# **RETENTION CAPACITY AND ENVIRONMENTAL MOBILITY OF Pb IN SOILS ALONG HIGHWAY CORRIDOR**

#### LORETTA Y. LI

*Department of Civil Engineering, The University of British Columbia, 6250 Applied Science Lane, Vancouver, Canada V6T 1Z4 (e-mail: lli@civil.ubc.ca; Tel.:* +*604-822-1820, Fax:* +*604-822-6901)*

(Received 4 October 2004; accepted 9 September 2005)

**Abstract.** Although lead (Pb) emissions have dropped drastically with the phase-out of tetra-ethyl lead (TEL) as a fuel additive, Pb deposited along highway corridors continues to be of concern because of its toxicity. This paper provides comprehensive data on the extent and distribution of Pb in roadside soils, Pb interaction with soils as a function of soil composition, the retention capacity of soil based on batch adsorption tests, the retention mechanism of Pb using selective sequential extraction, the potential for mobility using batch desorption tests with simulated rain and winter road salt, and column leach tests. Highway soils on high-traffic sections near Burnaby, Canada were found to have Pb accumulations up to 1628 mg/kg soil. Contamination was mainly in the top 0.3 m, with concentrations rapidly decreasing to the background level at a depth of 0.6 m. The top layer contained more organic material and had a high adsorption capacity. Highway soils were found to have 3–10 times higher Pb adsorption capacities than the amount currently deposited. Selective sequential extraction indicated low exchangeable Pb in highway soils. Batch desorption tests with leaching solutions of  $H_2O$  (pH 5.5),  $HNO<sub>3</sub>$  solution (pH 4.0) and aqueous NaCl solution (0.17 M) indicate low likelihood of significant leaching. Selective sequential extraction, leachate extraction and desorption tests show that Pb has limited mobility in highway soil.

**Keywords:** highway pollution, leachability, mobility, Pb, retention, sequential extraction

## **1. Introduction**

Lead (Pb) accumulation in roadside soils has been studied since the 1970s, but it is still a subject of major importance because Pb is toxic, adversely affecting the human nervous and blood systems, while also being toxic to marine life and other non-human species and reducing crop yields. Although tetra ethyl lead was phased out during the 1970s as a fuel additive to improve the octane rating of automotive fuels and has been banned for more than 10 years in North America, there has been a marked increase in the number of motor vehicles in developing countries, some of which continue to use leaded gasoline. In the US, the USEPA (1996) estimated that 4 to 5 million metric tons of Pb were emitted from automobile tailpipes as fine dust particles prior to the phase-out of leaded gasoline. This remains in soils and represents approximately 75% of the total Pb added to gasoline. The remaining 25% was deposited on internal engine surfaces as dust particles, with much of this also eventually ending up in the soil.

Water, Air, and Soil Pollution (2006) 170: 211–227 DOI: 10.1007/s11270-005-9002-0

<sup>C</sup> Springer 2006

212 L.Y. LI

Studies in the last four decades have demonstrated significant accumulation of automobile-associated trace metals in soils and vegetation near highways, exponentially decreasing with distance (Cannon and Bowles, 1962; Lagerwerff and Specht, 1970; Gish and Christensen, 1973; Wheeler and Rolfe, 1979; Rodriguez-Flores and Rodriguez-Castellon, 1982; Harrison and Johnston, 1985; Hewitt and Rashed, 1991; Mao and Chen, 1996; Chatterjee and Banerjee, 1999; Bhuie *et al.*, 2000). These studies characterized temporal and spatial contamination patterns of Pb in surface soils; they focused primarily on the top 150 mm at distances of no more than 100 m from the roads. Despite the studies examining the concentration of trace metals, particularly Pb, with distance from roads, there remain gaps in our current knowledge. Few studies have examined the distribution of Pb within the first 8 m from the road where it is primarily located. Deroanne-Bauvin *et al.* (1987) reported on ten years of Pb deposition monitoring near highways. Surface soil samples every 5 m along a highway at distances of 0–40 m from the road edge found that Pb in the soil was primarily within the first 5 m; the concentration decreased almost to the background level at 10 m. Recently, Oztas and Ata (2002) studied the relationship between Pb accumulation in soils and the distance from the road edge, and defined vertical and horizontal distribution patterns of Pb accumulation. Soil samples were collected on three transects separated by 1 km intervals and perpendicular to the motorway, at distances of 1–500 m from the road at incremental depths between 0 and 200 mm. Fakayode and Olu-Owolabi (2003) measured heavy metal concentrations for topsoil (0–50 mm) samples taken 5, 15, 30 and 50 m from the road.

Various sequential extraction procedures have been used extensively in an effort to estimate metal speciation, retention and mobility, and potential plant availability. In past work, sequential extraction has been used to characterize geochemical properties and to speciation of heavy metals (Zhang *et al.*, 1999; Sutherland *et al.*, 2000; Turer *et al.*, 2001). Backstrom *et al.* (2004) examined metal leachability and anthropogenic signals in roadside soils, estimated from sequential extraction using Tessier (1987) procedures. Gracia and Millan (1998) applied DTPA extraction to determine the available metal contents and acid digestion for total metal contents. Only soluble, exchangeable and chelated metal species in the soils are mobile and potentially mobile, and hence readily available for uptake by plants. Turer *et al.* (2001) used the extraction steps reported by Sposito *et al.* (1982) in an effort to determine the mechanisms controlling both retention and remobilization of metals on five soil samples. Sequential soil extraction indicated less Pb associated with organic matter than expected based on the correlation of metals to % organic carbon (C) in the soil. Measurement of organic C in the residues of the sequential extraction steps revealed that much of the carbon was not removed for the conditions studied.

Despite this work, there has been a lack of systematic and comprehensive studies on the fate of Pb along highways, fundamental parameters that control the partitioning and fate of heavy metals along highway corridors, the adsorption capacity

of roadside soils, and the leachability of Pb related to changes caused by acid rain and winter conditions with high concentrations of road salt. In additions, retention mechanisms have received little attention.

The objectives of this investigation were: (1) to identify the extent of Pb contamination in surface and subsurface soils as a function of depth and distance from the roadside; (2) to investigate retention and potential mobility of Pb using batch adsorption and batch desorption tests; (3) to investigate relationships between estimated soil adsorption capacity and current Pb concentration, and soil physical and chemical properties; (4) to investigate Pb-soil interaction, in particular the retention mechanism. Overall, the results of this study provide a comprehensive data-base with respect to Pb at a representative highway site, helping to elucidate mechanisms and providing information for engineers and regulators who must deal with contamination of roadside soils by heavy metals.

### **2. Materials and Analytical Methods**

## 2.1. BACKGROUND INFORMATION OF THE STUDIED SITE

The interchange at the intersection of Willingdon Ave and Highway #1 in Burnaby, British Columbia was constructed in 1963, together with shouldering of ramps and highway alignment. Ramps and shoulders were constructed from local sand and gravel imported by truck. Local organic material was used for soil surfacing, and grass was then seeded. The traffic counts for eastbound and westbound were 68,232 and 69,431 vehicles per day, respectively, for all 3 lanes as of June 2002. The truck count, based on visual count in 1996 was 27% of average daily traffic. The highway intersection is situated at an elevation of 137 m. The daily mean temperature of 10.3  $°C$ . The annual rainfall is 1850 mm, and the annual snowfall is 60 mm.

# 2.2. SAMPLING AND ANALYSIS

Sampling was carried out in mid-June 1999. Seventeen boreholes of 3 transects (A, B, and C) were drilled to a depth of 2.2 m, and samples were taken every 0.1 m. The sampling locations are shown in Figure 1. Samples from Transect A were labeled as A1 to A9, Transect B with B1 to B4, and Transect C with C1 to C4. Location of Transects C and B represent similar traffic number and speed, while Transect A represents lower traffic number and speed. Of the 17 borehole locations, A5, A8, B2 and C2, were selected for detailed study because their soil characteristics were representative of the profiles sampled. Both samples B2 and C2 are 2.3 m from the asphalt surface of the road; whereas samples A5 and A8 are 3.5 and 9.5 m from the asphalt surface of the road; the examination of these samples will provide





*Figure 1*. Sampling locations and soil profiles at chosen interchange and topography of three sampling profiles in Greater Vancouver Regional District in British Columbia, Canada.

information of the extent of Pb pollution due to traffic, speed and distance from highway surface.

A total of 139 soil samples from 17 borehole locations were analysed for total metals using digestion in nitric acid and metals analysis by Inductively Coupled Plasma (ICP). Soil samples from A5, A8, B2 and C2, were used for leachate analysis according to the Leachate Extraction Procedure (LEP) described in the B.C. Waste Management Act, Special Waste Regulation (1992). This procedure is very similar to the better-known US TCLP procedure. In addition, duplicate water samples were collected from the 6 ditches, direct run-off from the road as indicated in Figure 1. These non-filtered water samples were analyzed for total Pb and dissolved Pb concentrations using Atomic Absorption Spectrophotometry (AAS).

X-ray diffraction (XRD) was employed for mineralogical characterization of the fine fraction of the soil, particle-size  $\langle 74 \mu \text{m} \rangle$ . Slides were prepared as described by Kittrick and Hope (1963). XRD analysis was then conducted over a range of 3–70◦ 2θ with CuKα radiation on a standard Siemens D5000 Bragg-Brentan Diffractometer and a Siemens Kristalloflex (Germany). Sieve analysis was used to measure particle size distributions for particles  $>53 \mu$ m. Surface areas of samples were determined using the B.E.T. method for the external area of soil, and the ethylene glycol monoethyl ether (EGME) method for the total surface area (Sheldrick,

1984). The organic content in the surface and subsurface soil was determined by a Leco induction furnace equipped with a carbon analyzer.

Heavy metal adsorption isotherms for the soil were determined from batch equilibrium tests (USEPA, 1987) with a 1 g:10 mL soil:solution ratio. Lead nitrate solutions of various concentrations at pH 3.6 ensured that no precipitated forms of Pb were introduced into the adsorption process. Duplicate samples were prepared for each concentration, and a kaolinite sample of known adsorption properties was also analysed to verify the accuracy of the test and for  $QA/QC$ . The nominal  $Pb^{2+}$ ion concentrations (expressed in mol/ $m<sup>3</sup>$ ), used to determine adsorption isotherms for all samples from boreholes A5, A8, B2 and C2, at depths from 0 to 2.2 m were 0, 0.24, 0.48, 0.72, 1.21, 2.41, 3.62, 4.83, 9.65 mol/m<sup>3</sup>. Samples were shaken for 24 h and then centrifuged for 15 min at about 2000 rpm in a Beckman GS-6 centrifuge to separate the solids and supernatant. Residual Pb concentrations in solution were then determined using a Video 22 Thermo Jarrell Ash AA/AE Spectrophotometer-Model 957 (AAS); pH was measured with an Orion model 1 420A pH meter.

The heavy metal sorption concentration for the sorbent is calculated from

$$
q_a = \frac{(C_i - C_f)V}{M} \tag{1}
$$

where  $q_a$  is the Pb sorption concentration (mg/kg) obtained from a batch adsorption test,  $C_i$  is the initial concentration of the lead nitrate solution (mol/m<sup>3</sup>),  $C_f$  is the equilibrium (final) Pb concentration after 24 h of shaking (mol/m<sup>3</sup>), *V* is the volume of lead nitrate solution  $(dm<sup>3</sup>)$  in the batch test, and *M* is the dry mass of the soil sample (kg).

Selective Sequential Extraction (SSE) was used to investigate the Pb retention mechanism and to evaluate the potential mobility of heavy metals in surface/subsurface soils along the highway. The extraction and rinse sequence, described in detail by Li  $(2002)$ , was as follows:  $(0)$  Initial – distilled water;  $(1)$ Exchangeable cations extraction  $-1$  M KNO<sub>3</sub>; (2) Weak acid extraction (to remove metals ionically bound to amorphous materials)  $-1$  M sodium acetate (NaOAc) at pH5.0; (3) Weak acid/complexing agent extraction – 0.04 M hydroxylamine hydrochloride (NH<sub>3</sub>OH·HCl) in 25% (v/v) HOAc heated to 96  $\pm$  3 °C; (4) Organic matter digestion – 0.02 M nitric acid (HNO<sub>3</sub>) and 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at pH2 heated to  $85 \pm 2$  °C, then, addition of 5 mL of 3.2 M NH<sub>4</sub>OAc in 20% (v/v)  $HNO<sub>3</sub>$ ; and (5) Residual digestion –  $HNO<sub>3</sub>$ . The total digestion was consistent with the SSE results, i.e. the summation of all the extraction Pb concentrations was very nearly equal to the total digestion result. Total digestion procedures were the same as in the final step of the SSE procedure, i.e. digestion by  $HNO<sub>3</sub>$ .

Batch equilibrium desorption tests were carried out to evaluate the potential mobility of the Pb, following the same procedures as the batch adsorption test (USEPA, 1987). Distilled water (pH5.5) and nitric acid (pH4) were used as the leaching solutions to simulate normal precipitation and acid rain conditions, respectively. A

# 216 L.Y. LI

0.17 M sodium chloride solution was employed to simulate the addition of salt under winter road conditions. Pb concentrations leached out in the desorption tests were compared with the total Pb content in the soil to determine the availability and mobility of Pb under different leaching conditions.

## **3. Results and Discussion**

#### 3.1. Pb CONCENTRATIONS IN SOIL SAMPLES

ICP results of 139 samples from the 17 boreholes show that high Pb concentrations occur mainly between depths of 0 and 0.3 m. Distributions with depth are summarized in Table I. As in previous studies (Harrison *et al.*, 1981; Albasel *et al.*, 1985; Dierkes and Geiger, 1999; Pagotto *et al.*, 2001) Pb concentrations generally decrease with distance from the highway. Profiles B1 and C1, closest to (0.3 m) the highway asphalt surface have lower concentrations than the next boreholes (B2 and C2) due to different soil compositions. Transect A has less Pb deposition than B or C because of ligher traffic and reduced speeds along the exit (see Figure 1). The variability with depth could be due to different soils.

# 3.2. CHARACTERISTICS OF SOILS AND RELATIONSHIPS WITH DEPOSITION Pb CONCENTRATIONS IN THE FIELD

The XRD, SSA and BET results all indicate a coarse material with little clay. Mineralogical compositions of 29 samples indicate similar X-ray diffraction patterns. The semi-quantitative XRD technique shows that the soils are dominated by quartz, with small amounts of clay minerals, belonging mainly to the chlorite and illite groups.

Particle size analysis indicates that the particle size distributions of borehole samples vary with depth, as well as with location and distance from the highway surface. Samples below 1.5 m generally have higher percentages of particles finer than 75  $\mu$ m than surface samples. The texture of the surface soil ranges from silt to sand and is well sorted. These characteristics are likely due to the introduction of foreign soil during highway construction. Soils at 1.0 to 1.5 m depth appear to be generally native soils.

The percentages of samples finer than 74 and 53  $\mu$ m at each depth are summarized in Figure 2 and Table II. Most samples have at least 80% of particles larger than 74  $\mu$ m. Clay minerals generally have particles smaller than 2  $\mu$ m. These results are consistent with the XRD analysis and are significant since clay minerals are expected to interact strongly with heavy metals such as Pb.

Specific surface area measurements for the highway soils measured using BET are summarized in Table II for two boreholes. A5 soil was analysed as a bulk sample, and a separate measurement was made of the  $\lt 63 \mu$ m fraction; only the

Summary of lead concentrations in 17 boreholes 318 237 $\overline{ }$ 624 629 $\circ$ Transect A 288 569 5 418 500 4 69 807 3 $\overline{a}$ 1040 $\mathbf{C}$ $\overline{2}$ 63								1020 355 ∞	Pb (mg/kg soil) 835 554 ç	105 237	Transect B 925 894 2	95 260 3	25 4	303	Transect C 1650 391 $\mathbf 2$	1650 755 3	34 180 4
$0.5 - 0.6$ $0.2 - 0.3$	23 $\supseteq$	86	$\circ$ Ξ	679	667 520	865 $\Xi$	597 $50\,$	503	966 22	72 I	$\mathbf{13}$			$\overline{4}$ $\overline{\phantom{a}}$	$\Xi$	$\overline{\phantom{a}}$ I	n
$0.8 - 0.9$ $1.2 - 1.3$	$\overline{24}$ 4	$\overline{2}$	247 $\overline{\phantom{a}}$	324	13	$\frac{4}{9}$ $\overline{\phantom{a}}$		$\mathrel{\sim}$		Ī	I I	I		$\overline{\phantom{a}}$	$\overline{1}$	$\overline{\phantom{a}}$	
$1.4 - 1.5$	I	$\overline{1}$	$\overline{\phantom{a}}$	$\overline{\phantom{a}}$	$\overline{1}$	$\overline{1}$	$\overline{1}$	$\overline{1}$	$\overline{\phantom{a}}$	$\Box$		Ī	Ī		I		I
$1.5 - 1.6$		$\frac{4}{2}$			보			25		Ī	I			I		$\mathbf{\sim}$	
$1.8 - 1.9$		C					$\mathcal{C}$						I	I		$\overline{\phantom{a}}$	
$2.1 - 2.2$							$\mathrel{\sim}$		Ī					$\mathrel{\sim}$		Ī	

TABLE I TABLE I

218 L.Y. LI

Summary of physical properties of particle-size and specific surface area of the transect samples



Note: " $-$ " = not determined.



*Figure 2.* Pb retained and soil properties as functions of depth for boreholes A5, A8, B2, and C2.

bulk sample was characterized at A8. The specific surface measurements range from 1.2 to  $7.0 \,\mathrm{m}^2/\mathrm{g}$ . Measured pH values were relatively uniform, almost all between 5.0 and 6.5.

The total carbon (sum of organic and inorganic carbon) content of the highway soils vs depth is shown in Figure 2. Local organic material was used for soil surfacing. Below 0.5 m, the carbon content is lower, except for boreholes A5 and A8 at 1.5 m depth. These two boreholes were located at an exit ramp where foreign soil may have reached a depth of 1.5 m. The high levels of organic material in the top 0.3 m correlate loosely with metal adsorption. The upper organic layers of the roadside soils appear to have high adsorption capacity for Pb, with little leaching to the lower layers.

Measured soil properties and local Pb concentrations are plotted vs depth in Figure 2. As in previous studies, Pb is deposited mainly in the top 0.3 m of the soil, dropping to background levels by a depth of 0.6 m.

# 3.3. Pb ADSORPTION CAPACITY OF HIGHWAY SOILS

Freundlich and Langmuir isotherms were used to fit adsorption data for each sample. The model parameters of the adsorption results are summarized in Table III, providing estimates of Pb adsorption for soils at various depths. These isotherms indicate that the capacity of the soil to absorb Pb in a strong solution is 3 to 10 times the maximum concentration found on the site. These values represent the accumulation of Pb deposits between the construction of the interchange in 1963 and 1999, including ∼26 years of leaded gasoline usage. After phase-out of leaded gasoline in Canada in the late 1980s, source inputs virtually ceased. An air pollution study along the highway at a different location (Li and Preciado, 2004) indicates that the Pb input due to vehicle emissions has decreased significantly. Therefore, the sorption capacity is unlikely to be reached in the foreseeable future.

The extent of the adsorption capacity correlates with total Pb concentration, soil pH, silt and clay. A single soil adsorption capacity value is interpolated from each adsorption isotherm for A5, A8, B2 and C2 at which the equilibration solution Pb concentration is  $0 \text{ mol/m}^3$  in soil pore water. Figure 3 shows that the absorption capacity is significantly correlated  $(r^2 = 0.782)$  with carbon content. Other properties such as pH, silt and clay have no significant correlation with adsorption for this highway soil.

#### 3.4. PARTITIONING AND FATE OF Pb

As noted above, SSE was used to determine the likely forms of Pb and how these might partition in different circumstances. The SSE results for field samples as a function of depth are summarized in Figure 4 as: (1) normalized concentrations, referring to Pb extracted from each phase as a percentage of the total Pb in the soil, and (2) absolute amounts extracted, i.e. sum of fractions (mg Pb/kg soil). The results indicate that the top 0.1 m of the soil has only about 10% exchangeable Pb. This Pb fraction, involving mostly clay minerals, soil organics and amorphous materials, is considered to be non-specifically adsorbed, ion exchangeable, and able



# TABLE III

Langmuir and Freundlich model parameters for adsorption isotherms for boreholes A5, A8, B2 and C2 at different depths

		Langmuir $C^* = K_1 C / (1 + K_2 C)$		Determination coefficient	Freundlich $C^* = K_1 C^{K_2}$		Determination coefficient
	Transect						
	Depth (m)	$K_1$	$K_2$	r <sup>2</sup>	$K_1$	$K_2$	r <sup>2</sup>
A <sub>5</sub>	$\mathbf{0}$	408.731	0.026	0.788	3742.851	0.221	0.965
	0.1	266.268	0.022	0.839	2638.176	0.231	0.949
	0.2	445.656	0.049	0.567	3138.770	0.165	0.863
	0.5	58.677	0.006	0.862	988.122	0.306	0.977
	0.8	44.106	0.006	0.742	803.187	0.300	0.977
	1.2	59.980	0.006	0.853	964.114	0.322	0.804
	1.5	403.493	0.0246	0.947	3527.793	0.2270	0.938
	1.8	111.922	0.0156	0.556	1258.591	0.2443	0.508
	2.1	55.799	0.0071	0.733	866.026	0.2904	0.591
A8	$\mathbf{0}$	91.036	0.006	0.875	1371.185	0.332	0.973
	0.1	40.112	0.001	0.933	170.672	0.719	0.948
	0.2	195.349	0.021	0.873	1562.785	0.276	0.892
	0.5	162.527	0.021	0.821	1426.800	0.248	0.756
	0.8	39.368	0.002	0.890	535.643	0.446	0.915
	1.2	55.698	0.006	0.860	762.673	0.343	0.774
	1.5	115.395	0.013	0.758	1523.664	0.244	0.619
	1.8	260.038	0.020	0.896	2406.918	0.240	0.764
	2.1	44.158	0.004	0.733	548.193	0.390	0.638
<b>B2</b>	$\boldsymbol{0}$	1901.431	0.147	0.875	4303.257	0.167	0.757
	0.1	1275.034	0.113	0.867	2562.556	0.239	0.909
	0.2	418.360	0.060	0.760	1344.482	0.254	0.820
	0.5	9.038	1.16E-07	0.715	8.73E-09	4.108	0.936
	1.2	8.131	2.42E-07	0.652	6.02E-12	5.139	0.957
	1.5	13.491	5.52E-08	0.828	0.0013	2.391	0.952
	1.8	9.058	2.25E-07	0.666	5.36E-09	4.155	0.961
	2.1	34.717	0.006	0.839	642.845	0.297	0.799
C <sub>2</sub>	$\mathbf{0}$	5704.766	0.447	0.817	4058.186	0.213	0.972
	0.1	241.800	0.021	0.733	3011.516	0.196	0.892
	0.2	81.443	0.007	0.856	1295.436	0.299	0.947
	0.5	7.332	0.002	0.895	88.188	0.486	0.857
	1.2	11.878	0.004	0.799	233.961	0.327	0.818
	1.5	10.695	0.001	0.920	121.130	0.521	0.913
	1.8	14.472	0.002	0.840	201.538	0.446	0.859
	2.1	56.101	0.004	0.859	736.234	0.383	0.812

Curve fit using Langmuir or Freundlich: *C*<sup>∗</sup> = Pb-sorbed concentration onto the soil (mg/kg); *C* = equilibrium concentration of lead in solution (ppm);  $r^2$  = determination coefficient;  $K_1, K_2$  = constants.

RETENTION CAPACITY AND ENVIRONMENTAL MOBILITY 221



*Figure 3.* Relationship between carbon content and Pb retention on soil. Line ( $y = 1170x + 1430$ ) is least squares linear fit with  $r^2 = 0.78$ .

to be replaced by competing cations. Since the chemical used for this extraction is the weakest of those in the five steps (Li and Li, 2003; Tessier *et al.*, 1979; Yong, 2001), the corresponding fraction is considered to be most readily released to the environment. The soil at 0.2 to 2.1 m depths has a relatively higher exchangeable Pb content, possibly due to the presence of clay minerals. This result is consistent with those from the determination of particle size and SSA showing a higher percentage of 53  $\mu$ m particles below a depth of 0.3 m than at higher levels.

All samples have pH  $\approx$  6, indicating little or no carbonate in the soil. Therefore, data from step 2 estimates metals specifically sorbed to amorphous materials. The results indicate that all samples had relatively little Pb specifically sorbed to amorphous materials, typically 5–20%. Figure 4 indicates that Pb adsorption in highway soils is dominated by this oxide/hydroxide phase, with readings as high as 50%. This could be because the Pb was oxidized to PbO during combustion of the gasoline.

The binding mechanisms for Pb in association with organic matter can include complexation, adsorption and chelation (i.e. step 4 of SSE). Because of the different binding mechanisms, some overlap is obtained with those methods designed to determine exchangeable cations. Figure 4 indicates that the soil at 0–0.1 m has at most an organic phase of approximately 30–40% of the total adsorbed Pb, consistent with carbon contents (Figure 2). It is likely that the Pb is largely deposited as oxide and to a lesser degree amorphous, followed by slow dissolution of the oxide phase due to leaching of the sparingly soluble oxide. The dissolved Pb is then likely reabsorbed by the organic fraction. Other Pb may be released as metal, then slowly oxidize and dissolve. The residual fraction of Pb was a small proportion (about 5%) of the total soil Pb (Figure 4) indicating that most of the Pb pollutant is anthropogenic, resulting from highway traffic.





*Figure 4*. SSE for natural samples plotted as a function of depth for four boreholes. Steps: (1) ECE-Exchangeable cations extraction; (2) CE-Weak acid extraction (to remove metals ionically bound to amorphous materials); (3) OHD-Oxide and Hydroxide weak acid/complexing agent digestion; (4) OD-Organic matter digestion; and (5) RD-Residual HNO<sub>3</sub> digestion.

Figure 4 can be viewed in terms of the ease of removal of sorbed Pb, showing how strongly various contaminants are held by the soil fractions. The Pb held by the soil fractions by mechanisms associated with cation exchange capacity (CEC) constitutes the easily extractable Pb, expected to be most mobile. The retention due

to exchangeable and carbonate- or amorphous- materials-bound Pb (categories 1 and 2 above) is sensitive to pH (McQuarrie and Rock, 1991; Tan, 1998; Li and Li, 2000) because of the solubility of the Pb hydroxide species. Pb forms hydroxyl species when pore water reaches a certain pH level. Precipitated Pb can be released if the immediate environment is acidified. Bonding between Pb and amorphous or poorly crystallized Fe, Al, and Mn oxides is relatively strong. This work suggests that determination of the exchangeable Pb provides a quick method to estimate the potential mobility of Pb retained in soils.

## 3.5. LEACHIBILITY AND MOBILITY OF Pb IN HIGHWAY SOILS

As noted above, Pb was mainly limited to the top 0.3 m of the soil along the highway corridor, with insignificant Pb below this depth. The results of batch desorption tests to demonstrate the potential for Pb release from the original Pbcontaminated soils are shown in Table IV. In each case Pb concentrations in the leachate were less than  $9.6 \times 10^{-3}$  mol/m<sup>3</sup>, in spite of total Pb concentrations, as high as 1628 mg per kg soil. Thorough mixing and low soil:solution ratios in the leaching tests should have led to overestimation of the leaching in the field (USEPA, 1999; Harter and Naidu, 2001). The results suggest a low likelihood of significant leaching, even under aggressive acid conditions or high road salt loadings.

Results for the water samples collected at the locations indicated in Figure 1, analyzed for total and dissolved Pb concentration using ICP indicate that Pb was detected only in the duplicate sample from Water Sample 6 of the same ditch as total metals, while no Pb was detected in the dissolved metal tests. This confirms that dissolved Pb should not be a concern in ditches at this site; however, Pb may be associated with fine suspended particulates.

## **4. Conclusions**

- 139 samples from 17 boreholes were analyzed for their Pb concentrations. Four boreholes were studied comprehensively. The results provide a relatively large data-base to help elucidate the fate and transport of Pb in soil and to design rights-of-way along highways.
- Significant Pb accumulations of up to 1628 mg/kg were found in soils along the corridor of a major highway interchange site. The distribution of contamination was consistent with previous findings. Soil Pb concentrations rapidly decreased to background levels at a depth of 0.6 m. The top 0.3 m contained more organic material and had high Pb adsorption capacity.
- Adsorption capacities ranged from 2000 to 12,000 mg Pb/kg soil, 3 to 10 times the soil concentrations found on the site. Since the primary source of contamination



Summary results of batch desorption tests using desorption agents: H<sub>2</sub>O at pH 5.5, HNO<sub>3</sub> solution at pH 4.0, and an aqueous 0.17 M NaCl solution Summary results of batch desorption tests using desorption agents:  $H_2O$  at pH 5.5, HNO<sub>3</sub> solution at pH 4.0, and an aqueous 0.17 M NaCl solution **TABLE IV** TABLE IV

L . Y . LI

has been phased out, it is unlikely that the sorption capacity of the soil for Pb will be reached in the foreseeable future.

- The relative amount of exchangeable Pb in the highway soils was low. Pb has very limited mobility in the highway soil investigated.
- Despite the high total Pb concentrations in the soils, all leachants have Pb concentrations below  $9.6 \times 10^{-3}$  mol/m<sup>3</sup>.
- Step 1 of the SSE (i.e. determination of the exchangeable Pb) provides a quick method to estimate the potential mobility Pb retained in soils.

## **Acknowledgments**

I would like to thank the B.C. Ministry of Transport and Highways for supporting this study. I am also grateful to Dr. John Grace for reviewing and editing the manuscript, R.G. Buchanan and Scott Tomlinson for their technical support, Joan Liu, Juan Garifias, Linlin Hui for performing the analytical tests, Susan Harper, Paul Parkinson, Karen Ferguson and Carol Dyck for their assistance with laboratory equipment and analytical procedures.

#### **References**

- Albasel, N. and Cottenie, A.: 1985, 'Heavy metal contamination near major highways, industrial and urban areas in Belgian grassland', *Water Air Soil Pollut.* **24**, 103–109.
- Backstrom, M., Karlsson, S. and Allard, B.: 2004, 'Metal leachability and anthropogenic signal in roadside soils estimated from sequential extraction and stable lead isotopes', *Environemntal Monitoring and Assessment*, **90**, 135–160. Kluwer Academic Publishers. Netherlands.
- Baekken, T.: 1994, 'Effects of highway pollutants on a small Norwegian lake', *The Science of the Total Environment* **146/147**, 131–139.
- Bhuie, A. K., McLaughlin, D. and Roy, D. N.: 2000, 'Exposure of urban ecosystems to Mn and Pb contaminants from gasoline additives beside a major highway in the Greater Toronto Area, Canada', *Forestry Chronicle* **76**, 251–258.
- Cannon, H. L. and Bowles, J. M.: 1962, 'Contamination of vegetation by tetraethyl lead', *Science* **137**, 765–773.
- Chatterjee, A. and Banerjee, R. N.: 1999, 'Determination of lead and other metals in a residential area of greater Calcutta', *The Science of the Total Environment* **227**, 175–185.
- Deroanne-Bauvin, J., Delcarte, E. and Impens, R.: 1987, 'Monitoring of lead deposition near highways: A ten years study', *The Science of the Total Environmental* **59**, 257–266.
- Dierkes, C. and Geiger, W. F.: 1999, 'Pollution retention capabilities of roadside soils', *Water Science Technology* **39**, 201–208.
- Fakayode, S. O. and Olu-Owolabi, B. I.: 2003, 'Heavy metal contamination of roadside topsoil in Osogbo, Nigeria: Its relationship to traffic density and proximity to highways', *Environmental Geology* **44**, 150–157.
- FHWA: 1998, 'Is Highway Runoff a Serious Problem?' Office of Infrastructure R&D. Turner-Fairbank Highway Research Center. McLean, VA. http:/www.fhwa.dot.gov/terp/prog.htm#I129.
- Ge, Y., Murray, P. and Hendershot, V. H.: 2000, 'Trace metal speciation and bioavailability in urban soils', *Environmental Pollution* **107**, 137–144.
- Gish, C. D. and Christensen, R. E.: 1973, 'Cadmium, nickel, lead and zinc in earthworms from roadside soil', *Environmental Science and Technology* **7**, 1060–1062.
- Gracia, R. and Millan, E.: 1998, 'Assessment of Cd, Pb and Zn contamination in roadside soils and grasses from Gipuzkoa (Spain)', *Chemosphere* **37**, 1615–1625.
- Harrison, R. M., Laxen, P. H. and Wilson, S. J.: 1981, 'Chemical association of lead, cadmium, copper, and zinc in street dusts and roadside soils', *Environment Science & Technololy* **15**, 1378–1383.
- Harrison, R. M. and Johnston, W. R.: 1985, 'Deposition fluxes of Lead, Cadmium, Copper and polynuclear aromatic hydrocarbons (PAH) on the verges of a major highway', *Sci. Total Environ.* **46**, 121–135.
- Harter, R. and Naidu, R.: 2001, 'An assessment of environmental and solution parameter impact on trace-metal sorption by soils', *Soil Sci. Am. J.* **65**, 697–612.
- Hewitt, C. N. and Rashed, M. B.: 1991, 'The desorption of selected pollutants adjacent to a major rural highway', *Atmospheric Environment* **25**, 979–983.
- Hoedrejaerv, H., Vaarmann, H. and Inno, I.: 1997, 'Heavy metals in roadside: Chemical analysis of snow and soil and the dependence of the properties of heavy metals on local conditions', *Proceedings of the Estonian Academy of Science & Chemistry* **46**, 153–167.
- Kittrick, J. A. and Hope, E. W.: 1963, 'A procedure for the particle-size separation of soils for x-ray diffraction analysis', *Soil Science* **96**, 319–325.
- Lagerwerff, J. V. and Specht, A. W.: 1970, 'Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc', *Environmental Science and Technology* **4**, 583–586.
- Li, R. S. and Li, L. Y.: 2000, 'Enhancement of electro-kinetic extraction of heavy metals from contaminated soils', *American Society of Civil Engineering (ASCE), Journal of Environmental Engineering* **126**, 849–857.
- Li, L Y. and Li, R. S.: 2000, 'The role of clay minerals and  $H^+$  ion effect on removal of a heavy metal (Pb) from contaminated soils', *Canadian Geotechnical Journal* **37**, 1–12.
- Li, L. Y. and Li, F. C.: 2001, 'Heavy metal sorption and hydraulic conductivity studies using three types of bentonite admixes', *American Society of Civil Engineering (ASCE), Journal of Environmental Engineering* **127**, 420–429.
- Li, R. S., Yong, R. N. and Li, L. Y.: 2001, 'Mathematical prediction of lead removal from carbonaterich illite', *Engineering Geology*, Specialty issue for Geoenvrionmental Engineering, R.N. Yong and H.R. Thomas, editor, **60**, 159–171.
- Li, L. Y., 2002: *Environmental Fate of Lead in Surface Soils along Highway Corridors*, Project # 02402, Ministry of Transportation and Highways, B.C. Canada.
- Li, F. and Li, L.Y.: 2003, 'Modelling of multi-component adsorptivity and compatibility of dissolved heavy metals for various soils', *Environmental Technology* **24**, 1479–1490.
- Li, L. Y.: 2003, 'Multi-component of heavy metal contaminants adsorptivity and compatibility onto variable charge clay mineral', *Clay Science* **12**, 73–80.
- Li, L. Y. and Preciado, H.: 2004, 'Air, runoff and soil monitoring of highway pollution by metals along highway corridors', *Air Pollution 2004, Twelfth International Conference on Modelling, Monitoring and Management of Air Pollution*, 30 June–2 July 2004, Rhodes, Greece. pp. 529–540.
- Mao, I. F. and Chen, M. L.: 1996, 'Airborne lead pollution in metropolitan TaiPei (Republic of China)', *Water Air Soil Pollut.* **91**, 375–382.
- McQuarrie, D. A. and Rock, P. A.: 1991, *General Chemistry*. W.H. Freeman, New York.
- Mikkelsen, P. S., Hafliger, M., Ochs, M., Tjell, J. C. Jacobsen, P. and Boller, M.: 1996, 'Experimental assessment of soil and groundwater contamination from two old infiltration systems for road run-off in Switzerland', *The Science of the Total Environment* **189/190**, 341–347.
- Norovtny, V., Muehring, D., Zitomer, D. H., Smith, D. W., Facey, R., Grabow, W. O. K., Dohmann, M., Haas, C., Hall, E. R., Lesouef, A., Orhon, D., Van Der Vlies, A., Watanable, Y., Milburn, A.,

Purdon, C. D. and Nagle, P. T.: 1998, 'Cyanide and metal pollution by urban snowmelt: Impact of deicing compounds', *Water Science and Technology* **38**, 223–230.

- Norrstroem, A. C. and Jacks, G.: 1998, 'Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts', *The Science of the Total Environment* **218**, 161–174.
- Pagotto, C., Remy N., Legret, M. and Le Cloirec, P.: 2001, 'Heavy metal pollution of road dust and roadside soil near a major rural highway' *Environmental Technology* **22**, 307–319.
- Rodriguez-Flores, M. and Rodriguez-Castellon, E.: 1982, 'Lead and cadmium levels in soil and plants near highways and their correlation with traffic density', *Environmental Pollution (Series B)* **4**, 281–290.
- Sheldrick, B. H. (ed.): 1984, *Analytical Method Manual*, Land Resource Research Institute, Research Branch, Agriculture Canada, *LRRI contribution, No. 84–30.*
- Sposito, G., Land, L. J. and Chang, A. C.: 1982, 'Trace-metal chemistry in arid-zone field soils amended with sewage-sludge.1. fractionation of Ni, Cu, Zn, Cd, and PB in solid-phases', *Soil Science Society of America Journal* **46**, 260–264.
- Sutherland, R. A., Tack, F. M. G., Tolosa, C. A. and Verloo, M. G.: 2000, 'Operationally defined metal fractions in road deposited sediment, Honolulu, Hawaii', *J. Environmental Quality* **29**, 1431–1439.
- Tan, K. H.: 1998, *Principles of Soil Chemistry*, Marcel Dekker, New York.
- Tessier, A., Campbell, P. G. C. and Bisson, M.: 1979, 'Sequential extraction procedure for the speciation of particulate trace metals', *Anal. Chem.* **51**, 844–851.
- Turer D., Maynard J. B. and Sansalone J. J.: 2001, 'Heavy metal contamination in soils of urban highways: Comparison between runoff and soil concentrations at cincinnati, Ohio', *Water Air Soil Pollut.* **132**, 293–314.
- USEPA: 1999, *Understanding Variation in Partition Coefficient, K<sub>d</sub> Values. U.S. Environmental* Protection Agency, Washington, D.C.
- USEPA: 1993, *Integrated Risk Information System on Lead*, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati.
- USEPA: 1987,*Batch Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals.* Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, EPA/530-SW-87-006, Washington, D.C.
- Wheeler, G. L. and Rolfe, G. L.: 1979, 'The relationship between daily traffic volume and the distribution of lead in roadside soil and vegetation', *Environmental Pollution* **18**, 265–274.
- Yassoglou, N., Kosmas, C., Asimakopoulos, J. and Kallianou, C.: 1987, 'Heavy metal contamination of roadside soils in the greater Athens area', *Environmental Pollution* **47**, 293–304.
- Yong, R. N.: 2001, *Geoenvironmental Engineering Contaminated Soils, Pollutant Fate, and Mitigation*, CRC Press LLC.
- Yong, R. N. and Phadungchewit, Y.: 1993, 'pH influence on selectivity and retention of heavy metals in some clay soils', *Canadian Geotechnical Journal* **30**, 821–833.
- Zhang, H., Ma, D., Xie, Q. and Chen, X.: 1999, 'Approach to studying heavy metal pollution caused by modern city development in Nanjing, China', *Environmental Geology* **38**, 223–228.