HEAVY METAL CONTENT AND HEALTH RISK ASSOCIATED WITH MAGNETIC PARTICLES IN URBAN ROAD DUSTS FROM THESSALONIKI CITY CENTER, GREECE: PRELIMINARY RESULTS

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ABSTRACT

Over the last decades, an increased attention on the heavy metal contamination associated with roadside soils and dusts has been observed, because of the associated health hazards and risks. The aim of the present study was to define the accumulation and enrichment of heavy metals in magnetic extracts from urban road dusts. Road dust samples from selected sites in Thessaloniki's city core and roads near big industrial units were collected. Magnetic extracts were separated using a hand magnet sealed in a polyethylene bag and the mass of the magnetic fraction (MF) in the road dust samples was found ranging between 2.2 and 14.7 wt %. Mass-specific magnetic susceptibility (χ_{lf}) varied widely from 122.5×10^{-8} to 638.7×10^{-8} m^3 kg^{-1} indicating high variation of ferrimagnetic minerals in the road dusts (bulk samples). The total mean Pb, Cr, Cu, Ni, Zn, and Cd contents (191, 187.3, 526.2, 95.71, 671, 0.59 μg g^{-1} dry weight, respectively) in urban road dusts were higher than their corresponding natural background values and decreased in the order of Zn>Cu>Pb>Cr>Ni>>>Cd. Compared with the non-magnetic fractions (NMFs), heavy metal concentrations in MFs were enriched and the enrichment ratios, defined as the concentration ratio of metals in MFs to NMFs, were ranging between 2.05 (Pb) and 39.36 (Cr), suggesting that these metals are highly associated with the ferromagnetic dust particles. Furthermore, the toxic metals content was eliminated in the NMFs compared to the total metal content suggesting that magnetic separation could be considered as a potential and attractive cleaning method. The non-carcinogenic health risk for adults and children resulting from exposure to the potentially toxic metals (total concentrations) in road dusts was investigated and found higher for children than adults. The Hazard Index (HI) for both children and adults decreased in the order Cr>Pb>Cu>Ni>Zn>Cd. For children the HIs were all within the safe level (1), whereas HIs for Pb (0.52) and Cr (0.58) approached it. Additionally, based on the studied heavy metal concentrations in the NMFs, the HI related to childrens' exposure in Cr was decreased from 0.58 to 0.39. Though in all cases the HIs were all within the safe level, the possible health risk due to exposure to road dust in pollution hotspots cannot be overlooked and further investigation is needed.

Keywords: road dust, heavy metals, magnetic extracts, health risk

1. Introduction

Road dust, an accumulation of solid particles on outdoor ground surfaces, is a valuable medium for characterizing urban environmental quality. Road dust may act as a temporary sink of metals from a variety of sources and may also act as a source of metals contributing to atmospheric pollution through resuspension (Amato *et al*. 2010). Over the last several decades, there has been increased attention on the heavy metal contamination associated with road dusts due to its importance to urban environmental quality and related health hazards and risks (Liu *et al*. 2014; Zheng *et al*. 2010). The concentrations of heavy metals and toxic elements in road dust can provide valuable information about pollution levels in urban and industrial areas as, in most cases, such concentrations reflect the extent of the emissions of these elements from anthropogenic sources.

Many studies have been reported from different metropolitan areas worldwide on the contamination of urban road dusts with various elements, especially heavy metals (Lu *et al*., 2009; Gunawardana *et al*. 2011; Han *et al*. 2014; Liu *et al*. 2014).However, for the city of Thessaloniki which is the second largest of Greece and road dust has been estimated as a main contributor to ambient PM10 (Samara *et al*. 2003), only sporadic studies have reported the contents of toxic heavy metals in road dust (Misaelides *et al*. 1989; Samara *et al*. 2003; Ewen *et al*. 2009; Bourliva *et al*. 2011, 2012), while no investigation was focused on the heavy metal content and health risk associated with magnetic particles extracted from them. The aim of the present study was to define the accumulation and enrichment of trace elements in magnetic extracts from urban road dusts and to assess the potential health risk associated with them.

2. Materials and methods

2.1. Site description and sampling

A total of 10 road dust samples (~100 g) were collected in April and September 2014 (before and after dry season, respectively) from the accumulated matter at the edges of selected roads in Thessaloniki's city core and roads near big industrial units. The dust samples were mainly collected by gently sweeping an area of about 1 m^2 from road surface using clean plastic dustpan and brushes for each sampling site. The samples (bulk sample) were dried in an oven at 35^oC for 3 days, mechanically sieved, while the <250 μm fraction was used for further investigation since it is the particle size that adheres to children's hands. Magnetic extracts were obtained by using a hand magnet sealed with a propylene bag and the extracted magnetic fractions (MFs) and the residue (hereafter called non-magnetic fractions, NMFs) were collected and weighed.

2.2. Analytical procedures

Total heavy metal contents of the bulk road dust samples, magnetic fractions (MFs) and non-magnetic fractions (NMFs) were determined using inductively coupled plasma mass spectrometry (ICP-MS) after a multi acid (HF-HNO_3-$HClO_4$-HCl) digestion procedure at the accredited Acme Analytical laboratory, Canada. QA/QC included reagent blanks, analytical duplicates and analysis of certified reference materials. The mass specific magnetic susceptibility (χ) of dust samples was measured at low (0.46 kHz) and high (4.6 kHz) frequency using a Bartington MS2 laboratory magnetic susceptibility meter (Bartington Ltd., UK), equipped with a dual frequency MS2B sensor. Frequency-dependent magnetic susceptibility (χ_{fd}) was defined as χ_{fd} (%) = $[(\chi_{lf}-\chi_{hf})/\chi_{lf}]\times100$, where χ_{lf} and χ_{hf} represent magnetic susceptibility values at 0.46 and 4.6 kHz, respectively. The magnetic measurements were performed in the Department of Geophysics in the Aristotle University of Thessaloniki.

3. Results and discussion

3.1. Magnetic properties and mass of MFs

The magnetic properties values and mass of MFs of road dusts are shown in Table 1.

Table 1: Magnetic properties and mass of MFs in road dusts.

Samples	χ_{lf} 10^{-8} m^3/kg	χ_{fd} %	Mass of MFs %	Fe %
min	122.5	0.3	2.2	0.6
max	638.7	4.1	14.7	3.9
mean	404.4	1.1	7.6	2.5
median	424.2	0.8	8.2	2.4

As shown, the values of mass specific magnetic susceptibility (χ_{lf}) of the studied road dusts ranged from 122.5×10^{-8} to 638.7×10^{-8} m^3 kg^{-1}, demonstrating a considerable amount of ferromagnetic iron oxides in the investigated road dust samples. The magnetic susceptibility values of the road dusts samples from the Thessaloniki city were much higher than those reported from other metropolitan areas (Shilton *et al*. 2005; Yang *et al*. 2010). On the other hand the low values of χ_{fd} (except of sample RD6) are a characteristic feature of road dusts indicating an almost lack of superparamagnetic grains (Magiera *et al*. 2011). The contents of MFs in road dusts varied between 2.2 and 14.7 wt%.

3.2. Enrichment of heavy metals in MFs

The range and mean concentrations of major and trace elements in different fractions (MF, NMF and bulk sample) are listed in Table 2.

Table 2: Heavy metals content in bulk road dusts along with NMFs and MFs.

Element	Element Concentrations (n=10)		
	Bulk road dusts	**Non-magnetic fractions**	**Magnetic fractions**
Major Elements (%)			
Ca	12.08-27.22 (16.91±5.04)	12.02-28.24 (17.36±5.13)	2.81-6.99 (4.51±1.52)
Mg	0.5-1.27 (0.95±0.2)	0.51-1.3 (0.97±0.21	0.6-1.59 (1.03±0.28)
Na	0.37-1.24 (0.92±0.26)	0.31-1.18 (0.95±0.28)	0.21-0.57 (0.32±0.11)
K	0.34-0.84 (0.68±0.16)	0.29-0.91 (0.71±0.19)	0.15-0.40 (0.26±0.07)
Al	1.04-3.92 (2.92±0.81)	0.96-4.04 (2.98±0.87)	1.02-1.72 (1.31±0.27)
Fe	0.61-3.91 (2.51±0.89)	0.49-2.09 (1.42±0.39)	32.28-47.01 (41.89±4.19)
Trace Elements (mg kg^{-1})			
Cd	0.2-1 (0.59±0.24)	0.3-2.1 (0.69±0.52)	1.1-2.7 (1.87±0.55)
Cr	43-307 (187.3±75.4)	27-208 (122.6±55.74)	2973-7636 (4734±1586)
Cu	125.5-1667 (526.2±480.9)	55-983 (406.3±383.7)	1388-9943 (4501±2930)
Ni	43.8-215.6 (95.71±53.6)	35.1-140.1 (78.49±35.33)	755.6-1874 (1107±359.4)
Pb	56-492 (191±135)	40.3-569.7 (220.6±170.3)	270.9-444.7 (360.9±46.63)
Zn	154-2153 (671±592)	148-1712 (554.3±443.2)	1907-4970 (2760±927.3)

As it is shown, Fe as expected was depleted in NMFs and enriched in MFs exhibiting total iron contents in MFs and NMFs in the range of 32.28–47.01% (mean 41.89%), and 0.49–2.09% (mean 1.42%), respectively. On the other hand Ca, Al, Na and K were depleted in MFs, indicating that these elements are associated with the non-magnetic dust particles mainly of crustal origin. Mg showed almost the same enrichment in MFs (mean 1.03%) and NMFs (mean 0.97%) indicating its presence and relevance with both MFs and NMFs.

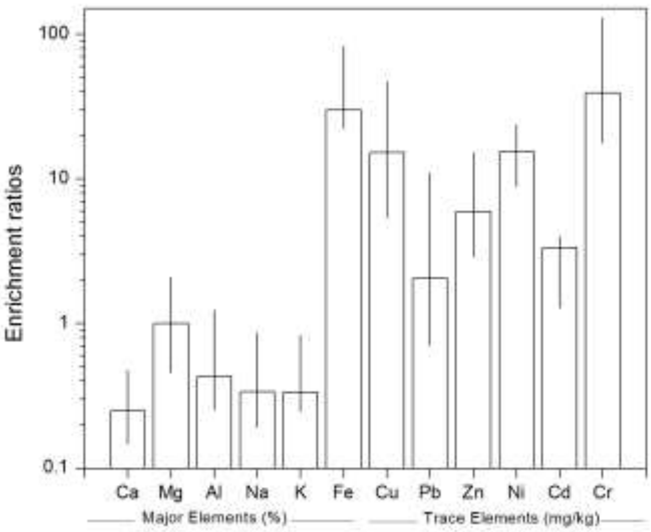

Figure 1: Enrichment ratios of major and trace elements in magnetic fractions.

On the contrary, as shown in Table 2, the potential toxic metal elements were highly enriched in the MFs. The enrichment ratios of elements, which is defined as the concentration ratio of elements in magnetic fraction to non-magnetic fraction, are illustrated in Figure 1. The mean enrichment ratio of Fe in MFs was calculated to be 29.8, while for heavy metals it ranged between 2.1 (Pb) and 39.4 (Cr). The fact that MFs contain significantly higher concentrations of heavy metals as compared to NMFs suggests that Fe and other trace elements such as Cd, Cr, Cu, Pb and in particular Cr, are preferably gathered in magnetic fractions, as indicated by their significantly higher enrichment ratios. Furthermore heavy metal concentrations in the residual NMFs (except of Pb, Cd and As) were lower than those exhibited in the bulk samples. For example, Cu was reduced by 22.8% since its mean concentration was decreased from 526.2mg/kg in the bulk road dust samples (range 125.5-1666.9mg/kg) to 406.3mg/kg in the residual NMFs (range 55-983mg/kg).

3.3. Health risk assessment

The enrichment of heavy metals in MFs raises environmental concern issue with road dust in the urban environments. For this reason models developed by USEPA were used in order to assess the health risk of the potentially toxic metals in road dusts. Chronic daily intake (CDI) and hazard quotient (HQ) for adults and children were calculated separately for each metal and for each exposure pathway (direct ingestion, inhalation and dermal absorption) according to the equations given by USEPA (1989) and are presented extensively by other workers (Chabukdhara and Nema, 2013; Zheng *et al*. 2010). It was assumed that the magnitude of adverse effect is accumulative for each exposure pathway, thus the Hazard Index (HI) is presented as the sum of HQ for each metal.

The HQs and HIs for adults and children were calculated taking into account the heavy metal contents in both bulk road dust samples and residual NMFs in order to determine the possible reduction of the impact on human health due to the lower concentrations present in the NMFs. The results of non-carcinogenic and health risks for children and adults due to metal exposure in road dusts are presented in Table 3. As shown, the non-carcinogenic health risk for children is always higher compared to adults. Regarding the exposure pathway, ingestion of dust particles appears to be the main risk followed by dermal and inhalation routes. For the studied heavy metals HIs were all lower than the safe level (= 1), however as far as children health risk is concerned, HIs for Cr (0.58) and Pb (0.52) in the bulk samples were close to the safe level signifying that children exposure to the road dusts can potentially trigger adverse non-cancer health effects. On the other hand the reduced heavy metals content in the residual NMFs resulted in a decrease in the HI related to children exposure to Cr.

Table 3. Non-carcinogenic hazard quotients (HQ) and hazard index (HI) of metals due to exposure to urban road dusts for children and adults in Thessaloniki, Greece.

		HQ_{ing}		HQ_{inh}		HQ_{derm}		HI=ΣHQ	
		Adults	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**
Bulk samples	Cd	5.13E-03	4.79E-03	1.51E-07	2.68E-07	2.05E-03	1.34E-03	2.56E-03	6.13E-03
	Cr	5.42E-02	5.06E-01	1.67E-03	2.97E-03	1.08E-01	7.09E-02	1.64E-01	5.80E-01
	Cu	1.61E-02	1.50E-01	4.74E-06	8.41E-06	2.14E-03	1.40E-03	1.83E-02	1.52E-01
	Ni	4.47E-03	4.17E-02	1.31E-06	2.33E-06	6.60E-04	4.32E-04	5.13E-03	4.21E-02
	Pb	5.42E-02	5.06E-01	1.59E-05	2.83E-05	1.44E-02	9.44E-03	6.86E-02	5.15E-01
	Zn	2.58E-03	2.41E-02	7.58E-07	1.34E-06	5.14E-04	3.37E-04	3.09E-03	2.44E-02
Non-magnetic fractions	Cd	9.91E-04	9.24E-03	2.91E-07	5.17E-07	3.95E-03	2.59E-03	4.94E-03	1.18E-02
	Cr	3.64E-02	3.40E-01	1.12E-03	1.99E-03	7.26E-02	4.75E-02	1.10E-01	3.89E-01
	Cu	1.65E-02	1.54E-01	4.84E-06	8.59E-06	2.19E-03	1.43E-03	1.87E-02	1.55E-01
	Ni	3.49E-03	3.25E-02	1.03E-06	1.82E-06	5.15E-04	3.37E-04	4.00E-03	3.29E-02
	Pb	6.43E-02	6.00E-01	1.89E-05	3.35E-05	1.71E-02	1.12E-02	8.14E-02	6.11E-01
	Zn	2.01E-03	1.87E-02	5.90E-07	1.05E-06	4.00E-04	2.62E-04	2.41E-03	1.90E-02

4. Conclusions

In this study, the enrichment of heavy metals in MFs extracted from road dusts was investigated. It was noted that road dusts MFs showed significant enrichment of heavy metals suggesting that removal of the magnetic fraction from urban road dusts especially as it comprises a considerable proportion of the bulk road dust samples, would reduce significantly the amount of these metals in the road dust residues (NMFs) and could diminish the pollution of heavy metals. Finally, removal of MFs could lead, in some cases, to a decrease in the non-carcinogenic health risk related mainly to children exposure to heavy metals.

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