## THE UNIVERSITY OF MANITOBA

## A SURVEY OF SOIL LEAD LEVELS IN THE

## CITY OF WINNIPEG

by

### BERT PAUL KRAWCHUK

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## A THESIS

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## A SURVEY OF SOIL LEAD LEVELS IN THE

## CITY OF WINNIPEG

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### BERT PAUL KRAWCHUK

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

### MASTER OF SCIENCE

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### ABSTRACT

Lead has been mined and used for thousands of years. Today, lead is the most common non-ferrous heavy metal pollutant of the environment. In particular soils by major roadways and around smelters have been found to be contaminated by lead.

A survey of soil was carried out in the city of Winnipeg during the period September 1978 to September 1979. Seventy-five sites, ranging from residential through heavily trafficked arteries to industrial areas were sampled on a seasonal basis. In the winter a number of snow samples were collected and examined. The samples were prepared using a nitric-perchloric acid digest. Extracts were analysed for lead by atomic absorption spectroscopy. An extraction of 95% or better was obtained. The survey found high leadin-soil levels (>1000 µg Pb/g soil) beside major arteries and at busy intersections. As well, high lead-in-soil levels were found in areas surrounding secondary lead smelters. Snow samples showed the same trend, high lead levels along major arteries, low lead levels in residential areas.

Lead levels in roadside soil are traffic volume dependent. Soils from along major routes had lead-in-soil levels greater than 1000  $\mu$ g/g while residential area soils gave levels of less than 500  $\mu$ g/g. The three smelter sites were found to have high lead-in-soil levels (1,000 to 12,000  $\mu$ g/g) in the soil around them. A factor influencing the lead level observed in the soil was found to be site location of the sampling point within the area of study. As well, site history (topography, physical disruption of the soil) is believed to be a factor for the lead observed in the soil at that site. The salt spread during the winter was found to reduce the accumulated lead levels along major arteries from fall to spring.

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#### I, INTRODUCTION

Lead has been mined and used by man for about five millenia. The Greeks and Romans used lead in cooking utensils and in the plumbing of the homes of the wealthy. It has often been speculated that this widespread use of lead was one of the contributing factors in the deterioration of the Roman Civilization due to the resulting effects of lead poisoning within the ruling class.

1

Today lead is the most widely used non-ferrous metal and as a result it is also the most common heavy metal pollutant in the environment.

#### 1.1 Sources of Lead

Lead naturally occurs in soil, water, plants, animals, and air. However, man's use of lead has raised the natural background level far above that which would be in existence naturally. The main sources of lead pollution are mining and smelting (primary and secondary) operations and the combustion of organolead compounds, tetramethyl- and tetraethyllead, used as anti-knock agents in automobile engines. Other sources of lead pollution are lead-based pigments in paint and lead in the glaze from improperly-fired ceramic ware.

1.1a Atmospheric Lead

We solowski <u>et al.</u>(1) recorded the ambient air levels of a number of heavy metals in an area 32.2 km northwest of San Francisco. Episode peak lead levels ranged from 4.15  $\mu$ g/m<sup>3</sup> to 9.40  $\mu$ g/m<sup>3</sup> for a two hour sampling period over a twenty-four hour period (12 - 2 hour samples taken). These peaks occurred at different periods of the day and could be correlated with the wind's direction and velocity. Neutron activation analysis was used to identify non-automotive sources of lead by correlation with other heavy metals present.

Measurements done in the south of Norway (2) have illustrated the long range transport of heavy metal pollutants. When the air flow was from industrial areas in continental Europe, the observed lead-in-air level was 0.28  $\mu$ g/m<sup>3</sup> for a 24 hour period, whereas when the air flow was from the North Atlantic Ocean and the Norwegian Sea the lead-in-air level was less than 0.001  $\mu$ g/m<sup>3</sup>. In Germany, the wind direction was found to influence the lead-in-rain levels (3). Observed levels ranged from 13 to 73  $\mu$ g/L for rain and fresh snow in an industrial area and a recorded pH of about 4 for the precipitation.

Lead-in-air values have been reported for a number of urban and rural areas around the world. Perry <u>et al.</u>(4) have reported the following average lead-in-air levels for varing time periods,  $6.0 \pm 2.0 \ \mu\text{g/m}^3$  in a carpark,  $4.3 \pm 1.7 \ \mu\text{g/m}^3$  and  $3.8 \pm 1.5 \ \mu\text{g/m}^3$  at curbside on a busy street in London. In Teheran (5) lead-in-air ranged from 2.8 to 4.8  $\mu\text{g/m}^3$  with a monthly mean range of 3.12 to 4.05  $\mu\text{g/m}^3$ . At a rural control site the lead-in-air level was undeterminable by the dithizone method used. In the American southwest (6,7) values of 0.69 to 0.72  $\mu\text{g/m}^3$  and 0.055 to 0.067  $\mu\text{g/m}^3$  were reported for urban and rural localities respectively.

A 42 month study in Denver, Colorado (8) found maximum lead-in-air levels in the winter which coincided with atmospheric minima in mixing heights. During the winter months lead-in-air levels of around 2  $\mu$ g/m<sup>3</sup> were recorded at four of the six sampling sites whereas in the summer the lead-in-air level was below 1  $\mu$ g/m<sup>3</sup> at all six sites.

A St.Louis study (9) reported a range of 0.115 to 0.640  $\mu$ g/m<sup>3</sup> leadin-air for a 2 hour sample time. Daines <u>et al</u>.(10) found the lead-in-air

levels decreased as the distance from the roadway increased and that leadin-air levels were related to traffic volume. The higher the traffic volume, the higher the lead-in-air level observed.

Chamberlain <u>et al</u>.(11) calculated the downwind lead-in-air levels and compared them to reported values. At distances close to the roadway the values agreed but as the distance from the roadway increased the values diverged due to upward diffusion of the plume.

A downward trend in lead-in-air levels has been noted (12) with the increase in use of unleaded gasoline in the Los Angeles Basin area. For the period 1971-1976 the winter lead-in-air average dropped from 7 to 5  $\mu$ g/m<sup>3</sup> and the summer average dropped from 4.5 to 2  $\mu$ g/m<sup>3</sup>.

In Germany (13) a decrease in lead emissions of 45% was observed when the maximum amount of lead in gasoline was lowered from 600 mg/L to 150 mg/L.

The American Petroleum Institute (14) is advocating a return to lead tolerant automobiles as an energy conservation measure. This would yield a savings in costly aromatics which are currently used to raise the octane rating of unleaded gasoline. The emission of lead would be controlled by the inclusion of a lead trap in the exhaust system.

Deposition of air-lead occurs either directly or in rain. As well, deposited lead is washed off leaf surfaces, window ledges and roofs of buildings. As noted by Ho and Tai (15), an average decrease of about 50% was observed after a period of rain in leaf-surface-lead.

The deposition of air borne lead is of concern where it involves human foodstuffs. Samples of summer grass had lower lead levels than samples of winter grass and as a result Tjell <u>et al.(16)</u> concluded that 90 to 99% of the lead observed was due to atmospheric deposition. Only 1 to 10% of the lead observed was in the green parts as a result of root uptake from the

soil. Atmospheric deposition of lead was found to contribute to the lead content of leaf lettuce(17) due to the large surface area, but other crops like tomatoes, potatoes, beans, and corn were unaffected.

Servant(18) has documented the lead levels in rain for a number of regions in France over a period of years. For the period 1972 - 1973 a range of 75 to 8100  $\mu$ g/L lead-in-rain was observed for an industrial area, 4 to 38  $\mu$ g/L for a rural area, 2 to 22  $\mu$ g/L for a mountain area, and 6 to 67  $\mu$ g/L for an urban area. These values showed an increase in lead levels over the ones for the same areas in 1971 - 1972 (19). The lead levels observed in a river system(20) during high and low flow seasons were attributed to natural sources as an increase in the lead level was not observed during the low flow season as was expected if man-made pollution was present.

It has been noted(21) that the lead content of precipitation can be correlated to the amount of leaded gasoline consumed in the area of sample collection. Some of this deposited lead finds its way into the water system either by direct precipitation or in run-off. It has been estimated (22) that Lakes Huron and Superior both receive on the order of 1 tonne/day of lead from the atmosphere. Lake Michigan has been reported(23) as having a lead level of 40  $\mu$ g/L. In the central and northern parts of Norway a background lead level of  $\leq 0.5$  to 2.0  $\mu$ g/L was reported(24). Lead-in-precipitation levels ranged from 10 to 80  $\mu$ g/L and a correlation was seen between the acid level and other long-range pollutants. Lakes in the southeastern part of Norway were found to have lead levels in the range of 2 to 4  $\mu$ g/L.

The concentration of lead in drinking water is of concern where the water has a source of lead pollution. A survey done on drinking water across Canada(25) found a range of <1.0 to 65  $\mu$ g/L lead in the distributed

water. In the British Isles a range of 0 to 86  $\mu$ g/L lead-in-drinking water has been reported(26). In the city of Debrecen, Hungary the water pipes were found to have a high lead level in the iron-manganese-oxide-hydroxide precipitate(27). In an Australian mining community(28) the reservoir sediment contained from 30 to 650  $\mu$ g/g lead and the lead-in-water level ranged from 5 to 69  $\mu$ g/L. As long as the pH did not decrease dramatically there was no danger of increased lead-in-water levels due to the natural sink in the sediment of the reservoir and the precipitate in the water pipes.

All of these reported values are below the limit established by the World Health Organization(WHO) of 100  $\mu$ g/L lead-in-drinking water. However, Germany has a limit of 40  $\mu$ g/L and the United States has a limit of 50  $\mu$ g/L for lead-in-drinking water(29,30).

The lead in drinking water level is of particular concern where young children and mothers are exposed to a continual source of lead. Young children are particularly susceptable to lead poisoning both at subclinical and clinical levels. More will be said about this problem area in a later section.

1.1b Lead in the Soil

The lead which has been emitted into the atmosphere eventually deposits onto the ground where it becomes a problem with respect to plant uptake. Also, children playing in contaminated soils may ingest the soil or inhale the fine lead aerosol(31). Spittler and Feder(32) analysed 900 soil samples taken from backyards, playgrounds, play areas, and large community gardens in the Boston area for lead. A range of 100 to 2000  $\mu$ g/g lead-in-soil was observed with an average of 800  $\mu$ g/g. They attribute the

high lead-in-soil levels observed in some of the cases to the past use of lead-based paints. The following recommendations were made to gardeners: where lead-in-soil exceeded 1000  $\mu$ g/g, gardening should be confined to fruiting crops which show minimal uptake of lead; in the range 500 to 1000  $\mu$ g/g lead-in-soil root crops can be safely grown but the leafy tops( i.e., beets and turnips) should not be harvested. They also note the general problem of high lead-in-soil levels where small children are concerned. Due to their inherent closeness to the soil and their habit of putting dirty fingers and food into their mouths, children have a greater exposure to lead than most adults.

Some studies (33,34) have looked at the effect of adding lead-containing newsprint to the soil. No significant increase in lead uptake was observed in the vegetables grown on the newsprint amended soil over those grown on control soils.

Motto <u>et al</u>, (35) examined the lead content of soils and grasses adjacent to a number of highways, and compared the lead level in vegetables grown in fields by highways with greenhouse grown vegetables. The field vegetables had a higher leaf to root lead ratio than the greenhouse controls did, which indicated the role of surface contamination. The edible portions of carrots, corn, potatoes, and tomatoes had the lowest lead levels for the entire plant and showed the least effect of an increased lead supply. Davies (36), in England, examined lead uptake by radishes and potatoes grown on lead contaminated soils. A rural soil of pH 6.7 and a lead-in-soil level of 510 µg/g yielded radishes with a lead level of 3.1 µg/g fresh weight (56.7 µg/g dry weight) whereas an urban soil of pH 4.7 and a lead in-soil-level of 2636 µg/g yielded radishes with a lead level of 2.0 µg/g fresh weight (33.5 µg/g dry weight). Another soil with a pH of 7.1 and a lead-in-soil level of

242 µg/g yielded radishes containing 0.2 µg/g fresh weight. A similar level was obtained for radishes grown on a rural soil which had a pH of 6.9 and a lead-in-soil level of 27 µg/g. Likewise, potatoes grown on high lead soils contained more lead than potatoes grown on low lead soils, but the lead levels observed in potatoes were much lower than those observed in the radishes. In another study(37), radishes were grown on soils contaminated by mining activity (lead-in-soil levels ranged from 35 to 47,995 µg/g). Radishes from three of the seventeen gardens surveyed exceeded the British statutory limit of 2.0 µg/g for lead in fresh produce.

Beavington(38) found high metal levels in leaf vegetables grown in the vicinity of a copper smelter, John and Van Laerhoven (39) examined the effect of added lime and nitrogen on the uptake of various forms of lead by lettuce and oats. Lime caused a three-fold decrease in lead levels for both species but the addition of nitrogen had no effect on the lead uptake of either the lettuce or the oats. Page et al.(40) ascertained the lead content of 27 consumer crops and plants which were grown near highways. The samples were collected at various distances from major highways which had daily traffic volumes approaching 75,000 motor vehicles. The following were field sampled: oranges, lemons, tomatoes, carrots, parsnips, sugarbeets, corn, lima beans, red pepper, wheat, alfalfa, strawberries, romaine lettuce, cauliflower, cabbage, and the freeway landscape. As well, celery, collards, artichokes, spinach, romaine lettuce, carrots, potatoes, strawberries, beans, broccoli, and canned stewed tomatoes were market surveyed. The soils were found to have an extractable lead-in-soil range of 70 to 118  $\mu$ g/g. None of the vegetables surveyed showed any significant uptake of lead from the soil. The lead present in the samples was primarily due to surface contamination; washing and/or removal of the

surface layer greatly reduced the observed lead content. The lead content was found to be influenced by a) the distance from the highway, b) the extent to which the surface was exposed, c) the nature of the collecting surface, d) the duration of the exposure, e) the motor vehicle density, and f) the direction of the prevailing winds.

Chow(41) has shown that wind direction will affect the lead levels at the sides of a highway. The east side of U.S. Highway #1 in Maryland had higher lead levels than the west side at various distances from the highway. Samples were taken near the US Department of Agriculture Plant Industry Station at Beltsville, and the Baltimore-Washington Parkway at Bladensburg.

Kirkham(42) found no accumulation of lead in corn grown on sludge-treated soil compared to non-treated soil(1015  $\mu$ g/g and 613  $\mu$ g/g lead-in-soil, respectively). He found that the amount of extractable lead was the same for both soils(0.2  $\mu$ g/g). Webber and Corneau(43) found that the extractability of the lead from a sludge-treated soil was independent of the soil's properties.

Barry and Clark(44) studied the natural plant cover of land that was contaminated by mining wastes. They noted interspecies, as well as intraspecies differences in lead uptake from the soil. These differences were attributed to two main groups: soil properties such as pH, material content, concentrations of various nutrient salts, and others; and clonal differences within the plant species, where one clonal strain may be more lead-tolerent than another.

Ho(45,46) determined lead levels in street dust for 82 sites on the island of Hong Kong and 50 sites in the New Territories. On the island the lead-in-dust levels ranged from 271 to 19,073  $\mu$ g/g with an average of 2974  $\mu$ g/g. In the New Territories, lead-in-dust levels ranged from 109 to 8487  $\mu$ g/g with a mean level of 1039  $\mu$ g/g. Ho noted no direct relationship between concentration of the lead in the dust and the traffic volumes of

the site. This lack of correlation may be due to the high density of traffic on the whole island. Lines of contamination probably overlap to such a degree that there exists a uniform 'background' level for the entire island.

A survey of the city of Birmingham, England (47) gave a range of 160 to 50,000  $\mu$ g/g and an average of 1630  $\mu$ g/g for lead in the soil. A busy city thoroughfare gave a range of 160 to 10,000  $\mu$ g/g for lead-in-soil with a mean of 1050  $\mu$ g/g. An industrial street ranged from 160 to 50,000  $\mu$ g/g lead-in-soil with a mean of 2574  $\mu$ g/g. Archer and Barrett(47) state that the value reported is just the level of lead in a given place at the time of sampling. The lead-in-soil level at any given site is directly influenced by the history of the site. Such influences as topography, surface cover, physical disruption by pedestrian traffic and automobile traffic can all affect the lead level observed at a particular time.

During the spring of 1976, street dust from the city of Glasgow was quantitated with respect to lead content(48). A lead-in-soil range of 150 to 8900  $\mu$ g/g with a mean of 960  $\mu$ g/g was reported, and a natural background level of 78 ± 35  $\mu$ g/g lead-in-soil was given. Parkland soils bordering major roadways had lead-in-soil levels ranging from 460 to 744  $\mu$ g/g. From this it was stated that automobile traffic contributes significant amounts of lead to areas adjacent to the road. Another survey (49), of major roadways and residetial streets in five residential areas of Greater London, England yielded lead-in-soil values ranging from 430 to 3500  $\mu$ g/g with a mean value of 1200  $\mu$ g/g. In the winter of 1972-1973, Day <u>et al</u>.(50) collected street dust, dirt, and soil from the central area of Manchester, England. Like Ho (45), no apparent correlation between lead-in-soil levels and major roads was found. They claim that the lead from various sources remains airborne for several weeks, thus resulting in thorough mixing before deposition

Wesolowski et al. (51) have reported on a former wet-acid battery factory site in Oakland, California which was converted into an urban park. Soil at the site gave lead-in-soil values ranging from 57 to 95,588  $\mu$ g/g. Sufficient areas of the site were contaminated with significantly high levels of lead to warrant the removal of the top 30 cm of soil from the entire site. The removed soil was replaced with 45 to 50 cm of fresh soil which contained only 15 to 18  $\mu$ g/g lead-in-soil. Lagerwerff and Sprecht(52) have reported lead-in-soil values at a number of distances from a major highway and at a number of depths. As distance or depth increased the lead-in-soil level decreased. In 1967, Page and Ganje(53) were able to compare lead-in-soil values with values from samples collected thirty-five to forty years earlier. They noted an increase in soil lead of up to three times. The increase was noted to be traffic dependent, where the traffic density was less than 100 vehicles/square mile no increase was observed, but where the traffic density was greater than 1500 vehicles/square mile an increase by a factor of three was observed in the lead-in-soil value. All sites were generally one mile or more in distance from a major highway. This illustrates the effect that long range dispersal can have on lead levels even in remote areas.

Solomon and Hartford(54) found lead-in-dust levels ranging from 170 to 1440  $\mu$ g/g for a household sample and a range of 360 to 3380  $\mu$ g/g for a non-residential sample. In soil, they found high lead levels both near the road and near the house. Away from the house lead-in-soil values ranged from 240 to 6640  $\mu$ g/g, while near the house the levels ranged from 130 to 11,760  $\mu$ g/g. This higher level near the house was attributed to

leach-out of lead from the paint and wash-off of the surface accumulation of settled airborne lead from the roof and window sills. The same sort of pattern was observed in the non-residential samples. The high lead level at the road side decreased as the distance from the road increased, but the greatly increased at the side of the building. The values observed in the non-residential area were double those observed in the residential ares. A New York study(55) also noted high lead levels in the accumulated dust in residences.

The deposition of lead with respect to particle size and distance from the road surface has been studied by Little and Wiffen(56). The large particles were found to deposit within a short distance of the road surface, whereas the small particles were carried a long distance. From their observations they stated that only 10 to 30 % of the lead emitted from automobile traffic is deposited within 100 metres of the road surface. A comparison between the theoretical calculation of total lead emitted by automobile traffic and the fraction deposited within the 100 metre borders since the roadway(M4) had been oppened(historical lead) and the levels observed, showed that only 22 % of the historical lead was present at the time of the determination. A road side depth survey yielded the following values;

depth	north side	south side
СЩ	μg/g	lead-in-soil
0 - 5	1621	3740
5 - 10	1207	737
10 - 15	289	135
15 - 20	186	106

The median area of the roadway gave a lead-in-soil level of 6835  $\mu$ g/g for the surface(0 - 1.5cm) layer sample while a deep(17 - 20cm) soil layer

had a level of 22  $\mu$ g/g.

Wheeler and Rolfe(57) have developed a double exponential function relationship between the lead emitted from automotive sources and that found in road side soil and vegetation. The expression(I) takes into

$$Pb = A_1 e^{-k_1 D} + A_2 e^{-k_2 D}$$
 (1)

account the two families of particle size in the exponential portion and the  $A_1$  and  $A_2$  terms are linear functions of the daily traffic volume. The larger particles settle within 5 metres of the road surface and the smaller particles settle within 100 metres.  $k_1$  and  $k_2$  are the settling constants and D is the distance from the road. Wheeler and Rolfe also estimated the historical lead input into the soil and found that about 72% of the lead had been removed by leaching or run-off from the top 10 cm of the soil. Ward <u>et al</u>.(58) found that the lead-in-soil level observed at road side could be related to the traffic volume on the highway.

In 1974, Ragaini <u>et al</u>.(59) sampled air and soil for lead and other heavy metals in Kellogg, Idaho, where 90% of the children tested showed abnormally high lead-in-blood levels. Lead-in-soil levels ranged from 170 to 7900  $\mu$ g/g with a mean of 4640  $\mu$ g/g. For lead-in-air, 24 hour samplings gave a mean value of 10.8  $\mu$ g/m<sup>3</sup> for a range of 0.5 to 30.3  $\mu$ g/m<sup>3</sup>.

The type of soil which receives the lead may be a factor in the later availability of lead. Colbourne and Thornton(60) have examined various lead compounds and their extractability from soil. Certain soils, Trent warp for example, removed lead from solution to maintain a concentration of less than 50  $\mu$ g/L until the total soil lead was greater than one percent. The extraction of certain lead compounds was also examined. For example, dilute nitric acid only extracted 1% of the added PbSO<sub>4</sub>, 13% of the added PbCO<sub>3</sub>, and 30% of the added Pb<sub>3</sub>O<sub>4</sub>, whereas 80 - 86% extrac-

tion was obtained from a soil from a smelter site. The soil type and the nature of the compound both affect the extractability and the availability of the lead for plant uptake. Zimdahl and Skogerboe(61) found that soils varied in their ability to fix lead with an observed range of 3000 to 71,000  $\mu$ g/g. The pH and the cation-exchange capacity of the soil are two of the variables which determine the fixation ability of the soil. Precipitation of the lead as the carbonate, fixation by soil organic matter, and sorption by the hydrous oxides may enhance this ability, either individually or collectively. The major indication is that the majority of the fixed lead is associated with organic matter. A lead-in-soil accumulation rate of 30 mg/m<sup>2</sup>/year was obtained from the analysis(62,63) of soil samples covering a sixteen year period for a forest in the American Northwest.

Mills and Zwarich(64) determined that the lead-in-soil levels in farm land around Winnipeg was slightly higher than in rural areas (30  $\mu$ g/g versus 17  $\mu$ g/g average).

Stevenson and Welch(65) found that lead applied to soil migrated downward and to some degree horizontally.

A preliminary survey(66) done in the city of Winnipeg by the Provincial Government during the summer of 1979 after this study was nearly complete but not reported until February 1980, gave lead-in-soil values ranging from 970 to 1200  $\mu$ g/g along major arteries. This same survey reported lead-in-soil levels of 290 to 7800  $\mu$ g/g in a residential area around a secondary lead smelter. Sampling done around two other secondary smelters in Winnipeg gave lead-in-soil values ranging from 520 to 5900  $\mu$ g/g and 530 to 19,000  $\mu$ g/g.

1.2 Lead Compounds of Automotive Origin

Olson and Skogerboe(67) characterized soil lead compounds which are

emitted from automobile exhausts. The major compound emitted is the lead bromochloride with trace amounts of lead oxide and lead sulphate(31,67,68). In soil, the chemical form of lead was found to be lead sulphate; this was attributed to the solubilization of the lead bromochloride and precipitation as the lead sulphate by soil sulphates. The lead bromochloride compound was found to be stable to photodegradation under laboratory conditions(69), so that the loss of bromine observed in environmental samples can not be a direct product of this process. A number of other lead compounds have been identified(31,70,71) as being present in automotive exhaust. They are PbBrCl·2NH<sub>4</sub>Cl and  $\alpha$ -PbBrCl·NH<sub>4</sub>Cl. As well, PbBrCl·(NH<sub>4</sub>)<sub>2</sub>BrCl and  $PbSO_4 \cdot 2(NH_4)_2 SO_4$  were found in the soil along with  $PbSO_4$  (72). Hunt(73) outlines the combustion process of the organolead compounds that are added to gasoline. Under normal operating conditions an engine exhausts 75 to 80% of the lead present in fuel. Provenzano (74) lists a number of factors (vehicle related) which affect the nature of the lead emitted from the exhaust system. Emission rate is speed related, 27 to 71% emission at 72 kph and 49 to 91% at 115 kph. At high speed or during periods of heavy acceleration emission can be as high as 900 to 2000%, as some of the deposited lead is re-entrained into the exhaust. The build-up of lead in the exhaust system stabilizes as mileage accumulates so that 70 to 80% of the consumed lead is exhausted over the lifetime of the car. Lead emission also depends on the lead concentration in the gasoline, as well as the fueleconomy of the vehicle. The mass balance for lead deposition was determined (75) for the Los Angeles Basin area for 1972. Of the 24 tonnes of lead consumed each day as antiknock additive, 18 tonnes of lead was exhausted into the atmosphere and 6 tonnes was deposited within the automobile exhaust and oil systems. Two-thirds(12 tonnes) of the exhausted lead

deposits within the Basin area, the other one-third is advected out of the Basin area. Half of the anthropogenic lead input into coastal waters is of automotive origins.

1.3 Lead from Other Sources

1.3a Lead from Power Plants and Smelters

The soil around a coal-fired power plant was found(76) to be enriched with heavy metals. Fly ash from coal was found(77) to have a lead-in-ash level of 73 to 278  $\mu$ g/g. Under strongly acidic conditions(78) it has been found that metals are strongly mobilized out of fly ash. Lead leached-out of a fly ash pond was found(79) to be precipitated in the soil, by soil <sup>components.</sup> The pH and the concentration of various factors of the soil determined the partitioning of the heavy metals between the solution and particulate phases.

Woody plants grown on fly ash showed(80) little or no uptake of lead. Wastes containing lead, when incinerated, have the greater part of the lead oxidized(81). Some of this lead is vented into the atmosphere as fine particulates (lead content 97,000 ± 2,600  $\mu$ g/g ash) with the remainder in the bottom ash (1700 ± 800  $\mu$ g/g) and fly ash (7200 ± 3200  $\mu$ g/g). Such municipal waste ash is often used as land fill(82). The ash studied in this case had a lead content ranging from 82 to 1333  $\mu$ g/g. Cabbage grown on a soil containing this ash showed a lower lead level than the controls grown on the same soil without the added ash. It was suggested that the ash was 'fixing' some of the 'natural' metal present into insoluble forms in the soil.

Smelter flue dusts were characterized(83) by wet chemical techniques for the compounds present. Lead was found to be emitted in the forms:  $PbSO_{\Delta}$  and  $PbO \cdot PbSO_{\Delta}$ . In Missouri(84) lead levels ranging from 25,150 to 274,000 µg/g were found in the soil within the smelter complex. Levels in the sediment of the two creeks which drain the site ranged from 819 to 227,000 µg/g with a level of 283 µg/g at a site 9.6 km downstream from the smelter complex. Elevated lead levels were also observed in the vegetation of the area. Bewley(85) found lead levels ranging from 100 to 400 µg/g (dry weight) in vegetation from fields 0.35 to 1.85 km away from a smelter. An acid wash removed 50 to 80% of the observed lead indicating that the majority of the lead was due to atmospheric deposition. A survey conducted around a secondary smelter and metal refinery in London, England(86) gave lead-in-soil levels ranging from 304 to 1169 µg/g and lead-in-dust levels ranging from 1041 to 6508 µg/g, at various compass points around the smelter and at distances ranging from 30 to 150 metres. Lead-in-air levels ranged from a low of 0.20 µg/m<sup>3</sup> to a high of 1.64 µg/m<sup>3</sup> for a 30 minute sampling period in this area. Long-term sampling indicated a lead-in-air value below 2.0 µg/m<sup>3</sup> with the lead-in-air value being affected by the prevailing weather.

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In the areas where they are exposed to high lead levels, insects(87) and earthworms(88) accumulate lead and are a potential hazard to higher organisms which include them in their diets.

The heavy metal fallout from the smelter complex located at Flin Flon, Manitoba has been studied(89). Precipitation(snow) results for 1976 -1977 showed a range of 1.7 to 42 mg/m<sup>2</sup> for distant(72km) to near(4.3km) sites(southerly downwind) respectively. Lead-in-snow ranged from 0 to 40  $mg/m^2$  for samples from 32 lake surfaces collected during the winter of 1975-76. For the winter of 1976-77, 53 lake surfaces were sampled giving a range of 0.2 to 81 mg/m<sup>2</sup>, for lead-in-snow. The estimated mass of metals deposited is given as 1.1 to 125 kg per lake surface (0.19 to 13.12 km<sup>2</sup>).

Ragaini et al. (59) studying the mining and smelting center of Kellogg,

Idaho, found the lead-in-soil levels just outside a smelter complex to be equal to levels within the smelter complex. A downtown site, 2 km away from the smelter had a lead-in-soil level of 6700  $\mu$ g/g, while the mean of several non-smelter sites was found to be 4640 ± 3030  $\mu$ g/g. A Zambian study(90) found a range of 92 to 2580  $\mu$ g/g for lead-in-soil around a smelter, while Lusaka, which served as the control, had a lead-in-soil range of 1.1 to 40  $\mu$ g/g. Acid extractable (2.5% acetic acid) portions were reported to be 2.9 to 492  $\mu$ g/g and 0.01 to 3.18  $\mu$ g/g, respectively.

A Swedish study(91) of children living near a smelter found low lead-in-blood levels. A mean of 7.3  $\mu$ g/100mL was reported for these children. A Winnipeg study(92) reported mean blood lead levels of 24.09  $\mu$ g/100mL and 19.55  $\mu$ g/100mL for children living near a smelter and for children in a non-smelter area, respectively. Lead-in-blood will be dealt with in greater depth in a later section.

#### 1.3b Lead from Ceramic Ware

Krinitz(93) screened 90 samples of ceramic dinnerware for lead extractability using 4% acetic acid. Of the 90 samples, 48 had no extractable lead, 23 gave lead-in-solution levels ranging from 0.01 to 0.9  $\mu$ g/mL, and the remaining 19 samples gave extractabilities ranging from 1.0 to 568  $\mu$ g/mL. Henderson <u>et al.</u>(94) surveyed both homemade and commercial ceramic ware using a 5% acetic acid extraction at 85°C for one hour. None of the commercial pieces exceeded the regulatory limit of 7  $\mu$ g/mL set by the Food and Drug Administration(FDA), but 17 of the 33 homemade pieces exceeded this limit and 11 of the pieces gave a level equal to or exceeding 100  $\mu$ g/mL. Of the 90 pieces sampled by Krinitz(93), 13 exceeded the FDA limit for extractability. A Spanish study(95) also found glazed ceramic ware which

exceeded both the Spanish Food Codex and the FDA guidelines for amounts of lead extracted.

1.3c Lead from Food

Capar(96) found that canned foods stored in their original containers after opening absorbed lead from the container. Peas increased from 0.20 to 0.44  $\mu g$  Pb/g, orange juice from 0.05 to 0.36  $\mu g$  Pb/g, and grapefruit juice from 0.05 to 0.32  $\mu$ g Pb/g during the five day storage period at  $6^{\circ}$ C. A number of studies(35,40,97,98) have found that the lead content of a number of fruits and vegetables was mainly due to surface contamination from atmospheric fallout. Elfving et al.(34) found that an increase in the lead-in-soil level from 14 to 65  $\mu$ g/g produced a very small increase in uptake of lead by a number of vegetables grown on a soil amended with coloured newsprint. A Danish study(99) of cereal grains and other components of a typical diet showed a decrease in lead levels over a 15 year period. The decrease was attributed to a switch in fertilizers, from one which was contaminated with lead to one which was relatively lead-free. Moore et al. (100) found that lead in tap water used to cook vegetables and pasta was significantly absorbed by both. Tea and coffee brewed in water containing lead both decreased the soluble lead by complexation with the natural polyphenols.

Golimowski <u>et al</u>.(29,101) and Oehme and Lunde(102) determined the lead content of a number of European red and white wines. The International Wine Office in Paris has set a maximum value of 400  $\mu$ g/L for lead-in-wine. Germany has its own limit of 300  $\mu$ g/L for wine while its lead-in-drinking water limit is 40  $\mu$ g/L. Golimowski(29) reported that 35 of 36 red and white wines had lead levels ranging from 37 to 170  $\mu$ g/L, with one wine having an excessively high level of 467  $\mu$ g/L. Twenty-five of these wines exceeded the German drinking water limit for lead but all except one were under the German lead-in-wine limit. Oehme and Lund(102) reported a range of 70 to 230  $\mu$ g Pb/L in European red wines and a range of 65 to 200  $\mu$ g Pb/L for white wines. A collaborative study of four British beers(103) gave lead levels ranging from 123 to 350  $\mu$ g/L, all under the British statuatory limit of 500  $\mu$ g Pb/L.

The lead in wine is attributed to surface contamination of the grapes by atmospheric fallout. As well, the lead in beer is probably due to atmospheric contamination of any of a number of ingredients used in the brewing(hops, yeast, barley, and the water) .

#### 1.4 Health Effects

The Occupational Safety and Health Administration(OSHA) final standard(104) for lead-in-air levels for occupational exposure was set at 50  $\mu$ g/m<sup>3</sup> for an eight hour time-weighted average. This level was chosen to keep the health effects of lead at a minimum.

Health effects which result from ingestion of lead include damage to the nervous, urinary, and reproductive systems, and the inhibition of heme synthesis. The adverse effects range from acute, relatively mild inhibition of enzyme activity, reduction of motor nerve conduction, behavioral changes, and mild central nervous system(CNS) symptoms to permanent damage to the body, chronic disease, and death.

#### 1.4a Heme Synthesis Inhibition

Inhibition of delta-aminolevulinic acid dehydrogenase(A-LAD) (104,105), an enzyme responsible for the synthesis of a precursor to heme,

has been observed at blood lead levels below 20  $\mu$ g/100mL. At a level of 40  $\mu$ g/100mL, 20% of the population would have 70% inhibition of A-LAD. Another enzyme, ferrochelatase, is inhibited by the build-up of one of the products of A-LAD inhibition. This inhibition is the primary step in a progression of health effects due to lead exposure. The degree of the effect is dependent on the individual's biological response to the stress.

## 1.4b Neurological Effects

The effects of lead(104,105) on the nervous system range from acute intoxication, coma, cardiorespiratory arrest, and fatal brain damage to mild symptoms, subtle behavioral and electrophysiological changes associated with lower exposure levels. In the last several years evidence has accumulated that demonstrates neurological damage can occur at low blood lead levels. The location and degree of neurological damage depends on the dose and duration of exposure. A positive correlation was found(106) between lead-in-blood levels and conduct (disruptive behavior), motor activity/attention span, and learning difficulties for a group of inner city children. Children with at least one symptom of plumbism have been noted(107) to do poorly in school even though standard psychometric tests indicate normal intelligence. This failure in school was attributed to behavioral disorders, lack of attention, perseveration, and visual-motor impairment.

Bryce-Smith <u>et al</u>.(108) have stated that the body lead levels considered 'normal' are significantly associated with pathogenic effects on mental health in children. The observable symptoms include disturbances in intelligence, as evidenced in learning disabilities, and hyperactivity. There is a significant causal relationship between body-lead levels and

the symptoms observed; improvements in behavior and intelligence are observed upon treatment for lead poisoning.

1.4c The Renal System

Routine screening is ineffective in diagnosing the early stages of renal damage. Once damage(104,105,109) is detected, about two-thirds of kidney function is lost to irrepairable damage. The question has been raised as to whether exposure at high lead-in-blood levels is similar to exposure at lower lead-in-blood levels for a longer period of time. Dr. Wedeen(104) has stated that in very few of the renal-damaged patients is there a leadin-blood level in excess of 60  $\mu$ g/100mL. Renal failure in children(107) who were exposed to lead for a prolonged period of time has been observed.

1.4d Reproductive Effects

Male workers exposed to lead(104,105,109) have experienced a decreased sexual drive, impotence, a decreased ability to produce healthy sperm, and sterility. These alterations are produced by a direct toxic effect on the male gonads.

Female workers exposed to lead(104,105,109) risk damage to their germ cells which could lead to genetic damage, miscarriage, stillbirth, and birth defects. Also abnormal ovarian cycles, premature birth, menstrual disorders, and sterility have been observed in lead exposed women.

The child is also exposed to lead in the mother's system(104,105,109). It has been shown that lead can and does cross the placental barrier(105). Children of lead-exposed women suffer from low birth weights, slower growth, and nervous system disorders. Children are more susceptable to the toxic effects. Some experience central nervous system damage at low lead-in-

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blood levels. Hyperactivity related to lead has been associated with leadin-blood levels between 25 and 55  $\mu$ g/100mL(109). As well, a definite correlation exists between mental retardation and lead in blood and drinking water(107).

1.4e Immune System and Endocrine System Effects

Damstra(109) found that lead may interfere with the immune response. Certain parts of the endocrine system are affected, iodine uptake is inhibited, pituitory hormone secretion is decreased, and adrenal gland function is impaired by lead. The question of long-term effects from lowlevel exposure is raised again.

1.5a Lead Uptake - Nutritional Aspects

Levander(112) has published a review which points out some of the effects an individual's diet has on the uptake of lead by the system and on the susceptability of one's health. A diet which is either very high or very low in protein(105,112) has been found to increase lead uptake. The kind and quality of dietary fat(112) greatly influences lead absorption. Butterfat caused an increase in lead uptake, while polyunsaturates(i.e., rapeseed and sunflower seed oils) had little effect. A low-calcium diet showed a marked increase in lead absorption over a high-calcium diet(105, 112). Individuals who have a negative calcium balance may be more susceptable to lead poisoning than those in a positive calcium balance. Similarly, an iron deficiency enhanced the toxicity of lead. Dietary supplements of copper and/or iron were found to enhance lead absorption from the digestive system while zinc decreased lead absorption(105,112)

Vitamin C is believed to have a protective effect by helping to

eliminate lead from the body(105,113). Vitamin E also has shown a protective effect. Vitamin E deficiency in the rat has been shown to cause red blood cells to become more fragile and more susceptable to the effects of lead poisoning(112). Vitamin D on the other hand, appears to increase lead absorption from the digestive tract(105)

#### 1.5b Lead Uptake - Physiological Aspects

Grandjean(114) has published a review on the literature covering lead pollution. The 'natural' lead concentration in air was estimated to be  $0.0005 \ \mu\text{g/m}^3$ . In urban areas the actual level may be three to four orders of magnitude greater than the 'natural' level. An urban dweller may inhale up to 60  $\mu$ g of lead per day with 35 to 40% absorption.

The 'natural' amount of lead absorbed from the diet was calculated (114) to be about 0.3  $\mu$ g of lead per day from geochemical data. Actual measurements gave a range of 200 to 300  $\mu$ g Pb/day consumed with 20 to 30  $\mu$ g Pb/day absorbed. A comparison of modern tissue with mummified tissue(115) from the second and third millenia B.C. showed an increase in lead concentration of the recent tissue by two to three orders of magnitude over the ancient tissue.

On the average, a human adult absorbs 30 to 40  $\mu$ g Pb/day, of which most is excreted. The biological half-life of lead in the blood is about 25 days(68) and in the bone it is on the order of years. Of the body burden of lead, 90% of it resides in calcified tissues(68,114), so a blood lead level may not give a true indication of the body's lead level. Toxicity may eventually occur even at low blood-lead levels. Children are especially sensitive to lead in their time of developement. Bridboard(116) states that, blood lead levels at and above 30  $\mu$ g/100mL significantly alters heme
synthesis and that at levels above 30 to 40  $\mu g/100 \text{mL}$ , adverse effects have been seen in the neurological system of children.

Mahaffy(117) and others(105,118,119) have reported values of absorption for adults and children for lead from the diet. Adults consume from 150 to 250  $\mu$ g Pb/day with about 10% absorption. Of the inhaled portion of lead about 40% is absorbed. Children have a much higher absorption rate of about 50% for dietary lead with a retention of about 18%. The maximum level for lead consumption is set at 3 mg/week for adults and at 0.7 mg/week for children.

Rosen and Sorell(120) support these absorption values and state that dietary deficiencies may alter the absorption rate. They found that lead decreased the liver's tolerance to a number of endotoxins. In children, lead seeks out the areas of bone in which new bone formation, bone remodelling, and rapid bone turnover predominate. Renal failure in adults has been correlated to the transfer of lead from the bone reservoir to the kidney.

1.6 Other Sources of Lead

Marzulli <u>et al</u>.(121) and others(122,123) have found that cosmetic preparations which contain lead can lead to elevated lead levels in the blood, either through absorption through the skin or, in some cases by consumption of these products by small children.

Eaton <u>et al</u>.(124) found that the lead contained in the coloured inks used in comics was totally extractable under physiological conditions. One American tabloid was found to have significant quanties of lead in its printed pages in a comparison of a number of American and Canadian newspapers.

### 1.7 Lead in Blood

Posner(125) and others(105) state that blood-lead levels are more of a reflection on recent exposure than of total body burden. The term 'normal' is somewhat ambiguous as what may be 'normal' for one individual may be fatal to another. In the blood, 90% of the lead is associated with the erythrocytes, both in the membrane and within the cell.

A group of workers (126) dismantling a lead-painted bridge were found to have elevated blood-lead levels. A followup of these workers found that some of them exhibited clinical symptoms of lead poisoning. Watson <u>et al</u>. (127) found elevated blood-lead levels in the children of lead storage battery workers. The 'exposed' children had a mean blood-lead level of 31.8  $\mu$ g/100mL whereas 'unexposed' children from the same community had a mean blood-lead level of 21.4  $\mu$ g/100mL. A Newark study(128) of children aged one to eight years found that 5% had a blood-lead level exceeding 60  $\mu$ g/100mL. The mean of this group was 40  $\mu$ g/100mL with a range of 9 to 102  $\mu$ g/100mL. A Detroit study(129) found that the proximity of highways made little difference in blood-lead levels. The major contributor was found to be housing. The poorer the quality of the housing(old paint) the higher the observed blood-lead levels.

Eisinger <u>et al</u>.(130) found that 77% of the workers in a secondary smelter had blood-lead levels greater than 60  $\mu$ g/100mL, while the control population was totally below this level. The average blood-lead level ranged from 60 to 79  $\mu$ g/100mL, dependent on the length of exposure. Twenty-two percent of the workers at a smelter in the Netherlands were found(131) to have blood-lead levels greater than 60  $\mu$ g/100mL. Children living within one kilometre of the smelter had blood-lead levels ranging from 12.3 to 32.7  $\mu$ g/100mL with a mean of 19.6  $\mu$ g/100mL. In the one to

two kilometre range the level dropped to 14.7  $\mu$ g/100mL(average) and past two kilometres the average was 11.9  $\mu$ g/100mL.

In a 1979 follow-up(132) to a 1976 study(92) of school children in Winnipeg, the average blood lead level dropped from 23 to 14  $\mu$ g/100mL at Weston School and from 19 to 11.2  $\mu$ g/100mL at Lord Nelson School. Of the students tested, 25% had been over 30  $\mu$ g Pb/100mL blood in 1976. This dropped to 1% in 1979 at Weston School. At Lord Nelson School it dropped from 9 to 0.4% of the population tested. The interpretation of these results is difficult because different sample collection methods were used for the two surveys. For one survey whole, venous blood was taken, but in the other the finger-prick method was used.

Hunt(73) notes that, in Britain, legal action has been taken against Shell, BP, Octel, and FMC by parents who claim damages for assault, trespass, negligence, and nuisance on the grounds that their childrens'health has been damaged by inhalation of lead from exhaust fumes. Duggan and Williams(49) extrapolated their data and found that a range of 20 to 200  $\mu$ g of lead/day would be consumed by a child from the soil. Using a consumption value of 50  $\mu$ g Pb/day and an absorption factor of 0.25 they state that 12  $\mu$ g of lead will be absorbed from street dust/soil ingestion. The lack of definite information on any sort of recommendation is illustrated by the variance in recommended intakes of lead by researchers.

#### 1.8 Purpose of Study

When this study was begun, the Provincial lead-in-blood study had been carried out(92) but the results had not yet been released. There was an indication that elevated lead levels existed in the soil in one area of the city of Winnipeg from the analysis of some soil samples brought

to this department in 1975. The present study was undertaken to determine whether there was a lead pollution problem in the City of Winnipeg, to determine the sources if possible, and to determine if there was any sort of distribution pattern. The sites would range from residential areas to industrial areas with both high- and low-volume traffic arteries being sampled.

There are conflicting reports in the literature as to whether soillead levels could be correlated to traffic levels. In Winnipeg there exist a number of east-west and north-south major traffic arteries. If soil-lead levels are traffic volume related then elevated levels should be seen along these arteries. Of the three lead smelters in the City of Winnipeg, one of them was forced to close down for a period of time due to excessive airlead levels within the smelter. These smelters are supposedly equipped with emission control devices. If these devices are operating efficiently then there should not be any significant emission of lead into the surrounding environment. It has been noted(57) that sodium chloride leaches lead out of the surface layer(10cm) of soil at low temperatures. If this is the case, a decrease in soil-lead should be observed from a fall sampling to a spring sampling since salt is used to control ice on the streets during the winter. This study attempted to determine the validity of these points. Further questions have arisen from some of the findings of this study.

#### 2. EXPERIMENTAL

## 2.1 Apparatus and Reagents

Perkin-Elmer Model 306 atomic absorption spectrophotometer with a 10 cm single slot burner and Westinghouse lead and tin lamps, Cathodeon 1ead lamp, and a Perkin-Elmer antimony lamp.

Nuclear Semiconductor beryllium-windowed silicon detector mounted on an Union Carbide Cryogenic Refrigerator. Power was supplied by a Tennelec TC909 power supply, and a Nuclear Semiconductor Bias Protection Module was used to monitor liquid N<sub>2</sub> coolant levels. The signal was passed through a Nuclear Semiconductor 512 Amplifier and was displayed on a Tracor Northern TN 1705 Pulse Height Analyser. Hard copies of the displayed spectrum were obtained by outputting to a Houston Instruments "Omniscribe" B5126-1 strip chart recorder.

Glassware was washed with detergent and rinsed twice with de-ionized water.

A lead solution containing 1003  $\mu$ g/mL lead was prepared by dissolving 1.6402 g of Pb(NO<sub>3</sub>)<sub>2</sub> in sufficient 1M HNO<sub>3</sub> to make 1 litre of solution. Standards in the range of 0 to 50  $\mu$ g/mL lead were made by dilution of the stock solution with 0.1M HNO<sub>3</sub>.

A tin solution containing 1056  $\mu$ g/mL tin was prepared by dissolving 0.2640 g of tin metal in 25.0 mL of concentrated HCl and diluting to 250.0 mL with triply distilled water. Standards in the range of 0 to 200  $\mu$ g/mL tin were prepared by dilution of the stock solution with 10%(v/v) HCl.

An antimony solution containing 1419  $\mu$ g/mL antimony was prepared by dissolving 0.3789 g of antimony potassium tartrate, (K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·<sup>1</sup><sub>2</sub>H<sub>2</sub>O), in triply-distilled water and diluting to 100.0 mL. Standards in the range of 0 to 40  $\mu$ g/mL antimony were prepared by dilution of the stock solution with triply-distilled water.

All water used for solutions was triply distilled. The house-distilled water was re-distilled twice more in a glass double still which contained potassium permanganate in the first pot and potassium dichromate in the second. All water collected was stored in glass or polyethylene containers.

The antimony potassium tartrate was obtained from The McArthur Chemical Company, Ltd. of Montreal. The tin metal (granular) was obtained from J.T.Baker Chemical Co., Phillipsburg, N.J.. The lead nitrate was obtained from Fisher Scientific Co., Chemical Manufacturing Division, Fairlawn,N.J.. All chemicals and reagents used were of reagent grade.

All calculations and least-squares regressions were performed on a Texas Instruments SR 58 calculator, mounted on a PCA 100 printer, using the built in library programs.

2.2 Sampling

A large(24" x 38") City of Winnipeg street map ('Street Number Guide' of Winnipeg © Roy Pickard) was overlaid with plastic and a grid was drawn using the alphanumeric coordinants provided on the map borders. For the initial survey, 150 points were picked from the grid to give an overall sampling of the inhabited areas of the city. During the survey 34 of these points were excluded because they were unsuitable for sampling on a continuous basis. From the remaining 116 sites a surface soil sample consisting of 30 to 50 grams was taken using an aluminium garden trowel. This sample consisted of the top two centimetres of the soil. At 94 locations a subsurface sample was taken below the surface sample(2 - 4 cm deep). At 19 sites a sample of 5 to 10 grams of vegetation was taken using clippings of grass or weeds growing adjacent to the soil sampling site. All sites were within 15 cm of the curb. Where possible, samples were taken at curb edge. In some cases, where there was an accumulation of soil on the road surface at the curb edge, a sample was taken there. All samples were placed in separate plastic bags('baggies', Colgate-Palmolive Canada, Distr.). If the soil sample was moist or wet, or if the sample consisted of vegetation it was allowed to dry and come to constant weight under ambient laboratory conditions.

From the results of the initial survey 75 sites were selected for further monitoring Surface soil, consisting of the top 1 to 2 cm, was collected in each case. Large stones(>1 cm diameter) were excluded.

# 2.3 Sample Preparation

There are a number of procedures in the literature regarding the preparation of a sample containing organic and inorganic material. A combination of wet and dry ashing has been used in the analysis(133) of edible oils. Snyder(134) found that an extraction method using dilute aqua regia compared favourably with a Soxhlet extraction method for heavy metals. Lead in bubblegum was determined using both dry and wet ashing methods(135). Williams(136) has outlined a wet digestion method for biological materials where the sample is digested in a closed container using concentrated nitric acid at  $70^{\circ}$ C. Pressure buildup in the container was vented by a special mechanism in its cap. Ritter <u>et al.</u>(137) evaluated dry ashing, wet ashing(HNO<sub>3</sub>-HC1O<sub>4</sub>, HNO<sub>3</sub>-HC1, and HF), and a nitric acid extraction for a number of heavy metals in soil and sewage sludge. A wet digestion method(HNO<sub>3</sub>-HC1O<sub>4</sub>) was comparable to dry ashing for the analysis of lead, cadmium, and zinc in the samples. A number of methods for the

destruction of organic matter have been outlined(138) by the Analytical Methods Committee. Advantages and disadvantages of wet and dry ashing methods are discussed.

The wet digestion of organic matter by the action of various acids is almost of universal application. Conditions are adjustable to prevent loss of volatile components. Generally the method is fast and easily controlled. Disadvantages include the dependence on reagents which form insoluble salts, the incomplete destruction of organic matter, and the violent destruction of organic matter causing splattering of the sample. Wet ashing requires constant attention to ensure that the sample does not evaporate to dryness since some of the salts formed are unstable and volatilization may occur.

Using dry ashing, larger samples can be analysed. Reagents which could form insoluble salts are eliminated and little attention is required to monitor the ashing. Disadvantages of this method include loss of material through volatilization and vigorous combustion, incomplete extraction from some samples due to incomplete combustion, formation of insoluble salts and other compounds by excessive heating, and formation of poisonous fumes by the slow ignition of some organic materials.

The wet digestion method which uses nitric acid and perchloric acid for the destruction of organic material, was chosen on the basis of speed and ease of control. The perchlorates formed are all fairly soluble and loss due to volatilization is small since lower temperatures are used. The main disadvantage of this method is that some heterocyclic nitrogen compounds may escape complete destruction. Digests should not be allowed to go to complete dryness because some of the reaction products may undergo vigorous reactions.

### 2.4 Method

A soil sample of 4 to 6 grams (average 5.4 grams) was weighed into a 150 mL beaker and 25 mL of concentrated nitric acid was added. The beaker was heated on a steam bath for two hours, the removed and allowed to cool to room temperature. At this time 15 mL of concentrated(60%w/w) perchoric acid was added and the sample was gently heated overnight on the steam bath. Both digests were performed in a fume cupboard. In the morning, triply distilled water was added carefully to give an approximate volume of 40 mL. The solution was allowed to cool to room temperature. The sample was filtered through a Whatman #2V or #1, llcm filter into a 100 mL volumetric flask. The beaker and filter were washed into the flask with the triply-distilled water and the filtrate was made up to volume.

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For the vegetation samples, 2 to 4 grams of dried matter was weighed into a beaker and prepared as above.

For each group of analyses a beaker wich contained no sample was included. This blank was treated the same as the other samples.

During the standard addition study a soil obtained from a residential vegetable garden was analysed in replicate. The first analysis looked at 10 samples from this soil and the lead content(backgroud level) was determined. The results of this analysis which are tabulated below showed an average lead-in-soil level of 49.6  $\pm$  5.5 µg/g for a range of 44.2 to 61.6 µg/g. Of the ten lead-in-soil values obtained nine of the values fell within the range of one standard deviation of the mean value (i.e., 44.1 to 56.1 µg/g).

A second study gave a lead-in-soil average of  $46.5 \pm 4.1$  g/g for five samples of the same soil(range 41.2 to 51.2 g/g). The average was slightly lower in this second study than in the first. However all five samples fell

	weight of sample	lead level µg/g	weight of lead level sample µg/g	· · ·
	first s	tudy	second study	····
1,	5.42 grams	61.6	1. 5.25 grams 43.3	1
2,	5,22 grams	48.2	2. 5.57 grams 48.3	
3,	5,33 grams	55.8	3. 5.03 grams 48.6	
4,	5.66 grams	52.2	4. 5.45 grams 41.2	
5,	5.53 grams	48.1	5. 5.97 grams 51.2	
6,	5.20 grams	44.2		
7.·	5.45 grams	47.1	Average weight 5.45 ± 0.35 gra	ams
8.	6.03 grams	44.5	Average lead level 46.5 ± 4.1	µg/g
9.	6.10 grams	48.8		
10.	5.31 grams	45.1		

within the one standard deviation range of the first study.

Average weight  $5.53 \pm 0.32$  grams Average lead level  $49.6 \pm 5.5 \mu g/g$ 

2.5 Atomic Absorption Spectroscopy

2,5a Introduction

As early as 40 A.D. it had been observed that light passing through a triangular piece of glass produced a rainbow spectrum. In 1666, Sir Isaac Newton concluded that white light was a 'confused aggregate of rays imbued with all sorts of colours'. With the aid of a lens to focus the light from a pinhole he managed to produce a solar spectrum 25 cm in length. Due to the use of a circular pinhole as the source Newton did not observe the dark lines in the solar spectrum that Franhofer observed in 1817 using a homemade grating to disperse the spectrum. Bunsen noted that the colour observed when a chemical compound was burned in the flame was related to the element rather than the compound in which it was bound; as a result of this, two new elements were discovered in mineral water. Other workers reported finding a number of new elements once news of this technique spread. Kirckhoff, a collaborator of Bunsen remeasured the wavelengths of many of the Franhofer lines and compared the lines with ones obtained in the laboratory. He showed that the lines present in the solar spectrum arose from the same elements, thus, these elements were present in the sun. The reversed appearance of some of the lines was due to the absorption of the emission rays as they passed through the cool outer layers of the sun's atmosphere. Kirckhoff also noted that absorption only occurs at the same wavelength as emission. The forerunner of absorption spectroscopy, emission spectroscopy began to appear in 1925, and it was not until 1955 that two papers appeared describing the method of atomic absorption spectroscopy. From Australia, Walsh, and from the Netherlands, Alkemade and Milatz, described a system in which the analyte solution was sprayed into a flame, and the flame was irradiated with a lamp or other source with the same spectrum as the analyte element. The intensities of the unabsorbed and the absorbed beams were compared. It was not until 1962 however, that commercial equipment became readily available for the method to become popular (139,140,141,142).

2.5b The Atomic Absorption Spectrophotometer

The instrument is composed of three major blocks of components, the lamp, the flame, and the detection system.

The lamps commercially available are of the sealed hollow cathode variety. In monoelement specific lamps the cathode is composed of or coated

with the element of interest; multi-element lamps are also available which have a cathode composed of a mixture of similar elements. The lamp is filled with an inert gas like argon, neon, or helium with a pressure of a few tenths of a millimetre of Hg to a few millimetres. A current is passed through the cathode to cause the emission of light from the cathode which is element specific.

The flame provides the medium in which the excitation and absorption take place. The analyte solution is aspirated into a mixing chamber where it forms a mist with the burner gases. When the mixture leaves the burner slot the combustible gases burn and the solvent evaporates leaving molecules which are then broken apart into the atomic state by the energy in the flame to provide a population of ground-state atoms. Rising in the flame due to pressure the monoatomic element crosses the light path and absorbs a quantum of energy raising an electron to an excited state high energy level.

In a double beamed instrument, such as the one used, the beam from the source is sent along two paths by a mirror system, one the analyte beam, through the flame and the second, the reference beam, in a path around the flame to the monochronometer. From the monochronometer the beam travels to a photomultiplier where it is converted into an electrical signal and boosted in strength. This signal is the converted by way of an amplifier and/or rectifier system into a form which is readable, ie. a digital readout or a voltmeter reading. The detection system is set to monitor a particular wavelength by adjusting the monochronometer. Initially, aspirating a blank solution the analyte and reference beams are set to be equivalent to give an absorbance reading of 0.000 absorbance units.

## 2.5c Basis of the Method

Bohr gave the initial explanation that is still accepted for the absorption and emission of specific wavelengths or lines of light. The element in the monoatomic state is composed of a heavy nucleus surrounded by 'shells' of electrons at specific energy levels. In the ground state all the electrons in the valence 'shell' are in their lowest energy state. Upon absorption of a quantum of energy one of these ground state valence electrons is raised to a higher energy level known as an excited state. The atom de-excites itself by re-emitting this quantum of energy when the excited electron drops back down to its ground state energy level. The amount of light or numbers of quantums of energy absorbed depends on the number of monoatomic ground states that are present, which is concentration dependent. Absorption increases linearly with concentration up to a certain concentration where the process of self absorption starts taking place.

A series of solutions of known concentration (in the linear working range) are aspirated into the flame and the absorbance for that concentration recorded. The results are plotted, the absorbance versus the concentration of the standards. The analyte solutions are then aspirated into the flame and the absorbances recorded, then the concentration for the element in solution is determined by extrapolation from the standard graph.

The absorbance given is a measure of the difference in intensities of an analyte beam and the reference beam. The intensity of the analyte beam is decreased by a certain amount for each solution concentration(139,141, 142,143).

### 2.6 Calibration

The initial set of standards consisted of 0,2,4,6,8,10,12,14,16,18,20,

25,30,40, and 50 µg/mL lead. Later sets consisted of 0,4,8,12,16,20,25,30, 40, and 50 µg/mL lead. The instrument was set up to give a reading of 0.200  $\pm$  0.010 for a 50 µg/mL lead solution at 283.3 nm. Using these conditions, 49 standard determinations gave an average correlation coefficient of 0.9993 with a standard deviation of  $\pm$  0.0009. Analyte solutions which gave an absorbance reading greater than 0.200 were diluted by a factor of 10. The graph of absorbance versus concentration was plotted with the aid of a Texas Instruments SR 58 calculator using the built-in least-squares regression routine to determine the slope of the line, the y-intercept, the correlation coefficient, and to interpolate between standards to yield sample concentrations. Ratios of the weight of lead per dry weight of sample were inferred from the calculated solution concentrations.

## 2.7 X-Ray Fluorescence

X-ray fluorescence involves the absorption and emission of energy. A quantum of energy(x-ray) is absorbed by the atom. This absorption of energy results in the ejection of an electron from an inner 'shell' either the K or the L 'shell' depending on the size of the atom. The resulting hole is filled by an electron which releases a quantum of x-ray energy and jumps from an outer 'shell' into this inner 'shell' hole. The resulting ion returns to neutrality after a period of time by picking up a free electron. The quantum of energy released by the dropping electron has a characteristic energy for that particular energy level transition(140,141,144).

## 2.8 X-Ray Fluorescence Method

Two to three grams of a soil was placed in a plastic container.

The opening was covered with Mylar and sealed. The sample was positioned Mylar-face down, over the detector. The excitation source consisted of a 0.5 Curie Americium 241 y-source located in a ring about the sample. The spectrum was accumulated over a 2000 second period and the output signal was routed to a stripchart recorder for a hard-copy of the spectrum. Elements were identified by the X-ray energy and by comparison with a standard graph of atomic number versus channel number (energy).

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### **RESULTS AND DISCUSSION**

# 3.1 The Initial Survey

The initial survey was done during September, 1978, when 116 sites were sampled. 224 samples of surface(0-2cm), subsurface(2-4cm) soil, vegetation were collected. The results of this survey are presented in Table 3.1. All values are in  $\mu g$  of lead per g dry weight of soil or vegetation.

This survey was done to determine whether this type of study was feasible, i.e., whether lead pollution was widespread or a localized phenomenon in Winnipeg. The 116 samples of surface soil represented 107 different sites within the city. The average lead-in-soil concentration for these sites was 750  $\pm$  1300 µg/g with a range of 30 to 12,960 µg/g. The large deviation arises when one site by a secondary smelter, which gave a lead-in-soil level of 12,960 µg/g is included. Dropping this value gives and average of 640  $\pm$  520 µg Pb/g soil with a range of 30 to 2920 µg Pb/g soil. Subsurface soil gave a lead-in-soil average level of 410  $\pm$  450 µg/g with a range of 0 to 2220 µg/g. The vegetation gave an average level of 120  $\pm$  130 µg Pb/g vegetation (dry weight) with a range of 0 to 470 µg/g.

As was expected, if pollution control devices were not 100% effective, sites by secondary smelters(#51,#52, and #60) showed higher lead levels in the soil than other sites. Site #52, which was close to a smelter building, showed a lead level which was four times higher than the level at site #51, which was by a road at the same location. This observed difference could be due to the deposition of lead fallout from the roof by rain wash-off, whereas at site #51 the lead is mainly due to atmospheric fallout from the smelter and automobile traffic along the street. Sites along Pembina Highway, Waverley Street, Taylor Avenue, Grant Avenue, Portage Avenue, Mountain

	Location	surface soil	subsurface soil	vegetation
		µgrams of	lead per gram dry	weight
1.	Virgin bush in a residential area	<b>30</b> ;	30	50
2,	Chancellor Drive and Chancellor Drive	30	40	
3.	Waverley Street and Lake Crest Road	60	20	120
4.	Waverley Street at Bison Drive	120	260	180
5.	Ducharme Avenue and Rue Lemaire	30	20	20
6.	Pembina Highway at Turnbull Drive	210		170
7.	Dalhousie Drive and Radcliff Road	160	120	150
8.	University Crescent and Markham Road	390	310	50
9.	University Crescent and Thatcher Drive	250	330	0
10.	Pembina Highway at Adamar Road	530	210	160
11.	Waverley Street and Clarence Avenue	370	130	200
12.	Pembina Highway and McGillivray Boulevard	1450	1240	130
13.	South Drive in the 500's	180	20	0
14.	Waverley Street and Wilkes Avenue	1790	730	210
15.	McGillivray Boulevard and Brockville Avenue	110	100	0

Table 3.1 Lead Levels in Surface and Subsurface Soils and in Vegetation - Initial Survey

Location	surface soil	subsurface soil	vegetation	
	µgrams of	lead per gram dry	y weight	
16. McGillivray Boulevard and Front Street	130	90	0	
17. McGillivray Boulevard and Kenaston Boulevard	380	80		
18. Kenaston Boulevard at the Railway Crossing	420	150	<del></del>	
19. Roblin Boulevard at the Perimeter Highway	250	160	300	
20. Rannock Avenue and Dale Boulevard	110	90	30	
21. Rannock Avenue and Charleswood Road	50	20	40	
22. Roblin Boulevard and Charleswood Road	460	130	360	
23. Roblin Boulevard and Harstone Road	720	330	470	
24. Grant Avenue and Shaftsbury Boulevard	400	200	60	
25. Assiniboine Park East Gate	230	120	20	
26. Nanton Boulevard and Girton Boulevard	170	150	50	
27. Grant Avenue and Edgeland Boulevard	380	310		
28. Taylor Avenue and Borebank Street	1250	130	· <u></u>	
29. Grant Avenue and Borebank Street	660	760		
30. Kingsway and Beaverbrook Street	410	410		
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Location	surface soil	subsurface soil	vegetation	
	µgrams of	lead per gram dry	weight	
31. Kingsway and Cambridge Street	200	160	. <b></b>	
32. Rockwood Street and Fleet Avenue	320	160	· <u></u> ·	
33. Pembina Highway and Taylor Avenue	680	500	· <b></b>	
34. McMillan Avenue and Hugo Street N.	30	<b>50</b> <sup>1</sup> ( <sup>2</sup>		
35. Broadway Avenue and Kennedy Street	1150	390		
36. Main Street and River Avenue	570	840	(	
37. Portage Avenue and Ingorsol Street	660	550		
38. Portage Avenue and Empress Street	580	700		
39. Portage Avenue and Olive Street	1050	450		
40. Portage Avenue and Sturgeon Road	1110	900	<b></b>	
41. Sansome Avenue and Rouge Road	1010	780		
42. Portage Avenue and the Perimeter Highway	450	60		
43. Perimeter Highway at Assiniboia Downs	1100	870		
44. Perimeter Highway and Saskatchewan Avenue	520	410	<b></b>	
45. Cavalier Drive and Hamilton Avenue	290	70	, 	

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Location	surface soil	subsurface soil	vegetation	
	ugrams of	lead per gram dry	v weight	
46. Ness Avenue and Sturgeon Road	780	310		
47. Ness Avenue and Braintree Crescent	640	480		
48. Ness Avenue and Duffield Street	1210	740		
49. Ness Avenue and Berry Street	470	70	. '	
50. St.James Street by Canada Metals Limited	1290			
51. Wellington Avenue by Canada Metals Limited	2920			
52. Wellington Avenue beside Canada Metals Limited	12960			
53. Wellington Avenue at the Railway Crossing	860	· · · · ·		
54. Wellington Avenue and King Edward Street	260	60		
55. The Winnipeg International Airport	630	140		
56 Notre Dame Avenue and Bangor Avenue	630	730		
57 Notre Dame Avenue and Sherwin Road	90	10		
58 Notre Dame Avenue and Brookside Boulevard	450	480		
59. Rvan Road east of North West Smelting and Refining	Ltd. 610			
60. Rvan Road east of North West Smelting and Refining	Ltd. 1520			

Location		surface soil	subsurface soil	vegetation	
		$\mu$ grams of 1	lead per gram dry	weight	
61. Selkirk Avenue and Keewatir	n Street	1120	520		
62. Church Avenue and Keewatin	Street	530	800		
63. Adsum Drive and Jefferson A	lvenue	840	160		
64. McPhillips Street and Leila	a Avenue	390	220	· · · · · ·	
65. Inkster Boulevard and Fife	Street	410	310		
66. McPhillips Street and Mount	tain Avenue	960	240		
67. Arlington Street and Mounta	ain Avenue	1080	920	` <b>_</b> ~	
68. McGregor Street and Duffer	ine Avenue	1110	830		
69. McPhillips Street and Logar	n Avenue	690	310		
70. Wellington Avenue and Ingo	rsol Street	440	310		
71. Isabel Street and Cumberla	nd Avenue	1500	1010	<del></del> .	
72. Main Street and Manitoba Av	venue	1800	1170	-	
73. Salter Street and Bannerman	n Avenue	1090	680		
74. McGregor Street and Perth	Avenue	850	360		
75. Kildonan Park south of Sell	kirk Creek Bridge	290	190		

Location	surface soil	subsurface soil	vegetation	
·	ugrams of	lead per gram dry	weight	
76. Templeton Avenue and Sly Drive	210		 L_	
77. Templeton Avenue and Sly Drive	310			
78. Perimeter Highway and Lagimodiere Boulvard	190	100		
79. Henderson Highway and Valhalla Drive	990	730		
80. Roch Street and Kingsford Avenue	60			<u>_</u>
81. Hazel Dell Avenue and Golspie Street	500	350		
82. Henderson Highway and Chelsea Avenue	1330	880	·	•
83. Watt Street and Thames Avenue	230	240		
84. Munroe Avenue and Grey Street	1100	250		
85. Panet Road and Concordia Avenue	450	300		<i>٦</i>
86. Lagimodiere Boulevard and Concordia Avenue	360	0		
87. Day Street and McMeans Avenue	310	180	·	
88. McMeans Avenue and Redonda Street	390		·	
89. McMeans Avenue and Redonda Street	130		, <del></del> .	,
90. Day Street and Regent Avenue	830			÷

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	Location	surface soil	subsurface soil	vegetation
		µgrams of	lead per gram dry	weight
91.	Day Street and Regent Avenue	1090		·
92.	Regent Avenue and Brewster Street	570	460	<b>۔۔۔</b> ب
93.	Regent Avenue and Lagimodiere Boulevard	2030	2200	
94.	Nairn Avenue and Chester Street	1240	680	
95.	Archibald Street and Provencher Boulevard	630	680	
96.	Tache Avenue and Rue Grandin	230 ~	> 230	
97.	Marion Street and Des Meurons Street	750	760	
98.	Archibald Street and Fermor Avenue	750	2220	
99.	St.Mary's Road and Carriere Avenue	540	270	
100.	Lyndale Drive and Balsam Place	300	70	
101.	St.Anne's Road and Fermor Avenue	2150	1960	
102.	St.Anne's Road and LaVallee Avenue	700	90	
103.	St.Mary's Road and Norberry Drive	930	70	
104.	St.Mary's Road and Avalon Road	70	20	
105.	River Road and Falconer Bay	70	30	

vegetation subsurface surface Location soil soil µgrams of lead per gram dry weight ` 30 30 106. River Road and Woodlawn Avenue 1380 1000 107. Osborne Street and Jubilee Avenue  $120 \pm 130(23)$  $410 \pm 450(93)$  $750 \pm 1300(107)$ Average lead level (number of samples) Average of surface soil lead excluding #52  $640 \pm 520(106)$ 0 - 470  $30 - 12,960(107) \quad 0 - 2220$ Range of lead levels for the above averages 30 - 2920 (106)

Avenue, Main Street, Salter Street, Henderson Highway, Nairn Avenue, Regent Avenue, Lagimodiere Boulevard, St.Anne's Road, St.Mary's Road, and Osborne Street all showed elevated lead levels with the majority of these having a lead-in-soil level in excess of 1000  $\mu$ g/g. One of the sites, at Lagimodiere Boulevard and Regent Avenue, exceeded 2000  $\mu$ g Pb/g soil.

Residential streets were found to reflect the lower traffic levels in their lead-in-soil levels. Sites #2 and #3, in the Waverley Heights area, had low lead levels (30 and 60  $\mu$ g Pb/g soil, respectively) at the time of this sampling whereas one year later the levels had increased (70 and 810  $\mu$ g Pb/g soil, respectively). At the time of the initial sampling the Waverley Heights area was still undergoing development. A year later the development was complete with about 90 % occupancy. Site #3 is located beside the left turn lane from south-bound Waverley Street to Lake Crest Road, one of the access roads into the area.

Where there is only local traffic, residential streets are observed to have a lead-in-soil level of 100  $\mu$ g/g or less. Beside residential streets which serve as throughways, a lead-in-soil level between 100 and 500  $\mu$ g/g was observed. Semi-major routes had lead-in-soil levels greater than 500  $\mu$ g/g but less than 1000  $\mu$ g/g.

Subsurface soil lead levels were generally lower than the surface soil levels although the reverse was true in some cases. These higher subsurface values could be due to a number of local conditions. The surface may lack a natural grass cover and therefore be subject to 'caking' during wet-dry cycles. After rain the soil may form 'cakes' upon dying. The cracks created may extend two to four centimetres below the surface. As a result the subsurface soil would be exposed to direct deposition of lead from the atmosphere and to drifting of surface-deposited lead particulates. As well,

surface phenomena like wind and rain will determine how much lead will remain on the surface to sink into the lower soil layers. The lead particulates which are not blown or washed away are carried down into the soil as suspended particulates in rain water. One would expect a build-up of lead in the lower layers of the soil as it is carried down by surface water. It has been found(57) that salt will leach lead from soil at low temperatures. During the winter the City of Winnipeg spreads a large quantity of sand containing salt on the city street. In the spring runoff this salt would leach some of the previous years accumulation of lead from the surface section(0-10cm) of the soil. Some of the lead may be transported deeper into the soil as the ground thaws.

The lead levels in vegetation also reflect the amount of traffic in the local environment. The lead is in the form of particulate matter on the surface of the vegetation.

The background level for lead-in-soil appears to be 30  $\mu$ g/g. Site #1 was located in an undeveloped area which was part of a natural clearing in a stand of bush. The nearest roadways to this sample site were 300 metres to the north and east. The surface(0-2cm) and subsurface(2-4cm) samples gave almost identical values for lead content. The vegetation showed a higher level(50  $\mu$ g Pb/g,dry weight) suggesting long range dispersal from the highway 300 metres to the east. As a result, the 'background' level may not represent a true natural background level but rather a low-level contaminated background.

3.2 Monitoring Survey,

From the initial survey 75 site were selected, 25 sites where the lead level was less than 500  $\mu$ g/g, 25 sites where the lead level was

between 500 and 1000  $\mu$ g/g, and 25 sites where it was above 1000  $\mu$ g/g were chosen. These sites were sampled in April, June, and September of 1979. The results, together with those from the initial survey, are tabulated in Table 3.2.

On the whole, one trend is noted: the lead level is high in the fall (average  $680 \pm 570 \ \mu g \ Pb/g$ ), drops in the spring (average  $410 \pm 600 \ \mu g \ Pb/g$ ), and then returns to high values through the summer (average  $560 \pm 530 \ \mu g \ Pb/g$ ), and the fall (average  $850 \pm 750 \ \mu g \ Pb/g$ ). As already stated the drop from a high fall value to a low spring value is attributed to the leaching of the soil lead by salt during the spring thaw(57).

A number of anomalies are visible in Table 3.2. These are probably due to local conditions, environmental and traffic patterns. A change in traffic density is reflected by a change in soil lead levels as shown at sites #2 and #74. Site #2 (Waverley Street and Lake Crest Road) is located at the exit from a major artery into a residential area, which was still under development when the initial survey was done and which was completed when the final sample was taken a year later. Site #74 (St.Mary's Road and Avalon Street) was originally an access road into a residential area as reflected by the low lead level in the fall of 1978. During the winter and continuing through the summer of 1979 construction of a major shopping center (St.Vital Center) occurred to the east of this point. A higher lead level was observed in the spring and summer due to traffic involved in the construction. The shopping center opened in the late summer with four major entrances. This sample site was on one of these four main entrance ways, and the 1979 fall sampling shows a great increase in soil lead content.

The sites which experienced the greatest drop in winter to spring lead levels were at major intersections, where a greater amount of salted sand was used. Site location and history are factors which influence observed

# Table 3.2

Lead Levels in the Surface (0-2cm) Layer of Soil Monitering Survey

	Location	Traffic Volume #vehicles/12hr	Sept.1978 µgrams of	May 1979 lead per	) June 1979 gram soil dry	Sept.1979 weight
1.	Chancellor Drive and Chancellor Drive	1843	30	50	70	50
2.	Waverley Street and Lake Crest Road		60	420	310	810
3.	Bison Drive curve		120	370	480	570
4.	Ducharme Avenue and Rue Lemaire	986	30	70	.80	80
5.	Pembina Highway at Turnbull Drive		210	<b>9</b> 0	100	320
6.	Dalhousie Drive and Radcliff Road		160	80	630	370 -
7.	University Crescent and Markham Road		390	450	400	480
8.	University Crescent and Thatcher Drive		250	90	560	390
9.	Pembina Highway at Adamar Road	· · · ·	530	350	180	450
10.	Pembina Highway and McGillivray Boulevard	40297	1450	400	1800	2070
11.	South Drive in the 500's		180	120	100	200
12.	Waverley Street and Wilkes Avenue	21633	1790	1180	1120	2290
13.	Waverley Street and Clarence Avenue	17242	370	500	370	150
14.	Kenaston Boulevard at the Railway Crossing		420	330	750	450
15.	Taylor Avenue and Borebank Street		1250	110	580	880
16.	Grant Avenue and Borebank Street	· · ·	660	110	760	950

Location	Traffic Volume #vehicles/12hr	Sept.197 µgrams	8 May 1979 of lead per	June 1979 gram soil dry	Sept.1979 weight
17. Grant Avenue and Edgeland Boulevard		380	290	460	470
18. Grant Avenue and Shaftsbury Boulevard	11637	400	230	280	380
19. Roblin Boulevard and Harstone Road	12534	720	630	380	1070
20. Rannock Avenue and Charleswood Road	1180	50	90	130	160
21. Rannock Avenue and Dale Boulevard		110	130	120	170
22. Roblin Boulevard and Charleswood Road	9001	460	520	460	150
23. Assiniboine Park East Gate		230	170	490	270
24. Nanton Boulevard and Girton Boulevard		170	150	150	150
25. Kingsway and Beaverbrook Street		410	260	230	490
26. Kingsway and Cambridge Street		200	130	420	450
27. Pembina Highway and Taylor Avenue	23251	680	410	620	620
28. Osborne Street and Jubilee Avenue		1000	1650	1000	2000
29. McMillan Avenue and Hugo Street N.		30	170		390
30. Main Street and River Avenue	52582	570	750	640	1070
31. Lyndale Drive and Balsam Place		300	220	310	450
32. Broadway Avenue and Kennedy Street		1150	530	720	1280

Table 3.2 cont:	inuea
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Table 3.2 continued	•	- - -			
Location	Traffic Volume #vehicles/12hr	Sept.1978 µgrams	May 1979 of lead per	June 1979 gram soil dr	Sept.1979 y weight
33. Portage Avenue and Ingorsoll Street		660	400	450	1050
34. Portage Avenue and Empress Street	47315	580	700	1180	1430
35. Portage Avenue and Olive Street		1050	440	530	830
36. Portage Avenue and Sturgeon Road	34333	1110	120	460	1110
37. Portage Avenue and the Perimeter Highway		450	650	1030	1270
.38. Perimeter Highway at Assiniboia Downs		1100	480	1280	2060
39. Ness Avenue and Sturgeon Road	16929	780	200	610	490
40. Ness Avenue and Braintree Crescent		640	90	340	420
41. Ness Avenue and Duffield Street		1210	230	720	1140
42. St.James Street and Wellington Avenue	11603	2920	4770	2570	3640
43. Winnipeg International Airport		630	480	830	1370
44. Notre Dame Avenue and Bangor Avenue		630	550	920	1090
45. Notre Dame Avenue and Sherwin Road		90	300	230	410
46. Notre Dame Avenue and Brookside Boulevard		450	390	160	170
47. Logan Avenue and Ryan Road			250	2570	2650
48. Logan Avenue and King Edward Street			880	<b></b> '	1420

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Location	Traffic Volume #vehicles/12hr	Sept.1978 µgrams (	May 1979 of lead per	June1979 gram soil di	Sept.1979 ry weight
- 49. Selkirk Avenue and King Edward Street			400	190	1270
50. Adsum Drive and Jefferson Avenue		840	60	40	470
51. Mountain Avenue and McPhillips Street		960	<b></b>	610	860
52. Mountain Avenue and Arlington Street		1080	330	580	840
53. Isabel Street and Cumberland Avenue		1500	130	190	520
54. Main Street and Manitoba Avenue	16859	1800	1180	770	1640
55. Kildonan Park south of Selkirk Creek Bridge	· .	290	150	180	250 ×
56. Templeton Avenue and Sly Drive		210	120	270	660
57. Henderson Highway and Valhalla Drive	13872	990	310	360	1300
58. Roch Street and Kingsford Avenue		60	320	70	300
59. Henderson Highway and Chelsea Avenue		1330	270	1060	1550
60. Hazel Dell Avenue and Golspie Street		500	80	180	200
61. Munroe Avenue and Grey Street		1100	270	350	2120
62. Watt Street and Thames Avenue		· 230	150	190	490
63. Nairn Avenue and Chester Street	23177	1240	100	580	890
64. Regent Avenue and Lagimodiere Boulevard	38498	2030	1450	2090	2720

	Location	Traffic Volume #vehicles/12hr	Sept.1978 µgrams of	May 1979 E lead per	June1979 gram soil dry	Sept.1979 y weight
65. Regen	t Avenue and Day Street	11154	830	340	490	710
66. Day S	treet and McMeans Avenue		· / 310	250	270	360
67. McMea	ns Avenue and Redonda Street	•	390	50	120	160
68. Regen	t Avenue and Brewster Street		570	490	500	410
69. Archi	bald Street and Provencher Bouleva	rd	630	440	610	800
70. Archi	bald Street and Fermor Avenue	26296	750	490	920	1630
71. St.An	ne's Road and Fermor Avenue	30709	2150	780	1730	2480
72. St.An	ne's Road and LaVallee Avenue		700	30	50	630
73. St.Ma	ry's Road and Norberry Drive	11755	930	210	670	560
74 St Ma	ry's Road and Avalon Road	5196	70	160	180	500
75 Pivor	Road and Falconer Bay	588	70	70	80	150
76. Chanc	ellor Drive and Gaylene Place gar	den			110	160
,			-			
	Numb	er of samples	72	75	75	76
	Aver	age lead levels	680±570	410±600	560±530	850±730
	Rang	e of lead levels	30 - 2920	50 - 4770	40 - 2570	50 - 3640

# Figures 3.1 to 3.15

These fifteen figures illustrate the location of the 76 sampling sites listed in

Table 3.2

# Figure 3.1

Sample sites #1 to #7 located

in the south section of Winnipeg



# Figure 3.2

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Sample sites #7 to #13 and #73 to #76 located in the south central section of the City of Winnipeg.


Sample site #9,#10 and #12 to #17 in the southwest section of the City of Winnipeg.



Sample sites #12,#15 to #18, #23 to #27, #29 and #34 in the central section of the City of Winnipeg south of the Assiniboine River.



Sample sites #19 to #22 and #36 to #39 in the west section of the city of Winnipeg.



Sample sites #26 to #33 and #71 in the central section of the City of Winnipeg.



Sample sites #35 to #41 in the west central

section of the City of Winnipeg.



Sample sites #23 to #26, #29 to #34, #42 and #53 in the central section of the City of Winnipeg.



Sample sites #33,#34, #42 to #46, and #53 in the northwest section of the City of Winnipeg.



Sample sites #44 to #49 and #51 and #52 in

the northwest section of the City of Winnipeg.



Sample sites #50, #51, #55 and #56 in the central north section of the City of Winnipeg.



Sample sites #55 and #57 to #60 in the north

-east section of the City of Winnipeg.



Sample sites #61 to #64 and #69 in the east central section of the City of Winnipeg.



Sample sites #65 to #68 in the eastern section of the City of Winnipeg.



Sample sites #70 to #75 in the southeast

section of the City of Winnipeg.



lead levels. The effects of site location will be dealt with in a later section. Site history takes into account factors like traffic levels, weather, and human disturbances, such as disruptions of the surface soil by automobile traffic and construction. All influence the observed lead levels in some manner.

3.3 Recovery Study

Two sets of recovery experiments were performed to determine the percent extraction/recovery of lead from the samples.

The first experiment consisted of five sets of five beakers to which 1 mL of 1008 µg/mL lead standard solution had been added. The samples were processed in the usual manner. The results of this study are tabulated in Table 3.3 along with the average recovery for each set and for the total set. The average recovery ranged from 92.2 to 100.9 % for the five sets with an overall average of 97.7  $\pm$  4.3 %. Four of the five sets averaged better than 95 % recovery/extraction.

In the second experiment a quantity of garden soil from 939-941 Chancellor Drive was analysed to determine the average lead content. Ten samples were weighed-(range 5:20 to 6.10 grams, average 5.53  $\pm$  0.32 grams) and analysed for lead using the previously described method. An average lead-in-soil value of 49.6  $\pm$  5.5 µg/g was obtained with a range of 44.2 to 61.6 µg/g (page 33). A further set of 10 soil samples were weighed (3.03 to 5.95 grams) into beakers and to 5 of the samples 1 mL of the 1008 µg/mL lead standard was added. Two blanks were also run, one a reagent blank, the other a standard addition blank (1 mL 1008 µg/mL lead standard plus reagents, no soil). The results of this study are recorded in Table 3.4 along with a calculation of a theoretical value based on the lead recovery from the

	Set #1	Set #2	Set #3	Set #4	Set #5
	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL
	924	978	958	1022	970
	929	1024	1004	1015	995
	912	1008	1002	1002	995
	937	999	989	998	958
	947	999	1131	993	953
Average	930 ± 13	1002 ± 17	1017 ± 66	$1006 \pm 12$	974 ± 20
	92.2 ± 1.3%	99.4 ± 1.7%	100.9 ± 6.6%	99.8 ± 1.2%	96.6 ± 2.0%

Table 3.3 Recovery Study using 1 mL of standard Lead solution, concentration 1008  $\mu$ g Pb/mL

Average for the 25 samples 986  $\pm$  44  $\mu$ g/mL or 97.7  $\pm$  4.3 %

sot	11	soil plus	lmL of	calculated
		standard	lead	lead level
weight grams	μg/g	weight grams	µg/g	µg/g
5.25	43.3	5.25	227.8	229.9
5.57	48.3	5.23	224.5	230.6
5.03	48.6	5.81	205.0	212.3
5.45	41.3	5,95	224.5	208.4
5.97	51.2	5.64	238.2	217.3
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Table 3.4 Standard Addition-Recovery Study from Soil

Average lead levels 46.5 ± 4.1

 $224.0 \pm 12.0$  219.7 ± 10.1

12.0 21007 = 1003

a lmL sample of the 1008  $\mu$ g/mL gave a recovery of 963  $\mu$ g (95.5%)

Calculated lead level = 963 ÷ sample weight + average of soil lead level

example  $963/5.25 + 46.5 = 229.9 \ \mu g/g$ 

standard addition blank. This theoretical value is obtained by dividing the recovery value (963  $\mu$ g) by the sample weight and adding the average of the soil lead value to it, i.e., (963÷5.25) + 46.5 = 229.9  $\mu$ g Pb/g soil for the first standard addition sample of garden soil. Based on this percent recoveries are tabulated in the last column of Table 3.4 . The recoveries ranged from 96 to 109% with an average of 102 ± 6%, thus indicating that at least 95% of the lead present both original and added is being recovered.

#### 3.4 Snow Survey

Two snow surveys were carried out. The first, in the latter part of February 1979, sampled 35 sites bordered by the Red River on the east and Portage Avenue on the north (site #1 to #35 from the second soil survey). The second survey was done in the Weston area of the city of Winnipeg involving 30 sites. In both cases, fresh snow (24-48 hours) was gathered where possible. In some cases, because of drifting, old and fresh snow or just old snow, was gathered. Some of the fresh snow samples gathered along major arteries were observed to be greyish coloured in the top 1 - 2 cm. Some of the old snow samples collected were quite discoloured(almost black).

Snow samples were gathered by a scoop-and-pack method. A horizontal layer was scooped into a 150 mL preweighed beaker and packed in. This was repeated until the beaker was filled. An average weight of 57.86 ± 6.29 g with a range of 44.49 to 69.72 g was obtained for the first study. The samples were heated on a steam-bath to melt the snow and to reduce the volume to about 20 mL. Samples were then processed according to the standard proceedure used for soils.

For the February 1979 study only 35 of the possible 75 samples were

Table 3.5 Lead Levels in Fresh Fallen Snow

	Location	Lead Level
		µg/g
1.	Chancellor Drive and Chancellor Drive	0.5
2.	Waverley Street and Lake Crest Road	6.3
3.	Bison Drive curve	6.7
4.	Ducharme Avenue and Rue Lemaire	<0.5
5.	Pembina Highway and Turnbull Drive	1.1
6.	Dalhousie Drive and Radcliff Road	7.1
7.	University Crescent and Markham Road	4.2
8.	University Crescent and Thatcher Drive	3.7
9.	Pembina Highway at Adamar Road	3.6
10.	Pembina Highway and McGillivray Boulevard	4.4
11.	South Drive (544)	<0.5
12.	Waverley Street and Wilkes Avenue	1.4
13.	Waverley Street and Clarence Avenue	7.9
14.	Kenaston at the railway crossing	9.5
15,	Taylor Avenue and Borebank Street	2.4
16.	Grant Avenue and Borebank Street	1.5
17.	Grant Avenue and Edgeland Boulevard	5.9
18.	Grant Avenue and Shaftsbury Boulevard	2.6
19.	Roblin Boulevard and Harstone Road	3.3
20.	Rannock Avenue and Charleswood Road	1.7
21.	Rannock Avenue and Dale Boulevard	1.4
22.	Roblin Boulevard and Charleswood Road	1.2
23.	Assiniboine Park East Gate	<0.5
24.	Nanton Boulevard and Girton Boulevard	<0.5
25,	Kingsway and Beaverbrook Street	1.9

#### Table 3.5 continued

	Location	Lead Level
		µg/g
26.	Kingsway and Cambridge Street	6.5
27.	Pembina Highway and Taylor Avenue	1.9
28.	Osborne Street and Jubilee Avenue	2.8
29.	McMillan Avenue and Hugo Street N.	<0.5
30.	Main Street and River Avenue	5.8
31.	Broadway Avenue and Kennedy Street	8.6
32.	Portage Avenue and Ingorsoll Street	1.0
33.	Portage Avenue and Empress Street	5.9
34.	Portage Avenue and Olive Street	5.0
35.	Portage Avenue and Sturgeon Road	8.8

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Average Lead Level (<0.5 taken as being 0.0) 3.6 ± 2.9

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collected due to inclement weather in the afternoon of the sampling day. The new snow and further ground drifting would alter the conditions of sampling. The results which are tabulated in Table 3.5 show a great range in lead-in-snow levels from a level which was not detected (ie below 0.5  $\mu$ g/g) to a level almost reaching 10  $\mu$ g/g. In residential areas where there is only local traffic the snow's lead content is very low. Along major routes the snow's lead content is quite high. Drifting is a major factor in the lead-in-snow levels observed as it not only gathers snow into drifts but also carries the lead aerosol across the rough snow surface where it can be trapped. Ideally this sort of study should be done after a quiet(no wind) snowfall where no drifting has occurred.

For the 35 sites surveyed the average lead-in-snow level was 3.6  $\pm$  2.9 µg/g. Grandstaff and Meyer(145) found a lead level ranging from 0.034 to 0.056 µg/g snow in freshly fallen snow in Philadelphia. A linear relationship between lead by dry deposition and time was found. Site location influenced the rate of accumulation. A site by a four lane high-way was found to have a lead-in-snow level of 2.7 µg/g after 800 hours whereas a site beneath a bridge had a lead-in-snow level of 2.2 µg/g after only 36 hours. A 1978 study(146) from Toronto, Ontario gave a lead level of 1.0 to 1.6 µg/mL in the runoff from the final snowmelt.

The second study was undertaken in response to concern raised about the possibility of lead emission from the smelter in the Weston area. The results of this survey are tabulated in Table 3.6 . They show elevated lead levels along Logan Avenue reflecting the trend seen in the first study above. Figure 3.16 illustrates the location of 28 of the 30 sites sampled in this area. Of the 13 sites south of Logan Avenue, only one at Pacific Avenue W and Jordon Street, had a lead level greater than 5 µg Pb/g

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Location and Sample Description	Lead Level	-
1. Logan Avenue and Ada Street sw corner fresh snow	0.6 ± 1.8	
2. Logan Avenue and Wiens Street s side old and fresh	snow 5.0 ± 1.9	
3. Logan Avenue (1658) n side fresh snow	1.2 ± 3.0	
4. Logan Avenue and Quelch Street ne corner old snow	$14.1 \pm 0.5$	
5. Quelch Street and Alexander Avenue ne corner old an	nd fresh snow $3.0 \pm 0.5$	
6. Alexander Avenue and Weston Street nw corner fresh	snow 1.9 ± 1.4	
7. Logan Avenue and Jordon Street sw corner old and fr	resh snow 1.9 ± 1.5	
8. Logan Avenue and Vine Street ne corner old and free	sh snow 9.7 ± 1.4	
9. Vine Street and Whyte Avenue sw corner old and free	sh snow 4.9 ± 1.3	
10. Whyte Avenue and Bury Street ne corner old and free	sh snow 5.6 ± 1.7	
11. Bury Street and Irysh Avenue nw of Weston Shop entra	ance fresh snow 3.8 ± 1.1	
12. Irysh Avenue and Blake Street n side old and fresh	snow 11.9 ± 0.9	
13. Logan Avenue and Blake Street s side old and fresh	snow 2.4 ± 0.6	
14. Cecil Street and Pacific Avenue W se corner old and	fresh snow 0.9 ± 1.2	
15. Pacific Avenue and Quelch Street nw corner old and	fresh snow 1.2 ± 1.1	

Table 3.6 Lead Levels in Snow from the Weston Area of the City of Winnipeg

Table 3.6 continued

Location and Sample Description	
	µg/g
16. Pacific Avenue W and Jordon Street n side fresh snow	5.4 ± 0.7
17. Alexander Avenue and Blaine Street se corner old and fresh snow	$2.5 \pm 1.0$
18. Logan Avenue and Electra Street ne corner dirty old snow	34.1 ± 3.3
19. Roy Avenue and Cecil Street sw corner old and fresh snow	$0.7 \pm 1.3$
20. Roy Avenue and Quelch Street nw corner fresh snow	3.8 ± 1.8
21. Roy Avenue and Jordon Street e side old and fresh snow	0.7 ± 1.1
22. Ross Avenue and Langford Street nw corner fresh snow	1.0 ± 1.4
23. Ross Avenue and Jordon Street e side old and fresh snow	1.1 ± 0.7
24. Elgin Avenue and Langford Street se corner fresh snow	3.7 ± 0.7
25. Elgin Avenue and Jordon Street e side old ice crystals	1.0 ± 0.9
26. Gallagher Avenue and Blake Street se corner fresh snow	$0.9 \pm 1.2$
27. Gallagher Avenue and Vine Street e side fresh snow	$2.2 \pm 0.6$
28. Gallagher Avenue and Electra Street nw corner fresh snow	$1.7 \pm 0.8$
29. Gallagher Avenue and Quelch Street ne corner old and fresh snow	10.1 ± 0.6
30. Pacific Avenue and Yeoman Street fresh snow	1.1 ± 1.1
## Figure 3,16

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Map of the Weston area of the City of Winnipeg illustrating the snow sampling locations.



snow. Eight sites had a lead level below 2  $\mu$ g/g snow. North of Logan Avenue only one site of the eight had a lead-in-snow level below 2  $\mu$ g/g. Two of the sites in this area had lead-in-snow levels exceeding 10  $\mu$ g/g. One of these sites is south of the smelter, the other is to the northwest, The south site, located at Gallagher Avenue and Quelch Street is opposite a grocery store so lead from automobile exhausts may be above average. The other site located at Irysh Avenue and Blake Street is by an apartment parking-lot and so only experiences local traffic. It is not on a major access route into the industrial area to the east. With the exception of one site at Pacific Avenue W. and Jordon Street all the sites with a lead-insnow level equal to or greater than 5  $\mu$ g/g are along or north of Logan Avenue. The site at Pacific Avenue W. and Jordon Street showed an elevated level due to the heavy traffic at this site, which serves to funnel traffic to and from the residential area to Logan Avenue.

Overall, the area north of Logan Avenue showed lead-in-snow levels which were higher than similar sites in the area south of Logan Avenue. The higher lead-in-snow levels may be a reflection of the heavy traffic in the area due to the industry or due to emissions from the smelter. The high lead-in-snow levels observed along Logan Avenue follow the same trend observed along other major traffic arteries.

From the results tabulated in Table 3.5 it can be seen that lead accumulates quite rapidly in the snow along streets that are heavily trafficked. There is a buildup of lead evident even on some of the residential streets but not at the same rate as on some of the heavily trafficked streets. The results tabulated in Table 3.6 support the above observations where fresh snow was collected. The inclusion of old snow in this study offers the opportunity to observe the accumulation of lead

in the snow with time. Two sites on Logan Avenue gave very high lead-insnow values. The snow collected in both cases was old and discoloured. By old, it is meant that the snow had lain on the ground for a long period of time. Both of these samples as well as others which included old snow contained ice crystals which were present as a result of thawing and freezing cycles. Samples #4 and #18 (Table 3.6) Quelch Street and Logan Avenue, and Electra Street and Logan Avenue respectively, are about one block apart. The first on the south side of Logan Avenue, the second on the north side of Logan Avenue. The lead level in the sample from site #18 was more than twice the lead level at site #4 indicating either a greater accumulation rate or a longer accumulation time. From the condition of the snow that was collected the latter case is the more probable cause. Of the other snow samples gathered in this locality only those which contained some old snow contained a level of lead approaching the level found at the above two sites. Of the samples which were composed of fresh snow entirely only two showed a somewhat elevated lead level. One of these samples taken from Pacific Avenue W. and Jordon Street has already been mentioned as having a fairly high traffic flow due to its position as a feeder channel into and out of the residential area south of Logan Avenue, This high traffic volume would yield a high accumulation rate of lead in a short period of time.

3.5 Smelters and Surrounding Areas.

During May 1979, two samplings were done around three smelters and one lead user in Winnipeg. The results of the soil analysis appear in Tables 3.7 to 3.10. The results for the area around Dominion Bronze (lead user) on Chevrier Avenue gave no indication of lead emission from the plant on the south or

east sides. The four samples taken from the east side of the plant, between the property line and the CNR tracks, show lead levels which are near background levels. Samples taken along the south-side along the north side of the road are generally indicative of a well trafficked street, with the high-low variations due to parked cars along the street. These variations are probably due to the cold start-up of the parked vehicles. This results in resuspension of lead particulates in the exhaust system and venting of them into the atmosphere. The first two samples were taken from the same location, the first on May 2nd and the second on May 9th. Over the period of a week the lead-in-soil level was observed to increase by 72%. An anomaly is observed with samples #2 and #3, where the second of the pair(#3) taken from the road edge showed a lower lead-insoil level than the sample taken 3 metres away. The other two pairs of samples, #4 and #5, and #6 and #7, show a high lead-in-soil level by the road and a decreased lead-in-soil level when the distance increased to 3 metres from the road surface.

The first of the smelter sites sampled was around North West Smelting and Refining Ltd. (Fig. 3.17) with the first sample taken from an area west-southwest of the plant which was under development. The level in the first sampling was about twice background lead level. At the time of the second sampling the lead-in-soil level had dropped by about 20%. The second sample was taken from a point midway between the first site and the smelter itself. The initial sampling gave a fairly high lead-in-soil level (Table 3.8) but the second gave a much lower value. The site location and history may account for the observed changes in lead-in-soil values. The third sample was taken from a site directly south of the plant on Logan Avenue and gave a very high(4780µg/g) lead-in-soil level. The second

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Table 3.7 Lead Levels in the Soil in the area of Dominion Bronze Ltd.

	Sample Location	Lead Level
		µg/g
1. 5	southwest fence corner - 8 feet east May 2, 1979	90
2. s	southwest fence corner - 8 feet east May 9, 1979	160
3. r	road edge south of #2	40
4.1	15 paces east of #3 at road edge	220
5. ł	beside the fence by the 5th pole from the southwest corner	90
6.2	22 paces east of #4 at road edge	315
7. t	peside the fence by the 2nd pole west of the gate	190
8.8	3 inches from the curb edge opposite the west windows	370
9. f	from curb edge east of the sidewalk	180
10.6	5 inches from the curb edge 25 paces east of $\#9$	195
11. f	from the path on the east side opposite the 2nd pole from the ne corn	er 35
12. f	from the path on the east side opposite the 7th pole from the ne corn	er 55
13. f	from the path on the east side opposite the 14th pole from the ne cor	ner 30
14. f	from the path on the east side opposite the 22nd pole from the ne cor	ner 40

Map of the area around North West Smelting and Refining Limited in the City of Winnipeg showing the location of the six sample sites listed in Table 3.8



Sample Site Location	Lead	Leve1
	μ	g/g
	May 14	May 28
1. Logan Avenue and Omand's Creek Boulevard	60	50
2. Logan Avenue east end of S curve	1600	. 380
3. Logan Avenue opposite North West Smelting and Refining Limited	4780	8160
4. Ryan Road at the northeast corner of the fence around NWS&R Ltd.	640	260
5. Ryan Road at the entrance to the yard	1400	1840
6. Logan Avenue and King Edward Street - the northwest corner	60	180

Table 3.8Soil Lead Levels in the Area of North West Smelting and Refining Limited

sampling on May 28th almost doubled the May 14th value for lead-in-soil. Of the two sites located east of the smelter the second or more southerly one gave the higher lead-in-soil level. This site was directly east of the stack and as a result would receive lead fallout when the wind was from the west. Also, as it is located by the side entrance, vehicular traffic may carry particulates out of the yard itself and deposit them in the outside. The sixth location sampled was at the corner of a busy intersection and it had a lead-in-soil level characteristic of a moderately busy traffic artery. During the sampling period the prevailing winds were from the north, so sites south (i.e., #3) of the smelter would experience fallout of-stack emmisions. The Provincial Study(66) has reported a leadin-soil level of 19,000  $\mu$ g/g at a location just outside the smelter and a level of 710  $\mu$ g/g at a site corresponding to site #2 where this work found lead-in-soil levels of 1600 and 380 µg/g. Wind direction influences the areas polluted by stack emission as seen here. The area south of the smelter showed the greatest increase in lead levels with time.

The second smelter-area was Canadian Bronze Ltd. and the Weston area around the smelter. The results for this area, which are given in Table 3.9, show high lead-in-soil levels along Logan Avenue, as expected from studies of other areas of the city. One site in the smelter area, at Whyte Avenue and Bury Street was found to have an excessively high lead-in-soil level for a residential area. Two other sites in the area, Irysh Avenue and Blake Street, and Whyte Avenue and Vine Street, also showed high lead-in-soil levels. In fact, these levels were almost the same as certain sites along Logan Avenue. This smelter was shut down for two months during the summer of 1979 because of excessive lead-in-air levels within the smelter itself. During this period(at the beginning of July and the end of August) the

Provincial Government(66) surveyed a number of sites in the area. Values reported by the provincial study for sites in close proximity to those sampled by this work appear in Table 3.9. The values in 3 of the 4 cases are higher for the provincial results than the results obtained in this work. This is to be expected since lead accumulates with time. At the one site which is lower, the lead level decreased between July and August in the provincial study(66). This may be due to the shut-down of the smelter and the resulting decrease in the traffic along Quelch Street.

The lead-in-soil levels in some areas of this region appear to be above what would be expected from studies of other areas of the city with similar characteristics. Some of the residential streets in this area would appear to carry a high traffic level as shown by the lead-in-soil values obtained for the soils bordering these streets.

The third smelter surveyed was Canada Metals Ltd. located at Wellington Avenue and St.James Street. The first sample site was located about one kilometre east of the smelter on the east side of the old city dump, now Westview Park. The lead-in-soil level at this site was slightly higher than expected(195-230 µg Pb/g soil) for this area. Wellington Avenue feeds into two backlanes at this point because it is interrupted by the park. The lead-in-soil levels observed at Wellington Avenue and Empress Street are more representative of the type of environment. The site is located in the lee of a building, with respect to the smelter, and on a busy intersection. The site at Wellington Avenue at the railway crossing showed one of the greatest increases in lead-in-soil levels in this study. In the interval between the first and second samplings the level increased by a factor of 5.5, from 1410 to 7785 µg Pb/g soil. The site at Sargent Avenue and Empress Street, which is about one kilometre

	Sample Site Loca	Lead Level µg/g						
	· · · · · · · · · · · · · · · · · · ·			May 14	<u>May 28</u>	Provi July	ncial( <sup>6</sup> August	6) (1979)
<sup>′</sup> 1.	Logan Avenue and Ada Street se com	rner		140	250			
2.	Logan Avenue and Wiens Street se	corne	r	780	740			
3.	Logan Avenue - 1574 south side			300	300			
4.	Logan Avenue and Quelch Street	SW C	orner	- 870	980	1400	940	
5.	Alexander Avenue and Quelch Street	se co	orner	40	90			
6.	Logan Avenue and Electra Street	ne co	orner	1020	500			
7.	Irysh Avenue and Blake Street	nw c	orner	540	770	930	905	
8.	Whyte Avenue and Bury Street	ne co	orner	1590	2820	3500	3800	
9.	Whyte Avenue and Vine Street	SW C	orner	740	720			
10.	Logan Avenue and Vine Street	nw ce	orner	1470	2000			
11,	Roy Avenue and Keewatin Street	se co	orner	370	260			
12.	Roy Avenue and Worth Street	sw co	orner	150	140			
13.	Pacific Avenue W and Quelch Street	ne co	orner	440	600	440	290	
14.	Elgin Avenue and Worth Street	se co	orner	160	450			
15.	William Avenue and Cecil Street	ne co	orner	360	280			

Table 3,9 Soil Lead Levels in the Area of Canadian Bronze Limited and the Weston Area

	Table 5.10 Soll head levels in the Alea alound Canada Metals Limited (1979)									
		Sample Site Location	Lead Level µg/g							
		· , · ·	<u>May 14</u>	May 28	July(6	<u>6)August</u> (66)				
1.	. Wellington Avenue	west of Strathcona Street by hydro pole	195	230						
2.	. Wellington Avenue	and Empress Street nw corner	245	195	600	520 ·				
3.	. Wellington Avenue	south side by railway crossing	1410	7785	2000	3000				
4.	. Sargeant Avenue a	nd Empress Street nw corner 20m into a field	240	180						
5.	. Wellington Avenue	by Canada Metals Limited - fence corner		1380						

Table 3.10Soil Lead Levels in the Area around Canada Metals Limited (1979)

to the southeast of the smelter, gave lead-in-soil levels of 240 and  $180 \ \mu g/g$  . The provincial study(66) has also reported elevated lead levels in the soils in the vicinity of the smelter.

As can be seen in the above results there are differences in the reported lead levels for the same general area. Time, weather, and local history all influence the lead-in-soil level observed.

#### 3.6 Regional Surveys

In the previous section it was observed that lead values obtained for the same area, but from different sites within that area, differed. The influence that the site has on the lead-in-soil levels observed will be examined in this section.

From the 75 sample sites monitored 8 were selected for intensive study to determine if the choice of the sample site significantly affected the lead-in-soil level observed. These 8 sites ranged from residential areas through major traffic arteries to industrial areas.

#### 3.6a Chancellor Drive and Chancellor Drive

This first site located in the Waverley Heights area was situated at the junction of Chancellor Drive with itself. Chancellor Drive is the major access street for the area. The intersection studied is regulated by a three way system of stop signs(Fig. 3.18) with the southwest corner occupied by an elementary school. There is a bus stop on the north side of Chancellor Drive just east of the intersection. Sample site #7 was at the east end of the bus stop while site #8 was by the east stop sign at the curb edge. The first three samples were from the southeast corner, #1 and #2 from the curb edge and #3 from the intersection of the sidewalks.

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Sample Site Location	Lead	Level µg/g	
_	analysis #1	analysis #2	average
1. southeast corner north side curb edge	72	74	73±1
2. southeast corner northeast section from centre of curv	e 34	× 21	28±10
3. southeast corner east side 10 feet from road, by sidew	alk 31	22	26±7
4. southwest corner west side at curb edge	70	80	75±7
5. southwest corner northwest section at curb edge	127	81	104±30
6. southwest corner north side at curb edge	414	451	432±25
7. north side 9.5 feet east of busstop,at curb edge	22	11	17±8
8. north side by stop sign at curb edge	76	80	78±3
9. north side from weed patch in front of 1093 at curb edg	e 28	19	23±6
10. south side from hole in boulevard opposite 1091	51	35	43±11

Table 3.11 Soil Lead Levels in the Chancellor Drive - Chancellor Drive Area, A Regional Sampling

Sample site locations at the intersection of Chancellor Drive and Chancellor Drive in the Waverley Heights area of South Winnipeg



Both sites #2 and #3 gave lead-in-soil levels(Table 3.11) which were near background lead-in-soil level (30 µg/g) whereas site #1 gave a level of 75 µg Pb/g soil. The southwest corner (sites #4,#5,#6) showed a higher lead-in-soil level than the southeast corner. Levels increased from south to north (from #4 to #6). Site #6 had the highest level of the 10 sites in this area. The high lead level at this site is probably due to its location within the acceleration zone from the stop sign. Site #10, to the west of #6 is located in the deceleration zone just before the stop sign. The lead level at this site was ten times lower than at site #6. Site #9 across the street from #10 showed a lead level which was only one-half that at site #10. Site #8, which is located at the beginning of an acceleration zone, showed a very low level in comparison to the level at site #6.

At this location the south side of the street appeared to have a higher lead-in-soil level than the north side of the street for corresponding points. For a residential area, 9 of the 10 lead levels observed are 'normal'. The high value is probably due to resuspended lead particulates which are emitted from the exhaust system during acceleration from the stop sign. A similar but weaker effect was noted at the north side stop sign.

3.6b University Crescent at Markham Road and at Thatcher Drive

University Crescent carries traffic into and out of the University of Manitoba. The two cross-streets Markham Road and Thatcher Drive(Fig.3.19) are access routes to a golf and country club and a residential area, respectively. Traffic along University Crescent is heavy during the winter academic session and moderately heavy during the summer.

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Table 3.12	Soil Lead	Levels	for	the	intersections	of	University	Crescent	with	Markham	Road(11-15)	and
									•			
	Thatcher I	Drive(16	5-20)									

Sample Site Location	L	ead Level µg/{	g .
	analysis #1	analysis #2	average
ll, west side of crosswalk on east median	253	306	280±37
12. east side of crosswalk on east median	447	401	424±3 <b>2</b>
13. west end of east median	498	401	450±68
14. 12 feet from the end of the west median	341	357	349±11
15. east end of west median	473	476	474±2
16. west end of east median	669	557	613±79
17. south east corner at curb edge	306	413	360±76
18. south west corner at curb edge	263	383	323±85
19. east end of west median	418	432	425±10
20. north west corner by the street sign	270	193	231±54

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Sample site locations for the intersections of University Crescent with Markham Road and Thatcher Drive in the University Heights area of South Winnipeg.



At Markham Road and University Crescent five sites were examined on the median on both sides of the intersection. As can be seen from the values in Table 3.12 lead-in-soil levels at two adjacent sites(#11 and #12) differ by 140 µg Pb/g soil. Two sites on the opposite median gave similar results. For both of these areas, site history makes a significant contribution to what was observed. They are both located along pedestrian walk-ways and are subjected to disturbances. The grass cover at both sites has been worn away by pedestrian traffic.

The second area, at University Crescent and Thatcher Drive, was undisturbed at four of the five sites. Site #18 lacked grass cover. Both of the sites on the median(#16 and #19) gave higher lead-in-soil values than corresponding sites on the sides of the road. Here, the south side of the Crescent was observed to have a higher lead-in-soil level than the north side. The higher lead levels on the median are probably due to exposure and fallout of lead from both sides of the road as well as from traffic turning onto Thatcher Drive from University Crescent.

#### 3.6c Grant Avenue at Borebank Street

This third study area , illustrated in Figure 3.20,looked at the four corners of the intersection as well as points on the medians. Of the 10 sites sampled at this location, the southeast corner showed the highest lead-in-soil levels. As the results illustrate, Table 3.13, the lead-in-soil value determined varied within a sample(duplicate analysis-two sub-samples). The average lead-in-soil level ranged from 310 to 824  $\mu$ g/g with an average of 505 ± 180  $\mu$ g/g for the entire area. From these results it can be seen that geographic location can affect the lead-in-soil level at another site located just across the street from it(#28 - #27).

Sample Site Location	Lead Levels µg/g				
۲. ۲.	analysis #1	analysis #2	average		
21. southwest corner at curb edge	325	347	336±16		
22, southwest corner 9 feet back from the road	377	336	357±29		
23. south side west median	366	393	380±19		
24, north side west median	405	303	354±73		
25. northwest corner at curb edge	635	557	596±55		
26, southeast corner 8 feet back from the road	612	556	584±40		
27. southeast corner at curb edge	879	769	824±40		
28. south side east median	367	254	310±80		
29. north side east median	777	606	692±120		
30. northeast corner at curb edge	686	538	612±105		

Table 3.13 Soil Lead Levels for the intersection of Grant Avenue and Borebank Street

Sample site locations for the intersection of Grant Avenue and Borebank Street in the Fort Rouge area of the City of Winnipeg.



#### 3.6d Roblin Boulevard and Harstone Road

The fourth area to be sampled was located in the western portion of the city at the intersection of Roblin Boulevard by Harstone Road(Fig. 3.21). For the whole of the area sampled the average lead-in-soil level was 470  $\pm$  115 µg/g(Table 3.14) with a range of 318 to 644 µg/g. For the subarea along the south edge of the east median(5 sites) the average level was 510  $\pm$  115 µg Pb/g soil with a range of 362 to 644 µg Pb/g soil.

Even in this area a variation in lead-in-soils levels is evident for the samples taken from a similar area. Of the five samples (#36 - #40) taken along the median #38 showed the lowest lead-in-soil level while the neighbouring sites on either side were the higher of the outside pairs. This entire section of the median was devoid of surface cover for a distance of about 50 cm from the curb edge, resulting in a greater variety of disturbing influences like physical erosion by wind and rain runoff, and mechanical disturbances by man. Variability is also seen in the other five samples taken at this location. For example sites #34 and #33 were about 1 to 1.25 metres apart on a north-south line yet they differ by about 100 µg Pb/g soil. Also variability existed within the sample, as can be seen in the results from sites #34 and #37 where the difference between duplicate analyses is on the order of 100  $\mu$ g Pb/g soil. On the other hand some samples showed very little variation(i.e., #39) between duplicate analyses. From this it can be seen that the sample should be thoroughly mixed to give a uniform sample so that when subsamples are taken, that these subsamples should be representative of the whole sample. Each sample should be taken in the same manner so that the same soil layer is sampled.

Sample Site Location	Le	ad Level µg	/g
	analysis #1	analysis #2	average
31. southwest corner at the curb edge	346	289	318±41
32. southeast corner at the curb edge	386	343	365±31
33. south side west median	488	505	496±12
34. north side west median	668	524	596±102
35. north side Roblin Boulevard opposite Harstone Road	468	364	416±74
36. south edge of the east median at the west end	553	583	.568±21
37. south edge of the east median 10 paces east from $#36$	543	745	644±143
38, south edge of the east median 20 paces east from $#36$	370	355	362±11
39. south edge of the east median 35 paces east from $#36$	561	549	555±9
40. south edge of the east median 50 paces east from $#36$	396	431	413±25

Table 3.14 Soil Lead Levels for the intersection of Roblin Boulevard and Harstone Road

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Sample site locations for the intersection of Roblin Boulevard and Harstone Road in the Charleswood area of the City of Winnipeg.



#### 3.6e Assiniboine Park

The fifth area examined consists of four locations in and around Assiniboine Park. Figure 3.22 illustrates the four sampling site locations and Table 3.15 lists the results. The three samples(#41,#42,#43) taken at the southeast gate all showed high lead-in-soil levels and were fairly consistent. Two of the samples(#41 and #42) were taken from both sides of the entrance/exit. A difference of about 100  $\mu$ g Pb/g soil between the two is noted with the exit side having the higher level. The third sample, taken 20 metres inside the entrance side, showed a higher level than the site at the entrance.

At the west gate the entrance side showed a higher lead level than the exit side. The difference in lead levels was probably due to differences in traffic density and the position within an acceleration/deceleration zone.

Within the park a decrease in lead levels was observed, as was expected, as the distance from the roadway increased. The observed lead-in-soil level dropped from 238  $\pm$  21 µg/g at roadside to 78  $\pm$  14 µg/g at a distance of about 100 metres from the roadway.

At the east gate the lead level was observed to increase as distance from the gate decreased(#48 to #50). All three of these sites at the east gate were devoid of grass cover and so were exposed to factors which could affect lead levels.

#### 3.6f Broadway Avenue at Kennedy Street

The sixth location was downtown, located at the intersection of Broadway Avenue by Kennedy Street(Fig. 3.23). At this location only six sites were sampled due to recent construction in the area which had disturbed the roadside soils. The results(Table 3.16) show a high lead-in-soil level along Broadway Avenue at the curb edge. At a distance of about 4 metres Table 3.15 Soil Lead Levels for various sections of Assiniboine Park

Sample Site Location	Lead Level µg/g				
	analysis #1	analysis #2	average		
41. south east gate - east side of the entrance	474	679	576±146		
42. south east gate - west side of the exit	734	639	687±67		
43. south east gate - 20 metres inside east side entrance	638	667	653±20		
,					
44, at the crosswalk to the foot bridge	223	253	238±21		
45. at the 3rd lamp post on the walk to the pavillion	88	68	78±14		
46. west gate - west side by the concrete divider	374	315	344±42		
47. west gate - east side by gate	436	458	447±16		
48. east gate - north side by 'end way' sign	364	460	412±68		
49. east gate - north side 20 metres east of #48	399	367	383±22		
50. east gate - north side 100 metres east of #48	323	234	279±63		

### Sample site location in Assiniboine Park.

Southeast Gate

One half mile inside

East Gate on the perimeter

drive,

West Gate

East Gate



Table 3.16Soil Lead Levels for the Area Just West of the Intersection of Broadway Avenue and<br/>Kennnedy Street,

Sample Site Location

Lead Level µg/g

		analysis #1	analysis #2	analysis #3	average
51.	, south side median – northwest side of 1st tree	408	399	436	414±19
52.	south side median - south side 4th tree to west	531	589	531	550±23
53.	south side Broadway Avenue by 1st tree from Kennedy St.	49	39	39	42±6
54,	south side Broadway Avenue by the 4th tree from Kennedy	59	62	44	54±11
55.	north side median - north side of the fourth tree	1228	1160	1150	1179±43
56.	south side Broadway Avenue by the 8th tree on the		× ,		
	Legislature grounds	190	187	165	180±13

Sample site location at the intersection of Broadway Avenue and Kennedy Street in the Downtown area of the City og Winnipeg.


(site#56) from the road the level has dropped to one-half of the lowest level observed at curb edge (#51). Sites #53 and #54 were observed to be quite low and at the time of sampling it was noted that the old concrete sidewalk had been replaced with concrete paving stones(interlocking bricks) and that the soil around the trees along the road had been worked-up around them(turned and fresh soil added). The three sites along the median were undisturbed by the reconstruction of the roadway. However, they showed the effect of the closure of the roadway. At the time of the sampling the north side (west bound) had been open to traffic for a longer period of time than the south side(east bound), resulting in a greater accumulation of lead in the surface soil on the north side of the median. During the period of closure of the roadway there was no observable decrease in lead levels along a particular section of the roadway where a sample had been taken prior to closure. This would indicate that the lead is in the form of a stable compound which is not very soluble and is not removed from the soil, except under cation exchange conditions(salt leaching).

#### 3.6g Portage Avenue at Olive Street

The seventh location was located at the intersection of Portage Avenue by Olive Street(Fig. 3.24). It gave a wide range of lead-in-soil levels from a low of 138  $\mu$ g/g to a high of 2544  $\mu$ g/g in two sites 15 metres apart. Of the four sites located on the north side of Portage Avenue, one #70 was in a deceleration zone at the entrance to a service station. The other three sites(#61,#62,#63) were within a parking zone on the northeast corner. As can be seen from the results in Table 3.17 the values for lead-in-soil are fairly close together for the first three sites. The level at site #61 is lower because of its position at the edge of the parking zone. As a result its exposure to lead from the exhaust would be lower than at sites

Sample Site Location	1 <b>I</b>	ead Level	µg/g	
	analysis #1	analysis #2	analysis #	3 average
61. northeast corner by light standard	914	851	1024	930± 88
62. northeast corner 14 paces east of $#61$	2194	1063	1132	1289±509
63. northeast corner 31 paces east of $#61$	1146	1096	1585	1276±269
64, south side of west median	2616	2582	2430	2544±100
65, north side of east median	1398	1428	1722	1516±170
66, south side of east median	886	598	741	742±144
67. south side of Portage Avenue 1 foot west of drain	628	609	741	659± 72
68, south side of Portage Avenue west end of bus stop	300	374	319	331± 39
69. southwest corner at curb edge	973	1013	921	969± 46
70. northwest corner by the light standard	161	114	139	138± 23

Table 3.17 Soil Lead Levels for the Intersection of Portage Avenue and Olive Street

Sample site location for the intersection of Portage Avenue and Olive Street in the St.James area of the City of Winnipeg.



#62 and #63. These two sites show a greater variability within the sample as they show a standard deviation of 21 and 39%, respectively, for triplicate analyses. The majority of the other sites showed a sample variability of about 10%. The large observed deviation was probably due to the nature of the exhausted lead, which is emitted during start up. Some of it may be emitted as large particles which have accumulated in the exhaust system and are resuspended into the exhaust during start up. These large particles would settle out quite rapidly and unevenly so that there would be an uneven distribution in the soil.

On the medians three sites were sampled. They also showed a variability between sites and to some degree within the sample. One of the median sites, #64 had the highest lead-in-soil level for this location, while another site #66 similarly located on the next median only had a level one-third as high. Site #65 located across the median from site #66 had a lead-in-soil level twice the level at site #66 and only three-fifths the level at #64.

On the south side of Portage Avenue a great variability was again observed in the lead levels amoung the three sites. Site #69, on the southwest corner gave the highest level of the three, while the other two sites, lying on each side of #69, had levels of only 60 and 30% of the level at #69.

This location clearly illustrates the effect that the choice of sampling site can have on the value for the lead-in-soil level reported for that location. The average level at this location was  $1040 \pm 680 \ \mu g \ Pb/g$  soil with a range of 140 to 2544  $\ \mu g \ Pb/g$  soil. The site monitored in the major study corresponded to site #61 in this section and it reflects, in this case, the average lead level for the entire area.

3.6h Wellington Avenue by Canada Metals Ltd.

The eighth and last location was in an industrial area. The street surveyed bordered a secondary smelter, Canada Metals Ltd.. Figure 3.25 illustrates the position of the sample sites with respect to the intersection of Wellington Avenue by St.James Street and the smelter. The lead-in-soil levels, tabulated in Table 3.18, were higher on the north side(closest to the smelter) than the south side of Wellington Avenue. The average leadin-soil level for the whole area was 4485  $\pm$  2790 µg/g with the north side of Wellington Avenue having a higher average of 5305  $\pm$  3290 µg Pb/g soil. The south side of Wellington Avenue had a lower average of 3070  $\pm$  1885 µg Pb/g soil. The levels at this location ranged from 1417  $\mu$ g Pb/g soil (average for a high traffic area) to 9162  $\mu$ g Pb/g soil which was more than than four times the highest level observed for a busy intersection. As this is an industrial area the traffic in this region is not as dense as on some major arteries and there would be a greater amount of diesel fuel(which does not contain lead) used in this area. From these considerations the most probable source of the excess lead in the area is the secondary smelter located on the northeast corner of Wellington Avenue and St. James Street, Canada Metals Ltd.. Along the north side the lead-in-soil levels increase as the distance from St.James Street increased until the fourth site(#78). Decreases in the lead-in-soil levels begin at the fifth site(#79). The south side of Wellington Avenue shows two maxima, one at site #73 and the second at site #80. This variability may be due to wind direction and emission settling patterns from the stack. The north side may get a higher lead input due to rain wash off of particulate lead from the roof of the smelter. All of the sampling sites were from areas where there was good grass cover and so they were not subjected to major stresses from human or natural sources.

1

Table 3.18	Soil Lead Levels for the Intersection of Wellington Avenue and St. James Street,	along
	Wellington Avenue and parallelling Canada Metals Limited.	,

Sample Site Location		Lead Level	µg/g	
,	analysis #1	analysis #2	analysis #3	average
71. northeast corner at curb edge	2536	2296	1745	2193±405
72. southeast corner at curb edge	1278	1412	1562	1417±142
73. south side 25 paces east from #72	5402	5644	6682	5910±680
74. north side 25 paces east from #71	3295	3111	3661	3356±280
75. north side 50 paces east from #71	8893	8476	8363	8578±279
76. south side 50 paces east from #72	1900	2334	638	1624±881
77. south side 100 paces east from #72	2930	2204	2056	2397±468
78. north side 100 paces east from #71	10650	8152	8685	9162±1316
79. north side 150 paces east from #71	3218	3168	3304	3230± 69
80. south side 150 paces east from #72	2989	4297	4703	3997±896

Sample site location for the intersection of Wellington Avenue and St. James Street in an industrial section in the St. James area of the City of Winnipeg.



This location also gave a wide range in lead values within the samples for triplicate analyses. The deviation from the average ranged from a low of 2% to a high of 54% with an average deviation of 16% which was higher than normally observed (9 - 11%).

From the study of these eight locations it can be seen that sample site location affects the lead-in-soil level observed, as does sample homogeneity. The last grouping of samples taken from outside Canada Metals Limited, along Wellington Avenue illustrates the first point very well. All of these samples were taken from curb edge and all had some sort of vegetation cover. Samples taken from opposite sides of the street often differed greatly in their lead content, a comparison of the values in Table 3.18 shows a factor of two difference for lead levels from opposite sides of the street for some of the pairs. The precision or lack of precision of the sample is also well illustrated with this group of samples. For each sample taken three subsamples were prepared and analysed. Sample #76 shows a very high degree of imprecision as the standard deviation from the mean value is greater than 50%. On the other hand sample #79 shows a high degree of precision as the standard deviation was under 3% for the triplicate analysis. This range in sample precision was evident in the previous seven location analyses as well. In a number of the other analyses it was evident that a difference of a few feet between sample site locations would give a large difference in the leadin-soil levels observed. This sample precision or lack of precision was not isolated to one particular type of location but was evident in all of the eight locations sampled.

To overcome this problem of sample imprecision the whole sample collected should be meshed to remove large stones and ground to a uniform size.

This ground sample would then be meshed again to ensure that the particles were of an uniform size. Thorough mixing of the sample would ensure sample homogeneity. To ensure a representative sample of the site a pooled sample should be used. The pooled sample could be taken from five to ten areas at that location.

#### 3.7 Correlation with Other Metals

Table 3.19 reports the lead, tin, and antimony values as well as the antimony to tin, lead to antimony, and lead to tin ratios for 51 soil extracts which were re-analysed by atomic absorption spectroscopy for tin and antimony. Tin and antimony were selected for analysis from the X-ray fluorescence data on regional sample #78 which had a very high lead level. This was done to see if a correlation existed between lead and some of the other metals present in the soil sample.

Figure 3.26 illustrates an X-ray fluorescence spectrum of a lead, tin, and antimony standard with each of the peaks identified by channel(energy) position and fluorescence line. Table 3.20 lists the energies of these peaks as well as the peak designation and the channel numbers for the three elements. The spectrum of regional sample #78 (Fig. 3.27) showed a very intense pair of peaks at channel(energy) number 114 and 135 which were identified as being the  $L_{\alpha(1+2)}$  and the  $L_{\beta(1+2)}$  peaks of lead, by comparison with a standard. The  $L_{\gamma 1}$  peak is also evident at channel(energy) number 157. Tin was identified by its peaks at channel(energy) numbers 262 and 295, while antimony was identified by its doublet at channels #274 and #308. The triplet of peaks (channel #333,#375,#385) at the right of the spectrum were identified as belonging to barium while the pair on the 'hill' Table 3.19 Soil levels of lead, tin and antimony

Sample Site Location	Sn	SP SP	Pb	Sb/Sn	Pb <b>/</b> Sn	Pb/Sb
		µg/g				
26. Kingsway and Cambridge Street	1070	260	450	0.24	0.42	1.73
27. Pembina Highway and Taylor Avenue	1030	210	650	0.20	0.63	3.10
28. Osborne Street and Jubilee Avenue	870	210	1930	0.24	2.22	9.19
29. McMillan Avenue and Hugu Street N	670	200	. 390	0.30	0.58	1.95
30. Main Street and River Avenue	· 910	250	1050	0.28	1.15	4.20
31. Lyndale Drive and Balsam Place	640	200	470	0.32	0.73	2.35
32. Broadway Avenue and Kennedy Street	700	160	1250	0.23	1.79	7.81
33. Isobel Street and Cumberland Avenue	1050	230	520	0.22	0.50	2.26
34. Portage Avenue and Ingorsol Street	770	210	1000	0.27	1.30	4.76
35. Portage Avenue and Empress Street	590	170	1400	0.29	2.37	8.24
36. Portage Avenue and Olive Street	860	250	800	0.29	0.93	3.20
37. Portage Avenue and Sturgeon Road	870	220	1060	0.26	1.22	4.82
38. Portage Avenue and the Perimeter Highway	930	210	1220	0.22	1.31	5.81
39. Perimeter Highway at Assiniboia Downs	870	200	2000	0.23	2.30	10.00
40. Ness Avenue and Sturgeon Road	770	190	500	0.28	0.65	2.63

### Table 3.19 continued

	Sample Site Location	Sn	SÞ	РЪ	Sb/Sn	Pb/Sn	Pb/Sb
	· · · · · · · · · · · · · · · · · · · ·		µg/g	, 			
41.	Ness Avenue and Braintree Crescent	850	260	430	0.30	0.51	1.65
42.	Ness Avenue and Duffield Street	910	220	1170	0.24	1.29	5.32
43.	Wellington Avenue and St. James Street	970	260	3600	0.26	3.71	13.85
44,	Winnipeg International Airport	1020	290	1290	0.28	1.26	4.45
45.	Notre Dame Avenue and Bangor Avenue	1260	260	980	0.21	0.78	3.77
46.	Notre Dame Avenue and Sherwin Road	1280	220	430	0.17	0.34	1.95
47.	Notre Dame Avenue and Brookside Boulevard	1180	260	170	0.22	0.14	0.65
48.	Logan Avenue and King Edward Street	1310	250	1200	0.19	0.92	4.80
49.	Logan Avenue and Ryan Road	1220	280	2540	0.23	2.08	9.07
50.	Selkirk Avenue and King Edward Street	1360	230	1290	0.17	0.95	5.61
51.	Jefferson Avenue and Adsum Drive	1300	210	480	0.16	0.37	2.29
52.	Mountain Avenue and McPhillips Street	1030	200	860	0.19	0.83	4.30
53.	Mountain Avenue and Arlington Street	1210	190	840	0.16	0.69	4.42
54.	Main Street and Manitoba Avenue	980	200	1640	0.20	1.67	8.20
55.	Kildonan Park, south of Selkirk Creek Bridge	1170.	220	250	0.19	0.21	1.14

# Table 3.19 continued

Sample Site Location	Sn	Sb	рЪ	Sb/Sn	Pb/Sn	Pb/Sb
	<u> </u>	μg/g				
56. Templeton Avenue and Sly Drive	1270	200	660	0.16	0.52	3.30
57. Henderson Highway and Valhalla Drive	1190	240	1300	0.20	1.09	5.42
58. Roch Street and Kingsford Avenue	1060	180	300	0.17	0.28	1.67
59. Hazel Dell Avenue and Golspie Street	1170	220	200	0.19	0.17	0.91
60. Henderson Highway and Chelsea Avenue	960	200	1550	0.21	1.61	7.75
61. Munroe Avenue and Grey Street	1100	200	2120	0.17	1.93	10.61
62. Watt Street and Thames Avenue	1110	210	490	0.19	0.44	2.33
63. Nairn Avenue and Chester Street	1200	250	890	0.21	0.74	3.56
64. Regent Avenue and Lagimodiere Boulevard	1110	230	2720	0.20	2.45	11.83
65. Regent Avenue and Day Street	1150	200	710	0.17	0.62	3.55
66. Day Street and McMeans Avenue	1270	230	360	0.18	0.28	1.57
67. McMeans Avenue and Redonda Street	140	110	160	0.78	1.14	1.45
68. Regent Avenue and Brewster Street	800	190	410	0.24	0.51	2.16
69. Archibald Street and Provencher Boulevard	730	210	800	0.29	1.10	3.82
70. Archibald Street and Fermor Avenue	940	240	1630	0.26	1.73	6.79

# Table 3.19 continued

Sample Site Location	Sn	Sb	Pb	Sb/Sn	Pb/Sn	Pb/Sb
		μ <b>g/g</b>	1 			
1. St. Anne's Road and Fermor Avenue	920	240	2480	0.27	2.70	10.35
2. St. Anne's Road and LaVallee Avenue	940	220	630	0.23	0.67	2.86
3. St. Mary's Road and Norberry Drive	1010	220	560	0.22	0.55	2,55
4. St. Mary's Road and Avalon Road	830	180	500	0.22	0.60	2.78
75. River Road and Falconer Bay	800	170	150	0.21	0.19	0.88
6. 939-41 Chancellor Drive Garden	870	180	160	0,21	0.18	0.89
			~			
Average value	985	215	1010	0.22	1.05	4.52
Standard deviation	on ±225	±35	±745	±0.04	±0.77	±3.20
Range	140-1360	110-290	150-3600	0.16-0.32	0.14-3.71	0.88-13.85

X-ray Fluorescence Spectrum of

Lead, Tin, and Antimony

ы С 114 100 - L<sub>l</sub> Pb 114 - L<sub>a</sub> Pb 122 – L<sub>η</sub> Pb 135 - L<sub>β</sub> Pb  $156 - L_{\gamma 1} Pb$  $262 - K_{\alpha}$  Sn 160 - L<sub>y2</sub> Pb 295 - K<sub>β1</sub> Sn  $301 - K_{\beta 2}$  Sn 273 – K<sub>a</sub> Sb 273 307 – K<sub>β1</sub> Sb 314 - K<sub>β2</sub> Sb 295 156 307 100 122

line position (channel no.)	element	line designation	1 : •	energy KeV
100	Pb	L <sub>l</sub>	i. T	9.185
114	Pb	$L_{\alpha 1} \& L_{\alpha 2}$		10.552 & 10.454
122	Pb	L <sub>n</sub>		11.354
135	РЪ	L <sub>61</sub> & L <sub>62</sub>		12.625 & 12.613
156	РЪ	L <sub>γ1</sub>		14.760
160	РЪ	L <sub>Y2</sub> & L <sub>Y3</sub>		15.101 & 15.212
262	Sn	K <sub>al</sub> & K <sub>a2</sub>	·	25.251 & 25.047
273	Sb	κ <sub>α1</sub> & κ <sub>α2</sub>		26.379 & 26.101
295	Sn	ĸ <sub>β</sub> ť		28.501
301	Sn	K <sub>β2</sub>		29.104
307	Sb	K <sub>β1</sub>		29.732
314	Sb	K <sub>β2</sub>		30.388

Table 3.20 Tabulation of X-ray fluorescence Data from Figure 3.26

on the left at channel #72 and #79 belong to iron. Figures 3.28 to 3.38 illustrate the X-ray fluorescence spectra of some of a number of the soils from the September 1979 monitering survey. In most cases the lead peaks at channels 114 and 135 are quite low in intensity except for sample #48 from Logan Avenue and Ryan Road, outside of a secondary smelter(North West Smelting and Refining Ltd.). In these samples the antimony peak at 273-4 is evident. However, the tin peak at 262 is often lost in the broad peak at 255, where it often appears as a shoulder.

For the fifty-one samples analyzed, a high level of antimony(average 215  $\pm$  35 µg/g soil) and tin(average 985  $\pm$  22 µg/g soil) was observed. The antimony levels ranged from 110 to 290 µg/g soil while the tin level ranged from 640 to 1360 µg/g soil. One soil had a very low level of 140 µg Sn/g soil as well as a lower antimony level. As a result of this low tin level the the soil gave a very high antimony to tin ratio of 0.78. The average ratio for the other fifty samples was 0.22  $\pm$  0.04 with a range of 0.16 to 0.32. Hopke <u>et al</u>.(147) have reported a value of 2.2  $\pm$  0.3 µg Sb/g roadside dust and a level of 310  $\pm$  54 µg Ba/g roadside dust. Even though barium was not quantitated in this study the X-ray fluorescence spectra indicate a high level of barium in the roadside soils.

If a correlation existed between one of tin or antimony and lead then the lead to tin or antimony ratio would be constant and a plot of the ratio of lead to tin or antimony versus the soil concentration of lead should give a straight horizontal line. As can be seen from the data in Table 3.19 the lead to tin or antimony ratio is not constant and the plots of lead to tin/antimony versus soil lead concentration (Figures 3.39 and 3.40) yield straight lines but with positive slopes.

From these results it appears that there is no correlation between tin

or antimony and lead levels observed. The amounts of tin and antimony appear to be constant in the soils. It may be possible to use the ratio of lead to tin or antimony as an indicator of the degree of lead pollution in the soil, i.e., a Pb/Sb ratio of less than 1.0 would indicate a very low level of lead pollution while a Pb/Sb ratio greater than 8.0 would indicate a high level of lead pollution in the soil.

Figure 3.28

X-ray fluorescence spectrum of soil #78 (Table 3.18 & Figure 3.25) X-ray fluorescence spectrum of soil #1 from the monitoring survey(Chancellor Drive and Chancellor Drive, September 1979 sample)

Figure 3.29

X-ray fluorescence spectrum of soil #26 from the monitoring survey(Kingsway and Cambridge Street,September 1979 sample) Figure 3.30

X-ray fluorescence spectrum of soil #28 from the monitoring survey (Osborne Street and Jubilee Avenue, September 1979 sample)



X-ray fluorescence spectrum of Soil #35 from the monitoring

survey (Portage Avenue and Empress Street, September 1979 sample). X-ray fluorescence spectrum of soil #47 from the monitoring survey (Logan Avenue and King

Figure 3.32

Edward Street, September 1979

sample).

#### Figure 3.33

X-ray fluorescence spectrum of soil #48 from the monitoring survey (Logan Avenue and Ryan Road, September 1979 sample)

#### Figure 3.34

X-ray fluorescence spectrum of soil #53 from the monitoring survey (Main Street and Manitoba Avenue, September 1979 sample)



Figure 3.36

X-ray fluorescence spectrum of soil #63 from the monitoring survey (Regent Avenue and Lagimodiere Boulevard, September 1979 **sample**) X-ray fluorescence spectrum of soil #65 from the monitoring survey (McMeans Avenue and Day Street, September 1979 sample)

#### Figure 3.37

X-ray fluorescence spectrum of soil #75 from the monitoring survey (River Road and Falconer Bay, September 1979 sample)

#### Figure 3.38

X-ray fluorescence spectrum of soil #76 from the monitoring survey (939-41 Chancellor Drive Garden, September 1979 sample)



A plot of Pb/Sn versus the lead level in  $\mu g/g$  for the soils analysed for tin and lead



µg Pb / g soil

A plot of Pb/Sb versus the lead level in  $\mu$ g/g for the soils analysed for antimony and lead

5.-



µg Pb / g soil

Pb Sb

#### CONCLUSION

As shown in this work, elevated levels of lead do exist in the soils of the city of Winnipeg. The high soil lead levels are generally found along heavily trafficked streets or around lead smelting industries (see Plate no. 4.1) . Table 4.1 gives the average lead levels and ranges noted by others as well as those found in this work. On the whole the city-wide average found by this work is much lower than the averages reported for the cities in the British Isles. However, the average from the Provincial study(66) is higher than these cities and two to four times the averages found in this work. This difference in the values is probably due to the bias of the respective works. In this study, the average is based on 75 to 76 samples taken from different parts of the city whereas the provincial value is based on 35 to 36 samples which were taken from 6 locations where 5 to 8 samples were taken. With this sort of sample grouping the average would be biased towards the level where the greater number of samples were taken. For instance, the July average from the Provincial study(66) was 2085 ± 3365  $\mu$ g Pb/g soil with a range of 150 to 19,000  $\mu$ g Pb/g soil. The one sample with a level of 19,000  $\mu$ g Pb/g soil is biasing the average towards the high end.

A survey in the Weston area involving 15 sites yielded an average lead level of 725  $\pm$  745 µg/g soil with a range of 90 to 2820 µg Pb/g soil. The Provincial study(66) yielded an average of 2050  $\pm$  1780 µg Pb/g soil with a range of 440 to 5800 µg Pb/g soil for 9 sites. The provincial average was higher than the average obtained by this work for the same area due to sample groupings and survey time. The Provincial survey was done later in the summer allowing for greater lead accumulation.

An average of 26 sites from the September, 1979 survey along major

City	Population	Average Lev	vel Range	Reference
		µg Pb/g	g soil	
Hong Kong	4,500,000	2974	271 - 19,000	45
Birmingham	1,058,800	1630	160 - 50,000	46
Glasgow	816,265	960	150 - 8,900	47
London	7,028,200	1200	430 - 3,500	48
Manchester	490,000	970	90 - 10,200	49
Winnipeg , July 1979	553,000	2085	150 - 19,000	66
Winnipeg , August 1979	553,000	2065	115 - 18,800	66
Trail	12,000	1320	55 - 5,514	152
Nelson	10,000	192		152
Vancouver	1,172,200	1545		152
Winnipeg, September 1978	553,000	680	30 - 2,920	this work
Winnipeg, April 1979	553,000	410	30 - 4,770	this work
Winnipeg, June 1979	553,000	560 <sup>,</sup>	50 - 2,570	this work
Winnipeg, September 1979	553,000	850	50 - 3,640	this work

# Table 4.1 A Summary of Lead Level Averages and Ranges

# Plate 4.1

A map of lead levels in the city

of Winnipeg, Manitoba

Colour key

lead-in-soil less than 100 µg/g
lead-in-soil between 100 and 200 µg/g
lead-in-soil between 200 and 500 µg/g
lead-in-soil between 500 and 1000 µg/g
lead-in-soil greater than 1000 µg/g



arteries (Portage Avenue, Pembina Highway, Henderson Highway, etc...) gave a value of 1170  $\pm$  650 µg Pb/g soil which is comparible with the British Isles' averages. Even though the overall average is low in comparison to the averages from other major cities, the averages of certain groupings of samples (samples along major arteries) are comparable to these British Isle values. Whatever the lead level is in the soil there exists a danger to small children due to their habit of mouthing objects, dirty or clean. In the city of Winnipeg there are a number of playgrounds and school yards which border on major traffic arteries and the children who play in these areas may be exposed to high levels of lead both in the air and in the soil. This study was primarily concerned with roadside lead levels and it was noted that the use of road salt during the winter caused a decrease in accumulated lead, along roadways where salt was used, during the spring thaw. It is not known whether a similar drop in lead levels occurs at greater distances from the roadway(i.e., in playgrounds) or whether there is an annual accumulation in lead levels at these sites far removed from road salt exposure. At roadside about 50 to 70% of the annual accumulation is generally removed during the spring run-off while the amount removed from a playground is not known.

Needleham(148) in a recent study states that a child absorbs about 50% of the lead consumed. An adult absorbs about 10% of the lead consumed in contrast. He states that both soil and old paint can be sources of lead, especially where the child has a habit of eating foreign substances. He has found a relationship between body-lead levels and learning disabilities exhibited by the child. From the observation of behavioral difficulties and lead dosage he states that there is no 'threshold value' for this effect. As well others(149,150,151) have noted that there is no 'threshold value',

but that the onset of learning disabilities and other effects are of a variable nature with respect to blood-lead levels. Also the nature of the manifestation is variable among individuals.

Elevated levels of lead in the soil are of concern where young children are involved due to their increased uptake of lead as well as their greater sensitivity to the effects of lead poisoning even in subclinical doses.

With a shift in automobile production, from lead-tolerant vehicles to lead-intolerant vehicles, the use and emission of lead(TML and TEL) should decrease as older cars are removed from the road. However, with the energy shortage presently being experienced a shift back to the use of lead to increase fuel mileage and decrease the use of expensive aromatics may be instituted in the future. This shift back to lead useage in automobiles would require a trapping system in the exhaust system to reduce lead emission to a point where it would pose less of a problem to the environment.

The results from the monitoring survey show that elevated lead levels exist in the soil around the three smelters in the city, indicating that the pollution control devices mounted in the plants are not removing all the lead from the air or are not working at all in some cases. During the Weston School hearing it was revealed that Canada Metals Ltd. had suffered a stack knock-down resulting in uncontrolled emission from the plant into the atmosphere. This sort of occurrence is of concern where it affects workers in the area who have little control over their environment. A single occurrence of an elevated lead-in-air level may not manifest itself in an immediate health problem but a number of these occurrences over a period of time, or an exposure to low levels for a prolonged period, may cause an increase in the body burden of lead which at some future date may cause health problems.
Sites bordering major arteries showed elevated levels of lead in soils taken from roadside. The level of lead reflected the volume of traffic along the street. Where traffic volume was low, as on residential streets, the lead level was low, while on major arteries, where traffic volume was high, the lead level was high. This pattern was also observed in the snow samples collected. Samples from major arteries showed a discolouration (grey) within a short period of time while snow from a quiet residential area showed little lead accumulation in the same period of time.

A British Columbia study(152) gave similar results for roadside soils beside heavily trafficked streets in Vancouver. As well the smelter community of Trail was found to have a generally high lead-in-soil level when compared with the non-smelter community of Nelson. This is similar to the situation in Winnipeg around the smelter in the residential area.

Unlike the conclusion reported by Ho (45) and Day <u>et al</u>. (50) a relationship between the traffic volume and lead levels was observed for the city of Winnipeg.

Up to this time, this is the most comprehensive study done on lead-insoil levels for the urban area of Winnipeg. The Provincial study(66) of 1979 was a preliminary study done to see if soil and vegetation could be used to monitor lead levels. In 1980 a more comprehensive study is planned by the Province of Manitoba but the scope of this study is not known.

MacKenzie(153) has reviewed the finding of Schmitt and collegues(152) as well as others and commented on them. He states that current evidence suggests that environmental lead does not greatly affect the intellectual or behavioral development of children, but the possibility of minor or subtle impairment of fine motor or perceptual skills can not yet be excluded. Also he states that there is no evidence of a serious health threat to

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Canadian children from environmental exposure, then in the next sentence states that the data confirming this assumption is scanty and largely limited to hospital records.

The June 23rd,1980 issue of Chemical and Engineering News carried an article relating some of the health problems due to lead and some of the politicking occurring behind the issue(154). The main area of controversy is in the role of lead based paints as a contributing source of lead. One group of researchers says that paint does contribute to the lead observed in childrens' blood while the other group says that it does not.

In short, it appears that there is a great conflict as to the source of the lead observed in the human body as well as its affects on the body. In Canada, not much has been done in regard to identifying the problem and examining the effects. Much of the information available is from the United States and Great Britain. This information is not always in agreement, so it is often difficult to draw conclusions from it for the Canadian situation. This was evident at the Weston School hearings where the Province's medical representative could not or would not give a definite answer to the problem of lead-in-blood and its effects on the body.

In addition to the recommendations below on further soil testing, a more comprehensive study that the two Provincial lead-in-blood studies (66,132) should be undertaken. This study should identify the sources of lead and also identify the effects on the individuals observed and possibly correlate these effects with other factors(physical health, nutrition), as Canadian information in this area is lacking. Winnipeg could serve as a study site because of the three smelters within the city and the number of schools located on or near major traffic arteries as well as schools located in low trafficked residential areas.

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In the light of the results from this work, future work done in this area should investigate what effect the soil has on the deposited lead, the form or chemical composition of the lead before and after deposition, the source of the lead - automotive or smelter, and also the uptake by plants. Some of the following physical factors should be examined to determine their effect on the lead level observed at any given point: grass cover, mechanical disruption of the surface layer, and mixing with lower layers; and run-off from both bare and grass-covered sites. BIBLIOGRAPHY

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