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Manganese levels and chemical fractionation in street dust in South Africa

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Abstract: Mn in street dust and soil from selected roads was studied to assess the contribution of combustion of vehicular methylcyclopentadienyl manganese tricarbonyl (MMT) to Mn levels and distribution in Pretoria, South Africa. Total Mn concentrations ranged from (329.1–863.9 $\mu\text{g g}^{-1}$) for dust and (215.8–450.6 $\mu\text{g g}^{-1}$) for soil. These values were significantly higher than the mean value (278.9 $\mu\text{g g}^{-1}$) found on soil from a rural environment in Pretoria. The lowest value for the dust sample (329.1 $\mu\text{g g}^{-1}$) was close to the mean background level of 330 $\mu\text{g g}^{-1}$ for Mn in soil. Mn distribution in the samples was most in the residual fraction (178.18–487.50 $\mu\text{g g}^{-1}$) and (140.76–293.40 $\mu\text{g g}^{-1}$) for dust and soil respectively. Mn in the other fractions were 56.45–202.60 $\mu\text{g g}^{-1}$ oxides, 90.71–45.34 $\mu\text{g g}^{-1}$ organic, 45.36–12.65 $\mu\text{g g}^{-1}$ carbonates and 1.98–6.72 $\mu\text{g g}^{-1}$ exchangeable for dust and 32.54–167.31 $\mu\text{g g}^{-1}$ oxides, 34.23–70.45 $\mu\text{g g}^{-1}$ organic, 10.98–30.45 $\mu\text{g g}^{-1}$ carbonate and 1.0–4.87 $\mu\text{g g}^{-1}$ exchangeable for soil. Major source of Mn determined was mainly from the combustion of vehicular MMT.

Keywords: manganese level; chemical fractionation; street dusts; roadside soil; South Africa.

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1 Introduction

The widespread use of trace metals in various applications has led to high levels of these metals in environmental samples. This has become a global problem, especially since some of these metals have been recognised as health hazards. Metallic additives in petrol have contributed to the increased levels of trace metals, such as lead, in the urban environment, that has been observed over the years in many countries (Garcia-Miragaya et al., 1981; Schuhmacher et al., 1991; Sithole et al., 1993; Loranger and Zayed, 1994; von Schirnding and Fuggle, 1996; Okonkwo et al., 1999; Zafar and Mirza, 2000). Since lead has been implicated as a neurotoxin, there has been a global effort to drastically reduce, or completely eliminate, the addition of lead in petrol. This has prompted the search for alternatives. In some countries, including South Africa, methylcyclopentadienyl manganese tricarbonyl (MMT) is now in use (18 mg l^{-1}) in some parts of the country as a replacement for organo-lead compound in petrol (Zayed et al., 1999). The use of MMT as an additive (as a combustion enhancer and smoke suppressant) is presently controversial since the intake of manganese-containing MMT either through inhalation or ingestion, may result in pathology, particularly to the central nervous system (Keen and Zindenberg-Cherr, 1990; Mergler et al., 1990; Zayed, 2001). Recently, Wasserman et al. (2006) reported on the intellectual function in 142 10-year-old children exposed to tube-well water contaminated with high and low levels of Mn and As, respectively, in Araihaazar, Bangladesh. Water Mn was associated with reduced full-scale performance and verbal raw scores in the children studied.

Following vehicle emissions the deposition of manganese or any other metal on a road may result in incorporation into street dust as a result of their sizes, which range between 10^{-3} – $10 \mu\text{m}$ (Annegarn et al., 2002). Street dust has been shown to contain elevated levels of toxic metals that may emanate from airborne redistribution by vehicles (Sarto and Boyd, 1972; Pitt and Amy, 1973; Shaleen, 1975; Al-Chalaba and Hawker, 1996; Zayed et al., 2003). Of all the types of dust found in the urban environment,

one of the most highly enriched with toxic metals is roadway dust. Since such dust may be inhaled while airborne or discharged into rivers by storm-water runoff, roadway dust may represent a major pollution source within the urban environment (Harrison et al., 1981).

Total metal concentration is important, but it does not differentiate between different metallic species, forms or phases which determine the potential mobility and bioavailability of the metal (Ure et al., 1993). A comprehensive knowledge of interaction between the different species of the metal and environmental media, such as dust, is of importance in order to be able to predict their environmental impact.

Several studies have been conducted to determine the concentration and the different species of manganese and other elements in soil, sediment and street dust. Tessier et al. (1979) used a five-stage sequential extraction method for the speciation of manganese and other trace metals in sediment. High concentrations of exchangeable manganese were observed and this suggested that the metal existed in a reduced form. Harrison et al. (1981) used the same extraction procedure as Tessier et al. (1979) to study the chemical association of trace metals such as Cd, Cu, Pb and Zn in street dust and roadside soil. Trace metal fractionation and partitioning were observed for all the metals in this study. In another study, Hopke (1980) employed the HNO₃ acid digestion procedure to characterise manganese and other elements in urban roadway dust. The conclusion was that urban roadway dust originating from anthropogenic sources, particularly vehicle exhaust emissions contributed significantly to the levels of Mn determined. Fergusson and Kim (1991) studied the elemental composition of street dust from London (UK), New York (USA), Halifax (Canada), Christchurch (New Zealand) and Kingston (Jamaica). The metals, Cd, Pb, Cu, Zn, Mn and Fe were sequentially extracted from the dust into five fractions. Sutherland (2002) examined the relationship between the summed concentrations of Mn among other metals released by an optimised three-step standardised sequential extraction procedure and those released by a single HCl leach. Highly significant relationships between the two digestion procedures were found.

In an attempt to harmonise the methodology throughout the European Union, and to improve comparability between results, the Community Bureau of Reference (BCR) devised and used a three-stage extraction protocol for the operationally defined fractionation of trace metals, including manganese, in soil and sediment samples (Ure et al., 1993). Recently, Tokalioglu et al. (2003) applied the same three-stage extraction method to a speciation study of manganese and other trace metals in soil samples from Turkey. These studies attest that sequential extraction is still a much used extraction technique in elemental fractionation studies.

As part of ongoing automobile technology development in South Africa, oil companies in the country have introduced MMT to replace the phased out leaded petrol. The introduction of MMT has prompted research into health risk assessment of MMT within the South African environment. Recently Röllin et al. (2005) measured blood Mn concentrations of first grade schoolchildren in two South African cities, Cape Town and Johannesburg. Blood-Mn levels found in those subjects studied were 9.80 µg l⁻¹ and 6.74 µg l⁻¹ for Johannesburg and Cape Town, respectively. The study also examined dust and soil samples collected from the classrooms and playgrounds of some of the schools within the two cities. However, details of sample treatment before analysis were not given. Furthermore, Mn distribution among different fractions was not conducted.

In the light of the paucity of studies on the chemical fractionation of manganese in street dust in South Africa, the present study was embarked upon to determine the manganese levels in different roads in the Pretoria area. It is most likely that the chemical properties of street dust may, like those of soil and sediment, play an important role in manganese retention or removal from street dust. The impact of these properties may vary according to the nature of roads. There is, therefore, a need to investigate the behaviour of manganese distribution among different physical and chemical fractions of street dust samples obtained from roads with different characteristics. Furthermore, this is the first detailed study of manganese in street dust in South Africa. It is envisaged that the results of this study will provide a baseline against which the impact of exposure to manganese via vehicular fuel combustion of MMT, could be measured in the future in South Africa.

2 Materials and methods

2.1 Sampling sites

Based on the modelling results of traffic density in the city reported by the Tshwane (Pretoria) Metropolitan Council (Tshwane Interim Model, 2002), sampling sites were selected at the following major road junctions: Paul Kruger, DF Malan, Nelson Mandela and Potgieter. The aforementioned sites are with kerbs and, therefore, a distance of 1 m away from the kerb was chosen for in-situ street dust sampling. Four petrol stations (P Station) within the city centre (Eastern, Northern, Southern and Western directions) and a shopping mall, Menlyn, (about 15 km south-east from the city centre) were also selected. A suburban area orchard and a highway Ben Schoeman (located about 15 km north of Pretoria city centre) were also selected in order to get the general distribution of manganese levels within the different roads.

2.2 Sample collection and preparation

Samples were collected 1 m away from the kerb of street intersections of each site at 1-month intervals during the winter (dry) period in 2004–2005. Eight sampling points were identified at each four-way road junction. Analysis of initial samples collected from these junctions showed very close concentration values. Consequently, composite samples were prepared for all the points. Dust and soil samples were collected from a total of 16 road junctions. In the case of the petrol stations and the mall, dust samples were collected from the paved concrete. For the suburban orchard and Ben Schoeman highway, dust samples were collected from a distance of 1 m away from the kerb and 1 m distance inside the hard-shoulder lane, respectively. About 1 kg of street dust samples was collected from the sites by gently sweeping the road surface with a clean nylon broom into a thoroughly washed plastic scoop. The scoop was thoroughly washed with dilute acid and thereafter rinsed with deionised water and dried between sample collections in order to avoid cross contamination. The collected dust samples were thereafter placed into well-labelled, self-sealing propylene bags, stored in black plastic bags and transported to the laboratory. In the laboratory, the collected dust samples were air dried on a propylene sheet overnight. The air-dried dust samples were sieved with a 600 µm stainless steel sieve to remove large materials and the moisture content

determined at 105°C for 24 h. Roadside soil samples were collected within a depth of 1 cm where there were no intervening pavements at the sampling sites for comparison. Extraneous substances such as dead leaves and stones were removed from the soil. Approximately 100 g of soil were removed from each sample location using a clean stainless steel trowel. Adequate care was taken during sampling to avoid cross contamination of samples. Four soil samples were also collected (50 m off the road) from a rural environment within the Tshwane (Pretoria) Municipality (with the same soil type as those described earlier) in order to obtain some background levels. The samples were placed and treated as described above with the dust samples.

2.3 *Apparatus and reagents*

A Perkin Elmer 3030 atomic absorption spectrophotometer equipped with a single slot burner was used for the analyses. The analytical signals were recorded using a programme for data handling controlled by a microprocessor. Measurements were carried out in triplicate. All glass and propylene ware used were first soaked in dilute HNO₃, thoroughly washed with liquid soap and then rinsed with double distilled deionised water and acetone. Thereafter, all the glassware was dried in the oven at 100°C for 24 h, while the plastic ware was left to dry at room temperature. pH and Electrical Conductivity (EC) measurements were determined using Metrohm pH meter model 713 and Thermo Orion 145, respectively.

A 1000 mg l⁻¹ stock solution of manganese was purchased from Associated Chemical Enterprises from which standard working solutions were prepared. Lower concentrations were prepared as required. A normal linear fit working calibration curve was prepared for metal determination. All other reagents used were of analytical reagent grade.

2.4 *Determination of pH and Electrical Conductivity (EC)*

Deionised water (100 ml) was added to 40 g of air-dried and sieved dust and soil samples in separate beakers. The sample mixtures were agitated for 20 min and allowed to stand for 1 h. Thereafter the mixtures were filtered through pre-washed Whatman filter paper No. 42 and then the pH and EC of the filtrate determined.

2.5 *Determination of total manganese*

About 5 g dust samples (before fractionation into size fractions) were digested in ceramic crucibles with 60 ml aqua regia solution (HCl/HNO₃; 3 : 1) in a steam bath in a fume-cupboard. Additional volume of aqua regia solution was added to the digest as required and evaporated to near dryness. The digest was later filtered through Whatmann 48 filter paper with hot 1 M HNO₃ solution, allowed to cool, transferred to a 25 ml volumetric flask and made up to the mark with 1 M HNO₃ and then analysed using FAAS. The soil samples were also treated as described above.

2.6 Sequential extraction of manganese from various fractions

The extraction protocol has been validated for the selectivity of various fractions of trace elements in sediment samples; this is shown in Table 1 (Tessier et al., 1979). The method essentially involves weighing known amount of sample (in the present study, 5 g) and subjecting it to the first extractant treatment for exchangeable ions as shown in Table 1. The residue obtained was extracted with the second extractant for the carbonate fraction. Subsequent residues were then subjected to third, fourth and fifth extractants for oxide, organic and residue fractions, respectively. All extractions were performed in 50 ml polypropylene centrifuge tubes with a mechanical shaker for mixing and agitating. Thereafter, the extracts were centrifuged for 15 min at ± 2500 rev/min, supernatant liquor carefully transferred (with the aid of a pipette) into propylene vials and taken for manganese measurement.

Table 1 A five-stage sequential extraction protocol used in the present study

| <i>Fraction</i> | <i>Protocol</i> |
|-----------------|---|
| Exchangeable | 1 M MgCl ₂ (8 ml), pH 7.0, 1 h at 20°C, continuous agitation |
| Carbonate | 1 M NaOAc (8 ml), pH 5.0, at 20°C, continuous agitation |
| Fe-Mn oxides | 0.04 M NH ₂ OH.HCl in 25% acetic acid (20 ml), 6 h, 96°C, with occasional agitation |
| Organic | 0.02 M HNO ₃ (3 ml) + 30% H ₂ O ₂ (5 ml), pH 2.0, 2 h, at 85°C, occasional agitation; further 30% H ₂ O ₂ (3 ml) pH 2.0, 3 h, at 85°C occasional agitation; then 3.2 M NH ₄ Oac in 20% HNO ₃ , (5 ml), 0.5 h at 20°C continuous agitation |
| Residual | 15 ml concentrated HNO ₃ , 1 h refluxing, filtration, washing (sample + filter) with 10 ml hot 3 M HNO ₃ |

2.7 Quality assurance, method validation and detection limit

The performed analytical quality control included daily analysis of standards and triplicate analysis of samples and blanks. The instrument was calibrated using the method of standard addition in order to reduce matrix effect. The analytical method used in the present study was validated against Certified Soil Reference Material (Reference: GBW07401) supplied by the Industrial Analytical Company. The detection limit for manganese was determined using the lowest concentration of the element that gave the least detectable signal using flame AAS. Six replicates of standard manganese were prepared and analysed. The detection limits were determined from 3σ (σ = standard deviation) of the replicate determinations for each of the element (Miller and Miller, 1998). The results were analysed by the student *t*-test at 95% confidence limit.

2.8 Data analysis

The standard deviation for manganese from replicate measurements was determined. For the general subsequent evaluation of the data, the mean values were used. The linear correlation coefficients of dust and soil manganese were determined using the Pearson correlation coefficient.

3 Results and discussion

3.1 Quality control, detection limit and method validation

The calibration values gave correlation coefficients ranging from 0.95 to 0.97 and the detection limit obtained for manganese was 100 ng g^{-1} .

The results of manganese concentrations in different street dusts and soil chemical fractions against certified soil reference material are shown in Table 2. The high percentage recoveries of 81.7% and 79.0% for dust and soil samples, respectively, in the different chemical fractions and 88.0% for the total manganese value of $1552 \text{ } \mu\text{g g}^{-1}$ validate the methods used in the present study. Furthermore, as can be seen in the same table, there is good agreement between the sum of the total manganese concentrations in the individual fractions and the total metal concentration for both dust and soil samples. Also, the value for total manganese, $1552 \text{ } \mu\text{g g}^{-1}$, compares favourably with the reference value of $1760 \text{ } \mu\text{g g}^{-1}$.

Table 2 Validation of the chemical fractionation and aqua regia methods for manganese levels against soil certified reference material^b ($n = 3$)

| Chemical fraction | Manganese ($\mu\text{g g}^{-1} \pm \text{RSD}$) | | Total Mn ($\mu\text{g g}^{-1}$) |
|----------------------|---|------------------------------|--|
| | Dust sample | Soil sample | |
| Exchangeable cations | 20.72 ± 3.72 | 18.43 ± 5.3 | |
| Carbonates | 88.83 ± 1.02 | 81.87 ± 7.3 | |
| Oxides | 209.30 ± 1.09 | 195.87 ± 5.3 | |
| Organic matter | 197.40 ± 1.02 | 185.55 ± 6.2 | |
| Residual | 921.20 ± 2.02 | 908.71 ± 7.1 | |
| | 1437.45 (sum total) 81.7% | 1390.43 (sum total) 79.0% | |
| | | | ^a 1552.20 ± 2.12 (total Mn) |
| | | | ^b $1760 \pm 98 \text{ } \mu\text{g g}^{-1}$ |

RSD: Relative Standard Deviation.

^aValue obtained from the aqua regia digestion of certified reference sample.

^bCertified soil reference sample.

As can be seen in Table 2, the values for the dust samples are higher than those of the soil samples but they do not appear to be significantly different. This can be explained as follows: the tendency for manganese compounds to adsorb to soil can be highly variable depending on the cation exchange capacity and the organic composition among other properties of the soil. The lower values for both the organic and exchangeable fractions obtained for soil samples may have contributed to the observed difference between the values of dust and soil samples. Also, the residual fraction exhibited the highest concentrations, with 64% and 65% for street dust and soil samples, respectively. The other fractions followed similar trend for both street dust and soil samples: Fe-Mn oxide (15% and 15%) > organic (14% and 13%) > carbonate (6% and 6%) > exchangeable (1% and 1%) for dust and soil samples, respectively. This is perhaps not surprising as street dust, to a certain extent, is composed of soil material and hence,

chemical associations can be expected to be similar. The high association of manganese with the residual fraction was attributed to the high retention ability of the mineral crystal structure such as silicate minerals. Such mineral structure (although not determined in the present study) may hold trace metals within their crystal structure and the release of metals from such a structure will require a mixture of strong acid solutions. This overwhelming importance of this fraction was also shown by the results of Tessier et al. (1979) and Tokalioğlu et al. (2003) for manganese in sediment and soil samples, respectively. However, the values for the residual, Fe-Mn oxide and organic fractions for street dust and soil obtained in this study are significantly higher than those reported in sediment (Tessier et al., 1979). However, the work of Stone and Marsalek (1996) found that slightly less than half the Mn of street dust samples was in the residual fraction, with 27% in the Fe-Mn fraction followed by 16% in the carbonate fraction. Their mean levels of total Mn were double the values reported in this study. In another study (Droppo et al., 1998) found that Mn, proportionally, was highest in the Fe-Mn fraction, followed closely by the residual fraction and then the carbonate fraction. Their results were heavily influenced by atmospheric discharges from the steel mill operations and calcareous nature of the local bedrock. Robertson (2003) in a sequential extraction study found the Fe-Mn fraction to be the most important carrier of those metals studied (which included Mn) in the Manchester urban sediment. However, they reported low concentrations of exchangeable metal and this is in agreement with the low levels of exchangeable fraction reported in this study. In an attempt to find out possible sources for manganese obtained in the present study, the correlation coefficients between dust and soil samples were determined. A significant correlation between dust and soil manganese ($r = 0.92-0.99$) was found and this may suggest the same source, most probably from vehicle exhaust as a result of combustion of MMT, in the absence of any industrial activities within the study area. It is also possible that tyre wear and brake linings may have contributed to the manganese concentrations obtained in the present study since manganese and other metals have been reported to be present in these materials (Ondov, 1974).

3.2 Total mean manganese, pH and Electrical Conductivity (EC) measurement of street dust samples from selected sites

Results in Table 3 show the measured values of total mean manganese, pH EC and traffic count/day (Tshwane Interim Model, 2002) in street dust and soil samples from the selected sites. The total Mn values obtained for dust samples follow the trend: Ben Schoeman highway > P Kruger > P Station(N) > P Station(S) > DF Malan > Potgieter Street > Orchard suburban > P Station(W) > N Mandela Av > P Station(E) Tshwane Interim Model > Menlyn Mall. The trend for soil samples was as follows: Ben Schoeman highway > P Kruger > P Station(S) > P Station(N) > P Station(W) > Potgieter Street > DF Malan > Orchard suburban > N Mandela Avenue > P Station(E) > Menlyn Mall. The concentration values obtained in this study are within the upper range of those reported by Röllin et al. (2005) in classroom dust and playground soil obtained from Cape Town and Johannesburg in South Africa. This is not the case with the report by Boudissa et al. (2006) and Sutherland (2002) on roadside soil with total Mn concentrations of $26,600 \mu\text{g g}^{-1}$ and $1460 \mu\text{g g}^{-1}$, respectively. The high Mn concentrations obtained by these researchers was attributed to the direct deposition on the soil of solid Mn-rich residue from a manganese alloy production plant

(Boudissa et al., 2006) and traffic associated pollution (Sutherland, 2002). It can also be seen from Table 3 that all the manganese concentrations for the dust and soil samples from the selected roads are generally higher than the concentration for soil sample obtained from a rural environment, except the value for soil sample from Menlyn Mall.

Table 3 Total mean manganese ($\mu\text{g g}^{-1}$ dry wt) pH and Electrical Conductivity (EC) (μS) measurements of street dust samples from the selected sites

| Sampling sites | Total Mn | | pH | | EC (μS) | | *Traffic (count/day) |
|----------------|--------------------------|-----------------|-----------------|---------------|----------------------|-----------------|-------------------------|
| | Dust | Soil | Dust | Soil | Dust | Soil | |
| | (\pm RSD) | | | | | | |
| BS Highway | 863.8 \pm 1.5 | 450 \pm 1.0 | 8.2 \pm 2.5 | 7.7 \pm 2.2 | 136.6 | 58,916 | |
| | \pm 2.0123.1 \pm 1.2 | | | | | | |
| DF Malan St. | 594.7 \pm 2.3 | 324.4 \pm 0.7 | 7.9 \pm 0.1 | 8.1 \pm 1.6 | 312.4 \pm 2.9 | 291.4 \pm 2.1 | 31,194 |
| Menlyn Mall | 329.1 \pm 5.7 | 215.8 \pm 0.7 | 7.9 \pm 3.5 | 8.5 \pm 1.5 | 148.3 \pm 2.2 | 131.4 \pm 2.4 | 28,181 |
| N Mandela Av | 469.6 \pm 1.5 | 298.2 \pm 0.6 | 8.4 \pm 1.0 | 7.8 \pm 2.1 | 391.2 \pm 2.9 | 309.4 \pm 3.5 | 29,524 |
| Potgieter St. | 577.9 \pm 2.4 | 355.6 \pm 4.2 | 7.8 \pm 0.8 | 7.9 \pm 3.1 | 200.3 \pm 3.1 | 102.2 \pm 2.1 | 31,077 |
| P Kruger St. | 798.6 \pm 1.1 | 431.6 \pm 0.6 | 7.8 \pm 2.2 | 7.2 \pm 2.3 | 345.2 \pm 2.1 | 295.3 \pm 4.1 | 53,960 |
| P Station (E) | 447.3 \pm 2.9 | 278.9 \pm 2.1 | 8.1 \pm 0.2 | 7.4 \pm 4.2 | 185.5 \pm 3.8 | 150.1 \pm 3.2 | 22,218 |
| P Station (N) | 769.0 \pm 3.9 | 510.3 \pm 0.4 | 9.1 \pm 0.2 | 8.3 \pm 3.1 | 258.7 \pm 3.0 | 173.9 \pm 2.6 | 46,005 |
| P Station (S) | 728.6 \pm 0.6 | 416.5 \pm 1.6 | 8.2 \pm 1.2 | 9.1 \pm 2.1 | 567.4 \pm 2.6 | 475.4 \pm 1.2 | 33,763 |
| P Station (W) | 541.2 \pm 0.9 | 387.5 \pm 0.4 | 8.6 \pm 1.2 | 7.9 \pm 3.0 | 304.1 \pm 2.1 | 276.8 \pm 4.2 | 24,383 |
| Orchard sub | 542.1 \pm 6.7 | 303.6 \pm 1.2 | 7.8 \pm 2.7 | 7.0 \pm 2.1 | 173.1 \pm 4.9 | 120.6 \pm 2.3 | 23,679 |
| Rural En | | | 276.9 \pm 1.1 | | 7.2 \pm 0.7 | | 122.4 \pm 4.1 |

BS Highway = Ben Schoeman; DF Malan St = N; Mandela Av = Nelson Mandela Avenue; P Kruger St. = Paul Kruger Street; P Station = Petrol Station (E); P Station = Petrol Station (N) P Station = Petrol Station (S); P Station = Petrol Station (W); Orchard sub = Orchard suburban; Rural En = Rural Environment.

Source: *Tshwane Interim Model (2002)

The total mean manganese obtained for dust and soil samples summarised in Table 3 shows significant difference between the total mean values for dust (329.1–863.8 $\mu\text{g g}^{-1}$) and soil (215.8–450.6 $\mu\text{g g}^{-1}$). That the total mean values for soil are lower than those for dust can be explained as follows: the principal product of combustion of MMT in petrol is inorganic manganese, in the form of airborne particulates of hausmannite, (Mn_3O_4) along with traces of manganese sesquioxide (Mn_2O_3). These are quickly removed from the atmosphere by gravitational settling or by rain, depending on the sizes of the particles. The tendency of these particulates to adsorb to dust, soils and sediments depend mainly on the cation exchange capacity and the organic composition of the soil (Schnitzer, 1969; McBride, 1979; Curtin et al., 1980; Baes and Sharp, 1983; Kabata-Pendias and Pendias, 1984). Since the organic and exchangeable fractions of the dust samples are higher than those of the soil, the overall retention of Mn ions can be expected to be less in the soil sample than in the dust. Also Mn^{3+} is relatively unstable in the environment and its presence in soils can be altered by microbial activity

(Geering et al., 1969; Francis, 1985). If this is so the contribution of Mn^{3+} to the total manganese in soil may have been reduced. However, the range (215.8–450.6 $\mu\text{g g}^{-1}$) for the soil samples is lower than the range (720–1090 $\mu\text{g g}^{-1}$) reported by Tessier et al. (1979) for manganese in sediment samples and van Loon and Duffy (2000) for a similar study in Canada; but significantly ($p < 0.05$) higher than that reported by Hopke (1980) and Tokalioğlu et al. (2003) in street dust and soil samples, respectively. Tessier et al. (1979) reported a relatively higher concentration of exchangeable manganese than the values obtained in this study and this may explain the high values they obtained as well as the fact that their study was on sediment. The upper range value for dust samples is well within that reported by Tessier et al. (1979) in sediment samples.

A correlation analysis was performed which revealed a statistically significant relationship at 5% level between dust and soil Mn levels and traffic volume. Ben Schoeman highway and P Kruger Street showed fairly high mean levels of manganese in street dust and soil samples compared to the other sites. This is perhaps not surprising, as these roads also show high traffic count that may have contributed to higher levels of manganese in the roadside environment (Table 3). The concentrations for the other sites for dust samples were as follows: petrol station (N) > petrol station (S) > DF Malan > Potgieter Street > orchard suburb > petrol station (W) > Nelson Mandela Avenue > petrol station (E) and finally Menlyn Mall and these are in line with traffic count, except Menlyn Mall. This observation (except Menlyn Mall) agrees with the work of Zayed (2001) and Zayed et al. (2003) who have reported extensively on the combustion of MMT to the level of Mn in street dust, roadside soil, sediment and air as a result of traffic density in Canada; Fergusson and Kim (1991) have reported on elemental composition of street dust from large and small urban areas related to city types and Bolte et al. (2004) who attributed high outdoor atmospheric Mn to high traffic density. That Menlyn Mall showed the lowest concentration although ranking 6th on the traffic count can be attributed to the very frequent sweeping and cleaning of the car parks within the mall.

The concentrations obtained for the dust samples are significantly higher ($p < 0.05$) than the values found in soils ($278.9 \pm 1.1 \mu\text{g g}^{-1}$) collected 50 m off the road from a rural environment within the Tshwane (Pretoria) Municipality. This is not surprising since according to a National Research Council of Canada report (Stokes et al., 1988), manganese concentrations in air tend to be lowest in remote locations (about 0.5–14 ng m^{-3} on average), higher in rural areas (40 ng m^{-3} on average), and still higher in urban areas (about 65–166 ng m^{-3} on average). Similar concentrations have been reported elsewhere (WHO, 1999), leading to the conclusion that annual manganese concentrations average 10–30 ng m^{-3} in areas far from known sources and 10–70 ng m^{-3} in urban and rural areas without major point sources of manganese. Although the level of manganese in air was not measured in the present study, it is possible that the concentrations obtained for the dusts and soil samples reflect the atmospheric levels of manganese within the urban and rural environment studied. It is worth noting that these values are within the world soil levels of 100–4000 $\mu\text{g g}^{-1}$ (van Loon and Duffy, 2000). The value obtained for the soil sample from the rural environment is in good agreement with the estimated mean value of 330 $\mu\text{g g}^{-1}$ reported in the literature (USEPA, 1984; Schroeder et al., 1987; Eckel and Langley, 1988; Rope et al., 1988). As can be noted in Table 3, the high concentrations shown by DF Malan and Potgieter indicate that these roads are busy with traffic. The results for the petrol stations varied

from $447.7 \mu\text{g g}^{-1}$ to $769.0 \mu\text{g g}^{-1}$. The upper limit values were recorded for petrol stations north and south with very high traffic count, while petrol stations east and west showed values within the lower limits with lower traffic count. The lower values obtained for petrol stations east and west can be attributed to fewer vehicles making use of the services of these stations as well as good house keeping by the two petrol stations. That a higher concentration was recorded for orchard a suburban area than petrol stations east and west, Nelson Mandela Avenue (a dual-carriage way) and a busy shopping mall, Menlyn, is an indication of the extent of distribution of manganese within the selected roads. The soil followed a similar pattern as observed for dust from Ben Schoeman, P Kruger, Nelson Mandela, P Station(E) and Menlyn. There was no specific pattern for the other sites.

The correlation coefficient is used as a measure of the correlation between two variables. This tool has been employed to examine the relationship (with respect to possible sources) between trace metals and soil and vegetation (Harrison et al., 1981). This tool was employed in the present study to attempt to establish any correlation between dust and soil samples collected from selected roads, and dust and soil samples from these sites and the soil sample collected from a rural environment. A significant correlation ($r = 0.92\text{--}0.97$) was obtained between dust and soil from the selected roads. This may suggest similar source, most probably combustion of MMT from vehicle exhaust, since the closest industrial activity is 70–100 km from the study area. The contribution of transportation of Mn compounds by wind from the industrial areas to the study is expected to be minimal since Mn particulates are airborne for a very short time before they are quickly settled by gravity. However, no significant correlation was found between Mn dust and soil from selected sites and soil collected from a rural environment ($r = 0.12\text{--}0.65$). This may indicate different sources – anthropogenic and natural. It is important to note that the geological make up of the study area is that of shale which is very low in manganese as opposed to dolomite type of rocks. So the low level of manganese obtained for the rural soil sample is an attestation of the level of background manganese within the study area.

The pH and the EC are usually considered as indicators or measures of the chemical nature of street dusts and soils. The data in Table 3 show that the pH values obtained for all the sites are within the alkaline range 7.8–9.2. The amount of exchangeable manganese is, therefore, expected to be small at these pH values and this was so. Available information (Farrah and Pickering, 1977; Abd-Elfattah and Wada, 1981; Harter, 1983; Puls et al., 1991) indicates that the retention of metals in soil increases dramatically above pH 7 as a result of competitive bonding of CO_3^{2-} and OH^- anions with the metal cations. The resulting metal complexes are insoluble under these pH conditions and this may result in metals such as manganese becoming unavailable to plants. The EC measured the relative amount of total ions in the street dusts ($136.6\text{--}567.4 \mu\text{S/cm}$) and soil ($102.2\text{--}295 \mu\text{S/cm}$). The ECs for dust are generally higher than those of soil. The highest EC level was recorded for the petrol station (S) ($567 \pm 2.6 \mu\text{S}$) in the city centre as can be seen in Table 3.

3.3 Sequential extraction

Manganese levels obtained from the sequential extraction, based on the average values from the selected road sites, are shown in Table 4. The results in Table 4 show that for the 11 sites, the highest individual site mean of extractable manganese in the street dust

and soil was associated with the residual fraction. The other fractions follow the trend: Fe-Mn oxide > organic > carbonate > exchangeable. The highest concentrations for dust and soil were obtained for Ben Schoeman and the lowest values exhibited by Menlyn Mall and Potgieter Street for dust and soil under the residual fraction. Also, Ben Schoeman showed the highest values, and P Station (W) the lowest, for dust and soil samples under Fe-Mn oxide fraction. For the next abundant fraction, organic, Potgieter Street and P Kruger showed the highest values, and P Station (W) and Ben Schoeman the lowest values for dust and soil samples. P Kruger and P Station (E) exhibited the highest values for dust and soil samples under the carbonate fraction. Under the same carbonate fraction P Station (W) showed the lowest values and for dust and soil samples. Within the exchangeable fraction, P Station (E) showed the highest values for dust and soil; while P Station(S) and P Station(W) exhibited the lowest values for dust and soil.

The high association of manganese with the residual fraction was attributed to the high retention ability of the mineral crystal structure such as detrital silicate minerals and resistant sulphides, although this was not determined. This fraction accounts for an appreciable proportion of the total Mn for dust (11–31%) and soil (9–19%). The overwhelming importance of this fraction, amply shown by the results of Tessier et al. (1979) and Tokalioğlu et al. (2003) for manganese in sediment and soil samples, respectively, demonstrates very clearly the difficulty of distinguishing between background and anomalous levels of trace metal contamination when only total metal analyses are performed. However, the work of Stone and Marsalek (1996) found Mn among other metals to be predominantly bound to carbonates, Fe-Mn and organic. The Fe-Mn oxides fraction represents the second highest mean manganese with 2–13% and 2–11% for dust and soil, respectively (Table 4). These results are lower than the values reported by Tessier et al. (1979) for manganese in sediment samples. Fe-Mn oxides fraction is known to have a high capacity for trace metal adsorption and this is a testimony of the strong scavenging efficiency of Fe-Mn oxides for trace metals (Jenne, 1968). Robertson et al. (2003) found Fe-Mn to be the most important fraction for Mn in the Manchester urban sediment. The organic fraction showed a percentage manganese range of 3–6% and 2–5% for dust and soil, respectively, ranking it third in chemical fractionation behind the Fe-Mn fraction. The low levels shown by the organic fraction may be attributed to the unavailability of manganese since the metal was probably bound to various forms of organic matter; the formation of complexes and peptisation properties of natural organic matter (notably humic and fulvic acids) is well recognised. The concentration values shown by the carbonate fraction in Table 4, indicate the smaller importance of this fraction in controlling manganese retention and release in the street dust used in this study. It is probable that the street dust used in this study is not so calcareous in nature (although this was not investigated), since carbonate minerals such as calcium carbonate are widely distributed in nature, especially in soil. As street dust is composed mainly of soil materials, the carbonate fraction obtained from this fraction can be compared to that of soils. The mean manganese values obtained for the different sites are less than that reported by Tokalioğlu et al. (2003) in soil in Turkey. Using the same sequential extraction procedure, Tessier et al. (1979) found between 13–28% of manganese in the carbonate fraction in sediment compared to <1–3% and <1–2% for dust and soil samples, respectively, obtained in this study.

Table 4 Manganese concentrations ($\mu\text{g g}^{-1}$) and percentage distribution by mass in different chemical fractions of street dust and roadside soil ($<600 \mu\text{m}$) from selected road sites

| Sampling site | Chemical fractions (\pm RSD) | | | | | | | | | | | |
|---------------|---------------------------------|----------------|-----------------|-----------------|------------------|------------------|-----------------|-----------------|------------------|------------------|--|--|
| | Exchangeable | | Carbonate | | Fe-Mn oxides | | Organic | | Residual | | | |
| | Dust | Soil | Dust | Soil | Dust | Soil | Dust | Soil | Dust | Soil | | |
| BS Highway | 6.72 \pm 0.3 | 4.52 \pm 1.4 | 20.85 \pm 6.5 | 15.45 \pm 3.4 | 202.60 \pm 2.5 | 167.31 \pm 5.1 | 56.60 \pm 2.7 | 34.23 \pm 4.6 | 487.50 \pm 5.9 | 300.56 \pm 7.1 | | |
| DF Malan St. | 4.56 \pm 2.1 | 2.65 \pm 2.1 | 34.12 \pm 5.3 | 25.76 \pm 1.3 | 120.34 \pm 3.7 | 98.23 \pm 2.2 | 65.89 \pm 7.5 | 43.54 \pm 3.2 | 375.12 \pm 4.6 | 198.23 \pm 6.1 | | |
| Menlyn Mall | 2.12 \pm 1.0 | 1.76 \pm 0.4 | 17.56 \pm 2.8 | 12.54 \pm 6.2 | 68.95 \pm 7.5 | 45.45 \pm 4.5 | 50.55 \pm 5.3 | 35.23 \pm 2.4 | 178.18 \pm 2.5 | 140.76 \pm 7.2 | | |
| N Mandela A | 5.76 \pm 3.1 | 2.98 \pm 6.4 | 29.32 \pm 2.3 | 20.45 \pm 4.1 | 109.23 \pm 5.3 | 77.88 \pm 7.4 | 70.21 \pm 3.1 | 40.74 \pm 2.6 | 346.32 \pm 5.2 | 213.43 \pm 4.2 | | |
| Potgieter St. | 4.35 \pm 2.1 | 3.54 \pm 3.1 | 18.04 \pm 4.1 | 10.34 \pm 2.2 | 190.12 \pm 3.4 | 100.23 \pm 5.1 | 96.71 \pm 4.4 | 54.23 \pm 4.2 | 218.45 \pm 3.4 | 98.45 \pm 5.1 | | |
| P Kruger St. | 3.78 \pm 2.7 | 1.87 \pm 2.1 | 45.36 \pm 3.7 | 25.45 \pm 3.2 | 136.10 \pm 1.3 | 100.21 \pm 3.2 | 90.71 \pm 4.9 | 70.45 \pm 6.4 | 431.20 \pm 1.1 | 293.40 \pm 5.3 | | |
| P Station (E) | 7.32 \pm 5.4 | 4.87 \pm 1.2 | 40.54 \pm 7.2 | 30.45 \pm 4.1 | 150.11 \pm 9.1 | 127.31 \pm 7.5 | 86.54 \pm 1.5 | 65.87 \pm 4.9 | 460.45 \pm 3.3 | 278.30 \pm 2.1 | | |
| P Station (N) | 2.89 \pm 2.1 | 1.68 \pm 0.9 | 19.65 \pm 2.1 | 14.54 \pm 5.6 | 163.45 \pm 3.1 | 123.54 \pm 2.7 | 89.34 \pm 2.8 | 67.76 \pm 6.5 | 250.34 \pm 1.2 | 198.65 \pm 6.5 | | |
| P Station (S) | 1.98 \pm 0.8 | 1.34 \pm 0.6 | 16.76 \pm 6.5 | 11.11 \pm 2.1 | 100.32 \pm 6.4 | 78.67 \pm 5.3 | 66.54 \pm 5.4 | 46.61 \pm 2.4 | 219.17 \pm 6.1 | 168.53 \pm 2.1 | | |
| P Station (W) | 3.23 \pm 0.7 | 1.0 \pm 0.3 | 12.65 \pm 7.2 | 9.87 \pm 1.2 | 56.45 \pm 3.2 | 32.54 \pm 4.3 | 45.34 \pm 2.1 | 35.23 \pm 3.1 | 188.21 \pm 3.2 | 150.42 \pm 5.2 | | |
| Orchard sub | 2.12 \pm 0.6 | 1.10 \pm 0.5 | 14.32 \pm 6.4 | 10.98 \pm 5.4 | 60.34 \pm 6.5 | 40.65 \pm 7.4 | 50.12 \pm 5.4 | 40.24 \pm 6.3 | 200.52 \pm 5.3 | 160.69 \pm 2.5 | | |

The exchangeable fraction showed the lowest percentage compared to the other fractions (<1%) for both dust and soil samples. The relatively low concentration of exchangeable manganese suggested that the metal may have existed in the oxidised form, which led to lower exchange capacity and exchangeable cation. This is in agreement with the notion that the retention of metals in soil samples increases dramatically above pH 7 (Harter, 1983). Our results for exchangeable manganese agree with that reported by Robertson et al. (2003), but differ significantly from the findings of Tessier et al. (1979) who reported high concentrations of exchangeable manganese in sediment.

4 Conclusions

The results presented indicate that the urban dust and soil samples from the Pretoria area contained high levels of Mn compared to Mn levels in soil samples from a rural environment. Generally, there is a good correlation between Mn concentrations obtained in the present study and traffic density, suggesting vehicular sources as being the primary contributor to the street dust and soil studies. This trend was observed for all the sites except Menlyn Mall. The correlation coefficients calculated between dust and soil samples from the selected sites suggested, possibly, the same source of manganese. However, no significant correlation was obtained between soil obtained from a rural environment and dust and soil samples from the selected roads. This was a strong indication of different sources – anthropogenic and natural. The anthropogenic source was most probably the combustion of MMT emitted from vehicle exhaust, although contributions from tyre wear and brake linings may be possible.

The pH of the dust samples used in this study was found to be within the alkaline region and this may have played a significant role in the chemical fractionation, particularly with the exchangeable fractions.

Sequential extraction analysis indicates that most Mn was associated with the residual fraction. This was attributed to the binding of manganese to an aggregate of loosened solid bodies such as silicates. The next abundant fractions were the Fe-Mn oxide and organic fractions. The scavenging ability of the Fe-Mn oxide fraction may have contributed to the observed values obtained for this fraction in the present study. The organic fraction indicated non-availability of manganese due to the formation of complexes by humic substances. The carbonate fraction was low and may have been due to the small calcareous nature of the dust samples used in the present study, although no non-calcareous test was conducted. Very low levels of manganese were found in the exchangeable fraction, suggesting that Mn will be relatively immobile on street surfaces.

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