Exposure of urban ecosystems to Mn and Pb contaminants from gasoline additives beside a major highway in the Greater Toronto Area, Canada

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A study of manganese (Mn) and lead (Pb) deposition in soil was conducted adjacent to a multilane highway in the Greater Toronto Area (GTA), Ontario. The annual average daily traffic (AADT) volume was approximately 333 700 vehicles in 1993. Soil sampling was conducted at two different sites along the highway to determine the concentration and extent of Mn deposition from methylcyclopentadienyl manganese tricarbonyl, MMT (a gasoline additive). Samples were collected at distances up to 160 metres from the roadside, at each site. Parameters evaluated included total and exchangeable Mn and Pb (from historic use of leaded gasoline), soil particle size, pH, and cation exchange capacity. Mn concentrations decreased with increasing distance from roadside. Pb concentrations changed little from values reported in 1990, but have moved deeper into the soil, indicating a cessation of atmospheric deposition. In contrast, exchangeable Mn concentrations decreased with soil depth indicating recent atmospheric deposition. Although Mn concentration in soil decreased with the increase in the distance and the depth adjacent to the multilane highway, the difference was not statistically significant within the sites. More research is needed to provide better understanding of the extent of MMT and the complex behaviour of Mn contamination in the terrestrial urban environment.

Key words: manganese, lead, soil, methylcyclopentadienyl manganese tricarbonyl (MMT); gasoline additive; urban environment; greater Toronto area (GTA), Canada

Une étude sur les dépôts de manganèse (Mn) et de plomb (Pb) a été entreprise le long d'une autoroute à voies multiples de la région du Grand Toronto en Ontario. Le volume annuel moyen du trafic quotidien était d'environ 333 700 véhicules en 1993. L'échantillonnage du sol a été réalisé sur deux sites différents le long de l'autoroute pour déterminer la concentration et l'étendue des dépôts de Mn en provenance du méthylcyclopentadienyle tricarbonyle de manganèse, MMT (un additif pour le carburant). Des échantillons ont été recueillis sur des distances allant jusqu'à 160 mètres de la chaussée, sur chaque côté. Les paramètres évalués comprenaient le Mn et le Pb totaux et échangeables (selon l'utilisation historique des carburants avec plomb), la grosseur des particules du sol, le pH, et la capacité d'échange cationique. Les concentrations en Mn décroissaient selon l'augmentation de la distance à partir de la chaussée. Les concentrations en Pb changeaient peu par comparaison avec les valeurs rapportées en 1990, mais étaient plus profondément enfouies dans le sol, indiquant un arrêt des dépôts atmosphériques. Par contre, les concentrations de Mn échangeables diminuaient selon la profondeur du sol, indiquant la présence de récents dépôts atmosphériques. Même si la concentration en Mn dans le sol diminuait avec l'augmentation de la distance et de la profondeur le long de l'autoroute à voies multiples, la différence n'était pas statistiquement significative entre les sites. Il faut plus de recherche pour mieux comprendre l'étendue du MMT et le comportement complexe de la contamination en Mn dans l'environnement terrestre urbain.

Mots-clés : manganèse, plomb, sol, méthylcyclopentadienyle tricarbonyle de manganèse (MMT), additif de carburant, environnement urbain, territoire du Grand Toronto, Canada

Introduction

Increasing urbanisation, has led to a large increase in the range of trace metal contaminants in an urban environment. Trees in an urban and peri-urban areas are under severe environmental stress due to air pollution caused by coal and oil combustion (industrial, residential), the activities of steel and iron industries, pyrometallurgical processes,

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cement works, asphalt roads (building roads), road dust and automobile emissions (Pacyna *et al.* 1995). Several studies have reported that trace metal concentrations in surface soil in woodlands located within urban areas are elevated in comparison to peri-urban areas (Pouyat *et al.* 1995). These trace metals,

or pollutants, become part of the urban and peri-urban environment and have been reported to cause long-term detrimental effects on the health of trees (Watmough *et al.* 1998). Deposition over time has been reported to lead to an increase in the trace metal concentration and change in the wood composition of the tree growth rings (Takar *et al.* 1998). The present study has been divided in two phases. Phase one focuses on the study of urban soils and constitutes the text of the present paper. Phase two constitutes the analysis of tree matrixes and is in progress.

The phasing out of lead (Pb) compounds from gasoline has led to the search and use of other compounds that have anti-knock characteristics. Methylcyclopentadienyl manganese tricarbonyl (MMT), a gasoline additive, and its combusted products have recently been reported to create environmental stress (Zayed and Loranger 1994). The prolonged use of Pb by fuel manufacturers resulted in much research demonstrating that recipient ecosystems were adversely affected. It now appears that the continued use of MMT as a gasoline additive could be similarly detrimental to urban ecosystems. Phase one of the present study is designed to estimate the deposition effect of MMT – and its combusted products from automobile exhaust tail pipes – in soil beside major highways, which in turn influences the growth and decline of urban trees. Phase two of this work will be designed to study the impact of MMT on the stem matrix of urban trees located next to busy highways in very busy metropolitan areas with heavy traffic density. These trees could be used as bio-indicators of airborne toxic contaminants and their cumulative contribution to tree decline as evidenced by the study of growth rings (Takar *et al.* 1998). If the concentration of Mn deposition exceeds the normal levels in soils, then a physiological explanation of direct uptake from soil at high levels could be presented for the decline in health of urban trees. To produce a clearer understanding of long-term effects on the health of urban and peri-urban trees, we must be able to quantify the rate of heavy metal deposition in soil and the absolute quantities in other specified ecosystems.

MMT [$\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$] is an organic derivative of manganese (Mn) used as an anti-knock agent in unleaded gasoline (Cooper 1984). Introduced in Canada in 1976 (Environment Canada 1987), MMT has seen a substantial increase in utilization over the last few years (Zayed and Loranger 1994), and has now completely replaced lead in gasoline (Royal Society of Canada 1986, U.S. Dept. of Health and Human Services 1997a).

The combustion of MMT leads to the formation of Mn oxides, especially manganese tetraoxide (Mn_3O_4) (Tar Haar *et al.* 1975). The size of the particles emitted to the atmosphere is similar to that of Pb (Jaworski 1979) and varies from 0.1 to 0.45 μm (Mena 1980). Chemically, it is a negatively charged, organometallic compound that is pentate in structure (Fig. 1).

In 1990, the United States Environmental Protection Agency (USEPA) estimated that 30% of the Mn produced during the combustion of MMT-containing gasoline is emitted from the tailpipe (Lynam *et al.* 1994). It has been suggested that one of the main sources of inorganic Mn contamination in the urban environment may be the combustion of fuel containing MMT (Joselow *et al.* 1978, Davis *et al.* 1988, Zayed and Loranger

Fig. 1. Structure of MMT (methylcyclopentadienyl manganese tricarbonyl) (Cooper 1984).

1994). Since 1974, medical studies have attempted to predict the contribution of Mn from the combustion of MMT-containing fuels to the atmospheric Mn concentration. Manganese has long been known to be an occupational health hazard to workers at high doses. Its effects at low doses are poorly understood. At high doses, such as those found in some workplaces, Mn causes a degenerative neurologic condition almost indistinguishable from Parkinson's disease. This disease, known as manganism, begins as a loss of appetite, apathy, fatigue, psychotic behaviour, and clumsiness. At lower levels of exposure, delayed reaction time, poor hand-eye coordination, memory loss, and tremors have been reported (Mena 1974, Moran 1975, Tar Haar *et al.* 1975, USEPA 1975, Pierson *et al.* 1978, Barbeau 1984, Cooper 1984, Abbott 1987, Ethyl Corporation 1990, U.S. Dept. of Health and Human Services 1997b). Experimental data on animals have shown that exposure to MMT produces severe injury to the kidneys, liver, lungs and the central nervous system (Komura and Sakamoto 1992, U.S. Dept. of Health and Human Services 1997b).

Despite the occupational health issues associated with MMT / Mn exposure and the use of MMT fuels in Canada, no Canadian studies have been published on the impact of MMT or its derivatives on vegetation and soil. Inorganic Mn compounds produced through the vehicle combustion process will be emitted into the environment. As a consequence, airborne Mn eventually settles to the ground where it may potentially contaminate the surface of the soil (NRCC 1973). Like Pb, over time Mn accumulation may be particularly acute near roadways and in urban areas. While Mn impacts on human health can be estimated, the actual mechanism by which Mn is interacting with the environment has yet to be determined. It is unclear whether most of the Mn emitted from automobiles will remain on surface dust where it may intermittently become airborne again, whether it will be taken up by plants and soil organisms, or whether it has the potential to contaminate groundwater. Considering all the above given factors, information on terrestrial Mn needs to be properly explored and its deposition and fate in the ecosystem require attention. In

Fig. 2. Sampling locations/sites in the vicinity of Highway 401, City of Toronto, Ontario, 1996.

response, this study addresses the following issues: (1) the deposition of inorganic Mn in soil beside a major highway in an urban area, and (2) the change in soil Pb concentration over time, which had the same disputed position as Mn as a gaso-line additive.

Materials and Methods

Site Selection and Characteristics

Site selection was done in consultation with the Ontario Ministry of the Environment (MOE). Since the work is related to automobile pollution, it was important to select sites that were immediately adjacent to a busy highway. Highway 401 was selected because it is the busiest multilane highway in Canada and it transects the country's largest urban centre, Greater Toronto Area (GTA), Ontario. Data were collected at two different sites during a two-month period, August and September 1996. Both sites were Hydro transmission corridors; one crosses Highway 401 just west of Warden Avenue, and the second crosses the highway near Brock Road (Fig. 2). Both sites had similar vegetation management regimes and both transected similar urban areas. The sampling program was designed to determine the degree and extent of Mn and Pb soil contamination associated with vehicle exhaust on the north and south of the highway (the highway runs east-west). The Warden Ave. site was selected to examine the effects of noise barriers placed along the highway in 1973 and to compare the Pb concentration in the soil with previous studies by the MOE at the same site in 1975, 1979 and 1990 (Emerson 1992). There is a possibility that wind eddyding could concentrate Mn and Pb deposits on the leeward side of the 2–3 meter-high barriers located along some sections of the highway. Annual average daily traffic volumes (AADT) for both sites are similar and have increased steadily in proportion to urban expansion from about 126 400 vehicles in 1972 to about 333 700 vehicles in 1993 (MOT 1996) (Table 1).

Sample Collection

A total of 80 soil samples (0–2 cm depth) and 54 subsoil samples (0–5, 5–10, 10–15 cm depth) were collected at increas-

ing distances from the north and south sides of the highway by Warden Ave. and Brock Rd (Fig. 3). The soil sample collection was done at distances of 3 m, 15 m, 25 m, 40 m and 160 m, from the edge of the highway barrier. However, no soil collection was done at 3 m and 15 m on the south side of the highway by Brock Rd. because of the intersection of railway lines. At each distance, five transect lines perpendicular to the highway were chosen for soil sampling. Each transect line was separated by a distance of 20 m. The middle transect line was selected for subsoil samples (Fig. 3).

Analysis

The soil samples were collected into labelled plastic bags and transported to the laboratory at the Faculty of Forestry, University of Toronto. The soil samples were air dried and passed through a 45-mesh (355 micron) sieve. Particle size analysis, soil pH, and Cation Exchange Capacity (CEC) were determined to characterize the soil in order to provide an improved understanding of the presence, bio-availability, and toxicity of anthropogenic Mn oxides (Mena 1980, WHO 1981). Exchangeable Mn and Pb in the soil samples were estimated following the IN HNO₃ procedure (Smith *et al.* 1995). Total Mn and Pb concentrations in soil samples were determined by Neutron Activation Analysis (N.A.A) (Muecke 1987), using the Slow-poke Reactor facility at the University of Toronto.

Statistics

A complete systematic design was used to study these data to determine if the observed trends were statistically significant. The treatments in this study were the combination of sites (Warden Ave. and Brock Rd.), subsites (north and south sides of the highway), surface soil and subsoil samples. Analysis of Variance (ANOVA) was used to investigate if there was a difference in Mn deposition between the two sites, four subsites, and five transect lines chosen at specific subsites along the highway. Duncan's multiple range test was also used to determine the site and subsite variation for Mn and Pb in surface soil and subsoil samples. The Pearson correlation coefficient was used to determine the strength of the relationship

Table 1. Annual average daily traffic (AADT) volumes at Highway 401, Warden Ave. and Brock Rd., reported by the Ontario Ministry of Transportation (MOT 1996)

Year	Annual Average Daily Traffic Volume
1972	126 400
1979	190 300
1990	305 500
1993	333 700

between the two continuous variables (Mn and Pb) with respect to the distance from Highway 401 (Cody and Smith 1991).

Results

Soil Samples (0–2 cm depth)

Soil Particle Size Analysis

A significant difference was observed in silt and sand content between Warden Ave. and Brock Rd. Data showing the different percentage composition of soil samples is given in Table 2. According to the summarized data of soil particle size analysis, most of the soil is sandy in nature and classified as either loamy sand or sandy loam. The difference between the two sites is primarily in the sand and silt fractions. The Warden Ave. site was sandier and the Brock Rd. site was siltier. The sites have comparable clay content.

CEC and pH of Soil

Duncan's multiple range tests were done to compare the Cation Exchange Capacity (CEC) and pH values between sites. Significant differences were observed in pH and CEC between sites, but no significant differences were observed in pH and CEC within the subsites. Mean CEC and pH values of different subsites are summarized in Table 3. The Brock Rd. site revealed higher soil CEC values than the Warden Ave. site. The higher the CEC value the greater the tendency for metals to accumulate in the soil. Studies have shown that CEC increases with the alkalinity of soil (Tisdale *et al.* 1985). Data analysis has indicated that the Warden Ave. site is sandier, has a lower CEC, and a lower pH, whereas the Brock Rd. site has a higher silt content, and higher CEC and pH values. However, the Brock Rd. site showed a significant difference in pH within subsites ($p < 0.05$). Therefore, based on these basic soil characteristics, given similar traffic volumes metals like Mn and Pb would be more likely to accumulate in soil at the Brock Rd. site but would likely be more mobile in soil at the Warden Ave. site.

Exchangeable and Total Mn and Pb in Soil

Surface Soil Samples (0–2 cm depth)

A mean separation test was carried out to compare the Mn and Pb concentrations in surface soil samples between the two sample sites, the values of which are summarized in Tables 4a and 4b. Significant differences were observed between the exchangeable and total Pb in surface soil samples (0–2 cm depth) collected at the distances of 3 m, 15 m, 25 m, 40 m, and 160 m from the highway on both the north and south sides of both sample sites. Significant differences were observed in exchangeable Mn in surface soil samples at 3 m, and 40 m of the

Fig. 3. Sampling procedure of soil and subsoil samples collected along the Highway 401, GTA, 1996.

north and at 3 m, and 160 m of the south side of Warden Ave. Similarly, significant differences were observed in exchangeable Mn in surface soil samples at 3 m, 40 m, and 160 m of the north and the south side of Brock Rd. The relationship between total Mn and distance from the highway was less clear. Although there was a trend towards decreasing total Mn with increasing distance from the highway the differences were not significant at either the south side of Brock Rd. or the north side of Warden Ave. In contrast, the total Mn concentrations in surface soil were significantly higher at the sample sites closest to the highway compared to more distant sites at both the north side of Brock Rd. and the south side of Warden Ave.

The difference between the Pb and Mn data is that Pb concentrations tended to drop off more rapidly over a shorter distance and the Mn concentrations fall off more gradually and over greater distance. This suggests that Mn particles are smaller and lighter than Pb and are dispersed over a greater distance, or possibly that Mn particles, once settled on the ground, are held less tenaciously than Pb and are therefore more susceptible to localized re-entrainment, or both.

According to the literature Mn is a hard, brittle, greyish white metal widely distributed in the earth's rocks. In most soils concentrations range from 200 to 300 ppm, in many rocks concentrations range from 800 to 1400 ppm, and in some sedimentary rocks concentrations can range from 6000 to 8000 ppm (Labanauskas 1966). In Ontario urban surface soil not influenced by major roadways Mn concentrations typically range up to 1300 ppm (MOE 1993). It is generally accepted that Mn is deficient in plants at tissue concentrations of < 20 ppm, adequate between 20 and 500 ppm, and toxic to Mn sensitive plants at > 500 ppm (Zayed *et al.* 1994). Plant tissue samples were not collected as part of this study, so it not known if the

Table 2. Mean percentage composition of surface soil samples (dry weight, 0–2 cm depth) at the Warden Ave. and Brock Rd. sites along Highway 401, GTA, Ontario, 1996

Site	Subsite	Sand %	Clay %	Silt %	Σ	Triangle Classification
Warden Ave.	North Side	84.07	11.32	4.61	100.00	Sandy loam
	South Side	80.66	9.84	8.5	100.00	Loamy sand
Brock Rd.	North Side	65.21	10.32	24.47	100.00	Sandy loam
	South Side	61.3	12.32	26.38	100.00	Sandy loam

Table 3. Results of Duncan's range test for samples collected at the two study sites along Highway 401, GTA, Ontario, 1996

Site	Subsite	Cation Exchange Capacity	pH
Warden Ave.	North Side	17.57b	6.11c
	South Side	20.75b	6.19c
Brock Rd.	North Side	33.25a	6.41b
	South Side	33.83a	6.62a

CEC and pH values with the same letter are not significantly different at $p=0.05$.

higher soil Mn concentrations have affected plant tissue Mn levels. Even though the total soil Mn concentrations were higher nearer the highway they are still within the background Mn levels for Ontario soils.

Due to variability in valences, Mn occurs in different complex forms (MnO , MnO_2 and Mn_3O_4). However, Pb only occurs in two different valence forms (Pb^{2+} , Pb^{4+}), with the divalent form the most stable valence state in soil (U.S. Dept. of Health and Human Services 1997a). The divalent form of MnO is soluble, and gets leached into deeper layers of the soil. The effects of leaching depend on the soil texture and acidic conditions. The lower the pH, the higher the potential leaching of soluble Mn to deeper levels within the soil profile (Mahmoud and Grime 1977, U.S. Dept. of Health and Human Services 1997b). The north side of Warden Ave. has higher exchangeable and total Mn and Pb concentrations than the north side of Brock Rd., although these marginal differences are not statistically significant (Tables 4a and b). These subtle differences may be due to the texture and the pH of the soil, as the Warden Ave. site has a higher sand component and is more acidic in nature than the Brock Rd. site. The south side of both sites has a higher Mn deposition at 3 m distance from the highway than the north side. This may be due to the wind effect, since the prevailing wind is from the northwest in the GTA. The increase in Mn level at 3 m from the highway is likely due to the Mn fractions of the gasoline additive MMT.

Soil Correlation Study

There was negative correlation at each subsite between Mn and Pb concentration in surface soil samples and the distance from the highway (i.e., surface soil metal levels decreased with increasing distance from the highway). This relationship was stronger for Pb ($r = 0.839$) than for Mn ($r = 0.539$). On the other hand, a negative and positive correlation was observed for Mn and Pb respectively in subsoil samples collected at each subsite at increasing soil depth (i.e., Mn concentration decreased and Pb concentration increased with depth). Exchangeable Mn concentration decreased and Pb concentration increased with depth of the soil profile collected at 3 m, 15 m, 25 m, 40 m, and 160 m from the highway on the north and south sides of both sites. Mn has been introduced rather recently and is still being emitted. It is deposited on the surface and has not

had sufficient time to leach down into the soil profile. Lead has not been used as a gasoline additive since 1970 and with the cessation of surface deposition it has begun to work its way downward into the subsurface soil. The results also showed a positive correlation between soil CEC and pH with Mn and Pb deposition along Highway 401. The lower the pH, the lower the cation exchange capacity and the higher the dispersion effect of metals in the soil or vice versa (i.e., lower pH and CEC resulted in greater metal mobility in the vertical soil profile).

Subsite Variation Study

A statistically significant difference between the total Mn concentrations in surface soil samples was observed between the north and south sides of the highway at both Warden Ave. and Brock Rd. sites ($p \leq 0.05$). Duncan's multiple range test for different Mn and Pb variables in different subsites is summarized in Table 5. There were no significant differences in total soil Pb concentrations between the subsites at either site. Although there is no significant difference in exchangeable Mn between subsites, there is significant difference in exchangeable Pb (higher on the north side at both Warden Ave. and Brock Rd.). No significant difference was observed in exchangeable and total Mn and Pb between the north side of Warden Ave. and north side of Brock Rd. or the south side of Warden Ave. and south side of Brock Rd.

Site Variation Study

Statistically significant differences ($p \leq 0.05$) in soil exchangeable and total mean Pb concentrations were observed between the Warden Ave. and Brock Rd. sites. However, no significant difference ($p \geq 0.05$) in mean surface soil exchangeable and total Mn concentrations were observed between the sites. Duncan's multiple range test values are summarized in Table 6.

Subsoil Samples

Exchangeable Mn concentrations decreased and exchangeable Pb concentrations increased with soil depth. Significant differences in soil Pb concentrations were observed on the North side of Warden Ave. and on both sides of Brock Rd. A Duncan's range test was carried out to compare the mean Mn and Pb concentrations in subsoil samples collected at the two sites along Highway 401, the results of which are summarized

Table 4a. Exchangeable and Total values of Mn and Pb in surface soil samples (ppm dry weight, 0–2 cm depth) collected at Warden Ave. along Highway 401, GTA, Toronto, 1996

Sites	Subsites	Distance (m) from edge of HWY	Exchangeable and Total Values (ppm)			
			Exchangeable		Total	
			Mn	Pb	Mn	Pb
Warden Ave.	North Side	3	29.76a	20.36a	720.8a	88.76a
		15	25.87ab	15.95b	695.6a	61.83b
		25	23.89ab	13.89c	682.25a	56.93bc
		40	21.48b	11.54d	668.5a	47.89c
		160	20.18b	9.95d	658.5a	30.96d
	South Side	3	34.95a	14.27a	763a	138.25a
		15	29.98ab	12.73a	667.6b	91.64b
		25	24.76ab	11.03ab	593.6b	60.67bc
		40	21.26ab	8.46cb	588.6b	54.49bc
		160	24.88b	6.93c	628.5b	36.16c

Means within a column with the same letter are not significantly different at $p=0.05$.

Table 4b. Exchangeable and Total values of Mn and Pb in surface soil samples (ppm dry weight, 0–2 cm depth) collected at Brock Rd. along Highway 401, GTA, Ontario, 1996

Sites	Subsites	Distance (m) from edge of HWY	Exchangeable & Total Values (PPM)			
			Exchangeable		Total	
			Mn	Pb	Mn	Pb
Brock Rd.	North Side	3	28.64a	16.87a	687.6a	29.61a
		15	25.38ab	12.93b	647.4ab	27.01ab
		25	23.78abc	11.74b	645.6ab	24.96ab
		40	22.68bc	9.79c	622.2ab	21.75ab
	South Side	160	19.53c	8.46c	597.4b	18.53b
		25	34.68a	12.66a	761a	35.13a
		40	25.37b	9.69b	730.2a	24.27b
		160	17.98b	7.75c	715.75a	22.34b

Means within a column with the same letter are not significantly different at $p=0.05$.

Table 5. Results of Duncan's range test for Mn and Pb subsite deposition (ppm, dry weight) along Highway 401, GTA, Ontario, 1996

Subsite Variation Study	Duncan's Grouping			
	Exch. (ppm)		Total (ppm)	
	Mn	Pb	Mn	Pb
Warden Ave.				
North Side	24.24a	14.34a	690.10a	57.27a
South Side	27.17a	10.68 b	649.71b	76.24a
Brock Rd.				
North Side	24.01a	11.96a	639.57b	24.63a
South Side	26.02a	10.04b	737.07a	27.69a

For each subsite, values followed by the same letter are not significantly different at $p=0.05$.

Table 6. Results of Duncan's range test for Mn and Pb Total and Exchangeable values in surface soil samples (ppm dry weight, 0–2 cm depth) collected at sites along Highway 401, GTA, Ontario, 1996

Sites	Duncan's Grouping			
	Exch. (ppm)		Total (ppm)	
	Mn	Pb	Mn	Pb
Warden Ave.	24.24a	14.34a	673.47a	64.39a
Brock Rd.	25.42a	11.08b	676.46a	25.79b

For each site, values followed by the same letter are not significantly different at $p=0.05$.

in Table 7. Analysis of variance (ANOVA) was used to determine the variability of Mn and Pb according to the depth of the soil (0–5 cm, 5–10 cm and 10–15 cm). Pb showed a significant difference (higher concentration with depth) on the north side of Warden Ave. and on both sides of Brock Rd. However, no significant difference was found in the case of exchangeable Mn on either the north or south side of both sites. According to the literature, it is known that the prime medium for anthropogenic Mn and Pb transport is air and deposition should be consequently greater near the source (Barrie 1980). But most of the Mn or Pb particles deposited on the soil are retained and eventually become a part of the upper surface layer.

Pb or Mn accumulation occurs proportional to the rate of the deposition and relative to the physical and chemical properties of the soil. Over time, lower pH means more mobility of metals from the surface and accumulation of Mn and Pb in deeper layers of the soil (Mahmoud and Grime 1977). Pb was banned as a gasoline additive in 1970 and Mn was introduced as an anti-knock component in gasoline. However, Pb is persistent and it is still present in the terrestrial urban environment at concentrations greater than background levels. Data collected from this study clearly show that Pb is still present in considerable concentrations in soil adjacent to a major highway and the availability of Mn soil concentrations are increasing.

Table 7. Exchangeable values for subsoil samples (ppm dry weight, 0–5 cm, 5–10 cm, 10–15 cm depth) collected at Sites along Highway 401, GTA, Ontario, 1996

Site	Subsite	Depth(cm)	Mean Exch. Values (ppm)	
			Mn	Pb
Warden Ave.	North Side	0–5	32.50a	11.54c
		5–10	29.99a	17.38b
		10–15	22.66b	28.15a
	South Side	0–5	23.87a	11.54a
		5–10	25.48a	14.62a
		10–15	20.01a	14.93a
Brock Rd.	North Side	0–5	31.25a	10.62b
		5–10	31.72a	15.23ab
		10–15	29.84a	19.85a
	South Side	0–5	30.75a	7.95c
		5–10	26.75a	11.54b
		10–15	24.60a	14.11a

Means with the same letter are not significantly different between subsites at $p=0.05$.

Discussion

The field survey revealed that surface soil Mn concentrations at both sides of Warden Ave. and Brock Rd. sites were higher than historic lead levels (greater than 500 ppm). Surface soil Mn and Pb concentrations were highly correlated with distance from the highway. Lead concentrations have changed substantially over time from the values reported by the Ontario Ministry of Environment studies undertaken at the Warden Ave. site in 1972, 1979 and 1990. In these studies the mean total Pb concentration at Warden Ave. increased from 195 ppm in 1972 to 373 ppm in 1979 and again to 740 ppm in 1990 in surface soil samples collected at 3 m distance from the barrier located along the highway 401 (Emerson 1992). By 1996 the surface soil Pb concentration at this site had fallen to generally less than 100 ppm. This substantial reduction in surface soil Pb concentrations in such a relatively short period of time was unexpected and seems unrealistic. It is likely that the difference reflects a combination of factors; e.g., the sample sites are not exactly the same, sample collection protocols may have varied, and sample preparation and laboratory analytical procedures were different (from this study as compared to previous studies). Lead accumulation in soil is a long-term process and the reduction in soil Pb levels is likely to be a similarly lengthy process. Lead concentrations have changed with time through a leaching process with Pb moving deeper into the soil profile with cessation of aerial emission. In contrast, labile Mn concentrations decreased with depth because accumulation of ongoing surface deposition exceeds the vertical leaching potential of the soil. Many factors govern the deposition and subsequent availability of Mn in the soil, such as acidity, soil texture, soil moisture, soil micro-flora and micro-fauna, wind, and temperature. Considering the complexity and inter-relationships of all of these factors, more research is needed to identify the mechanisms of transport of MnO in air and its potential for deposition and accumulation in the terrestrial environment. Since two different sites were selected along the highway, one with a sound barrier and one without, Mn deposition characteristics were expected to be different adjacent to the barrier. However, no significant difference was observed in Mn deposition between the sites. This indicated that the noise barriers along the highway do not significantly impede the movement of the small dust particles away from the highway corridor. In conclusion, inorganic Mn from

automobile exhaust emissions is contributing to Mn contamination in the terrestrial environment adjacent to a major highway and is a likely contribution to the Mn burden in the urban environment at large. However, more research is required to provide a better understanding of the extent of MMT-related environmental contamination, its potential for accumulation, and the significance of an enhanced environmental Mn burden.

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