Characterizing Water Quality of Urban Stormwater Runoff:
Interactions of Heavy Metals and Solids in Seattle Residential Catchments

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Abstract

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Amy M. Engstrom

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Stormwater quality and quantity were investigated in urbanized catchments in the Pipers Creek watershed in North Seattle in order to characterize existing rates and processes of stormwater runoff in areas of moderate-density residential development. Hydrologic monitoring and water-quality sampling during storm events were performed as part of this project from fall 2002 through spring 2004.

Results of the sampling program indicate that concentrations of total and dissolved metals, total suspended solids, nutrients, total petroleum hydrocarbons, pesticides, herbicides, and E. coli and fecal coliform bacteria present in the runoff from these areas are significant, especially because they represent only a fraction of the total pollutant loading experienced by the receiving stream. Detailed analysis of heavy metal concentrations, total suspended solids concentrations, and concentrations of solids in the clay and silt size ranges has allowed for better understanding of how solids and metals interact in an urban stormwater environment.

Various hydrologic and water quality parameters affect the concentration and size distribution of solids and the concentration and partitioning of copper, lead, and zinc in stormwater runoff. Precipitation intensity and antecedent dry period influence the accumulation and sequential wash-off of both solids and metals. Total surface area on

particulate matter suspended in the runoff affects the concentrations and partitioning of metals between particulate and dissolved phases. Copper, lead, and zinc each have a distinct pattern of relationships with concentrations of solids of various sizes. Copper is most often associated with the coarser silts, zinc is most often associated with particles of the smallest size classes, and lead can be associated with all particles in runoff. Since solids of varying sizes have an effect on metals in aqueous environments and act as transportation mechanisms for these constituents, relationships between solids and metals in urban runoff must be taken into consideration when designing stormwater mitigation projects.

These findings indicate the importance of mitigating the impacts that urban development has had on the runoff from these catchments, given the regional goal of improved instream aquatic conditions for native biota, particularly salmon. This research is part of the City of Seattle's Natural Drainage Systems project, which has been responsible for several stormwater management projects already constructed within the Pipers Creek watershed. As additional projects are implemented in the coming years, results from this research will allow for a comparison of pre- and post-improvement stormwater runoff conditions. This should document the effectiveness of these various stormwater management techniques on alleviating the effects of urbanization, both in the catchments themselves and on downstream natural systems.

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1. Introduction

Increasing urbanization has led to significant changes in the natural systems of the Puget Sound Lowlands. These changes include alterations in the hydrologic flow regime as well as shifts in the chemical and biological makeup of stormwater runoff from these developing areas. As an area is developed, the natural ability of the catchment to withstand natural hydrologic variability is removed. Infiltration capacity is decreased due to the increase in impervious surface and disrupted native soils and vegetation. Natural retention and detention capabilities of a catchment are removed through channelization of natural waterways and the installation of formal drainage systems such as pipes and gutters. Anthropogenic activity also introduces chemical and biological constituents to the catchment. Trace metals, suspended solids, nutrients, pesticides, petroleum products, and E. coli and fecal coliform bacteria are generally found in higher concentrations in urbanized and urbanizing areas than in natural systems, due to increased numbers of people, vehicles, roads, and building materials introduced into the landscape.

Municipalities, state and federal governments, and government agencies have significantly improved the management of stormwater runoff in developed and developing areas within their jurisdictions. The City of Seattle has engaged in a variety of urban stormwater management efforts, including the large-scale stormwater management project called Natural Drainage Systems (NDS). This project includes multiple individual projects such as the already-constructed Viewlands and NW110th Street Cascades, the Street Edge Alternative (SEA Streets) Project, and the Broadview Green Grid, all of which located in the Pipers Creek Watershed in North Seattle (Figure 1). These projects emphasize using native vegetation and organic soils in combination with vegetated swales to promote infiltration and detention and retention of runoff.

Figure 1.1: Infiltration Swale at SEA Streets within the Pipers Creek Watershed in Northwest Seattle

Efforts to quantify the relative benefits of these individual projects that are part of the NDS effort have centered solely on hydrologic parameters, since water quantity is seen as the primary cause of downstream physical and biological habitat degradation in Pipers Creek. As additional projects become reality and more time and effort is dedicated to these projects, it is increasingly necessary to quantify the relative successes and failures of elements of these projects using both hydrologic and water-quality metrics. Currently, efforts are underway to quantify water quantity and quality conditions in catchments slated for future natural drainage systems improvements. Future phases of the NDS Project will include assessing the post-construction water quantity and water-quality status of the sites in order to measure the effectiveness of the individual NDS projects at mitigating the impacts of urbanization.

In order to quantify the effectiveness of stormwater BMPs, such as those future projects planned as part of the overall NDS effort, it is necessary to characterize the water quality and water quantity of stormwater runoff from the existing system prior to construction. This thesis covers the hydrologic and water-quality monitoring of two catchments slated for future NDS projects. As part of this work, flow monitors were installed and water-quality samples were taken during storm events in order to characterize the runoff from these existing catchments. Samples were analyzed for water-quality parameters from two catchments under existing pre-construction conditions. In addition, samples were taken from two monitoring locations in the same catchment as a paired upstream and downstream study to quantify the capabilities of the existing system in mitigating the effects of urbanization.

Heavy metals, especially copper, lead, and zinc, are by far the most common priority pollutants found in urban runoff, according to the U.S. EPA's Nationwide Urban Runoff Program (NURP) (USEPA, 1983b). In addition, constituents such as heavy metals have been found to be strongly associated with solids in urban runoff (Minton, 2002; Chebbo and Bachoc, 1992; Sansalone et al., 1998), especially TSS and concentration of smaller particles. Therefore, the parameters of total and dissolved metals and total suspended solids (TSS) along with results from the particle size distribution (PSD) analysis received the most attention and analysis in this report.

This research has concentrated on the relationships between solids and metals in urban runoff, specifically focusing on the following questions:

- How do the concentrations of total and dissolved metals in runoff from the Pipers Creek catchments compare to published water-quality criteria? How often are those criteria exceeded?
- Does TSS concentration affect metals concentrations or the distribution of total metals between particulate-bound and dissolved fractions in urban runoff?

- Does a relationship exist between concentrations of smaller particles and the concentration of total metals or the distribution of total metals between particulate-bound and dissolved fractions?
- How effective is the current existing informal drainage system of road ditches and diversion culverts at reducing the magnitude and attenuating the timing of peak flows and at removing solids and other constituents from stormwater runoff?

These questions were addressed by performing the monitoring program, site assessment, data analyses, and assessment of results as outlined by this thesis.

2. Literature Review

2.1. Constituents in Stormwater Runoff

2.1.1. Solids

Characteristics of Solids

Solids in stormwater runoff are classified using various methods, with most dependent on size. Total solids (TS) encompass all solids found in runoff, both suspended and dissolved. Total suspended solids (TSS) and total dissolved solids (TDS) are separated by what does and does not pass through a 0.45-µm filter (APHA, 1998). A PSD analysis further categorizes solids into size ranges. The American Association of State Highway and Transportation Officials (AASHTO) divide size classes for solids into gravel, sand, silt, and clay. Solids larger than 2,000 µm are referred to as gravel, between 75 and 2000 µm as sand, 2 and 75 µm as silt, and less than 2 µm as clay, with all particles less than 75 µm commonly referred to as fines (Das, 1998). Particles in stormwater runoff are referred to as *colloidal* if they are less than 1.0 micrometer (µm) in diameter and *macrocolloidal* if they are between 0.45 and 20 µm in diameter (Characklis and Wiesner, 1997).

The sizes of particles in stormwater runoff can significantly affect various physical and chemical processes. Fine particles may agglomerate, causing PSD to vary along the longitudinal path of stormwater runoff (Minton, 2002). Larger particles settle faster than smaller particles. This settling mechanism affects the relative concentrations of different sizes of particles depending on runoff velocity and depth of flow.

Surface area as a function of particle volume increases drastically with decreasing particle size. That is, smaller particles have a larger surface area to volume ratio than do larger particles. This physical characteristic is enhanced by the fact that actual particles are pitted and porous, increasing surface area over the estimate for surface area based on a completely spherical particle (Sansalone, 1998). In addition, any organic matter bound to solids will contribute to the non-spherical nature of the particle and therefore increase total surface area (Dempsey et al., 1993).

Solids in Stormwater Runoff

Solids enter stormwater runoff through erosion of natural soils. Both the amount of total solids present and the size distribution of those solids depend on catchment land use, the extent of construction activities, and the time since initial disturbance of the catchment (Minton, 2002). Solids also enter the runoff stream from vehicle emissions, vehicle tire, engine and brake wear, as well as through pavement wear and atmospheric deposition (Sansalone, 1998).

The concentration and size distribution of solids depend on runoff rate, runoff duration, traffic intensity and location of sampling within the watershed (Sansalone, 1998). TSS may demonstrate a “first flush” through a system, where the largest concentrations of solids are transported during the initial stages of the storm hydrograph. This trend may not hold for concentrations of finer particles, which often stay consistent throughout the hydrograph. This phenomenon is a consequence of differing settling velocities for different sizes of particles. PSD tends to be consistent throughout events and between sites of similar characteristics (Minton, 2002), but TSS concentrations vary greatly. Particles are smaller in stormwater than in street or highway sediments (Minton, 2002), with d_{50} for highway sediments nearing 100 μm and between 50 and 75 μm for stormwater sediments (Sansalone, 1998). Solids in stormwater runoff are mainly less than 250 μm, especially if best management practices (BMPs) such as street sweeping are in effect. PSD analyses indicate that most stormwater particles are quite small, especially those under low-flow conditions where larger particles are not in suspension. Pitt and

Bissonette (1984) found that 64% of all suspended matter in stormwater was associated with particle sizes less than 62 µm, and only 10% of suspended particles were larger than 250 µm.

Coagulation of smaller particles also occurs, altering the PSD of stormwater runoff over the runoff path. According to Atteia et al. (2001), a significant fraction of all particles greater than 10 µm lump together to form larger conglomerate particles. This agglomeration can affect settling capabilities and also PSD of solids in stormwater runoff.

2.1.2. Metals

Characteristics of Metals

Trace metals are introduced into catchments through anthropogenic activities. They are a cause for concern to due to their potential for toxicity. Once they are present, they cannot be chemically transformed or destroyed, as other constituents such as organic matter may be (Davis et al., 2001).

Metals are classified as particulate-bound or dissolved, with dissolved metal concentration determined by that which passes through a 0.45-µm filter (APHA, 1998). Total metals concentration consists of a sum of metal concentration in both the dissolved and particulate phases.

Metals in Stormwater Runoff

The final report of the U.S. EPA's Nationwide Urban Runoff Program (NURP) stated that heavy metals, especially copper, lead, and zinc, are the most prevalent constituents found in urban runoff (U.S. EPA, 1983b). Over the entire NURP project data, site median event-mean concentration (EMC) values were 34 micrograms per liter (µg/l) for copper, 144 µg/l for lead, and 160 µg/l for zinc, with 90th percentile urban site values at 93 µg/l, 350 µg/l, and 500 µg/l for copper, lead, and zinc, respectively. Total metal concentrations are generally higher in stormwater runoff from residential and commercial areas than in receiving streams and rivers where stormwater inputs are diluted. Concentrations in runoff from industrial catchments tend to be higher than those from residential and commercial catchments (Sanger et al., 1999).

Metals in urban areas come from various sources. Atmospheric deposition contributes cadmium, copper, and lead to urban runoff (Garnaud et al., 1999; Revitt et al., 1990; Davis et al., 2001). Vehicle emissions and tire and engine wear contribute sizable concentrations of all metals, particularly zinc from tire wear and copper from brake pad use. Metals also enter stormwater runoff from siding and roofing materials. Various studies have found significant correlations between traffic volumes and metals concentrations (Wang, 1981). Pavement can also contribute metals to runoff, especially lead and zinc (Ellis and Revitt, 1982).

Metal concentrations vary throughout the duration of a storm hydrograph. Metals tend to be present in suspended form under high flow conditions and in dissolved form under lower discharges (Prych and Ebbert, 1986). Constituents occurring naturally in a drainage system will decrease in streams during storms via dilution, but anything present in the catchment due to anthropogenic input will likely increase in concentration during storms because of increase in wash-off under wet-weather conditions (Characklis and Wiesner, 1997).

Factors Affecting Partitioning and Speciation of Metals in Stormwater Runoff

Various factors influence the relative concentrations of particulate-bound and dissolved forms of metals in urban runoff. These factors include total metal concentration, type of metal, TSS, pH, dissolved oxygen concentration, ionic strength, alkalinity, hardness, bacterial activity, and amount of organic material (Morrison et al., 1984; Morrison et al., 1990; Dempsey et al., 1993). If pH falls below approximately 7, the partitioning between the particulate-bound and dissolved forms shifts toward the dissolved as particulate-bound trace metals are released from particles as free ions (Dempsey et al., 1993). As pH increases, more metal complexes form and fewer spare metal ions are in solution, decreasing the dissolved form of the metal. Below approximately 5 milligrams per liter (mg/l) of dissolved oxygen, reducing conditions prevail and metal ion concentrations also tend to increase (Stone and Marsalek, 1996; Welch, 1980).

Speciation refers to the separation between the dissolved and particulate form. Chemical speciation of metals in natural waters is controlled by precipitation and dissolution reactions, attachment to ligands through the formation of complexes, and sorption to particles (Minton, 2002). The particulate form is further sub-divided into ion-exchangeable, reducible, oxidizable, acid-soluble, and residual phases. The dissolved form of metals is split into bioavailable and stable (Flores-Rodriguez et al., 1994). Morrison and others (1984) classified dissolved metals into classifications of “available”, “moderately bound”, and “strongly bound” based on their status within solution. In their study, strongly bound dissolved metals were mainly associated with colloids (particles from 0.2-10 µm having relatively large surface areas).

Trace metals have characteristic distributions between the particulate-bound and dissolved phases. Among cadmium, copper, lead, and zinc, Morrison and others (1983) found that between 5 and 50% of total metals were in the dissolved phase, with cadmium the most soluble and lead being most highly associated with particles, among cadmium, copper, lead, and zinc. Others have also found that lead is most often stable and particulate-bound (Gromaire-Mertz et al., 1999; Chebbo and Bachoc, 1992), whereas zinc and cadmium are most often found in dissolved ionic forms (Flores-Rodriguez et al., 1994; Morrison et al., 1990; Morrison et al., 1994). Lead is most often associated with the total suspended solids (TSS) fraction. Copper is most often bound to dissolved organic matter (50% of total) rather than TSS (Morrison et al., 1990). Revitt and others found that 82%, 88%, and 47% of total zinc, copper, and lead, respectively, were found in dissolved form (Revitt et al., 1990). These differences between metals have impacts on their interactions with other constituents within stormwater runoff.

Relevance of Metals Partitioning in Stormwater Runoff

The dissolved phase of a metal is the most detrimental to ecosystem health whereas the particulate-bound fraction is stable and therefore less toxic. Therefore, quantifying the dissolved fraction is more important than determining the concentration of total metal in the stormwater runoff (Lee and Jones-Lee, 1993). An accurate estimate for the concentration of metal that is biologically available is difficult to achieve. However, the dissolved concentration of a trace metal is an appropriate estimate for portion of total metal that is biologically available (Charlesworth and Lees, 1999).

The partitioning of metals is a dynamic process. Depending on conditions, metals will dissociate from particles and become dissolved and bioavailable, and dissolved metals will sorb onto particles and no longer be dissolved (Charlesworth and Lees, 1999). The dissolved phase is considered the most biologically available and the particulate phase has a high potential to become dissolved under the right conditions. Therefore, the particulate-bound metals can be the major source of bioavailable metals if released on contact with receiving waters (Morrison et al., 1984).

Toxicity of Metals in Stormwater Runoff

Trace metals in stormwater runoff are a problem because they are toxic to organisms and cannot be chemically transformed or destroyed in the same way as organic matter. Many factors influence the toxicity of the trace metals in stormwater, including hardness, pH, interval between storm events, and TSS.

The two primary factors affecting toxicity of metals in stormwater runoff are pH and hardness, because lower pH or hardness causes an increase in toxicity (Hall and Anderson, 1998). A decrease in pH leads to more metals existing in bioavailable free ionic form. The lower pH will lead to an increase in the dissolved fraction and presumably an increase in the reactivity (toxicity) and mobility of those trace metals. An increase in pH causes formation of insoluble hydroxides and oxides, which are then less bioavailable then the free ions themselves. This trend is especially true for zinc and lead (Dempsey et al., 1993).

Hardness is a measure of the concentration of ions in solution (Minton, 2002), with hardness usually measured as calcium carbonate ($CaCO_3$) equivalents in mg/l. An increase in hardness decreases the toxicity of metals, because calcium and magnesium cations compete with the metal ions for complexing sites, allowing fewer metal complexes to form and therefore resulting in a lower level of toxicity (Minton, 2002).

Outside factors other than hardness and pH affect the metals toxicity of metals in stormwater runoff. The length of an antecedent dry period before a storm event and the build-up of total metals directly affect the toxicity of stormwater runoff (Hall and Anderson, 1998). Highway runoff is much more toxic than stormwater from urban areas (Marsalek et al., 1999), though toxicity of urban stormwater is still substantial. TSS affects toxicity, although not as much as other factors.

Because particulate-bound metals can often become dissolved and therefore bioavailable depending on conditions, both dissolved and particulate-bound phases of metals are potential contributors to toxicity. This release of particulate metal could occur as a result of current or future pH swings (Sansalone et al., 1995). In addition, insoluble pollutants do not usually exhibit a first-flush effect during wet-weather events and therefore their contribution to toxicity persists throughout the duration of these events (Hall and Anderson, 1988).

2.1.3. Interactions of Metals and Solids

Characteristics of Solids and Metals in Stormwater

Solids have been found to be a main vector of pollution (Chebbo and Bachoc, 1992), with factors such as solid gradation, mass loading, surface area, and specific gravity affecting the composition of constituents attaching themselves to the solids (Sansalone et al., 1998). Parameters which measure this variability include TSS, PSD, and concentration of particles in each size class, each of which affect the concentration and partitioning of trace metals in urban stormwater runoff.

Lower TSS concentrations mean less area onto which metals can bind. Greater TSS concentrations, in contrast, are linked with greater percentage of total metal present in particulate form and, therefore, lower mobility and lower bioavailable metal fractions. Though the concentrations of total solids do affect metals partitioning, mechanisms involving the smallest particles most significantly determine relationships between solids and metals in stormwater runoff.

Mechanisms Affecting Metals-Solids Interactions

Sorption of constituents onto particles is an important mechanism for determining the relative concentrations of total and dissolved metals. Sorption is the attachment of dissolved organic and inorganic species to particles, and it depends on chemical bonding of solute and surface, as well as the electrostatic interactions between ions and charged surfaces (Morel and Hering, 1993).

Sorption is divided into three categories of ion exchange, adsorption, and absorption, with each involving varying extents of interaction between constituent and solid. In ion exchange, sorbent in the water places ions on the particle. Concentrations of other ions in the aquatic environment that compete with trace metals for binding sites (such as Ca^{2+} and Mg^{2+}) will affect binding abilities of trace metals. The higher the concentrations of other ions in solution, the more free metal ions that won't have binding sites available and be present in dissolved form (Stone and Marsalek, 1996).

In adsorption, no exchange of ions occurs. Rather, the sorbate penetrates to the molecular level. Through absorption, attachment occurs strictly at the surface of the particle. Absorption represents the least common form of sorption (Minton, 2002).

A much greater surface area-to-volume ratio exists for smaller particles compared to larger particles. The relatively large surface areas of smaller particles act as reservoirs for reactive constituents, including metals (Sansalone et al., 1998). Small particles account for only a small percentage of total mass load, but they are important for fate and transport of metals and organics because they make up a large portion of the total surface area available for sorption (Grout et al., 1999).

Viklander (1998) found that the smallest size fraction of particles had the highest concentration of heavy metals, and these concentrations decreased with increasing particle size for particles <75, 125, 250, 500, 1000, and 2000 μm. Zinc, copper, and lead concentrations were found to increase with increasing specific surface area and decrease with increasing particle size (Sansalone and Buchberger, 1997). This group of researchers has done extensive work, mainly on highway runoff, to determine correlations between metals concentrations and particle size and concentration. They found the strongest correlations between metals concentrations and particles less than 15 μm, no correlations in the 15-50 μm size range, and correlations in the 50-130 μm size range (Sansalone et al., 1995). They concluded that metals preferentially sorb to finer fractions of suspended solids in highway runoff, though no explanation was given for the concentrations in the larger size range. Sansalone and others were not alone in this conclusion regarding smaller particles and metals. Characklis and Wiesner (1997) found a disproportionate fraction of total metals associated with the smallest sediment particles, and that metals concentrations increased with decreasing particle size.

Each different metal has been found to be associated with different particle-size classes. Characklis and Wiesner (1997) found that 44-93% of total zinc is found in particles smaller than 0.45-µm. Copper and chromium, in contrast, have less of a tendency than zinc and lead to be attached to smaller particles (Wang, 1981).

Contaminants can be associated with particles even after suspension in runoff for long periods of time. This association has long-term impacts on reactivity, toxicity, and mobility of metals through the drainage system (Dempsey et al., 1993). Contaminants associated with particles will stay particulate-bound in storm events, especially if pH remains above approximately 7. Below pH of 7, the proportion of dissolved metal increases (Dempsey et al., 1993). Changes in the environment like rain acidification or extensive dilution of runoff may result in desorption of contaminants in particles, thereby affecting the relative concentrations of constituents between particulate and dissolved forms.

Trace metals in stormwater runoff preferentially bind to organic matter. Thus organic colloids have high affinity for metals and are a critical transport mechanism for metals (Morrison, 1988). This mechanism augments the association of metals concentrations associated with solids, as the majority of organic material is attached to fine inorganic sediment.

2.2. Stormwater Mitigation

BMPs are used to effectively remove larger solids from stormwater runoff. Street sweeping, the most common BMP, effectively removes particles larger than 250 μm (Ellis and Revitt, 1982). Basins and swales are effective at removal of larger particles through sedimentation. Vegetated swales can be more effective than other kinds of BMPs which use sedimentation as the primary mechanism of solids removal because of their ability to reduce velocities (Wang, 1981; Marsalek et al., 1999) and therefore increase sedimentation through increased residence times.

Wang (1981) found that grassy drainage channels remove a large portion of lead entering the system. He tested a 40-meter stretch of vegetated channel for lead inputs and outputs, noting that 80% of the original lead entering the system was removed. The study noted that 91% of all solids entering were greater than 20 μm. This indicates that a majority of the lead was tied up in larger particles rather then smaller particles and therefore could be removed more effectively using sedimentation then other metals, such as copper and zinc, would have been. Since lead is most often in particulate form more so than the other metals, lead removal is achieved beyond that of copper and zinc through sedimentation.

Stormwater ponds may be as or more effective than vegetated swales if they are built big enough. However, due to footprint size restrictions, stormwater detention ponds tend not to be of an adequate size to achieve settling of small particles. Greb and Bannerman (1997) found in a study of one wet detention pond over 16 separate wet-weather events that an average of 87% of TSS were removed between the pond inlet and outlet. However, Greb and Bannerman also concluded that over one-half of the influent solids by number were less than 4 μm in diameter. Very little of the smaller size fractions of clay and silt were removed by the pond. The PSD of the effluent shifted towards the smaller size classes, with the relative proportion of clay-size particles increasing from 36 to 72%. In the case of this study, the overall solids removal was greater then the overall pollutant removal, because pollutants are associated with the smaller particles.

However effective these BMPs are at removing larger particles, none of these methods can effectively remove solids with smaller diameters. Since metals preferentially sorb to smaller particles, a large portion of the particulate-bound fraction is associated with smaller particles. Therefore, stormwater BMPs relying on sedimentation alone for solids removal cannot remove this fraction of the particulate-bound metal, nor any of the dissolved metal. This is especially true with zinc, which is strongly associated with smaller particles and has a higher percent of total metal in the dissolved phase (Characklis and Wiesner, 1997). In order to effectively remove both solids and metals from stormwater runoff, BMPs must allow for both adsorption of dissolved metals onto substrate and filtration for particulate-bound fractions, especially for smaller particles (Sansalone, 1999). Given the failure of traditional BMPs to manage these critical sediment sizes, other stormwater management strategies are needed.

3. Methods

3.1. Study Area

Pipers Creek is the receiving water body for the Broadview neighborhood in northwest Seattle (Figure 3.1). This neighborhood is mainly medium-density residential with mixed commercial and residential land use along Greenwood Avenue N. The existing drainage system is informal, with ditches and culverts providing stormwater conveyance. There are no curbs or sidewalks in the area. Figure 3.2 contains a picture of a typical street right-of-way in the Broadview neighborhood.

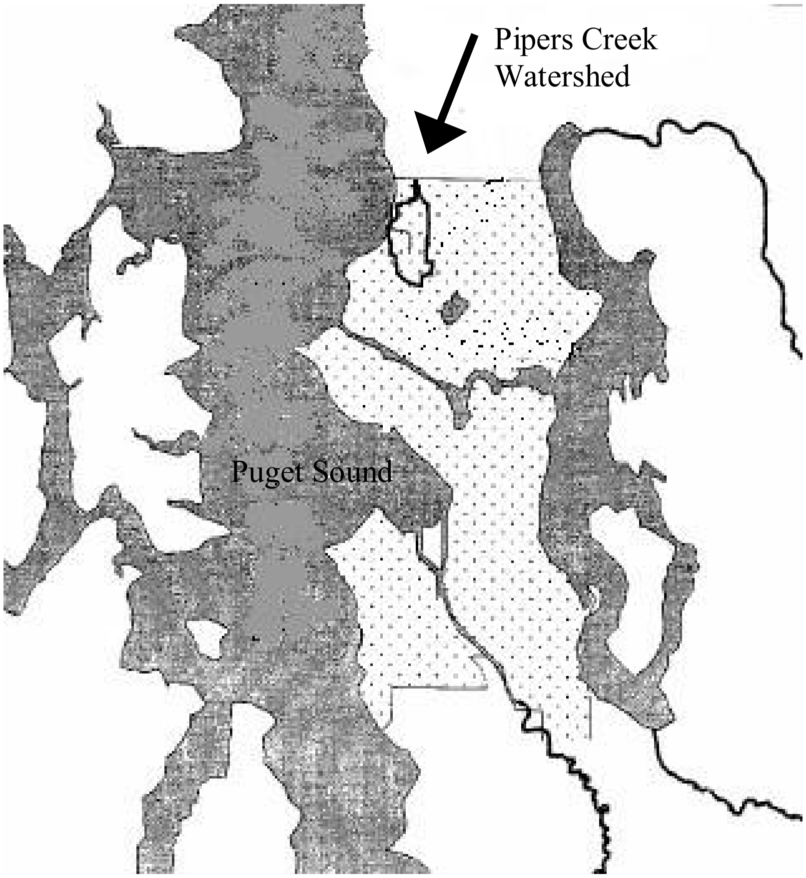


Figure 3.1: Pipers Creek Watershed Location

Figure 3.2: Typical Street Right-of-Way in Broadview Neighborhood, Northwest Seattle

Two catchments in the Pipers Creek watershed have been selected for future Natural Drainage Systems (NDSs) projects by Seattle Public Utilities (SPU). These are the NW107th and NW120th drainages. Both of these catchments drain to Pipers Creek, which enters Puget Sound after flowing through Carkeek Park.

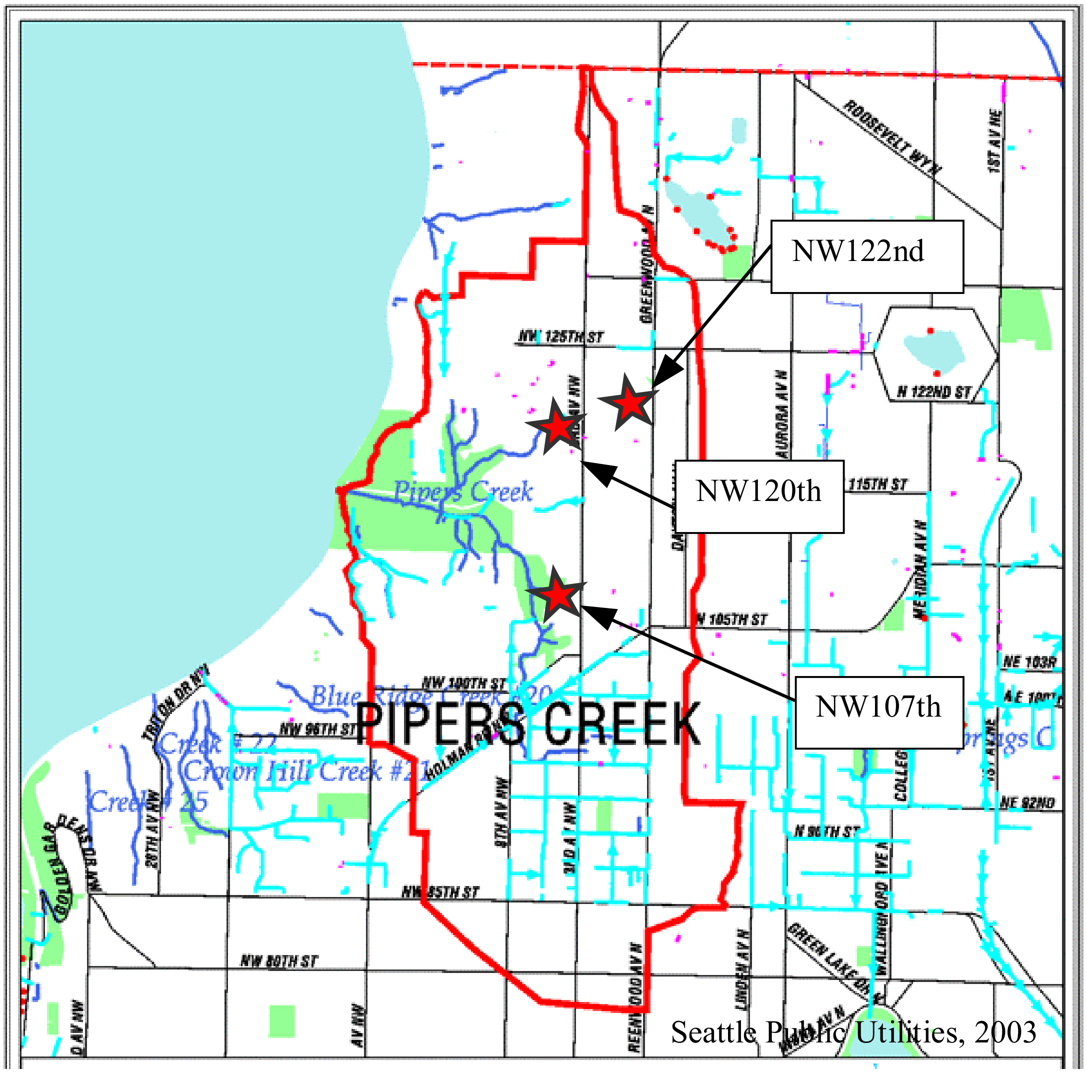
3.2. Site Selection

Three sampling stations were established in the NW107th and NW120th sub-basins. These are shown on Figure 3.3 and described in Table 3.1. The NW 107th station represents the total runoff exiting the NW107th sub-basin, which consists of 33.6 acres with a total impervious area of 42% (Seattle Public Utilities, 2003). An 18-inch Palmer-Bowlus flume was installed in the new manhole to improve the accuracy of flow measurements. Figure 3.4 shows the catchment area for the NW107th monitoring station.

Table 3.1: Descriptions of Monitoring Stations

Station ID	Sub-Basin	Location	Intersection
NW107th	NW107th, outlet	Newly installed manhole	4th Ave NW at NW107th St.
NW120th	NW120th, outlet	Existing manhole	NW120th St. and 5th Ave NW
NW122nd	NW120th, upper portion	Upstream end of grass-lined swale	NW122nd St. and Ridgewood Ave N

Upstream and downstream stations were established in the NW 120th sub-basin to quantify the extent of treatment provided by the existing informal drainage system. Most ditches in the sub-basin are asphalt-lined with the exception of the grass-lined swale on NW122nd Street. The upstream station (NW122nd) represents runoff that has been collected and conveyed in street edge and closed-pipe systems just upstream of this grass-lined swale. Monitoring this location in the upper portion of the NW120th sub-basin enabled an assessment of the quantity and quality of runoff from the upper portion of the NW120th catchment area upstream of the grass-lined swale, including approximately one-half of the NW120th sub-basin area and a stretch of Greenwood Avenue N. The downstream station (NW120th) represents the total surface runoff exiting the NW120th sub-basin. The NW120th catchment is 69.5 acres with a total impervious surface of 44% (Seattle Public Utilities, 2003). Flow measurements and samples have been collected from the NW122nd site at the outlet of a 9.75-inch pipe installed at the site upstream of the grass-lined swale. Monitoring equipment was installed at this location to serve the NW122nd site. Monitoring equipment was installed in an existing manhole at the NW120th site. An 18-inch pipe serves this existing manhole at NW120th. Figure 3.5 shows the locations of the NW120th and NW122nd monitoring stations in relation to the NW120th catchment area.



Seattle Public Utilities, 2003

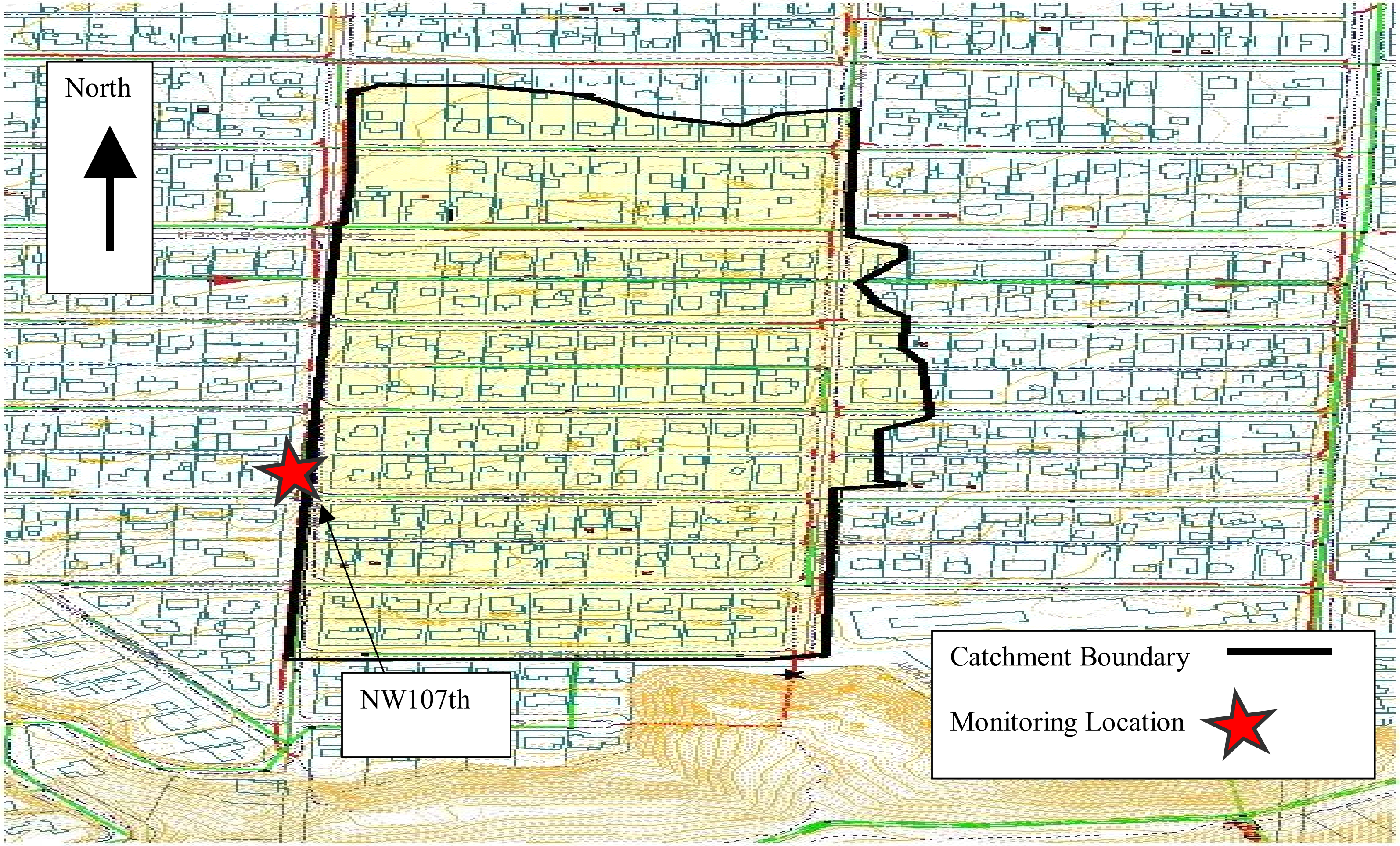
Figure 3:3: Pipers Creek Watershed Map

3.3. Sampling Plan Design and Implementation

3.3.1. Hydrologic Monitoring

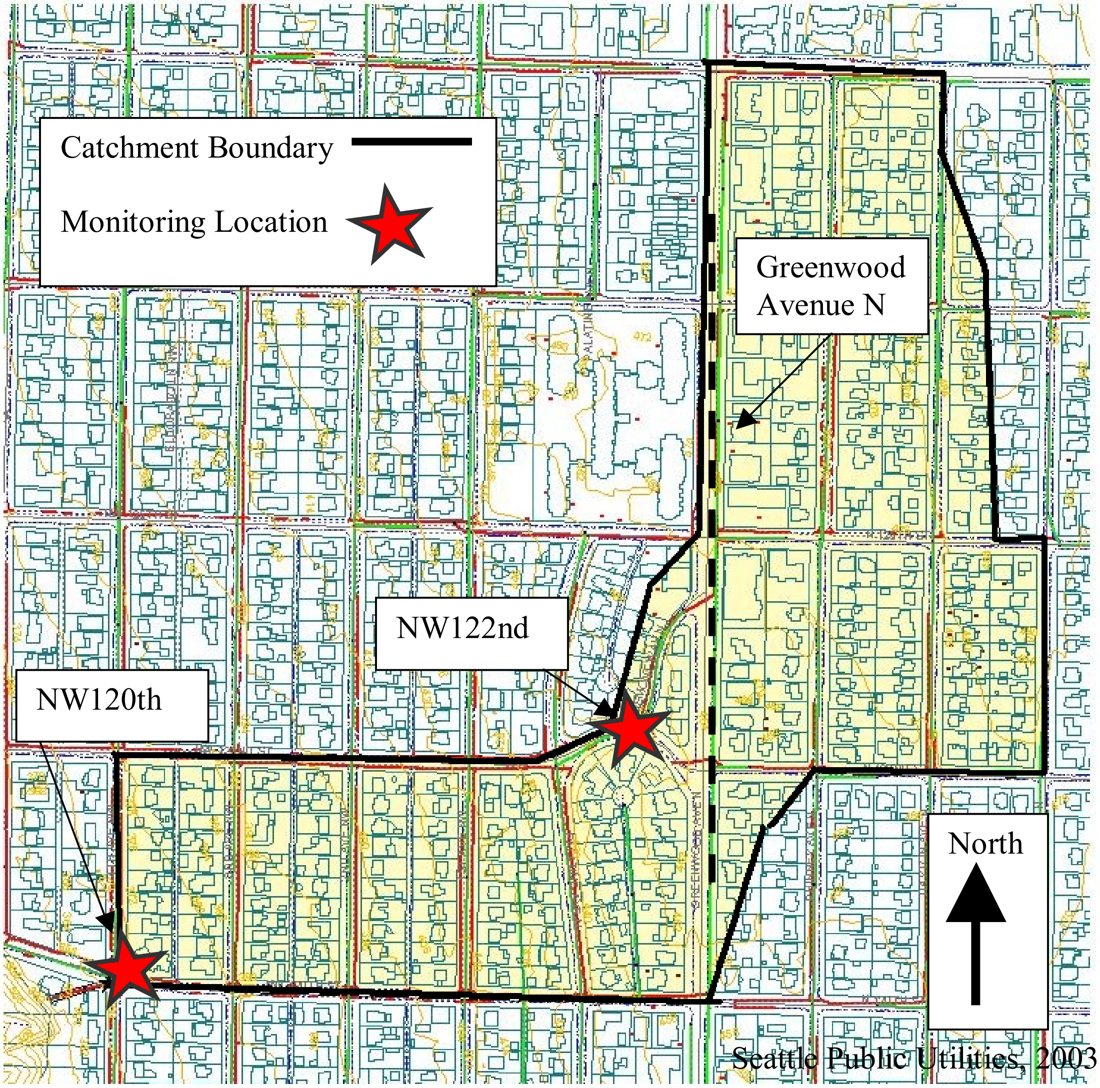
3.3.1.1. Precipitation

Precipitation data for this project were collected by Heungkook Lim as part of a long-term precipitation gage monitoring program headed by Stephen J. Burges at



Seattle Public Utilities, 2003

Figure 3-4: NW107th Catchment Area and Monitoring Station Location



Seattle Public Utilities, 2003

Figure 3-5: NW120th Catchment Area and Monitoring Station Locations

University of Washington. The data are in 15-minute intervals recorded in millimeters at a buried tipping-bucket gage located at Viewlands Elementary School, which is located within the NW107th catchment area Data were collected consistently through the monitoring period.

3.3.1.2. Surface Runoff

ISCO Model 730 bubbler flow modules were used at each monitoring location to measure level. Level data were used to calculate flow rate using Manning's equation at both the NW120th and NW122nd sites:

$$Q = \left(\frac{1.49}{n}\right) A R^{\frac{2}{3}} S^{\frac{1}{2}}$$

Where:
Q = Flowrate (cfs)
n = Manning's n
A = Area (ft^2)
R = Hydraulic Radius (ft)
S = Slope

At the NW107th station, flow was measured using an 18-inch Palmer-Bowlus flume discharge-head relationship from the manufacturer of the flume that was installed in the new manhole at that station. Table 3.2 contains parameters associated with these flow calculations.

Table 3.2: Parameters for Flow Calculations

Station ID	Method	Parameters
NW107th	Palmer-Bowlus Flume Equation	18" flume
NW120th	Manning's Equation	Diameter=1.5 ft Slope= 0.0486 n=0.012
NW122nd	Manning's Equation	Diameter=0.810 ft Slope= 0.06 n=0.009

Flow modules collected continuous level and flow data at the sampling location in 5-minute intervals. Flow monitoring was conducted continuously throughout the monitoring program to obtain information on runoff patterns in the two drainage basins. All hydrologic data were downloaded into Flowlink 4.13, a data-management tool.

3.3.2. Water-Quality Monitoring

3.3.2.1. Equipment

Sampling equipment consisted of an ISCO Model 6700 automatic sampler equipped with the Isco Model 730 bubbler flow module. At each sampling station, sampling equipment was housed in a storage cabinet located adjacent to the manhole or culvert. Sample suction tubing and bubbler tubing were then routed from the sampling station down into either the manhole or culvert. A stainless steel sample strainer was attached to the end of the suction tubing to weight and hold the tubing in the flow stream at the base of the manhole or culvert.

Samplers were configured to accommodate either four 1-gallon bottles or one 10-liter jug, depending on the analysis to be performed by the laboratory for that sampling event. Four one-gallon jars were utilized when sample analyses required both plastic and glass sample containers, and a 10-litre plastic jug was used when all analyses required a plastic sample container.

3.3.2.2. Sampling Design

Samples were collected during storm events from the three stations in the NW107th and NW120th sub-basins. To be determined acceptable for storm sampling, a storm event must have had at least 0.15 inches of total precipitation, an antecedent dry period of 12 hours with less than 0.04 inches of rain (both before and after the event), and have a minimum duration of 1 hour (Seattle Public Utilities, 2003). Composite samples were collected using the ISCO Model 6700 programmed to collect flow-weighted samples over the duration of the runoff hydrograph. A valid storm flow sample consisted of a minimum of 10 sample aliquots representing at least 75 percent of the runoff hydrograph.

Grab samples for bacteria analyses were collected and the field parameters pH and temperature were measured within the first hour of a storm event. Grab samples and field parameter measurements were obtained from the same storm as the composites as often as possible. However, because of the difficulty in obtaining representative grab samples and composite samples from the same storm, this was not always the case. Hannah 9023C field meters were used to measure pH and temperature.

3.3.2.3. Sample Analysis

Laboratory analytical procedures followed U.S. EPA Standard Methods (U.S. EPA, 1992; U.S. EPA, 1983a) and American Public Health Association (APHA et al., 1998). Analytical method designations and detection limits are presented in Table C-1 (Appendix C) for each parameter. Laboratory analyses were performed by Aquatic Research, Inc., Manchester Environmental Laboratory, and The University of Washington. Table C-1 contains detailed information on which parameters were analyzed at each laboratory.

The PSD analyses were performed at the University of Washington Laboratory. PSD was analyzed for all particles less than 250 µm in size by laser diffraction using a LISST portable particle size analyzer manufactured by Sequoia, Inc. Results of the PSD analyses are expressed as volumetric concentration in units of microliters of solid per liter of solution (µL/L). A concentration of particles is given for each bin size class and is reflective of the total volume of particles in that size class over the total volume of solution. Results of this analysis allow for the calculation of a percent-finer curve that is in units of %finer by volume.

3.3.2.4. Quality Control Procedures

3.3.2.4.1. Field Quality Control Procedures

The type of laboratory analysis to be performed determined the type of sampling container required. Sample containers of two different types of materials were used in this sampling effort. Glass jars were used for collecting samples for Total Petroleum Hydrocarbons (TPH), pesticides, and herbicides analysis. Plastic jars were used for collecting samples for metals and conventional analysis according to standard methods (APHA et al., 1998). With the exception of TPH, samples to be analyzed were poured off into the appropriate sample containers prior to delivery to the laboratory. The TPH sample was collected directly into a 1-gallon glass jar during composite sampling and then submitted to the laboratory for extraction and analysis. Glass sample jars were used for all grab samples, including bacteria and TPH.

After composite sampling, sample jars were iced in order to maintain sample temperature at 4° C. All samples were transported on ice at 4° C in a cooler to the analytical laboratory. Bacteria samples were delivered to the lab within 6 hours of sample collection, and nutrient samples were delivered within 30 hours of the start of the sampling event. Chain-of-custody records accompanied the samples. Holding times for sample analysis as specified by standard methods and the analytical laboratories are included in Table C-1 (Appendix C).

The equipment used for collecting samples was decontaminated in the University of Washington laboratory. All sampling equipment, including the 10-L sample jar, 1-gallon sample jars, ISCO pump tubing, suction tubing, and stainless-steel suction strainer, were decontaminated prior to each sampling event.

The 10-L and 1-gallon sample jars and the ISCO 6700 pump tubing and suction tubing were cleaned with phosphate-free detergent and given a tap water rinse and then a 10% hydrochloric acid rinse. Reagent grade water was then used as a rinse. Lastly, a methanol rinse was performed and the jars were allowed to air dry and then were capped. The pump tubing and suction tubing were capped with aluminum foil and bagged in clear plastic. The stainless steel suction strainer was washed with the phosphate-free detergent and given a tap water rinse. It was then rinsed with reagent-grade water followed by methanol. The strainer was allowed to air dry, and then it was wrapped in aluminum foil and bagged in plastic.

A separate sampler and associated tubing were installed to enable a field duplicate sample to be collected at each station throughout the sampling effort at a frequency of 5%. Equipment rinsate blank samples were collected by passing 10 L of distilled deionized water through field equipment already decontaminated. Equipment rinsate blank samples were collected at greater than 5% frequency.

3.3.2.4.2. Laboratory Quality Control Procedures

Method blanks comprised of reagent-grade water were analyzed by the laboratory and results were included in each laboratory report. The laboratory reviewed the blank results and noted in the case narrative whether the sample results are affected by the blank results.

Laboratory duplicate samples were analyzed in the same manner as the samples themselves. Precision of laboratory duplicate results were presented in each laboratory report. Precision of laboratory duplicate results were calculated according to the following equation:

$$RPD = 100 * \left(\frac{C_1 - C_2}{C_1 + C_2} \right)$$

Where:
RPD = Relative percent difference
C_1 = Larger of 2 values
C_2 = Smaller of 2 values

Results exceeding the objectives (Table 3.3) were noted and flagged as estimates. If the objectives were exceeded, then the associated values were rejected.

A matrix spike and matrix-spike duplicate samples were prepared by added known quantities of analyte and analyzing the sample in the laboratory in the exact same manner as the rest of the samples for that analysis. Matrix-spike results were presented in the laboratory reports. Accuracies of matrix spikes were calculated according to the following equation:

$$\%R = 100\% * \left(\frac{S - U}{C_{sa}} \right)$$

Where:
%R = Percent recovery
S = Measured concentration in spike sample
U = Measured concentration in unspiked sample
C_{sa} = Actual concentration of spike added.

If the analyte was not detected in the unspiked sample, then a value of zero was used in the equation. The laboratories also analyzed surrogate spikes and included the results of these analyses in the laboratory reports. Results exceeding the objective were noted and associated values were flagged as estimates.

3.4. Analytical Methods

3.4.1. Hydrology

The precipitation data from the Viewlands gage from the period of January 2003 through March 2004 were discretized into separate events. The criteria of 12 hours with no more than 0.04-inches of precipitation between events and a minimum event duration of one hour were used to separate the record into discrete events. This was chosen as the determining factor separating events because it was also the criteria used to determine if a wet-weather event qualified for sampling. All events occurring over the 15-month sampling period were analyzed and probability distributions were calculated for storm event duration and total event precipitation (Helsel and Hirsch, 2002). A comparison was made between all events and events during which samples were taken in order to determine the representativeness of the sampled events.

Summary statistics for the precipitation data were calculated for events during which water-quality samples were taken. Summary statistics were tabulated for event precipitation volume, maximum precipitation intensity, runoff event duration, runoff volume, peak flow rate, and antecedent dry period. These include arithmetic mean, median, minimum, maximum, 25th and 75th percentiles, 90-percent upper and lower confidence limits of the arithmetic mean and median, standard deviation of the arithmetic mean, and percent coefficient of variation. These statistical analyses were performed separately on events during which grab samples were taken, and then again separately on events when composite samples were taken.

3.4.2. Water Quality

3.4.2.1. Quality Analysis / Quality Control (QA/QC) Objectives

To determine whether or not QA/QC objectives had been met in this sampling effort, comments were made on any changes in the monitoring plan and on any significant problems encountered. Sample estimates and rejections were listed and comments were made on the limitations (if any) on the use of the data. A data quality assessment was performed using the metrics of precision, bias, representativeness, completeness, comparability, and reporting limits.

Precision is a measure of the scatter in the data due to random error, caused primarily from sampling and analytical procedures. Precision was assessed using laboratory duplicates, which were analyzed with every sample batch. Bias, the degree to which the analytical results reflect the true value of the sample, was assessed using analyses of method blanks, matrix spikes, and control spikes. Table 3.3 contains criteria for determining precision and bias.

Table 3.3: QA/QC Objectives

Parameter	Precision[a] (%RPD)	Bias[b] (%)
TSS	20	80-120
PSD	30	NA
Total phosphorus	20	75-125
Soluble reactive phosphorus	20	75-125
Total persulfate nitrogen	20	75-125
Fecal coliform bacteria	NA	NA
E. coli	NA	NA
Hardness	10	90-110
Metals, total and dissolved	20	75-125
NWTPH-diesel and heavy oil	NA	NA
Chlorinated pesticides	20	50-150
Organophosphorus pesticides	20	50-150
Nitrogen pesticides	20	50-150
Herbicides	20	20-150

NA = not applicable
cfu = coliform forming units
a. If measured concentration is less than 5 times the reporting limit, precision is ±40 percent.
b. Percent of true value.
(Adapted from Seattle Public Utilities, 2003)

The sampling program was designed to provide samples that represented a wide range of flow and water-quality conditions in the NW 107th and NW 120th Street sub-basins. Sample representativeness was ensured by employing consistent and standard sampling procedures. Sampling at consistent sites during storm conditions, along with adherence to standardized sampling and testing protocols, aided in providing complete data sets for this sampling program.

Completeness was judged by such criteria as compliance with established data quality criteria, holding times, and the storm and sampling event criteria established for this project. While the goal for completeness was 100% satisfaction of the above criteria, a level of 95% completeness was considered acceptable. Comments were made on the frequency and extent of any violations of the criteria set out in the sampling plan.

Data comparability was ensured through the application of standard sampling procedures, analytical methods, units of measurement, and reporting limits.

3.4.2.2. Analysis of Sampling Results

3.4.2.2.1. All Data

Sampling results for all parameters from al sampling stations were tabulated for all storm flow samples for both grabs and composites. Summary statistics were calculated, including the number of samples analyzed, number of samples with detected chemical concentrations, arithmetic mean, median, minimum, maximum, 25th and 75th percentiles, 90 percent upper and lower confidence limits of the arithmetic mean and median, standard deviation of the arithmetic mean, and percent coefficient of variation (Zar, 1996). For samples reporting non-detected concentrations, one-half the reporting limit was used to calculate summary statistics and all statistical analysis involving the data (Kayhanian, 2002).

More detailed calculations were performed on data for total and dissolved metals, total suspended solids (TSS), hardness, and on the data from the PSD analyses in accordance with the goals of this project.

Solids

The PSD analyses yielded volumetric concentration data for bin sizes from <1.36 µm through 250 µm. Percent finer curves (by volume) were developed for all events at all stations when and where PSD samples were taken and analyzed. Box-and-whisker plots were used to demonstrate the variability of solids concentrations in each size range from the PSD analysis.

Probability distributions were calculated based on TSS concentrations. This analysis was performed in order to develop a tool to predict the probability that a constituent concentration would be at or above a certain level (Helsel and Hirsch, 2002).

TSS and PSD were compared to meteorologic and hydrologic factors in an effort to identify if and how solids parameters depend upon these factors. These factors included total event precipitation, maximum precipitation event intensity, peak flow rate, total runoff volume, event duration, and time-to-peak (a measure of the time between the start of the event and the peak runoff). Various measures of antecedent conditions were then compared to the solids data. These parameters included total precipitation in the previous 12; 24; 48; and 168 hours; days since precipitation was greater than 0.04-inches over a 12-hour period; and days since precipitation was greater than 0.1-inches over both a 24-hour and 48-hour period.

The relationships between solids parameters and meteorologic and hydrologic parameters were analyzed using linear regressions and a test for significance (Zar, 1996). In addition, log-normal transformations were employed to determine if power and/or exponential equations provide better fits for data, because water-quality data commonly follow a log-normal distribution (Minton, 2002; Helsel and Hirsch, 2002).

Metals

Samples from this effort were analyzed for total and dissolved zinc, copper, and lead. Box-and-whisker plots were developed (Zar, 1996) to show the difference in partitioning between particulate-bound and dissolved phases for the three metals over the range of events. While the individual plots can show the range and dispersion of partitioning for any one metal, comparing the plots for each of the three metals can indicate the relative portion of the total metal that is commonly encountered in the dissolved rather than particulate form.

Probability distributions were calculated based on total and dissolved metals concentrations and on the percent of total metal present in dissolved form. This analysis was performed to develop a tool for predicting the probability that a constituent is present at or above a certain concentration or the probability associated with the percent of total metal present in dissolved form.

Metals data were used in combination with hardness data in order to quantify the toxicity of each metal in comparison with published water-quality standards. Washington State water-quality standards apply to end-of-pipe outlets. The monitoring locations that are part of this study do not quality as end-of-pipe outlets; however, acute and chronic toxicity criteria were applied for comparison purposes. Using these criteria assumes that aquatic life would come into contact with the runoff stream without the benefit of dilution in the receiving water.

Because this study concentrates on the relationships between trace metals and solids in urban runoff, it is relevant to discuss the relationship of these parameters with the meteorologic and hydrologic parameters that drive runoff. Total and dissolved metal concentrations, along with metals partitioning data, were compared to various meteorologic and hydrologic parameters mentioned previously. The relationships between metals concentrations and parameters were analyzed using linear regressions and log-normal transformations.

Metals compared to solids parameters

The data for total, dissolved, and partitioning of trace metals were compared to TSS data and data from the PSD analysis to test the hypothesis that concentrations of solids directly affect the concentration of total and dissolved metals and the partitioning of metals between the particulate and dissolved phase. Linear regression and log-transformation then linear regression (Zar, 1996) were performed in order to test for the dependence of metals concentrations (total, dissolved, dissolved as a portion of total) on total suspended solids concentrations and on the size-dependent concentrations from the PSD analysis.

3.4.2.2.2. Upstream and Downstream Paired Study Data

Comparisons of chemical concentrations between upstream (NW122nd) and downstream (NW120th) stations were conducted using a Wilcoxon rank sum tests for paired data (Zar, 1996) to test the hypothesis of equal variance between the populations from the two stations. These statistical tests were performed using a level of significance of 0.05. Results from these analyses would indicate if there is a statistical difference between the sites for each parameter analyzed. This analysis was performed for all water-quality parameters that were included in this sampling effort.

4. Results

4.1. Hydrology

Since precipitation drives runoff, an important part of an urban stormwater-quality analysis is the evaluation of a corresponding precipitation record. Using the criteria of a minimum event duration of one hour and an antecedent condition of less than 0.04 inches of precipitation over the twelve hours preceding the event, the precipitation record from the Viewlands Gage for the period of January 2003 through March 2004 was discretized into 111 events over the 15-month period of record. The median event duration over all events was 14.75 hours with a median event precipitation of 0.16 inches (Figure 4-1, Figure 4-2). The x-axis of the graphs are expressed in terms of quantiles of the standard normal deviation, or numbers of standard deviations away from the median. For example, 0.00 on the x-axis corresponds to a probability of exceedance of 50%, 1.00 corresponds to a probability of exceedance of 15.8%, and -1.00 to a probability of exceedance of 84.2%.

Both composite and grab sampling were conducted over a variety of storm events as characterized by both event duration and total precipitation. A summary of hydrologic statistics for the sampled events is included in Tables B-1 and B-2 (Appendix B). The median precipitation volume was 0.30 inches for composite-sampling events and 0.37 inches for grab-sampling events, both of which were less than one standard deviation from the mean event precipitation of 0.34 inches over the 111 events of the sampling period. The median event duration was 19 hours for composite-sampling events and 15 hours for grab-sampling events, which were both less than one standard deviation from the mean event duration of 19.75 hours over all events.

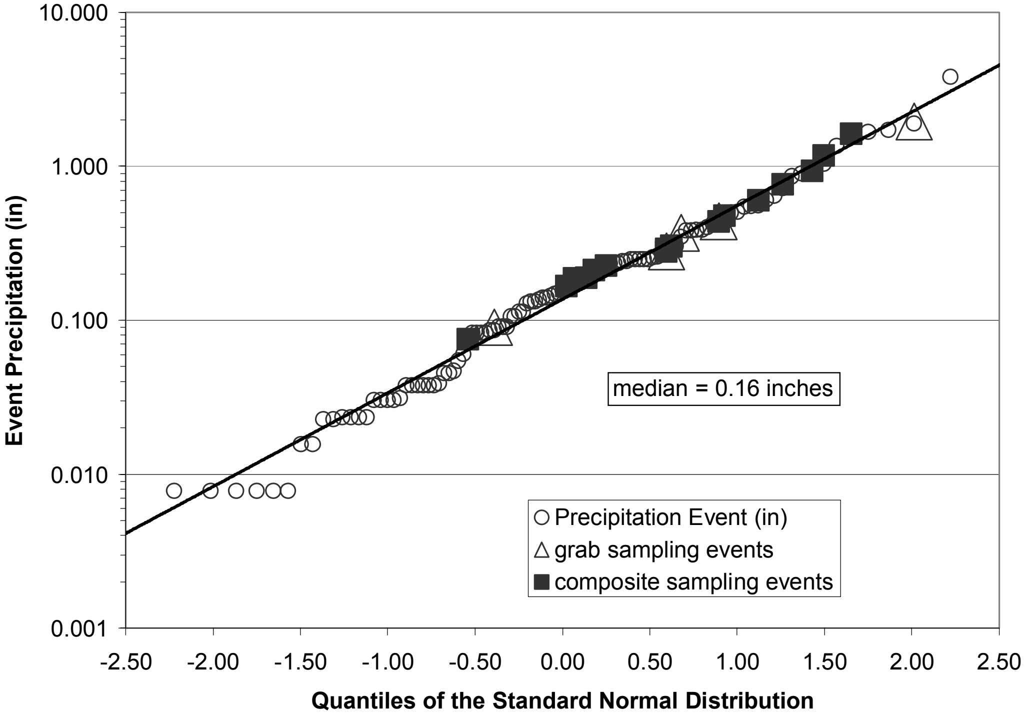


Figure 4-1: Event Precipitation Probability Distribution

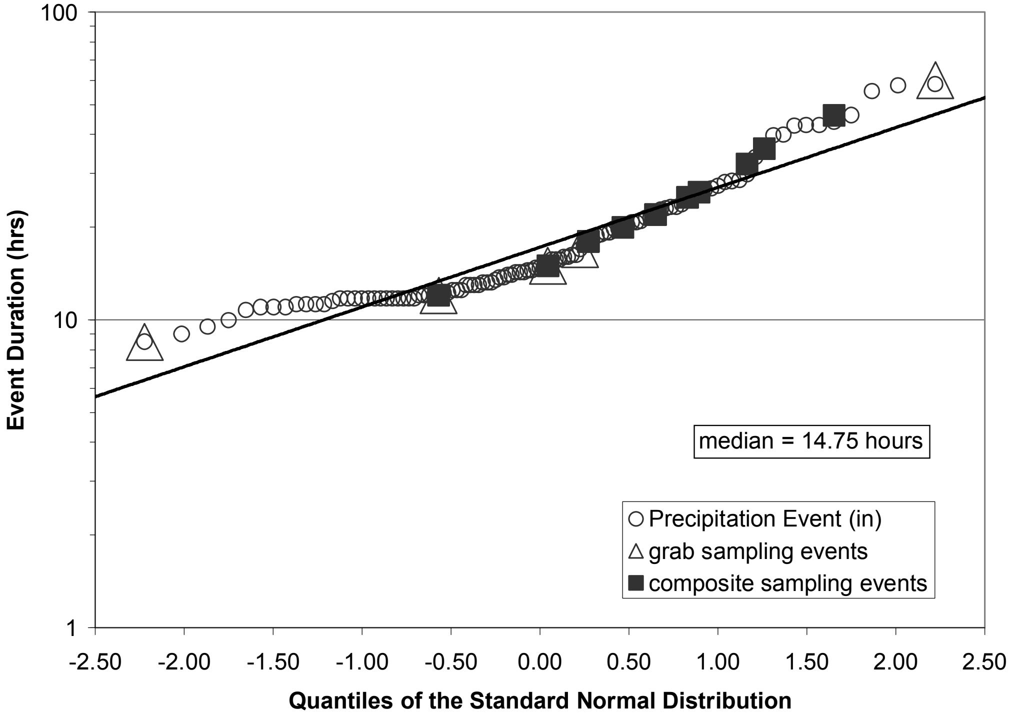


Figure 4-2: Event Duration Probability Distribution

4.2. Water Quality

4.2.1. QA/QC Objectives

The Sampling Analysis Plan (Seattle Public Utilities, 2003) contained several measures to insure accuracy and quality of resulting data. These include various laboratory and field quality control measures and guidelines.

Laboratory duplicate samples were analyzed at or above the frequency of 5% specified in the Sampling Analysis Plan (Seattle Public Utilities, 2003). One of the seventeen laboratory duplicate samples for soluble reactive phosphorus (SRP), from 1/13/03, exceeded the allowable relative percent difference (RPD) of 20% specified in the Sampling Analysis Plan (SAP). Because the RPD was 20.6%, however, the results from this sampling date were accepted and included in this report. No other sample results were listed as estimates and none were rejected.

Method blanks, matrix spikes, and control spikes are used to estimate bias, the degree to which the analytical results reflect the true value of the sample. Laboratory reports contained no comments on method blanks. However, chlorinated pesticides samples from 4/9/03 had a few detections at concentrations near the detection limit for a few of the parameters, but values for blanks did not exceed 2x the reporting limit for any parameters and so this was judged acceptable.

Field duplicate samples were taken twice over the sampling period, once each at the NW120th and NW122nd stations. Dissolved zinc and total lead field duplicate samples from 3/6/04 from the NW120th station exceeded 20% RPD. However, all samples were included in the analysis in this report. Equipment rinsate blanks were also taken above the minimum frequency. No analytes were detected in the equipment rinsate blanks. Appendix D contains summary tables with results from the QA/QC analysis.

Flow data for the 10/28/03 and 1/12/04 events at the NW120th site and for the 10/16/03 and 10/28/03 events at the NW122nd site are missing due to equipment malfunction and/or equipment theft. The grab-sample event on 10/28/03 and the composite-sampling event on 3/6/04 violated the criterion of a minimum of 0.15 inches of precipitation during the event. Samples from these events were included in the analysis even though they violated the criteria because of the lack of smaller storms incorporated in the sampling results. Results from the 3/6/04 and 10/28/03 events aid in characterizing water quality from smaller events. Antecedent and minimum duration requirements were not violated for any sampling event.

Composite and grab sampling was performed in a consistent manner throughout the sampling program. Procedures for sampling station set-up, including ISCO sampler programming, equipment decontamination, and sample preservation, were also consistent. In addition, laboratory holding times were met throughout the project.

4.2.2. Analysis of Sampling Results

4.2.2.1. All Data

Laboratory analytical results for all parameters are shown in Tables A-1 through A-6 (Appendix A). A total of twelve grab samples were taken. Two grab samples were taken at the NW107th station, and five were taken at each of the NW120th and NW122nd stations. A total of thirty-five composite samples were taken. Seven composite samples were taken at the NW107th station, with fourteen taken at each of the NW120th and NW122nd stations. Summary statistics for all parameters over all events are included in Appendix A.

For the dissolved lead and TPH samples reporting non-detected concentrations, one-half the reporting limit was used in statistical analysis involving the data (Kayhanian, 2002). The detection limit for dissolved lead was 1 µg/L and for TPH was 0.1 mg/L. Therefore, values of 0.5 µg/L and 0.05 mg/L were used in the summary statistics for dissolved lead and TPH, respectively. Ten of nineteen total samples for TPH were non-detects for diesel. Sixteen of thirty-four samples for dissolved lead were non-detects. All other parameters were detected in every sample taken.

Solids

Using volumetric concentration data from the PSD analysis, curves of percent finer by volume were constructed for all composite-sample events for all solids less than 250 µm in diameter (Figure 4-3). Very little variation occurs in these parameters, as is evidenced by the percent-finer curves in Figure 4-3 and by the low coefficients of variation (20, 17, and 13% for the d_{10}, d_{50}, and d_{90}, respectively). All curves are very similar in shape, indicating the low variability in the distributions of particle size.

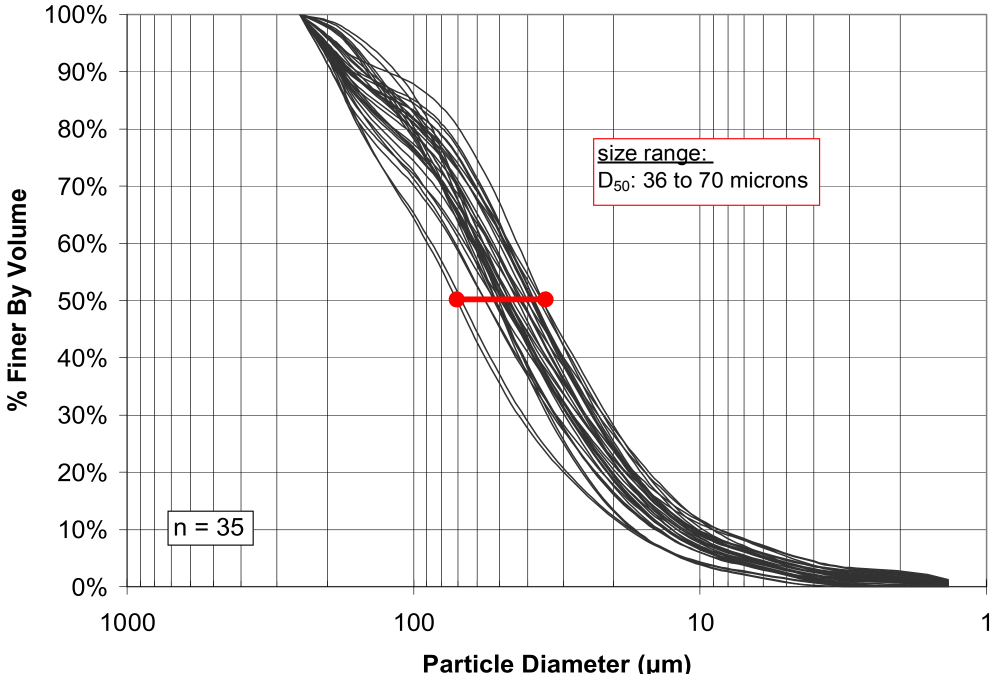


Figure 4-3: PSD for all Monitoring Stations

Two samples have larger d_{50} values and slightly different percent-finer curves than the others. These two samples are from the NW120th and NW122nd monitoring stations from the 3/7/04 event. This event had the lowest total precipitation (0.08 inches), and a lowest maximum intensity (0.03 in/hr) of all events during which composite sampling was performed. Therefore, it is possible that these samples had elevated concentrations of larger particles because high flow velocities were not present to flush the system of larger particles before sampling began.

Figure 4.4 contains box-and-whisker plots that show the variation in concentration (μL/L) within each size bin over all samples. The whiskers characterize the 10th and 90th percentiles, the box shows the 25th and 75th quadrants, and a horizontal line represents the median. The largest concentrations occur in the coarse silt range, with another maximum over the sand range.

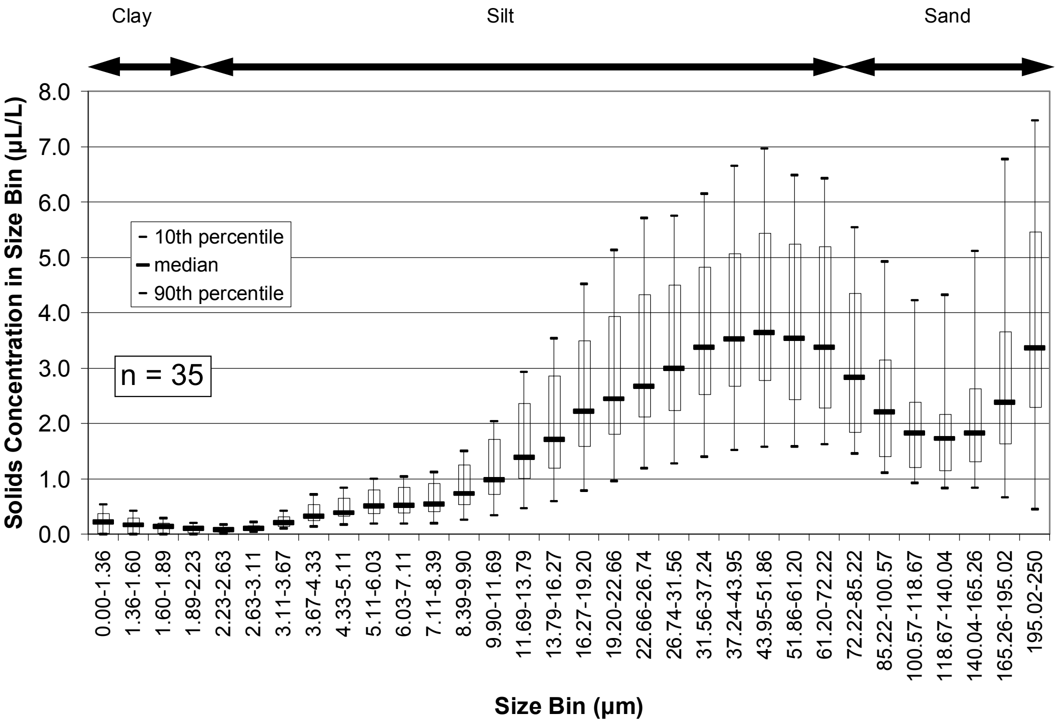


Figure 4-4: Solids Concentration Statistics from the PSD Analyses

Figure 4-5 contains the probability distribution TSS concentrations over the range of composite sampling events and monitoring stations, over the course of the monitoring program. The median value of TSS for this sampling program was 42 mg/L.

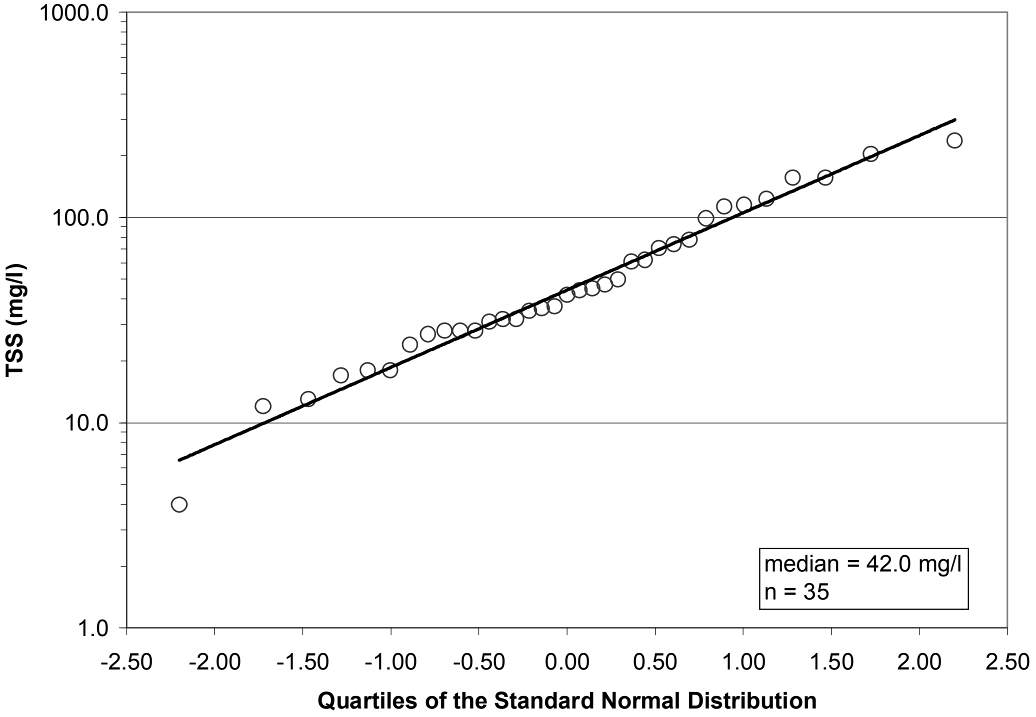


Figure 4-5: TSS Probability Distribution

None of the relationships between TSS and the hydrologic parameters had strong coefficients of determination (R^2) using either linear or log-transformed data in simple linear regression analyses. The log-transformation of the TSS data and maximum event precipitation intensity had the highest R^2 of 0.30 ($p<0.001$) (Figure 4-6). This indicates that the null hypothesis (H_o) must be rejected, and that TSS concentration does increase with maximum event precipitation intensity. Though the linear regression analysis did not show strong relationships between antecedent conditions and TSS concentrations, it is evident from Figure 4-7 that the highest TSS concentrations only occur during events following short dry periods. No significant relationships were found between TSS and any other hydrologic parameter such as total runoff volume or peak flowrate.

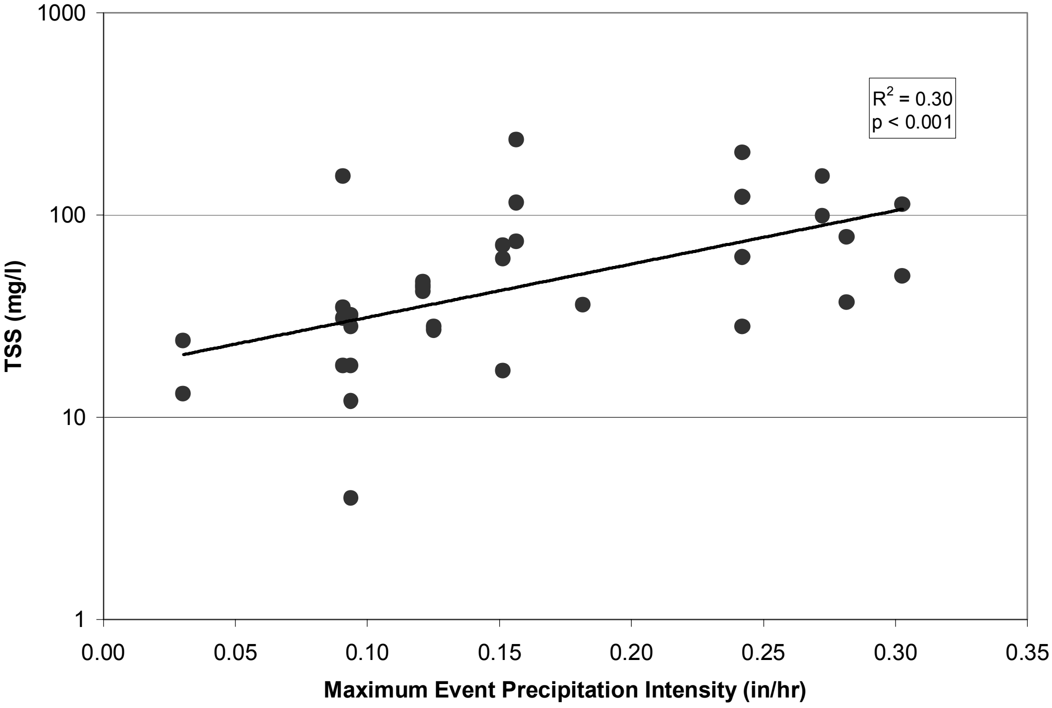


Figure 4-6: Total Suspended Solids and Maximum Event Precipitation Intensity

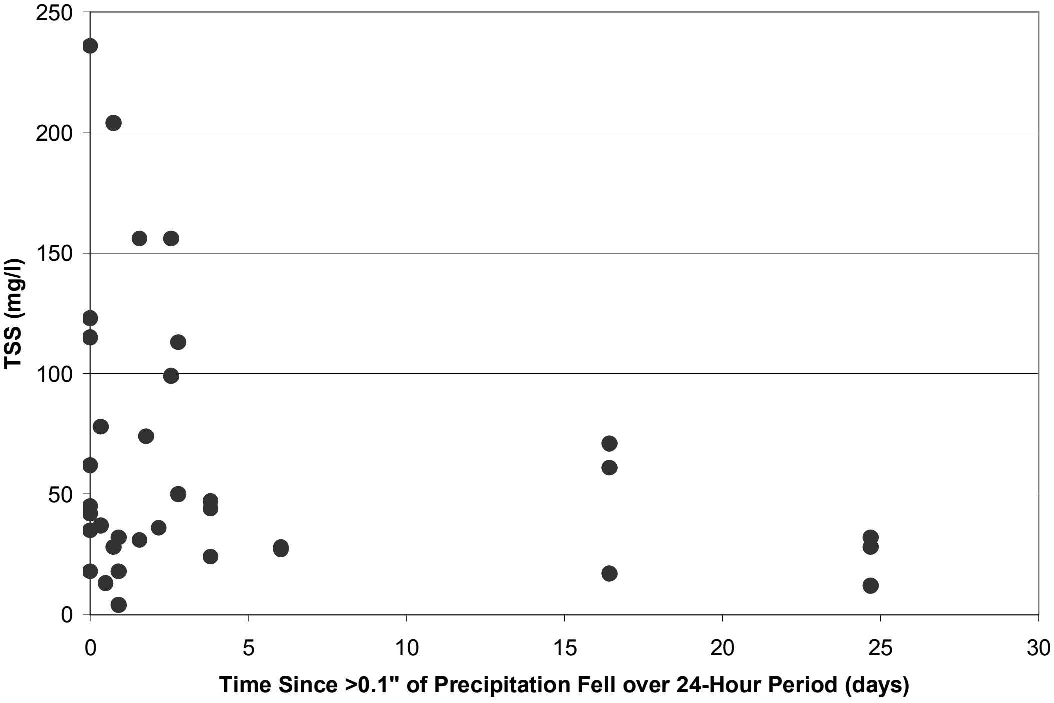


Figure 4-7: Total Suspended Solids and Antecedent Conditions

Data from the PSD analyses were compared to hydrologic data for all parameters listed previously. The most noticeable trends occurred between solids concentrations in the smaller size ranges and antecedent conditions. Figure 4-8 shows how solids concentration data vary with precipitation amount in the seven days (168 hours) prior to the storm event. Though the regression coefficients were not strong, the highest concentrations in these smaller size classifications apparently do not occur under wetter pre-event conditions.

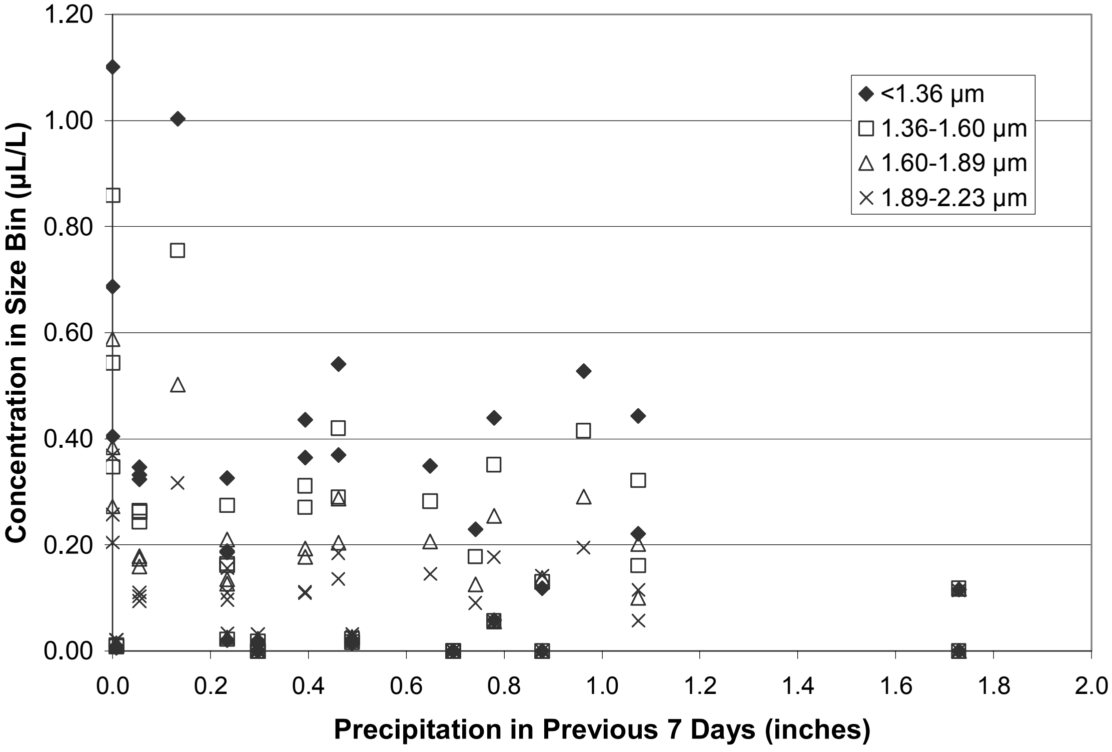


Figure 4-8: PSD and Antecedent Conditions

Solids concentrations and PSD were not found to be related to any other hydrologic parameters other than the precipitation parameters. Relationships between solids parameters and hydrologic parameters such as total runoff volume or peak flowrate were not significant.

Metals

A comparison between the partitioning of copper, lead, and zinc is shown in Figure 4-9. As is typical in urban runoff, a greater fraction of total copper and zinc is present in dissolved form because they are both more soluble than lead.

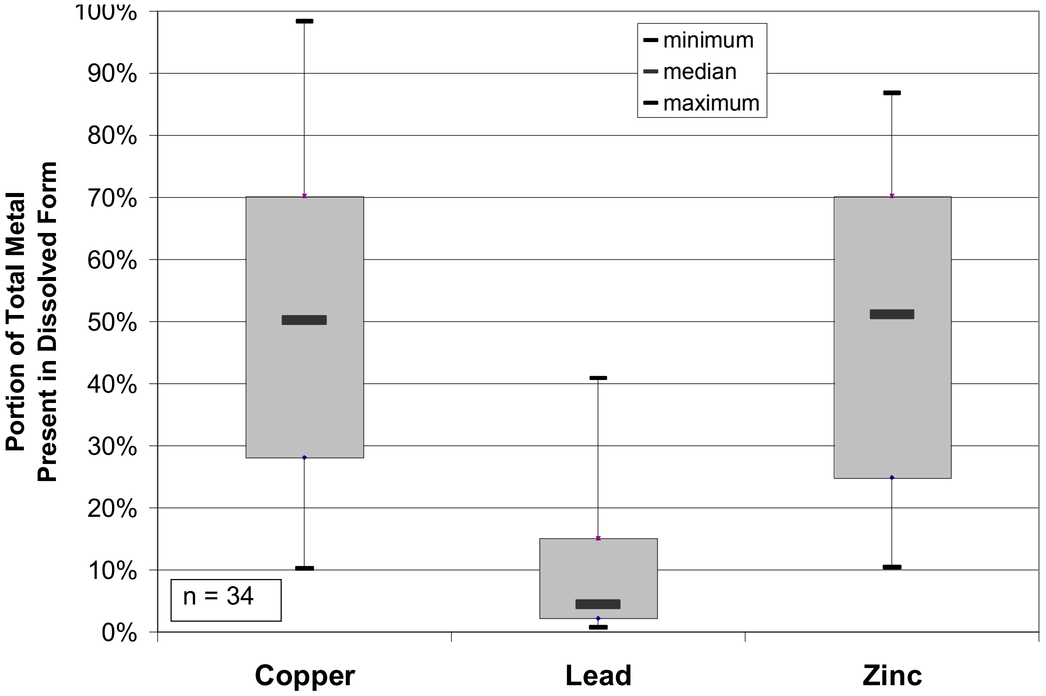


Figure 4-9: Partitioning of Copper, Lead, and Zinc

Figures 4-10 through 4-12 plot the probability distributions of total and dissolved metal concentrations over the range of sampling events. Generally speaking, the log-normal distribution is a good fit for all three parameters, both total and dissolved. Note the outlier of 14.2 μg/L for dissolved lead from 1/13/04 at the NW122nd site.

Several values for dissolved lead (Figure 4-11) are below the detection limit of 0.5μg/L specified in the sampling analysis plan. Results from samples analyzed by the Manchester Laboratory were occasionally expressed in concentrations below this value because analyses were performed to a lower limit of detection. Multiple samples at

0.5μg/L reflect one-half of the minimum detection level that applied to a majority of the samples.

Metals toxicity depends on hardness of stormwater runoff, which is expressed as mg/L of $CaCO_3$. Dissolved metals data were used in combination with hardness data in order to quantify the toxicity of each metal in comparison with published water-quality standards. Figures 4-10, 4-11, and 4-12 show how the analytical results for metals compare to State of Washington surface-water criteria for the protection of aquatic life (Washington State Department of Ecology, 2004; Washington State Standards Metals Criteria, WAC 173-201A), which are in terms of concentration of dissolved metal. These toxicity criteria were calculated based on a hardness value of 15.4 mg/L as $CaCO_3$, which is the median hardness of all samples analyzed during this effort. Appendix E contains graphical representation of how toxicity criteria vary with hardness, and how samples from this sampling effort compare to the published criteria. The equations for calculating acute and chronic toxicity based on hardness are included in Appendix E.

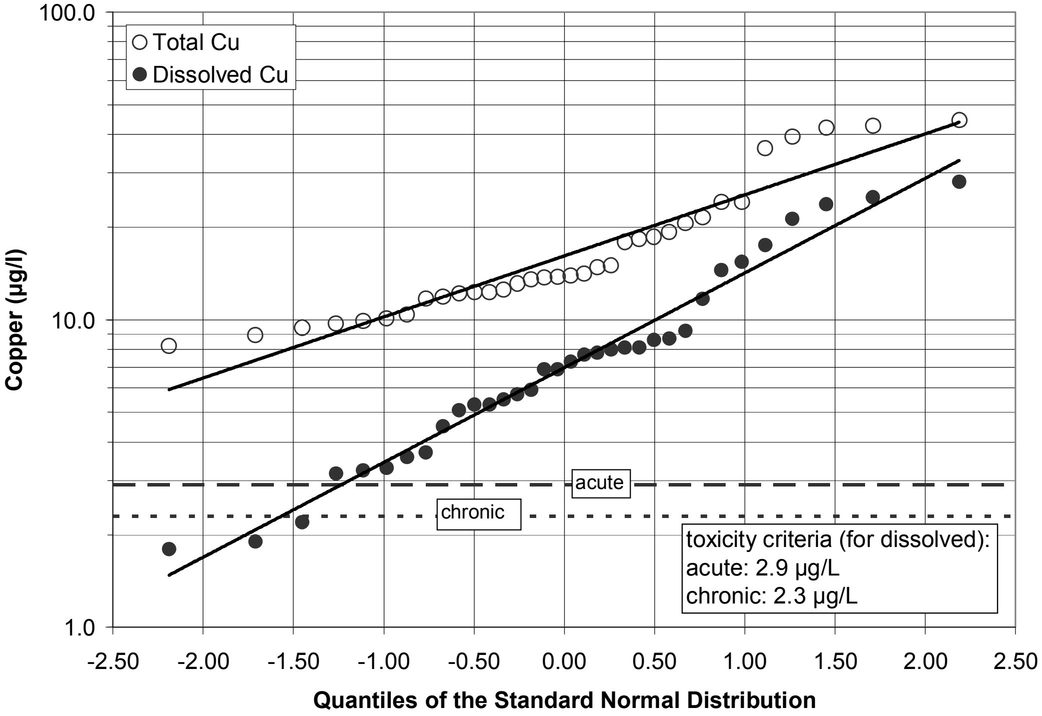


Figure 4-10: Probability Distributions of Total and Dissolved Copper

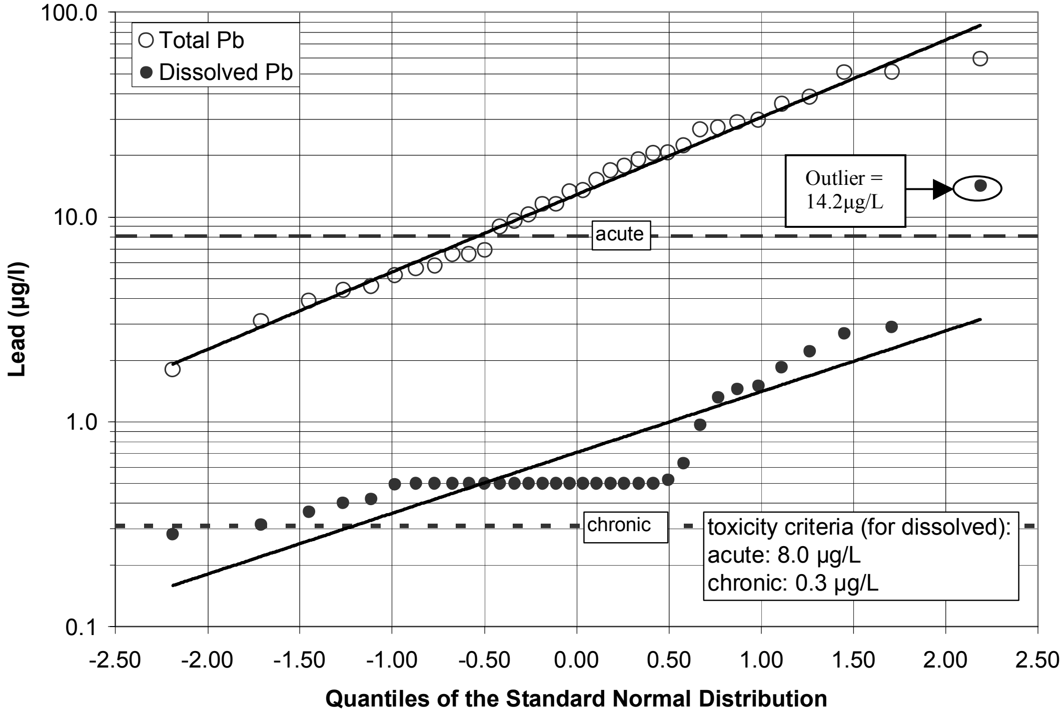


Figure 4-11: Probability Distributions of Total and Dissolved Lead

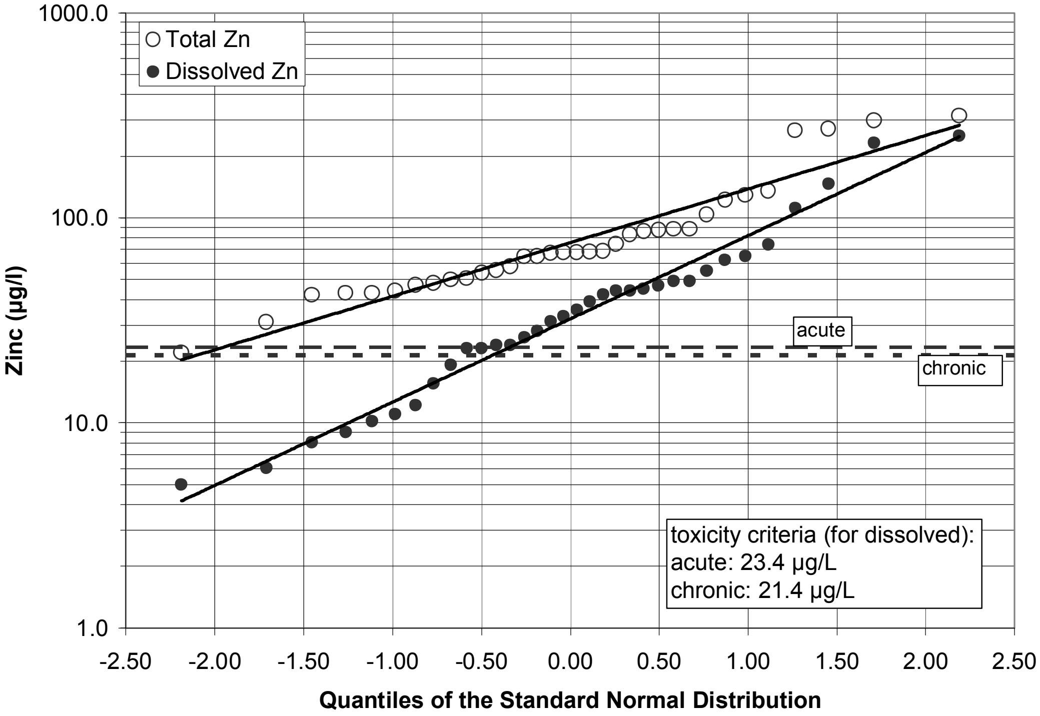


Figure 4-12: Probability Distributions of Total and Dissolved Zinc

Figures 4-10 through 4-12 show that a majority of dissolved copper results were above the acute and chronic toxicity criteria calculated based on the median hardness. For dissolved lead, all but the outlier of 14.2 µg/L were below the acute toxicity criteria. However, most samples analyzed for dissolved lead were above the chronic toxicity criteria. Almost all of the dissolved zinc samples were above both the acute and chronic toxicity concentrations.

Acute and chronic toxicity criteria were also calculated based on the hardness values for each composite event. These criteria were then compared with the corresponding dissolved metals concentrations from the same event. Table 4-1 includes a description of the frequency that dissolved metals concentrations exceeded the calculated acute and chronic toxicities.

Table 4.1: Frequency of Acute and Chronic Metals Toxicity Criteria Exceedances

Metal Parameter	Acute Toxicity Criteria, frequency of exceedance	Chronic Toxicity Criteria frequency of exceedance
Copper, dissolved (n=34)	32 of 34, 94%	34 of 34, 100%
Lead, dissolved (n=34)	0 of 34, 0%	31 of 34, 91%
Zinc, dissolved (n=34)	23 of 34, 68%	24 of 34, 71%

Total and dissolved metal concentrations along with metals partitioning data were compared to hydrologic data. The various measures of antecedent conditions were the only hydrologic parameters to have significant effects on most, if not all, of the metals parameters. Table 4-2 contains R^2 and p-values for the linear regressions for antecedent conditions and metal parameters; the sign of the correlation coefficient (R) gives the direction of slope. For these analyses of hydrologic data and metals data relationships, the outlier of 14.2 µg/L of dissolved lead was removed from the analysis because it was greater then five standard deviations away from the mean of 1.21µg/L.

Table 4.2: Linear Regression Analyses, Metal Parameters and Hydrologic Parameters

Dependent Metal Parameter	Independent Parameter: Precipitation total in the 7 days previous to start of event (inches)	Independent Parameter: Time since 48-hour precipitation total reached 0.1” (days)
Copper, total	$R^2 = 0.02$, $p=0.41$, $R<0$	**$R^2 = 0.26$, $p<0.005$, $R>0$**
Lead, total	**$R^2 = 0.19$, $p<0.05$, $R>0$**	$R^2 = 0.06$, $p=0.17$, $R<0$
Zinc, total	$R^2 = 0.10$, $p=0.075$, $R<0$	**$R^2 = 0.45$, $p<0.0001$, $R>0$**
Copper, dissolved	**$R^2 = 0.24$, $p<0.005$, $R<0$**	**$R^2 = 0.63$, $p<0.0001$, $R>0$**
Lead, dissolved	**$R^2 = 0.24$, $p<0.005$, $R<0$**	**$R^2 = 0.51$, $p<0.0001$, $R>0$**
Zinc, dissolved	**$R^2 = 0.16$, $p<0.05$, $R<0$**	**$R^2 = 0.43$, $p<0.0001$, $R>0$**
Copper, % of total as dissolved	**$R^2 = 0.22$, $p<0.005$, $R<0$**	**$R^2 = 0.18$, $p<0.05$, $R>0$**
Lead, % of total as dissolved	**$R^2 = 0.22$, $p<0.005$, $R<0$**	**$R^2 = 0.32$, $p<0.0005$, $R>0$**
Zinc, % of total as dissolved	**$R^2 = 0.17$, $p<0.05$, $R<0$**	$R^2 = 0.07$, $p=0.12$, $R>0$

BOLD = slope of regression is significant

For most of the metals parameters, a significant slope exists with the antecedent parameters. For all metals parameters except for total lead, the value of R is negative with the parameter of total precipitation in the previous seven days, indicating a decreasing metal concentration with increasing precipitation in the previous 168 hours. Positive R-values for all metals parameters except for total lead indicate that metals parameters increase as the time increases since 0.1-inches of precipitation occurred. The response of total lead concentrations is similar to that of TSS concentrations for antecedent parameters, where the greatest concentrations occur during events with the shortest dry period beforehand (Figure 4-7). Figure 4-13 shows the relationships between dissolved copper and total precipitation in the previous seven days, as an example of the results given in Table 4.2.

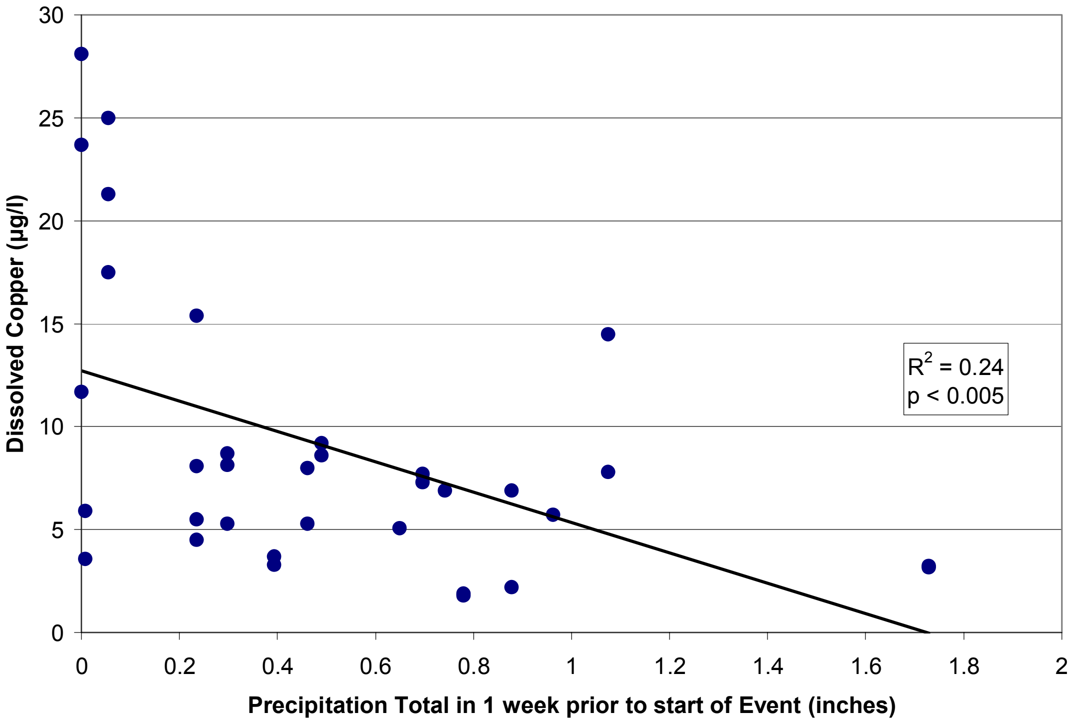


Figure 4-13: Dissolved Copper and Antecedent Conditions

In addition to the general relationships between antecedent conditions and metals concentrations and partitioning, individual metal parameters showed significant relationships with various other hydrologic parameters. The partitioning of metals into total and dissolved forms showed a significant relationship with maximum event precipitation intensity. Table 4.3 contains the linear regression R^2 values, p-values, and sign of the R values for metals partitioning versus maximum event precipitation intensity. A log-normal transformation was employed in this analysis, which provided a better fit for the data. Once again, the outlier of 14.2 µg/L of dissolved lead was removed from the analysis.

In each case listed in Table 4.3, a significant downward trend exists for the partitioning of total metal into the dissolved phase. That is, as event precipitation intensity increased, so did the portion of total metal present in particulate form. Figure 4.14 shows this trend for copper partitioning.

Table 4.3: Linear Regression Analyses, Precipitation Intensity and Metals Partitioning

Dependent Parameter, Metal Partitioning	Independent Parameter, Maximum Event Precipitation Intensity (in/hr)
Copper, % of total present as dissolved	**R^2 = 0.39, p<0.0001, R<0**
Lead, % of total present as dissolved	**R^2 = 0.18, p<0.05, R<0**
Zinc, % of total present as dissolved	**R^2 = 0.16, p<0.05, R<0**

BOLD = slope of regression is significant

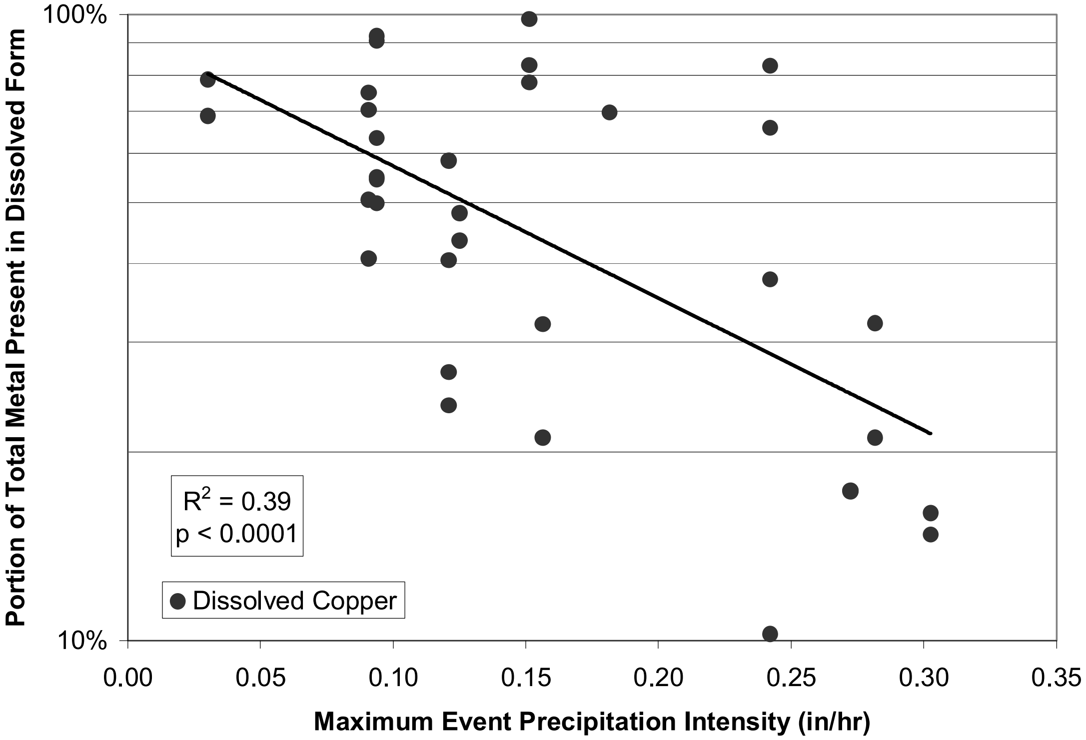


Figure 4-14: Copper Partitioning and Maximum Event Precipitation Intensity

Metals concentrations and partitioning were not found to be related to any other hydrologic parameters other than the precipitation parameters. Relationships between solids parameters and hydrologic parameters such as total runoff volume or peak flowrate were not significant.

Metals and solids parameters

Total, dissolved, and metal-partitioning parameters were compared to parameters describing solids in stormwater runoff. Total metal concentrations were compared to TSS concentrations over all sampled events in order to quantify the relative dependence of metals concentrations on TSS. Linear regressions are presented in Figure 4-15 for total copper ($R^2 = 0.15$, $p<0.05$) and total lead ($R^2 = 0.56$, $p<0.00001$). Total zinc was not found to be significantly dependent on TSS ($R^2 = 0.01$, $p=0.77$).

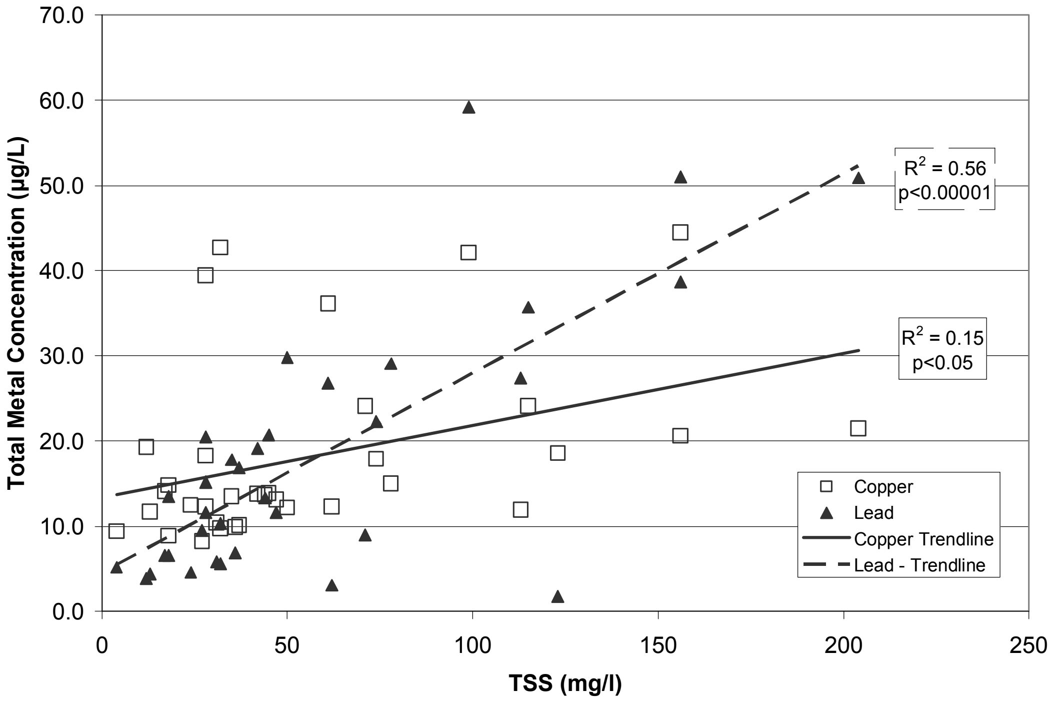


Figure 4-15: Total Metals and Total Suspended Solids

Total copper and total lead parameters were significantly correlated with TSS, with total lead the most significantly related to TSS. Lead tends to be particulate-bound, as it is the least soluble of the three metals.

While TSS was not significantly correlated with all total metals, significant correlations were found for all three metals in terms of metals partitioning. A log-normal transformation was used here because it provided a better fit for the data. Figure 4.16 shows the log-transformations and linear regressions for the metals partitioning data and TSS. It is notable that in the case of all three metals, significant negative correlations exist. As TSS increases, the fraction of total metal in particulate form increases.

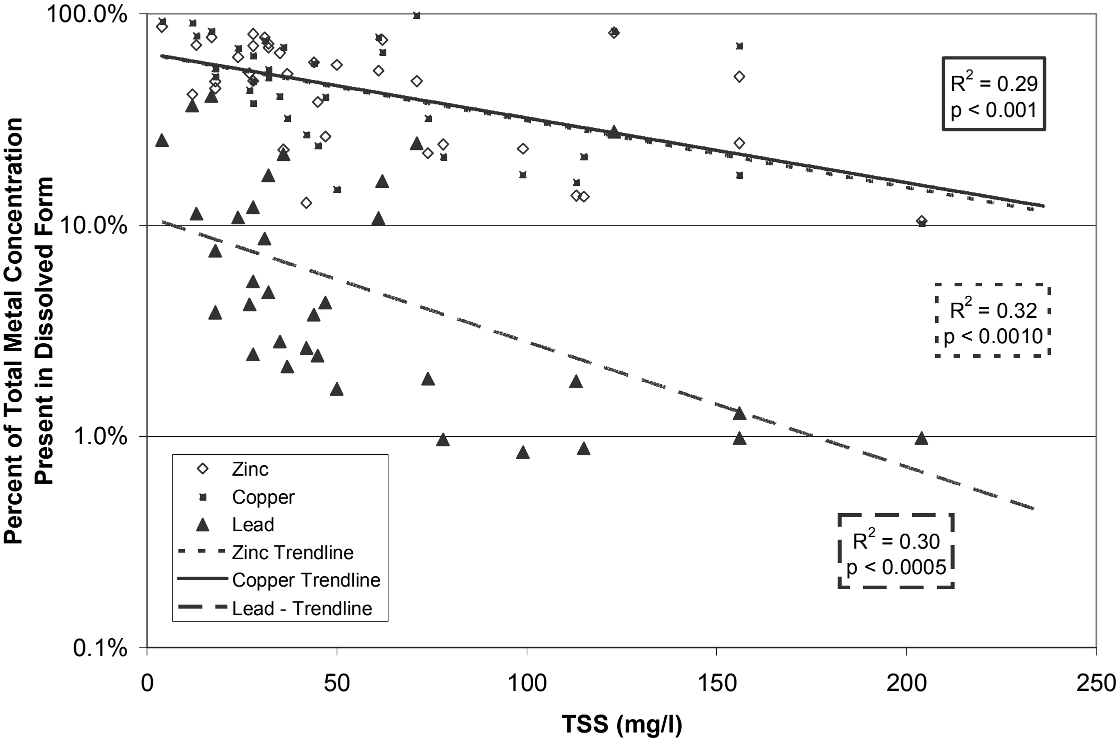


Figure 4-16: Metals Partitioning and Total Suspended Solids

Particulate, dissolved, and metals partitioning data were also compared to results from the PSD analysis. Linear regressions were performed to quantify their dependences on concentrations of solids in each of the size ranges as identified during the PSD analysis.

An R^2 and p-value were calculated for each linear regression between each metal parameter and solids concentration from each size bin. As an example, Figure 4-17 shows the linear regression for particulate zinc and concentration of particles in the 61.2-72.2 µm size bin. Note the low R^2 of 0.004 and high p-value of 0.71 associated with this regression.

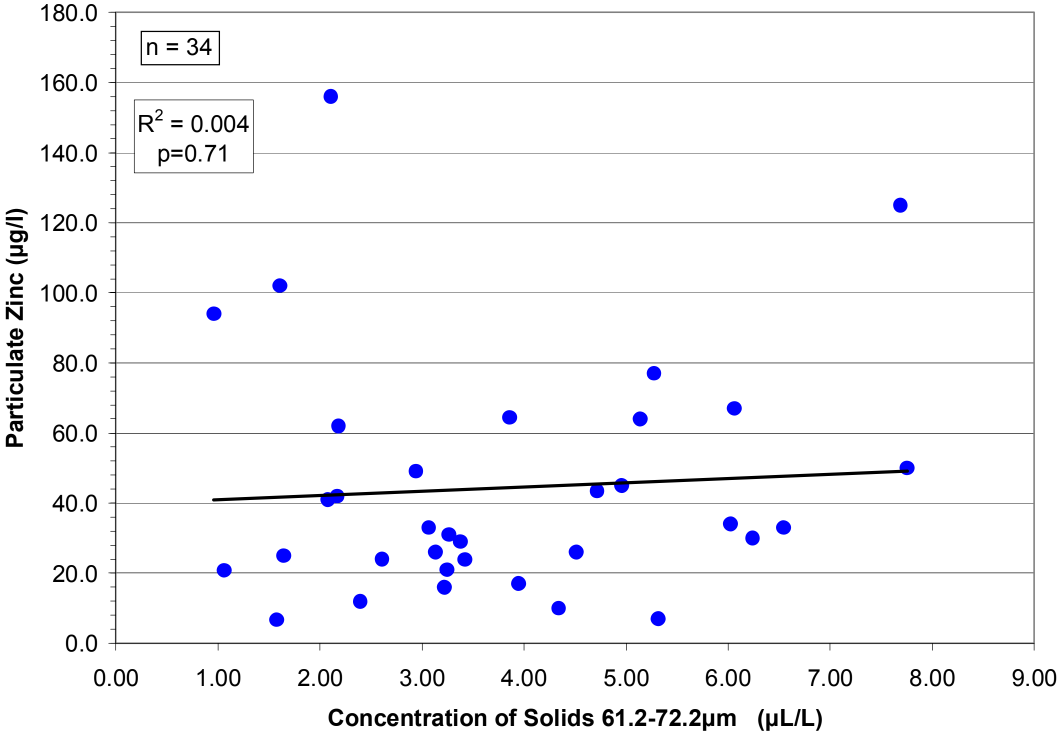


Figure 4-17: Linear Regression, Particulate Zinc and Concentration of Solids 61.2-72.2µm (not significant)

Two other example regressions shown in Figures 4-18 and 4-19, indicate increasingly stronger relationships. A higher R^2 of 0.10 and lower p-value of 0.06 exist between particulate zinc and solids 1.6-1.89 µm (Figure 4-18), with an even higher R^2 of 0.11 and lower p-value of <0.05 for particulate zinc and solids in the smallest size bin of <1.3 µm (Figure 4-19).

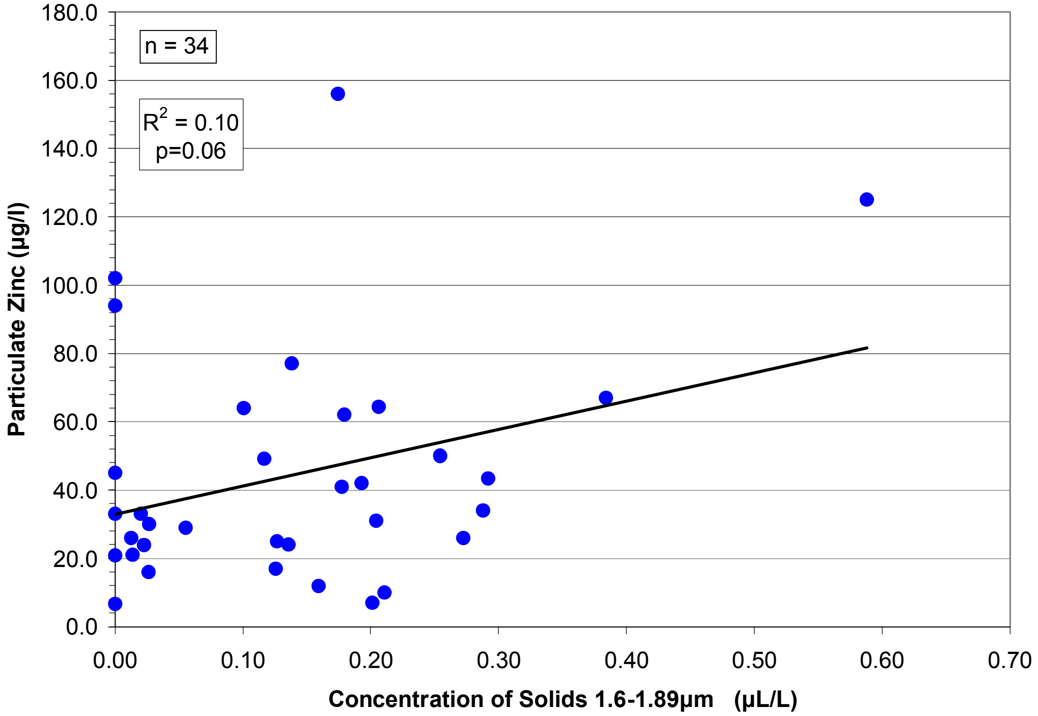


Figure 4-18: Particulate Zinc and Concentration of Solids 1.6-1.89 µm (not significant)

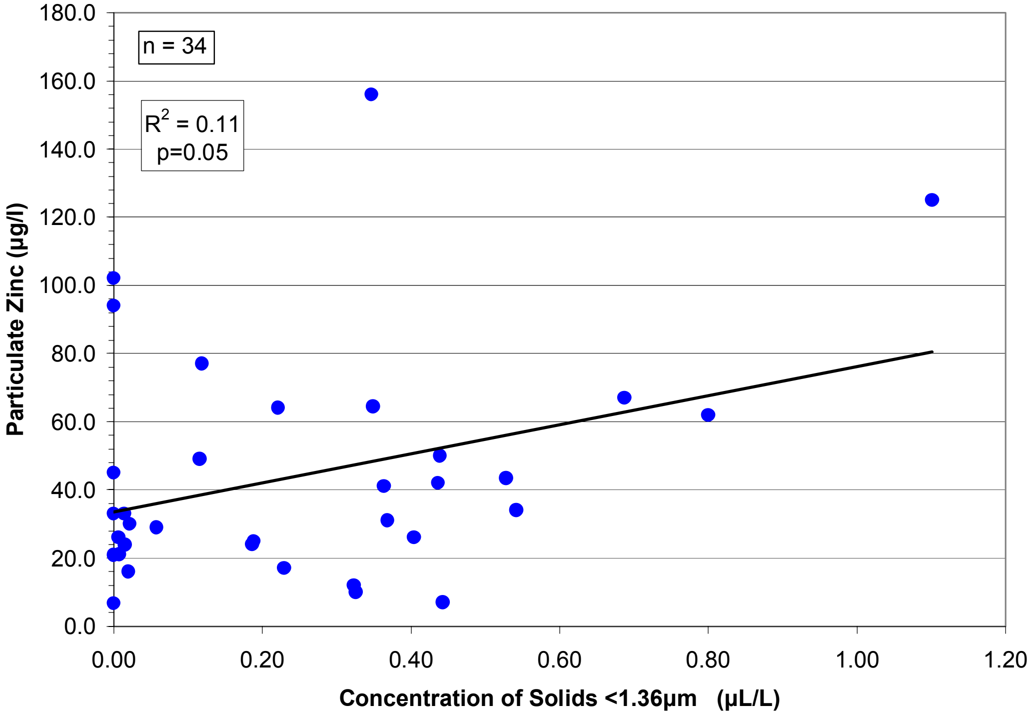


Figure 4-19: Particulate Zinc and Concentration of Solids <1.36 µm (significant)

Figures 4-17, 4-18, and 4-19 represent three linear regressions with increasing R^2 and decreasing p-values with decreasing size of solids. This series of three graphs suggests that particulate zinc concentrations are more dependent on concentrations of smaller particles than larger particles.

The R^2 values from regressions in Figures 4-17, 4-18, and 4-19, together with R^2 values from the linear regressions with solids concentrations from the other size bins, were graphed alongside one another in bar-graph format for dissolved zinc and particulate zinc in Figure 4-20. The trend suggested by comparing Figures 4-17, 4-18, and 4-19, is more completely displayed in Figure 4.20: R^2 values are largest for the smallest particle sizes for both dissolved and particulate-bound zinc, although a secondary peak occurs in the coarse silt range, mirroring the peak in PSD for all samples in that same size range (Figure 4-4). Figures 4-21 and 4-22 show similar plots for dissolved and particulate copper and particulate lead. Copper shows different trends than zinc. Where both dissolved and particulate-bound zinc R^2 values were largest for the smallest size classes, only dissolved copper shows this trend. Again, a secondary peak occurs in the coarse silt range. Particulate copper does not show this trend. In fact, the largest R^2 values correspond to the largest concentrations of solids found through the PSD analyses. Particulate lead shows no noticeable trend with R^2 values barely detectable. Dissolved lead shows the same trend as dissolved copper and dissolved zinc, though particulate lead shows no obvious trend.

The R^2 values for dissolved metal concentrations vary between metals and by size more so than do either of the other types of metals parameters, and they each show distinctive trends in generally decreasing dissolved metal R^2 with increasing particle size. For each dissolved metal parameter, the strongest R^2 values were for the smallest size classes of silt and clay, with a secondary peak in R^2 values in the coarse silt range.

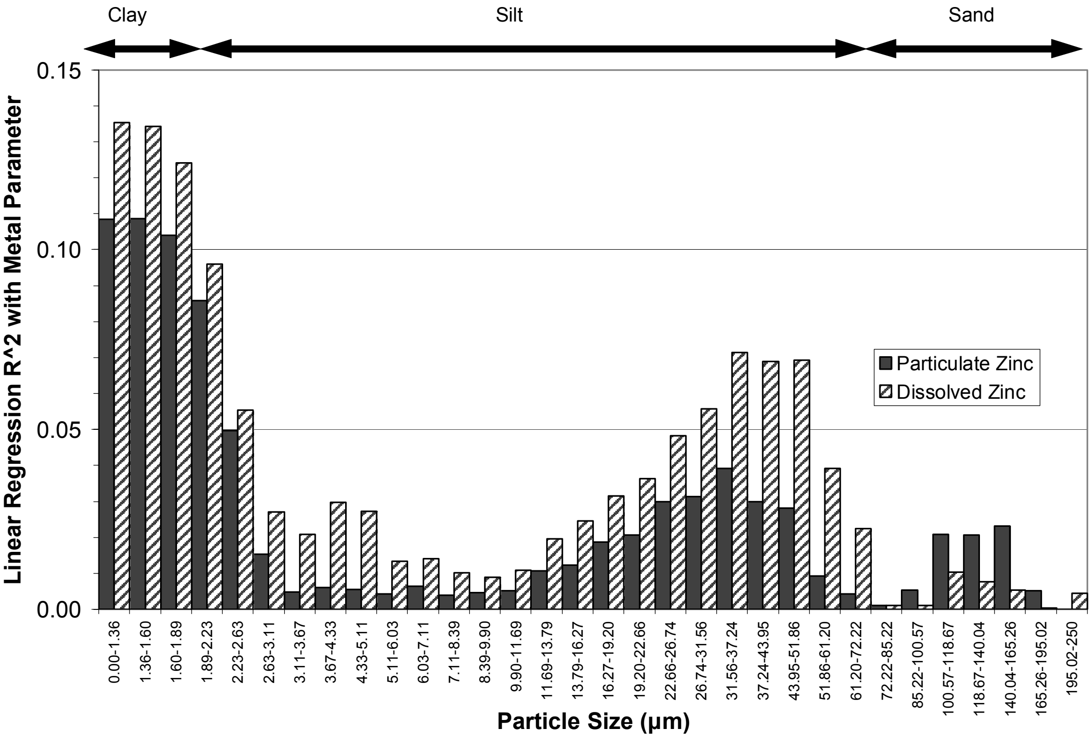


Figure 4-20: Linear Regression Analyses: PSD and Zinc

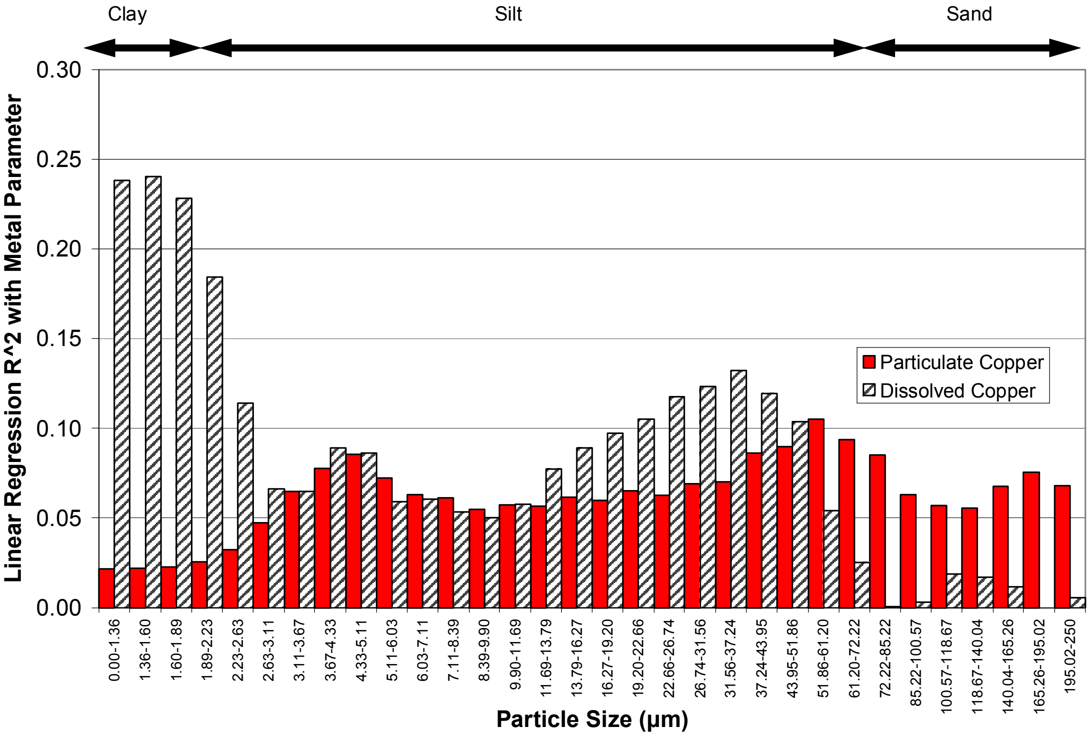


Figure 4-21: Linear Regression Analyses: PSD and Copper

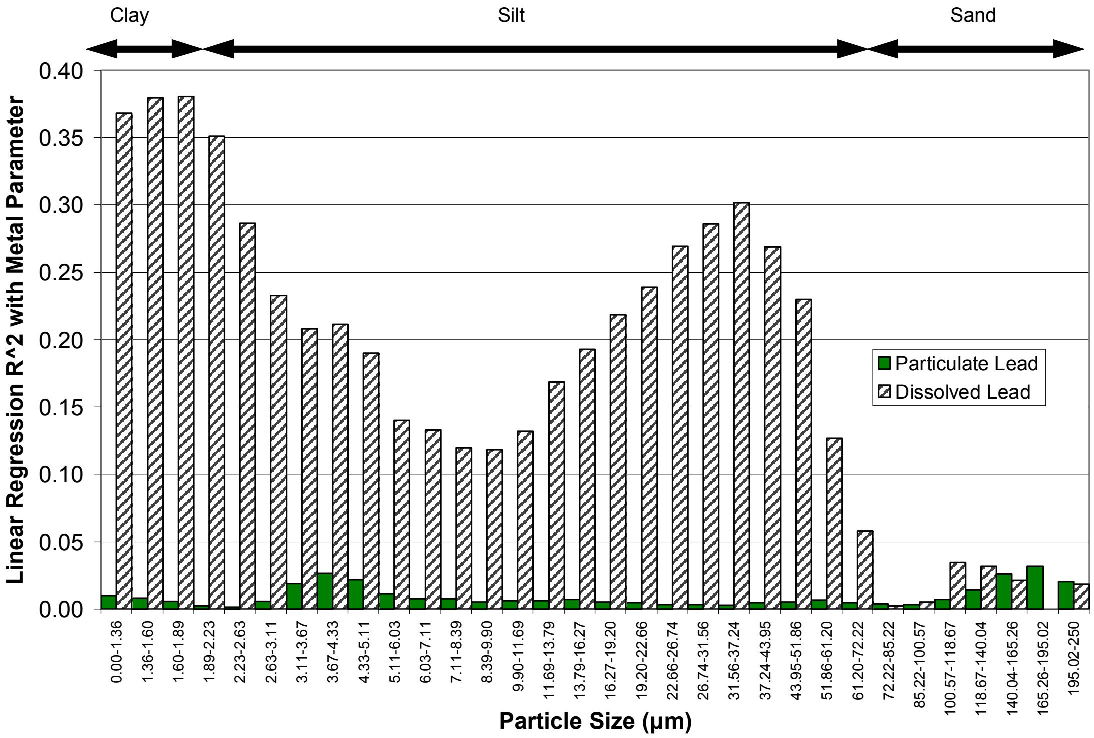


Figure 4-22: Linear Regression Analyses: PSD and Metals Lead

4.2.2.2. Paired Data

Comparisons of parameters between upstream (NW122nd) and downstream (NW122nd) stations were conducted at a level of significance of 0.05. The results indicate that total zinc shows a significant difference between upstream and downstream stations, with the NW122nd site higher than the NW120th site (Figure 4-23). No other parameters were significantly different between the two sites. The only other parameter that is close to significantly different is dissolved zinc, with $0.05<p<0.10$ (Figure 4-23). Just like with total zinc, the NW122nd site concentrations were higher than the NW120th concentrations for dissolved zinc. Appendix F contains the detailed calculations for these statistical tests.

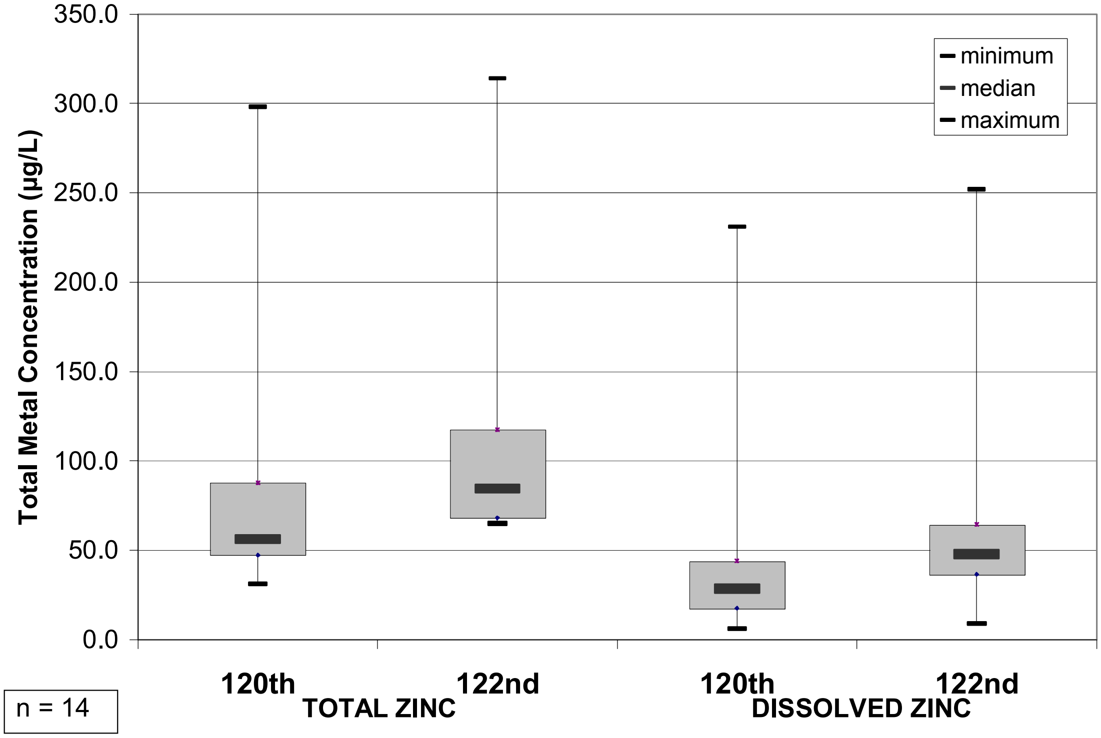


Figure 4-23: Paired study, statistically different parameters

5. Discussion

The results of the hydrologic and water-quality sampling performed as part of this research indicate significant hydrologic effects on water-quality parameters. In addition, solids concentrations are related to various metals parameters, which include total metals, dissolved metals, and metal partitioning between dissolved and particulate-bound fractions. Lastly, significant differences are evident between concentrations of certain constituents at different monitoring locations upstream and downstream of grass-lined culverts within the same catchment.

5.1. Solids Concentrations in Stormwater Runoff

TSS concentrations are affected by precipitation intensity and antecedent conditions. TSS concentrations increase with increasing maximum event precipitation intensity, presumably because higher rates of runoff induce erosion and wash-off of accumulated solids on catchment surfaces, which in turn increase TSS concentrations in runoff. In addition, increased velocities and turbulent flows maintain suspension of larger particles, which is reflected in higher TSS concentrations.

TSS is also related to the length of dry period before the wet-weather event. The largest TSS concentrations were found to occur during events with the shortest dry periods preceding them (Figure 4-7). This is not consistent with a hypothesis of longer dry periods causing more accumulation of solids on catchment surfaces. Winter conditions in the Puget Sound Lowlands often consist of back-to-back precipitation events of long duration and low intensity with little break between them. Six of the eight values for TSS over 100 mg/L occur during November, December, and January, which may explain the high TSS concentrations even under relatively short antecedent dry periods. The highest TSS value of the group is from the NW107th station on 5/15/03, which was a hydrologic event with a short duration and relatively high intensity following a series of similar events. Though this event occurred in the springtime, it followed a pattern typical of winter conditions in the area. Consistent wet-weather conditions can provide the transport capacity for a large amount of solids regardless of accumulation rates based on length of effective dry period.

Concentrations of particles in the smallest size classifications from the PSD analyses depend upon hydrologic parameters in the same manner as TSS concentrations. The greatest concentrations of solids in the smallest size classes occurred during events with the least precipitation occurring in the week prior to the start of the event. Again, the longer the dry period is before a wet-weather event, the greater the potential for solids accumulation on surfaces.

5.2. Metals Concentrations and Partitioning in Stormwater Runoff

Metals concentrations and partitioning are dependent upon hydrologic factors such as event precipitation intensity and antecedent conditions. A longer dry period before a wet-weather event allows for accumulation of metals on catchment surfaces. All dissolved metal parameters as well as total copper and total zinc are statistically dependent upon the parameter of days since the 48-hour precipitation total reached 0.1-inch. All dissolved metal parameters are statistically dependent on length of dry period before an event. As the precipitation total in the previous week increases, the dissolved concentrations of all three metals decrease significantly as do the portions of metals present in dissolved form. Generally speaking, the greater amount of precipitation occurring previous to the event, the fewer total and dissolved metals accumulated and the lower the fraction of total metal that was present in dissolved form. Increasing maximum event precipitation intensity also significantly reduces the portion of total metal present in dissolved form, presumably because mobility of particulates is increased with increased runoff, permitting a greater transport of non-dissolved metals.

Variation in results from many of the regression analyses highlight the differences among the three metals discussed in this report. Total lead, dissolved copper, and the partitioning of copper and zinc were all found to be dependent upon both precipitation intensity and precipitation in the week previous to the event. These results indicate that lead reacts differently than copper or zinc in an aqueous environment. Lead is most often particulate-bound in an aqueous environment. However, copper and zinc are more soluble and therefore most often in dissolved form (Figure 4-9). This characteristic of lead to be particulate-bound means that if even a small amount of total lead is present in runoff, most of that lead will find the sorption sites available on the solids. Also, not only could any existing lead sorb onto particles, but particles entering into the runoff could effectively transport a large amount of lead with them. In contrast, copper and zinc can be both associated with particles and dissolved within the water column, and are also more susceptible to disassociation from particulate form into dissolved form given the correct environmental conditions.

5.3. Interactions of Solids and Metals in Urban Stormwater Runoff

Each of the three metals discussed in this research interact in different ways and to different extents with particles of different sizes in stormwater runoff. With a majority of total lead present in runoff being associated with particles due to lead's relatively low solubility, it is conceivable that solids concentrations would have more of an effect on total lead than they would on total copper or total zinc. Since on average less than one-half of total copper and zinc were found to be particulate-bound in samples from this research, mechanisms affecting dissolved concentrations and metals partitioning would be much more obvious for copper and zinc than for lead.

The relevancy of this difference between lead and the other metals copper and zinc is quite significant. More variability exists for partitioning and dissolved concentrations of copper and zinc than for lead. In theory, therefore, it is possible to force copper and zinc into particulate-bound form from dissolved form depending on hydrologic and solids parameters. While changing precipitation amount or intensity is not possible, changing peak flows and runoff volumes is possible through mitigation efforts like reduction of impervious surface. Targeting certain sizes of particles for removal may be a method to remove certain types of metals and also certain portions of any one metal in either dissolved or particulate form. With the potential for zinc and copper to be present either in particulate or dissolved form, it is important to include allowances for removal of these metals in stormwater mitigation efforts.

Increasing TSS concentrations provide additional surface area onto which metals can bind and therefore decrease the dissolved fraction of total metal present in urban runoff. The partitioning parameters of all three metals were found to be statistically dependent upon TSS concentrations. In the case of copper, lead, and zinc, the portion of metal present in dissolved form decreases with increasing TSS concentration. This is consistent with the findings of Garnaud and others (1999), Sansalone and Buchberger (1997), and Stone and Marsalek (1996), who also found that dissolved meal concentrations tend to decrease slightly with increasing TSS. However, no significant trends of decreasing dissolved metal concentrations with increasing TSS were found in this study.

TSS concentrations can also affect the total concentrations of metals present in stormwater runoff. Total copper and total lead were found to increase with increasing TSS at statistically significant levels, with the relationship between total lead and TSS being the most significant ($p<0.00001$). The general trends of total metal concentrations increasing with solids concentrations indicate that solids are indeed a pathway for metals to enter runoff streams by providing potential sorption sites (Chebbo and Bachoc, 1992). Total zinc did not show a statistically significant positive slope with increasing TSS. This can be attributed to the fact that zinc is most often associated with the smallest particles which do not contribute a significant amount of mass to TSS.

Total metals concentrations increase and the portion of total metal present in dissolved form decreases with increasing TSS. It is unclear, however, if additional metals brought into the runoff with TSS actually just added particulate metal and did not change the concentration of dissolved metal. This would have the effect of not changing the dissolved concentration, only the fraction of the total present in dissolved form because of the increase in particulate-bound metal.

TSS is only a measure of total mass of particles, which does not accurately describe the true potential for the solids present to act as "carriers" of constituents such as metals in stormwater runoff. Since the concentration and partitioning of metals in stormwater depend more on total surface area rather than mass, it is preferable to relate metals parameters to either total effective surface area on particles or to volume of smaller particles, which contribute the greatest surface-area-to-volume ratio of any size group of particles.

Metals are associated with the smallest particles in urban stormwater runoff because of the higher surface-area-to-volume ratio for smaller particles. The relatively large surface areas of smaller particles act as reservoirs for metals. Even though small particles may represent only a fraction of the total volume of solids in runoff, they can significantly contribute concentrations of other constituents (Sansalone et al., 1998; Grout et al., 1999). Though the smallest particles contribute the greatest amount of surface area per unit volume, a large concentration of solids of any size class will also do the same. In this research, the greatest concentrations of solids were within the coarse silt range of approximately 40-60 µm. The median concentrations of these particles were approximately 4x that of the median concentrations in the smallest size fractions.

Particulate metals parameters show varying strengths of relationships to concentrations of solids in the smaller size classifications from the PSD analysis. Particulate lead is not significantly related to concentrations of smaller particles. This is because particulate lead is associated with larger particles represented in the TSS parameter and not in the smaller particles. Particulate copper is most strongly associated with particles in the coarse silt range, which coincides with the PSD results with the greatest concentrations of solids in that range. This is consistent with other research involving copper in stormwater runoff, with copper most often associated with organic particles of that size range, and not with smaller particles (Wang, 1981). Particulate zinc, however, is most often found associated with small particles, such as those in the smallest size ranges of the PSD analyses from this research (Characklis and Wiesner, 1997). This is evident in the trend of the strongest relationships between particulate zinc and solids concentrations occurring in the smallest size bins.

The strongest relationships exist for all three of the dissolved metals and solids concentrations in the smallest size bins, with the strength of the relationship decreasing with increasing particle size (Figures 4-20, 4-21, and 4-22). This result was not expected. Rather, the partitioning parameters were expected to depend upon concentrations of solids in the smaller size bins because of their large surface-area-to-volume ratios providing sorption sites for metal ions which would have otherwise been dissolved. However, relating partitioning of metals and concentrations of these solids showed no significant relationships and no trend between smaller and larger particles from the PSD analyses. The fact that dissolved concentrations of copper, lead, and zinc increase with increasing concentration of smaller particles indicates that another mechanism not covered in this research is affecting dissolved metal concentrations in a similar manner to how that mechanism is affecting concentrations of solids in varying size classes.

Figures 4-18, 4-19, and 4-20 show a secondary peak in R^2 values in the coarser silt range of approximately 20-80 μm. This secondary peak coincides with the results of the PSD analysis, which show that the greatest concentration of particles <250 μm are of approximately this same 20-80 μm size range (Figure 4-4). Results similar to these were found by Sansalone and others (1995) in highway sediments. These researchers found the strongest correlations between heavy metals and particles less than 15 μm, then another strong correlation in the 50-130 μm range, with no strong correlation between 15 and 50 µm. This second peak in higher R^2 values could be associated with the greater surface area available on particles of those size ranges because of the higher concentrations of particles in those size classes. Alternatively, the smaller particles could agglomerate to form larger particles in that 20-80 µm size range while maintaining the metal ions associated with their higher surface areas as individual particles. Also, organic matter associated with particulates would increase surface area available for sorption on those particulates. This would be especially true for copper, which tends to be associated much more with organic matter than with TSS (Morrison et al., 1990).

Stormwater ponds and infiltration basins provide removal of solids through sedimentation. Removal efficiencies of solids depend on settling velocities of particles and retention time. If constituents such as metals are associated with these solids, then reduction of constituents in the runoff will occur as a result of sedimentation. Extensive research has concentrated on nutrient removal through sedimentation in stormwater ponds. If greater than 60% removal of total phosphorus can be achieved through sedimentation within ponds (Gal et al., 2003; Greb and Bannerman, 1997), then it is possible to remove an equal or greater portion of total metals, based on the tendency for copper, zinc, and especially lead to be associated with particulates. The infiltration swales that are part of the NDS projects like SEA Streets and the Broadview Green Grid are shallow with long retention times. Therefore, these design components can be expected to remove a large amount of total metals from stormwater runoff.

5.4. Upstream and Downstream Study

The NW120th and NW122nd monitoring stations represent upstream and downstream locations within the same watershed, and so the differences between the water-quality parameters should indicate a difference in one or more aspects of the hydrology, morphology, and land cover and/or land use of the catchment areas contributing to the runoff.

The NW122nd station is noteworthy in that it is located less than 200 feet from the intersection of NW122nd and Greenwood Avenue N, the largest arterial in the catchment area of both sites. A large portion of total runoff experienced at the NW122nd station runs directly off of Greenwood Avenue N, whereas this runoff is significantly diluted at the NW120th station. The statistically significant difference in total zinc concentrations and corresponding difference in dissolved zinc concentrations between the NW122nd and NW120th monitoring stations suggest that the runoff is diluted after running over streets and neighborhoods under lower traffic loads before the runoff reaches the NW120th station. This may be a counterintuitive conclusion that urban land uses can actually dilute high levels of urban pollutants. It also suggests that vehicle use may be a more important indicator of potential pollutant generation than other measures of human activity based simply on urban land cover, housing density, or zoning.

It is clear from the statistical analysis that a majority of water-quality parameters are not different between the two monitoring stations. This indicates that there is no water-quality benefit of the existing drainage system.

6. Conclusions and Management Implications

This research has concentrated on the relationships between solids and metals in urban runoff and their dependence on hydrologic parameters. Conclusions drawn from the site assessment, data analyses, and assessment of results include the following::

- Hydrologic conditions determine the concentration and size distribution of solids. TSS concentrations increase with increasing precipitation intensity. The greatest concentrations of particles in the clay and finer silt ranges occur during events with the most extensive antecedent dry periods.
- Hydrologic conditions affect metals concentrations and partitioning between dissolved and particulate-bound. Events following dry periods have higher total and dissolved metals concentrations and higher fractions of total metal in dissolved form because catchment surfaces accumulate metals based on length of dry period.
- Copper, lead, and zinc behave differently in an aqueous environment based on their relative solubilities. Lead is most often associated with particulates, whereas copper and zinc are distributed between the dissolved and particulate phases depending on environmental conditions.
- Particulate copper, lead, and zinc exhibit different relationships with various sizes of particles:
    - Particulate copper is associated with the coarser silts, corresponding to the peak in solids concentrations from the PSD analyses.
    - Particulate zinc is associated with the smallest size classes of clay and fine silt.
    - Particulate lead is associated with all particles, though most obviously with the larger particles which comprise a majority of the mass represented in the TSS concentrations.

- Particulate size is an important factor determining the partitioning of total metals. Surface-area-to-volume ratio depends on particle size, with the smallest particles providing the greatest surface area. Therefore, small particles are key mechanisms of transport for constituents such as metals.
- Amount of surface area available (as measured by TSS and concentration in various size bins from the PSD analyses) determines the transport capacity of solids for parameters such as metals. The more surface area available for sorption, the lower the fraction of total metal present in dissolved form. However, solids can also bring additional particulate-bound metals into runoff.
- The existing informal drainage system in the Pipers Creek watershed is not effective at removing constituents.

Hydrologic parameters influence the concentrations of solids, total and dissolved metals, as well as PSD and the partitioning of total metals into particulate-bound and dissolved forms. Longer dry periods before storm events and more intense precipitation during an event both increase accumulation and wash-off of solids and metals on catchment surfaces. The interaction of solids and hydrology also affects the concentration of metals and the distribution of metals between dissolved and particulate-bound phases. The hydrologic factors that increase solids concentrations also decrease the portion of total metal present in dissolved form, because of the increase in available sorption sites due to the increase in total particulate surface area. Characteristics of the particulate matter also affect these mechanisms. Also, the type of metal and its relative solubility and characteristics can determine the extent of the affects of solids and hydrologic parameters.

Copper, lead, and zinc each have unique relationships with concentrations of solids in varying size classes. Particulate lead shows no obvious trend, whereas particulate zinc is associated with the smallest particles and particulate copper tends to be associated with particles in the coarse silt range. This has implications for effective removal efficiencies of the different metals based on the effective removal of particles of the various size classes. If the target constituent is copper, then removal of particles in the coarser silt range may effectively remove a large portion of copper present in the runoff. However, removing the smallest particles is necessary for effective removal of zinc. Removal of lead from runoff can be achieved through removal of even the largest of particles, noting the strong dependence of total lead on TSS concentrations.

Sedimentation can aid in removing constituents like metals from urban runoff. However, neither the smallest particles, which may carry a significant metal load, nor dissolved metals, can be removed effectively via this mechanism. It is imperative that future stormwater management efforts incorporate mechanisms for removal of smaller particles that affect the partitioning of metals between particulate-bound and dissolved phases. For instance, street sweeping is increasingly becoming more effective at removing smaller particles from catchment surfaces.

Most water-quality parameters are not different between the two monitoring stations part of the paired study in the NW120th catchment. Though total and dissolved zinc are different, this is perhaps a product of proximity to a major arterial and/or dilution rather than removal through the existing informal drainage system. It is clear from the statistical analysis that a majority of water-quality parameters are not different between the two monitoring stations. This indicates that there is no water-quality benefit of the existing drainage system.

The relationships between solids and metals indicate a promising method of removing trace metals from stormwater runoff. If solids of all sizes are removed from urban runoff, then presumably metals will be removed as well. Future research on these interactions would be helpful in order to further quantify relationships between certain metals and certain sizes of particles under various conditions. This would aid in concentrating removal efforts on certain particles sizes or on certain metals which are deemed most detrimental in any one specific catchment.

This research contains a quantification of the water quality and hydrologic status of the existing drainage system discharging to Pipers Creek. As additional NDS projects are designed and implemented in the area, results from this study should be used to rationalize including design components which provide both hydrologic and water quality benefits, capitalizing on the relationships between solids and metals discussed in this research. Then, after construction, similar water quality data can be compared to the results from this research in order to quantify project effectiveness.

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APPENDIX A:
Laboratory Analytical Results and Summary Statistics

		n=	12	10	12	12	6	6
		number of detects	12	10	12	12	6	0
		frequency of detection	100%	100%	100%	100%	100%	0%
		detection limit	2 cfu/100ml	2 cfu/100m	0.1 deg C	0.1	0.1 mg/l	0.1 mg/l
		arithmetic mean of sample	1330	688	12.0	6.9	1.22	0.05
		lower of 90% CI about arith. Mean	696	367	10.4	6.7	0.75	0.05
		upper of 90% CI about arith. Mean	1964	1009	13.5	7.1	1.69	0.05
		Std Dev of Sample	1336	617	3.2	0.4	0.70	0.00
		median	730	450	11.2	6.8	1.09	0.05
		lower of 90% CI about the median	400	200	7.7	6.5	0.00	0.00
		upper of 90% CI about the median	2000	1400	17.3	7.4	0.00	0.00
		minimum	180	180	7.7	6.3	0.51	0.05
		maximum	4400	2000	17.8	7.8	2.33	0.05
		25th percentile	400	200	10.9	6.6	0.69	0.05
		75th percentile	2000	950	12.7	7.1	1.60	0.05
		% coefficient of variation	100%	90%	27%	6%	57%	0%
			fecal	**ecoli**	**temp**	**pH**	**TPH**(mg/l)**	
			cfu/100ml	**cfu/100ml**	**(deg C)**	**units**	**oil**	**diesel**
1	1/30/2003	107th	1200	1000	10.7	6.8	■	■
2	1/30/2003	120th	3200	1400	10.9	6.6	■	■
3	1/30/2003	122nd	1000	800	11.0	6.5	■	■
4	3/12/2003	107th	400	400	11.4	7.3	■	■
5	3/12/2003	120th	4400	2000	11.3	7.0	■	■
6	3/12/2003	122nd	400	180	12.0	7.0	■	■
7	10/28/2003	120th	2000	200	17.3	7.4	0.51	0.05
8	10/28/2003	122nd	400	200	17.8	6.5	2.33	0.05
9	2/16/2004	120th	320	500	14.7	7.8	0.91	0.05
10	2/16/2004	122nd	180	200	11.0	6.8	1.71	0.05
11	3/4/2004	120th	2000	▓	7.7	6.6	0.61	0.05
12	3/4/2004	122nd	460	▓	7.7	6.3	1.27	0.05

░ not detected

▓ parameter was not tested for during this sampling event

**TPH samples were taken via composite on and before 10/15/03, and via grab after 10/15/03

Table A-1: Grab Samples, Summary Statistics

			Metals, Dissolved (ug/l)			Metals, Total (ug/l)			Nutrients (mg/l)			Hard-ness (mg/l)	TPH**(mg/l)		TSS (mg/l)	d10	d50	d90
			Cu	Pb	Zn	Cu	Pb	Zn	TP	SRP	TN		oil	diesel				
n=			34	34	34	34	34	34	34	34	34	35	13	13	35	35	35	35
number of detects			34	16	34	34	34	34	34	34	34	35	13	9	35	35	35	35
frequency of detection			100%	47%	100%	100%	100%	100%	100%	100%	100%	100%	100%	69%	100%	100%	100%	100%
detection limit			1 ug/l	1 ug/l	1 ug/l	1 ug/l	1 ug/l	1 ug/l	5 ug/l	2 ug/l	10 ug/l	0.5 mg/l	0.1 mg/l	0.1 mg/l	1 mg/l	0.01 mg/l	0.01 mg/l	0.01 mg/l
arithmetic mean of sample			8.96	1.21	49.96	18.26	18.07	94.29	0.21	0.04	1.90	19.28	1.71	0.09	63	12.14	46.57	164.56
lower of 90% CI about arith. Mean			7.02	0.53	33.93	15.30	13.87	72.72	0.18	0.03	1.51	16.03	1.04	0.06	47	11.46	44.34	158.75
upper of 90% CI about arith. Mean			10.90	1.88	65.99	21.21	22.27	115.85	0.24	0.05	2.28	22.54	2.38	0.13	78	12.82	48.80	170.37
Std Dev of Sample			6.87	2.39	56.83	10.47	14.89	76.44	0.11	0.05	1.35	11.72	1.46	0.08	56	2.46	8.03	20.89
median			7.10	0.50	34.30	13.85	13.40	68.00	0.18	0.02	1.44	16.20	1.20	0.05	42	11.65	46.39	167.62
lower of 90% CI about the median			5.30	0.50	24.00	12.30	9.00	55.60	0.14	0.01	1.14	13.10	10.80	42.66	32	10.80	42.66	162.15
upper of 90% CI about the median			8.13	0.50	45.00	18.30	20.50	86.00	0.24	0.04	1.65	18.00	12.98	48.45	61	12.98	48.45	177.18
minimum			1.80	0.28	5.00	8.23	1.80	22.00	0.07	0.00	0.48	8.60	0.30	0.05	4	8.57	35.56	115.61
maximum			28.10	14.20	252.00	44.50	59.20	314.00	0.50	0.25	5.51	66.40	5.40	0.31	236	17.74	70.70	193.38
25th percentile			4.65	0.50	20.08	11.98	6.60	50.18	0.13	0.01	1.04	11.65	0.64	0.05	28	10.42	40.47	149.81
75th percentile			9.08	0.88	49.00	20.28	25.68	88.23	0.29	0.04	2.08	23.05	2.20	0.10	76	13.21	50.02	180.72
% coefficient of variation			77%	199%	114%	57%	82%	81%	51%	128%	71%	61%	86%	83%	89%	20%	17%	13%
1	1/12/2003	120th	3.58	0.401	23	8.23	9.55	44	0.117	0.027	1.04	12.8	0.84	0.17	27	13.0	46.2	149.3
2	1/12/2003	122nd	5.92	0.627	62.3	12.3	11.6	88.3	0.119	0.02	1.82	16.6	2.20	0.17	28	13.2	47.7	158.1
3	1/25/2003	120th	3.16	0.282	15.6	15	29.1	64.7	0.178	0.013	1.12	10			78	12.0	42.3	178.1
4	1/25/2003	122nd	3.24	0.363	35.6	10.1	16.9	68.6	0.111	0.006	1.54	18			37	17.1	51.6	123.2
5	4/4/2003	107th	5.08	0.314	10.2	24.1	35.7	74.6	0.218	0.014	1.14	18.6	2.10		115	10.1	36.6	165.2
6	4/8/2003	107th	5.73	0.418	12.2	17.9	22.3	55.6	0.181	0.029	1.38	17.2	1.00		74	9.7	35.7	167.3
7	4/23/2003	107th	8.13	0.521	19.1	14.8	13.5	43	0.157	0.003	1.18	21.2	1.20	0.10	18	12.5	40.3	150.3
8	4/23/2003	120th	8.7	1.31	44	9.42	5.19	50.7	0.192	0.058	1.05	12.3	0.34	0.05	4	14.2	51.6	136.0
9	4/23/2003	122nd	5.3	0.494	46.5	9.72	10.3	67.3	0.181	0.003	1.25	11.6	3.30	0.05	32	12.0	49.0	142.6
10	5/15/2003	107th										33.2	2.00	0.31	236	12.5	47.6	179.8
11	6/20/2003	107th	21.3	0.96	31.1	42.7	5.59	43	0.305	0.122	4.34	24		0.08	32	10.9	41.9	174.1
12	6/20/2003	120th	17.5	1.44	111	19.3	3.9	267	0.314	0.111	5.51	34.6		0.05	12	10.2	38.6	169.6
13	6/20/2003	122nd	25	1.85	252	39.4	15.2	314	0.238	0.038	4.87	22.1	5.40	0.05	28	10.2	39.1	169.6
14	10/5/2003	107th	23.7	2.2	24	24.1	9	50	0.34	0.125	3.56	66.4	0.64	0.05	71	10.5	35.6	124.1
15	10/5/2003	120th	11.7	2.7	231	14.1	6.6	298	0.495	0.247	4.18	37.5	0.30	0.05	17	10.8	37.9	155.7
16	10/5/2003	122nd	28.1	2.9	146	36.1	26.8	271	0.381	0.113	4.8	39.1	2.56	0.05	61	10.3	38.0	162.2
17	10/15/2003	107th	6.9	1.5	5	9.9	6.9	22	0.128	0.037	0.907	27.2	0.35	0.05	36	11.0	38.5	166.2
18	11/15/2003	120th	15.4	0.5	44	18.6	1.8	54	0.377	0.08	2.47	16.2			123	10.5	47.1	183.7
19	11/15/2003	122nd	8.1	0.5	49	12.3	3.1	65	0.17	0.037	2.17	10.4			62	14.1	56.3	184.6
20	12/2/2003	120th	7.7	0.5	33	44.5	51	135	0.235	0.008	1.67	13.3			156	14.3	52.4	138.5
21	12/2/2003	122nd	7.3	0.5	28	42.1	59.2	122	0.235	0.008	1.58	13.9			99	11.6	48.5	145.6
22	12/4/2003	120th	6.9	0.5	42	18.3	20.5	87	0.099	0.016	1.27	17.6			28	16.9	50.3	115.6
23	12/4/2003	122nd	2.2	0.5	9	21.5	50.9	86	0.429	0.018	1.65	11.7			204	13.9	47.9	167.6
24	1/13/2004	120th	7.8	0.5	24	10.4	5.8	31	0.096	0.009	0.963	14.5			31	11.7	43.5	164.4
25	1/13/2004	122nd	14.5	14.2	65	20.6	38.7	129	0.3	0.011	2.51	28.5			156	13.2	46.4	143.1
26	1/28/2004	120th	1.9	0.5	8	11.9	27.4	58	0.314	0.013	1.610	9.58			113	13.1	55.7	193.4
27	1/28/2004	122nd	1.8	0.5	39	12.2	29.8	68	0.102	0.006	0.990	8.6			50	13.0	48.4	173.5
28	2/14/2004	120th	4.5	0.5	23	8.9	6.6	48	0.065	0.009	0.509	10.9			18	8.6	42.7	182.9
29	2/14/2004	122nd	5.5	0.5	45	13.5	17.8	69	0.141	0.025	0.827	13.1			35	9.0	40.7	181.6
30	2/16/2004	120th	3.7	0.5	6	13.8	19.1	47	0.118	0.011	0.480	10.9			42	9.0	46.2	177.2
31	2/16/2004	122nd	3.3	0.5	26	13.9	20.7	68	0.126	0.011	0.591	13.1			45	8.6	45.1	179.1
32	3/4/2004	120th	5.3	0.5	11	13.1	11.6	42	0.132	0.010	0.977	8.99			47	10.6	49.7	192.7
33	3/4/2004	122nd	8	0.5	49	13.7	13.3	83	0.246	0.051	1.390	10.9			44	11.3	51.8	187.4
34	3/7/2004	120th	8.6	0.5	55	12.5	4.6	88	0.159	0.030	1.490	16.4			24	17.7	70.7	187.2
35	3/7/2004	122nd	9.2	0.5	74	11.7	4.4	104	0.156	0.038	1.630	24			13	17.4	68.2	190.0

░ not detected

▓ parameter was not tested for during this sampling event

**TPH samples were taken via composite on and before 10/15/03, and via grab after 10/15/03

Table A-2: Composite Samples, Summary Statistics

site	120th		122nd		107th		107th		107th		120th		122nd	
date	01/12/03		01/12/03		04/09/03		05/15/03		06/20/03		06/20/03		06/20/03	
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.
2,4,6-Trichlorphenol	0.1	U	0.1	U	0.091	U	0.093	U	0.16	U	0.1	U	0.094	U
3,5-Dichlorobenzoic Acid	0.17	U	0.17	U	0.15	U	0.15	U	0.26	U	0.17	U	0.16	U
4-Notrophenol	0.3	U	0.3	U	**0.51**	**J**	0.27	U	**1.3**	**NJ**	0.3	U	0.27	U
2,4,5-Trichlorophenol	0.1	U	0.1	U	0.092	U	0.093	U	0.16	U	0.1	U	0.094	U
Dicamba I	0.17	U	0.17	U	0.15	U	**0.016**	**NJ**	0.26	U	**0.61**	**NJ**	0.16	U
2,3,4,6-Tetrachlorophenol	0.095	U	0.095	U	0.085	U	0.085	U	0.15	U	0.094	U	0.086	U
MCPP (Mecoprop)	0.34	U	0.34	U	0.31	U	**3.7**		**0.25**	**NJ**	2.8		**0.18**	**NJ**
MCPA	0.34	U	0.34	U	0.3	U	**0.1**	**NJ**	0.53	U	**0.37**	**NJ**	0.31	U
Dichlorprop	0.19	U	0.19	U	0.17	U	0.17	U	0.29	U	0.19	U	0.17	U
Bromoxynil	0.17	U	0.17	U	0.16	U	0.15	U	0.26	U	0.17	U	0.16	U
2,4-D	**0.037**	**NJ**	0.17	U	**0.071**	**NJ**	**2.5**		**0.28**	**NJ**	18		**0.11**	**NJ**
2,3,4,5-Tetrachlorophenol	0.095	U	0.095	U	0.085	U	0.085	U	0.15	U	0.094	U	0.086	U
Trichlopyr	0.14	U	0.14	U	0.12	U	**0.05**	**NJ**	**0.036**	**NJ**	10		**0.065**	**NJ**
Pentachlorophenol	**0.11**		**0.21**		0.078	U	**0.13**		**0.1**	**NJ**	0.085	U	**0.13**	**NJ**
2,4,5-TP (Silvex)	0.14	U	0.14	U	0.12	U	0.12	U	0.21	U	0.14	U	0.13	U
2,4,5-T	0.14	U	0.14	U	0.12	U	0.12	U	0.21	U	0.14	U	0.13	U
2,4-DB	0.21	U	0.21	U	0.18	U	0.18	U	0.32	U	0.2	U	0.19	U
Dinoseb	0.26	UJ	0.26	UJ	0.23	UJ	0.23	UJ	0.39	UJ	0.25	UJ	0.23	UJ
Bentazon	0.26	U	0.26	U	0.23	U	0.23	U	0.39	U	0.25	U	0.23	U
Ioxynil	0.17	U	0.17	U	0.16	U	0.15	U	0.26	U	0.17	U	0.16	U
Picloram	0.17	UJ	0.17	UJ	0.16	UJ	0.15	UJ	0.26	UJ	0.17	UJ	0.16	UJ
Dacthal (DCPA)	0.14	U	0.14	U	0.12	U	0.12	U	0.21	U	0.14	U	0.13	U
2,4,5-TB	0.15	U	0.15	U										
Acifluorfen (Blazer)	0.68	UJ	0.68	UJ	0.63	U	0.23	U	1.1	U	0.68	U	0.63	U
Diclofop-Methyl	0.26	U	0.26	U	0.24	U	0.26	U	0.39	U	0.25	U	0.23	U

U= Undetected
UJ = The analyte was not detected at or abovev the reported estimated result
NJ = There is evidence that the analyte is present. The associated numberical result is an estimate
REJ = The data are unusable for all purposes

Table A-3: Herbicides

site	120th		122nd		107th		107th		107th		120th		122nd	
date	01/12/03		01/12/03		04/09/03		05/15/03		06/20/03		06/20/03		06/20/03	
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.
Dichlorobenil	0.14	J	**0.0188**	**J**	0.062	UJ	0.62	UJ	0.11	UJ	**0.219**		0.14	U
Tebuthiuron	0.11	U	0.11	U	0.046	UJ	0.46	UJ	0.079	UJ	0.048	U	0.11	U
Propachlor (Ramrod)	0.17	U	0.18	U	0.074	UJ	0.74	UJ	0.13	UJ	0.077	U	0.17	U
Ethalfluralin (Sonalan)	0.11	U	0.11	U	0.046	UJ	0.46	UJ	0.079	UJ	0.048	U	0.11	U
Treflan (Trifluralin)	0.11	U	0.11	U	0.046	UJ	0.46	UJ	0.079	UJ	0.048	U	0.11	U
Simazine	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Atrazine	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Pronamide (Kerb)	0.29	U	0.29	U	0.12	UJ	1.2	UJ	0.21	UJ	0.13	U	0.29	U
Terbacil	0.22	U	0.22	U	0.092	UJ	0.92	UJ	0.16	UJ	0.096	U	0.21	U
Metribuzin	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Alachlor	0.26	U	0.26	U	0.11	UJ	1.1	UJ	0.19	UJ	0.12	U	0.26	U
Prometryn	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Bromacil	0.29	U	0.29	U	0.12	UJ	1.2	UJ	0.21	UJ	0.13	U	0.29	U
Metolachlor	0.29	U	0.29	U	0.12	UJ	1.2	UJ	0.21	UJ	0.13	U	0.29	U
Diphenamid	0.22	U	0.22	U	0.092	UJ	0.92	UJ	0.16	UJ	0.096	U	0.21	U
Pendimethalin	0.11	U	0.11	U	0.046	UJ	0.46	UJ	0.079	UJ	0.048	U	0.11	U
Napropamide	0.22	U	0.22	U	0.092	UJ	0.92	UJ	0.16	UJ	0.096	U	0.21	U
Oxyfluorfen	0.29	UJ	0.29	UJ	0.12	UJ	1.2	UJ	0.21	UJ	0.13	UJ	0.29	UJ
Norflurazon	0.14	UJ	0.15	UJ	0.062	UJ	0.62	UJ	0.11	UJ	0.064	UJ	0.14	UJ
Progargite					0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Fluridone	0.43	UJ	0.44	UJ	0.18	UJ	1.8	UJ	0.32	UJ	0.19	UJ	0.43	UJ
Eptam	0.14	U	0.15	U	0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Butylate	0.14	U	0.15	U	0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Vernolate	0.14	U	0.15	U	0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Cycloate	0.14	U	0.15	U	0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Benefin	0.11	U	0.11	U	0.046	UJ	0.46	UJ	0.079	UJ	0.078	U	0.11	U
Prometon (Pramitol 5p)	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Propazine	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Chlorothalonil (Daconil)	0.17	U	0.18	U	0.074	UJ	0.74	UJ	0.13	UJ	0.077	U	0.17	U
Triallate	0.22	U	0.22	U	0.092	UJ	0.92	UJ	0.16	UJ	0.096	U	0.21	U
Ametryn	0.072	UJ	0.074	UJ	0.031	UJ	0.31	UJ	0.053	UJ	0.032	U	0.071	U
Terbutryn (Igran)	0.072	UJ	0.074	UJ	0.031	UJ	`	UJ	0.053	UJ	0.032	U	0.071	U
Hexazinone	0.11	UJ	0.11	UJ	0.046	UJ	0.46	UJ	0.079	UJ	0.048	UJ	0.11	UJ
Pebulate	0.14	U	0.15	U	0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Molinate	0.14	U	0.15	U	0.062	UJ	0.62	UJ	0.11	UJ	0.064	U	0.14	U
Chlorpropham	0.29	U	0.29	U	0.12	UJ	1.2	UJ	0.21	UJ	0.13	U	0.29	U
Atraton	0.11	U	0.11	U	0.046	UJ	0.46	UJ	0.079	UJ	0.048	U	0.11	U
Triadimefon	0.19	U	0.19	U	0.08	UJ	0.8	UJ	0.14	UJ	0.083	U	0.19	U
MGK264	0.58	U	0.59	U	0.25	UJ	2.5	UJ	0.42	UJ	0.26	U	0.57	U
Butachlor	0.43	U	0.44	U	0.18	UJ	1.8	UJ	0.32	UJ	0.19	U	0.43	U
Carboxin	0.43	U	0.44	U	0.18	UJ	1.8	UJ	0.32	UJ	0.19	U	0.43	U
Fenarimol	0.22	U	0.22	U	0.092	UJ	0.92	UJ	0.16	UJ	0.096	U	0.21	U
Diuron	0.43	U	0.44	U	0.18	UJ	1.8	UJ	0.32	UJ	0.19	U	0.43	U
Di-allate (Avadex)	0.51	U	0.51	U	0.22	UJ	2.2	UJ	0.37	UJ	0.22	U	0.5	U
Profluralin	0.17	U	0.18	U	0.074	UJ	0.74	UJ	0.13	UJ	0.077	U	0.17	U
Metalazyl	0.43	U	0.44	U	0.18	UJ	1.8	UJ	0.32	UJ	0.19	U	0.43	U
Cyanazine	0.11	UJ	0.11	UJ	0.046	UJ	0.46	UJ	0.079	UJ	0.048	UJ	0.11	UJ

U= Undetected
UJ = The analyte was not detected at or abovev the reported estimated result
NJ = There is evidence that the analyte is present. The associated numberical result is an estimate
REJ = The data are unusable for all purposes

Table A-4: Nitrogen-Containing Pesticides

site	120th		122nd		107th		107th		107th		120th		122nd	
date	01/12/03		01/12/03		04/09/03		05/15/03		06/20/03		06/20/03		06/20/03	
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.
Demeton-O	0.051	UJ	0.051	UJ	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Sulfotepp	0.043	U	0.044	U	0.018	UJ	0.18	UJ	0.032	U	0.019	U	0.043	UJ
Demeton-S	0.051	UJ	0.051	UJ	0.022	UJ	0.22	UJ	0.037	UJ	0.022	UJ	0.05	UJ
Fonofos	0.043	U	0.044	U	0.018	UJ	0.18	UJ	0.032	U	0.019	U	0.043	UJ
Disulfoton (Di-Syston)	0.043	U	0.044	U	0.018	UJ	0.18	UJ	0.032	U	0.019	U	0.043	UJ
Methyl Chlorpyrifos	0.058	U	0.059	U	0.025	UJ	0.25	UJ	0.042	U	0.026	U	0.057	UJ
Fenitrothion	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Malathion	0.058	U	0.059	U	0.025	UJ	**3.7**	J	0.042	U	0.026	U	0.057	UJ
Chlorphyriphos	0.058	U	0.059	U	0.025	UJ	0.25	UJ	0.042	U	0.026	U	0.057	UJ
Merphos (1&2)	0.087	U	0.088	U	0.037	UJ	0.37	UJ	0.063	U	0.038	U	0.086	UJ
Ethion	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Carbophenothion	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	U	0.032	U	0.071	UJ
EPN	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	U	0.032	U	0.071	UJ
Azinphos Ethyl	0.12	U	0.12	U	0.049	UJ	0.49	UJ	0.084	U	0.051	U	0.11	UJ
Ethoprop	0.058	U	0.059	U	0.025	UJ	0.25	UJ	0.042	U	0.026	U	0.057	UJ
Phorate	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Dimethoate	0.058	UJ	0.059	UJ	0.025	UJ	0.25	UJ	0.042	UJ	0.026	UJ	0.057	UJ
Diazinon	0.058	U	**0.23**		0.0058	UJ	**3.5**	**J**	0.042	U	0.026	U	0.057	UJ
Methyl Parathion	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Ronnel	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Fenthion	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Parathion	0.058	U	0.059	U	0.025	UJ	0.25	UJ	0.042	U	0.026	U	0.057	UJ
Fensulfothion	0.072	U	0.074	U	0.031	UJ	0.31	UJ	0.053	U	0.32	U	0.071	UJ
Bolstar (Sulprofos)	0.051	U	0.051	U	0.022	UJ	0.22	UJ	0.037	U	0.022	U	0.05	UJ
Imidan	0.08	U	0.081	U	0.034	UJ	0.34	UJ	0.058	U	0.035	U	0.079	UJ
Azinphos (Guthion)	0.12	UJ	0.12	UJ	0.049	UJ	0.49	UJ	0.084	U	0.051	U	0.11	UJ
Coumaphos	0.087	UJ	0.088	UJ										
Dichlorvos (DDVP)	0.058	U	0.059	U										
Mevinphos	0.072	U	0.074	U										
Dioxathion	0.12	U	0.13	U										
Propetamphos	0.14	U	0.15	U										
Methyl Paraoxon	0.13	U	0.13	U										
Phosphamidan	0.17	U	0.18	U										
Tetrachlorvinphos (Gardona)	0.14	U	0.15	U										
Fenamiphos	0.11	U	0.11	U			0.46	UJ	0.079	U	0.048	U	0.11	UJ
Dribufos (DEF)	0.1	U	0.1	U										
Abate (Temephos)	0.43	UJ	0.44	UJ										

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UJ = The analyte was not detected at or abovev the reported estimated result
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REJ = The data are unusable for all purposes

Table A-5: Organophosphorus Pesticides

site	120th		122nd		107th		107th		107th		120th		122nd	
date	01/12/03		01/12/03		04/09/03		05/15/03		06/20/03		06/20/03		06/20/03	
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.
Alpha-BHC	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Beta-BHC	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Gamma-BHC (Lindane)	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Delta-BHC	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Heptachlor	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Aldrin	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Heptachlor Epoxide	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Trans-Chlordane (Gamma)	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Cis-Chlordane (Alpha-Chlorda	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Endosulfan I	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Dieldrin	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
4,4'-DDE	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Endrin	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Endosulfan II	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
4,4'-DDD	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Endrin Aldehyde	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Endosulfan Sulfate	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
4,4-DDT	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	REJ	0.026	REJ	0.016	REJ	0.036	REJ
Endrin Keytone	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Methoxychlor	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	REJ	0.026	REJ	0.016	REJ	0.036	REJ
Alpha-Chlordene	0.036	UJ	0.037	UJ	0.0077	UJ								
Gamma-Chlordene	0.036	UJ	0.037	UJ	0.0077	UJ								
Oxychlordane	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
DDMU	0.036	UJ	0.037	UJ										
Cis-Nonachlor	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Kelthane	0.14	UJ	0.15	UJ	0.031	UJ	0.62	REJ	0.11	U	0.064	U	0.14	U
Captan	0.098	UJ	0.1	UJ	0.021	UJ	0.42	REJ	0.071	REJ	0.043	REJ	0.096	REJ
2,4'-DDE	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Trans-Nonachlor	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	REJ	0.026	U	0.016	U	0.036	UJ
2,4'-DDD	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
2,4-DDT	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	REJ	0.026	REJ	0.016	REJ	0.036	REJ
Captafol	0.18	UJ	0.18	UJ	0.038	UJ	0.77	REJ	0.13	REJ	0.08	REJ	0.18	REJ
Mirex	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Hexachlorbenzene	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ
Pentachloroanisole	0.036	UJ	0.037	UJ	0.0077	UJ	0.15	UJ	0.026	U	0.016	U	0.036	UJ

U= Undetected
UJ = The analyte was not detected at or abovev the reported estimated result
NJ = There is evidence that the analyte is present. The associated numberical result is an estimate
REJ = The data are unusable for all purposes

Table A-6: Chlorinated Pesticides

APPENDIX B:
Hydrologic Summary Statistics

	n=	5	5	5	5	5	5	5	5	5	5	4	4	4
	arithmetic mean of sample	0.63	0.01	0.06	0.11	0.62	1.81	2.38	1.75	0.14	22.00	53,546	0.34	10.44
	lower of 90% CI about arith. Mean	0.07	0.00	0.02	0.02	0.29	0.04	0.39	0.11	0.11	6.08	1,140	0.15	8.54
	upper of 90% CI about arith. Mean	1.18	0.02	0.11	0.20	0.96	3.59	4.38	3.39	0.18	37.92	105,951	0.53	12.33
	Std Dev of Sample	0.75	0.01	0.07	0.12	0.46	2.41	2.71	2.23	0.05	21.64	63,721	0.23	2.31
	median	0.37	0.00	0.07	0.07	0.46	0.39	1.77	0.77	0.12	15.00	29,961	0.32	11.04
	lower of 90% CI about the median	0.09	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.09	6.00	6,938	0.09	7.17
	upper of 90% CI about the median	1.95	0.03	0.15	0.27	1.24	5.32	6.33	5.18	0.22	60.00	147,322	0.62	12.50
	minimum	0.09	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.09	6.00	6,938	0.09	7.17
	maximum	1.95	0.03	0.15	0.27	1.24	5.32	6.33	5.18	0.22	60.00	147,322	0.62	12.50
	25th percentile	0.28	0.00	0.00	0.00	0.39	0.00	0.00	0.00	0.12	12.00	18,845	0.20	9.79
	75th percentile	0.44	0.00	0.11	0.21	0.92	3.36	3.81	2.79	0.16	17.00	64,662	0.47	11.69
	% coefficient of variation	120%	224%	101%	112%	73%	133%	114%	128%	35%	98%	119%	68%	22%
	event date	**event precip (in)**	**precip in previous 12 hours (in)**	**precip in previous 24 hours (in)**	**precip in previous 48 hours (in)**	**precip in previous 168 hours (in)**	**time since 12 hour period > 0.04in (days)**	**time since 24 hour period > 0.1in (days)**	**time since 48 hour period > 0.1in (days)**	**max intensity (in/hr)**	**duration (hrs)**	**total runoff volume (gal)**	**peak flow (cfs)**	**time to peak (hrs)**
1	1/30/03	0.37	0.000	0.149	0.266	1.244	0.00	0.00	0.00	0.16	17.0	22,814	0.23	10.7
2	3/12/03	1.95	0.031	0.070	0.070	0.915	0.00	1.77	0.77	0.22	60.0	147,322	0.42	11.4
3	10/28/03	0.09	0.000	0.000	0.000	0.091	5.32	6.33	5.18	0.09	6.0			
4	2/16/04	0.44	0.000	0.106	0.212	0.393	0.39	0.00	0.00	0.12	15.0	6,938	0.09	12.5
5	3/3/04	0.28	0.000	0.000	0.000	0.462	3.36	3.81	2.79	0.12	12.0	37,108	0.62	7.2
	▨	flow data not collected for this sampling event												

Table B-1: Hydrologic Statistics, Grab Events

		event precip (in)	precip in previous 12 hours (in)	precip in previous 24 hours (in)	precip in previous 48 hours (in)	precip in previous 168 hours (in)	time since 12 hour period > 0.04in (days)	time since 24 hour period > 0.1in (days)	time since 48 hour period > 0.1in (days)	max intensity (in/hr)	duration (hrs)	total runoff volume (gal)	peak flow (cfs)	time to peak (hrs)
	n=	18	18	18	18	18	18	18	18	18	18	17	17	17
	arithmetic mean of sample	0.48	0.00	0.06	0.12	0.55	2.75	3.76	3.09	0.16	21.00	88,242	2.30	12.40
	lower of 90% CI about arith. Mean	0.33	0.00	0.03	0.07	0.37	1.22	1.24	0.64	0.13	17.20	36,804	0.92	9.76
	upper of 90% CI about arith. Mean	0.64	0.01	0.10	0.16	0.72	4.29	6.27	5.53	0.19	24.80	139,680	3.68	15.04
	Std Dev of Sample	0.41	0.01	0.09	0.12	0.45	3.96	6.49	6.31	0.08	9.79	128,938	3.46	6.62
	median	0.30	0.00	0.02	0.11	0.48	1.55	1.67	0.64	0.15	19.00	18,054	0.41	10.50
	lower of 90% CI about the median	0.23	0.00	0.00	0.01	0.23	0.48	0.33	0.00	0.12	15.00	7,055	0.21	7.17
	upper of 90% CI about the median	0.48	0.00	0.09	0.20	0.74	2.73	2.79	1.79	0.18	25.00	93,055	3.25	16.83
	minimum	0.08	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03	8.00	2,228	0.09	4.83
	maximum	1.63	0.04	0.28	0.34	1.73	16.57	24.69	23.69	0.30	46.00	457,337	9.88	26.75
	25th percentile	0.22	0.00	0.00	0.00	0.23	0.41	0.08	0.00	0.10	15.00	7,055	0.21	7.17
	75th percentile	0.57	0.01	0.10	0.21	0.77	3.21	3.56	2.54	0.23	25.00	93,055	3.25	16.83
	% coefficient of variation	84%	222%	143%	98%	82%	144%	173%	204%	48%	47%	146%	151%	53%
	event date	**event precip (in)**	**precip in previous 12 hours (in)**	**precip in previous 24 hours (in)**	**precip in previous 48 hours (in)**	**precip in previous 168 hours (in)**	**time since 12 hour period > 0.04in (days)**	**time since 24 hour period > 0.1in (days)**	**time since 48 hour period > 0.1in (days)**	**max intensity (in/hr)**	**duration (hrs)**	**total runoff volume (gal)**	**peak flow (cfs)**	**time to peak (hrs)**
1	1/12/03	0.939	0.000	0.000	0.000	0.008	6.542	6.042	5.042	0.125	25.0	253451.4	4.372	17.000
2	1/25/03	0.602	0.000	0.039	0.321	1.729	0.563	0.333	0.000	0.282	22.0	236537.9	9.876	16.833
3	4/3/03	0.211	0.000	0.282	0.336	0.649	0.281	0.000	0.000	0.156	15.0	7054.5	0.273	7.833
4	4/8/03	0.289	0.000	0.031	0.039	0.962	2.188	1.771	0.719	0.156	12.0	15186.3	0.293	6.667
5	4/23/03	0.438	0.000	0.000	0.133	0.297	1.073	0.906	0.000	0.094	36.0	18054.4	0.212	25.417
6	5/16/03	0.188	0.000	0.125	0.133	0.133	0.479	0.000	0.000	0.156	8.0	9696.5	0.299	5.417
7	6/20/03	0.305	0.000	0.000	0.000	0.055	6.073	24.688	23.688	0.094	18.0	4151.8	0.139	10.333
8	10/6/03	0.227	0.000	0.000	0.000	0.000	16.573	16.427	15.427	0.151	18.0	2228.1	0.138	4.833
9	10/16/03	1.180	0.000	0.000	0.000	0.742	2.573	2.167	1.167	0.182	32.0	30144.8	0.410	7.333
10	11/16/03	0.477	0.008	0.235	0.235	0.235	0.094	0.000	0.000	0.242	8.0	222225.7	9.523	6.500
11	12/2/03	0.303	0.008	0.030	0.030	0.696	2.729	2.563	1.563	0.272	22.0	11976.5	1.238	14.667
12	12/4/03	0.764	0.000	0.000	0.242	0.878	1.188	0.740	0.000	0.242	25.0	93054.8	3.251	17.000
13	1/12/04	0.166	0.000	0.000	0.008	1.075	1.906	1.563	0.563	0.091	26.0	▨	▨	▨
14	1/29/04	1.630	0.040	0.090	0.090	0.779	0.010	2.792	1.792	0.303	46.0	457337.1	7.825	26.750
15	2/14/04	0.189	0.023	0.204	0.204	0.235	0.135	0.000	0.000	0.091	20.0	7013.0	0.091	14.000
16	2/16/04	0.439	0.000	0.106	0.212	0.393	0.385	0.000	0.000	0.121	15.0	6937.8	0.091	12.500
17	3/3/04	0.280	0.000	0.000	0.000	0.462	3.365	3.813	2.792	0.121	12.0	37108.4	0.623	7.167
18	3/7/04	0.076	0.008	0.008	0.166	0.490	3.365	3.813	2.792	0.030	18.0	87957.7	0.418	10.500
	▨	flow data not collected for this sampling event												

Table B-2: Hydrologic Statistics, Composite Events

APPENDIX C:
QA/QC Methods

Parameter	type of sample	Lab	Method Number	Method	Units	Reporting Limit	Container	Preservation[a]
Conventional Pollutants								
Total suspended solids	composite	MEL	SM 2540-D	Gravimetric (104°C)	mg/L	1.0	P, G	Cool to 4°C
pH	grab	ARI	SM 4500-HB	Electrometric	pH units	-	P, G	Cool to 4°C
Hardness as $CaCO_3$	composite	MEL	SM 2340-B	Ca + Mg calculation	mg/L as $CaCO_3$	0.5	P, G	HNO_3 to pH <2. Cool to 4°C
Total phosphorus	composite	ARI	SM 4500-PF	Automated ascorbic acid	mg/L	0.005	P	H_2SO_4 to pH <2. Cool to 4°C
Soluble reactive phosphorus	composite	ARI	SM 4500-PF	Automated ascorbic acid	mg/L	0.002	P	Cool to 4°C
Total persulfate nitrogen	composite	ARI	SM 4500-N	Automated Koroleff	mg/L	0.01	P	H_2SO_4 to pH <2. Cool to 4°C
Fecal coliform bacteria[b]	grab	ARI	SM 9222-D	Membrane filtration	cfu/100 mL	1	P, G	Cool to 4°C
Escherichia coli[b]	grab	ARI	SM 9222-G	Membrane filtration	cfu/100 mL	1	P, G	Cool to 4°C
Total petroleum hydrocarbons-diesel	grab or composite[d]	MEL	Ecology 1997	NWTPH-Dx	mg/L	0.25	G	HCL to pH <2. Cool to 4°C
Total petroleum hydrocarbons-heavy oil	grab or composite[d]	MEL	Ecology 1997	NWTPH-Dx	mg/L	0.5	G	HCL to pH <2. Cool to 4°C
Particle size distribution	composite	UW		Laser diffraction	% by volume			Cool to 4°C
Metals (total and dissolved)								
Copper	composite	MEL	EPA 200.8 or 200.9	ICP-MS or GFAA	ug/L	1.0	P	HNO_3 to pH <2. Cool to 4°C
Lead	composite	MEL	EPA 200.8 or 200.9	ICP-MS or GFAA	ug/L	1.0	P	HNO_3 to pH <2. Cool to 4°C
Zinc	composite	MEL	EPA 200.8 or 200.9	ICP-MS or GFAA	ug/L	1.0	P	HNO_3 to pH <2. Cool to 4°C
Pesticides[c]								
Chlorinated pesticides	composite	MEL	SW 846 Method 8081/8085	GC/AED	ug/L	0.01-1.0	G	Cool to 4°C
Organophosphorus pesticides	composite	MEL	SW 846 Method 8085	GC/AED	ug/L	0.01-1.0	G	Cool to 4°C
Nitrogen pesticides	composite	MEL	SW 846 Method 8085	GC/AED	ug/L	0.01-1.0	G	Cool to 4°C
Herbicides	composite	MEL	SW 846 Method 8085	GC/AED	ug/L	0.1-1.0	G	Cool to 4°C

Labs: ARI = Aquatic Research, Inc.; MEL = Manchester Environmental Laboratory; UW = University of Washington
GFAA = graphite furnace atomic absorption spectrophotometric
ICP/MS = inductively coupled plasma mass spectrometry
GC = gas chromatography
AED = atomic emission detector

a. Samples will be maintained on ice in the field. Preservation will be performed by the laboratory.
b. Samples will be delivered to the laboratory immediately after field collection.
c. Samples were only analyzed for pesticides and herbicides for winter/spring 2003 events
d. TPH samples were taken as composite before 10/5/03 and as grab afterwards

Table C-1: Sampling Methods, Laboratory Methods, Detection Limits, and Holding Times

APPENDIX D:
QA/QC Results

CONVENTIONALS - COMPOSITE SAMPLES

	QC parameter	sites submitted			TSS	Hard-ness	SRP	TP	TN	Tot Cu	Tot Pb	Tot Zn	Diss Cu	Diss Pb	Diss Zn
	detection limit				0.5	2	0.001	0.002	0.1	0.001	0.001	0.005	0.001	0.001	0.005
	units				mg/l	mg CaCO3 per litre	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	event date	107th	120th	122nd	blank	blank	blank	blank	blank	blank	blank	blank	blank	blank	blank
1	1/12/2003		x	x	<1.0	<0.2	<0.001	<0.002	<0.100	<0.001	<0.0001	<0.005	<0.001	<0.002	<0.001
2	1/25/2003		x	x	<1.0	<0.2	<0.001	<0.002	<0.100	<0.001	<0.0001	<0.005	<0.001	<0.002	<0.001
3	4/4/2003	x			<1.0	<0.2	<0.001	<0.002	<0.100	<0.001	<0.0001	<0.005	<0.001	<0.001	<0.001
4	4/8/2003	x			<1.0	<0.2	<0.001	<0.002	<0.100	<0.001	<0.0001	<0.005	<0.001	<0.001	<0.001
5	4/23/2003	x	x	x	<1.0	<0.2	<0.001	<0.002	<0.100	<0.001	<0.0001	<0.005	<0.001	<0.001	<0.001
6	5/16/2003	x			<1.0	<0.2	▨	▨	▨	▨	▨	▨	▨	▨	▨
7	6/20/2003	x	x	x	<1.0	<0.2	<0.001	<0.002	<0.100	<0.001	<0.0001	<0.005	<0.001	<0.001	<0.001
8	10/6/2003	x	x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.002	<0.005	<0.001	<0.002	<0.005
9	10/16/2003	x			<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
10	11/15/2003		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.002	<0.005	<0.001	<0.002	<0.005
11	12/2/2003		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.002	<0.005	<0.001	<0.002	<0.005
12	12/4/2003		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.002	<0.005	<0.001	<0.002	<0.005
13	1/12/2004		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.002	<0.005	<0.001	<0.002	<0.005
14	1/29/2004		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
15	2/14/2004		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
16	2/16/2004		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.002	<0.005	<0.001	<0.002	<0.005
17	3/3/2004		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
18	3/6/2004		x	x	<0.50	<2.00	<0.001	<0.002	<0.100	<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
	Samples Analyzed:				35	35	34	34	34	34	34	34	34	34	34
	Laboratory Duplicates Analyzed:				18	18	17	17	17	17	17	17	17	17	17
	Frequency (%)				51%	51%	50%	50%	50%	50%	50%	50%	50%	50%	50%

TPH - GRAB SAMPLES AND COMPOSITE SAMPLES

QC parameter				Diesel	Motor Oil
method				NWTPH-Dx	NWTPH-Dx
detection limit				0.05	0.1
units	sites submitted			mg/l	mg/l
event date	107th	120th	122nd	blank	blank
1/12/2003		x	x	<0.083	<0.21
4/4/2003	x			■	<0.13
4/8/2003	x			■	<0.13
4/23/2003	x	x	x	<0.048	<0.12
5/15/2003	x			<0.083	<0.21
6/20/2003	x	x	x	<0.05	<0.25
10/5/2003	x	x	x	<0.05	<0.10
10/28/2003		x	x	<0.05	<0.10
2/16/2004		x	x	<0.05	<0.10
3/3/2004		x	x	<0.05	<0.10

■ parameter not analyzed and QAQC analysis not performed
▨ QAQC method blank not analyzed
BOLD TYPE = criteria exceeded

BACTERIA - GRAB SAMPLES

QC parameter				fecal coliform	e coli
method				SM1892 22D	EPA100 29
detection limit				2	2
units	sites submitted			cfu/100 ml	cfu/100 ml
event date	107th	120th	122nd	blank	blank
1/30/2003	x	x	x	<2	<2
3/12/2003	x	x	x	<2	<2
10/28/2003		x	x	<2	<2
2/16/2004		x	x	<2	<2
3/3/2004		x	x	<2	■

■ parameter not analyzed and QAQC analysis not performed

Table D-1: Laboratory Method Blanks, Page 1 of 5

NITROGEN CONTAINING PESTICIDES

site	lab meth. blnk.I		lab meth. blnk.II		lab meth. blnk. I		lab meth. blnk. II		lab meth. blnk. III		lab meth. blnk. I		lab meth. blnk. II		lab meth
date	01/12/03		01/12/03		04/09/03		04/09/03		04/09/03		05/15/03		05/15/03		06/2
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l
Dichlorobenil	0.029	J	0.029	J	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Tebuthiuron	0.022	U	0.022	U	0.046	U	0.05	U	0.046	U	0.05	U	0.05	U	0.05
Propachlor (Ramrod)	0.035	U	0.035	U	0.074	U	0.07	U	0.074	U	0.08	U	0.08	U	0.08
Ethalfluralin (Sonalan)	0.022	U	0.022	U	0.046	U	0.05	U	0.046	U	0.05	U	0.05	U	0.05
Treflan (Trifluralin)	0.022	U	0.022	U	0.046	U	0.05	U	0.046	U	0.05	U	0.05	U	0.05
Simazine	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Atrazine	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Pronamide (Kerb)	0.058	U	0.058	U	0.12	U	0.12	U	0.12	U	0.13	U	0.13	U	0.13
Terbacil	0.043	U	0.043	U	0.092	U	0.09	U	0.092	U	0.1	U	0.1	U	0.1
Metribuzin	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Alachlor	0.052	U	0.052	U	0.11	U	0.11	U	0.11	U	0.12	U	0.12	U	0.12
Prometryn	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Bromacil	0.058	U	0.058	U	0.12	U	0.12	U	0.12	U	0.13	U	0.13	U	0.13
Metolachlor	0.058	U	0.058	U	0.12	U	0.12	U	0.12	U	0.13	U	0.13	U	0.13
Diphenamid	0.043	U	0.043	U	0.092	U	0.06	U	0.092	U	0.1	U	0.1	U	0.1
Pendimethalin	0.022	U	0.022	U	0.046	U	0.05	U	0.046	U	0.05	U	0.05	U	0.05
Napropamide	0.043	U	0.043	U	0.092	U	0.09	U	0.092	U	0.1	U	0.1	U	0.1
Oxyfluorfen	0.058	UJ	0.058	UJ	0.12	UJ	0.12	U	0.12	U	0.13	UJ	0.13	UJ	0.13
Norflurazon	0.029	UJ	0.029	UJ	0.062	UJ	0.06	U	0.062	U	0.067	UJ	0.067	UJ	0.067
Progargite	▨	▨	▨	▨	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Fluridone	0.087	UJ	0.087	UJ	0.18	UJ	0.19	U	0.18	U	0.2	UJ	0.2	UJ	0.2
Eptam	0.029	U	0.029	U	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Butylate	0.029	U	0.029	U	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Vernolate	0.029	U	0.029	U	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Cycloate	0.029	U	0.029	U	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Benefin	0.022	U	0.022	U	0.046	U	0.05	U	0.046	U	0.05	U	0.05	U	0.05
Prometon (Pramitol 5p)	0.014	U	0.014	U	0.031	UJ	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Propazine	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Chlorothalonil (Daconil)	0.035	U	0.035	U	0.074	U	0.07	U	0.074	U	0.08	U	0.08	U	0.08
Triallate	0.043	U	0.043	U	0.092	U	0.09	U	0.092	U	0.1	U	0.1	U	0.1
Ametryn	0.014	UJ	0.014	UJ	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Terbutryn (Igran)	0.014	UJ	0.014	UJ	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Hexazinone	0.022	UJ	0.022	UJ	0.046	UJ	0.05	U	0.046	U	0.05	UJ	0.05	UJ	0.05
Pebulate	0.029	U	0.029	U	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Molinate	0.029	U	0.029	U	0.062	U	0.06	U	0.062	U	0.067	U	0.067	U	0.067
Chlorpropham	0.058	U	0.058	U	0.12	U	0.12	U	0.12	U	0.13	U	0.13	U	0.13
Atraton	0.022	U	0.022	U	0.046	U	0.05	U	0.046	U	0.05	U	0.05	U	0.05
Triadimefon	0.038	U	0.038	U	0.08	UJ	0.08	U	0.08	U	0.087	U	0.087	U	0.087
MGK264	0.12	U	0.12	U	0.25	U	0.25	U	0.25	U	0.27	U	0.27	U	0.27
Butachlor	0.087	U	0.087	U	0.18	U	0.19	U	0.18	U	0.2	U	0.2	U	0.2
Carboxin	0.087	U	0.087	U	0.18	U	0.18	U	0.18	U	0.2	U	0.2	U	0.2
Fenarimol	0.043	U	0.043	U	0.092	U	0.09	U	0.092	U	0.1	U	0.1	U	0.1
Diuron	0.087	U	0.087	U	0.18	U	0.19	U	0.18	U	0.2	U	0.2	U	0.2
Di-allate (Avadex)	0.1	U	0.1	U	0.22	U	0.22	U	0.22	U	0.23	U	0.23	U	0.23
Profluralin	0.035	U	0.035	U	0.074	U	0.07	U	0.074	U	0.08	U	0.08	U	0.08
Metalazyl	0.087	U	0.087	U	0.18	U	0.19	U	0.18	U	0.2	U	0.2	U	0.2
Cyanazine	0.022	UJ	0.022	UJ	0.046	UJ	0.05	U	0.046	U	0.05	UJ	0.05	UJ	0.05

U= Undetected
UJ = The analyte was not detected at or abovev the reported estimated result
NJ = There is evidence that the analyte is present. The associated numberical result is an estimate
REJ = The data are unusable for all purposes
▨ QAQC method blank not analyzed

Table D-1: Laboratory Method Blanks, Page 2 of 5

CHLORINATED PESTICIDES

site	lab meth. blnk.I		lab meth. blnk.II		lab meth. blnk. I		lab meth. blnk. II		lab meth. blnk. III		lab meth. blnk. I		lab meth. blnk. II		lab meth
date	01/12/03		01/12/03		04/09/03		04/09/03		04/09/03		05/15/03		05/15/03		06/2
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l
Alpha-BHC	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Beta-BHC	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Gamma-BHC (Lindane)	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Delta-BHC	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Heptachlor	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	UJ	0.017	U	0.017	U	0.017
Aldrin	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Heptachlor Epoxide	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Trans-Chlordane (Gamma)	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Cis-Chlordane (Alpha-Chlordane	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Endosulfan I	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Dieldrin	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
4,4'-DDE	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Endrin	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Endosulfan II	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
4,4'-DDD	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Endrin Aldehyde	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	UJ	0.017	U	0.017	U	0.017
Endosulfan Sulfate	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
4,4-DDT	0.0072	UJ	0.0072	UJ	0.016	U	0.016	U	0.0077	UJ	0.017	REJ	0.017	REJ	0.017
Endrin Keytone	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	UJ	0.017	U	0.017	U	0.017
Methoxychlor	0.0072	UJ	0.0072	UJ	0.016	U	0.016	U	0.0077	UJ	0.017	REJ	0.017	REJ	0.017
Alpha-Chlordene	0.0072	U	0.0072	U	**0.016**		▨	▨	▨	▨	▨	▨	▨	▨	▨
Gamma-Chlordene	0.0072	U	0.0072	U	**0.016**		▨	▨	▨	▨	▨	▨	▨	▨	▨
Oxychlordane	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
DDMU	0.0072	U	0.0072	U	**0.016**		▨	▨	▨	▨	▨	▨	▨	▨	▨
Cis-Nonachlor	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Kelthane	0.029	U	0.029	U	0.063	U	0.063	U	0.031	UJ	0.067	REJ	0.067	REJ	0.067
Captan	0.02	UJ	0.02	UJ	0.042	U	0.042	U	0.021	UJ	0.045	REJ	0.045	REJ	0.045
2,4'-DDE	0.0072	U	0.0072	U	**0.016**		0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Trans-Nonachlor	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	REJ	0.017	REJ	0.017
2,4'-DDD	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	U	0.017	U	0.017	U	0.017
2,4-DDT	0.0072	U	0.0072	U	0.01	U	0.01	U	0.0077	U	0.017	REJ	0.017	REJ	0.017
Captafol	0.036	U	0.036	U	0.016	U	0.016	U	0.038	UJ	0.083	REJ	0.083	REJ	0.083
Mirex	0.0072	U	0.0072	U	0.016	U	0.016	U	0.0077	UJ	0.017	U	0.017	U	0.017
Hexachlorbenzene	0.0072	U	0.0072	U	**0.016**		0.016	U	0.0077	U	0.017	U	0.017	U	0.017
Pentachloroanisole	0.0072	U	0.0072	U	**0.016**		0.016	U	0.0077	U	0.017	U	0.017	U	0.017

U= Undetected
UJ = The analyte was not detected at or abovev the reported estimated result
NJ = There is evidence that the analyte is present. The associated numberical result is an estimate
REJ = The data are unusable for all purposes
▨ QAQC method blank not analyzed

Table D-1: Laboratory Method Blanks, Page 3 of 5

ORGANOPHOSPHOROUS PESTICIDES

site	lab meth. blnk.I		lab meth. blnk.II		lab meth. blnk. I		lab meth. blnk. II		lab meth. blnk. III		lab meth. blnk. I		lab meth. blnk. II		lab meth
date	01/12/03		01/12/03		04/09/03		04/09/03		04/09/03		05/15/03		05/15/03		06/2
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l
Demeton-O	0.01	UJ	0.01	UJ	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Sulfotepp	0.0087	U	0.0087	U	0.019	U	0.02	U	0.018	U	0.02	U	0.02	U	0.02
Demeton-S	0.01	UJ	0.01	UJ	0.022	U	0.02	U	0.022	UJ	0.023	UJ	0.023	UJ	0.023
Fonofos	0.0087	U	0.0087	U	0.019	U	0.02	U	0.018	U	0.02	U	0.02	U	0.02
Disulfoton (Di-Syston)	0.0087	U	0.0087	U	0.019	U	0.02	U	0.018	U	0.02	U	0.02	U	0.02
Methyl Chlorpyrifos	0.012	U	0.012	U	0.025	U	0.02	U	0.025	UJ	0.027	U	0.027	U	0.027
Fenitrothion	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Malathion	0.012	U	0.012	U	0.025	U	0.02	U	0.025	U	0.027	U	0.027	U	0.027
Chlorphyriphos	0.012	U	0.012	U	0.025	U	0.02	U	0.025	UJ	0.027	U	0.027	U	0.027
Merphos (1&2)	0.017	U	0.017	U	0.038	U	0.04	U	0.037	U	0.04	U	0.04	U	0.04
Ethion	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Carbophenothion	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
EPN	0.014	U	0.014	U	0.031	U	0.03	U	0.031	U	0.033	U	0.033	U	0.033
Azinphos Ethyl	0.023	U	0.023	U	0.05	U	0.05	U	**0.049**		0.053	U	0.053	U	0.053
Ethoprop	0.012	U	0.012	U	0.025	U	0.02	U	0.025	U	0.027	U	0.027	U	0.027
Phorate	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Dimethoate	0.012	UJ	0.012	UJ	0.025	U	0.02	U	0.025	UJ	0.027	UJ	0.027	UJ	0.027
Diazinon	0.012	U	0.012	U	0.025	U	0.02	U	0.025	U	0.027	U	0.027	U	0.027
Methyl Parathion	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Ronnel	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Fenthion	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Parathion	0.012	U	0.012	U	0.025	U	0.02	U	0.025	U	0.027	U	0.027	U	0.027
Fensulfothion	0.014	U	0.014	U	0.031	U	0.03	U	0.031	UJ	0.033	U	0.033	U	0.033
Bolstar (Sulprofos)	0.01	U	0.01	U	0.022	U	0.02	U	0.022	U	0.023	U	0.023	U	0.023
Imidan	0.016	U	0.016	U	0.034	U	0.03	U	0.034	U	0.037	U	0.037	U	0.037
Azinphos (Guthion)	0.023	UJ	0.023	UJ	0.05	U	0.05	U	0.049	U	0.053	U	0.053	U	0.053
Coumaphos	0.017	U	0.017	UJ											
Dichlorvos (DDVP)	0.012	U	0.012	U											
Mevinphos	0.014	U	0.014	U											
Dioxathion	0.025	U	0.025	U											
Propetamphos	0.029	U	0.029	U											
Methyl Paraoxon	0.026	U	0.026	U											
Phosphamidan	0.035	U	0.035	U											
Tetrachlorvinphos (Gardona)	0.029	U	0.029	U											
Fenamiphos	0.022	U	0.022	U							0.05	U	0.05	U	0.05
Dribufos (DEF)	0.02	U	0.02	U											
Abate (Temephos)	0.087	UJ	0.087	UJ											

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▨ QAQC method blank not analyzed

Table D-1: Laboratory Method Blanks, Page 4 of 5

HERBICIDES

site	lab meth. blnk.		lab meth. blnk.		lab meth. blnk. I		lab meth. blnk. II		lab meth. blnk. I		lab meth. blnk. II	
date	01/12/03		04/09/03		05/15/03		05/15/03		06/20/03		06/20/03	
units	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.	ug/l	qual.
2,4,6-Trichlorphenol	0.1	U	0.092	U	0.1	U	0.1	U	0.1	U	0.1	U
3,5-Dichlorobenzoic Acid	0.17	U	0.16	U	0.17	U	0.17	U	0.17	U	0.17	U
4-Notrophenol	0.29	U	0.3	U	0.29	U	0.29	U	0.29	U	0.29	U
2,4,5-Trichlorophenol	0.1	U	0.093	U	0.1	U	0.1	U	0.1	U	0.1	U
Dicamba I	0.17	U	0.16	U	0.17	U	0.17	U	0.17	U	0.17	U
2,3,4,6-Tetrachlorophenol	0.092	U	0.087	U	0.092	U	0.092	U	0.092	U	0.092	U
MCPP (Mecoprop)	0.33	U	0.31	U	0.33	U	0.33	U	0.33	U	0.33	U
MCPA	0.33	U	0.31	U	0.33	U	0.33	U	0.33	U	0.33	U
Dichlorprop	0.18	U	0.17	U	0.18	U	0.18	U	0.18	U	0.18	U
Bromoxynil	0.17	U	0.16	U	0.17	U	0.17	U	0.17	U	0.17	U
2,4-D	0.17	U	0.16	U	0.17	U	0.17	U	0.17	U	0.17	U
2,3,4,5-Tetrachlorophenol	0.092	U	0.087	U	0.092	U	0.092	U	0.092	U	0.092	U
Trichlopyr	0.14	U	0.13	U	0.14	U	0.14	U	0.14	U	0.14	U
Pentachlorophenol	0.084	U	0.079	U	0.084	U	0.084	U	0.084	U	0.084	U
2,4,5-TP (Silvex)	0.13	U	0.13	U	0.13	U	0.13	U	0.13	U	0.13	U
2,4,5-T	0.13	U	0.13	U	0.13	U	0.13	U	0.13	U	0.13	U
2,4-DB	0.2	U	0.19	U	0.2	U	0.2	U	0.2	U	0.2	U
Dinoseb	0.25	UJ	0.24	UJ	0.25	UJ	0.25	UJ	0.25	UJ	0.25	UJ
Bentazon	0.25	U	0.24	U	0.25	U	0.25	U	0.25	U	0.25	U
Ioxynil	0.17	U	0.16	U	0.17	U	0.17	U	0.17	U	0.17	U
Picloram	0.17	UJ	0.16	UJ	0.17	UJ	0.17	UJ	0.17	UJ	0.17	UJ
Dacthal (DCPA)	0.13	U	0.12	U	0.13	U	0.13	U	0.13	U	0.13	U
2,4,5-TB	0.15	U	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Acifluorfen (Blazer)	0.67	UJ	0.64	UJ	0.67	U	0.67	U	0.67	U	0.67	U
Diclofop-Methyl	0.25	U	0.25	U	0.25	U	0.25	U	0.25	U	0.25	U

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Table D-1: Laboratory Method Blanks, Page 5 of 5

CONVENTIONALS - COMPOSITE SAMPLES

	QC parameter	sites submitted			TSS			PSD			Hardness			SRP			TP		
	detection limit				0.5			0.001			2			0.001			0.002		
	units				mg/l			ul/l			mg CaCO3 / l			mg/l			mg/l		
	goal RPD:				20			30			10			20			20		
	event date	107th	120th	122nd	original	duplicate	RPD	original	duplicate	RPD	original	duplicate	RPD	original	duplicate	RPD	original	duplicate	RPD
1	1/12/2003		x	x										**0.002**	**0.002**	**20.59%**	0.131	0.134	2.39%
2	1/25/2003		x	x										0.013	0.015	10.90%	0.120	0.119	0.72%
3	4/4/2003	x												0.001	0.001	3.27%	0.041	0.039	4.57%
4	4/8/2003	x												0.023	0.024	2.91%	0.041	0.039	4.57%
5	4/23/2003	x	x	x	32.0	32.0	0.00%							0.003	0.003	4.16%	0.075	0.071	5.54%
6	5/16/2003	x																	
7	6/20/2003	x	x	x	12.0	13.0	8.33%							0.037	0.037	4.13%	0.150	0.015	2.90%
8	10/6/2003	x	x	x	48.0	52.0	8.00%				25.2	24.6	2.35%	0.045	0.048	6.37%	0.245	0.242	1.23%
9	10/16/2003	x			4.5	5.0	10.53%	71.7	69.5	3.04%	20.9	21.5	2.76%	0.067	0.067	0.53%	0.151	0.147	2.12%
10	11/15/2003		x	x	62.0	69.0	10.69%	46.7	45.0	3.58%	10.4	10	3.85%	0.037	0.036	2.61%	0.047	0.047	0.24%
11	12/2/2003		x	x	8.0	9.0	11.76%	20.0	18.6	7.19%	11.7	12.1	3.28%	0.008	0.008	0.00%	0.048	0.047	2.49%
12	12/4/2003		x	x	8.0	9.0	11.76%				11.7	12.1	3.28%	0.018	0.019	2.45%	0.048	0.047	2.49%
13	1/12/2004		x	x	156.0	160.0	2.53%				25	25.8	3.08%	0.011	0.010	5.94%	0.045	0.042	6.98%
14	1/29/2004		x	x	50.0	49.0	2.04%				71.5	69.2	3.33%	0.006	0.006	2.99%	0.024	0.023	1.43%
15	2/14/2004		x	x	42.0	40.0	4.88%				83.8	82.9	1.17%	0.025	0.026	1.11%	0.054	0.053	2.85%
16	2/16/2004		x	x	35.0	35.0	0.00%				83.8	82.9	1.17%	0.025	0.026	1.11%	0.211	0.219	3.59%
17	3/3/2004		x	x	46.0	48.0	4.26%				24	23.6	1.64%	0.052	0.052	0.05%	0.013	0.014	3.04%
18	3/6/2004		x	x	13.0	12.0	8.33%	87.6	78.0	10.93%	24	23.6	1.64%	0.038	0.038	0.36%	0.153	0.154	0.88%
	Samples Analyzed:				35			35			35			34			34		
	Laboratory Duplicates Analyzed:				14			4			12			18			18		
	Frequency (%)				40%			11%			34%			53%			53%		

	QC parameter	sites submitted			Total Cu			Total Pb			Total Zn			Diss Cu			Diss Pb		
	detection limit				0.001			0.001			0.005			0.001			0.001		
	units				mg/l			mg/l			mg/l			mg/l			mg/l		
	goal RPD:				20			20			20			20			20		
	event date	107th	120th	122nd	original	duplicate	RPD	original	duplicate	RPD	original	duplicate	RPD	original	duplicate	RPD	original	duplicate	RPD
1	1/12/2003		x	x										0.0036	0.0036	0.00%	0.0004	0.0004	0.50%
2	1/25/2003		x	x										0.0032	0.0032	0.93%	0.0004	0.0004	1.10%
3	4/4/2003	x																	
4	4/8/2003	x																	
5	4/23/2003	x	x	x															
6	5/16/2003	x																	
7	6/20/2003	x	x	x															
8	10/6/2003	x	x	x	0.0344	0.0320	7.23%	0.0109	0.0100	8.61%	0.176	0.158	10.78%	0.0228	0.0216	5.41%	0.0016	0.0014	13.33%
9	10/16/2003	x			0.0055	0.0055	0.73%	<0.001	<0.001	NC	0.176	0.158	10.78%	0.0228	0.0216	5.41%	0.0016	0.0014	13.33%
10	11/15/2003		x	x	0.0023	0.0024	4.26%	<0.001	<0.001	NC	0.062	0.079	24.11%	<0.001	<0.001	NC	<0.001	<0.001	NC
11	12/2/2003		x	x	0.0015	0.0015	0.00%	<0.001	<0.001	NC	0.086	0.095	9.94%	<0.001	<0.001	NC	<0.001	<0.001	NC
12	12/4/2003		x	x	0.0015	0.0015	0.00%	<0.001	<0.001	NC	0.086	0.095	9.94%	<0.001	<0.001	NC	<0.001	<0.001	NC
13	1/12/2004		x	x	0.0131	0.0130	0.77%	0.0071	0.0073	2.78%	0.431	0.432	0.23%	0.0187	0.0186	0.54%	0.0017	0.0017	0.00%
14	1/29/2004		x	x	0.0033	0.0035	5.88%	<0.001	<0.001	NC	0.033	0.029	12.90%	0.0018	0.0018	3.31%	<0.001	<0.001	NC
15	2/14/2004		x	x	0.0089	0.0088	1.13%	0.0066	0.0057	14.63%	0.015	0.014	6.90%	0.0123	0.0122	0.82%	<0.001	<0.001	NC
16	2/16/2004		x	x	0.0109	0.0104	4.69%	0.0063	0.0055	13.56%	0.018	0.019	5.41%	0.0037	0.0033	11.43%	<0.001	<0.001	NC
17	3/3/2004		x	x	0.0131	0.0135	3.01%	0.0116	0.0135	14.40%	0.010	0.012	18.18%	0.0024	0.0022	8.70%	<0.001	<0.001	NC
18	3/6/2004		x	x	0.0092	0.0089	3.31%	<0.001	<0.001	NC	0.010	0.012	18.18%	0.0086	0.0084	2.35%	<0.001	<0.001	NC
	Samples Analyzed:				34			34			34			34			34		
	Laboratory Duplicates Analyzed:				11			5			11			10			5		
	Frequency (%)				32%			15%			32%			29%			15%		

■ samples not analyzed for this event
▒ QAQC laboratory duplicate not analyzed
BOLD TYPE = RPD goal exceeded

Table D-2: Laboratory Duplicate Samples, Page 1 of 2

TPH - GRAB SAMPLES AND COMPOSITE SAMPLES

QC parameter				Diesel			Motor Oil		
method				NWTPH-Dx			NWTPH-Dx		
detection limit				0.05			0.1		
units	sites submitted			mg/l			mg/l		
event date	107th	120th	122nd	original	duplicate	RPD	original	duplicate	RPD
1/13/2003		x	x	insufficient volume					
4/4/2003	x			insufficient volume					
4/8/2003	x			insufficient volume					
4/23/2003	x	x	x	insufficient volume					
5/15/2003	x			insufficient volume					
6/20/2003	x	x	x	insufficient volume					
10/5/2003	x	x	x	<0.05	<0.05	NC	<0.1	<0.1	NC
10/28/2003		x	x	5.61	5.28	6.06%	56.80	61.90	8.59%
2/16/2004		x	x	1.94	2.16	10.73%	1.08	1.18	8.85%
3/3/2004		x	x	0.31	0.38	20.29%	0.73	0.65	11.59%

BACTERIA - GRAB SAMPLES

QC parameter				fecal coliform			e coli		
method				SM189222D			EPA 10029		
detection limit				2			2		
units	sites submitted			cfu / 100ml			cfu / 100ml		
event date	107th	120th	122nd	original	duplicate	RPD	original	duplicate	RPD
1/30/2003		x	x	5200	5400	3.77%	est 3200	est 3600	NC
3/12/2003	x	x	x	est 3000	est 2000	NC	est 1600	est 1600	NC
10/28/2003		x	x	est 2000	est 2600	NC	<200	<200	NC
2/16/2004		x	x	est 180	est 160	NC	est 200	est 160	NC
3/3/2004		x	x	460	560	19.61%	■	■	■

■	samples not analyzed for this event
▒	QAQC laboratory duplicate not analyzed

BOLD TYPE = RPD goal exceeded

Table D-2: Laboratory Duplicate Samples, Page 2 of 2

	detection limit				0.5	2	0.001	0.002	0.1	0.0010	0.0010	0.005	0.0010	0.0010	0.005
	units				mg/l	mg CaCO3 / l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	%R goal (range)				80 to 120	90 to 110	75 to 125	75 to 125	75 to 125	75 to 125	75 to 125	75 to 125	75 to 125	75 to 125	75 to 125
	event date	107th	120th	122nd	% recovery	% recovery	% recovery	% recovery	% recovery	% recovery	% recovery	% recovery	% recovery	% recovery	% recovery
1	1/12/2003		x	x	97%	103%	103%	114%	99%	98%	99%	90%	100%	102%	97%
2	1/28/2003		x	x	99%	90%	101%	105%	108%	104%	110%	102%	98%	106%	92%
3	4/4/2003	x			100%	104%	98%	95%	92%	108%	105%	114%	96%	100%	95%
4	4/8/2003	x			99%	96%	97%	95%	105%	108%	105%	114%	101%	102%	102%
5	4/23/2003	x	x	x	95%	102%	98%	94%	95%	104%	102%	106%	102%	102%	102%
6	5/16/2003	x			97%	103%	■	■	■	■	■	■	■	■	■
7	6/20/2003	x	x	x	99%	104%	100%	104%	106%	104%	103%	113%	99%	103%	112%
8	10/6/2003	x	x	x	░	99%	99%	104%	90%	91%	106%	100%	100%	113%	114%
9	10/16/2003	x			░	104%	96%	94%	93%	88%	108%	100%	101%	113%	114%
10	11/15/2003		x	x	░	100%	96%	101%	100%	98%	110%	102%	110%	107%	101%
11	12/2/2003		x	x	░	102%	100%	103%	90%	116%	95%	93%	110%	112%	114%
12	12/4/2003		x	x	░	102%	100%	103%	90%	116%	95%	93%	110%	112%	114%
13	1/12/2004		x	x	░	104%	100%	103%	115%	94%	101%	98%	87%	114%	91%
14	1/29/2004		x	x	░	101%	96%	102%	110%	98%	89%	97%	91%	95%	88%
15	2/14/2004		x	x	░	99%	100%	98%	86%	94%	112%	107%	100%	102%	107%
16	2/16/2004		x	x	░	99%	100%	99%	86%	99%	102%	105%	96%	93%	103%
17	3/3/2004		x	x	░	102%	98%	97%	OR	98%	113%	113%	104%	105%	89%
18	3/6/2004		x	x	░	102%	99%	OR	OR	90%	118%	113%	102%	103%	89%
	Samples Analyzed:				35	35	34	34	34	34	34	34	34	34	34
	Laboratory Duplicates Analyzed:				7	18	17	16	15	17	17	17	17	17	17
	Frequency (%)				20%	51%	50%	47%	44%	50%	50%	50%	50%	50%	50%

TPH - GRAB SAMPLES AND COMPOSITE SAMPLES

	QC parameter				Diesel	Motor Oil
	method				NWTPH-Dx	NWTPH-Dx
	detection limit					
	units	sites submitted			mg/l	mg/l
	event date	107th	120th	122nd	% recovery	% recovery
1	1/12/2003		x	x	107.00%	■
2	4/4/2003	x			114.00%	■
3	4/8/2003	x			113.00%	■
4	4/23/2003	x	x	x	114.00%	■
5	5/15/2003	x			101.00%	■
6	6/20/2003	x	x	x	95.60%	■

■ samples not analyzed for this event
░ QAQC laboratory duplicate not analyzed
BOLD TYPE = % Recovery goal exceeded

Table D-3: Matrix Spike / Matrix Spike Duplicates, Page 1 of 3

NITROGEN CONTAINING PESTICIDES

site	Lab Contr.	Lab Contr.	Lab Contr.	Lab Contr.	Lab Contr.	Lab Contr.
date	01/12/03	01/12/03	04/09/03	04/09/03	05/15/03	06/20/03
units	%rec	%rec	%rec	%rec	%rec	%rec
Dichlorobenil	81	62	▨	▨	112	▨
Tebuthiuron	95	59	▨	▨	62	▨
Propachlor (Ramrod)	85	67	▨	▨	69	▨
Ethalfluralin (Sonalan)	53	48	▨	▨	62	▨
Treflan (Trifluralin)	64	54	▨	▨	60	▨
Simazine	147	94	▨	▨	64	▨
Atrazine	80	57	▨	▨	55	▨
Pronamide (Kerb)	84	68	▨	▨	74	▨
Terbacil	84	65	▨	▨	149	▨
Metribuzin	93	67	▨	▨	716	▨
Alachlor	78	69	▨	▨	62	▨
Prometryn	96	71	▨	▨	84	▨
Bromacil	60	48	▨	▨	58	▨
Metolachlor	82	69	▨	▨	116	▨
Diphenamid	72	65	▨	▨	85	▨
Pendimethalin	101	91	▨	▨	63	▨
Napropamide	97	76	▨	▨	113	▨
Oxyfluorfen	165	136	▨	▨	68	▨
Norflurazon	52	32	▨	▨	70	▨
Progargite	▨	▨	76	76	▨	101
Fluridone	43	134	▨	▨	18	▨
Eptam	▨	▨	70	74	▨	116
Butylate	▨	▨	54	60	▨	119
Vernolate	▨	▨	57	63	▨	158
Cycloate	▨	▨	84	34	▨	148
Benefin	▨	▨	52	59	▨	133
Prometon (Pramitol 5p)	▨	▨	25	16	▨	32
Propazine	▨	▨	60	60	▨	134
Chlorothalonil (Daconil)	▨	▨	50	62	▨	98
Triallate	▨	▨	146	166	▨	152
Ametryn	▨	▨	72	78	▨	75
Terbutryn (Igran)	▨	▨	26	27	▨	54
Hexazinone	▨	▨	0	0	▨	0
Pebulate	▨	▨	92	112	▨	184
Molinate	▨	▨	65	73	▨	128
Chlorpropham	▨	▨	89	100	▨	234
Profluralin	▨	▨	53	53	▨	
Cyanazine	▨	▨	36	42	▨	51

CHLORINATED PESTICIDES

site	Lab Contr.	Lab Contr.	Lab Contr.
date	01/12/03	01/12/03	04/09/03
units	%rec	%rec	%rec
Alpha-BHC	196	95	78
Beta-BHC	457	188	91
Gamma-BHC (Lindane)	87	66	84
Delta-BHC	84	66	105
Heptachlor	49	39	72
Aldrin	49	49	53
Heptachlor Epoxide	75	69	82
Trans-Chlordane (Gamma)	77	65	78
Cis-Chlordane (Alpha-Chlord	69	61	77
Endosulfan I	82	64	78
Dieldrin	74	65	82
4,4'-DDE	75	65	103
Endrin	90	65	132
Endosulfan II	78	53	130
4,4'-DDD	113	81	137
Endrin Aldehyde	66	57	90
Endosulfan Sulfate	71	55	122
4,4-DDT	91	10	91
Endrin Keytone	53	29	87
Methoxychlor	22	5	77
Oxychlordane	▨	▨	74
Cis-Nonachlor	▨	▨	133
Kelthane	▨	▨	92
Captan	▨	▨	263
2,4'-DDE	▨	▨	102
Trans-Nonachlor	▨	▨	108
2,4'-DDD	▨	▨	52
2,4-DDT	▨	▨	260
Captafol	▨	▨	96
Mirex	▨	▨	0
Hexachlorbenzene	▨	▨	72
Pentachloroanisole	▨	▨	84

▨ This parameter was not tested for in these samples

Table D-3: Matrix Spike / Matrix Spike Duplicates, Page 2 of 3

HERBICIDES

site	lab. Control sample I	lab. Control sample II	lab. Control sample I	lab. Control sample I	lab. Control sample I
date	01/12/03	01/12/03	04/09/03	05/15/03	06/20/03
units	%rec	%rec	%rec	%rec	%rec
2,4,6-Trichlorphenol	99	97	83	100	59
3,5-Dichlorobenzoic Acid	62	64	75	98	65
4-Notrophenol	85	86	80	95	89
2,4,5-Trichlorophenol	138	158	146	198	139
Dicamba I	50	48	94	90	45
2,3,4,6-Tetrachlorophenol	102	98	79	92	79
MCPP (Mecoprop)	44	47	91	90	54
MCPA	48	42	81	93	51
Dichlorprop	57	46	99	85	44
Bromoxynil	117	112	78	91	76
2,4-D	50	52	101	79	39
2,3,4,5-Tetrachlorophenol	100	96	86	95	83
Trichlopyr	52	55	99	94	47
Pentachlorophenol	103	105	80	92	84
2,4,5-TP (Silvex)	75	77	100	112	78
2,4,5-T	62	48	93	92	43
2,4-DB	52	44	92	98	61
Dinoseb	18	74	40	42	141
Bentazon	79	100	83	98	93
Ioxynil	114	122	87	86	94
Picloram	18	26	21	29	16
Dacthal (DCPA)	25	31	89	40	87
2,4,5-TB	66	62	▨	▨	▨
Acifluorfen (Blazer)	10	24	76	45	37
Diclofop-Methyl	37	38	88	90	39

▨ This parameter was not tested for in these samples

ORGANOPHOSPHOROUS PESTICIDES

site	Lab Contr. Sample I	Lab Contr. Sample II	Lab Contr. Sample I	Lab Contr. Sample II	Lab Contr. Sample I	Lab Contr. Sample I
date	01/12/03	01/12/03	04/09/03	04/09/03	05/15/03	06/20/03
units	%rec	%rec	%rec	%rec	%rec	%rec
Demeton-O	30	18	128	130	▨	82
Sulfotepp	46	34	70	76	▨	94
Demeton-S	37	16	19	19	▨	35
Fonofos	85	66	67	74	▨	83
Disulfoton (Di-Syston)	40	31	72	73	▨	80
Methyl Chlorpyrifos	38	31	31	35	▨	100
Fenitrothion	42	31	86	98	▨	114
Malathion	44	34	77	89	▨	95
Chlorphyriphos	39	34	30	39	▨	94
Merphos (1&2)	48	37	86	75	▨	▨
Ethion	42	35	81	95	▨	85
Carbophenothion	45	33	79	91	▨	96
EPN	41	33	87	102	▨	112
Azinphos Ethyl	41	33	▨	▨	▨	75
Ethoprop	▨	▨	▨	▨	79	▨
Phorate	▨	▨	▨	▨	50	▨
Dimethoate	▨	▨	▨	▨	59	▨
Diazinon	▨	▨	▨	▨	49	▨
Methyl Parathion	▨	▨	▨	▨	62	▨
Ronnel	▨	▨	▨	▨	40	▨
Fenthion	▨	▨	▨	▨	48	▨
Parathion	▨	▨	▨	▨	43	▨
Fensulfothion	▨	▨	▨	▨	56	▨
Bolstar (Sulprofos)	▨	▨	▨	▨	49	▨
Imidan	▨	▨	▨	▨	50	▨
Azinphos (Guthion)	▨	▨	▨	▨	45	▨

▨ This parameter was not tested for in these samples

Table D-3: Matrix Spike / Matrix Spike Duplicates, Page 3 of 3

QC parameter				TSS	Hardness	SRP	TP	TN
detection limit				0.5	2	0.001	0.002	0.1
units	sites submitted			mg/l	mg CaCO3	mg/l	mg/l	mg/l
event date	107th	120th	122nd	RPD	RPD	RPD	RPD	RPD
3/3/2004			x	4.55%	5.50%	1.96%	15.04%	1.44%
3/6/2004		x		0.00%	6.10%	3.33%	0.63%	0.67%
Samples Analyzed:				35	35	34	34	34
Field Duplicates Analyzed:				2	2	2	2	2
Frequency (%)				6%	6%	6%	6%	6%

QC parameter				Total Cu	Total Pb	Total Zn	Diss Cu	Diss Pb	Diss Zn
detection limit				0.001	0.001	0.005	0.001	0.001	0.005
units	sites submitted			mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
event date	107th	120th	122nd	RPD	RPD	RPD	RPD	RPD	RPD
3/3/2004			x	14.60%	12.78%	6.02%	0.00%	0.00%	12.24%
3/6/2004		x		19.20%	**73.91%**	4.55%	4.65%	0.00%	**34.55%**
Samples Analyzed:				34	34	34	34	34	34
Field Duplicates Analyzed:				2	2	2	2	2	2
Frequency (%)				6%	6%	6%	6%	6%	6%

QC parameter				fecal coliform	e coli
detection limit					2
units	sites submitted			#/100ml	#/100ml
event date	107th	120th	122nd	RPD	RPD
2/16/2004		x		0.00%	20.00%
Samples Analyzed:				12	10
Field Duplicates Analyzed:				1	1
Frequency (%)				8%	10%

Table D-4: Field Duplicate Samples, page 1 of 1

CONVENTIONALS - COMPOSITE SAMPLES

QC parameter				TSS	Hardness	SRP	TP	TN
detection limit				0.5	2	0.001	0.002	0.1
units	sites submitted			mg/l	mg CaCO3 / l	mg/l	mg/l	mg/l
event date	107th	120th	122nd	blank	blank	blank	blank	blank
3/7/2004			x	<0.5	<2	<0.001	<0.02	<0.1
3/7/2004		x		<0.5	<2	<0.001	<0.02	<0.1
Samples Analyzed:				35	35	34	34	34
Rinsate Blanks Analyzed:				2	2	2	2	2
Frequency (%)				6%	6%	6%	6%	6%

QC parameter				Total Cu	Total Pb	Total Zn	Diss Cu	Diss Pb	Diss Zn
detection limit				0.001	0.001	0.005	0.001	0.001	0.005
units	sites submitted			mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
event date	107th	120th	122nd	blank	blank	blank	blank	blank	blank
3/7/2004			x	<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
3/7/2004		x		<0.001	<0.001	<0.005	<0.001	<0.001	<0.005
Samples Analyzed:				34	34	34	34	34	34
Rinsate Blanks Analyzed:				2	2	2	2	2	2
Frequency (%)				6%	6%	6%	6%	6%	6%

Table D-5: Equipment Rinsate Blanks, page 1 of 1

APPENDIX E:
Metals Toxicity Criteria and Calculations

Formulas:

Dissolved Copper:

$$\text{Acute:} \le (0.960) * e^{(0.9422*(\ln(hardness))-1.464)}$$

$$\text{Chronic:} \le (0.960) * e^{(0.8545*(\ln(hardness))-1.465)}$$

Dissolved Lead:

$$\text{Acute:} \le (CF) * e^{(1.273*(\ln(hardness))-1.460)}$$

$$\text{Chronic:} \le (CF) * e^{(1.273*(\ln(hardness))-4.705)}$$

$$\text{With: CF} = 1.46203 - [\ln(hardness)] * 0.145712$$

Dissolved Zinc:

$$\text{Acute:} \le (0.978) * e^{(0.8473*(\ln(hardness))+0.8604)}$$

$$\text{Chronic:} \le (0.986) * e^{(0.8473*(\ln(hardness))+0.7614)}$$

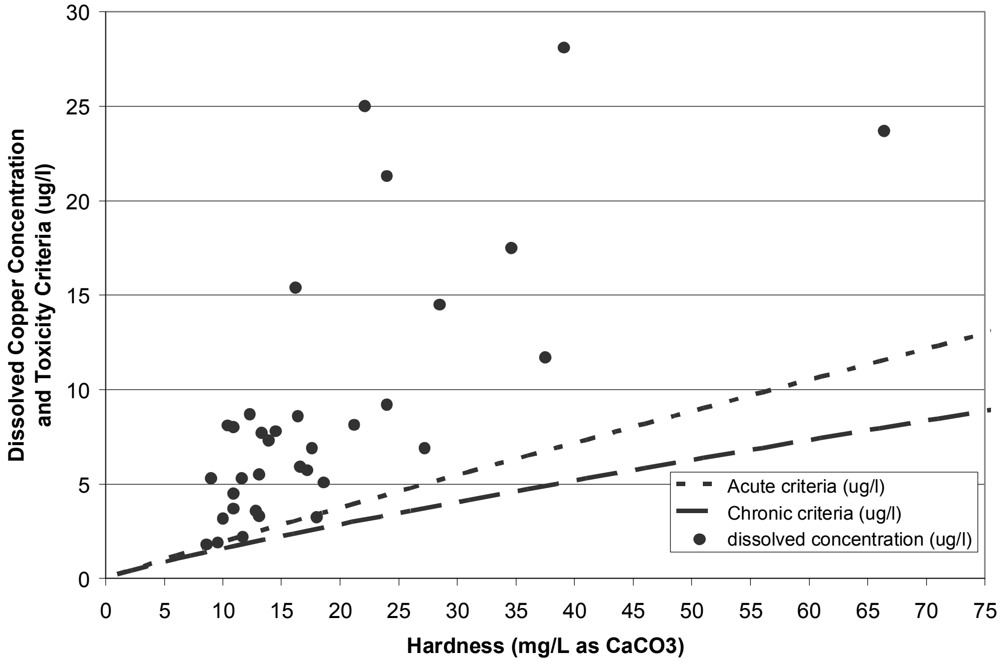

Figure E-1: Acute and Chronic Metals Toxicity Criteria Compared to Dissolved Copper Concentrations

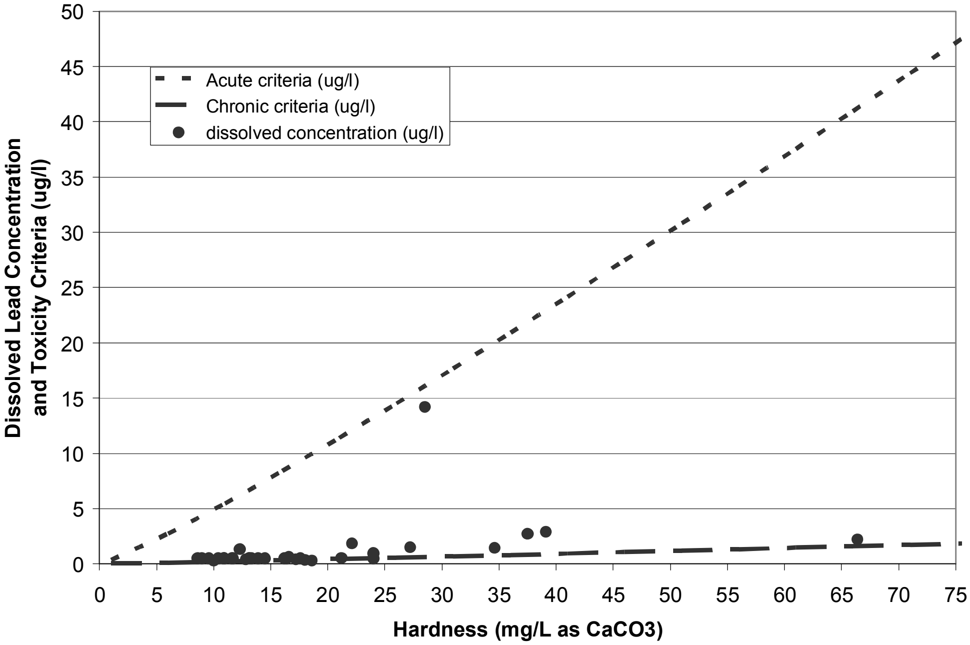

Figure E-2: Acute and Chronic Metals Toxicity Criteria Compared to Dissolved Lead Concentrations

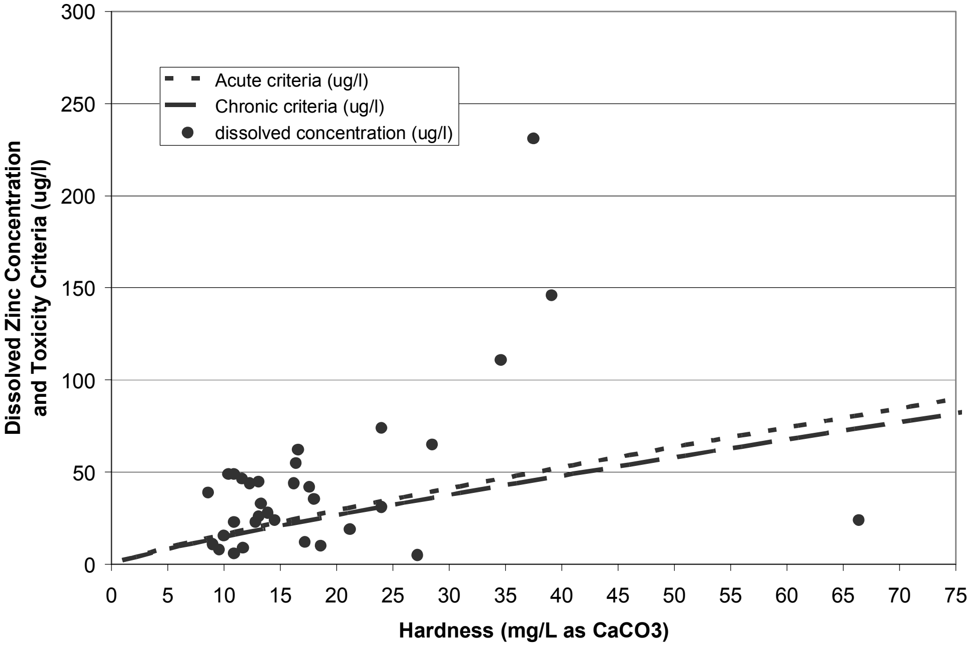

Figure E-3: Acute and Chronic Metals Toxicity Criteria Compared to Dissolved Zinc Concentrations

APPENDIX F:
Paired Study Statistical Analysis

Table F-1: Paired Study Statistical Analysis, Composite Samples
Page 1 of 2

non-parametric
Mann-Whitney or Wilcoxon Rank Sum
2-tailed hypothesis
H0: 120th and 122nd are the same

		n1=	14	14	14	14	14	14	14	14
		n2=	14	14	14	14	14	14	14	14
		R1=	192.5	214.5	180	189	175.5	192.5	214.5	180
		R2=	213.5	191.5	226	217	230.5	213.5	191.5	226
		U=	108.5	86.5	121	112	125.5	108.5	86.5	121
		U'=	87.5	109.5	75	84	70.5	87.5	109.5	75
			108.5	109.5	121	112	125.5	108.5	109.5	121
alpha = 0.2		test statistic	127	127	127	127	127	127	127	127
		if U > test statis, Ho rejected	ok	ok	ok	ok	ok	ok	ok	ok
alpha = 0.1		test statistic	135	135	135	135	135	135	135	135
		if U > test statis, Ho rejected	ok	ok	ok	ok	ok	ok	ok	ok
alpha = 0.05		test statistic	141	141	141	141	141	141	141	141
		if U > test statis, Ho rejected	ok	ok	ok	ok	ok	ok	ok	ok

🟨	no detect	n=	14	14	14	14	14	14	14	14
		number of detects	14	14	14	14	14	14	14	14
		detection limit (ug/l)	5	2	10	500	1000	5	2	10
		arithmetic mean of sample	0.21	0.05	1.74	16.11	51.43	12.33	48.21	166.02
		Std Dev of Sample	0.07	0.01	0.48	8.99	4.00	8.59	37.94	115.61
		median	0.50	0.25	5.51	37.50	156.00	17.74	70.70	193.38
		minimum	0.12	0.01	0.99	10.90	19.50	10.53	42.86	150.93
		maximum	0.29	0.05	1.66	16.35	70.25	13.91	51.26	183.54
		25th percentile	0.12	0.01	0.99	10.90	19.50	10.53	42.86	150.93
		75th percentile	0.29	0.05	1.66	16.35	70.25	13.91	51.26	183.54
		% coefficient of variation	31%	17%	28%	56%	8%	70%	79%	70%
			Nutrients (mg/l)			Hardness (mg/l)	TSS (mg/l)	median, 10%, 90% size		
			TP	SRP	TN			d10	d50	d90
1	1/12/2003	120th	0.117	0.027	1.04	12.8	27	12.978	46.236	149.335
2	1/25/2003	120th	0.178	0.013	1.12	10	78	12.049	42.312	178.054
3	4/23/2003	120th	0.192	0.058	1.05	12.3	4	14.181	51.581	135.966
4	6/20/2003	120th	0.314	0.111	5.51	34.6	12	10.221	38.643	169.570
5	10/5/2003	120th	0.495	0.247	4.18	37.5	17	10.803	37.940	155.715
6	11/15/2003	120th	0.377	0.08	2.47	16.2	123	10.508	47.124	183.736
7	12/2/2003	120th	0.235	0.008	1.67	13.3	156	14.312	52.375	138.453
8	12/4/2003	120th	0.099	0.016	1.27	17.6	28	16.891	50.297	115.612
9	1/13/2004	120th	0.096	0.009	0.963	14.5	31	11.651	43.456	164.427
10	1/28/2004	120th	0.314	0.013	1.610	9.58	113	13.089	55.673	193.381
11	2/14/2004	120th	0.065	0.009	0.509	10.9	18	8.590	42.664	182.944
12	2/16/2004	120th	0.118	0.011	0.480	10.9	42	8.999	46.250	177.180
13	3/4/2004	120th	0.132	0.010	0.977	8.99	47	10.607	49.743	192.702
14	3/7/2004	120th	0.159	0.030	1.490	16.4	24	17.739	70.697	187.208

🟨	no detect	n=	14	14	14	14	14	14	14	14
		number of detects	14	14	14	14	14	14	14	14
		detection limit (ug/l)	5	2	10	500	1000	5	2	10
		arithmetic mean of sample	0.21	0.03	1.97	17.26	63.86	12.49	48.48	164.88
		Std Dev of Sample	0.10	0.03	1.31	8.52	54.10	2.64	7.57	20.08
		median	0.1755	0.019	1.605	13.5	44.5	12.49282	48.19409	168.6205
		minimum	0.10	0.00	0.59	8.60	13.00	8.57	38.02	123.23
		maximum	0.43	0.11	4.87	39.10	204.00	17.37	68.16	190.01
		25th percentile	0.13	0.01	1.29	11.63	32.75	10.59	45.45	148.75
		75th percentile	0.24	0.04	2.08	21.08	61.75	13.71	50.92	180.98
		% coefficient of variation	49%	105%	66%	49%	85%	21%	16%	12%
			Nutrients (mg/l)			Hardness (mg/l)	TSS (mg/l)	median, 10%, 90% size		
			TP	SRP	TN			d10	d50	d90
15	1/12/2003	122nd	0.119	0.02	1.82	16.6	28	13.166	47.695	158.144
16	1/25/2003	122nd	0.111	0.006	1.54	18	37	17.094	51.551	123.229
17	4/23/2003	122nd	0.181	0.003	1.25	11.6	32	11.982	49.042	142.579
18	6/20/2003	122nd	0.238	0.038	4.87	22.1	28	10.211	39.057	169.620
19	10/5/2003	122nd	0.381	0.113	4.8	39.1	61	10.349	38.015	162.151
20	11/15/2003	122nd	0.17	0.037	2.17	10.4	62	14.093	56.331	184.605
21	12/2/2003	122nd	0.235	0.008	1.58	13.9	99	11.624	48.452	145.624
22	12/4/2003	122nd	0.429	0.018	1.65	11.7	204	13.869	47.941	167.621
23	1/13/2004	122nd	0.3	0.011	2.51	28.5	156	13.246	46.394	143.137
24	1/28/2004	122nd	0.102	0.006	0.990	8.6	50	13.003	48.447	173.537
25	2/14/2004	122nd	0.141	0.025	0.827	13.1	35	9.019	40.652	181.610
26	2/16/2004	122nd	0.126	0.011	0.591	13.1	45	8.574	45.130	179.078

Table F-1: Paired Study Statistical Analysis, Composite Samples
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non-parametric
Mann-Whitney or Wilcoxon Rank Sum
2-tailed hypothesis
H0: 120th and 122nd are the same

		n1=	14	14	14	14	14	14
		n2=	14	14	14	14	14	14
		R1=	202.5	201.5	162	189	170.5	158
		R2=	203.5	204.5	244	217	235.5	248
		U=	98.5	99.5	139	112	130.5	143
		U'=	97.5	96.5	57	84	65.5	53
			98.5	99.5	139	112	130.5	143
alpha = 0.2		test statistic	127	127	127	127	127	127
	if U > test statis, Ho rejected		ok	ok	reject	ok	reject	reject
alpha = 0.1		test statistic	135	135	135	135	135	135
	if U > test statis, Ho rejected		ok	ok	reject	ok	ok	reject
alpha = 0.05		test statistic	141	141	141	141	141	141
	if U > test statis, Ho rejected		ok	ok	ok	ok	ok	reject

🟨	no detect	n=	14	14	14	14	14	14
		number of detects	14	14	14	14	14	14
		detection limit (ug/l)	1	1	1	1	1	1
		arithmetic mean of sample	7.60	0.76	47.90	15.58	14.48	93.89
		Std Dev of Sample	1.90	0.28	6.00	8.23	1.80	31.00
		median	17.50	2.70	231.00	44.50	51.00	298.00
		minimum	3.90	0.50	17.45	10.78	5.34	47.25
		maximum	8.68	0.50	44.00	17.48	20.15	87.75
		25th percentile	3.90	0.50	17.45	10.78	5.34	47.25
		75th percentile	8.68	0.50	44.00	17.48	20.15	87.75
		% coefficient of variation	25%	37%	13%	53%	12%	33%
			Metals, Dissolved (ug/l)			Metals, Total (ug/l)		
			Cu	Pb	Zn	Cu	Pb	Zn
1	1/12/2003	120th	3.58	0.401	23	8.23	9.55	44
2	1/25/2003	120th	3.16	0.282	15.6	15	29.1	64.7
3	4/23/2003	120th	8.7	1.31	44	9.42	5.19	50.7
4	6/20/2003	120th	17.5	1.44	111	19.3	3.9	267
5	10/5/2003	120th	11.7	2.7	231	14.1	6.6	298
6	11/15/2003	120th	15.4	0.5	44	18.6	1.8	54
7	12/2/2003	120th	7.7	0.5	33	44.5	51	135
8	12/4/2003	120th	6.9	0.5	42	18.3	20.5	87
9	1/13/2004	120th	7.8	0.5	24	10.4	5.8	31
10	1/28/2004	120th	1.9	0.5	8	11.9	27.4	58
11	2/14/2004	120th	4.5	0.5	23	8.9	6.6	48
12	2/16/2004	120th	3.7	0.5	6	13.8	19.1	47
13	3/4/2004	120th	5.3	0.5	11	13.1	11.6	42
14	3/7/2004	120th	8.6	0.5	55	12.5	4.6	88

🟨	no detect	n=	14	14	14	14	14	14
		number of detects	14	14	14	14	14	14
		detection limit (ug/l)	1	1	1	1	1	1
		arithmetic mean of sample	9.10	0.77	66.17	19.22	22.76	114.51
		Std Dev of Sample	8.11	0.71	62.28	11.40	16.76	78.61
		median	6.61	0.5	47.75	13.6	17.35	84.5
		minimum	1.80	0.36	9.00	9.72	3.10	65.00
		maximum	28.10	2.90	252.00	42.10	59.20	314.00
		25th percentile	3.80	0.50	36.45	12.23	12.03	68.15
		75th percentile	8.93	0.50	64.33	21.28	29.05	117.50
		% coefficient of variation	89%	93%	94%	59%	74%	69%
			Metals, Dissolved (ug/l)			Metals, Total (ug/l)		
			Cu	Pb	Zn	Cu	Pb	Zn
15	1/12/2003	122nd	5.92	0.627	62.3	12.3	11.6	88.3
16	1/25/2003	122nd	3.24	0.363	35.6	10.1	16.9	68.6
17	4/23/2003	122nd	5.3	0.494	46.5	9.72	10.3	67.3
18	6/20/2003	122nd	25	1.85	252	39.4	15.2	314
19	10/5/2003	122nd	28.1	2.9	146	36.1	26.8	271
20	11/15/2003	122nd	8.1	0.5	49	12.3	3.1	65
21	12/2/2003	122nd	7.3	0.5	28	42.1	59.2	122
22	12/4/2003	122nd	2.2	0.5	9	21.5	50.9	86
23	1/13/2004	122nd	14.5	0.5	65	20.6	38.7	129
24	1/28/2004	122nd	1.8	0.5	39	12.2	29.8	68
25	2/14/2004	122nd	5.5	0.5	45	13.5	17.8	69
26	2/16/2004	122nd	3.3	0.5	26	13.9	20.7	68

Table F-2: Paired Study Statistical Analysis, Grab Samples
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Mann-Whitney or Wilcoxon Rank Sum
non-parametric

2-tailed hypothesis	n1=	5	4	5	5
H0: 120th and 122nd are the sam	n2=	5	4	5	5
	R1=	36	32.5	27.5	36
	R2=	19	22.5	27.5	19
	U=	4	-6.5	12.5	4
	U'=	21	3.5	12.5	21
	larger of U vs. U'	21	3.5	12.5	21

alpha = 0.2	test statistic	20	13	20	20
	if U > test statis, Ho rejected	reject	ok	ok	reject
alpha = 0.1	test statistic	21	15	21	21
	if U > test statis, Ho rejected	ok	ok	ok	ok
alpha = 0.05	test statistic	23	16	23	23
	if U > test statis, Ho rejected	ok	ok	ok	ok

no detect

n=	5	4	5	5
number of detects	5	4	5	5
detection limit (ug/l)	500	500	500	500
arithmetic mean of sample	2384.00	1025.00	12.38	7.09
lower of 90% CI about arith. Mean	1263.26	345.56	9.66	6.71
upper of 90% CI about arith. Mean	3504.74	1704.44	15.10	7.47
Std Dev of Sample	1523.57	826.14	3.70	0.52
median	2000	950	11.3	7.04
minimum	320.00	200.00	7.70	6.60
maximum	4400.00	2000.00	17.30	7.80
25th percentile	2000.00	425.00	10.90	6.62
75th percentile	3200.00	1550.00	14.70	7.40
% coefficient of variation	64%	81%	30%	7%

			fecal col	ecoli	temp	pH
1	1/12/2003	120th	3200	1400	10.9	6.6
2	1/25/2003	120th	4400	2000	11.3	7.04
3	4/23/2003	120th	2000	200	17.3	7.4
4	6/20/2003	120th	320	500	14.7	7.8
5	10/5/2003	120th	2000		7.7	6.62

no detect

n=	5	4	5	5
number of detects	5	4	5	5
detection limit (ug/l)	500	501	502	503
arithmetic mean of sample	488.00	345.00	11.90	6.62
lower of 90% CI about arith. Mean	263.29	95.41	9.20	6.42
upper of 90% CI about arith. Mean	712.71	594.59	14.60	6.82
Std Dev of Sample	305.48	303.48	3.68	0.28
median	400	200	11	6.5
minimum	180.00	180.00	7.70	6.30
maximum	1000.00	800.00	17.80	7.00
25th percentile	400.00	195.00	11.00	6.50
75th percentile	460.00	350.00	12.00	6.80
% coefficient of variation	63%	88%	31%	4%

			fecal col	ecoli	temp	pH
1	1/12/2003	122nd	1000	800	11	6.5
2	1/25/2003	122nd	400	180	12	7
3	4/23/2003	122nd	400	200	17.8	6.5
4	6/20/2003	122nd	180	200	11	6.8
5	10/5/2003	122nd	460		7.7	6.3

Table F-3: Paired Study Statistical Analysis, TPH Samples
Page 1 of 1

Mann-Whitney or Wilcoxon Rank Sum			
non-parametric			
2-tailed hypothesis	n1=	7	6
H0: 120th and 122nd are the sar	n2=	7	6
	R1=	47.5	28
	R2=	57.5	77
	U=	29.5	29
	U'=	19.5	-20
	larger of U vs. U'	29.5	29
alpha = 0.2	test statistic	36	27
	if U > test statis, Ho rejected	ok	reject
alpha = 0.1	test statistic	38	29
	if U > test statis, Ho rejected	ok	ok
alpha = 0.05	test statistic	41	31
	if U > test statis, Ho rejected	ok	ok

		n=	7	6
		number of detects	3	6
		detection limit (mg/l)	0.05	0.05
		arithmetic mean of sample	0.07	0.59
		lower of 90% CI about arith. Mean	0.04	0.42
		upper of 90% CI about arith. Mean	0.10	0.75
		Std Dev of Sample	0.05	0.25
		median	0.05	0.56
		minimum	0.05	0.30
		maximum	0.17	0.91
		25th percentile	0.05	0.38
		75th percentile	0.05	0.78
		% coefficient of variation	68%	43%
			TPH (mg/l)	
			diesel	heavy oil
1	1/12/2003	120th	0.17	0.84
2	4/23/2003	120th	0.05	0.34
3	6/20/2003	120th	0.048	
4	10/5/2003	120th	0.05	0.3
5	10/28/2003	120th	0.05	0.51
6	2/16/2004	120th	0.05	0.91
7	3/4/2004	120th	0.05	0.61

		n=	7	7
		number of detects	3	7
		detection limit (mg/l)	0.05	0.05
		arithmetic mean of sample	0.07	2.68
		lower of 90% CI about arith. Mean	0.04	1.84
		upper of 90% CI about arith. Mean	0.10	3.53
		Std Dev of Sample	0.04	1.36
		median	0.05	2.33
		minimum	0.05	1.27
		maximum	0.17	5.40
		25th percentile	0.05	1.96
		75th percentile	0.06	2.93
		% coefficient of variation	65%	51%
			TPH (mg/l)	
			diesel	heavy oil
1	1/12/2003	122nd	0.17	2.2
2	4/23/2003	122nd	0.048	3.3
3	6/20/2003	122nd	0.054	5.4
4	10/5/2003	122nd	0.06	2.56
5	10/28/2003	122nd	0.05	2.33
6	2/16/2004	122nd	0.05	1.71
7	3/4/2004	122nd	0.05	1.27