Magnetic properties of urban street dust and their relationship with organic matter content in the West Midlands, U.K.

V.F. Shilton[1] ; C.A. Booth[2]*; J.P. Smith[2], P. Giess[1]; D.J. Mitchell[2] and C.D. Williams[2]

[1]The Competitiveness Centre, Wolverhampton Science Park, Glashier Drive, Wolverhampton, West Midlands WV10 9RU, U.K.

[2]Environmental & Analytical Science Division, Research Institute in Advanced Technologies (RIATec), The University of Wolverhampton, Wulfruna Street, Wolverhampton, West Midlands WV1 1SB, UK.

*Correspondence to Dr Colin A. Booth, Environmental & Analytical Science Division, Research Institute in Advanced Technologies (RIATec), The University of Wolverhampton, Wulfruna Street, Wolverhampton, West Midlands WV1 1SB, U.K.; Tel. 01902 322410; Fax. 01902 322680; international code +44 1902; Email: c.booth@wlv.ac.uk

Abstract

This study demonstrates significant correlations between the organic matter content of urban street dust and certain mineral magnetic properties, which accords with previous work that indicates magnetic parameters offer potential as a proxy for organic content. However, site-specific data demonstrate the relationship can be different for particular roads, even within the same area. This indicates the association may be more complex than previous work proposes and a cautionary note is required. It is recommended that the nature of the relationship between magnetic and organic properties should be fully explored for particular urban environments and individual field settings, before using magnetic measurements as a proxy for organic matter content. Furthermore, whilst soil is believed to significantly contribute to urban street dust, magnetic values in this study are much higher than those previously reported for top-soils and indicate the influence of other sources, such as anthropogenic pollutants. This suggests that using magnetic measurements to discriminate sources of urban particulates has considerable potential for development.

Keywords: Environmental Magnetism, Data Correlation, Anthropogenic Pollutants, Public Health, Diesel Emissions, Top-soil.

1. Introduction

Advancement of geophysical technology has enabled the ‘atmospheric’ application of mineral magnetic techniques to expand extensively during recent decades (Oldfield *et al*., 1979; Chester *et al*., 1984; Hunt *et al*., 1984; Charlesworth & Lees, 1997; Robertson *et al*., 2003). Compared with other analytical methods, mineral magnetics provides a compositional tool, which is reliable, rapid, non–destructive, inexpensive and sensitive to low detection levels (Thompson & Oldfield, 1986; Walden *et al*., 1999; Maher & Thompson, 1999). Consequently, this has assisted the understanding of linkages between health and respirable airborne particulate matter (Morris *et al*., 1995), progressed spatial and temporal pollution studies (Beckwith *et al*., 1986; Flanders, 1994; Hoffman *et al.,* 1999; Muxworthy *et al*., 2001, 2003) and has promoted its suitability for aiding biomonitoring of air quality (Matzka & Maher, 1999; Hanesch *et al*., 2003; Moreno *et al*., 2003; Urbat *et al*., 2004).

Magnetic particles have long been recognised to be associated with atmospheric particulates (Hunt *et al*., 1984; Hunt, 1986), especially as fossil fuels contain traces of iron, which may melt to form magnetic spherules during combustion processes. It is therefore possible to use easily measured magnetic properties to identify and trace combustion-generated particulate pollutants in the environment (Muxworthy *et al*., 2002). For instance, Flanders (1994) demonstrated relationships between particle concentration and magnetic properties away from source. Hoffman *et al*. (1999) displayed the usefulness of magnetic techniques in discriminating fly ash and vehicular derived particles in roadside samples, while Shu *et al*. (2000, 2001) and Spassov *et al*. (2004) used magnetic properties of urban atmospheric particulates to discriminate types of air-borne particles.

Street dust often becomes a sink for both industrial and vehicle-generated pollutants and can be a significant human exposure source of both metals and organic matter (Fergusson & Ryan, 1984; Glikson *et al*., 1995). Rogge *et al*. (1993) noted several potential sources of organic materials in fine dusts on roads, including vehicle exhaust, tyre wear, vegetative plant fragments and garden soil. Within such street dusts there may be several minerogenic components, including metallic fragments, concrete/cement, products of tyre wear, salt spray, de-icing salt, vehicle emissions and soil. In urban areas, both vehicle exhaust emissions and soil typically contribute most street dust (Hopke *et al*., 1980; Fergusson & Kim, 1991; Spassov *et al*., 2004). Street dust organic matter in the City of Liverpool (U.K.) has specific magnetic signatures (Xie *et al*., 1999, 2000). Both studies acknowledged strong correlations between organic matter content and some mineral magnetic parameters, and proposed they may be used to determine the presence of heavy metal contaminants and as a proxy for street dust organic matter content.

This paper presents the results of a similar study to Xie *et al*., (1999, 2000), with notable improvements in field sampling strategy and provides the opportunity for greater discrimination between sites. Organic matter content and its relationship to magnetic properties are reported for a comparable equivalent industrial U.K. city. Using a much larger database of samples, the work tested and extended the findings of Xie *et al*., (1999, 2000) to dusts containing a much wider range of organic matter contents. Furthermore, this work studies the magnetic-organic relationship of particular sample sites, rather than treating all dust samples from a single city as one population. It also aims to discriminate between different types of urban dusts, especially high organic content diesel engine particulates and other urban street dusts, on the basis of their distinctive magnetic properties.

2. Samples

2.1 Sample Sites

Street dust was collected from three roads within the urban West Midlands, U.K. Two of the three roads are located in Wolverhampton City Centre, with the third road in a residential area of Dudley (~10 km south of Wolverhampton): (i) *Urban Road 1* (National Grid Reference: SO 391650 298730) is Lichfield Street, which is the main approach road to the main bus station in Wolverhampton City Centre. The road is closed to most vehicles except buses and taxis; hence buses contribute almost 100% of traffic, with two to three thousand buses using the route daily. Frequently, buses are delayed at traffic lights at one end of the road, regularly causing queues of vehicles idling outside buildings. Four and five storey buildings on both sides of the road aid a small street canyon effect, which may impede the dispersion of traffic related emissions, thus contributing to high concentrations of airborne particulate matter (Giess, 1998); (ii) *Urban Road*

2 (National Grid Reference: SO 391460 298840) is Wulfruna Street, which is also situated in Wolverhampton City Centre, ~200 m from Urban Road 1. In contrast, this road is only occasionally used by heavy duty vehicles, does not carry high traffic flows and the buildings do not produce any significant street canyon effect; and (iii) *Residential Road* (National Grid Reference: SO 393580 291420) is Meadow Road, which is a residential road located in suburban Dudley, which is infrequently used by heavy duty vehicles and carries very low traffic flows, with no local industries nearby.

2.2 Sample collection

Street dust was collected from six regularly spaced locations along each road on a monthly basis, for one year (May 2000 to April 2001). Typically, flat pavement surface dust samples of between 10–50 g, representing the net accumulation per month (irrespective of weather conditions and foot traffic during the month), were collected by brushing with a small paint brush inside a 1 m^2 quadrat. Dust was transferred to clean, pre-labelled, self-seal, airtight plastic bags. In the laboratory, samples were visibly screened to remove macroscopic traces of hair, animal and plant matter. Samples were then oven-dried at <40°C and fractionated through a 63 μm sieve. The decision to analyse only the <63 μm diameter fraction was because these particles are easily transported in suspension, with the finest among them capable of remaining airborne for considerable durations. Samples were then weighed and prepared for analysis.

3. Laboratory methods

3.1 Mineral Magnetic Analyses

All samples were subjected to the same preparation and analysis procedure (Walden *et al.*, 1999). Initial, low-field, mass-specific, magnetic susceptibility (χ_{LF}) was measured using a Bartington MS2 susceptibility meter. By using a MS2B dual frequency sensor, both low and high frequency susceptibility were measured (χ_{LF} & χ_{HF}), allowing the frequency dependent susceptibility to be calculated ($\chi_{FD\%}$). Anhysteretic Remanence Magnetisation (ARM) was induced with a peak alternating field of 100 mT and small steady biasing field of 0.04 mT using a Molspin A.F. demagnetizer. The resultant remanence created within the samples was measured using a Molspin 1A magnetometer and the values converted to give the mass specific susceptibility of ARM (χ_{ARM}). Samples were then demagnetized to remove the induced ARM and exposed to a series of successively larger field sizes up to a maximum 'saturation' field of 800 mT, followed by a series of successively larger fields in the opposite direction (backfields), generated by two Molspin pulse magnetisers (0–100 and 0–800 mT). After each 'forward' and 'reverse' field, the isothermal remanent magnetisation (IRM) of the sample was measured using the magnetometer. From these data, a number of standard parameters and ratios were calculated.

3.2 Determination of organic matter content

After samples' magnetic properties were analysed, the same samples were subjected to loss on ignition (LOI), to determine the percentage of combustible organic matter content. Samples were oven dried at 105°C, weighed and then ignited in a muffle furnace at 375°C for 16 hours before being re-weighed to determine organic material loss (Ball, 1964). All mass measurements were performed on a Mettler Toledo micro-balance with a readability of 0.1 mg.

4. Results

Mineral magnetic results for street dust samples are summarized in Table 1. Low frequency magnetic susceptibility (χ_{LF}) represents the total contribution of ferrimagnetic minerals, (Dearing, 1999). Frequency dependent magnetic susceptibility ($\chi_{FD\%}$) reflects almost exclusively the presence of ultra-fine superparamagnetic ferrimagnetic grains (diameter <0.03 μm, (Dunlop, 1973)), particularly those grains between 0.01–0.025 μm (Dearing *et al.*, 1997; Maher, 1988). Soft parameters are approximately proportional to the concentration of the ferrimagnetic minerals (e.g. magnetite (Fe_3O_4) and maghaemite (γFe_2O_3)) within a sample, while Hard parameters are approximately proportional to the concentration of the canted antiferromagnetic minerals (e.g. haematite (αFe_2O_3) and goethite ($\alpha FeOOH$)) within a sample (Oldfield & Richardson, 1990). The S-ratio is a reverse field measurement that discriminates between ferrimagnetic and canted antiferromagnetic minerals (Robinson, 1986), while the χ_{ARM}/SIRM quotient is particularly sensitive to magnetic domain size changes and can distinguish between superparamagnetic (high values), stable single domain and multidomain (low values) sizes (Dearing *et al.*, 1997).

Magnetic concentration–dependent parameters indicate street dusts contain a moderately high concentration of magnetic minerals (mean values χ_{LF} 58.83 10^{-7} m^3 kg^{-1}; χ_{ARM} 2.67 10^{-7} m^3 kg^{-1}; SIRM 5952.99 10^{-5} Am^2 kg^{-1}) compared to other environmental materials (Dearing, 1999). Magnetic mineralogy–dependent parameters indicate the content of ‘magnetite-type’ (low coercivity) minerals (mean 17.59%) are more dominant than ‘haematite-type’ (high coercivity) minerals (mean 4.27%). The S–ratio further supports this, which is indicative of dominantly magnetically soft minerals (mean –0.76). Based on a semi–quantitative mixing model (Dearing *et al.*, 1997), using the $\chi_{FD\%}$ and χ_{ARM}/SIRM parameters, the domain size data indicate samples are almost exclusively coarse stable single domain size and that some contain an admixture of superparamagnetic and coarser grains (mean values χ_{FD} 4.37% and χ_{ARM}/SIRM 0.51 10^{-5} Am^{-1}).

Anderson-Darling normality tests performed on the data sets necessitated the use of non-parametric Spearman’s rank correlation analyses. These were calculated between various magnetic parameters and dust organic matter contents (Table 2). Associations for all the roads, collectively, show the most significant relationships for organic matter content exist with $\chi_{FD\%}$ (r_s = 0.65, n = 216, $p<0.001$) and χ_{ARM}/SIRM (r_s = –0.63, n = 216, $p<0.001$) parameters (Figures 1a and 2a). Clearly, our data originates from a collection of three sample populations and demonstrates some evidence of clustering, which should be treated separately for correlation analyses. However, previous workers have collected samples from a greater number of sites, indiscriminate of known land-use patterns, and have presented collective data without showing the same clarity of sample origin. Therefore, a cautionary note is required here as our data indicate the association may not be as simple as previous work proposes.

When the data are separated into site-specific relationships, the significance of the $\chi_{FD\%}$ association continues to be evident for each sample site (Figure 1b–d). However, the χ_{ARM}/SIRM association becomes insignificant for each sample site and the trend of the relationship changes (Figure 2b–d). This is perhaps expected, as the data for each road is remarkably conservative. For several parameters display low percentage coefficient of variation values (Table 1), indicating relatively low intra-site variability throughout the year. This suggests the dusts are mostly locally-derived, well-mixed and consistent in provenance. Hence, they show relatively little systematic seasonal trend. SIRM, on the other hand, is less conservative and may reflect dilution effects of paramagnetic materials. Furthermore, besides confirming the significance of any parameter associations, these data provide an indication that individual sample sites considerably influence the relationship between organic and magnetic parameters and hence the magnitude of inter-site variability is relatively high.

Non-parametric Kruskal-Wallis *H*-tests determined whether any parameters provide evidence of significant variations between each of the sample sites (Table 3). The critical-*H*-value (at $p < 0.01$) is 9.21 and since all the parameters have higher calculated-*H*-values, the sample site populations for each parameter significantly differ. However, variations of temporal analyses are not statistically significant and reveal no apparent trends (data not presented).

5. Discussion

Comparison of West Midland data with Xie *et al*. (1999, 2000) highlights some remarkable similarities and differences. Firstly, it is noteworthy that our data contain a much wider range of organic matter contents than reported previously, yet it is noticeable the trend of the relationship continues to be observed with higher readings. Secondly, graphic plots of both $\chi_{FD\%}$ and χ_{ARM}/SIRM parameters have previously been shown to significantly correlate with organic matter, and not only does our data support these findings, but the correlation strengths are also comparable. However, it is important to note the range of χ_{ARM}/SIRM values recorded in our work does not overlap with those recorded by Xie *et al*. (1999) and the trend of the χ_{ARM}/SIRM and organic relation is opposite to the one presented in previous work. This is attributed to inter-site variation, particularly urban road 1, which, in contrast to urban road 2 and the residential road, possess high organic matter contents and low χ_{ARM}/SIRM values. Based on the interpretation of this parameter, this indicates the nature of the magneto-organic correlation is influenced by magnetic grain size.

Typically, superparamagnetic and stable single domain size grains dominate free-draining surface soils and therefore, are proposed as the principal source of street dusts (Maher, 1986; Maher & Taylor, 1988; Dearing *et al*., 1996a). This interpretation accords with Xie *et al*. (2000), who identified surface soils as the significant source component of street dusts in Liverpool. Previous magnetic pedological studies (Dearing *et al*., 1996b; Hay *et al*., 1997) have shown the mean χ_{LF} and $\chi_{FD\%}$ of top-soils to be 7.3 $\times 10^{-7}$ m^3 kg^{-1} and 4.1%, respectively. On this basis, Xie *et al*. (1999) described their mean χ_{LF} street dust data (23.7 $\times 10^{-7}$ m^3 kg^{-1}) as being over two-times higher than typical top-soils and their mean $\chi_{FD\%}$ data (1.7%) as notably lower than top-soils. When our results are compared to these data, the mean χ_{LF} (58.8 $\times 10^{-7}$ m^3 kg^{-1}) of West Midland street dusts are more than eight times higher than typical top-soils and twice the concentration of Liverpool street dusts. It is also noticeable that the mean $\chi_{FD\%}$ (4.4%) of West Midland street dusts is comparable to typical top-soils and considerably higher than Liverpool street dusts. A possible explanation for differences in the mean magnetic values between both cities is that the West Midland data has high inter-site variability, which is influenced by the very high magnetic values attributed to Urban Road 1. This is where high buildings on both sides of the road aid a small street canyon effect, which impedes the dispersion of traffic related emissions, thus contributing to high concentrations of airborne particulate matter possessing strong magnetic signatures. A further contributory factor, perhaps not as notable, is that, although both cities are of similar size and have industrial heritages, comparatively, the West Midlands are relatively continental and Liverpool is maritime. Therefore, the urban West Midlands may receive a greater volume of soil-derived dusts.

Long-term monitoring of agricultural soils surrounding Wolverhampton has shown their organic matter content to be ~2–4 % (Fullen, 1998). This suggests that, in addition to surface soils, West Midland street dusts contain significant contributions of other sources (Beckwith *et al*., 1986). Recently, Matzka & Maher (1999) analysed the magnetic properties of dusts adhering to leaf surfaces as a pollution indicator. Based on this evidence, it is proposed that decaying and disintegrated leaves are the source of high organic matter contents and any adhering pollutant-particles are the source of associated high magnetic readings. However, since trees and types of vegetation are scarce along Urban Road 1 (the site with the highest organic matter content and magnetic readings) this indicates substantial leaf matter is either transported into the road from outside the sample site or another source, perhaps anthropogenic origin is responsible.

Scanning Electron Microscopy (SEM) micrographs of dust samples collected from Urban Road 1 shows Fe-rich, spherical, dust particulates (Plate 1). Sphericule sizes (0.2–2 μm) are similar to pseudo-single-domain grains (0.7–10 μm (Smith, 1999)). Hanesch & Petersen (1999) used electron microscopy to demonstrate the presence of combustion-generated, metallic spherules in brown earths. Therefore, it is plausible the source of coarse stable-single-domain grains is an anthropogenic pollutant, particularly as Urban Road 1 has restricted access and several thousand diesel engine buses use the route daily. Therefore, the likely source is from diesel emissions.

Xie *et al*. (1999, 2000) has suggested a strong correlation between several magnetic parameters and organic matter content, offering the potential for using simple magnetic measurements as a proxy. However, this study suggests we need to be more cautious about such apparently simple relationships. For instance, within a given site there is no significant correlation between gross magnetic concentration and organic matter content, but they exist between sites. Based on the evidence presented, one suggested interpretation is that the magnetic assemblage of street dust can be portioned between that associated with the inorganic mineral fraction (perhaps dusts from primary earth materials, such as soil and concrete residues, amongst others) and a magnetic fraction associated in some way with the organic fraction (perhaps airborne dust derived from combustion and processed organic materials (tyre debris)). Figure 3 shows a schematic summary of this interpretation.

6. Conclusions

This study demonstrates site-specific correlations between organic matter content of urban street dust and certain mineral magnetic properties. Significant correlations were observed for organic matter content and the parameters $\chi_{FD\%}$ and χ_{ARM}/SIRM. These correlations exist over a wider range of organic matter contents in street dusts than previously reported. It is possible that some magnetic parameters may have potential to be used as a proxy for organic content in street dust. However, this should be attempted with caution, as the relationships are not necessarily 'universal'. These data demonstrate the relationship can be different for particular roads even within the same area. Therefore, for most parameters, the mineral magnetic approach is unsuitable as an organic matter proxy. Consequently, it is recommended that the nature of the relationship between magnetic and organic properties should be explored fully for particular urban environments and individual field settings, before using magnetic measurements as a proxy for organic matter content.

Data originated from three sample populations and demonstrated strong evidence of clustering. However, previous workers have collected samples from a greater number of sites, indiscriminate of known land-use patterns, and have presented collective data without showing the same clarity of sample origin. Therefore, our data indicate the association may not be as simple as previous work proposes and a cautionary note is required.

The fact that the measured magnetic susceptibility of the urban West Midlands is eight times higher than previously reported values for U.K. surface soils is an indication of some additional magnetic material, suggested to be anthropogenic pollutants, which contributes to the dust magnetic signature. SEM analyses support the identification of metal-rich, combustion-generated pollutants in the dust samples as being an important anthropogenic source.

Data separation into the three different source streets demonstrated distinct differences between the χ_{ARM}/SIRM of samples taken from the first urban road and those taken from the second urban and residential roads. Given the first road is used almost exclusively by diesel powered buses, producing a distinct diesel aerosol, this raises the possibility of using magnetic measurements to discriminate between differing sources of urban particulate. Further work is required to test this assumption.

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