Influence of Highway Runoff Chemistry, Hydrology and Residence Time on Non-Equilibrium Partitioning of Heavy Metals – Implications for Treatment at the Highway Shoulder

Donald W. Glenn III[1], Dingfang Liu[1], and John J. Sansalone, Ph.D., P.E.[2] (corresponding author)

[1]Louisiana State University, Department of Civil and Environmental Engineering, 3502 CEBA Building, Baton Rouge, Louisiana 70803-6405; 225.578.8652 (fax)
[2]Louisiana State University, Department of Civil and Environmental Engineering, 3502 CEBA Building, Baton Rouge, Louisiana 70803-6405; 225.578.6047 (office); 225.578.8652 (fax)

Word Count: 5000 text and 2500 for tables and figures

ABSTRACT

The control and treatment of highway pavement storm water at the edge of the highway shoulder pose unique challenges due to the unsteady nature of processes including rainfall runoff, mobilization and partitioning of heavy metals, variations in storm water chemistry, residence time on the pavement and delivery of particulate mass. This study presents heavy metal partitioning results as influenced by pavement runoff chemistry and hydrologic parameters from a series of eight rainfall runoff events over a two-year period. Water quality characteristics such as low alkalinity, low hardness and short pavement residence times results in a majority of the heavy metal mass remaining 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.

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 design should be based on the concept that BMPs, to be effective, are essentially garbage cans for heavy metals and solids and as such must be emptied and maintained.

Keywords: heavy metals, partitioning, highway storm water, alkalinity, in-situ treatment

INTRODUCTION

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 (1). 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 (2-5). 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 (6).

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 (7). 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 (8).

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 (6). 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 $CaCO_3$) 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 (9):

$$Cu > Ni > Co > Pb > Cd > Zn > Mg > Sr \qquad (1)$$

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 (9):

$$Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb \qquad (2)$$

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 (9):

$$Pb > Cu > Zn > Co > Ni > Cd > Mn \qquad (3)$$
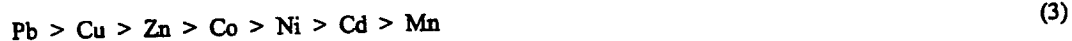
METHODOLOGY

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 (10, 11). 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 (6). Figure 1 illustrates the location of the experimental facility with respect to

the Millcreek Expressway portion of inter state 75 approximately 3-km north of downtown Cincinnati. Figure 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 various laboratory methodologies and analyses as well as the experimental protocols are provided elsewhere (*6, 7*).

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 (*12*). 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 HNO_3. 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 (*13*). 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.

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:

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

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:

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

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:

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

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:

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

$$f_p = P/(D+P) = c_p/c_T = [(K_d)(m)]/[1+K_d(m)] \qquad (8)$$

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 (6). 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_{sf} volume (v_i) representative of the discrete time increment to determine heavy metal or solids mass (m_i) as shown in equation 9.

$$m_i = (c_i)(v_i) \qquad (9)$$

To evaluate the study objectives, these data (m_i) were evaluated for both dissolved fraction and for Kd 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 $CaCO_3$ provide sufficient protection for most fresh and salt-water fish (14). 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 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, the delivery of suspended solids as the ratio of TSS/VSS is plotted in Figure 4 along with the pavement hydrograph, q_{sf} 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 (7). The entrainment and delivery of suspended solids concentration, as well as total mass fractions shown in Table 1, have an impact on heavy metal partitioning as will be discussed shortly. In 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_{sf} tabulated in Table 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 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 6. Hardness is the sum

of the calcium (Ca^{2+}) and magnesium (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 (15). Since

hardness is measured in terms of a concentration, it rapidly diminishes for all events to approximately 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 $CaCO_3$ hardness levels, the Ohio criteria start at a minimum hardness

of 100-mg/L as $CaCO_3$.

Non-Equilibrium Partitioning – Heavy Metal K_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_d values, TSS

(as a mass concentration) has a direct influence on heavy metal K_d values. Plots of K_d values for Pb, Cu, Cd and Zn

as a function of elapsed time are presented in Figure 7. There are a number of important results portrayed in these

figures. First, K_d values vary in a discernible trend across several orders of magnitude and sometimes more for

many events. Second, an equilibrium K_d condition in the range of 10^4 to 10^5 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_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 such as TSS and flow are constant. Finally, the variations in flow and TSS are mirrored shortly

afterwards by resulting changes in K_d. This can be clearly discerned for the 18 June 1996 event. Finally, the

variation in the relative magnitude of K_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-m^2 instrumented asphalt pavement drainage area 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 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 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 effective capture, reasonable time between disposal and an optimal cost between treatment alternatives.

ACKNOWLEDGMENTS

REFERENCES

1. Hamilton, R.S., and R.M. Harrison. *Highway Pollution.* Elsevier Science Publishing Company Inc., New York, 1991, pp. 350.

2. Armstrong, L.J. *Contribution of Heavy Metals to Storm Water from Automotive Disc Brake Pad Wear.* Report for Santa Clara Valley Nonpoint Source Pollution Control Program, Woodward-Clyde Consultants, 1994, pp. 1-37.

3. Ball, D., Hamilton, R., and R. Harrison. *The Influence of Highway-Related Pollutants on Environmental Quality.* R. Hamilton and R. Harrison, eds., Highway Pollution, Elsevier Science Publishing Company, Inc., New York, NY., 1991, pp. 1-47.

4. Lygren, E., Gjessing, E., and L. Berglind. Pollution Transport from a Highway. *The Science of the Total Environment,* Vol. 33, 1984, pp. 147-159.

5. Muschack, W. Pollution of Street Run-Off by Traffic and Local Conditions. *The Science of the Total Environment,* Vol. 93, 1990, pp. 419-431.

6. Sansalone, J.J., and S.G. Buchberger. Partitioning and First Flush of Metals and Solids in Urban Highway Runoff. *J. Envir. Engrg. Div.* ASCE, Vol. 123, No. 2, 1997, pp. 134-143.

7. Sansalone, J.J., Koran, J.M., Smithson, J.A., and S.G. Buchberger. Physical Characteristics of Urban Roadway Solids Transported during Rain Events. *Journal of Environmental Engineering,* ASCE, Vol. 124, No. 5, 1998, pp. 427-440.

8. Klein, L.A., Lang, M., Nash, N., and S.L. Kirschner. Sources of metals in New York City wastewater. *J. Water Pollution Control Federation,* Vol. 46, No. 12, 1974, pp. 2653-2662.

9. McBride, M. *Environmental Chemistry of Soils.* Oxford University Press, New York, 1994, pp. 406.

10. Morrison, G., Revitt, D., Ellis, J., Svensson, G., and P. Balmer. Variation of Dissolved and Suspended Solid Heavy Metals Through an Urban Hydrograph. *Environmental Technology Letters,* Vol. 7, 1984, pp. 313-318.

11. Harrison, R., and S. Wilson. The Chemical Composition of Highway Drainage Waters I. Major Ions and

Selected Metals. *Science of the Total Environment*, Vol. 43, 1985, pp. 63-77.

12. American Public Health Association. *Standard Methods for Water and Wastewater*, 18th edition. A.

Greenberg, L. Clesceri, and A. Eaton, eds., Washington, D.C., 1992, pp. 823.

13. USEPA. *Test Methods for Evaluating Solid Waste*. Physical/Chemical Methods, SW 846, 3rd edition, final

update, Washington, D.C., 1990, pp. 312.

14. Loyless, J.C., and R.F. Malone. A sodium bicarbonate dosing methodology for pH management in freshwater-

recirculating aquaculture systems. *The Progressive Fish-Culturist*, Vol. 59, 1997, pp. 198-205.

15. Cusimano, R.F., Brakke, D.F., and G.A. Chapman. Effects of pH on the toxicities of cadmium, copper, and

zinc to steelhead trout (*Salmo gairdneri*). *Can. J. Fish. Aquat. Sci.*, Vol. 43, 1986, pp. 1497-1503.

LIST OF TABLES

LIST OF FIGURES

TABLE 1 Dissolved and Particulate Solids Mass for Each Event

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

[a]standard deviation
[b]relative standard deviation
[c]total solids
[d]total suspended solids
[e]volatile suspended solids
[f]total dissolved solids
[g]volatile dissolved solids

TABLE 2 Hydrologic Indices and Residence Time Data for Each Event

Event Measured	Rainfall Duration (min)	Rain Depth (mm)	Runoff Volume (L)	IPRT (min)[c]	APRT (min)[d]	LEMF (L/min·m)[e]	LPF (L/min·m)[f]
21 May 1996	35	0.9	97	4	6	0.05	0.92
18 June 1996	63	11.3	2779	5	2	2.29	16.3
7 July 1996	50	40.4	9644	4	2	11.08	21.50
8 August 1996	51	14.1	3877	7	3	4.31	26.10
17 October 1996	616	29.1	3693	5	7	0.40	2.95
25 November 1996	150	3.1	216	8	10	0.09	0.61
16 December 1996	340	3.4	268	14	15	0.05	0.24
12 June 1997	20	2.0	464	3	5	0.52	5.14
All events mean	165.6	13.0	2629.8	6.3	6.3	2.3	9.2
All events median	57.0	7.4	1621.5	5.0	5.5	0.5	4.0
All events SD[a]	210.0	14.5	3260.5	3.5	4.5	3.8	10.5
All events RSD[b] (%)	126.8	111.2	124.0	56.6	71.4	163.2	113.4

[a] standard deviation
[b] relative standard deviation
[c] initial pavement residence time
[d] average pavement residence time
[e] lateral event mean flow
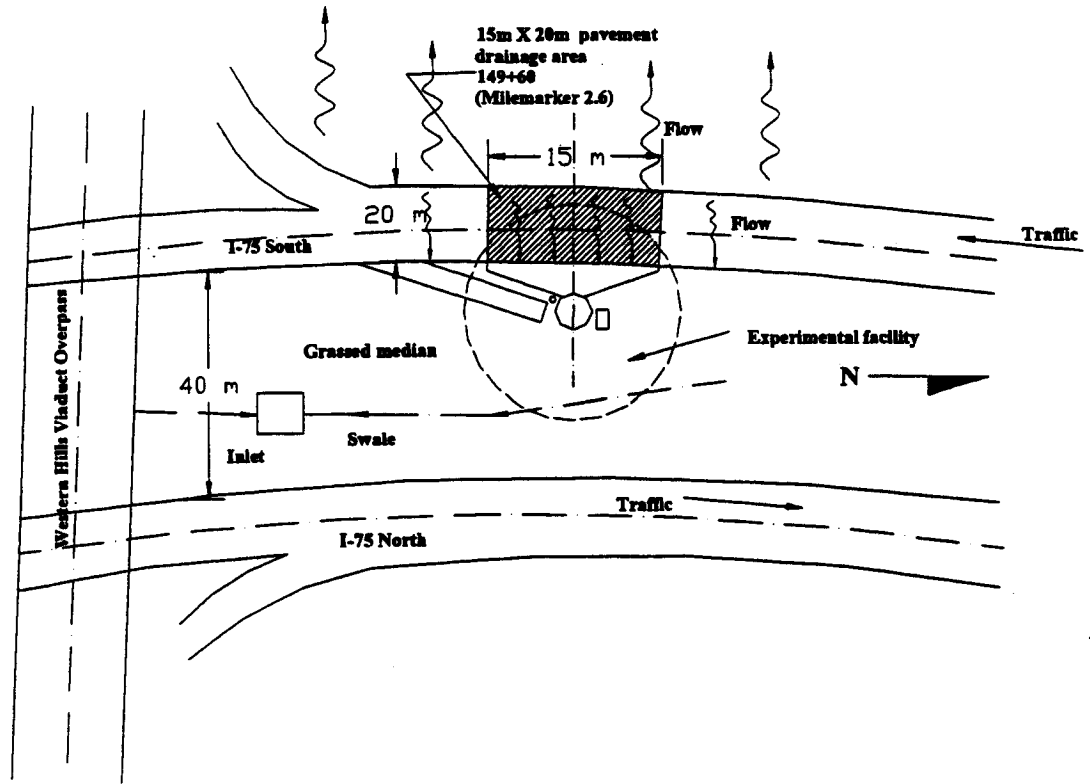[f] lateral peak flow

FIGURE 1 Location of site in SW Ohio and in Cincinnati.
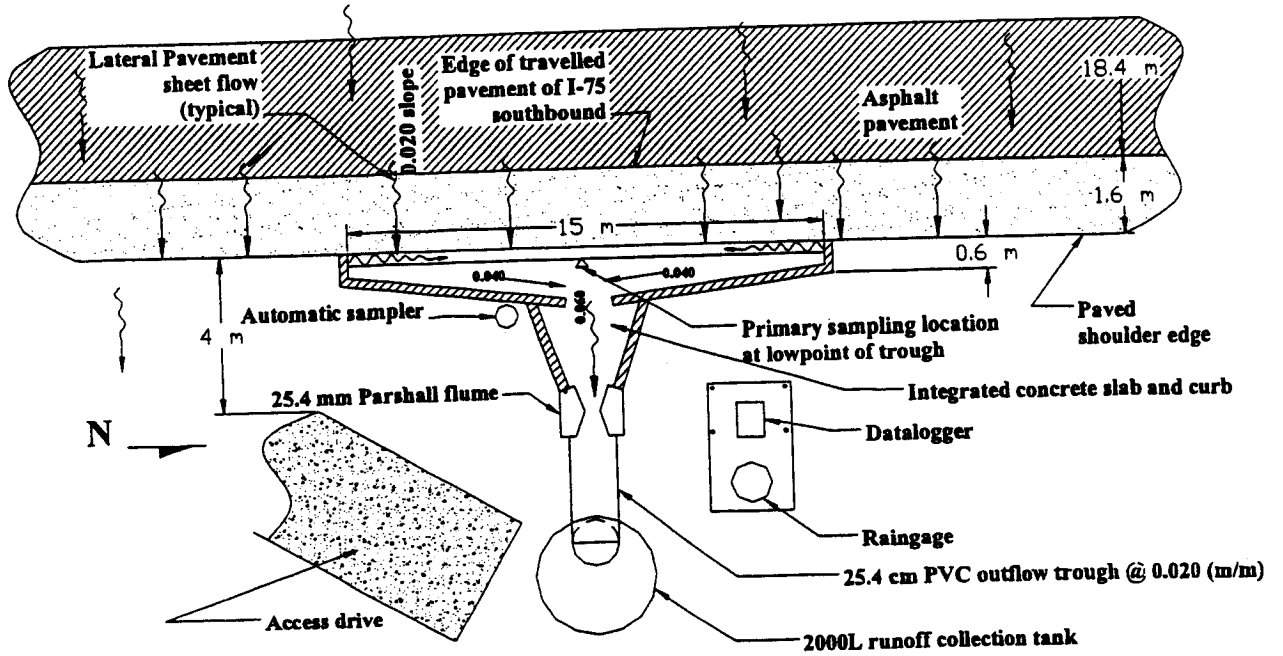
Glenn, Liu and Sansalone (Paper # 01-0336)

FIGURE 2 Experimental facility capturing highway shoulder runoff.
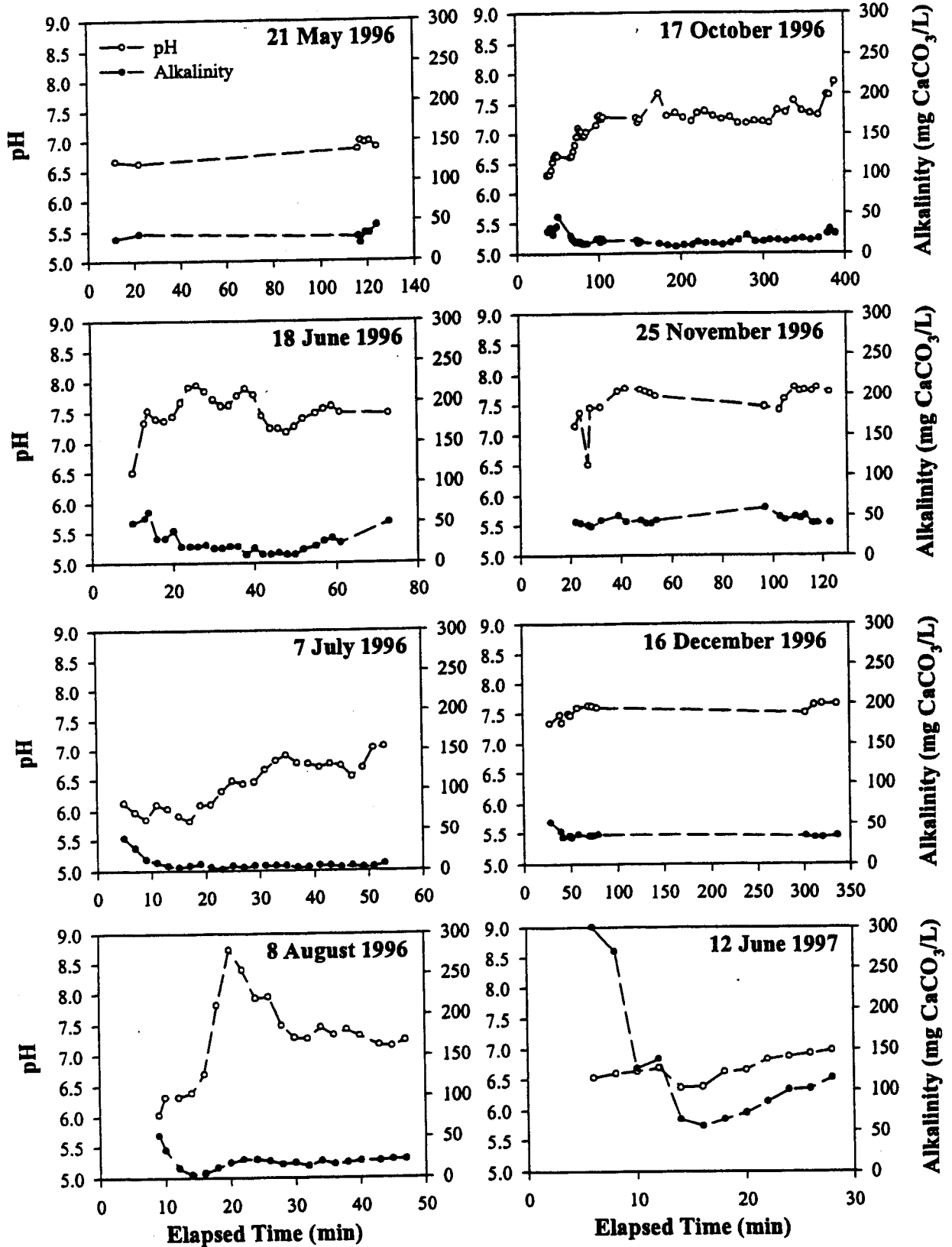
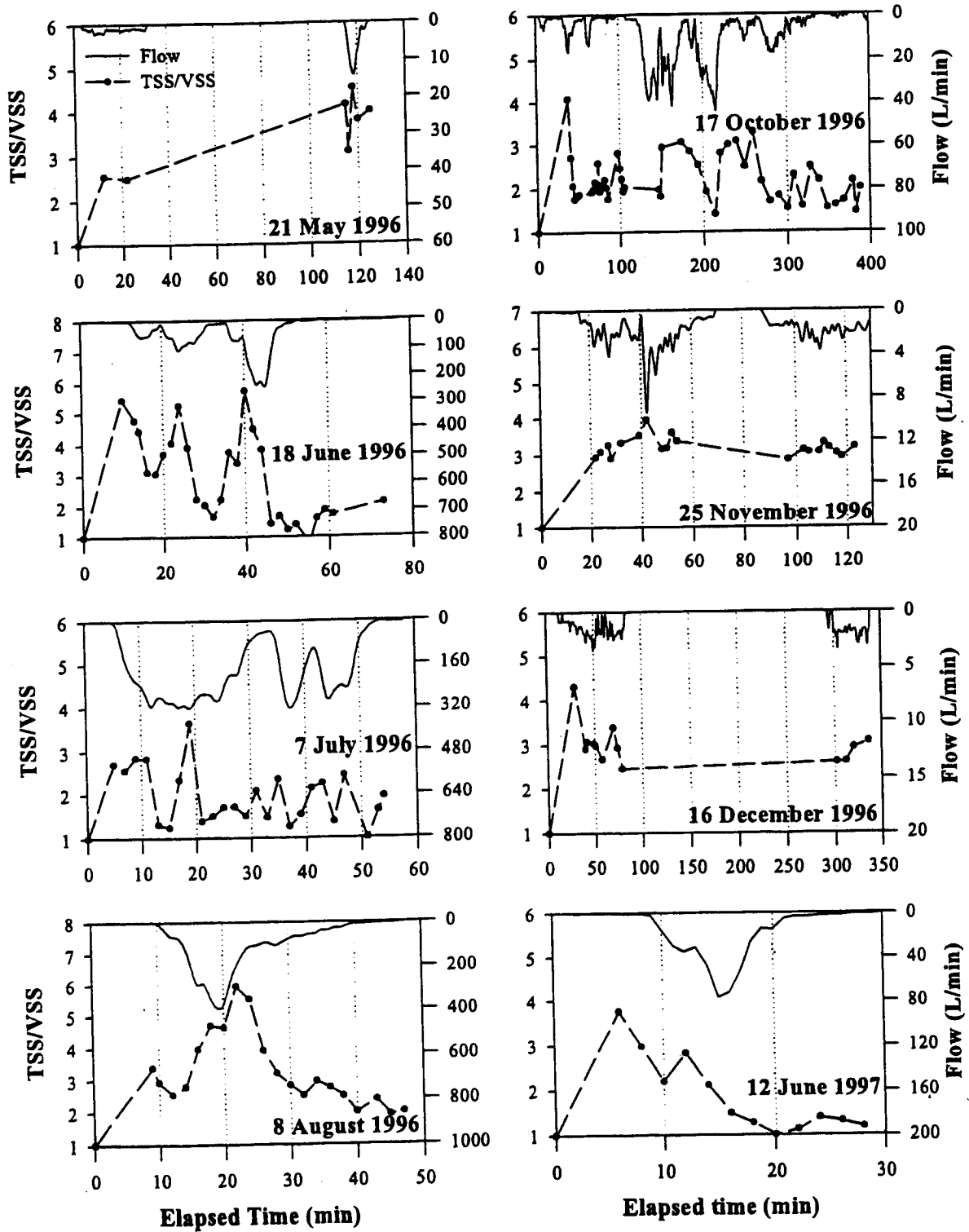FIGURE 3 pH and alkalinity for all rainfall events at I-75 site.

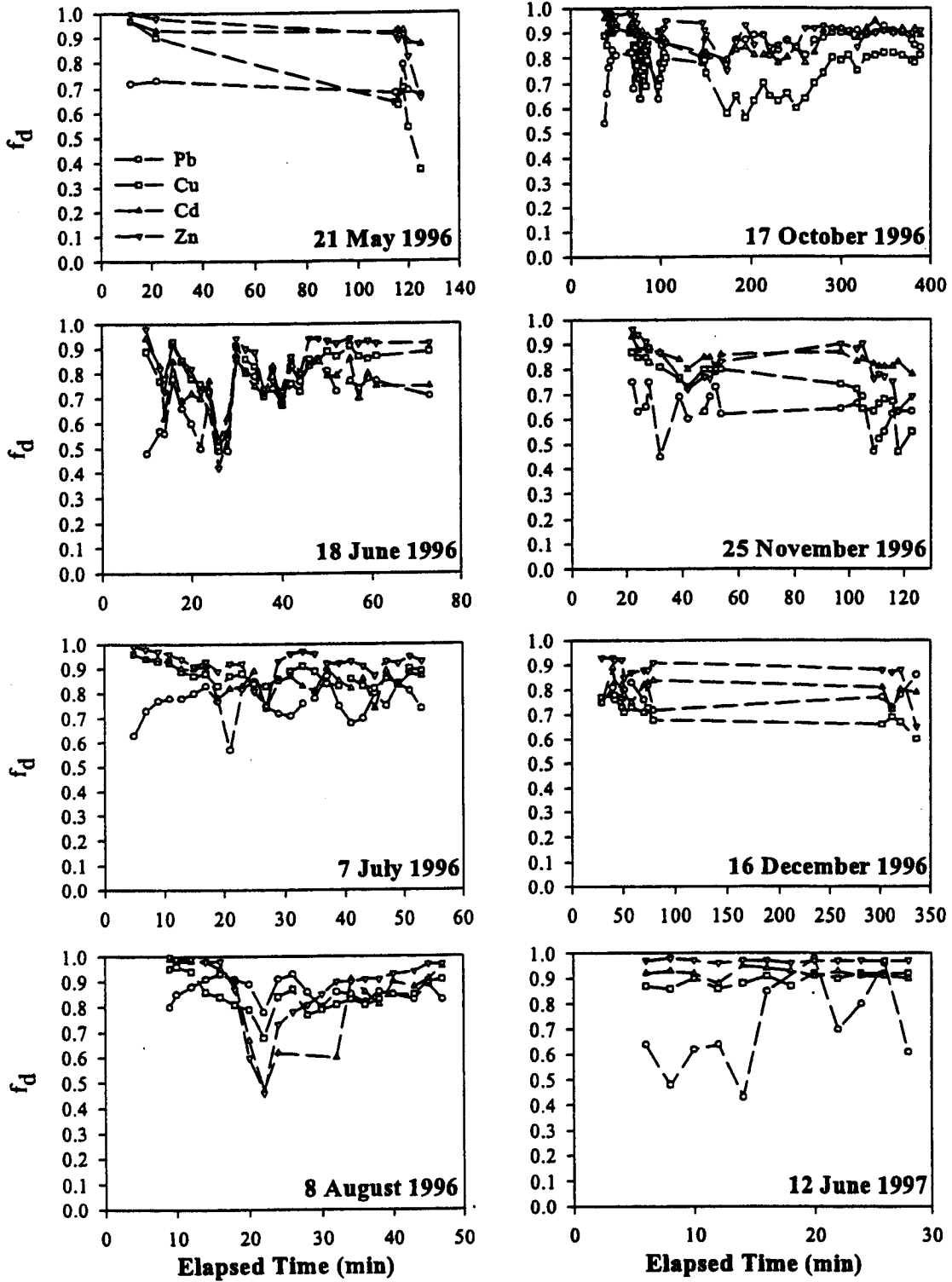FIGURE 4 The ratio of TSS/VSS compared to hydrology for each event.

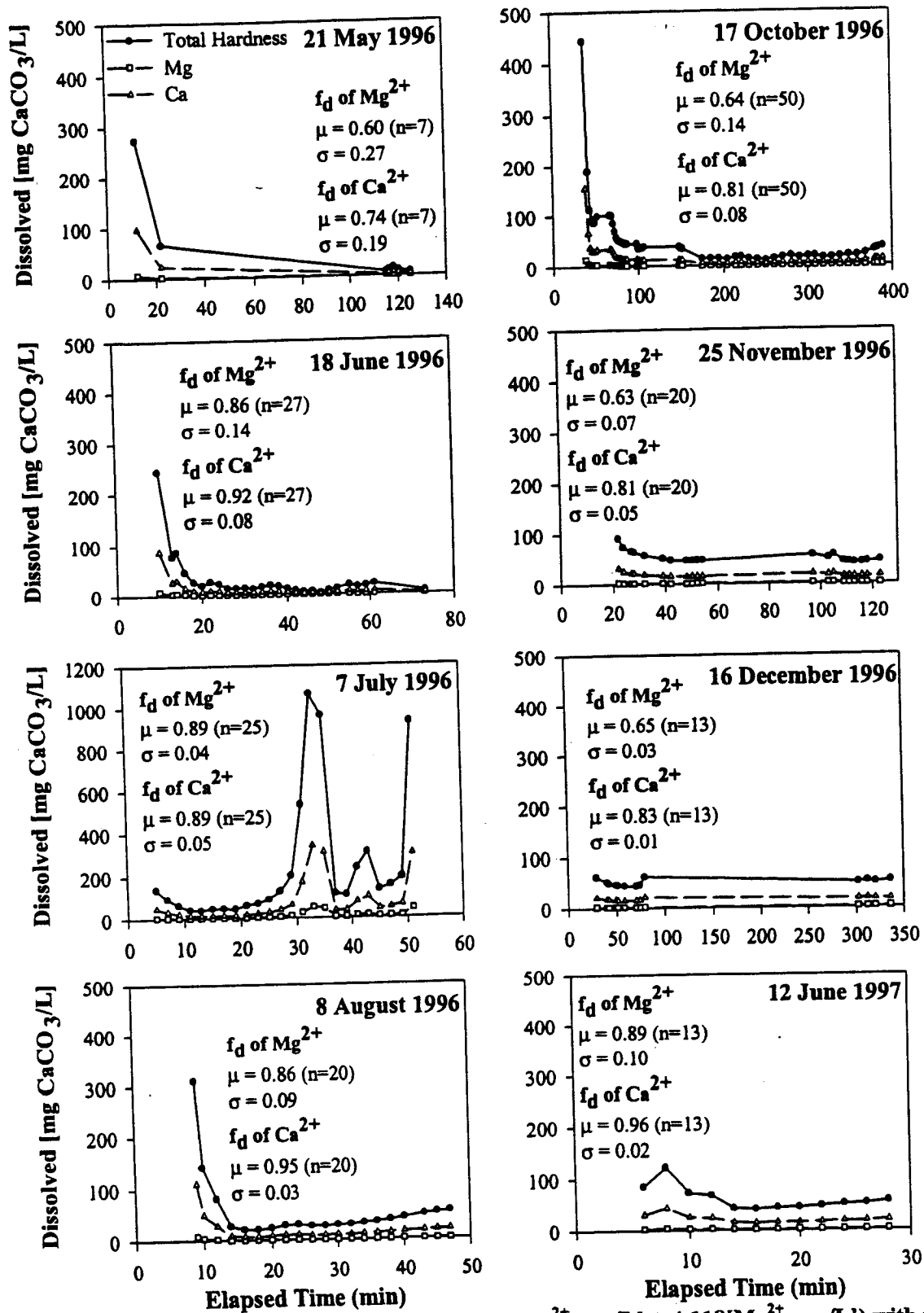FIGURE 5 Temporal variations of dissolved fraction (f_d) with respect to Pb, Cu, Cd and Zn.

FIGURE 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.
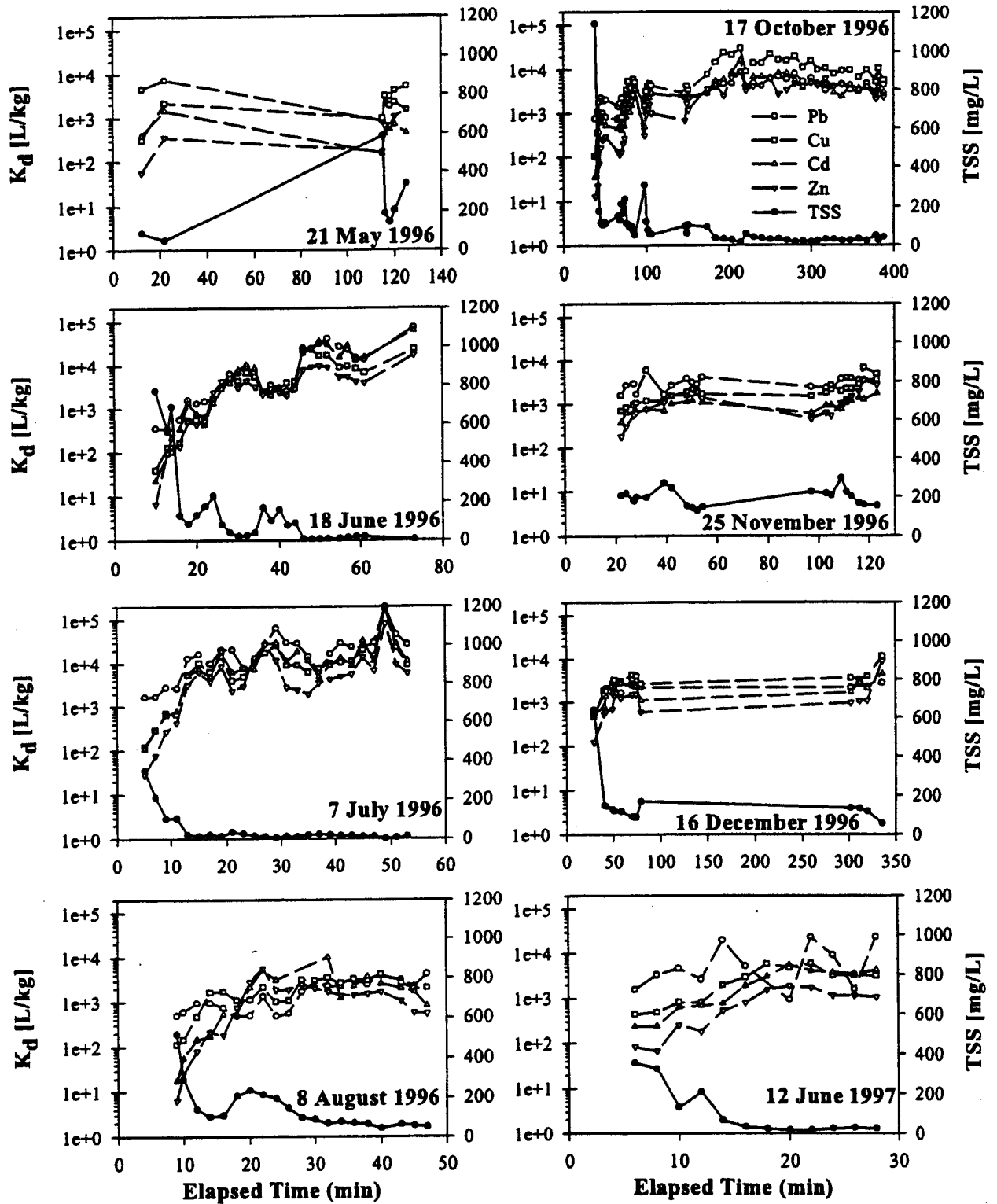
FIGURE 7 Temporal variations of TSS and K_d values with respect to Pb, Cu, Cd and Zn.

(a) Typical highway cross-section during rainfall-runoff event

(b) Typical highway detention basin

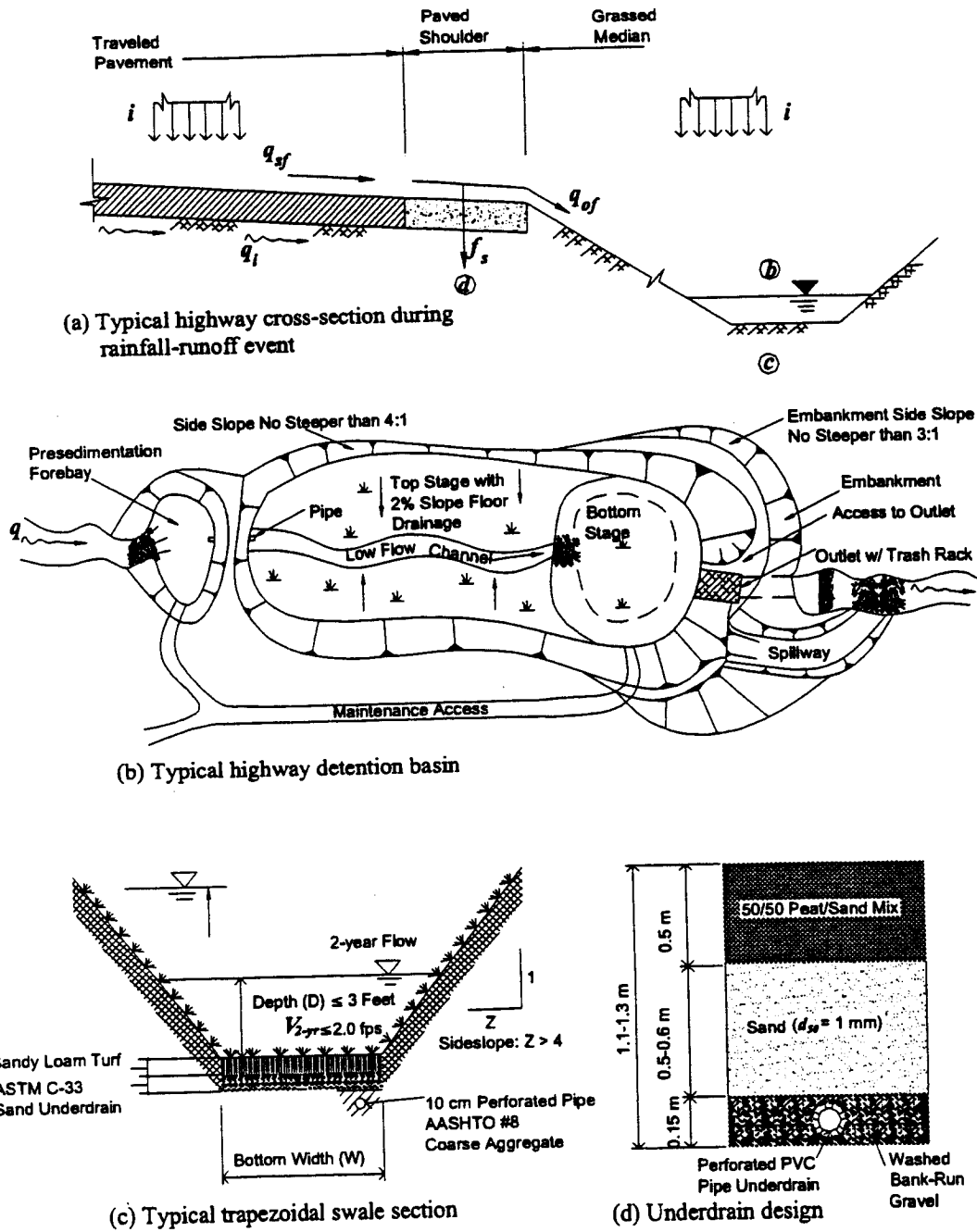(c) Typical trapezoidal swale section

(d) Underdrain design

FIGURE 8 A typical highway shoulder section with several common in-situ treatment (as BMPs) alternatives.