‘hard’) magnetic minerals, and tall, thin, loops indicates low coercivity (‘soft’) magnetic minerals

(Thompson and Oldfield 1986). Thermosusceptibility measurements (χ-T curves) were performed on a KLY-3S Kappabridge with a CS-3 high temperature furnace attached to it and Curie temperatures were calculated using the graphical method referred to in Moscowitz (1981).

2.2.2.3. Chemical analyses

To determine the concentrations of some selected trace elements (Fe, Ni, Mn) in plants, five samples (harvested and oven-dried shoots) from each soil treatment were ground and sub-samples were prepared for microwave-assisted digestion using a CEM Mars 5 microwave digestion oven. The digested samples were later analysed using inductively-coupled plasma optical emission spectroscopy (ICP-OES; Thermo Jarrell Ash Corporation IRIS).

Soil samples were also subjected to chemical analysis. Prior to the analysis, about 500 g of soil was dried and sieved (with 2 mm sieve size) to remove gravel and plant litter. To determine mineralogical transformations of the iron minerals, only the magnetic extracts (obtained by extraction from suspended material using a hand magnet sealed in plastic), were examined using X-ray diffraction (Rikagu MiniFlex^{TM}). Rather than attempting to identify all of the minerals included in the spectra, only the most common magnetic minerals, which were represented by the highest peaks on the X-ray diffractograms, were identified and their relative abundances in the soil were noted. As soil pH can influence the magnetic characteristics of anthropogenic particles (Kapicka et al. 2001), the pH of the background and post-harvest soils were measured. About 40 g of the dried and sieved soil was mixed with 40 g of distilled water (soil to water ratio = 1:1), and pH was measured in the supernatant using a pH meter (Hanna Instruments®, type HI 98127; sensitivity 0.1 pH)**.** All pH readings were automatically temperature compensated.

2.2.3. Data analysis

The variance and significance of the differences among treatments in plant height, dry biomass, MS and trace element concentrations were analyzed using analysis of variance (one way-ANOVA) after testing and determining that the data distribution was normal. Further analysis using a Bonferroni multiple comparison test (BMCT) was done (referring to Norusis 2000) to identify the treatments that are significantly different from one another. The confidence interval was set at 95 % for the purpose of this study and hence the statistical significance was defined as the level of $p = 0.05$.

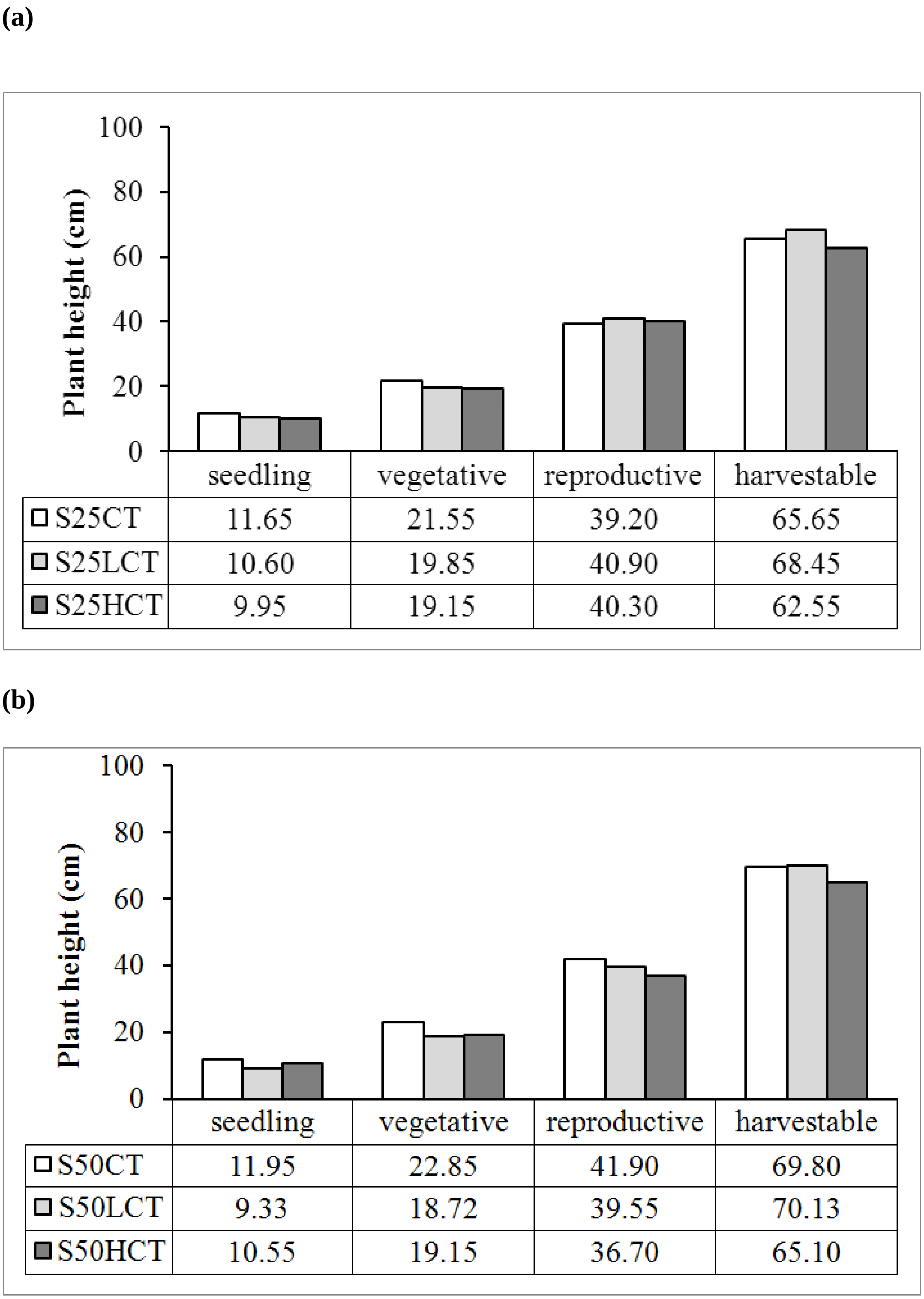
The standard diffraction patterns produced by the Joint Committee on Powder Diffraction Standards (J.C.P.D.S.) were compared to our XRD results in order to identify the magnetic mineral phases in soil. Match! software (developed by Crystal Impact, Bonn, Germany) was used to assist in mineral identification. Hysteresis results were analyzed using the program VFTB Analyzer 1.8 and the temperature variation of MS was processed using Cureval 16.0 (provided by AGICO).

2.3. Results

2.3.1. Plant morphology

The effects of the exposure of tomato plants to different concentrations of magnetite powder was assessed using three variables: plant height, biomass and green color saturation, which are standard measurements of plant health and have good visual changes associated with the treatment. No visual symptoms attributable to toxicity by magnetite powder, such as reduction in leaf size, wilting of shoots, yellowing or dieback of oldest leaves (Snowden and Wheeler 1993), nor were Fe- deficiency symptoms, such as iron-chlorosis and stunted growth (Brown and Jolley 1989), were observed during the course of this experiment. Some growth-related patterns, however, were observed in terms of plant height and biomass. The CT plants were taller than those from the other two treatments in the early growth stage, but the LCT plants overtook them during the late growth stages. The maximum average height at the harvestable stage differed by 1 to 4 cm between the controls and plants grown in contaminated soils, but such a difference is slightly higher between LCT and HCT plants (Fig. 2.1).

When testing the significance of the differences in average heights between the treatments for both soil types, it was found that the significance level (*p* values) between the treatments in S25 is greater (0.192) than the level of significance set for the purpose of this study, whereas in S50 the significance level is less (0.027) (Table 2.1). This indicates that there is a significant difference in plant heights within the S50 soil, but not within the S25 soil. To further investigate this difference, BMCT was performed on the S50 soil. In Table 2.2, each row corresponds to a comparison of two treatments. The average height of HCT plants is significantly different from the average height of LCT plants; however, the height of the CT plants is not significantly different from plants of other two treatments.



	seedling	vegetative	reproductive	harvestable
□ S25CT	11.65	21.55	39.20	65.65
▨ S25LCT	10.60	19.85	40.90	68.45
■ S25HCT	9.95	19.15	40.30	62.55

	seedling	vegetative	reproductive	harvestable
□ S50CT	11.95	22.85	41.90	69.80
▨ S50LCT	9.33	18.72	39.55	70.13
■ S50HCT	10.55	19.15	36.70	65.10

Fig. 2.1 Mean height variation in plants at different growth stages: (**a**) S25 plants, (**b**) S50 plants.

Table 2.1 One-way ANOVA results for height differences of S25 and S50 plants at the harvestable stage

	Sum of squares	*df*	Mean square	*F*	Sig.
S25					
Between groups	174.200	2	87.100	1.757	0.192
Within groups	1338.475	27	49.573		
Total	1512.675	29			
S50					
Between groups	158.440	2	79.220	4.152	0.027
Within groups	515.180	27	19.081		
Total	673.620	29			

Table 2.2 BMCT on height differences of S50 plants at the harvestable stage

Treatment (*I*)	Treatment groups (*J*)	Mean difference (*I*-*J*)	SE	Sig.	95% Confidence interval	
					Lower bound	Upper bound
Dependent variable: *height difference*						
S50CT	S50LCT	–0.333	1.953	1.000	–5.319	4.653
	S50HCT	4.700	1.953	0.070	–0.286	9.686
S50LCT	S50CT	0.333	1.953	1.000	–4.653	5.319
	S50HCT	5.033(*)	1.953	0.047	0.047	10.019
S50HCT	S50CT	– 4.700	1.953	0.070	–9.686	0.286
	S50LCT	–5.033 (*)	1.953	0.047	–10.019	0.047

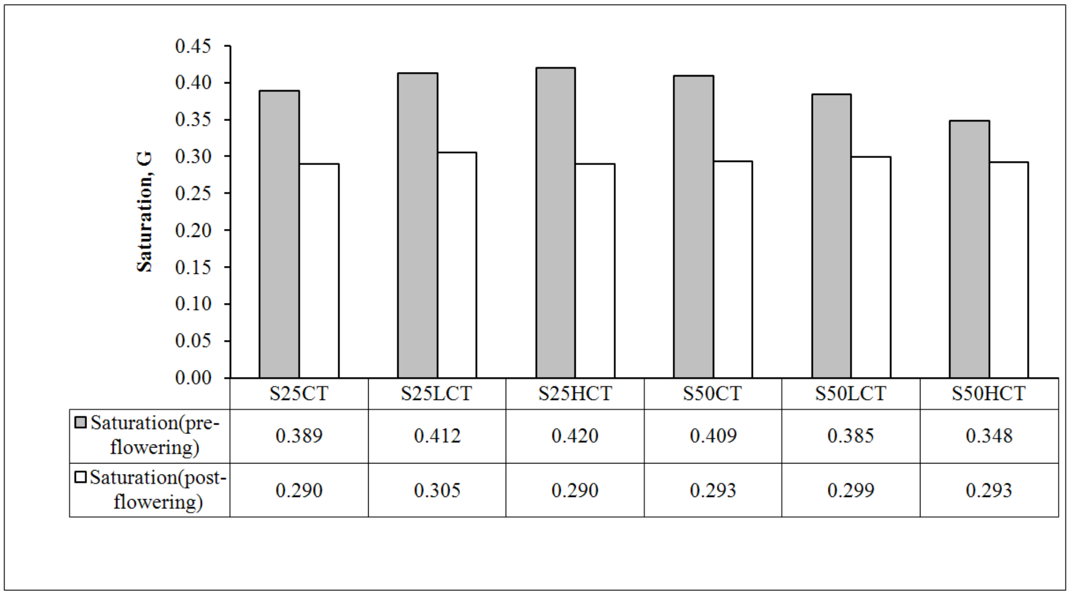
* The mean difference is significant at the .05 level.

Regarding dry biomass, although the total dry biomass is higher in LCT plants than other treatments in both soil types, the difference between the treatments is statistically insignificant as the observed significance level is higher (0.798 for S25 and 0.563 for S50) than the one set for this study (Table 2.3).

Table 2.3 Dry biomass of plants

Treatment	Average biomass per treatment (g)
S25CT	33.75
S25LCT	34.03
S25HCT	32.71
S50CT	35.77
S50LCT	35.78
S50HCT	33.48

Green color saturation measurements were not consistent when compared between the soil types, and, therefore, this parameter was not useful in differentiating growth response of plants between treatments. The S25 pre-flowering stage did show a small but statistically insignificant increase in saturation from CT to LCT plants (7.8%), and also from LCT to HCT plants (2.4%), while a reverse pattern was observed in plants grown in S50, where a 5% decrease from CT to LCT plants and 10.5% decrease from LCT to HCT plants were observed. In the post-flowering stage, however, the saturation levels remain constant in plants from all the treatments in both soil types (Fig. 2.2).



	S25CT	S25LCT	S25HCT	S50CT	S50LCT	S50HCT
▨ Saturation(pre-flowering)	0.389	0.412	0.420	0.409	0.385	0.348
☐ Saturation(post-flowering)	0.290	0.305	0.290	0.293	0.299	0.293

Fig. 2.2 Mean green color saturation in leaves at pre- and post-flowering stages.

2.3.2. Magnetic susceptibility results

The mass-specific susceptibility of the initial soil mixtures (BG) was 69 × 10^{-8} m^3/kg for S25 and 52 × 10^{-8} m^3/kg for S50, suggesting that S25 was slightly more enriched in magnetic material than S50. This could be due to a higher content of topsoil in S25, which had higher MS ($\chi = 127 \times 10^{-8}$ m^3/kg) than sand ($\chi = 40 \times 10^{-8}$ m^3/kg). In addition, the measured surface susceptibility values in the initial stage are not in proportion to the level of contamination applied (Fig. 2.3), which could be due to the heterogeneous distribution of the pollutant on the soil surface that may have resulted in variable pollutant distribution in the MS measurement locations. During the experiment, the bulk MS of the soils decreased substantially in all treatments (Fig. 2.3) from the initial values to the seedling stage, which was considered to be the first growth stage where all the containers had four plants. The decrease was between 14 and 29% in S25, and between 25 and 31% in S50, with the greatest occurring in HCT and the least occurring in the CT for both soil types. With a single plant growing in the successive stages (from vegetative to harvestable stage), the MS decrease is slightly less, with a range of 10–13% for S25 and 4–5% for S50. The overall MS decrease (from initial to harvestable stage) was found to be 25–36% for S25, and 29–34% for S50. When tested for significance, the level that the overall MS decreased between the treatments for both soil types is less than the level of significance chosen for this study (Table 2.4 and 2.5). This indicates that there is a significant difference in the overall decrease of MS between the treatments. Further analysis was done using a BMCT and the results show that in S25, the overall MS decrease in the CT is significantly different from both LCT and HCT, whereas in S50, a significant difference was observed only between the CT and HCT. In both soil types, the MS decrease between LCT and HCT is not significantly different. These results suggest that the decrease of MS from initial values through harvestable stage is dependent on treatment.

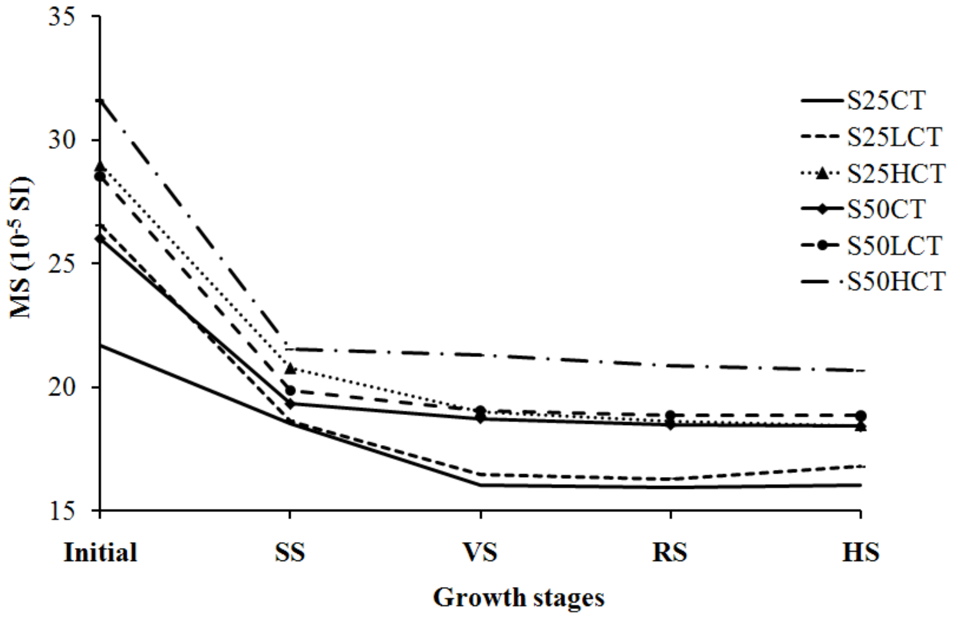


Fig.2.3 MS change in soil during the growth experiment (SS=seedling stage, VS=vegetative stage, RS=reproductive stage, and HS=harvestable stage).

Table 2.4 One-way ANOVA and BMCT on overall MS differences in S25 soil

One-way ANOVA

S25	Sum of squares	*df*	Mean square	*F*	Sig.
Dependent variable: *MS difference*					
Between groups	139.245	2	69.622	10.1	0.001
Within groups	184.662	27	6.839		
Total	323.907	29			

BMCT

Treatment (*I*)	Treatment groups (*J*)	Mean difference (*I-J*)	SE	Sig.	95% Confidence interval	
					Lower bound	Upper bound
Dependent variable: *MS difference*						
S25CT	S25LCT	–4.1300 (*)	1.1696	0.005	–7.1152	–1.1448
	S25HCT	–4.9100 (*)	1.1696	0.001	–7.8952	–1.9248
S25LCT	S25CT	4.1300 (*)	1.1696	0.005	1.1448	7.1152
	S25HCT	–0.7800 (*)	1.1696	1.000	–3.7652	2.2052
S525HCT	S25CT	4.9100 (*)	1.1696	0.001	1.9248	7.8952
	S25LCT	0.7800 (*)	1.1696	1.000	–2.2052	3.7652

* The mean difference is significant at the 0.05 level.

Table 2.5 One-way ANOVA and BMCT on overall MS differences in S50 soil

One-way ANOVA

S50	Sum of squares	*df*	Mean square	*F*	Sig.
Dependent variable: *MS difference*					
Between groups	55.909	2	27.954	3.4	0.047
Within groups	220.646	27	8.172		
Total	276.555	29			

BMCT

Treatment (*I*)	Treatment groups (*J*)	Mean difference (*I-J*)	SE	Sig.	95% Confidence interval	
					Lower bound	Upper bound
Dependent variable: *MS difference*						
S50CT	S50LCT	–1.8100	1.2784	0.505	–5.0732	1.4532
	S50HCT	–3.3400(*)	1.2784	0.044	–6.6032	–0.0768
S50LCT	S50CT	1.8100	1.2784	0.505	–1.4532	5.0732
	S50HCT	–1.5300	1.2784	0.725	–4.7932	1.7332
S50HCT	S50CT	3.3400(*)	1.2784	0.044	0.0768	6.6032
	S50LCT	1.5300	1.2784	0.725	–1.7332	4.7932

* The mean difference is significant at the .05 level.

χ was also determined for random samples from the post-harvest controls and treated soils. Because the soil samples were collected once the plants were removed from the soil, the conditions for measuring volume and mass specific susceptibility were not the same, and therefore, absolute differences in magnetic susceptibility between surficial soil and bulk soil could not be determined. In addition, while the dry weight volume susceptibility of plant samples was also measured, the values were almost negligible (values ranging between $+1\times 10^{-5}$ SI to -1×10^{-5} SI), suggesting either a lack of magnetic enhancement, or an inability to measure any enhancement using this instrument. The susceptibility values for background, post-harvest controls and treated soils are provided in Table 2.6.

Table 2.6 Average χ values for background, post-harvest controls and treated soils

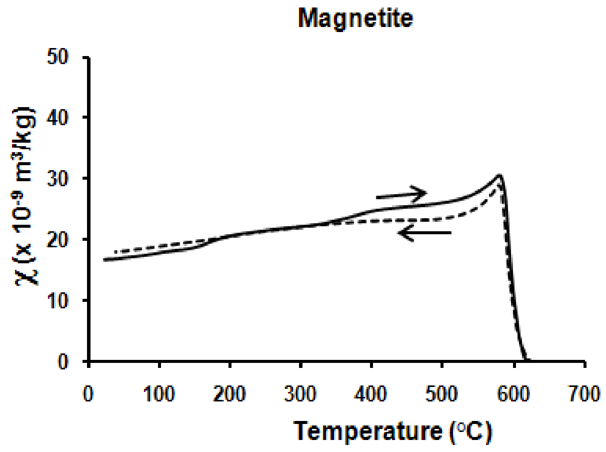
Soil sample	χ (x 10^{-8} m^3/kg)
S25BG	69.00
S50BG	52.00
S25CT	40.13
S25LCT	42.94
S25HCT	42.54
S50CT	42.97
S50LCT	42.16
S50HCT	45.84

2.3.3. Magnetic mineral transformations in soil

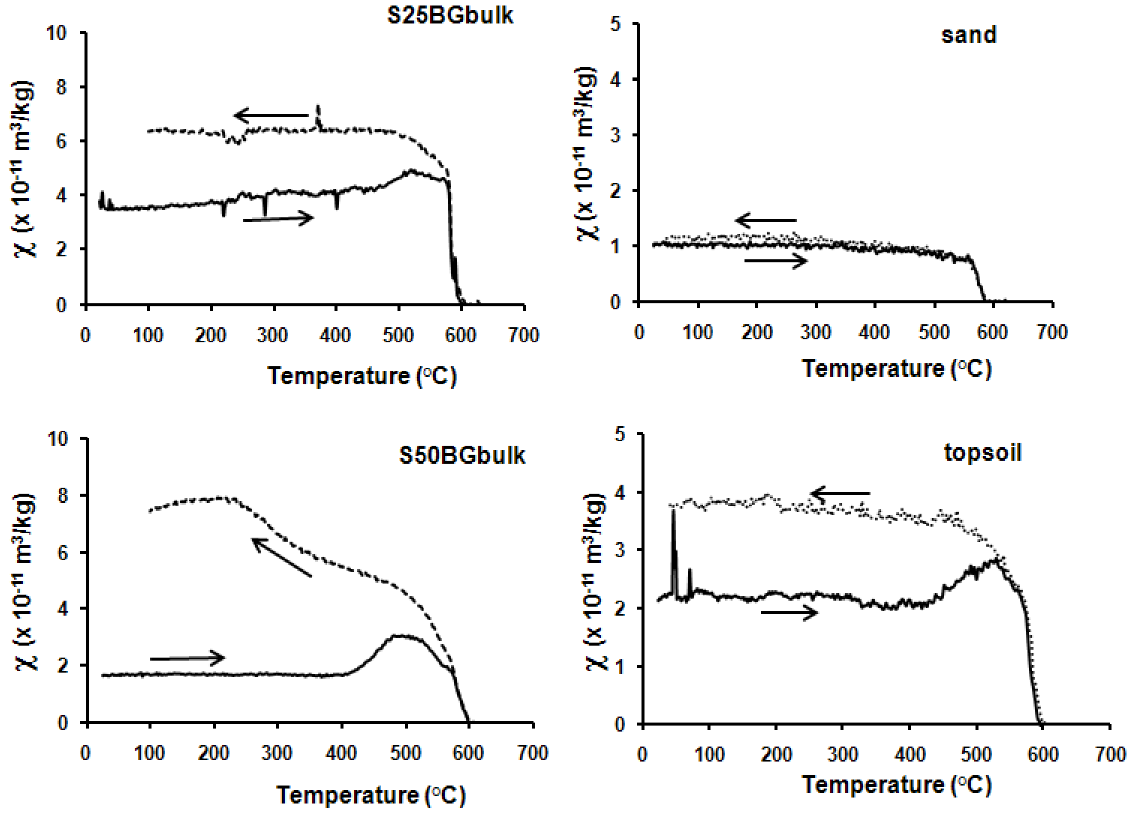
2.3.3.1. Rock magnetic measurements

The thermosusceptibility curves for the magnetite contaminant (Fig.2.4a) show that the Curie temperature (Tc) is about 615 °C, which is higher than that for pure magnetite (580°C). Although use of a graphical method in determining the Curie temperature may yield a temperature above the inflection point (Petrovsky and Kapicka 2006), it could also be due to the presence of small amounts of impurities in the magnetite, which is quoted to be only 98% pure from the company (READE Advanced Materials), or due to surface oxidation during storage into maghemite. The fact that the curves are not quite reversible also suggests some chemical alterations (such as generation of more magnetic minerals during cooling) have occurred. Similarly, the χ–T curves for the background soil and its components (Fig. 2.4b), and magnetic extracts from post-harvest soils (Fig. 2.4c) are irreversible, suggesting chemical alteration. The Curie point for all samples was between 590 and 600°C.

(a)


Magnetite
χ (x 10-9 m3/kg)
50
40
30
20
10
0
0
100
200
300
400
500
600
700
Temperature (°C)

(b)


S25BGbulk
χ (x 10-11 m3/kg)
10
8
6
4
2
0
0
100
200
300
400
500
600
700
Temperature (°C)
sand
χ (x 10-11 m3/kg)
5
4
3
2
1
0
0
100
200
300
400
500
600
700
Temperature (°C)
S50BGbulk
χ (x 10-11 m3/kg)
10
8
6
4
2
0
0
100
200
300
400
500
600
700
Temperature (°C)
topsoil
χ (x 10-11 m3/kg)
5
4
3
2
1
0
0
100
200
300
400
500
600
700
Temperature (°C)

(c)

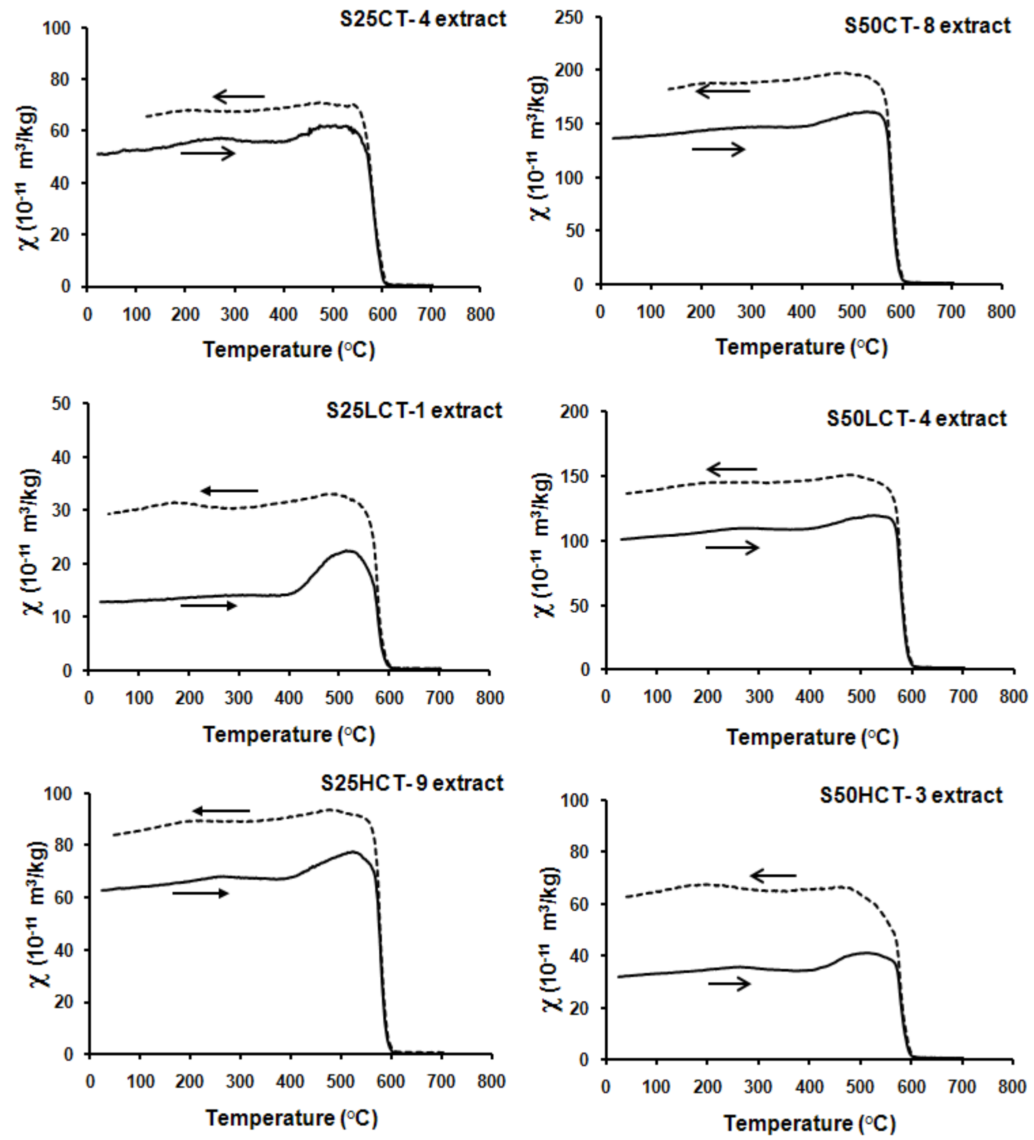


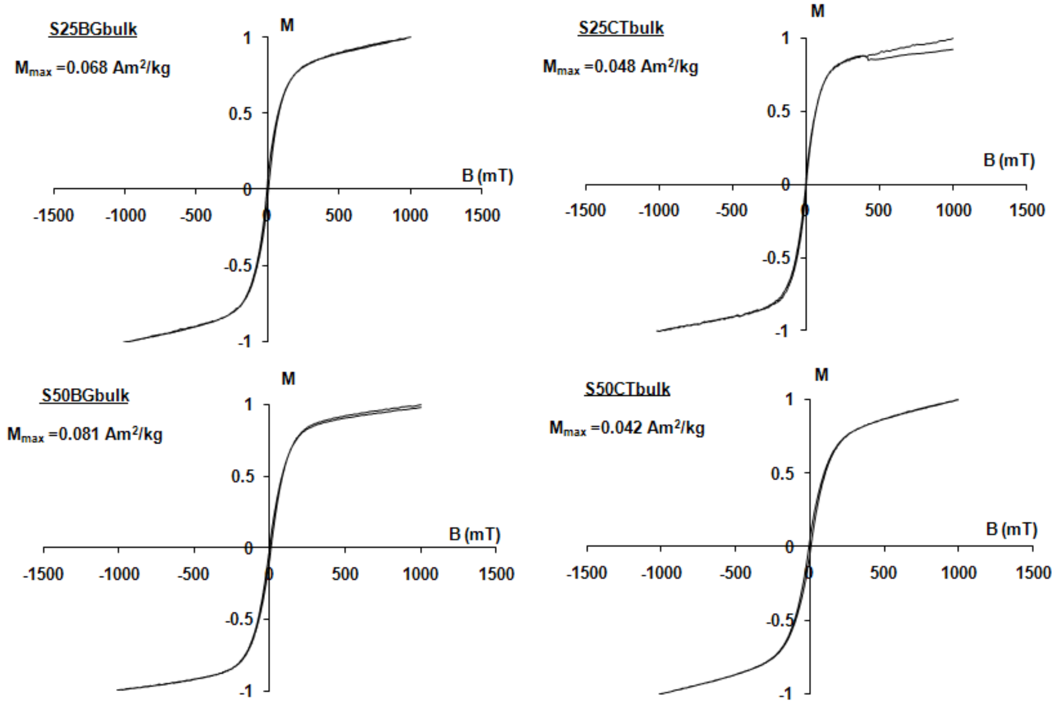
Fig.2.4 χ-T curves for: (**a**) magnetite contaminant, (**b**) background soil and its components, (**c**) magnetic extracts from post-harvest soils of S25 and S50. Measurements were made in air for all but the magnetite contaminant (χ in 10^{-11} m^3/kg).

Figure 2.5 shows typical hysteresis loops for the bulk soils, magnetic extracts (background and post-harvest soils) and the plant samples. The hysteresis loops for bulk soil samples and magnetic extracts are thin, closed, have steep central sections and approach magnetic saturation in the field of ~300 mT; all of which indicate that the magnetic minerals are dominated by low coercivity ferrimagnets (i.e., mainly magnetite). The slope of the loop above 300 mT in bulk soils and magnetic extracts of contaminated samples is greater, indicating a mixture of ferrimagnetic and paramagnetic components. The sigmoid-shaped loops of most of these samples imply a coarse grained assemblage (PSD or MD), as indicated by the Day Plot (Fig. 2.6). The hysteresis parameters of magnetic extracts (Table 2.7) show higher ratios of M*rs*/M*s* for contaminated soils than for background and control soils, indicating contaminated soils have lower saturation magnetization (M*s*). This potentially indicates an increase in the amount of high coercivity magnetic minerals. In addition, because the initial susceptibility of HCT and LCT was higher than the CT due to addition of magnetite, the reduced magnetization in these soils after plant growth may indicate a mineralogical change. With respect to the plant samples, the hysteresis loops are straight and are dominated by diamagnetic components.

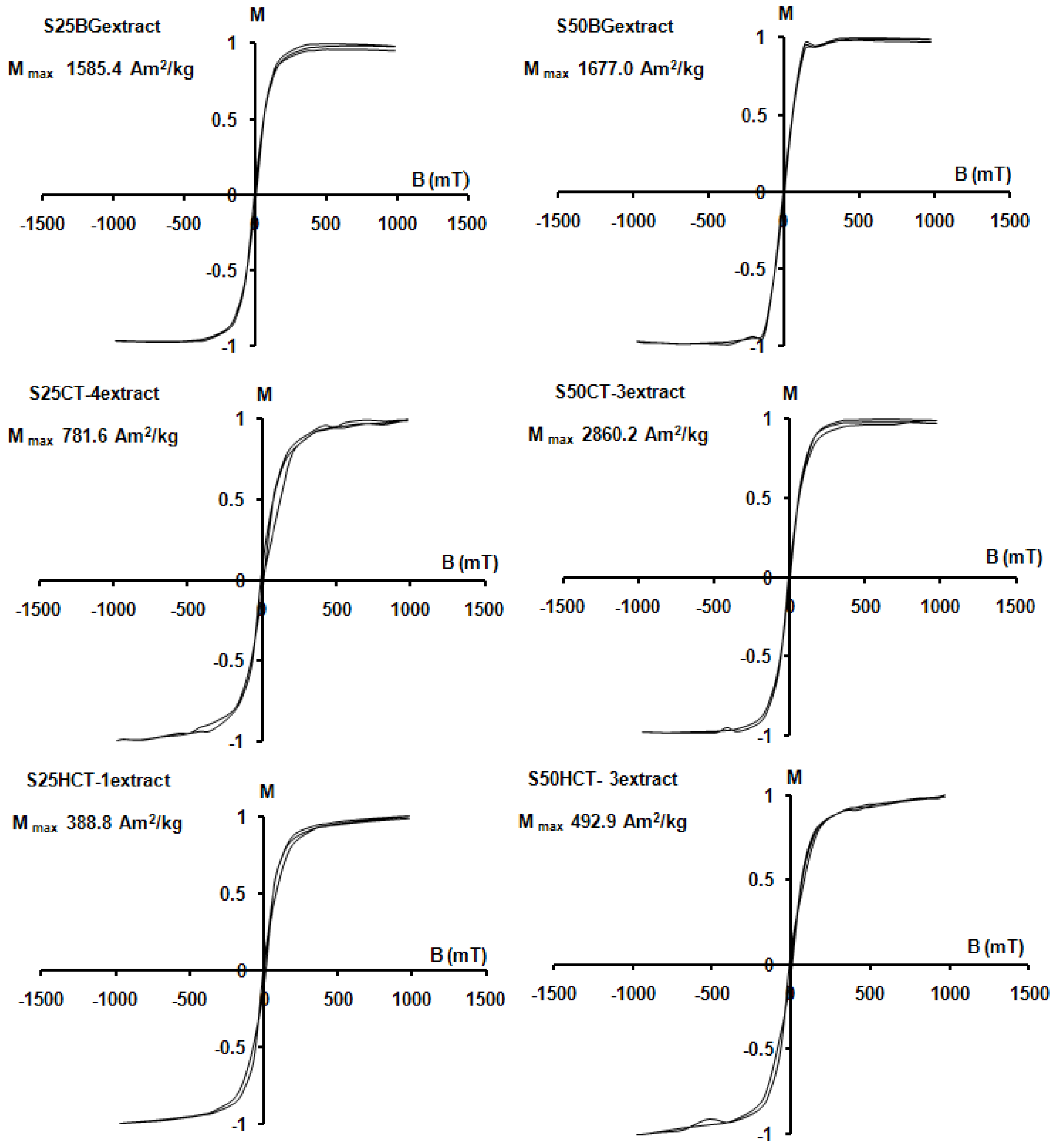
Table 2.7 Hysteresis parameters (Mrs/Ms, Bcr/Bc, Bc) for magnetic extracts of Fig. 5b

Soil sample	M*rs*/M*s*	B*cr*/B*c*	B*c* (mT)
S25BG	0.06	3.31	6.58
S25CT-4	0.07	2.56	8.64
S25HCT-1	0.08	3.18	7.78
S50BG	0.04	6.32	4.28
S50CT-3	0.04	6.23	4.11
S50HCT-3	0.07	4.16	7.62

(a)



(b)


S25BGextract
M max 1585.4 Am²/kg
S50BGextract
M max 1677.0 Am²/kg
S25CT-4extract
M max 781.6 Am²/kg
S50CT-3extract
M max 2860.2 Am²/kg
S25HCT-1extract
M max 388.8 Am²/kg
S50HCT- 3extract
M max 492.9 Am²/kg
M
B (mT)
1
0.5
0
-0.5
-1
-1500
-1000
-500
500
1000
1500

(c)

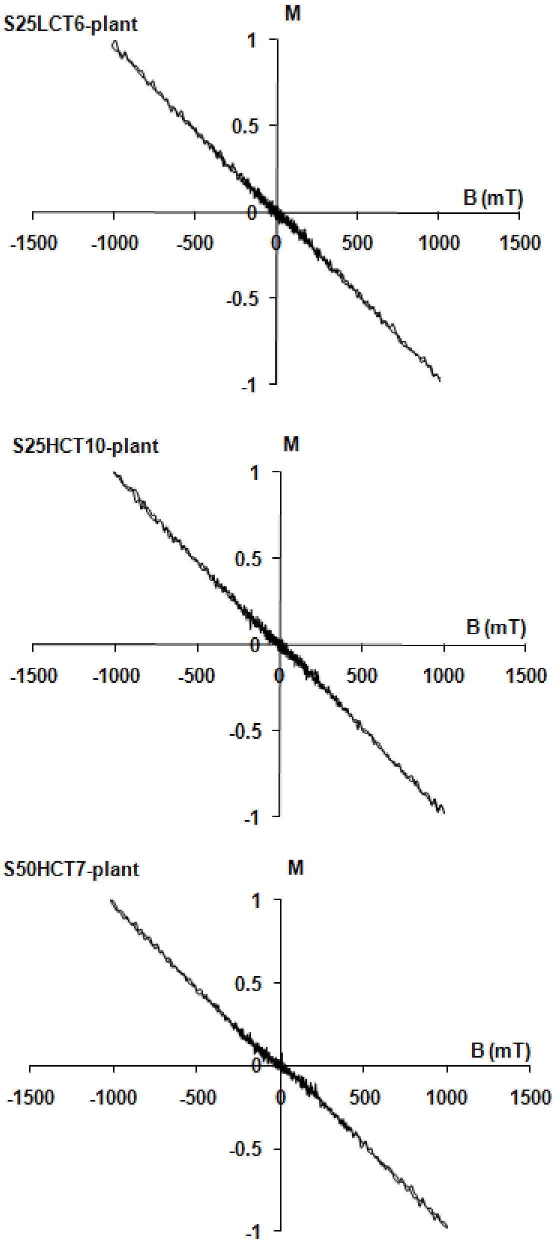


Fig. 2.5 Hysteresis loops for: (**a**) bulk soils, (**b**) magnetic extracts from background and post-harvest soils, and (**c**) high contamination plant samples (magnetization normalized in all).

The grain sizes of the magnetic minerals were determined using a Day plot (Day et al. 1977). The magnetic mineral grains are all of pseudo-single domain (PSD) or multidomain (MD) size and they showed no variation in grain size during plant growth (Fig. 2.6).

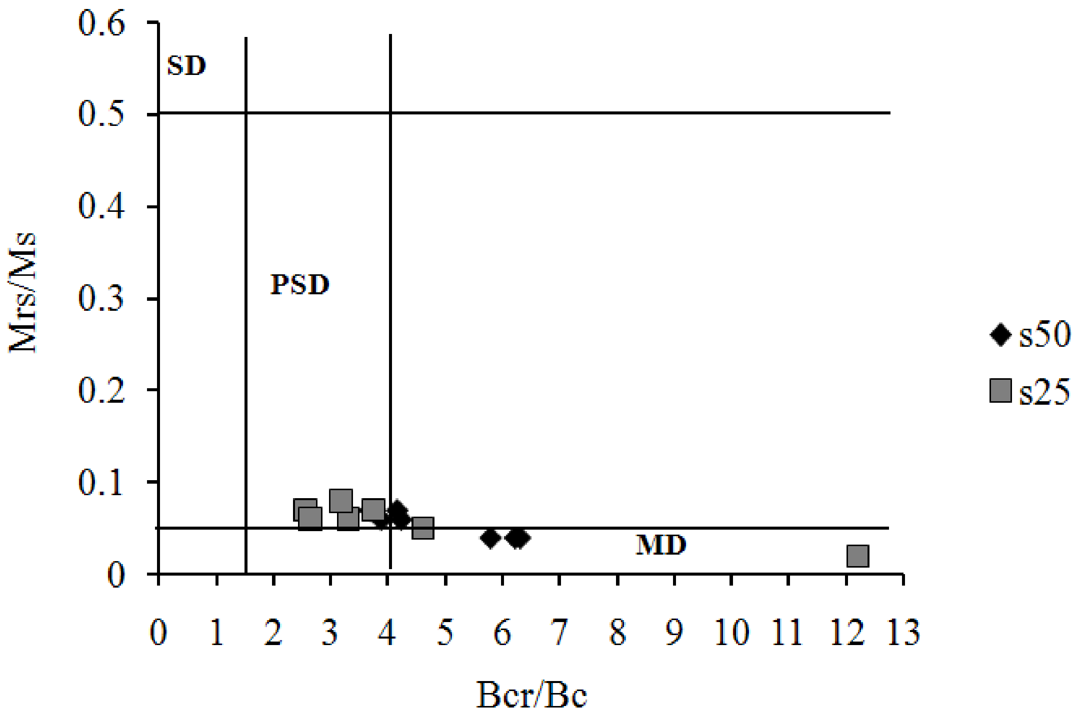
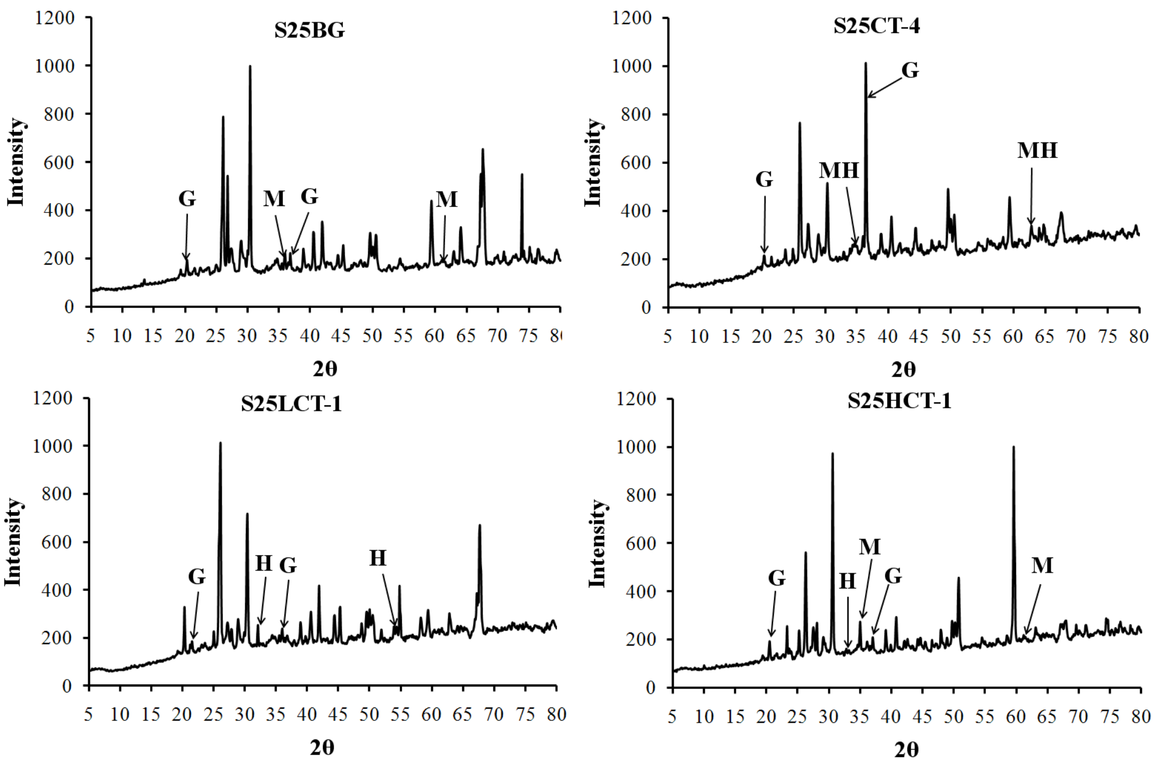


Fig. 2.6 Biplot of Mrs/Ms versus Bcr/Bc for magnetic extracts from post-harvest soils using method of Day et al. (1977).

2.3.3.2. X-ray diffractograms

Examples of X-ray diffractograms are provided in Figure 2.7. Only the diffractogram peaks that correspond with magnetic mineral phases are labelled. The results indicate that the magnetic extracts from the background (untreated) soil mixture contained both reduced (e.g., magnetite) and oxidized (e.g., goethite) iron minerals. In post-harvest soils, maghemite and goethite were present in control; however, in contaminated soils, goethite, maghemite and hematite were observed in addition to the magnetite that was added.

(a)



(b)

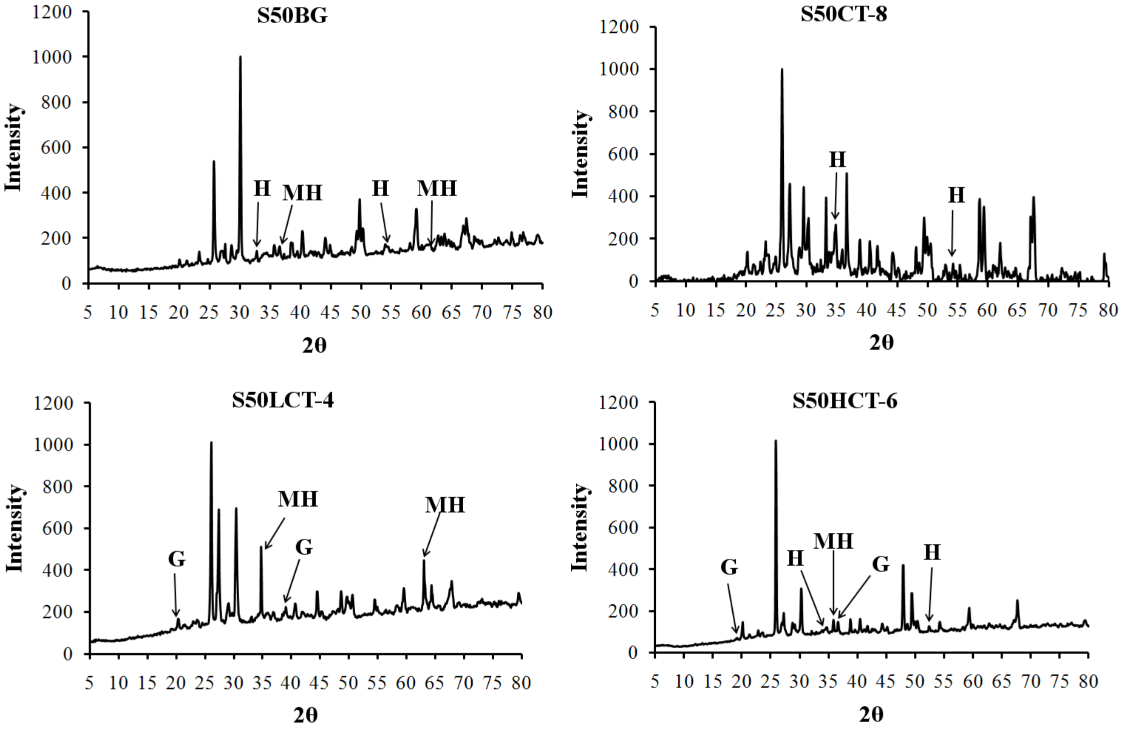


Fig. 2.7 X-ray diffractograms of magnetic extracts from background and post-harvest soils (θ in degrees; Minerals: M=magnetite, G= goethite, MH= maghemite, H=hematite): (**a**) S25 soil, (**b**) S50 soils.

2.3.4. Soil pH

The pH of the S50 background soil was found to be slightly more basic (pH= 8.0) than that of the S25 soil (pH=7.6). The pH values of post-harvest soils from all the treatments in both soil types, however, did not deviate significantly from background values. The pH of the S25 was in the range of 7.3 –7.5, and the S50 was in the range of 7.6–7.9.

2.3.5. Trace element concentrations in plants

Because the soil treatments were Fe-based, the *a priori* assumption was that Fe concentrations in plants between treatments would be higher than the other trace elements. Table 2.8 shows that the maximum difference in [Fe] between treatments ranges from 2 to 14%, while [Ni] ranges from 7.7 to 9 %, and [Mn] from 4 to 5 %. [Fe] was higher in the LCT and HCT plants than in the controls. Such differences in trace element concentrations in plants between treatments are found to be statistically insignificant (*p*-values > 0.05) for all of the trace elements examined. In addition, while the results are highly repeatable and therefore precise, the variation in results is within the accuracy of the ICP-OES.

Table 2.8 Concentration of trace elements in plant biomass (µg/g)

Soil type	Treatment	[Fe]	Fe%	[Ni]	Ni%	[Mn]	Mn%
S25	CT	15.33	32.40	0.40	38.46	8.68	31.00
	LCT	15.72	33.22	0.32	30.77	9.89	35.32
	HCT	16.27	34.38	0.32	30.77	9.43	33.68
	Max. diff.		*1.99*		*7.69*		*4.32*
S50	CT	14.46	27.46	0.40	28.57	9.76	31.50
	LCT	16.41	31.17	0.47	33.57	9.96	32.15
	HCT	21.78	41.37	0.53	37.86	11.26	36.35
	Max. diff.		*13.90*		*9.29*		*4.84*

2.4. Discussion

Examination of Figure 2.3 shows that the MS drops significantly between the initial and the post-harvest measurements. Similar results were also obtained in a controlled experiment conducted by Sapkota and Cioppa (2009). Post-hoc tests showed that the MS decrease is significantly different between the control and the other two treatments, but not between the LCT and HCT. In addition, it is clear that most of the change occurs between the initial and the seedling stage in both soil types. One of the reasons for the substantial decrease in MS during this early growth stage could be the larger number of plants (four plants) grown in each container until the seedling stage, which may have accelerated the decrease in soil Fe and other trace elements. Alternatively, rapid alteration of minerals by irrigation could have occurred (discussed later).

There are a number of potential reasons for the overall MS decrease, including trace element uptake by plants, vertical migration of Fe-particles within the container and magnetic mineral transformations. With regard to the possibility of the trace element uptake by plants, Fe-uptake in most plants is so small that it does not necessarily alter the [Fe] in soil or the soil ferromagnetic concentrations (the most common range of [Fe] in soils is from 0.5 to 5%, according to Kabata-Pendias and Pendias 1984). In addition, there are no relevant reports that mention tomato plants as hyperaccumulators of Fe, though it has been used for cleaning soil polluted with Co (Woodard et al. 2003). Although the tomato plants in this study do not show statistically significant differences in trace element uptake between the treatments (Table 2.8), the observed pattern of an increase in [Fe] in the plant biomass with higher contamination levels is inversely proportional to the MS decrease in the soils. [Fe] is higher in HCT plants and this could be due to the fact that they were grown in soil contaminated with magnetite and, therefore, had greater chances for Fe-uptake. As the contaminant used is of very small size (average size less than 1 micron), such colloidal iron could have increased the bioavailability of iron for the plants. Although there is an increasing trend of [Fe] from the controls to the LCT and HCT soils, as determined from chemical analysis (see Table 2.8), the anticipated magnetic enhancement in shoots could not be detected by the MS2 system. While the [Fe] changed between the treatments, the concentration of the other two trace elements (Ni, Mn) remained relatively constant, which shows that addition of the magnetite powder did not affect their concentrations.

The LCT plants responded positively to the addition of Fe (Fig. 2.1), however, the HCT plants had shorter heights and slightly lower biomass, which could be due to Fe acting as a stressor rather than as an essential nutrient. Bell and Treshow (2002) suggested that air pollutants may serve as plant nutrients at low deposition rates, and the LCT plants may mimic these conditions. Connolly and Guerinot (2002), however, suggested that accumulation of Fe within cells can be toxic for plants, and the HCT plants could have shown manifestations of this toxic effect. For both LCT and HCT plants, Fe could be accessed continuously by the plants throughout the growth period, as opposed to the controls where Fe might have been reduced to insufficient amounts for late growth stages.

Fe is an essential micronutrient with numerous cellular functions (Hell and Stephan 2003), and is essential for chlorophyll formation in plants (Marsh et al. 1963). The saturation value was reduced in the post-flowering stage in this study, and a similar loss was observed by Novel (1977) in a desert perennial, which resulted in progressive bleaching (yellowing) of the plants from their original grayish green color. Such distinct color variation, however, was not observed in this study. Because all the other conditions were kept the same during the growth period, the observed differences in plant growth and saturation values between soil treatments may be a function of the [Fe]. It is also noted that the growth media (S25 vs. S50) seems to have had some effect on plant growth (Fig. 2.1).

Because the plant uptake of Fe is not statistically correlated with MS decrease, the other two possibilities need to be considered: vertical migration of Fe particles and magnetic mineral transformations. The reduction in surficial soil MS could be due to the migration of Fe-containing particles vertically downward in the container during the growth cycle due to either gravitational effect or due to watering. Macropores caused by root penetration change soil structure (Angers and Caron 1998), which may ease migration of iron particles down the container. The loosened soil could have resulted in an increased potential for Fe-particles to move downward with continuous irrigation of plants in the initial stages of plant growth (until seedling stage). In the later stages of growth, the rate of migration could have decreased as the soil became more compact. This migratory effect on Fe-containing particles might have reduced the signal for the sensor. According to Lecoanet et al. (1999), about 90% of the MS signal is recorded in the first centimetre of soil underlying the sensor. This migration effect was not controlled in this study, however, it is being evaluated in a separate investigation.

This study did, however, evaluate whether magnetic mineral transformations play a significant role in the decrease in soil MS. It is well known that the magnetic properties of soils are affected by ferrimagnetic mineral neoformation and dissolution (Grimley et al. 2004). In our study, the potential magnetic mineral phase transformation is probably associated with the transition from reduced to oxidized Fe species. Constant wetting and drying (through watering) and exposure to atmospheric gases could be the potential factors influencing the redox state of the magnetic minerals in soils. The results show that the background soils contained a mixture of oxidized and reduced magnetic minerals, but the post-harvest soils contained relatively more oxidized magnetic minerals, suggesting that magnetite in the background soil is being altered into its oxidized (hematite) and oxy-hydroxide (goethite) forms, which are magnetically less strong. Such mineral transformation would have contributed in reducing the overall MS in soil, as well as decreasing the Ms values obtained from hysteresis measurements, both of which were observed in this study. While the XRD results show clear evidence for specific iron minerals in some samples at low concentrations, distinct peaks in the diffractograms often could not be easily identified using the Match! software. The compositional complexity of the soil (i.e., a mixture of topsoil, sand, and manure) made it difficult to interpret the results. Thus, the exact mechanism for oxidation cannot be determined, because Fe^{3+} can be oxidized abiotically by molecular O_2 (Stumm and Lee 1961), biotically by anaerobic phototrophic and nitrate reducing, as well as by aerobic Fe^{2+}-oxidizing microorganisms (Emerson 2000, Kappler and Straub 2005).

Overall, the rock magnetic measurements show that the dominant magnetic mineral in all treatments and in both soil mixtures is magnetite and, therefore, more subtle mineralogical changes were difficult to observe. The chemical and magnetic methods of mineral determination show consistent results. Magnetic susceptibility measurements, however, were more discriminatory for thermosusceptibility measurements when compared to X-ray diffraction. A common method of determining the amount of alteration occurring in a sample is to compare the intensity of the heating and cooling curves (Housen and Musgrave 1996). In the thermosusceptibility (χ–T) curves of the bulk soil and its magnetic extracts, the susceptibility measurements during cooling had higher intensities than during the warming cycle and the Curie point was between 580 and 600 °C, which suggests the generation of magnetite or maghemite during heating. Examination of Figure 2.4 shows that the values of $\chi_{100heating}$/ $\chi_{100cooling}$ of the magnetic extracts of background soils lie between 0.58 and 0.67, while those for post-harvest control soils range between 0.76 and 0.78 and for post-harvest contaminated soils between 0.40 and 0.70. This suggests that less chemical transformation of magnetite occurred in the control soils compared to the contaminated soils; therefore the degree of mineral transformation was apparently higher. Comparison of the background and post-harvest control data suggest that the either plant growth or biotic and abiotic chemical reactions have altered the magnetic mineralogy of the soil. The hysteresis curves of the post-harvest contaminated soils have much lower saturation magnetization and higher coercivity values, indicating the possible contribution of high coercivity magnetic phases, like hematite or maghemite. These results provide support to the mineral transformations determined from X-ray diffractograms. The changes in soil pH can also affect mineral transformations. For example, a slightly basic pH (7 to 8) favors the formation of hematite (Schwertmann and Murad 1983). In this experiment, the pH of the post-harvest soil was between 7.3 and 7.9, suggesting that this environment would favor formation of oxidized minerals. Our results, however, show that pH does not alter to any significant degree in such a controlled environment and, therefore, possible mineralogical changes due to changes in soil pH alone cannot be assessed.

Some other factors that were not investigated in this study but could influence the mineral transformations are plant growth and bacterial activity. According to Hell and Stephan (2003), plant roots penetrate the substrate in anaerobic zones, and the air channels they contain rapidly introduce oxygen into the soil. This could result in the oxidation of reduced magnetic minerals present in soil. Fe (III) reducing bacteria reduce Fe^{3+} (ferric) to the Fe^{2+} (ferrous) state in anaerobic conditions (Dong et al. 2000, Roden and Zachara 1996); however, anaerobic conditions were unlikely to be present throughout the containers used in this experiment because the containers had drainage holes in the bottom and water logging of the soil was not observed after watering.

The results show that magnetic mineral transformations in soil, caused by both biogenic (plant growth) and abiogenic (the wetting and drying) processes during plant growth, must be the potential causes of MS decrease. As plant uptake of Fe is in small quantities, this may not have contributed significantly to the MS decrease. Another possible factor could be migratory effect, which is not controlled in this study.

2.5. Conclusions

Soil magnetic properties changed during plant growth, showing a significant decrease in surficial soil MS. The decrease in MS could be attributed to magnetic mineral transformations, Fe uptake by plants and the vertical migration of Fe-containing particles. Some evidence for the first two possibilities has been obtained from magnetic and geochemical measurements; however, it seems crucial to investigate the third possibility, i.e., vertical migration of Fe-containing particles during the growth cycle.

Magnetic methods used in this study seem to be complementary to the chemical methods, indicating that they can be used as a proxy for chemical methods, as a monitoring tool for tracing the pollutant uptake by plants and be beneficially applied to phytoremediation.

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CHAPTER 3

USING MAGNETIC AND CHEMICAL MEASUREMENTS TO DETECT ATMOSPHERICALLY-DERIVED METAL POLLUTION IN ARTIFICIAL SOILS AND METAL UPTAKE IN PLANTS

An earlier version of this chapter was submitted to *Environmental Pollution* (submitted on 13 October 2011). This chapter accommodates the comments from thesis committee and has been re-formatted according to the guidelines of the University of Windsor, to maintain consistency throughout the thesis.

Citation:

Sapkota, B., Cioppa, M.T. Using magnetic and chemical measurements to detect atmospherically-derived metal pollution in artificial soils and metal uptake in plants. *Environmental Pollution (in revision)*

3.1. Introduction

Atmospheric pollution is derived primarily from the emissions of gasses and solid particulates into the atmosphere. Although atmospheric pollution may have natural sources (e.g., volcanic eruptions, forest fires), the term is usually used to refer to the gaseous or solid by-products of anthropogenic processes such as energy production, industrial operations, waste incineration, transport and agriculture (Canter et al. 2000). Through a number of past studies (e.g., Blaha et al. 2008, Hoffmann et al. 1999, Kukier et al. 2003, Magiera et al. 2007, Shi and Cioppa 2006), it is now well-documented that such solid by-products can possess a significant mineral magnetic component. Studies examining the effects of atmospheric pollution on surface soil have found that anthropogenic magnetic minerals (consisting of Fe and other coexisting heavy metals) contribute significantly to their magnetic properties (Boyko et al. 2004, Chapparo et al. 2010, Kapicka et al. 1999, Strzyszcz and Magiera 1996).

While many of the previous environmental magnetic studies have dealt with pollution detection and magnetic characterization in soils and sediments from lithogenic and anthropogenic sources, monitoring of soil pollution using magnetic parameters is still rare. Kapicka et al. (2011) conducted an experimental study of fly-ash migration in sands of different porosity and under a simulated rain regime, and determined a stable peak value of magnetic susceptibility (MS) only a few millimeters below the surface. A similar vertical migration study, conducted by Sapkota and Cioppa (2012) in natural clay-rich glacial soil that was treated with magnetite powder, showed that the contaminant migrated vertically downwards to a maximum depth of 9 cm, with an average maximum peak at ~ 5 cm. While these two studies aimed to assess the vertical migration behaviour of atmospheric pollutants, Sapkota et al. (2012) used an artificial contaminant (magnetite powder) in synthetic soils in a closed (greenhouse) environment, and monitored the changes in soil magnetic and chemical properties during plant growth. They detected a decrease in surficial soil MS during plant growth, and suggested that changes in soil magnetic mineralogy brought about by both biotic and abiotic processes were responsible. The current study eliminates the artificial Fe-contaminant (i.e., magnetite powder) but retains the synthetic soil, isolating ambient atmospheric pollution as the variable, and thus examining the effects of atmospheric pollution on magnetic and chemical properties of the synthetic growth media (i.e., soils) and the plants grown therein.

The Ambassador Bridge connects Windsor, Canada's southernmost city, to Detroit, Michigan, and is the busiest international commercial vehicle-crossing in North America, averaging 4880 heavy-duty diesel trucks each day (http://www.citywindsor.ca), and contributing to increased gaseous and particulate air pollutants. Proximity to the Ambassador Bridge was found to be a significant predictor of outdoor levels of traffic-related pollutants in land use regression models for Windsor (Wheeler et al. 2008). Shi and Cioppa (2006) determined that the MS values near major truck routes were nearly five times higher than near county roads. While this is the only magnetic study in the area, gravimetric and chemical analyses determined that the $PM_{2.5}$ content is very high in the Windsor and Detroit areas (Hammond 2008). Dabek-Zlotorzynska et al. (2011) reported that the $PM_{2.5}$ mass by monitoring site (as measured by the speciation samplers of the Canadian National Air Pollution Surveillance (NAPS) network for the years 2003 to 2008), was the highest (>30 µg/m^3) in Windsor (Ontario) and southern Quebec in comparison to all other locations across Canada. Thus, because of the high potential for significant atmospheric pollution, the University of Windsor campus, located close to the Ambassador Bridge (Fig. 3.1), was considered to be an excellent site for evaluating the potential effect of atmospheric pollution on soils. We aim that this research will provide qualitative estimates of changes in magnetic properties of soils as a result of ambient air quality in the Windsor-Essex area.

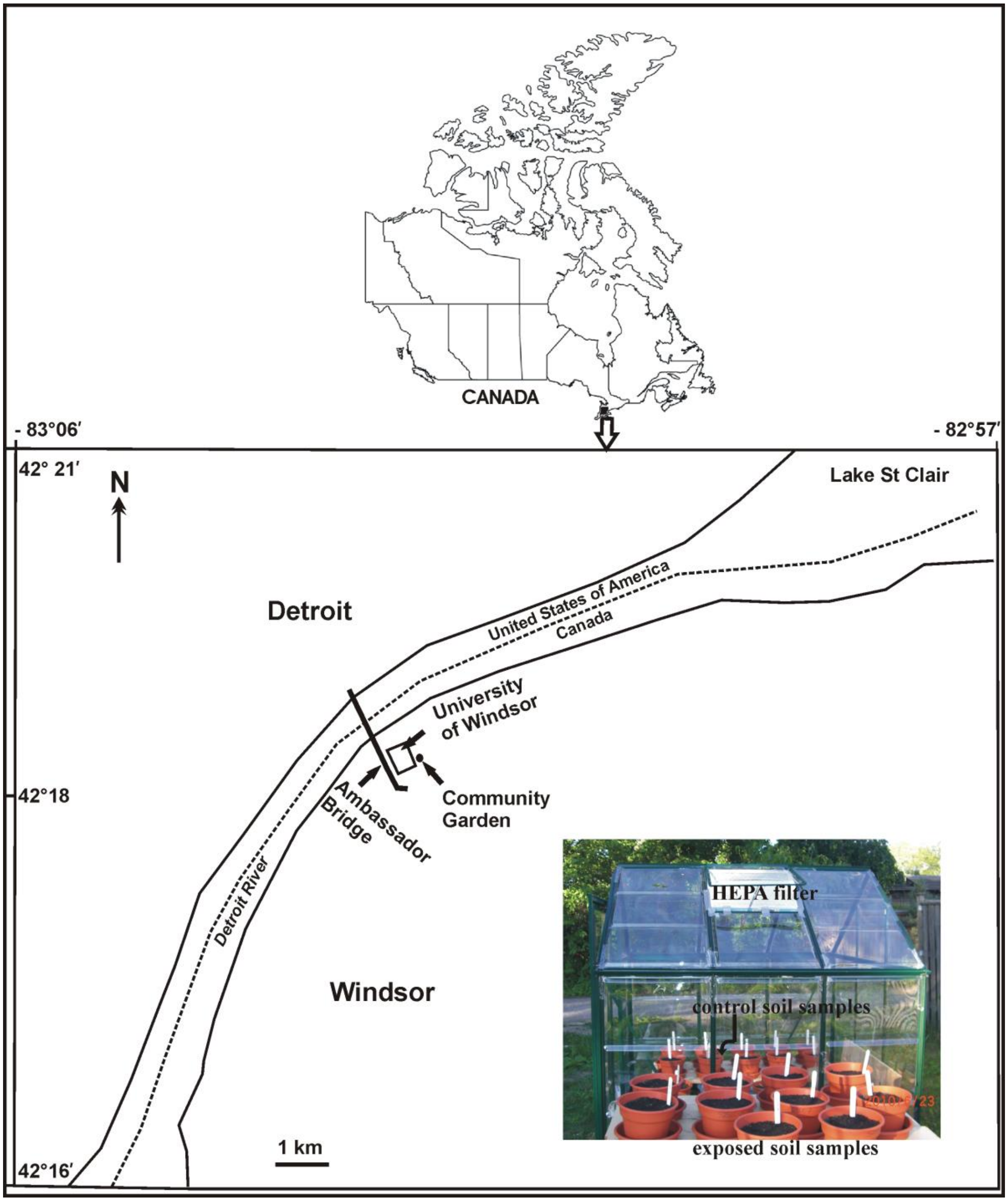

Fig. 3.1 Site location; the image in the lower-right corner shows control soil sets inside a greenhouse, and exposed soil sets placed outside the greenhouse.

3.2 Methodology

3.2.1 Materials and treatments

Synthetic soils were prepared by mixing (vol:vol) Alltreat Farms® (http://www.alltreat.com) play sand (screened and washed sand from a gravel pit), natural topsoil and manure (both consisting of peat sedge, leaf and yard compost). Alltreat Farms had collected the peat sedge from farmland, and leaf and yard compost from various municipalities across Ontario, mixed them together, and composted the mixture till it acquired a soil-like texture. Two soil mixtures were prepared: S50 had equal amounts of sand and topsoil, while S25 had a sand to topsoil ratio of 1:4. From these two soil mixtures, four treatments were prepared: two controls consisting of 10 pots (20 cm diameter) each of S25C and S50C mixtures and an equal number of exposure pots (S25UC and S50UC), thus totaling 40 samples. The controls were placed into a $1.9 \times 3.1 \times 2.2\ m^3$ greenhouse, with the open vents of the greenhouse covered with HEPA (high efficiency particulate air) furnace filters to trap the majority of the atmospheric particulates while allowing air to pass through and maintaining the inside temperature. The exposure pots were left in the open air nearby the greenhouse. The same patio hybrid variety of tomato (http://www.stokeseeds.com) used in Sapkota et al.'s (2012) study was used, in order to be able to compare this experiment to the previous one. Four seeds were sown in each pot to a depth of 0.5 cm, and were reduced to one (the visibly healthiest candidate among those that germinated) per container after emergence and establishment. The containers were irrigated daily and fertilized using equal quantities of water and fertilizer in all pots. The irrigation water was Windsor tap water, which was treated to safe drinking water standards, and was not treated or filtered further.

3.2.2 Magnetic measurements

Surficial MS measurements of the growth media were made during all four growth stages[1] (seedling, vegetative, reproductive and harvestable), using the Bartington MS2 system and a MS2F probe. Measurements were always made on dry (non-saturated) soils to avoid the possible diamagnetic effects of water. For statistical purposes, individual measurements were taken in five equally spaced locations (3 replicate readings were collected in each location to ensure repeatability) in each container and averaged to give the MS reading per container at the time of measurement.

MS measurements of vertical profiles through the post-harvest control soils (Fig. 3.2) were conducted to determine if measurable vertical migration of Fe-containing particles from the original mixture had occurred. In Sapkota et al. (2012), this was suggested as a potential reason for the overall MS decrease, but was not evaluated therein. Two assumptions were made while measuring the vertical MS profiles: first, that soil volume and root density remained constant throughout the container soil, and the second, that the background soil mixture was chemically and magnetically homogeneous, as the individual soil components (sand, topsoil, manure) were thoroughly mixed prior to placing in the containers and planting. Because the goal was to assess vertical migration

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[1] *Seedling* plants established, about 4 weeks of growth; *vegetative* until first flower opened, about 8 weeks of growth; *reproductive* until first fruiting occurred, about 10 weeks of growth; *harvestable* plant terminated after fully grown, about 12 weeks of growth (Sapkota et al. 2012).

in the absence of other potential inputs (e.g., atmospheric particulate matter), vertical MS profiles were not measured on the exposed soil samples, with the concern that their magnetic mineralogy, concentration and granulometry at any depth could be altered by the presence of or the translocation of Fe-containing atmospheric pollutants. Pollutant migration behavior between controls and contaminated tubes, however, are investigated in detail in a separate study (Sapkota and Cioppa 2012).

Fig. 3.2 Preparation and measurement of vertical MS profiles: (**a**) recovered soil from container, (**b**) longitudinal soil section, and (**c**) MS measurement along the longitudinal section using the MS2 system and a MS2F probe.

Low-frequency mass-specific MS (χ_{lf}) for each pot was determined, using a Bartington MS2B sensor, for the post-harvest bulk soils that were sieved (2 mm sieve size) and then mixed to assure homogeneity. To prevent cross-contamination, the precaution of using separate sieve sets for the control and exposed soil, was taken.

However, in order to identify the carriers of the magnetic signal in soils, magnetic extracts (obtained by using a hand-held magnet) were used. The extraction efficiency was calculated from the ratio of $\chi_{\text{residual soil}}/\chi_{\text{initial soil}}$ (Walden et al. 1998). The values were determined to be approximately 75% for topsoil and bulk soils, and 92% for sand, and these relatively high values were considered to be representative of the magnetic particles in soil samples. Hysteresis loops and magnetic parameters were measured on a Magnetic Measurement variable field transition balance (MMVFTB-EM) and the susceptibility dependence on temperature (K–T) was measured on a KLY-3S Kappabridge with the CS-3 high temperature furnace attachment at the Paleomagnetics and Rock Magnetics Laboratory, University of Windsor.

Plant roots (both main root and rootlets) were cleaned using a solid-state ultrasonicator (Fisher Scientific®) and distilled (Millipore®) water. This method of cleaning roots was chosen, instead of chemical methods, such as the use of $PbNO_3$ (Markert 1995), to avoid possible contamination and leaching of elements by the chemicals. The cleaned roots were oven-dried (50°C for 24 hours) to avoid microbial decomposition, and homogenized using an agate mortar and pestle. χ_{lf} of dried plant roots was measured in order to detect any magnetic enhancement. As roots are the most important sites for storing metals absorbed from the soil before translocation into the shoots and leaves (Collins et al. 2011), detection of magnetic enhancement in roots, if any, would suggest considerable absorption/storage of Fe and other trace/heavy metals by the plants, which could contribute to a decrease in surface soil MS.

3.2.3 Chemical measurements

Magnetic extracts from the background soil mixtures and components therein, and from post-harvest soils were investigated using an SEM (scanning electron microscope, Quanta 200 ESEM FEG), equipped with EDS (energy-dispersive X-ray spectroscopy). To ensure that representative particles from the samples were investigated, observations were carried out in all four quadrants of the sample, followed by a detailed investigation of bright particles in the back-scattered electron images, which are likely metal particles and tend to appear brighter than silicate minerals (Adachi and Tainosho 2004). While the number of Fe-rich bright particles present were counted using EDAX GENESIS software, the EDS quantification was determined using the standardless ZAF correction method (where all the elements present in the sample volume were analyzed and the sum of the concentrations was set to unity) and recalculated directly with the software to 100% (weight%).

SEM-EDS techniques are often used to provide detailed information on the morphology and composition of magnetic minerals in fly ashes, (Blaha et al. 2008) or contaminated sediments and soils (Hanesch and Petersen 1999, Jordanova et al. 2004). This information can provide clues about the source and/or combustion process. While Xie et al. (2005) suggested that spherical, fine particles, containing Fe, Si and Al, would originate from coal combustion, Kim (2007) found magnetic particles originating from vehicles contained aggregates of Fe-oxides and Fe-C-S materials or pure Fe and aggregates of Al-Ca-Fe-K-Mg-Si. In this study, the goal was to compare possible sources of particles in the post-test control and exposed soils using SEM-EDS analysis. However, SEM-EDS investigation may sometimes be restricted by particle size. Therefore, an alternative analytical technique that allowed analysis of smaller particles, ICP-OES (inductively-coupled plasma optical emission spectrometry) (Thermo Jarrell Ash Corporation IRIS) was used to determine the distribution of metals on soil magnetic extracts and on roots. The plant root samples (sub-sampled by weight from the total dried roots) were digested with *aqua regia*, using a CEM Mars 5 microwave digestion oven. Certified standard reference materials (DORM–fish protein and PL1547–Peach Leaves) were analyzed as part of the QA/QC protocol. Reagent blanks and analytical duplicates were also used where appropriate to determine limits of detection and to quantify the precision in the analysis, respectively. Both the ICP-OES and the SEM-EDS analyses were done at the Great Lakes Institute for Environmental Research (GLIER), University of Windsor.

3.2.4 Data analysis

Statistical analyses of the experimental data (mean values of MS, element concentrations from chemical analyses) were performed using the SPSS_12.0 and Excel (Microsoft Inc.) software packages. The variance and significance of the differences between the MS of two treatments (controls vs. exposed soils) from S25 and S50 soils were analyzed using a Linear Mixed Model, with confidence interval set to 95%. Statistical tests of pair-wise comparisons between parameters (treatment and soil mixture) were made using a post-hoc Fisher's Least Significant Difference (LSD) technique. The LSD test computes the smallest significant difference between two means (Williams and Abdi 2010) and is considered powerful in determining whether the difference found between two treatments is due to the treatment or simply due to a random chance (Saville 1990). Comparisons between the surficial MS of the soils and some selected element concentrations (Fe, Ti, Mn) in plant biomass and bulk soils were made by calculating the coefficient of determination.

3.3 Results

3.3.1 Surface magnetic susceptibility of soils

Initial surface MS (K) values (mean ± STD in 10^{-5} SI units) in samples intended as controls were 34.57 (±3.9) and 39.92 (±4.1) for S25C and S50C, respectively, whereas in the samples intended for exposure, the S25UC values were 33.84 (±3.9) and 30.27 (±3.7) for S50UC (note that these soils and the measurements made on these samples prior to plant growth are referred to as 'background measurements and soils' hereafter). The MS difference in initial S50C and S50UC could have resulted from the heterogeneous distribution of iron minerals in the various soil components. The surficial MS values decreased (with respect to the background values) substantially (16–28%) in all but the S50UC treatment (increased by 3.3%) at the vegetative growth stage, which is considered to have occurred ~ 4 weeks after the removal of the seedlings. Compared to the vegetative stage, small variations (+/- <10%) in the MS values were observed in the controls, whereas a considerable increase (+14–19%) was observed in the exposed soils, in reproductive stage. In the harvestable stage, the changes (compared to the reproductive stage) in MS values were smaller (+/- <6%) in all but the S25UC treatments (-13.7%). Overall, the magnetic signal increased in the exposed soils more than the control soils during the growth period (Fig. 3.3). Statistical analysis shows that 'treatment' had a statistically significant effect (*p* = 0.000, Table 3.2) in causing these MS differences; however, 'soil mixture' did not (*p* = 0.230). The statistical parameters are reported in Tables 3.1 and 3.2.

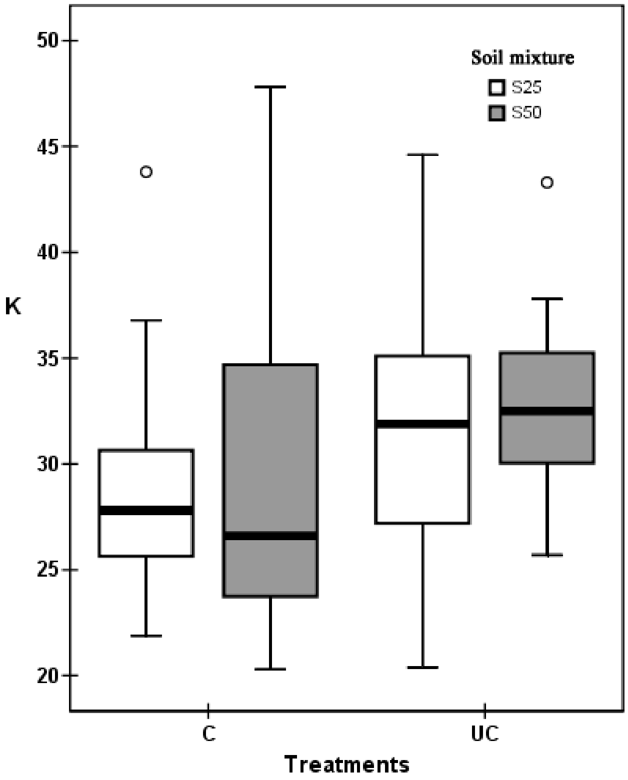

Fig.3.3 Box plots showing overall surficial MS (K x 10^{-5} SI) variation between treatments during the growth period (C- control soils; UC- exposed soils; open circles represent outliers).

Table 3.1 Means of overall MS measurements, together with the 95% confidence interval (CI) for the estimates

Factors	Mean MS (x 10^{-5} SI)	SE	*df*	95% Confidence interval	
				Lower bound	Upper bound
Soil mixture					
S25	29.962	0.505	36	28.937	30.987
S50	30.829	0.505	36	29.804	31.854
Treatment					
C	29.007	0.509	36	27.976	30.039
UC	31.784	0.509	36	30.752	32.816

SE – standard error, *df* – degree of freedom

Table 3.2 Post-hoc (LSD) pair-wise comparisons of parameters (soil mixture and treatment) contributing to the significant differences in MS values

Soil mixture (*I*)	Soil mixture (*J*)	Mean difference (*I-J*)	SE	*df*	Sig.	95% Confidence interval	
						Lower bound	Upper bound
Soil mixture							
S25	S50	–0.867	0.710	36	0.230	–2.307	0.573
S50	S25	0.867	0.710	36	0.230	–0.573	2.307
Treatment							
C	UC	–2.776(*)	0.719	36	0.000	–4.235	–1.317
UC	C	2.776(*)	0.719	36	0.000	1.317	4.235

3.3.2 Magnetic properties of post-harvest bulk soil samples

χ_{lf} values (two random samples each, 10^{-8} m^3/kg units) were found to be 63 and 65 for the S25 and S50 background soils, respectively. However, mean χ_{lf} values of the post-harvest controls were reduced to 55 for S25 and 46 for S50 soils (both in 10^{-8} m^3/kg units), and MS for the post-harvest exposed soils showed a similar range. Note that although the surface MS measurements were quite different between two treatments (Fig. 3.3), this variation was not observed in the χ_{lf} of the post-harvest bulk soils (Fig. 3.4). As the measurement of surficial MS values were made on initially homogeneous synthetic soil, and by applying uniform pressure on the probe throughout the measurements, this procedure largely rules out the possibility of having significant MS variations due to pressure variations (Lecoanet et al. 1999). Therefore, the observed results suggest that the increased MS in exposed soil is primarily surficial.

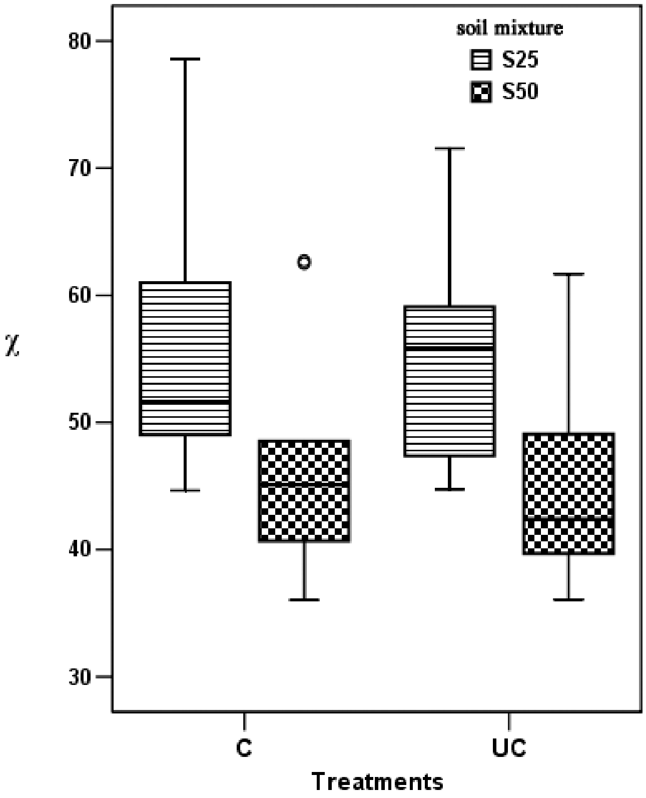

Fig. 3.4 Box plots showing χ_{lf} (10^{-8} m^3/kg) of post-harvest bulk soils (C- control soils, UC- exposed soils, open circle indicates an outlier).

The K–T curves (Fig. 3.5) show that the Curie temperature of the magnetic extracts is between 590 and 610˚C, suggesting the presence of magnetite and/or maghemite. All curves are irreversible, and the MS increase during cooling suggests formation of magnetic minerals (possibly magnetite) due to chemical alteration. The amount of alteration determined using $\chi_{100heating}$ / $\chi_{100cooling}$ (Housen and Musgrave 1996) is between 0.90 and 0.95 for background soil, 0.80 to 0.86 for controls, and 0.75 to 0.77 for exposed soils. Alteration appears to be greater in the post-harvest soils than the background soil (Fig. 3.5), suggesting that chemical and/or biogenic effects have made the magnetic minerals less stable. Hysteresis measurements on all magnetic extracts (from background and post-harvest soils), however, are characteristic of low-coercivity ferrimagnets, most probably magnetite (thin, closed loops with steep central sections and approach magnetic saturation near 300 mT; Fig. 3.6).

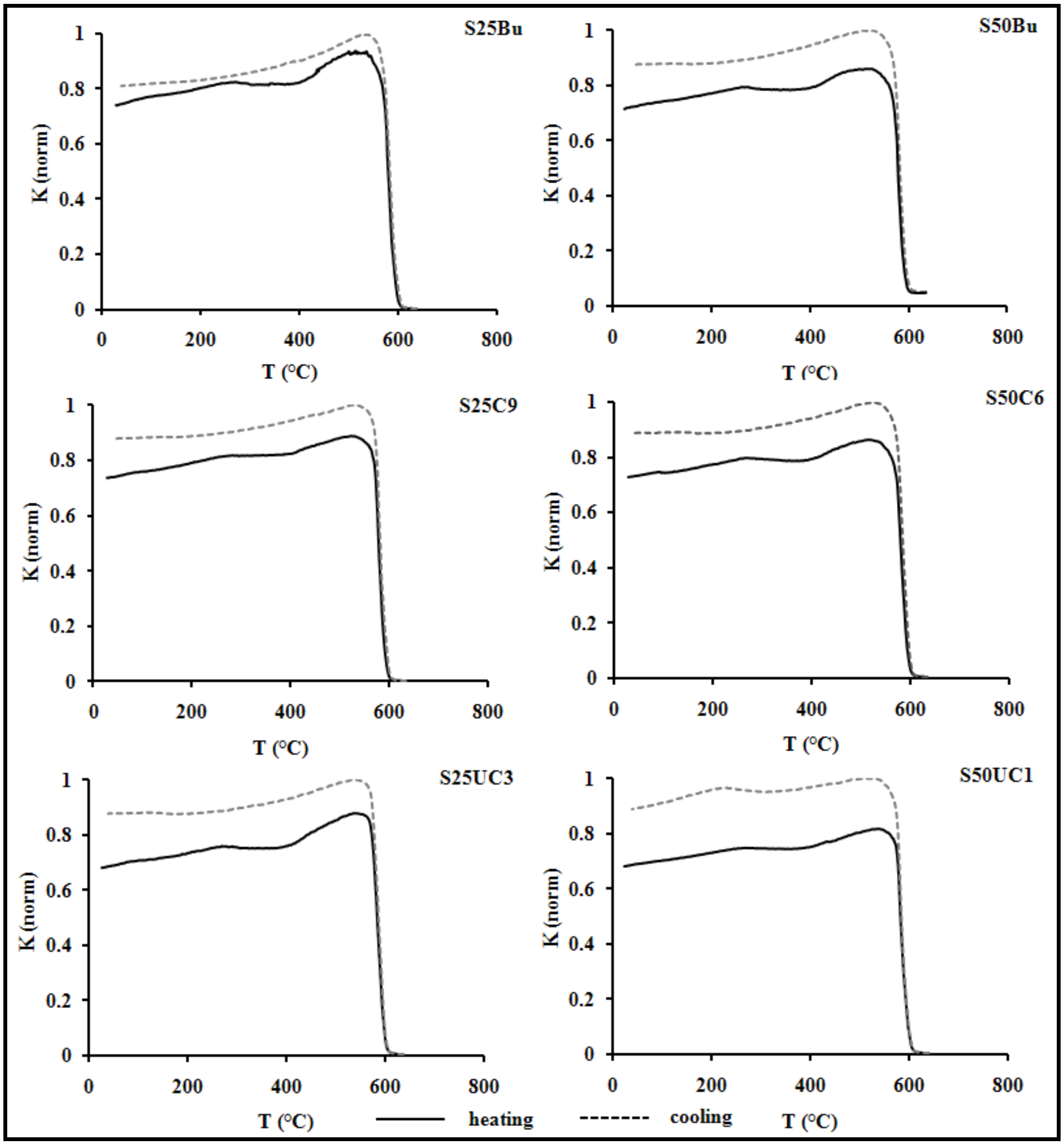

Fig. 3.5 Thermosusceptibility curves (K-T) of magnetic extracts from background soils (S25Bu, S50Bu), post-harvest control soils (S25C9, S50C6), and exposed soils (S25UC3, S50UC1).

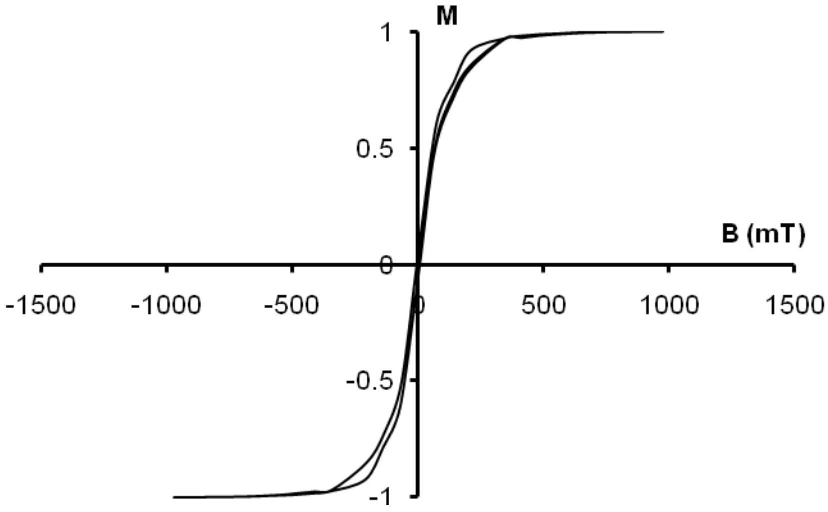

Fig. 3.6 Typical hysteresis loop for magnetic extracts from background and post-harvest soils (intensity normalized to saturation magnetization).

3.3.3 Vertical MS profiles in control soils

The top 5 cm of the 8 cm deep longitudinal section of the container soil was used to construct MS profiles. In each pot, three profiles were taken, one in the centre (P1) and the other two (P2 and P3) near the edges of the pot. Fig. 3.7 shows MS profiles of representative samples from the control pots. The near surface (depth of 1 cm) MS differs only slightly (± 7 SI) within each container, with two exceptions (S25C2, S50C9), and the profiles are similar within a single container. The results show magnetic enhancement (compared to the near surface values) at depths of 2 to 5 cm in some samples (S25C2, S25C4 and S50C2), while MS is almost constant in others (S25C3, S50C1 and S50C9). Such magnetic enhancement at depths may suggest that Fe-containing particles that were present in the background mixtures have been concentrated at this depth, potentially by downward migration.

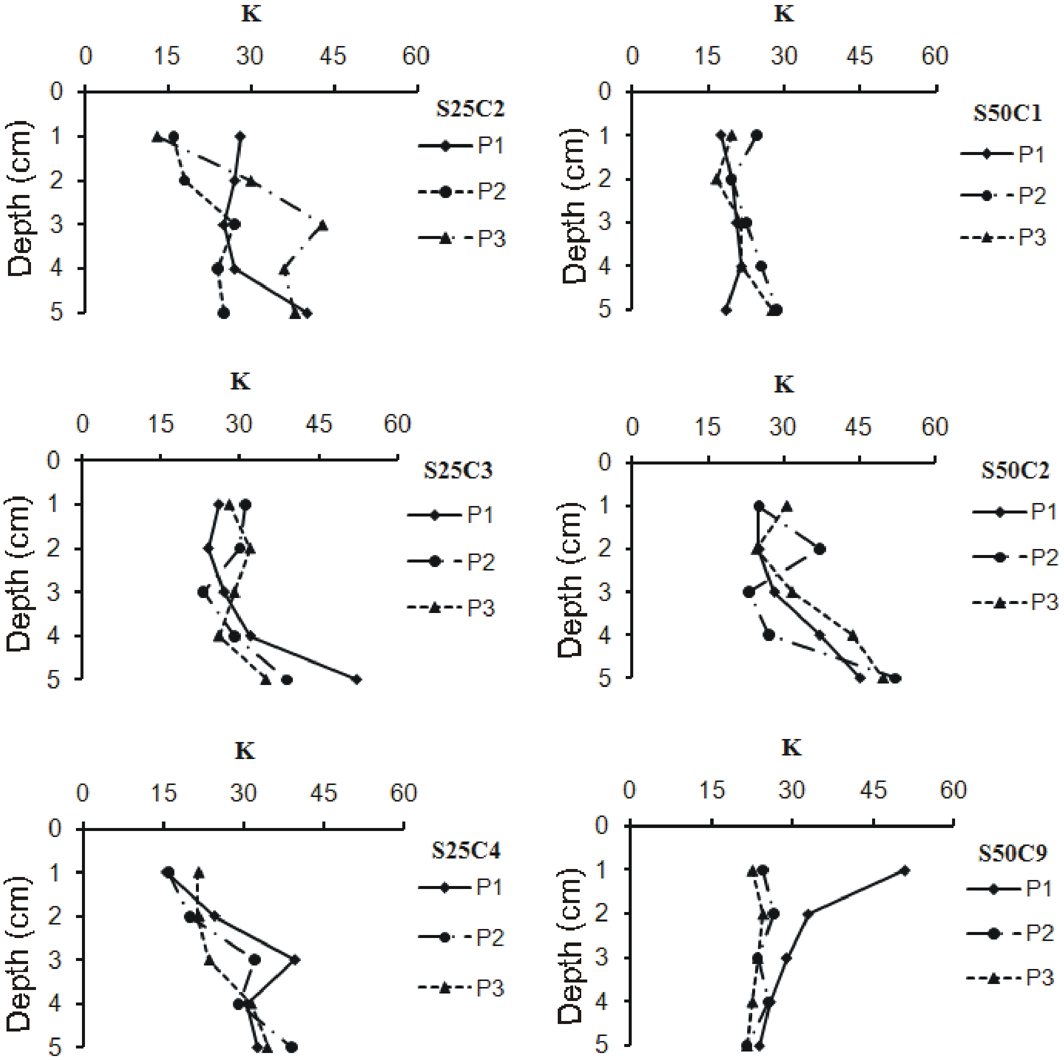

Fig. 3.7 MS (K× 10^{-5} SI) profiles from longitudinal sections of representative soils from controls

3.3.4 SEM-EDS investigation of magnetic particles

The bright (metal-rich) particles investigated can be grouped into 3 morphological types: angular particles, aggregates and spherules. The most frequently observed magnetic particles in all samples were angular particles between 5 and 10 μm in length, and oval aggregates (~ 25 to 100 μm) (Fig. 3.8). Relatively fewer spherules were observed in the soil components and in the control soils than the exposed soils, and those were generally found agglomerated with other particles (Fig. 3.9). Examination of the exposed soils revealed more spherules (Fig. 3.10). In addition, the number of Fe-rich particles, including spherules, which for this study included all particles having a minimum Fe concentration of 38%, was counted using the EDAX® GENESIS® software and was found to be approximately double in the exposed soils. For example, in one set of paired samples, of the 103 total bright particles in S25C3 and 85 in S25UC3, only 5% of the total number was Fe-rich in the former and 12% in the latter. While no statistical analysis could be made of the number of spherules in the specimens due to the nature of the observations, this empirical evidence suggests that the exposed soils contain more Fe-containing particles than the controls. Amount of metal deposition could be determined by directing measuring the particulate amount retained by the HEPA filter; however, this was not performed in this study.

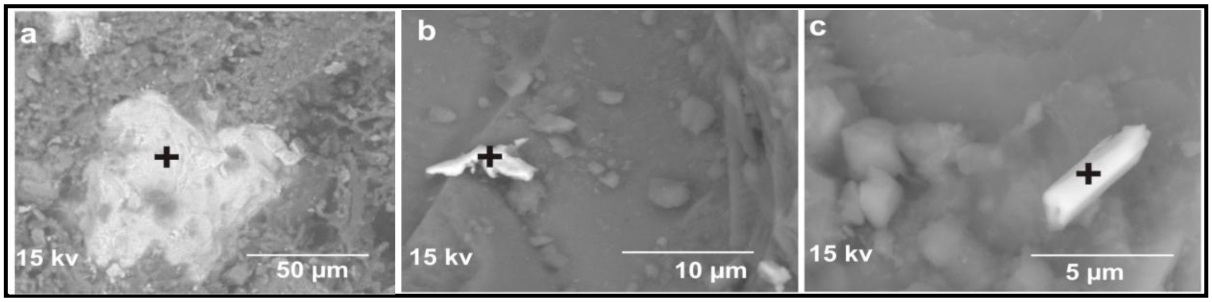

Fig. 3.8 SEM images (BSE mode) of bright, Fe-rich particles: (**a**) aggregates, and (**b, c**) angular particles. EDS analyses were made on locations marked with a positive sign (+) and results are presented in Table 3.3.

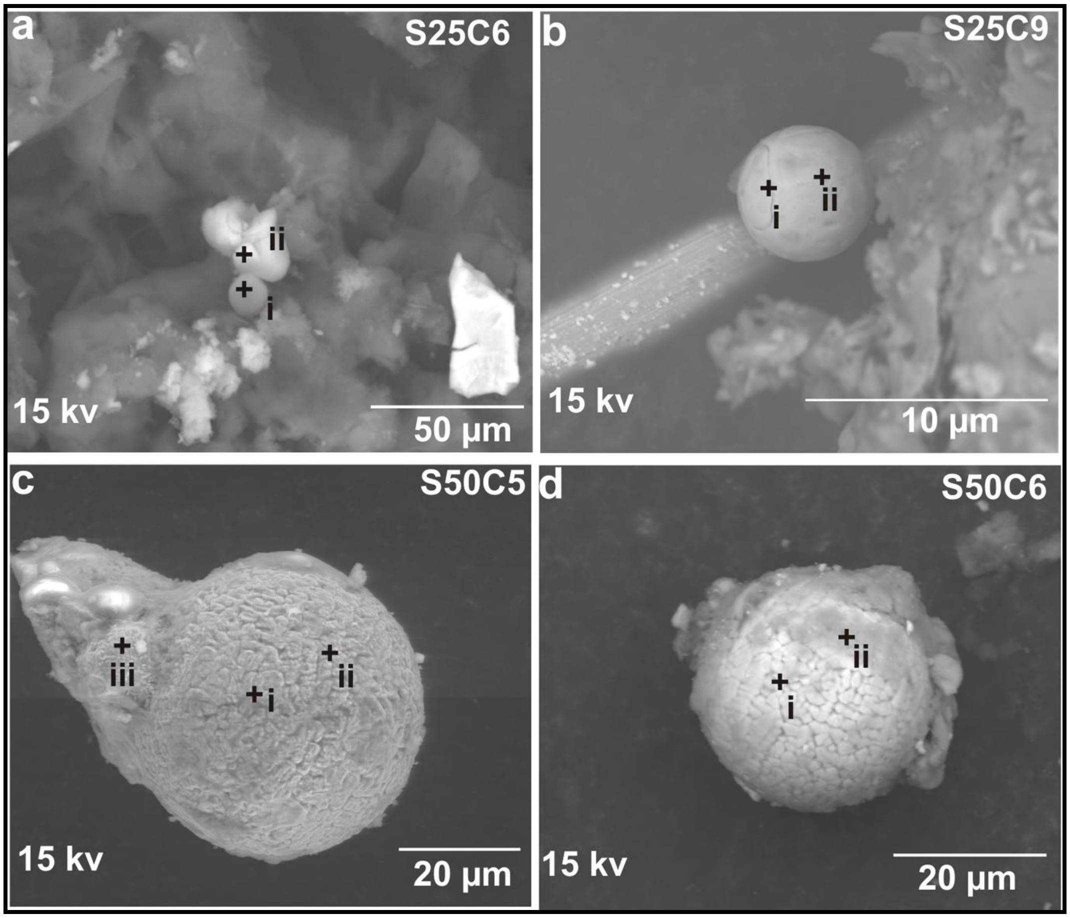

Fig. 3.9 SEM images (BSE mode) of magnetic spherules from individual soil components and control soil samples.

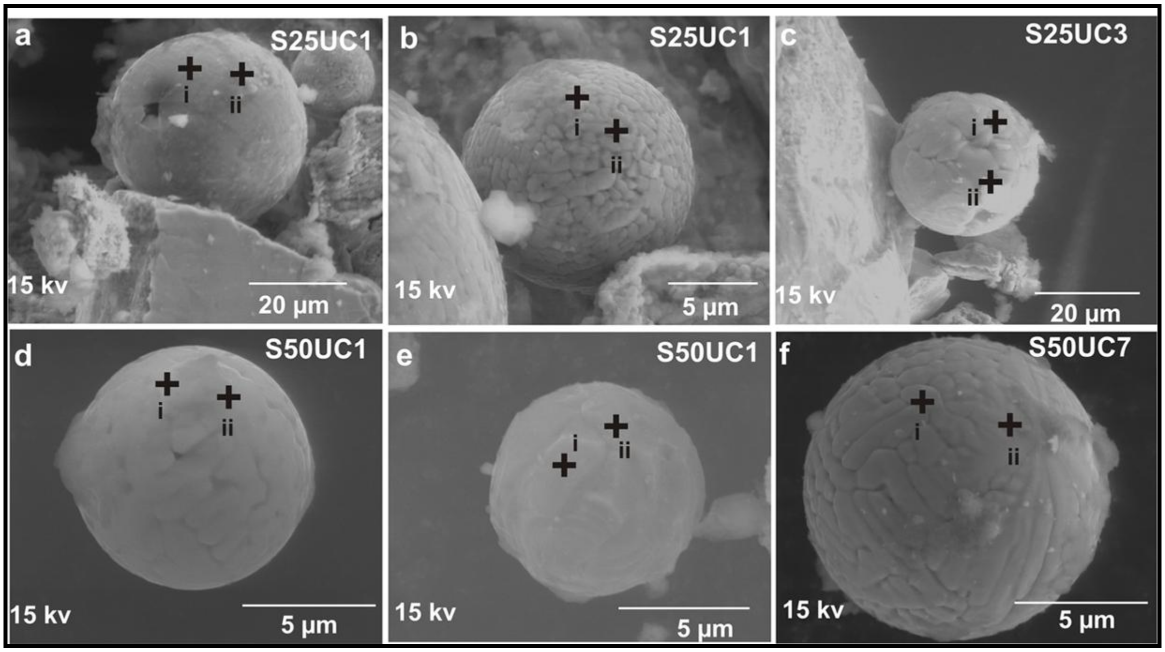

Fig. 3.10 SEM images (BSE mode) of magnetic spherules from exposed soil samples.

EDS analysis showed that carbon was present in all samples analyzed, constituting between 9 and 30%, as were iron and oxygen, indicating the presence of Fe or Fe-containing minerals. The weight percentage of Fe was higher (50 to 82%; mean 68.62%) in exposed samples than in the control samples (37 to 68%; mean 53.75 %; Table 3.3), and the mean difference in Fe% was found to be statistically significant between the treatments ($p = 0.001$). Because Fe is present in both the background mixture and the post-test soils, some of the iron must be inherited; however, enrichment must have also occurred. While silicon and aluminium were much lower in the spherules than the angular particles, their higher concentration in the darker particles suggested that they are alumino-silicates. Titanium and cobalt were present in some spherules from the exposed soil; however, metals such as copper, zinc, molybdenum and lead were below the detection limit in all samples.

Table 3.3 EDS results for angular particles and aggregates from Fig. 3.8, and for spherules from Fig. 3.9 and 3.10.

Particle	Particle figure referral	Elemental weight percentage (normalized to 100%)												
		Na	O	Mg	Al	Si	P	K	Ca	Ti	Cr	Mn	Fe	Co
Aggregates	8-a(i)	–	32.14	–	0.81	2	–	–	1.06	–	–	–	64.14	–
	8-a(ii)	–	36.99	–	–	1.61	–	–	1.28	–	–	–	60.28	–
Angular particle	8-b(i)	0.78	22.79	3	2.22	6.53	–	–	2.3	–	–	–	62.3	–
Angular particle	8-b(ii)	1.02	56.38	8.13	5.17	17.58	–	–	5.76	–	–	–	5.79	0.51
Angular particle	8-c	–	54.49	1.08	4.8	19.24	14	1.79	–	–	–	–	4.13	–
Spherule (S25C6)	9-a(i)	–	43.6	–	1	3.8	1.4	–	5.5	–	–	–	44.7	–
	9-a(ii)	–	31	1.4	1.5	4.7	1.5	–	7.7	–	–	–	52	–
Spherule (S25C9)	9-b(i)	–	21.9	1.4	1.8	5.8	–	–	3.3	–	–	–	63.7	–
	9-b(ii)	–	18.9	1.5	1.7	5.2	–	–	3.4	–	–	–	68.7	–
Spherule (S50C5)	9-c(i)	–	43.2	–	1.2	2.4	–	–	–	–	–	–	53.1	–
	9-c(ii)	–	35.2	–	1	2.6	–	–	–	–	–	–	60.8	–
	9-c(iii)	–	36.4	0.8	2.2	4.3	–	–	1.8	–	–	–	54.1	–

Table 3.3 continued

Spherule (S50C6)	9-d(i)	–	44.5	–	0.8	2.7	–	–	1.7	–	–	–	49.6	–
	9-d(ii)	–	50.7	1	0.9	2.7	1.9	–	5.2	–	–	–	37.1	–
Spherule (S25UC1)	10-a(i)	–	32.36	–	–	1.02	–	–	–	–	–	–	66.62	–
	10-a(ii)	–	30.16	–	–	1.39	–	–	–	–	–	–	68.45	–
Spherule (S25UC1)	10-b(i)	–	30.2	–	1.16	1.96	–	–	–	–	–	–	66.69	–
	10-b(ii)	–	29.13	–	–	1.68	–	–	–	–	–	–	69.19	–
Spherule (S25UC3)	10-c(i)	–	39.61	–	–	1.02	–	–	–	1.45	–	–	57.63	–
	10-c(ii)	–	22.19	0.45	0.64	1.22	–	–	0.69	3.11	–	–	71.42	0.22
Spherule (S25UC3)	10-d(i)	–	41.65	–	0.77	1.38	–	–	–	–	–	–	56.21	–
	10-d(ii)	–	46.73	–	0.74	1.47	–	–	–	–	–	–	50.82	–
Spherule (S50UC1)	10-e(i)	–	33.85	–	–	1.1	–	–	–	–	–	–	65.05	–
	10-e(ii)	–	30.33	–	–	1.48	–	–	–	–	–	–	68.19	–
Spherule (S50UC7)	10-f(i)	–	27.96	1.25	2.4	5.02	–	–	4.49	–	–	–	59	–
	10-f(ii)	–	10.92	0.46	1.11	2.36	–	–	1.89	–	–	–	82.97	–

3.3.5 ICP-OES investigation of plant biomass and magnetic extracts of soils

Before selecting plant samples for chemical analysis, the MS of the cleaned plant roots was measured to detect magnetic enhancement due to uptake and storage of Fe and other coexisting trace/heavy metals. The values were almost negligible (between $+1\times 10^{-5}$ and -1×10^{-5} SI), suggesting either a lack of magnetic enhancement, or an inability to measure any enhancement using this technique and instrument. Therefore, random samples (5 from each of the four sets of samples) were selected for chemical analysis in the ICP-OES. Table 3.4 shows a clear difference in element concentrations in plant roots between the treatments. In exposed plants, while concentrations of some metals, such as Cd, Co, Mo, Ni, Zn, are just slightly higher than in the controls, other metals such as Al, Fe, Mn, Pb and Ti are nearly double. This indicates that plants grown in exposed soils have uptaken more of these metals from the soil. Visual observation, however, suggests that the growth of these plants was not affected.

Table 3.4 Average element concentrations (mean, µg/g) in plant biomass (dry weight) derived from the four treatments (n = 20).

Elements	Treatments			
	S25C	S50C	S25UC	S50UC
Al(*)	631.72	584.65	1010.22	1142.86
B	20.89	20.39	23.54	25.95
Cd(*)	0.52	0.47	0.62	0.81
Co	0.76	0.73	0.85	1.11
Cr(*)	0.96	DL	1.76	1.76
Cu	14.98	15.02	20.08	19.68
Fe(*)	652.33	627.65	1065.25	1296.27
Mg(*)	2216.59	2259.04	3445.06	3467.37
Mn(*)	32.81	29.02	56.41	64.05
Mo	0.83	1.93	1.39	1.48
Ni	2.16	2.32	2.95	3.23
Pb(*)	2.08	DL	2.96	4.75
Ti(*)	21.62	21.96	31.32	38.53
V	3.28	4.01	3.43	4.11
Zn(*)	37.21	32.77	46.72	57.48

DL - detection limit of the instrument
(*) indicates increase in concentration in exposed plants

Element concentrations in magnetic extracts from soils are reported in Table 3.5. There is no obvious trend in the distribution of elements between the treatments as was observed in the plant biomass results (Table 3.4). While concentrations of some metals (Co, Mg, Mn, Ti) in post-harvest soils are less than the background mixtures, other metals such as Cr, Ni, Pb and Zn, have higher concentrations. When comparing element concentrations between treatments within the 25C/25UC soil mixtures, however, many of the elements such as Fe, Co, Ni, Ti, Zn, Pb are present in higher concentrations in the UC samples but the reverse is true for the S50 soil mixture.

Table 3.5 Average element concentrations (mean, µg/g) in post-harvest soils and background soil mixtures (dry weight) (n = 24).

Elements	Treatments				Background soil mixtures	
	S25C	S50C	S25UC	S50UC	S25C	S50C
Al(*)	9450.58	11303.88	9889.97	11460.63	10128.18	11446.2
B	15.45	11.04	17.46	13.38	20.92	16.41
Cd(*)	4.87	7.47	5.31	5.5	5.75	5.31
Co	16.72	27.2	19.54	19.51	17.88	21.54
Cr(*)	142.75	253.07	121.55	141.1	141.65	124.51
Cu	30.45	13.57	57.29	24.87	31.59	30
Fe(*)	86564.37	138844.95	93865.03	99267.34	104616.53	91635.44
Mg(*)	9397.22	10008.01	9988.72	10040.32	10476.82	10608
Mn(*)	597.52	802.28	557.58	583.34	581.1	935.22
Mo	2.55	2.69	14.51	1.95	3.03	1.45
Ni	42.07	55.92	68.25	47.27	42.96	40.59
Pb(*)	25	24.42	44.49	23.18	26.42	21.3
Ti(*)	2184.15	5986.86	2473.02	3035.99	2684.01	4255.97
V	174.68	338.75	146.8	219.56	176.75	242.23
Zn(*)	205.5	222.48	231.92	147.76	172.36	130.1
Ca	18073.05	11627.77	19056.28	14416.49	20343.01	15951.7
K	2222.97	1701.47	2002.79	1567.77	4390.33	2953.71
Na	946.2	760.77	766.65	673.53	1234.83	865.47

(*) indicates elements of major differences between two treatments (S25C and S25UC; S50C and S50UC)

3.3.6 Correlations between magnetic and geochemical measurements

As mentioned previously, both the volume and mass susceptibility of the plant biomass could not be measured due to detection limits of the instruments used. It was, therefore, decided to examine whether measurements of MS from the surface soil could be compared with selected ICP-OES geochemical parameters from the plant biomass and soil magnetic extracts. Scatter plots of Fe, Ti and Mn concentrations in the plant biomass as a function of MS (Fig. 3. 11a) of surface soils at the harvestable stage show some correlation (coefficient of determination, R^2 in the range of 0.55 to 0.63). It is clear that the measurements fall into two groups: the higher values of MS in the soil correspond to higher concentrations of these elements in the plants grown in the exposed soils. When the same test was run on the soils (Fig. 3.11b), the correlations observed were not as high (R^2 in the range of 0.05 to 0.12), and the grouping of the controls and exposed sample sets was not as distinct, although the MS values in the exposed soils were again generally higher than in the control soils.

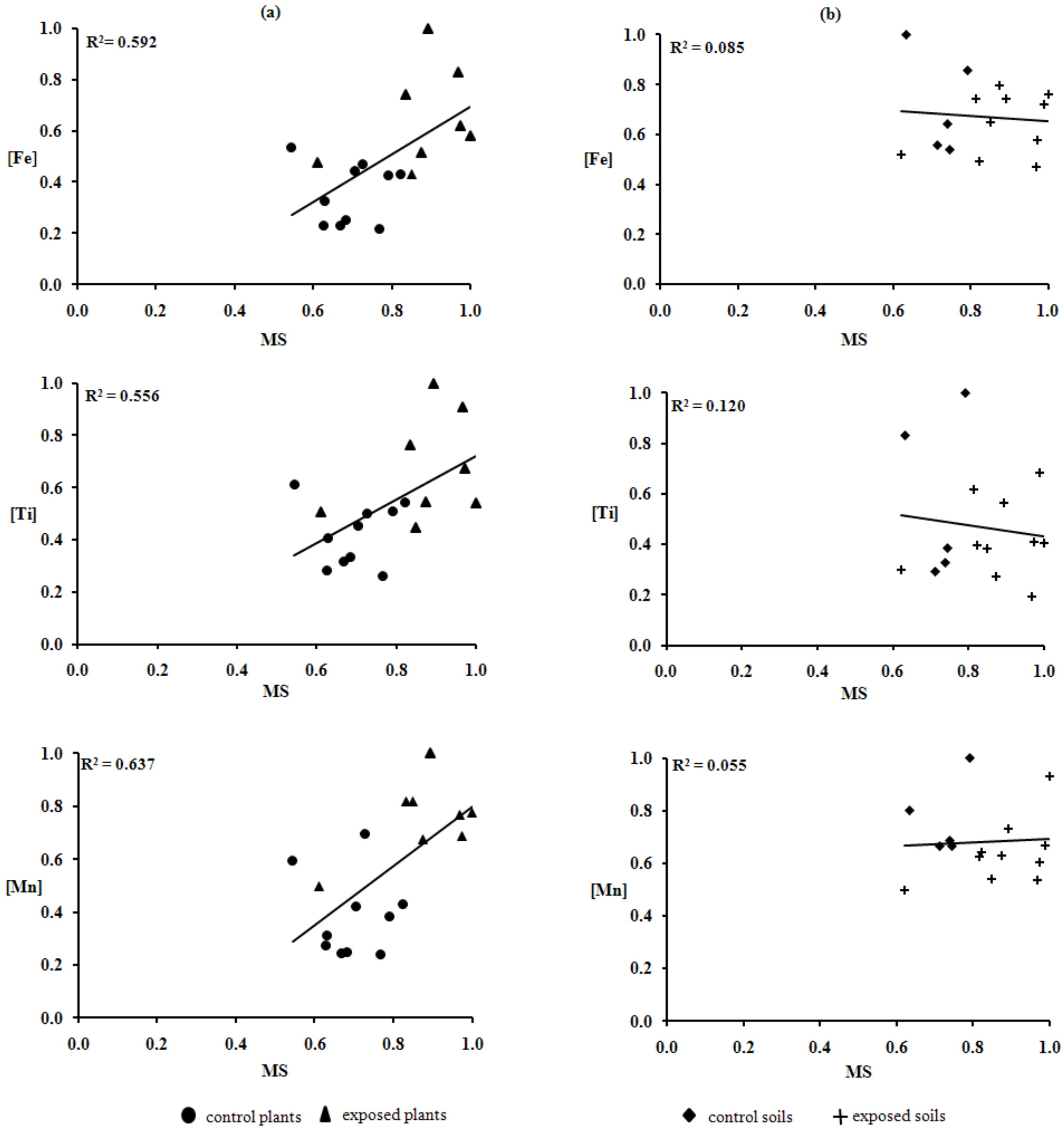

Fig. 3.11 Scatter plots (normalized values) between surficial MS values at the harvestable stage and the ICP-OES geochemical measurements, with their coefficient of determination (R^2) indicated: (**a**) plants, (**b**) magnetic extracts from post-harvest soils.

3.4 Discussion

The MS decrease in the control samples is in agreement with the results obtained in a similar greenhouse growth experiment by Sapkota et al. (2012). The authors suggested three reasons for the decrease: Fe uptake by plants, magnetic mineral transformations, and downward vertical migration of iron containing particles. Mineralogical transformation from highly magnetic to less magnetic minerals was postulated to be the major contributor to the overall MS decrease; however, vertical migration could not be excluded. In this study, the potential contributions of the vertical migration of Fe-containing particles and trace/heavy metal uptake and storage by plant roots were explored.

Angers and Caron (1998) suggested that vertical migration of particles could occur through macropores caused by root penetration, or through channels created by watering. Irrespective of the cause, downward migration of Fe-rich (i.e. ferrimagnetic) particles would result in a reduction in the quantity of these particles at the soil surface, and a reduction in surface MS would be expected. In a separate migration experiment, Sapkota and Cioppa (2012) determined that artificially-introduced Fe particles migrated vertically to a depth of 2–9 cm and the surficial soil MS decreased significantly from the initial values. In this experiment, we considered migration in the absence of artificially-introduced Fe particles in a synthetic, initially homogenous soil. Fig. 3.7 shows magnetic enhancement (or susceptibility maxima) in some container soils (S25C2, S25C3, S25C4 and S50C2) at depths between 2 and 5 cm, together with a decrease in surficial soil MS. These results, and those from past studies (e.g., Kapicka et al. 2011, Sapkota and Cioppa

2012), allow us to conclude that translocation of Fe-containing particles has occurred and is measurable using the MS technique. A plant-free control set, however, would have been useful to examine the role of plant growth or mechanical perturbation, as well as chemical changes related to wet-dry cycles, in the downward migration of the Fe-containing particulate.

While the initial surface MS values in the controls were slightly greater than the exposed soils, the overall MS (between initial to harvestable stages) decreased in the controls and increased in the exposed soils (Fig. 3.3). Statistical analysis of the MS values showed a significant difference, with the exposure to unfiltered air contributing the most to the MS increase in exposed soil (Tables 3.1 and 3.2). This result, as well as the differences observed in both the EDS measurements and the ICP-OES measurements (particularly the trace metal concentrations), clearly reflect an additional input of Fe-containing particles. Given experimental and environmental settings, this additional source of particles is most likely to be deposition of atmospheric particulate pollutants.

There are a number of potential sources of atmospheric pollution nearby including automotive and transportation sources, auto manufacturing plants, refineries and waste incinerators and steel plants (Hammond et al. 2008). In addition, dust from coal-fired power plants and steel mills could also enhance the surface soil MS values, but their contribution to the total MS can vary with proximity to these sources, redistribution by erosional processes, and post-depositional dissolution (Kapicka et al. 1999). Since fine (0.05 to 2 µm) particles can be transported some 1000 km, the Windsor area could contain such particles. It was also noted that street reconstruction was occurring near (approximately 200 meters west) the experiment, which may have influenced the atmospheric composition by producing the particulates.

In the soils, the SEM images showed agglomerations of spherical and irregular particles composed of mainly inorganic constituents. Because topsoil and manure used in the synthetic soil mixture consisted of leaves and yard compost that have been exposed to atmospheric particulates, there is the potential for observing Fe-containing spherules in controls soils as well as in the exposed soils. The likelihood of observing magnetic spherules, however, was higher in exposed soils than in the control and background soils, indicating an enrichment of Fe-containing spherules in these soils. The observed particle morphology is typical of coal fly ash and exhaust from steel mills and vehicles (Blaha et al. 2008, Giordano et al. 2005, Kim et al. 2007) and the relative proportions of Fe, O and C compared to elements such as Si and Ca determined using EDS, suggest coal combustion products (Xie et al. 2005). In comparison, the Fe-rich angular particles could either be of traffic origin (e.g., brake dust, abrasion or corrosion of vehicle bodies; Lu et al. 2010, Matzka and Maher 1999) or may have a natural origin. There are several potential industrial sources in the Detroit area that emit $PM_{2.5}$ particulates including oil refineries, steel mills (National Steel, Ford Rouge Foundary, Bean Steel and Hascall Steel Companies) and power plants in Michigan (Morishita et al. 2006). The prevailing wind direction, which would have carried emissions from these potential sources from Detroit to the Windsor area, probably contributed to most of the particulates observed in exposed soil. In addition, power plants such as Nanticoke, the largest coal-fired power plant in Ontario (roughly 300 km northeast from Windsor) could also influence the atmospheric particulate matter within the studied area due to the long-range transport of the atmospheric aerosols. As further evidence of strong atmospheric particulate pollution in the area, a preliminary chemical and SEM biomonitoring survey done on the leaves of two species of trees in Windsor also found smooth spherules of iron (pers. comm. Dr. Joel Gagnon, University of Windsor).

The connection between, and potential use of, the magnetic-geochemical observations of the increase in surface soil MS and trace/heavy metal concentrations in the roots due to the presence of atmospheric particulate pollutants (most likely anthropogenic) was examined further. Bivariate scatter plots (Fig. 3.11) were used to evaluate correlations between element (Fe, Ti and Mn) concentrations in soils, plant biomass and surficial soil MS. It was observed that increased MS was associated with the increased element concentrations mainly in the plant biomass and to a lesser extent in the bulk exposed soils (correlations in the soils were much weaker than in the plant biomass). This implies that the Fe concentration in the plants is influenced by the magnetic particles in soil, rather than the total iron concentration in soil. Given that the variation in atmospheric particulate matter was the only difference between the two treatments, the correlations between the Fe, Mn and Ti concentrations in the plant biomass and the surficial soil MS imply that not only does the atmospheric particulate matter increase the MS of the exposed soil surface (as has been observed in numerous studies), but that it also leads to increased uptake of trace/heavy metals by the plants grown in the affected soil. In phytoextraction studies, a significant correlation has been observed between heavy metal doses in soils and corresponding effects on plants through roots (cf., Punz and Sieghardt 1993). In our study, geochemical analysis of plant roots showed that plants grown in exposed soils had higher (twice as much) metal concentrations (Al, Fe, Mn, Pb and Ti) than those from the controls (Table 3.4), which suggests that the bioavailable metal content was higher in the exposed soils than in the controls. The observed correlation suggests that measurements of surficial soil MS, when calibrated properly, may be used to indicate the potential concentration of metals, such as Fe, Mn, Pb and Ti, in the plant biomass as well, in addition to indicating the rate of change in soil metal concentrations. The predictive equations for determining the biomass metal concentration, however, are likely to be site (based on soil characteristics) and plant specific.

In summary, the higher concentrations of trace/heavy metals in plant roots and the higher values of MS in post-test exposed soils show that these soils and plants have become enriched with such metals relative to the controls. Similarly, Pandey and Pandey (2009) showed that concentrations of heavy metals (Zn, Pb, Cu, Ni, Cd) in field grown vegetables were significantly higher than those grown inside a glasshouse, and concluded that atmospheric pollution was the major contributor of these metals. These results suggest that even organic (i.e., pesticide/fertilizer free) produce can contain significant amounts of anthropogenic contaminants. Furthermore, it is clear that areas considered as 'pristine' could also be affected by atmospheric particulates. In previous studies (e.g., Han et al. 2007, Sun et al. 2004), background PM deposition has been recognized, however, many case studies consider the 'background soil' (and associated MS values) to be clean and non-polluted with respect to polluted soils near point sources such as industries/mills. As this study shows that background soils can collect atmospherically-derived metals, therefore, estimates of anthropogenic contamination which simply remove the 'background' values may underestimate the actual pollutant concentration.

Our study shows that an enhancement in Fe and other associated toxic metals due to atmospheric pollution in soils can be detected by measuring surficial soil MS (if the elements are present in high enough concentrations), as well as by standard geochemical methods. In addition, comparisons of magnetic parameters (surficial soil MS) and elemental concentrations (obtained from ICP-OES) show that magnetic parameters can be a good proxy for detecting and quantifying toxic (heavy) metal uptake by plants grown in polluted soil.

3.5 Conclusions

Measurements of soil surface MS and soil and plant magnetic and chemical properties were used to detect the effect of atmospheric pollution on synthetic soils and plant biomass in a controlled experiment. Although the soil surface MS decreased in early growth stages in all treatments (probably due to vertical migration of Fe-containing particles and Fe uptake by plants), the overall MS in exposed soil was significantly greater than in the control samples. The exposed soils collected atmospherically-derived particulate matter, which not only increased the surficial MS over time but also increased the potential for increased trace/heavy metal uptake by plants grown in this soil. Correlations evaluated between element (Fe, Ti and Mn) concentrations in plant biomass, post-harvest soils and surficial soil MS, showed that increased MS is associated with increased element concentrations in both the exposed soils and the plant biomass.

Examination of the magnetic extracts under SEM-EDS revealed that both soil treatments are rich in Fe-containing particles. Evidence of Fe-enrichment in the exposed soils (i.e., higher Fe concentrations and more Fe-rich particles), however, suggests significant input from atmospheric particulates, consistent with the increase in MS values. Based on the environmental setting, it is inferred that angular magnetic particles may be derived from traffic-related sources as well as natural sources. Similarly, spherical magnetic particles may be derived from coal-fired power plants and steel plants located in close vicinity to Windsor. These results suggest that traffic emissions and industrial combustion are the dominant external sources of the magnetic particles present in the soils.

In this, and other studies, magnetic measurements have been shown to be good proxies for detecting atmospherically-derived toxic metal particulates in soils. However, in an effort to better understand how these particulates affect soil and biomass magnetic and chemical properties, continuous biomonitoring studies are essential. Such experimental studies may be able to define localized variations in air pollution very effectively.

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CHAPTER 4

ASSESSING THE USE OF MAGNETIC METHODS TO MONITOR VERTICAL MIGRATION OF METAL POLLUTANTS IN SOIL

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4.1 Introduction

Heavy (i.e., toxic) metal pollution in soils is on the rise in industrial and urbanized areas of developing nations, and is of significant concern for human health, both because of the high quantities involved, and the widespread dispersion of fine particles that can easily be carried by wind and are inhalable (Jarup 2003). One of the major sources of such metal pollution in soil is atmospheric pollution (Li et al. 2001), which is mainly caused by energy production, mining, metal smelting and refining, manufacturing processes, transport and waste incineration (Nriagu 1990). Heavy metals generated from such anthropogenic activities settle through wet/dry deposition on soils, and then accumulate by sedimentation, impaction or interception (Li et al. 2001). Depending on their chemical origin and soil quality factors, only the mobile heavy metals move below the surface topsoil and migrate down through the underlying soil horizons.

Heavy metal transport within soil profiles is a major environmental problem, as elevated concentrations can have adverse effects on soil quality and biota (Giller et al. 1998), affecting the ecosystem function, and potentially leading to deterioration of groundwater quality (Behbahaninia et al. 2008). Because of the concern about the environmental danger that these metals could represent if mobilized, a number of studies have attempted to clarify the different factors that contribute to metal solubility and transportability in soils. Alloway and Jackson (1991) cite several studies that reported some downward metal translocation in specific soils. According to their report, the movement of heavy metals within sewage sludge-amended soils is limited to the first few centimeters below the depth of sludge injection. Because such studies rely primarily on traditional sampling and chemical analysis, which are not particularly rapid and efficient, the use of these techniques for quick screening and monitoring of potential heavy (toxic) metal pollution and migration in soils is difficult. Therefore, it would be advantageous to develop fast and inexpensive screening techniques, which can serve as complementary and alternative tools to the standard chemical analyses of pollutants (Duan et al. 2010).

Several studies (e.g., Boyko et al. 2004, Schmidt et al. 2005) have shown that magnetic measurements can serve as a simple, fast, inexpensive, and nondestructive tool for pollution screening and monitoring. Mineral magnetic measurements provide detailed information about the composition, chemical state and grain size of iron-oxides, the most common ferrimagnetic minerals in soil (Schmidt et al. 2005). *In situ* magnetic measurements of topsoil have been successfully applied in polluted areas for estimating anthropogenic pollution (e.g., Gautam et al. 2005, Kapicka et al. 1999, Petrovsky et al. 2000), outlining polluted areas, and assessing the level of contamination (e.g., Durza 1999, Hanesch and Scholger 2002, Lecoanet et al. 2003). Similarly, magnetic measurements of vertical profiles from polluted areas, such as areas around power plants and steel mills, can discriminate the anthropogenic and lithogenic influences on topsoil magnetic susceptibility (Magiera et al. 2006). To date, however, there are no relevant reports using the magnetic screening technique to monitor vertical migration of pollutants in soil, or to calculate quantitative migration rates. A recent study that used magnetic susceptibility (MS) distributions within a column experiment (Kapicka et al. 2010) determined that both fly ash and fine-grained magnetite moved only a few centimeters vertically downward in sand of various particle sizes. Such laboratory metal leaching studies performed on homogenous soils, however, might under or overestimate metal mobility in the field, and may not necessarily represent the range of physical conditions that result from natural weather variability. In this context, the present study was aimed at investigating the migratory behavior of iron particles in natural soils, using magnetic methods.

4.2. Materials and Methods

4.2.1 Site description and materials

A controlled experiment was performed on grass-covered ground near a woodlot in Belle River (42° 12' N and 82° 43' W), Ontario, during August to December 2009, to monitor migration behavior of the Fe-pollutant in one season. The studied area is more than 20 km from any local industries (primarily chemical) and even further from potential heavy metal emission sources, and is considered *a priori* a non-polluted area. The soil is Quaternary in age, consisting primarily of glacial till (Tavistock Till) overlain by localized alluvium deposits, and exhibits grey-brown Podsolic characteristics under the vegetative and climatic conditions that prevail in the area (Soil Survey of Essex County Report 1949). On a textural basis, the soil at the site can be classified as a silty-clay, heavy textured soil, with poor drainage characteristics.

Twenty PVC tubes (16" in length and 8" in diameter) were cleaned and then inserted to a depth of 14" vertically into the ground as test capsules (Fig. 4.1), in order to avoid contaminating the surrounding area and prevent lateral migration. The length of the tube was chosen based on an estimate of the extent of potential metal accumulation in the upper few centimeters of soil, as described in the literature (Alloway and Jackson 1991, Kapicka et al. 2010, Spiteri et al. 2005). The tubes were placed randomly over an area of approximately 50 m^2, with at least a meter distance between each. The existing grass inside the tubes was removed prior to contaminating half the number of tubes with iron oxide powder (magnetite milled to <5 µm by READE Advanced Materials®, USA), because thick grass often acts as a biological filter to these pollutants, however, the tubes were not weeded during the experimental period so as not to affect the magnetic properties of surface soil and the migration process. Iron oxide was chosen to simulate contamination because several forms of iron oxide have been studied intensively in environmental magnetic studies because they constitute the most common magnetic particles in pollutants (Huliselan et al. 2010). The amount of the pollutant to be distributed per tube was determined by reference to the study of Magiera et al. (2007) which found, using metal analysis of polluted soils, that the Iron (Fe) concentration was in the range of 0.7 to 9.7 g/kg in soil cores, and that the highest concentration of dust per area in the region (Upper Silesia, Poland) was 600 g/m^2. In our experiment, within each tube, the internal surface area was 0.0324 m^2, and the necessary amount of pollutant was calculated to be 19.44 g/tube, using the concentration value of 600 g/m^2 determined in Magiera's study. Instead, 10 grams of pollutant/tube was used to simulate a moderate level of pollution, consistent with the lesser time of pollutant accumulation within this study area. After the pollutant was distributed (manually by hand) on the soil, the pollutant was covered with a very small amount of non-contaminated, background surface soil and then with a thin (~ 1 mm) sheet of cheesecloth in order to prevent the pollutant from being blown away or removed by rainwater, as well as to prevent a direct loss of the pollutant during measurements. Precipitation was measured using a Tru-chek® rain gauge that was mounted to a wooden post with an aluminium bracket. Readings less than 0.05 mm were recorded as trace and others are presented in a tabular format (Table 4.4).

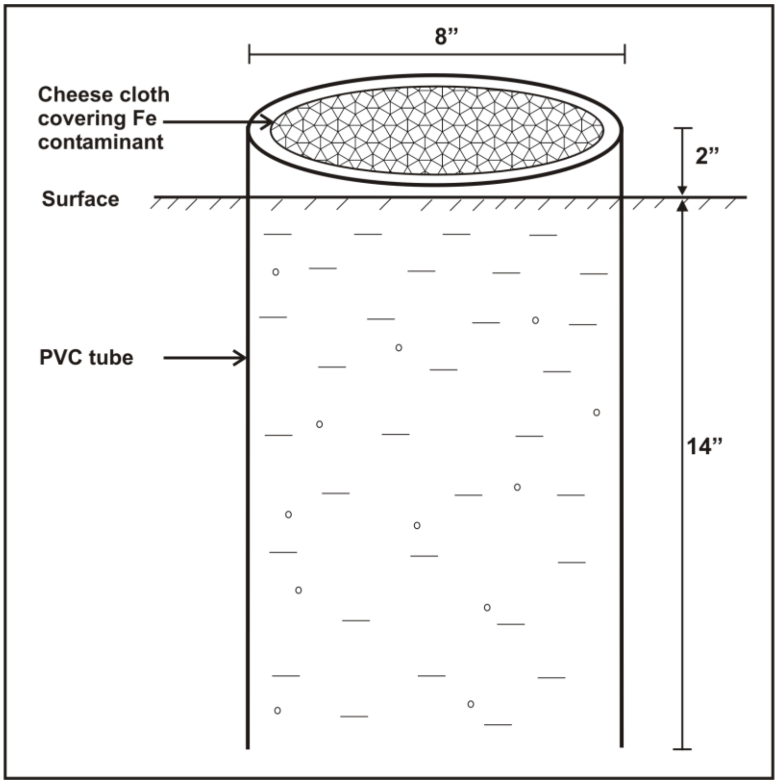

Fig. 4.1 Schematic representation of a typical tube after insertion into the ground.

4.2.2 In situ magnetic measurements

MS measurements were used for both ongoing surface monitoring and pre- and post-treatment vertical migration assessment. MS measurements of the surface soils were made periodically using the Bartington MS2 system and a MS2F probe (Bartington

Instruments, Oxford, UK). Each time the measurements were made, readings were taken in five locations in each tube, four at the edges and one at the centre (3× at each location to ensure repeatability), and averaged to give the MS reading per tube. From these measurements, the changes in surficial MS over time were determined and surficial MS profiles were plotted. The significance of the differences in average MS values of tubes at different measurement times were analyzed using a Linear Mixed Model in SPSS. The confidence interval was set at 95% for the purpose of this study and, hence, the statistical significance was defined as the level of $p = 0.05$.

4.2.3. Laboratory magnetic and chemical measurements

Soil cores were collected from a nearby (background) site and from each test capsule after the experiment. Two cores were collected within each capsule, one from near the centre and the other from the edge, respectively labeled as C1 and C2. The cores were sliced at 1 cm scale to prepare sub-samples that were inserted into cleaned, demagnetized cylindrical plastic containers for laboratory analysis. Volume of the solid sub-samples was determined from their dimensions (height and diameter), while for loose samples, it was determined from artificially-designed cubes of known volumes. These samples were then subjected to volumetric magnetic susceptibility (K) measurement using the MS2B sensor and the MS2 susceptibility meter, operating at 470 Hz. This K value would, however, represent the susceptibility of the sample occupying the total volume of the cylindrical container (6.58 cm^3). Because the containers were not completely filled, the true K for soil samples was calculated by multiplying the volume susceptibility with the ratio of sample volume to the container volume. With true *K* being determined, the mass-specific low frequency susceptibility (χ) was calculated by dividing true *K* of the sample by its mass. This parameter is used frequently because it approximates concentration of magnetite in the sample (Huliselan et al. 2010). χ – depth profiles were plotted for the vertical assessment of MS (Fig.4.4, 4.5 and 4.6).

After the vertical MS profiles were constructed, any soil layers with an enhanced magnetic signal were identified and were then further investigated using a ESEM (Scanning Electron Microscopy, Quanta 200 ESEM FEG), equipped with EDS (Energy-dispersive X-ray Spectroscopy), for visual observation and compositional analysis. The SEM-EDS techniques are often used to provide detailed information on the morphology and composition of magnetic minerals in fly ashes, (e.g., Blaha et al. 2008) and in contaminated soils and sediments (e.g., Chaparro et al. 2010, Jordanova et al. 2004). This type of analysis was done to ensure that the enhanced magnetic signal could be attributed to the contaminant, rather than to natural processes or materials. The analysis was carried out on magnetic extracts (physical extraction using a hand magnet) from selected soil samples, and on a sample of the contaminant itself. The morphology of the magnetic particles were visually analyzed using SEM, and EDS analysis was performed to identify the chemical composition of the magnetic minerals, particularly to determine the weight% of iron and oxygen. Furthermore, the iron mineralogy was also determined on these magnetic extracts by measuring the susceptibility dependence on temperature on an AGICO KLY-3S Kappabridge with a CS-3 high temperature furnace attachment in ambient air.

4.3. Results and Discussion

4.3.1. Magnetic susceptibility of surface soil

The initial surface MS values in the controls ranged from 6 to 16 x 10^{-5} SI, while those from contaminated tubes were two to three orders of magnitude larger (ranging from 182 to 468 x 10^{-5} SI) (Table 4.1) than controls. Despite the uniform dose of pollutant in all contaminated tubes, these tubes had a larger range of initial values, which may have resulted from a heterogeneous distribution of the contaminant, minor wind issues or very minute changes in the topography inside the tube.

Table 4.1 Initial surface MS (K) values in controls and contaminated tubes.

Control tubes	Initial MS (x 10^{-5} SI)	Contaminated tubes	Initial MS (x 10^{-5} SI)
2	8.2 (± 0.8)	1	246.0 (± 105.8)
4	10.3 (± 1.5)	3	182.2 (± 45.1)
5	11.3(± 1.9)	6	326.7 (± 88.6)
7	11.4 (± 0.9)	8	215.5 (± 116.0)
10	16.0 (± 2.5)	9	197.0 (± 59.0)
12	6.4 (± 1.1)	11	345.5 (± 117.5)
15	11.1(± 2.1)	13	459.5 (± 127.9)
16	7.3 (± 1.8)	17	468.0 (± 165.2)
18	9.8 (± 1.3)	14	*****
20	6.9 (± 1.3)	19	*

*****During the course of the experiment, these tubes were disturbed and are not considered in this study*

After the four-month period of the study, the MS values had decreased by 15 to 60% in the contaminated soil tubes, while in the uncontaminated (control) soil tubes, the results were highly variable, and both increases (9 to 65%) and decreases in MS values (3 to 26%) were observed (Fig. 4.2). There was a substantial decrease in MS value in the first three weeks of measurement in most of the contaminated soil tubes.

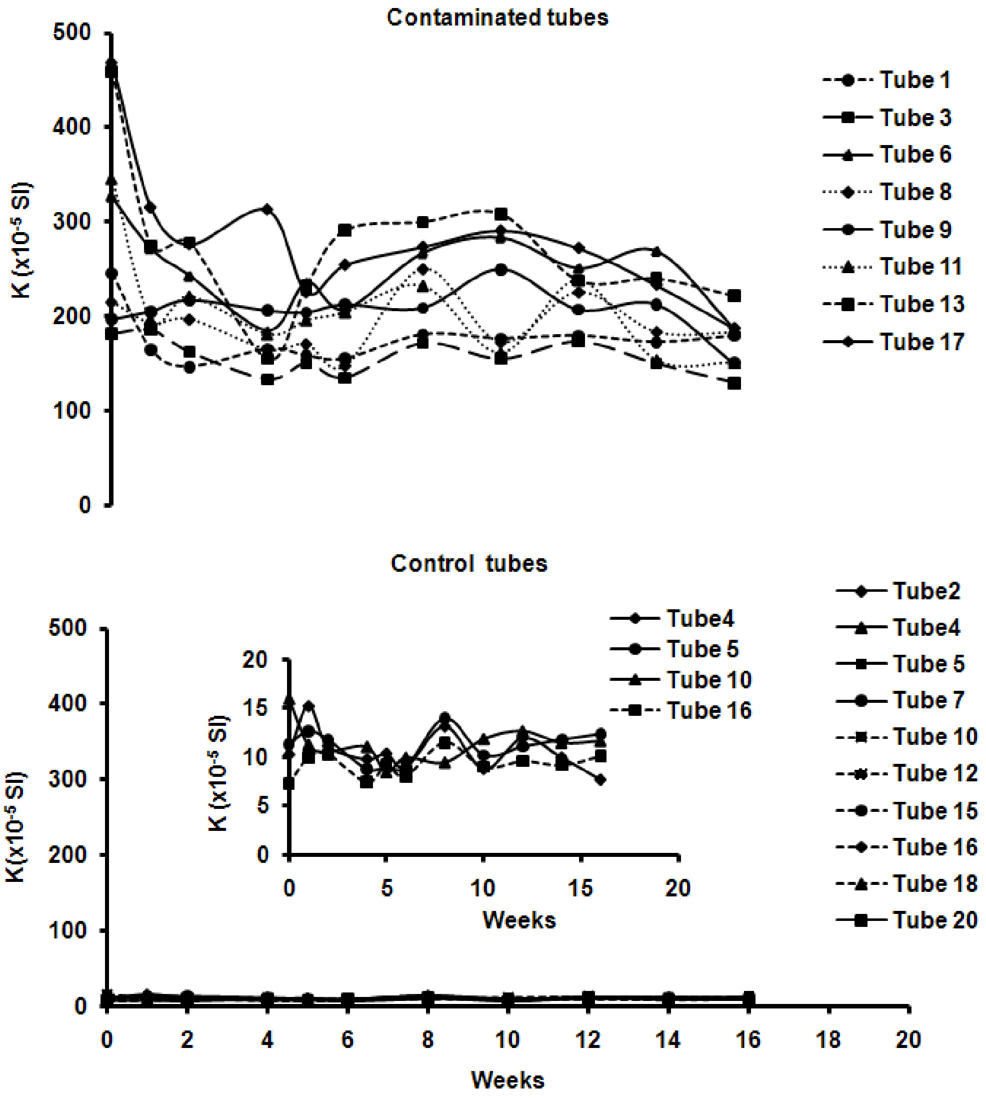

Fig. 4.2 Mean surficial MS (K) profiles for controls and contaminated soil tubes, plotted to the same scale to show comparative differences. *Inset:* four control tubes plotted at a larger scale, showing the variation discussed in section 4.3.1.

We turn first to the potential reasons for the results from control tubes. According to Mullins (1977), MS enhancement can occur in soils due to *in situ* conversion of a small proportion of the weakly magnetic forms of iron oxides and hydroxides to strongly magnetic microcrystalline magnetite and maghemite. Furthermore, repeated reduction-oxidation cycles in soil can release iron from weakly magnetic minerals, and strongly magnetic minerals can be generated by microbial activities, through either formation of magnetite and maghemite, or by iron coagulation with organic materials (Fassbinder et al. 1990, Maher and Taylor 1988, Sapkota et al. 2012). Although these possibilities were not specifically considered in this study, it is likely that such processes would result in changes in all samples, and be identifiable as consistent trends in the control tubes. However, no such trends were observed. It is also possible that atmospheric fall-out (particularly iron containing particles released from industries) might have contributed to the minor increase in surface MS in some of the tubes. Decreases in these values could be due to air-water mediated removal of pollutants. In summary, the uncontaminated tubes have irregular increases and decreases of MS values (with respect to the initial values) during the experimental period. Statistical analysis, however, showed that the overall changes are not significant, with calculated p-values being higher (0.216) than the statistical significance level defined for this study ($p = 0.05$).

The contaminated soil tubes show decreases of between 15 and 60% (mean 38, standard deviation 17) from the initial MS values, suggesting that either the contaminant had been removed from the surface soil due to atmospheric processes (wind) or had been transported downward through the soil. Because specific actions (i.e., use of a soil cover and cheesecloth cover) were undertaken to prevent atmospheric/wind removal, it is more probable that downward migration had occurred.

Fig. 4.2 shows that decreases in surficial MS occurred primarily in the first three weeks, and the MS values varied only slightly between the fourth and the sixteenth weeks. With the highest rainfall in the first three weeks and a greater decrease in the surface MS in the same time period, it is probable that the rainfall pattern was more deterministic than any other factors in controlling pollutant transport. An experiment by Rousseau et al. (2004) tested the effects of physicochemical properties of soil and infiltrating water on the transport of soil particles, and found that particle mobilization is more extensive at high rainfall intensities. During the first three weeks, when heavy rainfall occurred, there could have been a significant downward movement of colloidal particles (both clay particles and the contaminant used). Such an infiltration of large amounts of colloidal particles increases the physical exclusion of pore spaces due to clogging (Rousseau et al. 2004), thereby leading to the retention of colloids at a certain depth. This also means that the drainage characteristics (on a local scale) change when a large amount of clogging particles infiltrate the soil. Such a change could have affected the downward migration of the pollutant during the period between the 4th and the 16th week. As all the parameters (both biotic and abiotic) likely to have an influence on the dynamics of metal pollutant have not been taken into account in this study, it is difficult to explicity state the cause of the temporal MS variation due to pollutant migration.

Statistical tests showed that the overall change (i.e., decreases in final MS values with respect to initial values) in MS is significant (calculated *p*-value is 0.004).

Interestingly, Fig. 4.3 shows that the specimens that had the highest initial MS showed the greatest decrease. This also argues against atmospheric removal, as one would expect that, if atmospheric removal were the cause, the percent removed would be consistent from tube to tube, because the contaminant amount used and its grain size were similar.

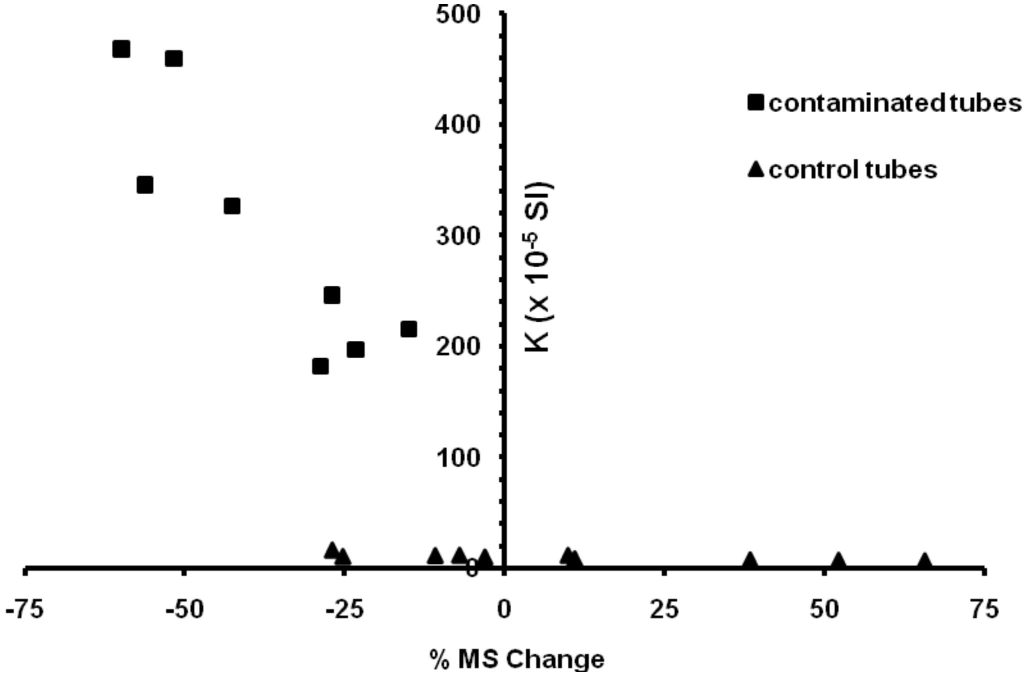

Fig. 4.3 Total change in surface MS (K), normalized to the initial values in both the controls and contaminated soil tubes.

4.3.2 Vertical assessment of soil cores

Decreases in surficial MS in the contaminated tubes suggested that downward migration of the pollutant may have occurred. Therefore, to examine the migration pattern of the pollutant in soil, soil cores from the tubes were analyzed. MS profiles of background soil cores, taken from outside both the control and the contaminated soil tubes, show that the mean χ is about 0.48 x 10^{-8} m^3/kg units (Fig. 4.4). Background soil cores are used as standards for comparing the changes in MS values in both control and contaminated soil tubes.

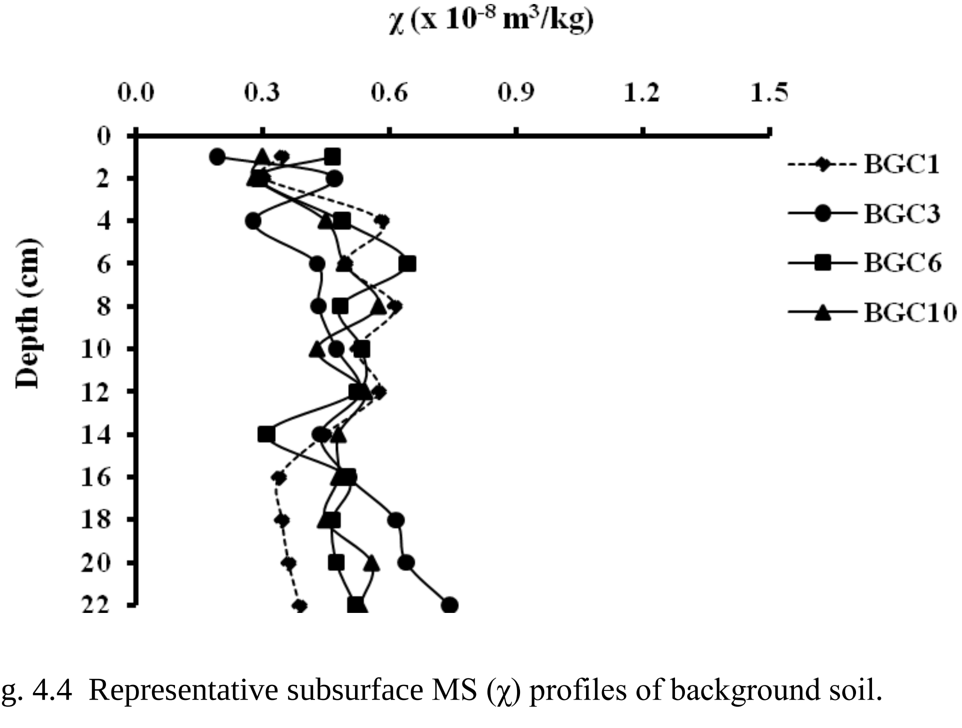

Fig. 4.4 Representative subsurface MS (χ) profiles of background soil.

In the cores from the post-test control soil tubes, the MS soil profiles (Fig. 4.5) are very similar to the background soil profiles (Fig. 4.4), as would be expected. The variability also resembles the background profiles, as some profiles show slightly elevated MS in the top 2 to 3 cms (as seen in BGC1 and BCG3), with lower MS below this depth. The stronger signal on the soil surface could be due to the deposition of heavy metals from the atmosphere (as mentioned in section 4.3.1). In two of the control soil cores (T7C2 and T12C2, Fig. 4.5), a strong peak was observed at depths of 16 to 18 cm, similar to BCG3. Given that these peaks at greater depth are present in both the background and controls, it is reasonable to assume that they are not due to downward migration of the contaminant used. There could, however, be a number of potential reasons for such enhancement, including leaching and dissolution, microbial activity and some form of natural barrier in the soil. Contribution from leaching of metals is less likely because the topsoil with lower MS values possibly is poor in heavy metal content. Furthermore, weathering of the parent material is unlikely because the Quaternary deposit at the test site is quite thick (few to more than 50 meters, according to Hudec 1998) and the soil cores were taken from the upper 20 centimeters. Because the possibility of microbial activity is not tested in this study, we suggest that the enhancement could possibly be related to some form of natural barrier or agricultural effects at those locations.

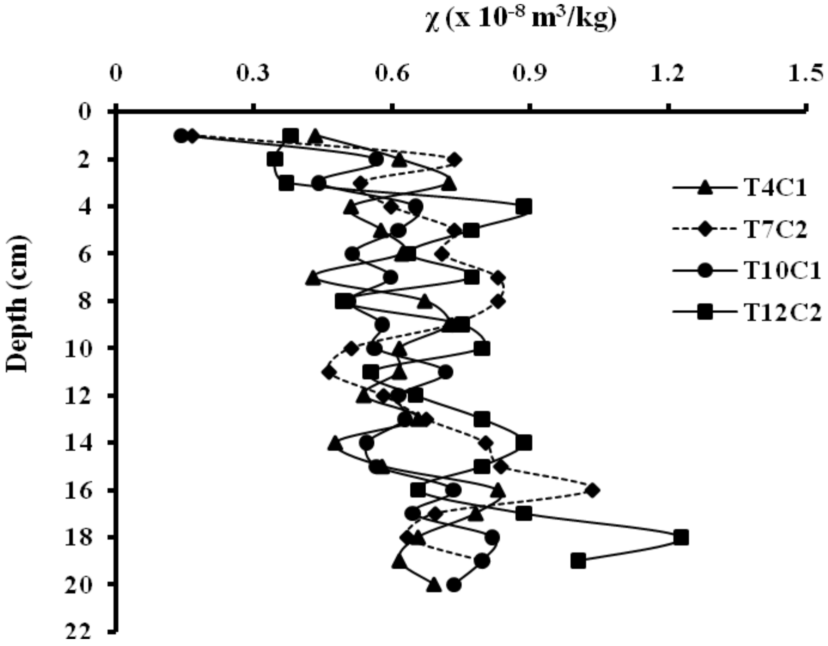

Fig. 4.5 Representative subsurface MS (χ) profiles from the control tubes.

MS profiles from soil cores of contaminated tubes show that the magnetic susceptibility reaches a maximum at depths between 2 and 9 cm (Fig. 4.6) and most of the soil cores have the strongest signal between 4 and 6 cm. The MS peak enhancement depth is also different for soil cores taken from the central and peripheral locations within each tube. In three out of eight tubes (T1,T8 and T13), core C2 had an enhanced signal at greater depth than core C1 (Fig. 4.6) and this could possibly be due to preferential transfer of pollutants in these tubes where soil could have been disturbed more in edges than in the centre, while inserting tubes into the ground. Specific conductive paths unrelated to the experiment, however, such as fracture cracks in soil, were not observed. In the other five tubes, the peak enhancement was either at the same depth (T6, T9, T17) or C1 had peak enhancement at greater depths than C2 (T3, T11).

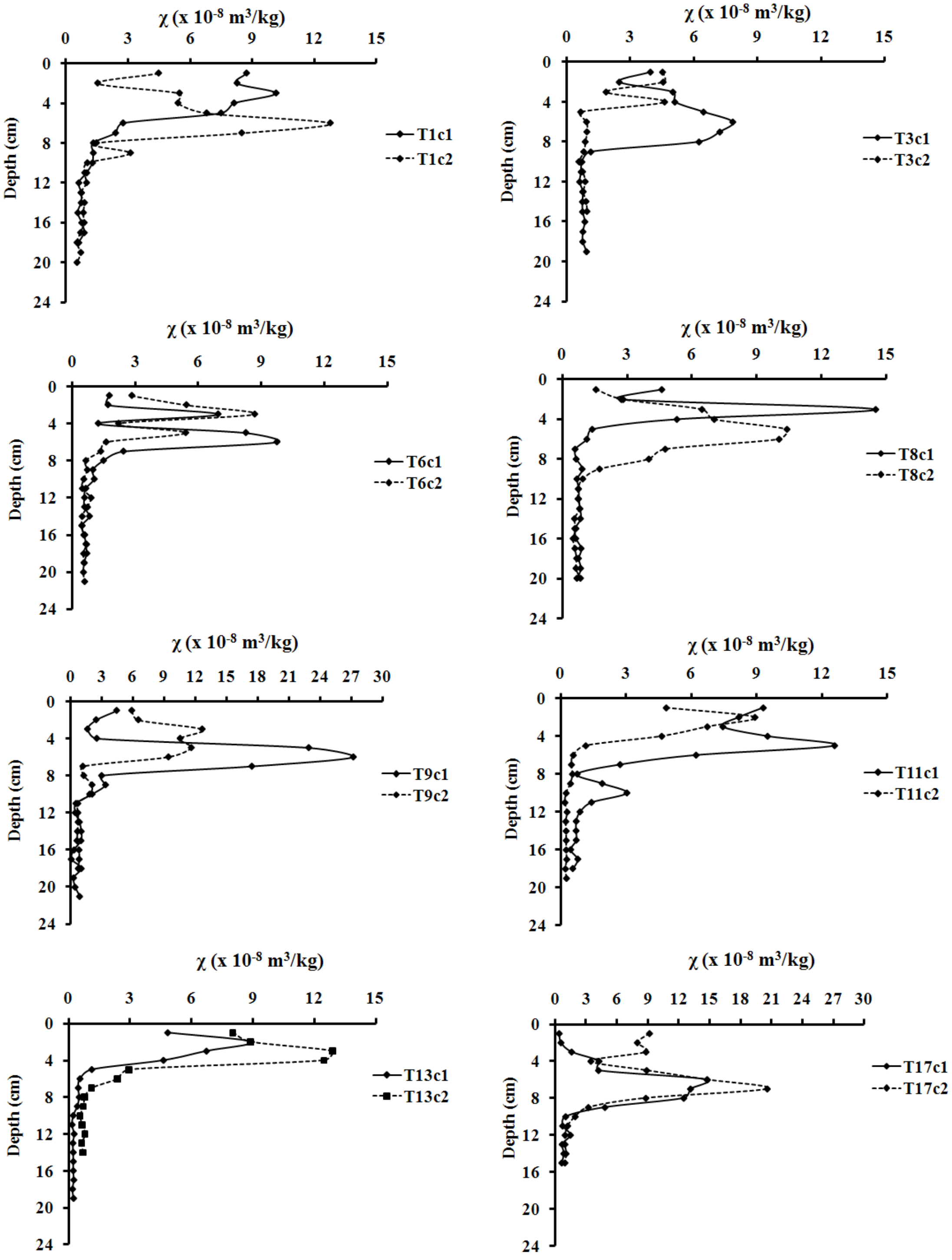

Fig. 4.6 Representative subsurface MS (χ) profiles from the contaminated tubes.

4.3.3 Thermosusceptibility measurements

Prior to discussing quantitative vertical migration, it is necessary to ensure that the MS enhancement observed below the surface is indeed due to the contaminant used. Some of the samples from these enhanced soil layers **(**T8C2-5, T9C2-3, T13C1-3 and T17C2-7; Fig. 4.7) were subjected to thermosusceptibility measurements, where the behavior of susceptibility of minerals upon heating is monitored, and the Curie temperature is determined. Major changes in magnetic properties of specific minerals occur at their Curie temperatures, defined as the temperature at which ferrimagnetic minerals start to behave like paramagnetic minerals (Hanesch et al. 2006). In this study, the thermosusceptibility (K–T) curves for heating and cooling processes of the magnetic extracts are irreversible, i.e., the measurements during cooling had higher intensity (Fig. 4.7) due to chemical changes in the minerals. The results, however, confirmed the presence of magnetite in these enhanced soil sections, with Curie temperatures for all the samples between 590 and 600 °C, confirming vertical migration of the synthetic contaminant.

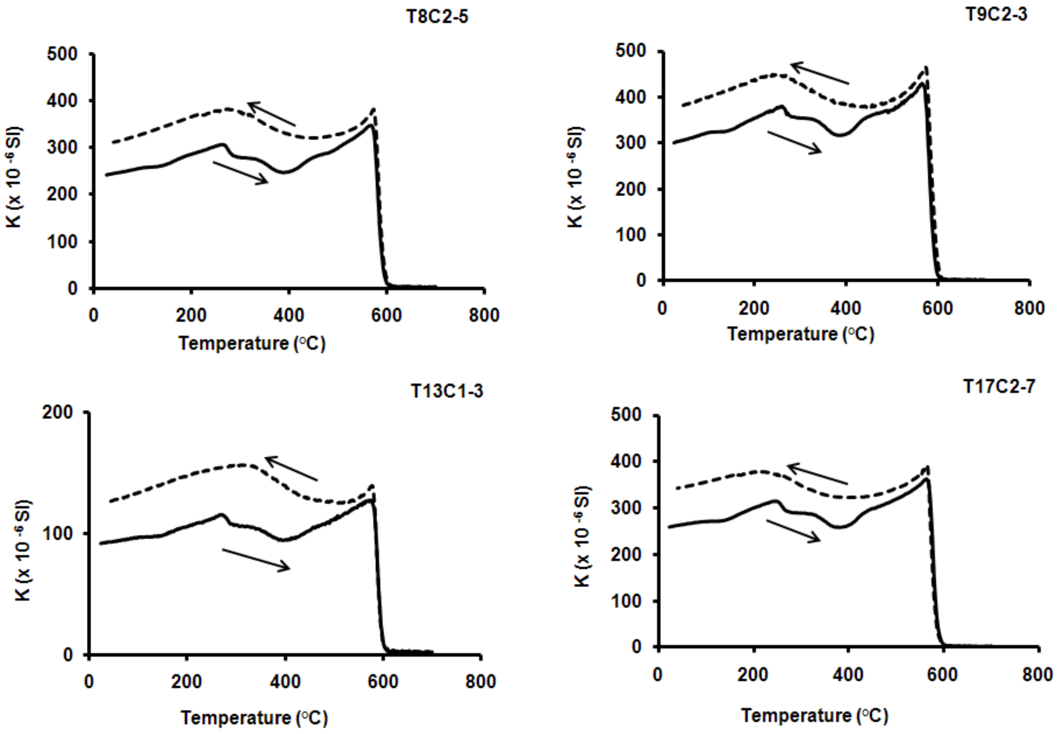

Fig. 4.7 Thermosusceptibility curves (K-T) of magnetic extracts from the contaminated soil, collected after the end of the experiment. Naming convention for samples: T8C2-5 is sub-sample from core C2 of tube T8 at a depth of 5 cm.

4.3.4 SEM-EDS analysis

Magnetic particle extracts from contaminated soil cores showed similar sizes (smaller than 5 µm) and shapes (cubic) to the original contaminant (magnetite powder) when observed using SEM (Fig. 4.8). In addition to having similar surface morphologies, these iron-containing particles (determined using EDS) were randomly distributed on the surface of larger soil particles, and were not part of the actual grains (Fig. 4.8 c, d). These results confirm that magnetic particles must have migrated downward from the soil surface. Similar examination of magnetic extracts from the control soil cores showed very different surface morphologies to that observed in the magnetite powder (Fig. 4.9). The magnetic particles in the control samples were irregular rather than cubic crystals and were part of the larger soil and mineral grains. Such differences in the morphologies of magnetic particles between control and contaminated soils allow distinction between the natural Fe-rich grains and the contaminant, and thus can be used to distinguish between *in situ* grains and those that migrated from the surface.

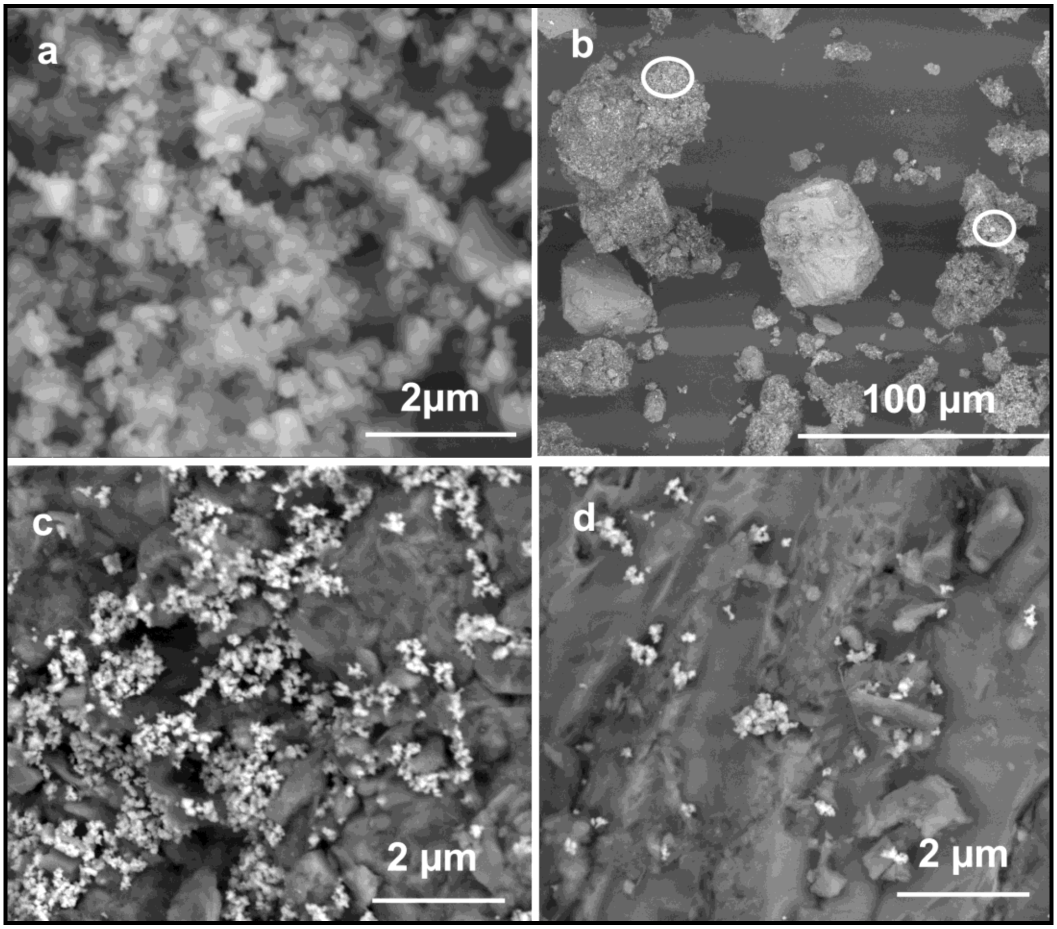

Fig. 4.8 Photomicrographs (BSE mode) showing surface morphology of: (**a**) magnetite powder (contaminant), (**b**) a contaminated soil sample (T9C1-6) with the light and dark differences indicating highly reflective and less reflective particles, (**c**–**d**) magnification of areas circled in (**b**). The lighter portions had high Fe content, and had particles with morphologies (shape and size) similar to the contaminant.

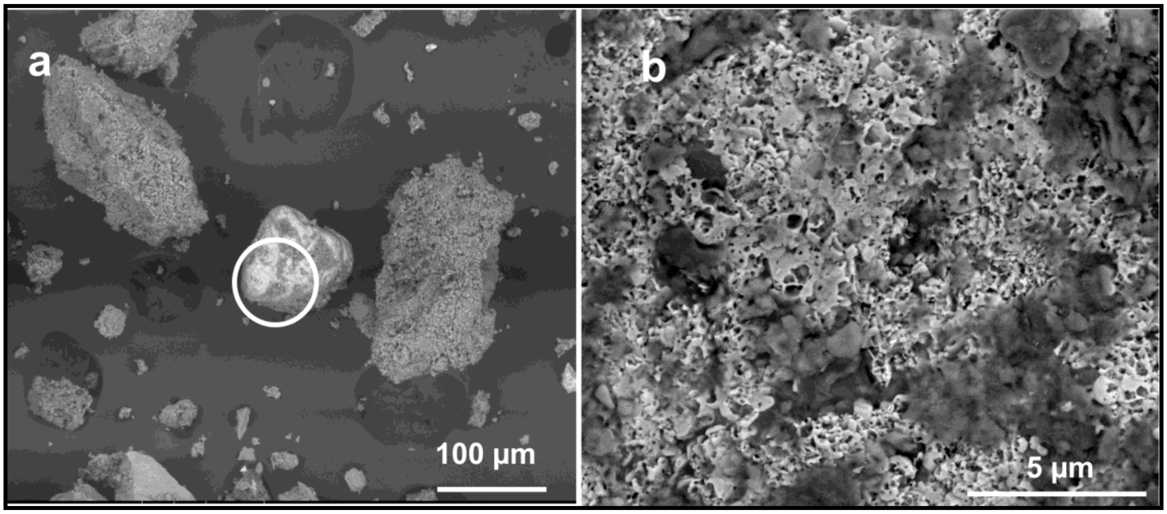

Fig. 4.9 Photomicrographs (BSE mode) showing surface morphology of a control soil sample (T12C2-18): (**a**) single grain, with the light and dark differences indicating highly reflective and less reflective particles, and (**b**) magnification of an area circled in (**a**). The lighter portions also had high Fe content, but different morphology than the contaminant.

Although the surface morphology was different for bright or highly reflective (HR) magnetic extracts from both contaminated and control soils (cubic in contaminated; irregular in controls), EDS analysis show that these extracts contained a high weight percent of iron and oxygen (Table 4.2 and 4.3), confirming the presence of iron oxides. In contrast, particles that were dull (less reflective, LR) in texture contained a higher weight% of Silicon (Si), Aluminium (Al), and Oxygen, and could either be glassy parts of the magnetic grains or purely non-magnetic grains. These results support the argument that the enhanced magnetic signal in soil layers at depths of 2 to 9 cm of the contaminated tubes must be due to migration of surface-deposited magnetite particles.

Hence, both the results from thermosusceptibility measurements and the SEM-EDS measurements show a clear evidence of magnetite in the enhanced soil layers.

Two of the control soil samples (T7C2-16 and T12C2-18), which showed a small enhancement of the magnetic signal at 16 to 18 cm, contained high levels of Fe and Ti (Table 4.3) at that depth. As discussed previously, this enhancement may be related either to some form of natural barrier in the soil or to agricultural effect, wherein soil disturbances such as plowing or tilling affect the soil at shallower depths. While there is no historical record of such disturbance (pers. comm., farm owners) at this specific location, this possibility cannot be eliminated due to the widespread agricultural use of the Essex County for the last 150 years.

Table 4.2 EDS analysis on magnetic extracts from contaminated soil showing their elemental compositions (in wt%)

Samples	Wt.% of elements											
	Fe	Ti	V	Co	Ca	Mg	Al	Si	O	C	K	Na	Br
T17C2-7: HR	27.23	–	–	–	9.43	0.68	0.99	3.03	38.60	19.52	0.52	–	–
LR	33.28	–	–	–	9.28	1.14	0.90	2.75	31.89	20.16	0.60	–	–
LR	1.97	–	–	–	4.84	0.35	8.95	27.46	46.63	–	9.80	–	–
T13C1-3: HR	52.70	–	–	–	3.18	1.47	1.09	2.65	24.55	14.35	–	–	–
HR	38.33	–	–	–	6.75	0.88	1.58	3.39	29.73	19.35	–	–	–
T13C2-3: HR	40.34	–	–	3.47	–	–	1.86	5.95	25.36	21.20	1.83	–	–
T9C1-6 : HR	46.07	–	–	–	2.00	1.01	0.68	3.88	19.79	26.57	–	–	–
T9C2-3 : HR	52.04	–	–	–	3.70	1.24	0.65	2.16	21.83	18.38	–	–	–
T8C1-3 : HR	40.00	–	–	–	3.81	2.08	0.65	2.35	27.78	23.23	–	–	–
T8C2-5 : HR	43.00	–	–	–	3.46	1.72	0.58	1.93	25.84	23.48	–	–	–
LR	8.47	–	–	–	11.77	7.73	–	2.35	41.69	27.99	–	–	–
T3C1-6 : HR	31.43	–	–	–	2.03	0.94	3.62	4.87	35.78	21.32	–	–	–
HR	20.78	–	–	–	2.04	0.84	3.44	5.63	36.32	30.32	0.63	–	

Table 4.2 continued

LR	1.50	–	–	–	1.40	0.41	8.81	22.76	35.34	25.16	0.41	4.21	–
T1C2-6: HR	31.53	–	–	–	4.23	2.33	0.94	2.36	33.57	24.65	0.38	–	–
LR	3.11	–	–	–	0.87	–	0.65	32.03	45.56	17.79	–	–	–

HR indicates magnetic (Fe-rich) particles, and LR indicates either non-magnetic particles or glassy part of magnetic particles.

Naming convention for samples: T17C2-7 is sub-sample from core C2 of tube T17 at a depth of 7 cm

Table 4.3 EDS analysis on magnetic extracts from controls showing their elemental compositions (in wt%)

Samples	Wt.% of elements												
	Fe	Ti	V	Co	Ca	Mg	Al	Si	O	C	K	Na	Br
T12C2-18: HR	35.65	7.67	–	–	–	–	2.11	3.5	29.21	21.43	0.43	–	–
LR	7.09	1.22	0.04	–	0.6	0.97	6.33	16.33	41.99	23.95	1.56	–	–
LR	9.88	0.82	0.02	_	5.16	3.77	5.22	16.78	36.73	19.75	1.22	0.65	–
T12C2-16: HR	55.32	–	–	–	–	–	–	6.23	14.36	18.58	_	_	5.51
HR	51.08	–	–	–	–	–	2.23	5.3	28.02	13.38	_	_	–
LR	4.83	–	–	–	–	0.63	8.86	21.72	37.03	24.09	2.84	_	–
LR	7.93	–	–	–	–	1.35	8.67	22.7	38.74	17.27	3.34	_	–
T10C1-11: HR	48.76	–	–	–	–	–	2.4	5.54	27.96	15.33	_	_	–
HR	51.69	–	–	–	–	–	2.04	5.24	26.36	14.67	_	_	–
HR	50.14	–	–	–	–	–	2.15	5.26	27.21	15.25	_	_	–
LR	11.63	–	–	–	–	0.97	5.81	20.82	42.01	18.76	_	_	–
LR	–	–	–	–	–	–	2.39	36.87	48.19	12.55	_	_	–
LR	6.49	–	–	–	–	0.73	7.12	26.28	45.41	13.96	_	_	

Table 4.3 Continued

T7C2-16: HR	34.44	6.78	0.13	–	–	0.46	2.78	4.89	35.39	14.66	0.48	_	–
T4C1-8 : HR	28.31	–	–	–	–	1.01	4.6	9.01	33.9	23.17	_	_	–
HR	24.34	–	–	–	–	0.63	6.24	10.79	35.18	22.82	_	_	–
LR	16.31	–	–	–	–	–	3.8	15.72	37.77	25.6	_	0.80	–
LR	–	4.71	–	–	–	–	6.41	17.98	37.87	30.22	_	2.81	–
LR	3.49	5.19	0.87	–	–	–	2.47	21.28	39.04	27.66	–	–	–

HR indicates magnetic (Fe-rich) particles, and LR indicates either non-magnetic particles or glassy part of magnetic particles.

Naming convention for samples: T7C2-16 is sub-sample from core C2 of tube T7 at a depth of 16 cm

4.3.5 Metal (Fe) migration

Our results show that the contaminant migrated downward to a maximum depth of 9 cm into the soil. The strongest signal is recorded at depths between 4 and 6 cm, suggesting that this is the potential average depth of pollutant migration in the given environment during the four-month experimental period.

Although understanding natural processes governing migration of toxic elements in soils is important, we limit our discussion to only the most likely modes of metal transport in this study, because our objective is assessing the usefulness of magnetic measurements in determining downward migration of metal contaminants in soil. The primary mode of vertical migration of Fe-containing particles from the surface down the soil profile is likely to be physical transport of these particles as a result of rainwater infiltration and/or gravity. Rainfall data, collected weekly to biweekly, showed that precipitation ranged between 0.64 and 53 mm per event (Table 4.4), totaling 20.5 cm during the experimental period. A substantial decrease in MS in contaminated tubes in the first week of measurement (Fig. 4.2) can probably be related to a high rainfall amount (53.34 mm on Aug 14, 2009) that may have transported the pollutant vertically downward from the surface.

There are no obvious signs of physical disturbances in the soil cores, such as burrows or root cracks, suggesting that biota-mediated physical transport is unlikely to be significant. Metal transport and the resulting migration depth could also be influenced by factors such as soil texture, surface area, organic matter, pollutant concentration and pH. They were, however, not considered to be significant in this study because of the constant surface area in each test capsule, similar soil texture at the site, similar environmental conditions, and equal amount of contaminants distributed.

Table 4.4 Rainfall data collected during experimental period

Date (month/day/year)	Rainfall (mm)	Cumulative rainfall (mm)
08/06/09	0.00	0.00
08/14/09	53.34	53.34
08/21/09	15.24	68.58
09/03/09	44.45	113.03
09/11/09	5.59	118.62
09/17/09	0.64	119.25
10/05/09	33.02	152.27
10/20/09	29.21	181.48
11/02/09	21.34	202.82
11/13/09	1.65	204.47
12/07/09	0.00	204.47

Vertical assessment of soil cores showed that about 40% of the contaminated tubes showed increased infiltration near the edge of the tube, where the most disturbances could have occurred while inserting tubes into the ground. Such disturbance of the soil may create preferential pathways for downward migration of contaminants. The most significant implication of this finding is that farming areas, which consistently are plowed/tilled, have greater potential for migration and uptake by plants (Sapkota et al. 2012), and should therefore be monitored closely.

In the control tubes, where the signal was enriched in the upper 2 to 3 cm, the iron containing particles from atmospheric deposits could have accumulated in the topsoils due to their affinity with the organic matter (as was observed by Davis et al. 1988). In the contaminated tubes, the contaminant migrated mostly to a depth of 4 to 6 cm, and potentially, most of the migration may have occurred during the first three weeks. Although it is tempting to calculate the pollutant transport rate considering this time, when the maximum reduction in surficial MS occurred, the extrapolation of such transport processes may need to consider drying and wetting cycles and geochemical processes (Jacques et al. 2008). Therefore, we feel it is inappropriate to suggest a migration rate based on the results of the first three weeks only. The predicted average vertical migration rate, however, was calculated to be approximately 14 cm/yr using a simple linear approximation and a 5 cm depth penetration, and ranged between a minimum of 6 cm/yr for 2 cm, and a maximum of 27 cm/yr for 9 cm migrated depth. Our results are comparable to previous studies on heavy metal transport in soil profiles that had an application of sludge and wastewater. Behbahaninia et al. (2008) reported the maximum movement of Cu and Cd to be 20 cm/yr in agricultural soil treated with wastewater. Maskall et al. (1995) determined the mean vertical migration of Pb and Zn in historical smelting sites to be approximately 1cm/yr, and found higher rates of vertical migration at sites with soils underlain by sandstone than clay. Similarly, while observing the movement of metals (Cd, Cr, Pb, Zn) downwards from the grassland soil treated with sewage sludge, Davis et al. (1988) found that most of the metals (mean 87%) remained in the upper 5 cm of soil in each of the four year experimental periods.

Using these metal migration results, predictions can be made for long-term continued downward migration over years, which can be important to understand the zone(s) of pollutant accumulation in soils. This could be particularly useful to areas that are likely to be exposed to continued pollution, or where anthropogenic activity is high. In particular, where the water table is at shallow depths (less than 1 m), the migration of pollutants may reach the water table in only a few years (about 8 years based on this study and conditions at the site) and could eventually pollute drinking water. On a cautionary note, with diverse site-specific conditions (such as contaminant type, soil chemistry, soil type, geology, precipitation), the migratory rates of pollutants are probably site-dependent. Therefore, it is imperative to conduct such studies with detailed site-by-site description and determine depth of metal transfer, and the possible transport-related processes responsible for redistributing metal contaminants.

4.4. Conclusions

Vertical migration of iron particles and the potential depth of soil contamination were examined for 4-month period. The particles migrated to a maximum depth of 2 to 9 cm, but the strongest magnetic signal in most of the test tubes was at depths of 4 to 6 cm. Our study shows that a magnetic susceptibility-based monitoring technique can provide valuable information on the migration behavior of the metal pollutants, and the potential depth of soil contamination, and is therefore recommended as a sensitive and fast tool for detecting metal movement in soils in polluted areas. Using magnetic measurements, in conjunction with chemical analytical techniques to study metal migration, can give valuable information that may help determine the focus of remediation efforts at high-priority locations.

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CHAPTER 5

CONCLUSIONS

The research presented in this dissertation represents a comprehensive analysis of the usefulness of environmental magnetic techniques in determining the effect of atmospheric pollution on magnetic and chemical properties of plants and their growth media (i.e., synthetic soils) in both controlled and test/experimental situations. The determinations were accomplished through *in situ* and laboratory magnetic measurements, visual observations and elemental analysis using SEM-EDS, and geochemical compositional analysis (XRD, ICP-OES). Three experiments were designed to assess independently the effect of possible variables on the magnetic and chemical properties of soils and plant biomass, and, in particular their contributions to *in situ* MS measurements that are often used to evaluate pollutant distributions. The conclusions drawn from these experimental studies are presented below.

5.1 Experiment 1: Effects of Fe-contaminant on magnetic and chemical properties of soil and plant biomass during growth

The plants grown in high contamination soils had slightly lower height and less biomass than those grown in low contamination soils. The low contamination soils, in turn, tended to have plants with slightly greater biomass than those grown in control soils. This suggests that high contamination level mimics the pollutant and lowered the biomass, but the lower level acts as an essential nutrient and increased the biomass. While the differences in plant height were significant only in the S50 soils, the differences in total plant biomass between these two contamination levels were not statistically significant.

The background (pre-growth) soil surface MS values decreased substantially (14 to 29% in S25 and 25 to 31% in S50) in all three treatments at seedling stage, with greater decreases in the high contamination samples and the lowest in the controls. For a single plant growing through the successive stages (from vegetative to harvestable stage), the MS decrease was smaller. The overall MS decrease (from initial to harvestable stage) was found to be statistically significant between the treatments in both soil types, especially between the controls and treated soils. Fe uptake by plants and magnetic mineral transformations were considered to be mainly responsible for the MS decrease.

Geochemical analysis of plant shoots showed that high contamination plants had slightly higher concentrations of Fe and some selected trace elements (Ni, Cr, Mn), which indicated higher bioavailability of these elements in the treated plants than in the controls. Among the factors that regulate the availability of these elements to the plants, soil acidity is considered to be the most decisive factor (Sauerbeck 1991). Lowering the rhizosphere pH (by plant roots and associated microorganisms) favors the formation of Fe(II) from Fe (III) and enhances the Fe availability to plants (Romheld 1987). The pH value, however, was found to be similar in all treatments and in both soil types. Because all the experimental parameters, except for the Fe concentration levels, were similar, the variation in element concentrations (including Fe) in the plant biomass is most likely due to the treatment level.

The post-harvest treated soils contained relatively more oxidized minerals than the controls, suggesting that magnetite was being altered into its oxidized (i.e., hematite) and oxy-hydroxide (e.g. goethite) forms. Compared to the control and background soils, the treated soils had lower maximum magnetization (M*s*) values and greater chemical alteration as determined from thermosusceptibility measurements, both of which indicate a greater degree of magnetic mineral transformation. According to Maher and Thompson (1991) and Verosub et al. (1993), MS variations in soils can be caused by post-depositional alteration and/or formation of the magnetic phases by pedogenic processes. In this study, however, MS variations due to pedogenic processes are largely excluded as a possibility due to the nature of the experiments and the synthetic soils used, and, therefore, transformations of magnetic minerals due to favorable ion dynamics between the surface of iron-oxides and soil solution were probably largely responsible for the reduction in soil surface MS.

5.2 Experiment 2: Detection of atmospherically-derived metal pollutants in soils and metal uptake in plants

The overall surficial soil MS (from the pre-growth to the harvestable stage) was significantly less in the controls than in the exposed soils, and between the two parameters evaluated (soil mixture and treatment), ‘treatment’ (i.e., exposure to the atmosphere) had a significant influence in causing the difference. This indicated that the exposed soil had more Fe-containing particles than the controls. SEM-EDS analysis on these soils revealed relatively greater number of magnetic particles (bright particles with high [Fe]) and spherules, whose morphologies are typical of industrial combustion and transportation byproducts. The evidence from SEM-EDS analysis suggested that the enhanced MS in exposed soil is probably directly linked to the influence of atmospheric pollutants derived from transportation and industrial combustion in Windsor and nearby Detroit. Other possibilities, however, cannot be ruled out, such as bacterially-generated magnetic minerals.

The plants grown in the exposed pots had considerably higher concentrations of trace metals (Cd, Co, Mo, Ni, Zn, Al, Fe, Mn, Pb and Ti) than the controls. These results suggest that deposition of atmospheric particulates not only contributed to the increased soil magnetic signal but also to increased metal uptake by plant roots. Comparisons between the surficial soil MS and chemically-determined concentrations of selected elements (Fe, Ti, Mn) in both root biomass and soils showed some correlations, indicating that magnetic parameters could potentially serve as a proxy to estimate and trace anthropogenically-enhanced trace metals in polluted soils.

Overall, this experimental study demonstrated that local sources of pollution, such as, the proximity of the studied area (West Windsor) to the Ambassador Bridge and to the power plants and industries nearby, strongly influenced the soil geochemical properties, and that influence can be measured by magnetic methods more rapidly and cost-effectively than performing geochemical analysis. In addition, as this experiment started with synthetic soils of known composition and magnetic properties, the changes observed can be considered absolute changes, rather than the relative changes that are inferred from most ‘case-style’ environmental magnetic studies where the polluted areas are compared to distant areas that are considered non-polluted, but which cannot be evaluated separately as such.

5.3 Experiment 3: Vertical migration of metal pollutants in soil

Over the four-month period, the surficial soil MS decreased substantially (up to 60%) in the contaminated soil tubes; however, only a minor MS variation was observed in the control tubes. Provided that the exposure conditions were same for both treatments, the processes contributing to an increase in surface MS in control samples are likely to affect contaminated samples as well; however, these processes seem to have had little effect in contaminated samples relative to the effect contributed by the synthetic contaminant, and as a result decreases in MS were predominant. Because the contaminant was covered with a thin layer of soil (1 mm) and then with a thin cloth cover to prevent redistribution by wind or water, any decrease in MS due to atmospheric removal of the contaminant particles is unlikely, and the most probable cause for an observed reduction at the sample surface is downward migration of the pollutant. Downward migration of Fe-rich particles would reduce the number of these particles, and as a consequence reduce the surficial soil MS, while potentially increasing the subsurface MS. Magnetic measurements of soil cores from the contaminated tubes obtained at the end of the experiment showed magnetic enhancement at depths between 2 and 9 cm, with a average depth of maximum enhancement in the range of 4 to 6 cm. The fact that the magnetic particles from contaminated soil cores showed similar sizes (smaller than 5 µm) and shapes (cubic) to the original contaminant (magnetite powder) when observed using the SEM, and that they did not resemble the actual soil grains which were mostly (sub)angular and many times larger than the contaminant used, confirms that magnetic particles that caused enhancement likely were sourced from the surface and must have migrated downward.

Two major reasons for potential vertical migration of particles are the presence of macropores caused by root penetration, or the effect of channels created by watering (Angers and Caron 1998). In this study, as there were no obvious signs of physical disturbance in the soil cores, such as burrows or root cracks, we considered that significant biota-mediated transport was unlikely, and rainfall infiltration is the most probable cause for downward migration. Fine rootlets present in soil, however, may affect the migration to some degree due to capillary action, and this cannot be evaluated as a potential effect. A substantial decrease in MS in the contaminated tubes in the first week of measurement, however, can probably be related to high rainfall amount during that time, which may have transported the pollutant vertically downward from the surface at a greater rate. One way of determining any potential hydrological effect on metal migration due to infiltration would be to compare magnetic enhancement profiles with the rainfall data. In this study, however, soil cores were not taken during the experimental stage because doing so would create preferential paths and affect migration within the tube.

In the published paper, in order to provide a minimum estimate of the migration rate of the particles, an average maximum enhancement depth of 5 cm was used, and transport rate was assumed to be linear, which yielded a vertical contaminant migration rate of nearly 14 cm/year. The migration rate calculated is more likely a seasonal estimate than a year round average. Similarly, the potential that the pollutant migration stopped after the significant rainfall event was also not discussed, but the possibility of non-linearity in transport cannot be eliminated. Based on this linear extrapolation, however, predictions show that in similar areas likely to be exposed to continued pollution or where anthropogenic activity is high, a similar pollutant could easily migrate into shallow water tables (less than 1 m in depth) in less than a decade, and could therefore eventually pollute both surface and subsurface drinking water. Although these magnetic and chemical studies assist in making long-term predictions, it must be noted though that this sort of extrapolation to the overall infiltration rate of pollutants could be somewhat inaccurate, as natural biophysical factors are not constant.

5.4 Inter-experimental comparisons

The main objective of the two growth experiments (Experiments 1 and 2) was to examine the effects of contaminants (artificial or anthropogenic) on magnetic and chemical properties of soils and plants. To allow inter-experimental comparisons, the synthetic soil composition, plant species, and growth conditions were kept the same for the control sample sets. Experimental sample sets from Experiment 1, however, were treated with an artificial contaminant (magnetite-powder) and were kept inside a greenhouse, while those from Experiment 2 were untreated but exposed to open air. The surficial MS values of soils from all treatments of the two experiments decreased considerably from their background values in the early growth stages of plants. In the late growth stages, however, the MS values decreased to a lesser degree or stayed constant in the treated soils in Experiment 1, but were increased in the exposed soils from Experiment 2, suggesting that there must have been a constant input of particulate matter, whereas in the greenhouse there was only a single pollutant-event.

The MS variations provided the potential for examining a range of interacting factors. Fe uptake by plants, thought to be one of the potential reasons for the MS decrease, was determined through the geochemical analysis of plant parts – in shoots (Experiment 1) and in roots (Experiment 2). The difference in control and treated concentrations of Fe and other elements in the shoots was minimal in Experiment 1. In Experiment 2, however, the exposed soils had significantly greater MS values than the controls, the root biomass of the plants grown in these soils had considerably higher metal uptake, and the elemental concentrations of the root biomass correlated well with MS values. A possible implication of this result is that root products may carry more of a pollutant load than the shoot products. Although the actual levels of contamination and the contaminant composition are different for the two growth experiments and, therefore, their effects on soils and plants cannot be directly compared, both experiments did show that higher concentrations of contaminants (sourced experimentally or from the atmosphere) affect soil magnetic properties and plant uptake of metal nutrients. Statistical analysis also showed that among the two parameters, soil mixture and treatment, ‘treatment’ (controls vs. experimental) had a significant effect on the variations (MS and metal uptake) observed.

The vertical MS profiles examined in the control soils (Experiment 2) showed varying patterns, but magnetic enhancement most commonly occurred at depths between 2 and 5 cm. A similar observation was made in the migration experiment where some of the soil cores obtained from the control tubes had elevated MS in the top 2 to 3 cm, but others showed little variation down the profile. In the contaminated tubes, however, the MS profiles were clearly different, with sharply defined MS peaks at depths of 2 to 9 cm. This confirms that in the presence of contaminants, the soil MS profiles show peaks near the surface, which is commonly considered to be characteristic of anthropogenic activity; while in the absence of such contaminants, other influences (e.g., lithology, pedogenesis) dominate the signal. These two experiments also provided some insights into spatial distribution of contamination: the traffic and industry derived contaminants seen in the exposed samples from Experiment 2 are not apparent in the control samples from Experiment 3, suggesting that with increased distance (~ 30+ km in this case), most of the local atmospheric particulate pollutants were reduced, but not eliminated.

The results obtained from these three separate studies show that inter-experimental comparisons are useful in isolating the effects of a number of variables (e.g., contaminant level effects on surficial soil MS and plant biomass, atmospheric exposure effects on soil MS and plant uptake, pollutant distribution in soils). The observed variations in the set of studies for this research were ensured through routine analysis of both magnetic and chemical measurement on soils and plants.

5.5 Usefulness of susceptibility-based monitoring techniques for pollution studies

This research investigated the effects of the atmospheric deposition of particulate pollutants in soils and plants, examined through the controlled use of magnetic and geochemical measurements. As Fe-oxides constitute the most magnetic particles in pollutants (Huliselan et al. 2010), magnetite-powder was considered as a reasonable substitute for atmospheric contamination to treat soil in both the growth and migration experiments. As determined from growth Experiment 1, the soil surface MS values decreased during growth and were found to be significantly different among the three treatments. Similarly, laboratory magnetic measurements (thermosusceptibility and hysteresis) provided meaningful interpretations of the magnetic mineral transformations in the growth media and the determinations of the dominant magnetic carriers in both the background soil mixtures and post-harvest soils. These intriguing *in situ* and laboratory magnetic results provided the potential for testing a range of other possible biotic-abiotic mechanisms causing the MS variations in soils. In the follow-up growth experiment (Experiment 2), MS values of the soils exposed to the natural atmosphere were significantly higher and trace metal contents of exposed plants were higher than the controls, which were grown in a greenhouse. These results indicated that deposition of atmospheric particulates was likely the cause of both. The magnetic measurements from these growth experiments showed that the MS2 system and the probe used (MS2B) were sensitive enough to detect such minute changes in soil magnetic properties, but were not sensitive enough to detect small concentration differences of trace metals in the plant biomass (shoots and/or roots). Higher concentrations of Fe and other trace elements in high contamination plants (in Experiment 1) and exposed plants (Experiment 2), however, indicated higher bioavailability of these elements in these plants. Because the plant uptake of Fe and other coexisting trace/heavy metals change and affect the soil magnetic properties, and such changes can be detected by magnetic methods, there is significant potential for the use of magnetic methods in phytoremediation studies through soil monitoring.

While there is a potential for the contaminants to settle on the surface soil or be taken up by plants, there is also the possibility for pollutants to migrate downward through the soil profile when exposed to infiltrating rainwater. The results from the migration experiment showed that the metal pollutant migrates down the soil profile, causing a reduction in surficial MS but enhancing the magnetic signal of the sub-surface soil horizons.

From these three experimental studies, it is clearly seen that magnetic parameters could serve as a proxy to estimate and trace anthropogenically-enhanced trace metals in soils. In this set of studies, MS measurements were used to not only determine the surficial MS variations, but also to explore other potential factors (e.g., biomass, distance, contaminant level, soil mixture type) that might affect the observed variation. Such factors have generally been measured using other techniques, primarily chemical methods. The combination of the two sets of techniques has provided additional knowledge about the different processes (biotic and abiotic) and pathways of contaminant movement.

5.6 Future work

This research has shown the usefulness of environmental magnetic methods in biomonitoring studies that are often needed in polluted or brownfield sites, and thus there is a significant potential for the future use of these techniques.

- This research provided evidence that the soil magnetic properties differ significantly depending on their exposure to anthropogenic contamination. Because only synthetic soils were considered for the growth experiments and clay-rich glacial till for the migration experiment, the most obvious direction forward is to conduct a series of similar studies in different soil type, in order to enhance our understanding of the interacting processes in diverse environments. In particular, the migration experiment needs to be conducted in common crop soils, because this is where an obvious application for this research is most likely.
- In three experimental studies, the behaviour of both artificial and natural (atmospheric) pollutants on soil and plant magnetic properties were investigated, and potential reasons for the observed variation were explained, limiting the evidence to that obtained from the magnetic and chemical measurements. Other soil characteristics such as hydrocarbon content, soil biota, which play an important role in changing soil magnetic mineralogy, also should be considered. Natural biogenic Fe oxides are often reported as the dominant oxides associated with bacteria (Fortin and Langley 2005) and bacterial transformation of iron oxides may lead to changes in soil MS (Wang et al.2008). Although natural and anthropogenic processes and pathways for the formation and transportation of magnetic iron minerals are often coupled,

making it difficult to isolate a single cause (Maher et al. 2003), such results indicate that bacterial-mediated MS variation is also a possibility in the synthetic soils and, therefore, it is strongly recommended that this be considered in future biomonitoring studies.

- In the migration experiment, only the potential for vertical migration of the contaminant was examined. Lateral migration, however, should also be considered in order to cover the broader spectrum of the potential migration phenomenon for environmental pollutants. In addition, to increase the depth of coverage and to assess the in situ dynamics of the contaminant migration in soil, the use of advanced magnetic sensors, such as the SM400, would be appropriate.
- In this research, Fe pollutant was used for the ease of detecting the magnetic signal and as a tracer. In the environment, however, other metals are often thought to be the problem. Therefore, a similar experiment that uses both Fe and other coexisting metals (e.g., Ni, Ti, Cr), would allow evaluation of the Fe as a tracer for specific metals.
- The potential use of soil magnetic measurements as proxies for the effect of phytoremediation is suggested by this research. Future work could include magnetic and geochemical measurements to confirm our initial correlations between soil MS and root biomass geochemistry, and to determine if the suggested technique is indeed accurate and practical.

5.7 References

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APPENDIX

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