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Heavy metal distribution for aqueous and solid phases in urban runoff, snowmelt and soils

Donald W. Glenn III
Louisiana State University and Agricultural and Mechanical College

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HEAVY METAL DISTRIBUTION FOR AQUEOUS AND SOLID PHASES IN URBAN RUNOFF, SNOWMELT AND SOILS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

Donald W. Glenn, III
B.S., Auburn University, 1993
M.S., Louisiana State University, 1998
December 2001
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\tau_{sf}$</td>
<td>mean pavement residence time</td>
</tr>
<tr>
<td>CMA</td>
<td>calcium magnesium acetate</td>
</tr>
<tr>
<td>COD$_d$</td>
<td>dissolved chemical oxygen demand</td>
</tr>
<tr>
<td>COD$_p$</td>
<td>particulate chemical oxygen demand</td>
</tr>
<tr>
<td>COD$_t$</td>
<td>total chemical oxygen demand</td>
</tr>
<tr>
<td>ITS</td>
<td>intelligent traffic system</td>
</tr>
<tr>
<td>M</td>
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<tr>
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<td>milligrams per liter</td>
</tr>
<tr>
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<td>miles per hour</td>
</tr>
<tr>
<td>mS/cm</td>
<td>milliSiemens per centimeter</td>
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<td>pH</td>
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</tr>
<tr>
<td>q$_{sf}$</td>
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<td>method detection limit</td>
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<tr>
<td>SA</td>
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</tr>
<tr>
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<td>specific surface area ($L^2/M$)</td>
</tr>
<tr>
<td>SS</td>
<td>settleable solids</td>
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<td>D</td>
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<td>P</td>
<td>particulate-bound (µg/L)</td>
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<tr>
<td>$f_d$</td>
<td>dissolved fraction (unitless)</td>
</tr>
<tr>
<td>$f_p$</td>
<td>particulate-bound fraction (unitless)</td>
</tr>
<tr>
<td>$K_d$</td>
<td>partition coefficient (L/kg)</td>
</tr>
</tbody>
</table>
C \text{ = flow weighted average concentration for entire event (M/L^3)}

°C \text{ = degrees Celsius}

C_c \text{ = coefficient of concavity}

C_i \text{ = incremental heavy metal mass concentration per dry mass of solid [µg/g]}

\text{c(t) = time variable solid or dissolved fraction (M/L^3)}

C_u \text{ = coefficient of uniformity}

d_{10} \text{ = particle size at which 10% of particle size gradation mass is finer (L)}

d_{30} \text{ = particle size at which 30% of particle size gradation mass is finer (L)}

d_{50} \text{ = particle size at which 50% of particle size gradation mass is finer (L)}

d_{60} \text{ = particle size at which 60% of particle size gradation mass is finer (L)}

EGME \text{ = Ethylene-Glycol-Monoethylether}

EMC \text{ = event mean concentration (M/L^3)}

M_{e_i} \text{ = mass of heavy metal for a given increment (M)}

PSD \text{ = particle size distribution}

RSD \text{ = relative standard deviation}

SD \text{ = standard deviation}

t \text{ = time (T)}

\text{t_r = duration of event (T)}

UHP \text{ = ultra high pure}

V \text{ = total volume of flow over entire event duration (L^3)}

W_a \text{ = measured weight of EGME retained by sample (M)}

W_s \text{ = measured weight of dried sample (M)}

\rho_l \text{ = density of water (assumed to be 1.0 g/cm^3)}

\rho_{sg} \text{ = specific gravity of residual particulate matter}

\rho_s \text{ = particle density of residual particulate matter (\rho_s/\rho_l)}

PZC \text{ = point of zero charge}

R \text{ = Reference site}

A \text{ = Asphalt}

N \text{ = north}

S \text{ = south}

E \text{ = east}

W \text{ = west}

LS \text{ = low speed}

HS \text{ = high speed}

ICDD \text{ = International Centre for Diffraction Data}

n\lambda \text{ = whole number of wavelengths}

d \text{ = interplanar spacing}

\theta \text{ = angle of incidence of the primary radiation with crystal planes.}

V_S \text{ = true sample volume (cm^3)}

V_C \text{ = cell volume (cm^3)}

V_R \text{ = reference volume (cm^3)}

P_I \text{ = initial pressure (psi)}

P_2 \text{ = final pressure (psi)}

M_s \text{ = mass of sample specimen prior to placement in the pycnometer (g)}

SA_{i} \text{ = surface area of solids having particle diameter i (m^2/kg)}

m_i \text{ = mass of solids having particle diameter i (g)}
SSAi = specific surface area of solids having particle diameter i (m²/g)
Tm = total dry mass from PSD (kg).
m_i = mass of the ith increment (M)
Abstract

At the start of the third millennium, over 50% of the world’s population lives in urban areas. Anthropogenic activities associated with urban development such as traffic generate significant particulate and heavy metal mass loadings. Ten urban highway sites located throughout the metropolitan area of Cincinnati, Ohio were studied. Storm water, snow and transportation land use soil/residual complexes (RSCs) were collected at each site. For the storm water, results are presented for a series of eight rainfall runoff events over a two-year period and included analyses between dissolved and particulate-bound fractions of heavy metals (Pb, Cu, Cd and Zn), and water quality characteristics such as hydrology, alkalinity, hardness and pH. For all sites, results are presented for a 460-mm snowfall in 1998 and included analyses between dissolved and particulate-bound fractions of heavy metals, particle size distributions (PSD), specific surface area (SSA), total surface area (SA), particle density ($\rho_s$), and water quality characteristics such as hardness, pH, conductivity, chloride, chemical oxygen demand (COD), and total suspended (TSS) and dissolved (TDS) solids. The role of climate and traffic were examined with respect to these results. For the RSCs, results included PSD, SSA, SA, $\rho_s$, particulate-bound fractions of heavy metals, mineralogical constituents and potentiometric titrations. Overall, partitioning analysis for storm water runoff indicated that heavy metals were predominately dissolved due to low pH, low alkalinity and short pavement residence times ($\tau_{sf}$). Snow however had a much greater capacity to accumulate and retain particulate-bound metals due to a neutral pH, increased hardness and longer $\tau_{sf}$ in terms of days instead of minutes. The RSCs which retain and export storm water and snow had decreased levels of heavy metals when compared to the reference site. Although similar in parent material, the RSCs had different mineralogical constituents than the reference and exhibited a greater buffering capacity and net
surface charge density. Heavy metal concentration at the undisturbed reference site indicated the potential of high atmospheric deposition from historical coal combustion. Characterization of partitioning, accretion and distribution of heavy metals is necessary for development of best management practices as source control in urban transportation land use areas.
Chapter 1
Introduction

Transportation activities can be a significant source of pollutant generation and transport during rainfall runoff events and snow melt in the urban environment. Heavy metals in urban rainfall runoff partition between the particulate and dissolved fraction, favoring the dissolved fraction for low rainfall pH levels and pavement residence times in terms of minutes (Sansalone and Buchberger 1997). The literature is quite limited, however, when it comes to temporal accretion and partitioning of heavy metals in urban snow. High heavy metal concentrations and the persistence of heavy metals influence characteristics of rainfall and snowmelt runoff, receiving waters, the existing soil/residual complex, and ultimately the aquatic life and food chain.

The United States is dependent on its roadways for the movement of people and services. The roads and highways are expected to be maintained to provide safe traveling conditions, particularly during winter storms. De-icing salts applied to roads as well as other chemical additives may be carried by surface runoff into streams and waterways or may infiltrate the soil bordering the highway, be carried to groundwater, remain in the soil solution or become adsorbed by soils.

In storm water or snow melt, complexation and interaction with high levels of organic matter should reduce toxicity of these metals (Amrhein et al. 1992). However, most metals pose a threat to the development of aquatic species as a result of low pH condition or high metal concentration. With the promulgation of the Final Rule for Phase II Storm Water under the National Pollutant Discharge Elimination System (NPDES) regulations on 29 October 1999, heavy metals in roadway storm water have now come into direct focus at the national regulatory
level. No less attention should be placed upon heavy metals in urban snow and transportation land use soil/residual complexes.

The unique nature of urban highway snow banks makes urban snow a significant sink for both heavy metals and particulates generated by traffic and winter maintenance activities. These heavy metals can be predominantly associated with the particulate matter suspended and trapped within the snow bank. The emphasis on treatment for urban snow varies according to site and available space. Leachates as well as snow chemistry affects quality of runoff and treatment strategies. Apart from peak concentrations of suspended solids during short intense street runoff from rain, concentrations of suspended solids in snowmelt runoff are 2 to 5-fold higher than in rain runoff (Daub et al. 1994). In fact, the size and velocity of snowflakes as compared with raindrops enable a higher scavenging efficiency for gaseous and particulate atmospheric pollutants. Snow pack contamination in urban areas has been correlated with proximity to large industries or major roadways as well as snow pack age (White et al. 1995).

Without best management practices (BMPs), these materials are deposited, accumulate and then are transported by storm water and snowmelt. Soils subject to years of such loading can serve as a sink and a potential source for heavy metals depending on loading and drainage conditions. Surficial soils in the urban environment serve as an interface between the subsurface, surface water and the atmosphere. Transportation land use soil/residual complexes have been subjected to particulate and heavy metal loading and will be subjected to the same, if not more loadings in the future. As a result, accretion and export of heavy metals in urban soil/residual complexes will remain of interest especially when affected by urban activity.

Partitioning is a concept used in both rainfall runoff and snowmelt when describing the highly dynamic complexes of different physical-chemical phases that can vary in orders of
magnitude in a single event. The dynamic nature of an event is due to the changing total suspended solids, pH, alkalinity, residence time, flow regime and urban surface conditions. These concepts can be applied to organics and other water constituent classes, however, in the case of this dissertation, this concept is applied towards heavy metals. Partitioning is typically defined as an interaction between the dissolved fraction, the colloidal fraction (<50-μm) and the particle-bound fraction. These interactions can be forward (sorption) or reverse reactions (desorption) that occur during the partitioning reaction (Figure 1.1). However, sorption tends to dominate with high pH (8 to 9) and high total suspended solids (USDOT 1990). This partitioning includes specific mass transfer mechanisms such as ion exchange, surface complexation and precipitation (Stumm and Morgan 1996). Chemical species in complex environmental systems eventually attain different equilibrium concentrations in the phases comprising these systems (Weber and Digiano 1996). The concentrations in theory should be quantifiable as sediment-water partitioning and thus should be a “first-cut” estimator of the distribution of solute between two phases.

Modeling metal ion adsorption has been a subject of interest in recent years. Surface complexation modeling such as the triple layer model (TLM) has became more widely used especially in the environmental engineering and science area. The general scope of the surface complexation model has been developed and summarized by a number of scientists (Dzombak and Morel 1990; Stumm and Morgan 1996). Application of TLM assumes that the surfaces on which adsorption of metal ions takes place are composed of a number of discrete sites undergoing ionization in the aqueous environment. Adsorption occurs as a result of the formation of complexes between the metal ions and the ionized sites as well as between the hydrolysis products of the ions and ionized sites. The reactions between metal ions and surface
hydroxyl groups are analogous to the formation of soluble complexes and can be described by mass law equations. However, the corresponding equilibrium constants are not, in fact, constant. Ionization of the surface sites, the formation of complexes between these sites and different ionic species implies that the oxide surfaces, in general are charged. These charges are influenced by the presence of an electrostatic field which, in turn, affects the equilibrium between the oxide surface and the aqueous environment. These surface reactions distinguished from reactions among solutes are the variable electrostatic energy of interaction caused by the variable charge on the surface (Dzombak and Morel 1990). In addition, ionized sites may also form complexes with electrolyte ions present in the aqueous environment outside the oxide surface. For example, cations may be adsorbed on a positively charged surface and anions on a negatively charged surface (specific adsorption), and the primary adsorption can reverse the net surface charge (McKenzie 1989).

![Diagram showing partitioning between dissolved and particulate form of heavy metals](image)

**Figure 1.1.** Partitioning between dissolved and particulate form of heavy metals (2-partition model).

Kinetic rates, equilibrium are functions of:
- TSS, pH, redox, TS properties, salinity
- RTD, mixing and flow regime, temperature
- Heavy metal and competitive interactions
The majority of the particulate mass and heavy metal partitioning is not to the colloidal fraction but to the fraction of particles that 50-µm or larger in anthropogenically-impacted urban conditions. A current example of such data (Figure 6.5) is provided to clarify this point. Figure 6.5 clearly demonstrates that if one examines the entire gradation of transported particulate matter in “overland” flow, at the upper end of the urban watershed from a particular storm event, most of the heavy metal mass is associated with the coarser fraction not the colloidal fraction. These data are representative of storm water, rainfall runoff, snowmelt or sediment-residual urban complexes subject to overland flow. Certainly, one can argue for additional and finer partitions to separate the storm water particle gradation into, but in urban storm water the vast majority of particle total surface area (settleable, suspended and colloidal) as well as heavy metals is associated with greater than 50-µm, generally in the settleable or in some cases larger overland-entrained sizes. As one follows the hydrograph further down the urban watershed, particles capable of being entrained in overland flow are progressively removed. Only as flow is incorporated into downstream receiving waters, or as effluent from a BMP facility such as a quiescent settling basin, does the relative portion of colloids with respect to the remaining mass gradation, becomes increasingly important. In fact, past studies have examined more homogeneous and pure (single mineral) surfaces (not anthropogenically-modified and heterogeneous surfaces) and conditions not represented by urban overland flow (Stumm and Morgan 1996). Any one particulate from any of the storm water particulate gradations (10,000 to less than 15 µm) contains measurable mineral concentrations of quartz, calcite, dolomite, anhydrite, K-feldspar, Ca and Na plagioclase, kaolinite, illite, chlorite, pyrite, augite and amphibole. This is complex system for rainfall-runoff parameters and water quality parameters change by orders of magnitude in a single event. The ability of a mineral to sorb chemical
species from either liquids or gases is strongly dependent on the surface area that a unit mass or volume of the solid presents to the liquid or gas phase, that is, the specific surface area (SSA). This exposed solid surface at the solid/liquid or solid gas interface contains the functional groups and/or lattice ions and atoms that interact with liquid or gas phase species to effect sorption reactions.

These studies include the adsorption of heavy metals by goethite and hematite in the order of Cu > Pb > Zn > Cd > Co > Ni > Mn except for an interchange in position of Cu and Pb for hematite (Schwertmann and Taylor 1989). Adsorption of heavy metal cations is highly sensitive to pH. As pH increases, a steep rise in adsorption occurs within a narrow pH range. The pH range of maximum increase in adsorption is found to be linearly related the first hydrolysis constant of the metal (Schwertmann and Taylor 1989). Alkalinity is also important in that the greater the total alkalinity, the more acid the solution could neutralize (Kehew 2001). In any solution, a charge balance exists where the sum of the normalities of the positively charged species equals the sum of the normalities of the negatively charged species. The only process that could change the alkalinity would be the precipitation of solid phases such as calcite (Kehew 2001).

Under conditions where a number of heavy metals are present in solution, the competitive order of partitioning (sorption) can be compared to bonding preferences as predicted using covalent theory, electrostatics or the tendency of a metal element to undergo hydrolysis followed by sorption. Electronegativity is an important factor in determining which heavy metal will complex to a hydrated inorganic surface, such as an iron oxide surface, with the highest preference. The more electronegative heavy metals form the strongest covalent bonds with the oxygen atoms of the surface hydroxyl groups. According to covalent theory for divalent metal
ions, the predicted order of bonding preference would be Cu > Ni > Co > Pb > Cd > Zn > Mg > Sr (McBride 1994). However, based on electrostatics, bonding preference is for the metals with the greatest charge-to-radius ratio, producing a different order of preference for this group of divalent metals Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb (McBride 1994). Electrostatics would also predict that trivalent metal ions such as Cr$^{3+}$ would have a greater bonding preference to all divalent metal ions. Finally, based on the tendency to hydrolyze, the bonding preference of selected metal ions to iron oxides would be Pb > Cu > Zn > Co > Ni > Cd > Mn (McBride 1994).

Knowledge of the partitioning and the relative fractions of dissolved ($f_d$) and particulate-bound ($f_p$) mass delivered for treatment are of fundamental importance for in-situ treatments where residence times on the urban surface or in the upper end of the urban watershed in the presence of entrained particulate matter are less than minutes for storm water and hours to months for snowmelt. With respect to partitioning, the edge of the highway shoulder receives a mixture of aqueous heavy metals and entrained particulate matter. Therefore, there will be a competitive process of partitioning. Even for the complexities of the highway environment, trends predicted by theory can be used to explain actual competitive partitioning results.

Partitioning is based on defining two partitions, for a given constituent, in the dissolved and particulate-bound fractions. The dissolved fraction is defined as $C'_d$ in [M/L$^3$], where $M =$ mass of constituent and $L^3 =$ volume of aqueous solution (or non-aqueous solution). The particulate form is defined as $C_p$ in [M/L$^3$], where $M =$ mass of constituent and $L^3 =$ volume of solid plus water (the bulk volume). Therefore, the form $C_p$ is the mass of the constituent “sorbed” on and in the solid relative to the total volume of solids and water (Thomann and Mueller 1987). In the sediment zone (i.e. benthic layer of a storm water detention basin) then
there will be porosity, $\eta$, which is the volume of water per bulk volume in [$L^3_w/L^3_{s+w}$].

Therefore, in the water column or in the sediment layer, total concentration is

$$C_T = C_p + \eta C_d'$$  \hspace{1cm} (1)

or

$$C_T = C_p + C_d$$  \hspace{1cm} (2)

where:  \hspace{1cm} $C_d = \text{the “porosity-corrected” dissolved constituent} \ [M/L^3_{s+w}]$

In many upper sediment layers, $\eta$ ranges from 0.7-0.8. For the balance of this analysis let us assume we are in the water column and that the dissolved form is porosity corrected.

Therefore, all constituent concentrations are on a bulk volume basis:

$$C_d = \eta C_d' \hspace{1cm} (\eta = 1)$$  \hspace{1cm} (3)

The particulate form, $C_p$ is expressed as mass of constituent per bulk volume of solids and water.

For a given concentration of solids, $C_p$ can also be expressed as

$$C_p = C_s m$$  \hspace{1cm} (4)

where:  \hspace{1cm} $m$ = the solids concentration in [M/L$^3$]

$L$ = bulk aqueous volume with solids strained (essentially TSS)

$C_s$ = constituent concentration expresses on a dry weight basis [M/M]

i.e. mass of metal on or in solid / mass of dry solid; Units for $C_s$ are typically $\mu g/g$; noting the $\mu g/g$ is equivalent to a part per million

Assuming linear kinetics (Thomann and Mueller 1987; Figure 1.2), a representation of the mechanism of sorption of the chemical to the particulates and desorption from the particulates back into the dissolved phase is described in Equation 5 and 6:

$$\frac{dC_p}{dt} = K_u m C_d' - K C_p$$  \hspace{1cm} (5)
\[ \eta \frac{dC'_d}{dt} = -K_u mC'_d + KC_p \]  

(6)

where:  
\( K_u \) = sorption rate \[L^3/M \cdot T\]  
\( K \) = desorption rate \[1/T\]  

For a fixed solids concentration, Equation 5 becomes

\[ \frac{dC_s}{dt} = K_u C'_d - KC_s \]  

(7)

We then can express \( K_d \) as:

\[ K_d = \frac{C_s}{C'_d} = \frac{K_u}{K} \]  

(8)

and units of \( K_d \) are:

\[ K_d = \frac{\text{Mass of metal}}{\text{Mass of solid}} \times \frac{\text{Mass of metal}}{\text{volume of solution}} \]

where \( K_d \) is the equilibrium partitioning coefficient.

Figure 1.2. Conceptual relation between particulate bound and dissolved phases.
In pavement runoff, meltwater or any aqueous system, there is a temporal partitioning between heavy metals in solution and solids. These partitioning reactions are generally non-linearly reversible between the solid-phase and soluble phase concentrations. Operationally, the soluble or dissolved fraction is that fraction that passes the 0.45-µm membrane filter, and therefore contains both the dissolved and part of the colloidal-bound heavy metals. When the rate of sorption and desorption are equal, concentration equilibrium exists between the dissolved and solid-phase concentrations of a heavy metal. The ratio of these phases is referred to as the partitioning coefficient \( K_d \) for a particular heavy metal at a particular pH and redox level:

\[
K_d = \frac{C_s}{C_d} = \frac{\left( \frac{P}{m} \right)}{D} \quad (9)
\]

where, \( D \) is the dissolved mass of a heavy metal (µg/L), and \( P \) is the particulate-bound mass of a heavy metal (µg/L). Substitution of equation (2) and (3) into equation (1) yields the dissolved fraction \( (f_d) \) and the particulate-bound fraction \( (f_p) \) as defined by:

\[
f_d = \frac{D}{(D + P)} = \frac{C_d}{C_T} = \frac{1}{[1 + K_d(m)]} \quad (10)
\]

\[
f_p = \frac{P}{(D + P)} = \frac{C_p}{C_T} = \frac{[K_d(m)]}{[1 + K_d(m)]} \quad (11)
\]

\[f_d + f_p = 1 \quad (12)\]

where, \( m \) in this case is the total suspended solid mass in terms of mass/volume of aqueous solution \( (O’Connor 1988) \). For \( f_d > 0.5 \), the heavy metal mass is mainly in dissolved form. The product of \( (K_d)(m) \) is dimensionless and \( K_d \) is usually expressed as liters per kilogram \( (L/kg) \). The larger the \( K_d \) value the greater the partitioning of a heavy metal to the solid phase. The greater the dissolved fraction, or the more soluble the heavy metal, the lower the \( K_d \) value. The sum of the dissolved and
The overall goal of this dissertation research is to identify and characterize heavy metal distribution in urban runoff, snowmelt and soils subject to traffic and urban practices. The contributions from this research are five fold. First, it was to examine metal concentrations as a function of particle size distribution (PSD) for rainfall/snow residuals and soil/residual complexes. Secondly, it was to determine the demonstrable impact of traffic and climate influences on loadings during a rainfall or snow event. Thirdly, it was to demonstrate that the mineralogical and surface characteristics of anthropogenic snow residual and soil/residual complexes are a function of PSD. Another contribution was to demonstrate that at the upper end of the urban watershed that heavy metals in rainfall runoff can be highly dissolved. Finally, the dissertation was to demonstrate that at the upper end of the urban watershed that heavy metals in snow can be highly particulate bound.

There are seven major objectives or chapters of this research. These objectives will be carried out for data collected at ten experimental study sites on major transportation roadways in urban Cincinnati, Ohio. The format of this dissertation is set for the guidelines presented in the American Society of Civil Engineer’s *Journal of Environmental Engineering*. Chapters two and three of this research examines heavy metal distribution between the dissolved and particulate fractions in storm water. Chapters four through six addresses studies related to urban snow pollution generated by traffic. Chapters seven and eight addresses studies related to anthropogenically-loaded transportation land use urban soil/residual complexes.

**Literature Cited in Chapter 1**


Urban highway storm water often contains elevated levels of heavy metals and particles. These heavy metals, principally Pb, Cd, Cu, Ni, Zn, and Cr, can pose acute and chronic threats to receiving water bodies and soils. In receiving water, the dissolved fraction of these heavy metals has the potential for acute and long-term chronic toxicity for aquatic life. What is unique about heavy metals is that unlike organic compounds, heavy metals are not eventually degraded in the environment. With recent signature of the Final Rule for Phase II Storm Water NPDES regulations on 29 October 1999, issues related to heavy metals in roadway storm water have now come into direct focus at the national regulatory level. In the urban highway environment, heavy metals are generated primarily from the abrasion of metal-containing vehicular parts, including the abrasive interaction of tires against pavement, leaching of heavy metals from infrastructure, oil and grease leakage and industrial discharges (Lygren et al. 1984; Muschack 1990; Ball et al. 1991; Armstrong 1994). The majority of traffic/vehicular generated solids come from abrasion of tires and pavement (Kobriger and Geinopolos 1984). Pavement and vehicle part abrasion are sources of solids, ranging from colloidal to gravel size particles. These solids (washed off in lateral pavement sheet flow, $q_{sfs}$) during rainfall runoff events as part of a heterogeneous mixture of heavy metals, organic compounds, oil and grease, can influence partitioning of heavy metals to and from the dissolved phase, $f_d$.

Heavy metal concentrations in urban runoff can range from essentially background levels to milligram/liter levels during a single rainfall runoff event. Since the concentration of hydrologically transported constituents can vary by orders of magnitude during a single runoff event, a single index, designated as an event mean concentration (EMC), has been used often to

Chapter 2
Temporal Variations in Heavy Metal Loading in Urban Highway Pavement Sheet Flow – Implications for In Situ Treatment Design
characterize concentrations. EMCs represent a flow average concentration for the event. In addition, EMCs at a particular site can vary depending on average daily traffic (ADT), vehicles during storm (vds), rainfall runoff intensity, previous dry days and climate conditions. While the benefits of EMC data include simplicity and economics, drawbacks of EMC data include the inability of such data to quantify the temporal variation of water quality parameters and partitioning throughout a rainfall runoff event.

Traffic and roadway maintenance activities are further sources of particulates and solids that either initially are abraded heavy metals that dissolve in the low pH rainfall runoff of low alkalinity, are solids that contain heavy metals, or are solids that act as a substrate to which dissolved heavy metals can partition. Abraded pavement accounts for 40-50% and abraded tires account for 20-30% of the total particulate matter generated (Kobriger and Geinopolos 1984). Most of these abraded solids and particulates contain heavy metals. Abraded tire particles have a mean diameter of 20-µm, a density ($\rho_s$) of 1.5 - 1.7 g/cm$^3$ and are significant sources of Zn and Cd (Sansalone and Tribouillard 1999).

**Study Objectives**

There were three objectives of this study. These objectives were carried out at an instrumented experimental site on interstate 75 in urban Cincinnati for eight fully analyzed rainfall runoff events over two years. The primary objective illustrates the temporal relationship between cumulative loadings (mass) of dissolved and particulate heavy metals as well as suspended and dissolved solids. This objective intended to demonstrate the need for quantification of heavy metal partitioning in $q_{df}$ when considering the design and operation of in-situ treatment systems, for example, in-situ water quality control practices such as BMPs. The second objective quantified the mean and standard deviation of the heavy metal dissolved
fractions across each event and evaluated the temporal variation of partitioning in q_{sf} during an event. Results from this objective intended to illustrate the variation in heavy metal f_d values across the duration of the rainfall runoff event to assess implications of such variations when considering the design of in-situ treatment systems. The final objective compared the temporal washoff of the heavy metal dissolved and particulate with respect to q_{sf} volume. Results from this objective intended to examine implications for capture and treatment of the “first flush” from a rainfall runoff event.

**Previous Work**

Because of the difficulty and expense associated with obtaining and analyzing discrete samples throughout the progression and duration of a rainfall runoff event, many State DOTs, consultants and researchers have utilized EMC data as inputs for their regulatory, water quality characterization and treatment needs. Previous work at the Cincinnati experimental site has demonstrated the variation in heavy metal site EMCs and also demonstrated that significant partitioning can occur within approximately six hours of initial sample collection for heavy metals such as Cu in runoff having a pH of 6.5 (Sansalone and Buchberger 1997). Such findings demonstrated that composite storm water samples collected for EMC determination, while economical, could in fact provide erroneous partitioning results due to sample holding time. Heavy metal EMCs were calculated for this site from many discrete rainfall runoff samples, and analyses were taken at two to ten minute intervals over the event duration during a two-year period (Sansalone and Buchberger 1997).

Heavy metals transported in urban storm water partition into dissolved and particulate-bound fractions as a function of pH (-log{H_{3}O^+} where activity coefficient, \( \gamma = 1.0 \)), runoff alkalinity (as CaCO₃), runoff pavement residence time, solids concentration (as TSS) and solids
surface (as specific surface area) characteristics. Urban storm water characterization of heavy metal partitioning in urban roadway areas of London reported dissolved fractions for Cd of 69%, Cu of 87%, Pb of 47%, and Zn of 82% (Revitt et al. 1990). These partitioning findings for roadway storm water, $q_{sf}$ and the high dissolved fractions for heavy metals have significant implications for the development or selection of effective treatment methods.

Because of the expense associated with water quality analyses, specifically with trace and heavy metals, researchers have investigated the potential use of surrogates for equilibrium measurements of ionic species, heavy metals and nutrients. These surrogates include the use of solid indices for total suspended solids (TSS), volatile suspended solids (VSS), and total dissolved solids (TDS) (Thomson et al. 1997). For the particulate fraction, other researchers have investigated the relationship between particle size and metal concentration (Xanthopoulos and Hahn 1990). For rainfall runoff, correlations between heavy metal concentration and particle size in roadway storm water indicate that higher concentrations are associated with smaller particles (Xanthopoulos and Hahn 1990; Price and Yonge 1995). Design and operation guidance for water quality devices based on particle and particulate-bound constituent removal require quantification of both particles and particulate-bound mass. From an ecological viewpoint, heavy metal partitioning has significant implications for potential toxic effects in receiving waters and surficial soil (Barrett et al. 1998). In receiving waters, organic solids, iron and manganese oxides are considered the main solid components that mediate the partitioning of heavy metals (Muller and Sigg 1990).

**Methodology**

**Experimental site**

An experimental facility, utilized since 1995, was designed to sample and analyze representative lateral pavement sheet flow ($q_{sf}$) at the pavement edge. Measurements of $q_{sf}$ are
critical for design of in-situ treatment systems such as BMPs loaded by such flow. At the site, the downstream edge of the pavement section was saw-cut and removed to allow the construction of a 15-m wide instrumented sampling facility. The drainage area to the site was a well defined 15-m wide by 20-m long (across the super-elevated four lanes of pavement) asphalt pavement drainage area. Details of the sampling and instrumentation configuration are provided elsewhere (Sansalone and Buchberger 1997).

**Sampling and field data collection**

During 1996 and 1997, eight rainfall runoff events were sampled and analyzed at the experimental site. The analysis for this study focused on characterization of heavy metal partitioning and temporal washoff of heavy metals and solids.

Hydrologic and water quality field data were collected during all sampled events at the experimental site. The rain events varied in duration, intensity, inter arrival times and generated flows (ranging from the low-flow to high-flow capacity of the flume). Samples were analyzed for metals and solids for all events and pH, redox, and conductivity for selected events. Details of hydrology, sampling, analyses and QA/QC protocols are provided elsewhere (Sansalone and Buchberger 1997; Sansalone et al. 1998).

**Heavy and trace metal protocol**

After the completion of a runoff event, the samples were immediately transported to the nearby laboratory. Metal partitioning between the dissolved and particulate-bound phases is a dynamic process. Therefore, samples were fractionated between dissolved and particulate-bound heavy metals and acidified within hours of being logged at the laboratory.

The dissolved fraction is defined as heavy metals of an unacidified sample that pass through a 0.45-µm membrane filter (APHA 1992). Each one-liter sample was mixed on a magnetic stirrer,
and a 50-ml sample was passed through a membrane filter. The 50-ml dissolved fraction was immediately acidified with 2.5 ml of trace-metal HNO₃. The particulate-bound heavy metal fraction, retained in the membrane filter, was subsequently digested using a microwave-assisted procedure based on SW-846 Method 3015 (USEPA 1990). Heavy metal analyses conducted on a Perkin-Elmer Optima 3000 Inductively Coupled Plasma Spectrometer included scans for Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb.

Characterization indices for water quality and heavy metal mass

Because non-point heavy metals, H₂O⁺, organics, oil, grease, particulate matter and solids indices (total solids, TS, total suspended solids, TSS, volatile suspended solids, VSS) concentrations often vary by several orders of magnitude during a runoff event, a single index, known as an event mean concentration (EMC), is often used to characterize such concentrations. The EMC of a rainfall runoff event for a particular constituent, is defined as:

\[
EMC = \bar{C} = \frac{M}{V} = \frac{\int_{0}^{tr} c(t)q(t)dt}{\int_{0}^{tr} q(t)dt}
\]

where:
- \(M\) = total mass of constituent (heavy metal fraction, H₂O⁺, TSS, etc.)
- \(V\) = total liquid volume of flow or sample
- \(\bar{C}\) = flow-weighted concentration average
- \(c(t)\) = time-variable concentration
- \(q(t)\) = time-variable flow
A “first flush” can be defined as the delivery of a disproportionately large load of constituents during the early part of the runoff hydrograph (Schueler 1987). For the development of a criterion to determine whether the delivery of a disproportionately large load of constituents occurs with respect to the q_{sf} runoff volume, incremental heavy metal or solid mass and flow can be normalized to the respective total of mass or flow. The resulting normalized incremental results can be plotted as a function of normalized time. Normalized time is simply each increment of time normalized to the total duration of q_{sf}. The definition given in (Schueler 1987) can be generalized for the entire storm based on normalized mass and flow volume results. This more general definition would indicate that mass plotted above the normalized flow volume line would demonstrate the occurrence of a “first flush” with respect to flow volume during any time increment of the rainfall runoff event (Sansalone and Buchberger 1997).

Whether in pavement runoff, urban storm water or any aqueous system, there is a temporal partitioning between heavy metals in solution and solids whether these solids are in suspension (TSS, VSS) or as settleable solids that may be part of a fixed or mobile bed load. This partitioning includes specific mass transfer mechanisms of sorption, ion exchange and surface complexation with both organic and inorganic sites on the solid matter. These partitioning reactions are generally non-linearly reversible between the solid-phase and soluble phase concentrations. Total concentration of a heavy metal is therefore the sum of the dissolved (c_d) and the particulate-bound concentrations (c_p) where:

\[ c_T = c_d + c_p \]  

(2)
Operationally, the soluble or dissolved fraction is that fraction that passes the 0.45 micron membrane filter and therefore contains both the dissolved and part of the colloidal-bound heavy metals. The solid phase concentration, \( c_p \), is defined as the product of the heavy metal concentration on the solid phase, \( c_s \), in terms of mass/mass of solids and the concentration of the adsorbing solid material in the aqueous system, \( m \), typically measured as either TS or TSS in terms of mass/volume of aqueous solution:

\[
c_p = (c_s)(m)
\]  

(3)

Under equilibrium conditions, when the rate of sorption and de-sorption are equal, concentration equilibrium exists between the dissolved and solid-phase concentrations of a heavy metal (Sansalone et al. 1998). The ratio of these phases at equilibrium is referred to as the partitioning coefficient, \( K_d \) for a particular heavy metal at a particular pH and redox level:

\[
K_d = \frac{c_p}{c_d}
\]  

(4)

Substitution of Equation (3) and (4) into Equation (2) yields the dissolved fraction \( f_d \) and the particulate-bound fraction \( f_p \) are defined as:

\[
f_d = \frac{D}{(D+P)} = \frac{c_d}{c_T} = \frac{1}{[1+K_d(m)]}
\]  

(5)

\[
f_p = \frac{P}{(D+P)} = \frac{c_p}{c_T} = \frac{(K_d)(m)}{[1+K_d(m)]}
\]  

(6)

where, \( D \) is the dissolved mass of a heavy metal (mg) and \( P \) is the particulate-bound mass of a heavy metal (mg). For \( f_d > 0.5 \), the heavy metal mass is mainly in dissolved form. The product of \( (K_d)(m) \) is dimensionless and \( K_d \) is usually expressed as liters per kilogram (L/kg). The larger the \( K_d \) value, the greater the partitioning to the solid phase. Heavy metals in pavement runoff have \( K_d \) values that range from \( 10^2 \) to over \( 10^6 \) (Sansalone et al. 1998).

For each discrete sample obtained, dissolved and particulate heavy metal concentrations were obtained after sample preparation and digestion through ICP-AES analysis. Each respective
sample concentration ($c_i$) (dissolved or particulate) was multiplied by the $q_{sf}$ volume ($v_i$) representative of the discrete time increment to determine heavy metal or solids mass ($m_i$) as shown in Equation 4.

$$m_i = (c_i)(v_i) \quad (7)$$

To evaluate the study objectives, these data ($m_i$) were then plotted for both dissolved and particulate fractions as a function of elapsed time. To illustrate the temporal variation in partitioning, sample statistics were calculated to describe the characteristics of the dissolved fraction for an event in terms of a sample mean ($\mu$), standard deviation ($\sigma$) and skewness ($\gamma$).

**Results**

Results are presented graphically in two formats. The first format is presented as cumulative washoff plots illustrating the temporal variation in dissolved and particulate mass. Descriptive statistics for $f_d$ are summarized in each plot. The second format is normalized data (mass, flow) for both the dissolved and particulate mass, plotted as a function of normalized time. These plots provide a comparison for the delivery of the dissolved and particulate mass with respect to the flow volume. Both formats are provided side by side in Figures 2.1 through 2.8. The figures are presented in chronological order, and each figure contains plots for a single rainfall runoff event.

**21 May 1996 rainfall runoff event (Figure 2.1)**

This event was a low runoff volume, short duration event composed of two separate and distinct hydrographs with an intervening period of no runoff and a mean runoff pH of 6.86. Cumulative mass trends across the entire event demonstrate that the dissolved mass of each
Figure 2.1. Cumulative mass plots (left) and normalized washoff plots (right) for 21 May 1996 event.
heavy metal dominated the particulate fraction. TDS mass dominated that of TSS across the entire event. The descriptive statistics indicate a high event $f_d$ mean for all heavy metals with small standard deviations except for Cu and TDS. Plots of normalized delivery generally indicated that dissolved mass was more rapidly transported by $q_{sf}$ than particulate mass in the first half of the event. Delivery of all dissolved fractions, except Pb, proceeded the flow volume curve.

18 June 1996 rainfall runoff event (Figure 2.2)

This event was a high runoff volume, short duration event composed of a series of three back to back hydrographs and a mean runoff pH of 7.50. The influence of these hydrographs can be observed in the three variations of slopes in the plots. Cumulative mass trends across the entire event demonstrate that the dissolved mass of each heavy metal dominated the particulate fraction. In contrast to these results, TSS mass clearly dominated that of TDS across the entire event. The descriptive statistics indicate a high event $f_d$ mean for all heavy metals with small standard deviations. Plots of normalized delivery generally indicate that dissolved mass is more rapidly transported by $q_{sf}$ than particulate mass and flow volume over a majority of the event, although the difference is not as great as for 21 May 1996.

7 July 1996 rainfall runoff event (Figure 2.3)

The results presented in Figure 3 represent an interesting contrast to the results from the first two events. This event was a high runoff volume, short duration event also composed of three back to back hydrographs and mean runoff pH of 6.20. Cumulative mass trends across the entire event demonstrate that the dissolved mass of each heavy metal dominated the particulate fraction. These plots are unique in that the slope of the cumulative dissolved mass curve for all heavy metals is much steeper at the end of the event than near the beginning. In contrast to the
Figure 2.2. Cumulative mass plots (left) and normalized washoff plots (right) for 18 June 1996 event.
Figure 2.3. Cumulative mass plots (left) and normalized washoff plots (right) for 7 July 1996 event.
dissolved heavy metal mass, the TSS mass dominated that of TDS for much of the event. The
descriptive statistics indicate a higher event $f_d$ mean for all heavy metals with small standard
deviations. TDS exhibited a low mean $f_d$ and a high standard deviation. In contrast to the first
two events described, plots of normalized delivery generally show little difference in delivery
between the dissolved and particulate mass. Delivery of both fractions lagged behind the flow
curve for all metals, yet ahead of the flow curve for TSS and TDS.

8 August 1996 rainfall runoff event (Figure 2.4)

This event was a high runoff volume, short duration event composed of a single, distinct
hydrograph and a mean pH of 7.29. Cumulative mass trends across the entire event demonstrate
that the dissolved mass of each heavy metal dominated the particulate fraction. As with the 7
July 1996 event, TSS mass dominated that of TDS across much of the event. The descriptive
statistics indicate a high event $f_d$ mean for all heavy metals with small standard deviations except
for Cd and TDS. Plots of normalized delivery generally indicate that dissolved mass is more
rapidly transported by $q_{sf}$ than particulate mass during the rising limb of the runoff hydrograph.
The delivery of the dissolved and particulate fractions did not demonstrate a clear trend when
proceeding or lagging the flow volume curve.

17 October 1996 rainfall runoff event (Figure 2.5)

This event was a high runoff volume, long duration event composed of multiple, distinct
hydrographs and a mean pH of 7.12. Cumulative mass trends across the entire event
demonstrate that the dissolved mass of each heavy metal dominated the particulate fraction. The
TDS fraction dominated the TSS fraction through much of the event but not significantly as
indicated by a mean $f_d$ of 0.56. The descriptive statistics indicate a high event $f_d$ mean for all
heavy metals with small standard deviations. Plots of normalized delivery generally indicate that
Figure 2.4. Cumulative mass plots (left) and normalized washoff plots (right) for 8 August 1996 event.
Figure 2.5. Cumulative mass plots (left) and normalized washoff plots (right) for 17 October 1996 event.
dissolved mass is more rapidly transported by \( q_{d} \) than particulate mass throughout much of the event, with the exception of Pb. In contrast to the 7 July 1999 event, delivery of the dissolved and particulate fractions proceeds the flow volume curve.

**25 November 1996 rainfall runoff event (Figure 2.6)**

The cumulative mass profile plots presented in Figure 6 are similar to those of the 7 July 1996 event. This event was a low runoff volume, moderate duration event of two distinct hydrographs separated by an approximately 40 minute low flow period that can be discerned from the lack of data points between elapsed time of 55 and 95 minutes. The runoff mean pH was 7.56. Cumulative mass trends across the entire event demonstrate that the dissolved mass of each heavy metal dominated the particulate fraction, although the mean \( f_{d} \) for Pb (0.63) was the lowest of all the events. These plots are similar to the corresponding plots for the 7 July 1996 event in that the slope of the cumulative dissolved mass curve for all heavy metals does not taper off towards the end of the event, indicating the continued availability for transport of dissolved material. The TDS fraction dominated the TSS fraction through much of the event but not significantly as indicated by a mean \( f_{d} \) of 0.55. The descriptive statistics indicate a high event \( f_{d} \) mean for all heavy metals, except Cu, and small standard deviations for all metals except Cu. Plots of normalized mass and flow indicate little difference in delivery between the dissolved mass, particulate mass and flow volume.

**16 December 1996 rainfall runoff event (Figure 2.7)**

The cumulative mass profile plots presented in Figure 2.7 are similar to those of the 25 November 1996 event. This event was a low runoff volume, moderate duration event of two distinct hydrographs separated by an approximately 200 minute low flow period that can be discerned from the lack of data points between elapsed time of 70 to 290 minutes. The runoff
Figure 2.6. Cumulative mass plots (left) and normalized washoff plots (right) for 25 November 1996 event.
Figure 2.7. Cumulative mass plots (left) and normalized washoff plots (right) for 16 December 1996 event.
mean pH was 7.54. Cumulative mass trends across the entire event demonstrate that the dissolved mass of each heavy metal dominated the particulate fractions. These plots are similar to the corresponding plots for the 25 November 1996 event in that the slope of the cumulative dissolved mass curve for all heavy metals (except possibly Zn) does not decrease towards the end of the event, indicating the continued availability for transport of dissolved material. The TDS and TSS mass transported during the event were nearly equal, and the solids $f_d$ was 0.56. The descriptive statistics indicate a high event $f_d$ mean and small standard deviations for all heavy metals. Plots of normalized mass and flow indicate little difference in delivery between the dissolved mass, particulate mass and flow volume, except for solids where interestingly TSS proceeds both the flow volume curve and the delivery of TDS.

12 June 1997 rainfall runoff event (Figure 2.8)

This event was a low runoff volume, short duration event composed of a single, distinct hydrograph and a mean runoff pH of 6.70. Cumulative mass trends across the entire event demonstrate that the dissolved mass of each heavy metal strongly dominated the particulate fraction, although Pb had a mean $f_d$ of 0.64. TDS mass dominated the TSS mass across much of the event. The statistics indicate a high event $f_d$ mean with small standard deviations for all metals except Pb and TDS. The delivery of the dissolved and particulate fractions did not demonstrate a clear trend with respect to the flow volume curve.

Conclusions

This study presented cumulative heavy metal and solid loadings and partitioning results from a series of eight rainfall runoff events loading a 300-m$^2$ instrumented asphalt pavement drainage area located on inter state 75 in urban Cincinnati. With respect to source control design and in-situ treatment of lateral pavement sheet flow for water quality enhancement and
Figure 2.8. Cumulative mass plots (left) and normalized washoff plots (right) for 12 June 1997 event.
mitigation of ecological impacts, there are a number of conclusions that can be drawn from this study.

The first and most important conclusion is that even for moderate event mean pH values (6.20 to 7.56) the dissolved mass of heavy metals in q_{sf} dominates the particulate mass for Zn, Cd, Cu and even Pb. For this site, the mean pavement residence time (τ_{sf}) of q_{sf} for each event was less than 10-minutes with the exception of the 16 December 1996 event with a τ_{sf} of 15-minutes. Despite relatively neutral pH values, the low q_{sf} event mean alkalinity (less than 40 mg/L as CaCO_3 for all events) coupled with low τ_{sf} resulted in less dissolved heavy metal contact time with flow-entrained TSS. These factors, in aggregate produced a dissolved mass that dominated the particulate mass for Zn, Cd, Cu and even Pb through the duration of each event. These conclusions are applicable to all events despite a wide variation in event hydrology.

The second conclusion that follows from the first is that the degree to which each heavy metal was dissolved across the duration of each event was relatively constant. Across the entire duration of each event, standard deviations in each heavy metal dissolved fraction were generally small. Results demonstrate that the low pH events exhibited smaller standard deviations for the heavy metal f_{dl}, than for higher pH events.

For the designer of in-situ treatment systems, the above conclusions indicate that treatment will require the effective use of adsorption or precipitation as physico-chemical mechanisms for immobilization of the dissolved mass. In fact, any reasonable degree of overall mass removal efficiency for an in-situ treatment system design will require a high degree of adsorption or precipitation because of the high dissolved heavy metal mass. This requirement is valid whether the designer exploits such mechanisms to partition dissolved metals onto entrained
TSS that is subsequently treated by filtration or sedimentation, or to directly remove dissolved metals by mass transfer onto adsorptive media.

**Implications for BMP Design**

The conclusions identify several critical heavy metal partitioning and loading results that have significant implications when considering treatment process viability of in-situ treatment design for BMPs. Each of the results reported have an important effect on initial selection and then on the details of treatment design for the selected in-situ BMPs.

First, partitioning results for all the heavy metals (including Pb) indicate that partitioning is dominated by the dissolved fraction of the heavy metal mass for all but the early portion of each rainfall runoff event. This conclusion is consistent across all events despite a random selection of hydrologic events to characterize over a two-year period and despite the variation in runoff event mean pH values of 6.20 to 7.56. These partitioning results are consistent with the fact that $\tau_{sf}$ is typically less than 10 minutes for pavement sheet flow, $q_{sf}$ (Sansalone et al. 1998). In addition, the runoff leaving the pavement is very poorly buffered with a site event mean alkalinity of 25 mg/L (as CaCO$_3$). Therefore despite variations in event hydrology and some variation in event mean pH, the partitioning results demonstrated that towards the upper end of the urban catchment, which is the location for in-situ source control BMPs, heavy metals can predominately partition towards the dissolved phase, as $f_d$.

In terms of implications for BMPs, these results indicate that in-situ treatment BMPs, placed near the upper end of an urban pavement watershed with similar pH, alkalinity, TSS and residence time, can be effective if they are selected and then designed to provide capture (a function of hydrology and hydraulics) and then treatment of the dissolved fraction (either through sorption or precipitation). If the BMP is not designed with a treatment mechanism for
the dissolved fraction, the heavy metal trap efficiency of the BMP can at best be equal to only the \((1-f_d)m_i\) for a given heavy metal, \(i\), assuming full runoff capture by the BMP. For example, consider Zn for the 18 June 1996 event. If a BMP was designed to treat only the particulate-bound fraction of Zn and was not designed with a mechanism to remove the dissolved fraction (sorption, precipitation, etc.), the removal efficiency (in percent) for the total mass of Zn would be \((1-0.83)m_i\) or 17 percent of \(m_i\). This assumes that through filtration or sedimentation mechanisms, the BMP captures the entire particulate-bound mass.

At the upper end of the watershed there is relatively little time for heavy metal contact with entrained TSS, another reason for the predominate dissolved fraction, \(f_d\), for each event. Any process at environmental pH levels (5.5 to 8.5) that promotes increased residence time and interfacial contact will increase the probability of heavy metal solutes partitioning to solid matter, either as entrained TSS as in a detention basin or in a fixed media device such as a PET. This partitioning of solute to solid is by definition adsorption, whether in a detention basin or a fixed media device. In fact, the only mechanisms available to remove non-volatile heavy metal solutes from the water column in a detention basin are: partitioning to solids and then sedimentation; an increase in pH to promote precipitation; or through various biological uptake vectors. Many basins, particularly retention basins can have residence times in terms of many hours or days as opposed to minutes, thus promoting partitioning at environmental pH levels. However, once heavy metals become part of the basin sediments, the potential exists for the sediment in the benthic zone to become anaerobic, releasing the heavy metals and permitting advection and diffusion of the heavy metals back into the water column.

Many current BMP designs utilize mechanisms of filtration and sedimentation, therefore removal of particles, solids (TSS) and particulate-bound constituents including heavy metals.
While these mechanisms are important and must be utilized, the only way that such mechanisms can effectively remove the dissolved fraction of a heavy metal is if that metal is first partitioned to entrained or suspended solids and then filtered or removed through sedimentation. In addition, if a filter media is to be utilized to remove dissolved heavy metals, it must be designed to sorb and retain the dissolved heavy metal and have sufficient surface area for a reasonable design life.

**Literature Cited in Chapter 2**


Chapter 3
Influence of Highway Runoff Chemistry, Hydrology and Residence Time on Heavy Metals – Implications for Treatment at the Highway Shoulder

Storm water runoff, impacted by both urban transportation activities and associated urban transportation infrastructure, transports significant loads of dissolved, colloidal and suspended solids in a complex heterogeneous mixture that includes heavy metals, inorganic and organic compounds. Compared to drinking water and domestic wastewater, storm water treatment continues to pose uniquely difficult challenges due to the unsteady and stochastic nature of processes including traffic, rainfall-runoff, heavy metal partitioning and transport of entrained solids. Heavy metals from these sources are not degraded in the environment and constitute an important class of acute and chronic contaminants. Highway storm water levels of Zn, Cu, Cd, Pb, Cr and Ni can be above ambient background levels, and for heavily traveled highways often exceed surface water discharge criteria on an event basis for both dissolved and particulate-bound fractions. Storm water transports a wide gradation of particulate matter ranging in size from smaller than 1-µm to greater than 10,000-µm. From a treatment perspective, entrained solids or engineered media having reactive sites and large surface-to-volume ratios mediate partitioning and transport of heavy metals while serving as reservoirs for reactive constituents.

Since passage of the 1972 Clean Water Act, storm water non-point pollution has advanced from being a problem that was understood only well enough to realize the difficulties associated with application of conventional treatment process design, to now becoming our most recent water treatment challenge. Since the National Pollution Discharge Elimination System (NPDES) Storm Water Phase I permitting regulations in the 1980s, there has been a proliferation of suggested in-situ storm water “best management practices”, BMPs. However, experience over the last decade has demonstrated that there continues to be a significant gap in knowledge
between conventional in-situ BMP design/analysis and design based on the actual physical and chemical characteristics of storm water loadings. Such an understanding of these physical and chemical characteristics of storm water loadings at the point of treatment, such as the edge of the highway shoulder, is critical to the success of a new generation of storm water treatment systems that will develop in response to the new February 2000 Phase II Storm Water Final Rule. This knowledge will require an understanding of temporal storm water chemistry, temporal heavy metal partitioning between solid and solution phases, physico-chemical characteristics of transported particulate matter, and highway hydrology as influenced by traffic and pavement conditions.

**Study Objectives**

There were three objectives of this study. These objectives were carried out at an instrumented experimental site on inter state 75 in urban Cincinnati for eight fully analyzed rainfall runoff events over two years. The goal of the paper is to demonstrate that an understanding of heavy metal partitioning and pavement hydrology at the edge of the pavement shoulder is a critical prerequisite for in-situ BMP design focused on heavy metal capture. As a result, there are three objectives of this paper. The first is to demonstrate that despite relatively low alkalinity and essentially neutral pH values, heavy metal mass can be predominately dissolved at the edge of the highway shoulder. The second objective is to demonstrate the role of residence time and hydrology on delivery of heavy metals at the edge of the highway shoulder. The final objective is to examine the trends in non-equilibrium heavy metal partitioning in terms of temporal heavy metal partitioning coefficients and delivered suspended solids at the edge of the highway shoulder. Finally, the paper will discuss implications of these findings for the selection, design and efficacy of in-situ BMPs loaded by highway pavement sheet flow.
Previous Work

Storm water runoff from roadways transports significant event and annual loads of heavy metals and a wide gradation of particulate matter to receiving waters (Hamilton and Harrison 1991). In urban environments, heavy metals are generated primarily from the abrasion of metal-containing vehicular parts, including the abrasive interaction of tires against pavement, leaching of metal elements from infrastructure, and oil and grease leakage (Lygren et al. 1984; Muschack 1990; Ball et al. 1991; Armstrong 1994). Storm water from urban and transportation land uses is a complex physico-chemical heterogeneous mixture of heavy metals, particulate matter, inorganic and organic compounds with variations in flow, concentrations and mass loadings that sometimes vary by orders of magnitude during a single hydrologic event. This complexity has made storm water very difficult to treat. For example, two years of research results from data collected on an instrumented urban transportation roadway site located at the edge of the highway shoulder on inter state 75 in urban Cincinnati demonstrates the variation in magnitude of event mean concentration (EMC) values between discrete hydrologic events. For total Zn, EMCs ranged from 15,244 to 459 µg/L, total Cu from 325 to 43 µg/L, total Pb from 88 to 33 µg/L, total Cr from 35 to 13 µg/L, and total Cd from 11 to 5 µg/L (Sansalone and Buchberger 1997).

From urban inter state highway pavement alone, annual heavy metal, total suspended solids (TSS), chemical oxygen demand (COD) loadings and storm water flows have been shown to equal or exceed annual loadings and flows from untreated domestic wastewater for a given urban area (Sansalone et al. 1998). The urban inter state and major arterial pavement area typically constitutes less than a factor of 10 of the total pavement area for an urban area while generating a disproportionate pollutant load especially with respect to heavy metals. In fact, it was been reported in the literature as early as 1974 that storm water runoff from urban pavement
represented a greater pollutant loading to receiving water than point source wastewater discharges from that same urban area (Klein et al. 1974).

**Background**

Heavy metal partitioning between the dissolved and particulate-bound fractions in storm water is a dynamic process. This partitioning, which varies significantly between hydrologic events and traffic patterns is a function of pH, alkalinity, residence time, mixing and solids characteristics (Sansalone and Buchberger 1997). As a result of very low rainfall alkalinity, low rainfall pH (4 to 5.5) and low pavement residence time, urban roadway runoff can be of moderate to low alkalinity (< 50 mg/L as CaCO₃) with slightly acidic to neutral runoff pH. This results in dissolution of finely abraded metallic particles generated from traffic activities, and therefore metal mass partitions predominately to the dissolved fraction for short residence times. Understanding the kinetics of this non-equilibrium partitioning is critical for proper monitoring, conceptual design and viability of unit operations and processes that may be applied as in-situ or source control treatment.

For sampling and monitoring, previous results indicate for such pH and alkalinity conditions that the originally dissolved Cu mass partitions to the particulate-bound fraction within 6 hours of transport from the pavement. Additionally, in the presence of suspended or entrained solids, a resulting change in the partitioning coefficient, K_d as a function of time for Pb, Cu, Cd and Zn during the passage of the rainfall runoff event, can occur. Knowledge of the partitioning kinetics and the relative fractions of dissolved (f_d) and particulate-bound (f_p) mass delivered for treatment are of fundamental importance for in-situ treatments where residence times on the urban surface or in the urban drainage system in the presence of entrained particulate matter are less than several hours.
With respect to partitioning, the edge of the highway shoulder receives a mixture of aqueous heavy metals and entrained particulate matter. Therefore, there will be a competitive process of partitioning. Even for the complexities of the highway environment, trends predicted by theory can be used to explain actual competitive partitioning results.

Under conditions where a number of heavy metals are present in solution, the competitive order of partitioning (sorption) can be compared to bonding preferences as predicted using covalent theory, electrostatics or the tendency of a metal element to undergo hydrolysis followed by sorption. Electronegativity is an important factor in determining which heavy metal will complex to a hydrated inorganic surface, such as an iron oxide surface, with the highest preference. The more electronegative heavy metals form the strongest covalent bonds with the oxygen atoms of the surface hydroxyl groups. According to covalent theory for divalent metal ions, the predicted order of bonding preference would be (McBride 1994):

\[ \text{Cu} > \text{Ni} > \text{Co} > \text{Pb} > \text{Cd} > \text{Zn} > \text{Mg} > \text{Sr} \]  

(1)

However, based on electrostatics, bonding preference is for the metals with the greatest charge-to-radius ratio, producing a different order of preference for this group of divalent metals (McBride 1994):

\[ \text{Ni} > \text{Mg} > \text{Cu} > \text{Co} > \text{Zn} > \text{Cd} > \text{Sr} > \text{Pb} \]  

(2)

Electrostatics would also predict that trivalent metal ions such as \( \text{Cr}^{3+} \) would have a greater bonding preference to all divalent metal ions. Finally, based on the tendency to hydrolyze, the bonding preference of selected metal ions to iron oxides would be (McBride 1994):

\[ \text{Pb} > \text{Cu} > \text{Zn} > \text{Co} > \text{Ni} > \text{Cd} > \text{Mn} \]  

(3)
Methodology

Experimental Site

An experimental facility, utilized since 1995, was designed to sample and analyze representative lateral pavement sheet flow ($q_{sf}$) at the edge of the highway shoulder. The focus on $q_{sf}$ is a departure from work of other researchers who sampled flow as an aggregation of sheet flow, gutter flow and pipe flows (Morrison et al. 1984; Harrison and Wilson 1985).

Measurements of $q_{sf}$ are critical for design of in-situ treatment systems such as BMPs loaded by such flow. At the site, the downstream edge of the pavement section was saw-cut and removed to allow the construction of a 15-m wide instrumented sampling facility. The drainage area to the site was a well defined 15-m wide by 20-m long (across the super-elevated four lanes of pavement) asphalt pavement drainage area. Details of the sampling and instrumentation configuration are provided elsewhere (Sansalone and Buchberger 1997). Figure 3.1 illustrates the location of the experimental facility with respect to the Millcreek Expressway portion of interstate 75 approximately 3-km north of downtown Cincinnati. Figure 3.2 provides details of the geometry of the experimental facility and the relative location of experimental appurtenances.

Sampling and field data collection

During 1996 and 1997, eight rainfall runoff events were sampled and analyzed at the experimental site. Samples were obtained using an automated sampler programmed to acquire discrete 1-liter samples at timed intervals of between 2 to 10 minutes for the duration of the runoff. Hydrologic and water quality field data were collected during all sampled events at the experimental site. The rain events varied in duration, intensity, inter-arrival times and generated flows (ranging from the low-flow to high-flow capacity of the flume). Samples were analyzed for trace metals, solids and water quality parameters for all events. Details of hydrology, sampling, the
Figure 3.1. Location of site in SW Ohio and in Cincinnati.
Lateral Pavement sheet flow (typical)

Edge of travelled pavement of I-75 southbound

Paved shoulder edge

Integrated concrete slab and curb

Access drive

Automatic sampler

25.4 mm Parshall flume

Primary sampling location at lowpoint of trough

Datalogger

Raingage

25.4 cm PVC outflow trough @ 0.020 (m/m)

2000L runoff collection tank

Asphalt pavement

Figure 3.2. Experimental facility capturing highway shoulder runoff.
various laboratory methodologies and analyses as well as the experimental protocols are provided elsewhere (Sansalone and Buchberger 1997; Sansalone et al. 1998).

**Heavy metal and water quality protocols**

After the completion of a runoff event, the samples were immediately transported to the nearby laboratory. Metal partitioning between the dissolved and particulate-bound phases is a dynamic process. Therefore, samples were fractionated between dissolved and particulate-bound heavy metals and acidified within hours of being logged at the laboratory.

The dissolved fraction is defined as heavy metals of an unacidified sample that pass through a 0.45-µm membrane filter (APHA 1992). Each one-liter sample was mixed on a magnetic stirrer, and a 50-ml sample was passed through a membrane filter. The 50-ml dissolved fraction was immediately acidified with 2.5 ml of trace-metal HNO₃. The particulate-bound heavy metal fraction, retained in the membrane filter, was subsequently digested using a microwave-assisted procedure based on SW-846 Method 3015 (USEPA 1990). Heavy metal analyses conducted on a Perkin-Elmer Optima 3000 Inductively Coupled Plasma Spectrometer included scans for Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb.

In addition to heavy metal analyses, standard water quality measurements were carried out for the purposes of this study. These measurements included pH, redox, alkalinity and various suspended solids fractions including total and volatile suspended, and total and volatile dissolved solids (TSS, VSS, TDS, VDS) for all samples. All analyses quality assurance and quality control procedures were employed in the field and laboratory.

**Partitioning and heavy metal mass indices**

Whether in pavement runoff, urban storm water or any aqueous system, there is a temporal partitioning between heavy metals in solution and solids whether these solids are in suspension
(TSS, VSS) or as settleable solids that may be part of a fixed or mobile bed load. This partitioning includes specific mass transfer mechanisms of sorption, ion exchange and surface complexation with both organic and inorganic sites on the solid matter. These partitioning reactions are generally non-linearly reversible between the solid-phase and soluble phase concentrations. Total concentration of a heavy metal is therefore the sum of the dissolved ($c_d$) and the particulate-bound concentrations ($c_p$) where:

$$c_T = c_d + c_p \quad (4)$$

Operationally, the soluble or dissolved fraction is that fraction that passes the 0.45-micrometer membrane filter and therefore contains both the dissolved and part of the colloidal-bound heavy metals. The solid phase concentration, $c_p$ is defined as the product of the heavy metal concentration on the solid phase, $c_s$ in terms of mass/mass of solids and the concentration of the adsorbing solid material in the aqueous system, $m$ typically measured as either TS or TSS in terms of mass/volume of aqueous solution:

$$c_p = (c_s)(m) \quad (5)$$

When the rate of sorption and de-sorption are equal, concentration equilibrium exists between the dissolved and solid-phase concentrations of a heavy metal. The ratio of these phases is referred to as the partitioning coefficient, $K_d$ for a particular heavy metal at a particular pH and redox level:

$$K_d = c_p/c_d \quad (6)$$

Substitution of Equation (5) and (6) into Equation (4) yields the dissolved fraction ($f_d$) and the particulate-bound fraction ($f_p$) is defined as:

$$f_d = D/(D+P) = c_d/c_T = 1/[1+K_d(m)] \quad (7)$$

$$f_p = P/(D+P) = c_p/c_T = [(K_d)(m)]/[1+K_d(m)] \quad (8)$$
where, D is the dissolved mass of a heavy metal (mg) and P is the particulate-bound mass of a heavy metal (mg). For \( f_d > 0.5 \), the heavy metal mass is mainly in dissolved form. The product of \((K_d)(m)\) is dimensionless and \(K_d\) is usually expressed as liters per kilogram (L/kg). The larger the \( K_d \) value the greater the partitioning of a heavy metal to the solid phase. Heavy metals in pavement runoff have \( K_d \) values that range from \(10^1 \) to \(10^5 \) in rainfall runoff. The greater the dissolved fraction, or the more soluble the heavy metal, the lower the \( K_d \) value. Because of much longer residence times in the presence of highway solids, the dissolved fractions of heavy metals can be very low (Sansalone and Buchberger 1997). In comparison, \( K_d \) values for snowmelt are typically in the range of \(10^3 \) to \(10^6 \).

For each discrete sample obtained, dissolved and particulate heavy metal concentrations were obtained after sample preparation and digestion through Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) analysis. Each respective sample concentration \((c_i)\) (dissolved or particulate) was multiplied by the \( q_{ef} \) volume \((v_i)\) representative of the discrete time increment to determine heavy metal or solids mass \((m_i)\) as shown in Equation 9.

\[
    m_i = (c_i)(v_i)
\]

To evaluate the study objectives, these data \((m_i)\) were evaluated for both dissolved fraction and for \( K_d \) for Zn, Cd, Cu and Pb as a function of time for each event.

**Results**

**Alkalinity and pH**

While pH is a measured water quality parameter that is readily measured, understood and documented by many researchers examining highway runoff with an interest in heavy metals, alkalinity can also be an important parameter with respect to partitioning, speciation and toxicity of heavy metals, albeit a parameter that is not as easily measured and less documented than pH.
Higher alkalinities drive heavy metal partitioning towards the particulate-bound phase, reduce the ionic concentration of a heavy metal species and in addition to providing buffering capacity for pH also provides protection for aquatic species against toxic effects of dissolved heavy metals. Alkalinities above 200-mg/L as CaCO3 provide sufficient protection for most fresh and salt-water fish (Loyless and Malone 1997). There are many situations where highway right-of-ways are in direct hydrologic communication with receiving waters, such as along waterways or for elevated roadway infrastructure over shallow receiving waters such as estuaries, bayous, shallow lakes, reservoirs or source waters for drinking water supply. Figure 3.3 presents both alkalinity and pH trends for each rainfall runoff event.

Despite wide variability in event hydrology, pavement sheet flow alkalinity at the edge of the paved shoulder stabilized at or below 50-mg/L relatively rapidly within the initial third of the event runoff duration for most events. Although pH results were somewhat more variable, pH values stayed within a range of 6.5 to less than 8 for most of the storm event and were relatively stable during the latter half of each event.

Pavement hydrographs and delivery of suspended solids

Using the format of Figure 3.3, the delivery of suspended solids as the ratio of TSS/VSS is plotted in Figure 3.4 along with the pavement hydrograph, qsf as measured at the edge of the paved shoulder. Results clearly indicate that TSS dominates VSS and in particular this ratio increases as a function of flow indicating the increased mobility of the denser inorganic fraction as a response to increased flow. Results demonstrate that the mass delivery of suspended material is driven by flow as have been reported elsewhere for this site (Sansalone et al. 1998). The entrainment and delivery of suspended solids concentration, as well as total mass fractions shown in Table 3.1, have an impact on heavy metal partitioning as will be discussed shortly. In
Figure 3.3. pH and alkalinity for all rainfall events at I-75 site.
Figure 3.4. The ratio of TSS/VSS compared to hydrology for each event.
Table 3.1. Dissolved and particulate solids mass for each event.

<table>
<thead>
<tr>
<th>Event</th>
<th>TS mass (g)</th>
<th>TSS mass (g)</th>
<th>VSS mass (g)</th>
<th>TDS mass (g)</th>
<th>VDS mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 May 1996</td>
<td>52.3</td>
<td>17.5</td>
<td>4.7</td>
<td>34.8</td>
<td>16.0</td>
</tr>
<tr>
<td>18 June 1996</td>
<td>362.5</td>
<td>257.7</td>
<td>66.1</td>
<td>104.8</td>
<td>34.8</td>
</tr>
<tr>
<td>7 July 1996</td>
<td>454.9</td>
<td>275.6</td>
<td>137.7</td>
<td>210.5</td>
<td>121.6</td>
</tr>
<tr>
<td>8 August 1996</td>
<td>804.3</td>
<td>637.5</td>
<td>147.1</td>
<td>166.8</td>
<td>148.3</td>
</tr>
<tr>
<td>17 October 1996</td>
<td>854.6</td>
<td>400.5</td>
<td>156.9</td>
<td>454.1</td>
<td>192.1</td>
</tr>
<tr>
<td>25 November 1996</td>
<td>87.2</td>
<td>39.7</td>
<td>12.6</td>
<td>47.5</td>
<td>8.4</td>
</tr>
<tr>
<td>16 December 1996</td>
<td>97.4</td>
<td>37.9</td>
<td>12.7</td>
<td>59.6</td>
<td>11.1</td>
</tr>
<tr>
<td>12 June 1997</td>
<td>93.1</td>
<td>32.9</td>
<td>15.1</td>
<td>60.2</td>
<td>26.7</td>
</tr>
<tr>
<td>All events mean</td>
<td>350.8</td>
<td>212.4</td>
<td>69.1</td>
<td>142.3</td>
<td>69.9</td>
</tr>
<tr>
<td>All events median</td>
<td>230.0</td>
<td>148.7</td>
<td>40.6</td>
<td>82.5</td>
<td>30.8</td>
</tr>
<tr>
<td>All events SD</td>
<td>329.4</td>
<td>224.4</td>
<td>67.6</td>
<td>140.4</td>
<td>72.7</td>
</tr>
<tr>
<td>All events RSD (%)</td>
<td>93.9</td>
<td>105.7</td>
<td>97.7</td>
<td>98.7</td>
<td>104.0</td>
</tr>
</tbody>
</table>

SD = standard deviation  
RSD = relative standard deviation  
TS = total solids  
TSS = total suspended solids  
VSS = volatile suspended solids  
TDS = total dissolved solids  
VDS = volatile dissolved solids
addition, pavement hydrographs rapidly respond to variations in rainfall intensity with little intervening lag time. This can be discerned from the APRT (average pavement residence time) values for $q_{ar}$ tabulated in Table 3.2 for each event.

**Dissolved mass fraction of Pb, Cu, Cd and Zn**

For each event, the variation in the dissolved mass fraction for Pb, Cu, Cd and Zn are plotted as a function of elapsed time in Figure 3.5. These results indicate that the dissolved mass dominates the particulate-bound mass at the edge of the highway shoulder even for relatively insoluble heavy metals such as Pb. While the signature of the hydrograph can be clearly discerned in the dissolved heavy metal mass results, it is somewhat less pronounced than the delivery signature for the suspended solids. The major peaks of the hydrograph generally correspond to decreases in the dissolved heavy metal mass fraction as a result of partitioning to increased entrained solids mobilized by the higher flow.

The important point is that the dissolved mass fractions at the edge of the highway shoulder are typically greater than 80% for Zn and Cd, approximately 70% for Cu and approximately 60% for Pb. While the incremental values show some variability, dissolved fractions remain relatively high throughout each event. These results have important implications for design of in-situ treatment BMPs within the highway right-of-way.

**Generation of storm water hardness**

For each event, the variation of hardness is plotted as a function of elapsed time in Figure 3.6. Hardness is the sum of the calcium ($\text{Ca}^{2+}$) and magnesium ($\text{Mg}^{2+}$) ions. With regard to toxicity, hardness is similar to alkalinity in that the higher the hardness the lesser the toxicity effect for heavy metals discharged to receiving waters (Cusimano et al. 1986). Since hardness is measured in terms of a concentration, it rapidly diminishes for all events to approximately
Table 3.2. Hydrologic indices and residence time data for each event.

<table>
<thead>
<tr>
<th>Event</th>
<th>Rainfall Duration (min)</th>
<th>Rainfall Depth (mm)</th>
<th>Runoff Volume (L)</th>
<th>IPRT (min)</th>
<th>APRT (min)</th>
<th>LEMF (L/min·m)</th>
<th>LPF (L/min·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 May 1996</td>
<td>35</td>
<td>0.9</td>
<td>97</td>
<td>4</td>
<td>6</td>
<td>0.05</td>
<td>0.92</td>
</tr>
<tr>
<td>18 June 1996</td>
<td>63</td>
<td>11.3</td>
<td>2779</td>
<td>5</td>
<td>2</td>
<td>2.29</td>
<td>16.3</td>
</tr>
<tr>
<td>7 July 1996</td>
<td>50</td>
<td>40.4</td>
<td>9644</td>
<td>4</td>
<td>2</td>
<td>11.08</td>
<td>21.5</td>
</tr>
<tr>
<td>8 August 1996</td>
<td>51</td>
<td>14.1</td>
<td>3877</td>
<td>7</td>
<td>3</td>
<td>4.31</td>
<td>26.10</td>
</tr>
<tr>
<td>17 October 1996</td>
<td>616</td>
<td>29.1</td>
<td>3693</td>
<td>5</td>
<td>7</td>
<td>0.40</td>
<td>2.95</td>
</tr>
<tr>
<td>25 November 1996</td>
<td>150</td>
<td>3.1</td>
<td>216</td>
<td>8</td>
<td>10</td>
<td>0.09</td>
<td>0.61</td>
</tr>
<tr>
<td>16 December 1996</td>
<td>340</td>
<td>3.4</td>
<td>268</td>
<td>14</td>
<td>15</td>
<td>0.05</td>
<td>0.24</td>
</tr>
<tr>
<td>12 June 1997</td>
<td>20</td>
<td>2.0</td>
<td>464</td>
<td>3</td>
<td>5</td>
<td>0.52</td>
<td>5.14</td>
</tr>
<tr>
<td>All events mean</td>
<td>165.6</td>
<td>13.0</td>
<td>2629.8</td>
<td>6.3</td>
<td>6.3</td>
<td>2.3</td>
<td>9.2</td>
</tr>
<tr>
<td>All events median</td>
<td>57.0</td>
<td>7.4</td>
<td>1621.5</td>
<td>5.0</td>
<td>5.5</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>All events SD</td>
<td>210.0</td>
<td>14.5</td>
<td>3260.5</td>
<td>3.5</td>
<td>4.5</td>
<td>3.8</td>
<td>10.5</td>
</tr>
<tr>
<td>All events RSD (%)</td>
<td>126.8</td>
<td>111.2</td>
<td>124.0</td>
<td>56.6</td>
<td>71.4</td>
<td>163.2</td>
<td>113.4</td>
</tr>
</tbody>
</table>

SD   = standard deviation
RSD  = relative standard deviation
IPRT = initial pavement residence time
APRT = average pavement residence time
LEMF = lateral event mean flow
LPF  = lateral peak flow
Figure 3.5. Temporal variations of dissolved fraction ($f_d$) with respect to Pb, Cu, Cd and Zn.
Figure 3.6. Total hardness (hardness = 2.497[Ca$^{2+}$, mg/L] + 4.118[Mg$^{2+}$, mg/L] ) with respect to Mg and Ca for each rainfall event.
50-mg/L with the exception of the 7 July 1996 event where hardness is driven by the event hydrology. Many states, such as Ohio have numerical outside and inside zone mixing criteria for heavy metals, and these criteria are based in part on hardness. To provide a sense for 50-mg/L as CaCO₃ hardness levels, the Ohio criteria start at a minimum hardness of 100-mg/L as CaCO₃.

**Non-equilibrium partitioning – heavy metal K\textsubscript{d} values**

Water quality parameters such as alkalinity, pH, suspended solids and hardness play a role in partitioning of heavy metals in highway storm water. While each of these parameters influences partitioning and K\textsubscript{d} values, TSS (as a mass concentration) has a direct influence on heavy metal K\textsubscript{d} values. Plots of K\textsubscript{d} values for Pb, Cu, Cd and Zn as a function of elapsed time are presented in Figure 3.7. There are a number of important results portrayed in these figures. First, K\textsubscript{d} values vary in a discernible trend across several orders of magnitude and sometimes more for many events. Second, an equilibrium K\textsubscript{d} condition in the range of 10⁴ to 10⁵ L/kg appears to be approached as elapsed time increases given that all other conditions, such as TSS and flow remain relatively constant. In fact, K\textsubscript{d} values in the range of 10⁴ to 10⁵ L/kg are typical for rivers and large lakes where the residence time is in terms of days and conditions such as TSS and flow are constant. Finally, the variations in flow and TSS are mirrored shortly afterwards by resulting changes in K\textsubscript{d}. This can be clearly discerned for the 18 June 1996 event. Finally, the variation in the relative magnitude of K\textsubscript{d} for Zn, Cd, Cu and Pb tends to follow similar trends that can be explained by covalent bonding theory or tendency of the heavy metal to undergo hydrolysis.

**Conclusions**

This study presented heavy metal partitioning results from a series of eight rainfall runoff events over a two-year period loading a 300-m² instrumented asphalt pavement drainage area
Figure 3.7. Temporal variation of TSS and $K_d$ values with respect to Pb, Cu, Cd and Zn.
located on inter state 75 in urban Cincinnati. This study excluded snowmelt, which is addressed in a separate study. With respect to in-situ treatment for heavy metals at or near the edge of the highway pavement, a number of conclusions are important to State DOTs. As a result of recent regulations, State DOTs are increasingly focusing their resources to addressing challenging and expensive issues of in-situ treatment. The goal of this study was to demonstrate that heavy metals in pavement storm runoff could be predominately dissolved. Any treatment or BMP loaded by pavement sheet flow must be designed to provide the appropriate removal mechanisms for dissolved metals. Effective treatment will require a mechanism to either sorb heavy metals onto engineered sorptive filter media or onto entrained particulate matter that can subsequently be removed through liquid/solid separation processes such as filtration or sedimentation.

Water quality characteristics such as low alkalinity, low hardness and short pavement residence times for heavy metals entrained with pavement runoff TSS results in a majority of the heavy metal mass remaining in solution at the edge of the pavement. This high degree of dissolved heavy metal mass occurs despite pH values at the edge of the shoulder that range from 6.5 to 8. These same water quality issues present toxicity concerns for highway conditions where there are direct discharges to receiving waters that also have poor buffering capacity. One common example is elevated roadway infrastructure over shallow and limited volume receiving water that has a poor buffering capacity. This highway runoff chemistry, results in heavy metal $K_d$ values that can vary by several orders of magnitude or more across a storm event. These $K_d$, for all heavy metals, only approach equilibrium partitioning conditions towards the end of each event. This can be seen for relatively lengthy 17 October 1996 event (Figure 7).
Implications For BMP Design

The conclusions identify important water quality and hydrologic highway runoff parameters that have significant implications for non-equilibrium heavy metal partitioning and also toxicity. These parameters have a direct influence on the treatment selection of in-situ treatment design for BMPs. Each of the results reported have an important effect on initial selection and then on the details of treatment design for the selected in-situ BMPs.

Unlike the treatment of wastewater or source water for drinking water, storm water runoff at the edge of the pavement has not reached equilibrium conditions. A pavement storm water residence time of 15 minutes or less provides an indication of this when compared to a wastewater delivery residence time in term of hours to days and source waters with significantly longer residence times. As shown in Figure 3.7, as a result of low residence times and dynamic water chemistry, parameters such as $K_d$ can vary by orders of magnitude in less than an hour. High intensity runoff events such as 18 June 1996 and 7 July 1996 provide a clear indication of this. For these events, partitioning rate coefficients are large for all heavy metals.

There are two primary implications when considering the application of typical BMPs in the highway right-of-way, such as those shown in Figure 8, that are loaded by direct runoff from the edge of the paved shoulder. The first implication is to utilize a BMP, such as a detention basin or roadside swale as shown in parts b and c, to detain runoff and produce sufficient residence time so that heavy metal partitioning to the entrained solids fraction occurs. This requires the proper chemistry and mixing. Alkalinity and pH values must increase above runoff levels, which can occur where there are situations of overland flow, $q_{of}$. There must be sufficient suspension of entrained solids initially, to which the heavy metals will partition, while still settling within the BMP during the detention time. The benthic zone must remain sufficiently
aerobic in order that the heavy metals partition to settled solids and therefore not released back into the water column. Such BMPs require land area, a valuable commodity within the highway right-of-way. In addition, while many DOTs utilize basins at selected sites within the right-of-way, there are issues of sufficient drainage relief and safety that must be addressed for each application which may preclude their use despite favorable water chemistry conditions. While maintenance and disposal issues are in terms of years, State DOT must deal with these real issues.

The second implication is to utilize a BMP, such as an engineered infiltration trench as shown in part d of Figure 3.8, designed to provide surface complexation mechanisms for the dissolved fraction and filtration mechanisms for the particulate bound fraction of a heavy metal. There are a number of variations for infiltration trench design, including designs that also function as an underdrain, intercepting subgrade interflow, $q_i$ as well as lateral pavement sheet flow, $q_{sf}$. These designs are loaded by lateral sheet flow, not concentrated flow, directly off the edge of the paved shoulder. The engineered media is designed to provide an ion exchange or adsorption mechanism for removal of dissolved heavy metals while at the same time functioning as a filter media for separation of incoming particulate material. While efficiencies can be high, greater than 90%, such efficiency comes with costs associated with BMP maintenance to prevent issues such as clogging and the eventual recovery/disposal of trapped heavy metals and solids. There are no simple solutions for the removal of a heavy metal or particle once released in the highway environment, and there are BMPs that can be misapplied for the intended purpose, unfortunately at a significant cost. BMPs for heavy metals and solids are essentially garbage cans and as such must be emptied and cleaned occasionally. The purpose of design is to provide
Figure 3.8. A typical highway shoulder section with several common in-situ treatment (as BMPs) alternatives.
effective capture, reasonable time between disposal and an optimal cost between treatment
alternatives.

**Literature Cited in Chapter 3**


Chapter 4
Accretion of Pollutants in Roadway Snow Exposed to Urban Traffic and Winter Storm Maintenance Activities – Part I

As with most industrialized countries, the United States is dependent on its roadways for the movement of people, products and services. In areas that experience winter storms of snow and ice, we have come to expect that our roads and highways will be cleared and maintained to provide safe and uninterrupted vehicular travel conditions. In urban areas and transportation corridors linking urban, commercial and industrial areas, such expectations require significant material and financial resources, planning, personnel and equipment. However, because of an increase in urbanization and the commensurate vehicular traffic in urban areas, urban snow is exposed to increasing levels of pollutant loadings from traffic activities and winter storm maintenance practices.

In urban environments with traffic activities, heavy metals are generated primarily from the abrasion of metal-containing vehicular parts, including the abrasive interaction of tires against pavement, leaching of heavy metals from infrastructure, and oil and grease leakage (Lygren et al. 1984; Muschack 1990; Tong 1990; Ball et al. 1991; Armstrong 1994). Roadway storm water levels of Zn, Cu, Cd, Pb, Cr and Ni are significantly above ambient background levels, and for many heavily traveled roadways, Zn, Cu, Pb and Cd often exceed USEPA and State EPA surface water discharge criteria on an event basis (Sansalone and Buchberger 1997). These same heavy metals are present in storm water runoff and snowmelt. In comparison to storm water runoff, snowmelt levels for these metals and suspended solid materials can be several orders of magnitude higher (Sansalone and Buchberger 1996). Runoff (as either snowmelt or storm water) from urban transportation and land uses is a complex physico-chemical heterogeneous mixture of heavy metals, particulate matter, inorganic and organic...
compounds with variations in flow, concentrations and mass loadings that sometimes vary by orders of magnitude during a single event. The porous nature of the snow matrix that contains both heavy metals and entrapped particulate matter results in partitioning of pollutants towards the solid particulate phase as compared to storm water runoff, in part due to significantly longer residence times (Sansalone and Buchberger 1996). While the difficulties of storm water treatment are significant, options for snow treatment are even more challenging due to issues of high pollutant accretion and partitioning of these pollutants as a function of time.

Objectives

The major objectives of this study were threefold. These objectives were carried out for data collected at four experimental study sites on major transportation roadways in urban Cincinnati, Ohio. These sites were the primary sites of a total of ten highway sites where samples could be taken on a temporal basis. The first objective was to characterize the climate and traffic loadings as well as winter maintenance practices at a pair of these sites located at an experimental research facility along the Mill Creek Expressway of I-75. The second objective was to collect snow samples at each of these sites as a function of time to evaluate the accretion of pollutants, as determined by conventional water quality indices. Temporal variation in these water quality indices would be examined in light of traffic, local climatologic conditions and maintenance practices such as the application of de-icing salts. The final objective was to evaluate the temporal partitioning between particulate and dissolved phases of these water quality indices as determined from each site.

Background

Accumulation of pollutants in highway snow

Because snow plowed onto the highway shoulder is directly exposed to traffic and winter snow maintenance practices, pollutants generated from such activities can result in significant
accumulations in the highway snow. The porous matrix of snow, the high surface area of the snow and ice crystals, freezing and thawing, the extended residence times of the plowed snow exposed to these pollutant loadings and the physical barrier created by this plowed snow contribute to significant levels of pollutant accumulation. Snowmelt and chemistry within the snow pack generate differential partitioning between the dissolved and particulate-bound phases of trace metals (for urban highways, higher concentrations of heavy metals), whether the snow pack is from natural snow deposition or from anthropogenic activities such as highway snow plowing. The porous snow matrix is capable of scavenging fine particle-bound, pollutants from the urban environment. In urban areas, snow pack contamination has been correlated with proximity to large industries or major roadways as well as snow pack age (White et al. 1995).

Highway snow generated from plowing snow into linearly extended snowbanks along the shoulder is subject to freeze-thaw cycles for residence times that sometimes extend into days or weeks. This freeze-thaw process allows the pollutants to preferentially accumulate at the surfaces of ice particles. As the snow pack goes through freeze-thaw cycles, a further concentration of pollutants may result (Johannessen and Henriksen 1978; Ecker et al. 1990). The first melt water presumably forms near the snow surface and may later freeze due to either a change in air temperature or contact with colder snow as water percolates through the highway snow pack. This process may lead to the formation of essentially pure ice exposed to pollutant loadings from the highway.

Disposal of highway snow

Snow that falls on the pavement surface of a highway is typically plowed from the traveled pavement onto the shoulder of the highway. Along most roadways the plowing of snow from the pavement results in a linear snowbank that parallels the pavement surface from which it
was plowed. Plowing operations are generally carried out at regular intervals during and immediately after snowfall events depending on snowfall intensity and duration. There are two primary practices for disposal of this plowed snow in the USA. First, snow from roadways and highways is typically allowed to melt in-situ resulting in the discharge of snowmelt into the local environment presenting the potential threat to the local ecology and contamination of surficial soils and the groundwater supply. The other option practiced for snow disposal, in particular for significant snow events in densely populated urban areas, is the trucking of snow plowed from roadways and dumping into local streams or rivers (Pierstorff and Bishop 1980; Scott 1980; Scott and Wylie 1980; Estes 1996). Both the melted roadway snow and dumped snow contains increased concentrations of abraded solid matter, chlorides and associated calcium or sodium cations, heavy metals, organics such as oil and grease and inorganics such as cyanide. For example, both cyanide and lead are used in the production of de-icing salts as anti-caking agents for roadway pavement applications. Residual material that remains following a snow melt can contain very high levels of solids and pollutants adsorbed to those solids. Snow dumped near or into bodies of water have resulted in increased heavy metals and to an extent suspended and dissolved solids and lowered pH (Pierstorff and Bishop 1980).

**De-icing agents**

Traction and de-icing agents include a wide variety of substances that most typically range from grit or sand to de-icing salts and are winter storm maintenance practices that are sources of pollutants discharged from the highway environment. The major factor in the type of agent selected is generally cost. Since only de-icing agents were utilized at the study sites, a brief background is provided on de-icing agents. De-icing agents are used to minimize ice or snow on the pavement surface and facilitate snow clearing. The two most common and most
effective de-icing salts are sodium chloride (typically applied as a rock salt product) and calcium chloride (applied as a liquid or granular product). The leading states in highway salt consumption are Minnesota, Michigan, New York, Pennsylvania and Ohio which is where this study was performed (Novotny and Olem 1994).

Requirements for deicers are that the deicer must be soluble in water and lower the freezing point of water. Calcium chloride is more efficient at lower temperatures but costs 3 to 4 times more than NaCl. The environmental issues associated with these de-icing agents include damage to roadside vegetation, transport of high levels of chlorides and sodium to receiving waters or surficial groundwater, degradation of aquatic ecosystems, destruction of surficial soil structure by Na+, mobilization of heavy metals in the highway environment with potential contamination of water supplies and significant corrosion damage to highway infrastructure (Baboian 1992; Fritzsche 1992). The NaCl concentrations up to 600-mg/L stimulated growth in roadside plant material, but plant damage was evident at 1000 to 5000-mg/L. Plants sensitive to NaCl and CaCl₂ have increased leaf burn, leaf defoliation and limb dieback (Fritzsche 1991). Chloride concentrations as low as 400-mg/L can be harmful to fish (Scott and Wylie 1980). In South Ontario, levels of salt from road runoff affected drift of benthic invertebrates of urban streams when levels of Cl⁻ exceeded 1000-mg/L (Crowther and Hynes 1977). Snowmelt runoff with high concentrations of deicers can prevent spring turnovers in nearby lakes by creating a lower and denser saline water stratum (Hawkins and Judd 1972; Cherkauer and Ostenso 1976).

**Compounds of cyanide as anti-caking agents for de-icing salts**

Cyanide compounds and Pb are used as anti-caking coatings on granular de-icing salts such as rock salt to ensure the distribution of these salts as discrete granular material on the roadway (Field et al. 1974). Coatings of cyanide compounds typically are ferric ferrocyanide
(Prussian Blue) and sodium ferrocyanide (Yellow Prussiate of Soda) (Novotny et al. 1998). The sodium form is highly soluble in water and decomposition to cyanide (HCN\(_{aq}\) and CN\(^-\)) readily occurs in the presence of sunlight (photolysis). The generation of cyanide from ferrocyanide compounds in the presence of sunlight is accelerated in the presence of oxygen (Burdick and Lipschuetz 1980). Reactions in the presence of sunlight are reversible under dark conditions. In the presence of sunlight, acute toxicity was demonstrated to occur for laboratory fish test species \textit{Rhinichthys atratulus} and \textit{Semotilus atromaculatus} at 0.30-mg/L due to free cyanide species of HCN\(_{aq}\) and CN\(^-\) resulting in 50% mortality in less than 8 hours (Burdick and Lipschuetz 1980). This same research demonstrated acute toxicity to CN\(^-\) in sunlight resulting in 50% mortality in less than 48-hours for the same species at 0.19-mg of CN\(^-\)/L (Burdick and Lipschuetz 1980). These acute toxicity levels for free cyanide generated in sunlight occurred for total concentrations of ferrocyanide or ferricyanide compounds of 1 to 2-mg/L. Toxicity decreased significantly under simulated dark and diffuse light conditions. The free forms of cyanide can be volatilized [HCN\(_{g}\)] and are biodegradable. The free forms of cyanide are much more toxic than cyanide complexed with iron or hexacyanoferrates species such as Fe(CN)\(_6\)\(^{3-}\) or Fe(CN)\(_6\)\(^{4+}\) (Meeussen et al. 1992).

Under equilibrium conditions in surficial soils loaded by iron cyanide, iron cyanide complexes will typically dissociate to a significant extent to the free cyanide form (Meeussen et al. 1992). In groundwater containing iron cyanides, complexes of iron cyanide will normally tend to dissociate to free cyanide species, however, very slowly as governed by decomposition kinetics rather than chemical equilibrium from sites contaminated with cyanide. However, only complexed cyanide is predominately found, indicating that the speciation of cyanide is determined not by chemical equilibrium but by decomposition kinetics (Meeussen et al. 1992).
In groundwater, this slow decomposition is due in part to lack of light exposure. However, this complexed cyanide will rapidly decompose to free cyanide species when exposed to sunlight. The complexed forms will interact more with the soil solid phase because of their ionic nature and their ability to precipitate.

**CMA as an alternative de-icing agent**

An alternative to NaCl and CaCl$_2$ as another type of de-icing agent is calcium magnesium acetate (CMA). Calcium magnesium acetate has little or no impact on soils, vegetation, water supplies, aquatic and terrestrial organisms or infrastructure components of highways (Fritzsche 1992). CMA at a ratio of 3:7 (Ca:Mg) has been found to be an effective deicer, less toxic to fish, zooplankton, phytoplankton, and less corrosive than chloride salts (Amrhein et al. 1992). There are distinct differences between CMA and NaCl. NaCl is used as de-icing agent due to ready availability, low initial cost and adequate performance (McCrum 1991). However, NaCl is more corrosive to metals, damaging to concrete and the environment. Estimates of NaCl damages range from 6 to 40 times the initial cost of NaCl. The most readily quantifiable damage is due to corrosion and infrastructure damage. The initial cost of CMA is approximately 700-USD/ton compared to 150-USD/ton of corrosion-inhibitor-treated NaCl. As a result of the initial cost of CMA, CMA has been limited mainly to application on bridge decks.

**De-icing agents used at study sites**

De-icing salt is applied to various regions of the United States according to local site and weather conditions. On North American highways, greater than $10^7$-tons of rock salt are utilized for de-icing each year (Fritzsche 1992). For the study sites examined in this paper, both NaCl and CaCl$_2$ were utilized. The de-icing materials consisted of a mixture of NaCl (rock salt form) and liquid CaCl$_2$ at a mixture of 4.6-m$^3$ of NaCl as rock salt with 265-L of liquid CaCl$_2$. 
Application rates were 80 to 130-kg/lane-km of highway (37-km per application). This mixture of de-icing agents was discharged from a truck-mounted application device moving at 25-mph. The de-icing mixture was applied once every 2-hours in conjunction with snow plowing of traveled lanes during the period of snow accumulation. After snowfall ceased, the de-icing salt mixture was applied every night and early in the morning before each rush hour. The NaCl rock salt was determined to contain a cyanide-based anti-caking agent.

**Methodology**

**Highway study sites**

For this study, four primary highway sites were selected for snow sampling from a total of ten highway sites located within the metropolitan area of Greater Cincinnati. All were sampled for highway snow residuals. One site was located on Inter State 75 (I-75), a major north-south freeway between Michigan and Florida. The other site was located on U.S. Route 126, 1-km east of I-75. An additional site utilized as a control site was located in a residential area of urban Cincinnati. Snowfall at the control site had no direct exposure to highway or residential roadway traffic activity. Figure 4.1 illustrates the relative location of each site in metropolitan Cincinnati. Detailed plan views of the four primary sampling sites from which results of this study are based are shown in Figure 4.2. These four sites were designated 1SW, 1SE, 2ES and 3SW. For each designation the first number identifies the number of a particular site location, the first letter indicates the direction of traffic and the final letter indicates which side of the highway samples were obtained. A description and location of all snow and snow residual sampling sites is provided in Table 4.1. For all sites, drainage from the pavement was in the form of lateral pavement sheet flow, q_{sf} towards the pavement shoulder were the snowbanks were located.
Figure 4.1. Location of highway sampling sites and the control for the metropolitan Cincinnati study.
Figure 4.2. Plan view schematics of four primary snow sampling sites for metropolitan Cincinnati study (NTS).
Table 4.1. Description and location of all snow sampling sites for metropolitan Cincinnati study.

<table>
<thead>
<tr>
<th>Site</th>
<th>Highway</th>
<th>Mile Marker</th>
<th>Sampling Area</th>
<th>Drainage Area for qsf</th>
<th>qsf Area (m²/m)</th>
<th>Roadway Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>1SW</td>
<td>I-75 South</td>
<td>2.58S</td>
<td>low speed (west) shoulder</td>
<td>no qsf</td>
<td>0</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>1SE</td>
<td>I-75 South</td>
<td>2.60S</td>
<td>high speed (east) shoulder</td>
<td>4 lanes + 1.5 shoulders</td>
<td>20</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>2ES</td>
<td>126 East</td>
<td>11.1E</td>
<td>low speed (south) shoulder</td>
<td>1 lane + 1 shoulder</td>
<td>5.5</td>
<td>2 PCC lanes</td>
</tr>
<tr>
<td>3SW</td>
<td>I-75 South</td>
<td>5.90S</td>
<td>low speed (west) shoulder</td>
<td>1 lane + 1 shoulder</td>
<td>5.5</td>
<td>3 asphalt lanes</td>
</tr>
<tr>
<td>4NE</td>
<td>I-75 North</td>
<td>12.1N</td>
<td>low speed bridge (east) shoulder</td>
<td>1 lane + 1 shoulder</td>
<td>5.5</td>
<td>3 PCC lanes</td>
</tr>
<tr>
<td>5NE</td>
<td>I-75 North</td>
<td>16.1N</td>
<td>low speed (east) shoulder</td>
<td>2 lanes + 1 shoulder</td>
<td>9.1</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>6SW</td>
<td>I-75 South</td>
<td>16.0S</td>
<td>low speed (west) shoulder</td>
<td>1.5 lanes + 1 shoulder</td>
<td>7.3</td>
<td>3 asphalt lanes</td>
</tr>
<tr>
<td>7SW</td>
<td>I-75 South</td>
<td>11.9S</td>
<td>low speed (west) shoulder</td>
<td>2 lanes + 1 shoulder</td>
<td>9.1</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>8SW</td>
<td>I-75 South</td>
<td>0.90S</td>
<td>low speed (west) shoulder</td>
<td>2 lanes + 1 shoulder</td>
<td>9.1</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>9NE</td>
<td>I-75 North</td>
<td>1.70N</td>
<td>low speed (east) shoulder</td>
<td>no qsf</td>
<td>0</td>
<td>4 asphalt lanes</td>
</tr>
</tbody>
</table>

Legend:
N: north  
O: south  
P: east  
Q: west  
PCC: Portland cement concrete  
qsf: lateral pavement sheet flow
Climatologic and traffic loadings

Starting at 05:00 on 04 February 1998, the metropolitan Cincinnati area received a 470-mm snow event for which snow continued for 48-hours. Actual snow accumulation began at 06:00. At the control site, measurements of ambient air temperature and relative humidity were made for the duration of study period.

Traffic loading data was collected for the paired sites of 1SW-1SE using a recently installed network of Intelligent Transportation System (ITS) monitors located at a highway experimental site for storm water sampling where site 1SW and 1SE were located. The ITS monitors at the site were overhead cameras that recorded vehicle counts, vehicle spacing, vehicle size, vehicle velocity and vehicle lane location every 30-seconds. The ITS data was received electronically as an ASCII file, and a program was written to utilize these data. ITS field data was aggregated into vehicle counts of 1-hour increments.

Snow sampling

Snow samples were obtained from each of the four highway sites and from the control site every four hours for the duration of the highway snowbanks and then spaced in increasing increments of 6-hours to 24-hours. Typically, 18 snow samples were obtained at each of these sites for the 102-hour duration of the snowbanks. At each site, 4.0-L of snow were obtained from the leading edge of the snowbank exposed to traffic. From the snowbank, a rectangular area of snow was cut vertically out of the snowbank starting at the leading edge of the snowbank. The width of this area was approximately 150-mm in width and could extend back into the snowbank over 0.5-m depending on the depth of the snowbank. At each site, the sample was obtained from the leading edge of the snowbank using this procedure, with each subsequent sample cut from a section of the snowbank immediately adjacent (within a 0.3-m spacing) to the
previous sampled section. Each 4-L snow sample was placed in Zip-Loc bags, marked sealed and transported back to the laboratory frozen.

**Water quality analyses of snow samples**

Samples were returned to the laboratory in a frozen condition and immediately melted and placed in 2-L polypropylene containers. Aliquots from each sample were separated between the dissolved and particulate-bound fractions using a 0.45-µm membrane filter and vacuum filtration apparatus. Dissolved and particulate-bound fractions (total sample for chemical oxygen demand or COD) were acid-preserved or microwave acid-digested (particulate-bound metals) and analyzed for COD and heavy metals (in Part II). Water quality measurements and analyses protocols followed Standard Methods (APHA 1995). Measurement of pH followed Method 4500-H⁺ (electrometric); measurement of conductivity followed Method 2510 (electrode method); measurement of chlorides followed Method 4500-Cl⁻ (potentiometric); dissolved, suspended and settleable solids followed Method 2540; measurement of oxygen demand as COD followed Method 5220 C for dissolved and total analyses; and finally, measurement of hardness using separate inductively coupled plasma spectroscopy analyses for calcium and magnesium and calculation of hardness followed Method 2340 B. Sample bulk density, \( \rho_b \) was measured gravimetrically once the samples had completely melted and achieved laboratory temperature of 25°C. Duplicate samples were obtained, and replicate analyses were performed on the samples.

**Sampling and analyses of de-icing salts**

Both the City of Cincinnati and Ohio Department of Transportation (ODOT) Districts utilize and store de-icing salts mounded under dome-like structures that protect the stockpiles of salt from the weather while allowing for movement of loading and unloading equipment into and out of the structure. De-icing salt (NaCl rock salt) was obtained from three separate stockpiles of
salt stored in these structures at the ODOT District yard at I-75 and Paddock Road. The salt (~100-kg) was randomly shoveled from each stockpile to fill one of the three 20-L wide-mouth polyethylene containers totaling ~300-kg of dry rock salt. The containers were covered and transported back to the laboratory.

From the 300-kg of dry rock salt, 14 separate samples were obtained and placed in 250-mL high-density polyethylene wide-mouth bottles. Samples were analyzed using Method 9010, a reflux-distillation procedure under acidic conditions. Results were determined as total cyanide and reported in mg of total cyanide per kg of dry salt. The method detection limit was 0.5-mg of total cyanide/kg of dry salt.

Results

Climatologic and traffic loadings

Temperature and relative humidity data are plotted in Figure 4.3. For the entire 48-hour duration of snowfall, the ambient temperature remained below freezing. Only after the cessation of snowfall could a diurnal pattern of temperature be discerned. With respect to relative humidity, period of snowfall could be distinguished by relative humidity approaching 100%. At the cessation of snowfall the relative humidity dropped, and the relative humidity profile followed a similar but inverted pattern to temperature. Snow increment depths and cumulative depths in terms of water equivalents in mm were obtained in two-hour increments and plotted in Figure 4.4a. After hour 16 and before hour 36, the incremental snowfall diminished. Figure 4.4b illustrates the same data, but the cumulative snow depth is presented as in-situ measured snow depth on the ground at the control site. Figure 4.4b illustrates the influence of snow consolidation processes, melting and evaporation for snow depth measurements taken on the ground. The duration of the study extended for 102-hours which represented the duration of the highway snowbanks.
Figure 4.3. Temperature and relative humidity during snowfall study event (Time 0 = 6:00 am on 4 February 1998).
Figure 4.4a. Incremental and cumulative snow precipitation data (start of initial snowfall @ 6:00 am on 4 February 1998).

Figure 4.4b. Control site incremental precipitation and cumulative snow depth data (Time 0 = 6:00 am on 4 February 1998).
Figure 4.5a presents traffic counts for the duration of the study with respect to precipitation data. Figure 4.5a illustrates that traffic levels were significantly lower during the period of precipitation and only increased as winter maintenance practices removed much of the additional snowfall that fell on the Cincinnati area from hour 36 to 48. Since these data were collected at the experimental facility were sites 1SW and 1SE were located on southbound I-75 approaching downtown Cincinnati, rush hour traffic peaks occurred at hours 26 and 50 during the work week and then at hour 80 around noon on Saturday. Figure 4.5b presents the weekly clear weather pattern for traffic in terms of vehicles per day at site 1SW-1SE. Note that the cumulative 4-day level of average daily traffic (ADT) for the study period was 77% of the typical clear weather ADT for the same 4-day period. Figure 4.6 presents both the incremental and cumulative traffic.

**Snow pH, conductivity and chlorides**

Snow samples were returned to the laboratory and melted. Water quality measurements were conducted once samples had melted and reached achieved laboratory temperature. Figure 4.7 illustrates pH trends for each site and the control site. Each site produced slightly increasing pH profiles as a function of time. Sites 1SW, 1SE and 3SW produced pH increases of less than 1 pH standard unit (s.u.) while site 2ES, the only Portland cement concrete (PCC) pavement, produced a pH increase of 1.5 pH (s.u). These trends are compared to the control site, subject to background urban atmospheric deposition, that produced a rapid pH decrease from 6 to 4.7 during initial snowfall and then remained around 5 or just above for the duration of sampling.

Control site conductivity remained around 0.01-mS/cm. Conductivity at the four experimental sites was three orders of magnitude greater than the control site. Chloride values at
Figure 4.5a. Traffic during snowbank sampling period in comparison to incremental precipitation at site 1SE - 1SW.

Cumulative 4-day (96 hour) ADT = 360,695

Figure 4.5b. Traffic during snowbank sampling period (top plot) in comparison to representative clear weather traffic (bottom plot) at Site 1SE - 1SW.

Cumulative 4-day (96 hour) ADT = 466,957
daily $\mu = 110,251$ $\sigma = 20,271$
Figure 4.6. Incremental and cumulative traffic data at Site 1SE - 1SW (Time 0 = 6:00 am on 4 February 1998).
Figure 4.7. pH at the four principal highway sampling sites as compared to control site pH and conductivity (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
the control site were less than 1-mg/L while chloride concentrations at several sites approached 10,000-mg/L. When regressing trends in conductivity against trends in chlorides at each site, strong correlations with 95% confidence interval indicated that conductivity trends were mainly a function of chloride trends. These linear regression results are shown in the inset plots of each of the four plots in Figure 4.8.

**Dissolved and suspended solids**

Snow samples were analyzed for total dissolved solids (TDS) and volatile dissolved solids (VDS). At the control site, TDS values were less than 5-mg/L. As shown in Figure 4.9, TDS values increased rapidly at each site, approaching 10,000-mg/L in less than 10-hours from an initial value of approximately 100-mg/L. While the volatile fraction of dissolved solids also increased, the increase was not as significant as for TDS. In all cases, the volatile fraction represented less than 10% of the total dissolved mass. Trends in dissolved solids were erratic although an upper plateau of 10,000-mg/L occurred at each site. The high TDS levels resulted in precipitation of salt deposits that were readily observed in the TDS analyses.

Although suspended solid accretion in snow was erratic, there was a clearly increasing trend at all sites as a function of time as illustrated in Figure 4.10. Suspended solid concentrations approached an increase of five orders of magnitude as compared to the control site with suspended solids values that were below 1-mg/L. By the end of the study, total suspended solids had increased to 100,000-mg/L at several sites. The residual material had a consistency of a relatively thick slurry. Unlike dissolved solids were the volatile fraction was less than 10% of TDS, the volatile fractions ranged from 21 to 45% at the sites. High volatile dissolved fractions did not equate to high volatile suspended fractions at each site.
Figure 4.8. Temporal variation of conductivity and chloride concentration in urban roadway snow subject to traffic loadings. (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 4.9. Temporal variation of dissolved solids in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 4.10. Temporal variation of suspended solids in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
**Chemical oxygen demand**

At each site, chemical oxygen demand (COD) was determined for both the dissolved and particulate fractions. Results are plotted as total (dissolved + particulate) and dissolved in Figure 4.11. Total COD values increase rapidly within the first 10-hours of snowfall accumulation from less than 40-mg/L at time 0 to 1000-mg/L. This high level appeared to be a plateau until after the end of snowfall when COD values began to increase and approached 100,000-mg/L at several sites. Because of both the high COD levels and high chloride levels, dilutions were required for COD analysis. Dissolved CODs ranged from 3% to 7% of the total COD at each site. Dissolved CODs followed similar trends to total CODs at each site. Control site total COD was less than 1-mg/L.

**Sample bulk density**

Once snow samples were melted, a sample bulk density was determined gravimetrically and volumetrically. Results illustrated in Figure 4.12 indicate that for most samples through the end of snowfall at 48-hours, bulk density values remained relatively constant and just above 1-g/cm$^3$. However, as TSS accumulation continued and the snow matrix began to melt or evaporate, bulk densities increased rapidly. At site 3SW, the final bulk density of the residual material was similar to that of cultivated soil material such as sand that has a range of bulk densities from 1.2 to 1.8 g/cm$^3$ (Brady and Weil 1999).

**Hardness (as CaCO$_3$)**

For all the sites and for the control site, calcium and magnesium concentrations were determined. Because of the low values of Ca and Mg at the control site, graphite furnace atomic absorption spectroscopy was carried out. For the other sites, samples were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Hardness values at the
Figure 4.11. Temporal variation of COD in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 4.12. Temporal variation in melted snow sample bulk density @ 25°C (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
control site were less than 2-mg/L across the entire study period. As plotted in Figure 4.13, hardness values rapidly increased to between 100 and 200-mg/L and either remained approximately constant or showed a gradual increase as in the case of site 1SE to approximately 300-mg/L. Hardness was dominated by the calcium fraction.

**Cyanide as an anti-caking agent on de-icing salt**

Cyanide results were plotted as a frequency distribution plot with a normal probability distribution fit to the cyanide results as shown in Figure 4.14. Results from the 14 samples analyzed indicated that the mean concentration of total cyanide was 27.5-mg of total cyanide per kg of de-icing salt with a standard deviation of 6.35-mg/kg. These values are similar to those reported by other researchers (Novotny et al. 1998). The cyanide data fit a normal distribution.

**Conclusions**

This study examined urban highway snow that was sampled and analyzed for four heavily traveled urban highway sites and control site for accretion of selected pollutants as generated from traffic loadings and winter storm maintenance practices. Traffic, climate and de-icing salt loading were also examined in this study. A number of conclusions can be drawn from each facet of this study.

Highway snow samples exhibited approximately a 1-pH s.u. variation at each of the four highway sites. Hardness as CaCO₃ increased rapidly to approximately 100-mg/L during the initial hours of snow accumulation and remained relatively constant for each site ranging from 100 to 300-mg/L for much of the study period. This increase in hardness was likely due to a number of sources including the liquid CaCl₂ mixed with rock salt and CaCO₃ as part of the TSS captured by the snow matrix. This can be contrasted to the poorly buffered control site snow with a pH that dropped from 6 to 4.7 within the first 10-hours of snowfall due possibly to acid generating atmospheric pollutants that were adsorbed by the falling snow.
Figure 4.13. Total hardness (hardness = 2.497[Ca$^{2+}$, mg/L] + 4.118[Mg$^{2+}$, mg/L]) with respect to Ca and Mg in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 4.14. Frequency distribution of cyanide concentration in de-icing salt.
Trends in conductivity and chlorides as shown in Figure 4.8 can be tied to winter maintenance practices. The rapid initial increase in chlorides and conductivity was due to initial de-icing salt applications at each of the sites. Major peaks are associated with application of de-icing salts several hours before the onset of major morning rush hour. Peaks in chlorides and conductivity occur several hours before expected rush hour (hours 26, 50 and 80) for each of the I-75 sites southbound into downtown Cincinnati. A peak does not occur for site 2ES before 80 hours since this is an outbound highway site, and traffic is not significant in that direction at that time of day.

Some of the peaks in TDS profiles as shown in Figure 4.9 can be tied to application of de-icing salts as exemplified by site 1ES which is located on the downstream edge of the southbound I-75 pavement lanes. However, variability exists in the TDS trends that cannot be explained by winter maintenance practices and may be associated with snowbank melting and evaporation. In contrast to TDS, TSS shows a continued increase throughout the study duration. Other than some variability early in the study that may be a result of additional snow plowing and placing newer snow on existing snow, the snowbank matrix is an effective collector of TSS. COD trends are similar to TSS and much of the COD can be correlated to TSS. Bulk density values illustrate some variability but do not significantly increase until the snowbank is substantially dissipated through snowmelt and evaporation.

Based on cyanide analysis and winter maintenance practices the amount of cyanide released to the environment can be estimated. For the 27-km length of I-75 in the metropolitan Cincinnati area (Hamilton County) over 216,000-kg of NaCl as rock salt was applied for the study period (102-hours) with a resulting discharge of 6-kg of cyanide. Under the assumption that 90% of the snow became snowmelt, approximately $22 \times 10^6$-L of runoff were generated over
the 102-hour study from I-75. This resulted in an event mean concentration (EMC) of 0.27-mg of cyanide/L of snowmelt. Accounting for a standard deviation of 6.35-mg/kg from Figure 14 an approximate range of cyanide concentrations in snowmelt would be 0.21 to 0.34-mg of cyanide/L of snow melt. This approximation ignores any reactions such as volatilization or biodegradation of cyanide species that may result in somewhat lower concentrations. Results in Part II will demonstrate that measured cyanide in discrete snow samples taken at sites 1SW, 1SE and 3SW on I-75 ranged from approximately 0.05-mg/L up to 0.90 mg/L with a study event mean value of 0.16-mg/L. For the site subject to snow melt runoff (1SE), the mean site cyanide value was 0.24-mg/L. For the sites at the upslope side of the pavement that did not receive significant drainage from the pavement (1SW and 3SW), the event mean cyanide levels were 0.08-mg/L and 0.13-mg/L of cyanide, respectively. These results will be discussed further in Part II but illustrate that the cyanide analyses and loading calculations presented herein indicated a reasonable mass balance.

**Literature Cited in Chapter 4**


Chapter 5
Accretion and Partitioning of Heavy Metals Associated with Snow Exposed to Urban Traffic and Winter Storm Maintenance Activities – Part II

Transportation activities can be a significant source of pollutant generation and transport during rainfall runoff events in the urban environment. Heavy metals, organic and inorganic compounds, particulates and solids generated by vehicular traffic result from abrasion of vehicle components particularly tires, fuel leakage and residues, fluid leakage (oil, grease and radiator coolant), catalytic converter emissions and pavement degradation (Sansalone et al. 1998). High heavy metal concentrations in runoff from transportation activities and the persistence of heavy metals affect receiving waters, aquatic life and ultimately the food chain. With the promulgation of the Final Rule for Phase II Storm Water under the National Pollutant Discharge Elimination System (NPDES) regulations on 29 October 1999, heavy metals in roadway storm water have now come into direct focus at the national regulatory level, with significant implications for state and local transportation agencies (DOTs). No less attention should be placed upon heavy metals in urban snow, particularly at time of thaw.

The unique nature of urban highway snowbanks makes urban snow a significant sink for both heavy metals and particulates generated by traffic and winter maintenance activities. These heavy metals can be predominantly associated with the particulate matter suspended and trapped within the snowbank. Because the United States is so dependent on its roadways for the movement of people, goods and services, the public expects the roads and highways to be maintained to provide safe traveling conditions, particularly during winter storms. De-icing salts applied to roads as well as other chemical additives used to prevent the caking of such salt stocks may be carried by surface runoff into streams and waterways. They may also infiltrate the soil bordering the highway and be carried to groundwater or remain in the soil solution or become
adsorbed by the soils. Besides the direct effects of de-icing salts on water quality, the presence of these salts can influence heavy metal and trace metal partitioning, concentration and mobility and hence their potential environmental impact.

The partitioning of heavy metals in urban rainfall runoff between the particulate and dissolved fraction can favor the dissolved fraction for low rainfall pH levels and pavement residence times in terms of minutes (Sansalone and Buchberger 1997). The literature is quite limited, however, when it comes to temporal accretion and partitioning of heavy metals in urban snow. This study seeks to examine such accretion and partitioning, and provide a basis for developing management strategies and techniques for reducing water quality degradation from urban roadway snow.

**Objectives**

The goal of this study was to assess the accretion and partitioning of heavy metals over time generated by traffic activities for a series of highway sites in urban Cincinnati. For a 48-hour, 470-mm snowfall event across urban Cincinnati, this study had four primary objectives. The first objective was to evaluate the temporal accretion of heavy metals and selected constituents in highway snow at a series of highway sites in comparison to an urban control site located away from the highway environment. The second objective was to examine the partitioning characteristics of these metals between dissolved and particulate-bound phases. The third objective was to examine temporal trends in partitioning coefficients for selected heavy metals and trace metals. The fourth objective was to examine the range of distributions for heavy metals across the gradation of snow residuals. These objectives allow the comparison between heavy metal accretion and partitioning in snow to that of rainfall runoff and provide
insight into appropriate management techniques and best management practices (BMPs) for urban snow.

**Background**

**Snow pollution**

Many atmospheric pollutants are scavenged from the atmosphere by rain and snow. Since snowflakes have a larger surface area and lower velocity than raindrops, they more efficiently collect and retain particulates from the atmosphere. Snow is also capable of scavenging particle-bound, mutagenic organic pollutants from the atmosphere in an urban environment (White et al. 1995). In urban areas, snowpack contamination is correlated with proximity to large industries and major roadways and accumulation and concentration of pollutants as the snowpack or snowbank ages.

Snowmelt and chemistry within the snowpack generate differential retention of particulate-bound constituents and elimination of dissolved trace metals and solids. While the size and velocity of snowflakes as compared with raindrops enable a higher scavenging efficiency for gaseous and particulate atmospheric pollutants, ground snowcover accumulates dry deposited pollutants which are otherwise frequently washed off during rain events and thaw. Apart from peak concentrations of suspended solids during short intense street runoff from rain, concentrations of suspended solids in snowmelt runoff are 2 to 5-fold higher than in rain runoff (Daub et al. 1994).

Snowmelt runoff is similar to rainfall runoff, in highly developed areas that produce largest pollutant mass (Bennett et al. 1981). However, meltwater can follow preferred channels through the snowpack rather than percolating uniformly into the soil as does rainfall (Hibberd 1984). Snowmelt runoff further contains elevated levels of solids and pollutants transported
from urban surfaces, i.e. nutrients, COD, Pb, Cl, as well as atmospheric fallout, vehicular emissions, roadway deterioration, urban litter, anti-skid grit and chemical deicers (Field 1974; Oberts 1994). The specific sources of heavy metal pollutants from vehicles originate from tetraethyl lead in gasoline (Pb), diesel oil (Cd), tire attrition (Zn and Cd), steel parts attrition (Ni, Cr, V, W, Mo, Fe, Mn and Al), wear of bearings and bushings (Cu), wire corrosion, brake lining attrition (Pb, Cu and Zn), radiator fluid (Cu) and catalytic converter emissions (Pt, Pd and Rh) (Amrhein and Strong 1990; Amrhein et al. 1992).

Of the heavy metals present in snow, Pb, which is still generated by traffic activities despite the phase out of leaded gasoline, is considered of greatest concern (Zinger and Delisle 1988). Its soluble form is most toxic, very stable and difficult to eliminate. Due to the particle adsorption, the concentration of Pb is related to the quantity of suspended solids present in snow. Pb tends to displace Ca, Na and other plant nutrients through exchange complexation (Scott and Wylie 1980). In roadside dusts and soils collected in Cincinnati, Ohio, levels of Pb and Cu were higher than background levels for normal soil (Tong 1990). Anthropogenic Pb quantities are proportional to both density of vehicle traffic and the length of time snow remains along the roadside.

Other contaminants commonly found in snow include sulfur and nitrogen species and nitrate ions preferentially lost with respect to chloride during the melting process (Brimblecombe et al. 1987). Chloride is proportionally enriched in residual leached snow while \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) are proportionally enriched in initial meltwaters (Brimblecombe et al. 1987). Increased availability of metals in storm or meltwater with low pH may result from increased loading of metals, increased metal release rates due to deposition of acidifying components and changes in metal compounds to more soluble species (Cusimano et al. 1986). High concentration of \( \text{NO}_3^- \)
coincides with low pH and high concentration of Al. These are changed possibly by anthropogenic influences, the biological demand for atmosphere-derived nitrogen or the long-term increase in watershed nitrogen supply (deposition and mineralization).

Spatial variations in urban snowmelt are primarily due to heterogeneous conditions such as uneven snow distribution (in snowfall, drifting and the size of plowed snowbanks), subsequent rainfall events, spatial and temporal differences in insulation due to cloudiness and localized differences in shading and solar aspect and the resulting local differences in heating and temperature, and simply the localized differences in air temperature (Bengtsson and Westerstrom 1992).

**Mobility of metals**

Mobility of heavy metals in snowmelt or rainfall runoff depends on chemical characteristics of the water primarily pH. For unfrozen soils, infiltration into the ground is a concern and the ion composition of soil becomes a factor as well (Bauske and Goetz 1993). The Cd concentration of roadside soil samples exhibits high correlation with Na, Ca, Cl, whereas Zn exhibits moderate correlation. In the Don River, Canada, temperature and NaCl affect trace metal partitioning more than pH and thus influence the bioavailability of the metals (Warren and Zimmerman 1994). As temperature decreases, the accumulation of Cd, Cu and Zn in particulates decreases. An increase in NaCl decreases the concentration of Cd and Zn associated with particulate leachable phase and Zn, Cu and Cd (in decreasing order) in the oxidizable suspended particulate matter phase.

Mobilization of metals is mostly controlled by organic matter mobilization (Amrhein et al. 1992). With an increase in salt, concentrations of Cr, Pb, Ni, Fe, Cd and Cu also increase, suggesting ligand complexation and competitive exchange. Application of de-icing salts has
been shown to increase Pb mobility from the surficial layer of soils (Wheeler and Rolfe 1979). De-icing salts can also release Hg from bottom sediments. As NaCl or CaCl₂ increases, relative amounts of Hg in the water increase 2 to 5 orders of magnitudes. Changes in pH contribute to this phenomenon (Feick et al. 1972).

The proximity of snow to known anthropogenic sources such as traffic activities and winter maintenance practices has significant influence on concentration and wet deposition. The results present a dilemma for state DOTs responding to the new regulations. If snow is removed soon after deposition, contamination does not have time to accumulate in the snowbank to be later released when it melts. However, highway snow thus removed remains a complex matrix of solids, heavy metals, oil and grease, and other organic and inorganic constituents generated from highway traffic and winter maintenance activities. The treatment of the snow is also difficult due to the shear volume that must be handled.

**Impacts of snow pollution on the biota**

Ionic species of heavy metals are particularly toxic to organisms as are weak inorganic complexes in storm water (Paulson and Amy 1993). Effects of acidic deposition on microbial community depend on soil type, nature of vegetation and indigenous community itself (Thompson et al. 1987). In Scotland, spring melt causes bacterial numbers to decrease in upper soil horizon (3-cm), but to increase in lower profile due to protection from direct effects by soil exchange process and increased nutrient availability.

In storm water or snowmelt, complexation and interaction with high levels of organic matter should reduce toxicity of these metals (Amrhein et al. 1992). However, most metals pose a threat to the development of aquatic species as a result of low pH condition or metal concentration. For example, the amount of Al affects sensitive life stages of fish species at
certain times of the year (Hooper and Shoemaker 1985). Episodic exposure (snowmelt or precipitation) to acid and trace metals (Al and Cu) on brown trout (Salmo trutta) eggs and fry in soft water also has deleterious effects (Sayer 1991). In Norway, an increase in the acid concentration of low-buffered watercourses occasionally leads to severe physiological stress in fish and other aquatic organisms and even to massive fish kills (Johannessen and Henriksen 1978). Snowmelt runoff from roads and highways has a negative effect not only on aquatic species but upon vegetation as well. Although the threat to vegetation is comparatively much smaller, continuous pollution from snowmelt will affect and thus endanger larger areas, including vegetation along roadways.

Methodology

Experimental sites and field data collection

In February 1998, snow samples were collected from ten sampling sites in Cincinnati, Ohio located on I-75 and U.S. Route 126 E. A control site located in a residential urban area approximately 3-km from I-75 was sampled to evaluate background levels of heavy metals, sulfur, nitrogen, total organic carbon (TOC), total carbon and cyanide. Snow sampling at both the highway and control sites was described in Part I of this study for discrete samples taken during the 102-hour duration of the study. Of the ten sites (1SW, 1SE, 2ES, 3SW, 4NE, 5NE, 6SW, 7SW, 8SW and 9NE), four were analyzed extensively (1SW, 1SE, 2ES and 3SW) in this study.

Heavy metal analyses

Metals will partition between the dissolved and particulate-bound phases as a function of redox, pH, alkalinity, residence time, presence of solids and mixing generated from the flow. Throughout the snow event, samples from both the four highway sites and the control site were
immediately transported to the nearby laboratory for further analyses. The snow samples were separated into dissolved and particulate-bound constituents by taking a 100-mL aliquot and filtering the aliquot through a 0.45-µm acid-digestible membrane following Standard Method 3010 (APHA 1995). From the filtrate, 50-mL was preserved with 2.5-mL of nitric acid (HNO₃) and analyzed for metals. The solids retained on the filter were microwave digested in HNO₃ to release particulate-bound metals into solution following SW-846 Method 3015 (USEPA 1990).

For the highway sites samples, metals were analyzed using a Perkin Elmer Optima 3000 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) following Standard Method 3500 protocol (APHA 1995). For both dissolved and particulate-bound fractions, analyses were conducted for Pb, Cu, Cd, Zn, Al, Ca, Na, Mg and Fe. For control site samples with metal concentrations at significantly lower levels than for highway site samples, analyses were conducted on a Varian 220 Zeeman furnace using EPA method 200.9. Hg analyses were conducted using a cold vapor method following EPA 245.1 protocol.

In addition to heavy metal analyses, standard water quality measurements were carried out for the purposes of this study. These measurements included total suspended solids (TSS), settleable solids (SS), total carbon and dissolved and TOC. Total solids and TSS were determined using the Standard Method Section 2540, and SS were determined using the Standard Method Section 2540 F (APHA 1995).

The total carbon and TOC were determined from EPA Method 415.2 on the dried solids and analyzed on a Carla Elba carbon analyzer NA 1500. The dissolved TOC was first separated by centrifugation and the supernatant was analyzed. The solid material was dried and analyzed for total carbon.
Other water quality measurements for the highway sites and control site included total and dissolved sulfur and nitrogen as well as total Hg and cyanide. The determination of these measurements followed the following protocols: sulfur (Standard Method 3030 H), total kjeldahl nitrogen (TKN) (EPA Method 351.2), and cyanide (EPA Method 335.2 and SW 9010). Samples were fractionated between total and dissolved using 0.45-µm membrane filters and analyses conducted on each fraction. Samples used for sulfur analyses were digested following Standard Methods protocol 3030 H and analyzed by ICP-AES.

Characterization indices for heavy metal mass

In pavement runoff, meltwater or any aqueous system, there is a temporal partitioning between heavy metals in solution and solids. This partitioning includes specific mass transfer mechanisms of sorption, ion exchange and surface complexation with both organic and inorganic sites on the solid matter. These partitioning reactions are generally non-linearly reversible between the solid-phase and soluble phase concentrations. Total concentration of a heavy metal is the sum of the dissolved ($c_d$) and the particulate-bound concentrations ($c_p$):

$$c_T = c_d + c_p$$  \hfill (1)

Operationally, the soluble or dissolved fraction is that fraction that passes the 0.45-µm membrane filter, and therefore contains both the dissolved and part of the colloidal-bound heavy metals. The solid phase concentration ($c_p$) is defined as the product of the heavy metal concentration on the solid phase ($c_s$) in terms of mass/mass of solids and the concentration of the adsorbing solid material in the aqueous system, $m$ typically measured as TSS in terms of mass/volume of aqueous solution:

$$c_p = (c_s)(m)$$  \hfill (2)
When the rate of sorption and de-sorption are equal, concentration equilibrium exists between the dissolved and solid-phase concentrations of a heavy metal. The ratio of these phases is referred to as the partitioning coefficient \( K_d \) for a particular heavy metal at a particular pH and redox level:

\[
K_d = \frac{c_p}{c_d} = \frac{P}{D} \\
\text{(3)}
\]

where, \( D \) is the dissolved mass of a heavy metal, and \( P \) is the particulate-bound mass of a heavy metal. Substitution of Equation (2) and (3) into Equation (1) yields the dissolved fraction \( f_d \) and the particulate-bound fraction \( f_p \) as defined by:

\[
f_d = \frac{D}{(D+P)} = \frac{c_d}{c_T} = 1/[1+K_d(m)] \\
\text{(4)}
\]

\[
f_p = \frac{P}{(D+P)} = \frac{c_p}{c_T} = [(K_d)(m)]/[1+K_d(m)] \\
\text{(5)}
\]

where, \( m \) in this modeled case is the total suspended solid mass in terms of mass/volume of aqueous solution (O’Connor 1988). For \( f_d > 0.5 \), the heavy metal mass is mainly in dissolved form. The product of \( (K_d)(m) \) is dimensionless and \( K_d \) is usually expressed as liters per kilogram (L/kg). The larger the \( K_d \) value the greater the partitioning of a heavy metal to the solid phase. The greater the dissolved fraction, or the more soluble the heavy metal, the lower the \( K_d \) value. Because of much longer residence times in the presence of highway solids, the dissolved fractions of heavy metals can be very low in snow.

**Particle analyses**

The determination of the particle size gradation for residuals was performed according to ASTM D421 for the sample preparation (with the exception of air drying) and ASTM D422 for the sieve analysis (ASTM 1990; ASTM 1993). All samples were oven dried at 60°C. The set of sieves encompassed the 4750-µm (#4) through the 25-µm (#500) sieves. Dry residuals separated on each of the stainless steel sieves were weighed and stored separately in petri dishes or
polypropylene bottles depending on the volume of residual remaining on each sieve. A mass balance was computed for each particle size gradation from each site within 2% of the initial mass. Typically, a hydrometer analysis would be performed for particles less than 75-µm (ASTM 1993). However, for sample recovery, specific surface area (SSA) determination, specific gravity determination and heavy metal composition analysis, mechanical sieve analysis proved the best protocol. Across each size gradation, residuals were separated into 17 size classes.

The total surface area (SA) through the measurement of SSA provides, in part, a measure or index of the capacity of a particulate surface to adsorb aqueous heavy metals. The ethylene glycol monoethyl ether (EGME) method (Schwertmann and Cornell 1991) that did not require heating of the sample above 60°C was modified and utilized for experimental determination of SSA. The methodology to determine SA, SSA and specific gravity is presented elsewhere (Sansalone et al. 1998; Sansalone and Tribouillard 1999).

**Results**

**Inorganic species and TOC**

For sites 1SW, 2ES and 3SW sulfur, TKN (shown as N), total carbon, TOC and chemicals of Hg and cyanide were analyzed and plotted as a function of elapsed time in Figures 5.1 through 5.3. These results are compared to a control site located approximately 3-km from the highway and only receiving background urban loadings. Although sulfur concentrations vary throughout the study period, trends generally indicate an increase in accumulation of total and dissolved sulfur as a function of time at each site. While total nitrogen shows a more gradual increase in accumulation as compared to sulfur the dissolved fraction of nitrogen represents a more irregular pattern at site 1SW and 3SW while not significantly increasing beyond 1-mg/L at
Figure 5.1. Chemical analyses of selected inorganic species and organic indices accretion in snow at site 1SW. Control snow mean (μ) values for other constituents are: Total sulfur = 0.65 mg/L; Dissolved sulfur = 0.13 mg/L; Total and Dissolved nitrogen = 0.05 mg/L; TOC = 0.31 mg/L; and Dissolved TOC = 0.25 mg/L.
Figure 5.2. Chemical analyses of selected inorganic species and organic indices accretion in snow at site 1SE. Control snow mean (µ) values for other constituents are: Total sulfur = 0.65 mg/L; Dissolved sulfur = 0.13 mg/L; Total and Dissolved nitrogen = 0.05 mg/L; TOC = 0.31 mg/L; and Dissolved TOC = 0.25 mg/L.
Figure 5.3. Chemical analyses of selected inorganic species and organic indices accretion in snow at site 3SW.
Control snow mean (μ) values for other constituents are: Total sulfur = 0.65 mg/L; Dissolved sulfur = 0.13 mg/L; Total and Dissolved nitrogen = 0.05 mg/L; TOC = 0.31 mg/L; and Dissolved TOC = 0.25 mg/L.
site 1SE for the duration of the event. For all three sites, total sulfur and total nitrogen are at least an order of magnitude or higher as compared to the control site.

Total carbon either showed little to no increase (sites 1SW and 3 SW) or a variable trend as shown for site 1SE, the companion site to 1SW, but located on the down slope side of the pavement. While TOC values generally increased for 1SE and 3SW there was variability in the trends. TOC content at 1SW declined rapidly after the first sample, during the period of snowfall and recovered to the original TOC levels at the end of snowfall at 48-hours. For all sites, total carbon and TOC are at least an order of magnitude higher than the control site.

Cyanide levels, although demonstrating some variability, remained relatively constant at all sites (~154-µg/L) or increased with increases correlated to application of de-icing salts that contained cyanide compounds as anti-caking agents. For all sites, cyanide levels are at least an order of magnitude higher than the control site (20-µg/L). For all sites, Hg was at or below the method detection limit (MDL).

**Control site heavy metals**

For the control site, the concentration of total Pb, Cu, Ca, Na, Cd, Zn, Mg and Fe are plotted as a function of elapsed time in Figure 5.4. For each metal, MDL are plotted as a horizontal line in each plot. Results from each of the highway sites analyzed for temporal accretion of metals (1SW, 1SE, 2ES and 3SW) were compared to the control site that was subject only to background deposition from the urban environment. These results are above the MDL for the particular metal, except for Cd.

**Accretion and partitioning for highway site heavy metals**

The temporal accretion and temporal partitioning of specific heavy metals for sites 1SW, 1ES, 2ES and 3SW are presented in Figures 5.5 through 5.13. In addition, since most of the
Figure 5.4. Accretion of total heavy metals in snow at urban control site.
Figure 5.5. Temporal variation of Cu particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.6. Temporal variation of Cd particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.7. Temporal variation of Zn particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.8. Temporal variation of Pb particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.9. Temporal variation of Na particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.10. Temporal variation of Ca particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.11. Temporal variation of Mg particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.12. Temporal variation of Al particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.13. Temporal variation of Fe particulate and dissolved concentrations with partitioning in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
metals are predominately particulate-bound, the particulate-bound fraction, \( f_p \) is modeled using Equation 7 and compared with measured values shown as data points in the lower portion of each plot for each site. All concentration values are presented in terms of \( \mu g/L \). Note that the upper diagram of each plot has a logarithmic concentration axis and the lower diagram of each plot has an arithmetic axis for \( f_p \).

Figure 5.5 illustrates the accretion of dissolved and particulate-bound fractions for Cu. For the entire duration of the study the particulate-bound fraction of Cu dominates the dissolved fraction for all sites. This can be seen in the upper diagram of each plot by the separation between the two curves and seen in the lower diagram of each plot by the values of \( f_p \) that are typically greater than 0.80 indicating that 80\% of the Cu mass is particulate-bound. Modeled \( f_p \) results generally follow the same trend as measured data while predicting a slightly higher \( f_p \) than measured results indicate for all sites except 3SW.

Figure 5.6 illustrates the accretion of dissolved and particulate-bound fractions for Cd. Except for a number of specific instances, the particulate-bound fraction of Cd dominates the dissolved fraction for all sites, however the separation is not as great as with Cu. This can be seen in the upper diagram of each plot by the separation or lack there of between the two concentration curves. For Cd, \( f_p \) values show greater variability throughout the event as illustrated in the lower diagram of each plot. Modeled \( f_p \) results generally follow the same trend as measured data while predicting a higher \( f_p \) than measured results indicate for all sites. The difference between the modeled results and measured results increase as the value of \( f_p \) decreases.

Figure 5.7 illustrates the accretion of dissolved and particulate-bound fractions for Zn. Except for a few specific instances, the particulate-bound fraction of Zn dominates the dissolved
fraction for all sites, with the dominance increasing as a function of time at each site. This can be seen in the upper diagram of each plot by the increasing separation over time, in particular towards the end of the study. For Zn, $f_p$ values start out low at time 0 and rapidly increase within several hours at each site. Modeled $f_p$ results generally follow the same trend as measured data while predicting a higher $f_p$ than measured results indicate for all sites except site 3SW. The difference between the modeled results and measured results decrease at each site towards the end of the study period.

Figure 5.8 illustrates the accretion of the particulate-bound fractions for Pb. Nearly all of the Pb analyzed was particulate-bound with the dissolved fraction at or near MDL for all sites. Therefore only a particulate-bound concentration was plotted for most sites. For Pb, $f_p$ values were not modeled due to lack of a significant dissolved fraction.

Figure 5.9 illustrates the accretion of dissolved and particulate-bound fractions for Na. The primary sources of Na are from de-icing salts (NaCl) applied at the study sites. In contrast to Cu, Zn and Pb, Na is primary dissolved as illustrated by the dominance of the dissolved concentration with respect to the particulate-bound concentration in the upper diagram of each figure. Modeled $f_p$ results generally follow the same trend and fit the measured data through the first half of the study period while predicting a higher $f_p$ than measured for the second half of the study period at each site.

Figure 5.10 illustrates the accretion of dissolved and particulate-bound fractions for Ca. The primary sources of Ca are from de-icing salts (CaCl$_2$) applied at the study sites. For Ca, neither the dissolved nor the particulate-bound concentrations dominated the other fraction, except possibly for site 3SW. While modeled $f_p$ results generally follow the same trend as the measured data the modeled results predict a significantly higher $f_p$ than measured for Ca.
Figure 5.11 illustrates the accretion of dissolved and particulate-bound fractions for Mg. The particulate-bound fraction of Mg dominates the dissolved fraction for all sites. This can be seen in the upper diagram of each plot. For Mg, $f_p$ values start out low at time 0 and rapidly increase within several hours at each site. Modeled $f_p$ results generally follow the same trend as measured data while predicting a slightly higher $f_p$ than measured results indicate for all sites.

Figure 5.12 and 5.13 illustrate the accretion of dissolved and particulate-bound fractions for Al and Fe respectively. Both metals are strongly particulate-bound for all sites. This can be seen in the upper diagram of each plot. Modeled $f_p$ results fit measured $f_p$ results for both Al and Fe.

**Partitioning of metal elements and solids – $K_d$ values**

Water quality parameters such as solids, alkalinity, pH, hardness and residence time all play a role in partitioning of heavy metals. While each of these parameters affects partitioning and $K_d$ values, solids (as a mass concentration) have a direct relationship on $K_d$ heavy metal values as shown by Equation 5. For sites 1SW, 1SE, 2ES and 3SW, TS and TSS are plotted in the upper diagram of each plot along with $K_d$ values for Pb, Cu, Cd and Zn, and for Al, Ca, Fe, Mg and Na are plotted as a function of elapsed time, in the lower diagrams of each plot in Figure 14 and Figure 15 respectively. Here TS is defined as the sum of settleable and suspended solids. $K_d$ values are based on measured results from the dissolved and particulate-bound metal fractions. There are a number of important results portrayed in these figures. First, $K_d$ values vary in a discernible trend across three orders of magnitude ($10^3$ to $10^6$-L/kg). In comparison, heavy metals in pavement runoff have $K_d$ values that range from $10^1$ to $10^4$-L/kg in rainfall runoff (Sansalone and Buchberger 1997), indicating that a more significant fraction of the heavy metal mass is dissolved. Second, an equilibrium $K_d$ condition at $10^4$-L/kg appears to be approached for
Figure 5.14. Temporal variation of Pb, Cu, Cd and Zn with respect to Kd value, total suspended solids (TSS) and total solids (TS) concentration in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Figure 5.15. Temporal variation of Al, Ca, Fe, Mg and Na with respect to Kd value, total suspended solids (TSS) and total solids (TS) concentration in snowbank samples (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Pb, Cu, Cd and Zn as elapsed time increases for each site. In fact, $K_d$ values in the range of $10^4$ to $10^5$-L/kg are typical for rivers and large lakes where the residence time is in terms of days and conditions influencing $K_d$ remain relatively constant (Thomann and Mueller 1987).

**Particle analyses**

For all ten sites, a range of residual particle size distributions is plotted in Figure 5.16. These results indicate that there is a wide gradation of particulate material deposited from the highway snowbank and that the very coarse fraction (>1000-µm) dominates the total dry mass. The SSA results indicate that while SSA generally increases with decreasing particle size, the increase is not consistent and monotonic as would be expected for spherical particles. In contrast to SSA, the SA values indicate that the predominance is associated with the coarse size fraction of the gradation, that fraction greater than 500-µm.

With specific gravity, it is generally assumed that particulate specific gravity is constant across a gradation with a mean value of 2.82 g/cm³. Figure 5.16 illustrates the incremental particle density as a function of particle diameter. While density values range from a maximum of 3.13 g/cm³ to a minimum of 2.57 g/cm³ across the gradation, there is a fairly clear trend towards lower particle density values with decreasing particle diameter.

The plots also illustrate general metal trends for Pb, Cu, Cd and Zn. First, while variability in the mass distributions across each gradation does exist for all metals, results indicate that the predominance of heavy metal mass is associated with the coarse fraction of particles. In addition, the heavy metal mass trends more closely follow the total SA profile trends. The metals Pb, Cu and Zn show similar ranges as opposed to Cd which has a wider range to a minimum of 0 mg over the particle diameters.
Figure 5.16. Urban snow residual range of solid characteristics for all ten sites for sampling time February 8 at 12:00 am (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
Conclusions

This study examined the accretion and partitioning in urban snow of selected heavy metals and constituents generated by traffic activities and winter maintenance practices. Results were evaluated on a temporal basis for a series of 4 urban highway sites and compared to an urban control site subject to only ambient atmospheric deposition. Sampling and monitoring of these sites was carried out for the duration of the 48-hour, 470-mm snowfall event until the highway snowbanks at each site had nearly dissipated after 102-hours since the start of snowfall.

A number of important conclusions can be drawn from this study. First, traffic activities and winter maintenance practices generate significant levels of inorganic and organic constituents, many of which are predominately particulate-bound in the snowbank with increasing residence time. Accretion of these inorganic constituents at each highway site is an order of magnitude or higher than the control site. Accretion of particulate-bound heavy metals as illustrated in Figures 5.5 through 5.12 for the 4 highway sites are compared to the control site in Figure 5.4. These results indicate that heavy metal (Pb, Zn, Cu and Cd) accretion at each highway site is approximately two orders of magnitude greater than accretion of these metals at the control site. Accretion of Pb, Zn and Cu in snow at these highway sites resulted in concentrations that ranged from 1 to 10-mg/L depending on the site and heavy metal. Cd concentrations typically ranged from 10 to 100-µg/L depending on the site. All of these heavy metals, Pb, Cd, Cu and Zn are highly particulate-bound (>90% of mass is particulate-bound) throughout their residence time (4 to 102-hours) in the highway snowbank.

The results in this study differ sharply with highway rainfall runoff at a number of these sites. Two years of storm water analyses from site 1SW and 1SE indicate event mean concentration of total Pb is approximately 90-µg/L with approximately 57% of the Pb mass in
dissolved form, total Cu is approximately 150-µg/L with approximately 63% of the Cu mass in dissolved form, total Cd is approximately 12-µg/L with approximately 77% of the Cd mass in dissolved form, and total Zn is approximately 4500-µg/L with approximately 89% of the Zn mass in dissolved form. Residence times for rainfall runoff measured as average pavement residence time (APRT) ranged from 1.5 to 15 minutes at these sites (Sansalone et al. 1998).

Results of heavy metal mass trends across the particle size gradations for all ten sites indicate that the predominance of heavy metal mass is associated with the coarse size particle fraction (>250-µm). This trend is similar to that for residual mass retained and total SA where the predominance of both are associated with the coarse fraction of particles. These general trends are consistent and have similar ranges despite a physical separation of up to 27-km across urban Cincinnati and a wide range of conditions such as traffic levels, drainage area, pavement slopes, pavement type and localized wind patterns. Heavy metal mass trend results as a function of particle diameter provide information in the decision-making process for residual treatment, management strategies, regulations and disposal.

A number of important conclusions with respect to management can be drawn from these results. Pollutant accretion in highway snowbanks is relatively rapid within the first 12-hours of the snowbank exposure to traffic at all the highway sites examined. As a result of this rapid accretion, a decision must be made to either remove the snow from the immediate shoulder area rapidly or leave the snow in place and gradually dispose of it based on a given level of constituent accretion and applicable regulations. Finally, if snow is left in place and is to be treated on-site, or in local disposal areas such as a detention basin, the particulate-bound nature of constituents and potential re-partitioning to meltwater must be addressed in the design process.
The toxic effect of heavy metals on the environment is dependent on the concentration of these metals and hardness of the snowmelt. The USEPA sets standards for water quality so that locally sensitive aquatic species would not be affected as long as the metal concentration does not exceed a 4-day value and 1-hour value more than once every 3 years on average. In this study, Zn and Cu as well as cyanide exceeded these values. The limits for Zn and Cu were calculated from the mean hardness from each site (Part I). For Zn, a 4-day limit (170-μg/L) at site 1SW was exceeded by a Zn concentration of >1000-μg/L. The same was true for Cu which exceeded the 4-day limit of 357-μg/L at a concentration of ~1000-μg/L. The Pb and Cd were below water quality criteria with respect to mean hardness at each site. The implications of treatment for toxic levels as well as the effect on local biota must be taken into account.

The emphasis on treatment for urban snow is varied according to site and available space. Leachates as well as snow chemistry affects quality of runoff and treatment strategies. The use of best management practices (BMPs) to address snowmelt pollution can only improve and protect the environment. Complementing paper (Part I) collected and analyzed data on water quality during this event for a further database for BMPs.

**Literature Cited in Chapter 5**


Chapter 6
Physical and Chemical Characteristics of Urban Roadway Snow Residuals Generated from Traffic Activities

Traffic activities generate anthropogenic particulate matter in the urban roadway environment. This particulate matter can be dry deposited in the highway right-of-way or transported in storm water runoff after deposition and is generated from traffic activities that include vehicular component wear, pavement degradation, maintenance, spillage and littering (Sansalone et al. 1998). For example, tire and pavement interaction abrades both tire and pavement materials and is a major source of anthropogenic particulate matter (Muschack 1990). Pavement wear accounts for 40-50% and tire wear for 20-30% of particulates generated on a mass basis (Kobriger and Geinopolos 1984). Vehicular parts abrasions such as from the engine and brakes accounts for approximately an additional 15% of the total particulate mass generated from transportation activities, while deposition from urban atmospheric sources generated outside the right-of-way accounts for less than 3% of the total particulate mass that is dry deposited.

Much of this particulate mass that is dry deposited on urban pavement surfaces by traffic before and during a rainfall-runoff event can be mobilized and transported in a matter of hours, in part as a function of the intensity, duration and volume of storm water runoff generated by the event. In contrast to rainfall events, where storm water runoff has a pavement residence time exposed to traffic that is typically less than 10 minutes (Sansalone et al. 1998), highway snow has a residence time exposed to traffic that can extend into days or even weeks in northern climates. The exposed snow surface, typically plowed into a highway snowbank, is a porous and effective accumulator of particulate matter that is generated by traffic throughout the residence time of the snow. From a water quality perspective, this accumulated particulate matter having
reactive sites and large surface to volume ratios can mediate partitioning and transport of heavy metals while serving as reservoirs for many reactive constituents that accumulate on the particle surface.

Ultimately, decisions will be made regarding management and treatment of urban snow residuals which are deposited in highway snow and remain after the dissipation of the highway snow that is plowed into banks alongside the roadway. For example, these residuals might be removed by street sweeping or vacuuming before mobilization and transport by a subsequent rainfall runoff event. Such decisions will require knowledge of particulate gradations, mass loading, surface area, specific gravity and heavy metal distributions across the gradations. Results of this study provide information for residual management techniques such as street sweeping, vacuuming and disposal. With respect to in-situ treatment strategies, particulate characteristics and loadings are primary variables determining viability of settling basins, filtration systems and solid separation devices such as swirl separators.

Objectives

The major objectives of this study were threefold. These objectives were carried out for residuals recovered from each of the ten highway sites. The first objective was to characterize the mass gradation and specific gravity across the size gradation of particulate snow residual matter. The second objective was to experimentally measure specific surface area (SSA) of residuals across the gradation, integrate the SSA results over the gradation and determine the resulting surface area (SA) across the gradation. The final objective was to evaluate the heavy metal concentrations of Pb, Cu, Cd and Zn across each gradation. For each objective, results were evaluated in terms of incremental and cumulative distributions across each residual size gradation for each of the ten highway sites.
Previous Work

Various aspects related to the accretion and release or eventual deposition of anthropogenic particulate matter have been investigated by researchers. Apart from peak concentrations of suspended solids transported during short duration high intensity rainfall-runoff events, event mean concentration (EMC) of suspended solids, capable of entrainment in snowmelt runoff, are 2 to 5-fold or higher than in rainfall-runoff EMCs (Daub et al. 1994), where EMC is defined as (Huber 1993):

\[
EMC = \frac{M}{V} = \bar{C} = \frac{\int_{0}^{t_{r}} c(t)q(t)dt}{\int_{0}^{t_{r}} q(t)dt}
\]

where,
- \(M\) = total mass of a constituent over entire event duration (M)
- \(V\) = total volume of flow over entire event duration (L^3)
- \(\bar{C}\) = flow weighted average concentration for entire event (M/L^3)
- \(c(t)\) = time variable solid or dissolved fraction (M/L^3)
- \(q(t)\) = time variable flow (L^3/T)
- \(t_r\) = duration of the event (T)
- \(t\) = time (T).

The volumetric rate and total volume of snowmelt is generally significantly less than for rainfall runoff events. However, because the longer residence time of the highway snow bank results in a greater accumulation of particulate matter, snow melt EMCs can be an order of magnitude or larger than rainfall runoff EMCs for the same site. At the same time, particulate matter (as suspended and settleable solids) incorporated in the highway snow bank results in aqueous concentrations that can exceed 10,000-mg/L after a number of days of traffic exposure.
(Sansalone and Buchberger 1996). While the size and velocity of snowflakes as compared with raindrops enable a higher scavenging efficiency for gaseous and particulate atmospheric pollutants, it is the snow bank or snow cover alongside the highway that accumulates dry deposited pollutants generated by traffic that would otherwise be frequently washed off during rain events (Colbeck 1980). Urban roadway snow banks have been shown to be significant sinks for particulate and heavy metal accumulation (Sansalone and Buchberger 1996).

When suspended in a porous matrix of snow containing a heterogeneous mixture of particulate material and heavy metals, partitioning will occur. For example, Pb can adhere to fine insoluble particles. Due to the particle adsorption, the concentration of Pb is related to the quantity of suspended solids present in snow. Adsorbed Pb quantity has been shown to be proportional to both density of vehicle traffic and the residence time snow remains on roadside (Scott and Wylie 1980; Zinger and Delisle 1988). Equilibrium partitioning of heavy metals to particulate matter in snow has been shown to strongly favor the particulate-bound fraction for all heavy metals with the possible exception of Cd (Sansalone and Buchberger 1996; Viklander 1997). As the level of particulate material increases in the highway snow bank, the resulting pH of the snowmelt also increases (Viklander 1997). Both the increase in particulate matter and pH drives the equilibrium partitioning of heavy metals towards the particulate-bound fraction (Sansalone and Buchberger 1997). Therefore, snow residuals generated from transportation activities in the highway right-of-way contain high levels of particulate-bound heavy metals such as Pb, Cu, Cd and Zn.

A number of management strategies for snow particulate matter have been proposed in regions with urban areas that receive snow such as Quebec, Sweden and Ohio (Zinger and Delisle 1988; Sansalone and Buchberger 1996; Viklander 1997). These include the collection
and dumping of snow as soon as possible to avoid accumulation of particulate matter and heavy metals. A second strategy is to remove particulate matter from snow before disposal of snow. The third strategy is to avoid dumping of snow in receiving water by placing the snow in locations either designed for snow dumping with control of residuals and melt water or in storm water facilities such as detention basins capable of significant accumulation of snow. Separation of particulate matter residuals can be accomplished through melting of snow and settling of the particulate matter.

**Methodology**

**Climate and experimental sites**

Four primary highway sites were selected for snow sampling from a total of ten highway sites located within the metropolitan area of Greater Cincinnati. All were sampled for highway snow residuals. One site was located on Inter State 75 (I-75), a major north-south freeway between Michigan and Florida. The other site was located on U.S. Route 126, 1-km east of I-75. An additional site utilized as a control site was located in a residential area of urban Cincinnati. Snowfall at the control site had no direct exposure to highway or residential roadway traffic activity. These four sites were designated 1SW, 1SE, 2ES and 3SW. For each designation the first number identifies the number of a particular site location, the first letter indicates the direction of traffic and the final letter indicates which side of the highway samples were obtained. A description and location of all snow and snow residual sampling sites is provided in Table 6.1. For all sites, drainage from the pavement was in the form of lateral pavement sheet flow \((q_{sd})\) towards the pavement shoulder were the snow banks were located.

Starting at 05:00 on 04 February 1998, the metropolitan Cincinnati area received a 470-mm snow event for which snow continued for 48-hours. Actual snow accumulation began at
Table 6.1. Description and location of all snow sampling sites for metropolitan Cincinnati study.

<table>
<thead>
<tr>
<th>Site</th>
<th>Highway</th>
<th>Mile Marker</th>
<th>Sampling Area</th>
<th>Drainage Area for qsf</th>
<th>qsf Area (m²/m)</th>
<th>Roadway Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>1SW</td>
<td>I-75 South</td>
<td>2.58S</td>
<td>low speed (west) shoulder</td>
<td>no qsf</td>
<td>0</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>1SE</td>
<td>I-75 South</td>
<td>2.60S</td>
<td>high speed (east) shoulder</td>
<td>4 lanes + 1.5 shoulders</td>
<td>20</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>2ES</td>
<td>126 East</td>
<td>11.1E</td>
<td>low speed (south) shoulder</td>
<td>1 lane + 1 shoulder</td>
<td>5.5</td>
<td>2 PCC lanes</td>
</tr>
<tr>
<td>3SW</td>
<td>I-75 South</td>
<td>5.90S</td>
<td>low speed (west) shoulder</td>
<td>1 lane + 1 shoulder</td>
<td>5.5</td>
<td>3 asphalt lanes</td>
</tr>
<tr>
<td>4NE</td>
<td>I-75 North</td>
<td>12.1N</td>
<td>low speed bridge (east) shoulder</td>
<td>1 lane + 1 shoulder</td>
<td>5.5</td>
<td>3 PCC lanes</td>
</tr>
<tr>
<td>5NE</td>
<td>I-75 North</td>
<td>16.1N</td>
<td>low speed (east) shoulder</td>
<td>2 lanes + 1 shoulder</td>
<td>9.1</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>6SW</td>
<td>I-75 South</td>
<td>16.0S</td>
<td>low speed (west) shoulder</td>
<td>1.5 lanes + 1 shoulder</td>
<td>7.3</td>
<td>3 asphalt lanes</td>
</tr>
<tr>
<td>7SW</td>
<td>I-75 South</td>
<td>11.9S</td>
<td>low speed (west) shoulder</td>
<td>2 lanes + 1 shoulder</td>
<td>9.1</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>8SW</td>
<td>I-75 South</td>
<td>0.90S</td>
<td>low speed (west) shoulder</td>
<td>2 lanes + 1 shoulder</td>
<td>9.1</td>
<td>4 asphalt lanes</td>
</tr>
<tr>
<td>9NE</td>
<td>I-75 North</td>
<td>1.70N</td>
<td>low speed (east) shoulder</td>
<td>no qsf</td>
<td>0</td>
<td>4 asphalt lanes</td>
</tr>
</tbody>
</table>

**Legend:**
- N : north
- S : south
- E : east
- W : west
- PCC : Portland cement concrete
- qsf : lateral pavement sheet flow
06:00. At the control site, measurements of ambient air temperature and relative humidity were made for the duration of study period. Traffic loading data was also collected for the paired sites of 1SW-1SE using a recently installed network of Intelligent Transportation System (ITS) monitors.

Through a combination of evaporation, sublimation and melting, the highway snow banks located continuously along the back of the highway-paved shoulder dissipated over time. After the snowfall event (102 hours), only an icy sludge residual remained as a deposited remnant of the snow bank. Highway shoulders with a southern exposure were drier than northern exposure shoulders, but at all sites, snow and ice remained within a layer of residual material. Each of the ten sites was sampled to obtain a minimum of 4-L of residual material. A flat, 100-mm wide stainless steel trowel was used to sample the residual material across the entire cross-section that was typically less than 1-m in width and approximately 30-mm in depth. The pavement surface was scraped and brushed across each sampled cross section to ensure that all residual material down to the pavement surface was collected.

Physical analyses of particulate residuals

Measurement of particle size gradations and specific gravity are important from a management and treatment perspective. Physical processes such as advective transport, sedimentation, filtration, sweeping and re-entrainment of particles are influenced by particle size, gradation and specific gravity ($\rho_{sg}$). Many design procedures for physical unit operations, such as the design of sedimentation basins or holding basins to settle particulate snow residuals, will utilize the concept of minimum trapping efficiency based on a chosen design particle size and design surface overflow rate theory (Malcom 1989). However, designers of drainage systems,
sedimentation basins, water quality basins or filters rarely have access to particle gradations and specific gravity as a function of particle diameter.

**Particle gradations**

The determination of the particle size gradation for residuals was performed according to ASTM D421 for the sample preparation (with the exception of air drying) and ASTM D422 for the sieve analysis (ASTM 1990; ASTM 1993) for sampling time on 08 February at 24:00. All samples were oven dried at 60°C. The set of sieves encompassed the 4750-µm (#4) through the 25-µm (#500) sieves. Dry residuals separated on each of the stainless steel sieves was weighted and stored separately in petri dishes or polypropylene bottles depending on the volume of residual remaining on each sieve. A mass balance was computed for each particle size gradation from each site. All computed mass balances were determined to be within 2% of the initial mass. Typically, a hydrometer analysis would be performed for particles less than 75-µm (ASTM 1993). However, for sample recovery, SSA determination, \( \rho_{sg} \) determination and heavy metal composition analysis, mechanical sieve analysis proved the best protocol. Across each size gradation, residuals were separated into 17 size classes. Each size class for each site was stored separately so that all analyses could be performed across each gradation for these 17 increments.

From the particle size analysis, semi-logarithmic plots of percent finer by weight as a function of particle size can be constructed to yield large and small diameter particles of nearly equal weight (Bowles 1992). The effective size \( (d_{10}) \) of each gradation was determined from each of the resulting size gradations. This effective size is defined as the size at which ten percent of the material is finer by weight. From each gradation result, a \( d_{60} \), \( d_{50} \) and \( d_{30} \) were
interpolated, and a uniformity coefficient \( C_u \) and coefficient of concavity \( C_c \) were calculated. The \( C_u \) is defined as:

\[
C_u = \frac{d_{60}}{d_{10}} \tag{2}
\]

The uniformity coefficient provides an indication of the spread of particle sizes. A large value of \( C_u \) indicates that the \( d_{10} \) and \( d_{60} \) particles differ significantly. The coefficient of concavity is a measure of the shape of the gradation curve between the \( d_{60} \) and \( d_{10} \) particle sizes and is defined as:

\[
C_c = \frac{d_{30}^2}{d_{10} d_{60}} \tag{3}
\]

If \( C_c \) varies greatly from 1.0, particle sizes between \( d_{60} \) and \( d_{10} \) are missing (Das 1992). Visual observation of each particle size range indicated that solids retained on the #200 sieve and particles larger than 75-µm were inorganic material with a variable organic coating or asphaltic binder. Particles passing the #200 sieve appeared increasingly organic. Organic content of the minus-200 material may be approximated by the ratio of VSS to TSS mass (Sansalone et al. 1998).

**Specific gravity \( (\rho_{sg}) \)**

Measurement of particle specific gravity was carried out using an inert gas pycnometer. The measurement of specific gravity followed ASTM D 5550 – 94 (ASTM 1994). The gas utilized in this procedure was ultra-high pure (UHP) He. He gas was chosen for inertness and its ability to enter pore space approaching 1 angstrom \( (10^{-10}\text{-m}) \) in diameter. An inert gas pycnometer determines the true density of particles through measurement of the pressure difference when a known volume of He gas is introduced into a test cell of known volume and dry mass of solids. The basis for the procedure is the ideal gas equation. The gas pycnometer
procedure was selected in lieu of the more common liquid pycnometer procedure (Blake and Hartge 1996). First, sufficient material in the finer particle sizes was not available to utilize the liquid pycnometer technique. Secondly, because of the sorbed surface constituents such as metal elements, the liquid pycnometer procedure was potentially a destructive procedure with respect to analysis of surface constituents because of solid-solute partitioning in the liquid pycnometer.

A sufficient mass of sample from each particle size was obtained to provide three separate and independent sub-sample specific gravity measurements. This material was dried at 60°C before cooling in a dessicator and measuring dry solid mass. Individual sub-samples from the 9500-µm through 2000-µm particle sizes utilized 17 - 19 dry grams of particles and a 25.644-cm³ test cell. Sub-samples from the 1400-µm through pan particle sizes utilized 3 -5 dry grams of particles and a 12.561-cm³ test cell. Ambient laboratory temperature was held constant between 21 - 23°C. Triplicate aliquots were analyzed from each sample.

Specific surface area (SSA) and total surface area (SA)

The SA through the measurement of SSA provides, in part, a measure or index of the capacity of a particulate surface to adsorb aqueous heavy metals. The ethylene glycol monoethyl ether (EGME) method (Schwertmann and Cornell 1991) that did not require heating of the sample above 60°C was modified and utilized for experimental determination of SSA. More common methods such as the N₂-BET isotherm method require drying at 150°C, thus modifying the structure and SSA of many solids, and also volatilizing any organic coatings or surfaces of residuals resulting in a less accurate determination of SSA.

The EGME method determines the amount of EGME (HOCH₂CH₂OCH₂CH₃), a polar liquid with a relatively high vapor pressure adsorbed at a constant vapor pressure, by measuring the increase in sample weight due to the adsorbed monolayer of EGME. A representative sample
of 0.5 to 2.0 grams dry weight was selected for each discrete size range. Each sample was placed in a small glass petri dish for drying and EGME addition. All discrete size range samples from a single gradation were first dried to a constant weight at 60°C and then dried in an evacuated dessicator over phosphorus pentoxide, P₂O₅. Once a constant dry weight was obtained, each solid sample was saturated with EGME, completely wetting all particle surfaces, and placed in an evacuated glass dessicator over 600 grams of an EGME-CaCl₂ solvate. A constant vapor pressure was produced from this solvate. The EGME to CaCl₂ ratio was 1.5:1. Samples were held in an evacuated dessicator and weighted in four to eight hour intervals until a constant weight for each sample was obtained as determined by a weight differential of less than 1-mg across an interval of at least four hours. Each event generated 15 discrete size samples which were placed in the same dessicator with control samples. Each dessicator of 18 samples, including standards, required from 30 to 60 hours of drying time to produce monolayer coverage.

One EGME molecule has a cross section coverage of 0.52-nm² and a gram molecular weight of 90.12 grams per mole. Therefore, an EGME monolayer of 1-m² consists of 0.286-mg of EGME. Carter et al. (1986) present a thorough discussion of the EGME method along with a standard procedure. This method was modified to measure SSA of sieved solids of specific size increments in batches of 15 samples plus control samples per dessicator. Based on monolayer surface coverage and molecular weight of the EGME molecule, SSA was calculated according to the expression:

$$ SSA = \frac{W_a}{(0.000286)W_s} $$

where:

- SSA = specific surface area (m²/g)
- W_a = measured weight of EGME retained by sample (g)
- W_s = measured weight of dried sample (g)
Three materials of known SSA served as the control for the EGME method. These materials were research-grade kaolinite, research-grade hectorite and granular activated carbon, GAC. The research-grade kaolinite and hectorite have reported SSA values of 39.5 m$^2$/g and 461.5 m$^2$/g, respectively (Carter et al. 1965). The GAC was a Filtersorb F400 with a reported SSA of 1000 - 1100 m$^2$/g by the N$_2$-BET method (Calgon 1995).

Because of the gradation of particle sizes and SSA variation, a measure of total surface area was needed. SSA results were summed over each particle size distribution (PSD) to yield a SA distribution as a function of particle diameter using the following formulation for each particle diameter range,

$$\text{SA}_i = (m_i)(\text{SSA}_i)$$

where:

- $\text{SA}_i$ = surface area of solids having particle diameter $i$ (m$^2$)
- $m_i$ = mass of solids having particle diameter $i$ (g)
- $\text{SSA}_i$ = specific surface area of solids having particle diameter $i$ (m$^2$/g)

From these analytical results, residual mass retained, SSA and SA for each increment were determined, and these incremental results were summed across the gradation to yield a cumulative gradation of dry particle weight, SSA and SA as a function of particle size gradation.

**Chemical analyses of particulate residuals**

Chemical analyses focused on determination of heavy metal content for particulate residuals. Heavy metal analyses were conducted on each separate particle size increment. From each separate particle size increment, a representative portion, approximately 0.5 to 1-g of dry particulate matter, was measured to $\pm$ 0.1-mg and digested. Dry particulate matter samples were acid-digested (9.0-mL of trace-metal HNO$_3$ and 1.0-mL of trace-metal HF) using a microwave-assisted procedure based on SW-846 Method 3015 (USEPA 1990). Once digested and filtered,
aqueous heavy metal analyses, conducted on a Perkin-Elmer Optima 3000 Inductively Coupled Plasma Spectrometer (ICP), included scans for Na, Mg, Al, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb. The ICP concentration results were converted from µg/L to µg/g based on acid-digested volume dilutions and the measured dry particle mass digested. Heavy metal concentration results in terms of µg/g were converted to total metal element mass using:

\[ M_{ei} = (m_i)(c_i) \]  

(6)

where: \( M_{ei} \) = mass of the heavy metal associated with particulate matter having particle diameter \( i \) (g); \( m_i \) = dry mass of particulate matter solids having particle diameter \( i \) (g); and \( c_i \) = representative concentration of particulate-bound heavy metal for particle diameter \( i \) (µg/g).

From these analytical results, heavy metal mass (Pb, Cu, Cd and Zn) for each increment was determined, and these incremental results were summed across the gradation to yield a cumulative gradation of heavy metal mass as a function of particle size gradation.

**Results**

**Particle size distributions**

For each of the sites, residual particle size distributions are plotted in Figure 6.1. These results indicate that for each site there is a wide gradation of particulate material deposited from the highway snow bank. This gradation ranges from gravel size particles approaching 5000-µm to particles less than 25-µm. Particles smaller than 25-µm contribute little to the overall gradation, gravimetrically. However, their contribution in terms of particle counts, although not measured, would indicate the highest particle counts would be in the 5-µm to 1-µm range (Sansalone et al. 1998). Differences in gradations are a function of traffic, type of pavement, age of pavement, wind patterns, slopes and drainage. For example, the sites of 1SE and 1SW are paired sites where 1SE is located on the downslope shoulder and 1SW is located on the upslope...
Figure 6.1. Particle size distributions for snow event roadway residual solids for sampling time February 8 at 12:00 am (Time 0 = 6:00 am on 4 February 1998; start of snow accumulation).
The influence of slope and drainage can be discerned from these paired sites. Slope and snowmelt drainage results in larger particulate matter residuals transported and trapped in the downstream snowbank, site 1SE. In fact, site 1SE gradation remains coarser through much of the gradation, in particular for the d_{30} and larger sizes as compared to site 1SW.

From these gradations, distribution indices were determined. These indices are summarized in Table 6.2. The mean d_{50} for all the sites was 1225-\mu m with a standard deviation of 587-\mu m. While the relative standard deviation (RSD) was large (48.0%), all d_{50} values fell in the medium to coarse sand range of particle sizes. These particles are relatively easy to remove in grit separation processes. When comparing all sites, it should be noted that the standard deviations and RSDs consistently decreased when going from the d_{60} to d_{10}. While C_u values ranged from 6.5 to 36.2 indicating a fairly wide range of uniformities, C_c values were only slightly greater than 1 for two of the ten sites.

**Residual mass retained**

Figures 6.2 through 6.11 illustrate the incremental dry mass of particles for a given particle diameter on an incremental and cumulative basis. For all sites, the very coarse fraction (>1000-\mu m) dominates the total dry mass. In all cases, the gradient of cumulative dry mass decreases as a function of decreasing particle diameter. Such results would be expected for particulate residual matter consisting of such a wide gradation.

**SSA and total SA**

Figures 6.2 through 6.11 illustrate the incremental SSA and total SA for particles as a function of particle diameter on an incremental and cumulative basis. The SSA results indicate that while SSA generally increases with decreasing particle size, the increase is not consistent and monotonic as would be expected for spherical particles. Additionally, the actual measured
Table 6.2. Particle size distribution and particle analysis indices.

<table>
<thead>
<tr>
<th>Event measured</th>
<th>d_{60} (μm)</th>
<th>d_{50} (μm)</th>
<th>d_{30} (μm)</th>
<th>d_{10} (μm)</th>
<th>C_u</th>
<th>C_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1SE</td>
<td>4000</td>
<td>1850</td>
<td>450</td>
<td>150</td>
<td>26.7</td>
<td>0.34</td>
</tr>
<tr>
<td>1SW</td>
<td>1800</td>
<td>1000</td>
<td>420</td>
<td>140</td>
<td>12.9</td>
<td>0.70</td>
</tr>
<tr>
<td>2ES</td>
<td>2100</td>
<td>1100</td>
<td>320</td>
<td>58</td>
<td>36.2</td>
<td>0.84</td>
</tr>
<tr>
<td>3SW</td>
<td>1700</td>
<td>850</td>
<td>350</td>
<td>120</td>
<td>14.2</td>
<td>0.60</td>
</tr>
<tr>
<td>4NE</td>
<td>3800</td>
<td>2300</td>
<td>750</td>
<td>170</td>
<td>22.4</td>
<td>0.87</td>
</tr>
<tr>
<td>5NE</td>
<td>1100</td>
<td>750</td>
<td>420</td>
<td>170</td>
<td>6.5</td>
<td>0.94</td>
</tr>
<tr>
<td>6SW</td>
<td>2950</td>
<td>1850</td>
<td>600</td>
<td>220</td>
<td>13.4</td>
<td>0.55</td>
</tr>
<tr>
<td>7SW</td>
<td>1000</td>
<td>700</td>
<td>360</td>
<td>120</td>
<td>8.3</td>
<td>1.08</td>
</tr>
<tr>
<td>8SW</td>
<td>1800</td>
<td>1300</td>
<td>600</td>
<td>170</td>
<td>10.6</td>
<td>1.18</td>
</tr>
<tr>
<td>9NE</td>
<td>900</td>
<td>550</td>
<td>220</td>
<td>92</td>
<td>9.8</td>
<td>0.58</td>
</tr>
<tr>
<td>All events mean</td>
<td>2115</td>
<td>1225</td>
<td>449</td>
<td>141</td>
<td>16.1</td>
<td>0.77</td>
</tr>
<tr>
<td>All events median</td>
<td>1800</td>
<td>1050</td>
<td>420</td>
<td>145</td>
<td>13.1</td>
<td>0.77</td>
</tr>
<tr>
<td>All events SD</td>
<td>1116</td>
<td>587</td>
<td>158</td>
<td>46.0</td>
<td>9.4</td>
<td>0.26</td>
</tr>
<tr>
<td>All events RSD (%)</td>
<td>52.8</td>
<td>48.0</td>
<td>35.2</td>
<td>32.6</td>
<td>58.6</td>
<td>33.8</td>
</tr>
</tbody>
</table>
Figure 6.2. Urban snow residual characteristics for site 1SE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.3. Urban snow residual characteristics for site 1SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.4. Urban snow residual characteristics for site 2ES. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.5. Urban snow residual characteristics for site 3SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.6. Urban snow residual characteristics for site 4NE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.7. Urban snow residual characteristics for site 5NE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.8. Urban snow residual characteristics for site 6SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.9. Urban snow residual characteristics for site 7SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.

Dry mass = 1076.95 g
Mass recovery = 99.6%
Figure 6.10. Urban snow residual characteristics for site 8SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
Figure 6.11. Urban snow residual characteristics for site 9NE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100% scale.
SSA values are approximately three orders of magnitude higher than SSA values calculated based on solid spherical particles of constant specific gravity. In contrast to SSA, the cumulative SA values indicate that the predominance of SA is associated with the coarse size fraction of the gradation, that fraction greater than 500-µm. While the gradation of SSA generally increased with decreasing particle diameter for all sites, the gradation of SA illustrated a corresponding decrease with decreasing particle diameter.

**Specific gravity (\(\rho_{sg}\))**

Design of urban storm water settling basins (snow melt basins or clarifiers) rarely account for the wide gradation of particulate matter when considering treatment. Many current regulations are based on a removal efficiency of a particular design particle for a given design event, for example, a 70% mass removal efficiency of the 40-µm design particle across a 2-year design storm (Malcom 1989). There are few design procedures in place to account for a wide particulate gradation but even less that account for variations in specific gravity across a gradation. For example, with specific gravity, it is generally assumed that particulate specific gravity is constant across a gradation with a value of 2.6 or 2.65 typically. Figures 6.2 through 6.11 illustrate the incremental particle density (\(\rho_s\)) as a function of particle diameter. Results are plotted as the mean of three replicate measurements. Because of the precision of the technique, error bars were generally contained within the width of the data points and therefore not shown. While \(\rho_s\) values range from 3.2 to 2.5 g/cm\(^3\) (\(\rho_{sg}\) of 3.2 to 2.5 with a \(\rho_l\) of 1.0) across the gradation below 100-µm, there is a fairly clear trend towards lower \(\rho_s\) values with decreasing particle diameter.
Heavy metal (Pb, Cu, Cd and Zn) mass distributions

After 102 hours, a very large percentage of the heavy metal mass was associated with the particulate matter, and the dissolved fractions of heavy metals were minimal. Although each site was loaded by heavy metals and solids differently as a function of primary variables such as traffic, one of the study goals was to evaluate the gradation of heavy metal mass as a function of particle diameter, both incrementally and on a cumulative basis as illustrated in the right-hand side plots in Figure 6.2 through 6.11. The plots illustrate several general trends. First, for all metals for all sites, while variability in the mass distributions across each gradation does exist, results indicate that the predominance of heavy metal mass is associated with the coarse fraction of particles. In addition, the heavy metal mass trends more closely follow the total SA profile trends with the exception of Zn for a number of sites.

The purpose for the form of these plots is two-fold. First, the cumulative heavy metal mass profiles allow one to examine the trends across the gradation for cumulative residual mass, SSA and SA with respect to heavy metal trends. These cumulative profiles indicate that while SSA plays a role in partitioned heavy metal mass as indicated by Equation 5, cumulative heavy metal mass trends more closely follow those of residual mass and SA. Secondly, cumulative heavy metal mass profiles as a function of particle diameter permit decision-making for residual management strategies. For example, if a settling basin design is used for clarification of residuals from melted snow, one could determine the heavy metal mass removal fraction based on the choice of effective settling of a design particle or a variable settling efficiency across the entire gradation.
Conclusions

This study focused on the physical and chemical characteristics of urban snow residuals from ten highway sites in urban Cincinnati. These residuals were collected from the paved highway shoulder from each site after the highway snow banks that collected this particulate residual matter from exposure to traffic activities dissipated 102 hours after the start of snowfall. Both the physical and chemical characteristics presented herein facilitate decision-making with respect to management strategies, regulations, treatment and potential disposal of these residuals. Despite a wide variation in site characteristics and a spatial separation as great as 27-km between sites, there are a number of conclusions that hold for all sites, with exceptions noted.

For all sites, the predominance of cumulative residual mass is associated with the very coarse fraction of residual particles, on average those particles larger than 1000-µm. Therefore if treatment efficiency were based on mass, unit operations such as grit separation or management strategies would focus on these particles first. A wide gradation of particulate residuals exists for all sites and ranged from greater than 5000-µm to less than 25-µm.

For all sites, incremental SSA results increase with decreasing particle diameter. While this trend is not monotonically increasing as would be expected for spherical particles and with some variability in the data, the incremental trend of increasing SSA with decreasing particle diameter is consistent for all sites. Also, the overall range of SSA values typically remain within an order of magnitude between 5 - 50 m²/g for all sites. This range is approximately three order of magnitude greater than SSA values calculated based on the assumptions of solid, spherical particles of constant specific gravity. For all sites, and in contrast to incremental SSA values, incremental total SA values decreased with decreasing particle diameter. Incremental total SA values closely followed those of incremental residual mass retained for each site. These results
are similar to results for storm water particles transported during rainfall runoff events, where SSA and SA demonstrated the same trends as reported herein (Sansalone et al. 1998).

Incremental measurement of $\rho_{sg}$ demonstrated that in general, there is a decrease in $\rho_{sg}$ with decreasing particle diameter, although a number of sites illustrate variability in this trend above 100-µm. Below 100-µm, a consistently decreasing gradation of $\rho_s$ is observed. Values of $\rho_{sg}$ range from 3.2 to 2.5 illustrating the inorganic and organic variability of the particulate residuals. In general, the higher $\rho_{sg}$ values are associated with the larger particles indicating their mainly inorganic content, and the lower $\rho_{sg}$ values are associated with smaller particles indicating a trend toward a higher relative organic content. It is expected that if enough particulate material less than 15-µm was recovered and separated for pycnometry analysis, $\rho_{sg}$ results would demonstrate a continued decline to less than 2.0 reflecting the influence of abraded tire material with a mean diameter of 15-µm and a $\rho_{sg}$ of 1.6 to 1.7 (Sansalone and Tribouillard 1999).

Results of cumulative heavy metal mass trends across the particle size gradations for each site indicate that the predominance of heavy metal mass is associated with the coarse size particle fraction (>250-µm). This trend is similar to that for residual mass retained and total SA where the predominance of both are associated with the coarse fraction of particles. These general trends are consistent for all sites, and while both the residual particulate mass and heavy metal mass may vary from site to site, the trends are consistent and similar despite a physical separation of up to 27-km across urban Cincinnati and a wide range of conditions such as traffic levels, drainage area, pavement slopes, pavement type and localized wind patterns. Heavy metal mass trend results as a function of particle diameter provide information in the decision-making process for residual treatment, management strategies, regulations and disposal.


Chapter 7  
Gradation-Based Characteristics of Anthropogenic Transportation Land Use Soil/residual Complexes Loaded by Snowmelt and Rainfall Runoff – Part I

Anthropogenic residual material from the highway directly influences soil matter located in the transportation corridor right-of-way, in particular, near the edge of the paved shoulder. This particulate matter ranging from silt to gravel size material can be dry deposited in the highway right-of-way or transported in storm water runoff, snowmelt or entrained in highway snowbanks. Traffic activity contaminants are generated from vehicular component wear, pavement degradation, maintenance, spillage and littering (Sansalone et al. 1998). A primary source of particulate matter is vehicular-infrastructure abrasion, including tire-pavement interaction. Abraded pavement accounts for 45% and abraded tires account for 25% of the total particulate mass while deposition from urban atmospheric sources generated outside the right-of-way accounts for less than 3% of the total particulate mass that is dry deposited (Kobriger and Geinopolos 1984). Because of an increase in urbanization and hence vehicular traffic, urban rainfall runoff and snow transport increasing levels of anthropogenic particulate and heavy metal loadings. Transportation land use surficial soils in the urban environment serve as an interface between the subsurface, surface water and the atmosphere.

Transportation land use storm water levels of Zn, Cu, Cd, Pb, Cr and Ni are significantly above ambient background levels, and for many heavily traveled roadways, Zn, Cu, Pb and Cd often exceed USEPA and State EPA surface water discharge criteria (Sansalone and Buchberger 1997). These heavy metals are also present in snowmelt. Snowmelt levels for these metals and suspended solid materials can be several orders of magnitude higher (Sansalone and Buchberger 1996; Glenn and Sansalone 2002). Runoff (as either storm water or snowmelt) from transportation and urban land use is a complex physico-chemical heterogeneous mixture of
heavy metals, particulate matter, inorganic and organic compounds with variations in flow, concentrations and mass loadings.

Much of this particulate mass that is dry deposited on urban pavement surfaces by traffic before and during an event can be mobilized and exported from the urban surface (Sansalone et al. 1998). Highway snow has a residence time that can extend into days or even weeks. The exposed snow surface, typically plowed into a highway snowbank, is a porous and effective accumulator of particulate matter. Apart from peak concentrations of suspended solids during short intense street runoff from rain, concentrations of suspended solids in snowmelt runoff are 2 to 5-fold higher than in rain runoff (Daub et al. 1994). Snow is also capable of scavenging particle-bound, mutagenic organic pollutants from the atmosphere in an urban setting due to its size and velocity (White et al. 1995).

Winter maintenance activities that provide safer driving conditions in snow influence particulate mass characteristics. For instance, de-icing salts applied to roads as well as other chemical additives used to prevent the caking of such salt influence heavy metal and trace metal partitioning, concentration and mobility. Trace metal partitioning was most affected by temperature and NaCl than pH in the Don River, Canada. As temperature decreased, the accumulation of Cd, Cu and Zn in particulates decreased (Warren and Zimmerman 1994). Mobility of heavy metals depends on the chemical characteristics such as pH and ion composition of the soil (Bauske and Goetz 1993). De-icing salts also infiltrate the soil bordering the pavement, are carried to surficial groundwater, remain in the soil solution or become adsorbed by the soils. In Ontario, Canada, variations in salt inputs between different point sources and between streams were related to the length and type of road draining into the stream, to the amount of salt applied prior to thaw periods, to the rate of rise in temperature at the start of
a thaw and to the duration of temperatures above freezing (Scott 1981). Calcium magnesium acetate (CMA) is an alternative for deicing highways and is less toxic to aquatic life and less corrosive than Cl⁻ salts (Amrhein and Strong 1990; Fritzsche 1991). While NaCl adversely effects environment, the effect of CMA on trace metal mobility in roadside soils should be more beneficial.

Because snow plowed onto the highway shoulder is directly exposed to traffic and winter snow maintenance practices, constituents generated from such activities can result in significant accumulations. While the difficulties of storm water treatment are significant (Malcom 1989), options for snow treatment are even more challenging due to the inherent nature of the snow and high levels of pollutant accumulation. The constituents of snowmelt and rainfall runoff affect the transportation land use soil/residual complex (SRC). By understanding this complex, by means of surface complexation and mineralogy, treatment strategies can be formulated. Depending on the residual characteristic, these may include adsorption, filtration or remediation. A general lack of information exists when considering anthropogenic complexation characteristics of soil/residuals within the highway environment. From traffic to runoff, the soil/residual complex adjacent to the highway accumulates and exports these constituents. The accumulation and export of these constituents, such as heavy metals can have an adverse effect on the environment specifically the biota.

Objectives

Particulate solids present on the roadway flow with the hydrologic gradient toward the shoulder. Transportation land use soil/residual complexes are directly influenced by pavement surface drainage. However, the environment of the highway mainly traffic and winter maintenance activities such as de-icing salt contributes to the physical and chemical structure of
the soil. Compared to storm water runoff and urban roadway snow, soil/residual complexes exposed to this changing environment have a capacity to accumulate and retrain particulate and dissolved material and other anthropogenic constituents as well as heavy metals for further enrichment. By understanding the surface complexation of the soil/residual complex, this includes the mineralogical constituents and point of zero charge (PZC), a treatment strategy for the removal of the particulate and entrained heavy metals can be better implemented. The unsteady nature of the highway environment and water chemistry from both storm water and snowmelt must also be understood for an effective best management practice.

There are four major objectives of this study. These objectives were carried out for surficial soil/residual complexes recovered from each of the four urban highway main sites (1SW, 1SE, 2ES and 3SW) and a reference site. The first objective was to examine mass gradations between transportation land use soil/residual complexes and an urban reference site soil subject to only background atmospheric deposition. Granulometric characteristics of snow residuals were compared to soil/residual complexes for each site. The second objective was to characterize predominant mineral species across a gradation in soils at the reference site, soil/residual complexes from transportation land use sites, and snow residuals at these sites using X-ray diffraction analyses. Gradation-based trends in mineral mass composition at selected sites based on X-ray diffraction results were examined and compared to the reference site, snow residual and surficial soil/residual complex compositions. The third objective was to examine and compare gradation-based trends in surface charge density between the reference site, snow residual and surficial soil/residual complexes. The fourth objective was to examine and compare gradation-based trends in acid-base titration between reference site, snow residual and surficial soil/residual complex.
Methodology

Experimental sites

For this study, four primary highway sites were selected for soil sampling from a total of ten highway sites located within the metropolitan area of Greater Cincinnati (Hamilton County). All were sampled for highway soil/residual complexes. An additional collection for site 1SE included snow residuals collected for an entire winter season. A 4.0-L sample of snow (a rectangular area cut vertically out of the snowbank) was obtained from the leading edge of the snowbank exposed to traffic. Further information concerning this snow site is presented elsewhere (Sansalone and Glenn 2002; Glenn and Sansalone 2002).

Site 1SE and 1SW were located on Inter State 75 (I-75), a major north-south freeway between Michigan and Florida. Site 2ES was located on U.S. Route 126, 1-km east of I-75. An additional site utilized as a reference site was located in a residential area of urban Cincinnati. Soil at the reference site had no direct exposure to highway or residential roadway traffic activity and had similar soil structure to highway sites (Soil 1982). For each designation, the first number identifies the number of a particular site location, the first letter indicates the direction of traffic and the final letter indicates which side of the highway the samples were obtained. A description and location of all soil and snow residual sampling sites is provided in Table 7.1. For all sites, drainage from the pavement was in the form of lateral pavement sheet flow ($q_{psf}$) towards the back of the pavement shoulder were the soil was collected.

The reference site was chosen for several reasons. First and foremost, it had no direct exposure to the highway, traffic and winter maintenance activities such as de-icing as did all ten soil/residual sites. Second, the urban soil and areas of the highway sites were of the same parent soil and primary USCS classification of CL (sandy lean clay). The four main land transportation
Table 7.1. Description and location of urban highway soil/residual and snow residual sampling sites and reference site for metropolitan Cincinnati study.

<table>
<thead>
<tr>
<th>Site</th>
<th>Highway</th>
<th>Mile Marker</th>
<th>Sampling Area</th>
<th>Drainage Area for qsf</th>
<th>qsf Area (m²/m)</th>
<th>Roadway Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>1SW</td>
<td>I-75 S</td>
<td>2.58S</td>
<td>LS (W) shoulder</td>
<td>no qsf</td>
<td>0</td>
<td>4 lanes (A)</td>
</tr>
<tr>
<td>1SE</td>
<td>I-75 S</td>
<td>2.60S</td>
<td>HS (E) shoulder</td>
<td>4 lanes + 1.5</td>
<td>20</td>
<td>4 lanes (A)</td>
</tr>
<tr>
<td>2ES</td>
<td>126 E</td>
<td>11.1E</td>
<td>LS (S) shoulder</td>
<td>1 lane + 1</td>
<td>5.5</td>
<td>2 lanes (PCC)</td>
</tr>
<tr>
<td>3SW</td>
<td>I-75 S</td>
<td>5.90S</td>
<td>LS (W) shoulder</td>
<td>1 lane + 1</td>
<td>5.5</td>
<td>3 lanes (A)</td>
</tr>
<tr>
<td>4NE</td>
<td>I-75 N</td>
<td>12.1N</td>
<td>LS bridge (E)</td>
<td>1 lane + 1</td>
<td>5.5</td>
<td>3 lanes (PCC)</td>
</tr>
<tr>
<td>5NE</td>
<td>I-75 N</td>
<td>16.1N</td>
<td>LS (E) shoulder</td>
<td>2 lanes + 1</td>
<td>9.1</td>
<td>4 lanes (A)</td>
</tr>
<tr>
<td>6SW</td>
<td>I-75 S</td>
<td>16.0S</td>
<td>LS (W) shoulder</td>
<td>1.5 lanes + 1</td>
<td>7.3</td>
<td>3 lanes (A)</td>
</tr>
<tr>
<td>7SW</td>
<td>I-75 S</td>
<td>11.9S</td>
<td>LS (W) shoulder</td>
<td>2 lanes + 1</td>
<td>9.1</td>
<td>4 lanes (A)</td>
</tr>
<tr>
<td>8SW</td>
<td>I-75 S</td>
<td>0.90S</td>
<td>LS (W) shoulder</td>
<td>2 lanes + 1</td>
<td>9.1</td>
<td>4 lanes (A)</td>
</tr>
<tr>
<td>9NE</td>
<td>I-75 N</td>
<td>1.70N</td>
<td>LS (E) shoulder</td>
<td>no qsf</td>
<td>0</td>
<td>4 lanes (A)</td>
</tr>
</tbody>
</table>

Reference: Historically urban residential land use. No highway exposure.

(A) : Asphalt
(PCC) : Portland cement concrete
N : north
S : south
E : east
W : west
qsf : lateral pavement sheet flow
LS : low speed
HS : high speed
sites and reference site were also silt loam (Soil 1982). Similarities do exist between the study sites and the reference site to the extent of soil type not to direct pollutant contamination. All sites received the same atmospheric deposition over time.

**Soil sampling**

Each of the ten sites was sampled on 05 August 2000 to obtain an approximate minimum dry mass (2000 g) of residual material. A stainless steel surficial soil sampler was used to sample the soil/residual material at a depth of 0 to 5 cm, within 1-m from the back (outside edge) of the paved highway shoulder. The samples were placed in a polyethylene container, sealed and marked. The sampler was cleaned with denatured alcohol before use at each site. The grass turf layer from the reference site was removed prior to sampling the surficial clayey glacial till soil immediately below. Samples were carried back to the laboratory, dried and stored in a 40°C (35% humidity) room for further analyses. The snow residuals were collected from the roadway before coming into contact with soil/residuals.

**Particle size distribution (PSD)**

Measurement of particle size gradations and specific gravity are important from a management and treatment perspective. Physical processes such as advective transport, sedimentation, filtration, sweeping and re-entrainment of particles are influenced by particle size, gradation and specific gravity ($\rho_s$). The determination of the particle size gradation for residuals was performed according to ASTM D421 for the sample preparation (with the exception of air drying) and ASTM D422 for the sieve analysis (ASTM 1990; ASTM 1993). The set of sieves encompassed the 9500-µm (#3/8 in) through the 25-µm (#500) sieves including sizes of 4750-µm (#4), 2000-µm (#10), 850-µm (#20), 600-µm (#30), 425-µm (#40), 300-µm (#50), 250-µm (#60), 180-µm (#80), 150-µm (#100), 106-µm (#140), 75-µm (#200), 63-µm (#230), 53-µm
(#270), 45-µm (#325) and 38-µm (#400). Dry residuals separated on each of the stainless steel sieves was weighted and stored separately in clear glass sampling jars depending on the volume of residual remaining on each sieve. A mass balance was computed for each particle size gradation from each site. All computed mass balances were determined to be within 2% of the initial mass. Across each size gradation, residuals were separated into 18 size classes. Each size class for each site was stored separately so that all analyses could be performed across each gradation for these 18 increments. A classification of size ranges included coarse (>425 µm), medium (425-75 µm) and fine (<75 µm).

From the particle size analysis, semi-logarithmic plots of percent finer by weight as a function of particle size can be constructed to yield large and small diameter particles of nearly equal weight (Bowles 1992). The effective size (d_{10}) of each gradation was determined from each of the resulting size gradations. This effective size is defined as the size at which ten percent of the material is finer by weight. From each gradation result, a d_{60}, d_{50} and d_{30} were interpolated, and a uniformity coefficient (C_u) and coefficient of concavity (C_c) were calculated. The C_u is defined as:

\[
C_u = \frac{d_{60}}{d_{10}}
\]  

(1)

The uniformity coefficient provides an indication of the spread of particle sizes. A large value of C_u indicates that the d_{10} and d_{60} particles differ significantly. The coefficient of concavity is a measure of the shape of the gradation curve between the d_{60} and the d_{10} particle sizes and is defined as:

\[
C_c = \frac{d_{30}^2}{d_{10}d_{60}}
\]  

(2)
If $C_c$ varies greatly from 1.0, particle sizes between $d_{60}$ and $d_{10}$ are missing (Das 1992). Visual observation of each particle size range indicated that solids retained on the #200 sieve or particles larger than 75-µm were inorganic material with a variable organic coating or asphaltic binder. Particles passing the #200 sieve appeared increasingly organic (Sansalone et al. 1998).

**Mineralogical analysis**

For the reference site, snow site (1SE), and soil/residual sites (1SE and 1SW), samples were separated and examined according to gradation. These particular sites were chosen for comparison due to their location. For example, sites 1SE and 1SW are paired sites where 1SE is located on the downslope shoulder subject to $q_{sf}$ and 1SW on the upslope shoulder not subject to $q_{sf}$. These sites should be representative of all ten-highway sites. The reference site was the control, and the snow residual sample offered a comparison to the soil/residual site at the same location of 1SE. Selected sizes of the gradations were analyzed. These included size ranges of 9500-4750 µm, 2000-850 µm, 600-425 µm, 300-250 µm, 180-150 µm, 106-75 µm, 63-53 µm and 45-38 µm. All samples were crushed and micronized to less than 5 µm.

A powder X-ray diffractometer (Siemens D5000 diffractometer) was employed in the present study on whole-soil subsamples. All the samples were carefully pressed into aluminum-glass holders before loading them. X-ray analysis was performed on randomly oriented samples using a kevex solid-state detector (Kevex Instruments, Valencia, CA) with Cu K$_{\alpha}$ radiation at 40 kV and 30 mA. The phenomenon of diffraction involves the scattering of x-rays by atoms of a crystal and the distance of separated atomic planes quantifies the subsequent reinforcement of these scattered rays. Diffraction can occur whenever Bragg’s law is satisfied, defined as,

$$n\lambda = 2d \sin \theta$$

(3)

where: $n\lambda$ = whole number of wavelengths
\[ d = \text{interplanar spacing} \]

\[ \theta = \text{angle of incidence of the primary radiation with crystal planes.} \]

A succession of equally spaced lattice planes results in a maximum diffraction with sufficient intensity to be recorded. The angles at which diffraction occurs will be unique for a particular mineral since no two minerals have exactly the same interatomic distances in three dimensions (Whittig and Allardice 1986).

Siemens Diffrac AT V3.1 was used to run the diffractometer. The XRD profiles were interpreted by MacDiff 4.0.0 using the ICDD (International Centre for Diffraction Data) powder diffraction file. Quantification by percent weight of minerals present in the soil samples was carried out by the program x-ray diffraction data analysis (XRDFIL). This program was written by Tai H. Le and sponsored by Ray E. Ferrell, Jr. at Louisiana State University. The Equation takes into account the total counts of a mineral divided by the sum of other peaks present utilizing the major intensity peak of quartz due to its stable crystal lattice. This was done for all minerals present for each gradation and site.

Potentiometric titration

Surface charge

The standard potentiometric titration method (Van Raij and Peech 1972) was modified to determine the surface charge of sediments across each size gradation for main four sites, snow residual (1SE) and reference site. A representative 0.5 to 1-g of dry sample (except for the coarse materials from which a representative materials were selected irrespective of weight limit) was suspended in 50-ml of 0.01-M KCl, and the pH was adjusted to a range between 6 and 10 with either HCl or KOH. The samples, blank (solution of 0.01-M KCl) and control (bentonite)
were set on a reciprocating table at 22 to 23°C in sealed airtight 50-ml centrifuge tubes for 24 hours. All samples were analyzed in triplicate.

After samples were allowed to settle overnight, pH was recorded from an aliquot of supernatant (25 ml) from each centrifuge tube. The amount of H⁺ and OH⁻ adsorbed by the sediment samples was estimated from the amount of acid or base (0.005-M HCl or KOH) necessary to bring the sample to the original pH, minus the amount necessary to bring 50-ml blank solution to the same pH. Taking into account the original soil mass, volume of centrifuge tube and volume of aliquot, surface charge was estimate in µmol/g. For each site, the mean and standard deviation for each gradation (or particle diameter) and original pH (6 to 10) were divided by the specific surface area (SSA; m²/g) having that particle diameter to calculate surface charge density (surface site density) in µmol/m². Surface site density can also be expressed in terms of sites/nm² using the following Equation (Langmuir 1997):

\[
N_S (\text{sites / nm}^2) = \Gamma_{\text{XOH}} \left(\text{µmol / m}^2\right) \times N_A \left(\text{sites / mol sites}\right) \times 10^{-24} \left(\frac{m^2}{nm^2} \times \frac{\text{mol}}{\mu\text{mol}}\right) \quad (4)
\]

\[
= \Gamma_{\text{XOH}} \left(\text{µmol / m}^2\right) \times 0.6022 \left(\frac{\text{sites}}{nm^2} \times \frac{m^2}{\mu\text{mol}}\right) \quad (5)
\]

where \(N_S\) is surface site density (sites/nm²), \(\Gamma_{\text{XOH}}\) is the surface site density (µmol/m²), and \(N_A\) is Avogadro’s number (6.022×10²³ sites/mole sites).

**Acid-base titration**

For the reference site, snow site (1SE), and soil/residual site (1SE), samples were separated and examined for specific sizes of the gradation. Only 3 of the 18 gradation ranges were analyzed due the similarity of anthropogenic soil/residuals between the ten highway sites. This included size ranges of 600-425 µm (coarse), 180-150 µm (medium) and 45-38 µm (fine).
These particular ranges represented one third of the gradations studied as significant differences were not expected between adjacent gradations. In addition, sufficient material was available in each of these sizes to conduct the analyses.

Acid-base titrations were performed using previously published methods (Dzombak and Morel 1990). For each gradation, a representative 0.50-g of dry sample was suspended in 100-ml of 0.01-M NaNO₃ along with a blank (solution of 0.01-M NaNO₃) and allowed to equilibrate overnight. Samples were placed for the duration of the experiment on a reciprocating table at 22 to 23°C in sealed 125-ml Erlenmeyer flasks with an inert headspace atmosphere of N₂. After equilibration, pH was measured and this pH represented initial pH at time 0. Blanks were adjusted (0.01-M HCl or KOH) to either a pH of 7 for the reference site or 9 for both the snow and soil residuals at site 1SE. All samples were analyzed in triplicate.

Samples were then monitored approximately every 3 hours for change in pH as 0.01-M HCl or KOH was added at predetermined increments (ml converted mM). The experiment ended when the pH reached either 3 or 10.5.

Results

Particle size distributions

For each of the sites (soil and snow residuals), particle size distributions are plotted in Figure 7.1. These results indicate that for each site there is a wide gradation of particulate material transported from the pavement, and in the case of the snow residual, deposition occurred within the snowbank. This gradation ranges from gravel size particles approaching 10,000-µm (5000-µm for snow residual) to particles less than 25-µm for soil/residual complex. Particles smaller than 25-µm contribute little to the overall gradation, gravimetrically. However, their contribution in terms of particle counts, although not measured, would indicate the highest
Figure 7.1. Particle size distributions for soil/residual complex (0 to 5 cm) and snow event roadway residual solids at each experimental site and reference site. Recoveries on a dry mass basis.
particle counts would be in the range of 1-µm to 5-µm (Sansalone et al. 1998). Differences in
gradations are a function of traffic, type of pavement, age of pavement, wind patterns, slopes and
drainage. For example, the sites of 1SE and 1SW are paired sites where 1SE is located on the
downslope shoulder (receiving q_{sf}) and 1SW is located on the upslope shoulder (not receiving
q_{sf}). The influence of slope and drainage can be discerned from these paired sites. Slope and
drainage from factors such as traffic, snowmelt and rainfall runoff result in larger particulate
matter residuals transported and trapped in the downstream snowbank, site 1SE. In fact, site 1SE
for snow residual gradation remains coarser through much of the gradation, in particular for the
d_{30} and larger sizes as compared to site 1SW. Although not as prominent for soil/residual
complexes at site 1SE, gradation remains coarser for d_{50} and larger sizes.

From both of these gradations, distribution indices were determined. These indices are
summarized in Table 7.2. The mean d_{50} for all the sites was 572-µm with a standard deviation of
491-µm for soil and 1225-µm with a standard deviation of 587-µm for snow residuals. While
the relative standard deviation (RSD) was large (85.8% for soil/residual complex and 48.0% for
snow residuals), all d_{50} values fell in the medium to coarse sand range of particle sizes with
exception of the reference site. When comparing all sites, it should be noted that the standard
deviations and RSDs consistently decreased from d_{60} to d_{10}. While C_{u} values ranged from 4.5 to
37.5 for soil/residual complex and 6.5 to 36.2 for snow residuals indicating a fairly wide range of
uniformities, C_{c} values were only slightly greater than 1 for both soil and snow residuals. For
soil/residual complex samples, a definite distinction between all sites could be seen in particular
between site 8SW and the reference site. In fact, the reference site subjected to only background
atmospheric deposition had d_{50} values below 145-µm, a C_{u} value of 2.5 and a C_{c} value of 1.06
suggesting a fine-grained clayey gradation.
Table 7.2. Particle size distribution and gradation indices for reference soil site, soil/residual complex sites (0 to 5-cm depth) and snow event roadway residual solids.

<table>
<thead>
<tr>
<th>Soil/residual site</th>
<th>$d_{60}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{30}$ (µm)</th>
<th>$d_{10}$ (µm)</th>
<th>$C_u$</th>
<th>$C_c$</th>
</tr>
</thead>
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<td>145</td>
<td>105</td>
<td>65</td>
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<tr>
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</tr>
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</tr>
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<td>250</td>
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<td>490</td>
<td>260</td>
<td>100</td>
<td>7.3</td>
<td>0.93</td>
</tr>
<tr>
<td>5NE</td>
<td>725</td>
<td>490</td>
<td>255</td>
<td>83</td>
<td>8.7</td>
<td>1.08</td>
</tr>
<tr>
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<td>675</td>
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<td>86</td>
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<td>1.45</td>
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<td>410</td>
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<td>72</td>
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<td>1.34</td>
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<td>2000</td>
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<td>120</td>
<td>37.5</td>
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<tr>
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<td>330</td>
<td>210</td>
<td>93</td>
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<td>1.13</td>
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<td>572</td>
<td>246</td>
<td>88</td>
<td>10</td>
<td>0.95</td>
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<td>725</td>
<td>490</td>
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<td>86</td>
<td>8</td>
<td>1.02</td>
</tr>
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<td>All events SD</td>
<td>1185</td>
<td>491</td>
<td>82</td>
<td>15</td>
<td>9</td>
<td>0.33</td>
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<tr>
<td>All events RSD (%)</td>
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<td>85.8</td>
<td>33.4</td>
<td>16.6</td>
<td>91.8</td>
<td>35.3</td>
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<table>
<thead>
<tr>
<th>Snow residual site</th>
<th>$d_{60}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{30}$ (µm)</th>
<th>$d_{10}$ (µm)</th>
<th>$C_u$</th>
<th>$C_c$</th>
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<tr>
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<td>4000</td>
<td>1850</td>
<td>450</td>
<td>150</td>
<td>26.7</td>
<td>0.34</td>
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<tr>
<td>2ES</td>
<td>2100</td>
<td>1100</td>
<td>320</td>
<td>58</td>
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<td>0.84</td>
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<tr>
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<td>850</td>
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<td>2300</td>
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<tr>
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<td>1100</td>
<td>750</td>
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<td>170</td>
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<td>0.94</td>
</tr>
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<td>2950</td>
<td>1850</td>
<td>600</td>
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<td>13.4</td>
<td>0.55</td>
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<td>700</td>
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<td>120</td>
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<td>1.08</td>
</tr>
<tr>
<td>8SW</td>
<td>1800</td>
<td>1300</td>
<td>600</td>
<td>170</td>
<td>10.6</td>
<td>1.18</td>
</tr>
<tr>
<td>9NE</td>
<td>900</td>
<td>550</td>
<td>220</td>
<td>92</td>
<td>9.8</td>
<td>0.58</td>
</tr>
<tr>
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<td>1225</td>
<td>449</td>
<td>141</td>
<td>16.1</td>
<td>0.77</td>
</tr>
<tr>
<td>All events median</td>
<td>1800</td>
<td>1050</td>
<td>420</td>
<td>145</td>
<td>13.1</td>
<td>0.77</td>
</tr>
<tr>
<td>All events SD</td>
<td>1116</td>
<td>587</td>
<td>158</td>
<td>46.0</td>
<td>9.4</td>
<td>0.26</td>
</tr>
<tr>
<td>All events RSD (%)</td>
<td>52.8</td>
<td>48.0</td>
<td>35.2</td>
<td>32.6</td>
<td>58.6</td>
<td>33.8</td>
</tr>
</tbody>
</table>

$d_x$: particle size at which $x\%$ of particle size gradation mass is finer (L)

$C_u$: coefficient of uniformity

$C_c$: coefficient of concavity

SD: standard deviation

RSD: relative standard deviation
According the Hamilton County soil survey (Soil 1982), the reference site had similar characteristics to the soil type described as RtB, a Rossmoyne-urban land complex. This particular complex is well drained with a surface layer that is a brown, friable silt loam about 15 cm thick on the Illinoian till plain. The primary USCS classifications is CL (sandy lean clay) with greater than 90% passing for sieve numbers above 40. The liquid limit is 30-40%, and plasticity index is 4-10. The characteristics of this urban land complex were different for the soil/residual site 2ES which was of the same complex.

The soil/residual sites of 1SW and 1SE although of a different urban land complex than 2ES were characteristically different in percentage passing sieve numbers by almost a quarter to half of what was expected. The soil type described is a UmB, a urban land-Martinsville complex that is gentle sloping, well drained with surface layer of dark grayish brown, friable silt loam about 23 cm thick. The liquid limit is 22-33%, and plasticity index is 4-12. The soil/residual site of 3SW was also characteristically different with a soil type described as BoE, a Bonnell silt loam that is well drained bordering stream valleys of the Illinoian till plain. The surface layer is very dark brown, friable silt loam about 10 cm thick. The difference in percentage passing sieve numbers was almost half of what was expected of sieves between 4 and 200. The liquid limit is 25-35%, and plasticity index is 4-12. The primary USCS classification for all of these sites is CL (sandy lean clay).

Mineralogical analysis

The X-ray diffraction patterns of the soil/residual complexes identified major clay and non-clay minerals within each site and identified mineralogical differences between gradations as shown through Figures 7.2 through 7.5. Each site had similar mineralogical constituents that either increased or decreased as particle size decreased from gravel to silt. The major minerals
Figure 7.2. X-ray diffractogram of reference site urban clayey glacial till soil at discrete particle sizes. Major diagnostic peaks are identified with mineral labels. Other peaks are additional reflections from the identified minerals. θ is diffraction angle.
Figure 7.3. X-ray diffractogram of site 1SE snowmelt particulate residuals at discrete particle sizes. Major diagnostic peaks are identified with mineral labels. Other peaks are additional reflections from the identified minerals. $\theta$ is diffraction angle.
Figure 7.4. X-ray diffractogram of site 1SE soil/residual complex (0 to 5 cm) at discrete particle sizes. Major diagnostic peaks are identified with mineral labels. Other peaks are additional reflections from the identified minerals. $\theta$ is diffraction angle.
Figure 7.5. X-ray diffractogram of site 1SW soil/residual complex (0 to 5 cm) at discrete particle sizes. Major diagnostic peaks are identified with mineral labels. Other peaks are additional reflections from the identified minerals. $\theta$ is diffraction angle.
as identified by peaks present with ICDD numbers in no general order, are as follows: quartz (SiO2; 33-1161); dolomite (CaMg(CO3)2; 36-0426); calcite (CaCO3; 05-0586); hornblende ((Ca,Na)2.26(Mg,Fe,Al)5.15(Si, Al)8O22(OH)2; 20-0481); pyrite (FeS2; 42-1340); clinochlore ((Mg,Fe)6(Si,Al)4O10(OH)8; 29-0701); biotite (K(Mg,Fe)3(Si3Al)O10(OH)2; 42-0603); anorthite ((Ca,Na)(Al,Si)2Si2O8; 20-0528); kaolinite (Al2Si2O5(OH)4; 29-1488); muscovite (KAl2(Si3Al)O10(OH,F)2; 06-0263); augite (Ca(Fe,Mg)Si2O6; 24-0201); and anhydrite (CaSO4; 37-1496). The differences between gradations and sites can be observed in these figures. For example, in the reference site, in contrast to the soil/residual complexes, hornblende and dolomite does not appear to be present, and calcite decreases after the coarse fraction (<600-425 µm). All sites are dominated by quartz, specifically the reference site. In the other three soil/residual complex sites, there is also a strong presence of calcite and dolomite.

Quantification by percent weight of minerals present in the soil samples was determined from size gradation (gravel, sand and silt) and mineral present as seen in Tables 7.3 through 7.6. Some minerals from above were grouped together for analysis due to their common characteristics, close wavelengths and program parameters. Specifically, plagioclase represents anorthite; k-feldspar represents a form closely linked to plagioclase; illite is general for micas representing both muscovite and biotite; chlorite represents clinochlore; and amphibole represents hornblende. As mentioned previously, the sites of 1SE and 1SW are paired sites where 1SE is located on the downslope and 1SW on the upslope shoulder. The influence of slope and drainage does not appear to be a factor for mineralogical differences. However, there is a difference in pyrite percent weight from 0.5 to 4.2% compared to the reference and snow site with a range of 0.2 to 2.0%. The sum of minerals across a gradation sometimes does not equal 100% showing real data and the variances in peak height and wavelength.
Table 7.3. Mass (%) mineral composition of reference clayey glacial till soil (0-5 cm depth) based on X-ray diffraction analyses of selected particle size ranges.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Gravel</th>
<th>Sand</th>
<th>Silt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7125</td>
<td>1425</td>
<td>513</td>
</tr>
<tr>
<td>Quartz</td>
<td>63.2</td>
<td>80.3</td>
<td>82.4</td>
</tr>
<tr>
<td>Calcite</td>
<td>13.0</td>
<td>2.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.5</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>1.6</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>1.5</td>
<td>2.3</td>
<td>3.8</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>2.8</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>7.2</td>
<td>4.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Illite</td>
<td>7.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.1</td>
<td>0.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Augite</td>
<td>2.9</td>
<td>2.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Amphibole</td>
<td>0.0</td>
<td>1.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Σ (%) 100.2 100.0 100.0 99.8 99.8 99.8 99.9 100.1

7125 µm : $d_{50i}$ for 9500-4750 µm size
1425 µm : $d_{50i}$ for 2000-850 µm size
513 µm : $d_{50i}$ for 600-425 µm size
275 µm : $d_{50i}$ for 300-250 µm size
165 µm : $d_{50i}$ for 180-150 µm size
91 µm : $d_{50i}$ for 106-75 µm size
58 µm : $d_{50i}$ for 63-53 µm size
42 µm : $d_{50i}$ for 45-38 µm size
Table 7.4. Mass (%) mineral composition of site 1SE snowmelt particulate residuals based on X-ray diffraction analyses of selected particle size ranges.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Gravel</th>
<th>Sand</th>
<th>Silt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7125</td>
<td>1425</td>
<td>513</td>
</tr>
<tr>
<td>Quartz</td>
<td>8.4</td>
<td>40.5</td>
<td>52.1</td>
</tr>
<tr>
<td>Calcite</td>
<td>24.7</td>
<td>14.5</td>
<td>14.4</td>
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<td>Dolomite</td>
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<td>1.2</td>
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<tr>
<td>Anhydrite</td>
<td>0.2</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>1.9</td>
<td>3.6</td>
<td>2.7</td>
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<tr>
<td>Plagioclase</td>
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<td>7.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Kaolinite</td>
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<td>4.2</td>
<td>0.1</td>
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<tr>
<td>Illite</td>
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<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Chlorite</td>
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<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.5</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Augite</td>
<td>4.6</td>
<td>4.1</td>
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</tr>
<tr>
<td>Amphibole</td>
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<td>2.1</td>
<td>1.2</td>
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</table>

Σ (%) 100.1 100.0 100.0 100.2 100.0 100.0 100.0 100.1

Median size ($d_{50}$) of selected particle size range (µm):
- 7125 µm: $d_{50}$ for 9500-4750 µm size
- 1425 µm: $d_{50}$ for 2000-850 µm size
- 513 µm: $d_{50}$ for 600-425 µm size
- 275 µm: $d_{50}$ for 300-250 µm size
- 165 µm: $d_{50}$ for 180-150 µm size
- 91 µm: $d_{50}$ for 106-75 µm size
- 58 µm: $d_{50}$ for 63-53 µm size
- 42 µm: $d_{50}$ for 45-38 µm size
Table 7.5. Mass (%) mineral composition of site 1SE surficial (0-5 cm depth) soil based on X-ray diffraction analyses of selected particle size ranges.

<table>
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<th>Gravel</th>
<th>Sand</th>
<th>Silt</th>
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<td>513</td>
</tr>
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<td>Quartz</td>
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<td>56.3</td>
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<td>K-Feldspar</td>
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<td>1.7</td>
<td>3.1</td>
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<td>5.9</td>
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<td>2.9</td>
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<td>Illite</td>
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<td>2.5</td>
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<td>0.5</td>
<td>0.3</td>
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<tr>
<td>Pyrite</td>
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<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Augite</td>
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<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Amphibole</td>
<td>12.8</td>
<td>0.9</td>
<td>1.8</td>
</tr>
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<td>Σ (%)</td>
<td>99.8</td>
<td>99.8</td>
<td>100.1</td>
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7125 µm : d_{50i} for 9500-4750 µm size
1425 µm : d_{50i} for 2000-850 µm size
513 µm  : d_{50i} for 600-425 µm size
275 µm  : d_{50i} for 300-250 µm size
165 µm  : d_{50i} for 180-150 µm size
91 µm   : d_{50i} for 106-75 µm size
58 µm   : d_{50i} for 63-53 µm size
42 µm   : d_{50i} for 45-38 µm size
Table 7.6. Mass (%) mineral composition of site 1SW surficial (0-5 cm depth) soil based on X-ray diffraction analyses of selected particle size ranges.

<table>
<thead>
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<th>Mineral</th>
<th>Gravel</th>
<th>Sand</th>
<th>Silt</th>
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<tbody>
<tr>
<td></td>
<td>7125</td>
<td>1425</td>
<td>513</td>
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<tr>
<td>Quartz</td>
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<td>34.9</td>
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<tr>
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<td>1.0</td>
</tr>
<tr>
<td>Anhydrite</td>
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<td>0.5</td>
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<tr>
<td>K-Feldspar</td>
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<td>3.2</td>
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<tr>
<td>Plagioclase</td>
<td>3.6</td>
<td>7.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.1</td>
<td>0.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Illite</td>
<td>0.2</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.6</td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Pyrite</td>
<td>1.4</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Augite</td>
<td>1.6</td>
<td>0.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Amphibole</td>
<td>17.1</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Σ (%)</td>
<td>99.9</td>
<td>100.1</td>
<td>99.9</td>
</tr>
</tbody>
</table>

- 7125 μm: $d_{50}$ for 9500-4750 μm size
- 1425 μm: $d_{50}$ for 2000-850 μm size
- 513 μm: $d_{50}$ for 600-425 μm size
- 275 μm: $d_{50}$ for 300-250 μm size
- 165 μm: $d_{50}$ for 180-150 μm size
- 91 μm: $d_{50}$ for 106-75 μm size
- 58 μm: $d_{50}$ for 63-53 μm size
- 42 μm: $d_{50}$ for 45-38 μm size
The soil/residual and snow residual particles had a range of minerals which would effect possible treatment strategies. These mineral surfaces are amphoteric with protons and hydroxyl ions co-existing at the surface in relative populations determined by solution pH (Brown et al. 1995; Langmuir 1997). Individual particles can contain constant and variable surface charges of varying strength and density, and furthermore, the effects of these heterogeneities in the form of intraplanar, interplanar and interparticle interactions are unknown (Sposito 1981; Zelazny et al. 1996).

**Potentiometric titration**

**Surface charge**

Surface charge is an important parameter when implementing treatment for dissolved and particulate bound heavy metals. Mineralogical constituents and SSA play an important role when considering absorption. In general, the trend of surface charge decreased and was reached as particle diameter decreased (Figures 7.6 to 7.11). For the higher particle ranges (>600-µm), a point of zero charge (PZC) was not reached up to a pH of 10. These ranges also had the highest surface charge densities. There is some variability for site 1SW and 2ES for which the particle gradation of >250-µm did not reach PZC up to a pH of 10. For particles <180-µm, the PZC varied depending on the site. The reference site had the lowest PZC at a pH of 7.5. For the snow residual and 2ES sites, the PZC was at a pH between 8 and 9. For sites 1SE and 3SW, the PZC occurred at a pH of 9. The highest PZC occurred at a pH of 10 for site 1SW.

The PZC is defined as the pH at which the net surface charge is zero. For example, since the PZC for site 1SW was 10, any surface runoff either from storm water (pH 6-8) or snowmelt (pH 7-8) containing high levels of heavy metals would most likely go directly to the groundwater. The reason being that the soil has a net positive surface charge at pH below 10.
Figure 7.6. Surface charge density from selected soil gradations for urban clayey glacial till soil at reference site.
Figure 7.7. Surface charge density from snowmelt residual gradations for site 1SE.
Figure 7.8. Surface charge density from selected soil gradations for soil/residual complex (0 to 5 cm) at site 1SE.
Figure 7.9. Surface charge density from selected soil gradations for soil/residual complex (0 to 5 cm) at site 1SW.
Figure 7.10. Surface charge density from selected soil gradations for soil/residual complex (0 to 5 cm) at site 2ES.
Figure 7.11. Surface charge density from selected soil gradations for soil/residual complex (0 to 5 cm) at site 3SW.
thereby heavy metals typically occurring as cations would not be removed from the liquid portion until the pH of the runoff was higher than 10. This would make the soil with a net negative charge attracting heavy metals in solution.

Overall, the snow residual site decreased more than any other site. The paired soil/residual sites of 1SE and 1SW showed more of a decrease in site 1SE. And in particular, site 2ES, the only site with Portland cement concrete (PCC), decreased the least across the gradations. All other sites except for the reference site had asphalt pavement residuals.

**Acid-base titration**

This particular study showed similar surface complexation absorption compared to surface charge when considering the site and pH decrease as seen in Figures 7.12 through 7.14. The experiment had a fixed mass of soil/residual complex with cumulative trends increasing or decreasing depending on the addition of base or acid. In a sense, these figures show the soil/residual buffering capacity for the individual gradations when taking into account SSA (Stumm and Morgan 1996; Langmuir 1997). In fact, acid-base titration data provides macroscopic information about surface charge characteristics of oxide surfaces (Dzombak and Morel 1990).

For the reference site, the volume of acid or base to either decrease or increase the pH over time was less when compared to the soil/residual and snow residual site of 1SE. With respect to the soil/residual complex, the trend in pH had a less of an effect when compared to the snow residuals from the same site for all gradations over time. For all the samples, a distinct trend of particle size is observed in that the larger particle gradations are more easily influenced by either a decrease or increase in pH over time when either acid or base was titrated.
Figure 7.12. Potentiometric titration of reference site soil (0-5 cm) at discrete soil particle sizes.
Figure 7.13. Potentiometric titration of site 1SE snowmelt particulate residuals at discrete particle sizes.
Figure 7.14. Potentiometric titration of site 1SE surficial (0-5 cm) soil containing anthropogenically deposited urban snowmelt particulates at discrete particle sizes.
Conclusions

This study focused on the granulometric and mineralogical characteristics of anthropogenic soil/residual complexes from four of the ten highway sites in urban Cincinnati. These residuals were collected from the back of the paved highway shoulder from each site. A reference site as well as a snow residual site was included. Results demonstrate differences between sites and as well as similarities despite a physical separation of up to 27-km across urban Cincinnati (Hamilton county) and a wide range of conditions such as traffic levels, drainage area, pavement slopes, pavement type and localized wind patterns.

First, it should be noted that there was a relationship between the soil/residual complex and the snow residuals of site 1SE. The mineralogical constituents mostly calcite and dolomite were similar across the gradations as well as the values of PZC at a pH of 9. This shows that a high particulate fraction of snow resides in the soil/residual complex at the edge of the shoulder, and this material influences heavy metal accumulation and export as will be discussed in paper II. The reference site was different than the transportation land use soil/residual sites and thus the snow residuals in that this site had relatively no calcite with a low PZC of 7.5. Even though the parent material of all the sites was glacial till according to the Hamilton county soil survey (Soil 1982), the constituents at the experimental sites were vastly different.

The value of PZC can help to determine surface complexation of heavy metals. The reason that the surface charge did not reach PZC for higher gradations was due to the fact that these particles contained calcite as well as had low SSA. The buffering capacity of these larger gradations was lower than the smaller gradations due to their low SSA. Part II goes into more depth about SSA for each site. The reference site had the lowest buffering capacity and PZC because, although similar parent material, the soil/residual complex contained little calcite and compared to the highway sites was mostly clayey material.
These characteristics can facilitate decision-making with respect to urban management strategies and potential disposal of highway particulates. Overall, a wide gradation of particulate soil/residuals exists for all sites and ranged from greater than 10,000-µm to less than 25-µm. If treatment efficiency were based on mass, unit operations such as grit separation would focus on the larger particles first. This would leave the smaller particles associated with the minority of heavy metals for removal with adsorption or filtration processes. Particle size and heavy metals is discussed further in paper II.

There are no simple solutions for the removal of a particle or heavy metal once released into the environment, and there are remediation strategies or best management practices (BMPs) that can be misapplied for the intended purpose. While there is little control of traffic levels, urban activities and past accretion, soils in the vicinity of highways can accumulate these particulates and metal loadings by the processes of sedimentation, adsorption and surface complexation. Unit processes for in-situ storm water and potentially snowmelt partitioning or heavy metal removal must be based on an understanding of the parameters and constraints of the urban environment. This includes mineralogical and PZC of the existing complex. Combined unit operations of filtration and processes of surface complexation for a range of treatment configurations can be applied to remove the pollutant mass.

**Literature Cited in Chapter 7**


Chapter 8
Gradation-Based Characteristics of Anthropogenic Transportation Land Use Soil/residual Complexes – Part II: Surface Area and Metal Elements

As we anthropogenically modify our global environment, issues related to human health and our ability to sustain natural and built environments have come into increasing focus. For example, urban surface contamination from atmospheric deposition and anthropogenic activities such as motor vehicle transport has become a major concern for urban environmental management. Years of transportation activities as well as historical urban atmospheric deposition can be a significant source of pollutant generation and transport between (dry deposition) and during (wet deposition) rainfall runoff and snowmelt events in the urban environment (Cusimano et al. 1986; Hoyer et al. 1995). Storm water and snowmelt runoff to the surrounding environment including surficial soils, surface water and groundwater contains heavy metals, organic and inorganic compounds, de-icing salts, oil, grease, and suspended and dissolved solids (Pierstorff and Bishop 1980; Buttle and Xu 1988; Paulson and Amy 1993; Daub et al. 1994). The soil/residual complex of heavy metals is important in assessing the bioavailability of these metals and thus their toxicity to the biota.

Traffic activities generate anthropogenic particulate matter containing heavy metals in the urban roadway environment (Zinger and Delisle 1988; Pagotto et al. 2001). Cincinnati urban soil as in any surficial transportation land use soils is subject to loadings from storm water and snow melt runoff and constituents such as particulates and heavy metals. The urban environment is open to these heavy metals from sources of traffic activities that include vehicular component abrasion, pavement degradation, roadway maintenance and in particular abrasion between tires and pavement (Scott and Wylie 1980; Fritzsche 1992; Sansalone et al. 1998). Particular sources of metals originate from tetraethyl lead in gasoline (Pb), diesel oil (Cd), tire attrition (Zn and Cd), steel parts attrition (Ni, Cr, V, W, Mo, Fe, Mn and Al), wear of bearings and bushings (Cu),
wire corrosion, brake lining attrition (Pb, Cu and Zn), radiator fluid (Cu) and catalytic converter emissions (Pt, Pd and Rh) (Amrhein and Strong 1990; Amrhein et al. 1992). These relatively high heavy metal concentrations and the persistence of heavy metals impact rainfall and snow runoff quality, receiving soils and waters.

**Toxicity**

The total concentration of heavy metals gives an idea of the capacity of a reactive element which could under certain circumstances be mobilized. Heavy metals are expected to migrate downward and not accumulate at the surface due to changes in pH. Storm water from these experimental sites has low pH values between 6-8 and low alkalinity thereby mobilizing the metals (Glenn et al. 2001).

Of the heavy metals present in snow, Pb, which is still generated by traffic activities, is considered a significant concern (Zinger and Delisle 1988). Its soluble form is most toxic, very stable and difficult to eliminate. Pb can adhere to fine insoluble particles and therefore the risk of bioaccumulation is greater. Increased availability of Pb and other heavy metals in storm water or melt water with low pH may result in increased loading of metals, increased metal release rates due to deposition of acidifying components and changes in dissolved metal species (Cusimano et al. 1986). This availability may have an impact on vegetation and the local biota. The total metal concentrations in soil and pH were found to most effect metal content in plants (Jung and Thornton 1996).

Soil biological and biochemical processes are sensitive to heavy metals depending on the soil type, since sorptive capacity thus availability of metals to soil biota differs. The heavy metal content of native soil is largely dependent on the rocks from which the soil parent material was derived, and on the process of weathering to which the soil-forming materials have been
subjected. The more aged and older the soil, the less the influence of the parent rocks (Adriano 1986). In urban transportation land use dusts and soils collected in Cincinnati, Ohio, levels of Pb and Cu were higher than background levels for normal soil (Tong 1990). Similar results were found for Pb in an urban residential neighborhood in Chicago (Shinn 2000). Typical values of metals in uncontaminated soil have been reported on dry material and include Pb at 15 mg/kg, Cu at 12 mg/kg, Cd at 0.4 mg/kg, Zn at 40 mg/kg, Mn at 450 mg/kg, and Cr at 50 mg/kg (Forstner 1995).

At high enough concentrations, these metals may become detrimental to the urban environment. Recognition of the factors that influence toxicity of metals is important in determining the risk of local populations. These include interactions with essential metals, formation of metal-protein complexes, age and stage of development, lifestyle factors, chemical form, and immune status of host (Klaassen 1996). Of the heavy metals studied, As, Cd, Cr, and Pb are the most toxic with multiple effects such as renal dysfunction. The metals of Cu, Fe, Mg, Mn and Zn are considered essential with the potential for toxicity. Cr and As are also considered essential to humans and animals yet have toxicological significance. All these particulate-bound metals have the potential to cause harm either from entering a water supply, uptake in a plant or direct consumption.

The nature of urban highway soil/residual complexes directly influenced by rainfall runoff, snowmelt and drainage makes it a significant sink for both heavy metals and particulates generated by traffic and winter maintenance activities. These heavy metals can adversely affect the physical and chemical properties of the soil and thus biota.

**Historical background - Cincinnati**

Cincinnati, Ohio was founded in 1788 with a strategic position straddling the Ohio River. Within a generation, by the mid 1800’s, Cincinnati had become the fifth largest city in the US
and second largest industrial and manufacturing center fueled by an increase of German immigrants (Sansalone 1998; Glazer 1999). From the mid 1800s through the end of WWII, coal was the dominant fuel for individual dwelling and commercial heating, and coal-fired power plants are still the major source of power in Greater Cincinnati. By the early part of the 20th century, Cincinnati had developed a significant rail network, a network of canals, river transport facilities and urban trolley cars. These once dominant forms of transport gave way to motor vehicle transportation land use corridors. After WWII, these corridors were shaped, in part, based on the topography and major drainage patterns of this portion of the Ohio valley. One example that illustrates the alignment between topography, drainage patterns and transportation land use is inter state 75 that parallels the Mill Creek and along which most of our study sites are located. This section of inter state 75 along Mill Creek was constructed in 1960 and 1961.

Cincinnati receives on average 1,020 mm of rainfall and 420 mm of snow per year. The average summer temperature is 23.4ºC, and winter temperature is 0ºC. The highest monthly rainfalls are March with 106 mm and July with 104 mm. The highest monthly snowfall is January with 150 mm (Soil 1982). Because of its geographic location and as a major city, Cincinnati was used as a model for anthropogenic particulate characterization from rainfall runoff, snowmelt and soil/residual complexes and best management practices (BMPs).

Objectives

Nearly all studies that have examined heavy metal contamination of anthropogenically-impacted surficial soils or anthropogenic-generated particulate matter have examined these materials with respect to the total gradation or possibly the sand, silt and clay fractions of the gradation. Physical indices and gradation-based heavy metal distributions have an influence on remediation and treatment strategies. Therefore, the major objectives of this study were
threefold. These objectives were carried out for surficial soil/residual complexes recovered from each of the ten urban highway sites and reference site. The first objective was to examine gradation-based trends in mass, specific surface area (SSA) and total surface area (SA) for soils loaded directly by lateral pavement sheet flow in comparison to surficial clayey glacial tills from an upland reference site removed from the vicinity of transportation land use corridors. The second objective was to examine gradation-based trends in particle density of these soil/residual complexes in comparison to the urban reference site soil. The final objective was to examine gradation-based trends in heavy metal mass of the soil/residual complexes loaded directly by lateral pavement sheet flow in comparison to the urban reference site soil. For each objective, results were evaluated in terms of incremental and cumulative distributions across each residual size gradation for each of the ten highway sites and references site. The purpose was to achieve a characterization of the soil/residual complex that would aid in the identification of best management practices or remediation suitable for adoption across a wide area rather than for each individual site.

Methodology

Experimental sites

Ten highway sites located within the metropolitan area of Greater Cincinnati were selected for soil/residual sampling. Nine of the ten sites were located on Inter State 75 (I-75), a major north-south freeway between Michigan and Florida. The other site was located on U.S. Route 126, 1-km east of I-75. An additional site utilized as a reference site was located in a residential area of urban Cincinnati. Soil at the reference site had no direct exposure to highway or residential roadway traffic activity. For each designation the first number identifies the number of a particular site location, the first letter indicates the direction of traffic and the final
letter indicates which side of the highway samples were obtained. A description and location of all soil residual sampling sites is provided in Part I. For all sites, drainage from the pavement was in the form of lateral pavement sheet flow (q_{sf}) towards the back of the pavement shoulder were the soil was collected. Site 1SW was the only site not to receive direct q_{sf}. Soil/residual sampling at both the highway and control sites was described in Part I of this study.

**Particle gradations**

The determination of the particle size gradation for soil/residuals complexes are described in Part I of this paper. Across each size gradation, residuals were separated into 18 size classes. Each size class for each site was stored separately so that all analyses could be performed across each gradation for these 18 increments. A classification of size ranges included coarse (>425 µm), medium (425-75 µm) and fine (<75 µm).

**Particle density (ρ_s)**

Measurement of particle density was carried out using an inert gas pycnometer. The measurement of particle density followed ASTM D 5550 – 94 (ASTM 1994). The gas utilized in this procedure was ultra-high pure (UHP) He. He gas was chosen for inertness and its ability to enter pore space approaching 1 angstrom (10^{-10}-m) in diameter. The gas pycnometer procedure was selected in lieu of the more common liquid pycnometer procedure (Blake and Hartge 1996). First, sufficient material in the finer particle sizes was not available to utilize the liquid pycnometer technique. Secondly, because of the sorbed surface constituents such as metal elements, the liquid pycnometer procedure was potentially a destructive procedure with respect to analysis of surface constituents because of solid-solute partitioning in the liquid pycnometer.
An inert gas pycnometer determines the true density of particles through measurement of the pressure difference when a known volume of He gas is introduced into a test cell of known volume \((V_R)\) and dry mass of solids. True solid volume can be calculated using Equation (1):

\[
V_s = (V_c) - (V_R)(P_1)/(P_2) - 1
\]

where:

- \(V_s\) = true sample volume (cm\(^3\))
- \(V_c\) = cell volume (cm\(^3\))
- \(V_R\) = reference volume (cm\(^3\))
- \(P_1\) = initial pressure (psi)
- \(P_2\) = final pressure (psi)

Density of the sample then can be calculated using Equation (2):

\[
\rho_s = \frac{(M_s)}{(V_s)}
\]

where:

- \(\rho_s\) = particle density (g/cm\(^3\))
- \(M_s\) = mass of the sample specimen determined prior to placement in the pycnometer (g)

A sufficient mass of sample from each particle size was obtained to provide three separate and independent sub-sample particle density measurements. This material was dried at 40°C before measuring dry solid mass and held in sealed glass jars. Individual sub-samples from the 9500-µm through 2000-µm particle sizes utilized ~165 dry grams of particles and a 147.499-cm\(^3\) test cell. Sub-samples from the 850-µm through 38-µm particle sizes utilized ~18 dry grams of particles and a 25.644-cm\(^3\) test cell. Sub-samples from the 25-µm through pan particle sizes utilized ~1.5 dry grams of particles and a 12.561-cm\(^3\) test cell.
Specific surface area (SSA) and total surface area (SA)

Total SA measured through the measurement of SSA provides, in part, a measure or index of the capacity of a particulate surface to adsorb aqueous heavy metals. The ethylene glycol monoethyl ether (EGME) method (Schwertmann and Cornell 1991) did not require heating of the sample above 60°C was modified and utilized for experimental determination of SSA. The use of low temperature was important due to potential changes in structure and changes to organic content both resulting in changes to surface area.

The EGME method determines the amount of EGME ($\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$), a polar liquid with a relatively high vapor pressure, by measuring the increase in sample weight due to the adsorbed monolayer of EGME on particles in presence of EGME at a constant vapor pressure. A representative sample of known (~1 g) dry weight was selected for each discrete size range (except for the coarse materials from which a few representative materials were selected regardless of weight limit). Each sample was placed in a small glass petri dish for drying and EGME addition. All discrete size range samples from a single gradation were dried in a desiccator cabinet over phosphorus pentoxide, $\text{P}_2\text{O}_5$. Once a constant dry weight was obtained, each solid sample was saturated with EGME, completely wetting all particle surfaces, and placed in an evacuated glass dessicator over 800 grams of an EGME-$\text{CaCl}_2$ solvate (1.0:2.3). A constant vapor pressure was produced from this solvate. Samples were held in an evacuated dessicator and weighted in four-hour intervals after an initial 24 hours in the desiccator until a constant weight for each sample was obtained as determined by a weight differential of less than 1-mg across an interval of at least four hours. Each event generated 18 discrete size samples which were placed in different desiccators with control samples. Each dessicator of 21 samples,
including standards, required ~48 hours of drying time to produce monolayer coverage. All
discrete particle sizes and control were analyzed in triplicate.

One EGME molecule has cross section coverage of 0.52-nm² and a gram molecular
weight of 90.12 grams per mole. Therefore, an EGME monolayer of 1-m² consists of 0.286-mg
of EGME. Carter et al. (1986) present a thorough discussion of the EGME method along with a
standard procedure. This method was modified to measure SSA of sieved solids of specific size
increments in batches of 18 samples plus control samples per dessicator. Based on monolayer
surface coverage and molecular weight of the EGME molecule, SSA was calculated according to
the expression:

\[
SSA = \frac{W_a}{(0.000286)W_s}
\]

where:  
SSA = specific surface area (m²/g)  
W_a = measured weight of EGME retained by sample (g; ± 1 mg)  
W_s = measured initial weight of dried sample (g; ± 1 mg)

Granular activated carbon (GAC) of known SSA served as the control for the EGME method.
The GAC was a Filtersorb F400 with a reported SSA of 1100 m²/g by the N₂-BET method
(Calgon 1995).

Because of the gradation of particle sizes and SSA variation, a measure of total surface
area was needed. SSA results were summed over the entire particle size distribution (PSD) to
yield a total SA distribution as a function of particle diameter using the following formulation for
each particle diameter range,

\[
SA_i = \frac{(m_i)(SSA_i)}{(T_m)}
\]

where:  
SA_i = surface area of solids having particle diameter i (m²/kg)


\[ m_i = \text{mass of solids having particle diameter } i \text{ (g)} \]

\[ SSA_i = \text{specific surface area of solids having particle diameter } i \text{ (m}^2/\text{g)} \]

\[ T_m = \text{total dry mass from PSD (kg)} \]

For comparison between sites, total SA as a function of particle diameter was divided by total dry mass from each individual site resulting in a 1000.0 g basis. From these analytical results, mass retained, SSA and total SA for each increment were determined, and these incremental results were summed across the gradation to yield a cumulative gradation of dry mass, SSA and total SA as a function of size gradation.

**Chemical analyses of particulate residuals**

Chemical analyses focused on determination of heavy metal content for particulate residuals. Heavy metal analyses were conducted on each separate particle size increment. From each separate particle size increment, a representative portion, approximately 0.5 to 1-g of dry particulate matter, was measured to \( \pm 0.1 \)-mg and digested. All discrete particle sizes were analyzed in duplicate. Dry particulate matter samples were acid-digested (9.0-mL of trace-metal \( \text{HNO}_3 \) and 3.0-mL of trace-metal \( \text{HCl} \)) using a microwave-assisted procedure based on SW-846 Method 3015 (USEPA 1990). Once digested and filtered, aqueous heavy metal analyses, conducted on a Perkin-Elmer Elan 6000 Inductively Coupled Plasma Spectrometer (ICP), included scans for Mg, Al, As, Cr, Mn, Fe, Cu, Zn, Cd and Pb. The ICP concentration results were converted from \( \mu \text{g/L} \) to \( \mu \text{g/g} \) based on acid-digested volume dilutions and the measured dry particle mass digested. Heavy metal concentration results in terms of \( \mu \text{g/g} \) were converted to total metal element mass using:

\[ Me_i = \frac{(m_i)(c_i)}{(T_m)(1000)} \] (5)
where: $M_{e_i} = \text{mass of the heavy metal associated with particulate matter having particle diameter } i \ (\text{mg/kg})$; $m_i = \text{mass of solids having particle diameter } i \ (\text{g})$; $c_i = \text{representative concentration of particulate-bound heavy metal for particle diameter } i \ (\mu \text{g/g})$; and $T_m = \text{total dry mass from PSD (kg)}$. For comparison between sites, heavy metal mass as a function of particle diameter was divided by total dry mass from each individual site resulting in a 1000.0 g basis. From these analytical results, heavy metal mass for each increment was determined, and these incremental results were summed across the gradation to yield a cumulative gradation of heavy metal mass as a function of particle size gradation. Analytical controls were also maintained throughout the process including the use of control, blank samples and standard solution quantity checks every 10 samples. A Pearson’s correlation coefficient (Excel 2000) will also be run between all cumulative heavy metals, total SA and mass retained to determine if a relationship exists.

Results

The form of Figure 8.1 through 8.22 has a three-fold purpose. First, the cumulative profiles allow one to examine the trends across the gradation for cumulative residual mass, SSA, SA and heavy metal trends. These cumulative profiles indicate that while SSA plays a role in partitioned heavy metal mass as indicated by Equation 4, cumulative heavy metal mass trends more closely follow those of residual mass and SA. Secondly, cumulative heavy metal mass profiles as a function of particle diameter permit rapid identification of the portion of the gradation with the highest heavy metal mass for separation or remediation. Finally, by correcting the profiles to a 1000.0-g basis, the figures can be used to quantify, by inspection, mass levels, concentration levels and medial levels for each gradation providing a comparison to each site. The figures are designed to read off a median cumulative concentration (mg/kg) and the particle size at which 50% of the metal mass is associated. For example, at the reference site,
Figure 8.1. Urban clayey glacial till (0 to 5-cm depth) as reference soil. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.2. Urban clayey glacial till (0 to 5-cm depth) as reference soil. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.3. Urban soil residual complex from upper 0 to 5-cm depth at site 1SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.4. Urban soil residual complex from upper 0 to 5-cm depth at site 1SW. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.5. Urban soil residual complex from upper 0 to 5-cm depth at site 1SE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.6. Urban soil residual complex from upper 0 to 5-cm depth at site 1SE. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.7. Urban soil residual complex from upper 0 to 5-cm depth at site 2ES. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.

Dry mass = 4236.86 g
Mass recovery = 99.1%
Figure 8.8. Urban soil residual complex from upper 0 to 5-cm depth at site 2ES. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.

Mass retained (%) 
Dry mass = 4236.86 g 
Mass recovery = 99.1%

Total SA (m²) 
Cumulative (%)
Figure 8.9. Urban soil residual complex from upper 0 to 5-cm depth at site 3SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.10. Urban soil residual complex from upper 0 to 5-cm depth at site 3SW. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.11. Urban soil residual complex from upper 0 to 5-cm depth at site 4NE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.12. Urban soil residual complex from upper 0 to 5-cm depth at site 4NE. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.13. Urban soil residual complex from upper 0 to 5-cm depth at site 5NE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.14. Urban soil residual complex from upper 0 to 5-cm depth at site 5NE. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.15. Urban soil residual complex from upper 0 to 5-cm depth at site 6SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.16. Urban soil residual complex from upper 0 to 5-cm depth at site 6SW. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.17. Urban soil residual complex from upper 0 to 5-cm depth at site 7SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.18. Urban soil residual complex from upper 0 to 5-cm depth at site 7SW. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.19. Urban soil residual complex from upper 0 to 5-cm depth at site 8SW. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.20. Urban soil residual complex from upper 0 to 5-cm depth at site 8SW. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.21. Urban soil residual complex from upper 0 to 5-cm depth at site 9NE. Total SA, Pb, Cu, Cd and Zn are each 1000.0-g basis. Cumulative axes are 0 to 100%.
Figure 8.22. Urban soil residual complex from upper 0 to 5-cm depth at site 9NE. Total SA, Mg, Cr, Fe, Al, Mn and As are each 1000.0-g basis. Cumulative axes are 0 to 100%.
50% of the heavy metal mass is associated with particles greater than 128-µm (mean between 106 to 150-µm), and the median Pb mass concentration for the entire sample gradation level is ~60 mg/kg (or ppm).

**Soil/residual mass retained**

Figures 8.1 through 8.22 illustrate the distribution of dry mass of particles for a given particle diameter on an incremental and cumulative basis. All computed mass balances were determined to be within 2% of the initial mass. For all soil/residual samples from transportation land use sites, the coarse fraction (>600-µm) dominates the total dry mass with the median particle mass ~2000 g. For the reference site, the medium size fraction dominates with the median particle mass ~1270 g. Field sampling, laboratory analysis and data QA/QC were followed.

**SSA and total SA**

Figures 8.1 through 8.22 illustrate the distribution of SSA and total SA for particles as a function of particle diameter on an incremental and cumulative basis. The SSA is plotted as a mean of three replicate measurements. For all sites, the SSA results indicate that while SSA generally increases with decreasing particle size, the increase is not consistent and monotonic as would be expected for spherical particles. Additionally, the actual measured SSA values are approximately three orders of magnitude higher than SSA values calculated based on solid spherical particles of constant specific gravity. In contrast to SSA, the total SA values indicate that the predominance of SA is associated with the coarse size fraction of the gradation, that fraction greater than 500-µm. While the gradation of SSA generally increased with decreasing particle diameter for all sites, the gradation of SA illustrated a corresponding decrease with
decreasing particle diameter. For the reference gradation, the 50% cumulative particle mass is associated with particles larger than 128-µm as is the 50% cumulative total SA.

**Particle density (ρₚ)**

Figures 8.1 through 8.22 illustrate the incremental particle density (ρₚ) as a function of particle diameter. Results are plotted as the mean of three replicate measurements. Because of the precision associated with the gas pycnometer, error bars were generally contained within the width of the data points and may not be visible in the plots. While ρₚ values range from 2.8 to 2.1 g/cm³ across the gradation, there is a slight trend towards lower ρₚ values with decreasing particle diameter. The ρₚ for < 25 µm, although shown, had a high standard deviation possibly due to insufficient material for experimental procedure (< 1 g).

**Heavy metal mass distributions**

Although loadings to soils of heavy metals and particulate residuals were unique and independent for each site, one of the study goals was to evaluate the gradation of heavy metal mass as a function of particle diameter, both incrementally and on a cumulative basis as illustrated in the right-hand side plots in Figure 8.1 through 8.22. The plots illustrate a general trend. For metals such as Pb, Cu, Cd, Zn, Mg, Cr, Al, Mn, Fe and As, while variability in the mass distributions across each gradation does exist, results indicate that the predominance of heavy metal mass is associated with the medium to coarse fraction of particles where 50% of the heavy metal mass is associated with particles greater than 250-µm. In addition, the heavy metal mass trends generally follow the total SA profile trends specifically for all heavy metals in the reference site. For cumulative heavy metals, total SA and mass retained, a Pearson’s correlation coefficient in showed a direct relationship (r = 0.99) for all the reference site parameters. Similar results were found for the soil/residual sites with a greater than 0.95 value.
Conclusions

This study focused on the gradation-based physical and heavy metal associations of soil/residual complexes from ten highway sites in urban Cincinnati and a reference site. These soil/residuals were collected within 1-m of the edge of the paved shoulder for each site. The reference site was included to show characteristics of natural undisturbed particles contaminated by only atmospheric deposition within the area of highway sampling. Both the physical and chemical characteristics presented facilitate decision-making with respect to urban management strategies, regulations, treatment and potential disposal of highway residuals. Despite a wide variation in site characteristics and a spatial separation as great as 27-km between sites, there are a number of conclusions that hold for all sites.

For all transportation land use sites, the predominance of cumulative residual mass is associated with the coarse fraction of residual particles, on average those particles larger than 600-µm. The reference site had a higher overall mass than the other sites in a medium silt-size range of particles from 180 to 63 µm. The reason for this difference is due in part to the undisturbed nature of the upland reference site located away from traffic and direct drainage. Overall, a wide gradation of particulate residuals exists for all sites and ranged from greater than 10,000-µm to less than 25-µm, based on particle mass analysis.

For all sites including the reference site, incremental SSA results increase with decreasing particle diameter. While this trend is not monotonically increasing as would be expected for spherical particles and with some variability in the data, the incremental trend of increasing SSA with decreasing particle diameter is consistent for all sites, including the reference site. Also, the overall range of SSA values typically remain within an order of magnitude between 1 - 20 m²/g for all soil/residual sites and 1 - 70 m²/g for the reference site.
This range is approximately three order of magnitude greater than SSA values calculated based on the assumptions of solid, spherical particles of constant specific gravity. For all soil/residual sites, and in contrast to incremental SSA values, incremental total SA values decreased with decreasing particle diameter. Incremental total SA values closely followed those of incremental residual mass retained for each site including the reference site. These results are similar to results for storm water and snowmelt particles transported during runoff events, where SSA and SA demonstrated the same trends as reported herein (Sansalone and Glenn 2002).

Incremental measurement of $\rho_s$ demonstrated that in general, there is a decrease in $\rho_s$ with decreasing particle diameter, although a number of sites illustrate variability within this general trend. Values of $\rho_s$ range from 2.8 to 2.1 illustrating the predominately inorganic nature of the soil/residual particles. In general, the higher $\rho_s$ values are associated with the larger particles indicating their mainly inorganic content, and the lower $\rho_s$ values are associated with smaller particles indicating a trend toward a higher relative organic content as seen from mineralogical data in Part I of this paper.

Results of cumulative heavy metal mass trends across the particle size gradations for each site indicate that the predominance of heavy metal mass is associated with the coarse size particle fraction (>250-µm). This trend is significantly similar to that for residual mass retained and total SA where the predominance of both are associated with the coarse fraction of particles. The same conclusion can be drawn with the reference site where the predominance of residual mass retained, total SA and heavy metal mass is associated with the medium fraction of particles. For the majority of heavy metal mass at the reference site, the concentration was similar or higher than the metal concentrations at the highway sites. One of the main reasons is that this site was left undisturbed and that with continued coal consumption for heating in older urban
areas of Cincinnati, atmospheric deposition of coal combustion products have accumulated in undisturbed surficial soils for over 200 years. Furthermore, levels of Pb were found to be higher in older neighborhoods probably due to leaded gas and lead-based paint.

These general trends for SSA, SA and heavy metals mass are consistent for all transportation land use sites, and while both the residual particulate mass and heavy metal mass may vary from site to site, the soil/residual trends are consistent and similar despite a physical separation of up to 27-km across urban Cincinnati and a wide range of conditions such as traffic levels, drainage area, pavement slopes and pavement type. Results allow the development of gradation-based remediation and best management practices (BMPs) for urban surficial contamination.

**Literature Cited in Chapter 8**


Chapter 9
Summary and Conclusions

As we anthropogenically modify our global environment, issues related to human health and our ability to sustain natural and built environments have come into increasing focus. Years of transportation activities can be a significant source of pollutant generation and transport in rainfall runoff and snowmelt events. Storm water and snowmelt runoff to the surrounding environment including surficial soils, surface water and groundwater contains heavy metals, organic and inorganic compounds, de-icing salts, oil, grease, and suspended and dissolved solids. It is important to characterize the highway environment that is subjected to particulate and heavy metal anthropogenic loadings and assess the bioavailability of these metals and thus their toxicity to the biota. Three environmental partitions or reservoirs exist including rainfall runoff (storm water), snow (snowmelt) and soil/residual complexes that potentially can affect treatment strategies.

The first environmental reservoir for anthropogenic loadings is urban storm water. In-situ treatment design for pavement storm water runoff poses unique challenges due to the unsteady nature of processes including rainfall runoff, mobilization, partitioning and delivery of heavy metals. Storm water from pavements and roadways transports dissolved, colloidal and suspended solids in a heterogeneous mixture, and with additional parameters of pH, alkalinity, traffic levels and residence time, influences the partitioning of heavy metals. For effective in-situ treatment design, an understanding of heavy metal partitioning and temporal washoff during a rainfall runoff event is a prerequisite. This study investigates Zn, Cd, Cu and Pb partitioning, cumulative loadings and washoff in storm water pavement sheet flow from an urban inter state pavement site, typical of heavily traveled urban inter states. Results are presented for a series of eight rainfall runoff events collected at an instrumented urban inter state site. Results from
partitioning analysis (heavy metal mass transfer) between the dissolved and particulate-bound fractions indicate that Zn, Cd and Cu mass are predominately dissolved in pavement sheet flow, \( q_{sf} \). Although Pb mass is a relatively insoluble heavy metal, it was also predominately dissolved. These high dissolved fractions can be attributed to low urban rainfall pH levels, relatively short pavement residence times for the \( q_{sf} \) and low pavement runoff alkalinity. The majority of heavy metal mass remains in solution at the edge of the pavement with partitioning coefficients only approaching equilibrium conditions towards the end of the event as heavy metals partition to entrained solids. Plots of cumulative heavy metal mass as a function of elapsed runoff time clearly demonstrate that for the duration of all events the \( q_{sf} \) dissolved fractions dominated the particulate fractions for Zn, Cd, Cu and Pb. In terms of delivery, results also indicate that the dissolved mass for Zn, Cd, Cu and Pb generally exhibited a “first flush” in comparison to their particulate mass. Design of in-situ treatment systems or source control best management practices (BMPs) loaded by \( q_{sf} \) require data on partitioning and loading for effective treatment.

There are two primary implications when considering the application of typical best management practices (BMPs) for highway runoff within the right-of-way. The first implication is to utilize a BMP such as a detention basin or roadside swale to detain runoff and produce sufficient residence time so that partitioning to the entrained solids occurs. The second implication is to utilize a BMP such as an engineered infiltration trench to provide surface complexation for dissolved metals and filtration mechanisms for the particulate bound metals. While no simple solutions exist for the removal of a heavy metal or particle once released in the highway environment, knowledge of the dynamic processes in highway runoff can provide insights for the proper selection of BMPs depending on the conditions at the highway site.
A second environmental reservoir for anthropogenic loadings is urban roadway snow. This snow is impacted by traffic activities and winter maintenance practices that result in significant accretion of dissolved, colloidal and suspended solids in a complex heterogeneous snow matrix that includes heavy metals, inorganic and organic compounds. Extended residence times of snow as a roadway snowbank in the presence of these pollutant-generating activities lead to significant pollutant accretion and partitioning in the snow matrix. This study analyzed four highway sites in urban Cincinnati with respect to specific water quality indices for the residence time of the roadway snow. Chloride levels in roadway snow illustrate a direct correlation to application of de-icing salts. While accretion of total dissolved solids (TDS) was initially rapid with a decrease late in the event, total suspended solids (TSS) accretion demonstrated a more gradually increasing trend for the duration of roadway snow, approaching $10^5$-mg/L. Temporal trends towards increasing total chemical oxygen demand (COD$_t$) exerted by roadway snow are similar to TSS, with COD$_t$ values approaching $10^5$-mg/L. Applications of $2.2 \times 10^5$-kg of de-icing salt containing cyanide as an anti-caking agent, along a 27-km section of interstate, resulted in approximately 6-kg of cyanide discharged along this major north-south interstate in the study area.

Compared to storm water runoff, urban roadway snow exposed to traffic and winter maintenance practices has a much greater capacity to accumulate and retain heavy metals and other anthropogenic constituents. Heavy metals once released in the highway environment are not degraded and partition between the dissolved and particulate-bound fractions. Residence time, solids loadings, alkalinity, hardness and pH influence partitioning. Accretion and partitioning of Pb, Cu, Cd, Zn, Al, Ca, Na, Mg and Fe from a series of urban highway sites in Cincinnati, Ohio are compared to temporal accretion trends at a control site removed from the
highway environment. Results from partitioning analysis indicate Pb, Cu, Cd, Zn, Al, Mg and Fe were all highly particulate-bound, while Na and Ca are mainly dissolved for all highway sites. Partition coefficients for most heavy metals in snowmelt ranged from $10^3$ to $10^6$-L/kg. Concentrations for Pb, Cu, Cd, Zn and cyanide were orders of magnitude higher than the control site and exceeded storm water runoff concentrations by one to two orders of magnitude.

Characterization of accretion and partitioning of these metals is a necessary first step towards development of management and treatment strategies designed to address urban highway snow pollution. These solids accumulate in urban highway snow and remain as residual deposition material after the melting and recession of the snow from the pavement shoulder. This study analyzed the physical characteristics of these residuals and the associated heavy metals for 10 urban highway sites located throughout metropolitan Cincinnati. Results from the residuals analyses indicate that for all sites particle gradations ranged from greater than 5000-µm to less than 25-µm with a mean $d_{50}$ of 1225-µm. Particle density ($\rho_s$) of residual solids ranged from 2.5 to 3.2 as evaluated for intervals across the gradations, with the lower specific gravity associated with particles less than 100-µm. For each gradation, specific surface area (SSA) generally increased with decreasing particle size while the predominance of total surface area (SA) was associated with the coarser size fractions. Cumulative analysis for Pb, Cu, Cd and Zn associated with snow residuals indicated that more than 50% of the heavy metal mass was associated with particles greater than 250-µm and more than 80% was associated with particles greater than 50-µm. Results provide guidance for management focused on these residuals.

A third environmental reservoir for anthropogenic loadings is soil/residual complexes. Transportation land use soils are directly impacted by traffic activities, rainfall and snowmelt pavement runoff and winter maintenance practices that result in importation, enrichment and
potential export of dissolved, colloidal suspended and settleable anthropogenic particulate matter. These loadings are a complex heterogeneous matrix that includes heavy metals, inorganic and organic compounds. These soil/residual complexes are exposed to pollutant-generating activities that lead to significant pollutant accretion and export. This study analyzed the physical characteristics of these soil/residual complexes for 10 urban highway sites, a snowmelt site and a reference site, all located in metropolitan Cincinnati. Results from the soil/residuals analyses indicate that for all sites particle gradations ranged from greater than 10,000-µm to less than 25-µm with a mean d₅₀ of 572-µm. In comparison, the clayey glacial till soils not subject to residual enrichment of the urban reference site had a d₅₀ of 145-µm. The soil/residual complexes investigated had mixed clay mineralogy with a dominance of k-feldspar, plagioclase, illite and kaolinite, whereas major non-clay minerals were predominantly, dolomite, quartz and calcite. The percent weight of these minerals varied across the size gradation and from site to site. The point of zero charge was more distinct as particle diameter decreased. For the smaller particle diameters, less of an effect was observed as the pH changed over time during the acid-base titration. Results indicate that physical and mineralogical characteristics can have a significant impact on pollutant accretion and export into the urban environment.

It was hypothesized that such soil/residual contamination, either as particulate matter or metal species could be analyzed and explained as a function of size gradation. Within the urban highway environment, a wide size fraction of such particulate residuals and associated metals are incorporated into the soil matrix through dry or wet deposition and can be a potential source of soil, surface water and groundwater contamination over time. This study analyzed the gradation-based physical characteristics for a series of soil/residual complexes and the associated metals for 10 urban transportation land use sites located throughout metropolitan Cincinnati and a
reference site. Results were compared to a reference site in urban residential Cincinnati subject only to historical urban atmospheric deposition. Particle density ($\rho_s$) of residual solids ranged from 2.8 to 2.1 as evaluated for intervals across the gradations, with the lower specific gravity associated with particles less than 100-µm. For each site, specific surface area (SSA) generally increased with decreasing particle size while the predominance of total surface area (SA) was associated with the coarser size fractions except for the reference site. Cumulative analysis for Pb, Cu, Cd and Zn associated with soil indicated that more than 50% of the heavy metal mass was associated with particles greater than 250-µm and more than 80% was associated with particles greater than 106-µm. Overall, the results provide guidance for urban pollution management and potential treatment design when dealing with soil/residual complexes influenced mainly by drainage.
Vita

Donald W. Glenn, III, was born December 15, 1967, in Birmingham, Alabama. He is the oldest of five siblings, two brothers and two sisters. He has lived in Georgia, Connecticut, California, and Illinois. He attended Mountain Brook High School in Mountain Brook, Alabama. Upon graduating, he attended Auburn University, receiving a Bachelor of Science degree in marine biology in August 1993. During the following year, he worked for Southern Ecosystems Research in Florida, relocating the threatened gopher tortoise. In Fall 1994, he enrolled in the master’s program in Fisheries (Aquaculture) at Louisiana State University. The primary focus of his research was storage of eggs and the cryopreservation of sperm of koi, *Cyprinus carpio*. In Fall 1996, he was hired as a Research Associate to study growth and mortality of channel catfish fry using different feed as well as net culture to prevent predation and increase survival and growth of fry. He was also involved in the hatchery phase and rearing of fry from channel catfish broodstock. He was awarded a Master of Science degree May 1998. In Fall 1998, he was hired as a Doctoral Research Assistant in Civil and Environmental Engineering at Louisiana State University. The primary focus of his research was the characterization of heavy metals within urban storm water, snowmelt and soil located in Cincinnati, Ohio. He is currently a candidate for a Doctor of Philosophy degree to be awarded on December 21, 2001.