Magnetic studies of dusts in the urban environment

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Abstract

Dusts are one of the major public health concerns in the urban environment. This study investigates the application of magnetic techniques in the studies of urban dust pollution. Measurements of magnetic properties, element concentrations, and the organic matter content were carried out on Liverpool (UK) street dust and/or Bootle (UK) deposited dust.

Mixed dominant ferrimagnetic phases are found in Liverpool street dust although magnetite is probably a major one. The partial susceptibility technique is able to model the contributions of main magnetic components satisfactorily in Liverpool street dust. There are similar spatial distributions for some measurements, such as χ_{LF} and Pb, whilst there are different patterns for some measurements, such as χ_{LF} and the organic matter content. There are good linear correlations between the organic matter content and some magnetic mineral concentration-related parameters for < 1mm (bulk) samples. Among them, frequency dependent susceptibility (χ_{FD}) shows the highest correlation coefficient value. χ_{FD} percentage demonstrates a significant correlation with the organic matter content for size fraction and bulk samples. This suggests that re-entrainment of soil is probably a major source of the organic material present in street dust. The ratio χ_{ARM} /SIRM shows a highly significant correlation with the organic matter content for $<150\,\mu$m fraction samples. The study demonstrates that the simple, rapid, and non-destructive magnetic measurements may be used as proxies for the organic matter content in street dust. Associations between magnetic properties and element concentrations are investigated by using correlation analysis and factor analysis, which may be a potential approach for source identification of magnetic material in the environment.

The study suggests that ferrimagnetic minerals are the dominant magnetic component in Bootle dust samples. Both studied sites show similar magnetic properties, but they can be differentiated using some magnetic parameters, such as χ_{LF}, SIRM, and Hcr / Hc. The difference of magnetic properties in two sites may provide a potential application of magnetic techniques in the study of dust sources in the urban environment.

This study makes a useful contribution to environmental magnetism, especially the application of magnetic techniques to the study of dusts in the urban environment. The results also have practical implications for pollution studies in Liverpool and Bootle areas.

Chapter 1. Introduction

1.1 Recent research developments

Dusts in the environment include surface dust and atmospheric dust: the former referring to the material accumulated on the earth's surface, such as on streets and in living and working environments, the latter to the particulate material suspended in the atmosphere (Fergusson, 1992). This project focuses on magnetic studies of street dust and deposited dust (see Section 1.2). Here a review is given of recent research developments on street dust and dust deposition, in particular the application of magnetic techniques.

Street dust, as pollution material, has received much attention due to its potential health risk to children through hand-to-mouth activities (Fergusson and Kim, 1991; Fergusson, 1992). Street dust is also an important source of house dust (Adgate *et al.*, 1998) and urban atmospheric particulate matter (Harrison *et al.*, 1997). In addition, street dust can degrade the quality of urban water runoff (Sartor and Caboury, 1984). Many studies on street dust have focused on element concentrations and source identification (e.g., Fergusson and Kim, 1991; Fergusson, 1992; De Miguel *et al.*, 1997; Nageotte and Day, 1998). Among them, Pb has been the most frequently investigated element because of its human health hazard (Linton *et al.*, 1980; Nageotte and Day, 1998). The significant findings from studies of element concentrations are that the main component of street dust is soil and that the elements in street dust fall into two groups: those that are primarily soil based, and those that are from pollution sources (Fergusson and Kim, 1991). Dust deposition, particularly acid deposition from fossil fuel combustion, is one of major environmental concerns. Due to dust nuisance, Vallack and Chadwick (1993) reported dust deposition monitoring in a high density coal-fired power station region in North Yorshire, UK. Modaihsh (1997) analysed particle size distribution, physio-chemical and mineralogical compositions of the falling dust sediments on Riyadh city, Saudi Arabia. In short, there are continued interests in studies of dusts in the urban environment, including street dust and dust deposition (e.g., Soylak *et al.*, 2000; Shahin *et al.*, 2000).

On the wider topic of applications of magnetic techniques on pollution studies, Petrosky and Ellwood (1999) have already given a comprehensive literature review. The focus here is on the application of magnetic measurements to the study of dusts in the environment, particularly the latest developments after the publication of their work. Chester *et al.* (1984) were able to distinguish between and characterize dust source types by plotting aluminium concentration against the magnetic susceptibility / aluminium concentration quotient. Soil-derived dusts of North African origin fell at one extreme, with high aluminium concentrations and a low quotient, whereas urban / industrial dusts rich in magnetic spherules fell at the opposite extreme. Hunt *et al.* (1984) applied magnetic measurements to distinguish between fly ash originating from power stations and the particulates in automobile emissions. In another pioneering work, Oldfield *et al.* (1985), on the basis of the magnetic variation in magnetic grain size, proposed magnetic methods for characterizing atmospheric dusts and aerosols derived from different sources, whether the differentiation results from seasonal variations at a single collection site or large scale spatial variations. Using the statistical procedure discriminant analysis, Hunt (1986) established variations in magnetic signature between groups of dust samples collected from the marine aerosols of the North Atlantic Ocean and the Arabian Sea, and from a sampling station on the island of Barbados. Later, Flanders (1994) reported that a significant percentage of magnetic material in many air-borne dust samples consists of spherical magnetite from coal-burning utilities and from iron / steel manufacturing with particle diameters 2 – 10 µm. He also found that the amount of air-borne magnetic material settling to the ground varies inversely with distance from its source. Hay *et al.* (1997) suggested that magnetic susceptibility parameters may be used as a first approximation to identify English topsoils whose magnetic susceptibility can be attributed to the presence of anthropogenically produced magnetic particles. Recently, Hoffmann *et al.* (1999) reported extensive mapping of the magnetic enhancement of the soil surface due to road traffic pollution along a German motorway. They found that profiles of magnetic susceptibility clearly reflect the prevailing wind direction with a sharp maximum within 2 - 5 m of the road. In short, these pioneering studies demonstrate different magnetic characteristics of atmospheric dusts derived from soil, coal-fired power stations, and vehicular exhausts, and suggested that simple, rapid, and non-destructive magnetic measurements can be of considerable value in characterising atmospheric dust sources.

In connection with magnetic sediment tracing (e.g. Beckwith *et al.*, 1986; Brilhante *et al.*, 1989, Beckwith *et al.*, 1990; Charlesworth and Lees, 1997; Flanders, 1999), some authors have carried out magnetic measurements on street dust: an important component of urban sediments. The results suggest the possible relationship between magnetic properties and some element concentrations. Hunt *et al.* (1984) also investigated linkage between magnetic properties and heavy metals in atmospheric particulate matter of anthropogenic origin from power station fly ash and motor vehicle emissions. Morris *et al.* (1995) observed a strong linear correlation between mutagenicity and magnetic susceptibility of respirable airborne particulate matter in Hamilton, Canada. They suggested that magnetic susceptibility measurements could be used to pre-select filters for more extensive evaluations such as by organic compound analyses or biological assays. Recently, Petrosky and Ellwood (1999) suggested that the links between magnetic minerals and heavy metals form the basis for the use of magnetic methods in pollution studies, including magnetic studies of dusts in the environments.

More recently, Matzka & Maher (1999) reported the novel use of magnetic measurements to investigate the spatial and temporal pattern of urban dust loadings on leaves of roadside trees. They suggested that the magnetic analyses enable detailed mapping of the spatial and temporal variations of vehicle-derived particulates. Flanders (1999) made a very useful and important contribution to the application of magnetic techniques to the study of air pollution particulates, using the coercive force field Hc to identify power station fly ash in dust samples. In general terms, his approach and also his findings are useful in that the Hc of dust samples may indicate the proportion of fly ash relative to the total amount of airborne magnetic material, but some caution is required (Xie & Dearing, 1999). First, there is a wealth of environmental magnetic results that shows the difficulties of quantifying the magnetic component where there is evidence of variable grain sizes and mineral types. For example, the rapid oxidation of magnetite into haematite in fly ash (Querol *et al.*, 1996) may be expected to affect the Hc values described. Other magnetic parameters, such as the 'hard' remanence expressed as the difference between the saturation (1T) remanence and a moderate (100mT) or high (300mT) back field remanence, can be used to semi-quantify the haematite component (Thompson & Oldfield, 1986; Oldfield & Richardson, 1990). Second, samples of dust in and around urban areas, especially close to ground level, contain magnetic particles from various sources (e.g. fly ash, vehicle exhaust, degradation products, emissions from metallurgical industries, surface soil) (Beckwith *et al.*, 1986; Hunt *et al.*, 1984). Our knowledge of the importance of each source is presently inadequate but it cannot normally be assumed that fly ash or surface soil magnetic particles dominate the magnetic properties. Third, the claim that distance-dependent deposition of magnetic spheres represents only a minor control on particle-size distribution and Hc values is counter to other evidence. For example, the mean particle size of fly ash in the first 30 km around a large coal-fired power station in Spain (Querol *et al.*, 1996) was > 10 μm, reducing to <10 μm at 46.8 km. Measurements, such as frequency-dependent susceptibility, suggest that there is a small but significant fine (< 0.03 μm) superparamagnetic magnetite component in fly ash samples (Oldfield *et al.*, 1985), a range of grain sizes where Hc values are highly variable. It may be argued that atmospherically - dispersed magnetic particles will show different size distributions with distance from source and may have significant effects on Hc values. An explanation for the measured differences in Hc values for dust samples shown in Figures 6a and 6b in Flanders (1999) may be that there are more larger magnetic particles present in the dust sample from Conesville. Finally, Hc values for fine soil particles are extremely variable with a unimodal distribution peaking in the stable single domain region (~ 0.05 - 0.10 μm). The magnetic properties of well-drained fertile soils (Dearing *et al.*, 1996b) are very often dominated by ultrafine secondary superparamagnetic magnetite / maghemite with low bulk Hc values ~ 2mT or less. Such low background Hc values may accentuate the discrimination of fly ash particles by Hc values, but the simple linear expression of proportions (Flanders, 1999) may be difficult to justify without full calibration against samples of wind-blown soil. In conclusion, there is sufficient evidence to argue that the proposed quantitative interpretation of Hc values in terms of fly ash proportions (Flanders, 1999) needs further development. Most recently, Shu *et al.* (2000) reported results from a pilot investigation into the value and sensitivity of using magnetic techniques to define the types, sources, and transport mechanisms of total suspended particulates in adjacent districts of Shanghai, China, over daily periods. They showed that ferrimagnetic concentration parameters appear to discriminate the different dusts from a range of sources, including iron and steel manufacturing, coal-fired combustion, construction industries and wind-blown soil. Their results suggest that magnetic measurements may provide an exceptionally simple and effective approach for identifying daily variations in particulate loadings and sources in the urban environment.

In summary, urban dusts are an important topic in pollution studies and magnetic measurements provide a new dimension in the area which needs further studies to explore the potential of the techniques.

1.2 Objectives of the project

Despite the progress in the studies of street dust and particularly its magnetic measurements, many topics need further investigation. First, magnetic properties, particularly the main magnetic components, are not well documented. Second, the organic matter content is not well understood. Third, previous studies observe a general trend that element concentrations increase as sizes decrease, but there is lack of knowledge about particle size variations of magnetic properties and the organic matter content. Finally, spatial and temporal variations of magnetic properties and the organic matter content need investigation.

The primary objective of this project is to investigate the application potential of magnetic techniques to studies of dust pollution in the urban environment. Using Liverpool street dust and Bootle deposited dust, measurements were carried out of magnetic properties, element concentrations, and the organic matter content. Then the associations between magnetic properties and the organic matter content, and between magnetic properties and element concentrations were investigated and discussed with regard to the implications for the applications of magnetic measurements to studies of urban dust pollution. Interpretation of magnetic data by the partial susceptibility approach was also examined.

Liverpool is one of the UK's original industrial cities and is still a major port in the NW of England, located on the north-eastern shore of the Mersey Estuary (Fig. 1.1). The population of the city itself is 468, 300 (1998); but the population of its metropolitan area (Merseyside) is 1,400,000 (1998). Traditionally, Liverpool used to handle most of Britain's imported raw cotton and wool, but it also imports sugar, grain, oilseeds, minerals, and crude petroleum and exports manufactured goods of all kinds. Liverpool's manufacturing industries were at first those associated with its foreign commerce, such as grain milling and soap making, but automobile and electrical engineering, chemicals, and petroleum refining have been added and are now more important (see http://www.merseyguide.ndo.co.uk/origin.htm). Tourism and the service sector are increasingly important to the economy. The city also attracts film and television companies who use its unspoilt streets and buildings for location filming. Major regeneration strategies are being applied all around the city, especially in the city centre (see http://www.liverpool.gov.uk/htm/frames1.htm). Urban regeneration activities may cause dust nuisance. For example, some residents brought a legal battle over dust nuisance caused by demolition work (Liverpool Echo, October 8, 1999). In the past 20 years, studies of street dust have been carried out in a number of cities in the UK, including London, Birmingham, Manchester (e.g., Leharne *et al.*, 1992; Davies *et al.*, 1987; Nagerotte & Day, 1998). In spite of the dust nuisance problem, however, no such studies in Liverpool have been reported in the literature.

Bootle, about 5 km north-east of Liverpool city centre (Fig. 1.1), is one of the principal towns in the Borough of Sefton. It is the industrial and commercial heart of Sefton, a port town containing the Port of Liverpool and Liverpool Freeport, now the most successful Freeport in the UK (see http://www.sefton.gov.uk/). A dust deposition monitoring programme is undertaken in the Bootle area, in response to local residents' complaints of dust nuisance in houses (Beer *et al.*, 1994)

Therefore, this project intends to make a useful contribution to the development of environmental magnetism in general, and the application of magnetic techniques to studies of dusts in the urban environment in particular. The results also have practical implications for pollution studies in Liverpool and Bootle.

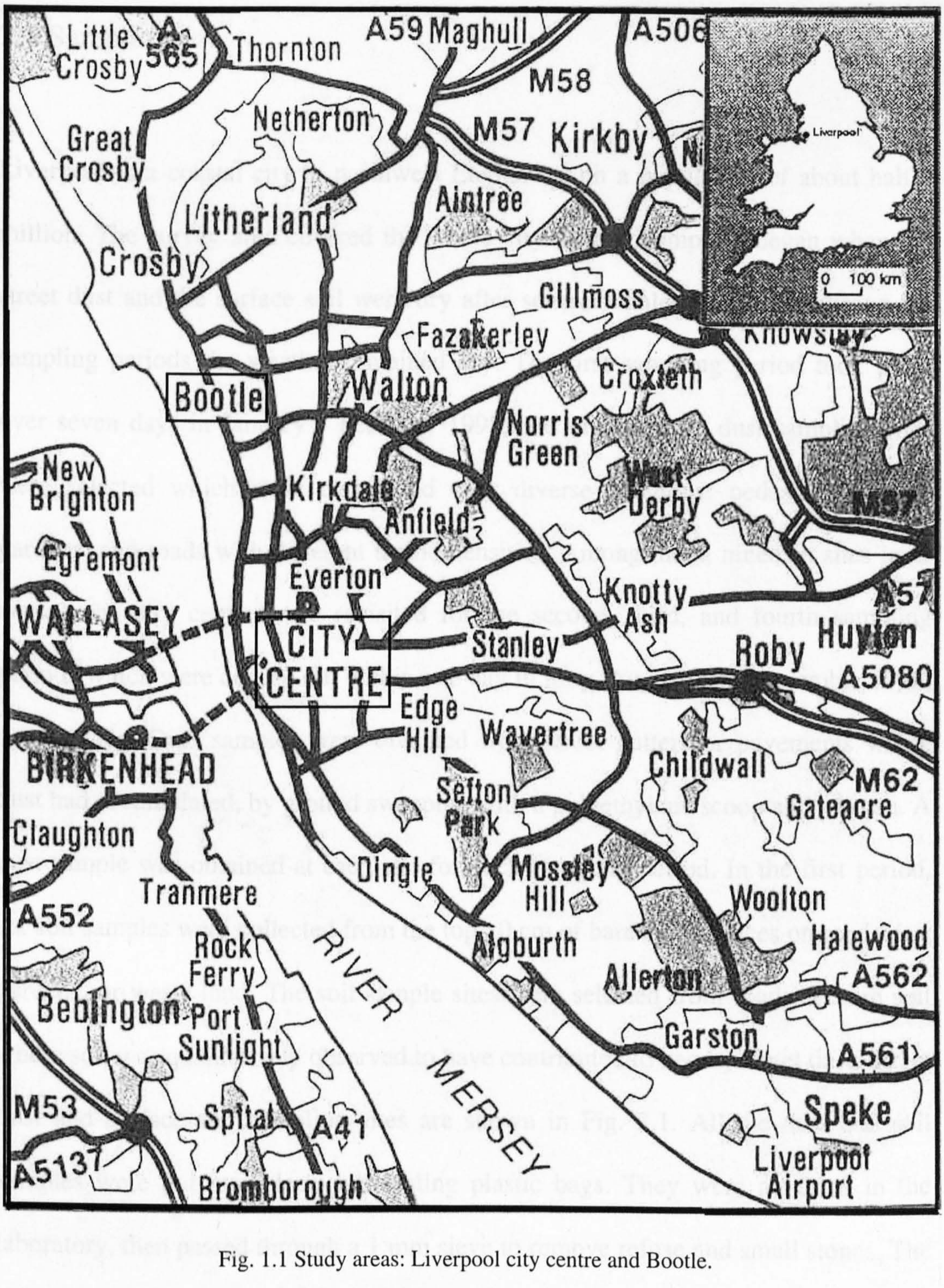

Fig. 1.1 Study areas: Liverpool city centre and Bootle.

Chapter 2. Sampling and measurements of Liverpool street dust

2.1 Sampling

Liverpool is a coastal city in northwest England, with a population of about half a million. The survey area covered the whole city centre. Sampling began when the street dust and the surface soil were dry after several rainless days, and during the sampling periods the weather remained dry. The first sampling period took place over seven days in January – February 1998, and ninety-seven dust sampling sites were selected which were distributed over diverse locations: pedestrian streets, gardens, and roads with different traffic densities. Among them, nineteen sites in or around the city centre were revisited for the second, third, and fourth sampling periods which were carried out within one day in May, August, and November 1998, respectively. Dust samples were obtained from street gutters or pavements where dust had accumulated, by ground sweeping with a polyethylene scoop and a brush. A dust sample was obtained at each site for each sampling period. In the first period, six soil samples were collected from the top 10 cm of bare soil surfaces on roadsides, gardens, or waste land. The soil sample sites were selected from roadside bare soil where soil was qualitatively observed to have contributed to nearby street dust. Street dust and surface soil sampling sites are shown in Fig. 2.1. All the dust and soil samples were put into clean self-sealing plastic bags. They were air-dried in the laboratory, then passed through a 1 mm sieve to remove refuse and small stones. The < 1 mm bulk samples were weighed before being sieved into five fractions with a range of aperture sizes of 63, 150, 300, and 500 μm. The mass of these subsamples (size fractions 1,2 3, 4, and 5: <63, 64-150, 151-300, 301-500, and 501-1000μm) was also measured.

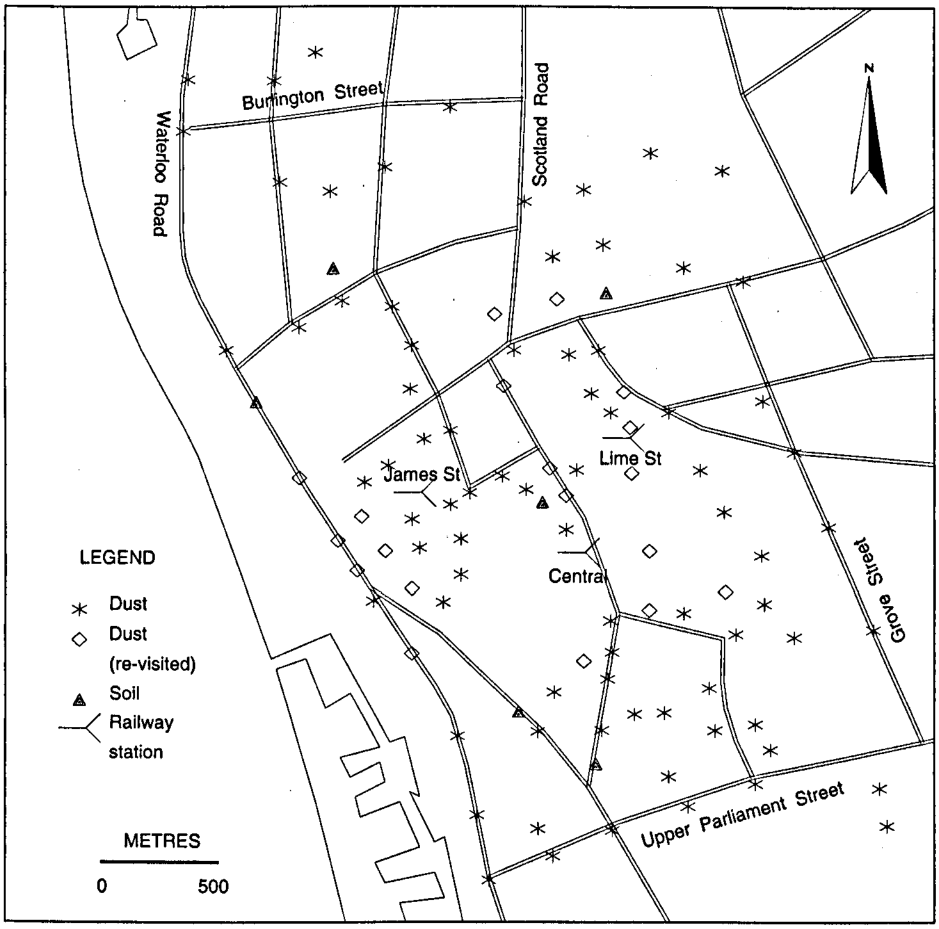

Fig.2.1 Liverpool street dust and surface soil sampling sites, showing 97 sites for the first sampling period (January -February 1998) and 19 revisited sites for subsequent three sampling periods (May, August, and November 1998).

2.2 Magnetic measurements

Low field AC magnetic susceptibility was measured on 10 cm^3 samples using a dual-frequency (470 and 4700 Hz) Bartington Instruments MS2 sensor on the 0.1 scale.

The difference between low and high frequency susceptibility (χ_{LF} - χ_{HF}) is expressed as a mass specific term (χ_{FD} 10^{-8} m^3 kg^{-1}) and as a percentage of the low frequency susceptibility (χ_{FD} percentage). Anhysteretic remanent magnetisation (ARM) was induced in a steady field of 0.1mT with a parallel peak alternating field of 100mT using a DTECH AF demagnetiser and measured on a Molspin spinner magnetometer. Measurements are expressed as susceptibility of ARM (χ_{ARM} 10^{-8} m^3 kg^{-1}) by dividing the remanence by the steady field. Acquisition of isothermal remanent magnetisation (IRM) in the fields of 1T (SIRM), -20mT (reverse) (IRM_{-20mT}), and –300mT (reverse) (IRM_{-300mT}) was carried out using a Molspin pulse magnetiser, and measured on a Molspin spinner magnetometer. Measurements are expressed in 10^{-5} A m^2 kg^{-1} for SIRM, SOFT (= (SIRM - IRM_{-20mT}) / 2), and HIRM (= (SIRM - IRM_{-300mT}) / 2) on a mass specific basis, and as percentages (%) for reverse field ratios of SOFT (-20mT) and HARD (–300mT) (SOFT percentage = 100 × SOFT / SIRM, HARD percentage = 100 × HIRM / SIRM). High field susceptibility χ_{HIGH} was obtained on 1 cm^3 samples using a Molspin vibrating sample magnetometer in the field of 0.8-1 T. Measurements are expressed as a mass specific term (10^{-8} m^3 kg^{-1}).

Ten of the first period bulk samples, 9 dust and 1 soil, were selected. The 9 dust samples were selected across the whole range of the magnetic parameter values and from sites in different quadrants of the city and of different distances from the city centre, which are assumed to represent the variability in magnetic properties in Liverpool street dust. Low and high temperature magnetic susceptibility and low temperature remanent magnetisation measurements were carried out on these 10 selected bulk samples. High temperature susceptibility measurements were also carried out on the 64 - 150 μm fraction of the ten selected bulk samples. Low and high temperature magnetic susceptibility measurements were achieved using a dual-frequency Bartington Instruments MS2 sensor on low frequency and the 1.0 scale. The change in susceptibility value from liquid nitrogen (–196 °C) to room temperature (20 °C) (for low temperature measurements) or first from room temperature to 800 °C then from 800 °C to room temperature (for high temperature measurements) was monitored continuously, and sample temperature recorded using a type-T thermocouple; and measurements are normalized by dividing by their maximum values. For low temperature remanent magnetisation measurements, first, samples were cooled using liquid nitrogen, then SIRM was acquired using a Molspin pulse magnetiser. Remanent magnetisation was measured on a Molspin spinner magnetometer every 10 s as the samples were heating to room temperature in the air. The relationship between heating time and temperature was obtained by simulating the heating process in a Minispin spinner magnetometer. Remanent magnetisation measurements are normalized to values at room temperature.

2.3 Measurements of the organic matter content

Loss-on-ignition is a current common technique to estimate the organic matter content in soil samples. Ignition at 375 °C removes organic matter without structural water loss from inorganic soil components, or the loss of inorganic carbon compounds, which occurs at > 400 °C; the removal of both of these will result in an overestimation of the organic matter content (Boon *et al.*, 1998). Ignition at temperatures below 375 °C removes appreciably less of the carbonaceous matter and is, therefore, not suitable (Ball, 1964). In terms of heating time, Ball (1964) employed the procedure of ignition at 375 °C for 16 h on soil samples, which resulted in > 90% organic matter removal without loss of structural water. Recently, Boon *et al.* (1998) applied the LOI technique (ignition at 375 °C for 4 h) to measure the organic matter content of suspended and deposited dusts in Australia. Their laboratory test shows that the lower limit for acceptable replicated results is 0.0012 g for the dust samples.

Some authors have used the LOI method to measure the organic matter content in street dust (e.g. Fergusson and Ryan, 1984; Al-Chalabi and Hawker, 1996). However, there seems to be some discrepancy in just how the loss-on-ignition method should be applied and different temperatures and different periods of time were used. For the purpose of comparison, several ignition procedures were carried out on bulk dust samples (Table 2.1). Ignition at 375 °C for 4 h, at 375 °C for 16 h, and at 850 °C for 0.5 h was carried out on the same subsamples, and at 450 °C for 4 h on further subsamples.

Weighed subsamples (> 1 g) of bulk dust and soil samples were oven-dried at 105 °C overnight, reweighed and then ignited in a muffle furnace. The value of loss-on-ignition is then expressed as the percentage of weight lost after the 105 °C oven-drying. Table 2.1 shows good correlations between the LOI values at 375 °C for 4 h and those of other ignition procedures. However, as expected, the LOI values at 375 °C for 4 h are lower than or equal to those at 375 °C for 16 h. Due to loss of structural water from inorganic soil compounds or of inorganic carbon compounds at 450 °C, the LOI values at 450 °C for 4 h are generally higher than those at 375 °C for 4 h. Nevertheless, the mean differences between the LOI values at 375 °C for 4 h and those at 375 °C for 16 h or at 450 °C for 4 h are 10.2 and 17.9 %, respectively. Therefore, the procedure of ignition at 375 °C for 16 h or at 450 °C for 4 h may be used to estimate the organic matter content in street dust, in spite of the possible underestimation or overestimation of the organic matter content. An ignition temperature at 850 °C causes greater loss of structural water from inorganic soil compounds or of inorganic carbon compounds. As a result, the LOI values at 850 °C for 0.5 h are more than double of those at 375 °C for 4 h, on average. In this study, the procedures of ignition at 375 °C for 16 h or 4 h are used to measure the organic matter content of the Liverpool street dust and surface soil samples.

Table 2.1 Comparison between loss-on-ignition values of ignition at 375 °C for 4 h and those of other ignition procedures (the first sampling period 97 bulk dust samples).

Ignition procedure	At 375 °C for 4 h	At 375 °C for 16 h	At 450 °C for 4 h	At 850 °C for 0.5 h
Correlation coefficient	1.000 [a]	0.957 [a]	0.932 [a]	0.834 [a]
Mean ± Standard deviation	3.9 ± 1.7	4.3 ± 1.8	4.6 ± 1.8	8.4 ± 2.3
Mean difference (%)	0.0	10.2	17.9	115.4

[a] Correlation is significant at the 0.01 level. The mean difference between mean LOI values of ignition procedure i (LOIi) and those of ignition procedure j (LOIj): (LOIj - LOIi) / LOIi.

A further test of the LOI method was achieved by comparison between the organic carbon content measurements using the Walkley-Black method (Hesse, 1971) and the LOI values on selected dust subsamples. Ten subsamples were selected from each size fraction and bulk samples of the first sampling period, respectively, totalling 60 subsamples, across the whole range of the LOI values and from sites in different quadrants of the city and of different distances from the city centre, which are assumed to represent the variability in the LOI values in Liverpool street dust. Fig. 2.2 shows a good positive correlation between the organic carbon content measurements and LOI values for the 60 selected subsamples, indicating that ignition at 375 °C for 4 h is a reasonably good procedure for estimating the organic matter content of Liverpool street dust samples.

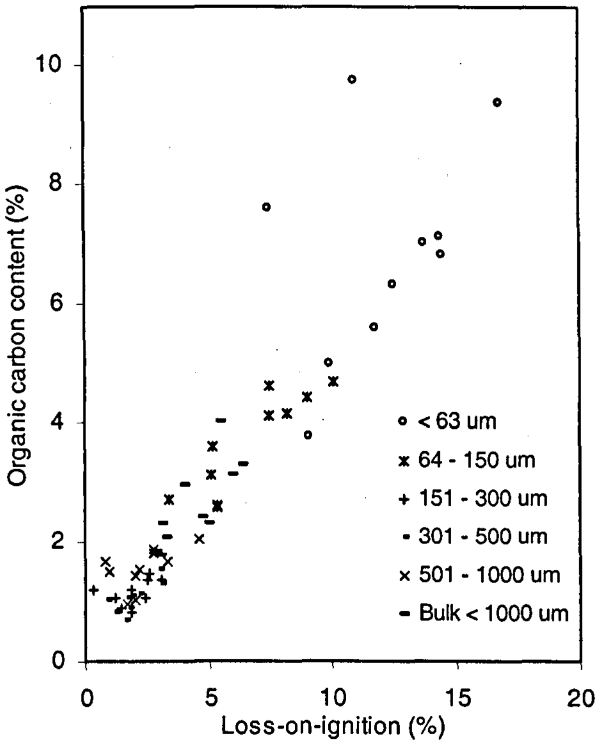

Fig. 2.2 Comparison between organic carbon content measurements and loss-on-ignition values of 60 selected particle size fraction and bulk dust subsamples from the first sampling period, showing that ignition at 375 °C for 4 h is a reasonably good procedure for estimating the organic matter content in Liverpool street dust samples.

2.4 Isotope source X-ray fluorescence (XRF) analysis

Boyle (2000) reported that total concentrations of 15 elements can be determined in soils and sediments with sufficient accuracy using isotope source X-ray fluorescence (XRF) analysis with a Metórex oy (Finland) XMET920 system. This technique was used to measure total concentrations of elements in Liverpool street dust samples. The system consists of software, two X-Met PC system (XPCS) boards, and two analysis probes: a heavy element probe (3-20 keV) using a ^{109}Cd source and a light element probe (0.8-5.9 keV) using a ^{55}Fe source. The measurement procedure and the signal deconvolution method used in this study are the same as those described by Boyle (2000). It was found that total concentrations of Mn, Cl, Nb, and Ni in quite a number of samples were below the detection limits. As a result, only the measurement results of 11 elements (Si, Ti, Ca, K, Fe, S, Pb, Rb, Sr, Zn, and Zr) were analysed in this study. The particle size effect on XRF quantification was tested by comparison of the measurements between ground and unground samples. Twenty samples of the coarsest fraction (501-1000 μm) were chosen. Each of them was split into two subsamples and one subsample was ground finely. Results of the two-tailed Student's t-test revealed that the differences of Pb, Zn, Rb, and S concentrations between the two subsample sets are not significant at the 0.05 level, suggesting insufficient evidence of a particle size effect. Therefore, for the finest size fraction (< 63 μm) samples 11 element (Si, Ti, Ca, K, Fe, S, Pb, Rb, Sr, Zn, and Zr) concentrations were analysed, whilst for > 63 μm fraction and bulk (< 1000 μm) samples only 4 element (Pb, Zn, Rb, and S) concentrations were analysed.

Chapter 3. Magnetic properties of Liverpool street dust

3.1 Introduction

In connection with magnetic sediment tracing studies (e.g. Beckwith *et al.*, 1986; Brilhante *et al.*, 1989, Beckwith *et al.*, 1990; Charlesworth and Lees, 1997; Flanders, 1999), some authors have carried out magnetic measurements on street dust. However, more detailed analysis of magnetic properties of street dust is needed to identify the dominant magnetic components, which is essential both for inferring the origins of magnetic material and for investigating the applications of magnetic techniques in studies of dusts in the urban environment.

In this chapter, magnetic properties of Liverpool street dust are analysed. First, magnetic properties of bulk samples (< 1000 μm) from the first sampling period are analysed. Then, magnetic properties of the different size fractions are investigated. Finally, magnetic properties of <63 μm fraction samples of the second, third, and fourth sampling periods are compared with those of the first period samples.

3.2 A brief discussion of interpretation of magnetic parameters

Detailed interpretation of magnetic parameters can be found in the literature (e.g., Thompson & Oldfield, 1986; Xie *et al.*, 1999a) and a brief discussion is given here. The magnetic susceptibility χ_{LF} represents the total contribution of magnetic minerals in a sample. For natural materials, it is mainly a function of their ferrimagnetic content (Thompson and Oldfield, 1986). Frequency dependent susceptibility χ_{FD} is related to the superparamagnetic (SP) ferrimagnetic component (Dearing *et al.*, 1996a), while the content of stable single domain (SSD) ferrimagnetic grains can be estimated by ARM or χ_{ARM} (King *et al.*, 1982; Maher, 1988). Weak field (e.g., 20mT) isothermal remanent magnetization (IRM) or low reverse field (e.g., –20mT) demagnetisation of saturation isothermal remanent magnetization (SIRM) can be used to identify the presence of soft components; mainly multidomain (MD) ferrimagnetic grains. Small MD grains could demonstrate pseudo-single domain (PSD) behaviour. Thompson's (1986) calculations suggest that SOFT is expected to be approximately proportional to the PSD + MD grain content of ferrimagnetic components in a sample. In addition to the contribution of PSD + MD grains, SOFT and IRM_{20mT} also include the contribution of fine viscous grains at the SSD / SP border. For magnetite, SP and SSD threshold grain sizes (in diameter) are estimated as 0.025 - 0.030 and 0.05 - 0.06μm (or 0.079 - 0.084μm) (Dunlop & Özdemir, 1997). Oldfield and Richardson (1990) suggested that HIRM can be used as a rough guide to canted antiferromagnetic components in a sample. HIRM, defined as (SIRM - IRM_{-300mT}) / 2, could exclude the contribution of some soft canted antiferromagnetic components. SOFT percentage (= 100 × SOFT / SIRM) and HARD percentage (= 100 × HIRM / SIRM) can be used as approximate indications of relative importance of ferrimagnetic and canted antiferromagnetic components in a sample, respectively (Oldfield and Richardson, 1990). Plots of the ratio χ_{ARM} /SIRM versus χ_{FD} percentage can be used to estimate grain sizes in ferrimagnetic minerals (Maher, 1988; Dearing *et al.*, 1997). High field susceptibility χ_{HIGH} detects the total contributions of paramagnetic, diamagnetic, and canted antiferromagnetic components (Richter & van der Pluijm, 1994).

3.3 Magnetic properties of the first period bulk samples

The magnetic measurements of bulk samples are summarised in Table 3.1. Because the dust organic matter content is not high (3.9 ± 1.7 %, see Table 2.1), its diluting effect on the dust magnetic concentration is not significant. Table 3.1 shows that the χ_{HIGH} / χ_{LF} values range from 1.5 to 7.0 % (average 2.6 %), indicating that the total contributions of paramagnetic, diamagnetic, and canted antiferromagnetic components to the total susceptibility are not significant. SOFT percentage (33.5 - 44.9 %) and HARD percentage (0.1 - 5.4 %) values and the mean χ_{LF} value (> 250×10^{-8} m^3 kg^{-1}) also suggest the dominance of ferrimagnetic minerals (Oldfield and Richardson, 1990; Dearing *et al.*, 1996a). By comparison of χ_{FD} percentage (0.6 - 2.5 %) and χ_{ARM} /SIRM ($0.09 - 0.20 \times 10^{-3}$ m A^{-1}) data in a semi-quantitative mixing model (Dearing *et al.*, 1997; see Fig. 3.1), the proportions of SP, SSD, and PSD + MD grains are estimated as ~ 10, ~ 0, and ~ 90 %, respectively. Therefore, the dominant magnetic component comprises PSD + MD ferrimagnetic grains, with SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals present in small magnetic concentrations.

It is suggested that there are few SP ferrimagnetic grains in samples with χ_{FD} percentage < 2.0 % (Dearing *et al.*, 1996a; Dearing, 1999a). However, recently, Worm & Jackson (1999) showed that χ_{FD} percentage = 0 must not be taken to imply the absence of superparamagnetic grains. Low temperature magnetic susceptibility measurements of ten selected bulk samples (the first period) show increasing susceptibility values with increasing temperature from -196 to 20 °C, indicating the existence of SP ferrimagnetic grains (Fig.3.2). Magnetic measurements of these ten selected bulk samples are listed in Table 3.2, showing similar magnetic properties to the whole dataset of 97 dust samples.

Table 3.1 Magnetic measurements of the first period bulk samples (< 1000 μ m).

Magnetic parameter	Unit	Range	Average	Standard deviation
χ_{LF}	$10^{-8}\,m^3\,kg^{-1}$	41.4 - 670.0	252.6	110.6
χ_{FD}	$10^{-8}\,m^3\,kg^{-1}$	0.5 - 10.3	4.1	1.7
χ_{FD} percentage	%	0.6 - 2.5	1.7	0.4
χ_{ARM}	$10^{-8}\,m^3\,kg^{-1}$	92.7 - 1162.8	484.9	185.2
SIRM	$10^{-5}A\,m^2\,kg^{-1}$	528.8 - 10655.6	3628.0	1587.4
SOFT	$10^{-5}A\,m^2\,kg^{-1}$	216.7 - 4046.8	1380.2	609.3
HIRM	$10^{-5}A\,m^2\,kg^{-1}$	2.6 - 303.6	54.5	43.8
χ_{ARM} /SIRM	$10^{-3}\,m\,A^{-1}$	0.09 - 0.20	0.14	0.02
SOFT percentage	%	33.5 - 44.9	38.1	2.1
HARD percentage	%	0.1 - 5.4	1.6	1.0
χ_{HIGH}	$10^{-8}\,m^3\,kg^{-1}$	1.4 - 15.9	6.5	2.9
χ_{HIGH} / χ_{LF}	%	1.5 - 7.0	2.6	0.8

High temperature susceptibility was also measured on the same ten selected bulk samples (Fig. 3.3). Seven of them show magnetite Curie temperatures (~ 580 °C) although during heating there are conversions of paramagnets into ferrimagnets. The remaining three samples (no14, no43, and no98) exhibit > 600 °C Curie temperatures (~ 620 °C), probably due to the contribution of maghaemite (Curie temperature ~ 600 °C) or haematite (Curie temperature ~ 675 °C). Some samples show negative susceptibility values at high temperatures (> ~ 580 °C), due to the contribution of diamagnetic components. In summary, high temperature susceptibility measurements demonstrate the presence of mixed magnetic phases although magnetite is probably a dominant one.

Table 3.2 Magnetic measurements of the ten selected first period bulk samples (< 1000 μ m) [a].

Magnetic Parameter	No.9	No.14	No.20	No.43	No.85	No.86	No.91	No.96	No.98	No.100
χ_{LF}	809.2	476.4	625.1	797.0	120.5	216.0	168.9	1053.7	563.4	382.9
χ_{FD}	7.3	8.4	9.6	4.7	2.3	2.4	0.8	12.8	5.6	6.2
χ_{FD} %	0.9	1.8	1.5	0.6	1.9	1.1	0.5	1.2	1.0	1.6
χ_{ARM}	1455.2	888.2	1065.3	1283.3	431.9	734.9	329.8	1595.8	1132.8	623.7
SIRM	10442.2	5364.2	6385.7	10091.8	2144.0	3831.6	1883.7	15284.9	5916.6	3829.9
SOFT	3681.7	1813.6	2056.5	3679.0	703.3	1174.7	664.1	4578.2	1909.9	1385.7
HIRM	184.7	73.6	103.0	131.8	101.0	163.5	26.6	289.4	65.6	56.6
χ_{ARM} /SIRM	0.14	0.17	0.17	0.13	0.20	0.19	0.18	0.10	0.19	0.16
SOFT %	35.3	33.8	32.2	36.5	32.8	30.7	35.3	30.0	32.3	36.2
HARD %	1.8	1.4	1.6	1.3	4.7	4.3	1.4	1.9	1.1	1.5
χ_{HIGH}	8.5	3.6	11.9	14.1	3.5	1.9	1.4	15.9	8.5	8.2
χ_{HIGH} / χ_{LF} (%)	1.8	2.8	2.7	2.3	2.9	2.5	3.3	2.4	2.6	5.3

[a] The units of magnetic parameters are the same as in Table 3.1. No.85 is a soil sample and the rest are dust samples. The soil sample shows the presence of SP grains (Fig. 3.2), dominance of magnetite in the bulk sample (Fig. 3.3) and non-magnetite phases in the 64 - 150 μ m fraction (Fig. 3.7). The Verwey transition is not observed for the bulk soil sample (Fig. 3.4).

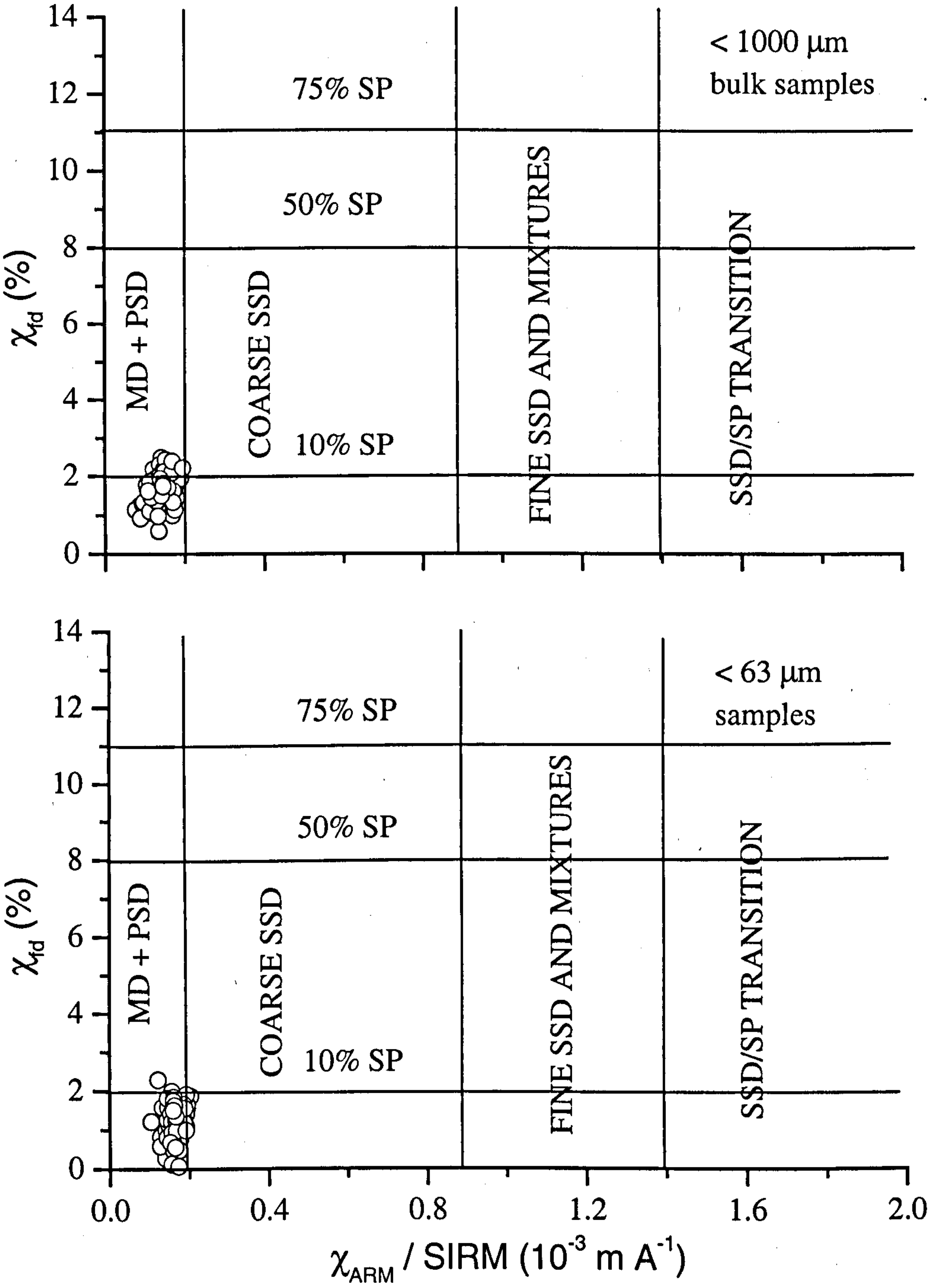

Fig. 3.1 Ferrimagnetic grain size analysis of Liverpool street dust samples: the plot of χ_{FD} percentage versus χ_{ARM} /SIRM (Dearing *et al.*, 1997) for bulk (< 1000 μm) and size fraction (< 63 μm) samples.

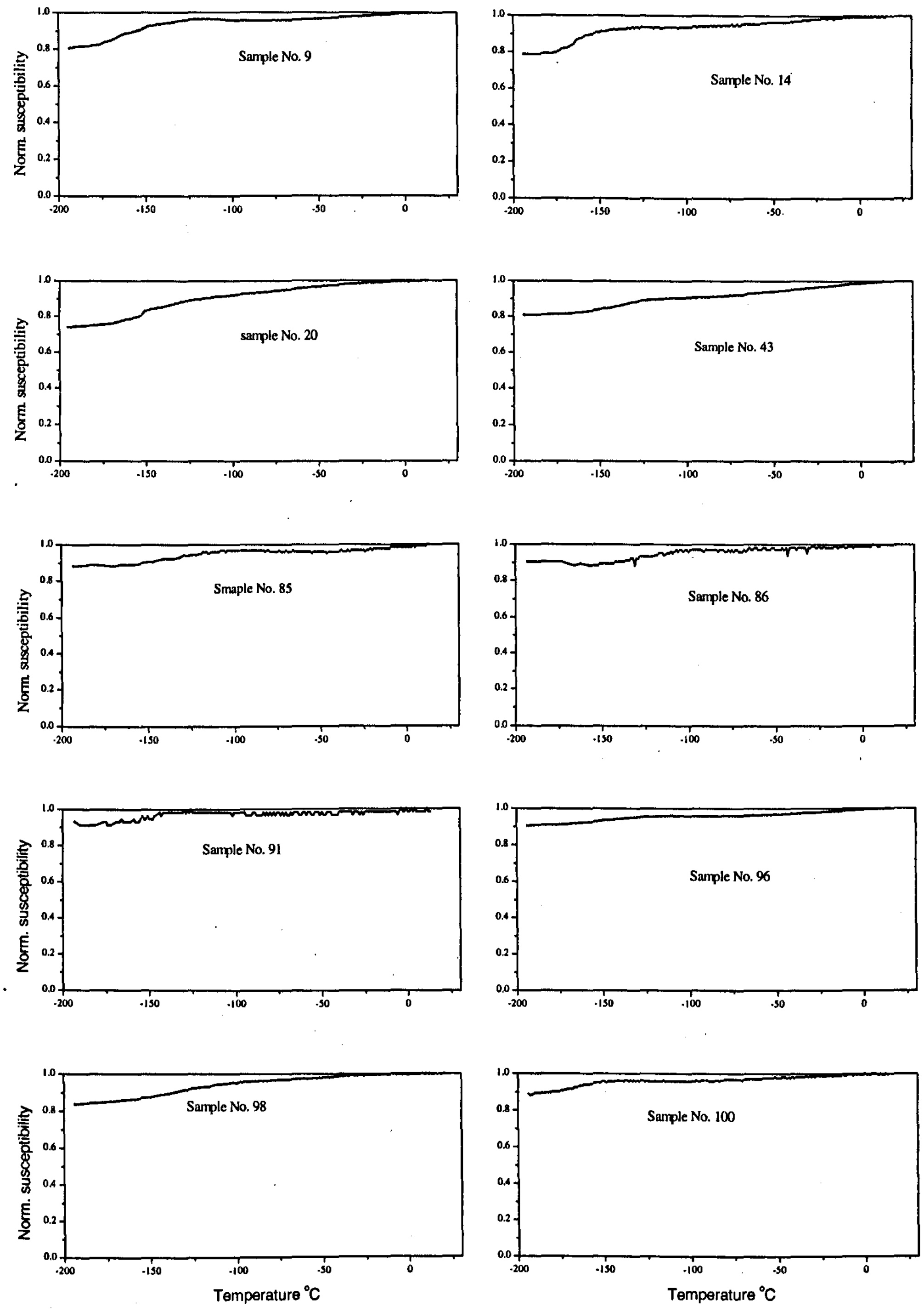

Fig. 3.2 Low temperature magnetic susceptibility measurements of ten selected bulk samples (the first sampling period). Increasing susceptibility values with increasing temperature from -196 to 20 °C indicates the existence of SP ferrimagnetic grains.

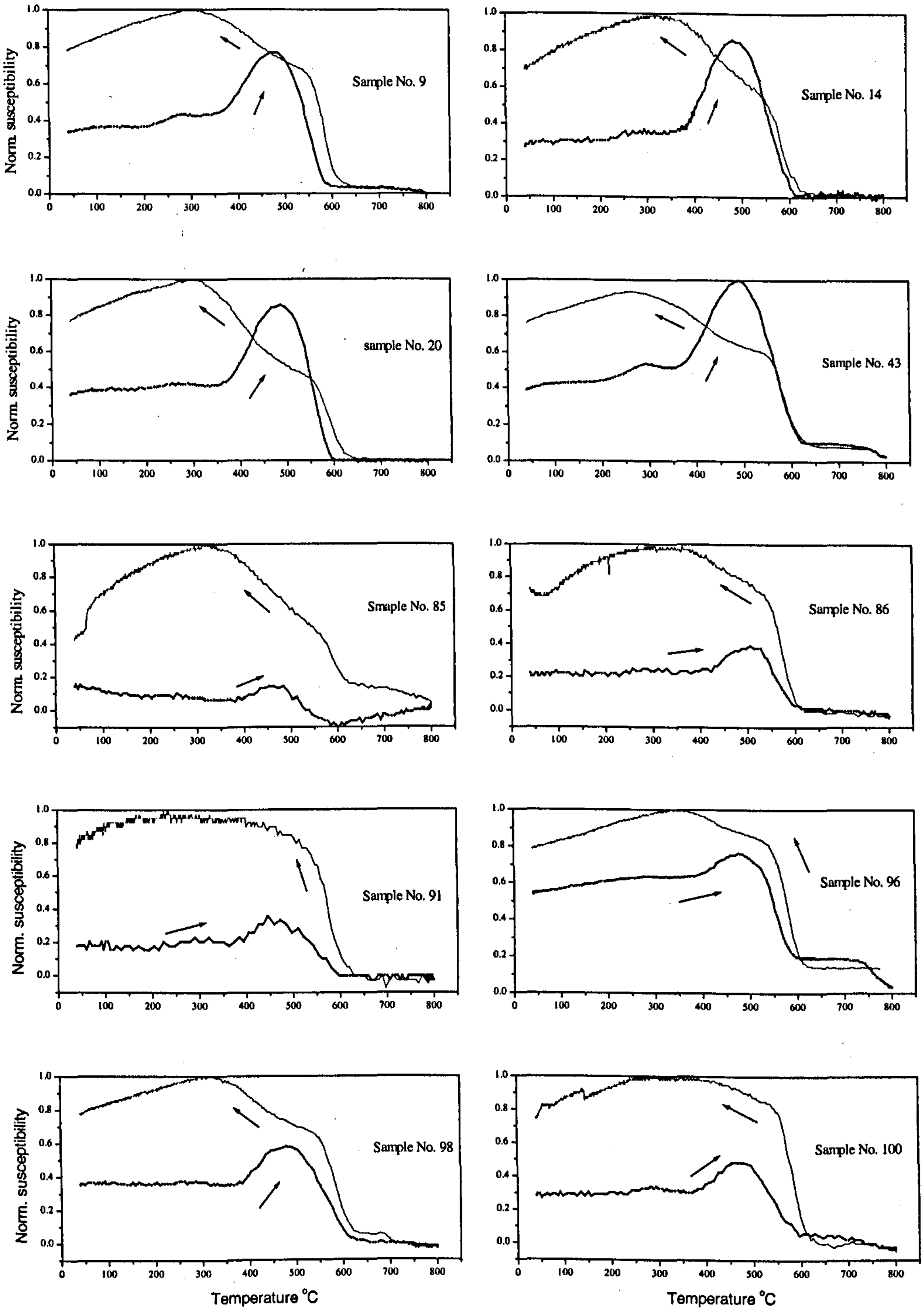

Fig. 3.3 High temperature susceptibility measurements of ten selected bulk samples (the first sampling period), suggesting the presence of mixed magnetic phases although magnetite is probably a dominant one.

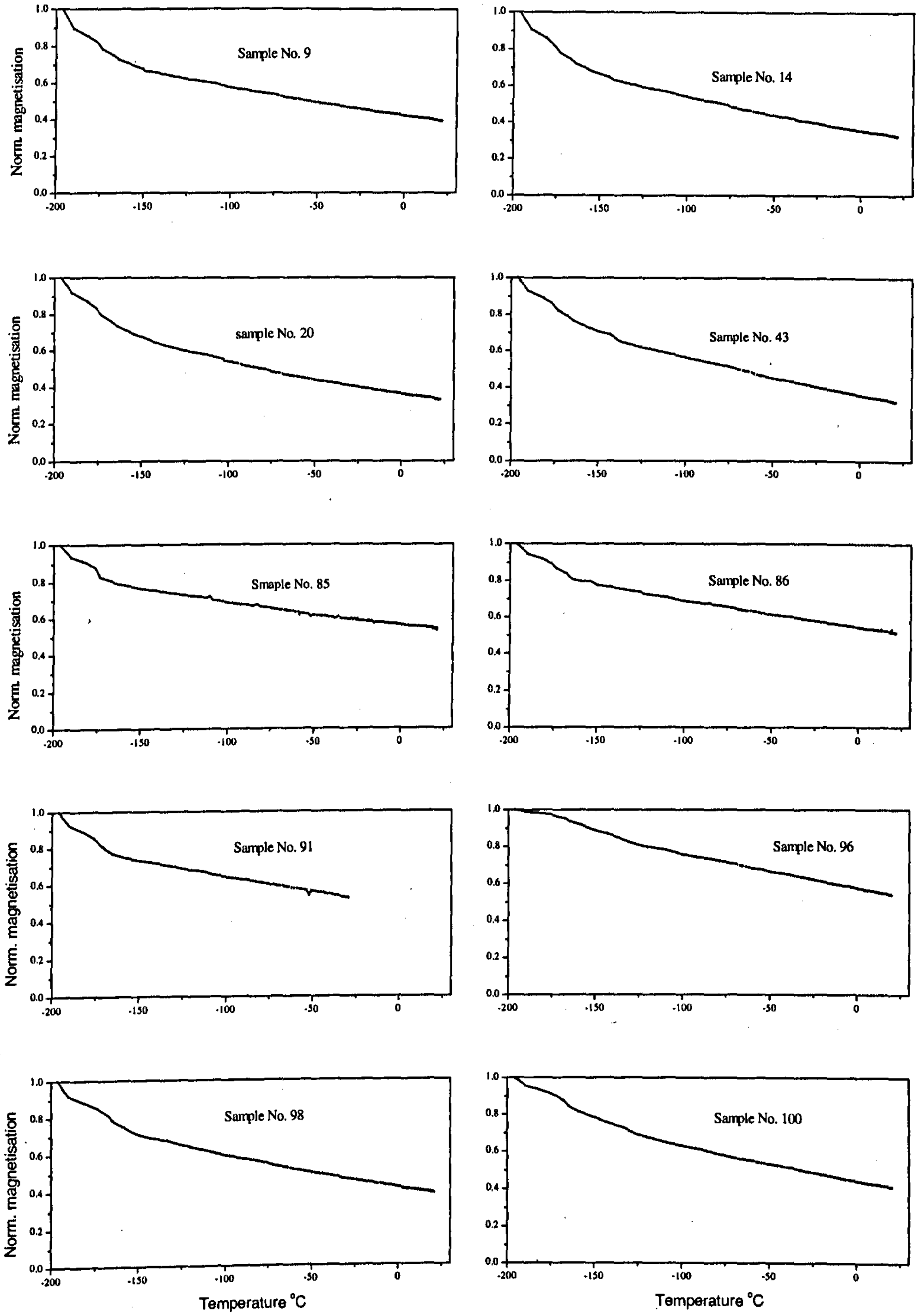

Fig. 3.4 Low temperature remanent magnetisation measurements of ten selected bulk samples (the first sampling period), showing gradual decrease of magnetisation values with increasing temperature.

Low temperature remanent magnetisation measurements of the same ten selected bulk samples show that magnetisation values gradually decrease with increasing temperature (Fig. 3.4). No abrupt changes of magnetisation values (the Verwey transition) are observed for magnetite dominant samples (mainly PSD + MD grains), possibly due to its impurity.

3.4 Magnetic properties of the first period size fraction samples

The magnetic measurements of size fraction samples are summarised in Table 3.3. Because the dust organic matter content is not very high (see Table 6.2), its diluting effect on the dust magnetic concentration is not significant. For the purpose of comparison, measurements of the bulk samples are also presented in Table 3.3. Although χ_{LF} values vary with particle size, the average values are still relatively high ($> 150 \times 10^{-8}$ m^3 kg^{-1}) (Table 3.3), suggesting the dominance of ferrimagnetic minerals (Dearing *et al.*, 1996a). High values of SOFT percentage (29.2 - 48.3 %) and low values of HARD percentage (0.0 - 4.6 %) for five fractions also indicate the dominance of ferrimagnetic minerals (Oldfield and Richardson, 1990). Similar to the analysis of the bulk samples, comparing size fraction χ_{FD} percentage (0.1 - 2.8 %) and χ_{ARM} /SIRM ($0.04 - 0.25 \times 10^{-3}$ m A^{-1}) data in a semi-quantitative mixing model (Dearing *et al.*, 1997; see Figs. 3.1, 3.5, and 3.6), the proportions of SP, SSD, and PSD + MD grains are estimated as ~ 10, ~ 0, and ~ 90 %, respectively. In summary, the size fraction sample measurements also suggest that dominant magnetic component comprises PSD + MD grains, with SP and SSD grains and non-ferrimagnetic minerals present in small magnetic concentrations, similar to those of the bulk samples (see Section 3.3).

Table 3.3 Magnetic measurements of the first period samples (mean ± standard deviation).

Size fraction	< 63 μm	64 - 150 μm	151-300 μm	301 - 500 μm	501-1000 μm	< 1000 μm
χ_{LF}	502.8	333.5	157.1	235.2	529.0	252.6
(10^{-8} m^3 kg^{-1})	± 149.8	± 126.4	± 73.8	± 119.4	± 316.8	± 110.6
χ_{FD}	6.1	5.3	2.8	2.9	7.6	4.1
(10^{-8} m^3 kg^{-1})	± 2.7	± 1.9	± 1.3	± 1.3	± 4.5	± 1.7
χ_{FD} percentage	1.2	1.6	1.8	1.3	1.5	1.7
	± 0.4	± 0.4	± 0.5	± 0.4	± 0.3	± 0.4
χ_{ARM}	963.3	605.6	281.2	404.0	925.5	484.9
(10^{-8} m^3 kg^{-1})	± 225.4	± 180.9	± 107.5	± 171.5	± 465.1	± 185.2
SIRM	6069.6	4259.5	2122.4	3291.4	8015.1	3628.0
(10^{-5} Am^2 kg^{-1})	± 1976.1	± 1513.4	± 911.6	± 1581.9	± 5240.4	± 1587.4
χ_{ARM}/SIRM	0.16	0.15	0.14	0.13	0.12	0.14
(10^{-3} m A^{-1})	±0.18	± 0.18	± 0.02	± 0.03	± 0.03	± 0.02
SOFT	2050.6	1448.3	775.2	1228.2	3113.4	1380.2
(10^{-5} Am^2 kg^{-1})	± 682.0	± 544.1	± 344.9	± 586.8	± 1905.5	± 609.3
SOFT percentage	33.7	33.9	36.2	37.5	39.3	38.1
	± 1.8	± 1.8	± 2.0	± 2.3	± 2.6	± 2.1
HIRM	100.3	16.4	34.6	19.3	79.2	54.5
(10^{-5} Am^2 kg^{-1})	± 38.2	± 19.7	± 19.5	± 16.2	± 93.1	± 43.8
HARD	1.7	0.5	1.7	0.8	1.1	1.6
percentage	± 0.6	± 0.7	± 0.7	± 0.7	± 1.2	± 1.0

Maher (1986) illustrated that higher values of some magnetic parameters (e.g., χ_{LF}, χ_{FD} percentage, ARM, SIRM, SIRM/ARM) are associated with <63 μm fractions in soils which have undergone magnetic enhancement as a consequence of pedogenic formation and/or atmospheric deposition. In contrast, Table 3.3 shows higher values of magnetic concentration-related parameters χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, SOFT, and HIRM in the finest (<63μm) and coarsest (501-1000μm) fractions than those in other fractions (64-150, 151-300, and 301-500μm), significantly at the 0.01 level, with one exception that the difference between the mean χ_{FD} value in fraction <63μm and that in fraction 64-150μm is not significant at the 0.05 level. This, therefore, indicates magnetic enhancement in the finest and coarsest fractions. Quotient parameters χ_{FD} percentage, χ_{ARM} /SIRM, SOFT percentage, and HARD percentage, however, do not demonstrate the same size variation trend as concentration-related parameters (Table 3.3). The six surface soil samples do not show magnetic enhancement in the finest or coarsest fraction, although this may be inconclusive because of the small number of soil samples.

Magnetic measurements of English topsoils show a mean χ_{LF} of 73×10^{-8} m^3 kg^{-1} (median 38×10^{-8} m^3 kg^{-1}) and a mean χ_{FD} of 4.53×10^{-8} m^3 kg^{-1} (mean χ_{FD} percentage: 4.1 %) (Dearing *et al.*, 1996b; Hay *et al.*, 1997). Mean χ_{FD} values in the Liverpool street dust samples (~ 4.0×10^{-8} m^3 kg^{-1}) are remarkably similar to that in English topsoils. However, street dust shows considerably higher mean χ_{LF} values (~ 250×10^{-8} m^3 kg^{-1}), more than two times higher, than English topsoils. As a result, mean χ_{FD} percentage values in Liverpool street dust (~ 1.7 %) are notably lower than that in English topsoils. The considerably higher mean χ_{LF} values of street dust than those of English topsoils suggest that dust magnetic material is largely from non-soil urban sources. Beckwith *et al.* (1986) suggested that the possible non-soil sources of magnetic minerals in the urban environment include atmospheric deposition, automobile derived particulates, and surface constructional materials.

High temperature susceptibility was also measured on some size fraction samples. Fig 3.7 shows the measurement results on the 64 - 150 μm fraction of the ten selected bulk samples in Figs. 3.2 - 3.4. They show Curie temperatures of > 600 °C, suggesting the dominance of non-magnetite phases, different from those of the bulk samples showing magnetite Curie temperatures (~ 580 °C) for seven of the ten samples (Fig. 3.3). This suggests that dominant magnetic minerals in street dust may be various in different particle size fraction samples.

3.5 Magnetic properties of the second, third, and fourth period samples

Magnetic measurements of the finest fraction (<63 μm) of the samples taken in the second, third, and fourth sampling periods from the same sites demonstrate relatively high mean χ_{LF} and SOFT percentage values and low mean HARD percentage, χ_{FD} percentage, and χ_{ARM} /SIRM values, very similar to those of the first period samples (see Table 5.2). This also suggests that the dominant magnetic mineral assemblage comprises PSD + MD ferrimagnetic grains, with SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals present in small magnetic concentrations in street dust at different periods of the year.

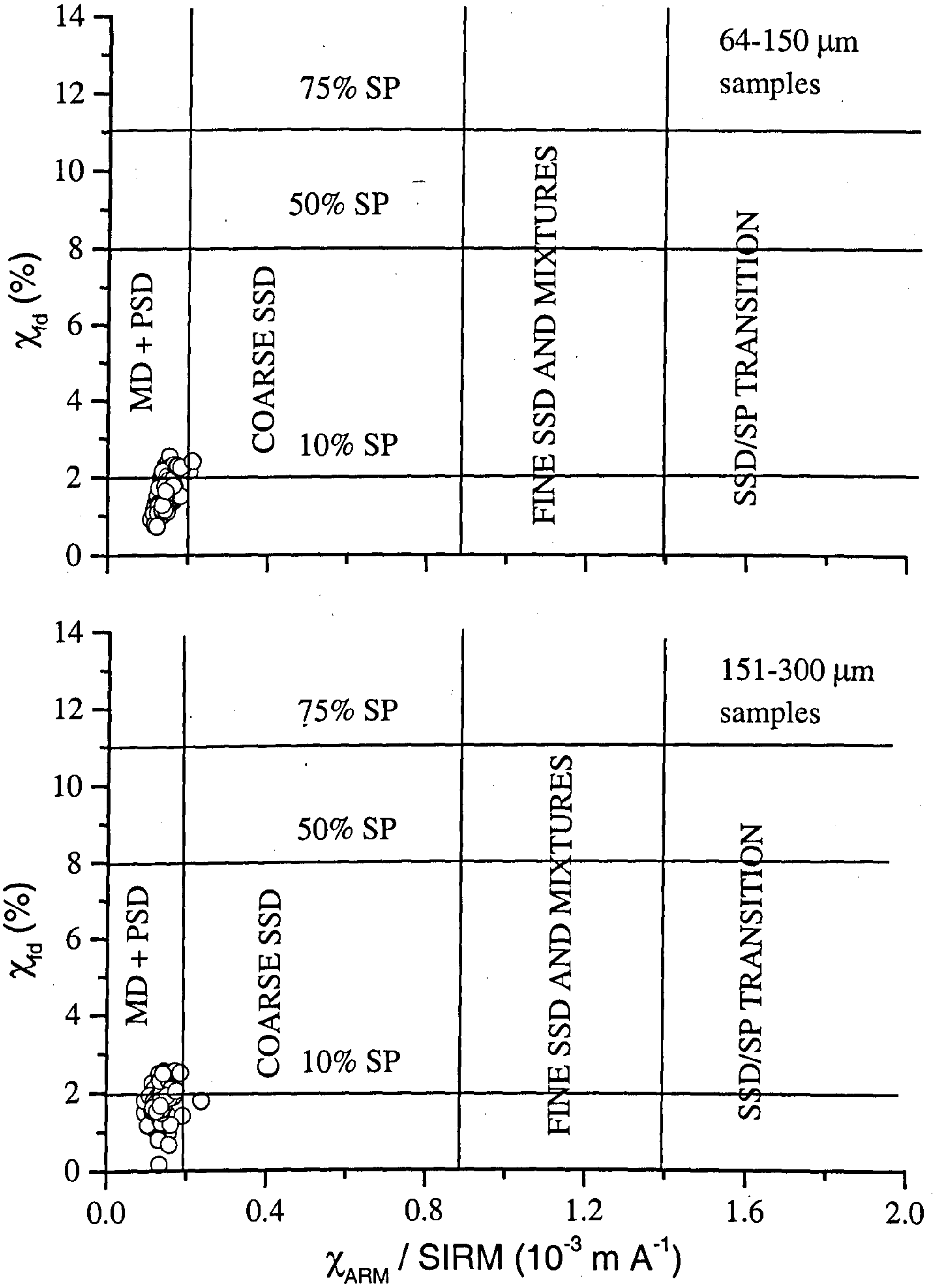

Fig. 3.5 Ferrimagnetic grain size analysis of Liverpool street dust samples: the plot of χ_{FD} percentage versus χ_{ARM} /SIRM (Dearing *et al.*, 1997) for size fraction (64 - 150 and 151 - 300 μ m) samples.

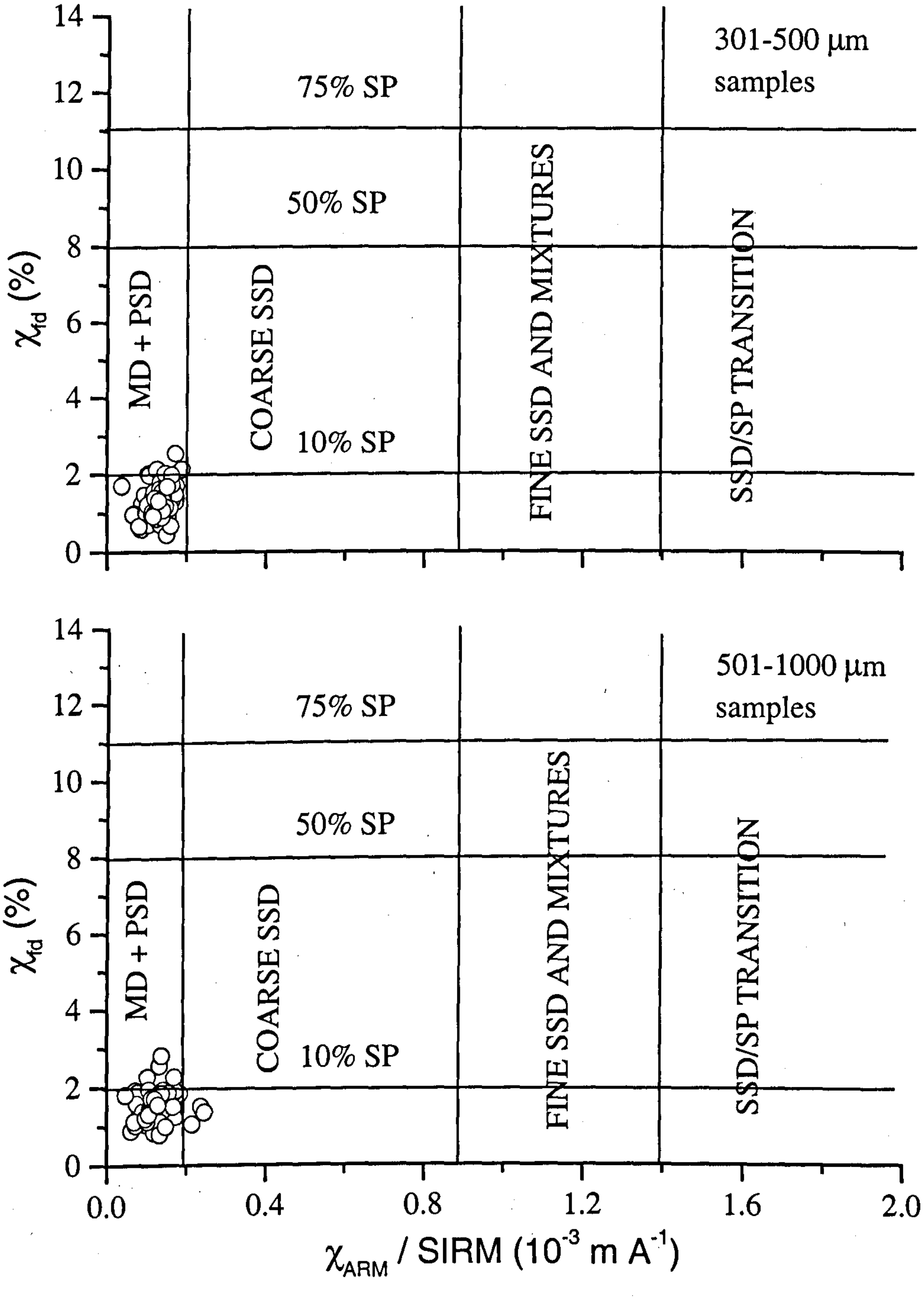

Fig. 3.6 Ferrimagnetic grain size analysis of Liverpool street dust samples: the plot of χ_{FD} percentage versus χ_{ARM} /SIRM (Dearing *et al.*, 1997) for size fraction (301 - 500 and 501 - 1000 μ m) samples.

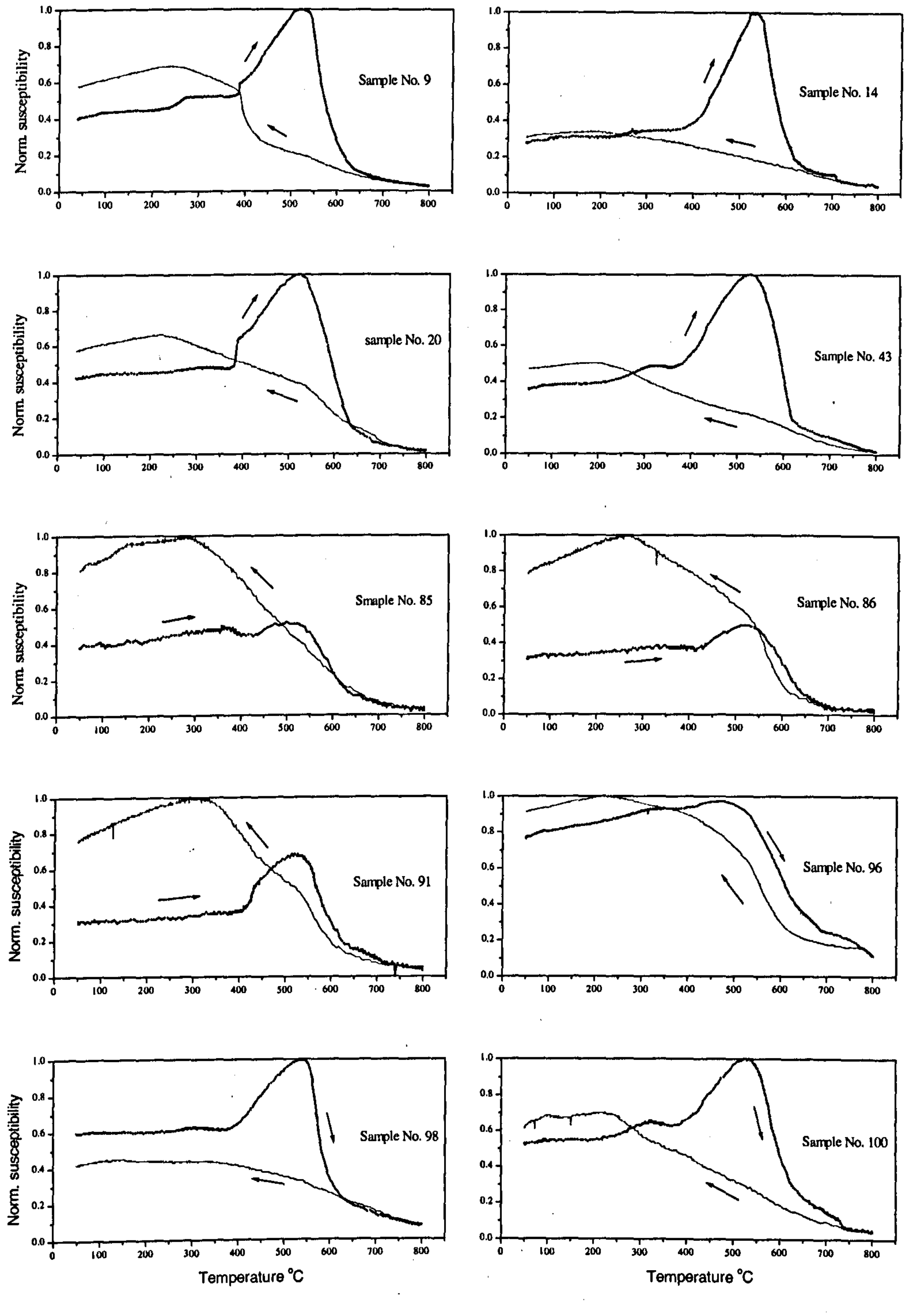

Fig. 3.7 High temperature susceptibility measurements of the 64 - 150 μ m fraction of the ten selected bulk samples (the first sampling period), showing Curie temperatures of > 600 °C, indicating the contribution of non-magnetite phases.

3.6 Summary

High temperature susceptibility measurements demonstrate mixed dominant ferrimagnetic phases in Liverpool street dust although magnetite is probably the major magnetic mineral. In terms of grain size, the dominant component comprises PSD + MD grains, with SP and SSD ferrimagnetic grains and paramagnetic, diamagnetic, and canted antiferromagnetic minerals representing minor magnetic concentrations. Samples of different particle sizes and of different sampling periods show similar magnetic properties.

Chapter 4. A case study of the partial susceptibility approach using Liverpool street dust samples

4.1 Introduction

One of the most urgent needs in environmental magnetism is to present magnetic measurement results in terms of mineral and grain size contributions quantified by both empirical and theoretical models of the relationships between magnetic properties and magnetic components (Oldfield, 1991; 1999a). Several complementary attempts have been made. Hunt (1986) used discrimination analysis to establish variations in magnetic signature between groups of dusts. Thompson (1986) described two approaches to modelling magnetization data, the first modelling the magnetic properties of natural materials in terms of mixtures of possible source materials, the second modelling the magnetic properties of natural materials in terms of mixtures of magnetite and haematite crystals of varying concentrations and grain sizes. Another attempt is represented by the development of empirically derived mixing models to estimate the contributions of magnetically differentiated source material types (e.g., Yu & Oldfield, 1989; Lees, 1997). On the basis of magnetic properties of some synthetic sub-micron magnetites, Maher (1988) proposed a method of magnetic granulometry using a sequence of measurements, such as the ratio χ_{ARM} /SIRM and χ_{FD} percentage which has been further tested by Oldfield (1994) and Dearing *et al.* (1997). Robertson and France (1994) and Stockhausen (1998) tried to discriminate different magnetic phases using cumulative log Gaussian functions to model IRM acquisition curves. Recently, von Dobeneck (1998) and Frederichs *et al.* (1999) introduced the concept of partial susceptibilities for quantitative analysis of carriers of magnetic susceptibility in marine sediments.

In this chapter, the approach of von Dobeneck (1998) and Frederichs *et al.* (1999) proposal is developed. First, the concept of partial susceptibilities and the relevant concentration dependent parameters are described. Then, Liverpool street dust bulk samples from the first sampling period are used as a case study. Last, factors which may have a significant impact on the approach are discussed.

4.2 Methods

The observed total magnetic susceptibility of an environmental sample, χ_{TOTAL}, is the sum of partial susceptibilities of discrete particles, domains or mineral fractions. The partial susceptibilities are of ferrimagnets, χ_{FERRI}, canted antiferromagnets, $\chi_{ANTIFERRO}$, paramagnets, χ_{PARA}, and diamagnets, χ_{DIA}. The susceptibility of ferrimagnetic components (χ_{FERRI}) in a sample can also be considered as the total contributions of superparamagnetic domain (SP), stable single domain (SSD), and pseudo-single domain and multidomain (PSD + MD) grains (χ_{SP}, χ_{SSD}, and χ_{MD}). Therefore, χ_{TOTAL} can be expressed as

$$\chi_{TOTAL} = \chi_{SP} + \chi_{SSD} + \chi_{MD} + \chi_{ANTIFERRO} + \chi_{PARA} + \chi_{DIA} \qquad (4.1)$$

χ_{TOTAL} is usually routinely measured by means of low field AC susceptibility χ_{LF} (low frequency), which represents the total contributions of magnetic materials in a sample, but partial susceptibilities are rarely directly measured except high field susceptibility χ_{HIGH}, which detects the total contributions of paramagnetic, diamagnetic, and canted antiferromagnetic components (Richter & van der Pluijm, 1994). However, the concentrations of discrete magnetic minerals and their fractions can be estimated by other magnetic concentration-related parameters. There is evidence that some concentration dependent parameters can be used as proxies for the related magnetic components in a sample. First, χ_{FD} is related to SP components. When the SP grain concentration, rather than the grain size distribution, dominates both χ_{FD} and χ_{SP} values, a linear relationship between χ_{SP} and χ_{FD} is expected. Measurements of environmental materials show that χ_{FD} values can be considered loosely as an indication of the amount of SP material present in a sample (Dearing *et al.*, 1996). Second, SSD grains can be estimated by anhysteretic remanent magnetization (ARM) or susceptibility of ARM (χ_{ARM}). χ_{SSD} can be regarded as independent of grain sizes. However, χ_{ARM} values are associated with SSD grain sizes (King *et al.*, 1982; Maher, 1988). Therefore, when χ_{ARM} is dominated by the SSD grain concentration, rather than the grain size distribution, χ_{ARM} is expected to linearly relate to χ_{SSD}. Dearing *et al.*'s (1997) study on representative Welsh soil samples suggests that where soils have reasonably constant proportions of grains in the SP and SSD size ranges, χ_{ARM} may be used to estimate the concentration of fine (SSD) ferrimagnetic grains. Third, weak field (e.g., 20mT) isothermal remanent magnetization (IRM) or low reverse field (e.g., –20mT) demagnetization of saturation isothermal remanent magnetization (SIRM) can be used to identify the presence of soft components (mainly PSD + MD grains). Thompson's (1986) calculations suggest that (SIRM - IRM_{-20mT}) is expected to be approximately proportional to the PSD + MD grain content of ferrimagnetic components in a sample, although it may also be affected by fine viscous grains at the SSD / SP border. Finally, high reverse field (e.g. –300mT) demagnetization of SIRM may represent the contributions of canted antiferromagnets. Oldfield & Richardson (1990) suggested that HIRM can be used as a rough guide to the canted antiferromagnetic components, e.g. haematite, in a sample. As long as these magnetic parameters are related to the relevant components linearly and essentially independently, they can be used to determine partial susceptibilities by the multiple linear regression methods (von Dobeneck, 1998; Frederichs *et al.*, 1999).

4.3 Case study

Liverpool street dust bulk samples from the first sampling period are used as a case study of the partial susceptibility approach. The sampling program and the magnetic measurements are described in Chapter 2. Chapter 3 shows that the dominant magnetic minerals are ferrimagnetic, in which the proportions of SP, SSD, and PSD + MD grains are estimated as ~ 10, ~ 0, and ~ 90 %, respectively. In this case study, the units of χ_{ARM}, SOFT, and IRM_{20mT} are 10^{-5} m^3 kg^{-1}, 10^{-7} A m^2 kg^{-1}, and 10^{-7} A m^2 kg^{-1}, respectively, in order to obtain similar orders of magnitude for regression coefficients in the regression equations.

Two variable selection procedures (the simultaneous method and the stepwise method) were applied to generate regression equations in the case study. In the simultaneous method, all the available independent variables are included in the regression model. On the other hand, in the stepwise method, probably the most commonly used procedure, the variables are entered or removed from the model depending on the significance (probability) of the F values (0.05 for entry and 0.10 for removal in this study).

Modelling of ferrimagnetic susceptibility χ_{ferri}

Since the sum of the partial susceptibilities of paramagnetic, diamagnetic, and antiferromagnetic components ($\chi_{\mathrm{PARA}} + \chi_{\mathrm{DIA}} + \chi_{\mathrm{ANTIFERRO}}$) is estimated by χ_{HIGH}, from eq. (4.1), therefore, $\chi_{\mathrm{FERRI}} = \chi_{\mathrm{TOTAL}} - \chi_{\mathrm{HIGH}}$, or $\chi_{\mathrm{FERRI}} = \chi_{\mathrm{LF}} - \chi_{\mathrm{HIGH}}$. χ_{SP}, χ_{SSD}, and χ_{MD} can be determined by means of the multiple linear regression using χ_{FD}, χ_{ARM}, and SOFT [= (SIRM - $\mathrm{IRM}_{-20\mathrm{mT}}$) / 2] or $\mathrm{IRM}_{20\mathrm{mT}}$. Therefore, the multiple linear regression equations to calculate χ_{FERRI} can be written as

$$\chi_{\mathrm{FERRI\,(cal)}} = \alpha_1 \chi_{\mathrm{FD}} + \alpha_2 \chi_{\mathrm{ARM}} + \alpha_3\,\mathrm{SOFT} \qquad (4.2)$$

$$\chi_{\mathrm{FERRI\,(cal)}} = \alpha_1 \chi_{\mathrm{FD}} + \alpha_2 \chi_{\mathrm{ARM}} + \alpha_3\,\mathrm{IRM}_{20\mathrm{mT}} \qquad (4.3)$$

Where α_1, α_2, and α_3 are the partial regression coefficients.

Using the simultaneous method, the regression result of eq. (4.2) is

$$\chi_{FERRI\,(cal)} = 11.023\,\chi_{FD} + 36.061\,\chi_{ARM} + 13.355\,SOFT \qquad (4.4)$$

The multiple linear regression correlation coefficient R^2 is 0.988, close to unity, and the difference between $\chi_{FERRI\,(obs)}$ and $\chi_{FERRI\,(cal)}$ is 2.3 % on average (Table 4.1), indicating a high degree of agreement between observations and calculations. A test of the regression results is made by comparison between the partial susceptibility contributions from modelling and those from another approach. In eq. (4.4), the calculated χ_{SP}, χ_{SSD}, and χ_{MD} contribute 18.8, 7.1, and 74.1 % to $\chi_{FERRI\,(cal)}$ on average. Considering the grain size dependence of magnetic susceptibility, which shows higher values for SP grains than those for SSD or PSD + MD grains (Maher 1988), the regressed partial susceptibility results are consistent with those of the mixing model (SP, SSD, and PSD + MD grain proportions ~10, ~0, and ~90 %).

Using the stepwise method, from eq. (4.2), eq. (4.5) is obtained:

$$\chi_{FERRI\,(cal)} = 12.887\,\chi_{FD} + 14.047\,SOFT \qquad (4.5)$$

As shown in Table 4.1, eq. (4.5) also gives a good estimate of $\chi_{FERRI\,(obs)}$ and the contributions of SP, SSD, and PSD + MD grains. Examination of the partial regression coefficients in eq. (4.4) shows that α_1 and α_3 are significant at the 0.01 level, but α_2 is not significant at the 0.05 level, suggesting that χ_{ARM} does not contribute reliably to the regression equation. This is confirmed by the stepwise method resulting in eq. (4.5) which does not include χ_{ARM}. Therefore, eq. (4.5) is more appropriate for application than eq. (4.4).

Table 4.1 The modelling results of the partial susceptibilities of Liverpool street dust bulk samples.

Eq.[a]	Multiple R^2	Mean difference (%)	SP proportion (%)[b]	SSD proportion (%)[b]	PSD + MD proportion (%)[b]
(4.4)	0.988[c]	2.3[c]	18.8	7.1	74.1
(4.5)	0.988[c]	2.2[c]	22.0	0.0	78.0
(4.6)	0.984[c]	3.3[c]	26.6	0.0	73.4
(4.9)	0.929[d]	0.5[d]	19.7	9.5	70.8
(4.10)	0.928[d]	0.6[d]	23.7	0.0	76.3
(4.11)	0.904[d]	1.1[d]	28.3	0.0	71.7

[a] Eq. (4.4): modelling χ_{FERRI} by using SOFT and the simultaneous method, eq. (4.5): modelling χ_{FERRI} by using SOFT and the stepwise method, eq. (4.6): modelling χ_{FERRI} by using IRM_{20mt} and the stepwise method, eq. (4.9): modelling χ_{TOTAL} by using the simultaneous method (only including three independent variables: χ_{FD}, χ_{ARM}, and SOFT), eq. (4.10): modelling χ_{TOTAL} by using SOFT and the stepwise method, eq. (4.11): modelling χ_{TOTAL} by using IRM_{20mt} and the stepwise method (only including the first two independent variables entered).

[b] SP, SSD, and PSD + MD proportions: proportions of ferrimagnetic components.

[c] Between $\chi_{FERRI\,(obs)}$ ($= \chi_{LF} - \chi_{HIGH}$) and $\chi_{FERRI\,(cal)}$, difference: $(\chi_{FERRI\,(cal)} - \chi_{FERRI\,(obs)}) / \chi_{FERRI\,(obs)}$.

[d] Between $\chi_{TOTAL(obs)}$ ($= \chi_{LF}$) and $\chi_{TOTAL(cal)}$, difference: $(\chi_{TOTAL\,(cal)} - \chi_{TOTAL\,(obs)}) / \chi_{TOTAL\,(obs)}$.

For eq. (4.3), using the simultaneous method, an erroneously negative α_2 value is obtained, because the relationship between χ_{SSD} and χ_{ARM} is positive. Alternatively, using the stepwise method, eq. (4.6) is obtained:

$$\chi_{FERRI\,(cal)} = 15.486\,\chi_{FD} + 30.765\,IRM_{20mT} \qquad (4.6)$$

The modelling results of eq. (4.6) are similar to those of eq. (4.5) (see Table 4.1). As discussed above, IRM_{20mT} can be used for the same purpose as SOFT on the basis that they both represent soft components in a sample. Fig. 4.2 shows a good linear correlation between SOFT and IRM_{20mT} in our data set. In practice, reverse field remanence can be precisely remeasured and confirmed much more easily.

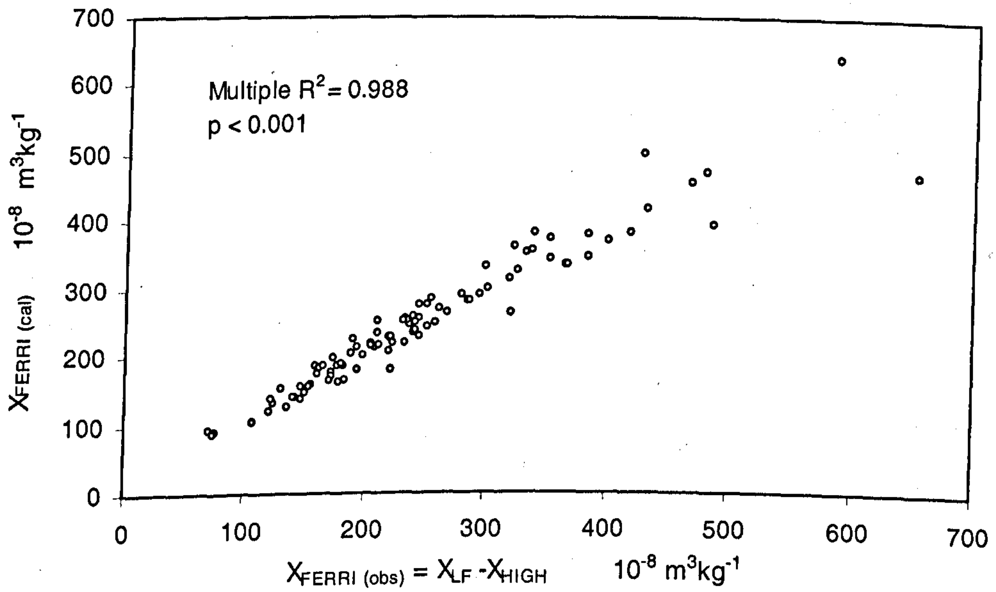

Fig.4.1 Comparison between $\chi_{FERRI\,(obs)}$ (= χ_{LF} - χ_{HIGH}) and $\chi_{FERRI\,(cal)}$ from eq. (4.5), showing a good estimate of $\chi_{FERRI\,(obs)}$.

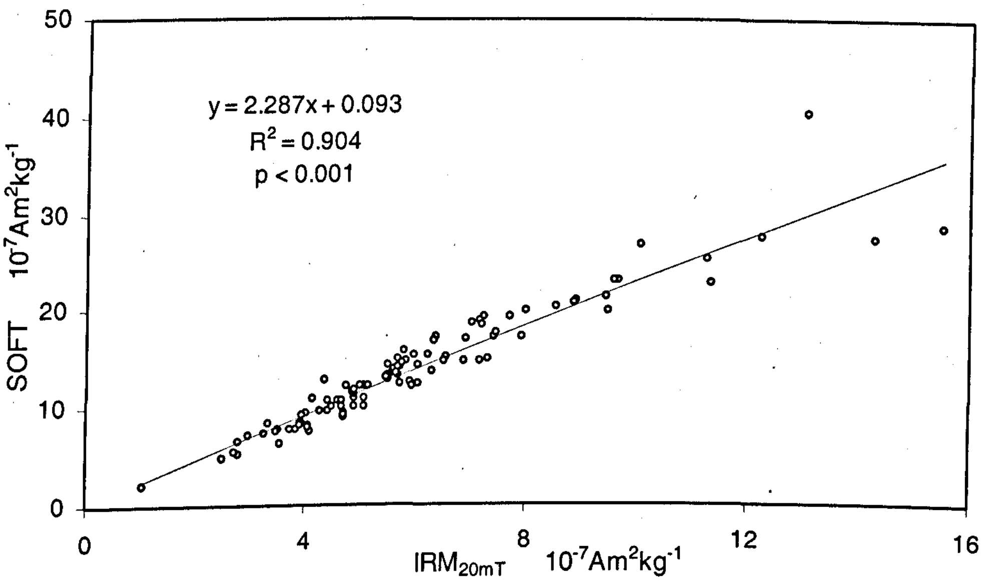

Fig.4.2 Relationship between SOFT and IRM_{20mT} measurements of Liverpool street dust bulk samples, showing a good linear correlation between SOFT and IRM_{20mT}.

Modelling of total susceptibility χ_{total}

Using HIRM as a proxy for the concentration of canted antiferromagnetic components, from eq.(4.1) - (4.3), the regression equations for modelling χ_{TOTAL} can be expressed as

$$\chi_{TOTAL\,(cal)} = \alpha_0 + \alpha_1\,\chi_{FD} + \alpha_2\,\chi_{ARM} + \alpha_3\,SOFT + \alpha_4\,HIRM \quad (4.7)$$

$$\chi_{TOTAL\,(cal)} = \alpha_0 + \alpha_1\,\chi_{FD} + \alpha_2\,\chi_{ARM} + \alpha_3\,IRM_{20mT} + \alpha_4\,HIRM \quad (4.8)$$

Where α_0, α_1, α_2, α_3, and α_4 are the partial regression coefficients.

For eq. (4.7), using the simultaneous method, an erroneously negative α_4 value is obtained, because the relationship between $\chi_{\mathrm{ANTIFERRO}}$ and HIRM is positive. Eliminating the HIRM term, using the simultaneous method, eq. (4.9) is obtained:

$$\chi_{\mathrm{TOTAL\ (cal)}} = -12.284 + 12.373\,\chi_{\mathrm{FD}} + 50.955\,\chi_{\mathrm{ARM}} + 13.675\ \mathrm{SOFT} \qquad (4.9)$$

R^2 is 0.929, and the difference between χ_{LF} and $\chi_{\mathrm{TOTAL\ (cal)}}$ is 0.5 % on average (Table 4.1), indicating a high degree of agreement between χ_{LF} and $\chi_{\mathrm{TOTAL\ (cal)}}$. The estimated χ_{SP}, χ_{SSD}, and χ_{MD} contribute 19.7, 9.5, and 70.8 % to $\chi_{\mathrm{FERRI\ (cal)}}$, consistent with the results of the mixing model (SP, SSD, and PSD + MD grain proportions ~10, ~0, and ~90%). R^2 between $\chi_{\mathrm{FERRI\ (obs)}}$ and $\chi_{\mathrm{FERRI\ (cal)}}$ is 0.842, and the difference between $\chi_{\mathrm{FERRI\ (obs)}}$ and $\chi_{\mathrm{FERRI\ (cal)}}$ is 8.5 %, on average. The constant term, which may reflect magnetic measurement uncertainties, contributions of $\chi_{\mathrm{ANTIFERRO}}$, χ_{PARA}, and χ_{DIA}, and deviations from the linear proportional relationships between χ_{SP} and χ_{FD}, χ_{SSD} and χ_{ARM}, and χ_{MD} and SOFT, is unlikely to represent the contributions of any major magnetic components.

Using the stepwise method, the regression result of eq. (4.7) is

$$\chi_{\mathrm{TOTAL\ (cal)}} = -10.076 + 14.719\,\chi_{\mathrm{FD}} + 14.600\ \mathrm{SOFT} \qquad (4.10)$$

Comparison between $\chi_{\mathrm{TOTAL\ (obs)}}$ (= χ_{LF}) and $\chi_{\mathrm{TOTAL\ (cal)}}$ is shown in Fig. 4.3. The modelling results of eq. (4.10) are similar to those of eq. (4.9) (see Table 4.1). Similar to that between eq. (4.4) and eq. (4.5), comparison between eq. (4.9) and eq. (4.10) suggests that eq. (4.10) is more suitable for application than eq. (4.9) since α_2 in eq. (4.9) is not significant at the 0.05 level.

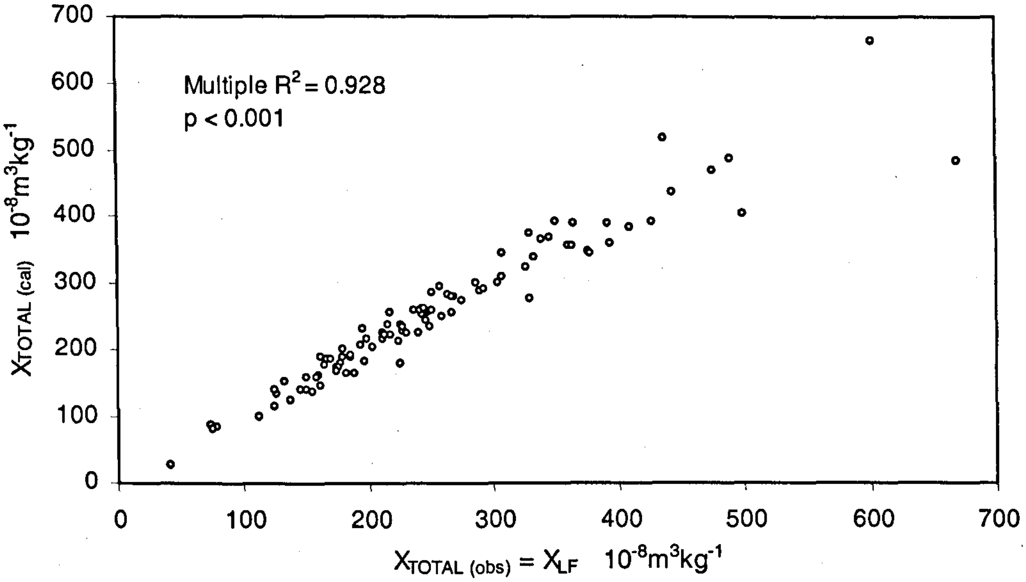

Fig.4.3 Comparison between $\chi_{TOTAL(obs)}$ (= χ_{LF}) and $\chi_{TOTAL(cal)}$ from eq. (4.10), showing a good estimate of $\chi_{TOTAL\ (obs)}$.

For eq. (4.8), the simultaneous method is also unsuccessful due to negative α_2 and α_4 values. When the stepwise method is applied and three independent variables (χ_{FD}, IRM_{20mT}, and HIRM) are included in the model, the α_4 value is again negative. However, if the regression model only includes the first two independent variables entered, eq. (4.11) is obtained:

$$\chi_{TOTAL\ (cal)} = -21.442 + 18.597\ \chi_{FD} + 32.836\ IRM_{20mT} \qquad (4.11)$$

Table 4.1 shows that the modelling results of eq. (4.11) are similar to those of eq. (4.10), suggesting the success of eq. (4.11). However, eq. (4.11) has a higher negative value of the constant term than eq. (4.10). As a result, for eq. (4.11), the mean difference between $\chi_{FERRI\ (obs)}$ and $\chi_{FERRI\ (cal)}$ (23.4 %) is higher than that of eq. (4.10) (18.3 %). Comparison between eq. (4.10) and eq. (4.11), the former using SOFT and the latter IRM_{20mT}, to estimate the content of PSD + MD grains, suggests that the partial susceptibility approach may be sensitive to some magnetic parameters, such as SOFT and IRM_{20mT}. The regression process of eq. (4.8), using the stepwise method, shows that an inadequate model will cause the failure of the partial susceptibility approach.

Discussion and conclusions

The partial susceptibility approach assumes linear positive proportional relationships between χ_{SP} and χ_{FD}, χ_{SSD} and χ_{ARM}, χ_{MD} and SOFT or IRM_{20mT}, and $\chi_{ANTIFERRO}$ and HIRM. As discussed above, there is evidence to support these assumptions. However, in some situations, some assumptions do not hold. Dearing *et al.* (1997) suggested that zero χ_{FD} value does not result in zero content of SP grains in the Welsh soil samples, indicating the non-proportional relationship between χ_{SP} and χ_{FD}. Recently, Worm & Jackson (1999) also showed that χ_{FD} percentage = 0 must not be taken to imply the absence of superparamagnetic grains. In the Liverpool street dust data set, the relationship between SOFT and IRM_{20mT} is not proportional (see Fig. 4.2), suggesting that the relationship either between χ_{MD} and SOFT or between χ_{MD} and IRM_{20mT} is non-proportional. In addition to the contribution of PSD + MD grains, SOFT and IRM_{20mT}

also include the contribution of fine viscous grains at the SSD / SP border which may not be significant in our samples due to small concentrations of SP grains. HIRM, defined as (SIRM - IRM_{-300mT}) / 2, could exclude the contribution of some soft canted antiferromangetic components. Deviations from the assumptions of linear proportionality will lead to increased uncertainties in the regression results. Contributions of more than one ferrimagnetic mineral and effects of grain interactions in the samples may also cause violations of the assumptions of linear proportionality.

The case study results are summarised in Table 4.1. They demonstrated the success of the partial susceptibility approach in modelling the contributions of main magnetic components. The case study shows that several factors may have a significant impact on the regression results. First, different variable selection procedures, e.g. the simultaneous method and the stepwise method, may generate considerably different regression equations. Second, an adequate regression model is important to obtain a reasonable regression result. Finally, the technique may be sensitive to some magnetic parameters, such as SOFT and IRM_{20mT}. It is unlikely that the constant term in the regression equation represents the contributions of any discrete magnetic components. As a consequence, in some circumstances, the regression equations fail to model the contributions of the partial susceptibilities. Two points are essential in the application of the partial susceptibility technique. First, different regression models and methods (e.g., the simultaneous method and the stepwise method) should be tested for selecting suitable variables and developing regression equations. Second, the technique is successful only if the modelling results give a reasonable estimate of the contributions of the partial susceptibilities, which can be assessed by comparison with those of other approaches. In this study, the semi-quantitative mixing model (Dearing *et al.*, 1997) was used. Other possible alternatives for future validation include transmission electron microscopic (TEM) studies of magnetic extracts and studies of synthetic samples.

The advantage of the technique is that complex magnetic data are reduced to magnetic susceptibilities, which can then be compared quantitatively against each other in the percentage or ratio form. In other words, based on routine magnetic measurement data, this technique provides an approach to presenting magnetic mineralogy, grain size, and concentration in terms of partial magnetic susceptibilities.

4.4 Summary

The partial susceptibility approach expresses the magnetic properties of environmental materials in terms of contributions of the magnetic susceptibilities of specific magnetic components and links the partial susceptibilities of discrete particles, domains or mineral fractions with the concentration dependent parameters by means of multiple linear regression methods. The case study, using the Liverpool street dust data set, demonstrates that the technique is able to model the contributions of main magnetic components satisfactorily. Several factors may have a significant impact on the regression results. They include the validity of the linear proportional relationships between partial susceptibilities and the relevant concentration dependent parameters, the adequacy of the variable selection procedure and the regression model, and the suitability of certain magnetic parameters.

Chapter 5. Spatial and temporal variations of magnetic properties, element concentrations, and the organic matter content of Liverpool street dust

5.1 Introduction

Recent developments in magnetic pollution studies showed that spatial and temporal analysis of magnetic properties may provide a useful tool for investigating sources of magnetic material in roadside soil (Hoffmann *et al.*, 1999), dust deposition (Matzka & Maher, 1999; Flanders, 1999), and total suspended particulates (Shu *et al.*, 2000). Although there is growing interest in using magnetic methods in sediment tracing in the urban environment (e.g. Beckwith *et al.*, 1990; Flanders, 1999), spatial and temporal variations of magnetic properties in street dust have been little reported in the literature although potentially they have significant impact on source tracing results (Lees, 1997; Charlesworth and Lees, 1997). Some researchers (e.g. De Miguel *et al.*, 1997; Chon *et al.*, 1998) have examined spatial and temporal variations in street dust and found different variations between elements. Few researchers, however, have studied spatial and temporal variations of the organic matter content in street dust (Yang and Baumann, 1995).

This chapter investigates spatial and temporal variations of magnetic properties, element concentrations, and the organic matter content of Liverpool street dust. The results represent a step toward a better understanding of spatial and temporal variations of street dust measurements and provide useful information for future environmental monitoring and assessment of street dust, particularly magnetic studies of sediment tracing in the urban environment.

In this chapter, only the finest size fraction (<63 μm) was used for the study of spatial and temporal variations since fine dust particles cause more environmental concerns than coarse particles. Chapter 2 illustrates the sampling program and measurement methods of magnetic properties, total concentrations of 11 elements (Si, Ti, Ca, K, Fe, S, Pb, Rb, Sr, Zn, and Zr), and the organic matter content (ignition at 375 °C for 4 h). For discussions of magnetic properties of Liverpool street dust, see Chapter 3.

Measurement results are presented in Tables 5.1 and 5.2. The χ_{LF} values are similar to those obtained by Beckwith *et al.* (1990) and Charlesworth and Lees (1997). The measurements of Si, Ti, Ca, K, Fe, Pb, and Zn concentrations fall within the ranges of medians in other studies (Fergusson and Kim, 1991), but Rb and Zr concentrations are higher and Sr lower. Hildemann *et al.* (1991) reported 5.6 mg g^{-1} of S concentration in their fine road dust samples. In general, the results of element levels are consistent with those of previous studies. The results of the organic matter content also fall within the ranges of other studies (see Chapter 6).

The coefficient of variation (C.V.) [= standard deviation (S.D.) / mean] was used to analyse spatial variations. The C.V. value allows comparisons between magnetic properties, element concentrations, and the organic matter content as it is independent of unit. The statistical procedure t-test and one-way analysis of variance (ANOVA) (the Tukey HSD test) were applied to test differences of mean measurement values for significance in the analysis of spatial and temporal variations.

Table 5.1 Measurements of magnetic parameters, element concentrations, and the organic matter content (dataset AA: 97 site samples in January -February 1998).

Measurement	Range	Mean	S.D.	C.V.
χ_{LF} (10^{-8} $m^3 kg^{-1}$)	168.9 - 1166.3	502.8	149.8	0.30
χ_{FD} (10^{-8} $m^3 kg^{-1}$)	0.4 - 19.3	6.1	2.7	0.44
χ_{FD} percentage	0.1 - 2.3	1.2	0.4	0.33
χ_{ARM} (10^{-8} $m^3 kg^{-1}$)	329.9 - 1751.7	963.3	225.4	0.23
SIRM (10^{-5} $Am^2 kg^{-1}$)	1883.7 - 15284.9	6069.6	1976.1	0.33
χ_{ARM}/SIRM (10^{-3} $m A^{-1}$)	0.10 - 0.20	0.16	0.02	0.13
SOFT (10^{-5} $Am^2 kg^{-1}$)	664.1 - 4693.9	2050.6	682.0	0.33
SOFT percentage	30.0 - 39.5	33.7[a]	1.8	0.05
HIRM (10^{-5} $Am^2 kg^{-1}$)	26.6 - 289.4	100.3	38.2	0.38
HARD percentage	0.9 - 4.3	1.7	0.6	0.35
Si (mg g^{-1})	109.8 - 251.5	167.5	19.7	0.12
Ti (mg g^{-1})	2.84 - 7.09	3.80	0.62	0.16
Ca (mg g^{-1})	23.7 - 136.9	77.5	17.5	0.23
K (mg g^{-1})	7.0 - 15.6	10.6	1.8	0.17
Fe (mg g^{-1})	21.7 - 98.5	44.2	9.6	0.22
S (mg g^{-1})	1.6 - 13.3	5.2	2.0	0.38
Pb (μg g^{-1})	254 - 4187	892	536	0.60
Rb (μg g^{-1})	15 - 176	70	25	0.36
Sr (μg g^{-1})	138 - 465	192	41	0.21
Zn (μg g^{-1})	337 - 4733	1469	602	0.41
Zr (μg g^{-1})	171 - 583	302	83	0.27
Organic matter (%)	4.1 - 19.9	11.7	3.4	0.29

[a] The difference between the mean value of 97 site samples (dataset AA) and that of 19 revisited site samples (dataset A) (Table 5.2) is significant at the 0.01 level.

Table 5.2 Mean values of magnetic parameters, element concentrations, and the organic matter content for 19 revisited site samples.

Dataset [a]	A (Jan-Feb)	B (May)	C (Aug)	D (Nov)	E
χ_{LF} (10^{-8} m^3 kg^{-1})	529.2	691.6	800.2 [b]	587.0	652.0
χ_{FD} (10^{-8} m^3 kg^{-1})	7.4 [c]	12.3	13.0	11.6	11.1
χ_{FD} percentage	1.4 [b]	1.8	1.6	2.0 [b]	1.7
χ_{ARM} (10^{-8} m^3 kg^{-1})	978.7	1015.5	1101.5	944.8	1010.1
SIRM (10^{-5} Am^2 kg^{-1})	6332.7	7384.0	8357.6	6717.8	7198.0
χ_{ARM}/SIRM (10^{-3} m A^{-1})	0.16 [c]	0.14	0.13	0.15	0.15
SOFT (10^{-5} Am^2 kg^{-1})	2057.5	2488.5	2923.9	2321.7	2447.9
SOFT percentage	32.6 [c]	33.8	35.1	34.5	34.0
HIRM (10^{-5} Am^2 kg^{-1})	100.4	114.6	128.4	110.2	113.4
HARD percentage	1.7	1.6	1.6	1.7	1.6
Si (mg g^{-1})	166.3 [c]	200.6	204.9	193.4	191.3
Ti (mg g^{-1})	3.71	3.76	3.88	3.75	3.77
Ca (mg g^{-1})	78.2	85.8	91.4	92.0	86.8
K (mg g^{-1})	11.1 [c]	15.0	15.8 [b]	15.0	14.2
Fe (mg g^{-1})	43.2	44.1	48.2	43.6	44.8
S (mg g^{-1})	5.6	4.3	3.9	6.7	5.1
Pb (μg g^{-1})	957	1013	993	978	985.3
Rb (μg g^{-1})	71	80	80	79	77.3
Sr (μg g^{-1})	189	197	203.4	203	198.3
Zn (μg g^{-1})	1476	1529	1648	1473	1531
Zr (μg g^{-1})	323	444	502 [b]	353	406
Organic matter (%)	12.1	13.0	11.7	10.0	11.7

[a] Datasets A, B, C, and D: 19 revisited site samples in January- February, May, August, and November 1998, respectively; dataset E: all 76 samples from datasets A, B, C, and D.

[b] The difference between the mean of dataset A, B, C, or D and that of dataset E is significant at the 0.05 level.

[c] The difference between the mean of dataset A, B, C, or D and that of dataset E is significant at the 0.01 level.

5.2 Spatial variations

Charlesworth and Lees (1997) reported C.V. values of 0.49 and 0.18 for χ_{FD} and χ_{ARM} in their < 63 μm samples, which are similar to the results in Table 5.1. Among the magnetic parameters, χ_{FD} and HIRM demonstrate the highest C.V. values. For element concentrations, C.V. values range from 0.12 to 0.60. Pollution elements Pb and Zn show the highest C.V. values, 0.60 and 0.41, respectively. However, soil derived element Si demonstrates the lowest C.V. value of 0.12. This appears consistent with previous studies that concentration variations of elements originating primarily from soil are less than those of pollution-type elements (Fergusson, 1987; Vermette *et al.*, 1991). The organic matter content shows a C.V. value of 0.29.

Comparison between mean values of the first period 97 site samples (dataset AA) and those of 19 revisited site samples (dataset A) (t-test) shows that, except for SOFT percentage, the differences are not significant at the 0.05 level (Table 5.1). Therefore, the results suggest that a relatively small number of samples may be used to obtain representative mean values of magnetic parameters (except SOFT percentage), element concentrations, and the organic matter content for a large region. Duggan's (1984) study on Pb level variations in London street dust shows that a representative mean Pb concentration for a large area can be obtained by taking a comparatively small number of samples, which is supported by this study. Although the difference between the mean SOFT percentage value of dataset AA (33.7 %) and that of dataset A (32.6 %) is significant at the 0.01 level, both values suggest the dominance of ferrimagnetic minerals.

Table 5.3 Comparison between major and minor roads (dataset AA: 97 site samples in January - February 1998, mean ± standard deviation)[a].

Measurement	Major road	Minor road
χ_{LF} (10^{-8} m^3 kg^{-1})	512.3 ± 151.0	477.0 ± 146.5
χ_{FD} (10^{-8} m^3 kg^{-1})	6.3 ± 2.6	5.3 ± 2.9
χ_{FD} percentage	1.3 ± 0.4	1.1 ± 0.5
χ_{ARM} (10^{-8} m^3 kg^{-1})	970.3 ± 205.1	944.0 ± 277.1
SIRM (10^{-5} Am^2 kg^{-1})	6118.6 ± 1986.4	5935.8 ± 1980.6
χ_{ARM}/SIRM (10^{-3} m A^{-1})	0.16 ± 0.02	0.16 ± 0.02
SOFT (10^{-5} Am^2 kg^{-1})	2045.9 ± 682.4	2063.5 ± 694.1
SOFT percentage	33.4 ± 1.6	34.8 ± 1.9
HIRM (10^{-5} Am^2 kg^{-1})	103.3 ± 40.2	92.4 ± 31.6
HARD percentage	1.7 ± 0.6	1.6 ± 0.6
Si (mg g^{-1})	165.1 ± 16.9	174.2 ± 25.1
Ti (mg g^{-1})	3.76 ± 0.62	3.91 ± 0.64
Ca (mg g^{-1})	79.3 ± 15.5	72.7 ± 21.8
K (mg g^{-1})	10.7 ± 1.7	10.6 ± 2.2
Fe (mg g^{-1})	43.5 ± 7.4	46.2 ± 14.0
S (mg g^{-1})	5.4 ± 2.2	4.8 ± 1.4
Pb (μg g^{-1})	838 ± 527	1040 ± 541
Rb (μg g^{-1})	69 ± 24	73 ± 27
Sr (μg g^{-1})	190 ± 29	199 ± 64
Zn (μg g^{-1})	1481 ± 621	1437 ± 555
Zr (μg g^{-1})	297 ± 62	317 ± 123
organic matter (%)	11.7 ± 3.3	11.7 ± 3.9

[a] The difference between major road and minor road is significant at the 0.01 level for SOFT percentage, but not significant at the 0.05 level for other measurements (the 2-tailed t – test).

The dust samples were subdivided into two groups according to the type of locality (major streets with heavy or moderate traffic, 71 samples, and minor streets with light traffic, 26 samples). The mean values and standard deviations of magnetic parameters, element concentrations, and the organic matter content are listed in Table 5.3 for major and minor streets. The 2-tailed t-test shows that the difference between the mean value from major road sites and that from minor road sites is significant at the 0.01 level for SOFT percentage, but not significant at the 0.05 level for other magnetic parameters, element concentrations, and the organic matter content. This suggests insufficient evidence of the significant contribution of the traffic-related sources for magnetic properties (except SOFT percentage), element concentrations, and the organic matter content.

The spatial distribution of magnetic parameters, element concentrations, and the organic matter content was examined by using the software package SURFER. Table 5.1 suggests that the difference between mean values of 97 site samples and those of 19 revisited site samples is not significant, except for SOFT percentage. However, all the measurements show some degree of spatial variability, with high and low value areas in the sampling region, possibly reflecting their localised sources. The spatial distribution of χ_{LF}, Pb, and the organic matter content will be discussed in detail. The areas around James Street railway station, and between Lime Street railway station and Scotland Road show high χ_{LF} values, whilst there are some low value areas in the city centre (Fig. 5.1). Pb shows a similar distribution to χ_{LF} with high values in the above two high χ_{LF} areas (Fig. 5.2). Table 8.1 shows that there is a highly significant correlation between χ_{LF} and Pb. The organic matter content shows a different distribution from χ_{LF} and Pb. The area around James Street railway station, with high values of χ_{LF} and Pb, shows low values of the organic matter content (Fig. 5.3). Correlation analysis shows that the correlation between the organic matter content and χ_{LF} or Pb is not significant at the 0.05 level. Therefore, spatial analysis illustrates high value, as well as low value, areas for measurements. Combined with correlation analysis, similar spatial distributions of some measurements may provide useful information about their sources.

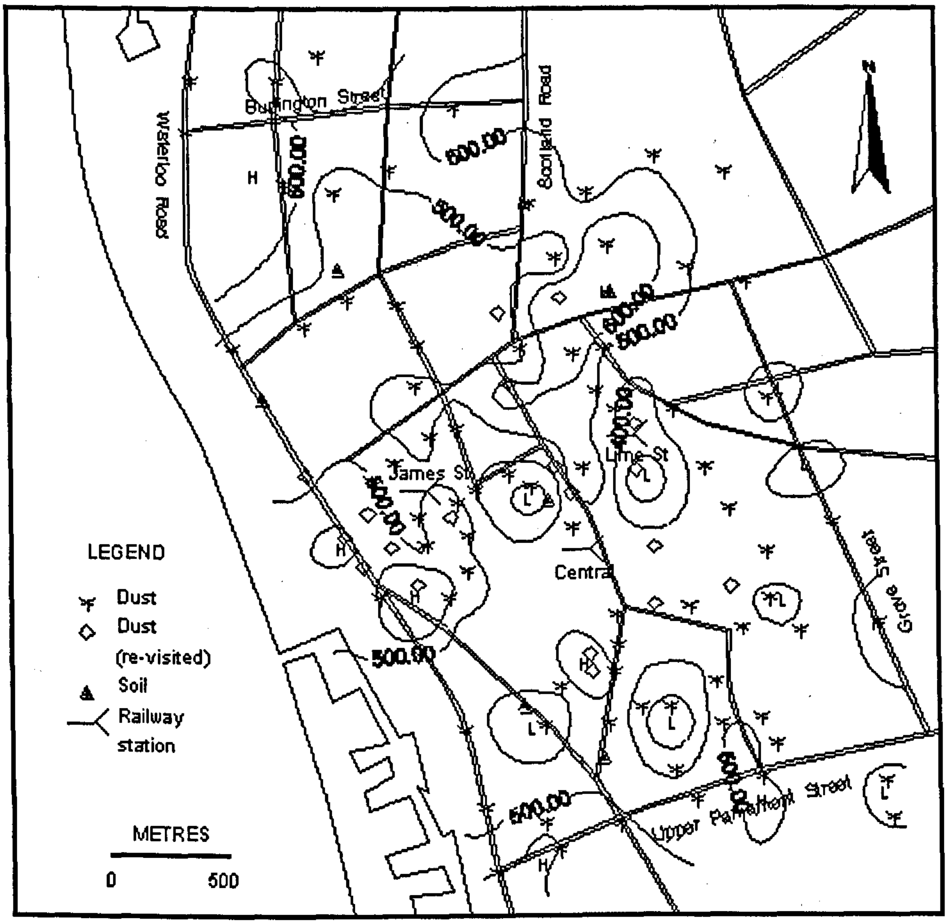

Fig. 5.1 χ_{LF} spatial distribution of Liverpool street dust (<63 μm fraction) (dataset AA: 97 site samples in January -February 1998), unit: 10^{-8} m^3 kg^{-1}.

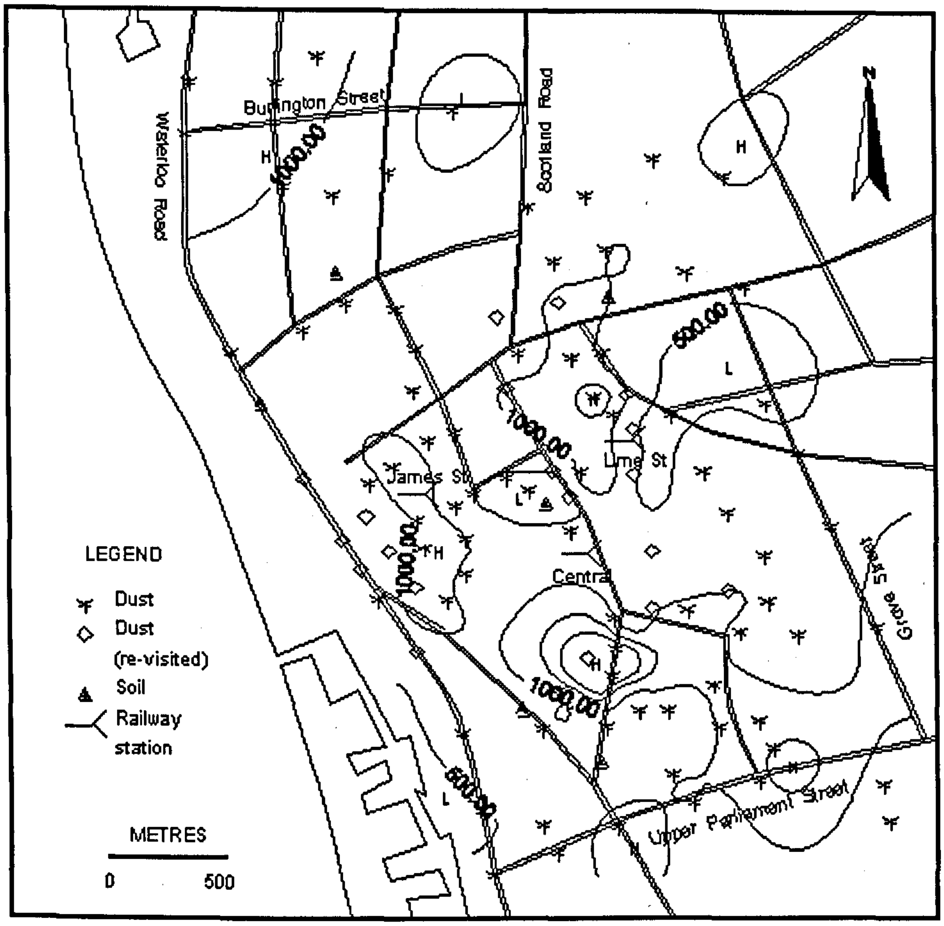

Fig. 5.2 Pb spatial distribution of Liverpool street dust (<63 μm fraction) (dataset AA: 97 site samples in January -February 1998), unit: $\mu g\ g^{-1}$.

5.3 Temporal variations

The ANOVA results show that the differences between mean values of dataset A, B, C, or D and those of dataset E are significant at the 0.05 or 0.01 level for χ_{LF}, χ_{FD}, χ_{FD} percentage, χ_{ARM}/SIRM, SOFT percentage, Si, K, and Zr (Table 5.2). Significant temporal variations of these magnetic parameters suggest that more than one sampling period is needed to obtain their representative mean values. Nevertheless, datasets A, B, C, D, and E (Table 5.2) suggest similar magnetic properties (see

Chapter 3). This implies that the mean values of several samples from a sampling period of one or several days may still provide reliable information about magnetic properties. Table 5.2 also shows insufficient evidence for significant differences between the mean values of dataset A, B, C, or D and those of dataset E for Ti, Ca, Fe, S, Pb, Rb, Sr, Zn, and the organic matter content. This suggests that the representative mean values of these element concentrations and the organic matter content may be also obtained with several samples from a sampling period of one or several days. Duggan (1984) suggested that representative mean Pb levels in street dust may be obtained by a sampling period of a relative short time, which is supported by this study.

5.4 Summary

There are several high and low value areas for magnetic parameters, element concentrations, and the organic matter content, maybe due to the localised sources. Some measurements, such as χ_{LF} and Pb, show a similar spatial distribution, whilst some measurements, such as χ_{LF} and the organic matter content, show different distribution patterns. Comparison between ninety-seven sampling sites and nineteen revisited sites suggests that representative magnetic properties, and mean values of some element concentrations and the organic matter content may be obtained with a small number of samples from a sampling period of one or several days. These results provide useful information for future environmental monitoring and assessment of street dust, particularly magnetic studies of sediment tracing in the urban environment.

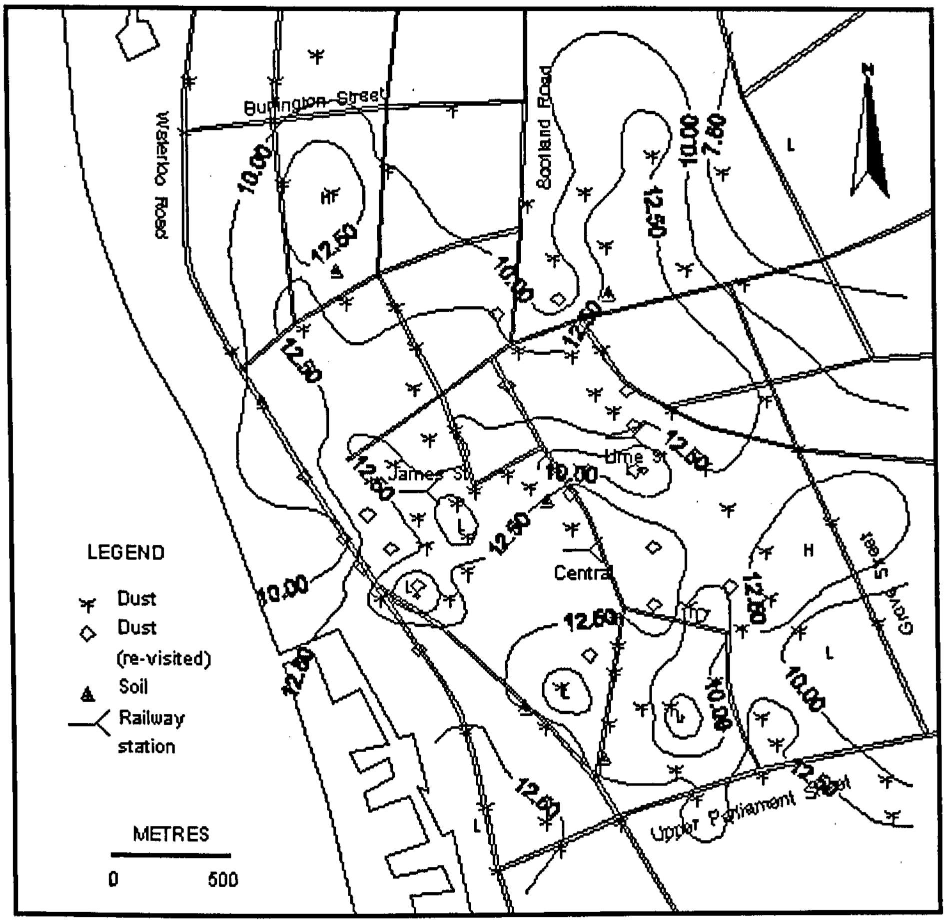

Fig. 5.3 The organic matter content spatial distribution of Liverpool street dust (<63 μ m fraction) (dataset AA: 97 site samples in January -February 1998), unit: % .

Chapter 6. Association between the organic matter content and magnetic properties of Liverpool street dust

6.1 Introduction

Many studies of street dust have focused on element concentrations and source identification (e.g., Fergusson and Kim, 1991; Fergusson, 1992; De Miguel *et al.*, 1997; Nageotte and Day, 1998). Few studies, however, have been carried out on the organic matter content of street dust. Moreover, little work has been reported in the literature about the particle size variation of the organic matter content, despite the fact that the size effect is an important factor in the study of street dust (Al-Rajhi *et al.*, 1996). Fergusson and Ryan (1984) estimated the organic matter content of street dust samples from two large urban areas (London, UK; and New York, USA) and three small cities (Halifax, Canada; Christchurch, New Zealand; and Kingston, Jamaica), ranging from 3.5 to 18.3 %, by means of loss-on-ignition (LOI) measurements. Hildemann *et al.* (1991) reported 11 % of the organic matter content in fine road dust particles (< 2μm) in Los Angeles area, USA, and Rogge *et al.* (1993) estimated that vehicle exhaust emissions and tyre dust contribute no more than 32.7 and 4.3 %, respectively, to the organic matter content of the road dust. Yang and Baumann (1995) analysed seasonal variations of polycyclic aromatic hydrocarbon (PAH) concentrations of street dust in some German cities, and suggested that street dust is contaminated by PAHs about 2-12 times more in winter than in summer. Al-Chalabi and Hawker (1996) also estimated the organic matter content (mean ± standard deviation: 4.1 % ± 0.3 %) in the street dust samples of

Brisbane, Australia. Toxic components of organic matter in the urban environment, such as PAHs, are a cause of environmental concern (National Research Council, 1983). Hildemann *et al.* (1991) estimated that fine particulate road dust is the third largest source of organic carbon to that of urban fine atmospheric particulate, following vehicle exhaust and meat cooking emissions, in Los Angeles area, USA. In addition, Glikson *et al.* (1995) suggested that the organic composition of dust may have important health implications for asthma sufferers. Therefore, organic material in street dust has significant environmental implications. However, in despite of the development in magnetic applications to pollution studies (see detailed discussions in Chapter 1), little work has been reported in the literature on association between the organic matter content and magnetic properties in urban street dust.

Associations between the organic matter content and magnetic properties in Liverpool street dust are investigated in this chapter. First, the organic matter content and its association with magnetic concentration dependent parameters in the first period bulk samples are examined. Then, size variations of the organic matter content and its associations with magnetic properties are analysed by using the first period samples. Last, associations between the organic matter content and magnetic properties are investigated for 19 revisited site samples (< 63 μm fraction) from four sampling periods. Some implications are also discussed. Laboratory tests show that the procedure of ignition at 375 °C for 4 or 16 h is suitable for estimating the organic matter content in Liverpool street dust (see Chapter 2). In this chapter, the procedure of ignition at 375 °C for 4 h is used to estimate the organic matter content of Liverpool street dust and surface soil bulk samples.

6.2 Analysis of the first period bulk samples

The dust organic matter level ranges from 0.5 to 9.4 % (average 3.9 %, standard deviation 1.7 %). The organic matter content of surface soil is between 2.2 and 7.1 % (average 4.9 %, standard deviation 1.7 %). It seems that the organic matter content of dust is lower than that of soil, but the comparison may be inconclusive because of the small number of soil samples. Fergusson and Ryan (1984) estimated the organic matter content of street dust samples from different city types, ranging from 3.5 to 18.3 %, by ignition at 500 °C for 16 h. Al-Chalabi and Hawker (1996) reported a mean organic matter content of 4.1 % in their samples (ignition at 500 °C for 12 h). Their results may overestimate the organic matter content due to the high ignition temperature (> 400 °C). Hildemann *et al.* (1991) showed a high level (17 %) of organics in their fine particulate road dust samples. In general, the present results fall within the ranges of previous studies.

The mean organic matter contents are also examined for major and minor streets (See Chapter 5), resulting 4.1 % (standard deviation 1.6 %) and 3.4 % (standard deviation 1.9 %) for major and minor streets, respectively. Similar to $< 63\,\mu\mathrm{m}$ fraction samples, the bulk samples do not show significant difference between the organic matter content for major streets and that for minor streets (at the 0.05 level, using the t-test). This also suggests insufficient evidence of the significant contribution of the organic matter of the bulk samples from the traffic-related sources. Qualitative observation of the street dust during the field work and under a microscope in the laboratory shows the presence of soil material, weathered building material, plant fragments, and urban refuse, which may be the major sources of dust organic material.

Magnetic measurements of dust bulk samples suggest that the dominant magnetic component comprises PSD + MD ferrimangetic grains, with SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals present in small magnetic concentrations (see Chapter 3). Table 6.1 shows that there are good correlations between the organic matter content and χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, or χ_{HIGH} and that there is insufficient evidence of correlation between the organic matter content and SOFT or HIRM. The linear regression for the organic matter content and frequency dependent susceptibility is shown in Fig. 6.1. Rogge *et al.* (1993) identified a variety of sources of organic materials in fine road dust particles, including vehicle exhaust, tyre wear, vegetative plant fragments, and garden soil. The minerogenic components of street dust derive from metallic fragments, concrete/cement, products of tyre wear, salt spray, de-icing salt, vehicle emissions, and soil which contributes more than half of dust material (Hopke *et al.*, 1980; Fergusson and Kim, 1991; Fergusson, 1992). Most of these street dust sources will contribute a suite of magnetic particles.

Studies so far suggest that the most common source of SP grains is surface soil (Dearing *et al.*, 1996b) and pollution ferrimagnetic minerals are mainly within the ranges of SSD and PSD + MD grains (Hunt *et al.*, 1984; Flanders, 1994; Hay *et al.*, 1997; Flanders, 1999). In their method of magnetic differentiation of atmospheric dusts, Oldfield *et al.* (1985) showed that χ_{FD} percentage is sensitive to the contribution of soil derived material. Although there is evidence of other SP grain sources, such as fly ash (Xie and Dearing, 1999), and urban sources may contribute to SP grains in Liverpool street dust (see Chapter 8), it is suggested that the close association between the organic matter content and χ_{FD} in Liverpool street dust may reflect the contributions of soil organic material to the organic matter content of street dust. Strong linear correlations between the organic matter content and some magnetic mineral concentration-related parameters, particularly frequency dependent susceptibility, may enable simple, rapid, and non-destructive magnetic measurements to be used as proxies of the organic matter content in street dust.

Table 6.1 Correlation coefficients between the organic matter content and magnetic concentration dependent parameters from the first period bulk samples.

Magnetic parameter	χ_{LF}	χ_{FD}	χ_{ARM}	SIRM	SOFT	HIRM	χ_{HIGH}
Correlation coefficient	0.298 [a]	0.651 [a]	0.378 [a]	0.264 [a]	0.186	0.102	0.402 [a]

[a] Correlation is significant at the 0.01 level.

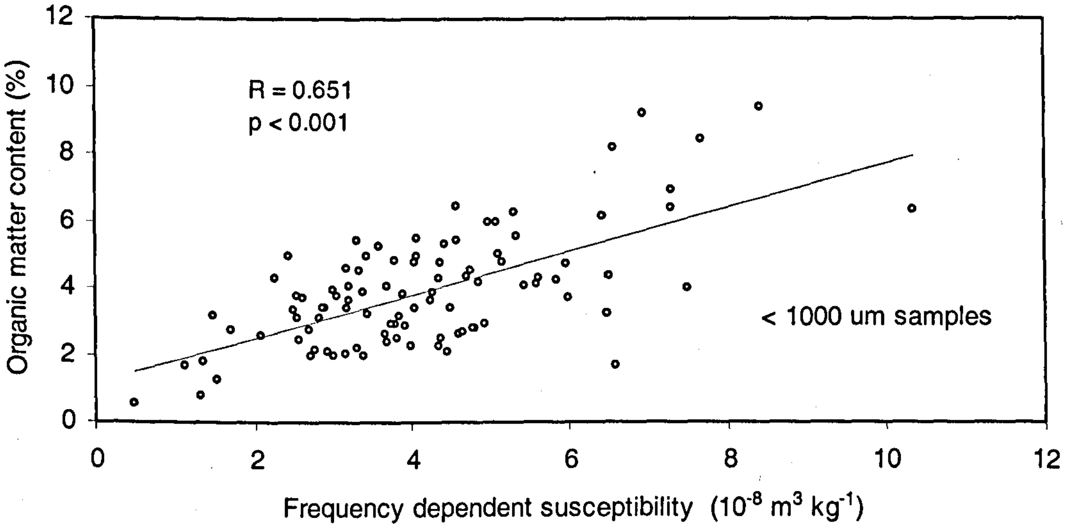

Fig. 6.1 Correlation between the organic matter content and frequency dependent susceptibility for <1000 μ m bulk samples from the first sampling period.

6.3 Analysis of the first period size fraction samples

Since fine dust particles cause more environmental concerns than coarse particles and the particle size effect is an important factor in the study of street dust, the previous section is extended to study the variation of the organic matter content with particle size and to examine the possible applications of magnetic measurements to source apportionment of organic matter in street dust. First, the organic matter content of size fractions from the first sampling period is analysed. Associations between the organic matter content and magnetic properties are investigated. Emphasis is placed on the organic matter content of fraction samples and its association with dust magnetic measurements, particularly ratio parameters.

The statistical procedure one-way analysis of variance (ANOVA) (the Tukey HSD test) was applied to test the mean differences of the organic matter content between size fractions for significance. Table 6.2 presents the measurement results of the organic matter content for five size fraction samples. For the purpose of comparison, the organic matter content of bulk samples is also presented in Table 6.2. The results fall within the ranges of previous studies (Fergusson and Ryan, 1984; Hildemann *et al.*, 1991; Al-Chalabi and Hawker, 1996). The organic matter content decreases with increasing particle sizes for fractions < 300 μm, significantly at the 0.01 level, but the differences of the organic matter content are not significant at the 0.05 level for fractions > 300 μm. It is, therefore, suggested that the investigation of organic matter in street dust should place emphasis on fine particles because the content is highly elevated in fine particles and fine particles cause more environmental concerns than coarse particles.

Table 6.2 Measurement results of the organic matter content of the first period size fraction samples (mean ± standard deviation).

Size fraction	< 63 μm	64 - 150 μm	151 - 300 μm	301- 500 μm	501- 1000 μm	< 1000 μm
Organic matter content (%)	11.7 ± 3.4	6.2 ± 2.7	2.2 ± 1.1	2.3 ± 1.4	3.2 ± 2.3	3.9 ± 1.7

The study of Liverpool street dust bulk samples suggests that soil is probably an important source of organic matter present in street dust (see Section 6.2). Rogge *et al.* (1993) identified a variety of sources of organic materials in fine road dust particles (< 2 μm), including vehicle exhaust, tyre wear, vegetative plant fragments, and garden soil. The organic matter content (%) of the six surface soil samples is (mean ± standard deviation) 11.7± 3.0, 6.5± 1.1, 3.2± 4.6, 3.3± 1.0, and 5.8± 2.8 for size fractions <63, 64-150, 151-300, 301-500, and 501-1000 μm, respectively. The difference of the soil organic matter content is significant at the 0.01 level for fractions < 150 μm, but not significant at the 0.05 level for fractions > 150 μm. This trend may be inconclusive because of the small number of soil samples. However, it provides evidence of size variations of the soil organic matter content. Vehicle exhaust consists mostly of fine particulate matter, with the majority of particles < 2.5 μm in diameter (Silva and Prather, 1997). In addition, fine particles of street dust and soil may have a higher specific surface area, and therefore a higher capacity for adsorbing vehicle-derived organic matter material. As a result, the contribution of organic matter from vehicle exhaust to fine street dust fractions may be higher than it is to coarse fractions. Using Pierson and Brachaczek's (1974) observations on size distributions of tyre wear particles in roadway gutters, it is estimated that the contributions of tyre wear particle mass are relatively 1.0, 1.16, 0.57, 0.66, 1.10 for fraction <63, 64-150, 151-300, 301-500, and 501-1000 μm, respectively, in Liverpool street dust. The values are relative to that of the <63 μm fraction which is assigned as 1.0. It is therefore suggested that the higher organic matter content in fine dust particles (< 300 μm) may be partly due to contributions from soil, vehicle exhaust, and tyre wear.

Magnetic measurements of dust bulk and size fraction samples suggest that the dominant magnetic component comprises PSD + MD ferrimagnetic grains, with SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals present in small magnetic concentrations (see Chapter 3). Table 6.3 shows that the correlation between the organic matter content and χ_{FD} is significant for 64 - 500 μm fractions at the 0.01 level, but not significant at the 0.05 level for other fractions. The 64 - 500 μm fractions make up 95.6 % of bulk sample mass, on average. As a result, bulk samples also demonstrate a strong linear correlation between the organic matter content and χ_{FD} (Tables 6.1 and 6.3). χ_{FD} percentage also shows close associations with the organic matter content. The correlation between the organic matter content and χ_{FD} percentage is significant at the 0.01 level for > 63 μm fraction and bulk samples, but not significant at the 0.05 level for < 63 μm fraction samples (Table 6.3). Fig. 6.2 shows the linear regression for the organic matter content and χ_{FD} percentage for bulk samples. The ratio χ_{ARM} /SIRM shows a strong correlation (significant at the 0.01 level) with the organic matter content for < 150 μm fraction samples (Table 6.3). The linear regression for the organic matter content and χ_{ARM} /SIRM for < 63 μm fraction samples is shown in Fig. 6.3.

Table 6.3 Correlation coefficients between the organic matter content and magnetic parameters for size fraction and bulk samples (the first sampling period).

Size fraction	< 63 μm	64 - 150 μm	151 - 300 μm	301- 500 μm	501- 1000 μm	< 1000 μm
χ_{FD}	0.024	0.570 [a]	0.566 [a]	0.452 [a]	0.185	0.651 [a]
χ_{FD} percentage	0.129	0.585 [a]	0.390 [a]	0.290 [a]	0.458 [a]	0.450 [a]
χ_{ARM} /SIRM	0.447 [a]	0.446 [a]	0.133	0.082	0.017	0.074

[a] Correlation is significant at the 0.01 level.

The close associations between the organic matter content and χ_{FD} percentage in street dust fraction and bulk samples support the suggestion that re-entrainment of soil is probably a major source of the organic material present in street dust (see Section 6.2). The organic matter content and χ_{FD} show different size variation trends (Tables 6.2 and 3.3), probably reflecting the difference in their sources. This may partly explain the insufficient evidence of correlations between the organic matter content and χ_{FD} for < 63 and > 500 μm fractions. The highly significant correlation between the organic matter content and χ_{ARM} /SIRM for < 150 μm fraction samples implies that the organic matter is related to dust ferrimagnetic grain sizes.

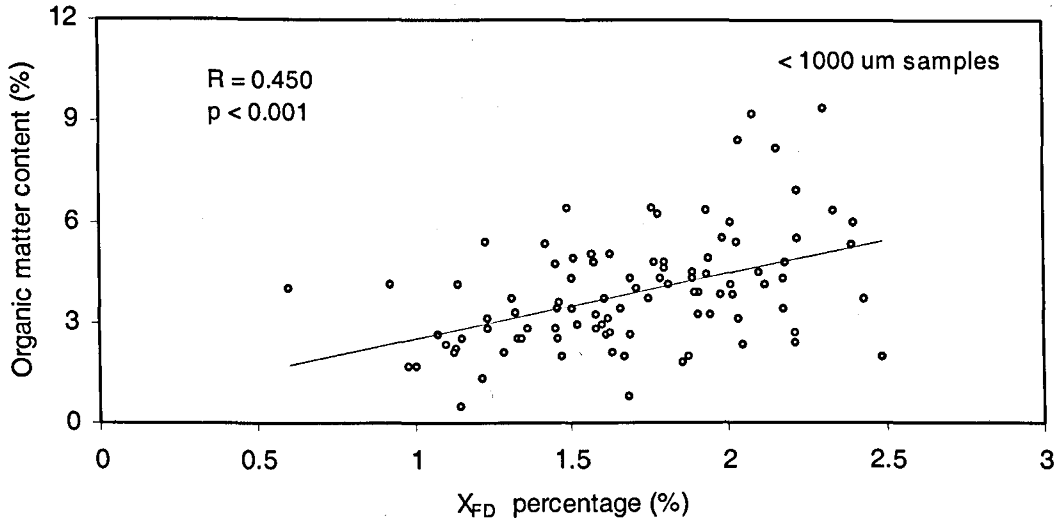

Fig. 6.2 Correlation between the organic matter content and χ_{FD} percentage for <1000 μm bulk samples of the first sampling period.

As discussed above, organic matter and magnetic particles in street dust come from a wide range of sources. As a result, R values in Table 6.3 are < 0.7, indicating a variety of controlling factors for the organic matter content and magnetic mineral concentrations. Rogge *et al.* (1993) estimated the contribution of tyre dust, vegetative detritus, and vehicle exhaust aerosol to organics in the fine road dust (< 2 μm) by using several groups of organic tracer compounds such as steranes, hopanes, and higher molecular weight n-alkanes. The highly significant correlation between the organic matter content and χ_{FD}, χ_{FD} percentage, and/or χ_{ARM} /SIRM suggest that the organic matter is related to SP grains and/or ferrimagnetic grain sizes in street dust. Thus, simple, rapid, and non-destructive magnetic measurements could provide useful information about source apportionment of street dust organic matter once origins of dust ferrimagnetic components are satisfactorily resolved. Dearing *et al.* (1996a) and Dearing (1999) suggested that there are few SP grains in samples with χ_{FD} percentage < 2.0 %. However, this study demonstrates that small concentrations of SP grains still have significant environmental implications.

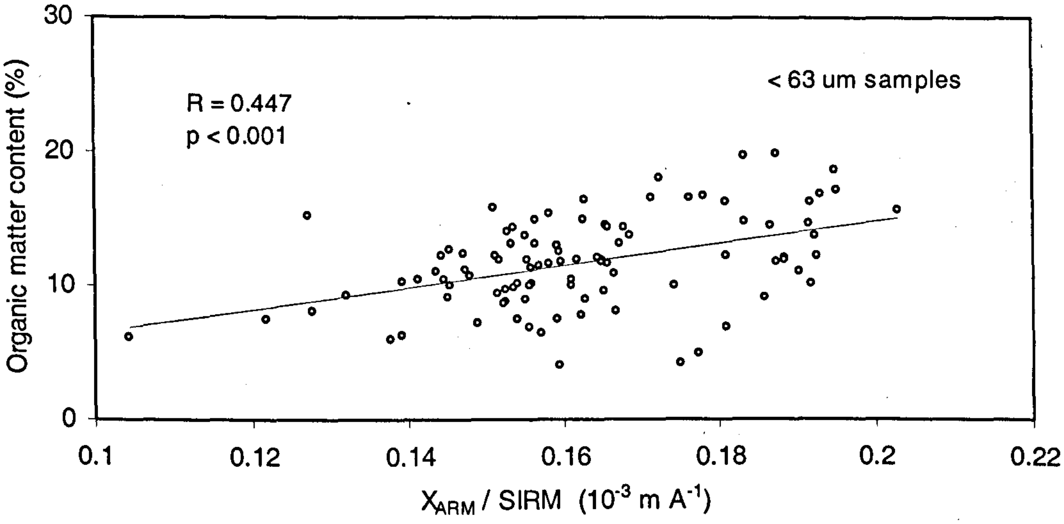

Fig. 6.3 Correlation between the organic matter content and χ_{ARM} /SIRM for < 63 μm fraction samples of the first sampling period.

6.4 Analysis of revisited site samples

In this section, associations between the organic matter content and magnetic properties are examined by using 19 revisited site samples from the first sampling period (dataset A) and from four sampling periods (dataset E) to assess the impact of the limited number of sampling sites and/or their distribution and various sampling periods on the analysis results (Table 6.4). For the purpose of comparison, the correlation coefficient between the organic matter content and χ_{ARM} / SIRM of the first period 97 site samples (dataset AA) is also shown in Table 6.4. It is found that the correlation between the organic matter content and χ_{ARM} / SIRM is significant at the 0.05 level for datasets A and E. But for dataset AA, it is significant at the 0.01

level. This implies that the number of sampling sites and/or their distribution may have a significant impact on the analysis results of associations between the organic matter content and magnetic properties.

Table 6.4. Correlation coefficients between the organic matter content and χ_{ARM} / SIRM for < 63 μm fraction [a].

Magnetic parameter	Dataset AA	Dataset A	Dataset E
χ_{ARM} / SIRM	0.447 [c] (97)	0.487 [b] (19)	0.256 [b] (76)

[a] Dataset AA: 97 site samples of the first sampling period (January- February, 1998), dataset A: 19 revisited site samples of the first sampling period (January- February, 1998), and dataset E: all 76 samples from 19 revisited site samples of four sampling periods (January- February, May, August, and November 1998). Values in ( ): samples numbers.

[b] Correlation is significant at the 0.05 level.

[c] Correlation is significant at the 0.01 level.

6.5 Summary

The study demonstrates good linear correlations between the organic matter content and some magnetic mineral concentration-related parameters (χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, or χ_{HIGH}) in the bulk samples. Among them, χ_{FD} shows the highest correlation coefficient value, suggesting that re-entrainment of soil is probably a major source of the organic material present in street dust.

The organic matter content of the first period samples is 11.7, 6.2, 2.2, 2.3, 3.2, and 3.9 % on average for size fractions of <63, 64-150, 151-300, 301-500, 501-1000 μm, and <1000 μm bulk samples, respectively. The organic matter content significantly decreases with increasing size for fractions < 300 μm, but the variation is not substantial for fractions > 300 μm. There is a strong correlation between the organic matter content and χ_{FD} for 64 - 500 μm fraction samples, but insufficient evidence of a correlation for other fraction samples. χ_{FD} percentage also demonstrates a close association with the organic matter content, with a highly significant correlation for > 63 μm fraction and <1000 μm bulk samples. This supports the suggestion that soil is probably an important contributor of dust organic material. The quotient χ_{ARM} /SIRM shows a highly significant correlation with the organic matter content for <150 μm fraction samples. 19 revisited site samples (<63 μm fraction) show a significant correlation between the organic matter content and χ_{ARM} / SIRM

This study demonstrates several implications for the application of magnetic methods in the study of street dust. First, the simple, rapid, and non-destructive magnetic measurements may be used as proxies for the organic matter content in street dust. Second, magnetic measurements could provide useful information about source apportionment of street dust organic matter, provided the origins of the relevant dust magnetic components are satisfactorily resolved. Finally, small concentrations of magnetic components, such as SP ferrimagnetic grains, may still have significant environmental implications.

Chapter 7. Variations of element concentrations with particle size of Liverpool street dust

7.1 Introduction

Particle size is a controlling factor of element concentrations in street dust (Al-Rajhi *et al.*, 1996). Few researchers, however, have paid much attention to its effect. Furthermore, the particle size effect of street dust is an important aspect for the assessment of potential human health risk (Rinehart and Rogers, 1995), the contribution to atmospheric particulate matter (Harrison *et al.*, 1997) to house dust (Adgate *et al.*, 1998), and to degradation of urban run-off quality (Ellis and Revitt, 1982) and for source identification (Beckwith *et al.*, 1985).

In a study of street dust in Champaign - Urbana, Illinois, USA, Linton *et al.* (1980) and Hopke *et al.* (1980) examined Pb and other element concentration variations with particle size. Ellis and Revitt (1982) reported that for highways carrying the highest traffic densities the concentrations of Cd and Pb are greatest for grain sizes between 100 and 500 μm and that residential side street samples show a marked affinity of Cd, Fe, and Zn with the coarsest grain fractions. Fergusson and Ryan (1984) observed an overall increase of element levels with decreasing particle size, by analysing eleven street dust samples from two large urban areas (London, UK; and New York, USA) and three small cities (Halifax, Canada; Christchurch, New Zealand; and Kingston, Jamaica). In their investigation of relationships between metal levels and particle size across a residential street in NW London, UK, over a six-month period, Beckwith *et al.* (1985) demonstrated a higher affinity of Cu, Pb, and Zn with smaller sizes. With five collections of street dust from three major sites in the urban area of Brisbane, Australia, Al-Chalabi and Hawker (1996) found that Pb is primarily associated with smaller particles ($< 90\,\mu$m). A survey of the particle size effect for metal pollution of atmospherically deposited urban dust in Riyadh city, Saudi Arabia, shows that the overall trend of metal concentrations decreases as particle size increases in the study fraction (< 2 mm) (Al-Rajhi *et al.*, 1996). In short, these studies observe a general trend that concentrations increase as sizes decrease, but there are differences between elements and there is evidence for enhanced concentrations in coarse particle sizes in some cases. Therefore, more research is needed to investigate size variation patterns of element concentrations in street dust.

Pb has been the most frequently investigated element in street dust because of its human health implications (Day *et al.*, 1975; Linton *et al.*, 1980; Nageotte and Day, 1998). Traffic Pb is the most significant source of street dust Pb, but there are also contributions from Pb contaminated soil, lead paint, and local industrial emission (Fergusson and Kim, 1991; De Miguel *et al.*, 1997). In the UK, leaded petrol was still supplied for traffic consumption when the sampling work of this study was carried out. In some countries, traffic Pb in street dust still causes environmental concerns (e.g., Al-Chalabi and Hawker, 1996).

This chapter extends the study of size variations of element concentrations in street dust, using Liverpool dust samples of the first sampling period. Pb, Zn, Rb, and S concentration variations with particle size are examined. Pb concentrations are analysed in further detail. Some potential implications are also discussed.

The total Pb, Zn, Rb, and S concentrations of five size fraction (<63, 64-160, 151-300, 301-500, and 501-1000μm) and bulk (< 1000μm) dust samples of the first sampling period were measured using isotope source X-ray fluorescence (XRF) analysis. The test of the particle size effect on XRF quantification suggests insufficient evidence of significance of the particle size effect (see section 2.4).

The statistical procedure one-way analysis of variance (ANOVA) (the Tukey HSD test) was applied to test the mean differences of the element concentrations between size fractions for significance. The dust element concentrations are presented in Table 7.1. The measurements of Pb and Zn concentrations fall within the ranges of medians in other studies, but Rb concentrations are higher (Fergusson and Kim, 1991; De Miguel *et al.*, 1997). For S, Hildemann *et al.* (1991) reported a concentration of 5.6 mg g^{-1} in < 2μm paved road dust.

7.2 Analysis of element concentrations

Two methods are used in this study to present mean values of element concentrations for a certain particle size for a number of samples. One is the calculation of average concentrations for the particle size over the number of samples, and the other is the average particle ratio approach. Based on a study of cross-correlation and comparison for two sets of atmospherically deposited dust samples, Al-Rajhi *et al.* (1996) recommended the average particle ratio method for analysing metal concentration trend with particle size. The particle ratio of an element concentration for a certain particle size *i*, in sample *n*, is expressed as the ratio between the element concentration of the particle size, α_{in}, and the sum of α_{in} for all the particle sizes m. Thus, the average particle ratio β_i* over the sample number N is given by

$$\beta_i^* = \sum_{n=1}^{N} (\alpha_{in} / \sum_{i=1}^{m} \alpha_{in}) / N \qquad (7.1)$$

The β_i* value allows comparisons between element concentrations as it is independent of unit. The calculated average particle ratios (Fig. 7.1) show the same trends to those illustrated by the mean concentration method (Table 7.1). Pb, Zn, and Rb concentrations decrease with increasing particle size for fractions < 300 μm, all significantly at the 0.01 level. From fraction 151-300 to 301-500 μm, the differences of Pb and Zn concentrations are not significant at the 0.05 level, but Rb concentrations decrease significantly at the 0.05 level. For fractions >300 μm, Pb, Zn, and Rb concentration increase significantly at the 0.01 level. S shows a different trend. The concentrations do not change significantly at the 0.05 level with increasing particle size for fractions < 150 μm, but decrease significantly at the 0.01 level from fractions 64-150 to 151-300 μm, then do not change significantly at the 0.05 level for fractions > 150 μm.

Ellis and Revitt (1982) found that for highways carrying the highest traffic densities the concentrations of Cd and Pb are the greatest for grain sizes between 100 and 500 μm. Al-Chalabi and Hawker (1996) reported that, at sites with active street dust resuspension, Pb was found to be associated more with the medium size fraction (90-250 μm). They suggest the existence of an aggregation process. The overall trends in

Liverpool street dust show that the aggregation process is not likely to be a controlling factor.

Table 7.1 Variations of dust element concentrations with particle size (the first period 97 samples) (mean ± standard deviation).

Element	Pb ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)	Rb ($\mu g\ g^{-1}$)	S (mg g^{-1})
< 63 μm	892 ± 536	1469 ± 602	70 ± 25	5.2 ± 2.0
64-150 μm	454 ± 293	908 ± 488	57 ± 16	4.4 ± 1.4
151-300 μm	208 ± 151	454 ± 300	37 ± 11	3.3 ± 1.4
301-500 μm	195 ± 138	433 ± 334	29 ± 10	3.4 ± 9.8
501-1000 μm	299 ± 207	645 ± 431	44 ± 15	3.8 ± 1.8
< 1000 μm	360 ± 237	654 ± 306	42 ± 12	4.1 ± 1.2
Crust (shale) [soil] [a]	12.5 (20) [74]	70 (90)[97]	90 (140)	0.3 (2.5)
Source [b]	Motor vehicle, weathered paint.	Combustion (oil, coal, refuse), tyre wear, metal corrosion & wear, weathered paint.	Soil, salt spray & de-icing salt, concrete & cement, metal corrosion & wear.	Tyre wear, plant fragments, etc.

[a] Average abundances in the Earth crust and shale (Krauskopf, 1982), values in [ ] are mean values in English and Welsh soils (McGrath and Loveland, 1992).

[b] Pb, Zn, and Rb references: Hopke *et al.* (1980), Fergusson (1992); S: based on Hildemann *et al.* (1991).

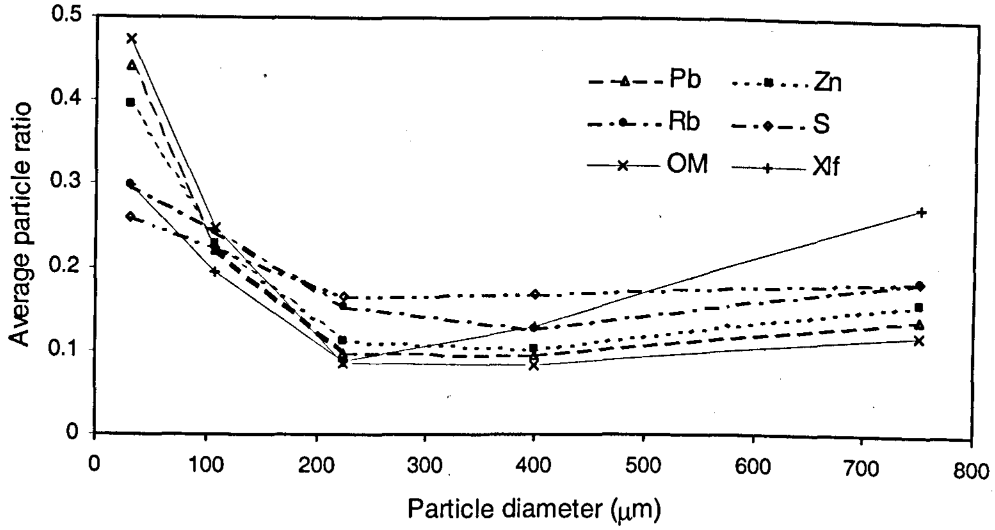

Fig.7.1 Variations of average particle ratios of element (Pb, Zn, Rb, and S) concentrations, the organic matter (OM) content, and magnetic susceptibility (χ_{LF}) with particle size (the first period 97 samples), demonstrating different size variations and relatively high concentrations in the finest particles (< 63 μ m).

Primarily, street dust consists of natural and anthropogenic source materials, the former mainly being soil material, the latter including vehicle exhaust, tyre wear, metal corrosion, weathered materials, refuse, and others (Fergusson and Kim, 1991; Fergusson, 1992). Qualitative observation of the Liverpool street dust samples during the field work and under a microscope in the laboratory shows the presence of soil material, weathered building material, plant fragments, and urban refuse. Comparisons between element concentrations in Liverpool street dust and background levels in the Earth crust and shale and English and Welsh soils show that Pb and Zn are dominated by non-natural sources and that Rb is a soil-derived element, which is consistent with previous studies (Table 7.1). The main sources of Pb, Zn, and Rb are summarised in Table 7.1. Hildemann *et al.*'s (1991) measurements show relatively high S levels in vehicle brake dust (12.8 mg g^{-1}) and vegetative detritus dust (6.2 mg g^{-1}), which may be important sources of S in street dust. Due to the difficulties of quantifying the contribution of specific sources, especially with respect to particle size, it is difficult in this study to link size variations of each element concentrations to the contribution of discrete sources.

The organic matter content (%) of Liverpool street dust, measured by means of the loss-on-ignition method (ignition at 375 °C for 4 h), is (mean ± standard deviation) 11.7 ± 3.4, 6.2 ± 2.7, 2.2 ± 1.1, 2.3 ± 1.4, and 3.2 ± 2.3 for size fractions <63, 64-150, 151-300, 301-500, and 501-1000 μm, respectively (see Table 6.2). The content decreases with increasing particle sizes for fractions < 300 μm, significantly at the 0.01 level (ANOVA, the Tukey HSD test), but the differences of the organic matter content are not significant at the 0.05 level (ANOVA, the Tukey HSD test) for fractions > 300 μm. The average particle ratios are also shown in Fig. 7.1. It is suggested that the higher organic matter content in fine dust particles (< 300 μm) may be partly due to contributions from soil, vehicle exhaust, and tyre wear (see Chapter 6). There is growing interest in the application of magnetic techniques to studies of dusts in the environment (e.g., Flanders, 1999; Xie *et al.*, 1999b). The magnetic measurements of Liverpool street dust indicate that the dominant magnetic component comprises PSD + MD grains of ferrimagnetic minerals, with SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals present in small magnetic concentrations (see Chapter 3). This study indicates magnetic enhancement in the finest (<63 μm) and coarsest (501-1000 μm) fractions (see Chapter 3). Beckwith *et al.* (1986) suggested that the possible non-soil sources of magnetic minerals in the urban environment include atmospheric deposition, automobile derived particulates, and surface constructional materials. Low frequency magnetic susceptibility (χ_{LF}) represents the total contribution of magnetic minerals in a sample. In Liverpool street dust, it is mainly a function of their ferrimagnetic concentration and can be used to represent dust magnetic properties in the size variation analysis. The average particle ratios of χ_{LF} are also shown in Fig.7.1. In the finest fraction (< 63 μm), organic matter, Pb, and Zn show higher average particle ratio values than χ_{LF}, Rb, and S, significantly at the 0.01 level (ANOVA, the Tukey HSD test). In the coarsest fraction (501-1000 μm), χ_{LF} demonstrates a higher average particle ratio value than Pb, Zn, Rb, S, and organic matter, significantly at the 0.01 level (ANOVA, the Tukey HSD test).

In summary, Fig. 7.1 demonstrates different size variations for element concentrations, the organic matter content, and magnetic properties and relatively high concentrations in the finest particles (< 63 μm). Therefore, this study suggests some implications. First, The particle size effect is an important factor to be considered in dust sampling, comparison of measurement data, and source tracing in the urban environment. Second, because element concentrations (such as Pb, Zn, Rb, and S), the organic matter content, and magnetic properties (such as χ_{LF}) show elevated values in fine particles and because fine dust particles cause more environmental concerns than coarse particles, studies of street dust should place emphasis on fine particles.

7.3 Analysis of Pb concentrations

The introduction of unleaded and reduced-lead petrol has cut the Pb traffic source greatly. Consequently, Pb concentration in street dust has decreased sharply (e.g., Ho, 1990; Nageotte and Day, 1998). However, it is found that the mean percentage Pb reduction in dust falls short of the percentage reduction of Pb in petrol (e.g., Ho, 1990). Nageotte and Day (1998) estimated that the total Pb emissions from motor vehicles in the UK in 1997 are about 20% of those in 1975. However, the fall in street dust Pb, in Manchester, to around 60% of the 1975 value, is only half of that which would have been expected from the trends in vehicle emissions. They suggest two possibilities. One is that up to half of the street dust Pb in 1975 arose from non-vehicle sources. The other is that vehicle Pb emissions in Manchester (or large cities in general) have not reduced as much as emissions nationally, perhaps if traffic densities in cities have risen disproportionately.

Pb levels in Liverpool street dust vary over a wide range, with quite high standard deviation values (Table 7.1). By comparison with other surveys (Leharne *et al.*, 1992; De Miguel *et al.*, 1997; Nageotte and Day, 1998), the results fit within the general framework of Pb concentrations in urban street dust. The Liverpool surface soil samples also show elevated Pb concentrations: average 829, 355, 259, 315, 378, and 287 μg g^{-1} for size fractions < 63, 64-150, 151-300, 301-500, and 501-1000 μm, and bulk samples (< 1000 μm), respectively, compared to the mean Pb concentration of 74 μg g^{-1} in English and Welsh soils (see Table 7.1). Soil is the main component of street dust, accounting for more than half of the materials in street dust (Fergusson and Kim, 1991; Fergusson, 1992). Moreover, urban street dust is frequently and effectively removed by activities like street cleaning and storm runoff. Consequently, dust Pb mainly consists of freshly deposited vehicle Pb and aged soil Pb. It is argued that the contribution of aged soil Pb, which accumulated from traffic emission since the use of leaded petrol, to dust Pb may partly explain the less reduction of dust Pb concentration than that of petrol Pb level. Therefore, it is expected that when leaded petrol is not available from 2000, Pb concentrations in Liverpool street dust will remain relatively high for some time.

Vehicle exhaust consists mostly of fine particulate matter, with the majority of particles <2.5 μm in diameter (Silva and Prather, 1997). In addition, fine particles of street dust and soil have higher specific surface area, therefore higher attachment for vehicle Pb. Consequently, the concentrations in fraction <63 μm are the highest. The increasing concentrations with increasing particle size in coarse particles (> 300 μm) may be due to the contribution of weathered paint. Since relatively higher Pb concentrations are usually associated with fine dust particles rather than coarse particles, the investigation of Pb in street dust should place emphasis on fine fractions.

The overall dust mass distribution is given in Fig. 7.2. The area of each block represents the proportion of the size fraction, with the highest in fraction 151-300 μm. The distribution profile is similar to the results observed by Fergusson and Ryan (1984) and Al-Rajhi *et al.* (1996). Pb concentration distributions are also shown in Fig. 7.2. Due to high Pb levels in fine particles, Pb concentration distributions are higher than those of mass for fractions <150 μm, but on the other hand lower for fractions 150-500 μm, both significantly at the 0.01 level (the t-test). In addition, the difference between the Pb concentration distribution and the mass distribution is not significant at the 0.05 level (the t-test) for fraction 501-1000 μm. The calculated mean Pb concentrations of different size ranges are shown in Table

7.2. There is a good linear correlation between the calculation and the observation for the particle size <1000 μm (correlation coefficient = 0.900, $p < 0.001$). Pb concentrations decrease substantially with increasing particle size for size ranges < 300 μm, significantly at the 0.01 level, but the concentration differences are not significant for size ranges > 300 μm. Therefore, the close association of Pb levels with particle size for size ranges < 300 μm supports the suggestion that comparison of Pb level measurements should consider the particle size effect (Al-Rajhi *et al.*, 1996), particularly for dust consisting mainly of fine particles.

Table 7.2 Variations of calculated Pb concentrations with particle size range (mean ± standard deviation: μg g^{-1}).

Size range	0-63 μm	0-150 μm	0-300 μm	0-500 μm	0-1000 μm
Concentration	892 ± 536	535 ± 332	325 ± 202	296 ± 182	296 ± 179

7.4 Summary

This chapter reports the study of element concentration variations with particle size (fractions < 63, 64-150, 151-300, 301-500, and 501-1000 μm), using the first period dust samples. Pb, Zn, and Rb concentrations decrease substantially with increasing particle size for size fractions < 300 μm, but increase considerably for size fractions >300 μm. S shows a different trend. The concentrations do not change significantly with increasing particle size for size fractions < 150 μm, but decrease considerably from size fraction 64-150 to 151-300 μm, then keep relatively unchanged for size fractions >150 μm. These variation patterns suggest that the aggregation process is not a controlling factor. This study confirms that the particle size effect is an important factor in dust sampling, comparison of measurement data, and source tracing in the urban environment and that studies of street dust should place emphasis on fine particles.

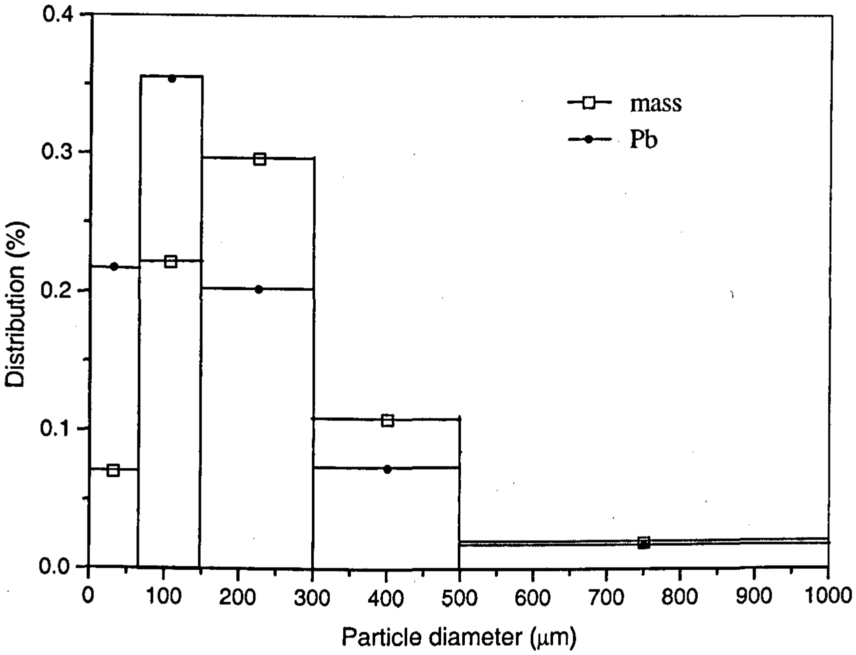

Fig. 7.2 Distributions of mass and Pb concentrations with particle size, showing that Pb concentration distributions are higher than those of mass for fractions <150 μm, but lower for fractions 150-500 μm, and the difference between the Pb concentration distribution and the mass distribution is not significant for fraction 501-1000 μm.

Pb shows the highest concentrations in the finest size fraction (<63 μm), confirming that the investigation of Pb concentrations should place emphasis on fine particles. Mean Pb levels are highly associated with particle size for size ranges < 300 μm, implying that comparison of Pb concentrations should consider the particle size effect, particularly for dust consisting mainly of fine particles. Dust Pb consists mainly of freshly deposited vehicle Pb and aged soil Pb. It is argued that the contribution of aged Pb in urban soil to dust Pb may contribute to the difference of Pb concentration reductions between petrol and dust.

Chapter 8. Association between magnetic properties and element concentrations of Liverpool street dust

8.1 Introduction

Street dust is an important pathway of pollution material in the urban environment. Some authors (Beckwith *et al.*, 1986; Brilhante *et al.*, 1989; Charlesworth and Lees, 1997) reported possible linkages between magnetic properties and heavy metals in street dust. Magnetic material in street dust comes from various sources (Beckwith *et al.*, 1986) and the knowledge of each is presently inadequate.

Magnetic properties and element concentrations of Liverpool street dust are discussed in Chapters 3 and 5, respectively. In this chapter, associations between magnetic properties and element concentrations of Liverpool street dust, using correlation analysis and factor analysis, and their implications are investigated. The results may provide useful information for future magnetic pollution studies, particularly source identification of magnetic material in the environment. Because fine dust particles cause more environmental concerns than coarse particles and only 4 element (Pb, Zn, Rb, and S) concentrations are available for $> 63\,\mu$m fraction and bulk ($< 1000\,\mu$m) samples (see Chapter 2), Only $< 63\,\mu$m fraction samples are analysed in this chapter.

8.2 Correlation analysis

The correlation between magnetic properties and between magnetic properties and element concentrations is examined for dataset AA (< 63 μm fraction of 97 site samples in January -February 1998) (Tables 8.1 and 8.2). It is found that there are positive correlations (significant at the 0.01 level) between concentration dependent magnetic parameters χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, SOFT, and HIRM, suggesting a possibly common source for magnetic material. For concentration independent parameters, there are positive correlations (significant at the 0.01 level) between χ_{FD} % and χ_{FD}, χ_{ARM}/SIRM and HARD %, SOFT % and SOFT, and HARD % and HIRM.

Tables 8.1 and 8.2 also show positive correlations (significant at the 0.01 level) between magnetic parameters χ_{LF}, χ_{ARM}, SIRM, and SOFT and elements Ti, Fe, Pb, and Zn. Street dust consists of both soil (or natural) and urban (or anthropogenic) material. The urban sources of street dust include metallic fragments, concrete/cement, products of tyre wear, salt spray, de-icing salt, and motor vehicle emissions (Fergusson and Kim, 1991; Fergusson, 1992). Previous studies (Beckwith *et al.*, 1986; Brilhante *et al.*, 1989; Charlesworth and Lees, 1997) have reported possible linkages between magnetic properties and heavy metals in street dust and suggested that magnetic measurements may be used as proxies for pollution levels. The main sources of Ti, Fe, Pb, and Zn in street dust are summarised in Table 8.2. Comparisons between Ti, Fe, Pb, and Zn concentrations in Liverpool street dust and background levels in the Earth crust and shale, and English and Welsh soils (Chapter 7 and Table 8.2) suggest that Pb and Zn are dominated by non-natural sources whilst

Ti is largely a soil-derived element and Fe an element of both soil and urban origin. In addition, Liverpool street dust shows much higher mean χ_{LF} values (~ 500×10^{-8} m^3 kg^{-1}) than that of English topsoils (73×10^{-8} m^3 kg^{-1}) (Xie *et al.*, 1999b). Therefore, the close correlations between magnetic parameters χ_{LF}, χ_{ARM}, SIRM, and SOFT and elements Ti, Fe, Pb, and Zn may suggest mixed contributions of magnetic material from urban and natural sources, probably mainly urban sources. Beckwith *et al.* (1986) suggested that the possible non-soil sources of magnetic minerals in the urban environment include atmospheric deposition, automobile derived particulates, and surface constructional materials. The partial soil origin of magnetic material is supported by previous studies suggesting that soil contributes to more than half of street dust material (Fergusson and Kim, 1991; Fergusson, 1992). χ_{LF} represents the total contribution of magnetic mineral in a sample. Fig.8.1 shows scatter plots of χ_{LF} versus elements Ti, Fe, Pb, and Zn for dataset AA.

Studies so far suggest that the most common source of SP grains is surface soil (Dearing *et al.*, 1996) and pollution ferrimagnetic minerals are mainly within the ranges of SSD and PSD + MD grains (Flanders, 1999). Nevertheless, there is evidence of other SP grain sources, such as fly ash (Xie and Dearing, 1999). Dearing *et al.*'s (1997) mixing experiment indicates that χ_{FD} is a reasonably good estimator of the SP grain concentration in mixed-domain assemblages. The significant correlation between χ_{FD} and Fe (at the 0.01 level) and between χ_{FD} and Zn (at the 0.05 level) (Tables 8.1 and 8.2) may suggest evidence of SP grains from urban contributions. More research is required to support this suggestion, which will be a topic in future studies.

Table 8.1 Correlations between magnetic properties and between magnetic properties and element concentrations for dataset AA (significant at the 0.01 or 0.05 level).

Variable		Magnetic parameter	Element
χ_{LF}	0.01 level	χ_{FD}, χ_{ARM}, SIRM, χ_{ARM}/SIRM [a], SOFT, HIRM, HARD % [a].	Ti, Fe, Pb, Zn.
	0.05 level		
χ_{FD}	0.01 level	χ_{LF}, χ_{FD} %, χ_{ARM}, SIRM, SOFT, SOFT % [a], HIRM.	Fe.
	0.05 level	χ_{ARM}/SIRM [a].	Zn.
χ_{FD} %	0.01 level	χ_{FD}, SOFT % [a].	
	0.05 level		
χ_{ARM}	0.01 level	χ_{LF}, χ_{FD}, SIRM, χ_{ARM}/SIRM [a], SOFT, HIRM.	Ti, Fe, Pb, Zn.
	0.05 level	HARD % [a].	Rb.
SIRM	0.01 level	χ_{LF}, χ_{FD}, χ_{ARM}, χ_{ARM}/SIRM [a], SOFT, HIRM. HARD % [a].	Ti, Fe, Pb, Zn.
	0.05 level		S [a], Rb.
χ_{ARM}/SIRM	0.01 level	χ_{LF} [a], χ_{ARM} [a], SIRM [a], SOFT [a], SOFT % [a], HIRM [a], HARD %.	Ti [a], Fe [a], S, Pb [a], Zr [a], organic matter.
	0.05 level	χ_{FD} [a].	Sr [a].
SOFT	0.01 level	χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, χ_{ARM}/SIRM [a], SOFT %, HIRM, HARD % [a].	Ti, Fe, S [a], Pb, Zn.
	0.05 level		Rb, organic matter [a].
SOFT %	0.01 level	χ_{FD} [a], χ_{FD} % [a], χ_{ARM}/SIRM [a], SOFT, HARD % [a].	Ti, Fe, S [a], organic matter [a].
	0.05 level		K [a], Pb.
HIRM	0.01 level	χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, χ_{ARM}/SIRM [a], SOFT, HARD%.	Si, Ti, K, S [a], Rb, organic matter [a].
	0.05 level		
HARD%	0.01 level	χ_{LF} [a], χ_{ARM}/SIRM, SOFT [a], SOFT % [a], HIRM.	Si, K, Fe [a], Pb [a], Zn [a].
	0.05 level	χ_{ARM} [a], SIRM [a].	

[a] Correlation coefficient (r) is negative.

Table 8.2 Correlation coefficients between magnetic properties and element concentrations for dataset AA.

Variable	Ti	Fe	Pb	Zn
χ_{LF}	0.459 ^{b}	0.645 ^{b}	0.366 ^{b}	0.505 ^{b}
χ_{FD}	0.040	0.396 ^{b}	0.178	0.258 ^{a}
χ_{FD} %	-0.193	0.026	-0.066	-0.016
χ_{ARM}	0.347 ^{b}	0.610 ^{b}	0.344 ^{b}	0.494 ^{b}
SIRM	0.437 ^{b}	0.634 ^{b}	0.359 ^{b}	0.406 ^{b}
χ_{ARM}/SIRM	-0.374 ^{b}	-0.487 ^{b}	-0.273 ^{b}	-0.106
SOFT	0.484 ^{b}	0.700 ^{b}	0.382 ^{b}	0.426 ^{b}
SOFT %	0.327 ^{b}	0.457 ^{b}	0.243 ^{a}	0.092
HIRM	0.305 ^{b}	0.181	0.071	0.002
HARD %	-0.052	-0.410 ^{b}	-0.289 ^{b}	-0.411 ^{b}
Crust [shale]{soil} ^{c}	5.00 [4.50]	54.0 [47.0]{27.8}	2.5 [20] {74}	70 [90] {97}
Source ^{d}	Soil, weathered paint.	Metal corrosion, concrete & cement, soil, motor vehicle.	Motor vehicle, weathered paint.	Tyre wear, metal corrosion, combustion, weathered paint.

[a] Correlation is significant at the 0.05 level.

[b] Correlation is significant at the 0.01 level.

[c] Average abundances in the Earth crust and shale (Krauskopf, 1982), values in { } are mean values in English and Welsh soils (McGrath and Loveland, 1992). Unit: mg g^{-1} for Ti and Fe, $\mu g\ g^{-1}$ for Pb and Zn.

[d] References: Fergusson and Kim (1991) and Fergusson (1992).

Dataset AA also shows positive correlations (significant at the 0.01 level) between HIRM and elements Si (r = 0.298), Ti (r = 0.305), K (r = 0.323), and Rb (r = 0.286), and between HARD % and elements Si (r = 0.366) and K (r = 0.297). This may suggest the possible contribution of soil material to the "hard" magnetic component, since Si, Ti, K, and Rb are largely soil-derived elements (Fergusson and Kim, 1991; Fergusson, 1992). χ_{ARM}/SIRM shows a positive correlation with S (r = 0.308) and the organic matter content (r = 0.447), significantly at the 0.01 level.

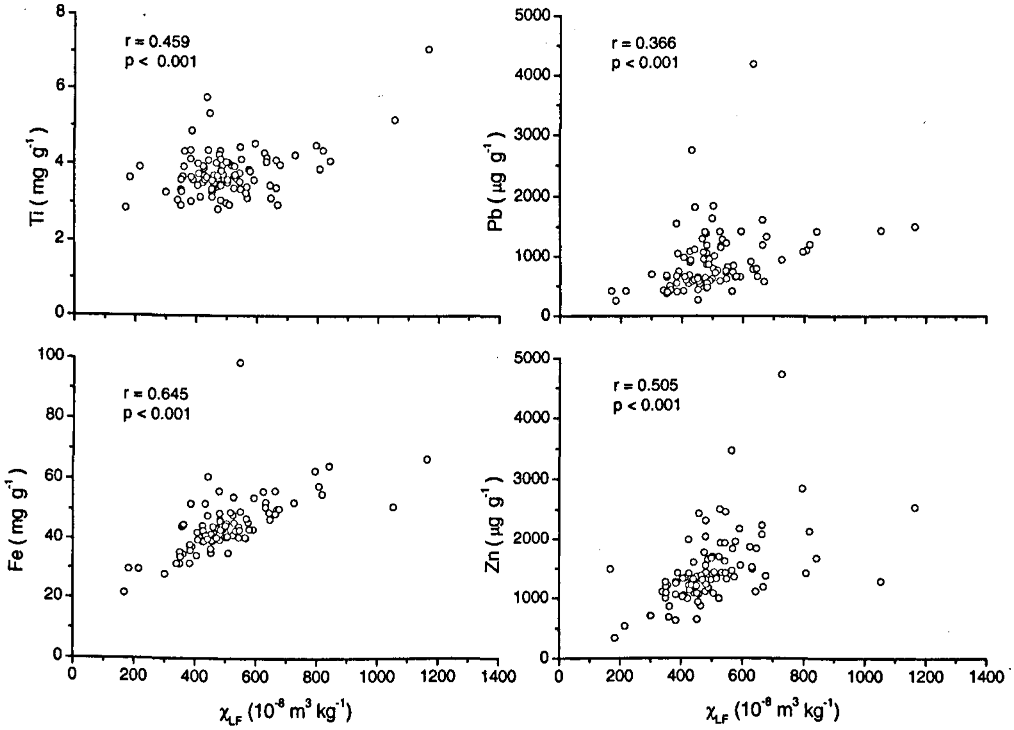

Fig. 8.1 Correlations between χ_{LF} and elements Ti, Fe, Pb, and Zn for dataset AA, all significant at the 0.001 level.

The correlation analysis for dataset E (< 63 μm fraction of all 76 samples from 19 revisited site for four sampling periods) are also carried out. There are positive correlations between concentration dependent magnetic parameters χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, SOFT, and HIRM, all significantly at the 0.01 level with the exception of the 0.05 level between χ_{FD} and HIRM. For concentration independent parameters, there are positive correlations (significant at the 0.01 level) between χ_{FD} % and χ_{FD}, χ_{ARM}/SIRM and HARD %, and HARD % and HIRM. There are also positive correlations between magnetic parameters χ_{LF}, χ_{ARM}, SIRM, and SOFT and elements Ti, Fe, Pb, and Zn, all significantly at the 0.01 level with the exception of the 0.05 level between χ_{LF} and Pb and between SOFT and Zn. χ_{FD} also shows a positive correlation with Fe and Zn (significant at the 0.01 level). HIRM shows a positive correlation with Si, Ti, K, Fe, Rb, and Sr, and HARD % with K, significantly at the 0.01 level. These results support the suggestion of mixed contributions of magnetic material from urban and natural sources, probably mainly urban sources.

8.3 Factor analysis

Factor analysis is a set of techniques to account for the correlations among a set of variables in terms of relatively few underlying dimensions, or factors. De Miguel *et al.* (1997) have used the method for the source apportionment of street dust in Madrid (Spain) and Oslo (Norway), satisfactorily. Here the method is applied to investigate associations between magnetic properties and between magnetic properties and element concentrations, using the SPSS package. Table 8.3 shows factor analysis results for dataset AA. Seven factors, with eigenvalues > 1, account for 80.8 % of the total variance. Factor 1 exhibits the highest loading of SIRM, χ_{LF}, SOFT, χ_{ARM}, Fe, and Zn, and a high loading of HIRM and χ_{FD}. Factor 3 shows the highest loading of HARD %, HIRM, and K, and factor 4 the highest loading of χ_{FD} and χ_{FD} %. For dataset E, factor analysis demonstrates that six factors (eigenvalues > 1) account for 84.0 % of the total variance. Factor 1 shows the highest loading of χ_{LF}, SOFT, SIRM, χ_{ARM}, Fe, χ_{FD}, and Zn, and a high loading of HIRM. Fig. 8.2

shows the plot of factor 1 versus factor 2 for dataset AA (see Table 8.3). Factor 1 shows a linkage between some magnetic parameters and some metals (e.g. Fe and Zn), whilst factor 2 explains a degree of variance according to the concentrations of sand (Si and Zr) versus organic matter (OM and S). Both factors seem relating to urban pollution and natural sources respectively. The spatial distribution of measurements with a high loading for factor 1 (SIRM, χ_{LF}, SOFT, χ_{ARM}, Fe, and Zn) or factor 2 (Si and Zr) are examined. The measurements with a high loading for the same factor (factor 1 or 2) show some similar high and/or low value areas. For information about the spatial distribution analysis method, see Section 5.2. The factor analysis results seem to support those of correlation analysis of mixed contributions of magnetic material from urban and natural sources, probably mainly urban sources.

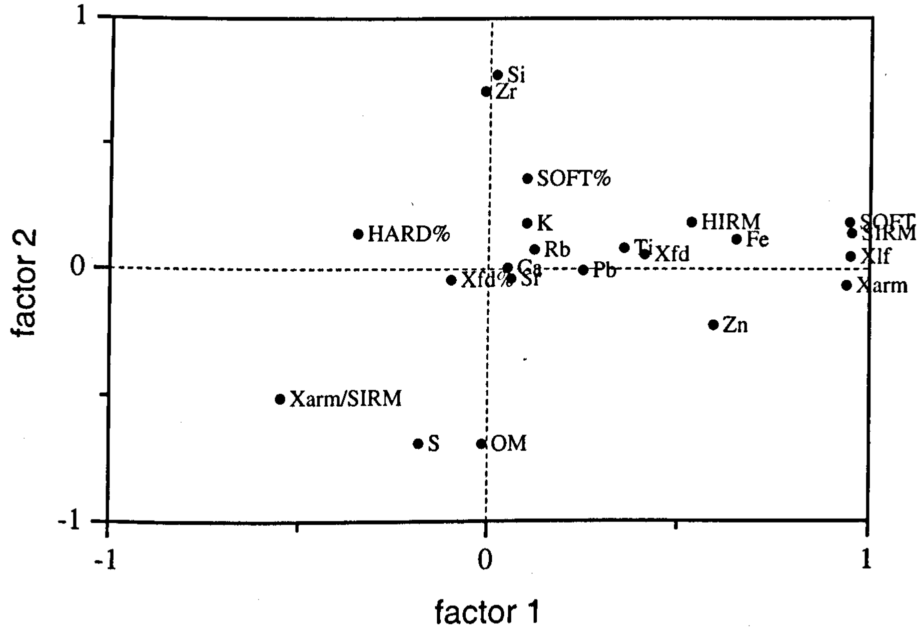

Fig. 8.2 Plot of factor 1 versus factor 2 for dataset AA (see Table 8.3).

8.4 Discussion

Some magnetic pollution studies demonstrate the linkage between magnetic properties and heavy metals, which forms the basis for the use of magnetic methods in pollution studies (Petrovsky and Ellwood, 1999). However, some studies suggest the potentially complex nature of relationships between magnetic minerals and heavy metals in the environment. For example, Charlesworth and Lees (1997) did not find evidence of relationships between heavy metals and mineral magnetic properties in the urban lake sediments and < 63 μm street dust in Coventry , although strong positive relationships did exist in < 2 mm street dust. On the other hand, covariances between magnetic properties and some element concentrations could be used to infer sources of magnetic minerals (see Dearing, 1999). As demonstrated above, associations between magnetic properties and between magnetic properties and element concentrations may provide useful evidence about sources of magnetic material. In addition, the analysis suggests evidence of SP grains from urban sources, information that has not been well recognized before about sources of magnetic material in the urban environment. Since the values of magnetic concentration-related parameters are also dependent on mineral phase and grain size (Thompson and Oldfield, 1986), results of correlation analysis and factor analysis should only be viewed as indicative of sources of magnetic material. Moreover, possible changes in dust magnetic properties both during transport and deposition and after deposition should be considered in interpretation of the analysis results. In this case, this effect should be insignificant because street dust comes mainly from local sources after relatively short distance transport and is frequently and effectively removed by activities like street cleaning and storm runoff

Source identification of magnetic variations is essential not only for obtaining detailed definition of the magnetic / climate connection (Hounslow and Maher, 1999) but also for magnetic pollution studies. For instance, chapter 6 suggests that magnetic measurements may be used as a source apportionment tool for organic matter in Liverpool street dust. Current methods for discriminating between magnetic sources include diagnostic magnetic measurements and complementary geochemical and microscopic analysis. Here, an alternative approach is suggested through the analysis of associations between magnetic properties and between magnetic properties and element concentrations, which can be achieved using some techniques, such as correlation analysis and factor analysis.

Finally, the particular results of spatial and temporal variations, and associations between magnetic properties and between magnetic properties and element concentrations in this study may be specific to Liverpool street dust. The way to investigate these issues, however, has wider validity and this study may provide useful information for future magnetic pollution studies.

8.5 Summary

The samples (< 63μm fraction) demonstrate positive correlations between concentration dependent magnetic parameters χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, SOFT, and HIRM, and between magnetic parameters χ_{LF}, χ_{ARM}, SIRM, and SOFT and elements Ti, Fe, Pb, and Zn. This suggests mixed contributions of magnetic material from urban and natural sources, probably mainly urban sources. Factor analysis seems to support this suggestion. This study implies that analysis of associations between magnetic properties and element concentrations may be a potential approach for source identification of magnetic material in the environment.

Table 8.3 Factor analysis: sorted rotated factor loadings for dataset AA [a].

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
SIRM	**0.953**	0.143	0.093	0.045	-0.111	0.130	0.099
χ_{LF}	**0.950**	0.049	-0.057	0.090	-0.072	0.100	0.100
SOFT	**0.947**	0.185	0.011	-0.044	-0.087	0.125	0.157
χ_{ARM}	**0.940**	-0.065	0.140	0.049	0.024	0.138	0.013
Fe	**0.651**	0.118	-0.308	0.097	0.214	0.141	0.466
Zn	**0.593**	-0.223	-0.346	0.033	0.218	-0.159	0.033
χ_{ARM} / SIRM	**-0.548**	-0.511	0.229	0.032	0.254	-0.083	-0.177
Si	0.017	**0.774**	0.320	-0.045	0.386	0.035	-0.048
Zr	-0.013	**0.709**	0.012	0.193	0.163	0.105	0.049
organic matter	-0.014	**-0.693**	-0.095	0.047	0.303	0.091	-0.414
S	-0.181	**-0.690**	-0.144	0.269	0.172	0.009	0.130
HARD %	-0.346	0.142	**0.845**	-0.044	0.045	-0.088	0.085
HIRM	0.533	0.186	**0.744**	0.013	-0.143	0.061	0.128
K	0.100	0.182	**0.555**	0.170	0.301	0.172	-0.162
SOFT %	0.099	0.361	**-0.478**	-0.459	-0.007	0.093	0.327
χ_{FD} %	-0.098	-0.043	0.069	**0.933**	0.016	-0.023	-0.043
χ_{FD}	0.411	0.058	-0.019	**0.871**	-0.007	0.075	-0.022
Ca	0.051	0.004	-0.170	-0.024	**-0.900**	0.020	-0.182
Sr	0.061	-0.038	0.144	0.028	**-0.611**	-0.034	0.438
Rb	0.121	0.077	0.200	-0.007	0.014	**0.918**	-0.074
Pb	0.250	-0.006	-0.221	0.027	0.005	**0.806**	0.346
Ti	0.357	0.083	-0.002	-0.134	0.013	0.159	**0.812**
% of variance	29.3	14.8	11.8	7.9	6.7	6.5	4.8

[a] Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Bold-face values represent the highest factor loadings for each variable.

Chapter 9. Magnetic measurements of Bootle dust deposition

9.1 Introduction

Dust deposition is one of the environmental concerns in the urban environment. It can cause indoor dust nuisance. Urban deposited dust comes from local sources, such as street dust, as well as sources outside the city. Acid deposition from fossil fuel combustion is also a current environmental problem. Although there were some studies on dust deposition pollution (See Chapter 1), little research, however, was reported in the literature on magnetic applications to dust deposition. In this chapter, magnetic properties of dust deposition samples from Bootle are analysed and their implications for applications of magnetic techniques in the study of deposited dust pollution are discussed.

A dust deposition monitoring programme was undertaken in the Bootle area (see Fig. 1.1), Sefton Metropolitan Borough Council, in response to local residents' complaints of dust nuisance in houses (Beer *et al.*, 1994). The dust analysed in this chapter was collected at the SDB and SDC sites from December 1995 to November 1996 (sampling every 4 weeks, 12 samples for each site), using a British Standard (BS) gauge which is recommended by the British Standards Institute (BSI) for the measurement of dust deposition in the U.K. The SDB site is located at the St. Joan of Arc School in the town centre, representing a dust nuisance area (the monitoring site), whilst the SDC site at the Buckley Hill Fire Station about 2 km north-east of the monitoring site, represents background dust deposition levels (the background site).

The mass of the dust was obtained before being packed in 1 cm^3 pots. Then the samples were subject to magnetic measurements including magnetic susceptibility, remanent magnetisation and hysteresis parameters. Magnetic measurements were also carried out on two blank filters (cellulose nitrate membrane) alongside the dust samples in order to assess and deduct the effects of packing and the blank filter. In addition to the magnetic parameters described in Chapters 2 and 3, some hysteresis parameters, obtained by using a Molspin vibrating sample magnetometer in the fields up to 1 T, are also used to analyse magnetic properties of Bootle dust samples. Saturation magnetisation (Ms), calculated by extrapolating the high field (0.8-1 T) magnetisation curve, is related to magnetic minerals and their concentrations and is unaffected by grain size. Saturation remanent magnetisation (at 1 T) derived from the hysteresis loop is denoted as Mrs in order to differentiate it from that obtained using a Molspin pulse magnetiser and a Molspin spinner magnetometer (SIRM, see Chapter 2). Coercivity (Hc) is the field reducing the saturation magnetisation to zero while coercivity of remanence (Hcr) is the field reducing the saturation isothermal remanence to zero. Hc is a measure of magnetic stability and particularly sensitive to magnetic mineralogy and grain size. Hcr is also a relatively straightforward, very useful hysteresis parameter which can be used in determining magnetic mineralogy and grain size and in helping to characterise magnetic mixtures. The magnetisation ratio of saturation remanence to saturation magnetisation, Mrs / Ms , is a sensitive indicator of magnetisation state whilst the coercivity ratio Hcr / Hc relates the coercivity of remanence to the saturation coercivity. Magnetic materials can be neatly classified by determining their magnetisation and coercivity ratios (Day *et al.*, 1977).

9.2 Magnetic properties of Bootle dust deposition

The magnetic measurements of Bootle dust samples are summarised in Table 9.1. χ_{HIGH} / χ_{LF} values range from 1.6 to 5.8 %, indicating that the total contributions of paramagnetic, diamagnetic, and canted antiferromagnetic components to the total susceptibility are not significant. SOFT percentage (26.8 - 37.8 %) and HARD percentage (1.3 - 3.6 %) values and χ_{LF} values ($> 350 \times 10^{-8}$ m^3 kg^{-1}) also suggest the dominance of ferrimagnetic minerals (Oldfield and Richardson, 1990; Dearing *et al.*, 1996a). Therefore, both sites show that ferrimagnetic minerals are the major contributor of magnetic properties.

Two approaches are applied to analyse grain size components of ferrimagnets. One is the magnetization ratio Mrs / Ms versus the coercivity ratio Hcr / Hc plot (Day *et al.*, 1977, modified by Thompson and Oldfield, 1986). Another is a semi-quantitative mixing model using the χ_{FD} percentage versus χ_{ARM} /SIRM plot (Dearing *et al.*, 1997). The Mrs / Ms v. Hcr / Hc plot (Fig. 9.1a) shows dominance of MD / PSD and SP grains. Two sites show distinguishable Hcr / Hc values, which is supported by plotting Hcr / Hc values over sampling periods for two sites (Fig. 9.2). The χ_{FD} percentage v. χ_{ARM} /SIRM plot (Fig. 9.1b) also suggests major contributions of MD / PSD and SP grains. However, the χ_{ARM} /SIRM values of 3 SDC site samples are > 0.20×10^{-3} m A^{-1}), falling into the coarse SSD grain size region. Inconsistent evidence of SSD contributions in the SDC site samples may be due to: (1) measurement errors in magnetic parameters caused by small amounts of dust (0.027 - 0.193 g and 0.015 - 0.051 g for the SDB and SDC site respectively); (2) uncertainties in the hysteresis loop parameters due to possibly high internal stress in ferrimagnets present in the samples (Flanders, 1999); and (3) effects of non-magnetite ferrimagnets in the samples. Obviously, independent evidence using other techniques, such as microscopic examination, is required to assess the presence SSD grains in the samples, which will be a topic in future studies.

Fig. 9.2 shows temporal variations of dust deposition and its magnetic properties. Dust deposition at the SDB site is higher than that at the SDC site, 13.9 - 229.7 % higher, 146.3 % on average, and over 2 times higher during the sampling periods of 28 February - 27 April, 25 May - 17 August, and 12 October - 10 November 1996. Although both the SDB and the SDC site show similar magnetic properties, they can be differentiated using some magnetic parameters, either concentration dependent or independent, such as χ_{LF}, SIRM, and Hcr / Hc. This implies a potential application of magnetic techniques in the study of dust deposition that magnetic measurements may be used as a source apportionment tool since the difference of magnetic properties in two sites may reflect their different sources.

9.3 Summary

This study suggests that ferrimagnetic minerals are the dominant magnetic component in Bootle dust samples and that MD / PSD and SP grains are the main contributors of magnetic properties although there is evidence of possible presence of SSD grains. Both two studied sites show similar magnetic properties, but they can be differentiated using some magnetic parameters, either concentration dependent or independent, such as χ_{LF}, SIRM, and Hcr / Hc. The difference of magnetic properties at the two sites may reflect their different sources, suggesting that magnetic measurements may be used as a source apportionment tool.

Table 9.1 Magnetic measurements of Bootle dust deposition.

Magnetic parameter	Unit	Range (SDB site)	Mean ± S.D. (SDB site)	Range (SDC site)	Mean ± S.D. (SDC site)
χ_{LF}	$10^{-8}\,m^3\,kg^{-1}$	715.3 – 1183.1	1001.7 ± 143.6	372.5 – 814.3	582.9 ± 135.1
χ_{FD}	$10^{-8}\,m^3\,kg^{-1}$	17.4 – 121.9	34.1 ± 29.4	0.0 – 65.1	26.0 ± 18.2
χ_{FD} percentage	%	1.7 – 11.7	3.5 ± 3.0	0.0 – 9.5	4.4 ± 2.7
χ_{ARM}	$10^{-8}\,m^3\,kg^{-1}$	1410.5 – 2236.5	1849.4 ± 257.8	578.1 – 2862.9	1131. 3 ± 589.5
SIRM	$10^{-5} A\,m^2\,kg^{-1}$	6929.1 – 9674.3	7598.1 ± 5811.5	3694.2 – 9674.3	5677.6 ± 1723.3
SOFT	$10^{-5} A\,m^2\,kg^{-1}$	2998.7 – 5244.4	4092.1 ± 692.3	1055.9 – 3377.2	1770.8 ± 683.2
HIRM	$10^{-5} A\,m^2\,kg^{-1}$	186.5 – 484.2	333.5 ± 104.0	61.0 – 348.5	139.7 ± 72.8
χ_{ARM} /SIRM	$10^{-3}\,m\,A^{-1}$	0.12 – 0.18	0.15 ± 0.02	0.15 – 0.30	0.19 ± 0.04
SOFT percentage	%	29.4 – 37.8	32.1 ± 2.6	26.8 – 36.7	30.7 ± 3.0
HARD percentage	%	1.3 – 3.5	2.6 ± 0.6	1.6 – 3.6	2.4 ± 0.5
χ_{HIGH}	$10^{-8}\,m^3\,kg^{-1}$	14.5 – 32.7	26.1 ± 6.0	10.1 – 40.9	20.7 ± 8.6
χ_{HIGH} / χ_{LF}	%	1.6 – 3.3	2.6 ± 0.5	2.2 – 5.8	3.5 ± 1.3
Ms	$10^{-5} A\,m^2\,kg^{-1}$	64689.1 – 167966.8	134217.2 ± 28849.4	400012.3 – 97003.3	61546.8 ± 18641.7
Mrs / Ms		0.10 – 0.11	0.10 ± 0.00	0.07 – 0.12	0.09 ± 0.01
Hc	mT	8.5 – 9.9	9.3 ± 0.4	6.5 – 9.2	8.2 ± 0.8
Hcr	mT	28.5 – 33.4	32.1 ± 1.5	28.6 – 36.9	33.5 ± 2.3
Hcr / Hc		3.3 – 3.7	3.5 ± 0.1	3.5 – 5.1	4.1 ± 0.4

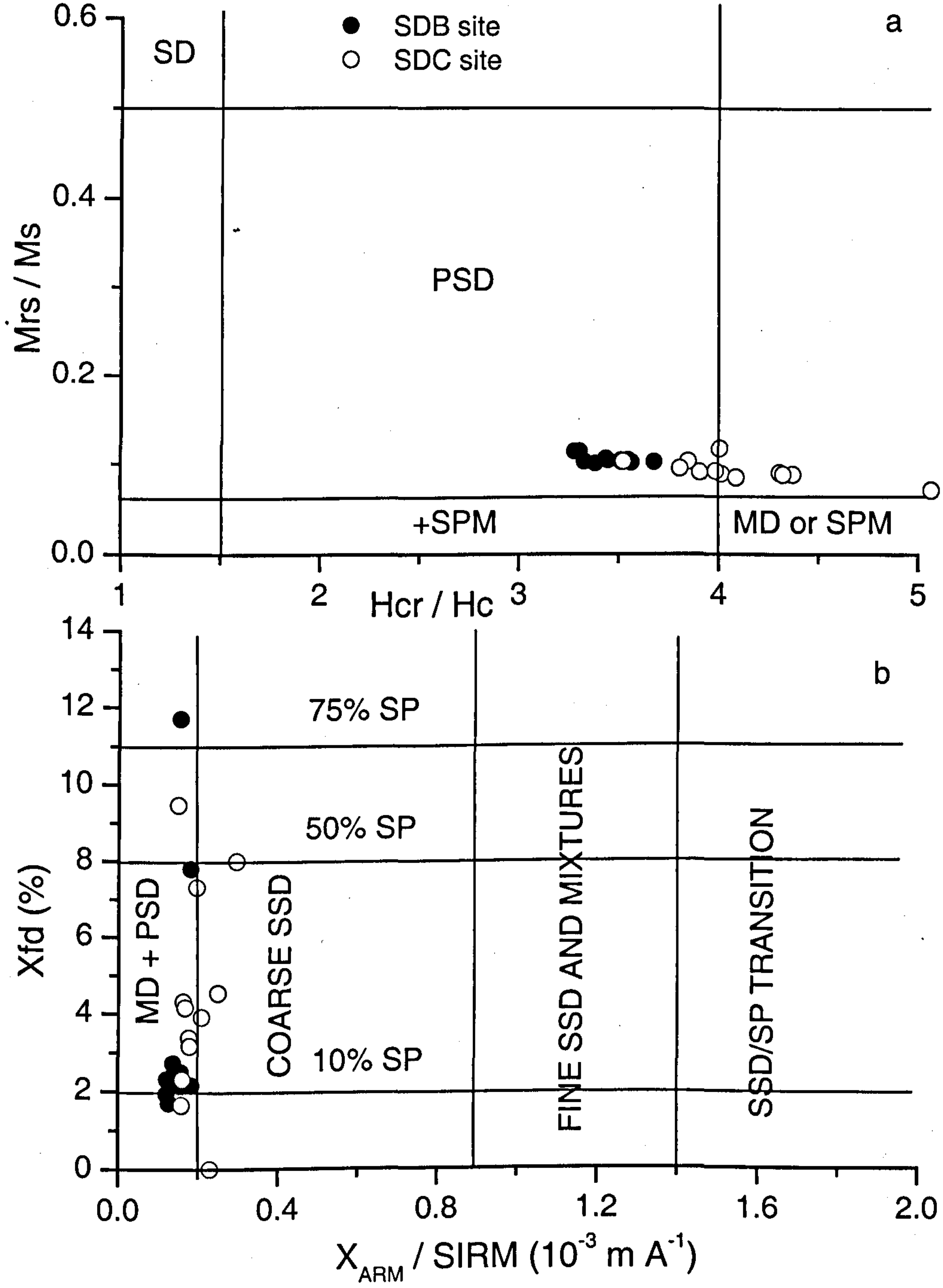

Fig. 9.1 Ferrimagnetic grain size analysis of Bootle dust samples (SDB and SDC sites). (a) The plot of the magnetization ratio Mrs / Ms versus the coercivity ratio Hcr / Hc (Day *et al.*, 1977, modified by Thompson and Oldfield, 1986). (b) The plot of χ_{FD} percentage versus χ_{ARM} /SIRM (Dearing *et al.*, 1997).

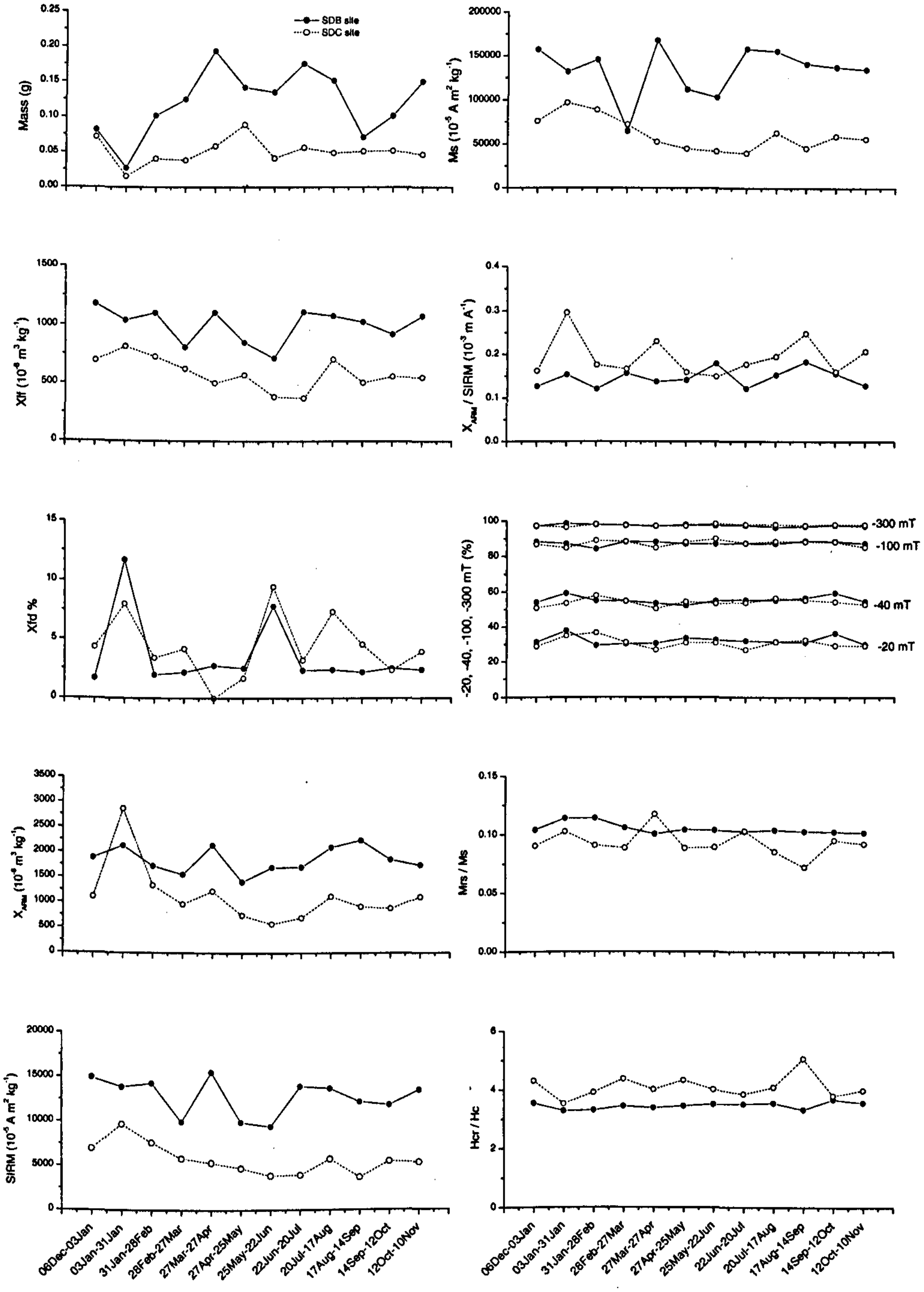

Fig. 9.2 Temporal variations of magnetic properties of Bootle dust samples. Although both the SDB and the SDC site show similar magnetic properties, they can be differentiated using some magnetic parameters, either concentration dependent or independent, such as χ_{LF}, SIRM, and Hcr / Hc.

This study also raises some questions for further investigations of magnetic measurements of dust deposition. First, the Mrs / Ms v. Hcr / Hc plot and the χ_{FD} percentage v. χ_{ARM} /SIRM plot suggests inconsistent evidence of SSD contributions in some samples. Further analysis is needed to provide independent evidence. Second, more information is required to support the interpretation of magnetic differences at two sites as source difference. This can be achieved by investigation of major component contributions to dust magnetic material. Finally, many magnetic pollution studies suggest that magnetic measurements could be used as proxies for heavy metal pollution (Petrovsky and Ellwood, 1999), mutagenecity (Morris *et al.*, 1995) and organic matter (see Chapter 6). Can these results be applicable for Bootle dust deposition?

Chapter 10. Conclusions

10.1 Conclusions

Since the publication of Environmental Magnetism (Thompson & Oldfield, 1986), there is increasing interest in the application of the methodology to a wide range of research tasks. At the same time, there is a persistent need for the theoretical and empirical basis for the interpretation of magnetic measurements to be improved (Oldfield, 1999b). Magnetic techniques have now been applied to study atmospheric particulates, a significant hazards for health in many urban areas worldwide, at diverse geographic locations in samples of modern suspended dusts, road dusts, polluted organic soils, contaminated building surfaces, polluted leaf and tree bark surfaces, and pre- and post-industrial sediment records. The presence of Fe in virtually all these dust types, existing in a variety of chemical and physical forms, provides a basis for characterizing and monitoring dusts using easily and non-destructively measured magnetic properties. Significant evidence exists to suggests that magnetic measurements may be successfully used to determine areas influenced by specific pollution sources, to identify pollution pathways, to classify particulate sources, to analyse their Fe-mineralogy and grain-size, to model multiple source contributions in bulk samples, and to provide an effective proxy for organic and inorganic compounds and potential health risk (See Shu *et al.*, 2000). This thesis presents an effort in the development of environmental magnetism, particularly the application of magnetic techniques in the study of urban dusts, using samples of Liverpool road dust and Bootle deposited dust.

1. This study suggests mixed dominant ferrimagnetic phases in Liverpool street dust although magnetite is probably a major one. In terms of grain size, the dominant component comprises MD + PSD grains, with SP and SSD ferrimagnetic grains and paramagnetic, diamagnetic, and canted antiferromagnetic minerals are present small magnetic concentrations. Samples of different particle sizes and of different sampling periods show similar magnetic properties.

2. Using the Liverpool street dust data set as a case study, this study demonstrates that the partial susceptibility technique is able to model the contributions of main magnetic components satisfactorily. The advantage of the technique is that complex magnetic data are reduced to magnetic susceptibilities, which can then be compared quantitatively against each other in the percentage or ratio form. In addition to the semi-quantitative mixing model (Dearing *et al.*, 1997), other possible alternatives, such as TEM studies of magnetic extracts and studies of synthetic samples, can be used to validate the partial susceptibility technique in future studies.

3. There are some high and low value areas for magnetic parameters, element concentrations, and the organic matter content, in the sampling region, which may be due to the localised sources. Some measurements, such as χ_{LF} and Pb, show a similar spatial distribution, whilst some measurements, such as χ_{LF} and the organic matter content, show different distribution patterns. Comparison between ninety-seven sampling sites and nineteen revisited sites suggests that representative magnetic properties, and mean values of some element concentrations and the organic matter content may be obtained with a small number of samples from a sampling period of one or several days. These results provide useful information for future

environmental monitoring and assessment of street dust, particularly magnetic studies of sediment tracing in the urban environment.

4. There are good linear correlations between the organic matter content and some magnetic mineral concentration-related parameters (χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, and χ_{HIGH}) in bulk samples of the first sampling period. Among them, frequency dependent susceptibility (χ_{FD}) shows the highest correlation coefficient value. χ_{FD} percentage also demonstrates a close association with the organic matter content, with a significant correlation for < 63 μm fraction samples and a highly significant correlation for > 63 μm fraction and bulk samples. This suggests that re-entrainment of soil is probably a major source of the organic material present in street dust. The ratio χ_{ARM} /SIRM shows a highly significant correlation with the organic matter content for <150 μm fraction samples. 19 revisited site samples (<63 μm fraction) of four sampling periods also show a significant correlation between the organic matter content and χ_{ARM} / SIRM. This study demonstrates several implications for the application of magnetic methods in the study of street dust. First, the simple, rapid, and non-destructive magnetic measurements may be used as proxies for the organic matter content in street dust. Second, magnetic measurements could provide useful information about source apportionment of street dust organic matter, provided the origins of the relevant dust magnetic components are satisfactorily resolved. Finally, small concentrations of magnetic components, such as SP ferrimagnetic grains, may still have significant environmental implications.

5. The samples (< 63 μm fraction) demonstrate positive correlations between concentration dependent magnetic parameters χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, SOFT, and

HIRM, and between magnetic parameters χ_{LF}, χ_{ARM}, SIRM, and SOFT and elements Ti, Fe, Pb, and Zn. This suggests mixed contributions of magnetic material from urban and natural sources, probably mainly urban sources. Factor analysis seems to support this suggestion. This study implies that analysis of associations between magnetic properties and element concentrations may be a potential approach for source identification of magnetic material in the environment.

6. Element concentration variations with particle size were examined using the first period samples. Pb, Zn, and Rb concentrations decrease substantially with increasing particle size for size fractions < 300 μm, but increase considerably for size fractions >300 μm. S shows a different trend. The concentrations do not change significantly with increasing particle size for size fractions < 150 μm, but decrease considerably from size fraction 64-150 to 151-300 μm, then keep relatively unchanged for size fractions >150 μm. These variation patterns suggest that the aggregation process is not a controlling factor. This study confirms that the particle size effect is an important factor in dust sampling, comparison of measurement data, and source tracing in the urban environment and that studies of street dust should place emphasis on fine particles. Dust Pb consists mainly of freshly deposited vehicle Pb and aged soil Pb. It is argued that the contribution of aged Pb in urban soil to dust Pb may contribute to the difference of Pb concentration reductions between petrol and dust.

7. This study suggests that ferrimagnetic minerals are the dominant magnetic component in Bootle dust samples and that MD / PSD and SP grains are the main contributors of magnetic properties although there is evidence of presence of SSD grains. Both studied sites show similar magnetic properties, but they can be

differentiated using some magnetic parameters, either concentration dependent or independent, such as χ_{LF}, SIRM, and Hcr / Hc. The difference of magnetic properties in two sites may reflect their different sources, suggesting that magnetic measurements may be used as a source apportionment tool.

Finally, some particular results presented in this study may be specific to Liverpool street dust and Bootle dust deposition; others probably are not, but are more general and thus may be useful elsewhere. Moreover, the way to investigate these issues has wider validity and the findings make a useful contribution to the application of magnetic techniques to pollution studies.

10.2 Future work

It appears that there are varying degrees of success in environmental applications of magnetic measurements. Some areas of applications are quite prominent and promising, e.g., loess studies, which have expanded out of all recognition. Some areas, e.g., atmospheric particulate studies, may not be addressing sufficiently important questions (See Oldfield, 1999b). This may reflect the limitations of magnetic measurements in some research areas. For example, small sample size still limits magnetic applications to the study of fine air-borne particulates. On the other hand, this may also suggest that new scientific insights are still to come.

1. In this study, a semi-quantitative mixing model using the χ_{FD} percentage versus χ_{ARM} /SIRM plot (Dearing *et al.*, 1997) is applied to analyse ferrimagnetic grain size components of dust samples. Supporting evidence of the partial susceptibility

technique, using the Liverpool street dust data set as a case study, is also provided by the mixing model. However, the precise nature of 'measured' SP mineral phases is the subject of debate (e.g., Wörm, 1998) and remains enigmatic. Due to a wide range of possible applications of SP grains (usually iron oxides) in environmental studies as proxies for present or past environmental conditions, hence, there is a clear need to provide unequivocal information about SP grains in natural environmental samples. Progress is hindered for the following reasons: a) calibration of magnetic measurements on 'pure' samples of SP grains is frustrated by the difficulty of extracting grains with small magnetic moments from natural samples; b) microscopic (TEM) examination of SP iron oxides (typically 0.005 - 0.025 μm) is time-consuming and requires initial magnetic extraction; c) SP iron oxides produced by chemical precipitation are not easily controlled for a known and narrow grain-size distribution, and degree of interaction; d) the nature of superparamagnetism in natural weakly magnetic minerals, like haematite, is poorly understood. SP grains display magnetic properties dependent upon temperature, grain volume, magnetic field frequency, and measurement time. Magnetic techniques are now available that can exploit all these properties and evaluate the different techniques against each other and against physical theory, to address the following questions (Dearing, 2000):

- How effective is each technique for identifying and quantifying SP grains and sizes?
- Can the techniques be used to identify weakly magnetic SP phases?
- Can a procedure be designed that optimises and standardises measurements of SP grains?

2. In Liverpool street dust, both SP ferrimagnetic grains and organic matter may come from a wide range of natural and urban sources. Further evidence is required to support the unsettling interpretation of correlations between χ_{FD} percentage and the organic matter content as reflecting re-entrainment of soil organic material in street dust. Combination of magnetic, microscopic, and geochemical analyses may offer an alternative means for identifying and quantifying source attributions of magnetic particles and organic matter.

3. The suggested approach through the analysis of associations between magnetic properties and element concentrations, which can be achieved using some techniques, such as correlation analysis and factor analysis, to the source identification of magnetic material provides a potential source apportionment tool for magnetic material in natural environmental samples. This approach needs further investigations using current methods for discriminating between magnetic sources include diagnostic magnetic measurements and complementary geochemical and microscopic analysis.

4. The study of Bootle dust deposition also raises some further research topics. First, the Mrs / Ms v. Hcr / Hc plot and the χ_{FD} percentage v. χ_{ARM} /SIRM plot suggests inconsistent evidence of SSD contributions in some samples. Further magnetic, microscopic, and geochemical analyses are needed to provide independent evidence. Second, more information is required to support the interpretation of magnetic differences at two sites as source difference. This can be achieved by investigating dust transport processes. Finally, many magnetic pollution studies suggest that magnetic measurements could be used as proxies for heavy metal pollution

(Petrovsky and Ellwood, 1999), mutagenecity (Morris *et al.*, 1995) and organic matter (See Chapter 6). Can these results be applicable for Bootle dust deposition?

5. Research progress in the application of magnetic techniques to dust pollution studies has shown that the sources of dusts may be distinguished by using sensitive magnetic parameters, based on the magnetic differences of source material, such as magnetic minerals (Hunt *et al.*, 1984), magnetic grain sizes (Oldfield *et al.*, 1985), and the stress developed in the formation of the magnetic oxides (Flanders, 1994; 1999). These results suggest the possibility for magnetically characterizing dusts derived from different sources. However, the present knowledge is inadequate about the distinctive magnetic signatures of various dust sources, such as from fossil-fuel combustion, from other industrial processes, and from soil erosion. As a result, the current magnetic detection methods are difficult and uncertain. Further developments in this direction, for example finding unique magnetic components and/or properties relating to specific source material, will enable the methodology, in pollution studies, to play a greater role, such as quantitative or semi-quantitative identification of source contributions in the dust samples by using magnetic markers, and to achieve a wider recognition, such as incorporating magnetic measurements into routine environmental monitoring of particulate matter.

In summary, this thesis attempts to make a useful contribution to environmental magnetic techniques, as well as their applications to the studies of urban dusts. It provides useful information for urban dust pollution studies, particularly in Liverpool and Bootle areas. This study also poses some questions for further investigations.

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The organic matter content of street dust in Liverpool, UK, and its association with dust magnetic properties

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Abstract

The organic matter content of street dust in Liverpool, UK, measured by means of the loss-on-ignition method, is 4.0% on average (standard deviation 1.3%). The magnetic measurements of the street dust samples indicate that the dominant magnetic component is multidomain grains of ferrimagnetic minerals and that superparamagnetic and stable single-domain ferrimagnetic grains and paramagnetic, diamagnetic, and canted antiferromagnetic minerals are present in small magnetic concentrations. Our study demonstrates good linear correlations between the organic matter content and some magnetic mineral concentration-related parameters: low-frequency susceptibility, frequency-dependent susceptibility, susceptibility of anhysteretic remanent magnetisation, and high-field susceptibility. Among them, frequency-dependent susceptibility shows the strongest correlation, suggesting that soil may be an important source of dust organic material. Finally, it is suggested that simple, rapid, and non-destructive magnetic measurements may be used as proxies for the organic matter content in street dust. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Organic matter; Loss-on-ignition; Magnetic properties; Frequency-dependent susceptibility; Street dust

1. Introduction

Street dust, as pollution material, has received much attention due to its potential health risk to children through hand-to-mouth activities (Fergusson and Kim, 1991; Fergusson, 1992). Street dust is also an important source of house dust (Adgate et al., 1998) and urban atmospheric particulate matter (Harrison et al., 1997). In addition, street dust could degrade the quality of urban water runoff (Sartor and Caboury, 1984). Many studies on street dust have focused on elemental contents (e.g., De Miguel et al., 1997). Among them, Pb has been the most frequently investigated element because of its human health hazard (Linton et al., 1980; Nageotte and Day, 1998). However, few studies have been carried out on the organic matter content of street dust. Fergusson and Ryan (1984) estimated the organic matter content of street dust samples from two large urban areas (London, UK; and New York, USA) and three small cities (Halifax, Canada; Christchurch, New Zealand; and Kingston, Jamaica), by means of loss-on-ignition (LOI) measurements. Hildemann et al. (1991) and Rogge et al. (1993) analysed the organic matter content and the organic constituents of fine road dust particles in Los Angeles area, USA. Yang and Baumann (1995) reported seasonal and areal variations of polycyclic aromatic hydrocarbon (PAH) concentrations of street dust in some German cities. Al-Chalabi and Hawker (1996) also analysed the organic matter content in the street dust samples of Brisbane, Australia. Toxic components of organic matter in the urban environment, such as PAHs, are a cause of environmental concern (National Research Council, 1983). Hildemann et al. (1991) suggested that fine particulate road dust is an important contributor of organic materials to urban fine atmospheric particulate. In addition, Glikson et al. (1995) suggested that the organic composition of dust may have important health implications for asthma sufferers. Therefore, organic material in street dust has significant environmental implications.

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Pioneering work in environmental magnetism has demonstrated different magnetic characteristics of atmospheric dusts derived from soil, coal-fired power stations, and vehicular exhausts, and suggested that simple, rapid, and non-destructive magnetic measurements can be of considerable value in characterising atmospheric dust sources (Oldfield et al., 1985; Thompson and Oldfield, 1986; Dearing et al., 1995; Hay et al. 1997). Hunt et al. (1984) also investigated linkage between magnetic properties and heavy metals in atmospheric particulate matter of anthropogenic origin from power station fly ash and motor vehicle emissions. Recently, Morris et al. (1995) observed a strong linear correlation between mutagenicity and magnetic susceptibility of respirable airborne particulate matter in Hamilton, Canada. They suggested that magnetic susceptibility measurements could be used to pre-select filters for more extensive evaluations such as by organic compound analyses or biological assays. In terms of street dust, Beckwith et al. (1986) and Charlesworth and Lees (1997) examined associations between heavy metal concentrations and magnetic properties. However, little work has been reported in the literature on association between the organic matter content and magnetic properties of urban street dust.

This paper reports a study of the organic matter content and its association with magnetic properties of street dust in Liverpool, United Kingdom. Firstly, the effect of ignition temperature and time on the loss-on-ignition measurements is examined. Secondly, the organic matter content and the magnetic properties of the street dust are analysed. Finally, the correlation between the organic matter content and the magnetic properties is investigated.

2. Materials and measurements

Liverpool is a coastal city in northwest England, with a population of about half a million. The street dust survey area was within ~1.5 km of the city centre. Sampling began when the street dust was dry after several rainless days and took place over seven days in January–February 1998. During this period, the weather remained dry. Ninety-seven dust samples were obtained from street gutters or pavements, where dust had accumulated, by ground sweeping with a polyethylene scoop and a brush. The dust sampling sites were distributed over diverse locations: pedestrian streets, gardens, and roads with different traffic densities. Six soil samples were collected from the top 10 cm of bare soil surfaces in roadsides, gardens, or waste land. The soil sample sites were selected from roadside bare soil where soil was qualitatively observed to have contributed to nearby street dust. All the dust and soil samples were put into clean self-sealing plastic bags. They were air-dried in the laboratory, then passed through a 1 mm sieve, to remove refuse and small stones.

Weighed subsamples (> 1 g) of the dust and soil samples were oven-dried at 105°C overnight, reweighed and then ignited in a muffle furnace. The value of loss-on-ignition is then expressed as the percentage of weight lost after the 105°C oven-drying. There seems to be some discrepancy in just how the loss-on-ignition method should be applied. Different authors have used different temperatures and different periods of time (e.g., Fergusson and Ryan, 1984; Al-Chalabi and Hawker, 1996). For the purpose of comparison, several ignition procedures were carried out (see Table 1). Ignition at 375°C for 4 h, at 375°C for 16 h, and at 850°C for 0.5 h was carried out on the same subsamples, and at 450°C for 4 h on further subsamples.

Magnetic measurements were carried out on different subsamples. Low-field AC magnetic susceptibility was measured on 10 cm^3 samples using a dual-frequency (470 and 4700 Hz) Bartington Instruments MS2 sensor on the 0.1 scale. The difference between low- and high-frequency susceptibility (χ_{LF}-χ_{HF}) is expressed as a mass specific term (χ_{FD} 10^{-8} m^3 kg^{-1}) and as a percentage of the low-frequency susceptibility (χ_{FD} percentage). Anhysteretic remanent magnetisation (ARM) was induced in a steady field of 0.1 mT with a parallel peak alternating field of 100 mT using a DTECH AF demagnetiser and measured on a Molspin spinner magnetometer. Measurements are expressed as susceptibility of ARM (χ_{ARM} 10^{-8} m^3 kg^{-1}) by dividing the remanence by the steady field. Acquisition of isothermal remanent magnetisation (IRM) in the fields of 1T (SIRM), −20 mT (reverse) ($IRM_{-20\ mT}$), and −300 mT (reverse) ($IRM_{-300\ mT}$) was carried out using a Molspin pulse magnetiser, and measured on a Molspin spinner magnetometer. Measurements are expressed in 10^{-5} A m^2 kg^{-1} for SIRM, SOFT (=(SIRM-$IRM_{-20\ mT}$)/2), and HIRM (=(SIRM-$IRM_{-300\ mT}$)/2) on a mass specific basis, and as percentages (%) for reverse field ratios of SOFT (−20 mT) and

Table 1
Comparison of loss-on-ignition values between ignition at 375°C for 16 h and other ignition procedures

Ignition procedure	Sample number[a]	Correlation coefficient	Mean difference (%)
At 375°C for 4 h	91	0.953[b]	− 9.9
At 450°C for 4 h	91	0.960[b]	9.0
At 850°C for 0.5 h	90	0.800[b]	114.6

[a] Samples with loss-on-ignition values more than 1.5 box-lengths away from the box of the boxplot are identified as outliers and excluded.

[b] Correlation is significant at the 0.01 level.

HARD (−300 mT) (SOFT percentage = 100 SOFT/SIRM, HARD percentage = 100 HIRM/SIRM). High field susceptibility χ_{HIGH} was obtained on 1 cm^3 samples using a Molspin vibrating sample magnetometer in the field of 0.8–1 T. Measurements are expressed as a mass specific term (10^{-8} m^3 kg^{-1}).

3. Results and discussion

3.1. Effect of ignition temperature and time on loss-on-ignition values

Loss-on-ignition is a current common technique to estimate the organic matter content in soil samples. Ignition at 375°C removes organic matter without structural water loss from inorganic soil components, or the loss of inorganic carbon compounds, which occurs at >400°C; the removal of both of these will result in an overestimation of the organic matter content (Boon et al., 1998). Ignition at temperatures below 375°C removes appreciably less of the carbonaceous matter and is therefore not suitable (Ball, 1964). In terms of heating time, Ball (1964) employed the procedure of ignition at 375°C for 16 h on soil samples, which resulted in >90% organic matter removal without loss of structural water. Recently, Boon et al. (1998) applied the LOI technique (ignition at 375°C for 4 h) to measure the organic matter content of suspended and deposited dusts in Australia. Despite a >1 g requirement of material in the LOI technique (Spain et al., 1983), the Boon et al. (1998) laboratory test shows that the lower limit for acceptable replicated results is 0.0012 g for the dust samples.

Samples with LOI values more than 1.5 box-lengths away from the box of the boxplot are identified as outliers and excluded in the following comparison analysis. Table 1 shows good correlations between the LOI values at 375°C for 16 h and those of other ignition procedures. However, as expected, the LOI values at 375°C for 4 h are lower than or equal to those at 375°C for 16 h. Due to loss of structural water from inorganic soil compounds or of inorganic carbon compounds at 450°C, the LOI values at 450°C for 4 h are generally higher than those at 375°C for 16 h. Nevertheless, the mean differences between the LOI values at 375°C for 16 h and those at 375°C or 450°C for 4 h are within 10% on average. Therefore, the procedure of ignition at 375°C or 450°C for 4 h may be used to estimate the organic matter content in street dust, in spite of the possible underestimation or overestimation of the organic matter content. An ignition temperature at 850°C causes greater loss of structural water from inorganic soil compounds or of inorganic carbon compounds. As a result, the LOI values at 850°C for 0.5 h are more than double of those at 375°C for 16 h, on average. The procedure of ignition at 375°C for 16 h is used to measure the organic matter content of the Liverpool street dust and surface soil samples.

3.2. The organic matter content of street dust

The dust organic matter level ranges from 1.0 to 10.1%. After eliminating six outliers, it ranges between 1.0 and 7.0% (average 4.0%, standard deviation 1.3%). No outlier in the surface soil samples is detected using the boxplot analysis. The organic matter content of surface soil is between 3.4 and 8.6% (average 5.6%, standard deviation 1.8%). It seems that the organic matter content of dust is lower than that of soil, but the comparison is inconclusive because of the small number of soil samples. Fergusson and Ryan (1984) estimated the organic matter content of street dust samples from different city types, ranging from 3.5 to 18.3%, by ignition at 500°C for 16 h. Al-Chalabi and Hawker (1996) reported a mean organic matter content of 4.1% in their samples (ignition at 500°C for 12 h). Their results may overestimate the organic matter content due to the high ignition temperature (>400°C). Hildemann et al. (1991) showed a high level (17%) of organics in their fine particulate road dust samples. In general, our results fall within the ranges of previous studies.

The Liverpool street dust samples were subdivided into two groups according to the type of locality (major streets with heavy or moderate traffic, 66 samples, and minor streets with light traffic, 25 samples; after excluding six outliers using the boxplot analysis). The mean organic matter contents are 4.1% (standard deviation 1.2%) and 3.6% (standard deviation 1.5%) for major and minor streets, respectively. The *t*-test result shows that the difference between the mean organic matter content for major streets and that for minor streets is not significant at the 0.05 level, suggesting insufficient evidence of the significant contribution of the organic matter from the traffic-related sources. Qualitative observation of the street dust samples during the field work and under a microscope in the laboratory shows the presence of soil material, weathered building material, plant fragments, and urban refuse, which may be the major sources of dust organic material.

3.3. Magnetic properties of street dust

The magnetic measurement results of dust samples are summarised in Table 2, where outliers are also identified as samples with values more than 1.5 box-lengths away from the box of the boxplot. Because the dust organic matter content is not high (1.0–10.1%), it is expected that its diluting effect on the dust magnetic concentration is not significant. The magnetic susceptibility χ_{LF} represents the total contribution of magnetic minerals in a sample. For natural materials, it is mainly a function of their ferrimagnetic content (Thompson and Oldfield, 1986).

Table 2
Magnetic measurement results of street dust

Magnetic parameter	Unit	Sample number[a]	Range	Average	Standard deviation
χ_{LF}	10^{-8} m^3 kg^{-1}	92	41.4–443.1	236.6	86.9
χ_{FD}	10^{-8} m^3 kg^{-1}	94	0.5–7.5	4.0	1.5
χ_{FD} percentage	%	96	0.9–2.5	1.7	0.4
χ_{ARM}	10^{-8} m^3 kg^{-1}	93	92.7–855.7	462.2	151.1
SOFT	10^{-5}A m^2 kg^{-1}	91	216.7–2297.0	1277.6	454.6
HIRM	10^{-5}A m^2 kg^{-1}	93	2.6–106.0	47.3	24.8
χ_{ARM}/SIRM	10^{-3} m A^{-1}	95	0.09–0.19	0.14	0.02
SOFT percentage	%	93	33.5–42.8	37.9	1.8
HARD percentage	%	95	0.1–4.2	1.5	0.9
χ_{HIGH}	10^{-8} m^3 kg^{-1}	96	1.4–14.1	6.4	2.8
χ_{HIGH}/χ_{LF}	%	93	1.5–3.8	2.5	0.5

[a]Samples with measurement values more than 1.5 box-lengths away from the box of the boxplot are identified as outliers and excluded.

Frequency-dependent susceptibility χ_{FD} is related to the superparamagnetic (SP) component (Dearing et al., 1996a), while the content of stable single domain (SSD) grains can be estimated by ARM or χ_{ARM} (King et al., 1982; Maher, 1988). Thompson's (1986) calculations suggest that SOFT is expected to be approximately proportional to the multidomain (MD) grain content of ferrimagnetic components in a sample. Oldfield and Richardson (1990) suggested that HIRM can be used as a rough guide to canted antiferromagnetic components in a sample. High-field susceptibility χ_{HIGH} detects the total contributions of paramagnetic, diamagnetic, and canted antiferromagnetic components (Richter and van der Pluijm, 1994). SOFT percentage and HARD percentage can be used as approximate indications of relative importance of ferrimagnetic and canted antiferromagnetic components in a sample, respectively (Oldfield and Richardson, 1990). Plots of the ratio χ_{ARM}/SIRM versus χ_{FD} percentage can be used to estimate grain sizes in ferrimagnetic minerals (Dearing et al., 1997). Table 2 shows that the χ_{HIGH}/χ_{LF} values range from 1.5 to 3.8% (average 2.5%), indicating that the total contributions of paramagnetic, diamagnetic, and canted antiferromagnetic components to the total susceptibility are not significant. SOFT percentage (33.5–42.8%) and HARD percentage (0.1–4.2%) values and χ_{LF} values ($>50\times10^{-8}$ m^3 kg^{-1}, with the exception of one sample) also suggest that the dominant magnetic minerals are ferrimagnetic (Oldfield and Richardson, 1990; Dearing et al., 1996a). By comparison of χ_{FD} percentage (0.9–2.5%) and χ_{ARM}/SIRM (0.09–0.19×10^{-3} m A^{-1}) data to a semi-quantitative mixing model (Dearing et al., 1997), the proportions of SP, SSD, and MD grains are estimated as ~10, ~0, and ~90%, respectively. Therefore, the dominant magnetic component is MD ferrimagnetic grains. SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals are present in small magnetic concentrations.

The most common source of SP grains is surface soil. The major formation machanisms of SP grains in soil are through weathering and fermentation processes and by burning (Dearing et al., 1996b). In their method of magnetic differentiation of atmospheric dusts, Oldfield et al. (1985) used the frequency-dependent component of total magnetic susceptibility (χ_{FD} percentage) to estimate the contribution of soil-derived material in atmospheric dusts. Our χ_{FD} measurements indicate the presence of soil material in the Liverpool street dust samples.

3.4. *Association of the organic matter content with magnetic properties*

Table 3 shows that there is a good correlation between the organic matter content and χ_{LF}, χ_{FD}, χ_{ARM}, or χ_{HIGH} and that there is insufficient evidence of correlation between the organic matter content and SOFT or HIRM. Outliers, identified as samples with values more than 1.5 box-lengths away from the box of the boxplot, are not included in the correlation analysis (Table 3). The linear regression for the organic matter content and frequency-dependent susceptibility is shown in Fig. 1. The correlation coefficient increases from 0.509 ($N = 88$, see Table 3) to 0.607 ($N = 84$, see Fig. 1) after eliminating other four outliers identified as samples with standardised residual values of more than two standard deviations above or below the regression line. Rogge et al. (1993) identified a variety of sources of organic materials in fine road dust particles, including vehicle exhaust, tyre wear, vegetative plant fragments, and garden soil. The minerogenic components of street dust derive from metallic fragments, concrete/cement, products of tyre wear,

Table 3
Correlation coefficients between the organic matter content and magnetic properties

Magnetic parameter	χ_{LF}	χ_{FD}	χ_{ARM}	SOFT	HIRM	χ_{HIGH}
Correlation coefficient	0.376[b]	0.509[b]	0.353[b]	0.164	0.109	0.397[b]
Sample number[a]	80	88	84	84	87	88

[a] Samples with measurement values more than 1.5 box-lengths away from the box of the boxplot are identified as outliers and excluded.
[b] Correlation is significant at the 0.01 level.

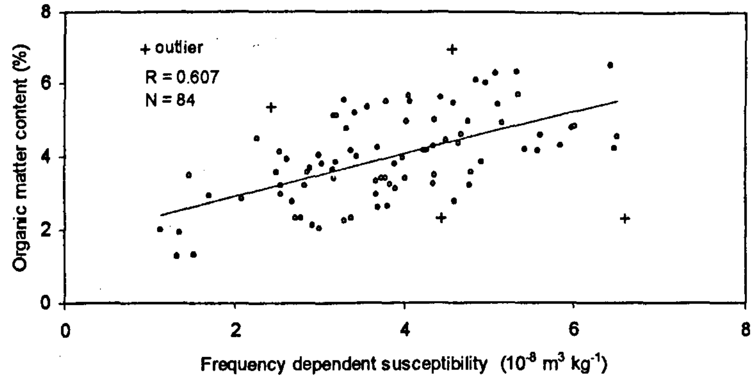

Fig. 1. Correlation between the organic matter content and frequency dependent susceptibility. The correlation coefficient increases from 0.509 ($N = 88$, see Table 3) to 0.607 ($N = 84$) after eliminating other four outliers identified as samples with standardised residual values of more than two standard deviations above or below the regression line.

salt spray, de-icing salt, vehicle emissions, and soil which contributes more than half of dust material (Hopke et al., 1980; Fergusson and Kim, 1991; Fergusson, 1992). Most of these street dust sources will contribute a suite of magnetic particles. Nevertheless, past studies have suggested that SP ferrimagnetic grains are directly tied to soil material. This study demonstrates a close association between the organic matter content and χ_{FD}. Hence this suggests that re-entrainment of soil is probably a major source of the organic material present in street dust. Strong linear correlations between the organic matter content and some magnetic mineral concentration-related parameters, particularly frequency-dependent susceptibility, may enable simple, rapid, and non-destructive magnetic measurements to be used as proxies of the organic matter content in street dust.

4. Conclusions

A study of the organic matter content and its association with magnetic properties of street dust in Liverpool, United Kingdom, is presented. There are good linear correlations between LOI values of ignition at 375°C for 16 h and those of other procedures (at 375°C for 4 h, at 450°C for 4 h, and at 850°C for 0.5 h). Compared with LOI at 375°C for 16 h, which is appropriate as a measurement of the organic matter content in street dust, LOI at 375°C for 4 h underestimates the organic matter level, while LOI at 450°C for 4 h overestimates it. However, the differences between LOI at 375°C for 16 h and LOI at 375°C or 450°C for 4 h are within 10% on average, suggesting that LOI values of ignition at 375°C or 450°C for 4 h may also be used to estimate the organic matter content of street dust. The dust organic matter content is 4.0% on average (standard deviation 1.3%). The results of dust magnetic measurements suggest that the dominant magnetic component is MD grains of ferrimagnetic minerals. SP and SSD ferrimagnetic grains and paramagnetic, diamagnetic, and canted antiferromagnetic minerals are present in small magnetic concentrations. Our study exhibits good linear correlations between the organic matter content and some magnetic mineral concentration-related parameters: low-frequency susceptibility χ_{LF}, frequency-dependent susceptibility χ_{FD}, susceptibility of anhysteretic remanent magnetisation χ_{ARM}, and high-field susceptibility χ_{HIGH}. Among them, χ_{FD} demonstrates the strongest correlation, suggesting that soil may be an important source of dust organic material. Based on this study, it is suggested that simple, rapid, and non-destructive magnetic methods may be used as proxies for the organic matter content in street dust.

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Comment on "Identifying Fly Ash at a Distance from Fossil Fuel Power Stations"

SIR: Flanders (*1*) makes a very useful and important contribution to the application of magnetic techniques to the study of air pollution particulates, using the coercive force field H_c to identify power station fly ash in dust samples. In general terms, we agree with his approach and also his findings that the H_c of dust samples may indicate the proportion of fly ash relative to the total amount of airborne magnetic material (*1*), but we would add some cautionary notes. First, there is a wealth of environmental magnetic results that show the difficulties of quantifying the magnetic component where there is evidence of variable grain sizes and mineral types. For example, the rapid oxidation of magnetite into haematite in fly ash (*2*) may be expected to affect the H_c values described. Other magnetic parameters, such as the 'hard' remanence expressed as the difference between the saturation (10 k_{Oe}) remanence and a moderate (1 k_{Oe}) or high (3 k_{Oe}) back field remanence can be used to semiquantify the haematite component (*3, 4*). Second, samples of dust in and around urban areas, especially close to ground level, contain magnetic particles from various sources (e.g., fly ash, vehicle exhaust, degradation products, emissions from metallurgical industries, surface soil) (*5, 6*). Our knowledge of each is presently inadequate, but it cannot normally be assumed that fly ash or surface soil magnetic particles dominate the magnetic properties. Third, the claim that distance-dependent deposition of magnetic spheres represents only a minor control on particle-size distribution and H_c values is counter to other evidence. For example, the mean particle size of fly ash in the first 30 km around a large coal-fired power station in Spain (*2*) was $>10\ \mu m$, reducing to $<10\ \mu m$ at 46.8 km. Measurements, such as frequency-dependent susceptibility, suggest that there is a small but significant fine ($<0.03\ \mu m$) superparamagnetic magnetite component in fly ash samples (*7*), a range of grain sizes where H_c values are highly variable. We would argue that atmospherically dispersed magnetic particles will show different size distributions with distance from source and may have significant effects on H_c values. An explanation for the measured differences in H_c values for dust samples shown in Figure 6a,b (*1*) may be that there are more larger magnetic particles present in the dust sample from Conesville. Finally, H_c values for fine soil particles are extremely variable with a unimodal distribution peaking in the stable single domain region ($\sim 0.05-0.10\ \mu m$). The magnetic properties of well-drained fertile soils (*8*) are very often dominated by ultrafine secondary superparamagnetic magnetite/maghemite with low bulk H_c values ~ 20 Oe or less. Such low background H_c values may accentuate the discrimination of fly ash particles by H_c values, but the simple linear expression of proportions (*1*) may be difficult to justify without full calibration against samples of wind-blown soil. In conclusion, there is sufficient evidence to argue that the proposed quantitative interpretation of H_c values in terms of fly ash proportions (*1*) needs further development.

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A partial susceptibility approach to analysing the magnetic properties of environmental materials: a case study

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SUMMARY

An approach to expressing the magnetic properties of environmental materials in terms of the contributions of the magnetic susceptibilities of specific magnetic components is reported. The approach links the partial susceptibilities of discrete particles, domains or mineral fractions with the concentration-dependent parameters by means of multiple linear regression methods. The case study, using the Liverpool street dust data set, demonstrates that the technique is able to model the contributions of the main magnetic components satisfactorily. Several factors may have a significant impact on the regression results. These include the validity of the linear proportional relationships between partial susceptibilities and the relevant concentration-dependent parameters, the adequacy of the variable selection procedure and the regression model, and the suitability of certain magnetic parameters.

Key words: concentration-related parameters, magnetic susceptibility, multiple linear regression, partial susceptibilities, street dust.

INTRODUCTION

One of the most urgent needs in environmental magnetism is to present magnetic measurement results in terms of mineral and grain size contributions quantified by both empirical and theoretical models of the relationships between magnetic properties and magnetic components (Oldfield 1991, 1999). There have been several complementary attempts to do this. Hunt (1986) used the statistical procedure of discrimination analysis to establish variations in the magnetic signature between groups of dusts. Thompson (1986) described two approaches to modelling magnetization data: the first modelling the magnetic properties of natural materials in terms of mixtures of possible source materials, and the second modelling the magnetic properties of natural materials in terms of mixtures of magnetite and haematite crystals of varying concentrations and grain sizes. Another attempt is represented by the development of empirically derived mixing models to estimate the contributions of magnetically differentiated types of source material (e.g. Yu & Oldfield 1989; Lees 1997). On the basis of the magnetic properties of some synthetic submicron magnetites, Maher (1988) proposed a method of magnetic granulometry using a sequence of measurements, such as the ratio χ_{ARM}/SIRM and χ_{FD} percentage, which has been further tested by Oldfield (1994) and Dearing *et al.* (1997). Robertson & France (1994) and Stockhausen (1998) tried to discriminate among magnetic phases using cumulative log Gaussian functions to model IRM acquisition curves. Recently, von Dobeneck (1998) and Frederichs *et al.* (1999) introduced the concept of partial susceptibilities for quantitative analysis of carriers of magnetic susceptibility in marine sediments.

In this paper, von Dobeneck (1998) and Frederichs *et al.*'s (1999) proposal is developed. First, the concept of partial susceptibilities and the relevant concentration-dependent parameters are described. Second, the Liverpool street dust data set is used as a case study. Finally, factors that may have a significant impact on the approach are discussed.

METHODS

The observed total magnetic susceptibility of an environmental sample, χ_{TOTAL}, is the sum of the partial susceptibilities of discrete particles, domains or mineral fractions. The partial susceptibilities are of ferrimagnets, χ_{FERRI}; canted antiferromagnets, $\chi_{ANTIFERRO}$; paramagnets, χ_{PARA}; and diamagnets, χ_{DIA}. The susceptibility of ferrimagnetic components (χ_{FERRI}) in a sample can also be considered as the total contribution of superparamagnetic domain (SP), stable single domain (SSD), and multidomain (MD) grains (χ_{SP}, χ_{SSD}, and χ_{MD}). Small MD grains could demonstrate pseudo-single domain behaviour. For magnetite, SP and SSD threshold grain sizes (in diameter) are estimated as 0.025–0.030 and 0.05–0.06 μm (or 0.079–0.084 μm) (Dunlop & Özdemir 1997). Therefore, χ_{TOTAL} can be expressed as

$$\chi_{TOTAL} = \chi_{SP} + \chi_{SSD} + \chi_{MD} + \chi_{ANTIFERRO} + \chi_{PARA} + \chi_{DIA}. \quad (1)$$

χ_{TOTAL} is usually routinely measured by means of low-field AC susceptibility χ_{LF} (low frequency), which represents the total contribution of magnetic materials in a sample, but partial susceptibilities are rarely directly measured except for high-field susceptibility, χ_{HIGH}, which detects the total contribution of paramagnetic, diamagnetic, and canted antiferromagnetic components (Richter & van der Pluijm 1994). However, the concentrations of discrete magnetic minerals and their fractions can be estimated by other magnetic-concentration-related parameters. There is evidence that some concentration-dependent parameters can be used as proxies for the related magnetic components in a sample. First, frequency-dependent susceptibility χ_{FD} is related to SP components. When the SP grain concentration, rather than the grain size distribution, dominates both χ_{FD} and χ_{SP} values, a linear relationship between χ_{SP} and χ_{FD} is expected. Measurements of environmental materials show that χ_{FD} values can be considered as a loose indication of the amount of SP material present in a sample (Dearing *et al.* 1996). Second, SSD grains can be estimated by anhysteretic remanent magnetization (ARM) or susceptibility of ARM (χ_{ARM}). χ_{SSD} can be regarded as independent of grain size. However, χ_{ARM} values are associated with SSD grain sizes (King *et al.* 1982; Maher 1988). Therefore, when χ_{ARM} is dominated by the SSD grain concentration, rather than the grain size distribution, χ_{ARM} is expected to be related linearly to χ_{SSD}. Dearing *et al.*'s (1997) study on representative Welsh soil samples suggests that where soils have reasonably constant proportions of grains in the SP and SSD size ranges, χ_{ARM} may be used to estimate the concentration of fine ferrimagnetic grains. Third, weak field (e.g. 20 mT) isothermal remanent magnetization (IRM) or low reverse field (e.g. −20 mT) demagnetization of saturation isothermal remanent magnetization (SIRM) can be used to identify the presence of soft components (mainly MD grains). Thompson's (1986) calculations suggest that ($\mathrm{SIRM} - \mathrm{IRM}_{-20mT}$) is expected to be approximately proportional to the MD grain content of ferrimagnetic components in a sample. Finally, high reverse field (e.g. −300 mT) demagnetization of SIRM may represent the contributions of canted antiferromagnets. Oldfield & Richardson (1990) suggested that HIRM [$=(\mathrm{SIRM} - \mathrm{IRM}_{-300mT})/2$] can be used as a rough guide to the canted antiferromagnetic components, for example haematite, in a sample. As long as these magnetic parameters are related to the relevant components linearly and essentially independently, they can be used to determine partial susceptibilities by multiple linear regression methods (von Dobeneck 1998; Frederichs *et al.* 1999).

Two variable selection procedures (the simultaneous method and the stepwise method) were applied to generate regression equations in the case study of the Liverpool street dust data set. In the simultaneous method, all the available independent variables are included in the regression model. In the stepwise method, probably the most commonly used procedure, however, the variables are entered or removed from the model depending on the significance (probability) of the *F*-values (0.05 for entry and 0.10 for removal in this study).

MATERIALS, MEASUREMENTS AND ANALYSIS

97 dust samples were obtained from street gutters or pavements in the city of Liverpool. The sampling sites were distributed over diverse locations: pedestrian streets, gardens, and roads with different traffic densities. All the samples were air-dried in the laboratory, and then passed through a 1-mm sieve to remove refuse and small stones.

Low-field AC magnetic susceptibility was measured on 10 cm^3 samples using a dual-frequency (470 and 4700 Hz) Bartington Instruments MS2 sensor on the 0.1 scale. The difference between low- and high-frequency susceptibility ($\chi_{LF} - \chi_{HF}$) is expressed as a mass-specific term (χ_{FD} 10^{-8} m^3 kg^{-1}) and as a percentage of the low-frequency susceptibility (χ_{FD} percentage). Anhysteretic remanence was induced in a steady field of 0.1 mT with a parallel peak alternating field of 100 mT using a DTECH AF demagnetizer, and measured on a Molspin spinner magnetometer. Measurements are expressed as susceptibility of ARM (χ_{ARM} 10^{-5} m^3 kg^{-1}) by dividing the remanence by the steady field. Acquisition of isothermal remanent magnetization in fields of 20 mT (IRM_{20mT}), 1 T (SIRM), −20 mT (reverse) (IRM_{-20mT}), and −300 mT (reverse) (IRM_{-300mT}) was carried out using a Molspin pulse magnetizer, and measured on a Molspin spinner magnetometer. Measurements are expressed in 10^{-7} A m^2 kg^{-1} for IRM_{20mT}, SIRM, (SIRM–IRM_{-20mT}), and (SIRM–IRM_{-300mT}) on a mass-specific basis, and as percentages (per cent) for reverse field ratios of SOFT (−20 mT) and HARD (−300 mT). High-field susceptibility χ_{HIGH} was obtained on 1 cm^3 samples using a Molspin vibrating sample magnetometer in a field of 0.8–1 T. Measurements are expressed as a mass-specific term (10^{-8} m^3 kg^{-1}).

The magnetic measurement data were then analysed. Samples with values more than 1.5 box-lengths away from the box of the box-plot were identified as outliers and excluded before carrying out other statistical analysis. In the linear regression analysis, samples with standardized residual values of more than two standard deviations above or below the regression line were also detected as outliers and eliminated.

The magnetic measurement results show that the χ_{HIGH}/χ_{LF} values range from 1.5 to 3.8 per cent (average 2.5 per cent), indicating that the total contribution of paramagnetic, diamagnetic, and canted antiferromagnetic components to the total susceptibility are not significant. SOFT percentage (33.5–42.8 per cent) and HARD percentage (0.1–4.2 per cent) values and χ_{LF} values ($> 50 \times 10^{-8}$ m^3 kg^{-1}, with the exception of one sample) also suggest that the dominant magnetic minerals are ferrimagnetic (Oldfield & Richardson 1990; Dearing *et al.* 1996). By comparing the χ_{FD} percentage (0.9–2.5 per cent) and χ_{ARM}/SIRM (0.09–0.19×10^{-3} m A^{-1}) data with a semi-quantitative mixing model (Dearing *et al.* 1997), the proportions of SP, SSD, and MD grains are estimated as ~10, ~0, and ~90 per cent, respectively. Therefore, the dominant magnetic minerals are ferrimagnetic, in which the main components are MD and SP grains.

MODELLING OF FERRIMAGNETIC SUSCEPTIBILITY χ_{FERRI}

Since the sum of the partial susceptibilities of paramagnetic, diamagnetic, and antiferromagnetic components ($\chi_{PARA} + \chi_{DIA} + \chi_{ANTIFERRO}$) is estimated by χ_{HIGH}, from eq. (1), we have $\chi_{FERRI} = \chi_{TOTAL} - \chi_{HIGH}$, or $\chi_{FERRI} = \chi_{LF} - \chi_{HIGH}$. χ_{SP}, χ_{SSD}, and χ_{MD} can be determined by means of the multiple linear regression using χ_{FD}, χ_{ARM}, and SOFT [$=(\mathrm{SIRM} - \mathrm{IRM}_{-20mT})/2$] or IRM_{20mT}. Therefore, the multiple linear regression equations to calculate

χ_{FERRI} can be written as

$$\chi_{FERRI(cal)} = \alpha_1 \chi_{FD} + \alpha_2 \chi_{ARM} + \alpha_3 \mathrm{SOFT}, \quad (2)$$

$$\chi_{FERRI(cal)} = \alpha_1 \chi_{FD} + \alpha_2 \chi_{ARM} + \alpha_3 \mathrm{IRM}_{20mT}, \quad (3)$$

where α_1, α_2, and α_3 are the partial regression coefficients.

Using the simultaneous method, the regression result of eq. (2) is

$$\chi_{FERRI(cal)} = 17.226\chi_{FD} + 7.646\chi_{ARM} + 11.800\,\mathrm{SOFT}. \quad (4)$$

The multiple linear regression correlation coefficient R^2 is 0.997, close to unity, and the difference between $\chi_{FERRI(obs)}$ and $\chi_{FERRI(cal)}$ is 0.6 per cent on average (Table 1), indicating a high degree of agreement between observations and calculations. A test of the regression results is made by comparison between the partial susceptibility contributions from modelling and another approach. In eq. (4), the calculated χ_{SP}, χ_{SSD}, and χ_{MD} contribute 30.9, 1.6, and 67.5 per cent to $\chi_{FERRI(cal)}$ on average. Considering the grain size dependence of magnetic susceptibility, which shows higher values for SP grains than for SSD or MD grains (Maher 1988), the regressed partial susceptibility results are consistent with those of the mixing model (SP, SSD, and MD grain proportions ~10, ~0, and ~90 per cent).

Using the stepwise method, from eq. (2), we obtain

$$\chi_{FERRI(cal)} = 17.593\chi_{FD} + 11.954\,\mathrm{SOFT}. \quad (5)$$

Fig. 1 compares $\chi_{FERRI(obs)}$ ($=\chi_{LF} - \chi_{HIGH}$) and $\chi_{FERRI(cal)}$. As shown in Table 1, eq. (5) also gives a good estimate of $\chi_{FERRI(obs)}$, and the contributions of SP, SSD, and MD grains. Examination of the partial regression coefficients in eq. (4) shows that α_1 and α_3 are significant at the 0.01 level, but that α_2 is not significant at the 0.05 level, suggesting that χ_{ARM} does not contribute reliably to the regression equation. This is confirmed by the stepwise method resulting in eq. (5), which does not include χ_{ARM}. Therefore, eq. (5) is more appropriate for application than eq. (4).

For eq. (3), using the simultaneous method, we get an erroneously negative α_2 value, since the relationship between χ_{SSD} and χ_{ARM} is positive. Alternatively, using the stepwise

Table 1. The modelling results of the partial susceptibilities of the Liverpool street dust data set.

Eq.[a]	Sample number[b]	Multiple R^2	Mean difference (per cent)	SP proportion (per cent)[e]	SSD proportion (per cent)[e]	MD proportion (per cent)[e]
(4)	79	0.997[c]	0.6[c]	30.9	1.6	67.5
(5)	79	0.997[c]	0.5[c]	31.6	0.0	68.4
(6)	72	0.995[c]	1.8[c]	31.1	0.0	68.9
(9)	79	0.964[d]	0.5[d]	30.7	0.0	69.3
(10)	78	0.964[d]	−0.9[d]	30.9	0.0	69.1
(11)	75	0.940[d]	0.8[d]	32.0	0.0	68.0

[a] Eq. (4): modelling χ_{FERRI} by using SOFT and the simultaneous method; eq. (5): modelling χ_{FERRI} by using SOFT and the stepwise method; eq. (6): modelling χ_{FERRI} by using IRM_{20mT} and the stepwise method; eq. (9): modelling χ_{TOTAL} by using the simultaneous method (only including three independent variables: χ_{FD}, χ_{ARM}, and SOFT); eq. (10): modelling χ_{TOTAL} by using SOFT and the stepwise method; eq. (11): modelling χ_{TOTAL} by using IRM_{20mT} and the stepwise method (only including the first two independent variables entered).

[b] After excluding outliers.

[c] Between $\chi_{FERRI(obs)}$ ($=\chi_{LF} - \chi_{HIGH}$) and $\chi_{FERRI(cal)}$; difference: $(\chi_{FERRI(cal)} - \chi_{FERRI(obs)})/\chi_{FERRI(obs)}$.

[d] Between $\chi_{TOTAL(obs)}$ ($=\chi_{LF}$) and $\chi_{TOTAL(cal)}$; difference: $(\chi_{TOTAL(cal)} - \chi_{TOTAL(obs)})/\chi_{TOTAL(obs)}$.

[e] SP, SSD, and MD proportions: proportions of ferrimagnetic components.

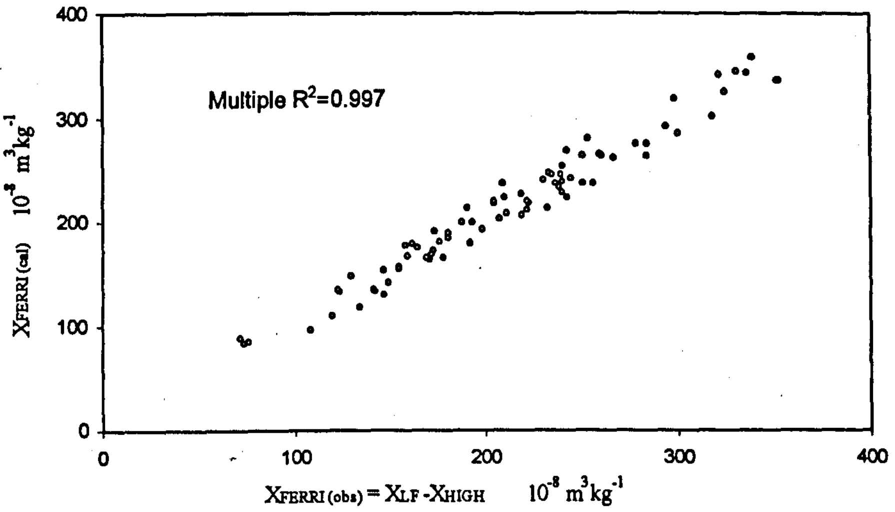

Figure 1. Comparison between $\chi_{FERRI(obs)}$ ($=\chi_{LF} - \chi_{HIGH}$) and $\chi_{FERRI(cal)}$ from eq. (5).

method, we obtain

$$\chi_{\mathrm{FERRI(cal)}} = 17.498\chi_{\mathrm{FD}} + 27.723\,\mathrm{IRM}_{\mathrm{20mT}}\,. \tag{6}$$

The modelling results of eq. (6) are similar to those of eq. (5) (see Table 1). As discussed above, $\mathrm{IRM}_{\mathrm{20mT}}$ can be used for the same purpose as SOFT on the basis that they both represent soft components in a sample. Fig. 2 shows a good linear correlation between SOFT and $\mathrm{IRM}_{\mathrm{20mT}}$ in our data set. In practice, reverse field remanence can be precisely remeasured and confirmed much more easily.

MODELLING OF TOTAL SUSCEPTIBILITY χ_{TOTAL}

Using HIRM as a proxy for the concentration of canted antiferromagnetic components, from eqs (1)–(3), the regression equations for modelling χ_{TOTAL} can be expressed as

$$\chi_{\mathrm{TOTAL(cal)}} = \alpha_0 + \alpha_1\chi_{\mathrm{FD}} + \alpha_2\chi_{\mathrm{ARM}} + \alpha_3\mathrm{SOFT} + \alpha_4\mathrm{HIRM}\,, \tag{7}$$

$$\chi_{\mathrm{TOTAL(cal)}} = \alpha_0 + \alpha_1\chi_{\mathrm{FD}} + \alpha_2\chi_{\mathrm{ARM}} + \alpha_3\mathrm{IRM}_{\mathrm{20mT}} + \alpha_4\mathrm{HIRM}\,, \tag{8}$$

where $\alpha_0, \alpha_1, \alpha_2, \alpha_3$, and α_4 are the partial regression coefficients.

For eq. (7), using the simultaneous method, we get an erroneously negative α_4 value, since the relationship between $\chi_{\mathrm{ANTIFERRO}}$ and HIRM is positive. Eliminating the HIRM term, using the simultaneous method, we obtain

$$\chi_{\mathrm{TOTAL(cal)}} = 1.256 + 17.560\chi_{\mathrm{FD}} + 0.107\chi_{\mathrm{ARM}} + 12.416\,\mathrm{SOFT}\,. \tag{9}$$

R^2 is 0.964, and the difference between χ_{LF} and $\chi_{\mathrm{TOTAL(cal)}}$ is 0.5 per cent on average (Table 1), indicating a high degree of agreement between χ_{LF} and $\chi_{\mathrm{TOTAL(cal)}}$. The estimated χ_{SP}, χ_{SSD}, and χ_{MD} contribute 30.7, 0.0, and 69.3 per cent to $\chi_{\mathrm{FERRI(cal)}}$, consistent with the results of the mixing model (SP, SSD, and MD grain proportions ~10, ~0, and ~90 per cent), since SP grains show higher magnetic susceptibility values than SSD and MD grains (Maher 1988). R^2 between $\chi_{\mathrm{FERRI(obs)}}$ and $\chi_{\mathrm{FERRI(cal)}}$ is 0.965, and the difference between $\chi_{\mathrm{FERRI(obs)}}$ and $\chi_{\mathrm{FERRI(cal)}}$ is 2.6 per cent on average. The constant term, which may reflect magnetic measurement uncertainties, contributions of $\chi_{\mathrm{ANTIFERRO}}$, χ_{PARA}, and χ_{DIA}, and deviations from the linear proportional relationships between χ_{SP} and χ_{FD}, χ_{SSD} and χ_{ARM}, and χ_{MD} and SOFT, is unlikely to represent the contributions of any discrete magnetic components.

Using the stepwise method, the regression result of eq. (7) is

$$\chi_{\mathrm{TOTAL(cal)}} = -1.291 + 17.635\chi_{\mathrm{FD}} + 12.388\,\mathrm{SOFT}\,. \tag{10}$$

Comparison between $\chi_{\mathrm{TOTAL(obs)}}$ ($=\chi_{\mathrm{LF}}$) and $\chi_{\mathrm{TOTAL(cal)}}$ is shown in Fig. 3. The modelling results of eq. (10) are similar to those of eq. (9) (see Table 1). Similar to that between eqs (4) and (5), comparison between eqs (9) and (10) suggests that eq. (10) is more suitable for application than eq. (9), since α_2 in eq. (9) is not significant at the 0.05 level.

For eq. (8), the simultaneous method is also unsuccessful due to negative α_2 and α_4 values. When the stepwise method is applied and three independent variables (χ_{FD}, $\mathrm{IRM}_{\mathrm{20mT}}$, and HIRM) are included in the model, the α_4 value is again negative. However, if the regression model only includes the first two independent variables entered, we have

$$\chi_{\mathrm{TOTAL(cal)}} = -25.775 + 20.808\chi_{\mathrm{FD}} + 31.693\,\mathrm{IRM}_{\mathrm{20mT}}\,. \tag{11}$$

Table 1 shows that the modelling results of eq. (11) are similar to those of eq. (10), suggesting the success of eq. (11). For eq. (11), the mean difference between $\chi_{\mathrm{FERRI(obs)}}$ and $\chi_{\mathrm{FERRI(cal)}}$ is 17.4 per cent, higher than that of eq. (10) (2.5 per cent), suggesting an overestimation of $\chi_{\mathrm{FERRI(obs)}}$ which results in a higher negative value of the constant term. Therefore, eq. (10) gives a better estimate of χ_{FERRI} than eq. (11). Comparison between eqs (10) and (11), the former using SOFT, the latter $\mathrm{IRM}_{\mathrm{20mT}}$, to estimate the content of MD grains, suggests that the partial susceptibility approach may be sensitive to some magnetic parameters, such as SOFT and $\mathrm{IRM}_{\mathrm{20mT}}$. The regression process of eq. (8), using the stepwise method, shows that an inadequate model will cause the failure of the partial susceptibility approach.

DISCUSSION AND CONCLUSIONS

The partial susceptibility approach assumes linear positive proportional relationships between χ_{SP} and χ_{FD}, χ_{SSD} and χ_{ARM}, χ_{MD} and SOFT or $\mathrm{IRM}_{\mathrm{20mT}}$, and $\chi_{\mathrm{ANTIFERRO}}$ and HIRM. As discussed above, there is evidence to support these assumptions.

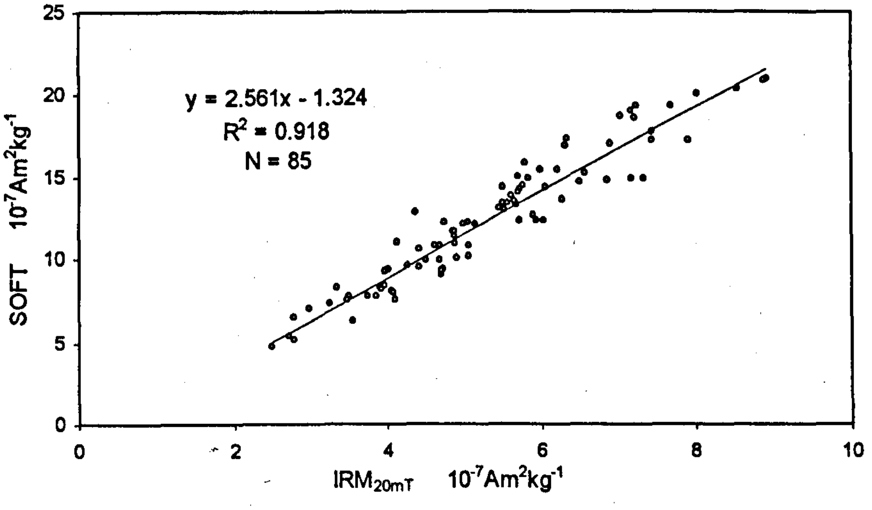

Figure 2. Relationship between SOFT and $\mathrm{IRM}_{\mathrm{20mT}}$ measurements of Liverpool street dust samples.

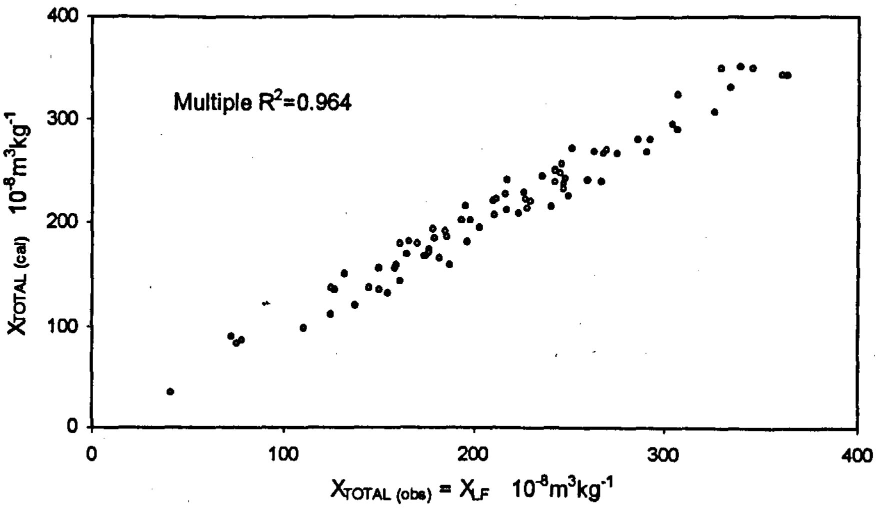

Figure 3. Comparison between $\chi_{TOTAL(obs)}$ $(=\chi_{LF})$ and $\chi_{TOTAL(cal)}$ from eq. (10).

However, in some situations, some assumptions do not hold. Dearing *et al.* (1997) suggested that a zero χ_{FD} value does not result in zero content of SP grains in the Welsh soil samples, indicating the non-proportional relationship between χ_{SP} and χ_{FD}. In the Liverpool street dust data set, the relationship between SOFT and IRM_{20mT} is not proportional (see Fig. 2), suggesting that the relationship either between χ_{MD} and SOFT or between χ_{MD} and IRM_{20mT} is not proportional. In addition to the contribution of MD grains, SOFT and IRM_{20mT} also include the contribution of fine viscous grains, which may not be significant in our samples due to the small concentrations of SP grains. HIRM, defined as $(SIRM - IRM_{-300mT})/2$, could exclude the contribution of some soft canted antiferromagnetic components. Deviations from the assumptions of linear proportionality will lead to increased uncertainties in the regression results. Contributions of more than one ferrimagnetic mineral and effects of grain interactions in the samples may also cause violations of the assumptions of linear proportionality.

The case study results are summarized in Table 1. They demonstrate the success of the partial susceptibility approach in modelling the contributions of the main magnetic components. The case study shows that several factors may have a significant impact on the regression results. First, different variable selection procedures, for example the simultaneous method and the stepwise method, may generate considerably different regression equations. Second, an adequate regression model is important to obtain a reasonable regression result. Finally, the technique may be sensitive to some magnetic parameters, such as SOFT and IRM_{20mT}. It is unlikely that the constant term in the regression equation represents the contributions of any discrete magnetic components. As a consequence, in some circumstances, the regression equations fail to model the contributions of the partial susceptibilities. Two points are essential in the application of the partial susceptibility technique. First, different regression models and methods (for example the simultaneous method and the stepwise method) should be tested for selecting suitable variables and developing regression equations. Second, the technique is successful only if the modelling results give a reasonable estimate of the contributions of the partial susceptibilities, which can be assessed by comparison with those from other approaches, such as the semi-quantitative mixing model (Dearing *et al.* 1997).

The advantage of the technique is that complex magnetic data are reduced to magnetic susceptibilities, which can then be compared quantitatively against each other in the percentage or ratio form. In other words, based on routine magnetic measurement data, this technique provides an approach to presenting magnetic mineralogy, grain size, and concentration in terms of partial magnetic susceptibilities.

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Association between the organic matter content and magnetic properties in street dust, Liverpool, UK

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Abstract

The organic matter content of street dust in Liverpool, UK, is measured for five particle size fraction and bulk samples. The content decreases significantly with increasing size for fractions < 300 μm (in diameter), but the variation is not substantial for fractions > 300 μm. The magnetic measurements indicate that the dominant magnetic component is multidomain grains of ferrimagnetic minerals and that superparamagnetic and stable single domain ferrimagnetic grains and non-ferrimagnetic minerals are present in small magnetic concentrations. There is a close association between the organic matter content and frequency-dependent susceptibility (χ_{FD} percentage), with a significant correlation for < 63-μm fraction samples and a highly significant correlation for > 63-μm fraction and < 1000-μm bulk samples. The ratio χ_{ARM}/SIRM shows a highly significant correlation with the organic matter content for < 150-μm fraction samples. This study suggests that simple, rapid, and non-destructive magnetic measurements could provide useful information about source apportionment of organic matter in street dust. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Organic matter content; Magnetic properties; χ_{FD} percentage; χ_{ARM}/SIRM; Correlation; Street dust

1. Introduction

Street dust is an important pathway of pollution material in the urban environment, acting as a sink for vehicle exhaust, deposited dusts, weathered material, and soil, and as a source of atmospheric particulate matter, house dust, and water run-off particulate matter. Many studies of street dust have focused on elemental concentrations and source identification (e.g. Fergusson and Kim, 1991; Fergusson, 1992; De Miguel et al., 1997; Nagerotte and Day, 1998). There is growing interest in the study of organic matter in street dust because of its potential human health implica-

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tions (Rogge et al., 1993; Yang and Baumann, 1995; Xie et al., 1999a), however, little work has been reported in the literature about the variation of the organic matter content with particle size, despite the fact that the size effect is an important factor in the study of street dust (Al-Rajhi et al., 1996).

Since Oldfield et al. (1985) demonstrated that simple, rapid, and non-destructive magnetic measurements can be of considerable value in characterising atmospheric dust sources, Beckwith et al. (1986), Brilhante et al. (1989) and Charlesworth and Lees (1997) have examined associations between heavy metal concentrations and magnetic properties in street dust from NW London, UK; Etrepagny, France; and Coventry, UK; respectively. Recently, Xie et al. (1999a) showed a strong linear correlation between the organic matter content and frequency dependent susceptibility in Liverpool street dust bulk samples and suggested that re-entrainment of soil is probably a major source of the organic material present in street dust.

Since fine dust particles cause more environmental concerns than coarse particles and the particle size effect is an important factor in the study of street dust, we extend this previous study to understand the variation of the organic matter content with particle size and examine the possible applications of magnetic measurements to source apportionment of organic matter in street dust with respect to particle size. First, we analyse the organic matter content and magnetic parameters for size fraction and bulk samples of Liverpool street dust, and then investigate associations between the organic matter content and magnetic properties. Emphasis is placed on the organic matter content of size fraction samples and its association with dust magnetic measurements, particularly ratio parameters.

2. Materials and measurements

Ninety-seven dust samples were obtained from street gutters or pavements in the city of Liverpool over a 7-day dry weather period in January–February 1998. The dust sampling sites were distributed over diverse locations: pedestrian streets, gardens, and roads with different traffic densities. Six soil samples were collected from the top 10 cm of bare soil surfaces in roadsides, gardens, or waste land. The soil sample sites were selected from roadside bare soil where soil was qualitatively observed to have contributed to nearby street dust. All the dust and soil samples were air-dried in the laboratory, then passed through a 1-mm sieve, to remove refuse and small stones. The < 1 mm bulk samples were sieved into five fractions with a range of aperture sizes of 63, 150, 300, and 500 μm. Further details of the sampling program are given by Xie et al. (1999a). Weighed subsamples (> 0.0722 g, mostly > 1 g) of size fraction and bulk samples were oven-dried at 105°C overnight, reweighed and then ignited in a muffle furnace (at 375°C for 4 h). The value of loss-on-ignition (LOI) is expressed as the percentage of weight lost after the 105°C oven-drying. Ignition at 375°C removes organic matter without structural water loss from inorganic soil components, or the loss of inorganic carbon compounds, which occurs at > 400 °C; the removal of both of these will result in an overestimation of the organic matter content (Boon et al., 1998). Ignition at temperatures below 375°C removes appreciably less of the carbonaceous matter and is therefore not suitable (Ball, 1964). The laboratory test of Boon et al. (1998) shows that the lower limit for acceptable replicated LOI results is 0.0012 g (ignition at 375°C for 4 h) for dust samples. Our study of the effect of ignition temperature and time on LOI values shows that the procedure of ignition at 375°C for 4 h is suitable for measuring the organic matter content of Liverpool street dust samples (Xie et al., 1999a). A further test of the LOI method was achieved by comparison between the organic carbon content measurements using the Walkley–Black method (Hesse, 1971) and the LOI values on selected dust subsamples. Ten subsamples were selected from each size fraction and bulk samples, respectively, totally 60 subsamples, across the whole range of the LOI values and from sites in different quadrants of the city and of different

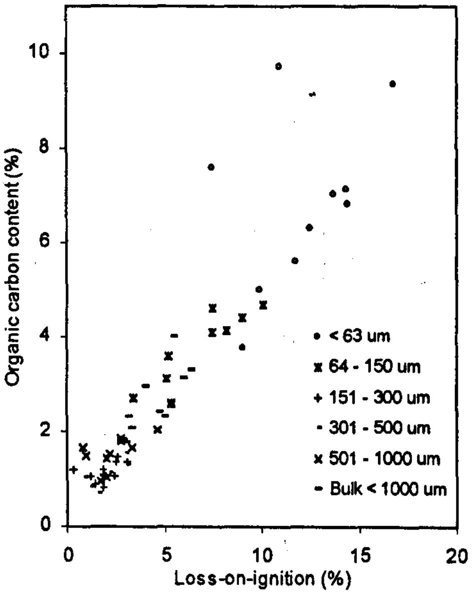

Fig. 1. Comparison between organic carbon content measurements and loss-on-ignition values of 60 selected size fraction and bulk dust subsamples, showing that ignition at 375°C for 4 h is a reasonably good procedure for estimating the organic matter content in dust samples.

distances from the city centre, which are assumed to represent the variability in the LOI values in Liverpool street dust. Fig. 1 shows a good positive correlation between the organic carbon content measurements and LOI values for the 60 selected subsamples, indicating that ignition at 375°C for 4 h is a reasonably good procedure for estimating the organic matter content of Liverpool street dust samples.

Magnetic measurements were carried out on different subsamples. Low field AC magnetic susceptibility was measured on 10-cm^3 samples using a dual-frequency (470 and 4700 Hz) Bartington Instruments MS2 sensor on the 0.1 scale. The difference between low and high frequency susceptibility ($\chi_{LF} - \chi_{HF}$) is expressed as a mass specific term (χ_{FD} 10^{-8} m^3 kg^{-1}) and as a percentage of the low frequency susceptibility (χ_{FD} percentage). Anhysteretic remanent magnetisation (ARM) was induced in a steady field of 0.1 mT with a parallel peak alternating field of 100 mT using a DTECH AF demagnetiser and measured on a Molspin spinner magnetometer. Measurements are expressed as susceptibility of ARM (χ_{ARM} 10^{-8} m^3 kg^{-1}) by dividing the remanence by the steady field. Acquisition of isothermal remanent magnetisation (IRM) in the fields of 1 T (SIRM), −20 mT (reverse) (IRM$_{-20\ mT}$), and −300 mT (reverse) (IRM$_{-300\ mT}$) was carried out using a Molspin pulse magnetiser, and measured on a Molspin spinner magnetometer. Measurements are expressed in 10^{-5} A m^2 kg^{-1} for SIRM, SOFT [= (SIRM−IRM$_{-20\ mT}$)/2], and HIRM [= (SIRM−IRM$_{-300\ mT}$)/2] on a mass-specific basis, and as percentages (%) for reverse field ratios of SOFT (−20 mT) and HARD (−300 mT) (SOFT percentage = 100 × SOFT/SIRM, HARD percentage = 100 × HIRM/SIRM). Low temperature magnetic susceptibility measurements were carried out on 10 selected bulk subsamples using a dual-frequency Bartington Instruments MS2 sensor on low frequency and the one scale. The subsamples were selected across the whole range of the magnetic parameter values and from sites in different quadrants of the city and of different distances from the city centre, which are assumed to represent the variability in magnetic properties in Liverpool street dust. The change in susceptibility value from liquid nitrogen (−196°C) to room temperature (20°C) was monitored continuously, and sample temperature recorded using a type-T thermocouple; and measurements are normalised to values at room temperature.

3. Results and discussion

The data were examined for outliers using the boxplot analysis. Samples with values more than 1.5 box-lengths away from the box of the boxplot were identified as outliers and excluded before carrying out other statistical analyses in order to eliminate the influence of outliers on the statistical results. The statistical procedure one-way analysis of variance (ANOVA) (the Tukey HSD test) was applied to test the mean differences of the organic matter content and magnetic parameters between size fractions for significance.

3.1. Variation of the organic matter content with particle size

Table 1 presents measurement results of the organic matter content for five size fraction and bulk samples. Our results fall within the ranges of other studies (Fergusson and Ryan, 1984; Hildemann et al., 1991; Al-Chalabi and Hawker, 1996). The organic matter content decreases with increasing particle sizes for fractions < 300 μm, significantly at the 0.01 level, but the differences of the organic matter content are not significant at the 0.05 level for fractions > 300 μm. It is therefore suggested that the investigation of organic matter in street dust should place emphasis on fine particles because the content is highly elevated in fine particles and fine particles cause more environmental concerns than coarse particles.

Our study on Liverpool street dust bulk samples suggests that soil is probably an important source of organic matter present in street dust (Xie et al., 1999a). Rogge et al. (1993) identified a variety of sources of organic materials in fine road dust particles (< 2 μm), including vehicle exhaust, tyre wear, vegetative plant fragments, and garden soil. The organic matter content (%) of the six surface soil samples is (mean ± S.D.) 11.7 ± 3.0, 6.5 ± 1.1, 3.2 ± 4.6, 3.3 ± 1.0, and 5.8 ± 2.8 for size fractions < 63, 64–150, 151–300, 301–500, and 501–1000 μm, respectively. No outlier in the surface soil samples was detected using the boxplot analysis. The difference of the soil organic matter content is significant at the 0.01 level for fractions < 150 μm, but not significant at the 0.05 level for fractions > 150 μm. This trend may be inconclusive because of the small number of soil samples. However, it provides evidence of size variations of the soil organic matter content. Vehicle exhaust consists mostly of fine particulate matter, with the majority of particles < 2.5 μm in diameter (Silva and Prather, 1997).

Table 1
Measurement results of the organic matter content and magnetic parameters (mean ± S.D.)[a]

Size fraction	< 63 (μm)	64–150 (μm)	151–300 (μm)	301–500 (μm)	501–1000 (μm)	< 1000 (μm)
Organic matter Content (%)	11.7 ± 3.4 (97)	6.2 ± 2.7 (97)	2.1 ± 0.8 (93)	1.9 ± 0.7 (84)	2.7 ± 1.4 (89)	3.7 ± 1.4 (93)
χ_{LF} (10^{-8} m^3 kg^{-1})	482.6 ± 85.9 (87)	315.2 ± 94.8 (92)	143.6 ± 55.4 (90)	220.0 ± 95.2 (93)	459.4 ± 187.6 (89)	236.6 ± 86.9 (92)
χ_{FD} (10^{-8} m^3 kg^{-1})	5.9 ± 2.3 (95)	5.3 ± 1.8 (96)	2.7 ± 1.1 (94)	2.8 ± 1.2 (95)	6.5 ± 2.8 (88)	4.0 ± 1.5 (94)
χ_{FD} percentage	1.2 ± 0.4 (95)	1.6 ± 0.4 (97)	1.8 ± 0.4 (96)	1.2 ± 0.3 (88)	1.4 ± 0.3 (93)	1.7 ± 0.4 (96)
χ_{ARM} (10^{-8} m^3 kg^{-1})	933.6 ± 166.4 (90)	588.1 ± 140.3 (92)	274.0 ± 95.7 (95)	388.3 ± 149.2 (94)	801.1 ± 301.7 (86)	462.2 ± 151.1 (93)
SIRM (10^{-5} A m^{-2} kg^{-1})	5622.0 ± 1083.8 (87)	3966.6 ± 1021.4 (88)	2037.0 ± 786.7 (94)	3178.1 ± 1377.3 (95)	7069.1 ± 3082.4 (91)	3433.7 ± 1268.1 (93)
χ_{ARM}/SIRM (10^{-3} m A^{-1})	0.16 ± 0.02 (96)	0.14 ± 0.02 (93)	0.13 ± 0.01 (84)	0.13 ± 0.02 (95)	0.12 ± 0.02 (91)	0.14 ± 0.02 (95)
SOFT (10^{-5} A m^{-2} kg^{-1})	1882.5 ± 374.3 (86)	1294.4 ± 297.8 (84)	743.3 ± 298.4 (94)	1141.2 ± 456.0 (92)	2733.6 ± 1159.3 (90)	1277.6 ± 454.6 (91)
SOFT percentage	33.5 ± 1.5 (93)	33.7 ± 1.4 (92)	36.1 ± 1.3 (92)	37.2 ± 1.8 (93)	38.9 ± 2.0 (92)	37.9 ± 1.8 (93)
HIRM (10^{-5} A m^{-2} kg^{-1})	98.4 ± 33.1 (96)	15.2 ± 17.9 (95)	32.3 ± 14.5 (94)	17.6 ± 13.8 (94)	75.8 ± 87.3 (96)	47.3 ± 24.8 (93)
HARD percentage	1.6 ± 0.4 (88)	0.5 ± 0.6 (94)	1.6 ± 0.6 (94)	0.6 ± 0.5 (88)	1.1 ± 1.1 (97)	1.5 ± 0.9 (95)

[a] Values in parentheses: sample numbers after excluding samples with measurement values more than 1.5 box-lengths away from the box of the boxplot.

In addition, fine particles of street dust and soil may have a higher specific surface area, and therefore a higher capacity for attachment of vehicle-derived organic matter material. As a result, the contribution of organic matter from vehicle exhaust to fine street dust fractions may be higher than it is to coarse fractions. Using the observations of Pierson and Brachaczek (1974) on size distributions of tyre wear particles in roadway gutters, it is estimated that the contributions of tyre wear particle mass are relatively 1.0, 0.92, 0.42, 0.51, 0.92 for fractions < 63, 64–150, 151–300, 301–500, and 501–1000 μm, respectively, in Liverpool street dust. It is therefore suggested that the higher organic matter content in fine dust particles (< 300 μm) may be partly due to contributions from soil, vehicle exhaust, and tyre wear.

3.2. Magnetic properties of size fraction samples

Because the dust organic matter content is not very high (Table 1), it is expected that its diluting effect on the dust magnetic concentration is not significant. χ_{LF} represents the total contribution of magnetic minerals in a sample. For natural materials, it is mainly a function of their ferrimagnetic concentration (Thompson and Oldfield, 1986). A mixing experiment of Dearing et al. (1997) indicates that χ_{FD} is a reasonably good estimator of the superparamagnetic (SP) concentration in mixed-domain assemblages while χ_{FD} percentage gives semi-quantitative estimates of the proportions of SP grains in the total ferrimagnetic mineral assemblages. The presence of stable single domain (SSD) grains can be estimated by χ_{ARM} (Maher, 1988). SIRM represents the contributions of remanence carrying components, and the calculations of Thompson (1986) suggest that SOFT is expected to be approximately proportional to the multidomain (MD) grain content of ferrimagnetic components in a sample. In addition to the contribution of MD grains, SOFT also includes the contribution of fine viscous grains at the SSD/SP border which may not be significant in our samples due to small concentrations of SP grains (low χ_{FD} percentage values). For magnetite, SP and SSD threshold grain sizes (in diameter) are estimated as 0.025–0.030 and 0.05–0.06 μm (or 0.079–0.084 μm) (Dunlop and Özdemir, 1997). Small MD grains could demonstrate pseudo-single domain behaviour. Oldfield and Richardson (1990) suggested that HIRM can be used as a rough guide to canted antiferromagnetic components in a sample. However, HIRM, defined as $(\mathrm{SIRM}-\mathrm{IRM}_{-300\ \mathrm{mT}})/2$, could exclude the contribution of some soft canted antiferromangetic components. SOFT percentage and HARD percentage can be used as approximate indications of the relative importance of ferrimagnetic and canted antiferromagnetic components in a sample, respectively (Oldfield and Richardson, 1990). The ratio χ_{ARM}/SIRM values are sensitive to grain size in ferrimagnetic minerals (Maher, 1988; Oldfield, 1994; Dearing et al., 1997).

Our study of the bulk samples suggests that the dominant magnetic component is MD grains of ferrimagnetic minerals and that SP and SSD ferrimagnetic grains and paramagnetic, diamagnetic, and canted antiferromagnetic components are present in small magnetic concentrations (Xie et al., 1999a,b). Although χ_{LF} values vary with particle size, the average values are still relatively high ($> 100 \times 10^{-8}$ m^3 kg^{-1}) (Table 1), suggesting that the dominant magnetic minerals are ferrimagnetic (Dearing et al., 1996a). Mean values of SOFT percentage (33.5–38.9%) and HARD percentage (0.5–1.6%) for five fractions also indicate dominance of ferrimagnetic minerals (Table 1) (Oldfield and Richardson, 1990). By comparison of size fraction χ_{FD} percentage (0.3–2.6%) and χ_{ARM}/SIRM ($0.07–0.20 \times 10^{-3}$ m A^{-1}) data to a semi-quantitative mixing model (Dearing et al., 1997), the proportions of SP, SSD, and MD grains are estimated as ~ 10, ~ 0, and ~ 90%, respectively. In summary, the fraction sample measurements suggest that the dominant magnetic component is MD grains and that SP and SSD grains and non-ferrimagnetic minerals are present in small magnetic concentrations.

Maher (1986) illustrated that higher values of some magnetic parameters (e.g. χ_{LF}, χ_{FD} percentage, ARM, SIRM, SIRM/ARM) are associated with < 63 μm fractions in soils which have undergone magnetic enhancement as a consequence of pedogenic formation and/or atmospheric deposition. In contrast, Table 1 shows higher values of magnetic concentration-related parameters χ_{LF}, χ_{FD}, χ_{ARM}, SIRM, SOFT, and HIRM in the finest (< 63 μm) and coarsest (501–1000 μm) fractions than those in other fractions (64–150, 151–300, and 301–500 μm), significantly at the 0.01 level, with one exception that the difference between the mean χ_{FD} value in fraction < 63 μm and that in fraction 64–150 μm is not significant at the 0.05 level. This, therefore, indicates magnetic enhancement in the finest and coarsest fractions. Ratio parameters χ_{FD} percentage, χ_{ARM}/SIRM, SOFT percentage, and HARD percentage, however, do not demonstrate the same size variation trend as concentration-related parameters (Table 1). The six surface soil samples do not show magnetic enhancement in the finest or coarsest fraction. This result, however, may be inconclusive because of the small number of soil samples.

Magnetic measurements of English topsoils show a mean χ_{LF} of 0.73×10^{-6} m^3 kg^{-1} (median 0.38×10^{-6} m^3 kg^{-1}) and a mean χ_{FD} of 45.3×10^{-9} m^3 kg^{-1} (mean χ_{FD} percentage: 4.1%) (Dearing et al., 1996b; Hay et al., 1997). Mean χ_{FD} values in the Liverpool street dust samples ($\sim 4.0 \times 10^{-8}$ m^3 kg^{-1}) are remarkably similar to that in English topsoils. However, street dust shows considerably higher mean χ_{LF} values ($\sim 236.6 \times 10^{-8}$ m^3 kg^{-1}), more than two times higher, than English topsoils. As a result, mean χ_{FD} percentage values in Liverpool street dust (~ 1.7%) are notably lower than that in English topsoils. Beckwith et al. (1986) suggested that the possible non-soil sources of magnetic minerals in the urban environment include atmospheric deposition, automobile derived particulates, and surface constructional materials.

3.3. Association of the organic matter content with magnetic ratio parameters

Table 2 shows that the correlation between the organic matter content and χ_{FD} is significant for 64–300-μm fractions at the 0.01 level, but not significant at the 0.05 level for other fractions. Fractions of 64–300 μm make up 64.7% of bulk sample mass, on average. As a result, bulk samples also demonstrate a strong linear correlation between the organic matter content and χ_{FD} (Table 2; Xie et al., 1999a). χ_{FD} percentage shows closer associations with the organic matter content than χ_{FD} for < 63- and > 300-μm fraction samples (Table 2). The correlation between the organic matter content and χ_{FD} percentage is significant at the 0.01 level for > 63-μm fraction and bulk samples, at the 0.05 level for < 63-μm fraction samples. Fig. 2 shows the linear regression for the organic matter content and χ_{FD} percentage for bulk samples. Outliers identified using the boxplot analysis are also shown in Fig. 2. A more reliable regression result can be obtained by eliminating more outliers. The R value increases from 0.418 ($N = 92$, see Table 2) to 0.536 ($N = 87$, see Fig. 2) after eliminating five samples

Table 2
Correlation coefficients between the organic matter content and magnetic parameters for size fraction and bulk samples[a]

Magnetic parameter	< 63 (μm)	64–150 (μm)	151–300 (μm)	301–500 (μm)	501–1000 (μm)	< 1000 (μm)
χ_{FD}	0.163	0.558[c]	0.338[c]	0.185	0.154	0.547[c]
	(95)	(96)	(92)	(83)	(80)	(91)
χ_{FD} percentage	0.204[b]	0.585[c]	0.334[c]	0.538[c]	0.313[c]	0.418[c]
	(95)	(97)	(92)	(82)	(87)	(92)
χ_{ARM}/SIRM	0.421[c]	0.420[c]	0.142	0.050	0.218[b]	0.020
	(96)	(94)	(84)	(89)	(83)	(91)

[a] Values in parentheses: sample numbers after excluding samples with measurement values more than 1.5 box-lengths away from the box of the boxplot.

[b] Correlation is significant at the 0.05 level.

[c] Correlation is significant at the 0.01 level..

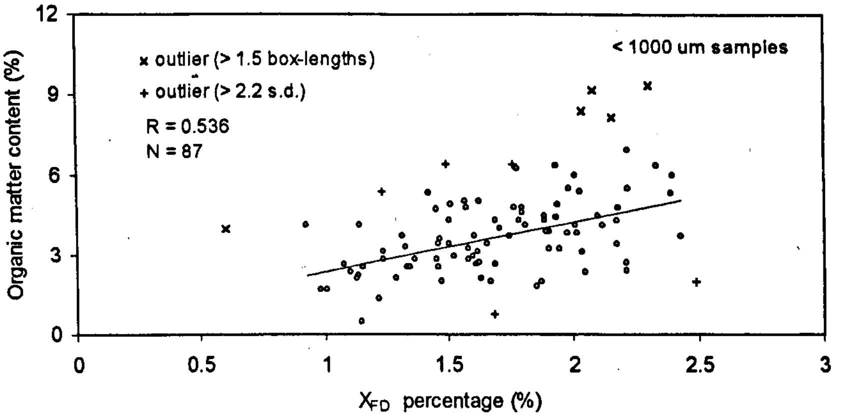

Fig. 2. Correlation between the organic matter content and χ_{FD} percentage for < 1000 μm bulk samples. Outlier (> 1.5 box-lengths): samples with measurement values more than 1.5 box-lengths away from the box of the boxplot. Outlier (> 2.2 S.D.): samples with standardised residual values of more than 2.2 standard deviations above or below the regression line. The correlation coefficient increases from 0.418 ($N = 92$, see Table 2) to 0.536 ($N = 87$) after eliminating five > 2.2 S.D. outliers.

with standardised residual values of > 2.2 S.D.s above or below the regression line. The ratio χ_{ARM}/SIRM shows a strong correlation, significant at the 0.01 level, with the organic matter content for < 150-μm fraction samples (Table 2). The linear regression for the organic matter content and χ_{ARM}/SIRM for < 63-μm fraction samples is shown in Fig. 3. Outliers identified using the boxplot analysis are also shown in Fig. 3. The R value increases from 0.421 ($N = 96$, see Table 2) to 0.561 ($N = 91$, see Fig. 3) after eliminating five samples with standardised residual values of > 2.2 S.D.s above or below the regression line.

Studies so far suggest that the most common source of SP grains is surface soil (Dearing et al., 1996b) and pollution ferrimagnetic minerals are mainly within the ranges of SSD and MD grains (Hunt et al., 1984; Flanders, 1994, 1999; Hay et al., 1997). In their method of magnetic differentiation of atmospheric dusts, Oldfield et al. (1985) showed that χ_{FD} percentage is sensitive to the contribution of soil derived material. The close

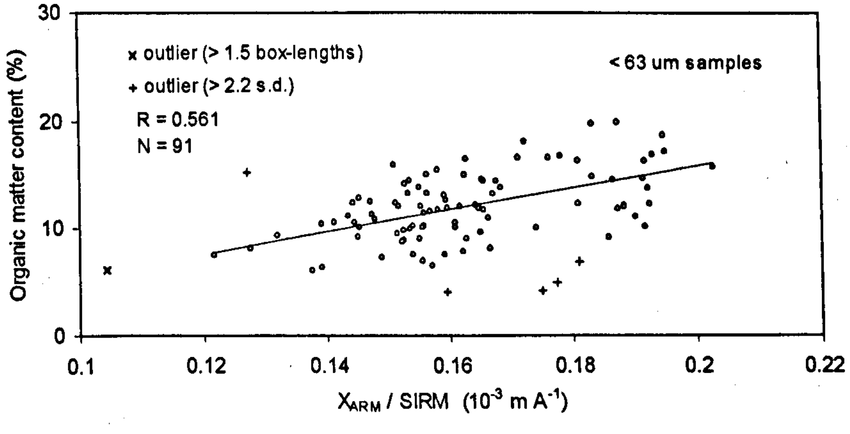

Fig. 3. Correlation between the organic matter content and χ_{ARM}/SIRM for < 63-μm fraction samples. Outlier (> 1.5 box-lengths): samples with measurement values more than 1.5 box-lengths away from the box of the boxplot. Outlier (> 2.2 S.D.): samples with standardised residual values of more than 2.2 standard deviations above or below the regression line. The correlation coefficient increases from 0.421 ($N = 96$, see Table 2) to 0.563 ($N = 91$) after eliminating five > 2.2 S.D. outliers.

associations between the organic matter content and χ_{FD} percentage in Liverpool street dust fraction and bulk samples support our suggestion that re-entrainment of soil is probably a major source of the organic material present in street dust (Xie et al., 1999a). The organic matter content and χ_{FD} show different size variation trends (Table 1), probably reflecting the difference in their sources. This may partly explain the insufficient evidence of correlations between the organic matter content and χ_{FD} for < 63- and > 300-μm fractions. The highly significant correlation between the organic matter content and χ_{ARM}/SIRM for < 150-μm fraction samples implies that the organic matter is related to dust ferrimagnetic grain sizes.

As discussed above, organic matter and magnetic particles in street dust come from a wide range of sources. As a result, *R* values in Table 2 are < 0.6. Rogge et al. (1993) estimated the contribution of tyre dust, vegetative detritus, and vehicle exhaust aerosol to organics in the fine road dust (< 2 μm) using several groups of organic tracer compounds, such as steranes, hopanes, and higher molecular weight *n*-alkanes. The highly significant correlation between the organic matter content and χ_{FD} percentage and/or χ_{ARM}/SIRM suggest that the organic matter is related to SP ferrimagnetic grain proportions and/or ferrimagnetic grain sizes in street dust. Thus, simple, rapid, and non-destructive magnetic measurements could provide useful information about source apportionment of street dust organic matter once origins of dust ferrimagnetic components are satisfactorily resolved. It is suggested that there are few SP ferrimagnetic grains in samples with χ_{FD} percentage < 2.0% (Dearing et al., 1996a; Dearing, 1999). Fig. 4 shows results of low temperature magnetic susceptibility measurements of two of ten selected bulk subsamples. Their high χ_{LF}, low χ_{FD} percentage, and low χ_{ARM}/SIRM values suggest dominance of MD ferrimagnetic grains. Fig. 4, however, demonstrates increasing susceptibility values with increasing temperature from −196 to 20°C, indicating the existence of SP grains. Therefore, this study demonstrates that small concentrations of SP ferrimagnetic grains still have significant environmental implications.

4. Conclusions

The organic matter content, measured by means of the loss-on-ignition method (ignition at 375°C for 4 h), is 11.7, 6.2, 2.1, 1.9, and 2.7% on average for size fractions < 63, 64–150, 151–300, 301–500, and 501–1000 μm, respectively. The content significantly decreases with increasing size for frac-

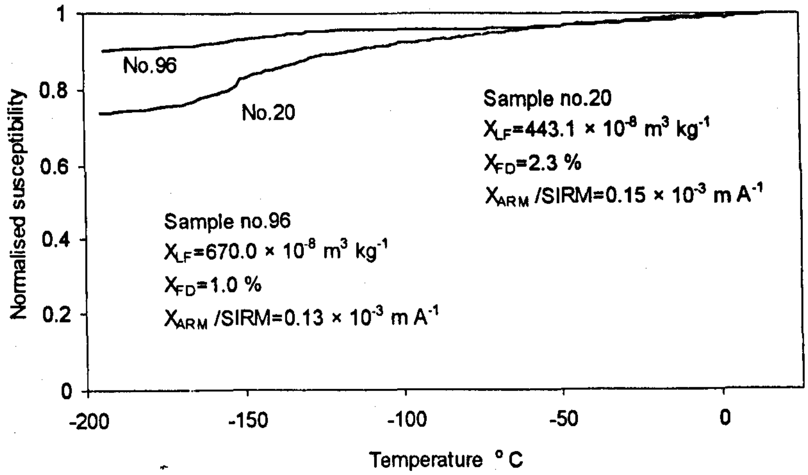

Fig. 4. Low temperature magnetic susceptibility measurements of two of 10 selected bulk samples. Increasing susceptibility values with increasing temperature from −196 to 20°C indicates the existence of SP ferrimagnetic grains.

tions < 300 μm, but the variation is not substantial for fractions > 300 μm. This size variation pattern suggests that the study of organic matter in street dust should place emphasis on fine particles. Due to the high organic matter content in the fine fraction, together with more environmental concerns of fine particles than of coarse particles, this study suggests that potential human health implications of organic matter in fine particles are more important than in coarse particles. The magnetic measurements indicate that the dominant magnetic component is MD grains of ferrimagnetic minerals. SP and SSD ferrimagnetic grains and non-ferrimagnetic minerals are present in small magnetic concentrations. There is a strong correlation between the organic matter content and χ_{FD} for 64–300-μm fraction and bulk samples, but insufficient evidence of a correlation for other fraction samples. Nevertheless, χ_{FD} percentage demonstrates a close association with the organic matter content, with a significant correlation for < 63-μm fraction samples and a highly significant correlation for other fraction and bulk samples. The ratio χ_{ARM}/SIRM shows a highly significant correlation with the organic matter content for < 150-μm fraction samples. Our study suggests that simple, rapid, and non-destructive magnetic measurements could provide useful information about source apportionment of street dust organic matter.

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