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Magnetic properties and heavy metal contents of automobile emission particulates*

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Abstract: Measurements of the magnetic properties and total contents of Cu, Cd, Pb and Fe in 30 automobile emission particulate samples indicated the presence of magnetic particles in them. The values of frequency dependent susceptibility (χ_{fd}) showed the absence of superparamagnetic (SP) grains in the samples. The $IRM_{20\ mT}$ (isothermal remanent magnetization at 20 mT) being linearly proportional to SIRM (saturation isothermal remanent magnetization) (R^2=0.901), suggested that ferrimagnetic minerals were responsible for the magnetic properties of automobile emission particulates. The average contents of Cu, Cd, Pb and Fe in automobile emission particulates were 95.83, 22.14, 30.58 and 34727.31 mg/kg, respectively. Significant positive correlations exist between the magnetic parameters and the contents of Pb, Cu and Fe. The magnetic parameters of automobile emission particulates reflecting concentration of magnetic particles increased linearly with increase of Pb and Cu content, showed that the magnetic measurement could be used as a preliminary index for detection of Pb and Cu pollution.

Key words: Automobile emission particulates, Magnetic properties, Heavy metal, Environmental magnetism
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INTRODUCTION

In recent years magnetic measurements, which are simple, rapid, inexpensive, and nondestructive, are increasingly being used in a wide range of environmental sciences such as identification of source of industrial pollutants and atmospheric particulates (Hunt *et al*., 1984; Kapicka *et al.*, 2003; Lecoanet *et al*., 2003; Moreno *et al*., 2003; Shu *et al*., 2001), mapping of soils and sediments pollution (Hanesch *et al*., 2003; Hoffmann *et al*., 1999; Matzka and Maher, 1999), and a proxy parameter for quantifying contents of heavy metals in certain environments (Chan *et al*., 2001; Petrovsky *et al.*, 1998; 2000). Many works on soils, sediments and atmospheric dusts have shown that the magnetic properties of airborne particles, industrially polluted soils and sediments were strongly associated with heavy metal concentration and mutagenic organic compounds (Hunt *et al*., 1984; Lecoanet *et al*., 2003; Morris *et al*., 1995). The finding of high coefficients of relation between certain pollutants and magnetic susceptibility or isothermal remanence (IRM) indicated that magnetic measurements could provide an inexpensive and rapid diagnostic alternative to other techniques.

Automobile emissions are considered as a significant source of pollutants. It was found that urban soils were heavily polluted by Pb from gasoline combustion (Chen *et al*., 1997; Imperato *et al*., 2003) and that dusts and roadside soils near motorways were polluted by heavy metal from automobiles. Roads and highways areas contaminated by traffic emissions can be easily mapped using magnetic susceptibility (Hoffmann *et al*., 1999). Spatial distribution of heavy metal in urban soils and industrial sites can be easily determined by magnetic measurements. Magnetic

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properties of airborne particles may be strongly associated with heavy concentrations and mutagenic organic compounds were also found in Asia and Europe (Lu, 2003; Thompson and Oldfield, 1986). These results indicated the link between the heavy metal contents and the magnetic parameters in soils, sediments and atmospheric particulates polluted by automobile emission and industrial activities. Some results are reported below on the use of magnetic parameters as a proxy for quantifying contents of heavy metals in soils or sediments (Chan *et al*., 2001; Petrovsky *et al*., 1998). However, details about the magnetic properties and heavy metal contents of automobile emission particulates are still unknown. This study was aimed at enhancing understanding of the relationship between magnetic properties and heavy metal contents in automobile emission particulates. This study was aimed at (1) determining the magnetic properties and contents of heavy metals in automobile emission particulates; (2) determining the statistical correlation of various magnetic parameters and heavy metal content; (3) examining further the feasibility of using magnetic susceptibility for pollution assessment.

MATERIALS AND METHODS

Sample collection

Automobile emission particulates were carefully collected from the exhaust pipe of 30 automobiles in Hangzhou City, China. To avoid any contamination, particulate samples (black ash) in inner wall of automobile exhaust pipe was carefully collected by using plastic scraper.

Magnetic and metal measurements

Low and high frequency magnetic susceptibility (MS, 0.47 kHz and 4.7 kHz) were measured using a dual frequency Bartington MS2 Susceptibility Meter. Anhysteretic remanent magnetization (ARM) with peak alternating field of 100 mT and decreasing amplitude was imposed on a steady field of 0.1 mT, and the remanence was measured with a Molspin spinner magnetometer. Isothermal remanent magnetization (IRM) was achieved by placing samples in increasing magnetic fields at room temperature using a Molspin pulse magnetizer. The IRM acquired at 1000 mT is referred to as the saturation isothermal remanent magnetization (SIRM). The magnetic parameters Hard IRM was calculated by the formula: Hard $IRM=(SIRM-IRM_{300\ \mathrm{mT}})$. All remanent magnetization measurements were made using a spinner magnetometer. Magnetic parameters are expressed on both mass specific (MS, $IRM_{20\ \mathrm{mT}}$, Hard IRM, and SIRM) and quotient bases (χ_{fd}) in order to give quantitative and qualitative information. Details of the methods and interpretation of magnetic parameters are given in Lu (2003) and Thompson and Oldfield (1986).

Samples were digested with a mixture of concentrated nitric acid, hydrofluoric acid and perchloloric acid in a microwave digestion oven. The contents of Cu, Cd, Pb and Fe were analysed using an atomic absorption spectrometer.

RESULTS AND DISCUSSION

Magnetic properties of automobile emission particulates

A set of magnetic parameters of automobile emission particulate provides information on concentration, mineralogy and grain size of ferrimagnetic minerals. Table 1 gives the range and mean of magnetic parameters of vehicle emission particulate. The mean values of mass specific magnetic parameters MS, $IRM_{20\ \mathrm{mT}}$, Hard IRM and SIRM were 179.7×10^{-8} m^3/kg, 3956.6×10^{-6}, 798.9×10^{-6} and 19942.4×10^{-6} $A\cdot m^2/kg$, respectively. MS represents the total contribution of Fe-bearing minerals in the sample. $IRM_{20\ \mathrm{mT}}$ is proportional to the concentration of ferrimagnetic minerals within the sample and strongly depends on the existence forms of the Fe-bearing minerals. SIRM is related to the total remanence carrying minerals and controlled largely by stable single domain (SSD) ferrimagnetic grain concentrations and the presence of canted antiferromagnetic minerals. Hard IRM can be used to estimate the total concentration of canted antiferromagnetic minerals (hematite). Fig.1 shows the relationship between $IRM_{20\ \mathrm{mT}}$ and SIRM. A highly significant linear correlation was found (R^2=0.901). These data showed that magnetic concentration and grain size varied widely among samples, suggesting the coexistence of ferrimagnetic magnetite phases and high coercivity hematite phase(Lu, 2003; Thompson and Oldfield, 1986).

Table 1 Magnetic parameters of automobile emission particulates (n=30)

Magnetic parameters	Range	Mean
MS ($\times 10^{-8}$ m^3/kg)	0.0~1072.5	179.7
χ_{fd} (%)	0.00~−0.12	0.01
ARM ($\times 10^{-6}$ A·m^2/kg)	1.7~1075.7	161.3
$IRM_{20\ mT}$ ($\times 10^{-6}$ A·m^2/kg)	72.5~23497.6	3956.6
Hard *IRM* ($\times 10^{-6}$ A·m^2/kg)	0.0~5795.4	798.9
SIRM ($\times 10^{-6}$ A·m^2/kg)	767.7~84274.0	19942.4

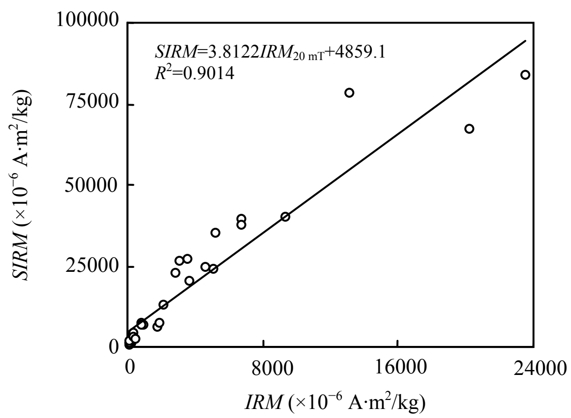

Fig.1 Relationship between $IRM_{20\ mT}$ and *SIRM* in automobile emission particulates

Variability in magnetic quotients is generally less than that of concentration parameters. Frequency-dependent susceptibility (χ_{fd}) approximates to the total concentration of superparamagnetic (SP) grains, while ARM approximates to the concentration of stable single domain (SSD) and fine pseudo-single domain (PSD) ferrimagnetic grains (Dunlop and Ozdemir, 1997). Very low values of χ_{fd} (~0.01%) indicated that the magnetic properties of the sample were not contributed by superparamagnetic (SP) particles; coarse multidomain (MD) grains were assumed to be the domain fraction. This result accords with the findings of many other authors (Hanesch *et al*., 2003; Hoffmann *et al*., 1999). Their work results demonstrated that ferrimagnetic minerals derived from industrial activity, fly ash from fossil fuel combustion and atmospheric particulates from traffic activity were dominated by MD and PSD domain sizes (Hanesch *et al*., 2003; Hunt *et al*., 1984; Moreno *et al*., 2003; Petrovsky *et al*., 2000).

IRM acquisition curves of typical samples are shown in Fig.2. The IRM reached remanence saturation at a magnetic field of 300 mT, indicating the prevalence of a magnetically soft, magnetite-like phase. Curves of demagnetization of SIRM, shown in Fig.2, also suggested the presence of magnetite-like phase. They confirmed a very soft magnetite present in the samples. A magnetite-like phase was found to be responsible for the enhancement of the MS.

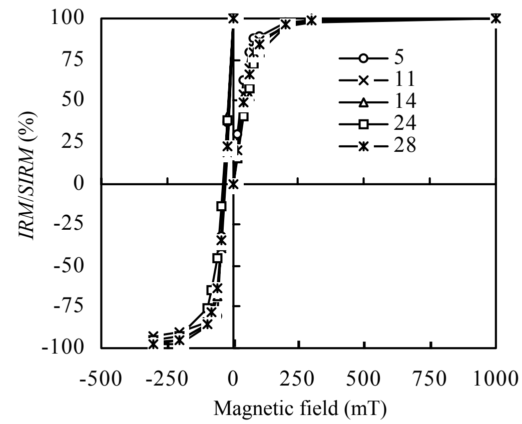

Fig.2 The acquisition curves of *IRM* and demagnetization curves of *SIRM* for typical vehicle emission particulates

Heavy metal contents of automobile emission particulates

The range and mean of Cd, Cu, Pb and Fe contents in automobile emission particulates are listed in Table 2, showing that the contents of Cd, Cu, Pb and Fe varied widely. The mean Cd, Cu, Pb and Fe contents were 22.14, 95.83, 30.58 and 34727.31 mg/kg, respectively. High heavy metal content in vehicle emission particulates was explained by the absorption of heavy metals onto the surface of particles and their incorporation into the structure of ferrimagnetic minerals. It is well known that such particles are excellent absorbers and carriers of heavy metals and PAHs due to their large specific surface area. That Cu, Pb and Zn were absorbed onto the surface of magnetite/hematite or incorporated into the structure of hematite were reported (Hoffmann *et al*., 1999; Kapicka *et al*., 2003; Petrovsky *et al*., 2000). The emission of Pb from automobile exhaust and its deposition near highways and roads has been reported worldwide. Roadside soils contained a higher heavy metal level than soils further away. Results from the present research and other studies support the finding that heavy metal emitted from gasoline combustion, especially roadside soils are important inputs to environment.

Table 2 The Cd, Cu, Pb and Fe contents of vehicle emission particulates (n=30)

Metals	Range (mg/kg)	Mean (mg/kg)
Cd	8.09~40.72	22.14
Cu	19.45~379.11	95.83
Pb	5.10~108.56	30.58
Fe	750.60~133739.00	34727.31

Coefficients of the linear correlation of the metals with each other are given in Table 3. Highly significant correlation (P<0.01) existed between Cu and Pb (R^2=0.521), Fe and Cu (R^2=0.374), and Fe and Pb (R^2=0.874). No significant correlation was observed between Cd and Cu, Cd and Pb, and Cd and Fe.

Table 3 Coefficients (R^2) of linear correlation between Cu, Cd, Pb and Fe and magnetic parameters (n=30)

	Cd	Cu	Pb	Fe
Cd	1.000			
Cu	0.089	1.000		
Pb	0.019	0.521**	1.000	
Fe	0.050	0.374**	0.874**	1.000
MS	0.0569	0.154*	0.419**	0.555**
ARM	0.0122	0.524**	0.791**	0.790**
$IRM_{20\ mT}$	0.0088	0.498**	0.734**	0.746**
Hard *IRM*	0.0296	0.199**	0.547**	0.385**
SIRM	0.0296	0.236**	0.859**	0.889**

*Significant at the 0.05 probability level; **Significant at the 0.01 probability level

Heavy metal-magnetic parameter relationships

The relationships between heavy metals and magnetic parameters provided interesting information on heavy metal sources and pathways. Total Pb, Cu and Fe contents were positively correlated with magnetic parameters MS, ARM, $IRM_{20\ mT}$, Hard IRM and SIRM (Table 3). Significant positive correlation between magnetic parameters and Pb and Cu contents in automobile emission particulates suggested that those two heavy metals have strong affinity with the ferrimagnetic minerals. Fig.3 shows the correlations between Pb content and magnetic parameters ($IRM_{20\ mT}$ and SIRM). Pb had highly significant positive correlations with $IRM_{20\ mT}$ (R^2=0.734) and SIRM (R^2=0.859). Ferrimagnetic minerals are supposed to carry toxic metals. The findings that Pb and Cu were enriched in ferrimagnetic component could be explained in term of incorporation of these elements into the lattice structure of ferrimagnetic minerals during the exhaust process or their absorption onto the surface of ferrimagnetic minerals already present.

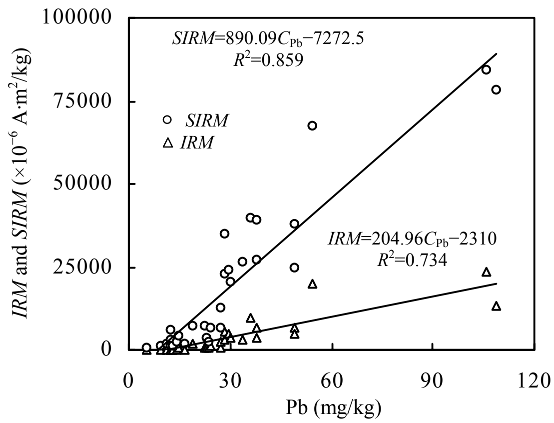

Fig.3 Correlation between Pb content and magnetic parameters ($IRM_{20\ mT}$ and SIRM) reflecting concentration of magnetic particles

The linear regression equation with Pb and Cu and magnetic parameters revealed that MS, $IRM_{20\ mT}$, Hard IRM and SIRM can be used to estimate the concentrations of heavy metals of automobile emission particulates or as indicator of heavy metal contamination from anthropogenic sources. Hoffmann *et al.*(1999) pointed out that the traffic pollution area mapping by magnetic parameters on the roadside of highway agreed well with data obtained by directly determining heavy metal contents. Shu *et al.*(2001) found that magnetic measurements could be used to estimate the concentrations of common heavy metals in total suspended particles (TSPs).

Relationships between Cd and magnetic parameters were statistically insignificant. Cd content had no correlation with Cu, Pb and Fe contents, in contrast to previous study results showing that linear relationship between Cd and magnetic susceptibility in atmospheric particulates (Hunt *et al*., 1984). Hunt *et al.*(1984) observed similar relationship between SIRM and susceptibility and Pb, Cu, Zn and Cd in atmospheric particulates.

CONCLUSION

Automobile emission particulates have relatively high concentrations of magnetic minerals and

heavy metals. A magnetite-like phase in multidomain (MD) size was found to be responsible for the remanent magnetization of automobile emission particulates. Pb, Cu and Fe have significant positive correlation with magnetic parameters MS, ARM, $IRM_{20\ mT}$, Hard IRM and SIRM. Magnetic parameters can be used to estimate the contents of Pb and Cu in automobile emission particulates. Rapid and non-destructive magnetic measurements provide a very useful method for estimating heavy metal contamination.

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