“Labile Manganese in the Terrestrial Environment - Increasing Manganese deposition in Soil from MMT, a gasoline additive, beside Highway 401, Ontario”.

by

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A thesis submitted in conformity with the requirements for the degree of Master in Science, Graduate Department of Faculty of Forestry, University of Toronto.

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0-612-28678-1
ABSTRACT

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“Labile Manganese in the Terrestrial Environment - Increasing Mn deposition in Soil from MMT, a gasoline additive, beside Highway 401, Ontario.”

The study was conducted on two Hydro rights-of-way, one which crosses Highway 401 at Warden Avenue in Scarborough, and another which crosses Highway 401 at Brock Road in Pickering, Ontario. Sampling was designed to determine the degree and extent of Mn and Pb deposition in soil. Samples were collected at distances up to 160 metres from the roadside. Selected tree corings of Norway maple and White spruce were conducted. Parameters evaluated included total and exchangeable Mn and Pb, soil particle size, pH, and cation exchange capacity. Mn concentrations decreased with increasing distance from roadside. Lead concentration changed little from values reported twenty years ago, but have moved deeper into the soil, whereas Mn concentrations decreased with soil depth. Soil Mn concentrations are measurably elevated adjacent to the highway. The most likely source is Mn emitted from vehicle exhaust as a result of the combustion of MMT-containing gasoline.
ACKNOWLEDGEMENT

I would like to thank Dr. D. N. Roy, my supervisor, for his guidance, support and enthusiasm during the course of this study.

A special thanks goes to Mr. D. L. McLaughlin for his unlimited help throughout the course of this work. Thanks also to Dr. M. Hubbes and Dr. A. Kenney for their guidance and unlimited support. I would also like to thank Dr. Ron Hancok and Susan of the University of Toronto Slowpoke Reactor facility for their instruction and friendly assistance.

Many thanks also goes to all those whose assistance and friendship made this thesis a reality: D. Charles, W. Mabee, Fatima, Teresa, H. Pande and others too numerous to mention.

Finally, I dedicate this thesis to my family, especially my brother, Dilraj Singh Bhuie, who passed away in 1993.
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1.0 INTRODUCTION

During the past decade considerable concern has been expressed by environmental scientists over the increasing levels of a range of toxic elements in the environment. Among the most potentially hazardous are the so-called ‘heavy metals’, a term applied to cover a range of transition elements, including copper, zinc, nickel, and other elements such as cadmium, mercury, and lead. Acutely toxic levels of these metals rarely occur, but ample evidence is available that demonstrates that their concentrations are increasing in many organisms.

There is clearly a need to investigate the rate of input of heavy metals into biological systems, and their subsequent behavior within such systems. Therefore, to produce a clearer understanding of the long-term effects of heavy metals, we must be in possession of information relating to both the rate of deposition and the absolute quantity of heavy metals deposited within a specified system.

An important concern is the atmospheric pollution in the urban environment caused by automobiles. The phasing out of lead (Pb) compounds from gasoline has led to the use of other compounds that have anti-knock characteristics. Among the most promising of such compounds, the use of which has already became commonplace, are the organic compounds of manganese. One widely used compound is methylcyclopentadienyl manganese tricarbonyl, commonly known as MMT.

Methylcyclopentadienyl manganese tricarbonyl \([\text{CH}_3\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3]\) is an organic derivative of manganese (Mn) used as an antiknock agent in unleaded gasoline (Cooper. 1984). Used in Canada since 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). The combustion of MMT leads to the formation of Mn oxides, especially manganese tetraoxide (MnO_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. It is known to cause pollution in the environment (Figure 1).

In 1990, the USEPA estimated that each automobile emits 30% of the Mn produced from the combustion of MMT-containing gasoline out of the tailpipe. It has been suggested that one of the main sources of inorganic Mn contamination in the urban environment may be the combustion
of MMT (Joselow et al., 1978; Davis et al., 1988; Zayed and Loranger, 1994). Since 1974, many studies have attempted to predict the contribution of Mn from the combustion of MMT to the atmospheric Mn concentration (Mena, 1974; Tar Haar et al., 1975; Moran, 1975; USEPA, 1975; Health and Welfare Canada, 1978; Pierson et al., 1978; Cooper, 1984; Abbott, 1987; Ethyl Corporation, 1990). While its impacts can be estimated, the actual mechanism by which Mn is entering the environment has yet to be determined.

Figure 1: Structure of MMT (methylcyclopentadienyl manganese tricarbonyl).

A number of American publications have documented the adverse health implications of MMT. However, no Canadian reports were published on the impact of MMT on Canadian vegetation and soil. Unavoidably, inorganic Mn compounds produced through the combustion process in toxic oxide forms will become a part of the urban environment. As a consequence, MMT can reach the soil through the acid rain process and then contaminate the organic matter and microflora of the soil (NRCC, 1973). Much effort has been put into studying the effects of chronic MMT exposure on human populations, but less attention has been paid to its relationship with the terrestrial ecosystem. Since Mn exists in soil at different oxidation states, it is neither well understood nor readily predicted, especially in terms of plant uptake. In general, information on terrestrial Mn has not been properly explored and its deposition in the ecosystem requires attention.
Manganese is an essential element for plants. It is involved in the enzymatic reactions of oxidative phosphorylation, decarboxylation, hydrolysis, Krebs cycle reactions, and the metabolism of carbohydrates in general, all of which are related to respiration (Gonzalez and Sanchez, 1977). Manganese is also involved in photosynthetic reactions and chlorophyll synthesis; there is evidence that it is firmly bound to the lamellae of chloroplasts and has a role in maintaining chloroplast structure (Foy, 1973). It also has functions in the enzymatic reduction of nitrate to ammonia and in plant hormone metabolism (Gonzalez and Sanchez, 1977).

Soil Mn toxicity usually occurs above 500 µg/g (Labanauskas, 1966). At the biochemical level, it has been suggested that excess Mn results in the destruction of auxin by producing increased levels of indoleacetic acid (IAA) oxidase (Morgan et al., 1966). Macroscopic symptoms of excess Mn include chlorosis, puckering and necrosis of leaves (Foy et al., 1978), and eventual shedding of older leaves (Horst, 1983).

In toxic conditions, plant species vary in their ability to accumulate and tolerate excess levels of Mn. Availability of Mn in soil is determined by pH, cation-exchange capacity (CEC), concentration of other cations, organic content, temperature, and microbial activity, as well as by the concentration of easily reducible Mn in parent material (Tisdale et al., 1985).

One of the most important factors affecting Mn availability is pH. Lowering pH increases the solubility of Mn. In well drained soils, Mn toxicity generally occurs only if the soil pH is below 5.5 (Foy, 1973). Foy (1973) also pointed out that even at pH 7.0, factors that increase reducing conditions can result in excess available Mn. Increasing the availability of water in soil promotes the reduction of Mn to the divalent (available) form. It has also been known that increased light intensity increases Mn toxicity. However, the acidification of soils can increase the mobility of a number of cations, including Mn. Acidic precipitation can mobilize Mn in surface waters.

At the human level, tricarbonyl (2-methylcyclopentadienyl) Mn is highly toxic, and can enter the body by inhalation, ingestion and skin absorption. 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).

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value - Time Weighted Average (TLV-TWA) of 0.2 mg/m³ for MMT, determined as Mn. The TLV-TWA for other Mn compounds and Mn dust is 5 mg/m³ (as Mn). The
maximum permissible amount of MMT in unleaded gasoline is 18 mg/l (as Mn) (Gaind et al., 1992).

MMT is used as an octane enhancer in leaded and unleaded gasoline in the USA, but in Canada it has only been used in unleaded gasoline. However, under the current provisions of the U.S. Clean Air Act, a waiver must be obtained from the Environmental Protection Agency (EPA) before it may be used in unleaded gasoline in the USA. In order to get this waiver, airborne Mn levels produced from the combustion of MMT need to be evaluated. To investigate this, the Ethyl Corporation has carried out several studies, including computer modeling, modeling based on lead-in-air data, and studies of personal exposures in Toronto where MMT is extensively used in unleaded gasoline.

Some investigators (USEPA, 1990) have attempted to predict the exposure to Mn that would result from adding MMT to the gasoline by comparing the Mn:CO ratio at the tailpipe and in various microenvironments. This method may lead to an inaccurate prediction because of the differences in the behavior of gases and particulates, and the diversity of sources for CO.

Tar Haar et al. (1975) showed that Mn particulates emitted from automobiles using MMT were of about the same mass, median, and aerodynamic diameter as Pb particulate emitted from automobiles. Thus, the behavior of Mn particulate in air should closely resemble that of Pb. In addition, the percentage of combusted Mn used in gasoline emitted from the tailpipe is similar to the percentage of Pb. In nature, background levels of airborne Pb are low; a large portion of the Pb emitted into the atmosphere in the USA was vehicular-related, and emitted before major reductions in Pb antiknock usage occurred. These facts suggest that Pb could be a useful surrogate for Mn in modeling the potential increase in airborne Mn from MMT usage.

Manganese-in-air concentrations at various sampling stations in Toronto were approximately 0.04-0.05 μg/m$^3$. A number of methods were utilized to estimate the impact on atmospheric levels of airborne Mn which resulted from adding MMT to unleaded gasoline. In the USA, MMT is added at a rate of 0.03125 g/gal (1 USgal=3.78541 litres). Even if MMT were used in all unleaded gasoline, environmental models have predicted that airborne Mn levels in most urban areas would be less than 0.02 μg/m$^3$, which is significantly lower than the actual levels being measured. Variations in measurements may be attributed to extremely high traffic density and unique atmospheric and geographic features; in Los Angeles, for instance, slightly higher levels are predicted when models take these features into account (Lynam et al., 1994).
MMT itself is not causing pollution in the environment. Since MMT has a low vapor pressure and a short half-life in sunlight, it is unlikely that significant concentrations of MMT could occur in the environment due to its use as a gasoline additive. Mn in its inorganic form, however, is posing a threat to the environment by causing a "manganism" effect, which can be related to various ailments such as Parkinson's disease in the human population. Mn can affect the brain dopamine level and Central Nervous Systems of the human body. It is also known that many potential toxins are detoxified by hydroxylation in the liver with P-450 cytochromes. Barbeau, (1984) suggested that people with defective hydroxylation mechanisms may be more susceptible if exposed to environmental neurotoxins and, as a result, may develop chronic degenerative disorders like Parkinson's disease. These findings may be particularly significant when one considers the effect that MMT could have on sensitive individuals. The subject of MMT in the environment cannot be dismissed without investigating its possible accumulation in dusts and soils over an extended time period, a process that has been responsible for the most intractable aspects of the Pb issue.

Unlike Pb particles, the MnO that reach the soil are not likely to remain concentrated in the upper few centimeters of earth for any length of time. The pH of the generally moist conditions prevailing in soils will cause mobilization of the Mn, which will move to lower depths and ultimately reach the groundwater or surface waters. Thus the Mn resulting from the combustion of gasoline that actually reaches the human population, and is directly inhaled or ingested, will only be present in incremental quantities, which is insignificant compared with the normal Mn exposure through food and respiration (0.3 μg/day additional intake against an uptake of 120μg/day without MMT) (Ethyl Corp., 1985).

This study addresses the issues of (1) the deposition of inorganic Mn to the terrestrial environment, and (2) the change in soil Pb concentration over time. To this end, the study has the following major objectives:

1) To identify and establish sample sites next to busy highways in urban corridors;
2) To collect soil and subsoil samples from these sites, at an increasing distance from the highway;
3) To sample a variety of tree species located at these sites, at an increasing distance from the highway; and
4) To determine the levels of Mn present, and to compare the levels of Mn with the residuals of Pb in the soil.

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2.0 REVIEW OF LITERATURE

MMT is added to much of the unleaded gasoline sold in North America as an antiknock compound. Levels of MMT in these gasolines average about 0.031g/US.gal. MMT was discovered and patented by the Ethyl Corporation, and to date there is little information in the scientific literature concerning the ecotoxicological characteristics of this compound. The current widespread distribution of MMT as a gasoline additive makes it important that a method be developed for its determination in environmental samples.

2.1 ENVIRONMENTAL CHEMISTRY:

Mn is an abundant element in the earth’s crust and a minor but ubiquitous constituent of surface waters. In igneous-rock minerals it is often present as Mn$^{2+}$, substituting for some other divalent ion of similar size (Hem, 1970). More common forms, however, are oxides, hydroxides and carbonates. The oxides adsorb other cations very strongly and hence, naturally occurring species have many impurities. Deposits of MnO occur as coatings on the surfaces of rocks in the beds of streams, in freshwater lakes and on the ocean floor.

A first-row transition element (atomic number 25; atomic weight 54.938; atomic structure $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$), Mn exists in a number of oxidation states ranging from −3 to +7 (Cotton and Wilkinson, 1972). Of these, the +2, +3 and +4 states are of primary importance in a geochemical context. The environmental chemistry of Mn is profoundly affected by changes in these oxidation states, notably from Mn(II) forms (reduced; soluble; geochemically mobile) to the higher valence states of Mn(III) and Mn(IV) (oxidized; relatively insoluble). In solution, Mn(III) is relatively unimportant as it rapidly disincorporates, as shown in the formula below:

$$\text{Mn(III)} \Rightarrow \frac{1}{2} \text{Mn(II)} + \frac{1}{2} \text{Mn(IV)}.$$ 

In oxidized precipitates, however, Mn(III) is often found in mixtures with Mn(IV).
2.1.1 Atmospheric Pathways and Characteristics:

The atmosphere is a significant pathway for the movement and redistribution of some metals within ecosystems. However, Mn is not one of these metals and it does not move primarily through the atmosphere. The physiochemical characteristics of Mn are of importance in determining atmospheric behaviour, pathways, residence time, and removal processes. Trace metals display a characteristic distribution of airborne particulate matter with respect to particle size (Lee and Von Lehmden, 1973), with the actual aerosol size distribution being dependent upon the nature of emission sources, physical and chemical transformation processes in the air, and scavenging and removal mechanisms.

Manganese is not expected to exist in ambient air in either the gaseous state or the elemental form because:

1. The vapor pressure of Mn is 133 Pa at 1251°C and \(1.3 \times 10^{-3}\) Pa at 717°C (Weast, 1973) and thus, its vapor pressure would be negligible at ambient air temperatures (Thompson, 1979);
2. The metal is quite reactive with oxygen and other substances in the atmosphere. In the troposphere, Mn is likely to be found in oxide, sulfate or nitrate forms, or as mineral complexes related to its natural origin in soil or rock.

As part of the emissions from combustion and metallurgical processes (i.e., high-temperature emission sources), Mn (in the form of an oxide) is thought to be associated with coarse particulate matter characterized by greater than 2 \(\mu\)m aerodynamic diameter (Hanel, 1982). It has also been suggested that trace elements (including Mn) and their compounds become volatile at the high temperatures encountered during fossil-fuel combustion, and then condense uniformly on the surfaces of particles in the stack gas or in the plume (Linton, et al., 1976). Consequently, from a bioavailability or toxicity point of view, anthropogenic sources could be more important than natural sources, because trace elements are generally bound chemically and structurally within the matrix of aerosols of natural origin. During transport in the atmosphere, trace metals associated with ambient aerosols are subject to physical and/or chemical interactions involving other substances. Manganese, for example, can catalyze the heterogeneous oxidation of sulfur dioxide in cloud water and raindrops (Barrie and Georgii, 1976).
2.1.2 Ambient Air Concentrations:

Concentrations of Mn and other trace elements in the atmosphere may vary by orders of magnitude as a function of time and space. In general, relatively low concentrations are found at remote sites and over the oceans, whereas the highest concentrations are observed at urban or industrial sites.

On the basis of measurements worldwide, the average concentrations of Mn in remote/background locations range from 0.5 to about 15 ng m\(^{-3}\). In nonpolluted urban and rural areas these values range from less than 10 to 30 ng m\(^{-3}\), while in large urban centers without foundry operations higher values from 200 to 300 ng/m\(^3\) are found. In locations close to foundry operations, the values may run to several thousand nanograms per cubic meter of air (Thompson, 1979). Analysis of air samples collected in the Montreal area in 1967-1968 showed values of approximately 30ng/m\(^3\) for Mn content that could be attributed to combustion (Leroux and Mahmud, 1970). Slightly higher levels of Mn content in air samples collected in various locations in Toronto have been reported. While the Mn content found in air samples in the vicinity of urban metal refineries averaged 62ng/m\(^3\), Mn levels reported in samples taken in the Toronto area averaged 69ng/m\(^3\) (Jervis et al., 1975).

The contribution of MMT-derived Mn to the total atmospheric Mn concentration was studied by Zayed and Loranger (1994) with the use of dispersion models near a major highway in the city of Montreal. Measurements were taken at distances of 25 and 250m from the road centerline. Both models gave similar Mn estimates for distances over 250m, with values ranging from 1 to 3 ng/m\(^3\). They concluded that the Mn contribution to total atmospheric emissions from vehicle MMT is less than 20%, whereas the contribution of CO to the atmospheric totals may reach 75%. The atmospheric concentrations of Mn, Pb and Total Suspended Particles (TSP) were measured in the Montreal Urban Community at three sampling densities (Zayed and Loranger, 1994) from 1981 to 1992. Results indicated stable Mn concentrations between 1981 and 1990 followed by a substantial decrease, in spite of annual increases of about 10% in Mn emissions from the combustion of MMT since 1981. The importance of air contamination by Mn in relation to other air pollutants, meteorological variables and traffic density was assessed by Forget et al., (1994). They concluded that Mn from MMT is an important constituent of the urban air pollution and that it is directly related to traffic density on a local scale. The roadside soil concentrations of
Mn were found to be 100-fold higher than Pb concentrations in the same samples (Smith et al., 1995).

2.2 ATMOSPHERIC SCAVENGING OR REMOVAL PROCESSES:

2.2.1 Wet Deposition:

Wet deposition involves removal of substances from the atmosphere by rain-out or washout processes. In rain-out processes, particles interact with water vapor in clouds to form droplets of water which subsequently fall out of the atmosphere. Washout removes particles suspended in the atmosphere beneath clouds through impaction and adsorption by falling raindrops as shown in Figure 2.

Figure 2: Atmospheric Scavenging or Removal Process

Relative Annual Mass Transfer Rates of Manganese to the Forest Floor (NRCC, 1973).
On the basis of a review of worldwide data for trace metals in precipitation, median concentrations of Mn in wet deposition are given as 23 μg/L (urban), 5.7 μg/L (rural) and 0.194 μg/L (remote locations) (Gallowway et al., 1982). In Ontario, Mn concentrations in 1980/81 were typically 4-5 μg/L (as measured in southern and south-central Ontario) (Chan et al., 1984). Existing data show that the distribution of Mn concentrations in precipitation across Ontario is irregular with no pronounced regional differences. Manganese deposition fluxes also have an irregular pattern. Furthermore, there was no marked seasonal variation in Mn concentration or deposition. Jeffries and Synder (1981) also found no obvious seasonal pattern in Mn deposition.

Wet deposition (in snow) has been examined by a chemical survey of the snowpack in eastern Canada (Barrie and Vet, 1984; Landsberger et al., 1982). These studies calculated a deposition rate of 1 μg/m²/yr a in Montreal (as measured in packed snow). To be able to link Mn deposition with ecological changes, it is necessary to know not only the rate of deposition but also the chemical form(s) of the metal.

2.2.2 Dry Deposition:

Dry deposition is a mechanism whereby aerosols are removed from the atmosphere by processes such as sedimentation, impaction, electrostatic or thermal deposition, advection and sorption in the absence of precipitation.

Measurements of metals in dry deposition suggest that the dry-deposited fraction is substantial, and general is greater than 10% of the total deposition. For Mn, dry deposition was estimated to constitute 50% of the deposition in marine, rural and urban areas (Tri-Academy Committee on Acid Deposition, 1985). In central Ontario, wet deposition of Mn predominates over dry deposition (Jeffries and Snyder, 1981). Barrie (1980) used a network of Harwell collectors to determine the rates and pattern of coarse-particle deposition around a power plant in northern Alberta. Manganese, together with aluminum and titanium, was most heavily deposited (at levels greater than 5 mg/m²/yr) either in areas where there was surface disturbance or close to dirt roads.

2.3 TERRESTRIAL COMPARTMENT:

Even though the atmosphere is not the most important route for mobilization of Mn, the atmosphere provides a significant pathway for Mn cycling in the terrestrial system. This section
summarizes the relatively few studies that have been published on the terrestrial cycling of Mn, omitting the biochemical processes that occur in plants.

2.3.1 The soil as a source of Mn for terrestrial plants:

The soil provides a reservoir of Mn for terrestrial plants. Mn is considered to be highly mobile in the plant/soil system (Hoffman et al., 1980). Concentrations of total Mn in soils, aside from those soils affected by pollution, can range from less than 1 to 4000µg/g (Adriano, 1986). McKeague and Wolynetz (1980) reported a mean Mn concentration of 520µg/g for Canadian soils, which is close to the most recently published world average of 450µg/g. The mean Mn concentration in Ontario soil is just less than 500µg/g, but the background range in urban parkland is up to 1,300µg/g. In rural parkland Mn in soil in Ontario can range up to 2,200µg/g (MOEE, 1993). Plant uptake processes of Mn have not been satisfactorily described, although there is a great deal of literature relating uptake and/or the biological effects of Mn to two major variables: hydrogen ion concentration and redox potential. These have clear and predictable effects on the solubility of Mn in soils, and solubility appears to be the major factor determining the availability of Mn to plants. This means that the "total Mn" in soils has little relevance in terms of the prediction of Mn toxicity or Mn deficiency, both of which are well known in crop plant studies.

Stahilberg and Sombatpanit (1974) showed that the chemistry and biochemistry of soil Mn are complex for the following reasons:

1. Mn has more than one oxidation state;
2. Mn exists in mixed oxidation states;
3. Higher oxides of Mn exist in several crystalline states;
4. Formation of coprecipitates, solids, or superstructures by higher Mn oxides exhibit amphoteric behavior;
5. Both oxidation and reduction processes involving Mn are probably influenced by both chemical and microbial processes.

2.3.2 The effect of pH on Mn in soil:

Water-soluble Mn in soils is directly proportional to pH. Availability as measured by plant uptake is not a simple function of pH, but there is still a general relationship between pH,
extractable Mn and plant uptake. As far as chemical extractants are concerned, soil pH plays an important role in the selection of a suitable extractant (Sharpe and Parks, 1982).

2.3.3 Sources of Mn in soils:

The major source of Mn in soils is a large reserve of crystalline metals within the soils. Addition of Mn to soils, however, can result from direct atmospheric deposition, wash-off from plant and other surfaces, leaching from plant tissues, and from shedding or excretion of material such as leaves, twigs, dead plant and animal material, and animal excrement. There are few studies which quantify these inputs to soils, but perhaps the most complete is provided by an account by Lindberg et al. (1979). These authors estimated that, on an annual basis, the relative fluxes of Mn to soil were 14% “external” (directly from the atmosphere) and 86% internal (via the plant canopy). Of this internal flux, 37% was from leaf fall, 49% from foliar leaching, and 11% from wash-off of dry deposition.

2.4 MANGANESE AND TERRESTRIAL PLANTS:

2.4.1 Plant Responses:

Mn is an essential element for plants. It is involved in the enzymatic reactions of oxidative phosphorylation, decarboxylation, hydrolysis, krebs cycle reactions and the metabolism of carbohydrates in general, which are related to respiration in plants (Gonzalez and Sanchez, 1977). Mn is also involved in photosynthetic reactions and chlorophyll synthesis. There is evidence that it is firmly bound to the lamellae of chloroplasts and has a role in maintaining chloroplast structure (Foy, 1973). The Mn content of the above ground portions of plants displaying Mn deficiency is generally less than 20μg/g (dry weight), whereas plants displaying neither deficiency nor toxicity have Mn concentrations ranging from 20 to 500μg/g (Labanauskas, 1966). At levels above this, toxicity usually occurs.

The mechanism of Mn toxicity is poorly understood, although its manifestations are well studied and described, largely in the literature related to agronomy, but also in that for plant physiology. At the biochemical level, it has been suggested that excess Mn results in destruction of auxin by producing increased levels of indole acetic acid (IAA) oxidase (Morgan et al., 1966). Excess Mn prevents the production of a precursor for protochlorophyll, or for chlorophyll itself. The most comprehensive treatment of Mn toxicity is by Foy et al. (1978), who described increases
in the peroxidase and polyphenol oxidase activities, and decreases in the activities of catalase, with lowered ATP and decreased respiration rates. Przemeck and Schrader (1981) also described the altered excretion of organic nitrogen metabolites into root xylem under conditions of excess Mn.

Toxicity is related to the accumulation of Mn in leaves and growing points. Certain crop species are known to be more Mn tolerant than others. Foy (1973) cited several studies that indicated that in more tolerant plants, excess Mn is "trapped" in roots and somehow prevented or limited from being translocated into stems and leaves.

Macroscopic symptoms of excess Mn include marginal chlorosis, puckering and necrosis of leaves (Foy et al., 1978) and eventual shedding of older leaves (Horst, 1983). Foy et al. (1978) also described browning of roots in severe cases, but this occurred only after the above ground parts had been affected.

Genotypic differences in Mn tolerance may occur as a result of heritable traits. This is important when considering the long term capability of plants to genetically adapt to chronic Mn pollution. For example, Wong et al. (1983) studied grass species in a Japanese coastal harbor and found that plants collected from an uncontaminated area were more sensitive to Mn compared to those collected from a contaminated area.

### 2.4.2 Hydrogen Ion Concentration:

One of the most important factors affecting Mn availability is pH. It is clear from the chemistry of Mn that lowering pH increases its solubility. In a study of four grass species, susceptibility to Mn toxicity was strongly correlated with the acid tolerance of the species (Mahmoud and Grime, 1977). When acidic soils were fertilized without the addition of lime, tobacco plants showed a great increase in Mn uptake (Lockman, 1970). Although specific anion effects may also have been involved, the salt effects of chloride nitrate or sulfate fertilizers are definitely associated. El-Kherbawy and Sanders (1984) showed increased uptake of Mn by clover species in silty-clay-loamy soil having low pH, which increased the amount of extractable Mn. Similar results were also found in a greenhouse study for blueberry cultivators (Haynes and Swift, 1985). For the yeast Candida utilis, Perkin and Ross (1985) showed that the optimum pH for Mn transport was 5.5.

Studies also demonstrated that Mn availability is enhanced through reducing conditions, including increases in organic matter or the inhibition of Mn-oxidizing bacteria. It has also been
known that several genera of common soil bacteria can precipitate MnO from Mn salts (NAS. 1973) and the formation of bog Mn ores is considered to be mediated by bacteria.

### 2.5 TEMPERATURE AND LIGHT:

Temperature and light are the other factors which have been shown to influence Mn toxicity in the soil. Heenan and Carter (1977) showed that increasing temperature eliminated symptoms of Mn toxicity in soybeans (Glycine max), and suggested that temperature induced higher growth rates of plants, as well as increased activity of Mn oxidizing bacteria. Munns et al. (1963) showed higher Mn in the tops of plants grown at higher temperatures, and Lohnis (1951) showed that plants remained healthy with higher Mn tissue levels when grown in warm greenhouses compared to cooler outdoor conditions. Studies have also shown that increased light intensity increased Mn toxicity, which may be related to increased chloroplast sensitivity to Mn at high light levels (Sutton and Hallsworth, 1958).

### 2.6 CALCIUM AND OTHER CATIONS:

Early studies by Sutton and Hallsworth (1958) and by Lohnis (1960) suggested competitive antagonism between Ca and Mn at the cell membrane, with a resulting decrease in Mn uptake into plants. According to Jauregui and Reisenauer (1982), Ca immobilized Mn through adsorption, precipitation and formation of manganocalcite. In essence, there was a competitive effect on the chemical form as well as competition at uptake sites. Clearly, liming, by increasing pH and by increasing Ca or Mg will prevent Mn toxicity.

#### 2.6.1 Iron:

A close association between the uptake levels of Fe and Mn has been identified. Mn addition may induce Fe deficiency, and increasing Fe may depress Mn uptake. In fact, early work suggested that it is difficult to differentiate between Fe deficiency and Mn toxicity. Evidence indicates competition between two cations such that adding Fe to soils causes an amelioration of Mn toxicity by reducing its uptake by plants (Heenan and Campbell, 1983).
2.6.2 Phosphorus:

Fertilization with phosphates may either reduce or enhance Mn availability and therefore affect Mn toxicity to plants. Heinz (1968) found that PO₄⁻ detoxified Mn by precipitating it into an inactive state within oats. Other research (Le Mare, 1977) determined that Mn uptake and toxicity were increased with phosphorus addition.

2.7 EXAMPLES OF MN TOXICITY TO PLANTS:

Under field conditions, it appears that Mn toxicity is rare, except in acidic soils. In such conditions the co-occurrence of Al toxicity may be observed (Foy and Campbell, 1984). As discussed earlier, hydrogen ion concentration and redox potential are major factors determining availability of Mn to plants. It is therefore not surprising that Mn toxicity to crop plants in well-drained soils is limited to soils of pH below 5.5 (NAS, 1973), or to waterlogged or flooded soils at higher pH. Damage to apple trees near Victoria, N. S. Wales, Australia was related to waterlogging, which induced Mn toxicity. Most potentially toxic situations can be remedied by liming (Adriano, 1986). In general, Mn toxicity, compared with that of other metallic pollutants in the terrestrial environment, does not appear to be a widespread problem.

Recent studies have estimated that bioaccumulation of Mn by plants may be motivated by the increased use of MMT as a replacement for Pb in gasoline. Studies have shown higher accumulation of Mn in fruits and stems of oats grown in organic and sandy soils. This indicated that the addition of MMT to gasoline may result in an increase in exchangeable Mn in organic soils (Forget et al., 1994).

Manganese concentrations in xylem from blue spruce (Picea pungens) growing close to and far from a road were measured as a function of the year of wood formation (Zayed et al., 1994). The results of the soil analysis showed that exchangeable Mn concentrations were about 10 times higher in soils near the highway which were exposed to contamination by MMT, in comparison with the concentrations found in soils remote from MMT exposure.
2.8 FORMS OF SOIL Mn:

There are three major forms of Mn in soils that are primarily responsible for Mn supply to the roots: exchangeable Mn, organically bound (complexes) Mn, and MnO (often mixed Mn$^{3+}$ and Mn$^{4+}$ oxides). The proportion of these forms of Mn vary with the soil type, soil pH and organic matter content. Generally, as soil pH decreases the proportion of exchangeable Mn steeply increases and the proportion of MnO and FeO decreases. In many neutral and alkaline soils, easily reducible Mn comprises the dominant fraction. Solubility of Mn is therefore strongly affected by pH according to the simplified reaction scheme:

$$\text{MnO}_2 + 4\text{H}^+ + 2e^- \leftrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}.$$ 

Additionally, microbial activity is also primarily responsible for oxidation of Mn$^{2+}$ in soils (Uren and Leeper, 1978).

2.9 GENOTYPIC DIFFERENCES IN Mn ACQUISITION:

Different rates of root to shoot transport may contribute to genotypic differences in the natural vegetation in susceptibility to Mn toxicity or deficiency. Genotypic differences between cereal species such as rye and wheat in Mn acquisition from soils are well known. Large differences between barley genotypes were demonstrated in Mn efficiency (relative yield decrease) when grown in a Mn deficient calcareous soil (Graham et al., 1988). These differences are related to the genotypic background (geographic origin) and are most probably due to the differences in Mn acquisition from the soil, not Mn utilization within the plants. Although breeding experiments with wheat and barley have achieved progress in increasing Mn efficiency and identifying those genes responsible for such efficiency, knowledge of the physiological factors responsible for genotypic differences in Mn acquisition is still rather vague.

2.10 PUBLIC HEALTH EFFECTS:

Exposure of the general population to MMT from its use in gasoline would be minimal, as very little (0.1 % of total MMT) is emitted in the exhaust. Since the most significant environmental consequence of the use of MMT as a fuel additive is the resulting discharge of Mn
to the air, this section deals mainly with the possible health effects of an increase in atmospheric Mn levels.

2.10.1 Emissions of Manganese:

Manganese is an essential element in animals and man. It is required as a cofactor in a number of enzymes; it is essential to arginase and alkaline phosphotase in the liver; it plays a role in the proper functioning of flavoproteins and in the synthesis of sulphated mucopolysaccharides, cholesterol, and hemoglobin; and it is impaired in carbohydrate metabolism, lipid metabolism, oxidative phosphorylation, growth, reproduction, and brain function (NRCC, 1973).

In animals, experimentally induced or naturally occurring Mn deficiency has resulted in the following: lack of growth, abnormalities of bone and reproductive function, and loss of equilibrium due to the disturbance of central nervous system (Masironi, 1973). Minimal human nutritional requirements for Mn have not been established. However, no Mn deficiency in humans has yet been documented and the normal daily Mn intake ranges from 2 to 7 mg per day (Pier, 1975).

2.10.2 Mammalian Toxicity of Manganese:

Manganese is regarded as one of the most least toxic elements. Chronic ingestion experiments in rabbits, pigs, and cattle at 1,000-2,000µg/g dose levels have shown no effects other than a change in appetite and reduction in metabolism of iron to form hemoglobin (NRCC, 1973). Toxicity of Mn varies with the valence state, the route of administration and, when inhaled, with particle size. The main routes of absorption of Mn are the respiratory and gastrointestinal tracts. Negligible amounts of inorganic Mn are absorbed through the skin. Organically-bound Mn may be absorbed by the cutaneous route (NRCC, 1973).

There have been some reports in the literature on the influence of Mn emissions on inhabitants living in the vicinity of Mn-producing industries (Mena, 1974). However, most animal studies have been conducted to evaluate possible toxicity resulting from chronic exposure to Mn aerosols at concentrations approaching ambient levels expected from the use of MMT in gasoline as a primary antiknock agent (Abbott, 1987).

The primary exhaust product of combustion of MMT, Mn₃O₄, is much less toxic than MMT. Consumption by rats of 4-8,900 mg/kg body weight of Mn₃O₄ caused no mortality or
apparent tissue damage (Exon and Koller, 1975). Even daily oral doses 150 times greater than the oral LD₅₀ of MMT to rats were only slightly toxic.

In monkeys and rats exposed continuously (9 months) to three different levels of MnO aerosol produced by combusting vapors of MMT (11.6, 112.5, 1152 μg/m³), no apparent adverse effects were observed (Ethyl Corporation, 1975). No toxic effects were observed in another study in which rhesus monkeys were exposed continuously for periods of up to 66 weeks to MnO particulates (100 μg/m³ Mn) generated through the combustion of vaporized MMT (Coulston and Griffin, 1976). Results showed small but statistically significant increases in Mn levels in the lungs, livers, pancreas, kidney and heart muscle (Komura and Sakamoto, 1992).

There are no reports to suggest that Mn is a human carcinogen. In summary, there is no evidence to suggest that small increments in the environmental Mn from the combustion of MMT would have any impact on health (Cooper, 1984). Toxicity in man is usually the result of chronic inhalation of high concentrations of Mn dusts from industrial sources (Hine and Pasi, 1975; Suzuki, 1970; Cotzias et al., 1971; Emara et al., 1971; Rosenstock et al., 1971). In such cases, there is apparently no correlation between age, duration of exposure and onset of symptoms. Symptoms differed from case to case. The severity of the symptoms, however, is often proportional to the length and intensity of exposure. The principal effects of long-term exposure to inorganic Mn compounds are the production of "manganese pneumonia" or pneumonitis and more commonly, manganism (Cotzias et al., 1971).

Based on the limited data available, there is no evidence to indicate that ambient Mn concentrations resulting from the use of methylcyclopentadienyl manganese tricarbonyl as an antiknock agent in gasoline, at a maximum level of 5μg/m³, would constitute a hazard to human health. Data available on the environmental effects are contradictory. No conclusions can be drawn about the possible health implications of such effects.

**2.11 ANTICIPATED SIGNIFICANCE OF THE WORK:**

The present debate on the use of MMT between car manufacturers, the petroleum industry, and the government, can be resolved by a systematic study of MMT and the products of its combustion in the environment. This work will contribute specific to Mn deposition to the terrestrial ecosystem adjacent to a major highway. Previous research done by the Ministry of Transportation describing the impact of MMT in relation to catalytic converters did not elaborate upon the effect that exhaust products may have on the surrounding environment. The
concentrations of MMT and its combusted products in the environment changes with relation to seasonal temperature and the presence and absence of foliage. This will alter the total impact that Mn has within the environment at its time of release. Precise knowledge of the seasonal impact of MMT could be used to consider changing the concentration of MMT in gasoline. The study is very relevant to the present public discussion, and will provide data to assist the scientific community to evaluate the continued use of MMT as a gasoline additive.
3.0 MATERIALS AND METHODS

3.1. MATERIALS:

3.1.1 Site Selection and Characteristics:

The study was conducted on two Hydro-right-of ways: one that crosses Highway 401 just west of Warden Avenue in Toronto, and one that crosses the Pickering Industrial Area near Brock St.. The sampling program was designed to determine the degree and extent of vehicular Mn and Pb contamination of soil and trees to the north and south of the highway.

Site selection was done with consultation of the Ministry of Environment and Energy (MOEE). In 1972, 1979, and 1990, the Phytotoxicology Section of the MOEE initiated a soil and vegetation Pb study at specific points along Highway 401. The present study resamples two of these sites. This would serve three purposes: (1) to determine the Mn contamination in the soil and tree species, (2) to determine if there has been a change in the Pb concentration over time, and (3) to examine the effects of noise barriers placed along the highway in 1973. There is a possibility that wind eddying could concentrate Mn/Pb deposits on the leeward side of the 2 to 3 meter-high barriers located along the highway.

Lead accumulation in soil is a long term process and the detection of low annual accumulations is complicated by the inherent natural variability in the Pb content of the soil. In contrast, vegetation (plant foliage) provides a better indication of current emissions. However, vegetation is subjected to environmental variables such as the cleansing action of rainfall and the heterogeneity of the foliage (particularly grasses) from one site to another.

Both sides of the highway were searched to locate areas where soil and trees could be sampled against a sound barrier and at increasing distances from the pavement edge. Uncontrolled variables could affect the validity of any direct numerical comparisons. Some of these include frequency and amount of rainfall, prevailing winds, and changes in annual traffic volume.

In the Warden Avenue study area the annual average daily traffic volumes reported by the
Ministry of Transportation have increased as shown in the following table:

<table>
<thead>
<tr>
<th>Year</th>
<th>Traffic Volume Mean daily vehicles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1972</td>
<td>126,400</td>
</tr>
<tr>
<td>1979</td>
<td>190,300</td>
</tr>
<tr>
<td>1990</td>
<td>305,500</td>
</tr>
<tr>
<td>1993</td>
<td>333,700</td>
</tr>
</tbody>
</table>

An annual average daily traffic volume on Highway 401 in 1996 is not available. The Ministry of Transportation found a similar increasing trend in the annual average traffic volume through the Pickering Industrial Area.

3.2 SAMPLE COLLECTION:

From the hydro corridor just west of Warden Avenue, and from the hydro corridor passing through the Pickering Industrial Area, 80 soil samples (0-2cm depth) and 54 subsoil samples (0-5, 5-10, 10-15cm depth) were collected at an increasing distance from the north and south sides of the Highway as illustrated in Figure 3.

Figure 3: Sampling Locations/Sites in the vicinity of Highway 401, Ontario, 1996.
Tree core samples were collected at the north sides of both sites. The collection of tree samples was not relative to increasing distance from the highway. Noise barriers were situated at the north and south sides of the Warden Avenue West site. A chain fence was located at the north and south side of the Pickering Industrial site approximately 5m (north) and 20m (south) from the highway. The soil sample collection was done, at distances of 3m, 15m, 25m, 40m and 160m from the edge of the highway barrier. At each distance, five transect lines perpendicular to the highway were chosen for soil sampling. Each transect line was separated by a distance of 20m (as shown in Figure 3). One transect line at each site was selected for soil subsamples. Tree core samples (Norway maple & White spruce) were collected at the north sides of Warden Avenue west and the Pickering Industrial Area. Core collection was done at breast height (160cm) from both sides of the tree, facing towards and away from the highway.
3.3 METHODS:

The soil samples were collected into labeled plastic bags and then transported to the laboratory at the Faculty of Forestry, University of Toronto, Canada. The soil samples were air dried and passed through a 45-mesh sieve. After collecting the tree core samples in plastic straws, they were labeled and stored in the freezer. All wood samples were analyzed for Mn and other trace elements including Ca, Mg, K, Cl, Na and Al by Instrumental Neutron Activation Analysis (INAA), using the Slowpoke Reactor facility at the University of Toronto. Similarly, soil and subsoil samples were assessed for total Mn, Pb and other trace elements such as Ti, Mg, Na, V, Al, Cl, and Ca at the Slowpoke reactor facility. The soil samples were leached with 1N HNO₃ to find out the exchangeable amount of Mn and Pb by Atomic Absorption Spectrophotometer. Soil pH, soil particle analysis and Cation Exchange Capacity (CEC) were determined to characterized the soil in order to provide an improved understanding concerning the presence, bioavailability and toxicity of anthropogenic Mn oxides (Mena, 1980; WHO, 1981).

3.4 PARTICLE SIZE DISTRIBUTION:

The particle size distribution method is used to determine the basic physical characteristics of soils. It is more widely known as a mechanical analysis, and consists essentially of two operations: 1) dispersion of the soil; and 2) grading the dispersed particles into size groups. Dispersion is obtained by the removal of cementing substances such as organic matter and free iron oxides. Organic matter is removed by hydrogen peroxide treatment of the soil. Acid treatments are used to remove iron oxides and flocculating ions. Among mechanical methods and dispersion, prolonged shaking and stirring of the suspended sample is most common. The dispersed particles are graded according to size by sieving and sedimentation. Using standard sieves, the various sand fractions can be separated. Determination of the finer sand separation is obtained through a sedimentation method.

The sedimentation method is based on the fact that a sphere attains a constant fall velocity in a setting medium, provided the sphere is large enough to be unaffected by Brownian movement and the rate of fall is influenced solely by the viscosity of the medium. The terminal fall velocity of a sphere is expressed by Stokes' Law.
\[ V = \frac{2}{9} g \left( D_p - D_w \right) r^2 \]

where:

\( V \) = velocity of fall (cm/sec);
\( g \) = acceleration due to gravity (cm/sec^2);
\( D_p \) = Density of particles (gm/cm^3);
\( D_w \) = Density of the fluid (dyne-sec/cm^2);
\( n \) = viscosity of the fluid (dyne-sec/cm^2);
\( r \) = radius of the sphere (cm);

With the velocity of fall known, it is possible to calculate the time that is necessary for suspended particles of given diameters to settle. Today, the hydrometer method is widely used in routine analysis of soil. The soil is dispersed mechanically by stirring and chemically by deflocculation with sodium ions (Day, 1963).

The procedure includes the use of a dispersing agent, which is formed by dissolving 96.4g of sodium hexametaphosphate \((\text{NaPO}_3)_6\) and 3.8g of anhydrous sodium carbonate in a litre of distilled water. Fifty grams of air-dried, fine textured soil was weighed in a large wax paper cup. The soil was then soaked for 15 minutes in a 10% dispersing agent solution. The whole suspension was then transferred into the metal collar of stirring motor and the mixture was stirred for 3 to 4 minutes until soil aggregates were broken down. The soil suspension was then transferred into a sedimentation cylinder. The hydrometer was placed into the soil solution and distilled water was added to the mark on the cylinder. The suspension was stirred vigorously, by turning the cylinder end-over-end several times.

The cylinder was then placed gently on the bench and, after exactly 40 seconds, the hydrometer reading was recorded. The temperature of the suspension was also recorded. After exactly 2 hours of sedimentation, a second reading was recorded by gently inserting the hydrometer into the suspension. Once again the temperature of the suspension was recorded.

**Calculations:**

The scale of the hydrometer is graded in grams of solid per litre of liquid. It is calibrated at 68°F. For each degree above 68°F, 0.2g/l is added to the obtained value.
1. Corrected reading = Reading + (°F - 68) 0.2;
2. Silt plus clay content = Corrected reading * 2;
3. Sand content = 100 - (% of silt plus clay);
4. Clay content = Reading after 2 hours of sedimentation + (°F - 68) 0.2;
5. Silt content = (Silt plus clay - Clay content).

3.5 ACIDITY AND ALKALINITY:

Acidity is the result of an excess of hydrogen ions over hydroxyl ions; alkalinity is the result of an excess of hydroxyl ions over hydrogen ions. The hydrogen ion concentration of a solution, which is more correctly identified as hydrogen ion activity, is expressed in pH units. The pH of the solution is defined as the logarithm (10) of the reciprocal of the hydrogen ion activity.

In soil, hydrogen ions are found free in solution and as exchangeable cations on the negatively charged surfaces of clay and organic matter particles. Both fractions exist in a state of equilibrium. This equilibrium can shift with a change in salt concentration of the solution (because metallic cations will replace hydrogen ions at the exchange sites), or with a change in the ratio of solids to liquids in the soil system.

The pH of a solution can be determined either colorimetrically, or potentiometrically. Potentiometric measurement, employing glass and reference electrodes, is the standard procedure of pH determination today. The United States Department of Agriculture determines the pH ratio in soil and water mixtures as 1:1. The most widely used method, however, is the "thin-paste method", in which the soil is wetted to the "liquid limit". This procedure most closely approximates field conditions and is employed in most laboratories.

The potentiometric method was used to determine the pH of the soil and soil subsamples. A pH meter, 50ml plastic beakers, stirring rods, and pH 7 and 4 buffer solutions were used. About 10gm of each sample was weighed in a beaker and a thin paste was made by the addition of 10ml of distilled water (1:1 ratio). The soil was stirred occasionally and was allowed to aggregate for 30 minutes. Finally, the pH of the soil suspension was measured with the pH meter (McLean, E. O., 1982).
3.6 CATION EXCHANGE CAPACITY:

The soil acts as a reservoir for plant nutrients. Colloidal particles of clay and organic matter have surface charges that attract positively charged nutrient ions, the cations. These cations are protected against leaching by water and remain available for absorption by plant roots. The most important soil cations are Ca++, Mg++, Na+, K+, H+, NH₄+ and Al+. When a cation is released from the surface of a colloidal particle, it is quickly replaced by another cation. This process is called cation exchange. Plate-shaped soil clay particles have a large surface area for their size, and contribute a large amount of surface activity even when only a small amount of clay is present. Determining the percent of the total cation exchange capacity that is occupied by the exchangeable basic cations gives the percent base saturation. The higher the percent base saturation, the higher the pH and generally more the fertile soil. Barium acetate Ba(C₂H₃O₂)₂ is the main chemical used to determine the cation exchangeable hydrogen capacity of the soil.

\[
2H^+ + 2Ba(C_2H_3O_2)_2 \Rightarrow 2Ba^{++} \text{Clay} + HC_2H_3O_2 + Ca(C_2H_3O_2)_2
\]

\[
\text{Ca}^{++} \quad \text{(Soil)} \quad \text{Clay} \quad \text{(Soil)} \quad \text{HC}_2\text{H}_3\text{O}_2 \quad \text{Acetic acid} \quad \text{(Calcium Acetate)}
\]

The hydrogen which existed on the soil colloids comes out in the leachate as acetic acid. One hundred ml of neutral 0.5N Ba(C₂H₃O₂)₂ was added to 10g of a soil sample weighed in a 250ml Erlenmeyer flask. The sample was shaken every 3 to 5 minutes over a period of 30 minutes. The liquid portion was decanted through a suction filter and filtrate was saved for further use. An additional 25ml of Ba(C₂H₃O₂)₂ solution was added three times and was decanted through the filter. Five drops of phenolphthalein was added to the filtrate and was titrated to a faint pink color with approximately 0.1 N NaOH. The exact normality of the base used was recorded and calculated as given below:

**Calculations:**

\[
\text{meq of base (NaOH) used} = \text{Titer(ml)} \times N \text{ base}
\]

At the end point:

\[
\text{meq acid} = \text{meq base}.
\]

\[
\text{Meq exchangeable H in soil} = \text{Titer(ml)} \times N \text{ base}
\]

\[
\text{meq exchangeable H/100g soil} = \text{meq base/sample wt. (G)} \times 100.
\]
Ammonium acetate is another leaching method which replaces the exchangeable cations on the soil complex in a similar reaction to that shown with barium acetate. Drying the leachate at high temperatures converts the basic cations (Ca++, Na+, K+, etc.) to their oxides, and drives off the hydrogen and excess ammonium acetate. Adding an excess amount of standard acid to the basic oxides gives the following reaction:

\[
\text{CaO} + (x)\text{HCl} \Rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + (x-2)\text{HCl}
\]

Approximately 25 ml of 1.0 N Ammonium acetate was added to 5g of soil in a flask (200 to 400 ml size). The flask was clamped to the mechanical shaker and shaken for 15 minutes. The liquid was decanted through a drip filter into a labeled porcelain evaporating dish. The dish was placed in a drying oven to evaporate. The next day, the evaporating dish was subjected to high heat in a muffle furnace at 475 to 500 °C for 1 hour. The ammonium acetate and hydrogen acetate was driven off in the furnace and the acetates of the basic cations (Ca++, Na+, K+ etc.) were decomposed to their oxides, which remains as a white residue. Thirty five ml of 0.1N HCl was added to the white powder and heated strongly over a burner for 3 minutes. The solution was then warmed gently on a hot plate for another 30 minutes. Finally, the solution was quantitatively transferred to a 125ml flask and 4 drops of methyl red indicator was added and then titrated with approximately 0.1 N NaOH. The exact N base was recorded until methyl red changed its color from red to yellow. This gave the meq of acid not neutralized by the bases of the soil (Rhoades, J. D. 1982).

**Calculations:**

\[
\text{meq acid used} = 35\text{ml} \times \text{normality of acid}
\]

\[
\text{meq based used} = \text{Titer(m1)} \times \text{normality of base}
\]

\[
\text{meq exchangeable bases in soil} = \text{meq acid} - \text{meq base.}
\]

\[
\text{Meq exch. bases / 100g soil} = \text{meq exch. bases in soil/Sample wt. (G)} \times 100
\]

\[
\text{Total CEC} = \text{meq exchangeable H}^+ + \text{meq exchangeable bases (per 100g of soil)}.
\]

\[
\text{Base saturation %} = \text{meq exchangeable bases/100g} \times 1/\text{total CEC/100g} \times 100.
\]
3.7 EXCHANGEABLE Mn AND Pb:

Five grams of dry soil and 50ml of 1N HNO₃ were placed in a 250ml Erlenmeyer flask and shaken on a reciprocating shaker for one hour and filtered, which was followed by the determination of HNO₃-extractable Mn and Pb in the supernatant through the use of an Atomic Absorption Spectrophotometer. Blanks were run with the same procedures (Smith et al., 1995).

3.8 INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INNA):

While several techniques have been used to identify and quantify inorganics in wood and soil samples, most of them require some sort of destructive sample pretreatment before actual measurements can take place. Instrumental Neutron Activation Analysis is a non-destructive method of elemental analysis well suited to both quantitative and qualitative analysis. Using INAA, wood and soil may be analyzed in solid or powder form. The limits of detection vary with the element under study and the irradiation conditions employed (Muecke, 1987).

The Instrumental Activation Analysis technique was chosen for this study since it is a non-destructive method and the samples could be used for subsequent chemical analysis. This method also accommodates very small sample sizes. INAA involves sealing the samples in 2.5cm by 1.1cm polyethylene vials and irradiating them with neutrons. For the determination of the elements in soil samples, with the exception of Pb, each sample was irradiated sequentially for 5 minutes at a thermal neutron flux of 1*10⁷ neutrons/cm/sec. For determination of the elements in tree core samples, each sample was irradiated sequentially for 2 minutes at a thermal neutron flux of 1*10⁷ neutrons/cm/sec.

The atoms of each element in the sample absorb the neutrons forming new isotopes. The isotopes are radioactive in nature and each has a characteristic energy that can be identified by its half life measurement. The radioactive emissions (gamma rays) of each element were measured. Before counting the gamma rays emitted by samples, a three minute delay time was applied to allow the emissions to “cool” and come into the detectable range. The intensity of gamma rays emitted by each sample was determined and recorded by detectors or counters (Camberra Ge (Li) Detectors) with manually selected spectral regions. The irradiated samples were mounted at different positions on the detectors according to the intensity of gamma rays emitted from each sample. The higher the intensity, the farther the position where the samples were mounted. By
Comparing the counts from each sample to the standard counts, the elemental concentration in each sample was determined. Concentrations, in parts per million (ppm), of the individual elements were determined by using:

\[
PPM = \frac{\text{Peak area activity/gm wood sample}}{\text{Peak area activity/\mu g standard}}
\]

Sometimes the delay time for a particular sample took more than the usual two minute delay interval. In this case, the following formula was used to calculate what the activity would have been with the normal two minute delay time:

\[
A_0 = \frac{A_1}{e^{-(\ln2 \cdot A_t) \cdot T/2}}
\]

where

- \(A_0\) = early activity;
- \(e = 2.718\);
- \(A_1\) = later activity;
- \(A_t = \text{final time minus two minutes}\);
- \(\ln2 = 0.693\);
- \(T/2 = \text{half life of isotopes of each element}\).

### 3.9 Statistical Design:

Data from the soil and wood samples were stored in SAS files. A complete systematic design was used to study this data to determine if there were significant/nonsignificant effects of Mn deposition from automobile exhaust in soil and subsoil samples, collected at the north and the south side of the two sites (Warden Avenue and Pickering Industrial Area).

The treatments in this study were the combination of sites (Warden Avenue and Pickering Industrial Area), subsites (north and south sides of the highway), soil, subsoil samples and tree species. Therefore, ten treatments were used from each site. Analysis of Variance (ANOVA) was used to investigate if there was a Mn deposition difference between the two sites, four subsites and five transect lines chosen at specific subsites along the highway. However, before carrying out an actual research analysis we had to reassure ourselves that the fundamental assumptions of ANOVA have been considered, and are appropriate to a given set of data. A fundamental assumption is that all ANOVAs require the random sampling of individuals. Equality of variances
in a set of samples is an important precondition for several statistical tests. Synonyms for this condition are homogeneity of variances or homoscedasticity; the converse condition (inequality of variances among the samples) is called heteroscedasticity. As it is assumed that each sample variance is an estimate of the same parametric error variance, the assumption of homogeneity of variances makes intuitive sense. The $F_{\text{max}}$ test method was applied to study the homogeneity of variances between soil samples collected at different sites. This test uses the statistic that is the ratio of the largest to the smallest of several sample variances; the values were compared with the tabular values as described by Sokal and Rohlf, (1981). The resulting ANOVA was found to be non-significant (i.e., the variances of the two soil samples at same site were equal). One-way ANOVA analysis was used to determine the deposition rate of inorganic Mn in soil subsoil samples collected along the highway. A “null-hypothesis” T-test was used to determine Mn variances in core samples collected at two different north subsites of the highway. Duncan’s multiple range test was also used to determine the site and subsite variation for Mn and Pb in soil and subsoil samples. The Pearson correlation coefficient was used to determine the strength of a relationship that exists between two continuous variables (Mn and Pb) with respect to the distance from Highway 401 (Cody and Smith, 1991).
4.0 RESULTS AND DISCUSSION:

4.1 SOIL SAMPLES (0-2cm, DEPTH):

4.1.1 Soil Particle Size Analysis:

Soil structure and its degree is the arrangement and development of the primary particles into the geometric patterns. Texture is used to classify the size distribution of the mineral particles forming the solid phase of the three phased soil system, i.e. sand, silt, and clay particles. Soil structure significantly influences soil moisture relations, structure, porosity and chemical activity, and, in turn plant growth. Therefore, it is important for the practitioner to perceive the relationships that soil texture has with these properties. Data showing different percentage composition of soil samples is illustrated in Table 1.

Table 1: Particle Size Analysis: Mean percentage composition of soil samples (0-2cm depth) collected at Warden Avenue & Brock Road/Pickering Industrial Sites along Highway 401, Ontario, 1996.

<table>
<thead>
<tr>
<th>Site</th>
<th>Subsite</th>
<th>Mean percentage composition of soil</th>
<th>Triangle Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warden Ave.</td>
<td>North Side</td>
<td>Sand % 84.25 Clay % 11.32 Silt % 4.61</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>(Site #1)</td>
<td>South Side</td>
<td>Sand % 80.66 Clay % 9.84 Silt % 9.5</td>
<td>Loamy sand</td>
</tr>
<tr>
<td>Brock Road</td>
<td>North Side</td>
<td>Sand % 65.21 Clay % 10.36 Silt % 24.43</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>(Site #2)</td>
<td>South Side</td>
<td>Sand % 61.3 Clay % 12.32 Silt % 26.38</td>
<td>Sandy loam</td>
</tr>
</tbody>
</table>

According to the summarized data of soil particles size analysis, most of the soil is sandy in nature. The difference is the silt and sand content at the Pickering Industrial site. Statistical analysis shows that there is a significant difference in silt and sand content between the two sites. The Warden Avenue site is higher in sand content, while the Pickering Industrial site is higher in silt content. Sand and silt particles are composed primarily of quartz and other light minerals. They are rounded or angular in shape, depending on their degree of weathering. These particles are chemically inert; i.e., they have very little surface activity or ability to adsorb nutrient ions, water or gases. Therefore, they contribute little to soil fertility. In contrast, clay particles are composed of interlayered sheets of alumina and silica giving them a plate-like shape. Though these particles are extremely small (less than 0.002mm diameter), their shape gives them a tremendous surface.
area for a unit volume of material, compared to sand and silt. In other words, clays contribute significantly to soil fertility, whereas sand and silt contribute relatively little (Tisdale, 1985).

Within the soil fabric, rounded sand particles are in contact with other particles at several points. This reduces the compactability of sandy soils. The same phenomenon applies to silt particles, but they are much smaller in diameter than sand grains and therefore can be more effectively packed into a small volume. Silty soils are compactable, especially if they have low organic matter content. The plate-like clays may become oriented in parallel plains under an applied force and compaction results. The swelling and shrinkage of soil on wetting and drying are caused by the amount and type of clay in the soil. On the other hand, sandy soils exhibit little swelling and shrinking since they contain small amounts of clay (Tisdale, 1985). Since both the sites are similar in clay content (as shown in Table 1), it is difficult to compare at this stage which site will be more likely contaminated by inorganic Mn. However, more explanation about the compactability and texture depends upon the cation exchange capacity and pH of the soil.

4.1.2 CEC and pH of Soil:

Soil has been defined as a dynamic system. A significant part of the system is the chemical reactions and processes that occur uniquely in the soil. Many of these reactions are simplification process, where very complex substances are transformed into simple products that can be utilized by plants and other organisms. These processes are governed by the composition of the soil parent material, the rate of removal of the end products, the level and character of organism activity, and the rate of reaction as influenced by environmental factors such as temperature, moisture content, and degree of aeration. All processes have the potential to occur everywhere, but the combined effects of the parent material and existing environmental conditions will favor one combination of processes over another. This is contributed to by the fact that different soils occur in different localities. Chemical properties are the more easily manipulated soil properties compared to physical properties. Consequently, chemical properties, especially the adjustment of soil reaction (pH) by liming or acidification and nutrients by fertilization, have received considerable attention by soil researchers (Brady, 1990).

The soil acts as a reservoir for plant nutrients. Colloidal particles of clay and organic matter have surface charges that attract positively charged nutrient ions, the cations. These cations are protected against leaching by water and remain available for absorption by plant roots. Total
CEC tends to be greatest in surface soils where organic matter from the forest floor or from agricultural crop debris accumulates through incorporation and decomposition by organism activity. It decreases as depth increases, and may show a limited increase in the silty and clayey soils. Sandy soils, because of their low organic matter and clay contents, do not have high cation exchange capacities. Therefore these soils have a relatively low fertility. Medium textured soils such as loams and silt loams, exhibit increasing CEC with increased clay and organic matter contents. The fertility of these soils increases accordingly. The effect of temperature also influences the CEC of the soil, such as humid temperate region soils formed on limestone parent material will have high Ca and Mg contents. In other words, they are alkaline in reaction (pH) and are fertile. Sandstone derived soils formed in the same region have high hydrogen ion contents as they are acid in reaction and not so fertile. Cation exchange capacity also influences soil buffering capacity, which is important for the maintenance of a stable pH. It has been found that soil reaction is correlated with the solubility of nutrient compounds. Hence, plant nutrition availability is indicative of the general character of the soil microorganism population and depends upon the rate and degree of organic mineralization, as well as the base saturation (Brady, 1990). Soil reaction is also correlated with the solubility and concentrations of toxic substances. The greater the base saturation the higher the pH value.

Mean CEC values of different subsites have been summarized in Table 2.

Table 2: Cation Exchange Capacity & pH: Mean Duncan's range test for samples collected at sites along Highway 401, Ontario, 1996.

<table>
<thead>
<tr>
<th>Site</th>
<th>Subsite</th>
<th>Cation Exchange Capacity</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warden Ave.</td>
<td>North Side</td>
<td>17.573b</td>
<td>6.102c</td>
</tr>
<tr>
<td>(Site #1)</td>
<td>South Side</td>
<td>20.748b</td>
<td>6.189c</td>
</tr>
<tr>
<td>Brock Road</td>
<td>North Side</td>
<td>33.246a</td>
<td>6.411b</td>
</tr>
<tr>
<td>(Site #2)</td>
<td>South Side</td>
<td>33.828a</td>
<td>6.612a</td>
</tr>
</tbody>
</table>

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

Ion exchange is a reversible process by which one type of cation or anion held on the solid phase is exchanged with another kind of cation or anion in the liquid phase. Studies have shown that the CEC of a soil is not a fixed quantity, but is dependent on the pH and concentration of the extracting solution used for its determination. CEC increases with the increase in pH values because of the ionization of the OH groups in soil organic matter. CEC of a soil will obviously be affected by the nature and amount of mineral and organic colloids present. As a rule, soils with
Large amounts of clay and organic matter will have higher exchange capacities than sandy soils which are lower in organic matter. According to the data summarized in Table 2, the Pickering Industrial site shows higher soil CEC values than the Warden Avenue site. No significant difference was found within subsites. The higher the CEC values, the higher the degree of Mn and Pb accumulation in the soil. CEC increases with the alkalinity of soil. Data analysis has shown that the Warden site is more sandy, has a lower in CEC and a lower pH, whereas the Pickering site was higher in silt content, higher in CEC values and higher in pH values. ANOVA values for the CEC and pH of soil samples is given in Appendix A. Duncan's multiple range test was done to compare the CEC and pH values between sites. The results showed significant differences in pH and CEC between sites, but no significant difference within the subsites. However, the Pickering site showed a significant difference in pH within subsites.

4.2 EXCHANGEABLE AND TOTAL MN/PB:

4.2.1 Soil Samples (0-2cm, Depth):

To compare the Mn and Pb concentrations in soil samples between the two sample sites, a mean separation test was carried out, the values of which are summarized in Table 3.

Table 3: Mean Duncan's multiple range test values: Total/Exchangeable values of Mn and Pb

<table>
<thead>
<tr>
<th>Sites</th>
<th>Subsites</th>
<th>Distance (m)</th>
<th>Mean Total &amp; Exchangeable Values (PPM)</th>
<th>Exchangeable</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Warden Ave.</td>
<td>North Side</td>
<td>3</td>
<td>29.76a</td>
<td>20.36a</td>
<td>720.8a</td>
</tr>
<tr>
<td>(Site #1)</td>
<td></td>
<td>15</td>
<td>25.87ab</td>
<td>15.95b</td>
<td>695.6a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>23.89ab</td>
<td>13.89c</td>
<td>682.25a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>21.48b</td>
<td>11.54d</td>
<td>668.5a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160</td>
<td>20.18b</td>
<td>9.95d</td>
<td>658.5a</td>
</tr>
<tr>
<td>South Side</td>
<td></td>
<td>3</td>
<td>34.95a</td>
<td>14.27a</td>
<td>763a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>29.98ab</td>
<td>12.73a</td>
<td>667.6b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>24.76ab</td>
<td>11.03ab</td>
<td>593.6b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>21.26ab</td>
<td>8.46cb</td>
<td>588.6b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160</td>
<td>24.88b</td>
<td>6.93c</td>
<td>628.5b</td>
</tr>
<tr>
<td>Brock Road</td>
<td>North Side</td>
<td>3</td>
<td>28.64a</td>
<td>16.87a</td>
<td>687.6a</td>
</tr>
<tr>
<td>(Site #2)</td>
<td></td>
<td>15</td>
<td>25.38ab</td>
<td>12.93b</td>
<td>647.4ab</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>23.78abc</td>
<td>11.74b</td>
<td>645.6ab</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>22.68bc</td>
<td>9.79c</td>
<td>622.2ab</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160</td>
<td>19.53c</td>
<td>8.46c</td>
<td>597.4b</td>
</tr>
<tr>
<td>South Side</td>
<td></td>
<td>25</td>
<td>34.68a</td>
<td>12.66a</td>
<td>761a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>25.37b</td>
<td>9.69b</td>
<td>730.2a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160</td>
<td>17.98b</td>
<td>7.75c</td>
<td>715.75a</td>
</tr>
</tbody>
</table>

Means with the same letter are not significant different at p=0.05.
Fig. 4: Soil Samples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil samples (0-2 cm depth), collected at North of Warden Avenue Site along the Highway 401, Toronto, Ontario, 1996.

Distance (m) from the HWY 401, 1 = 3 m, 2 = 15 m, 3 = 25 m, 4 = 40 m, 5 = 160 m.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing distance for Mn shows (A,AB,AB,B,B) letters but, for Pb it shows different letters i.e. (A,B,C,D,D). Marker size display extreme values.
**Fig. 5: Soil Samples:** Box Plot Graph showing Mean Total values for Mn & Pb in soil samples (0-2cm, depth), collected at North of Warden Avenue Site along the highway 401, Toronto, Ontario, 1996.

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m.

Left & Right Box Plots represent Mn & Pb concentration in ppm units.

Mean Duncan's range test values at an increasing distance for Mn shows the same letter (A) but for Pb it shows different letters i.e. (A,B,BC,C,D). Marker size display extreme values. Mn>500ppm = TOXIC.
Fig. 6: Soil Samples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil samples (0-2cm, depth), collected at South of Warden Avenue Site along the highway 401, Toronto, Ontario, 1996.

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m. Left & Right Box Plots represent Mn & Pb concentration in ppm units. Mean Duncan's range test values at an increasing distance for Mn shows (A, AB, AB, AB, B) letters and for Pb it shows (A, A, AB, CB, C) letters, less significant.
Fig. 7: Soil Samples: Box Plot Graph showing Mean Total values for Mn & Pb in soil samples (0-2cm, depth), collected at South of Warden Avenue Site along the highway 401, Toronto, Ontario, 1996.

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing distance for Mn shows (A, B, B, B) letters but, for Pb it shows different letters i.e. (A, B, BC, BC, C). Mn > 500ppm = TOXIC.
Fig. 8: Soil Samples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil samples (0-2cm, depth), collected at North of Pickering Industrial Site along the highway 401, Toronto, Ontario, 1996

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing distance for Mn shows (A,AB,AB,AB,B) letters and for Pb it shows (A,A,AB,CB,C) letters. Marker size displays mean extreme values.
Fig. 9: Soil Samples: Box Plot Graph showing Mean Total values for Mn & Pb in soil samples (0-2cm, depth), collected at North of Pickering Industrial Site along the highway 401, Toronto, Ontario, 1996

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing distance for Mn and Pb shows the same letters i.e. (A, AB, AB, AB, B). Marker size represents the extreme values. Mn > 500ppm = TOXIC.
Fig. 10: Soil Samples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil samples (0-2cm, depth), collected at South of Pickering Industrial Site along the Highway 401, Toronto, Ontario, 1996

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan’s range test values at an increasing distance for Mn shows same letters (A,B,B) but, for Pb it shows significantly different letters i.e. (A,B,C). Marker size display extreme values.
Fig. 11: Soil Samples: Box Plot Graph showing Mean Total values for Mn & Pb in soil samples (0-2cm, depth), collected at South of Pickering Industrial Site along the Highway 401, Toronto, Ontario, 1996

Distance (m) from the HWY 401, 1 = 3m, 2 = 15m, 3 = 25m, 4 = 40m, 5 = 160m.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing distance for Mn shows the same letter (A) but, for Pb it shows different letters i.e. (A, B, B). Marker size display extreme values. Mn > 500ppm = TOXIC.
One way analysis of variances (ANOVA) was used to determine the variability of Mn and Pb deposition in different transect lines, as shown in Appendix B. Exchangeable and total values of Mn and Pb in soil samples collected at the north and south sides of the hydro rights-of-way along Warden Avenue and at the Pickering Industrial sites have been illustrated in Figs. 4, 5, 6, 7, 8, 9, 10 and 11. Data analysis has shown no significant differences between exchangeable and total Mn values, but significant differences were observed between exchangeable and total Pb values at distances of 3m, 15m, 25m, 40m and 160m from the highway. However, there is a significant difference between exchangeable and total Mn values at the extreme distances, or 3m and 160m from the highway. This indicates that there is not a significant trend of Mn deposition in the soil. The total value of Mn in soil samples (at 0-2cm of depth) collected at both sites has been found to be higher than 500ppm known to be toxic in the terrestrial environment (Tisdale, 1985).

Even though the total Mn levels may indicate the possibility of toxic effects in the terrestrial environment, statistically these levels do not show any significant differences between different distances from Highway 401. This can be explained by the solubility and availability of the micro-nutrient-cations affected by the presence of complexing and chelating agencies, as well as the oxidation-reduction (redox) potential in the soil. The solubility of soil Mn is influenced by the soil pH, redox potential, and the formation of ion complexes with organic matter.

As stated before, Mn occurs at different valence states from Mn$^{2+}$ to Mn$^{7+}$; these valences can change constantly. Mn in soil exists as exchangeable Mn$^{2+}$, which is water soluble and is easily reduced to various forms of MnO. These various forms are in a state of equilibrium with one another; however, they differ in their degree of availability to plants. Two major processes are operative in this cycle. The first is oxidation-reduction, while the second is production and decomposition of natural chelating agents that can complex Mn in both soluble and insoluble forms. Factors influencing the solubility of soil Mn include pH, redox, and complexation. Soil moisture, aeration, and microbial activity influence redox, while complexation is affected by organic matter and microbial activity (Stahlberg and Sombatpanit, 1974).

Many soil seasonal, and management factors influence Mn availability and movement of Mn. Imbalance of heavy metal ions, and in particular high levels of copper, iron or zinc in the growth medium, will impede Mn uptake by plants. On the other hand, high pH favors the formation of less available organic complexes of Mn (Sharpe and Parks, 1982). The activity of the soil microorganisms, which oxidize soluble Mn to unavailable forms, reaches a maximum near
pH 7. Submerged or waterlogged soil has a lower redox potential and an increased amount of soluble Mn\(^{2+}\). While soluble Mn\(^{2+}\) concentration increases under submerged conditions, there is a corresponding decline in \(O_2\) levels.

Mn availability can be increased by poor aeration in compact soils. Due to variability in valences, Mn occurs in different complex forms (MnO, MnO\(_2\), Mn\(_3\)O\(_4\)). The divalent form of MnO is only soluble in nature which gets leached or accumulated into deeper layers of the soil. The effects of leaching depends upon the soil texture and acidic conditions. The lower the pH, the higher the accumulation or leaching of soluble Mn at deeper levels within the soil profile (Mahmoud and Grime, 1977). The Warden Avenue site has a higher exchangeable and total Mn and Pb concentrations than the Pickering Industrial site, although these marginal differences are not statistically significant (Table 3). These subtle differences may be because of the texture and the pH of the soil, as the Warden site has less organic matter, higher sand component, and is more acidic in nature than the Pickering site. As illustrated in Figures 6, 7, 10 & 11, the south sides of both the sites show a higher deposition of inorganic Mn than the north sides, at a 3m distance from Highway 401, although the difference is not statistically significant (\(p>0.05\)). This may be due to the wind effect, since the prevalent wind direction is northeasterly in Ontario. The increase in Mn level just beside the highway is likely due to the Mn fractions of the gasoline additive MMT. Automobile exhaust emitting inorganic Mn is contributing to Mn contamination of the terrestrial environment.

Lead is a normal constituent of the earth’s crust and it is found in small concentrations naturally in water, soil and food. The most significant amount of Pb released to the environment comes from man-made sources. Once released in the environment, it does not move readily through natural pathways to more remote locations. Therefore, like other heavy metals, it is environmentally persistent. Historically, Pb was one of the first metals to be widely used by man. In the last 1000 years, the global annual Pb production increased from 10,000 tones to more than 4,000,000 tones. Lead was first introduced in gasoline in 1923 (Waldron and Stoffen, 1974). The local, regional and global biogeochemical cycles of Pb have been affected by man to a greater degree than those of any other toxic element. The most important behavior of lead is that in natural deposits, if left undisturbed, is practically immobile. However, once it is released as aerosols from smelters, automobile exhausts and dust, it is globally dispersed. At both sample sites, there was a clear (and statistically significant) trend of decreasing Pb concentrations with increasing distance from the highway (Table 3).
4.2.2 TREE SAMPLE STUDY:

A correlation analysis was done to determine the correlation between Mn and Pb deposition in soil, distance from the highway and sample depth, (Appendix F). Results showed a negative correlation at each subsite between Mn and Pb deposition in soil samples and the distance from the highway (i.e. Mn concentration decreased with increasing distance from Highway 401). 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 soil subsamples collected at each subsite at increasing soil depth (i.e. Mn concentration decreased and Pb concentration increased with depth). The correlation between CEC and pH was also studied. The results showed a positive correlation effect between CEC and pH of soil with Mn and Pb deposition along Highway 401. The lower the pH, the lower the cation exchange capacity and the higher the toxic effect of contaminants in the soil or vice versa.

4.3 SUBSITE VARIATION STUDY:

4.3.1 North & South Subsites of Warden and Pickering Sites:

One way analysis of variance (ANOVA) was used to determine the deposition variability in soil samples collected at the north and the south sides of the hydro corridors along Warden Avenue and in the Pickering Industrial site, as shown in Appendix C. Duncan's multiple range test values for different Mn and Pb variables in different subsites have been summarized in Table 4. Results of exchangeable and total Mn and Pb have been illustrated in Figures 12 and 13.

Table 4: Subsite Variation Study: Mean Duncan's range test values for Mn/ Pb subsite deposition along Highway 401, Ontario, 1996.

<table>
<thead>
<tr>
<th>Subsite Variation Study</th>
<th>Mean Duncan's Grouping</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exch.(PPM)</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td>Warden Ave.</td>
<td></td>
</tr>
<tr>
<td>North Side</td>
<td>24.24a</td>
</tr>
<tr>
<td>South Side</td>
<td>27.17a</td>
</tr>
<tr>
<td>Brock Road</td>
<td></td>
</tr>
<tr>
<td>North Side</td>
<td>24.01a</td>
</tr>
<tr>
<td>South Side</td>
<td>26.02a</td>
</tr>
</tbody>
</table>

For each subsite, values not followed by the same letter are significantly different at ($P=0.05$).
Fig. 12: Subsite Variation: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil samples (0-2cm depth), collected at Warden Avenue & Pickering Industrial Sites along the Highway 401, Toronto, Ontario, 1996

Subsites 1 & 2 = North & South Sides of Warden Avenue Site.
3 & 4 = North & South Sides of Pickering Industrial Site.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at subsites for Mn shows the same letter (A) but for Pb it shows different letters i.e. (A,B,A,B). Diamonds in Box Plots display mean values & marker size display extreme values.
Fig. 13: Subsite Variation: Box Plot Graph showing Mean Total values for Mn & Pb in soil samples (0-2cm, depth), collected at Warden Avenue & Pickering Industrial Sites along the Highway 401, Toronto, Ontario, 1996

Subsites 1 & 2 = North & South Sides of Warden Avenue Site.  
3 & 4 = North & South Sides of Pickering Industrial Site.  
Left & Right Box Plots represent Mn & Pb concentration in ppm units.  
Mean Duncan's range test values at subsites for Mn shows (A,B,A,B) letters & for Pb it shows (A,B,A,A). Diamonds in Box Plot display mean values & marker size display extreme values. Mn > 500ppm = TOXIC.
Total Mn concentrations are significantly higher in soil on the north side of the highway at the Warden Avenue site and significantly higher on the south side at the Pickering site. There is no difference in total soil Pb concentrations relative to the higher 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 and Pickering). No significant difference was observed in exchangeable and total Mn and Pb between the north and north sides, or the south and south sides, of the two sites. Total Mn in soil samples (at a 0-2cm depth) collected at different subsites was higher than the literature threshold limit value (500ppm), and therefore potentially toxic to the terrestrial environment (*Tisdale, 1985*).

### 4.4 SITE VARIATION STUDY:

A one-way analysis of variance (ANOVA) was used to determine the deposition variability in soil samples collected at a depth of 0-2cm, along Highway 401 at the two sample sites, as shown in Appendix D. Duncan’s multiple range test values have been summarized in Table 5.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Mean Duncan's Grouping</th>
<th>Exchangeable(PPM)</th>
<th>Total(PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>Pb</td>
</tr>
<tr>
<td>Warden Ave.</td>
<td></td>
<td>24.24a</td>
<td>14.34a</td>
</tr>
<tr>
<td>(Site = 1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brock Road</td>
<td></td>
<td>25.42a</td>
<td>11.08b</td>
</tr>
<tr>
<td>(Site = 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of tests comparing the exchangeable and total Mn and Pb have been illustrated in Figures 14 and 15. There is no significant difference in mean soil Mn concentration, but that is a significant difference in soil Pb concentrations between the sites. The mean total Mn concentration, in soil samples taken at a depth of 0-2cm where higher than the literature threshold limit value (500ppm), and therefore potentially toxic to the terrestrial environment (*Tisdale, 1985*).
Fig. 14: Site Variation: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil samples (0-2cm depth), collected at Warden Avenue & Pickering Industrial Sites along the Highway 401, Toronto, Ontario, 1996

Site # 1 = Warden Avenue Site, Site # 2 = Pickering Industrial Site.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan’s range test values at sites for Mn shows the same letter (A) but, for Pb it shows different letters (A, B). Diamonds in Box Plot display mean values & marker size display extreme values.
Fig. 15: Site Variation: Box Plot Graph showing Mean Total values for Mn & Pb in soil samples (0-2cm, depth), collected at Warden Avenue & Pickering Industrial Sites along the Highway 401, Toronto, Ontario, 1996.

Site #1 = Warden Avenue Site., Site #2 = Pickering Industrial Site.
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at sites for Mn shows the same letter (A) but, for Pb it shows different letters (A,B). Diamonds in Box Plot display mean values & marker size display extreme values. Mn>500ppm TOXIC.
4.5 SOIL SUBSAMPLES:

To compare the variability of Mn and Pb in soil subsamples collected at the two sample sites along Highway 401, a Duncan’s range test was carried out, the results from which have been summarized in Table 6, and illustrated in Figures 16, 17, 18 and 19.

Table 6: Soil Subsamples: Mean Exchangeable values for soil subsamples (0-5cm, 5-10cm, 10-15cm) collected at Sites along the Highway 401, Ontario, 1996.

<table>
<thead>
<tr>
<th>Site</th>
<th>Subsite</th>
<th>Depth(cm)</th>
<th>Mean Exch. Values (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td>Warden Avenue</td>
<td>North Side</td>
<td>0-5</td>
<td>32.50a</td>
</tr>
<tr>
<td>(Site #1)</td>
<td></td>
<td>5-10</td>
<td>29.99a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-15</td>
<td>22.66b</td>
</tr>
<tr>
<td></td>
<td>South Side</td>
<td>0-5</td>
<td>23.87a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5-10</td>
<td>25.48a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-15</td>
<td>20.01a</td>
</tr>
<tr>
<td>Brock Road</td>
<td>North Side</td>
<td>0-5</td>
<td>31.25a</td>
</tr>
<tr>
<td>(Site #2)</td>
<td></td>
<td>5-10</td>
<td>31.72a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-15</td>
<td>29.84a</td>
</tr>
<tr>
<td></td>
<td>South Side</td>
<td>0-5</td>
<td>30.75a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5-10</td>
<td>26.75a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-15</td>
<td>24.60a</td>
</tr>
</tbody>
</table>

*Means with the same letter are not significant different between subsites at (P=0.05).*

Analyses of variance (ANOVA) was used to determine the variability of Mn and Pb according to the depth of the soil (0-5cm, 5-10cm and 10-15cm), as shown in Appendix E. Pb showed a significant difference (higher concentration with depth) on the north side of the Warden Avenue site and on both sides of the Pickering Industrial Site. Although there was a consistent trend towards higher Mn concentrations in the surface soil, these was statistically significant only on the north side of the highway at Warden Avenue. Generally Mn concentrations decreased and Pb concentrations increased with soil depth (Figure 16).

Substantial research has shown that changes in soil pH and redox potential increase the mobility and plant availability of Pb (Gambrell, 1994). Heavy metals tend to be adsorbed by soil colloids and organic matter. Leaching of heavy metals from the soil is relatively slow and
Fig. 16: Soil Subsamples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil subsamples collected at North of Warden Avenue Site along the highway 401, Toronto, Ontario, 1996

Depth of Soil (cm), 1 = (0-5 cm), 2 = (5-10 cm), 3 = (10-15 cm).
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing depth for Mn shows the same letter (A) but, for Pb shows different letters i.e. (C, B, A). Marker size display extreme values.
Fig. 17: Soil Subsamples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil subsamples collected at South of Warden Avenue Site along the highway 401, Toronto, Ontario, 1996

Depth of Soil (cm), 1 = (0-5cm), 2 = (5-10cm), 3 = (10-15cm).
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing depth for Mn & Pb shows the same letter (A), significantly not different. Marker size display extreme values.
Fig. 18: Soil Subsamples: *Box Plot Graph* showing Mean Exchangeable values for Mn & Pb in soil subsamples collected at North of Pickering Industrial Site along the highway 401, Toronto, Ontario, 1996

*Depth of Soil (cm), 1 = (0-5cm), 2 = (5-10cm), 3 = (10-15cm).*
*Left & Right Box Plots represent Mn & Pb concentration in ppm units.*
*Mean Duncan's range test values at an increasing depth for Mn shows the same letter (A) but, for Pb it shows different letters i.e. (B, AB, A). Marker size display extreme values.*
Fig. 19: Soil Subsamples: Box Plot Graph showing Mean Exchangeable values for Mn & Pb in soil subsamples collected at South of Pickering Industrial Site along the highway 401, Toronto, Ontario, 1996

Depth of Soil (cm), 1 = (0-5cm), 2 = (5-10cm), 3 = (10-15cm).
Left & Right Box Plots represent Mn & Pb concentration in ppm units.
Mean Duncan's range test values at an increasing depth for Mn shows the same letter (A) but, Pb shows different letters i.e. (C, B, A). Marker size display extreme values.
dependent on pH, CEC, field and soil conditions, temperature, interaction with other elements, valence state of the elements and soil type.

Mn exists in different valence states (Mn\(^{n+}\), Mn\(^{2+}\), Mn\(^{3+}\), Mn\(^{4+}\), Mn\(^{5+}\), Mn\(^{6+}\), and Mn\(^{7+}\)), is unstable and undergoes oxidation reduction quickly. Organometallic Mn, if left uncombusted in the atmosphere, will photochemically decompose into MnO forms (99.9% of the total mass will be decomposed). On the other hand, Pb mostly in two different valence forms. Pb (II) is most often found, while Pb (IV) is rarer. In the organic form, Pb can form up to 4 Pb-C bonds. It seems that about 5% of these Pb additives are emitted uncombusted to the air, rather than through biotransformation of inorganic environmental Pb. The flux of organometallic Pb is small compared with that of inorganic Pb on a global basis, but on a local basis it might be a significant factor.

The prime medium for anthropogenic Mn and Pb transport is air, because fine particulates (1\(\mu\)m diameter) generated by high temperature sources may travel a long distance before entering the terrestrial environment via wet, dry or cloud deposition. Deposition from the air is greater near the source (Barrie, 1980). Most of the Mn/Pb particles deposited on the soil are retained and eventually become a part of the upper surface layer. Lead or Mn accumulation occurs proportional to the rate of the deposition and relative to the physical and chemical properties of the soil. Lower pH means higher accumulation of Mn and Pb in deeper layers of the soil (Mahmoud and Grime, 1977). Seventeen years ago Pb was banned and Mn was introduced as an antiknock component in gasoline however, there is still persistent Pb in the terrestrial environment. Data collected from this study clearly shows that Pb is still present in considerable concentration in soil adjacent to the major highway and that Mn soil concentrations are increasing.

4.6 TREE SAMPLE STUDY:

Total Mn and other trace elements measured in tree core samples collected at the two sample sites have been summarized in Table 7. The results have been illustrated in Figure 20. Two different tree core samples were collected: Norway maple (Acer platanoides) and white spruce (Picea abies). Both were sampled at the north side of the two sample sites. Both species show different mean values for total Mn concentration, as well as for other trace elements.
Table 7: Tree Samples: Mean total Mn & other trace elements in the tree Core Samples collected at Sites in the vicinity of Highway 401, Ontario, 1996.

<table>
<thead>
<tr>
<th>Site</th>
<th>Tree Species</th>
<th>Mean total value of Mn &amp; other Trace elements in tree core samples (PPM)</th>
<th>Br</th>
<th>Mg</th>
<th>Na</th>
<th>V</th>
<th>K</th>
<th>Al</th>
<th>Mn</th>
<th>Ca</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Norway maple</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Warden Ave.</td>
<td>AN</td>
<td>0.2975*** 281.29 79.67 0.1209 762.1 24.43 7.894 2482.4 209.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Site #1)</td>
<td>AS</td>
<td>0.3582*** 317.55 75.96 0.115 760.7 24.64 11.57 2965.1 188.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North Side</td>
<td>Mean</td>
<td>0.3278 299.42 77.82 0.1179 761.4 24.54 9.732 2723.8 198.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>White spruce</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brock Road</td>
<td>CN</td>
<td>0.736** 176.34 185.6 0.4093 601.9 111.86 9.572 2158.9 354.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Site #2)</td>
<td>CS</td>
<td>1.565** 84.76** 193 0.3543 471.8 115.46 5.73 1464.3 308.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North Side</td>
<td>Mean</td>
<td>1.1505 130.55 189.3 0.3818 536.9 113.66 7.651 1811.6 331.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Increasing stars is equal to the decreasing significance of the value.

Statistically, there is no significant difference in the total Mn content between two tree species. Calcium content has been found in the highest concentration, as compared to the other trace elements in tree core samples. This is consistent with important role that Ca has in cell wall structure.

While Mn phytotoxicity may occur above 500ppm in soil, its impact on tree health in an urban environment is yet to be determined. The toxic levels of Mn in trees will likely be very species specific. Moreover, heavy metal tolerance varies within and between species in term of phenotypic variation, as well as with differences in soil pH, soil, physical and chemical conditions, wind characteristics effect, temperature, and nutrient availability. Changes in the acidity of the soil may lead to increased availability of potentially damaging elements, such as aluminum (Foy and Campbell, 1984). Root elongation and the solubility of different elements in the soil are important factors in uptake of elements from the soil. Most metals, including Zn, Cd, Mn, Cu and Pb, become increasingly soluble as pH drops. However, Innes (1993), has argued that soil acidification may result in the increased potential for mobilization of heavy metals stored in the upper horizons. Manganese reaches potentially toxic levels in many acidified soils, but there is little evidence that it has an adverse effect on trees at the concentrations normally found in acidic soils. Low pH may increase the mobility of Mn in soil, eventually resulting in Mn deficiency within the trees. High levels of Mn may induce Ca deficiency.
Fig. 20: Bar graph showing mean total Mn & other trace elements in the tree core samples collected at the North side of Warden and Pickering sites in the vicinity of the Highway 401, Toronto, Ontario, 1996.
5.0 CONCLUSION:

The sampling program was designed to determine the degree and extent of Mn contamination of soil adjacent to Highway 401. The sampling would also determine if there had been a change in the Pb concentration pattern over time and to examine the effects of noise barriers placed along both sides of the Warden Avenue site along Highway 401.

The field survey revealed that soil Mn concentrations in high traffic areas were up to 100-fold higher than historic lead levels (greater than 500 ppm). Soil Mn and Pb concentrations were highly correlated with the distance from the highway. Lead concentrations seem to have changed little from the values reported by the Phytotoxicology Section study done at the Warden site in 1972, 1979 and 1990, as shown in Appendix G. The Warden Avenue site has shown at least 100ppm Pb concentration that has decreased (as compared with the values reported by Phytotoxicology Section) in soil samples collected at 3m distance from the barrier located along the highway. Lead accumulation in soil is a long-term process. The detection of low annual accumulations is complicated by the inherent natural variability in the lead content of soil. Lead concentrations have changed with times likely through a leaching process with Pb moving deeper into the soil profile with cessation of aerial deposition. Labile Mn concentration decreased with depth likely because accumulation of surface deposition exceed the vertical leaching potential of the soil. Norway maple and White spruce xylem collected from the north sides of the highway were found to have a low Mn content in comparison to other trace elements. Mn contamination have increased in an urban environment since MMT was introduced as a gasoline additive in 1977. Many factors govern the availability of Mn in the soil, such as acidity, soil texture, soil moisture, soil microflora and microfauna, wind, and temperature. However, it is not possible to anticipate all the factors which may change the mobilization, pathways, bioavailability and effects of Mn on a global, regional and local basis. Other important factors to be considered are changes in the world economy, changes in national regulations concerning levels of Mn in gasoline, efficiency of vehicle, emission controls, acid rain, deforestation, global climatic change, demographic changes, and changes in the patterns of human and animal nutrition and diseases. 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 was expected to be different adjacent to the barrier. However, results showed that the variability in Mn deposition between the sites was not significant. 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. It can be concluded that inorganic Mn emitted from automobile exhaust is contributing to Mn contamination in the terrestrial environment.
6.0 RECOMMENDATIONS FOR FUTURE WORK:

1. New sites representing different vegetation types should be selected to evaluate the effects of Mn deposition. These sites should be large enough to allow for the comparison of several plant species at varying distances from the highway.

2. The impact of site orientation on the data is unclear. Sites oriented north/south and east/west of highways should be considered.

3. Sample sites should be established in a remote location and in a rural location, in order to provide appropriate control data.

4. More intensive data collection adjacent to the noise barriers is required to define their effect on the distribution of highway emissions.

5. The deposition of Mn from highway is likely exponential in nature, therefore the sampling strategy should be amended to include more sites closer to the highway to capture rate of maximum expected deposition rate, and extended further to define the maximum extent of deposition.

6. Vegetation collection should be done at different times during the year, to study the impact of seasonal variations on Mn deposition.
7.0 REFERENCES:


Moran, J. B. 1975. The environmental implications of manganese as an alternative antiknock. # 750926, SAE Publications Division, Detroit, Michigan, U.S.A.


Appendix A

ANOVA values for Table 2: Cation Exchange Capacity and pH of soil

**Dependent Variable: pH**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsite</td>
<td>3</td>
<td>2.9078</td>
<td>0.96929</td>
<td>15.88</td>
<td>0.0001</td>
</tr>
<tr>
<td>Transect</td>
<td>4</td>
<td>2.5206</td>
<td>0.63016</td>
<td>10.33</td>
<td>0.0001</td>
</tr>
<tr>
<td>Subsite*Transect</td>
<td>10</td>
<td>0.1168</td>
<td>0.01168</td>
<td>0.19</td>
<td>0.9963</td>
</tr>
</tbody>
</table>

**Dependent Variable: CEC**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsite</td>
<td>3</td>
<td>4295.82</td>
<td>1431.94</td>
<td>45.27</td>
<td>0.0001</td>
</tr>
<tr>
<td>Transect</td>
<td>4</td>
<td>98.634</td>
<td>24.658</td>
<td>0.78</td>
<td>0.5428</td>
</tr>
<tr>
<td>Subsite*Transect</td>
<td>10</td>
<td>450.866</td>
<td>45.086</td>
<td>1.43</td>
<td>0.1913</td>
</tr>
</tbody>
</table>
Appendix B

ANOVA values for Table 3: Exchangeable and Total values of Mn and Pb variables (Warden and Pickering Sites).

### Dependent Variable: Exchangeable Mn

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>1</td>
<td>23.759</td>
<td>23.759</td>
<td>0.95</td>
<td>0.3328</td>
</tr>
<tr>
<td>Subsite</td>
<td>2</td>
<td>101.335</td>
<td>50.667</td>
<td>2.03</td>
<td>0.1398</td>
</tr>
<tr>
<td>Transect</td>
<td>4</td>
<td>1135.47</td>
<td>283.868</td>
<td>11.38</td>
<td>0.0001</td>
</tr>
<tr>
<td>Site*Transect</td>
<td>4</td>
<td>34.808</td>
<td>8.702</td>
<td>0.35</td>
<td>0.8438</td>
</tr>
<tr>
<td>Subsite*Transect</td>
<td>6</td>
<td>385.089</td>
<td>64.182</td>
<td>2.57</td>
<td>0.0273</td>
</tr>
</tbody>
</table>

### Dependent Variable: Exchangeable Pb

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>1</td>
<td>181.624</td>
<td>181.624</td>
<td>81.58</td>
<td>0.0001</td>
</tr>
<tr>
<td>Subsite</td>
<td>2</td>
<td>38.135</td>
<td>19.067</td>
<td>8.57</td>
<td>0.0005</td>
</tr>
<tr>
<td>Transect</td>
<td>4</td>
<td>690.447</td>
<td>172.612</td>
<td>77.54</td>
<td>0.0001</td>
</tr>
<tr>
<td>Site*Transect</td>
<td>4</td>
<td>11.597</td>
<td>2.899</td>
<td>1.3</td>
<td>0.279</td>
</tr>
<tr>
<td>Subsite*Transect</td>
<td>6</td>
<td>8.967</td>
<td>1.494</td>
<td>0.67</td>
<td>0.6731</td>
</tr>
</tbody>
</table>

### Dependent Variable: Total Mn

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>1</td>
<td>836.115</td>
<td>836.115</td>
<td>0.25</td>
<td>0.6185</td>
</tr>
<tr>
<td>Subsite</td>
<td>2</td>
<td>122952.381</td>
<td>61476.191</td>
<td>18.42</td>
<td>0.0001</td>
</tr>
<tr>
<td>Transect</td>
<td>4</td>
<td>43865.861</td>
<td>10966.465</td>
<td>3.29</td>
<td>0.0167</td>
</tr>
<tr>
<td>Site*Transect</td>
<td>4</td>
<td>14055.915</td>
<td>3513.978</td>
<td>1.05</td>
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### Dependent Variable: Total Pb

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<th>M Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
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Appendix C

ANOVA values for Table 4: Subsite Variation Study.
of Mn and Pb variables.

Dependent variables: Exchangeable Mn/Pb for N & S of Warden & Pickering.

<table>
<thead>
<tr>
<th>Source</th>
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<th>Mean Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
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</thead>
<tbody>
<tr>
<td>Subsite</td>
<td>Warden Avenue Mn</td>
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<td>80.439</td>
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<tr>
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<td>Warden Avenue Pb</td>
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<td>1.86</td>
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<tr>
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<td>Pickering Ind. Pb</td>
<td>1</td>
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<td>21.48</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Dependent variables: Total Mn/Pb for N & S of Warden & Pickering.

<table>
<thead>
<tr>
<th>Source</th>
<th>Variable</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsite</td>
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<td>1.63</td>
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Appendix D

ANOVA values for Table 5: Site Variation Study.

Dependent variables: Exchangeable Mn/Pb Warden & Pickering Sites.

<table>
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<th>Source</th>
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<th>Mean Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Mn</td>
<td>1</td>
<td>23.759</td>
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<td>Site</td>
<td>Pb</td>
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<td>181.63</td>
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Dependent variables: Total Mn/Pb Warden & Pickering Sites.

<table>
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<th>Source</th>
<th>Variable</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Mn</td>
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<td>158.28</td>
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<td>25046.94</td>
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Appendix E

ANOVA values for Table 6: Soil Subsamples.
(Warden and Pickering Sites)

Dependent variables: Exchangeable Mn

<table>
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<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>P&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>1</td>
<td>197.163</td>
<td>197.163</td>
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<td>Subsite</td>
<td>2</td>
<td>279.838</td>
<td>139.919</td>
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<td>0.0158</td>
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<tr>
<td>Depth</td>
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<td>285.879</td>
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<td>Site*Depth</td>
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<td>24.985</td>
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<td>0.4476</td>
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<td>Subsite*Depth</td>
<td>4</td>
<td>73.377</td>
<td>18.344</td>
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<td>0.6635</td>
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Dependent variables: Exchangeable Pb

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>S of Squares</th>
<th>M Square</th>
<th>F Value</th>
<th>P&gt;F</th>
</tr>
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<tbody>
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<td>Site</td>
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<td>92.969</td>
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<td>Site*Depth</td>
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<td>Subsite*Depth</td>
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<td>252.698</td>
<td>63.174</td>
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Appendix F

Correlation matrix showing the relationship between Warden and Pickering sites.

Soil Samples (0-2cm, depth): Exchangeable Values:

<table>
<thead>
<tr>
<th>Variable</th>
<th>N</th>
<th>R-Square</th>
<th>p</th>
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<tbody>
<tr>
<td>Transect</td>
<td>100</td>
<td>1</td>
<td>0.0968</td>
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<tr>
<td>CEC</td>
<td>78</td>
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<tr>
<td>pH</td>
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<td>0.6194</td>
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<tr>
<td>Mn</td>
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<tr>
<td>Pb</td>
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<td>-0.8391</td>
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</table>

Soil Subsamples (0-5, 5-10, 10-15cm depth): Exchangeable Values:

<table>
<thead>
<tr>
<th>Variable</th>
<th>N</th>
<th>R-Square</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth</td>
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<tr>
<td>CEC</td>
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<td>0.3506</td>
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<tr>
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<td>Mn</td>
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<tr>
<td>Pb</td>
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### Table 1: Lead Concentrations in Soil and Grass in the Vicinity of Highway 401, Toronto - 1972, 1973, and 1980

<table>
<thead>
<tr>
<th>ULN</th>
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<th>0.9 m</th>
<th>1.3 m</th>
<th>1.7 m</th>
<th>2.1 m</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td>51</td>
<td>43</td>
<td>33</td>
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<td>43</td>
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<tr>
<td>4</td>
<td>68</td>
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<td>49</td>
<td>39</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>71</td>
<td>62</td>
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<td>43</td>
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South of Highway 401

<table>
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<td>3</td>
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<td>4</td>
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<td>71</td>
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</table>

North of Highway 401

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<th>2.1 m</th>
</tr>
</thead>
<tbody>
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</tr>
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</tr>
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<td>66</td>
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<td>69</td>
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<td>72</td>
<td>63</td>
<td>54</td>
<td>44</td>
<td>49</td>
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</tbody>
</table>

**Average** Lead Concentration (ppm, dry wt)

<table>
<thead>
<tr>
<th>Soil (0-3 cm)</th>
<th>Soil (3-10 cm)</th>
<th>Soil (10-30 cm)</th>
<th>Soil (30-100 cm)</th>
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<tbody>
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<td><strong>Average</strong></td>
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<td>3.5</td>
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**Appendix C**