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Date Jan 30, 2002
ABSTRACT

Tetra ethyl lead was used as a fuel additive to improve the octane rating of automotive gasoline until the early 1990s. Consequently soil lead concentrations in excess of the provincially determined standard are present at a number of highway construction sites. Presently, the Ministry of Transportation is obligated to mitigate risks by excavating and disposing of the contaminated soil present at each highway project at considerable cost. This is done without consideration of a significant risk-determining factor, the mobility of the contaminant. The contaminated soils of the 176th Street TransCanada Highway Interchange, Surrey BC were studied to determine whether it would be acceptable to leave lead-contaminated roadside soils in place. Significant lead accumulations of up to 1430 mg/kg were found in the roadside soils of the 176th Street TransCanada Highway Interchange Site. The distribution of lead contamination followed the characteristic distribution given in the literature. Soil lead concentrations decreased rapidly to background levels at 10 m away from the roadside and at the 60 cm depth. Leachant concentrations of all 24 samples (5 depths from 6 borehole sets) subjected to the batch desorption test (24 hours, pH 3.5) were below the 5 ppm method detection limit.

Estimated adsorption capacities of 24 samples (from 6 borehole sets) subjected to the batch adsorption test ranged from 4000-17000 mg/kg. Estimated capacities were 4 to 17 times the highest accumulated soil lead concentration found on the site. Annual source indicators have dropped drastically with the phase out of leaded gasoline, therefore it is unlikely that adsorption capacity will be reached in the near future. The results suggest leaving the lead-contaminated soil in place may be acceptable. A multiple regression analysis with commonly measured soil properties (soil pH, total soil lead, silt and clay fraction, soil carbon) showed estimated adsorption capacity was strongly correlated with soil carbon content. Therefore, organic matter is recommended as a remedial measure in the event of a lead spill.
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1 INTRODUCTION

Tetra ethyl lead was used as a fuel additive to improve the octane rating of automotive gasoline until the early 1990s. Consequently soil lead concentrations in excess of the provincially determined standard are present at a number of highway construction sites. At present the British Columbia Ministry of Environment, Lands and Parks uses the Contaminated Sites Regulation (CSR) to deal with the Ministry of Transportation and Highways' highway construction projects. In order to comply with the Contaminated Sites Regulation the Ministry of Transportation and Highways (MoTH) is required to conduct a site assessment whenever there is a possibility of disturbing contaminated soils. If soil lead concentrations within the construction limits of a project are above the CSR standard, risk mitigation is required. Presently, MoTH is obligated to mitigate risks by excavating and disposing of the contaminated soil present at each highway project at considerable cost. This is done without consideration of a significant risk-determining factor, the mobility of the contaminant. The mobility of lead in the contaminated soils of the 176th Street TransCanada Highway Interchange, Surrey BC was studied. If the mobility is low leaving the contaminated soil in place may be acceptable. The legal requirement for risk mitigation would be met without the costly excavation and disposal of contaminated soil.
2 OBJECTIVE AND SCOPE

To evaluate the mobility of lead in the soils at the 176th Street TransCanada Highway Interchange. Specific tasks are:

1. Identify extent of current Pb contamination in surface and subsurface soils with respect to distance from roadside, depth and longitudinal distribution along the highway.

2. Evaluate the leaching potential of samples by a 24 hour batch desorption test with dilute nitric acid, pH 3.5.

3. Estimate optimum adsorption capacity by 24 hour batch adsorption test.

4. Compare estimated remaining capacity against current input rates to determine whether soil will continue to sorb Pb in the future.

5. Investigate relationships between estimated soil adsorption capacity and:
   - current Pb concentration (total Pb by aqua regia digestion)
   - soil pH
   - silt and clay fraction (<53μm by wet sieving)
   - total carbon content (Leco analysis)
3 LITERATURE REVIEW

3.1 Lead in Roadside Soils

The main source of lead in roadside soils is vehicle emissions. In the early 1920s it was discovered that lead additives overcame the problem of incomplete combustion of gasoline in automobile engines and leaded fuel gasolines quickly became standard. Leaded fuel in Canada was phased out in the early 1990s. However large accumulations of Pb remain in roadside soils worldwide. Even today, vehicles contribute lead to the environment, albeit at much reduced volumes in comparison, in the forms of lead in paint, lead release from tire and brake wear and naturally occurring lead in today’s “unleaded” fuel (US Federal Highways 1998). Elevated soil Pb concentrations have been reported near roads in numerous studies worldwide. The most convincing direct evidence is derived from several studies of Pb isotope ratios, that conclude car exhausts are the main source of the Pb contamination near roads (Alloway, 1995).

Highway soil contamination literature provides both a characteristic distribution of highway soil lead contamination and proposed sources and transport mechanisms. This information was used to focus a search for the most highly contaminated soils at roadway sites. Numerous studies and compilations of studies identify two main features of the characteristic distribution of roadside soil lead contamination. First, elevated lead concentrations are normally restricted to a shallow depth. Second, lead concentrations rapidly decrease in an exponential fashion with distance from the highway (Harrison, 1981, Pagotto et al, 2001, Dierkes and Geiger, 1999, Albasel et al, 1985). This pattern has been attributed to reactions with organic matter, clay minerals, oxyhydroxides and formation of insoluble species. Numerous studies have shown organic matter, clay content and soil pH are important parameters determining the Pb fixation capacity of soils (Adriano, 1986).

The highest soil lead concentrations on a site could be expected in areas with the highest average daily traffic. Driving behavior also plays a role in predicting where peak soil lead concentrations can be found. Tire and brake wear are likely highest near highway off-ramps where vehicles must decelerate to city speed limits. Rapid acceleration from city
speed limits to highway speed limits has been shown to vastly increase lead emission (from 5% to 2000% of the lead consumed by the engine) in a study done before the phasing out of leaded fuel (Harrison 1981). Therefore high soil lead concentrations are likely near highway off-ramps and on-ramps.

Atmospheric deposition and runoff are the main mechanisms proposed for the transport of lead from vehicular emissions to roadside soil. In dry atmospheric deposition contaminants associated with airborne particulate matter deposit directly on soil or vegetation (with the dustfall). In wet atmospheric deposition, precipitation (rain/snow) scavenges particulates, washing them from the atmosphere. Atmospheric deposition accounts for no more than 15% of total lead contribution to soil, with dry and wet deposition each accounting for approximately half of this 15% contribution (Harrison, 1992). The remainder is from runoff.

In runoff, emissions associated with particulate matter accumulate on the road surface and are washed off into the soil during storm events. There is an order of magnitude increase in both lead concentration and total suspended solids (particulates in solution) during storm events versus during dry weather conditions (MacDonald, 1995). Highest soil lead concentrations could be expected in areas receiving the largest volumes of runoff, near culvert outfalls and along adjacent ditches.

In summary the highest soil lead concentrations can be expected:
- at a shallow depth, near the roadside
- where average daily traffic is highest
- near the on-ramp and off-ramp
- near culvert outfalls and along adjacent ditches

Significant and characteristic Pb contamination is expected at the 176th Street site due to the artifact of leaded fuel emissions. To what extent is Pb being released to roadside soils today?

3.2 Trends in Environmental Lead Indicators

Several environmental lead indicators have shown significant decreases in the past 30 years. The US EPA has maintained annual national lead emissions estimates since 1970.
Total estimated emissions as well as emissions for on-road vehicles are shown in Figure 3.2.1 below:

Figure 3.2.1 US Annual National Total and On Road Vehicle Lead Emissions 1970-1999

(EPA, 2001)

Total lead emissions decreased 94% between 1980 and 1999. Lead emissions from on-road vehicles decreased 99.7% between 1980 and 1991 and remained essentially constant until the most recent reporting year, 1999. (EPA, 2001). This was due in large part to regulatory efforts to reduce the lead content of automotive gasoline. Automotive sources accounted for 82% of total emissions in 1980, whereas automotive sources currently account for less than 1% of total emissions. Industrial processes now account for more than 75% of the total emissions and the highest ambient air concentrations are now found in the vicinity of industrial processes (primarily metals processing) (EPA, 2001). The statistic used to track ambient lead air quality is the maximum quarterly mean concentration for each year. The US EPA reports that the national average lead concentrations have decreased 94% between 1980 and 1998 and have stayed constant between 1998 and 1999 (approaching the minimum detectable level) (EPA, 2001).

Brody et al (1994) analyzed the results of the US National Health and Nutrition Examination Survey and found that mean blood levels in people 1 to 74 years of age declined 78% between 1978 and 1991. This decrease was likely the result of the phase out of leaded gasoline and lead in paint.
Environment Canada has compiled annual national mean airborne lead concentrations since 1974. The values from 1974 to 1990, the most recent reporting year are shown in Figure 3.2.2 below:

Figure 3.2.2 Canadian Annual Mean Airborne Lead Concentrations 1974-1990

(Furmanczyk, 1994)

The Canadian annual mean lead concentration decreased 97% between 1974 and 1990. Hall et al. (1999) reported decreasing Pb loading rates between 1970 and 1990 in the Burnaby Lake watershed based on dating a sediment core from Burnaby Lake. Hall et al. (1999) found that median Pb concentrations of street sediments in the Burnaby Lake watershed have decreased from 637 mg/kg (dry) in 1973/74 to 222 mg/kg (dry) in 1990, representing a 67% median difference. Environmental lead indicators show dramatic decreases following the phase out of leaded gasoline. However large accumulations of Pb remain in roadside soils. What is the risk posed by these accumulations?

3.3 Health effects of Lead

Lead is a very toxic element which causes a variety of health effects at low dose levels. Death from lead poisoning, brain damage, kidney damage and gastrointestinal distress are seen from acute (short term) exposure to high lead levels in humans. Chronic (long term) exposure to lead in humans results in effects on the blood (anemia), central nervous
system, blood pressure, kidneys and vitamin D metabolism. Children are particularly at risk because they absorb lead more readily than adults do (ATSDR, 1993). Slowed cognitive development and reduced growth effects have been reported. Animal studies have reported effects similar to those found in humans (ATSDR, 1993). Reproductive effects, such as decreased sperm count in men and spontaneous abortions in women, have been associated with exposure to lead. Prenatal exposure (of the developing fetus) effects include increased risk of pre-term delivery, low birthweight and impaired mental development. Human studies are inconclusive regarding the cancer risk from lead, while animal studies report increases in kidney cancer (EPA, 1993). The US EPA classifies lead as a probable human carcinogen.

Concern over exposure to lead is certainly justified. Roadside soil has been identified as a significant source. However a risk is only present when there is an operable pathway between the source and the receptor. The entire site is bounded by chainlink fences that run along both sides of the TransCanada Highway in the study area. No residential activities, commercial activities or sensitive ecological species are expected in the vicinity of this busy highway interchange. Therefore oral ingestion and dermal contact of soil is not considered as a real risk. Any inhalation of roadside soil would be negligible compared to inhalation of the source vehicular emissions present when traffic conditions make the interchange a virtual parking lot. The remaining pathway to ecological and human impact is leaching. Leaching of Pb from soils is controlled by its sorption behaviour.

3.4 Biogeochemistry of Lead in Soils

The average abundance of lead (Pb) in the Earth’s crust is 15 ppm. Two forms of lead are known in the terrestrial environment; primary lead incorporated into minerals at the time of their formation and secondary Pb from the decay of U and Th. Pb’s primary form in the natural state is galena (PbS). Pb occurs mainly as Pb\(^{2+}\) although it also has an oxidation state of +4. Pb sulfides slowly oxidize during weathering and can form carbonates as well as become incorporated in clay minerals, Fe and Mn oxides and organic matter. Pb can replace K, Ba, Sr and even Ca in minerals and on sorption sites. Most soils are likely to be enriched in Pb, especially in the top horizon, due to widespread
Pb pollution. The worldwide mean Pb concentration for surface soils could be estimated as 25 ppm. Mean surface soil Pb concentrations reported for various countries range from 3 to 189 ppm with levels above 100 ppm probably representing the impact of pollution (Kabata-Pendias, 2001).

Soil lead concentrations have reached as high as 21000 ppm at the most heavily polluted sites worldwide. These sites are usually involved in metal processing and battery processing. Roadside soil Pb concentrations range from 960 to 7000 ppm in the US (Kabata-Pendias, 2001).

Pb is reported to be the least mobile heavy metal. This is supported by the relatively low Pb concentrations in natural soil solutions. Pb is associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. The solubility of Pb can be greatly decreased by liming. A high soil pH may precipitate Pb as the hydroxide, phosphate or carbonate and promote the formation of stable Pb-organic complexes. Lowering pH may increase Pb solubility, but this mobilization is usually slower than accumulation in the soil organic matter (Kabata-Pendias, 2001). Pb has limited mobility except when soluble organic complexes are formed or when the soil-Pb exchange capacity approaches saturation. Methyllead species have been formed in the laboratory, however it has not been verified unequivocally that these processes occur in the environment (Fergusson, 1990). The lead sorption capacities for 3 pure clays: illite, montmorillonite and kaolinite were reported as 16640, 5000 and 3000 mg Pb/kg respectively (Hildebrand and Blum, 1975). The lead sorption capacities for 11 experimental humic soils ranged from 3768 to 10780 mg Pb/kg (Miller et al., 1975).

Several studies have related soil organic matter content to soil adsorption of lead. Ge et al. (2000) studied soils from three inactive railway yards in Montreal, Quebec. They found that Pb was largely immobilized at the soil particle surface because of high pH or organic matter content. Arnfalk et al. (1996) used the batch adsorption test to determine the Pb adsorption capacity of 14 different mineral and soil types. They found that adsorption capacity was positively correlated with organic content. Soldatini et al. (1976) used the batch adsorption test to determine the Pb adsorption capacity of 12 soils ranging in organic matter, clay and carbonate content. They found that adsorption capacity was positively correlated with organic content. Keijzer et al. (1991) conducted column and
batch leaching tests on soils from 19 locations in the Netherlands. They found the leachability of lead was significantly (negatively) correlated with the organic content of a soil. Sauve et al. (2000) reported that soil organic matter can either enhance or inhibit adsorption depending on other soil properties (pH, cation exchange, competing cations etc.). Soil humic acids can increase adsorption, reducing dissolved metal concentrations. However soil organic matter can increase dissolved organic matter and fulvic acid concentrations. This can increase total dissolved metal concentrations via complexation reactions in the soil solution, resulting in higher metal mobility. Sauve et al. (2000) conducted adsorption tests on 2 pedogenic oxides, ferrihydrite and leaf compost. Their results showed that increasing organic matter decreased Pb adsorption. They believed this was due to organic matter blocking the reactive sites on Fe oxides and formation of dissolved organo-lead complexes. Under certain conditions organic matter may maintain soil lead in a more soluble form than would be the case in the absence of organic matter.

3.5 Soil Sorption Processes

The mobility of a metal is limited by its ability to sorb onto the solid phase. When a contaminant is associated with the solid phase, it is not known if it was absorbed or precipitated as a 3-dimensional molecular structure on the surface of a solid. (Sposito, 1984) A generic term devoid of any mechanism used to describe the partitioning of aqueous phase metals to a solid phase is sorption. Sorption encompasses all of the above processes. In most natural systems, sorption is controlled by the electrostatic surface charge of the mineral phase. Most soils have net negative charges originating from permanent and variable charges. Permanent charge results from the substitution of lower valence cations for higher valence cations in the mineral structure. Permanent charge constitutes a majority of the charge in unweathered soils and is not affected by solution pH. Variable charge results from the ionization of surface functional groups. The magnitude and polarity of variable charge changes with a number of factors, including pH. As pH increases the surfaces becomes increasingly more negatively charged. The pH where the surface has a zero net charge is
known as the pH of zero-point-of-charge. Variable charge is the dominant charge of 
oxyhydroxides and organic matter (EPA, 1999).

Metal sorption in a natural soil, comprised of mineral and organic fractions, may involve 
any of three processes: cation exchange (adsorption), chemisorption (absorption) and 
precipitation (McBride, 1994).

Cation exchange is a reversible process where one ionic species on a solid phase is 
replaced by another ionic species taken from an aqueous solution in contact with the solid 
(EPA, 1999). This involves reversible types of bonding such as ion-dipole, dipole-dipole 
and van der Waals force interactions. In ion-dipole interactions an uncharged molecule is 
electrostatically attracted to a charged molecule because it possesses a dipole; a 
separation of charge within the uncharged molecule. These uncharged molecules are also 
owned as polar molecules. In dipole-dipole interactions two polar molecules interact by 
orienting their oppositely charged dipoles toward one another. Van der Waals 
interactions involve weak bonding between molecules with instantaneous dipoles 
(McBride, 1994). In general, cations of higher concentrations displace cations of lower 
concentrations, and higher valence cations displace the lower valence cations (Tan, 
1998). Organic matter and clay minerals are both high in cation exchange capacity. 
Organic matter accounts for up to 80% of the cation exchange capacity in many surface 
soils (Stevenson, 1982).

Chemisorption is a less reversible process where one ionic species in aqueous solution is 
specifically and chemically bonded to a charged surface species. The adsorbed metal 
becomes part of the solid surface. This involves ionic and covalent bonding. Ionic 
bonding is a strong, non-directional type of bonding involving a transfer of electrons 
between two atoms of very different energies. Covalent bonding is a strong, directional 
type of bonding involving a sharing of electrons between two atoms of similar energies. 
Chemisorption is usually slower than cation exchange and is weakly affected by the ionic 
strength of the aqueous phase (McBride, 1994; Sparks, 1995).

Precipitation may be seen as a continuation of adsorption and absorption. At low surface 
coverages surface complexation (such as adsorption and absorption) dominates and as 
surface coverage increases nucleation occurs on the surface. As surface loading further 
increases, surface precipitation becomes the dominant mechanism. When the precipitate
covers the entire surface it is referred to a "surface precipitate" and when the precipitate grows away from the surface it is known as a "surface cluster". (Sparks, 1995)

The adsorption isotherm is used to describe batch adsorption data. The sorbed amount of metal is plotted against the equilibrium concentration of heavy metal. The sorbed amount of heavy metal is calculated using the following equation (Sparks, 1995),

\[
q = \frac{V(C_i - C_f)}{m}
\]

where \( q \) is the mg of Pb sorbed per kg of soil, \( C_i \) and \( C_f \) are the initial and final solution concentrations in ppm Pb, \( V \) is the solution volume and \( m \) is the mass of soil.

Adsorption can be described by four general types of isotherms (S, L, H, C) shown in Figure 3.5.1 below (adapted from Sparks, 1995):

Figure 3.5.1 S, L, H, C general isotherm types

S,L,H,C general adsorption isotherm types

![Figure 3.5.1 S, L, H, C general adsorption isotherm types](image)

The S isotherm indicates a low affinity of soil for metal at low concentrations and a high affinity at higher concentrations. Eventually though, affinity decreases as sorption sites are filled. The L isotherm indicates a high affinity of soil for metal at low concentrations
and decreasing affinity as sorption sites are filled. The H isotherm indicates strong
interactions between soil and metal such as inner-sphere complexes. The C isotherm
indicates partitioning of soluble metal without any specific bonding between Pb and soil.
Pb sorption generally follows Langmuir and Freundlich adsorption isotherms (Fergusson,
1990). The Freundlich equation is

\[ q = KC^n \]

where \( q \) is the mg of Pb sorbed per kg of soil, \( K \) is a constant known as distribution
coefficient, \( C \) is final solution concentration in ppm Pb and \( n \) is a correction factor
(Sparks, 1995).

The Langmuir equation is

\[ q = \frac{KMC}{1 + KC} \]

where \( q \) is the mg of Pb sorbed per kg of soil, \( K \) is a constant related to binding strength,
\( M \) is the maximum amount of Pb that can be adsorbed (monolayer coverage) and \( C \) is
final solution concentration in ppm Pb (Sparks, 1995).

Pb is emitted from automobiles as water soluble PbBrCl which rapidly transforms into
PbSO₄ in the atmosphere. The exact chemical species of Pb in soil has not been
determined unequivocally either because 1) it is in the form of amorphous compounds
after only a few years to reach equilibrium or 2) it is adsorbed to strong adsorption sites
in the soil and not present in inorganic compounds (Chaney et al., 1988).
Often in interpreting adsorption isotherms a change in the slope or trend is attributed to
surface precipitation. However this is not entirely correct since surface complexation and
precipitation can occur simultaneously and often are hard to distinguish. Precipitation
can form on soil surfaces before precipitation of metal in bulk solution (Sparks, 1995).
Precipitation in bulk solution occurs when a new solid phase is formed in solution. This occurs when the product of the metal ion and ligand concentrations exceeds their solubility product (Tan, 1998). Precipitation is a strongly pH dependent process. For example at pH 4, lead precipitates if soluble concentrations exceed 4000 ppm. At pH 8, lead begins to precipitate at only 200 ppm (EPA, 1999).

### 3.6 Bioavailability

If mobile, soluble Pb is not adsorbed or precipitated it becomes available for uptake by plants. Plants can absorb and translocate available Pb from nutrient solution (Jaworski, 1978). Pb absorbed by a plant tends to accumulate in the root. The amount of Pb adsorbed by a plant relative to the concentration of Pb in soil solution is known as bioavailability. One approach to estimating the environmental impact of Pb in soils is to determine the bioavailability of the Pb in contaminated soil. Even when ingested, only a portion of the total Pb in soil is absorbed by the receptor of concern. Extraction of a heavy metal by chelating ion exchange resin is an attractive bioavailability determination method because the resin is embedded in the soil and the soil properties remain essentially unchanged. Therefore the amount of heavy metal adsorbed by the resin is closely related to the potential plant uptake (Lin et al, 2001).

Vaidyanathan and Nye (1966) used ion exchange resin paper placed on the soil surface as a standard adsorbing sink. The diffusive flux of nutrient cations in soils was measured in order to assess the bioavailability of the nutrient cations to the plant.

Jing and Logan (1991) developed a chelating resin procedure to predict plant uptake of Cd by municipal sewage sludge applied to land. Sludge suspensions were equilibrated with Chelex 100 resin placed in dialysis tubing. Resin-extractable Cd was compared with total sludge Cd, Cd$^{2+}$ in solution, total Cd and Cd$^{2+}$ in equilibrium with dilute Ca(NO$_3$)$_2$ and Ca(NO$_3$)$_2$/EDTA solutions and uptake by the sudax plant grown in sewage amended soil. The incremental increase in cation solubility between Ca(NO$_3$)$_2$ and Ca(NO$_3$)$_2$/EDTA solutions was used to estimate metal activity in soil-sludge systems. Resin extractable Cd was highly correlated with total Cd and Cd$^{2+}$ in equilibrium with dilute
Ca(NO₃)₂ and Ca(NO₃)₂/EDTA solutions and uptake by the sudax plant. Resin Cd was correlated to a lesser extent with total sludge Cd and Cd²⁺ in solution.

Yang et al. (1991) embedded a cation/anion exchange resin capsule in a saturated soil paste to measure nutrient ion diffusion. Fluxes determined by this technique were compared with results from the center-ring resin, resin batch and standard soil test techniques.

Lin et al. (2001) laid Amberlite IRC-718 resin flatly between two cells of soil paste dosed with heavy metal solutions to determine heavy metal bioavailability in contaminated soil. A more general theoretical solution to the diffusion process was developed to represent the short and long-term heavy metal diffusion in soil. Cd was found to have 2000x the bioavailability of Cu and Pb, while Zn was somewhere between these two extreme cases.

Lower pH was found to strongly favor desorption but did not influence effective diffusion in the soil, since pH does not strongly affect diffusion of ions in solution. The effective diffusion coefficients obtained for the four metals were strongly dependent on temperature but not dependent on initial heavy metal concentration or soil type.

Bioavailability is beyond the scope of this study and will not be explored further in this study.
4 MATERIALS AND METHODS

4.1 Site Selection

The TransCanada Highway is one of the busiest traffic corridors in the Greater Vancouver Regional District. Only sections of the TransCanada Highway within the Greater Vancouver Regional District were considered because sites beyond these boundaries would not have been a reasonable commuting distance from the UBC campus lab. Average daily traffic count was used as the first criteria for locating sites along the TransCanada Highway where the most highly contaminated highway soil could be found. According to B.C. Traffic Volumes Data from 1990-1994 the 176th Street section of the TransCanada Highway had an average daily traffic count of 81920 vehicles. Sites with planned construction were eliminated because of possible interference with this study. Sites with higher average traffic speeds were eliminated because soil contamination tends to be more diffuse at these sites. A preliminary study of lead mobility was conducted at the Willingdon and TransCanada Interchange (Li, 2000) located in the valley lowland soil region. To expand the database on contaminated highway soil mobility a site in the Surrey upland soil region was selected, the 176th Street and TransCanada Highway Interchange.

4.2 Site Description

The 176th Street (Pacific Highway Route 15) and TransCanada Highway (Route 1) Interchange is located in the northeast corner of the Surrey Municipality. (See Figure 4.2.1, 4.2.2 and 4.2.3 below) The center of the sites has a latitude of 49 degrees, 10 minutes, 54 seconds and a longitude of 122 degrees, 43 minutes, 59 seconds. The northwestern boundary of the site is bounded by a mixture of residential and undeveloped land. The northeastern boundary is bounded by undeveloped land. The southwestern boundary is bounded by a patch of agricultural land, the remainder is bounded by Tynehead Park. The grounds of Anniedale Elementary School bound the southeastern boundary. Access to the entire site is limited by a chainlink fence that runs
along the both sides of the TransCanada Highway interchange. No residential or commercial activities or sensitive ecological species are expected at the site.

Figure 4.2.1 Location of Site Within Greater Vancouver Region Indicated with a Star
Figure 4.2.2 Aerial photo of 176th Street TransCanada Highway Interchange Location
4.3 Sampling Program

4.3.1 Surface Sampling Program

The objectives of the surface sampling program were:

1. to identify the extent of current Pb contamination in surface soil with respect to distance from roadside and longitudinal distribution along the highway
2. to search for the most highly contaminated soils present at the site to be studied at depth in the subsequent drilling program.

The areas of highest traffic volume on the site were identified from MOTH records. The areas of highest runoff volume were identified from visual inspection of surficial topography and drainage patterns during storm events. These were the areas, based on the literature review, where the highest soil lead concentrations could be expected. The surface sampling program was conducted in three phases. An iterative approach was
taken for the surface sampling program. Results from previous phases were used to
design subsequent phases. The four phases are described in Table 4.3.1 below:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Focus</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>high traffic areas, on-ramp, off-ramp, culvert outfalls and adjacent ditches</td>
</tr>
<tr>
<td>B</td>
<td>one selected culvert outfall and adjacent ditch</td>
</tr>
<tr>
<td>C</td>
<td>along the TransCanada Highway only, roadside, ditch samples</td>
</tr>
</tbody>
</table>

Locations of each of sample point are shown on Figure 4.3.1 below:

Figure 4.3.1 Surface Soil Sampling Locations at the Highway Interchange
(1:10000 SCALE)

Surface Sampling Locations A, B, C
At each of the sample points indicated in the surface sampling plan map, a 250 mL plastic jar provided by Cantest Ltd. commercial lab was filled with soil and submitted for total lead, pH and water content determination.

4.3.2 Drilling Program

The objective of the drilling program was to produce samples of the most highly contaminated soils identified in preliminary surface sampling. Sufficient volume was taken so that planned laboratory investigations of lead mobility could be completed. Four drilling techniques were investigated.

Table 4.3.2 Comparison of Drilling Techniques for Soil Cores

<table>
<thead>
<tr>
<th>Drilling Technique</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger</td>
<td>cheap, fast</td>
<td>disturbed stratigraphy</td>
</tr>
<tr>
<td>76.2 mm Split Spoon Sampler</td>
<td>undisturbed stratigraphy, large sample volume</td>
<td>loss of dry gravel soils on withdrawal</td>
</tr>
<tr>
<td>44.5 mm Geoprobe chosen technique</td>
<td>undisturbed stratigraphy, capped against loss on withdrawal, sealed for storage (tube)</td>
<td>small sample volume</td>
</tr>
<tr>
<td>Sonic drill</td>
<td>undisturbed stratigraphy, capped against loss on withdrawal, sealed for storage (bag), large sample volume</td>
<td>limited availability, cost</td>
</tr>
</tbody>
</table>

The Auger was ruled out because a sample would be indiscriminately cross-contaminated between depths. Planned laboratory mobility investigations require discrete 5cm depth samples to study depth trends. The Split Spoon Sampler is not capped at the bottom; therefore it is prone to loss of drier, more gravelly soils on withdrawal. Also, the sample produced is open to the atmosphere, thus discrete samples must be transferred to closed containers on site to prevent oxidation. Geoprobe samples are sealed within a plastic tube; however the planned laboratory tests would require 4 cores to be taken per sample point to produce adequate sample volume. Sonic samples are sealed, large volume samples however the availability of the Sonic drill rig is limited. The approach chosen
was to use the Geoprobe and take 4 cores per sample point. The location and topographic profile of the sample points are shown on Figures 4.3.2 and 4.3.3 below:

Figure 4.3.2 Location of Borehole Sets 1 to 8 at the Highway Interchange (lines represent the two 0, 5, 10 m lines of boreholes sets; 2,3,4 and 5,6,7) (1:10000 SCALE)
Figure 4.3.3 Topographic Profile of Borehole Sets
Numbers refer to locations along transects shown in Figure 4.3.2

Topographic Profile of Borehole Set Locations

SKETCH ONLY
Figure 4.3.4 Borehole set location marked with paint
Figure 4.3.5 Drill rig maneuvers into position
Figure 4.3.6 Cores are extracted
Figure 4.3.7 Cores are cut open and laid out
Figure 4.3.8 Cores are measured
At each of the 8 sample points, 4 Geoprobe cores arranged in a square or line were taken according to utility considerations at each sample point. A spacing of 0.6 m was used between each core. The spacing was chosen based on the recommendations from the Geoprobe contractor, Mud Bay Drilling, who recommended 0.3 m as the closest cores could be taken before holes begin to collapse. A spacing of 0.6 m would allow a second set of cores to be taken between cores if necessary. The cores were split open on site and cut every 5 cm from the 0-120 cm depth, based on the grassy topsoil as the reference zero depth. The discrete 5 cm cuts were collected from the 4 cores and placed into double ziploc bags. In the lab the core sections in each bag were broken up by hand and mixed thoroughly. 5 g was then taken from each bag and submitted to Cantest for total lead determination.
4.4 Laboratory Materials and Methods

4.4.1 Total Lead determination by Cantest

Total lead was determined by the aqua regia digestion procedure (APHA et al., 1995). Approximately 10 mL nitric acid and 20 mL hydrochloric acid were added to a 5 g soil sample and heated until brown fumes disappeared and the solution volume was reduced to approximately 10 mL. The solution was cooled, filtered and the supernatant was analyzed on a Varian SpectrAA 220 Atomic Absorption Spectrometer.

Quality control procedures included:
1. A minimum of 2 blanks run per batch
2. A minimum of 1 in 10 samples done in duplicate
3. 1 certified reference material (NIST Montana soil) run per batch

4.4.2 Batch Adsorption Test Method

The method is based on the EPA (1992) method. The purpose of the batch adsorption test is to determine the optimum retention capacity of a soil. The method consists of several major steps:
1. Clean glassware and containers. All equipment was rinsed 3 times before and after submerging for 24 h in the acid bath and finally rinsed once with distilled water.
2. Make up lead dosing solutions. All solutions were prepared by dissolving lead nitrate crystals in distilled water adjusted to pH 3.5 with nitric acid. This was done to keep Pb cations in solution. Lead precipitates in bulk solution if the aqueous concentration exceeds 4000 ppm at pH 4 (EPA, 1999). The highest concentration used on field samples was 3000 ppm. The concentration of all lead dosing solutions was verified on the AAS before they were used to dose the soil samples, this was the initial concentration. Ionic strength is an important consideration in modeling field conditions. Measurements of the dosing solutions showed the ionic strengths to be within an order of magnitude of the ionic strength of 0.01 M sodium nitrate background electrolyte solution recommended by Harter and Naidu (2001) as a worldwide convention for simulation of field soil-solution conditions. (Appendix 1)
3. Prepare soil samples. Soil samples were air dried to within 0.005 g of constant weight (48 h in practice) and disaggregated by hand to pass through the 2 mm sieve. Water content determinations were by oven drying at 110 °C for 16 h.

4. React samples. A 1:10 soil:solution ratio was used. 4 g of soil and 40 mL of solution was placed into a 50 mL polypropylene centrifuge tube. The tubes were rotated end over end for 24 h at 22 rpm on a Dayton Model 4Z134 mechanical rotator. This was done in all cases at the ambient room temperature of the lab, 25 °C.

5. Centrifuge and filter supernatant. After 24 h the tubes were centrifuged at 3200 rpm for 15 minutes and the floating fractions were removed with a test tube prefiltter.

6. Analyse supernatant for equilibrium Pb concentration and pH. Pb determinations were done on a Thermo Jarrell Ash Atomic Adsorption Spectrometer Model 957 (AAS) calibrated to 0, 100, 200, 300, 400, 500 ppm standard solutions prepared from 1000 ppm Fisher reference standard. pH determinations were done on an Orion model 1 420A pH meter calibrated to standard pH 2, 4 and 7 solutions. The standard pH solutions were verified against litmus paper.

Adsorption isotherms were produced for Clinoptilolite, Illite-Grundite and Kaolinite Hydrite UF standard clays to verify the procedure was performed correctly. (Appendix 2) In order to determine the effect of water content on adsorption, tests were run on samples from 176th Street at both natural and air dried water content and compared. A shallow, medium and deep depth were selected from boreholes 5, 6 and 7. No significant difference was seen between natural water content versus air dried samples. (Appendix 2) Therefore adsorption isotherms were produced for air dried and 2 mm samples from boreholes 2-7.

Discrete 5 cm depths were selected from each borehole based on the distribution of total lead in each borehole and each depth was dosed at 8 different concentrations (0, 250, 500, 750, 1000, 1500, 2000, 3000 ppm).

Adsorption tests were run on the following samples:

- borehole 2: 0-5, 5-10, 15-20, 40-45, 60-65
- borehole 3: 0-5, 5-10
borehole 4: 0-5, 5-10
borehole 5: 0-5, 5-10, 15-20, 40-45, 60-65
borehole 6: 0-5, 5-10, 15-20, 40-45, 60-65
borehole 7: 0-5, 5-10, 15-20, 40-45, 50-55

Quality control procedures included:
• 1 in every 8 samples was done in replicate.
• Known additions were added to 1 in every 8 samples.
• 2 sets of duplicate standard soil samples were run with every batch, Kaolinite dosed at 500 ppm and Illite-Grundite dosed at 2000 ppm.

4.4.3 Batch Desorption Test Method

The method is based on the EPA (1992) method. The purpose of the batch desorption test is to determine the leaching potential of soil samples. The conditions and equipment of the test were identical to the batch adsorption test. Air dried, 2 mm samples were reacted at a 1:10 soil:solution ratio for 24 h with dilute nitric acid, pH 3.5 to simulate acid rain. The supernatant was centrifuged, filtered and analyzed for Pb concentration and equilibrium pH.

4.4.4 Preparation for <53 μm fraction, pH and C% determination

All samples were air dried for 48 h, thoroughly mixed and disaggregated by hand and run through the 2 mm sieve. The coarse fraction was weighed and discarded.

4.4.5 <53 μm fraction determination

The method is based on the Kettler et al. (2001) method. 15 g of 2 mm air dried, 2 mm soil was dispersed using 4% sodium metaphosphate, stirred thoroughly for at least 5 minutes to suspend all particles and left overnight. The soil suspension was then washed through a 53 μm sieve until the washings were clear. The suspension passing the sieve
was collected and left to settle overnight. The soil solution was then dried to a constant weight at 105 °C. The settled silt and clay fraction was measured to 4 decimal places on the analytical balance. The <53 μm (silt and clay) fraction was defined as the weight of the silt and clay fraction over the total weight of the 15 g sample.

4.4.6 Soil pH determination

The method is modified from the Krzic and Lavkulich (1999) method. pH was measured at a 1:2 soil:solution ratio in distilled water. 10 g of 2 mm soil was placed in a disposable wax paper cup and 20 mL of distilled water was added. The suspension was stirred for 30 minutes and left to settle for 30 minutes. The Orion model 1 420A pH meter was calibrated to fresh pH 4 and 7 buffer solutions and the pH was measured.

4.4.7 Carbon content determination

Carbon content (C%) was determined with a Leco induction furnace (model CN 2000) with a carbon analyzer. 1 g of 2 mm soil was placed in a crucible with iron chip (chemical accelerator) and ignited in a current of oxygen. Carbon dioxide, carbon monoxide and sulphur dioxide are formed. The sulphur dioxide was extracted through a sulphur trap and the carbon monoxide was converted to carbon dioxide in a catalytic convertor. The volume of the remaining gases, carbon dioxide and oxygen, were measured. Then the carbon dioxide was removed with KOH solution. The volume of oxygen was then measured and the volume of carbon was found by difference. The volume of carbon dioxide was converted into percent carbon by temperature and pressure correction.
5 RESULTS

5.1 Distribution of Total Pb, Soil pH, Silt and Clay Fraction and Carbon Content in Surface Samples

In order to clarify presentation of the results of the surface samples, a location matrix was created. Sample locations are arranged in relative spatial orientation to each other (see Figure 4.3.1). The sample locations were divided into 4 transects along the highway: westbound ditch samples, westbound roadside samples, eastbound roadside samples and eastbound ditch samples as shown in Table 5.1.1 below.

Table 5.1.1 Location Matrix for Soil Sample Collection

<table>
<thead>
<tr>
<th>Eastbound Ditch Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastbound Roadside Samples</td>
<td>c11d</td>
<td>c10d</td>
<td>a5</td>
<td>b5</td>
<td>b4</td>
<td>b3</td>
<td>b3</td>
<td>b1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Westbound Roadside Samples</td>
<td>c11r</td>
<td>c10r</td>
<td>c9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a3</td>
<td>a1</td>
<td>a2</td>
<td>c8r</td>
<td>c7r</td>
<td>a4</td>
<td></td>
</tr>
<tr>
<td>Westbound Ditch Samples</td>
<td>c2d</td>
<td>c1d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.1.1 presents the distribution of Pb concentrations in surface samples. There was no trend from west to east or north to south. Lower values were expected in the ditch samples since they were farther away from the roadside, however the samples also likely received more stormwater runoff. Most values were between 30 and 400 mg Pb/kg soil. One high value of almost 1400 mg Pb/kg soil was recorded at sample location c8d. The numerical results of the surface samples are given in Appendix 3.
Figure 5.1.1 Pb concentrations in surface soil samples by location along the TransCanada Highway

Figure 5.1.2 below shows the distribution of soil pH values in surface samples. There was no trend from west to east or north to south. The pH values were uniform almost all values were between pH 4.5 and 5.5. One high value of pH 7 was recorded at sample location a3, this sample was analyzed again with the same result. The numerical results of the surface samples are given in Appendix 3.
Figure 5.1.2 pH values of surface soil samples by location along the TransCanada Highway

Figure 5.1.3 below shows the distribution of silt and clay fraction values in surface samples. It appears that some areas near the middle of the interchange had higher silt and clay fractions. The numerical results of the surface samples are given in Appendix 3.
Figure 5.1.3 % Silt and clay fraction of surface soil samples by location along the TransCanada Highway

Figure 5.1.4 below shows the distribution of carbon in surface soil samples. There was no trend from west to east or north to south. Almost all values were below 7%. One high value of almost 17% was recorded at sample location a5. The numerical results of the surface samples are given in Appendix 3.
Figure 5.1.4 % Carbon content in surface soil samples by location along the TransCanada Highway

5.2 Distribution of Total Pb, Soil pH, Silt and Clay fraction and Carbon Content in Core Samples

4 cores were taken in each borehole set Discrete 5 cm cuts were taken from each core within a set and mixed in the lab into composite samples for every 5 cm interval within each borehole set. Figure 5.2.1 below presents the distribution of Pb in each borehole set. Borehole sets 2, 3, 4 and 5, 6, ,7 are both line transects of 3 sets 0, 5 and 10 m away from the roadside. Pb concentrations in all boreholes dropped to background levels by the 60 cm depth. Roadside samples had the deepest peaks and 10 m samples had the shallowest peaks. Surprisingly the highest concentration was found in borehole 3, a 5 m sample however an areal integration of the borehole 2 curve shows a greater total accumulation
of Pb. Clearly higher levels of Pb were found in the first line of borehole sets (2,3,4) than in the second line of borehole sets (5,6,7). The numerical results of the depth samples are given in Appendix 4.

Figure 5.2.1 Vertical profiles of Pb in each borehole set
Figure 5.2.2 below shows the distribution of soil pH values in each borehole set. pH values were uniform, almost all values were between pH 4 and pH 5.

Figure 5.2.2 Vertical profiles of soil pH in borehole sets

Figure 5.2.3 below shows the distribution of silt and clay fraction values in each borehole set. Borehole sets 3, 4 and 6 showed an increase in silt and clay fraction with depth.
Figure 5.2.3 % Silt and Clay Fraction with Depth in Boreholes

Figure 5.2.4 below shows the distribution of carbon content values in each borehole set. In all borehole sets the carbon content was highest in the surface horizons and decreased with depth.
5.3 Results of Leaching Test on Borehole Samples

In all 24 samples tested, the leachant concentrations were below the 5 ppm method detection limit. The method detection limit was defined as the median lab blank concentration plus three times the standard deviation of the well-characterized blank concentration (E. Hall, Dept. of Civil Engineering, UBC, Vancouver, B.C, pers. comm.). This was in spite of the high total Pb concentrations found in the soil which included the 4 highest values of 1160, 841, 459 and 407 mg Pb/kg. Thorough mixing and low soil:solution ratio in the leaching test likely overestimated leaching. More sites were
available for attack by the nitric acid than would occur in the field (EPA, 1999; Harter and Naidu, 2001). The results suggest a low likelihood of significant leaching even under aggressive acid conditions and with a conservative test.

5.4 Results of Adsorption Test on Borehole Soil Samples

The lead adsorption isotherms and equilibrium pH data for boreholes 2,3,4,5,6,7 are given below in Figures 5.4.2 to 5.4.13.

Figure 5.4.2 Adsorption data for soil sections from borehole 2
Figure 5.4.3 Equilibrium pH data for soil sections from borehole 2
Figure 5.4.4 Adsorption data for soil sections from borehole 3

Figure 5.4.5 Equilibrium pH data for soil sections from borehole 3
Figure 5.4.6 Adsorption data for soil sections from borehole 4

BH 4 Adsorption data

q (mg Pb retained/kg soil) vs. Equilibrium Pb conc (ppm)

Figure 5.4.7 Equilibrium pH data for soil sections from borehole 4

BH 4 pH data

pH vs. Equilibrium Pb conc (ppm)
Figure 5.4.8 Adsorption data for soil sections from borehole 5

![BH 5 Adsorption Data](image)

Figure 5.4.9 Equilibrium pH data for soil sections from borehole 5

![BH 5 pH data](image)
Figure 5.4.10 Adsorption data for soil sections from borehole 6

Figure 5.4.11 Equilibrium pH data for soil sections from borehole 6
Figure 5.4.12 Adsorption data for soil sections from borehole 7

Figure 5.4.13 Equilibrium pH data for soil sections from borehole 7
All boreholes followed an L isotherm to differing degrees. Depths with higher capacities had q values that just begin to plateau, whereas depths with lower capacities reached an asymptotic value well before the highest equilibrium concentration (3000 ppm initial dose). Q values at the highest equilibrium concentration (3000 ppm initial dose) for each of the 24 depths studied are shown in Figure 5.4.14 below:

Figure 5.4.14 Estimated adsorption capacity with depth in all boreholes

The q values ranged from 4x to 17x the highest 1160 mg/kg total soil Pb concentration found on site. This highest value represented the accumulation of all Pb sources between the construction of the interchange in the 1960s to the present, an estimated 30 years of leaded gasoline emissions. With Canada's final phase out of leaded gasoline in the 90s, source inputs have decreased dramatically. Therefore it is unlikely that sorption capacity will be reached in the near future.

The soil pH, solution pH at the 0 ppm dose and solution pH at the 3000 ppm dose are given in Figure 5.4.15 below.
In all cases the equilibrium pH started above the soil pH and decreased to slightly below pH 4. As more Pb cations are sorbed onto the soil surface, they replace more H\(^+\) cations, lowering the pH. All dosing solutions were adjusted to pH 3.5 before reaction. Lowering pH has two effects: increasing the concentration of competing cations and decreasing the surface negative charge as less dissociation of H\(^+\) cations occurs from functional groups (Sparks, 1995). Both effects likely caused an underestimation of adsorption capacity.

The batch adsorption test procedure has been criticized because in general it results in higher estimates of adsorption capacity than in flow through column tests. The thorough mixing and low soil:solution ratio make more adsorption sites accessible than would occur in the field (EPA, 1999; Harter and Naidu, 2001). Mixing was necessary to ensure uniformity of results. The soil:solution ratio was chosen to ensure sufficient solution for analysis and to make results comparable to other studies within this overall research program (Li, 2000). The batch method used in this study simulates static conditions in the micropores while the flow through column method simulates flow conditions in macropores. Both micropores and macropores are present in most soils. Therefore a
flow through column test is recommended as an area of further study in order to simulate conditions in macropores.

It is useful to fit adsorption isotherms to the 2 common empirical equations introduced in the Biogeochemistry of Lead literature review section, the Freundlich and the Langmuir equations. All 24 adsorption isotherms were fitted to both equations and their coefficients are given in Table 5.4.1 below.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Freundlich Equation</th>
<th>Langmuir Equation</th>
<th>R squared</th>
<th>R squared</th>
<th>Rf - RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-0-5</td>
<td>1759.8, 0.175, 0.935, 0.006</td>
<td>7633.6, 0.977, -0.042</td>
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<td>2-5-10</td>
<td>399.3, 0.304, 0.934, 0.002</td>
<td>5000.0, 0.971, -0.036</td>
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<td>2-15-20</td>
<td>278.8, 0.396, 0.940, 0.001</td>
<td>8000.0, 0.956, -0.016</td>
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<td>7092.2, 0.999, 0.043</td>
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<tr>
<td>2-60-65</td>
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<td>6896.6, 0.960, -0.037</td>
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<tr>
<td>5-15-20</td>
<td>99.5, 0.457, 0.939, 0.001</td>
<td>4902.0, 0.912, 0.027</td>
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</tr>
<tr>
<td>5-40-45</td>
<td>322.6, 0.321, 0.954, 0.002</td>
<td>4807.7, 0.968, -0.014</td>
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<td></td>
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<tr>
<td>5-60-65</td>
<td>525.3, 0.281, 0.965, 0.003</td>
<td>5291.0, 0.984, -0.018</td>
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<tr>
<td>6-0-5</td>
<td>2633.8, 0.273, 0.939, 0.021</td>
<td>17211.7, 0.994, -0.054</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6-5-10</td>
<td>2676.7, 0.241, 0.988, 0.009</td>
<td>17064.8, 0.985, 0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-15-20</td>
<td>685.3, 0.399, 0.986, 0.003</td>
<td>16447.4, 0.957, 0.029</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6-40-45</td>
<td>156.1, 0.480, 0.969, 0.001</td>
<td>8403.4, 0.955, 0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-60-65</td>
<td>575.7, 0.329, 0.957, 0.003</td>
<td>8547.0, 0.981, -0.024</td>
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<td></td>
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</tr>
<tr>
<td>7-0-5</td>
<td>139.8, 0.655, 0.742, 0.004</td>
<td>12360.9, 0.948, -0.207</td>
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<td></td>
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</tr>
<tr>
<td>7-5-10</td>
<td>3470.8, 0.207, 0.997, 0.012</td>
<td>16863.4, 0.983, 0.014</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7-15-20</td>
<td>661.2, 0.364, 0.991, 0.003</td>
<td>12345.7, 0.969, 0.022</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-40-45</td>
<td>615.6, 0.357, 0.973, 0.003</td>
<td>11001.1, 0.970, 0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-50-55</td>
<td>147.0, 0.522, 0.911, 0.001</td>
<td>12953.4, 0.821, 0.091</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Neither equation was statistically better at describing the data according to a t-test of the difference in R squared values (Rf - RI) at the 95% confidence interval. In all cases the M value capacity estimate was greater than the q value at the 3000 ppm dose. To be conservative the 3000 ppm dose estimate is used as the estimate of capacity. To what
degree is adsorption capacity correlated to total Pb concentration, soil pH, silt and clay fraction, and total carbon content?

5.5 Regression of Soil Characteristics Against Adsorption Capacity

The adsorption test is by far the most involved procedure so a relationship between estimated capacity and the more easily obtainable parameters would be useful in estimating capacity. In addition the correlations found should indicate the important factors that contribute to adsorption capacity. This would be useful in suggesting remedial options in the event of a Pb spill.

The data that were subject to regression analysis are given in the table below:

Table 5.5.1 Regression Data Set to Determine Relationships between Soil Characteristics and Adsorption Capacity

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>soil pH</th>
<th>%&lt;53um</th>
<th>Leco C%</th>
<th>Qi</th>
<th>q3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-0-5</td>
<td>4.99</td>
<td>9.66</td>
<td>3.11</td>
<td>77</td>
<td>7353</td>
</tr>
<tr>
<td>2-5-10</td>
<td>4.95</td>
<td>10.83</td>
<td>3.2</td>
<td>96</td>
<td>4424</td>
</tr>
<tr>
<td>2-15-20</td>
<td>4.99</td>
<td>11.47</td>
<td>2.18</td>
<td>459</td>
<td>6571</td>
</tr>
<tr>
<td>2-40-45</td>
<td>5.03</td>
<td>9.28</td>
<td>0.169</td>
<td>51</td>
<td>4501</td>
</tr>
<tr>
<td>2-60-65</td>
<td>5.25</td>
<td>17.53</td>
<td>0.315</td>
<td>0</td>
<td>5941</td>
</tr>
<tr>
<td>3-0-5</td>
<td>4.61</td>
<td>27.91</td>
<td>3.88</td>
<td>841</td>
<td>6650</td>
</tr>
<tr>
<td>3-5-10</td>
<td>4.41</td>
<td>24.33</td>
<td>3.03</td>
<td>1160</td>
<td>7113</td>
</tr>
<tr>
<td>4-0-5</td>
<td>4.44</td>
<td>35.23</td>
<td>4.07</td>
<td>51</td>
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<tr>
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<td>4.41</td>
<td>48.59</td>
<td>2.14</td>
<td>20</td>
<td>10130</td>
</tr>
<tr>
<td>5-0-5</td>
<td>4.31</td>
<td>10.08</td>
<td>5.07</td>
<td>77</td>
<td>8001</td>
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<tr>
<td>5-5-10</td>
<td>4.37</td>
<td>8.79</td>
<td>3.57</td>
<td>407</td>
<td>5501</td>
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<td>5-15-20</td>
<td>4.81</td>
<td>8.70</td>
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<td>5.39</td>
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<td>0.0537</td>
<td>0</td>
<td>4235</td>
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<td>5-60-65</td>
<td>5.28</td>
<td>6.30</td>
<td>0.0924</td>
<td>0</td>
<td>4749</td>
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<tr>
<td>6-0-5</td>
<td>4.41</td>
<td>15.13</td>
<td>11.4</td>
<td>99</td>
<td>17046</td>
</tr>
<tr>
<td>6-5-10</td>
<td>4.4</td>
<td>14.95</td>
<td>4.89</td>
<td>72</td>
<td>16584</td>
</tr>
<tr>
<td>6-15-20</td>
<td>4.09</td>
<td>14.22</td>
<td>4.77</td>
<td>5</td>
<td>14727</td>
</tr>
<tr>
<td>6-40-45</td>
<td>4.35</td>
<td>11.11</td>
<td>0.87</td>
<td>0</td>
<td>6633</td>
</tr>
<tr>
<td>6-60-65</td>
<td>4.46</td>
<td>38.60</td>
<td>0.388</td>
<td>0</td>
<td>7602</td>
</tr>
<tr>
<td>7-0-5</td>
<td>4.23</td>
<td>13.60</td>
<td>5.61</td>
<td>67</td>
<td>11075</td>
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<tr>
<td>7-5-10</td>
<td>4.21</td>
<td>14.99</td>
<td>5.5</td>
<td>28</td>
<td>16976</td>
</tr>
<tr>
<td>7-15-20</td>
<td>4.02</td>
<td>19.21</td>
<td>5</td>
<td>0</td>
<td>11226</td>
</tr>
<tr>
<td>7-40-45</td>
<td>4.04</td>
<td>11.29</td>
<td>2.59</td>
<td>0</td>
<td>9794</td>
</tr>
<tr>
<td>7-50-55</td>
<td>4.12</td>
<td>6.57</td>
<td>1.49</td>
<td>0</td>
<td>9199</td>
</tr>
</tbody>
</table>

NOTE:
%<53um = silt and clay fraction

52
Leco C% = % total soil carbon
qi = initial Pb concentration in mg/kg
q3000 = mg Pb sorbed by kg of soil at 3000 ppm Pb initial dose

Table 5.5.2 shows that absorption capacity (q3000) is significantly correlated with C% and pH. pH and C% are also correlated with one another. Significant correlations are underlined in Table 5.5.2.

Table 5.5.2 Correlation matrix of soil characteristics and Pb adsorption

<table>
<thead>
<tr>
<th></th>
<th>soil pH</th>
<th>%&lt;53um</th>
<th>Leco C%</th>
<th>qi</th>
<th>q3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>soil pH</td>
<td>1.00000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%&lt;53um</td>
<td>-0.22604</td>
<td>1.00000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leco C%</td>
<td>-0.51746</td>
<td>0.04363</td>
<td>1.00000</td>
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<td></td>
</tr>
<tr>
<td>qi</td>
<td>-0.00131</td>
<td>0.15999</td>
<td>0.08290</td>
<td>1.00000</td>
<td></td>
</tr>
<tr>
<td>q3000</td>
<td>-0.63718</td>
<td>0.19590</td>
<td>0.76224</td>
<td>-0.19687</td>
<td>1.00000</td>
</tr>
</tbody>
</table>

Scatterplots of each parameter vs q3000 were plotted in Figures 5.5.1-4.

Figure 5.5.1 Adsorption capacity vs soil pH
Figure 5.5.2 Adsorption Capacity vs silt and clay fraction

Figure 5.5.3 Adsorption capacity vs carbon content
An outlier value for C% in terms of C% value range was identified, however this value followed the overall relationship between C% values and q3000 values. Various curvilinear models were tested based on the scatterplot results. For each model the statistically insignificant variables were eliminated one by one and the regression equation was recalculated. This process was repeated until all variables were significant at the 95% confidence level. The final models were then compared for $R^2$ or $I^2$ values and standard error of estimate values. The “best” equation found was equation 1:

$$q_{3000} = -10206 + 737107(1/pH) + 934(C\%)$$  \hspace{1cm} (1)

$R^2 = 0.668$ \hspace{1cm} Standard error of estimate = 2488

As expected q was positively correlated with C%, a measure of organic matter content. The negative correlation with pH is due to the correlation with C% and the narrow range of soil pH values, which meant that effectively all samples were at the same pH. The adsorption edge where adsorption increases dramatically due to precipitation is at pH 3-4, all samples were above the adsorption edge.

The same procedure was then repeated for the same data set with the outlier removed resulting in equation 2:

$$q_{3000} = 5035 - 4.014(q_i) + 1484(C\%)$$  \hspace{1cm} (2)

$R^2 = 0.603$ \hspace{1cm} Standard error of estimate = 2520
The negative correlation with qi (initial soil Pb concentration in mg/kg) suggests that samples with higher current Pb loadings had lower total adsorption capacities. This would suggest the relatively small Pb loading influences surface properties and the total capacity. However the scatterplot of qi vs q does not support this and in fact highlights the highly skewed distribution of qi values. There are 20 values are under 100 and 4 values are unevenly distributed between 200 and 1200.

The $R^2$ values of these equations can not be compared because this statistic depends on the magnitude of the regression coefficient, number of observations and range of the independent variables, all of which are different. Equation 1 has the lower standard error of estimate. The lack of fit test for both equations (Figures 5.5.5 and 5.5.6) do not indicate bias.
Figure 5.5.6 (q – estimated q) vs estimated q for equation 2

Figure 5.5.7 shows neither equation is significantly better at estimating q or yields consistently greater (or smaller) q values.
Equation 1 had similar precision (standard error of estimate), however the distribution of pH values on which the equation is based has a more uniform distribution as compared to the qi values on which equation 2 is based. In addition pH is much easier to measure than qi in terms of time, cost and materials. Therefore equation 1 was chosen as the final equation. However the narrow pH range of the data set means that the equation would not be valid for estimating q when site soil pH conditions are beyond this narrow range. Clearly the results suggest organic matter application would be effective in the event of a Pb spill.
5.6 QA/QC Data for Adsorption Tests

Table 5.6.1 Variation in standard soil samples run with each batch or adsorption tests

<table>
<thead>
<tr>
<th>Kaolinite UF Hydrite dosed at 500 ppm</th>
<th>Illite-Grundite dosed at 2000 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>q (mg/kg)</td>
<td>%deviation from average</td>
</tr>
<tr>
<td>2650</td>
<td>8.7</td>
</tr>
<tr>
<td>2650</td>
<td>8.7</td>
</tr>
<tr>
<td>2566</td>
<td>5.2</td>
</tr>
<tr>
<td>2558</td>
<td>4.9</td>
</tr>
<tr>
<td>2324</td>
<td>-4.7</td>
</tr>
<tr>
<td>2400</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

Standard soil samples run with each batch were not significantly different between batches.

Table 5.6.2 Accuracy of lead measurement in soil samples

<table>
<thead>
<tr>
<th>Pb concentrations (ppm)</th>
<th>Actual</th>
<th>Measured</th>
<th>Actual - Measured</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>104</td>
<td>-4</td>
<td>-4.0</td>
<td></td>
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<tr>
<td>100</td>
<td>102</td>
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<td>-2.0</td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>119</td>
<td>-5</td>
<td>-4.4</td>
<td></td>
</tr>
<tr>
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<td>-7.4</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>117</td>
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<td>-0.9</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>140</td>
<td>-6</td>
<td>-4.5</td>
<td></td>
</tr>
<tr>
<td>119</td>
<td>124</td>
<td>-5</td>
<td>-4.2</td>
<td></td>
</tr>
<tr>
<td>127</td>
<td>120</td>
<td>7</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>119</td>
<td>-4</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>133</td>
<td>138</td>
<td>-5</td>
<td>-3.8</td>
<td></td>
</tr>
<tr>
<td>139</td>
<td>145</td>
<td>-6</td>
<td>-4.3</td>
<td></td>
</tr>
<tr>
<td>133</td>
<td>138</td>
<td>-5</td>
<td>-3.8</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>134</td>
<td>-6</td>
<td>-4.7</td>
<td></td>
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<tr>
<td>101</td>
<td>108</td>
<td>-7</td>
<td>-6.9</td>
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<td>114</td>
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<td>-1.8</td>
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<td>-1.5</td>
<td></td>
</tr>
<tr>
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<tr>
<td>125</td>
<td>123</td>
<td>2</td>
<td>1.6</td>
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</table>
Known additions recovery was within 10 ppm and 10% relative difference.

Table 5.6.3 Replicate analysis of soil samples for lead

<table>
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<tr>
<th>q (mg/kg)</th>
<th>Sample ID</th>
<th>1</th>
<th>2</th>
<th>1-2</th>
<th>% difference</th>
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</thead>
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<td>0.0</td>
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<td>0</td>
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<td>0</td>
<td>9.1</td>
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</table>

60
Replicate q values were all within 10% relative difference.
6 Discussion

Soil Pb concentrations decreased rapidly to background levels at 10 m away from the roadside and at the 60 cm depth. This is consistent with the characteristic distribution given in highway soil contamination literature, where elevated lead concentrations are normally restricted to a shallow depth and rapidly decrease in an exponential fashion with distance from the highway (Harrison, 1981, Pagotto et al, 2001, Dierkes and Geiger, 1999, Albasel et al, 1985). The highest surface lead concentration of 1430 mg/kg was within the range of 960 to 7000 mg/kg given for roadside soil Pb concentrations in the US (Kabata-Pendias, 2001). Leachant concentrations of all the 24 samples subjected to the batch desorption test were below the 5 ppm Pb method detection limit. This is consistent with the low Pb concentrations reported in natural soil solutions (Kabata-Pendias, 2001). Estimated adsorption capacities of 24 samples subjected to the batch adsorption test ranged from 4000-17000 mg/kg. These values are within the range of the lead sorption capacities reported for 3 pure clays: illite, montmorillonite and kaolinite (16640, 5000 and 3000 mg Pb/kg respectively) (Hildebrand and Blum, 1975) and for 11 experimental humic soils (3768 to 10780 mg Pb/kg) (Miller et al., 1975).

Estimated capacities were 4 to 17 times the highest soil Pb concentrations found on the site. This represented the accumulation of Pb emissions until the present day. Given that annual source inputs have dropped drastically with the phase out of leaded gasoline, it is unlikely that adsorption capacity will be reached in the near future. The results suggest leaving the Pb contaminated soil in place may be acceptable. The multiple regression analysis showed total adsorption capacity was strongly correlated with total soil carbon content. This is consistent with the many studies that have found correlations between organic matter and adsorption capacity (Adriano, 1986). Therefore, organic matter is recommended as a remedial measure in the event of a Pb spill.
Conclusions and Recommendations for Further Study

Significant Pb accumulations of up to 1430 mg/kg were found in the roadside soils of the 176th Street TransCanada Highway Interchange Site. The distribution of Pb contamination followed the characteristic distribution given in the literature. Soil Pb concentrations decreased rapidly to background levels at 10 m away from the roadside and at the 60 cm depth. Leachant concentrations of all the 24 samples subjected to the batch desorption test were below the 5 ppm Pb method detection limit. Estimated adsorption capacities of 24 samples subjected to the batch adsorption test ranged from 4000-17000 mg/kg. Estimated capacities were 4 to 17 times the highest soil Pb concentrations found on the site. This represented the accumulation of Pb emissions until the present day. Given that annual source inputs have dropped drastically with the phase out of leaded gasoline, it is unlikely that adsorption capacity will be reached in the near future. The results suggest leaving the Pb contaminated soil in place may be acceptable. The multiple regression analysis showed total adsorption capacity was strongly correlated with total soil carbon content. Therefore, organic matter is recommended as a remedial measure in the event of a Pb spill. Topics recommended for further study include:

- Multi-metal and multi-ligand effects on Pb mobility (not considered in this study other than the unknown concentrations of metals and ligands already present in the soil samples studied)
- Bioavailability of soil Pb
- Simulation of flow through leaching conditions (lysimeter or leaching column)
References


McCallum, Don. 1995. *An Examination of Trace Metal Contamination and Land Use in an Urban Watershed*. MASc Thesis. UBC Civil Engineering, Vancouver, BC.


Appendix 1 Ionic Strength of Solutions Used in Adsorption Test

0.01M NaNO₃ is the background electrolyte concentration recommended by Harter and Naidu (2001) to simulate field ionic strength. Ionic strength is measured by electrical conductivity and converted by the equation

\[ I = 0.0127 \times EC \]

where \( I \) is the ionic strength in moles per L and \( EC \) is electrical conductivity in dS/m. The electrical conductivities of 0.01M NaNO₃ the Pb dosing solutions is shown in the table below.

<table>
<thead>
<tr>
<th>Pb solutions adjusted to pH 3.5</th>
<th>EC (μS/cm)</th>
<th>I (moles/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ppm Pb</td>
<td>32</td>
<td>0.0004</td>
</tr>
<tr>
<td>500 ppm Pb</td>
<td>660</td>
<td>0.008</td>
</tr>
<tr>
<td>1000 ppm Pb</td>
<td>1160</td>
<td>0.015</td>
</tr>
<tr>
<td>2000 ppm Pb</td>
<td>2150</td>
<td>0.027</td>
</tr>
<tr>
<td>3000 ppm Pb</td>
<td>3050</td>
<td>0.039</td>
</tr>
</tbody>
</table>

Pb dosing solutions were within the order of magnitude of the recommended ionic strength for simulation of field conditions.
Appendix 2 Standard Clay Isotherms

Figure A.2.1 Adsorption isotherm for illite-grundite

Figure A.2.2 Adsorption isotherm for kaolinite hydrite UF
Appendix 3 Natural Water Content Versus Air Dried Water Content Isotherms

Figure A.3.1 Adsorption isotherms for natural water content vs air dried soil samples from borehole 5, 5 to 10 cm depth

Figure A.3.2 Adsorption isotherms for natural water content vs air dried soil samples from borehole 5, 15 to 20 cm depth
Figure A.3.3 Adsorption isotherms for natural water content vs air dried soil samples from borehole 5, 40 to 45 cm depth

$q$ values were not significantly different between air dried and natural water content samples reacted for 24 hours. $q$ values were not significantly different between air dried samples reacted for 24 and 28 hours.
Appendix 4

Table A.4 Surface Sample Results: Pb, pH, Silt and Clay fraction, Carbon Content

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>soil pH</th>
<th>%&lt;53um</th>
<th>Leco C%</th>
<th>qi (mg/kg)</th>
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</thead>
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<td>3.1</td>
<td>71</td>
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<tr>
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<td>5.9</td>
<td>89</td>
</tr>
<tr>
<td>a3</td>
<td>7.02</td>
<td>17.5</td>
<td>1.2</td>
<td>134</td>
</tr>
<tr>
<td>a4</td>
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<td>10.7</td>
<td>2.5</td>
<td>381</td>
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<tr>
<td>a5</td>
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<td>24.7</td>
<td>16.1</td>
<td>64</td>
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<td>b1</td>
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<td>3.2</td>
<td>32</td>
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## Appendix 5

Table A.5.1 Depth Sample Results: Pb, pH, Silt and Clay fraction, Carbon Content

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<th>Sample ID</th>
<th>soil pH</th>
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<th>Leco C%</th>
<th>qi (mg/kg)</th>
<th>q3000 (mg/kg)</th>
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NOTE: Sample ID 2-0-5 indicates soil sample from borehole set location 2, 0 to 5 cm depth in core.