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Monitoring of heavy metal levels in roadside dusts of Thessaloniki, Greece in relation to motor vehicle traffic density and flow

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Abstract In recent years, the level of heavy metal pollution in urban areas has been of considerable concern. The principal source has been attributed to the motor vehicle and increasing inner city congestion, which has lead to a change and enlargement of transport stop–start zones. These areas of high traffic density are associated with an increased release of heavy metals into the adjacent residential or commercial areas. Seventy-five roadside dust samples were collected throughout the inner city and by-pass motorway areas of Thessaloniki, Northern Greece. Samples were taken from arterial, major and minor roads, as well as the ring road, to compare and contrast the levels of heavy metals, namely Cu, Zn, Cd, Mn and Pb. Flame Atomic Absorption Spectroscopy (FAAS) was developed to quantitatively determine concentrations of both total element and geochemical fractionation, within the two dust particulate fraction sizes <75 μm and 75–125 μm. Acid digestion using *Aqua Regia* (3:1 conc. $HCl:HNO_3$) was employed for the total elemental analysis, a method that was validated through the use of certified reference materials (CRM). Fractionation studies involved a three-step sequential extraction method performed on five selected samples (representatives of high, mid and low total elemental concentrations). The resultant solutions were analysed for lead and zinc levels to ascertain fractionation throughout the different geochemical fractions, thus assessing bioavailability.

It was found that congestion/stop–start traffic patterns did influence and have led to increased levels of heavy metal deposition along inner city roads compared to levels observed on the new relief ring road. Dust particulate fraction sizes were only found to show statistically significant differences in cadmium and manganese, at the probability $P < 0.001$ or 99.9% confidence limit. Both Cd and Mn showed higher total levels in the smaller fraction sizes (<75 μm), implying that their major release source is exhaust emissions. There were no significant differences in the other elements, at the $P > 0.05$ or 95% confidence limit. Road type was seen to have little affect on cadmium and manganese, though lead, copper and zinc were all found to show higher levels on the inner city routes. This can be related back to the

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wear-and-tear of vehicle components as a result of the stop–start traffic patterns (brake pads etc). Both Pb and Zn have shown to be in chemical forms that are bio available to ecosystems.

Keywords Heavy metals • Pollution • FAAS • Total elemental analysis • Speciation analysis

Introduction

In today's modern society, urban developments and an ever-increasing traffic density have led to escalating amounts of motor vehicle pollution. During the past 25 years, the problem of heavy metal pollution was thought that lied within the inner city areas as well as motorways. In the first few minutes of a motor vehicle engine being engaged, the largest source of catalytic converter particulates is being deposited onto the road surface. As a result, several heavy metals are released, especially Pt, Pd and Rh (used as the catalysts) (Ward et al. 2004). Therefore, one of the major reasons behind the high heavy metal levels within inner cities is the 'stop–start' pattern that is often observed. Changes in traffic flow patterns and congestion in specific inner city areas (roundabouts, traffic lights/junctions) result in the possible release of many heavy metals, both from combustion particles and the wear-and-tear of the vehicle (especially tyres, brake linings etc.) (Charlesworth et al. 2003). Moreover, another important feature of inner city problems is the 'canyon' effect of buildings, which has a direct influence on dilution and dispersion pathways of the heavy metals released from motor vehicles (Namdeo et al. 1999). The effect of prevailing winds is not always evident within the environment of tall buildings and, as a result, particles tend to fall-out within the urban roadway 'canyon' resulting in higher heavy metal levels than found alongside motorways, where higher traffic densities are observed.

With regards to the urban/roadside environment the major contributor of pollution is the motor vehicle. It contains a complete spectrum of heavy and transition metals. In addition to the widely recognised exhaust emissions, there is also the wear of tyres, engine, chrome plating, brakes, wildings and bodywork (Rayson 1990), not to mention vehicle related contributors such as de-icers, accidental road spills and motorway surfaces (Hares and Ward 2004). All of the motorway-related elements such as Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, Al, Pt, Pd and Rh are dangerous in themselves, but as with any type of pollution, it is the interaction with other compounds and media in the environment that can lead to the most harmful consequences. In 1990, the internal combustion engine accounted for 60% of total anthropogenic lead in environment (Rayson 1990). Today, eighteen years later, leaded petrol is no longer sold yet lead is still seen in roadside media. This can often be directly related back to the availability of the metal.

Although many improvements have been made to reduce the amount of pollution from motor vehicles (unleaded petrol, catalytic converters, corrosion prevention etc.), these modifications combined with the increased volume and congestion on the roads counteract the benefits by simply providing new sources of different heavy metals (as illustrated by Pt from catalytic converters) (Ward et al. 2004; Rayson 1990).

In the present study, road side dust was used as the 'pollutant monitor' due to its availability on all urban routes and its association with particulate matter released from motor vehicles. Lead, copper, cadmium, manganese and zinc were chosen for quantitative determination since these heavy metals are extremely toxic for the human organism. Lead is an element that can affect almost every organ and system in the body. The central nervous and skeletal systems, particularly in children, are especially vulnerable. Moreover, damage can also occur in the kidneys, the reproductive system and the brain. In a dust form, lead can be easily inhaled or swallowed by children, both of which have similar effects. Copper is not as dangerous as other heavy metals due to it being used extensively within the body but, like any other element, an excess is toxic. Copper will deposit in the brain and liver and lead to both physical and psychological disorders. Hypoglycaemia and anaemia are linked to copper excess, as are symptoms such as hyperactivity and learning difficulties in children. Cadmium is an especially toxic heavy metal that is listed as a suspected carcinogen. Inhaling high levels can damage the lungs and ingestion will irritate the stomach. Cadmium accumulates in the kidneys and is a possible cause of kidney disease. Other symptoms can include alopecia, anaemia, arthritis, osteoporosis, growth impairment and hypertension. Manganese is a metal that is most harmful when inhaled. By this route, it is transported directly to the brain without being metabolised, hence, an excess can lead to some neurological disorders. Naturally, manganese is used in co-enzymes and, due to its metabolism being similar to that of iron, high levels can interfere with the absorption of dietary iron which leads to anaemia. Copper activity can also be affected through excess manganese. Zinc is an essential element that is used for enzymatic purposes. However, excess levels will interfere with the metabolism of iron and copper within the body. Large doses will lower manganese levels and increase susceptibility to autoimmune reactions. Further symptoms can include anaemia, growth retardation and increased low density lipoprotein (LDL) leading to raised cholesterol levels (Saryan and Zenz 1994). Listed above are some of the excess related toxicities of the metals examined in this study. It should be noted, though, other heavy metals will show similar symptoms and diseases, especially in terms of deficiencies in other essential metals within the body.

Methodology

Sample collection

The focus of the present study was the city of Thessaloniki, Greece's second biggest city after Athens. This metropolitan area was chosen for the urban traffic pollution investigation, due to its having both major and minor transportation routes within the city and a new ring road built to by-pass the city. For analysis, 75 roadside dust samples were collected from Thessaloniki during a week on November 2006 under dry meteorological conditions (see Fig. 1). Each sample was taken as a scoop sample and roughly filled a 10 ml sample tube with screw lid. The roadside dust samples of Thessaloniki were categorised into four differ-

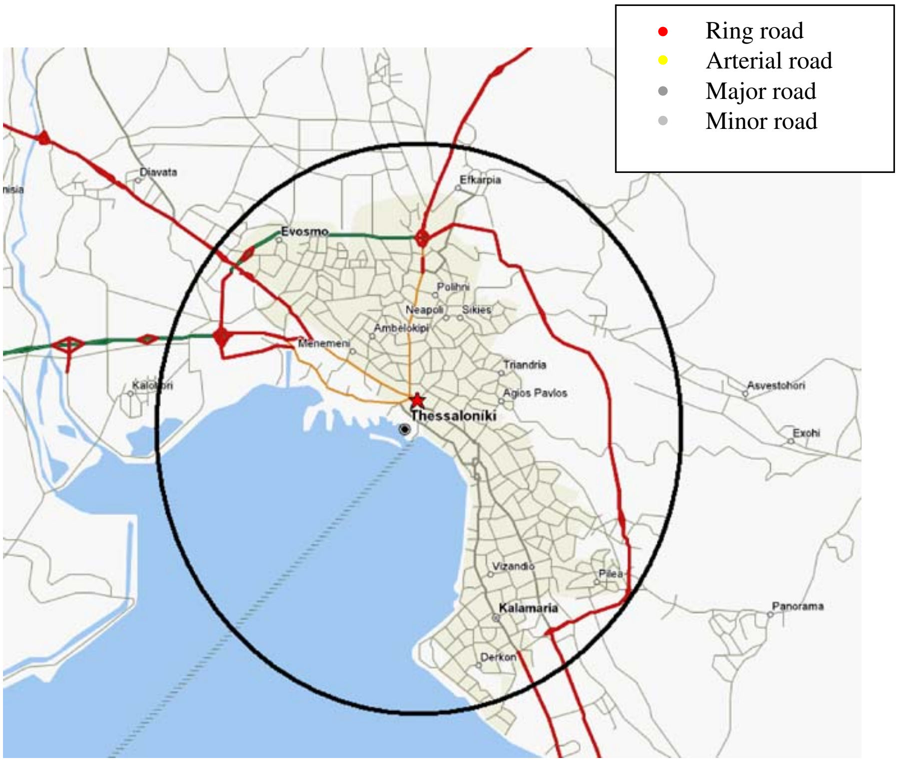


Fig. 1 Map of the city of Thessaloniki showing the sampling area into the *black circle*

ent road types: motorway/ringroad, arterial, major and minor roads.

The collected samples consisted of a variety of roadside dust particle sizes ranging from large grit to aerosols.

Sample preparation

All roadside dust samples were initially dried and ground, using a pestle and mortar, to ensure homogeneity. These were then sieved through 125 μm and 75 μm stainless steel sieves to create fractions <75 μm, 75–125 μm and >125 μm.

Total elemental analysis

It was decided to concentrate on the two smaller fractions, <75 μm and 75–125 μm, as the literature suggested these would yield the highest concentrations and they are known to be the most harmful if inhaled (Ward et al. 2004). By taking two size fractions knowledge about the distribution of the elements throughout the different sized particles was to be gained. Wet acid digestion by *Aqua Regia* (3:1, conc. $HCl:HNO_3$) was used for quantitative total elemental analysis. 0.2 ± 0.005 g of homogenised roadside dust sample were weighed out and transferred to a Kjeldahl tube. To this, 10 ml of *Aqua Regia* were added before heating in a Kjeldahl heating mantle at ~150°C. After two hours, the Kjeldahl tube was removed from the mantle and left to cool. The contents of the tube were transferred to a 50 ml plastic Sterilin^{TM} and with washing, the volume was made up to 25 ml using DDW (Distilled, De-ionised Water). Samples were centrifuged at 3,000 rpm for 10 min and stored in the fridge at 4°C prior to analysis.

Sequential extraction

When assessing the impact of a metal pollutant on the environment, it is often not adequate to just investigate total metal content. This derives from the fact that different geochemical forms of the same metal will interact and behave differently in relation to mobility and bioavailability (Stead et al. 2000). Sequential extraction is the method used to partition particulate metals depending on their affinity to certain soil types (Tessier et al. 1979). Although it is also described as 'speciation', the separation is due to geochemical forms as opposed to specific species, analysis of which would prove to be too difficult due to an amount of variables (Stead et al. 2000).

A range of different approaches have been developed and modified for this type of 'speciation'. The Rauret et al. (1999) extraction method involves fractionation relating to exchangeable, Fe–Mn oxide-bound, organic matter-bound and residual phases. Each step is more destructive than the previous. The exchangeable fraction involves the extraction of water soluble metals that are not specifically bound, hence the use of a mild reagent such as acetic acid. Fe–Mn oxides act as scavengers for trace metals so will bind to metals by adsorbing them onto their structure but are unstable in anoxic conditions, hence the use of a reducing agent such as hydroxyl ammonium chloride. Organic matter covers metals bound to anything organic including humic and fulvic acids. This matter is dissolved through oxidation by hydrogen peroxide and then released by ammonium acetate. The remaining content is the residual fraction (Tessier et al. 1979).

As with total analysis, roadside dust samples from both the <75 μm and 75–125 μm size fractions were taken. The roadside dust samples chosen for additional analysis by sequential extraction were sample numbers 34, 35, 47, 50 and 68. Examination of the total elemental levels led to these samples being selected as representatives of typical low (47, 50), middle (68) and high (34, 35) heavy metal pollution containing samples. The extraction procedure followed is stated below:

(1) 1.00 ± 0.01 g of homogenised roadside dust was placed in a 50 ml Sterilin^{TM}. To this, 40 ml of 0.11 M acetic acid were added and the mixture was shaken at 120 rpm for 4.5 h. Following this, the Sterilin^{TM} was centrifuged at 3,000 rpm for 5 min before the supernatant was removed using a Pasteur pipette (solution 1). The remaining roadside dust was washed twice by adding 20 ml of DDW, shaking for 15 min and then centrifuging at 3,000 rpm for 5 min. Each time the supernatant was discarded;

(2) To the remaining roadside dust, 40 ml of 0.5 M hydroxyl ammonium chloride were added and step (1) was repeated (solution 2). Furthermore, to the remaining roadside dust, 10 ml of 30% hydrogen peroxide were added. The Sterilin^{TM} was covered and left to digest at room temperature for 1 h. The sample was then transferred and heated at 85°C for 1 h in a polytetrafluorothene squat beaker, to reduce the volume to 3 ml. A further 10 ml of 30% hydrogen peroxide was added; the Sterilin^{TM} was covered and left to digest for 1 h. At this time the cover was removed and digestion continued until the volume was approximately 1 ml. Finally, 50 ml of ammonium acetate were added and the mixture was shaken at 120 rpm for 4.5 h before centrifuging as in step 1 (solution 3).

Method of analysis—Atomic Absorption Spectroscopy (AAS)

The AAS instrument used for analysis was a PerkinElmer AAnalyst400 (PerkinElmer Instruments LLC, Shelton, CT, USA). For all elements investigated, an air/acetylene flame was used. General Atomic Absorption Spectroscopy conditions for all elements were: acetylene flow rate = 2.50 l/min; air flow rate = 10.00 l/min; nebulizer flow rate = 1 ml/min; burner head length = 80 mm; dwell time = 2.0 s and repeat readings = 2. Each element had a calibration run before sample analysis. The standards used for each element, were chosen based on the linear range recommended for the AAnalyst400 software (WinLab32). The calibration curves were set for linear through zero and correlations averaged at 0.99846.

Method of validation

Three suitable Certified Reference Materials (CRM) were used to validate and compare results gained. The certified reference values for the reference materials used are: Ref1) NIST (National Institute of Standards and Technology) SRM 2557 Used Auto Catalyst (Monolith) = 13,931 mg/kg Pb and 1,131 mg/kg Pt, Ref2) NIST (National Institute of Standards and Technology) SRM 2556 Used Auto Catalyst (Pellets) = 6,228 mg/kg Pb and 697.4 mg/kg Pt and Ref3) Canmet Sudbury Matte = 7.31 mg/kg Pt. The certified reference materials were selected when it was thought that Platinum might also be investigated. For the actual measurement process, this was not possible due to the limitations posed by the detection limit for atomic absorption spectroscopy and the concentrations present in the samples. However, analysis was still performed on all three reference materials as it was considered the content might be useful for sequential analysis purposes. Comparison between the values calculated and certified reference values for the Certified Reference Materials showed some differences; reference 1 calculated as 15,483 mg/kg Pb and reference 2 as 6,858 mg/kg Pb. These differences showed that the results were not adequately matrix-matched and a correction factor was needed. The certified reference materials 1 and 2 values were plotted certified against calculated. The graph equation was used to correct the lead concentration results. Due to lack of certified values for the other elements, the correction for lead was taken as a semi-quantitative correction for copper, cadmium, zinc and manganese. The corrected values were used for the analysis and interpretation of the data.

Statistical analysis

All data from the total analyses were collated and the concentrations present in the original samples calculated using the matrix-matched calibration. Determination of any significant differences between the two particle fraction sizes (<75 μm and 75–125 μm) was carried out through assessment of the distributions (histograms) followed by comparisons of the variance, *F*-test and the mean, Student *t*-test (see “Results and discussion”).

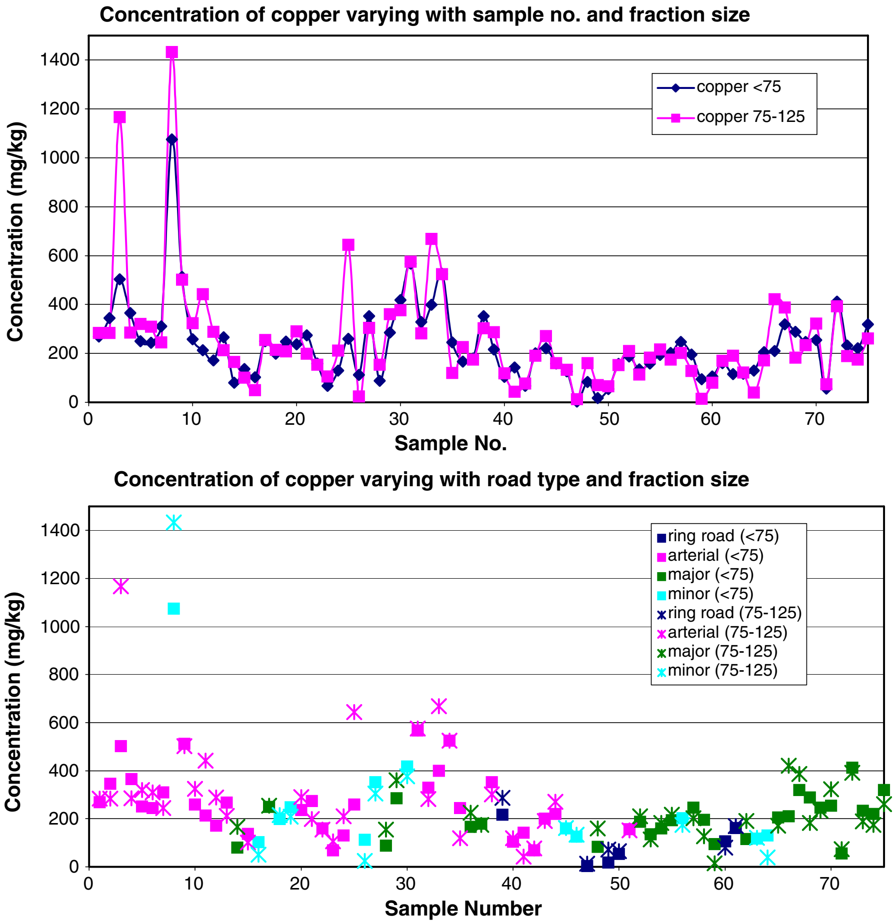
Results and discussion

Copper

Copper showed a similar pattern with regards to the roadside dust particle fraction sizes. There were, however, a couple of samples with high copper concentrations, which tended to be associated with the larger fraction sizes (75–125 μm). This is in accordance with the fact that copper is linked with the wear-and-tear of brake pads (Rayson 1990). These high Cu concentrations were found in samples 3 and 8, followed by samples 25 and 33. Sample sites 3 and 25 were junctions, 8 was a minor inner city road in a green area and 33 was a tourist attraction. Cross referencing these results with the second part of Fig. 2 showed that the highest Cu concentrations were found on a minor road but generally arterial roads provided the higher Cu levels (see Fig. 2). The major and minor roads seem to have resulted in about the same levels of copper whilst the ring road consisted of only a minor source. Interestingly, since the ring road is a new fast tract transport route it might be postulated that the low copper levels are a result of no or minimal copper release from the brake-linings, as the vehicles are not under going stop–start flow conditions. With there being very few exit junctions, there is also no significant wear-and-tear of vehicle brakes.

Zinc

Apart from a couple of samples, zinc showed a general trend to be at higher levels in the smaller road side dust particle fraction sizes. There were two samples (8, 14) which exhibited very high Zn concentrations. Sample no. 14 was collected at a junction just outside the university and 8 was collected from the inner city. As far as the road type is concerned, it was not very easy to see any significant differences in Fig. 3. Therefore Fig. 4, without samples 8 and 14, was produced to gain a better general comparison. Arterial roads tended to have the higher Zn levels followed by minor and major roads showing similar values. The ring


Concentration of copper varying with sample no. and fraction size

Concentration of copper varying with road type and fraction size

Fig. 2 Variation in copper content (mg/kg) due to roadside dust particle fraction size and road type

Fig. 3 Variation in zinc content (mg/kg) due to roadside dust particle fraction size and road type

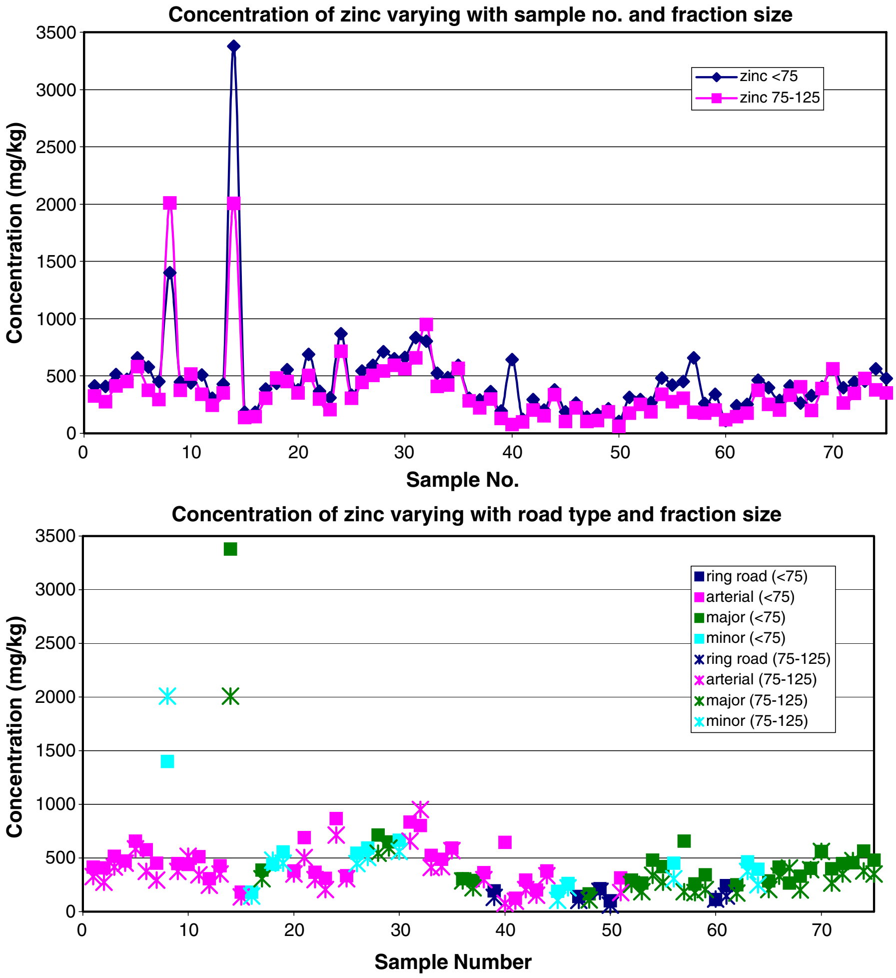
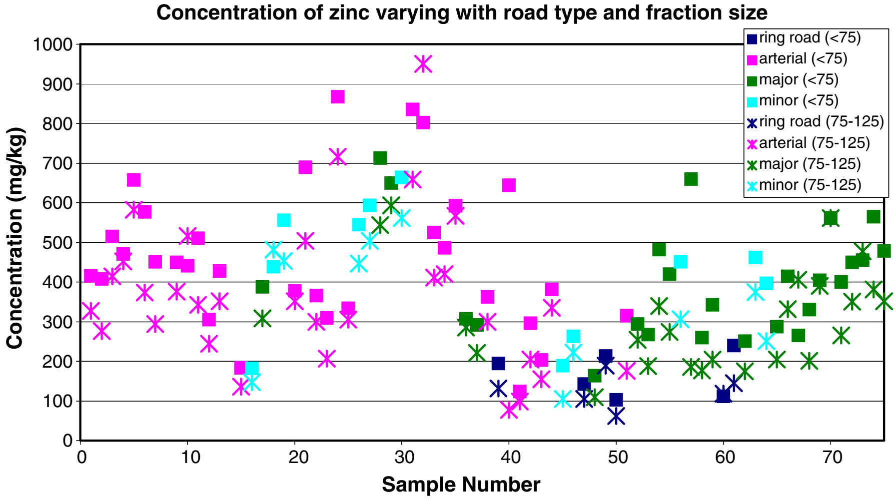


Fig. 4 Variation in zinc content (mg/kg) due to fraction size and road type (without samples 14 and 8)



road samples were seen at the low concentration end (refer to the explanation for copper).

Cadmium

Cadmium was the element that showed the clearest divide in road side dust particle fraction sizes in terms of the total elemental concentrations observed (see Fig. 5). This implies that the exhaust emissions of cadmium are greater than that which would be expected from a tyre wear contribution. In nearly all the samples (except two) the smaller particle sizes fraction was found to have the highest Cd levels. The two most highly contaminated samples, at sites 32 and 34, were situated on the arterial coastal road. However, apart from these two samples, there was not much spread in Cd concentrations throughout the study sites, especially for the smaller particle sizes fraction. The arterial and minor roads might be seen to have higher Cd levels than the other roads but this was only a marginal observation. The lowest Cd concentrations were found in two suburban roads (samples 16 and 75) along with sample 60, which was collected alongside the ring road. These findings are of

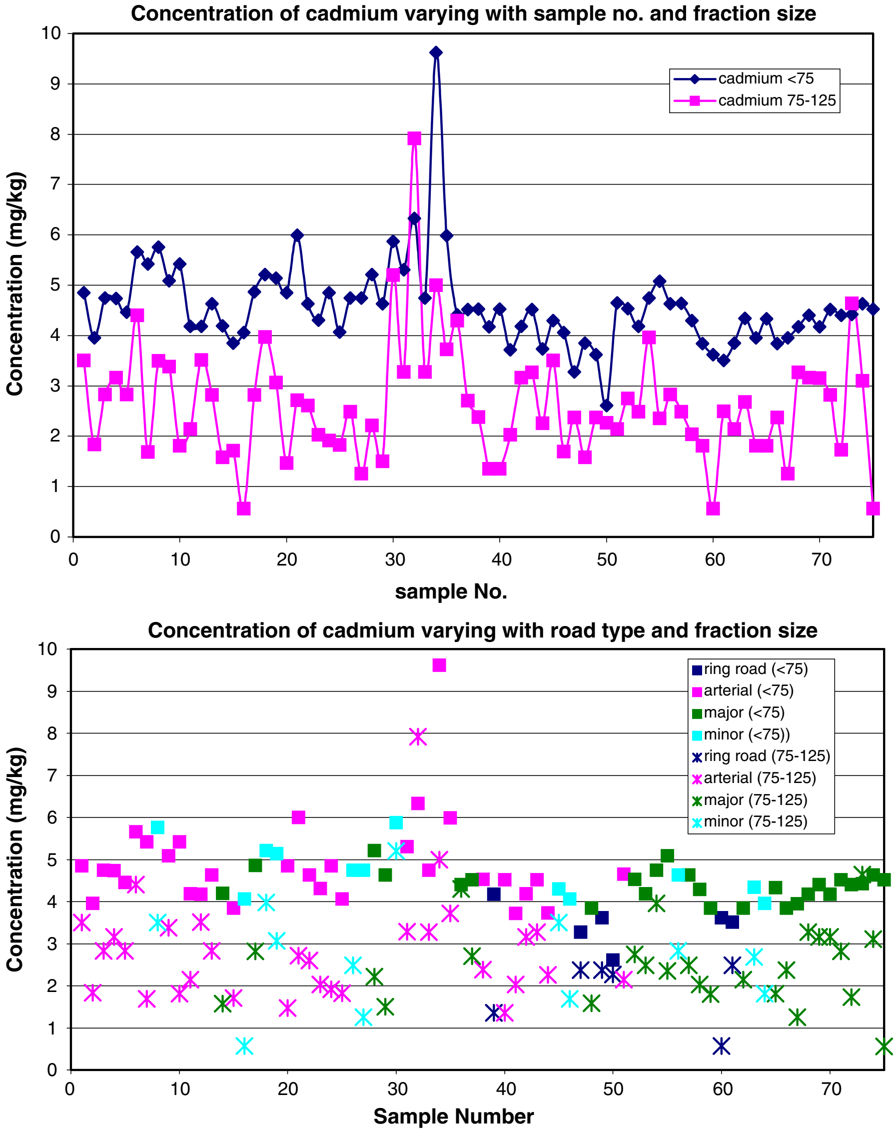


Fig. 5 Variation in cadmium content (mg/kg) due to roadside dust particle fraction size and road type

great importance as cadmium is considered to be a very toxic heavy metal in terms of human health. The fact that the small road side dust particles (<75 μm) had the highest levels of Cd contamination than the other size suggests that roadside dust could pose a serious health risk in urban environments. This is because the small particle sizes have the potential to be taken up by the lungs. The possible sources of Cd are limited as reflected in the narrow spread across the sampling sites. Although the wear-and-tear of tyres is recognised as a major source of cadmium alongside roadways, this study suggests that maybe the combustion of fuel (especially diesel) and oil/lubricants, which are known to contain trace levels of cadmium, may be a significant source of Cd as found in roadside dust within the Thessaloniki area.

Manganese

Manganese was another element that illustrated a tendency to be more highly concentrated in the small road side dust particles fraction. Figure 6 shows a consistency in the Mn levels of samples taken from the Thessaloniki area. Highest Mn concentrations were observed in sample no. 32, the coastal roadside dust sample, and samples 49 and 50. These two samples were collected from the ring road, which goes against the trends of the rest of the elements.

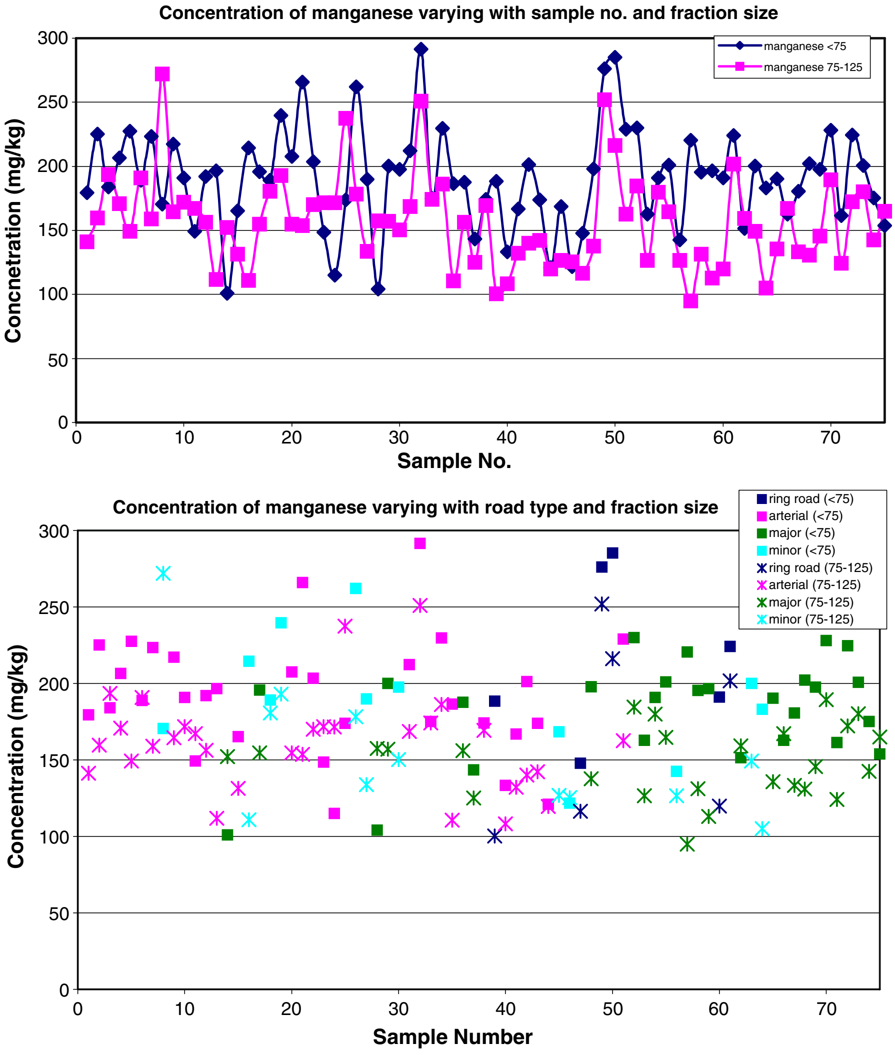


Fig. 6 Variation in manganese content (mg/kg) due to roadside dust particle fraction size and road type

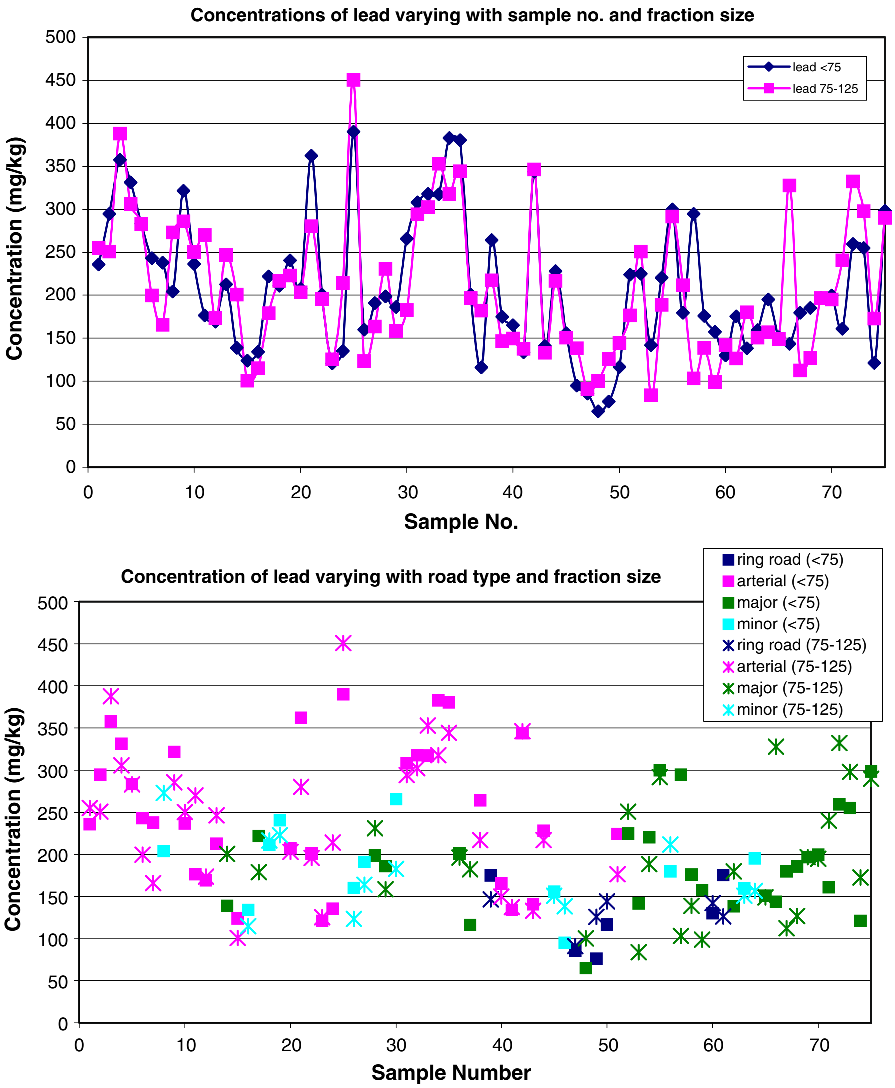


Fig. 7 Variation in lead content (mg/kg) due to roadside dust particle fraction size and road type

Lead

It can be seen from Fig. 7, on the whole, that samples varied very little in concentrations between the fraction sizes. Furthermore, the graph highlights the arterial roads as being the ones with the highest lead concentrations in both size fractions, though closely followed by major roads with the second highest levels. Minor roads are next and then the ring road following very closely behind.

This suggests that traffic flow patterns have an influence on the lead concentrations, not just traffic density. The highest concentrations were found in road side dust sample no. 25, which was collected at a site being a junction of several different road types. These high lead concentrations were observed in both size fractions. The lowest concentrations were seen in samples 48 and 53, both of which were collected from the suburbs. A possible explanation for this trend is not obvious in that the major source of lead, being added lead to fuel, is no longer in use in Greece. Residual lead from this source would not be expected to be evident in the present roadside dust samples, due to dust being considered a short-term contamination indicator (Xiangdong et al. 2001). The observed trend does show that the highest lead levels were found in busy/high traffic density roadways, namely the arterial roads. It is possible that modern cars via the wear-and-tear of wheel bearings are still releasing lead, but no evidence has been reported in the literature indicating this as a significant anthropogenic source in the urban environment. The data of the present study suggests that this might be possible in zones of vehicle acceleration and de-acceleration. However, if the release of lead were from wheel bearings it would be expected that the particle size profile would be higher in the smaller particle sizes (<75 μm), but the Student *t*-test confirmed no significant difference in the lead content of the two particle size fraction groups. It must therefore be concluded that whilst lead is high in these arterial and possible high traffic density areas, the source could be wheel bearings and other anthropogenic inputs (as yet not identified).

The overall results for Thessaloniki showed a significant improvement in the levels of lead alongside roadways since the 1981 and 1998 studies (Anagnostopoulos 1981; Anagnostopoulou and Day 2006) which had exhibited mean lead values of 1,150 μg/g or mg/kg and 519 μg/g or mg/kg respectively.

Table 1 gives a summary of all the elemental means for the separate particle fractions and a mean of the two fractions. Also listed in the Table 1 are comparisons with similar reported studies from other cities and the published mean elemental concentrations in their roadside dust. It should be noted that these studies were undertaken at different times (Istanbul 2004, Hong Kong 2001 and London 1991) which account for example, for the high levels of lead observed in the early London study before the removal of leaded petrol. The difference in elemental content emphasises that roadside dust is often an indicator of short-term contamination from vehicles (Xiangdong et al. 2001).

Speciation analysis—sequential extraction or fractionation

Two sequential analyses were done for lead and zinc. Lead was selected because of the concerns about residual levels of lead following the removal of leaded petrol; lead was a pollutant that was of significant concern about a decade ago. Since leaded petrol has been phased out it has been observed that lead levels in the roadside dust are lower but the question arises about the mobility of lead in the various environmental media, like dust, soil, plants and the aquatic ecosystems. It has already been seen in the present study that the lead content of roadside dust samples in Thessaloniki is fairly evenly distributed through both particle size fractions. This raises the question, maybe there is a different source of lead (such as wheel bearings or oil combustion products) or even that the roadside dust samples have input from a local domestic or commercial source (paint release as houses are refurbished, local small metal working sites). Zinc was chosen because of an increasing concern about the use of zinc-based compounds as lubricant additives, the potential poisoning of catalytic converters and enhanced release of zinc into the environment where it may have a detrimental effect on aquatic ecosystems. Furthermore, zinc was shown to exhibit vastly different concentrations in a selection of roadside dust samples as shown in Fig. 3. It was therefore thought that the

Table 1 Summary of the elemental mean values for the different roadside dust particle fractions in the present study relative to values reported in the literature

Fraction (μm)	Pb (mg/kg)		Cu (mg/kg)		Mn (mg/kg)		Zn (mg/kg)		Cd (mg/kg)	
	<75	75–125	<75	75–125	<75	75–125	<75	75–125	<75	75–125
Mean	206.5	206.9	255.4	282.9	211.0	173.0	515.4	410.3	5.1	2.9
Total Mean of both fractions.	206.7		269.2		192.0		462.9		4.0	
Istanbul[a]	211.88		208.49		397.90		526.81		1.91	
Hong Kong[b]	181		173		–		1450		3.77	
London[c]	1354		115		–		513		4.2	

[a] Sezgin et al. (2004)

[b] Xiangdong et al. (2001)

[c] Thorton (1991)

distribution of zinc through the geochemical fractions might be interesting and lead to explanations as to whether there are differing chemical forms of zinc whose origins are from various sources of the car (metal work, paint, exhaust system, tyres, oil additives, etc). Incidentally, the two samples that were chosen to represent high elemental concentrations (34, 35) were both collected from the coastal road. Samples reflecting low metal concentrations (47, 50) were both collected from the ring road (a new construction with very few exit points or traffic congestion problems) and the mid metal concentrations sample (68) was collected from a crossroad. These samples were selected by inspection of the overall elemental concentrations of the roadside dust samples (see Figs. 2, 3, 4, 5, 6 and 7) rather than by the location. The sequential fractionation graphs (see Figs. 8 and 9) were calculated using both total and sequential data. The three solutions, representing the exchangeable, Fe–Mn oxide and organic fractions were summed and then subtracted from the total elemental content to calculate the elemental levels in the residual fraction. All these sequential extraction fractions were then calculated to provide an estimate of the percentage of the total elemental level recorded relative to the total elemental analysis.

Lead

Lead showed quite a significant difference in the sequential fractionation pattern between the samples classed as having generally high lead concentrations (34, 35) and those classed as having mid (68) or low Pb concentrations (47, 50; see Fig. 8). None of the samples, except sample 47 (75–125 μm) showed any real association with the organic fraction. The roadside dust samples (34, 35) containing higher total lead levels showed a high affinity for the residual fraction. This might be expected as the roadside dust samples having higher lead levels may still reflect input from the use of leaded petrol. This also confirms that lead is

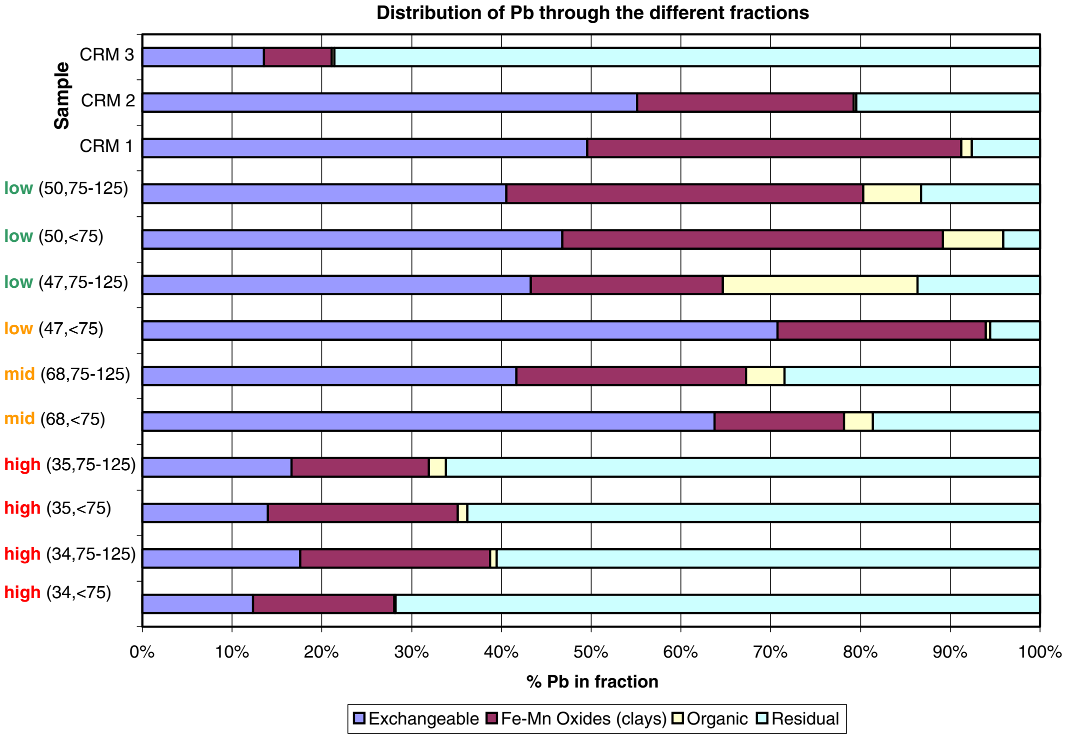


Fig. 8 Sequential fractionation of lead in selected roadside dust samples and certified reference materials (*CRM*) 1, 2 and 3 (with differing particle sizes, <75 μm and 75 to 125 μm)

not very mobile in soils and sediments (Stead et al. 2000), and therefore in the present study a similar observation is noted for roadside dusts. The other samples showed quite a high percentage of lead found in the exchangeable fraction. As far as particle size fraction differences, there was a similar split between the high and mid/low samples. The roadside dust samples containing high lead levels showed that the larger particle size fractions contained lead that had a high affinity for the residual fraction whereas the mid/low samples showed this reversed (see Fig. 8). However, overall the roadside dust samples reflected a tendency to have lead in the residual fraction for the larger particle sizes. This might also be expected in that residual matter is more likely to be the larger particles that are not so easily dispersed. Furthermore, the three certified reference materials showed differing sequential extraction patterns from each other and the road side dust samples under investigation. Reference materials 1 and 2 (Used Auto Catalyst) contained lead in the exchangeable and Fe/Mn oxide fractions, which is similar to the roadside dust samples from roadways that have low or mid lead levels (sites 47, 50 and 68). The Canmet Sudbury Matte certified reference material 3 (which is physically different in that it is very fine black powdered, origin unknown) is entirely different with the lead content being associated mainly with the residual fraction. This is similar to the roadside dust samples from sites 34 and 35, which contained some of the highest roadside dust lead levels, irrespective of particle size. These trends tend to suggest that there is a possibility that lead found in the road side dust samples of Thessaloniki not only varies in magnitude as a result of release from vehicles using the different road types (as a function of traffic density and flow conditions), but may also reflect different sources, and chemical forms, of lead.

Zinc

Figure 9 shows that zinc in roadside dust samples also exhibited a very low affinity for the organic phase, although maybe more (percentage wise) than lead. In summary, all of the road side dust samples showed a similar sequential extraction

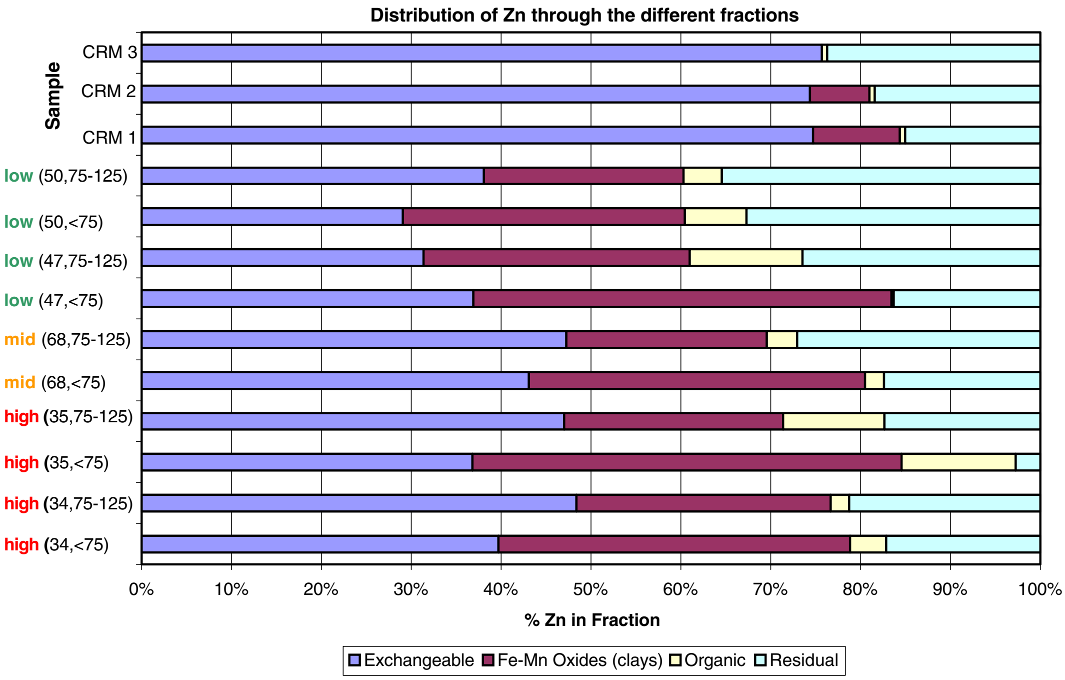


Fig. 9 Sequential fractionation of zinc in selected roadside dust samples and certified reference materials (*CRM*) 1, 2 and 3 (with differing particle sizes, <75 μm and 75 to 125 μm)

pattern throughout, with most of the zinc found in the following order: exchangeable >Fe–Mn oxide > residual > organic. This suggests that zinc may be very mobile in the environment or has an affinity to be associated with clay particles (Fe–Mn oxide fraction). This observation has also been found with zinc in motorway storm water drainage sediments (Stead et al. 2000). Interestingly, the extraction pattern for zinc was similar to that for lead in the low and mid lead level road side dust samples. Similarly, as with lead, there was no observable difference in the zinc sequential extraction pattern between road side dust particle size fractions. However, there was a significant difference in the zinc pattern between the road side dust samples from Thessaloniki and the three certified reference materials. Once again, the Canmet Sudbury Matte certified reference material 3 was slightly different from the other two Used Auto Catalyst materials, having little or no percentage of zinc associated with the Fe–Mn oxide fraction. This material contained zinc primarily associated with the exchangeable and residual fractions. Clearly, the reference materials and roadside dust samples contained different chemical forms of zinc. Although the total zinc analysis of the roadside dust samples showed that a couple of sampling sites had high zinc burdens (sites 8 and 14), the samples selected for the sequential extraction study (sites 34, 35, 47, 50, 68) did not appear to have any obvious variation in chemical forms of zinc. Therefore, this study can not provide any details about the possible sources that contribute to the release of zinc from motor vehicles (metal work, paint, exhaust system, tyres, oil additives, etc) (Rayson 1990; Hares and Ward 2004).

Synoptically, a wet acid digestion method was used, with the use of *Aqua Regia* and Kjeldahl tubes, for total elemental analysis. It was decided that the three step sequential extraction used by Rauret et al. (1999) would provide geochemical and bioavailability data. Data from the total elemental analyses were carried out first. According to calculated values using the F-test, copper was the only element that showed a statistically significant difference in the sample variance between the two fraction sizes, with an F_{cal} value of 2.098 which is significantly different at the probability, $P < 0.001$ or 99.9% confidence limit (F_{crit} of 2.07). Zinc and cadmium showed a significant difference at the $P < 0.05$ or 95% confidence limit. Only lead and manganese showed no significant difference at the $P < 0.05$ or 95% confidence limit. Once the F-test results were known, a Student t-test were carried out on the same data to assess whether there was any significant difference in the mean values between the two fraction sizes. Cadmium and manganese showed a statistically significant difference at the $P < 0.001$ or 99.9% confidence level, between the mean values of the two fraction sizes. Lead, copper and zinc showed no significant difference, at the $P > 0.05$ or 95% confidence limit. Fraction size is generally related to the source of the metal; smaller being associated with exhaust emissions and the engine, whereas larger particles with general wear-and-tear sources from all over the car's body. The results suggest that cadmium and manganese are being deposited more heavily through exhaust emissions while zinc, lead and copper are being deposited through several sources of the motor vehicle.

The other subcategory that was used to compare samples was different road types. The sample sites were divided, according to the map of Thessaloniki (see Fig. 1), into ring road, arterial, major and minor roads. The minor roads were noted to have an average of 10–100 cars/hr as opposed to the other roads which had an average density of >100 cars/h. This comparison enabled variations in traffic density and flow to be considered. In general, it was seen that the arterial roads had the highest metal concentrations followed by major, minor and then the ring road (Figs. 2, 3, 4, 5, 6 and 7). More specifically, road type was seen to have little effect on cadmium and manganese, though lead, copper and zinc were all found to show higher levels on the inner city routes. This can be related back to the wear-and-tear of vehicle components as a result of the stop–start traffic patterns (brake pads etc). Fractionation procedure revealed highly concentrated total Pb levels in samples to be greatly associated with the residual fraction, while mid and low level samples having a greater affinity for the exchangeable fraction. This suggests the presence of different chemical forms and sources of lead. Fractionation of dust samples for zinc showed less variation, with exchangeable and then Fe–Mn oxide association showing the highest levels.

The present study has confirmed that the highest levels of heavy metal pollution occur in the congestion/stop–start zones of inner city arterial, major and minor roads. Motorway ring roads, which display few acceleration/de-acceleration points, were seen to have lower levels of the named heavy metals. Both Pb and Zn have shown to be in chemical forms that are bio available to ecosystems.

Conclusions

1. The sample comparison enables variations in traffic density and flow to be considered. The arterial streets had the highest metal concentrations followed by major, minor and ring roads.
2. The highest metal concentrations were in junctions, supporting the notion of stop-start driving conditions being a major factor in the relationship of traffic to pollution levels.
3. Both Cadmium and Manganese showed higher total levels in the smaller fraction sizes (<75 μm), implying that their major release source is exhaust emissions. Lead, copper and zinc were all exhibited higher levels in the inner city routes. This can be related back to the wear-and-tear of vehicle components as a result of the stop–start traffic patterns (brake pads etc).
4. Fractionation studies revealed the presence of different chemical forms and sources of lead. Moreover, fractionation of road side dust samples for zinc showed less variation, with exchangeable and Fe–Mn oxide fractions showing the highest levels. Both lead and zinc have shown to be in chemical forms that are bio available to ecosystems.
5. Motorway ring road, which displays few acceleration/de-acceleration points, was seen to have low levels of heavy metals.
6. Last but not least, lead concentrations in the city of Thessaloniki exhibited a significant decrease since 1981 and 1998 lead studies of Thessaloniki obviously as a result of the exclusion of leaded petrol.

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