NCHRP

REPORT 767

NATIONAL
COOPERATIVE
HIGHWAY
RESEARCH
PROGRAM

Measuring and Removing Dissolved Metals from Stormwater in Highly Urbanized Areas

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Measuring and Removing Dissolved Metals from Stormwater in Highly Urbanized Areas

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NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM

Systematic, well-designed research provides the most effective approach to the solution of many problems facing highway administrators and engineers. Often, highway problems are of local interest and can best be studied by highway departments individually or in cooperation with their state universities and others. However, the accelerating growth of highway transportation develops increasingly complex problems of wide interest to highway authorities. These problems are best studied through a coordinated program of cooperative research.

In recognition of these needs, the highway administrators of the American Association of State Highway and Transportation Officials initiated in 1962 an objective national highway research program employing modern scientific techniques. This program is supported on a continuing basis by funds from participating member states of the Association and it receives the full cooperation and support of the Federal Highway Administration, United States Department of Transportation.

The Transportation Research Board of the National Academies was requested by the Association to administer the research program because of the Board's recognized objectivity and understanding of modern research practices. The Board is uniquely suited for this purpose as it maintains an extensive committee structure from which authorities on any highway transportation subject may be drawn; it possesses avenues of communications and cooperation with federal, state and local governmental agencies, universities, and industry; its relationship to the National Research Council is an insurance of objectivity; it maintains a full-time research correlation staff of specialists in highway transportation matters to bring the findings of research directly to those who are in a position to use them.

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The needs for highway research are many, and the National Cooperative Highway Research Program can make significant contributions to the solution of highway transportation problems of mutual concern to many responsible groups. The program, however, is intended to complement rather than to substitute for or duplicate other highway research programs.

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FOREWORD

By Christopher Hedges
Staff Officer
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This NCHRP report presents prototype best management practices (BMPs) for the removal of dissolved metals in stormwater runoff. Three conceptual configurations are presented in detail: two vault system configurations for urban and rural settings, and an inlet scupper with media for bridge deck drainage systems.

The report also includes standard protocols to accurately measure the levels of dissolved metals in stormwater. Practical guidance on the use of these protocols is provided in an appendix to the final report. The report is accompanied by an Excel spreadsheet on CD designed to assist in sizing the filter bed in the vaults and the bridge deck inlet scupper.

The report is suitable for immediate application by transportation practitioners in planning, design, and construction, particularly in areas where receiving waters are most susceptible to the impacts of dissolved metals.

Starting in the late 1980s, efforts to address polluted stormwater runoff have increased significantly, and the requirements for treating the runoff have gotten more stringent. Not long ago, most highway runoff could be treated using a few simple treatment methods such as bioswales, wet ponds, or vegetated filter strips. More recently however, the treatment requirements have been shifting to include the removal of dissolved metals. Dissolved metals in stormwater are becoming more of a concern to regulatory agencies, particularly in highly urbanized areas where land values and lack of available space limit the treatment options.

Furthermore, there are concerns about the current methods used to determine dissolved metal content. There is evidence that the measurements obtained can vary widely from the effects of a number of factors, including the measurement method and testing protocols, the testing equipment used, methods of cleaning the test equipment, and the scheduling of sampling times during storm events.

Under NCHRP Project 25-32, a research team led by the University of Texas at Austin studied the environmental chemistry of metals in highway runoff, reviewed key properties that control the chemical speciation of metals within water, and identified processes and parameters that affect the rate and extent of removal of metal ions from particulate matter. Based on the results, the team developed conceptual configurations for three design scenarios: highly urbanized areas, more rural locations with vegetated shoulders or embankments, and bridges. For each configuration, the design engineer is provided with guidance on integrating them with both new and existing drainage systems. Each configuration involves pretreatment of runoff, pH buffering, physical retention of the media, hydraulic design, and system maintenance.

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Note: Many of the photographs, figures, and tables in this report have been converted from color to grayscale for printing. The electronic version of the report (posted on the Web at www.trb.org) retains the color versions.

CHAPTER 1

Introduction

1.1 Background

This report provides the findings of the NCHRP Project 25-32: Measuring and Removing Dissolved Metals from Stormwater in Highly Urbanized Areas. This project was designed to improve the measurement of dissolved metals in highway runoff and to identify promising technologies for their removal in a highway environment. A variety of metals are associated with highway runoff, including copper, zinc, and lead, because of sources as varied as brake pads, wheel weights, and galvanized structures (signs, guardrails, etc.). The characterization and treatment of dissolved metals is a pertinent research topic because many receiving waters are impaired by dissolved metals concentrations, which can lead to the development of Total Maximum Daily Loads (TMDLs) or be subject to even more stringent requirements because of the presence of endangered species.

TMDLs often have water quality discharge requirements that are not achievable with conventional stormwater Best Management Practices (BMPs) appropriate for the highway environment. There are currently 417 waterbodies impaired by copper, 357 by zinc, and 392 by lead nationally. Many of these impaired waterbodies are located in highly urbanized areas where space for stormwater treatment is limited and hydraulic constraints of the existing stormwater drainage system limit the treatment options that are technically feasible. Examples of receiving waters located in urban areas impaired by metals include the Los Angeles River in California, and Des Moines and Hylebos Creeks in the Seattle metropolitan area in Washington State

The Endangered Species Act was passed to protect endangered and threatened species. Many salmon are on the endangered species list and this is a particular concern in the Pacific Northwest. Salmon have an especially low tolerance for dissolved copper, of which brake pad wear is a major source. Consequently, the regulatory limit for dissolved copper is even lower than the toxicity threshold.

One major challenge associated with characterization of receiving waters and stormwater runoff, as well as assessment of BMP effectiveness, are the low concentrations that must be achieved to meet water quality standards. For instance, the standard for copper, which is hardness dependent, is normally about 3 μg/L. Each aspect of sampling, processing, and analyzing water quality becomes increasingly critical as lower project reporting limits are required to evaluate concentrations of dissolved metals in waters in environmental samples.

1.2 Research Approach

This research was divided into two phases. The first phase was focused on a literature review, development of protocols for sampling and analyzing dissolved metals in runoff, identification of candidate materials for laboratory testing, and the development of a laboratory research plan, including the process for developing a synthetic stormwater cocktail. The second phase included execution of the laboratory evaluation of candidate materials and the creation of prototype BMPs for implementation in ultra-urban areas. The specific tasks are described in more detail in the following paragraphs.

1.2.1 Phase I

Task 1: The National Highway Runoff Water Quality Data and Methodology Synthesis (2003) provides the most comprehensive look at technical issues associated with sampling, processing, and analyzing dissolved metals in highway and urban runoff, but this compendium is nearly 7 years old and most studies included are at least 10 years old. The focus of this work was on obtaining and reviewing relevant research from the past 10 years that were designed to obtain representative and accurate measurement of all phases of metals in highway and urban runoff. Although detection limits are improving, large improvements in the ability to assess the accuracy and quality of many of the newer data sets was not anticipated. We

identified the uncertainties in current dissolved metals data and provided recommendations for addressing the cause. The data gaps and uncertainties in recent literature provided much of the focus for developing recommended protocol for a monitoring program designed for assessment of loads and concentrations of dissolved trace metals.

A Dissolved Metals Sampling and Analysis Guidance Manual was developed to provide general guidance for the design and implementation of stormwater monitoring efforts. The manual was designed for use by both field and laboratory staff. The intent was to produce a document that will serve as a practical working document rather than one that collects dust on a shelf. Protocols were presented that will assist staff in all phases of the process starting with designing a study and preparations necessary for successful implementation. These protocols include (1) batch cleaning of sampling equipment, bottles, and hoses; (2) quality checks necessary to verify that each batch of components subjected to cleaning meet project objectives; (3) tracking the use of all system components by batch so that they can be linked to the field samples; (4) establish requirements and guidelines for representative samples; (5) detailed sample handling and transportation procedures; (6) sample processing in the laboratory; and (7) the basic level of documentation necessary for final reports to allow others to assess the validity of the data set.

The overall objectives of monitoring programs for dissolved metals will be quite variable and may necessitate different monitoring strategies. For example, monitoring performance of dissolved metal removal as the tertiary portion of a treatment train may call for a different approach than one used to characterize dissolved metal loads and concentrations from a site with heavy sediment loads. The advantages and disadvantages of alternative strategies were presented and discussed. The manual is included as a standalone product in Appendix A of this report.

Task 2: Task 2 included a review and summary of all research findings and other relevant information related to the environmental chemistry of metals in natural surface waters. A particularly important effort was the identification of uncertainties in the speciation of metals and the potential for biotic ligand effects.

Task 3: This task had three main components: a review of the literature related to the removal of dissolved metals in stormwater, an identification of candidate materials for the laboratory testing program to be conducted under Task 6, and identification of potential structural design configurations for stormwater treatment systems focused on metals removal.

One focus of this task was the identification of candidate materials that appear to hold promise for removing metals in stormwater runoff. This portion of the task was conducted from two perspectives. The first was related to the literature review on previous research on metals removal in stormwater. A variety of materials have previously been tested, including various formulations of oxide-coated sands, zeolites, and other materials. These will be investigated to determine which, if any, have the potential to achieve water quality standards. The second perspective will be to consider the problem from a theoretical basis to determine whether other innovative materials might also be applicable for metals removal in the highway right-of-way. The deliverable for this portion of the task will consist of a list of selected materials for additional testing in Task 6.

Conceptual designs of stormwater treatment systems were developed to address different degrees of complexity in the urban environment: for example, one to address areas near steep embankments or areas with 50–75% impervious surface and another to address the most difficult cases with 75–100% impervious surface. Each consisted of an individual treatment or treatment train as required to meet the dissolved metals reduction objectives. The proposed designs provide practical, real world solutions that are applicable for use by departments of transportation.

Task 4: Task 4 consisted of a laboratory evaluation of the materials identified for metals removal in Task 3. There were two main experimental phases. The first of these consisted of evaluating the effect of pH on the partitioning coefficient, while the second phase explored the capacity of these materials, which bears on maintenance frequency. A critical element of this task was the development of an appropriate synthetic stormwater cocktail.

The recipe for the cocktail produced a synthetic stormwater with properties similar to that of edge of pavement highway runoff. The initial experiments were run using the synthetic stormwater runoff. Once initial testing to determine adsorption capacity and reaction rates was complete, the results were confirmed by using actual stormwater collected from the edge of pavement of a freeway in Austin, Texas.

Task 5: Task 5 was the development of an interim report to document Tasks 1 through 4 for review by the NCHRP.

1.2.2 Phase II

Task 6: The laboratory testing plan developed in Task 4 was conducted at the University of Texas at Austin upon NCHRP approval of the interim report.

Task 7: Task 7 consisted of a second interim report to document the results of Task 6 research for review by the NCHRP.

Task 8: After NCHRP approval, three examples of conceptual design specifications for stormwater treatment practices that could be used to effectively remove dissolved metals in highly urbanized areas were developed. The examples demonstrated how the laboratory data could be scaled up to address site-specific field conditions.

Task 9: Task 9 required the development of recommendations for further research necessary to validate the conceptual designs.

Task 10: Task 10 was the development of this final report. A PowerPoint presentation with speaker notes was also provided that summarized the background, objectives, research method, results, and benefits of this project.

1.3 Report Structure

Chapter 2 provides a summary of the characterization of highway runoff, including constituent concentrations and effects of varying particle size distribution. Chapter 3 summarizes the current state of knowledge regarding the transport and fate of dissolved metals in natural surface waters. Chapter 4 provides a literature review of previous studies investigating the removal of dissolved metals in stormwater runoff. Chapter 5 describes the synthetic stormwater cocktail and the laboratory evaluation of candidate materials for removal of dissolved metals in runoff. Chapter 6 presents the three conceptual BMPs developed for the removal of dissolved metals in ultra-urban areas, while Chapter 7 suggests directions for future research. Chapter 8 provides a brief summary and conclusions of this research project, while Appendices A and B provide guidance on the collection of samples for analysis of dissolved metal concentrations.

CHAPTER 2

Characterization of Highway Runoff

2.1 Stormwater Composition

Highway runoff is comprised of a number of soluble and insoluble constituents that vary with respect to their behavior in the environment. Metals such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) originate from sources as varied as brake pads, wheel weights, and galvanized structures (signs, guardrails, etc.). These metals are known to exist in a variety of different physical and chemical forms that dictate their mobility, bioavailability, and toxicity to aquatic organisms. A summary of observed metals concentrations in highway runoff from the FHWA database is presented in Table 2-1.

Review of these data suggests that the concentrations of heavy metals in highway runoff can be significantly higher than observed in natural waters. As a result, there is concern regarding the impacts of these discharges on ecosystems and water quality. Highway runoff has been shown to have acute and chronic effects on ecosystem biotic diversity and mortality rates downstream from discharge outfalls (Ellis et al. 1997). Metals constitute a common class of pollutants identified in numerous 303(d) lists for stormwater. In California, the most commonly listed metals are mercury, copper, lead, selenium, zinc, and nickel. Less frequently listed metals are cadmium, arsenic, silver, chromium, molybdenum, and thallium (California Stormwater Quality Association 2002). However, cadmium is one of the more frequent causes of impairment in New York, New Jersey, Maryland, and several other states (U.S. EPA 2010). Since both receiving water standards and the concentrations of dissolved metals in highway runoff are often near method detection limits, it is important to have appropriate protocols in place for sample collection and analysis. Guidance on these issues is provided in Appendices A and B.

An important consideration is that the distinction between dissolved and particulate associated metals is operational rather than chemically based. Laboratory methods for determining the fraction of a metal in the "dissolved" phase are based on the mass passing through a 0.45 μm filter. Clearly this is a rather arbitrary division, since many particles can be smaller than this threshold. In addition, metal ions can be associated with organic and inorganic ligands rather than existing as free ions. Consequently, dissolved is not synonymous with ionic.

A good example of this is a study conducted by the USGS on metals transport in the Sacramento River (U.S. Geological Survey 2001). This study analyzed for dissolved metals using ultrafiltration (equivalent to 0.005 μm pore size), in addition to the standard capsule filters (0.45 μm) to determine the amount of metal that is actually associated with colloidal size particles rather than actually being dissolved. They found that metal concentrations in the ultrafiltrates were about 40 to 70% lower than conventional filtrates, with the percentage for copper being higher than for zinc or cadmium. In the water column, colloids appeared to be the dominant form of aluminum, iron, lead, and mercury. This distinction is significant because the relative amounts of colloidal and dissolved metals influence the rates and mechanisms of metal bioaccumulation.

Organic constituents in highway runoff also have an important role in determining the bioavailability of dissolved metals and the effectiveness of various treatment processes. These constituents include oil, grease, humic acids, plastics, tire rubber, fecal material, PAH's, phthalates, pesticides, and herbicides, which are derived from a variety of natural and anthropogenic sources. A detailed study of the composition of stormwater runoff from Los Angeles, CA reveals the complex nature of the organic matter as shown in Table 2-2.

Dissolved metal complexes are often categorized as electrochemically available, chelex removable, and strongly bound. The chelex removable species are readily taken up by aquatic biota and include ionic species of metals as well as weakly bound organic species (Morrison et al. 1989). Strongly bound metals are less toxic, forming complexes with hydroxides, carbonates, and dissolved organic matter (DOM), which acts as a biogenic chelator (Ammann 2001).

Table 2-1. Summary of metals concentrations in highway runoff from the highway runoff database (Granato and Cazenas 2009).

Constituent	Mean (µg/L)	Median (µg/L)	Range (µg/L)
Dissolved Cu	15.9	9.2	< 1 - 620
Total Cu	50.1	26	< 1 – 9650
Dissolved Zn	94.8	41.0	3.6 – 14,786
Total Zn	273	150	1 – 21,060
Dissolved Pb[a]	5.6	< 1	< 1 – 480
Total Pb	246	32	< 0.5 – 13,100
Dissolved Cd[a]	0.36	< 0.2	< 0.1 – 9
Total Cd	5.0	0.7	< 0.1 – 400
Dissolved Ni	5.3	3	< 1 – 82
Total Ni	11.4	7.7	< 1 – 208
Dissolved Cr	3.4	2.1	< 1 – 54
Total Cr	13.8	7.2	< 0.5 – 190
Dissolved Fe	315	114	6 – 8,970
Total Fe	6,543	3,170	< 25 – 162,000
Dissolved Ca[b]	10.2 (mg/L)	10.6 (mg/L)	3.4 – 19.9 (mg/L)
Total Ca[b]	110 (mg/L)	44.5 (mg/L)	13 - 510 (mg/L)
Dissolved Mg[b]	0.8 (mg/L)	0.71 (mg/L)	0.3 – 2.35 (mg/L)
Total Mg[b]	48.5 (mg/L)	15 (mg/L)	5.3 - 270 (mg/L)
Dissolved Mn[b]	97	56	19.6 - 744
Total Mn[b]	295	229	106 – 932
Dissolved Organic C	19.6 (mg/L)	12.6 (mg/L)	0.2 – 440 (mg/L)

[a] > 50% nondetect, [b]limited dataset.

Table 2-2. Summary of molecular markers found in Los Angeles storm runoff (Eganhouse et al. 1981).

Anthropogenic	Recent Biogenic
Petroleum	**Microbial Based**
1. n-alkanes, n-C_{13-24}	1. n-alkanes
2. branched hydrocarbons	2. alkanoic acids
iso, anteiso, isoprenoids	iso, anteiso series, cyclopropane acids
3. cyclic compounds	3. β-hydroxy acids
cyclohexane series, steranes, diterpanes, triterpanes	iso, anteiso acids, normal acids < C_{20}
4. aromatic hydrocarbons	4. α,ω-dicarboxylic acids (?)
5. unresolved complex mixture	
Synthetics	**Higher Plants**
1. phthalates, adipates	1. n-alkanes > SC24
2. aromatic ketones (?)	2. n-alkanoic acids > 20:O
	3. dehydroabietic acid
	4. n-alkan-2-ones > c25 (?)
	5. chlorophyll derivatives
	CIS isoprenoid ketone, isoprenoid y-lactones
	6. α, ω –dicarboxylic acids (?)
	7. ω-hydroxy acids
	8. n-alkanols > C24
	9. phytosterols
	Higher Animals
	1. fecal sterols
	coprostanol, epicoprostanol

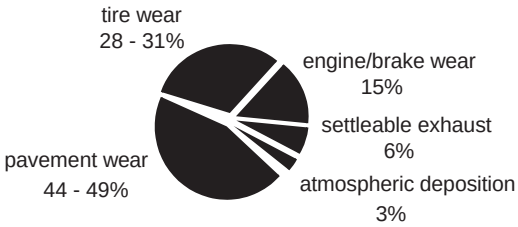


Figure 2-1. Relative fractions of traffic-generated particles (Sansalone et al. 1998).

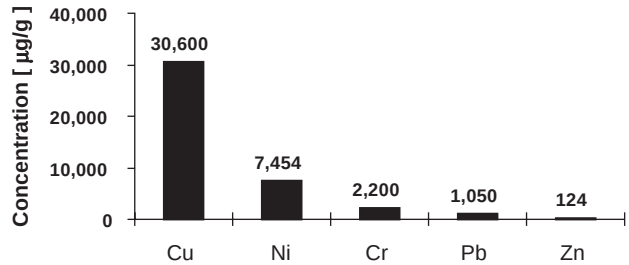


Figure 2-2. Selected metal content of typical 130-g brake pad (Sansalone and Hird 2002).

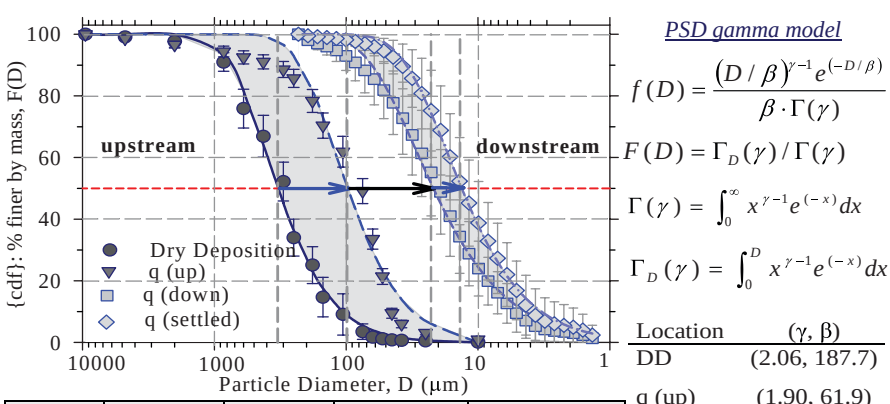
2.2 Particles in Highway Runoff

Stormwater runoff transports significant loads of dissolved, colloidal, and suspended particles in a complex mixture that includes metals and inorganic and organic compounds. While the temporal variability and complexity of rainfall-runoff chemistry is recognized, the focus herein is the transport, distribution, and partitioning of metals as mediated by the wide gradation of particles from highway systems. Particles are ubiquitous in transportation land use, and particles with associated metal accretion are in large part a function of traffic activities (Kobriger and Geinopolos, 1984; Hamilton and Harrison 1991; Glenn and Sansalone 2002).

Highway runoff transports a wide gradation of particles ranging in size from smaller than 1-µm to greater than 10,000-µm (Sansalone et al. 1998). From a water chemistry and treatment perspective, entrained particles having reactive sites and large surface-to-volume ratios are capable of mediating partitioning and therefore transport of metals. Figure 2-1 illustrates the relative contributions of abraded particles as generated by traffic.

In urban transportation corridors, metals are generated primarily from the abrasion of metal-containing vehicular parts, including the abrasive interaction of tires against pavement and oil and grease leakage (Armstrong 1994; Ball et al. 1991; Lygren et al. 1984; Muschack 1990). Abraded particles such as particles abraded by brakes have a high metal content (Sansalone and Hird 2002). Brake wear alone is estimated to contribute 15% of the total particles, and the relative contribution of selected metals for a typical 130-g brake pad is given in Figure 2-2 from data reported by Armstrong (1994). Some states, such as California and Washington, have recognized the significant source of copper in brake pads and have enacted legislation to reduce this source.

Given that particles can transport a significant fraction of metal mass and are a repository or sink for metals, the transformation of particle size distribution (PSD) as a function of distance from the edge of the pavement is of interest with respect to the fate of particles-based metals. This is illustrated in Figure 2-3 for measured particles data (1) initially as dry traffic deposition, (2) to particles in runoff at the edge of the



	DD Dry Deposition	q (up) Upstream Runoff	q (down) Downstream Runoff	q (settled) Settled (1 hour) Runoff
D_{50m}, µm	330.7	98.6	22.6	13.7

Figure 2-3. Transformation of PSD from dry traffic deposition through settled effluent. Range bars represent range of data (% finer by mass) for each event.

pavement, (3) to particles in runoff at the edge of the right-of-way (ROW) entering a settling tank, and (4) finally to particles in treated runoff effluent discharged to the adjacent receiving water (Ying and Sansalone 2010).

Results shown in Figure 2-3 illustrate two related phenomena. First, a significant fraction of coarse particles is potentially not mobilized during rainfall-runoff events or deposited in the drainage system (catch basin and storm drain in the ROW). Second, the drainage system can result in greater modification of the PSD than does one hour of sedimentation in a settling tank at the edge of the ROW.

2.3 Metal Partitioning and Complexation in Highway Runoff

PSD and loading of particles have a significant role in the partitioning (to and from particles) and transport of metals. While sediment particles (> 75 μm) are readily separated by size exclusion or sedimentation, suspended particles (< ~25 μm) such as, for example, organic particles from anthropogenic sources (tire particles) or biogenic sources (pollen), can be difficult to separate from runoff by sedimentation. Such suspended particles can require filtration or coagulation/flocculation if sufficient time for sedimentation is not available. Other parameters that are important from a treatment perspective include mass loading, PSD, specific gravity, specific surface area (SSA), and total surface area (SA). A typical relationship between PSD, SSA, and SA is illustrated in Figure 2-4 for particles (Sansalone and Tribouillard 1999).

SSA and SA results illustrated in Figure 2-4 demonstrate that although SSA does increase with decreasing particles diameter (by definition), the largest percentage of SA is associated with the mid-range of particles sizes. Additionally, the increase in SSA with decreasing particle size is not monotonically increasing as would be expected for spherical particles of constant specific gravity. Although SSA increases with decreasing particle diameter, calculations using the assumption of solid spherical particles grossly underestimate actual SSA values shown. Whether associated particles or engineered sorptive media for the separation of dissolved metals from runoff, the particle-water interfacial SA is an important parameter. The equilibrium distribution (> 24 hours) is shown in Figure 2-5 based on Cincinnati interstate data. Figure 2-5 illustrates strong correlations between particles-bound metal mass regressed against total particles SA. Although SSA does increase with decreasing particles diameter, the distribution of metal mass is correlated to SA of particles and not SSA.

The dissolved phase of metals is of particular concern for acute impacts since dissolved metals can be readily assimilated by aquatic biology and are more difficult to manage as compared to particles-bound metals (Yousef 1985). Due to the relatively acidic nature of rain in many urban areas, metals have the potential to leach into the dissolved phase at the upper end of the urban watershed as a function of residence time, pH, alkalinity, properties of particles, and the load of particles (Revitt and Morrison 1987). Previous research has suggested that Pb and Cu species leached after contact with acidic rain are complexed by organic matter or partition to suspended solids, while Cd and Zn remain primarily in solution (Morrison et al. 1990). During storage between runoff events in BMPs such as hydrodynamic separators or settling tanks, metals have been shown to re-partition and undergo re-distribution across the PSD (Ying and Sansalone 2010).

Metal partitioning between the dissolved and particle-bound fractions in stormwater is a dynamic process. Whether

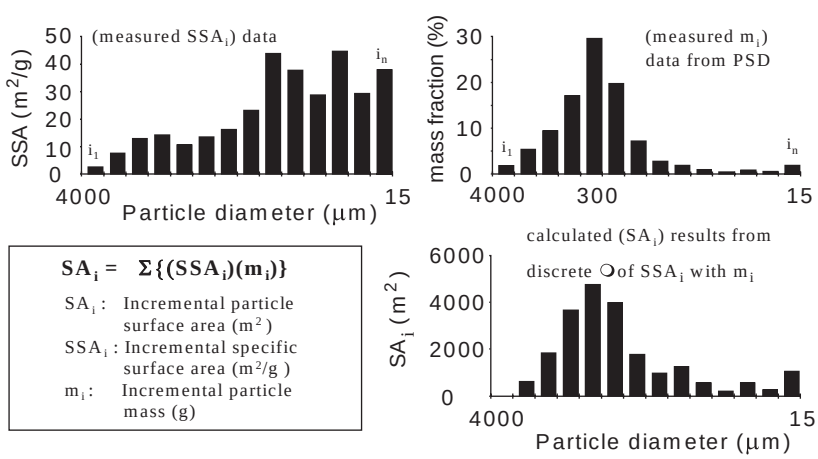


Figure 2-4. Relationship between the mass-based PSD, SSA, and total SA for runoff particles. The linkage between SSA and SA requires a mass-based PSD.

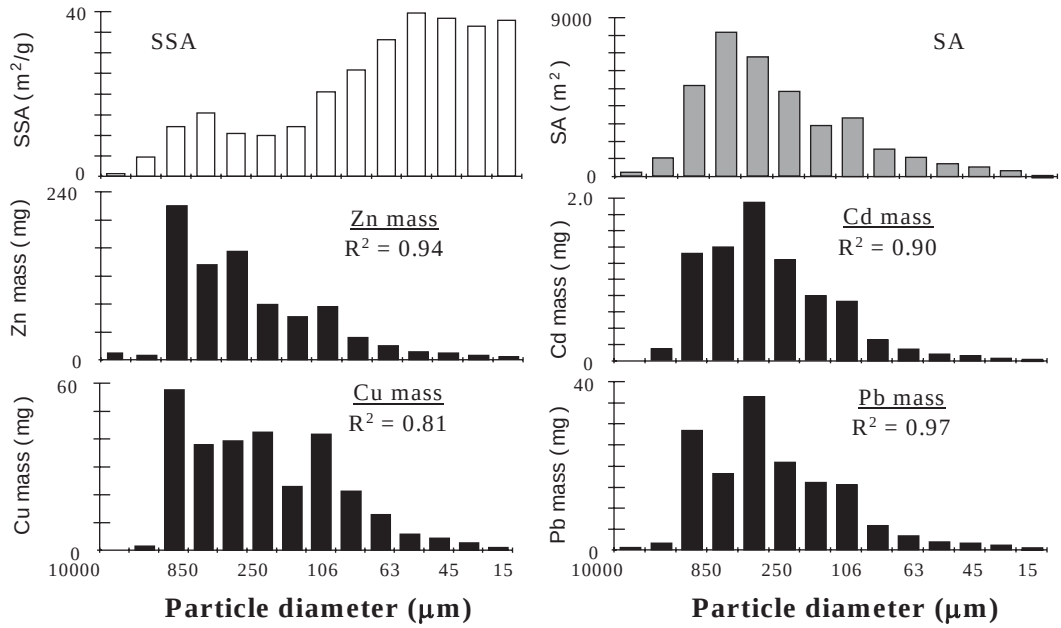


Figure 2-5. Distribution of metal mass as a function of runoff particles SA. For comparison to SA, the contrasting distribution of particles SSA is also illustrated.

in runoff or other aqueous systems, there is a temporal partitioning between metals in solution and the entire gradation of particles. This partitioning includes specific mass transfer mechanisms such as adsorption and ion exchange. These partitioning reactions are generally non-linearly reversible between the particles and soluble phase concentrations. If the colloidal fraction is considered a fraction of particles, the total concentration of a metal is therefore the sum of the dissolved (C_d) and the particulate-bound concentrations (C_p).

Under equilibrium, when the rate of sorption and desorption are equal, concentration equilibrium exists between the dissolved and solid-phase concentrations of a metal. The ratio of these phases *at equilibrium* is referred to as the partitioning coefficient, K_d ($K_d = C_p/C_d$) or a particular metal at a particular pH and redox level. From these definitions, a dimensionless dissolved fraction (f_d) ranging from 0 to 1, f_d can be computed. K_d is usually expressed as liters per kilogram (L/kg). The larger the K_d value, the greater the partitioning to the particles phase. Metals in pavement runoff have K_d values that range from 10^2 to over 10^6 (Sansalone and Buchberger 1997; Sansalone and Glenn 2003).

Metal partitioning in runoff also varies throughout a rainfall-runoff event and is influenced by intra-event rainfall-runoff chemistry (including pH, alkalinity, hardness, and particle concentration), transport residence time, hydrodynamics, traffic loading, and particle characteristics. Each of these parameters varies significantly between and during hydrologic events (Sansalone and Buchberger 1997).

Understanding the kinetics of this non-equilibrium partitioning is critical for proper monitoring, conceptual design, and viability of unit operations and processes that may be applied as in situ or source control treatment. Figure 2-6 provides an illustration of the time-dependent partitioning of Cu in stormwater samples for a fixed set of stormwater chemistry parameters (Sansalone and Buchberger 1997). For sampling and monitoring, this analysis indicates that after 6 hours for the given stormwater chemistry, the Cu mass is partitioning to the particulate-bound fraction. Additionally, a consistent trend in K_d as a function of time for Pb, Cu, Cd and Zn can be observed for the 8 August 1996 event despite the inverse trend in particles [measured as total suspended solidT(SS)].

Knowledge of the partitioning kinetics and the relative fractions of dissolved (f_d) and particulate-bound (f_p) mass delivered for treatment are of fundamental importance for in situ treatment where residence times on the urban surface or in the urban drainage system in the presence of entrained particles are less than several hours. An example of the relative fractions of dissolved and particles-bound metals is provided in Figure 2-7 for event-based data from a Cincinnati interstate catchment. Results in this figure illustrate that mass transfer from the aqueous phase (e.g., adsorption, ion exchange, or precipitation) in addition to particles-bound separation (sedimentation, filtration, coagulation/flocculation) require consideration in treatment design. Results also indicate that knowledge of partitioning for a given set of residence time and stormwater

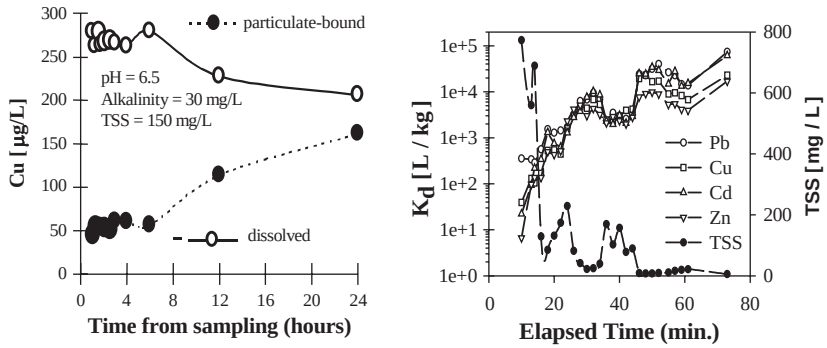


Figure 2-6. Time-dependent partitioning for Cu for 15 July 1995 runoff event and the temporal increase in heavy metal partitioning coefficient, K_d, for an 8 August 1996 event.

chemistry parameters is a necessary first step for conceptual and detailed treatment design.

The dominance of the dissolved mass for all metals, including relatively insoluble Pb for short urban surface residence times (initial pavement residence time < 15 minutes), with f_d values for Zn and Cd of approximately 0.8 or greater, Cu between 0.60 to 0.80, and Pb between 0.5 to 0.7 at this highway catchment, was typical of results from all 13 rainfall-runoff events characterized over two years at the urban Cincinnati highway catchment (Sansalone 1999). Controlling parameters of partitioning kinetics include pavement surface loading rate, suspended solids ratio, dissolved organic carbon (DOC) content, total dissolved solids (TDS), and ligand concentrations (organic and inorganic). These results illustrate the need for treatment of the dissolved as well as particle-bound fractions when considering in situ solutions.

In addition to metal ions and those associated with solids in runoff, metals can also form organic complexes and inorganic complexes. The mobility of the metals is directly dependent on the complex formed. Additional investigations carried out by Revitt et al. (1987) revealed that aqueous Cd, Cu, Pb, and Zn concentrations in transportation land-use runoff were predominately found in the chelex removable phase. However, only Zn and Cu were determined to be present as predominately divalent species, while Cu typically formed medium strength bonds with DOC. Results from this research indicated that 59%, 38%, 5%, and 53% of the total Cd, Cu, Pb, and Zn concentrations, respectively, in runoff were readily available to aquatic organisms. The results also revealed that Cu was predominately bound to organic complexes (Revitt and Morrison 1987). Investigations carried out by Flores-Rodriguez et al. (1994) verified that Zn and Cd were predominately bioavailable, while Pb tended to

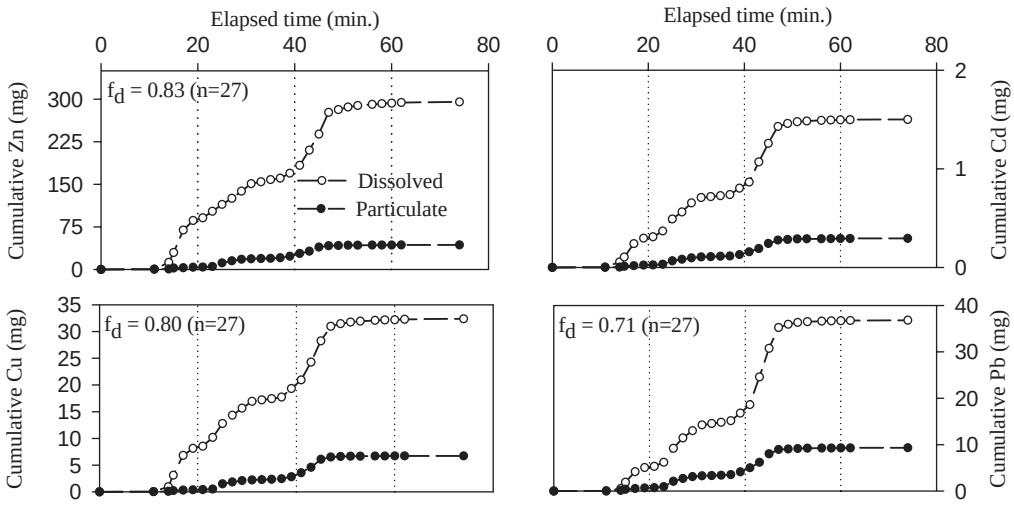


Figure 2-7. Dissolved fraction mass (f_d) partitioning and particles-bound fraction for an 18 June 1996 runoff event ($f_d + f_p = 1.0$) from I-75 in Cincinnati, OH.

form more stable complexes with inorganic and organic carbon in runoff.

2.4 Summary

Metals concentrations in highway runoff are elevated compared to most natural receiving waters and have been shown to have toxic effects on some aquatic species. Metals are divided into dissolved and particulate fractions (total metals being the sum of the two) based on the ability to pass through a 0.45 μm filter. Consequently, metals associated with very small particles are operationally defined as "dissolved." Metals can also form complexes with organic and inorganic ligands, rather than existing as an ionic species. These complexes make the metals less bioavailable and reduce their toxicity. Stormwater data also indicate that partitioning of metals with solids and ligands may not reach equilibrium for a number of hours. Consequently, treatment design for edge of pavement application should consider the non-equilibrium state of the runoff.

CHAPTER 3

Environmental Chemistry of Metals in Surface Waters

3.1 Introduction

3.1.1 Metal Speciation

The fate and transport of metals in natural surface waters is highly dependent on the properties of the particular metal, the solution chemistry of the water (i.e., pH, ionic strength, redox state, and presence of biotic, organic, and inorganic ligands), and interactions with resident particulate matter in the system. Figure 3-1 provides a schematic of the different potential reactions that affect metal ion speciation in water.

Water chemistry parameters such as pH, metal ion concentration, the presence of other reactive ligands and metals, ionic strength, and redox potential dictate metal ion speciation within the water column through complexation and oxidation/reduction processes. These processes impact the extent and rates of interaction with particulate matter and the bioavailability of metals.

Interactions with particulate matter include sorption to organic and inorganic phases as well as surface mediated transformation reactions (e.g., redox reactions). The mineralogy and available SA of solid phases in the systems, in conjunction with water chemistry parameters such as pH and ionic strength, dictate the rates and extent of adsorption. Sorption processes, as well as precipitation reactions, often control the rates and extent of migration and removal of metals in surface water, groundwater, stormwater, and highway runoff as well as the bioavailability of metal ions. The extent of sorption and precipitation are dependent on aqueous metal ion speciation such that metal ion speciation in the aqueous phase and sorption processes to inorganic, organic, and biological particulate matter are coupled.

Finally, colloids, which are particles small enough to pass through conventional filters used to separate dissolved and suspended phases, are major carriers of trace elements. As a result, sorption of trace elements to colloidal matter, including nanoparticles, can have a significant impact on metal ion mobility.

This chapter reviews the key properties that control the chemical speciation of metals within water, as well as the key processes and parameters that affect the rate and extent of removal of metal ions from particulate matter. A detailed understanding of these processes will not only facilitate predicting the fate, transport, and bioavailability of metal ions in natural water and stormwater, but will also guide the development of treatment strategies. Parameters to be explored within the literature include those associated with the metals (e.g., potential for adsorption to mineral surfaces and organic matter, oxidation/reduction, complexation, and precipitation) as well as properties of the water, potential ligands, and particulate matter surfaces. While the focus of this task will be on speciation in natural fresh waters, it is important to recognize that the processes that affect speciation in natural waters are the same as those that dictate speciation in stormwater and highway runoff. The major difference lies in the composition of the background water and particulate phases.

3.1.2 Natural Water Composition

Table 3-1 presents a summary of the concentrations of major elements in polluted and unpolluted river water (Maurice 2009). There are large variations of Ca^{2+}, HCO_3^-, and Na^+ that reflect differences in bedrock chemistry. For example, the presence of limestone ($CaCO_3$) in bedrock increases the hardness (sum of the multivalent cations) and alkalinity of the water.

Trace elements, defined as those present at concentrations less than 1 mg/L, constitute the remaining elements. Because their concentrations are low, they are not typically accounted for in measures of TDS. However, it is important to recognize that some of these other elements such as iron, aluminum, and titanium may constitute significant fractions of underlying bedrock. Aluminum, iron, and titanium have very limited mobility due to their solubility; however, their presence in the sediment layer often impacts the mobility of other trace elements. A compilation of data by Gaillardet et al. (2005)

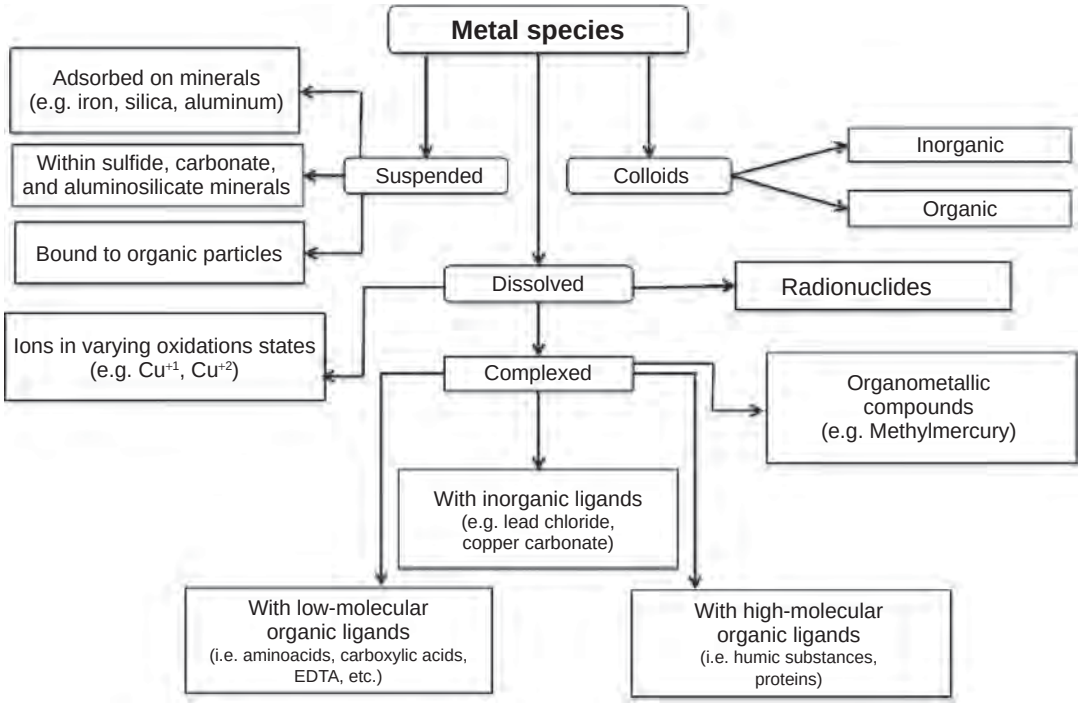


Figure 3-1. Speciation of metal ions in natural waters (adapted from Zaporozhets et al. 2010).

summarizes the concentration of trace elements in major rivers across the world. Average concentrations of selected elements are presented in Table 3-2.

Figure 3-2 depicts the wide variability among the different elements as well as the several order of magnitude span in concentration for each element. Correlations among different elements have also been studied. For example, by normalizing trace metal concentrations to continental crust composition, Gaillardet et al. (2005) identified average global mobility trends. Highly mobile elements were defined to have mobilities close to or greater than that of sodium. Included in this group are chlorine, carbon, sulfur, cadmium, boron, selenium, arsenic, calcium, magnesium, and strontium. The second group having mobilities approximately 10 times less than sodium includes silicon, lithium, potassium, manganese, barium, copper, cobalt, and nickel. The third group, referred to as the non-mobile group because their mobilities are 10–100 times less than sodium, includes zinc, chromium, vanadium, lead, and iron. The final group is defined by mobility indexes more than 100 times less than sodium and includes aluminum and titanium.

Thus, the heavy metals cadmium, copper, and zinc are expected to have varying mobilities in natural waters based on this analysis. These researchers (Gaillardet et al. 1999) utilized this data to develop a relationship between the fraction of an element in the dissolved phase based on the linear equilibrium partitioning coefficient, K_d (mg/gm of metal ion sorbed per

Table 3-1. Concentrations (in mmol/L) of major elements in world average "actual" and "natural (unpolluted)" river water (Maurice 2009).

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	SiO_2
World actual	0.36	0.15	0.31	0.03	0.23	0.12	0.87	0.18
World unpolluted	0.33	0.14	0.22	0.03	0.16	0.09	0.85	0.17

Table 3-2. Average concentrations (in μg/L) of selected trace elements in world river water (Gaillardet et al. 2005).

Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
32	0.62	0.08	0.7	1.48	66	34	0.801	0.079	0.6

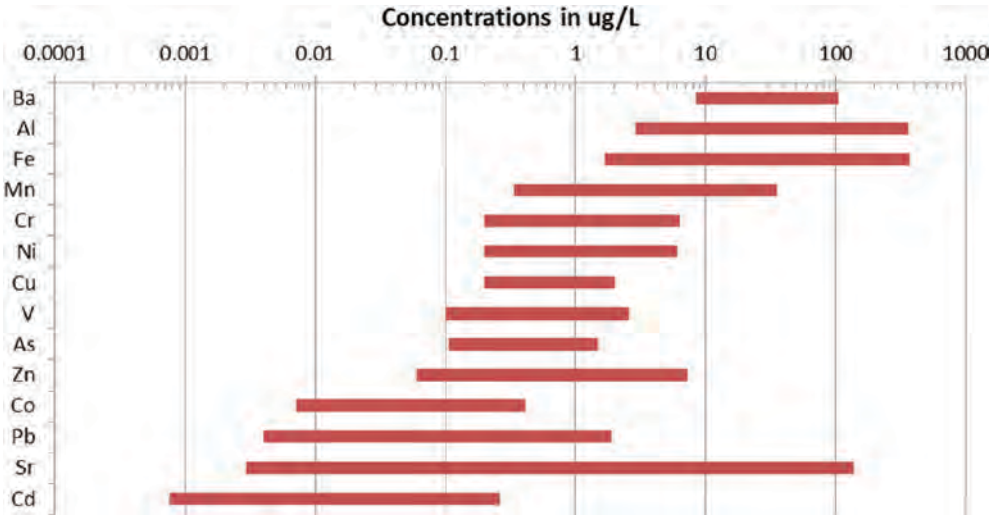


Figure 3-2. Selected trace element concentrations in world river waters (adapted from Gaillardet et al. 2005).

mg/L of metal ion in solution), and the TSS concentration. Their results are summarized in Figure 3-3 and suggest that for the world average TSS concentration of 350 mg/L, only the most mobile elements (e.g., Na, B, Se, As) will be transported in the dissolved phase.

Other correlations for estimating sorbed and dissolved fractions of metal ion have also been conducted based on cluster analysis or water quality parameters. Seyler and Boaventura (2001) reported that dissolved concentrations of vanadium, copper, arsenic, barium, and uranium are strongly positively correlated with major elements and pH. pH and major element composition can be affected by anthropogenic inputs depending on the natural bedrock composition. Thus, bedrock composition, chemical properties, and large scale processes such as acid rain can impact on metal ion concentrations within a river.

3.1.3 Characterization of Natural Organic Matter in Receiving Waters

The fate of metal ions in water is also highly dependent on the presence of natural organic matter that is ubiquitous in natural waters. Typical concentrations of DOM range from less than 2 to nearly 10 mg/L as C in freshwater streams and can be significantly higher in lakes (see Table 3-3). However, values as high as 80 mg/L have been reported for rivers draining wetlands (Walther 2005). While DOM is often quantified in terms of the concentration of carbon, the complexity and

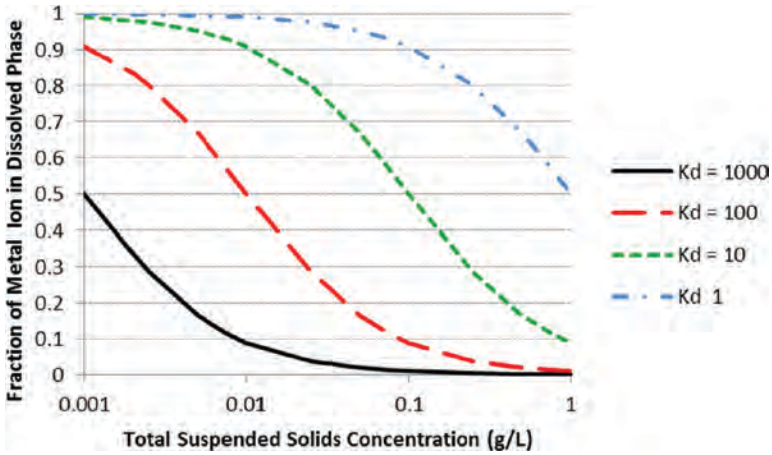


Figure 3-3. Predicted dissolved metal ion transport as a function of suspended solid concentration in river water (adapted from Gaillardet et al. 2005).

Table 3-3. Typical ranges of DOC concentrations and humic substance concentrations in natural waters (Thurman 1985).

Source	DOC (mg/L as C)	Humic Substances (mg/L as C)
Sea water	0.2 - 2.0	0.06 - 0.6
Groundwater	0.1 - 2.0	0.03- 0.6
River	1 - 10	0.5 - 4.0
Lake	1 -50	0.5 - 40

heterogeneity of natural organic matter has significant impacts on its reactivity.

The organic matter found in natural aquatic systems is a complex mixture of partially decomposed vegetation, animal matter, and other decaying parent material. As Figure 3-4 suggests, the composition of organic matter is made up of a range of chemical moieties including both soluble and insoluble fractions, carbohydrates, proteins, fats, and complex organic macromolecules (Abdulla et al. 2010). These substances range in size from low molecular weight dissolved substances to insoluble particulate matter (see Figure 3-5). The three main sources of DOM, such as fresh plant litter, microbial biomass, and humus, vary with respect to climate, season, and geology.

Humic substances (shown in the left side of Figure 3-5) formed during the decomposition of vegetation, animal matter, and other decaying parent material represent the most important components of aquatic DOM as they are present at significant concentrations in natural waters. The chemistry of their formation is quite complex and originates from both terrestrial origin (autocthonous sources) and biological activity within

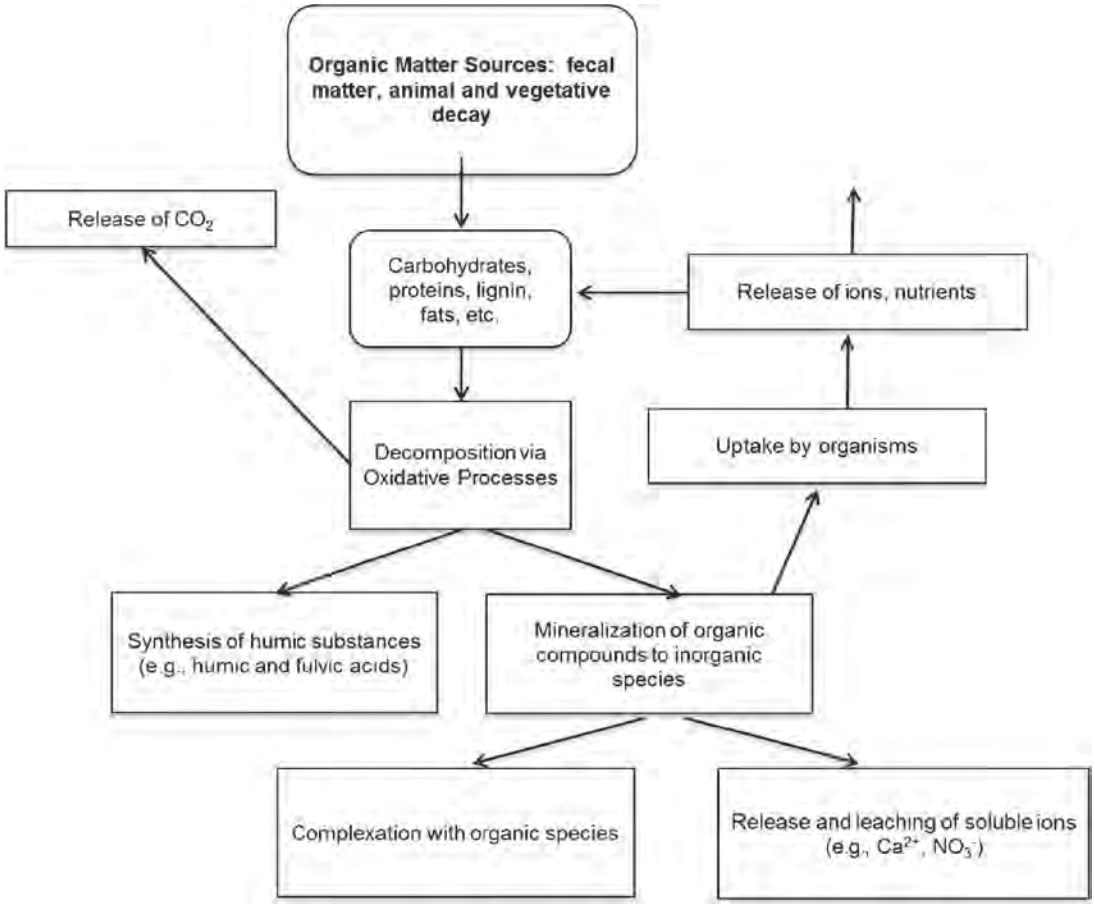


Figure 3-4. Formation of natural organic matter (adapted from Grunwald 1998).

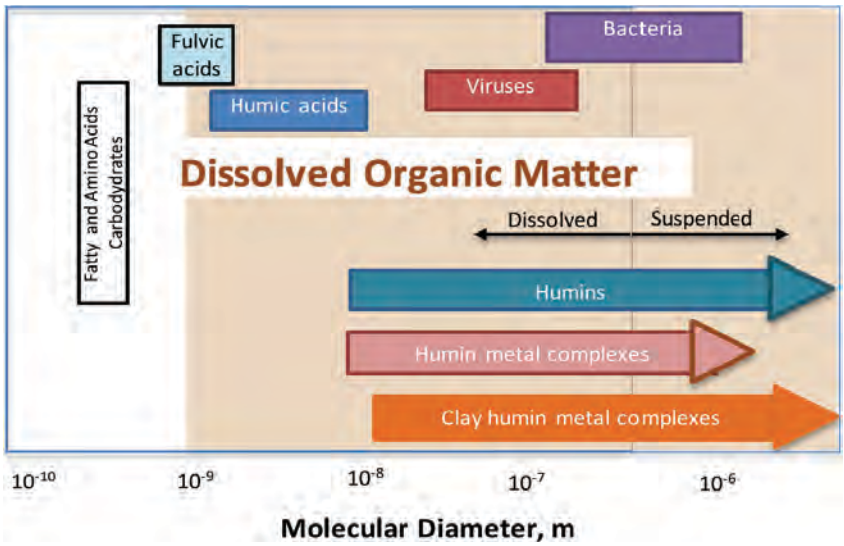


Figure 3-5. Distribution of sizes of various components of organic matter (adapted from Steinburg 2003).

the natural water (allocthanous sources). However, despite the wide variety of sources and decomposition pathways, there is significant uniformity in the macroscopic properties of humic matter. Thus, a significant amount of early research focused on generalizing these gross properties and developing classification schemes that were based on these properties. For example, elemental analysis indicates that humic substances contain carbon, oxygen, hydrogen, nitrogen, and sulfur. Forty to 50% of the mass is comprised of complex aliphatic carbon chains (e.g., C-C-C-C-) and 35% to 60% of the mass is 4, 5, and 6 member carbon rings (termed aromatic components due to the alternating double bonds) with C-C, C-N, and C=O components.

One of the most widely known classification schemes for humic substances is based on differences in solubility of various components of humic substances. The three major components, humin, humic, and fulvic acid, vary with respect to solubility in alkali and acidic solutions as shown in Figure 3-6.

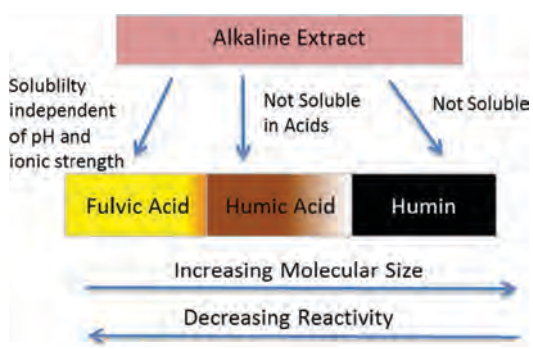


Figure 3-6. Operationally defined classification of humic substances (adapted from Steinburg 2003).

These different fractions vary with respect to color, composition, and reactivity. Humins are black in color and insoluble at any pH. In addition to improving water-holding capacity and improving soil structure, humins function as a cation exchange system in soils. Thus, it is not surprising that substances containing significant fractions of humins (e.g., peat) have been used as adsorbents for metal ions (Ringqvist and Oborn 2002; Liu et al. 2008; Shareef 2009).

Humic substances are ambiguous with respect to their affinity for water. They contain a hydrophobic (lipophilic) backbone that is made up of non-polar hydrocarbon bonds and hydrophilic, polar functional groups containing oxygen, nitrogen, and sulfur atoms. Thus, they are often referred to as hydrophobic acids. Non-humic and fulvic acid organic matter is often characterized by their hydrophobic and hydrophilic components as well. This type of classification is reflected in Figure 3-7, which shows that the relative distribution of organic matter varies from groundwater to surface water, and the ratio of humic to fulvic acid is slightly higher in lake and river water.

The acidic nature of the humic and fulvic acid polar, organic groups suggests that their presence can influence the pH and buffering capacity of natural water (Köhler et al. 1999). In addition, these functional groups provide binding or complexation sites for metal ions. The association of metal ions with humic substances has been shown to influence the rates of sorption and precipitation (Scheinost et al. 2001; Lin et al. 2005; Zhao et al. 2010). As a result, researchers have sought to more clearly elucidate the structure of humic substances and to quantify the number and reactivity of the various types of functional groups in humic substances.

Even though significant research has been conducted over the past several decades to characterize the properties

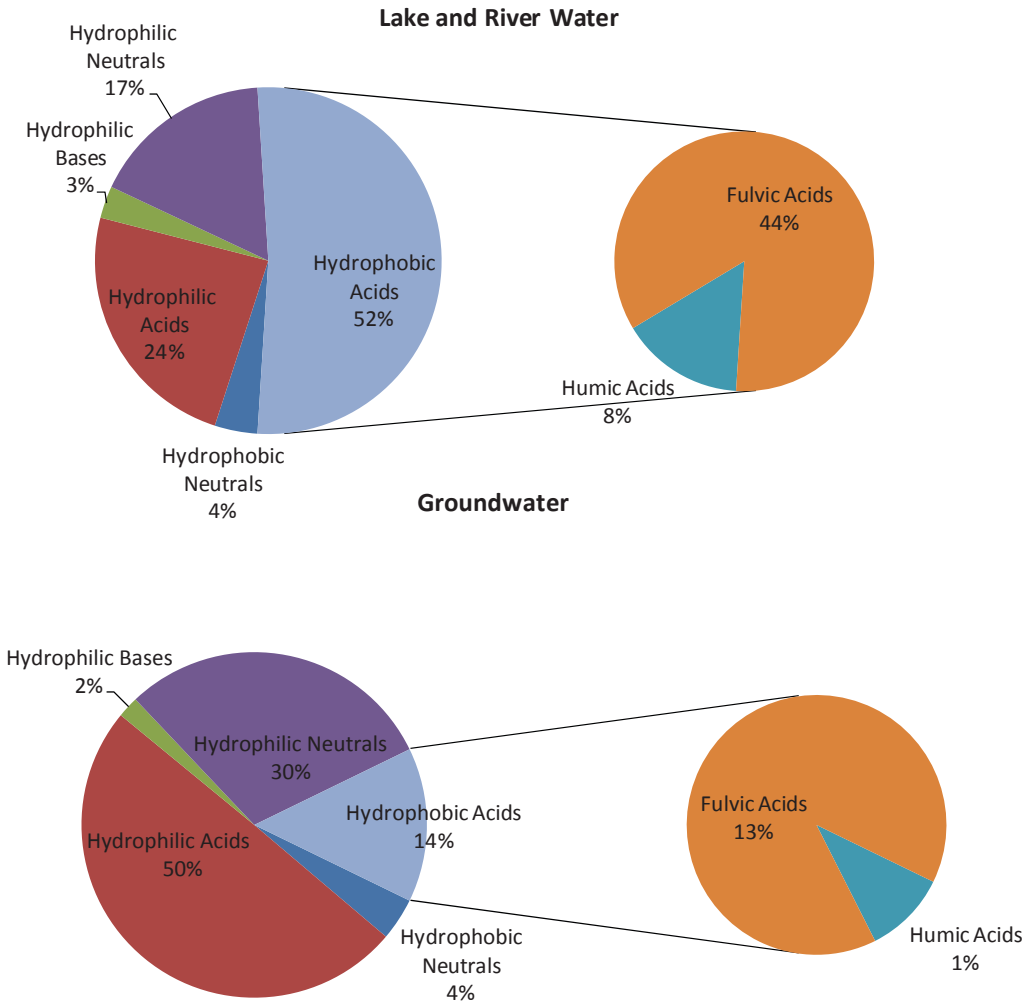


Figure 3-7. Distribution of hydrophilic and hydrophobic fractions of natural organic matter (adapted from Peuravuori and Pihlaja 2000).

and reactivity of humic substances, there is still a lack of consensus as to the nature of these complex materials (Hayes and Clapp 2001; Perminova et al. 2009). Researchers generally agree that much of the reactivity of humic and fulvic acids is due in large part to the presence of carboxylic (-COOH) and phenolic (C_6H_5OH) groups (Steinburg 2003). Carboxylic groups are much more acidic (Ka's on the order of $10^{-4.5}$) than phenolic groups (Ka's on the order of 10^{-10}). Thus, fulvic acids are expected to be more reactive than humic acids because they are higher in carboxylic acids and lower in phenolic content. These differences are evident in Table 3-4 and shown schematically in Figure 3-8 and Figure 3-9. The composition of organic matter and relative percentages of humic and fulvic acids varies depending on the origin of the organic matter. Terrestrial humic substances contain mainly lignoprotein (lignin + protein) complexes and humic and fulvic acids are major constituents. In contrast, aquatic humic substances are predominantly carbohydrate protein complexes composed mostly of fulvic acids. Thus, aquatic humic substances exhibit acidity to water, which is especially important in waters low in other natural buffers such as carbonate and bicarbonate ions (Köhler et al. 2001; Koopal et al. 1999).

Structural models of humic substances vary throughout the literature. Fulvic acids are a mixture of weak aliphatic and aromatic organic acids, but their shape and composition varies. In contrast, humic substances have traditionally been represented as flexible linear polymers that exist as random coils with cross-linked bonds to micelles. The most current views assume either that the structure of humic substances is macropolymeric with relatively large organic molecules considered as flexible linear synthetic polyelectrolytes (Figures 3-8 and 3-9), or humic substances are supramolecular associations of relatively small, chemically diverse organic molecules that have self-organized into large macromolecules. It is now thought that biomolecular moieties are also associated with these substances (Sutton and Sposito 2005).

Table 3-4. Elemental composition (weight %), mole ratios, and functional group content (meq/g) of humic and fulvic acids (Steinburg 2003).

Constituent	Humic Acid	Fulvic Acid	pKa	
C	54-59	41-51		
H	3.2-6.2	3.8-7.0		
N	0.8-4.3	0.9-3.3		
O	33-38	40-50		
S	0.1-1.5	0.1-3.6		
O/C	0.51	0.74		
H/C	1.0	1.4		
total acid functional groups	5.6-8.9	41-51		
carboxylic acids	1.5-5.7	5.2-11	6-9	typically deprotonated in circumneutral pH range
phenolic OH	2.1-5.7	0.3-5.7	9	
alcoholic OH	0.2-4.9	2.6-9.5	14	increases solubility
quinoide/keto, C=O	0.1-5.6	0.3-3.1		increases water solubility slightly
methoxy, OCH_3	0.3-0.8	0.3-1.2		

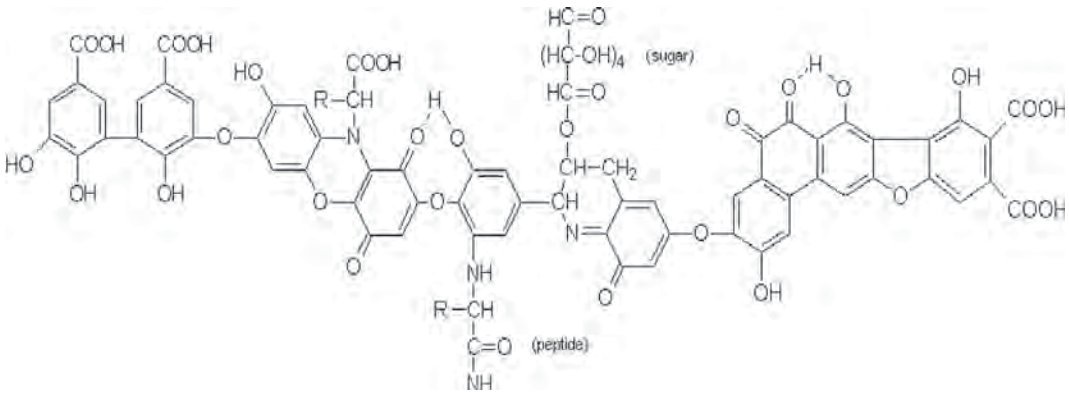


Figure 3-8. Structure of humic acid proposed by Stevenson (1982).

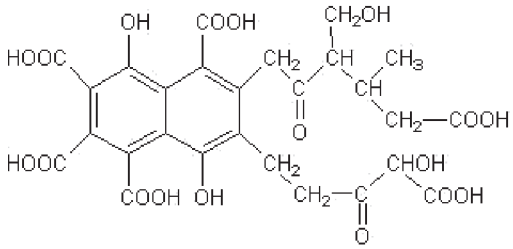


Figure 3-9. Structure of humic acid proposed by Buffle et al. (1977).

Regardless of which model of humic substances emerges from the on-going inquiry, it is clear that these humic substances provide functional groups and hydrophobic moieties that can interact with surfaces and dissolved metals ions in solution. These interactions can significantly impact the mobility and toxicity of metal ions in water.

3.1.4 Summary

Average concentrations of trace elements in freshwaters, stormwater, and highway runoff range over orders of magnitude, and their mobility in these systems vary depending on the metal ion, the chemical speciation, and the extent of

partitioning. For the average suspended solid concentration of 350 mg/L, only the most mobile elements (e.g., Na, B, Se, As) will be transported in the dissolved phase. As a result, partitioning to particulate matter and colloids in natural water is a key component to understanding fate and transport in water. Anthropogenic and natural organic matter also has a large impact on metal ion transport. The composition of natural organic matter is extremely complex and heterogeneous; however, the high reactivity and solubility of humic and fulvic acids suggests that these fractions are the key components for interaction with metal ions in natural waters. The research suggests that much of the reactivity of humic and fulvic acids is due in large part to the presence of carboxylic (-COOH) and phenolic (C_6H_5OH) groups. These same assumptions may not be true for anthropogenic inputs as they tend to be dominated by hydrophobic and lower molecular weight compounds.

3.2 Metal Ion Speciation in Solution: Complexation Reactions

Metal ions in solution are always associated with other ions, organic species, or particulate matter. Their coordination environment is dictated by the composition of the water including the pH, ionic strength, and the presence of other ions, organic molecules, and solid phases. Complexation reactions, in which a metal ion forms an association or bond with another ion (ligand), are the dominant reaction that controls metal ion speciation in water. Indeed, even in the absence of other molecules in the water, metal ions form complexes with the water molecules themselves, forming a primary hydration sphere around the metal ion.

3.2.1 Complexation with Inorganic Ligands

Metal ion speciation often dictates the mobility and toxicity in a particular aquatic environment because complexation reactions prevent metal ions from being precipitated, complexing agents act as carriers for trace elements in water, and metal ion bioavailability is often reduced by complexation. Metal ion speciation often involves the formation of a bond between a central metal ion and inorganic anions or functional groups that have electron pairs to donate. In natural waters, there are a number of simple inorganic ligands such as OH^-, Cl^-, NH_3, CO_3^{2-}, and PO_4^{3-}, as well as natural and anthropogenic organic ligands that may be available within the system to bind to a central metal ion (e.g., Cu, Fe, etc.) to form a soluble complex as shown in Figure 3-10.

The importance of complexation in natural waters depends on the pH of the water and the concentration and binding strength of available ligands. Stability constants describing the binding strength for the reaction between a particular metal ion and the common inorganic ligands are well estab-

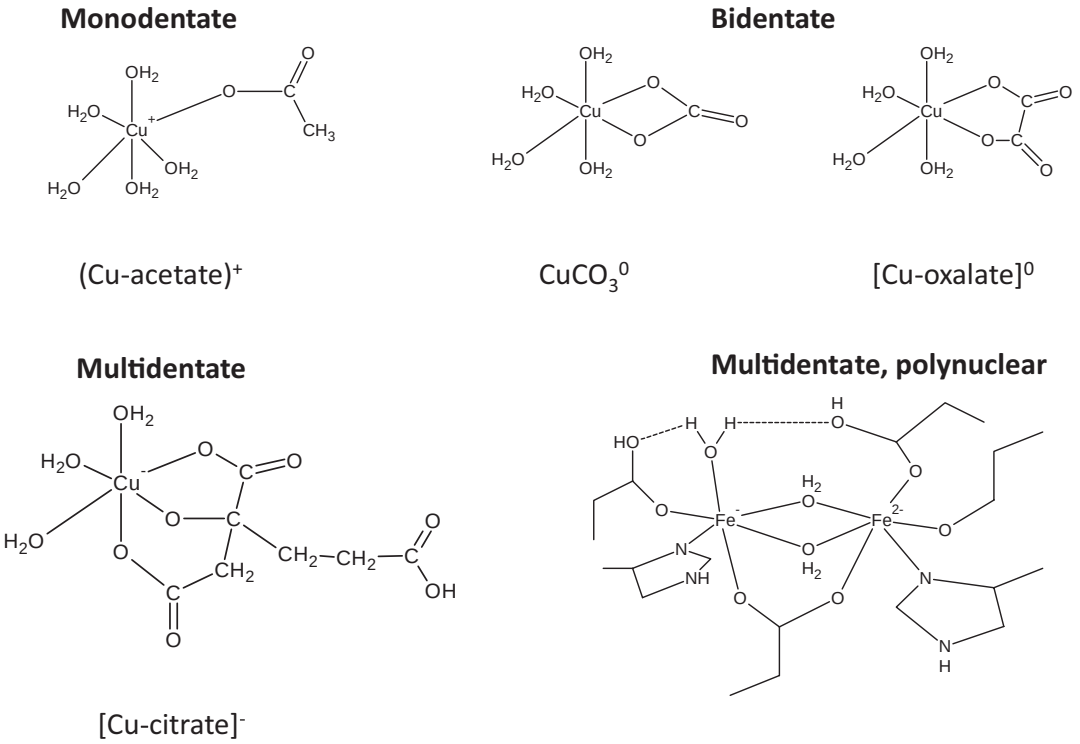


Figure 3-10. Examples of several types of metal-ligand complexes.

Table 3-5. Stability constants (β) for selected chloride complexes.

Reaction	β	Reaction	β	Reaction	β
$Hg^{2+} + Cl^- \Leftrightarrow HgCl^+$	$10^{7.2}$	$Hg^{2+} + 2\,Cl^- \Leftrightarrow HgCl_2$	10^{14}	$Hg^{2+} + 3Cl^- \Leftrightarrow HgCl_3$	$10^{15.1}$
$Pb^{2+} + Cl^- \Leftrightarrow PbCl^+$	$10^{1.6}$	$Pb^{2+} + 2\,Cl^- \Leftrightarrow PbCl_2$	$10^{1.8}$	$Pb^{2+} + 3Cl^- \Leftrightarrow PbCl_3$	$10^{1.7}$
$Cu^{2+} + Cl^- \Leftrightarrow CuCl^+$	$10^{0.5}$				
$Zn^{2+} + Cl^- \Leftrightarrow ZnCl^+$	$10^{0.4}$	$Zn^{2+} + 2\,Cl^- \Leftrightarrow ZnCl_2$	$10^{0.2}$	$Zn^{2+} + 3Cl^- \Leftrightarrow ZnCl_3$	$10^{0.5}$

lished in the literature and maintained in NIST databases (Martell and Smith 1974). Complexation reactions with simple monodentate, inorganic ligands such as those represented by the reactions of Hg, Pb, Cu, and Zn with the chloride ligand are shown in Table 3-5 and highlight the variability in binding strength for different metals.

The value of the stability constant, β value, for these reactions represents the equilibrium constant for the multi-step reaction of each metal ion with the associated number of chloride ligands. Note that the divalent metals can bond with more than one chloride ligand, but only one chloride ligand bonds with the metal ion.

Comparison of the different metals suggests that the strength of the metal-ligand complex follows the trend: Hg>Pb>Cu>Zn. Nevertheless, all of these binding constants are relatively weak and typical of ion pair associations with the exception of the $HgCl_n$ metal-ligand constants that display more covalent character. The low values of these stability constants indicate that chloride complexes of Pb, Cu, and Zn will not significantly affect metal ion speciation in freshwaters. In contrast, carbonate complexes range from approximately 10^5 to $10^{10.5}$ for these same metals, and their concentrations in solution can be significant as shown in Figure 3-11.

When the hydroxide ion is the dominant ligand in the system, many metal ions act as multiprotic acids in which protons are released from water molecules in the inner hydration sphere as shown in Figure 3-12.

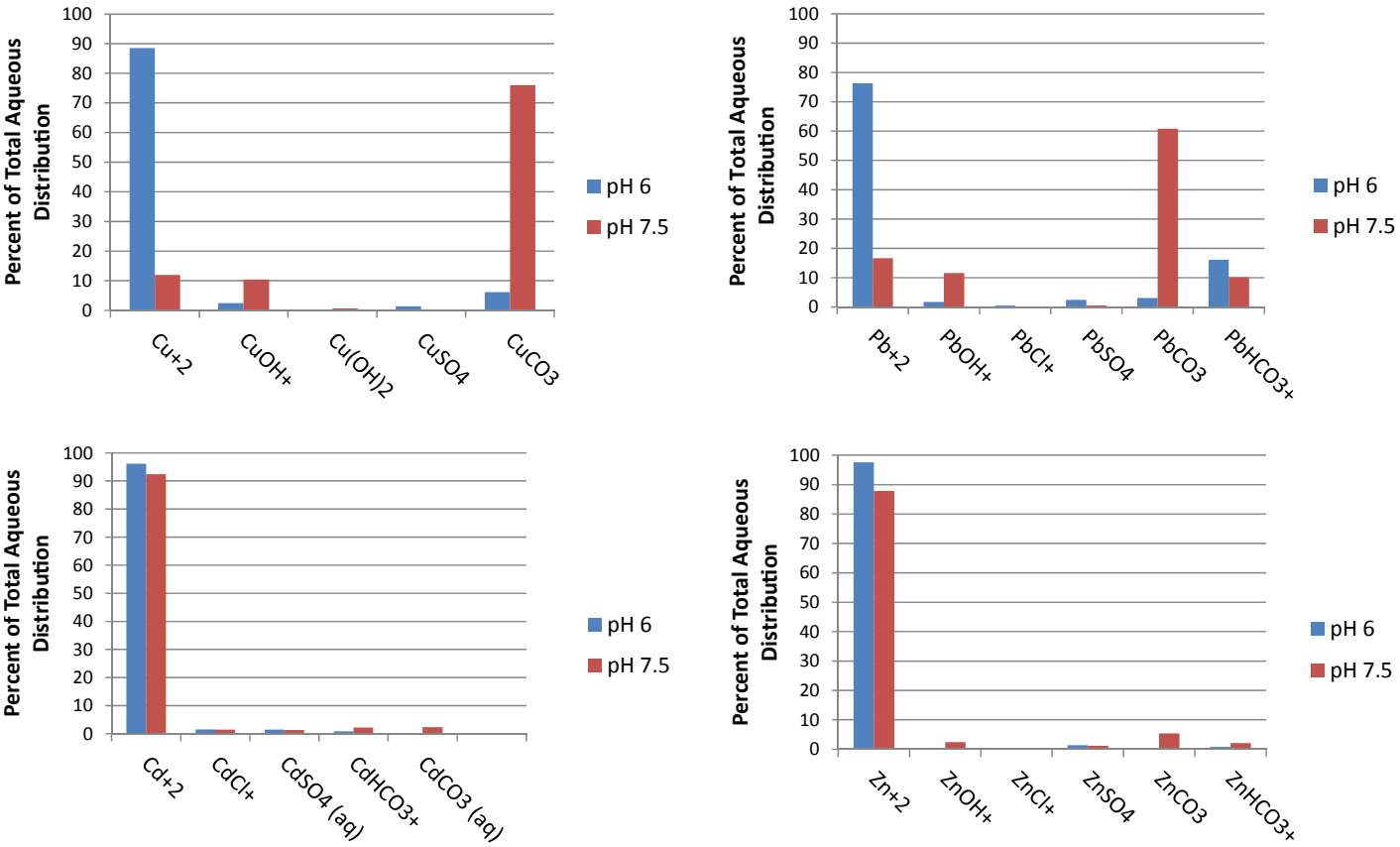


Figure 3-11. Impact of carbonate and sulfate complexes on metal ion speciation in solutions calculated using Visual MINTEQ and typical freshwater ligand concentrations.

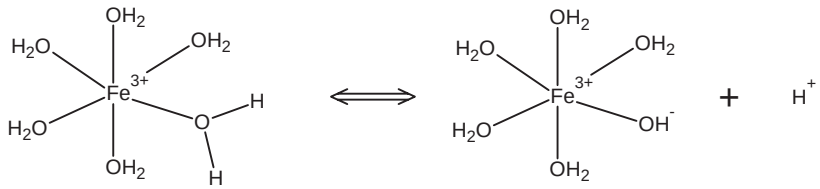


Figure 3-12. Representation of the acid/base properties of Fe^{3+} in water in octahedral coordination with water and hydroxyl ligands.

For example, the first hydrolysis reaction of Fe^{+3} [written with its waters of hydration as $Fe(H_2O)_6^{3+}$] with the hydroxide ligand can be written as either a complexation reaction:

$$Fe(H_2O)_6^{3+} + OH^- \Leftrightarrow Fe(H_2O)_5(OH)^{2+} + H_2O \qquad \beta = 10^{11.8}$$

or an acid/base reaction,

$$Fe(H_2O)_6^{3+} \Leftrightarrow Fe(H_2O)_5(OH)^{2+} + H^+ \qquad Ka = *\beta = 10^{-2.2}$$

where the $*$ indicates that the stability constant is written in terms of H^+ rather than OH^-. As pH is increased, hydroxide ligands can replace additional water molecules (i.e., more hydrogen ions are released) to sequentially form $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_3(OH)_3^0$, and $Fe(H_2O)_2(OH)_4^-$. The value of Ka = $*\beta = 10^{-2.2}$ suggests that $Fe(H_2O)_6^{3+}$ is a relatively strong acid. Lead, copper, zinc, and cadmium are significantly weaker acids with acidity equilibrium constants (Ka values) for their first proton dissociation of $10^{-7.71}$, $10^{-8.0}$, $10^{-8.96}$, and $10^{-10.0}$, respectively, compared to the value of $10^{-2.2}$ noted for Fe(III) above. Thus, Fe(III) acts as an acid that is as strong as phosphoric acid (H_3PO_4), whereas the acidity of zinc and cadmium are only slightly more acidic than bicarbonate (HCO_3^-). Figure 3-13 further demonstrates that the importance of hydroxide complexes on speciation is dependent on the particular metal ion.

The reactivity of metal cations in aqueous systems is often correlated with the values of $*\beta_1$ as shown earlier for the trends in complexation with chloride and ethylendiamine tetraacetate (EDTA). Of particular interest with respect to mobility is that complexation of metal ions has a significant effect on the charge of the species. For example, metal hydroxide complexes can be cations [e.g.,$Cu(OH)^+$], neutral molecules [e.g., $Cu(OH)_2^0$, (aq)], or anions [e.g., $Cu(OH)_3^-$]. The relative importance or dominance of each of these charged species is pH dependent. For example, speciation of Cr^{+3} and Cu^{2+} as a function of pH shown in Figure 3-14 and Figure 3-15, respectively, demonstrates the change in species charge as more hydroxide ligands or carbonate ligands are available for complexation.

Indeed, at pH values below 4, chromium speciation is dominated by the neutral species and at pH values above 7, a negatively charged hydroxide complex dominates. For Cu^{2+}, the presence of 10^{-3}M of carbonate impacts the speciation at circumneutral pH values where the neutral by charged $CuCO_3^o$ complex dominates. The distribution of charge affects both the

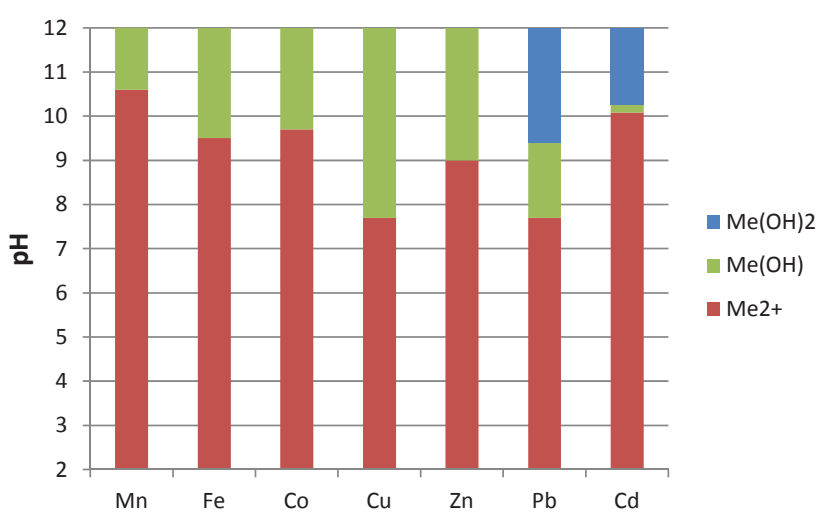


Figure 3-13. Distribution of metal hydroxide complexes as a function of pH (adapted from Essington 2005).

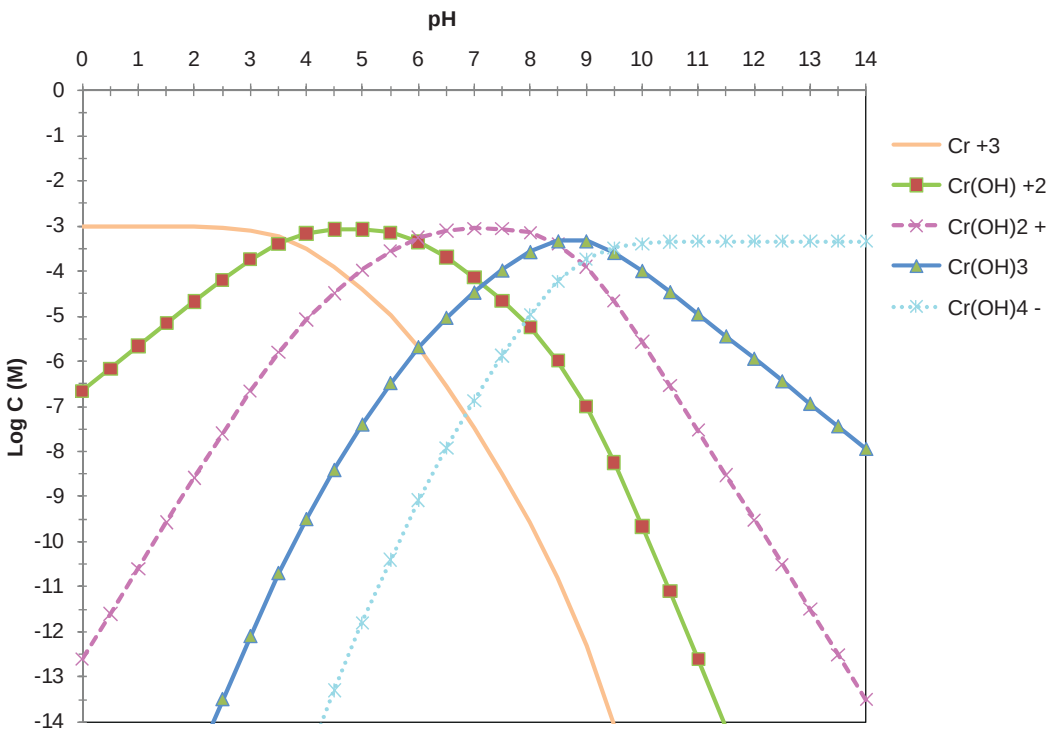


Figure 3-14. Speciation diagrams for 10^{-3} M Cr(III) in water at 25°C in the absence of competing ligands calculated using Visual MINTEQ.

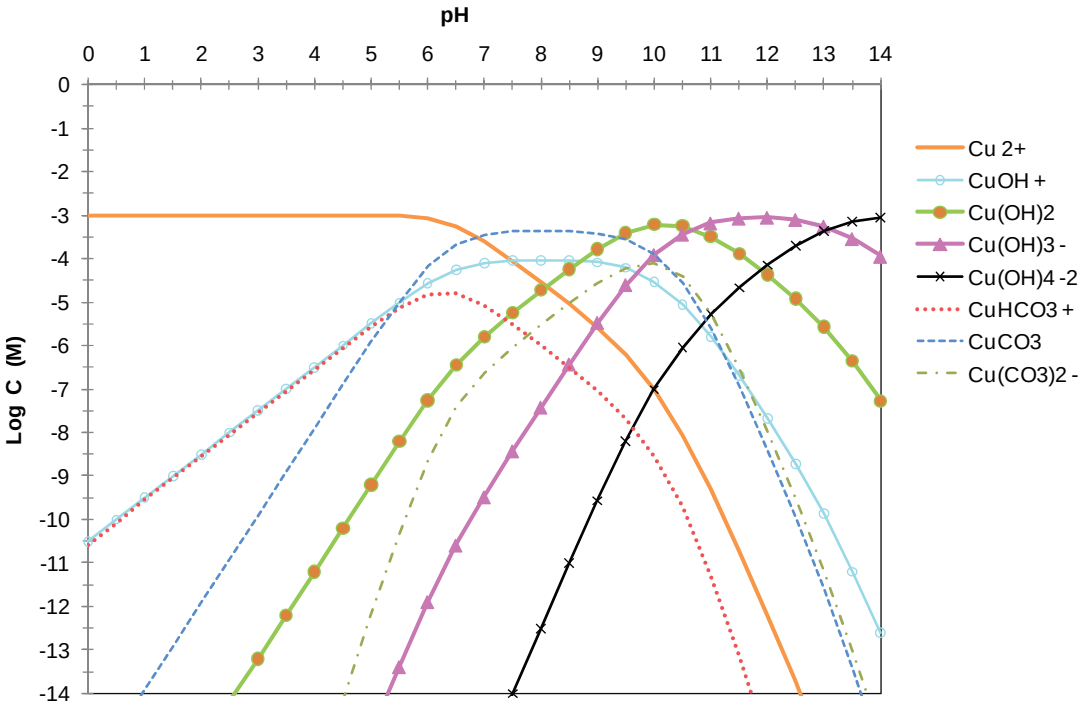


Figure 3-15. Speciation of 10^{-3} M Cu(II) in water at 25°C in the presence of 10^{-3}M total carbonate calculated using Visual MINTEQ.

Table 3-6. Stability constants for selected EDTA-metal complexes.

$Hg^{2+} + EDTA^{4-} \Leftrightarrow HgEDTA^{2-}$	$\beta = 10^{23.5}$
$Pb^{2+} + EDTA^{4-} \Leftrightarrow PbEDTA^{2-}$	$\beta = 10^{19.8}$
$Cu^{2+} + EDTA^{4-} \Leftrightarrow CuEDTA^{2-}$	$\beta = 10^{20.5}$
$Zn^{2+} + EDTA^{4-} \Leftrightarrow ZnEDTA^{2-}$	$\beta = 10^{18.3}$

adsorptive properties of the metal and transport across biotic membranes.

3.2.2 Complexation in the Presence of Chelating Agents

In many natural systems multidentate ligands or chelating agents are present. These types of species are also represented in Table 3-6. These chelating agents form stronger bonds with the central metal ion because they donate several pairs of electrons. Many of the chelating agents identified in natural waters are from anthropogenic sources. For example, the most well-known complexing agents are the aminopolycarboxylates, of which EDTA is a well-known representative. As shown in Table 3-6, the trend in binding strengths for the metal-EDTA complexes is similar to the chloride complexes; however, the binding strengths (as reflected in the value of the equilibrium constants) are orders of magnitude greater than those reported for the metal-chloride complexes. As a result, EDTA is mostly found bound to metal ions in natural waters.

The values of these stability constants suggest that when EDTA is added to water at concentrations comparable to or greater than the metal ions, EDTA-metal complexes will dominate the metal ion speciation and these complexes will carry a net negative charge. Natural chelating agents are also found in surface waters and are often generated from biological processes.

Ethylenediamine-succinate (EDSA) is a metabolite of the soil bacteria, *Amycolatopsis orientalis.* In contrast to EDTA, EDSA is readily biodegradable. Siderophores such as desferrioxamine-B (DFO-B) and azotochelin are naturally produced chelating agents that bind trace metals including Cu(II), Cd(II), and Pb(II) (Bellenger et al. 2007; Mishra et al. 2009). Complexation in these systems is a function of metal ion and pH. For example, Mishra et al. (2009) found minimal complexation of DFO-B with Pb at pH 3.0, but at pH 7.5 to 9.0, Pb was bound to three hydroxamate groups of the ligand in a "caged" hexadentate structure. At intermediate pH values (pH 4.8), a mixture of Pb-DFO-B complexes involving binding of the metal through one and two hydroxamate groups was observed. In contrast, Cd remained dissociated at pH 5.0, was present as a mixture of Cd-DFO-B and inorganic (hydroxide) species at pH 8.0, and was bound by three hydroxamate groups from DFO-B only at the highest pH value, pH = 9.0.

Stability constants for azotochelin and various metals are shown in Table 3-7. Of the metals shown in Table 3-7, copper exhibits the strongest affinity for azotochelin. Of particular interest is that this siderophore has recently been found to contain complex metals that form oxyanions such as molybdate, vanadate, and tungstate (Bellenger et al. 2007). Oxyanions are polyatomic ions that contain a metal ion and several oxygen atoms such as phosphate, sulfate, arsenate, and molybdate. They are relatively mobile in water due to their negative charge and relatively large in size compared to cationic metal ions such as Fe(III), Cu(II) and Zn(II).

Complexation can have a significant impact on metal bioavailability. In some cases, the presence of ligands shields the charge of the metal ion and allows it to pass across metal cell membranes. In other cases, the size of the metal-ligand cluster sterically hinders membrane transport (Finney and O'Halloran 2003; Manceau and Matynia 2010). Complexation also has a significant impact on metal ion solubility, and chelating agents are often used to extract metal ions from soils, sediments, and precipitated solids.

3.2.3 Complexation by Humic Substances

Humic and fulvic acids also serve as chelating agents for metal ions because they contain hydroxyl, phenoxylic, and carboxylic functional groups as shown in Figure 3-8 and Figure 3-9. As with other complexing agents, humic substances interact with and change the solubility and toxicity of trace elements in natural aqueous environments. In addition, major cations such as Na^+, Mg^{2+}, and Ca^{2+} can bind to organic matter to promote aggregation of smaller, dissolved natural organic molecules into colloidal particles. Due to the heterogeneity of these molecules,

Table 3-7. Complexation reactions of various metal ions with azotochelin, a naturally occurring siderophore (adapted from Bellenger et al. 2007).

Metal Ion	Reaction	Log of the Stability Constant, log β
Co^{2+}	$Co^{2+} + LH_5 \Leftrightarrow CoLH^{2-} + 4H^+$	Log β_1 = -23.0
	$Co^{2+} + LH_5 \Leftrightarrow CoLH_2^- + 3H^+$	Log β_1 = -13.5
Cu^{2+}	$Cu^{2+} + LH_5 \Leftrightarrow CuLH^{2-} + 4H^+$	Log β_1 = -12.9
Zn^{2+}	$Zn^{2+} + LH_5 \Leftrightarrow ZnL^{3-} + 5H^+$	Log β_1 = -24.1
	$Zn^{2+} + LH_5 \Leftrightarrow ZnLH^{2-} + 4H^+$	Log β_1 = -17.83

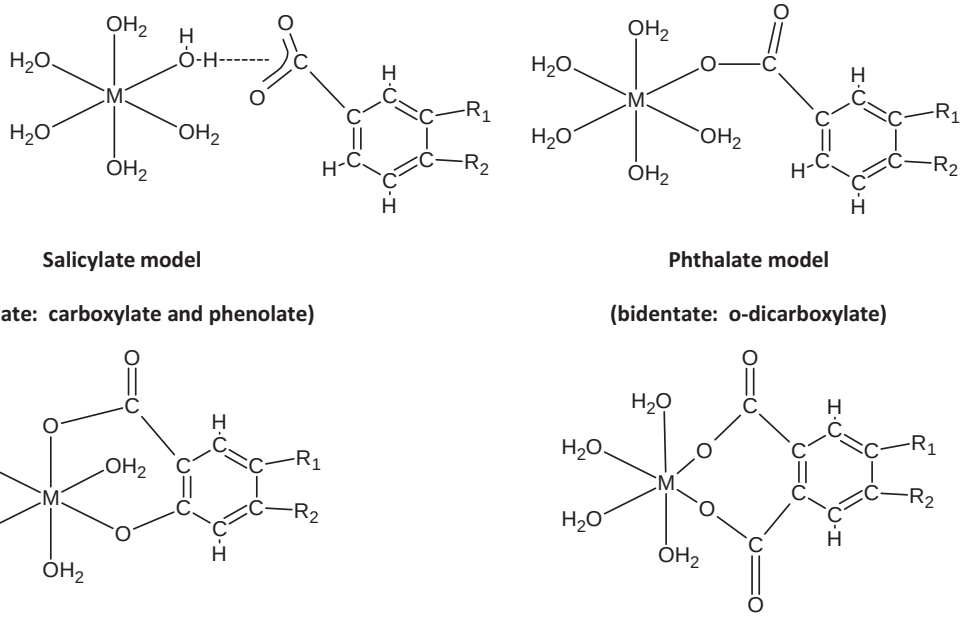


Figure 3-16. Organic molecules used to characterize metal ion binding to fulvic acid (adapted from Leenheer et al. 1998 and Essington 2005).

humic and fulvic acid binding is typically characterized using a range of ligand sites that vary with respect to their binding strength. Many researchers have employed small, monodentate organic acids such as those shown in Figure 3-16 to characterize weak binding of metals to fulvic acid, and multidentate ligands such as phthalate, salicylate, citrate, and oxy-succinate to quantify the strong binding sites (Leenheer et al. 1998; Nantsis and Carper 1998; Smith and Kramer 2000; Otto et al. 2001).

The stability constants (β values) for different metal–humic acid complexes typically follow a common order: Cu>Fe>Pb>Ni>Co>Ca>Cd>Zn>Mn>Mg. Note that this trend is not consistent with the previous order of reactivity shown for the inorganic ligands and anthropogenic chelating agents described earlier. Most notable is the relative stability of Cu-humic complexes. Manceau and Matynia (2010) used x-ray absorption spectroscopy to suggest that the stability of Cu-humic complexes is due to the abundance of dicarboxylate sites on the aliphatic portions of the molecule which provide good fits to the geometry of complexed Cu(II).

These spectroscopic results are supported by work of Meylan et al. (2004) in which in situ measurements of labile and dissolved copper and zinc in natural freshwater were compared to predictions from several models for the complexation by humic and fulvic substances. In all cases, the prediction of Zn^{2+} and complexed zinc concentrations were in agreement with the experimental data. However, model over-predictions of free Cu^{2+} concentrations were attributed to strong specific copper-binding ligands that were not accounted for in the models. This enhanced affinity for Cu suggests that the presence of humic acids in natural water will increase the overall solubility of Cu in water as both free Cu^{2+} and bound Cu will be present in solution.

Hoffmann et al. (2007) determined binding constants for copper and zinc with colloidal and dissolved organic ligands in river water on the order of $\beta = 10^{13}$. Equilibrium constants for the ligand-metal complex formation constants from ultrafiltered samples less than 3,000 Daltons were about 0.5 log units stronger than the values obtained from the 0.4 micron filterable fraction, suggesting the importance of colloidal humic matter. Nonetheless, the strength of these complexes is less than similar complexes formed with EDTA. Indeed, addition of EDTA to a solution containing metal organic matter complexes, led to dissociation of the complexes and formation of metal-EDTA complexes (Schmitt and Frimmel 2003).

While general trends in complexation with natural organic matter (NOM) have been observed, complexation with NOM is more difficult to define due to the complex and ill-defined nature of these organic complexes and the variability in the number and types of functional groups. Because the functional groups associated with humic substances are responsible for binding of humic and fulvic acids to mineral surfaces and metal ions, identifying the binding reactions with metal ions is difficult because (1) humic substances have different numbers of binding sites, (2) site competition is prevalent, (3) stoichiometry is metal ion dependent, and (4) electrostatics influence the extent of binding. In most studies, carboxylic acid and phenolic functional groups have dominated the speciation with metals. The relative importance of each is a function of the nature of the metal ion and the acidity of the functional group. In general, complexation of the carboxylic acid

and phenolic functional groups with metal cations increases with pH, decreases with metal ion concentration, and increases with humic acid concentration. Recent studies have suggested that acid polysaccharides participate in metal binding in colloidal organic matter and that binding of metals to humic acids greater than 1000 molecular weight units (Daltons) is associated with colloidal humic material depending on the metal ion and solution properties (Stordal et al. 1996; Quigley et al. 2002). Researchers have also emphasized the presence of sulfur moieties in humic substances, and have suggested that binding to sulfur sites may be important for adsorption of many metal ions (Smith et al. 2002; Karlsson et al. 2005).

Even with this complexity, reasonable agreement for binding of particular metals to humic substances extracted from natural waters frequently yields similar binding properties. For example, Cheng and Allen (2002) studied zinc binding to organic matter isolates (obtained using reverse osmosis) to isolate the organic matter. Using anodic stripping voltammetry and identical pH, ionic strength, and DOC concentrations, they found that the zinc titration curves from the different surface water sources were similar enough to suggest that the binding constants among the different waters were similar. They also demonstrated that the zinc-NOM complexes become more stable at higher pH. In contrast, Groenenberg et al. (2010) demonstrated that metal-fulvic acid binding parameters, optimized through modeling experimental data, showed substantial variation. Monte Carlo simulations showed differences in uncertainties depending on the affinity of the metal for the fulvic acids. For high affinity metals such as Cu and Pb, variations among samples were largely due to the natural variation in the log β values. However, for metals with a lower affinity such as Cd, uncertainty was associated with estimation of the fraction of fulvic acid in the organic matter.

Competition among different metal ions for complexation with humic and fulvic acids is also complicated due to the heterogeneous nature of these substances. While trace metal complexes such as Cu-NOM and Pb-NOM are generally stronger than major metal ion complexes such as Ca-NOM and Mg-NOM complexes, the concentration of major ions in natural waters makes them effective competitors for NOM complexation. Competition between trace metals and major ions is feasible even at these different concentration levels if the metal ions compete for the same sites on the organic matter. However, researchers have postulated that different ions preferentially complex to different functional groups of the humic and fulvic acids. For example, researchers have postulated that Cu complexation in natural waters occurs at the phenolic sites (Lu and Allen 2006) and phenolic and carboxylic functional groups (Benedetti et al. 1995). They attributed differences in pH dependency for Ca-NOM and Cu-NOM to the dominance of calcium complexation to the carboxylic sites, especially at high Ca concentration and low pH. Iglesias et al. (2003) also suggested that calcium only competes for specific copper sites. This research also suggested that only a fraction of the proton active sites are involved with Cu complexation.

Other researchers have focused on speciation to colloidal organic matter. Burba et al. (2001) developed a conceptual model based on the assumption that naturally occurring macromolecules and colloids ranging in size from nanometers to microns and comprised of irregular networks of organic and inorganic moieties are enriched in Al, Cu, Mn, Pb, and Zn. These so-called hydrocolloids compete for metal ions with organic matter and external ligands (e.g., EDTA and organic matter for Cu) and competition for organic matter occurs between different metal ions (e.g., Cu exchanges for Mn, Mg and Ca and Al and Fe exchange for Cu).

These results suggest that models for complexation of metal ions to humic and fulvic acids must incorporate multiple complexation sites, account for pH dependency associated with proton release from the sites, and include major ion and ligand competition. Two of the most challenging tasks for developing models to predict humic-metal ion competition are estimating the distribution and number of these different ligand sites and determining the stability (or equilibrium) constants for the formation of metal-ligand complexes.

3.2.4 Modeling Metal Complexation

A number of different models have emerged that describe the acid-base behavior of natural waters and metal ion binding to inorganic and organic complexes. The speciation of metal ions in waters containing simple inorganic ligands, anthropogenic chelating agents such as EDTA, and simple organic acids is well established and numerous chemical speciation models (PHREEQC, MINEQL, MINTEQA2, GEOCHEM) are adept at predicting the species distribution in systems containing metal ions and these ligands. However, the major challenge associated with speciation in natural waters has been describing and predicting chemical speciation in waters containing natural and anthropogenic organic matter. Such models must be able to predict metal ion binding over a wide range of conditions as a function of pH, concentration of organic matter, ionic strength, and the presence of competing metal ions and ligands. For example, each model must include a value for the total concentration of binding sites for each ligand, and a corresponding stability constant for the formation of each metal-ligand complex. The model must also describe how protons bind and dissociate by including reactions and equilibrium constants for each acid and base in the system. Thus, a complete model incorporates the equilibrium constants for each binding reaction and each proton dissociation reaction, mass balances for each type of ligand and each site on a ligand (e.g., phenolic and carboxylic if only two sites are used), mass balances for each metal ion, and a charge balance.

Over the past several decades several modeling approaches have evolved that have shown potential for predicting metal ion binding to NOM in these complex systems. The key to developing these models is to incorporate the chemical heterogeneity by providing a distribution of sites, competition among metals and protons, and a sub-model that describes the activity corrections resulting from the charge associated with the metal-ligand complexes (Milne 2000). In most cases, models for metal-humic acid complexation have utilized either discrete site or continuous site distributions. Two of the most well accepted models are WHAM Model VI (Windermere humic aqueous acid model) developed by Tipping et al. (1998) and the NICA-Donnan model (Kinniburgh et al. 1996). Both models assume two classes of binding sites attributable to carboxylic and phenolic groups (Tipping et al. 1998; Milne et al. 2001); however, at low metal concentration non-uniform binding and nitrogen and sulfur binding sites may be important (Frenkel et al. 2000).

Even though these models incorporate the basic tenants required for describing metal-ligand binding in complex systems, they each apply simplifications such as averaging the size, shape, and functional group behavior of humic substances and congruency of site heterogeneity for different metal ions. For example, each class of sites contains multiple binding constants whose values are distributed around a central log equilibrium constant. Both models have adopted the Donnan approach to account for electrostatic effects. Model VI utilizes a discrete distribution of sites assuming multidentate ligands (e.g., bi- and tridentate) in which humic substances are viewed as rigid spheres of uniform size with functional groups positioned on the surface. A large number of parameters are required to describe the site density, median values for the binding constants, and the distribution of constants around the means, but a number of assumptions are used to reduce the number of adjustable parameters. Nevertheless, a large number of parameters are required for the model as shown in Table 3-8.

Reasonable fits to a range of data have been observed for this model as well as with the NICA-Donnan model, which assumes that humic substances behave as a gel with a homogeneous charge and potential distribution. The NICA-Donnan was able to fit metal binding data from 124 data sets encompassing 23 metal ions over 16 orders of magnitude in metal ion concentrations from pH 2-16 using generic log K values for the two binding sites (Milne et al. 2001; Milne et al. 2003).

In a recent head-to-head comparison of two models for predicting Cu and Pb metal ion speciation for a soft water river, a hard water lake, and a hard water stream, it was concluded that predictions of the dominant species for each metal agreed reasonably well between the two models and the experimental data; however, both models under-predicted the concentrations of free metal ion concentrations by several orders of magnitude for the stronger complexing metals, Pb and Cu, when these concentrations represented only a small fraction of the total metal ion (Unsworth et al. 2006). Van Riemsdijk et al. found similar results for Ni complexation in six surface waters tested with Model VI. The model showed that the fraction of free metal ion in the waters increased with increasing Ni concentration, water hardness, and decreasing pH, and the model predictions overestimated the free Ni concentration even when all of the DOM was assumed to be comprised of the more reactive species, fulvic acid.

Cheng and Allen (2006) demonstrated that the prediction of Zn^{2+} free metal ion concentrations were reasonable at lower pH (below 7.0), but zinc binding for the natural waters tested was overestimated by Model VI at zinc concentrations below 10^{-6} M at pH 8.0. Better results were obtained by Bryan et al. (2002) for estimating Cu^{2+} concentrations in 15 freshwater samples in

Table 3-8. A summary of Model VI parameters (Tipping et al. 1998).

Parameter	Description
n_A	Density of type A sites (mol/g)
n_B	Density of type B sites (mol/g)
pK_A	Intrinsic proton dissociation constant for type A sites
pK_B	Intrinsic proton dissociation constant for type B sites
ΔpK_A	Distribution term to modify pK_A
ΔpK_B	Distribution term to modify pK_{VB}
Log K_{MA}	Intrinsic Equilibrium Constant for Metal Binding to Type A Site
Log K_{MB}	Intrinsic Equilibrium Constant for Metal Binding to Type B Site
ΔLK1	Distribution term to modify log K_{MA}
ΔLK_2	Distribution term to modify bidentate and tridentate binding strengths
P	Electrostatic parameter
K_{sel}	Selectivity coefficient for counterion accumulation
f_{prB}	Fraction of proton sites that can form bidentate complexes
f_{prT}	Fraction of proton sites that can form tridentate complexes
M	Molecular Weight of Fulvic Acid and Humic Acid
r	Molecular radius of Fulvic Acid and Humic Acid

which both humic and inorganic complexation were included using Model V and Model VI. The modeling effort incorporated competition with Mg, Al, Ca, Fe(II), Fe(III), and Zn, and the calculated Cu^{2+} concentrations from Model VI were within a factor of 3.6 in 95% of cases.

The application of these models to various natural waters has been tested for the past decade, and refinements to the approach to estimating parameters, predicting competition, and application to macrophytic organic matter have been a major focus. For example, Rey-Castro et al. (2009) developed a methodology which utilizes analytical expressions or average affinity distributions for the NICA-Donnan model and David et al. (2010) evaluated competition using the NICA model with a Conditional Affinity Spectra of the H+ binding at fixed total metal concentrations (CAScTM).

In the study by Rey et al. (2009), their approach allowed them to distinguish the binding locations of different groups of cations in a multi-component mixture: (a) Al, H, Pb, Hg, and Cr preferentially bound to the phenolic sites of fulvic acid; (b) Ca, Mg, Cd, Fe(II), and Mn preferred the carboxylic sites in the multi-component mixture; and (c) Fe(Ill), Cu, Zn, and Ni occupied both the phenolic and carboxylic sites. Using the Windermere Humic Aq. Model (WHAM) which incorporates Model VI, Tipping et al. (2008) showed that complexation constants for trace metal accumulation in bryophytes were similar to those for humic substances suggesting that these models can also be applied to plant uptake.

3.2.5 Summary

Metal ions in solution are always associated with other ions, organic species, or particulate matter. Their speciation is a function of the pH, ionic strength, and presence of other ions, organic molecules, and solid phases. Their speciation often dictates the mobility and toxicity in a particular aquatic environment because complexation reactions prevent metal ions from being precipitated, complexing agents act as carriers for trace elements in water, and metal ion bioavailability is often reduced by complexation. Simple inorganic ligands such as carbonate can control speciation in natural waters only in the absence of significant concentrations of stronger organic ligands. Naturally occurring and anthropogenic chelating agents that have binding constants that are orders of magnitude higher than the simple inorganic and organic acid functional groups can also dictate speciation if present at sufficient concentration. Because metal-ligand complexes can have significantly different charge than the metal ion itself, the mobility of these species can be increased dramatically. For example, Cu-EDTA species are typically negatively charged and highly mobile.

As with other complexing agents, humic substances interact with and change the solubility and toxicity of trace elements in natural aqueous environments. While general trends in complexation with NOM have been observed, complexation with NOM is more difficult to define due to the complex and ill-defined nature of these organic complexes and the variability in the number and types of functional groups. Recent studies suggest that the reactive components of NOM can be characterized using a series of simple organic acids that range from weakly binding carboxylate and phenolate to stronger binding salicylate, citrate, and phthalate molecules. In general, complexation of these functional groups with metal cations increases with pH, decreases with metal ion concentration, and increases with fulvic and humic acid concentration.

Chemical speciation models provide accurate tools for predicting chemical speciation in water. Speciation of metal ions with inorganic ligands, organic acids, and well-characterized anthropogenic ligands are available in a variety of chemical equilibrium software programs. Challenges associated with describing complexation with NOM still remain. Several models have emerged over the past several decades, and the two most promising models for characterizing speciation with organic matter are the NICA-Donnan model and Model VI. These models have demonstrated ability to predict metal ion binding over a range of conditions and represent the current state-of-the-art.

3.3 Oxidation/Reduction Processes

One of the key factors that controls reactivity and bioavailabilty of metals is the oxidation state of the metal in the system. Oxidation state is a number that is determined by the difference between the number of electrons associated with an atom in a compound as compared with the number of electrons in an atom of the element. Most of the divalent trace metal cations exhibit little redox activity in natural water columns indicating that they are typically present in only one oxidation state. Zn and Cd are examples of trace metals that do not typically undergo oxidation or reduction within natural waters. However, several metals including Cr, Se, Co, Pb, As, Ni, and Cu are redox active in natural systems and can exhibit different levels of toxicity, mobility, and bioavailability depending on the oxidation state of the metal ion. For example, the two major oxidation states of Cr are Cr(VI) and Cr(III). The most common form of Cr(VI) is as an oxyanion (e.g., $CrO_4^{=}$) which is extremely soluble, mobile, and toxic. Chromic acid is a relatively strong acid with pKa's of 0.86 and 6.51 for the first and second proton dissociation, respectively. In contrast, Cr(III), the reduced form, is relatively insoluble (e.g., Cr(OH)3(s)). In solution, it is typically present in cationic form, sorbs to many oxide minerals, complexes with natural and anthropogenic ligands, and forms both pure phase and mixed precipitates. Remediation strategies for Cr often involve reduction of Cr(VI) to Cr(III), followed by

precipitation of a chromium hydroxide solid (Gillham et al. 1994; Wilkin et al. 2005).

In general, trace metals do not dictate the redox conditions of a natural water. Rather, biochemical reactions involving major ions, nutrients, and minerals determine the availability of electrons in the water, and hence, the redox potential (oxidation/reduction status) of an element. Trace metals speciate based on the prevailing redox conditions. It is typical to represent the redox conditions of a water based on the electrical potential of the system, E_H (volts), or more typically the pe of the system which is related to the electrical potential by:

$$E_H = \frac{RT \ln 10}{F} pe$$

where F is Faraday's Constant (96484.56 Coulombs/mole), R is the ideal gas constant (8.314 Joules/degree Kelvin), and T is the temperature in degrees Kelvin. Natural waters are classified as oxic, suboxic, and anoxic based on their *pe* (or E_H) and pH values as shown in Figure 3-17. Thus, the key to understanding redox speciation in natural waters is to determine which redox couple (e.g., Fe^{+2}/Fe^{+3}, O_2/H_2O, NH_4^+/NO_3^-) controls the pe of the system. If the controlling redox couple is at equilibrium, then that couple defines the pe of the system. This pe can be calculated based on known values of the equilibrium constants for the so-called half-reactions for the two species. For example, the half reaction for $O_2(g)$ in equilibrium with H_2O(liquid) is

$$1/4O_2(g) + e^- + H^+ \Leftrightarrow 1/2H_2O(l) \qquad \log K = 20.75$$

Thus, in an oxic water zone at 25°C, pH 7, and a partial pressure of oxygen (PO_2) equal to 0.21 atm, the O_2/H_2O couple controls the redox environment, and the pe of the system will be equal to 13.5. The speciation of trace metals such as As, Cr, Cu, and Ni can then be calculated using the appropriate half reaction corresponding to a redox potential of 13.5. For example, the half reaction for the couple Cu^{2+}/Cu^+ is

$$Cu^{2+} + e^- \Leftrightarrow Cu^+ \qquad \log K = 2.6$$

and the ratio of Cu^{2+}/Cu^+ at a pe of 13.5 (E_H = 800 mV) is $10^{10.9}$, which suggests that Cu^{2+} is the stable copper species at neutral pH in an oxic water zone. Controlling redox couples for natural waters and soil systems are typically defined by the nutrient conditions prevalent in the system as shown in Figure 3-17. In oxic zones, reduced species such as H_2O, N_2, and Mn^{2+} will be oxidized to their corresponding oxidized forms (e.g., O_2, NO_3^-, and MnO_2, respectively). In suboxic and anoxic zones, the oxidized forms are reduced. The particular species formed during reduction depends both on the redox potential of the system (e.g., pe or E_H) and the presence of microorganisms capable of catalyzing the reduction reaction. As stated earlier, the redox potential in a system is controlled or defined by the most oxidized couple as long as the species are present. For example, if O_2 is present in a system, the O_2/H_2O couple will control the E_H of the system. As the oxidized species is reduced and disappears from the system, the next couple in the sequence controls.

It is also possible, to examine speciation of metal ions as a function of both pH and pe. pe vs. pH graphs can be prepared for each metal ion, and as long as the pe and pH of the system are known and equilibrium is established, speciation can be predicted. For example, As(III) and As(V) are both typically found as oxyanions, arsenite and arsenate, respectively. Metals such as, As, Se, and Cr can cause water molecules

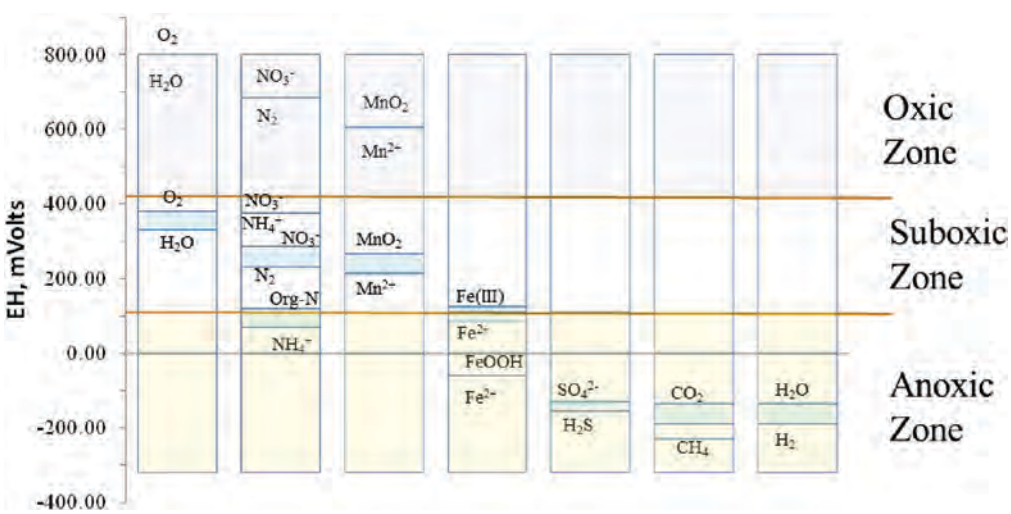


Figure 3-17. The oxidation (oxic zone) and reduction sequence observed in typical soils systems (adapted from Essington 2005).

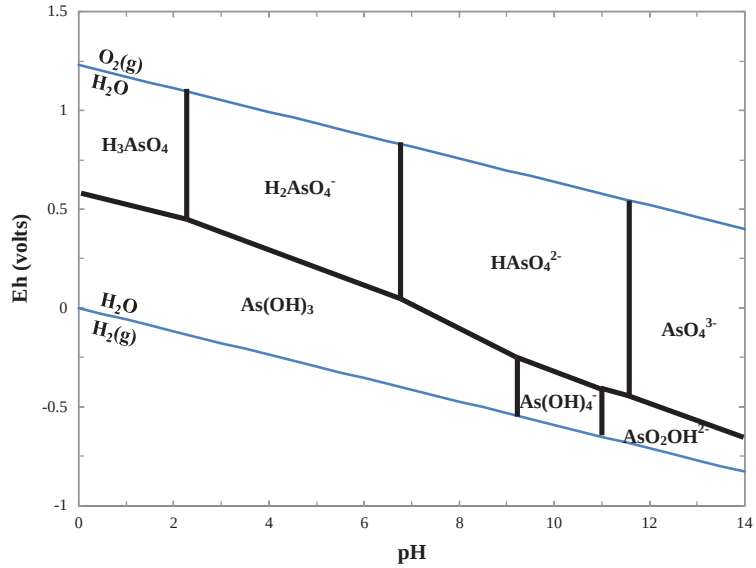


Figure 3-18. Arsenic speciation as a function of pH and redox potential (adapted from Cheng et al. 2009).

to deprotonate completely, forming the oxyanions AsO_3^{3-}, SeO_3^{2-}, and CrO_4^{2-}. These basic oxyanions undergo acid/base chemistry, forming either di- or tri-protic acid. Thus, arsenic can exist in solution in two different oxidation states and seven different states of protonation.

Figure 3-18 presents the speciation of these seven different forms of arsenic as a function of pH and pe. The stability region for water is also shown on this graph. The pKa for H_3AsO_3 of 2.24 is shown as a vertical line in Figure 3-18 that represents the pH at which equal concentrations of H_3AsO_3 and $H_2AsO_3^-$ are present. The vertical line is terminated at the pe at which the oxidized forms are in equilibrium with the reduced species $As(OH)_3$. Diagrams such as the one presented for the arsenic system can be extremely useful for understanding chemical speciation and for developing remediation strategies for water.

Arsenite is more toxic and less reactive, but can be oxidized to arsenate through homogeneous and heterogeneous (e.g., on mineral surfaces) oxidation processes (Sharma and Sohn 2009). For comparison purposes Table 3-9 shows that the ranges of Eh and pH for various freshwater systems are within ranges that encompass both oxidized and adsorbed arsenic species. The importance of adsorption to mineral surfaces to facilitate heterogeneous oxidation cannot be underestimated because homogeneous oxidation occurs slowly. Thus, understanding the distribution of arsenic species and potential remediation options for contaminated water requires an understanding of redox chemistry, as well as sorption reactions and precipitation reactions.

In general, equilibrium speciation is less appropriate for predicting the speciation of redox active metal ions because transformations between redox states are often kinetically controlled. Rates of oxidation are controlled by a number of water quality parameters. Craig et al. (2009) used a muti-parametric technique to demonstrate that Fe(II) oxidation rates were dependent on carbonate/bicarbonate, NOM, sulfate, chloride, the sulfate/fluoride interaction, and fluoride, in which the most influential parameters are listed first.

Table 3-9. Typical ranges of pH and Eh for various water bodies (Sanders 1998).

Type of Waters	Specific Conductance (mS/cm)	E_H (mvolts)	pH
Rain water	2 – 100	+400 to +600	4 – 7
Freshwater lakes/streams	2 – 100	+300 to +500	6.5 – 8.5
Groundwater	50 – 50,000	-200 to +100	6 – 8.5
Brines	Up to 500,000	-200 to -600	Near neutral
Ocean water	~ 50,000	+300 to +500	7.8 – 8.4
Wetlands/bogs	50 – 50,000	+100 to -100	variable

While the importance of redox chemistry is evident for redox active metals, it is important to recognize that while metals such as Zn and Cd are not directly influenced by the redox conditions of a system, their fate is dependent on the redox state of elements such as sulfur. In a reducing environment, rich in electrons, sulfate is reduced to sulfide and metal sulfides are extremely insoluble. Hence, in reducing environments many divalent metal ions, including Zn and Cd, can precipitate from solution [e.g., ZnS(s) and CdS(s)]. Changes in redox conditions have been shown to affect speciation in the water column of some lakes. Balistrieri et al. (1994) showed that dissolved Co, Cr, Fe, Mn, Ni, Pb, and Zn concentrations increased across the oxic-suboxic boundary (pe = 7 or $E_H = 400$) whereas dissolved As, Co, Cr, Fe, Mn, and V concentrations increased in the anoxic layer (pe < 2 or $E_H < 100$) of a meromictic lake. At greater depths, in the anoxic zones where sulfide was evident, significant decreases in dissolved Cu, Ni, Pb, and Zn concentrations were observed as well as increases in acid soluble particulate concentrations of As, Cr, Cu, Fe, Mo, Ni, Pb, V, and Zn.

3.3.1 Summary

Several metals including Cr, Se, Co, Pb, As, Ni, and Cu are redox active in natural systems and can exhibit different levels of toxicity, mobility, and bioavailability depending on the oxidation state of the metal ion. The particular oxidation state of a metal is typically controlled by dominant biogeochemical processes occurring within the system. Several metals such as Cr and As exhibit multiple oxidation states in natural waters and the relative rates of oxidation/reduction are often controlled by interactions with NOM and surfaces. In addition, metal fate and transport is affected by the dominant redox processes that affect speciation of major anions such as nitrate and sulfate. In reducing environments, nitrate reduction to ammonia increases, metal ion complexation, and sulfate reduction to sulfide can lead to precipitation of many of the trace metal ions.

3.4 Precipitation Processes

Precipitation processes are also typically rate limited, but may control the fate and transport of metal ions in natural waters due to the formation of mixed precipitates and metastable phases. Precipitation reactions are typically defined by Ksp or solubility reactions written in terms of the dissolution of the ionic solid. For example,

$$CuCO_3(s) \Leftrightarrow Cu^{2+} + CO_3^{2-} \qquad Ksp = 10^{-9.63}$$

$$CuOH_2(s) \Leftrightarrow Cu^{2+} + 2OH^- \qquad Ksp = 10^{-19.36}$$

The extent and rates of precipitation or dissolution are dependent on the solution phase concentrations of both species as well as the pH of the system. In all cases, precipitation occurs via a series of steps including nucleation, growth, and crystallization. The solution pH determines both the OH^- concentration and the concentration of other reactive ligands such as CO_3^{2-}, which undergoes acid/base reactions to maintain equilibria with HCO_3^- and H_2CO_3. Rates of precipitation are dependent on the degree of oversaturation defined by:

$$\frac{IAP}{Ksp} = \frac{\{Cu^{2+}\}\{CO_3^{2-}\}}{Ksp}$$

where IAP is the ion activity product determined from the product of the measured activities (NYSDEC) of the reaction products divided by the product of the activities of the reactants relative. If the ratio of IAP/Ksp is greater than one, then the system is oversaturated with respect to the solid phase. The rate of precipitation as a function of the relative supersaturation is typically expressed as a power law

$$R = k\left((IAP/Ksp)^{1/2} - 1\right)^n$$

where k is the apparent rate constant and n the apparent rate order. The degree of oversaturation often determines whether homogeneous or heterogeneous nucleation dominates. In heterogenous precipitation, a different surface or substrate acts as the site for ions of the crystal to properly orient whereas in homogeneous nucleation a few particles correctly orient in the course of their random movement through the water. One of the systems most commonly studied with respect to rates of precipitation, homogeneous and heterogeneous nucleation is the $CaCO_3(s)$ system. Numerous studies have investigated the relative degree of oversaturation required for homogeneous nucleation and the potential of other natural water particles to facilitate heterogeneous nucleation. Lin and Singer (2005) showed that at low degrees of supersaturation a nucleation site from another surface is required to overcome the activation energy barrier for precipitation. In their study of quartz, dolomite, and commercially available calcite and lime softening precipitates, only the calcite-based seed materials were capable of inducing calcite precipitation within a 2 hour time period and required a degree of oversaturation of greater than five. Impurities within the seed such as Mg^{2+} and NOM were reported to have poisoned the seed and reduced its catalytic ability. Other researchers have demonstrated similar effects at low supersaturation ratios. Lioliou et al. (2007) demonstrated that induction rates for homogeneous nucleation were proportional to the degree of supersaturation and suggested a polynuclear growth mechanism. At lower supersaturation ratios, the addition of calcite seed crystals led to immediate precipitation without an induction period. However, addition of quartz crystals did not lead to precipitation. Again the differences were attributed to

the lack of compatibility between the crystal lattices. Both of these studies emphasize the importance of lattice compatibility for nucleation. Similar findings have been reported for co-precipitation processes in which ion size is a key determinant for removal of trace metal ions in precipitating iron, aluminum, and silica systems (Maurice 2009).

It is important to also recognize that precipitation of a metastable phase may often precede formation of the most thermodynamically stable phase for a specific metal. For example, the presence of high concentrations of iron in water often leads to precipitation of amorphous iron hydroxide [$Fe(OH)_3$] in relatively short time periods (hours) whereas it takes significantly longer times to form stable goethite (FeOOH) or hematite (Fe_2O_3) phases. As each of these more stable phases is formed, the precipitate becomes more crystalline with a decreased SSA as shown in Figure 3-19.

The observed relationship between the crystallinity of a mineral and the SSA is typical of many oxide and hydroxide minerals (Schwertmann 1996). For iron oxides, the SSA is greatest for ferrihydrite and then decreases as the amorphous structure ages to the more crystalline structures of goethite and hematite. As a result, it is often necessary to calculate chemical speciation based on the operative redox state or based on knowledge of the metastable solid phase present.

The precipitation of metal hydroxides, oxides, carbonates, and sulfides can control the fate and transport of metal ions. Thermodynamic data for precipitation of metal species are tabulated in databases such as the Critical Stability Constants (Martell and Smith 1974), geochemical speciation databases contained in models such as MINTEQA2, MINEQL+, PHREEQC, and others. In many cases, values obtained from these sources differ significantly (by orders of magnitude in some cases) due to differences in experimental methods, particle size and crystallinity, experimental temperatures, pH values, aging times, analytical limitations, etc.

Dyer et al. (1998) reviewed solubility constants for a number of hydroxide solids and developed speciation diagrams for the more amorphous phases documented in the literature. An example of the type of solubility diagram developed is shown in Figure 3-20 for two metal hydroxide solids, $Cu(OH)_{2(s)}$ and

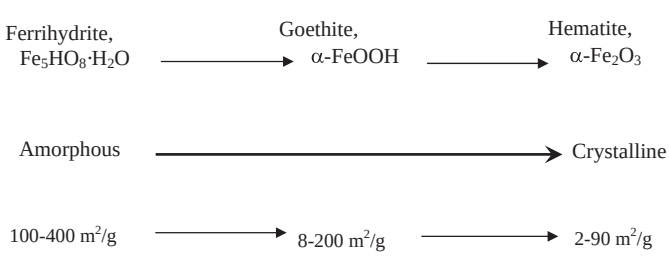


Figure 3-19. SA as a function of crystallinity for select iron oxides (adapted from Cornell and Schwertmann 1996).

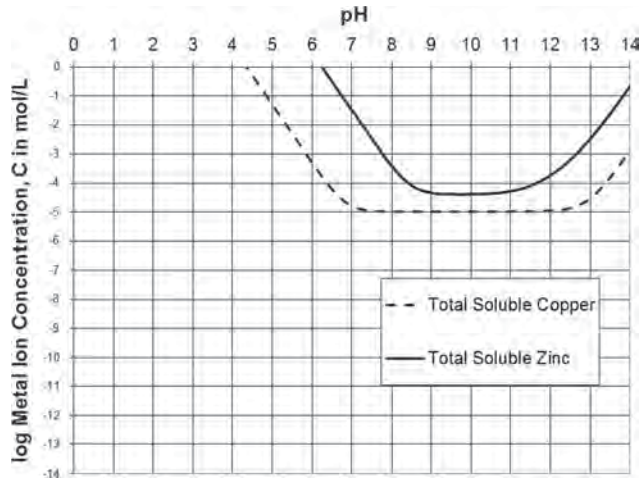


Figure 3-20. Comparison of $Cu(OH)_2$ and $Zn(OH)_2$ solubility model predictions.

$Zn(OH)_{2(s)}$. The solid line in these figures represents the equilibrium between the solid precipitate and the total aqueous concentration of the metal. The curvature in the solubility line is due to complexation reactions which change the dominant soluble species [e.g., Cu^{2+} to $Cu(OH)^+$ to $Cu(OH)_2^0$ to $Cu(OH)_3^-$] as described previously. Thus, the line represents the maximum solubility of the metal ion as a function of the pH of the water. Waters having concentrations of metal ion that fall above the line are oversaturated with respect to the metal ion.

Dyer et al. (1998) compiled model simulations for 12 different metals and their total solubilities in aqueous solution. Their data highlighted two important points. $Fe(OH)_3(s)$ and $Al(OH)_3(s)$ have minimum solubilities at lower concentrations and lower pH than all the other metal hydroxides except Ni(II). In addition, most of the trace metal ions have minimum solubilities that are above 0.1 ppm in the pH 6 to 8 range, suggesting that hydroxide precipitates will not control the mobility of trace metal contaminants in most systems. These results suggest that iron and aluminum hydroxides represent important sinks for metal ions and explain why these solids are frequently used in water treatment processes for coagulation processes.

Zn, Ni, and Co have been studied for their potential to sorb to aluminum oxides and clay minerals in laboratory and field studies. A thorough discussion of the adsorption process is presented in Chapter 5. However, not only do these metals adsorb to the surfaces of clays and iron, silica, and aluminum oxides and hydroxides, they also co-precipitate with them. The formation of mixed-metal-Al layered double hydroxide (LDH) phases similar to hydrotalcite has been well documented in the literature. The rates and thermodynamics of formation of these phases depend on a number of scenarios including the nature of the aluminum phase and the type of interlayer anion presence (Scheidegger et al. 1998; Thompson et al. 2000). Substitution of silica for carbonate and carbonate for sulfate led to a

more stable phase (Peltier et al. 2006). Again, the key to metal ion substitution is similarity in ionic size between the parent ion and the substituting cation. Thus, the presence of clay particles that can provide both aluminum and silica via dissolution can promote the formation of these mixed precipitates. Similar types of mixed metal precipitates have been identified for nickel and cobalt silicates in which the silica is derived from silica minerals. In all cases, the presence of these phases lowers the overall solubility of the metal ion. Thus, the solubility of both the trace contaminant phases and the dominant base mineral phases in the system will dictate the overall solubility of the metal contaminants.

For example, thermodynamic data suggests that Zn hydroxide [$Zn(OH)_2$], smithsonite ($ZnCO_3$) or hydrozincite [$Zn_5(OH)_6(CO_3)_2$] will control Zn solubility in contaminated neutral and calcareous soils (Saeed and Fox 1977; Jacquat et al. 2008). Jacquat et al. (2008) studied zinc contaminated soils and identified the presence of Zn-phyllosilicate and Zn-LDH phases from field samples. Not only did the precipitation of these phases control the total zinc concentration in solution at low and intermediate surface loadings of Zn, but separate experiments with synthetic phases suggested that zinc could be readily extracted from these phases using 1 M NH_4NO_3 followed by 1 M NH_4-acetate at pH 6.0. The implications of these studies are that the presence of dominant ions such as iron, aluminum, and silica in natural waters may impact trace metal concentrations through precipitation reactions even when the metal ions are present at levels below their saturation.

3.4.1 Summary

Precipitation processes can have a large impact on the speciation of metal ions in solution. In oxic waters, the major precipitates include hydroxide and carbonate phases. While published solubility constants are available for most of the potential solid phases, significant variability exists in the literature due to the experimental methods and conditions used to determine the values. Moreover, precipitation processes are often rate limited, and the most stable phase is often not the dominant phase found in natural waters. The kinetics of precipitate formation are dependent on the presence of nucleation sites from other similar phases or from homogenous solid formation. The evidence is also mounting that removal of metal ions in natural and engineered systems is due to the more rapid formation of mixed precipitates or co-precipitates formed from either dissolution of prevailing solid phases (e.g., clays and oxide minerals) or precipitation of more insoluble phases such as iron and aluminum hydroxide. Removal of metal ions from solution may also be controlled by adsorption to these other precipitating phases as is commonly noted in water treatment applications.

3.5 Sorption Processes

One of the dominant mechanisms for removing metal ions from natural waters is sorption to suspended solids, colloidal solids, and other particulate matter present in the system. By definition, sorption involves either adsorption or absorption, although macroscopic measurements of sorption rarely distinguish precipitation and surface precipitation from these other two processes. The term adsorption typically refers to the accumulation of compounds on a solid surface, and absorption is related to accumulation in the internal region of a solid phase.

Inorganic species, such as metal cations, have the potential to partition to solid surfaces present in aquatic systems. This interaction, generally termed sorption, involves distributing the metal species between the solid and aqueous phases in a manner analogous to the complexation reactions that occur in solution. Indeed, the interaction at the solid surface often involves the reaction between the metal species with surface functional groups, such as surface oxygens and hydroxyl groups. The extent of metal ion sorption is largely dependent on the type of solid mineral present, bulk aqueous concentration of the metal ion, solid concentration, pH, ionic strength, and the presence of aqueous ligands. The properties of solid minerals present in natural systems vary significantly for different minerals and surface functional groups; therefore, it is important to understand solid phase characteristics when discussing metal ion adsorption.

3.5.1 Charge Development in Clays and Clay Minerals

Both clays and clay minerals such as oxides, hydroxides, and oxyhydroxides provide surfaces for adsorption of metal ions. All of these minerals create charged surfaces when placed in solutions. Clays are comprised of sheets of silica tetrahedral and aluminum octahedra that are stacked as either 1:1 or 2:1 layers as shown in Figure 3-21, with the dimensions shown in angstroms (A°). Two types of charge are possible on the surfaces of clays: permanent charge surfaces and variable charge surfaces. Permanent charge on clays develops from isomorphic substitution of aluminum for silica in the tetrahedral sheet and Mg and other divalent metal ions for Al in the octahedral sheets. The substitution of an ion with lower charge [i.e., Al(III) for Si(IV) and Mg(II) for Al(III)] yields a net negative charge on the inner layer of the clay mineral as shown for montmorillonite in Figure 3-21. For expanding clays such as montmorillonite, this permanent charge is balanced by inner layer cations such as Ca^{2+} and Mg^{2+}. Ion exchange among these inner layer cations provides one mechanism for removal of metal ions from solution. However, since trace metals are present at substantially lower concentrations compared to the major cations of the system, competition with major cations must be considered.

In addition to the charge that develops due to isomorphic substitution, clays also develop charge on their edges where

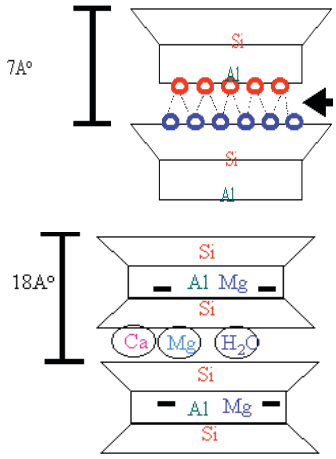


Figure 3-21. Structures of kaolinite, a 1:1 clay (top) and montmorillonite, a 2:1 clay (bottom). The arrow in the structure for kaolinite indicates the location of hydrogen bonding which gives kaolinite its rigid structure and prevents inner layer ion exchange.

oxygens terminate (Figure 3-22). These terminal oxygens of the clay are not fully coordinated as in the bulk clay structure and tend to protonate in water. As a result, they are often characterized as diprotic surface sites which undergo the following acid/base reactions:

$$\equiv SOH_2^+ \Leftrightarrow \equiv SOH + H^+ \qquad Ka_1$$

$$\equiv SOH \Leftrightarrow \equiv SO^- + H^+ \qquad Ka_2$$

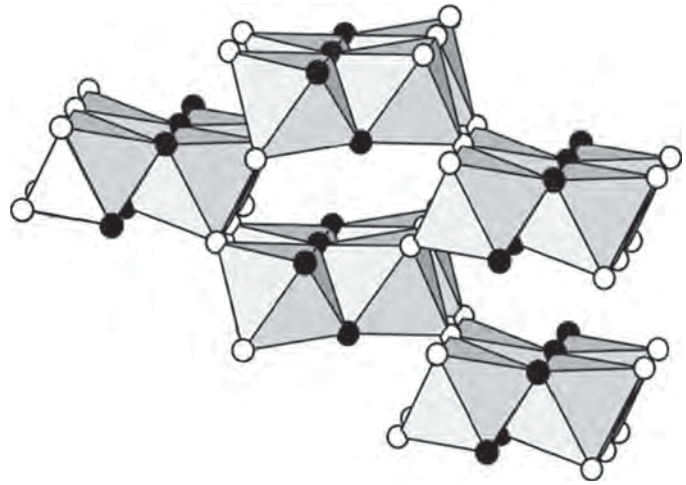


Figure 3-23. Goethite structure displaying octahedra formed by oxygen atoms.

where ≡S represents a generalized surface site. The pH at which the concentration of $[\equiv SO^-]$ is equal to the concentration of $[SOH_2^+]$, is termed the pH of the point of zero charge (pH_{pzc}). At this pH, the net charge on the surface is neutral. Below the pH_{pzc}, the surface will carry a net positive charge and above the pH_{pzc}, the mineral will carry a net negative charge.

Clay minerals such as oxides, hydroxides, and oxyhydroxides also contain terminal edge sites which develop charge in solution. For example, the goethite surface (FeOOH) is comprised of oxygen-hydroxyl sheets that form a hexagonal close-packed array in which iron resides in two-thirds of the oxygen octahedra, but in strips as shown in Figure 3-23.

In the goethite structure, surface oxygens can be singly, doubly, or triply coordinated to iron atoms, providing a range of reactivities. However, it is difficult to estimate differences in the reactivities of these different groups, and many researchers

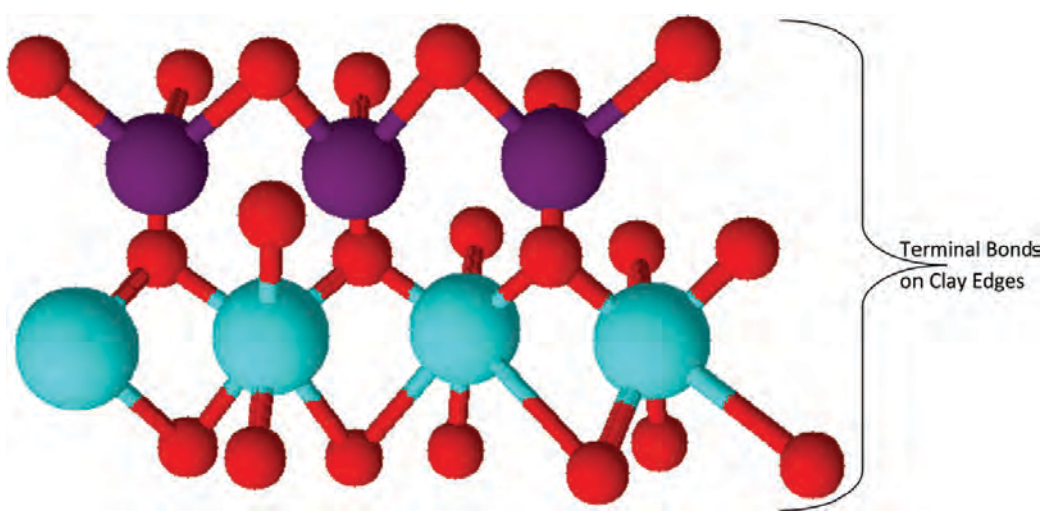


Figure 3-22. Terminal bonds on the edge of a 1:1 clay.

Table 3-10. Point of zero charge values for various clays and clay minerals (Sverjensky and Sahai, 1996).

Mineral	pH_{pzc}
Quartz (α-SiO_2)	2.9
Amorphous silica ($SiO_2 \cdot {}_2H_2O$)	3.5
Birnessite (δ-SiO_2)	3.76
Kaolinite	3.76
Rutile (TiO_2)	5.8
Anatase (TiO_2)	6.0
Magnetite (Fe_3O_4)	6.9
Muscovite	7.5
γ -Alumina (γ-Al_2O_3)	8.5
Hematite (α-Fe_2O_3)	8.5
Gibbsite ($Al(OH)_3$)	8.9
Corundum (α-Al_2O_3)	8.9
Goethite (α-FeOOH)	9.0

use a single set of diprotic acidity constants to describe proton release from these surfaces. This approach has been questioned as of late, and significant progress has been made that demonstrates that differentiating adsorption to different site types yields significant improvements in model fits to metal ion adsorption to geothites (Villalobos and Perez-Gallegos 2008; Villalobos et al. 2009; Salazar-Camacho and Villalobos 2010).

Of particular interest with respect to the acidity of these sites are the differences among the different oxide minerals as shown by the variation in pH_{pzc} values in Table 3-10. Since above the pH_{pzc}, the surface carries a net negative charge, minerals with a lower pH_{pzc} exhibit a higher tendency to attract cations. In contrast, minerals with a higher pH_{pzc} have greater affinity for anions.

Surfaces other than oxides also provide reactive sites for binding metal ions. Carbonate minerals also affect the biogeochemistry of natural waters and create surfaces for adsorption. Reactive sites on these minerals include $\equiv CaOH$ and $\equiv CO_3H$. On this surface, Ca, in addition to protons, affects the intrinsic surface charge as surface reactions including:

$$\equiv CO_3H \Leftrightarrow \equiv CO_3^- + H^+$$

$$\equiv CO_3H_2^+ \Leftrightarrow \equiv CO_3H + H^+$$

$$\equiv CO_3H + Ca^{2+} \Leftrightarrow \equiv CO_3Ca^+ + H^+$$

$$\equiv CaOH \Leftrightarrow \equiv CaO^- + H^+$$

$$\equiv CaOH + H^+ + CO_3^{2-} \Leftrightarrow \equiv CaHCO_3^0$$

$$\equiv CaOH + CO_3^{2-} \Leftrightarrow \equiv CaCO_3^-$$

Thus, the surface charge characteristics of calcium carbonate surfaces is complex. At low pH, adsorption of bicarbonate and calcium ions determine the surface charge. As pH increases, the adsorption and desorption of protons becomes the dominant source of charge.

In addition, many complications arise in determining the surface charge of calcite and other carbonate minerals due to the experimental challenges associated with establishing and maintaining equilibrium with the atmosphere which contains carbon dioxide and with the solid phase (Wolthers et al. 2008). Dissolution of carbon dioxide and precipitation of calcium carbonate are both pH dependent properties. The total aqueous carbonate concentration and the carbonate concentration both increase dramatically with increasing pH, and the time frame for establishing equilibrium with the atmosphere is on the order of hours and with the solid phase can be even longer. Thus, many experimental studies examining surface charge and adsorption to carbonate surfaces have been impacted by non-equilibrium artifacts. Thus, it is not surprising that the pH_{pzc} for calcite has been reported over a range of values from pH 7 to 11.

3.5.2 Surface Complexation

One of the most intriguing aspects of metal cation sorption is the ability of some metal ions to sorb at pH values below the pH_{pzc}. The sorption reaction, termed surface complexation, is thought to be analogous to the aqueous complexation of metal ions by ligands present in the bulk solution. The formation of surface complexes by divalent metal cations is often described by the following general chemical reaction:

$$\equiv SOH + Me^{+2} \Leftrightarrow \equiv SOMe + H^+$$

In this reaction, $\equiv S$ represents the generalized surface site acting as a complexing ligand. As a result of surface complexation, metal ions can sorb to oxide surfaces at pH values below the pH_{pzc} as shown for adsorption of Co by aluminum oxide in Figure 3-24. These pH adsorption edges are obtained from batch experiments in which identical concentrations of metal ion and solid (oxide mineral) are added to a series of reactors and the pH is varied through addition of strong acid or base. The shape of the adsorption edge is consistent with the complexation reaction shown above and suggests that for strongly sorbing metal ions such as cobalt, there is an increase in adsorption from near zero to 100% removal from solution over a fairly narrow pH range. The data also show that increasing the solids concentration or decreasing the amount of Co added to the solution shifts the edge to the left, which indicates increasing adsorption.

More typical isotherm plots may also be generated from metal ion adsorption data in which the solid phase concentration (or mass adsorbed/mass of sorbent) is plotted versus the aqueous phase equilibrium metal ion concentration as shown in Figure 3-25 for adsorption of Cu on iron oxide between pH 6 and 7. These model simulations (using the Diffuse Layer

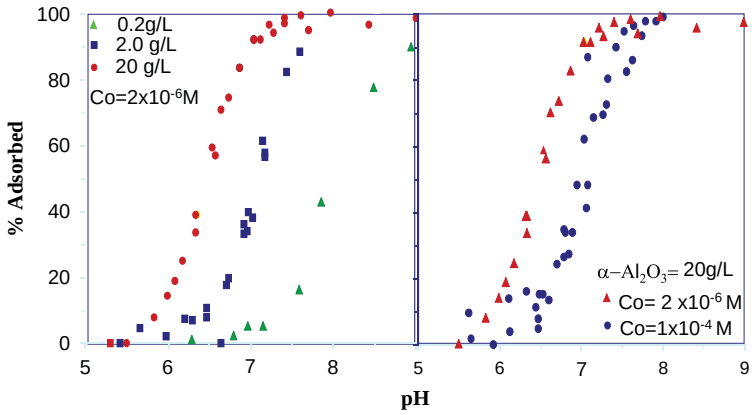


Figure 3-24. Sorption of Co(II) to α-Al_2O_3 (aluminum oxide, corundum) at constant initial Co concentration and aluminum oxide concentration as a) a function of aluminum oxide concentration and b) a function of initial Co concentration.

Model – DLM) show the non-linearity of the isotherms and the importance of incorporating pH into modeling approaches. As a result, descriptions of metal ion adsorption that utilize linear isotherms in which the sorbed phase concentration is related to the equilibrium solution phase concentration by a distribution coefficient, K_d, are inadequate for describing metal ion adsorption. In addition, non-linear empirical models such as the Langmuir and Freundlich isotherm models are also inaccurate, as they do not adequately capture the effect of pH.

Figure 3-26 shows the dramatic difference in adsorption of weakly sorbing Se(IV) and strongly sorbing Se(VI). The data also show a large impact of ionic strength on sorption of Se(IV) with reduced sorption at higher ionic strengths. The inability to achieve 100% adsorption at low pH in these systems can be due to site limitations or the change in speciation from the fully deprotonated oxyanion to a protonated acid form with lower charge (i.e., $SeO_4 + 2H^+ \Leftrightarrow H_2SeO_4$). Similar results have been reported from other oxides and other oxyanions (Essington 2005).

The presence of multiple adsorbing cations or cations and anions can lead to competition for sites on the surface. Competition for surface sites is just one possible affect that has been observed in multi-solute systems. The adsorption of oxyanions can reduce the negative surface charge on oxide minerals thereby promoting adsorption of cationic metals (Boyle-Wight et al. 2002; Zhang and Peak 2007). In addition, evidence for ternary complexes (see Figure 3-27) has been presented by a number of researchers and its impact on adsorption (Zhang and Peak 2007; Papadas et al. 2009; Swedlund et al. 2009). Thus, it appears that both competition and enhanced adsorption are possible in the presence of sorbing ligands.

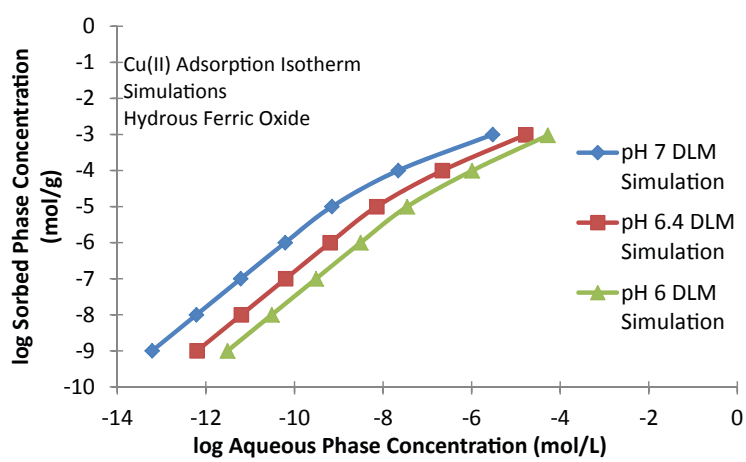


Figure 3-25. Effect of pH on sorption isotherms for Cu onto iron oxide (hydrous ferric oxide). Model simulations generated using Visual MINTEQ.

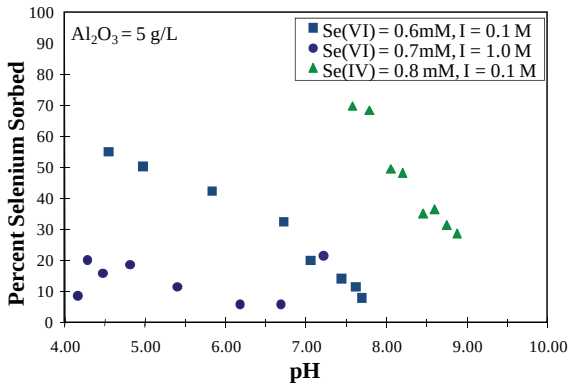


Figure 3-26. Adsorption of the oxyanions selenate Se(VI) and selenite Se(V) onto aluminum oxide. I denotes the ionic strength of the solution, M is molarity (mol/L), and mM is mmol/L.

Organic acids also adsorb to mineral surfaces. A number of researchers have studied the adsorption of organic acids and shown that they form inner sphere complexes that can affect both adsorption and dissolution rates of minerals (Ali and Dzombak 1996; Hwang et al. 2007; Hwang and Lenhart 2008a; Hwang and Lenhart 2008b; Hwang and Lenhart 2009; Hwang and Lenhart 2010). Research conducted in the mid- to late-1990s concluded that organic acids adsorption is similar to oxyanion adsorption and that carboxylic groups exhibit an adsorption maximum at low pH and phenolic groups have their adsorption maximum at higher pH (Gu et al. 1994; Gu et al. 1995; Evanko and Dzombak 1998). Figure 3-28 shows the proposed structure of two organic acids on the surface of hematite.

The adsorption of organic acids can also influence the surface charge and hence, the subsequent adsorption of metal cations (Johnson et al. 2005). The structure of the sorbed complex

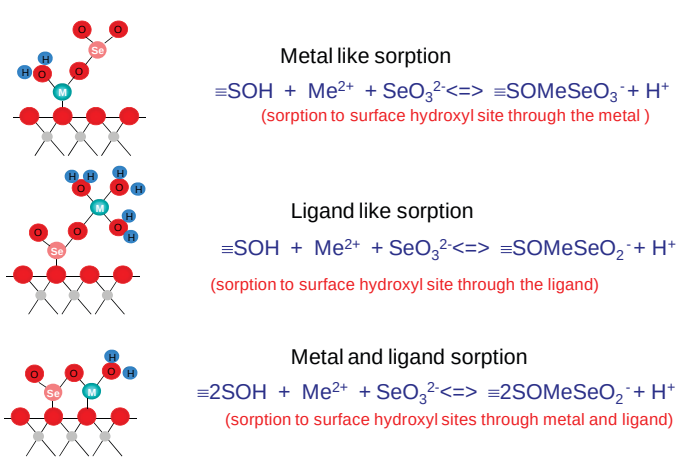


Figure 3-27. Representative ternary adsorption complexes for a representative oxyanion (SeO_3^{2-}) and a sorbing metal cation.

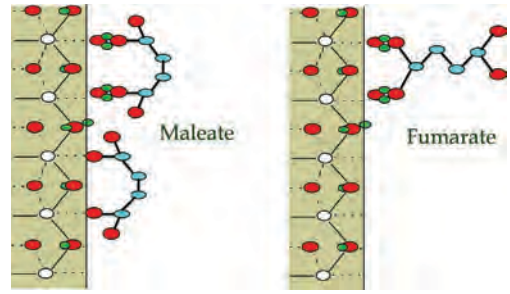


Figure 3-28. Proposed structures of adsorbed maleate and fumarate on iron oxide (adapted from Hwang and Lenhart 2008a).

depends on the affinity of the metal and oxyanion for the surfaces. For example, Buerge-Weirich et al. (2004) showed that the impact of organic acids on Cu, Ni, and Cd adsorption to goethite depended on pH, metal ion, and ligand. Competition for sorption sites led to a decrease in Cu and Ni adsorption at high pH values in the presence of the organic ligand, oxalate. However, below pH 6 surface complexation modeling of Cu adsorption was best described by defining a ternary complex of Type A (surface-metal-ligand). The adsorption of Cu in the presence of salicylate above pH 5 was also to a ternary complex of Type A. Increased adsorption of Cu and Cd in the presence of pyromellitate at acidic pHs was attributed to formation of Type B (surface-ligand-metal) ternary surface complexes. While these results were not verified by spectroscopic methods, they do provide evidence for the importance of both competing cations and complexing ligands for predicting metal ion adsorption to oxide surfaces. Of particular importance in this work is that the ligands selected for study are representative organic ligands used to simulate binding by humic acid moieties. Thus, this data also support the contention that humic and fulvic acids adsorb to oxide minerals.

The extension of this work to fulvic acids has been conducted by a number of researchers. Figure 3-29 shows the adsorption edges for removal of fulvic acid onto goethite. The adsorption behavior is typical of what is expected for oxyanion

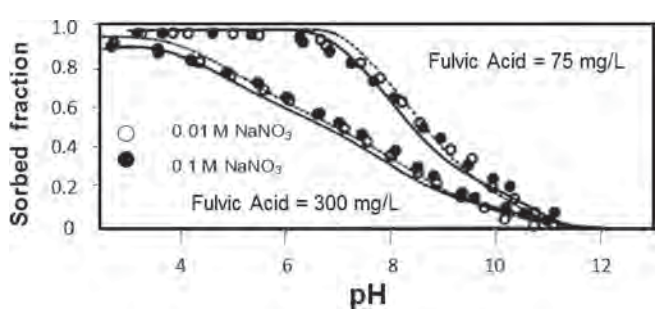


Figure 3-29. Adsorption of fulvic acid on goethite (adapted from Filius et al. 2000).

and organic acid adsorption; removal decreases with increasing pH and increased fulvic acid shifts the adsorption edge to lower pH (Filius et al. 2000). Bäckström et al. (2003) showed that 20 ppm of fulvic acid added to a goethite system followed adsorption trends consistent with anions in which the percent removed from solution decreased from over 90% to less than 10% as the pH increased from 7.5 to 10. Mercury and Cd(II) displayed typical cationic behavior in which adsorption increased with increasing pH. However, in studies of mercury adsorption, the presence of fulvic acid increased adsorption and had the largest impact at low pH. Fulvic acid also increased adsorption of cadmium, but only below pH 7. Above pH 7, the presence of fulvic acid decreased adsorption. Similar results for enhanced adsorption at low pH in the presence of fulvic acid were shown by Wu et al. (2003) for adsorption of Cu and Pb on gamma-aluminum oxide, and Weng et al. (2008) for Cu to goethite in the presence of fulvic acid.

These results suggest that pH, ionic strength, complexation with organic acids and fulvic acids, and competition by other adsorbing species must be considered in order to predict free metal ion concentrations in the presence of oxide minerals. Similar evidence for surface complexation to other particulate matter including the edges of clay minerals, bacteria, and algal matter has also been demonstrated in the literature.

3.5.3 Surface Complexation Models

Surface complexation models (SCMs) provide a thermodynamically based approach for describing adsorption in which solutes interact with functional groups on the surface either through ion pair association or solute-functional group complexation. In addition, these models also incorporate a description of the electrical double layer (EDL) surrounding the particle that describes the relationship between surface charge and potential, and this description is used to modify the activity coefficients for each surface species (Davis and Leckie 1979; Westall and Hohl 1980; Goldberg 1992). Thus, there are four basic tenants that all SCMs are founded upon: (1) the adsorption of ions occurs at specific sites on the mineral surface; (2) adsorption reactions can be explained thermodynamically through the use of mass-law expressions; (3) the electrostatic effects associated with adsorption are considered; and (4) adsorption of ions results in the surface being charged (Davis and Kent 1990; Dzombak and Morel 1990; Christl and Kretzschmar 1999).

A number of SCMs exist today including the Diffuse Double Layer Model (Dzombak and Morel 1990), the constant capacitance model (Schindler and Kramer 1968; Stumm et al. 1976; Stumm et al. 1980), the triple layer model, the modified triple layer model (Hayes and Leckie 1986; Hayes et al. 1988), and the CD-MUSIC model (Hiemstra et al. 1989a; Hiemstra et al. 1989b; Hiemstra and Van Riemsdijk 1996; Hiemstra et al. 1996). While these SCMs are all based on the four principles laid out above, each of them describes the structure of the mineral–water interface differently, resulting in mass-law expressions for surface reactions with electrostatic correction terms that are unique to a given model (Davis and Kent 1990). Parameters common to all SCMs include solids concentration (C_s) expressed in g/L, SSA normally in units of m^2/g, and surface site density (N_s) typically expressed in sites/nm^2.

The most simplistic description of the EDL incorporated into SCMs is the DLM (see Figure 3-30). In large part, model complexity is related to the complexity of the description of the EDL. Indeed, calculation of the surface potential for the DLM only requires knowledge of the surface charge and the ionic strength of the bulk solution. The constant capacitance model represents only slightly more complexity and is applicable to high and constant ionic strength systems. The model shown schematically in Figure 3-31 treats the double layer region as a parallel plate capacitor in which sorbing ions affect the intrinsic charge on the surface and the surface charged decays linearly with charge and distance. The relationship between surface charge and potential is described by a single parameter, the capacitance.

In order to more accurately capture the behavior of metal ion sorption over a broad range of ionic strengths, the triple layer model and modified triple layer model were developed. This model incorporates both aspects of the constant capacitance model and the DLM as seen in Figure 3-32. Sorbing anions and cations are located on the surface (or o-plane), on

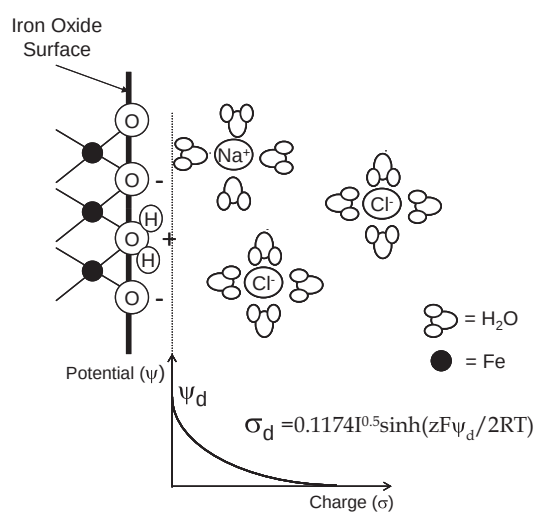


Figure 3-30. Representation of the diffuse layer for the DLM version of the surface complexation model in which Ψd represents the potential at the diffuse layer, σ_d is the diffuse layer charge, R is the ideal gas law constant, F is Faraday's constant, z is the ion charge, I is the ionic strength, and T is the temperature in K.

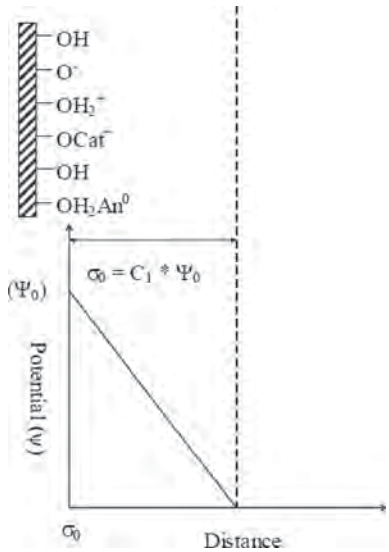


Figure 3-31. Description of the EDL for the constant capacitance model (Vieira 2006) where Ψo represents the potential at the surface, Ψd represents the potential at the diffuse layer, σ_0 is the diffuse layer charge, C_1 is the capacitance.

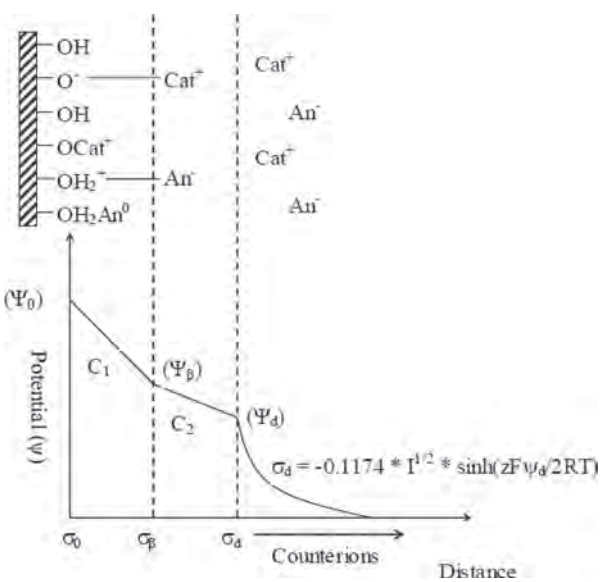


Figure 3-32. Representation of the EDL for the triple layer model where (Ψd represents the potential at the diffuse layer, σ_d is the diffuse layer charge, R is the ideal gas law constant, F is Faraday's constant, z is the ion charge, I is the ionic strength, and T is the temperature in K (Vieira 2006).

a plane located further from the surface (the β plane), or within the diffuse layer depending on the affinity of the sorbing ion for the surface. Two parallel plate capacitors and the DLM are placed in series to determine the potential on the surface as a function of charge. Thus, the model requires estimation of two different capacitances. Finally, the most rigorous model to be employed for surface complexation is the CD-MUSIC model. This model also utilizes the three plane approach but assumes that the surface is heterogeneous. Thus, a different representation of the three plane model is required for each different crystal face on the mineral.

The complete description of the surface complexation model also includes reactions for surface protonation and metal ion adsorption to the surface sites, and a value for the surface site density (i.e., the number of sites/m^2 of surface). While many trace metal cations bond directly to the surface oxygens in what is termed inner sphere adsorption, weaker binding background electrolytes are assumed to occupy the EDL. Their affinity for the surface is accounted for by the EDL equation shown in Figure 3-30, which incorporates ionic strength. More complicated SCMs utilize more sophisticated descriptions of the double layer with multiple adsorption planes at which strongly and weakly bound cations adsorb, and they include specific reactions for binding of background electrolyte ions such as Na^+ and Cl^-. However, as the models become more complicated, the number of fitting parameters increases.

SCMs must be capable of predicting adsorption as a function of solute and sorbent type, solute and sorbent concentration, pH, ionic strength, and the presence of aqueous ligands. Typical model results from the triple layer version of the surface complexation model show the effect of solute and sorbent concentration on cation sorption (Figure 3-33).

Studies of metal ion sorption to ferrihydrite indicate that sorption will occur in the following order, Pb(II)>Cu(II)>Zn(II)>Cd(II), with increasing pH as depicted in the figure. This behavior correlates with the first hydrolysis constant of a metal cation, the relative acidity of the solid surface, the surface site concentration, and the type of complex formed (Davis and Kent 1990). The hydrolysis constant is directly related to cation acidity; therefore a higher hydrolysis constant equates to higher acidity and sorption at lower pH values. Lead, which has its first hydrolysis constant of $10^{6.3}$, sorbs at a lower pH than Cd, with a hydrolysis constant of $10^{3.9}$.

An increase in the overall initial solute concentration, as shown in Figure 3-33b, results in a flattening of the adsorption edge. An increase in the sorbent concentration, or an increase in the available surface sites, results in the sorption edge shifting to lower pH values, as illustrated in Figure 3-33c. In contrast to the metal cation adsorption edges, oxyanion or ligand adsorption follows a trend in which maximum adsorption occurs at low pH as shown in Figure 3-26. Ionic strength has significant impact on weakly sorbing metal ions

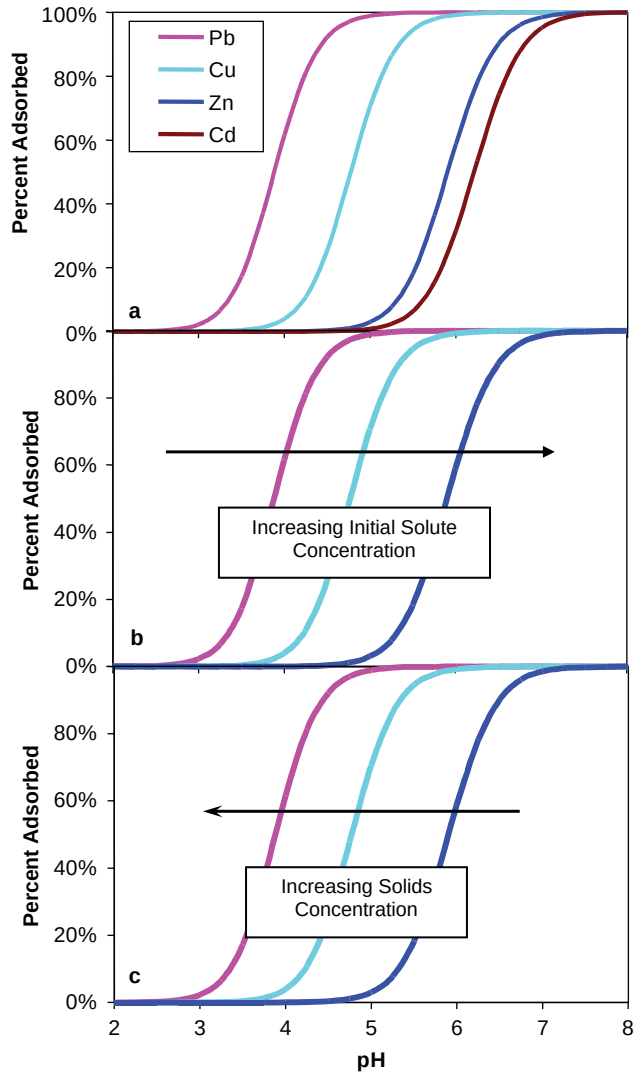


Figure 3-33. Surface complexation predictions of the location of cation sorption edges for (a) varying metal ions, (b) increasing solute concentration, and (c) increasing solid concentration.

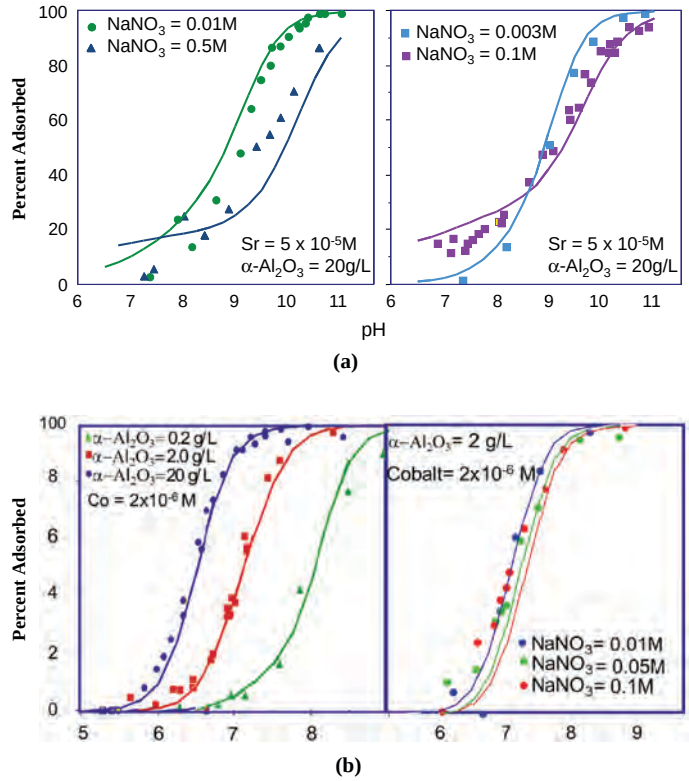


Figure 3-34. Triple layer model results for outer-sphere sorption of strontium (a) and inner sphere sorption of cobalt (b) on aluminum oxide as a function of ionic strength and solid concentration (for cobalt).

such as Sr, but little impact on strongly sorbing cations such as Co. Such dramatic changes in the adsorption behavior as a function of ionic strength have been used to distinguish inner and outer-sphere adsorption.

Model results for triple layer modeling of Co and Sr adsorption to aluminum oxide are shown in Figure 3-34. While Sr and Co are not typical metals found in natural waters, Sr is representative of other divalent alkaline earth metals such as Mg and Ca and Co is typical of many of the divalent heavy metals such as Cu, Pb, and Zn. Moreover, these results suggest that adsorption of the weakly sorbing metal ions such as Mg and Ca will be significantly impacted by the ionic strength of the water whereas adsorption of heavy metals will be independent of ionic strength.

The sorption of cations may also be strongly dependent on the presence of competing ions and ligands that can either compete for adsorption sites, or alter the speciation in solution through the formation of non-sorbing aqueous complexes. Stokes (2009) showed that competition between Cd and Zn and Cu and Pb on iron oxide could be modeled using the diffuse layer SCMs; however, the extent of competition was relatively low when both metal ions were added at similar concentrations.

Recent work has demonstrated that modeling competitive effects are highly dependent on the surface site density estimates. It was found that crystallographic estimates of the surface site density, along with an understanding of the reactivity of various sites, enhanced model predictions for all modeling approaches. While the most rigorous modeling approach, CD-MUSIC, seemed to best describe multi-solute adsorption behavior of Pb^{2+}, Cd^{2+}, and SeO_3^{2-} on goethite (Figure 3-35), all of the models benefit from enhanced approaches toward site density estimation.

All four of the SCMs described above have been widely used in laboratory studies to describe sorption in increasingly complex systems and all of the models are capable of describing single solute sorption in well-defined waters. How-

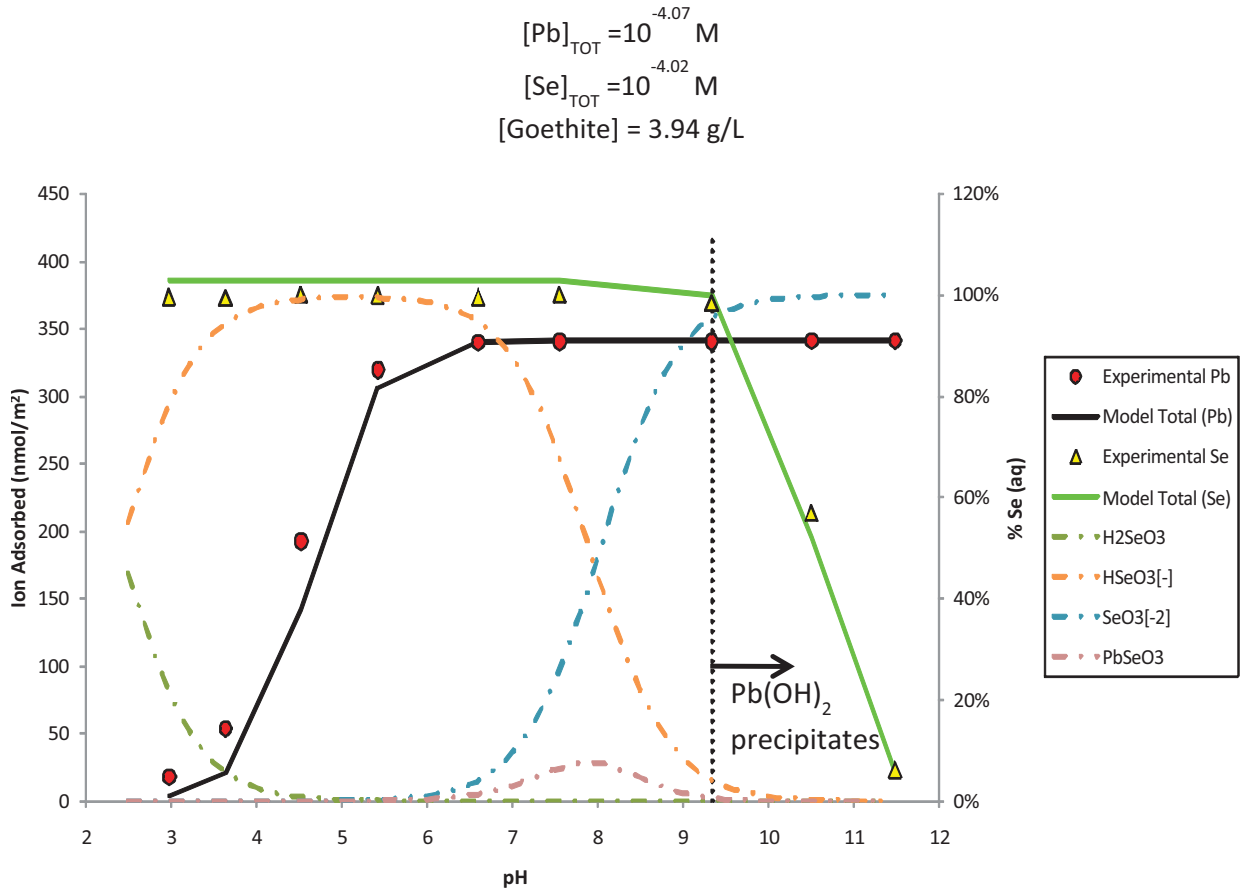


Figure 3-35. CD-MUSIC model predictions for Pb(II) and selenite bi-solute adsorption onto goethite (dashed lines represent aqueous species distribution).

ever, as the complexity of the system increases with the addition of multiple sorbents, multiple sorbing ions, and humic substances, the models appear less robust. Models such as the extended triple layer model (Sahai and Sverjensky 1997; Criscenti and Sverjensky 1999; Sverjensky 2006; Sverjensky and Fukushi 2006) and the CD-MUSIC model (Hiemstra 1996; Rietra et al. 2001; van and Hiemstra 2006; Weng et al. 2008) show the best potential for accurately predicting sorption in complex systems. However, these models require complete quantification of the solution and solid phase composition, even background electrolyte ions.

As a result, several researchers have taken a different approach to modeling metal ion sorption. Instead of increasing the complexity of the model to describe a more complex system, they have used a simplified version of the surface complexation modeling approach in which the EDL properties are ignored. The non-electrostatic model has been shown to provide reasonable predictions of sorption in a range of natural systems (Davis et al. 1998; Serrano et al. 2009). While the models do not accurately predict surface charge behavior, their ability to capture sorption over a range of conditions is often sufficient for field applications.

The DLM also represents a relatively simplistic model that can be applied readily to both simple and complex systems (Wen et al. 1998; Benyahya and Garnier 1999; Yang and Davis 1999; Lee and Davis 2000; Pretorius and Linder 2001; Swedlund and Webster 2001; Swedlund et al. 2003; Tonkin et al. 2003; Zhou et al. 2005; Bibby and Webster-Brown 2006; Hizal and Apak 2006; Allan et al. 2007; Carroll et al. 2008; Goldberg and Criscenti 2008; Lund et al. 2008; Song et al. 2008; Unuabonah et al. 2008; Hiemstra and Van 2009; Landry et al. 2009; Schaller et al. 2009; Stokes 2009; Swedlund et al. 2009; Reich et al. 2010). One of the distinct advantages of the DLM is that Dzombak and Morel (1990) compiled numerous data sets from previous research and developed a self-consistent data set for hydrous ferric oxide (amorphous iron oxide). This dataset has been used extensively in the literature and in commercially available computer codes such as MINEQL+ and MINTEQA2. Similar attempts to develop databases for other sorbents have emerged in the literature as well (Tonkin et al. 2003).

One of the most challenging aspects of modeling natural systems has been to distribute the sorption to different mineral phases. Landry et al. (2009) and Reich et al., (2010)

successfully applied the DLM to mineral assemblages containing amorphous iron oxide, quartz and kaolinite. Limitations in the modeling to the quartz component were attributed to failure of the DLM to capture the ionic strength effects.

SCMs have also been applied to describe sorption to bacteria, diatoms, and algae surfaces (Daughney and Fein 1998; Fein et al. 1999; Fowle and Fein 1999; Fein et al. 2001; Yee and Fein 2002; Yee and Fein 2003; Borrok and Fein 2004; Borrok et al. 2004; Borrok et al. 2005; Kaulbach et al. 2005; Gélabert et al. 2006; Alessi and Fein 2010; Deo et al. 2010). Much of this research assumes that the key functional groups on bacterial surfaces are carboxylic, phosphate, and hydroxyl/amine groups and that surface metal adsorption at acidic and circumneutral pH is dominated by interactions with the carboxylic groups and utilizes the non-electrostatic surface complexation model. More recently, this assumption has been questioned, and evidence suggests that both carboxylic groups and phosphate groups may be important (Ngwenya et al. 2009) as well as sulfhydril (Guine et al. 2006; Mishra et al. 2010). In the work of Ngwenya et al. (2009), the constant capacitance model was used to describe lanthanide adsorption to *Pantoea agglomerans* whereas the non-electrostatic surface complexation model was used in the work of Mishra et al. (2010).

3.5.4 Summary

Adsorption to metal ions is arguably the most important process affecting the fate and transport of metal ions. The high affinity of metal oxides for both inorganic and organic surfaces suggests that the major challenge for predicting adsorption is a lack of knowledge regarding the quantity of metal oxide phases in a system. Thus, one of the major challenges for describing adsorption in natural systems is identifying and characterizing the particulate matter within the system. As shown in this review, metal ions adsorb to functional groups on clays, oxide minerals, carbonate solids, bacterial surfaces, algae, fungi, and carbon. In addition, humic and fulvic acids also sorb to these surfaces and impart different surface properties to the particles. These processes must also be considered to understand metal ion sorption. Significant research has helped to elucidate the dominant functional groups and mechanisms of adsorption to surfaces present in natural waters. While the majority of this research has been conducted in well-controlled laboratory studies, research has also shown that the potential for scaling these studies to field scenarios is promising.

The development of SCMs has been a key tool that has significantly advanced both understanding of metal ion adsorption and provided reasonable predictions of sorption in complex systems. The refinement and application of these models has proceeded on two different fronts. Many researchers have focused on developing sophisticated models that accurately describe the structure or type of surface complexes, the location of the complexes relative to the surface, and the charge development at the surface from first principles. Others have focused on the application of more simplistic versions of SCMs that capture the trends in metal ion sorption behavior and the extent of sorption as a function of system conditions in complex laboratory systems and field systems. The results of these studies have provided the field with the key tools required for predicting metal ion sorption processes; however, in many cases the model parameters may require site-specific calibration.

3.6 Bioavailability and the Biotic Ligand Model

Consideration of aqueous speciation and bioavailability is required for predicting metal uptake by microorganisms and understanding metal ion toxicity in aqueous systems (Koster et al. 2004; Van Leeuwen et al. 2005). The fraction of total metal that can be taken up by an organism is termed the bioavailable fraction (Koster et al. 2005). According to Koster et al. (2005), there are three main components that determine the bioavailability of a particular chemical species to an organism. These components are the chemical reactivity of the species, the flux or concentration of these species to the microbial surface, and the internalization of the species by the organisms.

Figure 3-36 presents a conceptual model of metal-organism interactions (Campbell et al. 2002) that includes these three steps. Even though it is obvious that bioavailability is highly influenced by speciation, it is not clear which metal species are responsible for the final interaction with the organism. Current models for metal ion uptake by organisms assume that metal ion uptake is proportional to the free metal ion concentration. While this model is appropriate for many systems, exceptions do occur when metal complexes are transported by an

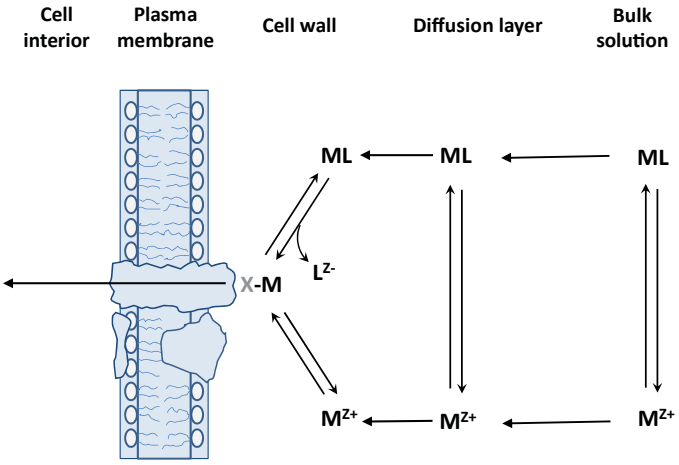


Figure 3-36. Conceptual model of metal–organism interactions (adapted from Campbell et al. 2002). M^{z+}, free metal ion; ML, metal complex in solution.

independent pathway that does not involve the pathway shown in Figure 3-36 in which dissociation of the complex to the free metal ion precedes uptake by a coordination site on the cell surface. This can include the transmembrane transport of lipophilic complexes [such as $Hg(CH_3)_2$] and nanoparticles. Metals such as $FeOH_3$ may be taken up by endocytosis, and metals with hydrated radii similar to common nutrients such as Pb, Cd, Mn, and Co can be taken up by active transport with ATP pumps and calcium channels (Markich and Jeffree 1994; Markich et al. 2001).

Over the past decade, the biotic ligand model (BLM) has emerged as the most accepted tool for linking metal ion speciation to bioavailability of metal ions (Di Toro et al. 2001). The modeling approach outlined in the BLM has been applied in the scientific community to study bioavailability and metal toxicity (e.g., Villavicencio et al. 2005; Schwartz and Vigneault 2007; Slaveykova 2007), in regulatory communities for establishing water quality criteria (Natale and Leis 2008), and for performing aquatic risk assessments for metals (Janssen et al. 2003). This model is currently used to develop freshwater criteria for copper (U.S. EPA).

The goal of the BLM is to successfully predict complexation of the metal ion with the biotic ligand, which is defined as "a specific receptor within an organism where metal complexation leads to acute toxicity" (Santore et al. 2001). The BLM incorporates an equilibrium chemical speciation model that includes competition of the free metal ion with major cations in the system (e.g., Ca^{2+}, Na^{+}, Mg^{2+}, H^{+}) and complexation by organic and inorganic ligands (e.g., humic substances, chloride, carbonates, and sulfide). The BLM quantitatively relates short-term binding to the biotic ligand to acute toxicity, with lethal accumulation (LA50) as a predictor for 96 h LC50 values for fish or 48 h LC50 values for daphnids (Niyogi and Wood 2004).

While the numerous applications of the BLM that appear in the literature are well beyond the scope of this report, a number of key review papers have emerged that summarize the major developments (Di Toro et al. 2001; Paquin et al. 2002; Santore et al. 2002; Batley et al. 2004; Niyogi and Wood 2004; Slaveykova and Wilkinson 2005; Worms et al. 2006). Most importantly for this work, the BLM can consider the effect of solution conditions, including pH, major cations such as Ca^{2+}, and competition with solution phase ligands on heavy metal toxicity. The basis of the model is that mortality occurs when the metal-biotic ligand complex reaches a critical concentration. The key assumptions inherent in the development of the BLM are that:

CHAPTER 4	Metal toxicity is associated with the free metal ion
CHAPTER 5	Complexation with inorganic ligands and NOM decreases metal ion toxicity by decreasing free metal ion concentrations
CHAPTER 6	Water quality parameters affect metal ion speciation and organism viability
CHAPTER 7	Mg and Ca ions that make up hardness reduce toxicity through competition for binding sites on the organism and by stabilizing paracellular junctions in fish gills
CHAPTER 8	Different metal ions bind with varying affinity to organisms

While the original development of the BLM was for fish tissue, recent research has revised and applied the model to other organisms such as daphnia (Di Toro et al. 2001; Niyogi and Wood 2004). As a result, the biotic ligand was assumed to be associated with the sodium or calcium channel proteins in fish gill surfaces that regulate the ionic composition of blood. Current applications to other organisms are modeled in the same way (see Figure 3-37) in that the biotic ligand is assumed to bind to metal cations, compete with other cations, and toxicity occurs when the metal-biotic ligand concentration reaches a critical value. Therefore, the amount of metal that binds is determined by competition for metal ions between the biotic ligand and the other aqueous ligands, particularly NOM, and the competition for the biotic ligand between the toxic metal ion and the other metal cations in solution, for example, calcium. Thus, the model incorporates metal complexation models such as the WHAM Model VI that was described previously. The BLM represents a significant improvement over models that only relate toxicity to the concentration of the free metal cation.

A number of recent criticisms of the BLM have emerged over the past several years. Bell et al., (2002) expressed concerns regarding the assumption of equilibrium between all metal

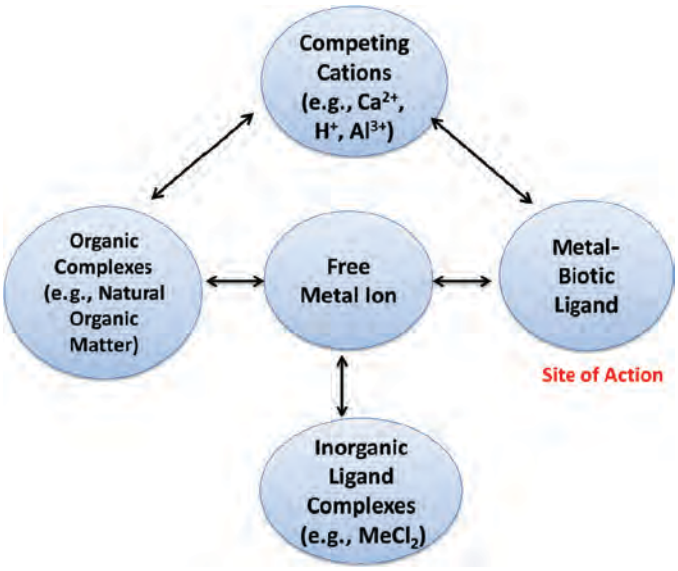


Figure 3-37. Representation of the BLM (Di Toro et al. 2001).

species in the bulk solution and the biotic ligand. Campbell et al. (2002) and de Schamphelaere et al. (2005) considered assumptions related to internalization which are assumed to be slow relative to the other steps involved in metal uptake, that internalization occurs via cation transport, and that internalization must occur for toxicity to appear. Others have focused on the assumption that competing metals can be modeled using an additive approach in which the sites for each metal are independent or the metal ions compete for the sites. However, recent data for Pb and Cu uptake by the green alga *Chlamydomonas reinhardtii* demonstrated that Cu plays a synergistic role for the uptake of Pb by aquatic organisms including bacteria (Chen et al. 2010). Thus, further improvements of the model will likely include the potential for different transport systems to dominate under different environmental scenarios including competition for sites, kinetics of internalization as well as other assumptions related to the bioavailability of different chemical species.

Recent developments in the BLM include the development of a terrestrial BLM that allows prediction of sediment metal toxicity (Di Toro et al. 2005). The model links measurable sediment and pore water parameters such as simultaneously extracted metals/acid-volatile sulfide (SEM/AVS), pore water-sediment partitioning, and the BLM to produce a median lethal concentration that is normalized to the sediment organic carbon concentration.

3.6.1 Summary

The bioavailability of metal ions is dependent on the speciation in solution, the affinity of metal species for surfaces on organisms, the modes of transport through biological membranes, and metal ion toxicity. The BLM represents the state-of-the-art with respect to predicting metal ion toxicity in natural waters. It incorporates chemical speciation models, sorption to the "biotic ligand" of an organism, and toxicity data to evaluate the impact of metal ions on aquatic life. The BLM has significant potential as a regulatory tool.

3.7 Conclusions

Chemical speciation in natural waters has significant implications for controlling the mobility, toxicity, and bioavailability of metals in water. Metal ion properties and solution chemistry dictate the speciation and determine the extent of sorption to inorganic, organic, and biological particulate matter. The key processes that must be considered for predicting metal ion speciation are acid/base chemistry, complexation with simple inorganic ligands, complexation with anthropogenic, autocthonous and NOM, oxidation/reduction reactions, precipitation and sorption. This literature review has presented a brief description of each of these processes and identified their impact on speciation of commonly identified metal ions. The review has identified state-of-the-art approaches used to predict metal ion speciation for each of these processes, and has highlighted interactions among these processes that affect metal ion speciation. The complexity of natural water chemistry was emphasized throughout the review, especially with respect to the heterogeneity of NOM, and approaches for incorporating NOM into predictive speciation models. Finally, the impact of metal ion speciation on bioavailability was addressed, and a description of the BLM was presented. The BLM represents an approach to incorporate all processes affecting metal ion speciation into a toxicity model for predicting the impact of metal ions on target organisms (the biotic ligand). The literature review demonstrates that the BLM has significant potential as a tool for incorporating metal ion speciation into bioavailability and toxicity assessment.

Average concentrations of trace elements in freshwaters, stormwater, and highway runoff range over orders of magnitude, and their mobilities in these systems vary depending on the metal ion, the chemical speciation, and the extent of partitioning. However, in most natural systems only the most mobile elements (e.g., Na, B, Se, As) will be transported in the dissolved phase. Thus, partitioning to particulate and colloidal matter is the key to understanding fate and transport in water. The composition of colloidal matter in natural water includes highly reactive humic and fulvic acids which impact metal ion speciation directly through complexation and indirectly through competition for adsorption sites. The research suggests that much of the reactivity of humic and fulvic acids is due to the presence of carboxylic (-COOH) and phenolic (C_6H_5OH) groups. Thus, models that describe metal ion speciation in waters must incorporate parameters that describe reactions with these functional groups as well as those that occur with inorganic ions and particulate phases.

Speciation of the dissolved metal ion fraction is a function of the pH, ionic strength, and presence of other ions, organic molecules, and solid phases. Complexation reactions prevent metal ions from being precipitated, complexing agents act as carriers for trace elements in water, and metal ion bioavailability is often reduced by complexation. Simple inorganic ligands such as carbonate can control speciation in natural waters only in the absence of significant concentrations of stronger organic ligands. Naturally occurring and anthropogenic chelating agents that have binding constants that are orders of magnitude higher than the simple inorganic and organic acid functional groups can also dictate speciation if present at sufficient concentration. Because metal-ligand complexes can have significantly different charge than the metal ion itself, the mobility of these species can be increased dramatically. For example, Cu-EDTA species are typically negatively charged and highly mobile. Chemical speciation models provide accurate tools

for predicting chemical speciation in water. The thermodynamic constants for complexation of metal ions with inorganic ligands, organic acids, and well-characterized anthropogenic ligands have been incorporated into databases that are tied to these programs. However, the approaches used to include the functional groups associated with humic and fulvic acids are variable, and the thermodynamic constants have significantly higher uncertainty.

While general trends in complexation with NOM have been observed, complexation with NOM is more difficult to define due to the complex and ill-defined nature of these organic complexes and the variability in the number and types of functional groups. Challenges associated with describing complexation with NOM still remain. Recent studies suggest that the reactive components of NOM can be characterized using a series of simple organic acids that range from weakly binding carboxylate and phenolate to stronger binding salicylate, citrate, and phthalate molecules. In general, complexation of these functional groups with metal cations increases with pH, decreases with metal ion concentration, and increases with fulvic and humic acid concentration. Several models have emerged over the past several decades, and the two most promising models that capture these general trends including the NICA-Donnan model and Model VI. These models have demonstrated ability to predict metal ion binding over a range of conditions and represent the current state-of-the-art.

Several metals including Cr, Se, Co, Pb, As, Ni, and Cu are redox active in natural systems and can exhibit different levels of toxicity, mobility, and bioavailability depending on the oxidation state of the metal ion. The particular oxidation state of a metal is typically controlled by dominant biogeochemical processes occurring within the system. Several metals such as Cr and As exhibit multiple oxidation states in natural waters and the relative rates of oxidation/reduction are often controlled by interactions with NOM and surfaces. In addition, metal fate and transport is affected by the dominant redox processes that affect speciation of major anions such as nitrate and sulfate. In reducing environments, nitrate reduction to ammonia increases metal ion complexation and sulfate reduction to sulfide can lead to precipitation of many of the trace metal ions. Incorporation of redox chemistry has also been included in most geochemical codes; however, in many cases these processes are rate limited, and thermodynamic approaches are not appropriate.

Precipitation processes also have a large impact on the speciation of metal ions in solution. In oxic waters, the major precipitates include hydroxide and carbonate phases. While published solubility constants are available for most of the potential solid phases, significant variability exists in the literature due to the experimental methods and conditions used to determine the values. Moreover, precipitation processes are often rate limited, and the most stable phase is typically not the dominant phase found in natural waters. The kinetics of precipitate formation are dependent on the presence of nucleation sites from other similar phases or from homogenous solid formation. The evidence is also mounting that removal of metal ions in natural and engineered systems is due to the more rapid formation of mixed precipitates or co-precipitates formed from either dissolution of prevailing solid phases (e.g., clays and oxide minerals) or precipitation of more insoluble phases such as iron and aluminum hydroxide. Removal of metal ions from solution may also be controlled by adsorption to these other precipitating phases as is commonly noted in water treatment applications. Finally, the importance of nanoparticle formation is emerging as a key process controlling the fate of a number of metal ions such as Zn and Hg. This area of research is only in its infancy, but has the potential to impact both the thermodynamics and kinetics of metal ion speciation.

Adsorption to metal ions is arguably the most important process affecting the fate and transport of metal ions. The high affinity of metal oxides for both inorganic and organic surfaces suggests that the major limitation to adsorption is the availability of surfaces. Thus, one of the major challenges for describing adsorption in natural systems is identifying and characterizing the particulate matter within the system. As shown in this review, metal ions adsorb to functional groups on clays, oxide minerals, carbonate solids, bacterial surfaces, algae, fungi, and carbon. Adsorption to oxide and carbonate minerals is highly pH dependent, with increasing adsorption at increasing pH for cation metal ion adsorption to oxide minerals. For strongly sorbing metal ions such as Pb, Zn, and Cu, ionic strength has only minimal impacts on the extent of adsorption. Competition among solutes can also have a major impact on adsorption, but in many cases the presence of oppositely charged metal ion species (e.g., divalent cations and oxyanions) can increase adsorption of both species through surface charge reduction or ternary species formation. In addition, humic and fulvic acids also sorb to these surfaces and impart different surface properties to the particles. These processes must also be considered to understand metal ion sorption.

Significant research has helped to elucidate the dominant functional groups and mechanisms of adsorption to surfaces present in natural waters. While the majority of this research has been conducted in well-controlled laboratory studies, research has also shown that the potential for scaling these studies to field scenarios is promising.

The development of SCMs has been a key tool that has significantly advanced both our understanding of metal ion adsorption and provided reasonable predictions of sorption in complex systems. The refinement and application of these models has proceeded on two different fronts. Many researchers have focused on developing sophisticated models that accurately describe the structure or type of surface complexes, the location of the complexes relative to the surface, and the charge

development at the surface from first principles. Others have focused on the application of more simplistic versions of SCMs that capture the trends in metal ion sorption behavior and the extent of sorption as a function of system conditions in complex laboratory systems and field systems. The results of these studies have provided the field with the key tools required for predicting metal ion sorption processes; however, in many cases the model parameters may require site-specific calibration.

The bioavailability of metal ions is dependent on the speciation in solution, the affinity of metal species for surfaces on organisms, the modes of transport through biological membranes, and metal ion toxicity. The BLM predicts complexation of the metal ion with a specific receptor site within an organism (the biotic ligand) where metal complexation leads to acute toxicity. The BLM represents the state-of-the-art with respect to predicting metal ion toxicity in natural waters. It incorporates chemical speciation models, sorption to the "biotic ligand" of an organism, and toxicity data to evaluate the impact of metal ions on aquatic life. The BLM has significant potential as a regulatory tool.

While the complexity of metal ion speciation hampers the a priori assessment of metal ion mobility, toxicity, and bioavailability, the availability of predictive models provides a set of tools that allow assessment of these if the key parameters of the system have been quantified. These parameters include the pH, ionic strength, organic carbon content and composition, the presence of competing and complexing solutes, and the composition and quantification of particulate and colloidal matter within the system. In many cases, the application of the most sophisticated predictive models is not suitable due to the lack of data describing the system. However, the literature suggests that even simplistic versions of these models that capture the general trends associated with key parameters such as pH and complexation may be adequate for many applications.

CHAPTER 4

Treatment of Metals in Highway Runoff

Highway runoff can contain dissolved and particle-bound metals at concentrations that require treatment, nominally with a unit process such as adsorption and unit operation such as sedimentation or filtration, respectively. The sources, magnitude, as well as the partitioning and distribution of these metals with particles have been reviewed. This review provides the basis for assessing the potential viability of a unit process such as adsorption for removing dissolved metals. It is noted that the term "adsorption" as used herein can represent a range of mass transfer phenomena including surface complexation, ion exchange, chemical precipitation, diffusion, and hydrolysis.

Treatment of highway runoff continues to pose unique challenges due to the unsteady nature of processes including rainfall runoff, mobilization, partitioning, and delivery of metals. There are no simple solutions for the removal of a metal or particle once released in stormwater, and there are BMPs that can be misapplied for the intended purpose, unfortunately at a significant cost. BMPs for metals and particles are essentially garbage cans and as such they must be emptied and cleaned occasionally. The purpose of effective design is to provide constituent capture given the complexities of runoff hydraulics and chemistry, reasonable time between media backwashing and replacement, and a preferred design life cost/benefit ratio among treatment alternatives. The strategies for removing dissolved metals in runoff have traditionally focused on infiltration and adsorption.

4.1 Infiltration

A variety of structural BMPs that are designed for infiltrating runoff into surrounding soils have been implemented. These include facilities where infiltration is the primary mechanism for stormwater treatment, such as infiltration trenches and basins. In addition, infiltration occurs as a secondary process in controls such as vegetated buffer strips and swales.

Infiltration is adaptable and potentially can remove dissolved and particle-bound constituents. There have been applications of infiltration concepts adopted in many parts of the world because of the potential benefits for stormwater chemistry and hydrologic control (Fujita 1993; Krejci et al. 1993; Jahangir-Issa 1998; Yu 1993; Sansalone 1999; Li et al. 1999; Teng and Sansalone 2004; Sansalone and Teng 2004).

For example, infiltration systems along the edge of a pavement have been used to attenuate stormwater runoff peak flow and to reduce the runoff volume to natural, predevelopment conditions. Swedish infiltration systems are utilized to promote shallow groundwater recharge and reduce surface drainage infrastructure in transportation systems (Hogland and Niemczynowicz 1986; Niemczynowicz and Hogland 1987).

Investigation of long-term hydraulic behavior of linear stormwater infiltration systems has demonstrated that infiltration is feasible even when the field saturated hydraulic conductivity of surrounding soils was as low as 10^{-6} m/s (0.14 in/hr) (Warnaars et al. 1999; Li et al. 1999). Li et al. (1999) used a numerical two-dimensional variably saturated flow model to evaluate transport and residence time distribution for a long linear trench. These studies indicate that infiltration systems offer the potential for infiltrating stormwater runoff from paved and urban areas.

Benefits of these infiltration BMPs are increased mean residence times relative to pre-BMP conditions, and promotion of discharges to surrounding soils, even for soils with low saturated hydraulic conductivity. Infiltration BMPs in soils of lower hydraulic conductivity (typically clayey materials of higher SA and surface charge) have a reduced risk for soil and groundwater contamination from increased loadings of pollution in urban and highway runoff, especially heavy metals (Li et al. 1999).

Water chemistry results for metals indicate that accumulation of metals occurs at the geotextile layer between the granular subgrade and surrounding soil. (Hogland and Niemczynowicz 1986). Long-term examination of such systems in clean granular soils is required to quantify any risk of elevated water chemistry constituents such as metals beyond the infiltration system (Hogland and Niemczynowicz 1986).

There are a variety of infiltration BMP systems that range from permeable pavement to sand filter inlets (Urbonas 1993). A common type of infiltration-exfiltration system is the combination of asphaltic permeable pavement and a granular-backfilled subgrade (clean, non-engineered gradation of sand and gravel) in a linear trench such as the Swedish Unit Superstructure. In comparison, a linear infiltration system implemented along an interstate catchment in Cincinnati, combined cementitious permeable pavement (CPP) and adsorptive-filtration media that had been tested in breakthrough studies.

The two major differences in these systems is the use of asphaltic as compared to CPP and the use of clean non-engineered granular backfill as compared to media engineered for adsorptive-filtration capacity as well as structural capacity. Both systems promote infiltration using permeable pavement and granular subgrade systems for hydrologic and water chemistry control.

Another common type of infiltration BMP that has been widely used is a vegetated or grassed swale infiltration system. Studies in Europe and the United States indicate that these vegetated swale infiltration systems can be effective at intercepting, conveying, and infiltrating stormwater runoff (Sieker 1998). For example the German "Mulden-Rigolen-System" (MR-System) provides in situ hydrologic and water chemistry control for stormwater. Swale infiltration trenches such as the MR-System are typically comprised of an upper layer of highly porous material such as gravel, with finer gradations of sand and soil in lower layers of the trench. The vegetated or grassed surface of the swale provides effective separation of the coarser sediment particles (>75 μm) trapping these particles at the surface of the swale. Infiltration treatment results from these systems indicate that water chemistry parameters such as metals can be attenuated by mechanisms of filtration and adsorption with resulting reductions in effluent concentration of greater than 90% by designs such as the MR-System (Sieker 1998).

Two long-term monitoring studies in the Washington, D.C., area on partial infiltration systems in suburban Maryland and Virginia (Schueler 1987) demonstrate the potential of such systems as in situ treatment for stormwater constituents. Both sites exhibited similar removal capability of TSS, with mass removal ranging from 85% to 95%. Approximately 65% of total phosphorus and 75–85% of the total nitrogen load were removed through partial infiltration, mainly volumetric reduction.

Passive infiltration systems, in particular those systems designed for dissolved metal treatment, cannot be considered sustainable if such systems are used to provide significant removal of particles and particles-bound constituents through mechanisms such as deep-bed filtration due to the potential for clogging and inability to backwash such in situ systems (Sansalone et al. 2009). Some form of particle separation is usually employed as pretreatment before stormwater is infiltrated. For example, an infiltration system under a highway shoulder or adjacent to the edge of pavement may be configured with an upper permeable pavement surface, which functions as both an infiltrating surface and provides surficial straining of particles transported from the traveled lanes. These surficially strained particles accumulate in a layer on the surface (commonly referred to as a "schmutzdecke") promoting further surficial straining.

Legret and Colandini (1999) investigated an asphalt permeable pavement with a lower reservoir structure for filtration of suspended particles and metals in runoff. The accumulation of particle-bound metals in the permeable asphalt and the absence of soil contaminant under the reservoir were demonstrated for a period of 8 years. Similar structures but with different sub-base stone were also constructed in the United Kingdom and initially reduced particles from 1000 mg/L to 50 mg/L although concerns over clogging and sustainability were recognized for such high particles loadings (Pratt et al. 1995).

Beyond costs and structural considerations, there are four primary design considerations (and failure modes) for passive infiltration systems: (1) hydrologic and hydraulic design, (2) filtration and filter ripening design, (3) dissolved constituent capacity and breakthrough design (in this case for metals), and (4) design for operation and maintenance (O & M) as well as constituent management.

4.2 Adsorption

Recent developments in stormwater treatment indicate that removal of dissolved metals through adsorption on engineered media is an effective strategy. Metal adsorption onto natural and engineered media, such as sand, soils, granular activated carbon (GAC), and oxide-coated media, has been studied (Stumm 1992). Specific media have been proposed for adsorption of metals transported in stormwater. While most of these media are inherently able to provide some level of particle-bound metals treatment depending on physical quantities such as surface loading rate, geometry of the media system, and the granulometry (size and gradation) of the media, there is a much greater variability with respect to adsorption of dissolved metals, and in many cases the adsorption by the media is only nominal.

Assuming that adequate hydrologic, hydraulic, filtration, and O&M design has been facilitated, the primary component of systems that adsorb dissolved metals is the media onto which the dissolved metal mass is transferred. The types of media that have been suggested for treatment of dissolved metals range from non-engineered media such as sand, gravel, limestone, perlite, or zeolite to organic/biogenic media that requires processing such as peat, litter pellets, or chitin/chitosan (from shells of crustaceans, insects and fungi); recycled or reclaimed infrastructure materials such as brick (clay), masonry, or concrete; or engineered media such as oxide-coated substrates.

In selecting a media the potential viability in an adsorptive-filtration system will be dependent upon the following factors:

1. Structural (required shear, compressive, and stability/degradation properties subject to cyclic wetting/drying and anaerobic/aerobic conditions),
2. Hydraulic (required hydraulic conductivity and internal/external pore distribution properties),
3. Filtration (particle separation, filter ripening properties),
4. Adsorptive (required equilibrium, kinetics, breakthrough and leaching properties),
5. Operation and maintenance properties for systems including the regeneration or replacement and ultimately the long-term management of material enriched with metals.

There are a plethora of media that are promoted in the marketplace for removal of metals in stormwater, media that may be well-intentioned from either a business point of view or from an intuitive point of view but simply cannot achieve dissolved metals removal efficiency (Liu et al. 2005a, 2005b). To meet current and expected water quality standards, in situ metals treatment technologies and materials require development and implementation based on knowledge of the loadings and chemistry of runoff combined with a quantitative knowledge of media behavior. These media-based technologies represent the combination of engineered media, an engineered system, and quantitative O&M practices that synthesize influent chemistry and loadings, effluent requirements, and the quantitative behavior of the engineered media and system.

Sand and fine gravel are the most common conventional media because of their initial economy, inertness, increased strength when subject to confining stresses, and availability. However, results from previous work (Sansalone 1999) demonstrated that plain sand or gravel media has insignificant SA ($< 0.1\ m^2/g$) and is ineffective for removal of dissolved metals.

Johnson et al. (2004) initially screened a suite of 12 media, after which the three best performing media for metals removal were further tested based on equilibrium and kinetics experiments. Results illustrated that a peat-sand mix had the highest metal capture capacity yet had the most detrimental impact on pH, the greatest headloss, and the highest potential for clogging. Organic compost had an intermediate metal capture capacity, colored the filter effluent, and had a lower impact on pH, headloss, and clogging. Zeolite had the lowest metal capture capacity, low impact on pH, lower headloss as a granular material, and less potential for clogging. Similar ineffectiveness was also shown for perlite with the additional weaknesses of friability and inadequate compressive strength. Any dissolved metal removal occurred by metal adsorption onto particles filtered by these plain substrates yet was subject to sloughing from the filter under changing hydrodynamic conditions (Liu et al. 2005b). Because of poor performance of sand, perlite, and gravel for metal adsorption and filtration, other substrates are needed for stormwater treatment (Sansalone 1999; Sansalone and Ma 2009).

After a decade of testing and evaluation of conventional media that demonstrated negligible to nominal adsorption capacity for dissolved metals in stormwater, research has concentrated on identifying more effective media. Within this same period, engineered media that combined oxides (Al, Fe, Mn, and Si) either singly or in combination have been applied to economical, stable, and competent substrates that provided sufficient SA and adhesion, including permeable clayey or cementitious substrates.

Oxide-coated metals have long been used for dissolved metal adsorption. In the presence of water, oxide surfaces such as Mn and Fe are covered with surface hydroxyl groups, protons, and coordinated water molecules. These mineral surfaces are amphoteric (net surface charge is a function of pH) with protons and hydroxyl ions co-existing at the surface in relative populations determined by solution pH. Consequently, the sorption of a metal ion to the hydrous oxide surface (manganese and iron) is strongly pH dependent.

This amphoteric behavior leads to the point of zero charge (PZC) definition. The PZC in its most simple definition is the pH at which the net surface charge is zero (net positive and negative charges sum to zero). Since many iron oxides have a PZC typically above 7 (in contrast, most manganese oxides have a PZC between 3 and 6), a stormwater solution pH greater than 7.0 can result in a predominance of negatively charged surface sites. Conversely, a solution pH less than 7.0 would result in an increasing amount of positively charged surface sites at least for Fe oxides.

Engineered amphoteric oxide-coated surfaces on filter media can have large SAs for adsorption in a chosen pH range. Amphoteric materials can be utilized for metal species adsorption because of their relatively high SA and their surface charge characteristics, which are generally negative at higher pH values. Having the opposite charge of the dissolved metal ions promotes adsorption. Therefore engineered media such as the oxide-coated filter substrates or cementitious media with high SA and amphoteric surface charge can be utilized to carry out the combined unit operations of filtration and processes of surface complexation for a range of treatment configurations for either decentralized treatment or centralized treatment. Such treatment can be designed as a passive and integral part of existing infrastructure, for example transportation infrastructure, or can be designed as a centralized stormwater treatment component.

To facilitate surface complexation of metals in stormwater by engineered amphoteric oxide-coated media, the pH of the stormwater must be considered in respect to the PZC of the media's surface coating. Utilizing pH, synthesizing mineral coatings of the appropriate PZC, or both will enhance removal capability and efficiency of the stormwater treatment device.

For example, an oxide-coated media surface with a net negative charge is preferred to remove the dissolved metals that exist as cations in stormwater.

Despite the high affinity of iron oxide for metal ions, iron oxide has not been widely used as a surface complexation media for stormwater because its physical properties are not conducive to this process. For example, it is bulky, hydrated, amorphous, flocculent material with extremely low hydraulic conductivity. However, iron oxide coated media was developed to overcome these physical limitations. Previous research with respect to performance of iron oxide-coated media for sorptive-filtration of stormwater has demonstrated proof-of-concept for oxide-coated media in systems such as partial exfiltration as applied as a full-scale passive treatment system in the highway environment (Sansalone 1999, Liu et al. 2005a, 2005b). Iron oxide can also remove dissolved metals to a lower level than that achieved by precipitation.

Granulated iron oxide media has also been used in a 1:1 combination with calcite (Steiner and Boller 2006) to treat roof runoff. The iron oxide provided the main copper and zinc adsorption capacity while the calcite controlled the pH and increased the mechanical and hydraulic stability of the system. This system has not been fully explored for applications in stormwater treatment, but the results from treatment of roof runoff suggest that this may be a good candidate for an adsorption system.

Negatively charged filtration media with a PZC sufficiently below the pH of stormwater could simplify the design for in situ stormwater treatment by eliminating any consideration of pH control. Compared to the iron oxide, manganese oxides have a very high negative surface charge in the range of typical stormwater pH values (usually pH 6–8). For example, at a pH of 7, a synthetic goethite (α–FeOOH) has a positive charge of approximately 0.2-μmol/m^2, while cryptomelane (α–MnO_2) has negative charge of 4.0-μmol/m^2, and birnessite (δ–MnO_2) has a negative charge of 18-μmol/m^2 (McKenzie 1981; 1989). Therefore, coating manganese oxide onto stormwater treatment media surfaces offers high potential for cationic metal removal.

Manganese oxide media, including manganese coated polymeric media (MOPM) and manganese oxide-coated cementitious media (MOCM) were evaluated by Liu and Sansalone (2004a, 2004b, 2005a, 2005b) in sorptive-filtration system as a rainfall-runoff or snowmelt unit operation and process media for treatment metal species. Birnessite-coated and cryptomelane-coated forms of manganese, as well as iron oxide coated media were tested by Liu et al. (2001a, 2001b), Sansalone (1999a, 1999b), Li et al. (1999). Sansalone and Buchberger (1995) utilized filtration and exfiltration systems for treatment of metals urban rainfall-runoff that included iron oxide coated media. Results indicate a significant capacity for metal species, with the surface chemistry favoring the adsorption of metal species as opposed to phosphorus.

Engineered media also include manganese oxide-coated polymeric media (MOPM) for adsorption of metals (Liu et al. 2001). Manganese oxides (MO) have a PZC below the typical pH range of 6 to 8 for runoff resulting in a negatively charged surface, allowing their use as adsorbents without pH control (Liu et al. 2001). MO has a high negative charge at higher pH levels and their cation adsorption capabilities increase with increasing pH. Metal adsorption at or below the PZC illustrates that a number of adsorption forces, in addition to electrostatic forces, are involved in the adsorption process (Murray 1974). Spectroscopic analyses of metal coordination by MO minerals utilizing extended X-ray absorption fine structure indicates that uptake of cationic metals at the pH lower than PZC is through the mechanism of ion exchange (Randall et al. 1998).

MOPM capacity has been shown to be significantly higher than polymeric media under the same set of loading conditions. MOCM provided the highest capacity of all media examined. Although manganese coated media offers potential for metal removal, little stormwater related research has been carried out (Liu et al. 2001a, 2001b). Compared to plain filter sand, cementitious media, or polymeric media the cost of oxide coating increases media costs by a factor of approximately five (approximately three for admixture MOCM). This cost increase is more than offset by greater breakthrough-exhaustion capacities, and breakthrough stability, in particular for MOCM. Results based on Cincinnati hydrologic and metals loadings (Sansalone and Buchberger 1997; Sansalone and Teng 2004) indicate breakthrough in an in situ system for filter sand or polymeric media are a fraction of a year, at least 5 years for an engineered Fe oxide-coated media configuration, and can exceed 10 years for MOCM.

Cementitious media such as graded concrete, masonry, rubble or brick, when coated, sprayed, or synthesized with oxides or oxide-admixture can also be an effective media for metal removal. Cementitious media has been generated from economical concrete rubble, recycled concrete, or crushed concrete with an oxide-admixture (Liu et al. 2005a, 2005b) and clay-based substrates effectively utilized for oxide-coated media (Sansalone and Ma 2009). The idea of using cementitious infrastructure material or recycled cementitious material is based on three advantages beyond the inherent economy of the substrate. First, after carbonation in the ambient environment, cementitious media creates a slightly alkaline aqueous environment since calcite ($CaCO_3$), portlandite [$Ca(OH)_2$], and calcium silicate hydrate ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) are major components of the concrete, and all contribute alkalinity to the aqueous solution. This alkaline environment will not only improve the metal removal efficiency by precipitation of dissolved metals, but also benefit from the electrostatic interaction between the oxide and dissolved cationic metal, because MO have larger negative surface charge in higher pH solutions. Another advantage is the rough surface of higher SA created by the coating.

While concrete media alone without an oxide coating or admixture is temporarily effective, the mass transfer is that of precipitation resulting in an unstable buildup of metals on the media surface with such physical precipitate buildup being sloughed off periodically into the effluent. This result is also observed for metal precipitates on concrete media (Liu et al. 2005a, 2005b). The use of dilute aqueous admixtures to the initial water-cement-sand mixture offer promise for cementitious materials from which such sorptive-filtration media can be produced. A mix of admixtures such as iron and manganese or coatings/admixtures combined with aluminum oxide can be effective for removal of cations (positively charged) and anions (negatively charged) such as phosphate.

Table 4-1 presents axial flow breakthrough experiments that were conducted to assess media capacity for metals utilized in snow or rainfall-runoff unit operation/processes. Results indicated that sand or polymeric media exhibited rapid breakthrough with little capacity and served as control to compare other media. While an improvement over control media, GAC's low capacity and low compressive strength limit applicability. Uncoated cementitious media had high capacity but breakthrough instability. Iron oxide coated sand (IOCS) had greater capacity compared to sand, and a combination of uncoated cementitious media and IOCS had improved capacity compared to IOCS.

Sansalone (1999) also illustrated media breakthrough behavior (equilibria and kinetics), comparing plain media substrates such as sand, perlite, or GAC to engineered media such as Fe oxide coated sand or in situ systems that combine Mn-oxide as either an admixture or coating to the portland cement concrete (PCC) or onto polymeric media. Specific media and combinations were based in an in situ partial exfiltration reactor (PER) design implemented along an interstate in Cincinnati (Teng and Sansalone 2004; Sansalone and Teng 2004; Sansalone and Teng 2005; Li et al. 1999). Based on annual hydrologic and water chemistry loads from the Cincinnati catchment as described earlier, results are summarized in Table 4-2. Natural organic or biogenic-based media were avoided in these tests due to deterioration of such media in a cyclically wet and dry environment, and the commensurate leaching of metals as well as nutrients from the biogenically-based media. Sansalone and Ma (2009) examined batch equilibrium for oxide-coated clay-based media in a parametric study that included media and water chemistry parameters. In this study they demonstrated that leaching from oxide-coated media was negligible.

In addition to oxide minerals, a number of recent studies have evaluated low cost adsorbents for metal ion removal from stormwater. While many of these have little potential for widespread application due to impacts on pH, headloss, and clogging, one particular material that has demonstrated potential for application to stormwater treatment is crabshell waste. Crabshells contain two important components, chitin and proteins (Lee et al. 2004). Chitin is a linear polymeric molecule containing the repeating unit 2-acetamido-2-deoxy-D-glucose-_Nacetylglucosamine. The combination of chitin and calcium carbonate has been proposed as an ideal media combination because the calcium carbonate promotes the formation of metal carbonate microprecipitates and chitin is a good adsorbent for these microprecipitates (Vijayaraghavan et al. 2010). In their recent study evaluating the potential of seven different sorbents including Amberlite XAD7, chitosan, crab shell, peat, *Sargassum* biomass, sawdust, and sugarcane bagasse to remove 11 different metals from simulated stormwater, Vijayaraghavan et al. (2010) found that crab shell media achieved capacities of 7.96, 7.94, 4.84, and 1.55 mg/g for Zn, Cu, Cd, and Pb, respectively. Based on these numbers, this media warrants further study.

Applications of oxide-coated media configurations for dissolved metal removal have applications in snow and rainfall-runoff control. In situ examples include partial exfiltration, infiltration systems, permeable pavement, filtration, and clarification systems. Ex-situ applications include deformable or tubular filters, upflow clarifiers, and many forms of in situ low impact development (LID) systems including permeable pavement. Media also provides filtration mechanisms; therefore, ex-situ systems require design, operation, and backwashing or replacement based on metal/particulate breakthrough and head loss considerations.

In situ systems have similar considerations, and many such systems are passive and not amenable to backwashing. As a result, some form of primary treatment, protection, or source control to reduce particulate loadings to passive systems is required. Examples include CPP or asphaltic permeable pavement functioning as surficial pretreatment for media in a PER and for upstream primary clarification/particle separation (Teng and Sansalone 2004).

While there have been many evaluations of BMPs containing media, for example, monitoring for total metal percent reduction; to date there has been little quantitative and mechanistic evaluations of adsorptive-filter media for dissolved stormwater metal (or other solutes) adsorption. Exceptions are the references identified herein. Media applications that do exist with reported information are still challenged due to the limited quantitative information of the mechanistic behavior of the media. Furthermore, many regulatory requirements require percent removal for total metal and thereby do not differentiate between dissolved metal adsorption and particles-bound metal filtration.

With respect to the economics of media, there is little examination of media lifetime and replacement costs; all too often the lowest initial cost media (which typically correlates to lowest capacity and lifetime) drives commercial applications. Some materials have abundant sources and relative low costs, such as those made from different types of waste; an examination of the

Table 4-1. Illustration of media breakthrough bed volumes, breakthrough, and exhaustion capacity for metal adsorption.

		Zn			Cu			Cd			Pb		
		X/M_b mg/g (mg/ml)	X/M_{exh} mg/g (mg/ml)	V_b (BV)	X/M_b mg/g (mg/ml)	X/M_{exh} mg/g (mg/ml)	V_b (BV)	X/M_b mg/g (mg/ml)	X/M_{exh} mg/g (mg/ml)	V_b (BV)	X/M_b mg/g (mg/ml)	X/M_{exh} mg/g (mg/ml)	V_b (BV)
Conventional mono-medium uncoated filter media													
Sand*		< 0.001 (< 0.001)	< 0.001 (<0.001)	< 10	< 0.001 (< 0.001)	0.0016 (0.003)	< 10	< 0.001 (< 0.001)	< 0.001 (< 0.001)	< 10	< 0.001 (< 0.001)	0.0015 (0.003)	< 10
GAC		0.40 (0.19)	1.63 (0.80)	45	3.51 (1.71)	4.10 (2.00)	300	0.02 (0.01)	1.11 (0.54)	15	1.63 (0.79)	3.33 (1.62)	120
Uncoated cementitious media		0.57 (0.66)	0.66 (0.77)	1300	0.60 (0.70)	0.67 (0.79)	1300	0.19 (0.23)	0.66 (0.77)	400	0.59 (0.69)	0.67 (0.78)	1300
Mono-medium iron oxide-coated sorptive media or dual-medium iron oxide coated media and cementitious media (BSPER)													
IOCS (iron oxide-coated sand)		0.013 (0.022)	0.019 (0.032)	< 10	0.006 (0.011)	0.122 (0.210)	< 10	0.013 (0.022)	0.017 (0.029)	< 10	0.19 (0.34)	0.36 (0.63)	80
BSPER (porous pavm over IOCS)		0.059 (0.10)	0.49 (0.86)	80	1.64 (2.83)	1.64 (2.83)	> 600	0.06 (0.10)	0.39 (0.67)	70	1.05 (1.81)	1.53 (2.64)	420
Manganese oxide-coated sorptive media													
MOCS (Mn-oxide-coated sand)		< 0.001 (< 0.001)	< 0.001 (<0.001)	< 10	0.028 (0.048)	0.15 (0.25)	100	< 0.001 (<0.001)	< 0.001 (<0.001)	< 10	0.084 (0.15)	0.11 (0.18)	100
MOPM (Mn-oxide polymeric media)		0.40 (0.46)	0.48 (0.55)	500	0.56 (0.64)	1.14 (1.30)	800	0.35 (0.40)	0.44 (0.50)	350	0.84 (0.96)	1.33 (1.51)	1000
MOCM	**Run #1**	2.18 (2.54)	> 4.57 (> 5.33)	2500	3.97 (4.64)	> 4.97 (5.80)	4000	2.33 (2.72)	> 4.64 (>5.41)	2500	3.69 (4.31)	> 4.83 (>5.63)	4000
	Run #2	1.04 (1.21)	1.50 (1.75)	900	1.08 (1.26)	1.78 (2.08)	1200	0.88 (1.02)	1.33 (1.55)	900	1.04 (1.21)	1.51 (1.76)	1200

X/M_b : Breakthrough capacity as $C/C_0 = 0.1$;
X/M_{exh}: Exhaustion capacity as $C/C_0 = 0.9$;
V_b: Number of bed volumes (BV) treated at an effluent breakthrough level of $C/C_0 = 0.1$;
The values in parentheses are the breakthrough or exhaustion capacities as the ratio of mass of metal per unit bed volumes.
> means breakthrough capacity are larger than the followed values (the experiment terminated before $C/C_0 = 0.9$).
Run #1: EBCT = 1.1 minutes, 1 mg/L each of Pb, Cu, Zn, and Cu, influent pH = 6.0;
Run #2: EBCT = 0.5 minutes, 1 mg/L each of Pb, Cu, Zn, and Cu, influent pH = 6.0;
* Uncoated polymeric media performance results very similar to sand performance, and had little metal adsorption capacity
MOCM: manganese oxide-coated cementitious media

Table 4-2. Comparative breakthrough times from a PER utilized as a replacement for conventional paved shoulder underdrain design and utilizing specific media tested to breakthrough. (Sansalone and Buchberger 1997; Sansalone et al. 1998; Glenn and Sansalone 2002).

Media	Time to breakthrough (years)	Media capacity at breakthrough [mg/g]
Plain silica sand or perlite	0.0015	0.0001 to 0.00015
CPP + Fe oxide coated sand	2.2	0.13
Granular activated carbon	2.8	0.19
Mn-oxide polymer media	6.9	0.46
Plain crushed concrete media	9.9	0.66
Mn-oxide concrete media	10^{+}	2.54

adsorptive performance for dissolved metal (or other solutes) removal is unknown and may present environmental/ecological challenges through the leaching or desorption of metals or in the case of biogenic pelletized materials, nutrients. Therefore media need to be tested and compared under both controlled surrogate loadings yet also subject to actual stormwater uncontrolled loadings to illustrate the performance difference.

4.3 Recommendation for Media Selections

The preferred matrix of choices, after a decade of work, includes crabshells and oxides of Fe, Mn, Al, and Si. The combination of chitin and calcium carbonate is a potential ideal media combination because the calcium carbonate promotes the formation of metal carbonate microprecipitates and chitin is a good adsorbent for these microprecipitates.

The metal oxides can be implemented as either coatings or admixtures, either singly or in combination onto or into rough, robust, inert, and porous substrates of concrete, clay, volcanic materials such as pumice, masonry rubble, and porous calcium-based materials. Each of these substrates have sufficient adhesive and SA to further support a higher SA of reactive oxide. It is also recognized that substrates such as fired clay or concrete retain their adsorptive and complexation properties to provide parallel mechanisms for dissolved metal treatment.

Biogenic or natural organically based substrates are not preferred as such media or media combinations (for example GAC, perlite, zeolite) have low capacity, leach constituents, desorb metals or do not have sufficient structural capacity. While it is well-known that organic and biogenic substrates can bind metals; such substrates are degradable in situ or in the conditions of a BMP. In addition, the presence of organics in the effluent from these systems can impact the speciation of metals and make them more mobile and less adsorptive. Non-engineered media such as sand, gravel, and perlite can be designed to physically separate metals in the particulate phase, but this process is reversible through leaching processes or specific deposit sloughing, requiring frequent O&M. The following are the media recommended for testing in this study.

- Iron and MO have demonstrated the highest potential for adsorbing the range of metals observed in highway runoff. Therefore, commercially available forms of these oxide metals will be evaluated as well as mixtures containing both types of media. The pH of the PZC is different for these two oxides. Therefore, both types of media will be tested over a range of pH values for a variety of metals that exhibit varying affinity for the oxides. Concentration ranges to be tested will be consistent with the concentrations observed in stormwater.
- Concrete materials and calcite offer the possibility of providing adsorptive capacity as well as pH buffering. Both of these materials will be assessed for their potential for adsorption of metal ions. While calcite represents a well characterized and less variable material, concrete provides the opportunity to recycle waste materials.
- Crab shell has also been shown to have potential for removal of metal ions from stormwater due to the presence of chitin and calcium carbonate. Thus, this sorbent will also be evaluated for its potential to synergistically promote adsorption of metal ions.

These five materials: iron oxide, manganese oxide, chitin, calcite, and concrete will be tested independently and in combination (as admixtures and dual media) to provide the maximum adsorption capacity for metal ions. Since maximum adsorption capacity will be pH dependent, the assessment will include evaluation of various combinations of the materials for pH control as well as adsorptivity. Selection of the particular source, size, and porosity of each of these materials will be based on optimizing SA while minimizing head loss. For all media, desorption potential will also be assessed as a function of pH (within expected pH ranges).

CHAPTER 5

Laboratory Testing and Modeling Methods

5.1 Introduction

This chapter describes the laboratory testing and modeling methods used to reduce the dissolved metals concentration in stormwater. The first objective of this work was to develop a standard protocol for evaluating effectiveness of various processes for treating highway runoff. As reported in Chapter 4, adsorption is the most promising technology for removal of metal ions from highway runoff, and the most appropriate adsorption media identified were oxide minerals, calcite-based minerals, and/or chitin based media (a waste material). Since the most promising application of these media may be a combination of media that includes oxide minerals for maximum adsorptive capacity combined with a calcite containing media such as limestone based PCC for pH control, various combinations of these media were tested.

A significant amount of research progress has been made with respect to collecting equilibrium adsorption data for metal ions on oxide minerals in well-defined solution matrices. These data provided a substantial head start for this project as they define a baseline of adsorption properties in well-defined systems. However, the major challenge that remained was to determine how well the results obtained from these well-defined systems are able to predict adsorption in the multi-component systems defined by highway runoff.

The difficulty associated with predicting adsorption in multi-component systems is to capture the impacts of background organic matter and other complexing ions on adsorption behavior. Very few studies have evaluated the ability of SCMs to predict adsorption in systems that contain NOM from highway runoff. Consequently, the series of experiments described included some with and without organic matter and at various pH and ionic strengths.

5.2 Development of the Laboratory Testing Protocol

5.2.1 Important Factors Affecting Laboratory Evaluation of Metal Adsorption

The protocol developed within this project is based on several observations that stem from the literature and experimental data collected within the scope of this project. These assumptions are described below.

- Metal cation adsorption is highly pH dependent as shown for Cu and Zn sorption onto iron oxyhydroxide in batch experiments (Figure 5-1) and for Cu adsorption in a column packed with iron oxide media (Figure 5-2). Thus, control of pH in protocols for evaluating media is essential. Moreover, optimal removal may occur in systems in which multi-media systems are utilized especially if one type of media is capable of raising the pH to promote adsorption or precipitation. In such systems, batch experiments are not easily correlated to data in flow-through systems. As such, protocols that employ column experiments for evaluating media options are preferred.
- Competition for sorption at the low concentrations encountered in highway runoff is often minimal as shown in Figure 5-3 and Figure 5-4 for data collected for sorption of Cu(II) and Pb(II) on iron oxyhydroxide in bi-solute batch experiments. Surface complexation modeling using the DLM also verifies the minimal impact of competition at low solute concentrations. These results suggest that cation-cation competition in stormwater, which has relatively low trace metal ion concentrations may be negligible; however, one should be aware that the more complex chemistry of actual runoff may affect this conclusion.
- Ionic strength effects on sorption of strongly sorbing metal ions is minimal and observed ionic strength effects can often be attributed to processes other than sorption. This

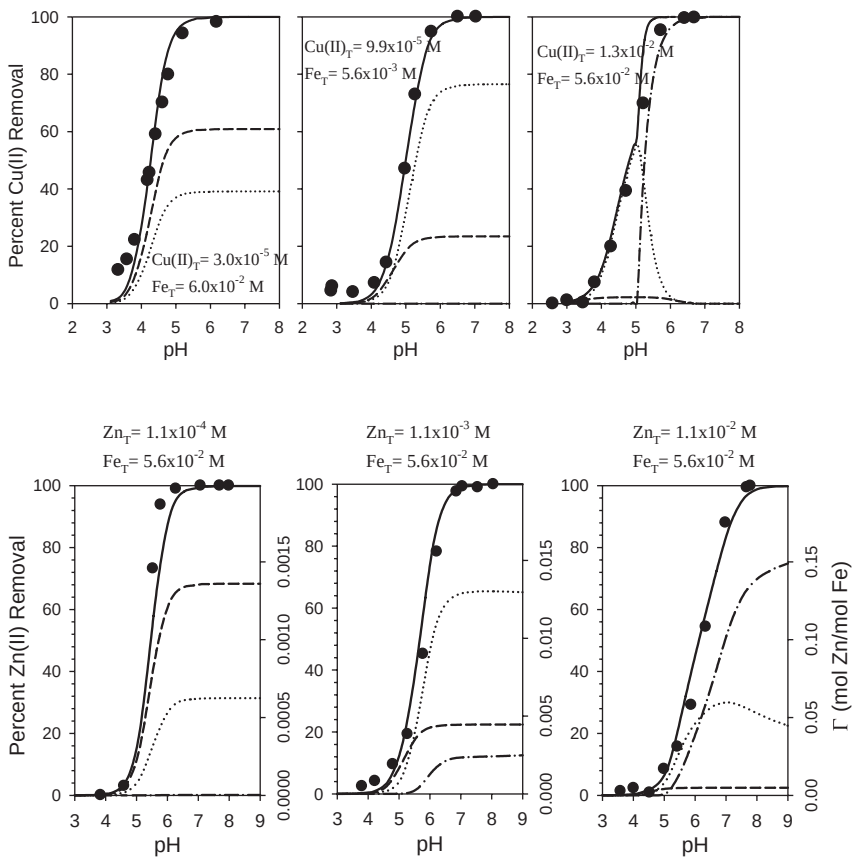


Figure 5-1. Adsorption data for single solute Cu(II) (top) and Zn(II) (bottom) onto hydrous ferric oxide using two site, mononuclear bidentate diffuse layer (DLM) surface complexation model. Dashed lines represent strong (dashed) and weak (dotted) site fractions of the total adsorption. Bulk precipitation is also included and represented by the dash-dotted lines.

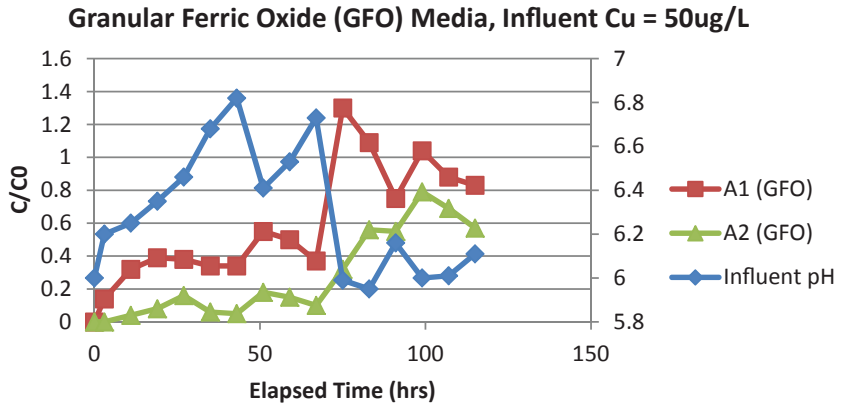


Figure 5-2. Fixed bed reactor data for Cu sorption onto granular iron hydroxide at pH = 6 in a synthetic stormwater solution. The column diameter was 1 cm ID, flowrate = 8 ml/min, and influent copper concentration of 50 μg/L. The influent ionic strength was 0.01M and the alkalinity was 2 meq/L. Two columns were connected in series with A1 being the first bed in the series. No attempt was made to control the influent pH during this experiment.

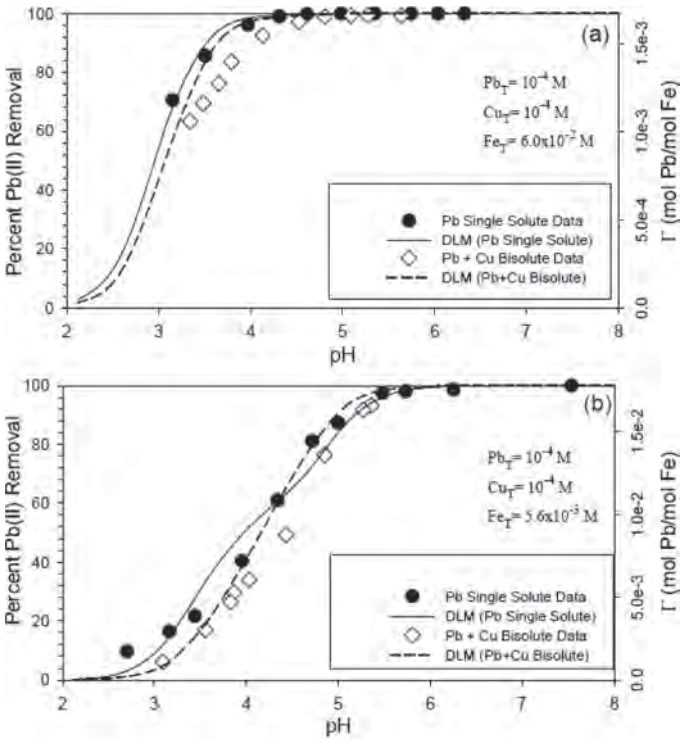


Figure 5-3. DLM and adsorption data for Pb(II) in bi-solute Pb(II)/Cu(II) system onto hydrous ferric oxide using two site, mononuclear bidentate single solute surface complex reactions for Cu(II) and monodentate and bidentate reactions for Pb(II). The Cu(II) constants are log K_{SCU} = 1.786 and log K_{wCU} = −0.035. The surface complexation constants for Pb(II) are log $K_s^{int}{}_{Pb}$ = 4.465 for the monodentate reaction and $K_s^{int}{}_{Pb}$ = 0.576 for the bidentate reaction.

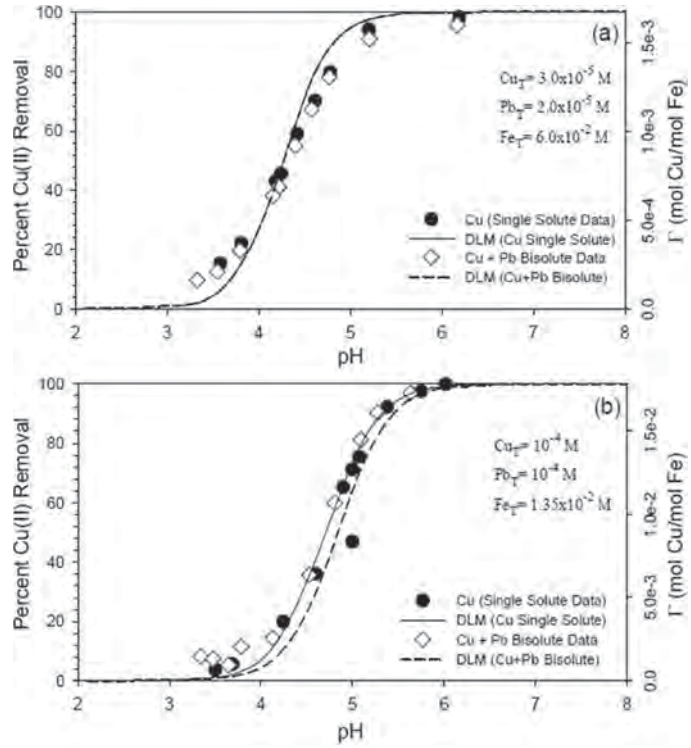


Figure 5-4. DLM and adsorption data for Cu(II) in bi-solute Pb(II)/Cu(II) onto hydrous ferric oxide using two site, mononuclear bidentate single solute surface complex reactions for Cu(II) and monodentate and bidentate reactions for Pb(II). Initial concentrations (e.g., Cu_T) are in units of mol/L (M). The Cu(II) constants are log K_{SCU} = 1.786 and log K_{wCU} = −0.035. The surface complexation constants for Pb(II) are log $K_s^{int}{}_{Pb}$ = 4.465 for the monodentate reaction and $K_s^{int}{}_{Pb}$ = 0.576 for the bidentate reaction.

is evident from data collected examining lead sorption onto silica. The data collected in batch experiments shown in Figure 5-5 indicates minimal impact of ionic strength for either the background electrolytes $NaNO_3$ or $NaClO_4$ that were used to control ionic strength, but at high ionic strengths reduction in sorption is evident for Pb sorption in a background electrolyte of NaCl. The reduction in sorption at higher ionic strengths was attributed to the presence of PbCl complexes.

- Table 5-1 indicates that as the concentration of chloride increases, PbClx complexes increase. Thus, protocols that address sorption of trace metal ions must consider the presence of complexes which typically do not sorb as strongly as free metal ions, especially since the amount of ionic copper and lead in runoff is a small fraction of the total.
- Complexation with organic ligands, including highway organic matter or NOM, can also affect metal ion adsorption, and the impact of the organic matter is a function of its composition, the ability of the metal ion to complex, the pH of the solution, and the potential for the organic matter to sorb to the media. Indeed, Grassi et al. (2000) showed that adsorption of a commercial humic acid onto aluminum oxide increased adsorption of copper at neutral pH; however, at higher pH, copper adsorption decreased due to formation of metal hydroxide, metal carbonate, and metal organic complexes. Nason et al. (2012) recently showed that increased dissolved copper concentrations were positively correlated with both DOC and alkalinity and negatively correlated with pH in first-flush highway stormwater. While the DOC correlation was quite strong, it is important to note that the relationship between log Cu concentration and log DOC was in µg/L for Cu and mg/L in DOC. Thus, an increase in DOC from 1 mg/L to 10 mg/L only produces an increase in dissolved copper from about 1 to 10 µg/L. A relatively weak correlation of the pH effect was attributed to a small variation in pH of the samples (less than 1 pH unit).

Copper is one of the most frequently studied metal ions with respect to organic complexation because it has a high affinity for binding to organic matter. However, metals such as zinc are not as strongly complexed to organic matter.

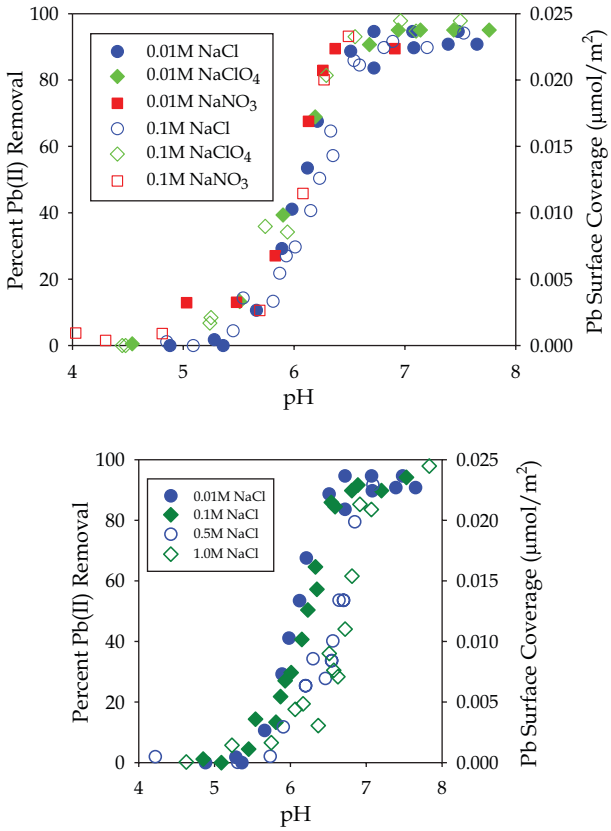


Figure 5-5. Pb(II) adsorption onto quartz as a function of background electrolyte and ionic strength at an initial Pb(II) concentration of 10^{-5}M added to each of a series of batch reactors containing 100 g/L quartz.

Binding constants for metal-ligand complexes are frequently an order of magnitude smaller for both inorganic species and one to three orders of magnitude smaller for organic species. Thus, the presence of organic matter may have little effect on sorption of zinc, unless the organic matter sorbs to the media and changes the affinity of zinc for the surface.

The variable impact of organic matter on sorption further suggests that protocols for evaluating media for metal ion removal of highway runoff should employ organic matter and background solution chemistry that closely mimics the composition of highway runoff. Moreover, given the widely different concentrations and affinities of the organic matter and the potential for the organic matter to coat media and block access to sorption sites over time warrants studies of sorption that are conducted in dynamic flow-through systems rather than batch experimental systems. In batch reactors, all constituents are added at the start of the experiment and changes in water and surface chemistry are minimized.

- Finally, precipitation of metal ions in highway runoff is also highly pH dependent and varies with metal ions [Ksp for $Cu(OH)_{2(s)} = 10^{-20.4}$ vs. Ksp for $Zn(OH)_{2(s)} = 10^{-16.8}$]. The types of precipitates that are expected in these systems include metal hydroxide solids, metal carbonate solids (although alkalinity values in many of these systems are low), and mixed metal precipitates such as metal-hydroxy-carbonates. The potential for dissolution of metal ions from the sorbent media also provides potential for formation of mixed metal precipitates. There is ample evidence in the literature, for example, that iron, aluminum, silica, and carbonates can form mixed precipitates with metal cations. Moreover, the formation of these mixed precipitates occurs well below the solubility limit for the pure phase precipitates [i.e., (Cu)x(Al)x(OH)x is less soluble that $Cu(OH)_{2)}$] as has been shown for cobalt mixed precipitates (Thompson et al., 1999). This mechanism has been suggested by Karthikeyan et al. (1999) for both iron and aluminum oxides. As dissolution of the media is affected by pH, ionic strength, and solution composition, it is necessary to evaluate the potential for both bulk precipitation and surface precipitation. However, in batch solutions, it is not possible to distinguish between sorption and precipitation. In contrast, precipitation can lead to breakthrough profiles that plateau at less than complete breakthrough (i.e., C/Co values less than 1) in column systems in which dissolution occurs dynamically.

The protocol developed for evaluating adsorptive media for metal ion sorption captures the important outcomes from these observations by primarily relying on performance of the media in column experiments and utilizing background solutions that are tailored to the expected composition of highway runoff. The test procedure was modified through the

Table 5-1. Percentage of total Pb(II) in various complexes as a function of NaCl concentration.

NaCl Concentration	Pb^{2+}	$Pb(OH)^{+}$	$PbCl^{+}$	$PbCl_2$	$PbCl_3^{-}$	$PbCl_4^{2-}$	total Pb-Cl
0.01	68.9	5.5	24.5	1.1	0.0	0.0	**25.6**
0.10	16.1	0.0	57.2	25.6	1.0	0.0	**83.8**
0.50	1.5	0.0	26.1	58.2	11.6	2.6	**98.5**
1.00	0.3	0.0	12.4	55.2	22.0	10.1	**99.7**

course of experimentation to ensure that the protocol could handle different media and solution compositions. Prefiltering and pH control were key modifications to the design to ensure that the tests could be conducted over suitable time frames and still capture the contaminant breakthrough profiles. Nonetheless, even with the in series short bed approach used in the column set up, it was not possible to capture the complete breakthrough profiles for all media/solution characteristics. Thus, a procedure for estimating capacity without complete breakthrough was developed to accommodate less than 100% contaminant breakthrough over the course of the experiments. The final protocol provides an efficient method for comparison of media under varying stormwater compositions which can be conducted within several days of experimentation.

The protocol includes isolation and concentration of the organic matter from actual highway runoff; developing a synthetic inorganic water that mimics the inorganic composition, ionic strength, and pH of highway runoff; and conducting experiments with various potential adsorbents using the background water in the presence and absence of organic matter and at varying pH and ionic strengths. The protocol was tested on two commercially available iron oxides and a manganese oxide. In addition, experimental columns were operated in series in which either crushed waste concrete or crab shell waste was evaluated for its ability to increase the pH prior to contact with the oxide media. Finally, a simplistic modeling approach, which can be applied to site-specific conditions, was used to model the effluent behavior from the columns. The model, CXTFIT/EXCEL (Tang et al. 2010), runs in Microsoft EXCEL and includes options to account for equilibrium and non-equilibrium transport in columns. Visual MINTEQ was used to assist in the evaluation of the effects of complexation with carbonate.

5.3 Development of a Synthetic Runoff Cocktail

The following sections describe how the synthetic runoff cocktail was developed. Descriptions are provided on the collection and processing of organic matter in highway runoff and the composition of the inorganic components in the synthetic cocktail.

5.3.1 Collection and Preparation of Highway Runoff Organic Matter

One of the goals of this project was to identify a means of conducting experiments with organic matter from actual highway runoff events while overcoming concerns of variability in water quality from different stormwater events and changes in stormwater composition during the course of the experimental system. To overcome these challenges, this research utilized an organic matter isolation approach developed by Pressman et al. (2010) in which runoff is pretreated to remove suspended solids and cations, and organic matter is then concentrated in a reverse osmosis system. This section describes this approach to concentrate organic matter.

Concentration processes employing reverse osmosis require significant pretreatment to prevent fouling of the reverse osmosis membrane. As a result, prior to concentration, pretreatment must remove suspended solids and excess ions from the water. In some cases, if the material is to be freeze-dried and the concentrate contains sulfate, sulfate precipitation may be required as well (Serkiz and Perdue 1990; Maurice et al. 2002; Pressman et al. 2010).

The pretreatment process consists of filtration followed by ion exchange. A schematic of the process is shown in Figure 5-6. This can be accomplished using in-line water filters.

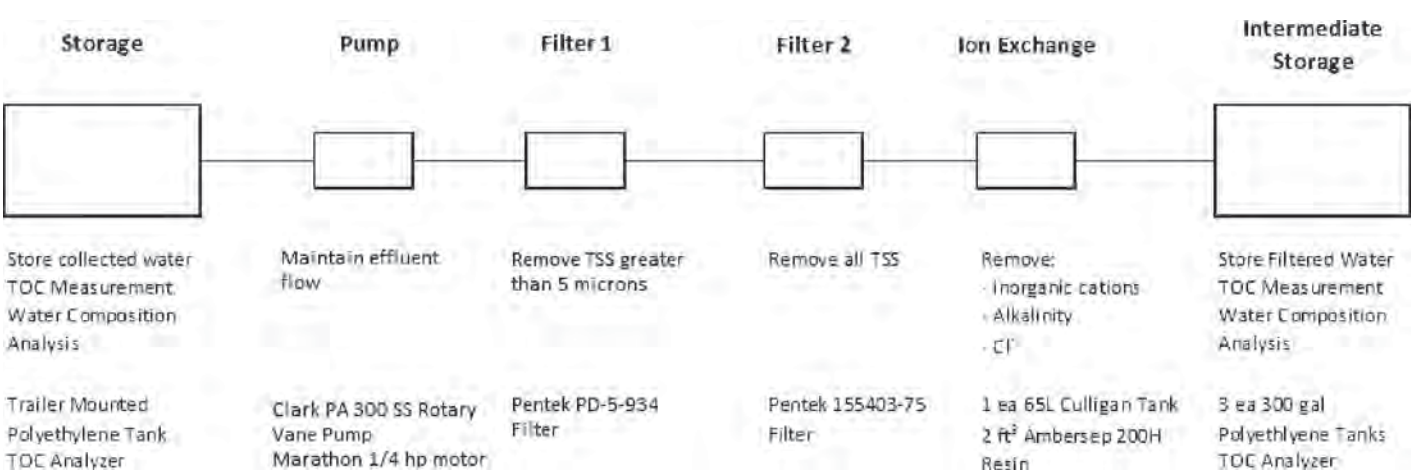


Figure 5-6. Schematic diagram of the organic matter pretreatment process using filtration and ion exchange. Specific brands of equipment are provided as examples.

Most in-line filters have a maximum operating pressure of about 100 psi and a maximum differential pressure of about 35 psi. Due to the variation in particle size in stormwater, a step-wise filtration process is justified. Previous research has shown that triple filtration accomplished using a series of three progressively smaller in-line filters is sufficient to remove suspended solids, maintain flow, and reduce system pressure (Serkiz and Perdue 1990; Maurice et al., 2002). The resulting water after passing through the 0.45 micron filter should be free of all suspended solids (TSS) and consist only of TDS. It is important to note that the TDS includes both organic and inorganic compounds. Inorganic compounds adsorbed onto suspended solids may have been lost in this process, but the loss of organic anions is likely minimal.

Following the removal of TSS from the water sample via filtration, the water sample is passed through an ion exchange resin to remove inorganic cations and isolate the organic anions. Since the objective is to isolate the organic anions in the water sample a hydrogen ion (H+) form macroporous resin is used to remove inorganic cations. During this phase, two reactions occur. Inorganic cations sorbed onto anionic compounds in the water desorb and then adsorb onto the H+ form resin, removing the cations from the water and releasing free hydrogen atoms. The free hydrogen ions then lower the pH of the effluent to a value of approximately 2 and react with the organic anions to form organic acids (Serkiz and Perdue 1990; Maurice et al. 2002; Speth et al. 2008; Pressman et al. 2010).

Selecting the appropriate ion exchange resin is critical to the successful removal of inorganic cations and, therefore, to the successful concentration of DOM through reverse osmosis. Failure to remove the cations completely will have two impacts on the outcome of the concentration process. First, inorganic compounds that remain in the water will concentrate alongside the organic matrix and could impact the results of the sorption studies. Secondly, higher influent TDS concentrations will result in higher osmotic pressure during reverse osmosis. It is because of this factor that a hydrogen ion form resin is used. Many types of resin are available on the market. For this application, it is generally agreed that macroporous resins are more effective and pose less of a threat to the integrity of the organic matrix than gel type resins (Serkiz and Perdue 1990; Speth et al. 2008; Pressman et al. 2010).

Once the resin is specified, it is critical to determine how much resin is required. The mass required is a function of the water sample volume, total inorganic cation concentration, and the exchange capacity of the resin. Typical exchange capacity values range from 1.8 to 2.25 eq/L. Constituent concentrations in stormwater and highway runoff differ significantly from those reported in typical natural waters and vary with each storm based upon location, environmental factors, human traffic factors, and storm frequency (Beck 1974; Weber 1974; Serkiz and Perdue 1990; Barrett 2008; Pressman et al. 2010; Sansalone 2011). Thus, analysis of the water composition prior to concentration is recommended to ensure that the ion exchange system is appropriately sized. One of the key design parameters for successful ion exchange is empty bed contact time (EBCT), which is calculated by dividing the resin container volume by the flow rate. EBCTs between 5 and 30 minutes are typical for ion exchange processes. A photograph of the complete filtration and ion exchange system is shown in Figure 5-7.

Concentration of the DOM is accomplished using reverse osmosis operated in a recycle mode as shown schematically and visually in Figure 5-8 and Figure 5-9, respectively. This membrane process is typically used to remove ions from water and provide ion free water for consumption or use. The concentrate stream containing the ions is then disposed. However, in this case, the goal is to utilize the concentrate flow. As the feed water passes through the reverse osmosis membrane, the organic constituents are retained in the concentrate flow and constituent free water flows in the permeate stream. Thus, the permeate stream is wasted in the system and the concentrate flow is recycled back to the feed and the system run in recycle mode until the desired concentration factor is achieved. During this process, the concentration of organic matter in the recycled feed water steadily increases as the constituent mass is retained and the "clean" water is wasted as permeate.

In the practical sense, several design and operation parameters can be manipulated to maximize permeate flow and constituent rejection to achieve optimal results depending on the operation. The primary parameters that are easily modified to meet the system requirements are the number, size, type, and alignment of membranes and the influent, permeate, and concentrate flow rates.

The type and size of the reverse osmosis membrane control the rejection properties and membrane SA of the system.

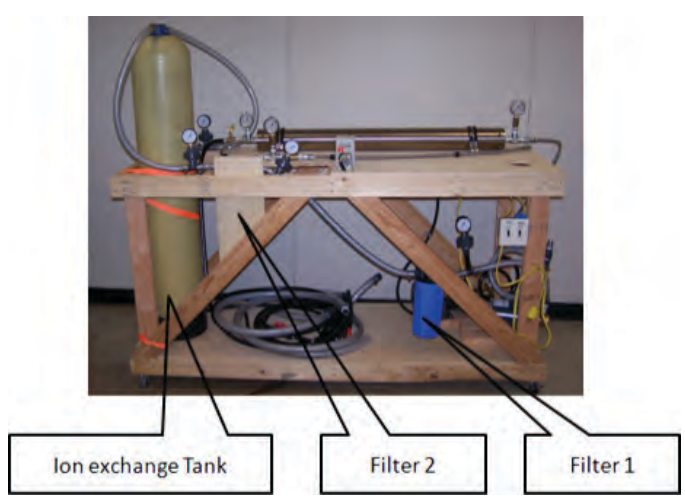


Figure 5-7. Photograph of a pretreatment process consisting of filtration and ion exchange.

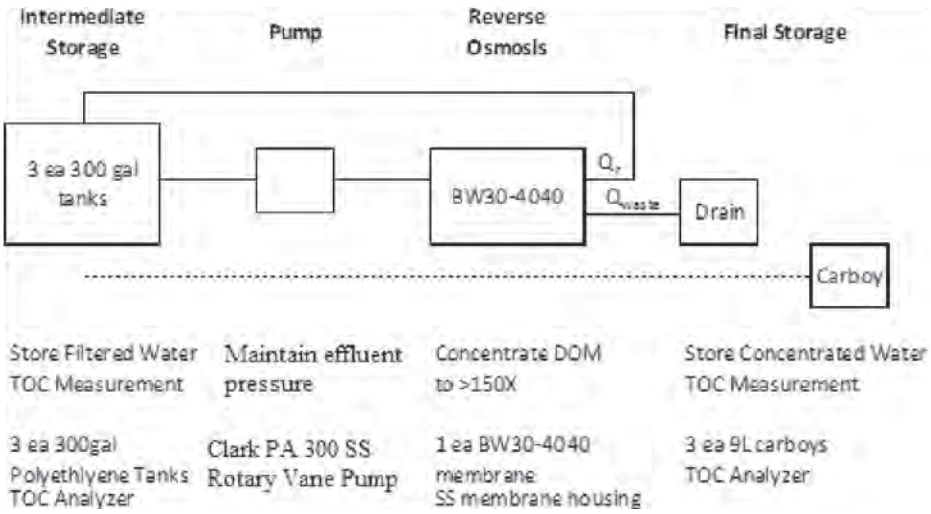


Figure 5-8. Schematic view of the concentration process using one Filmtech BW30-4040 membranes.

For this application, a brackish water membrane provides the tightness and pressure rating required to concentrate the DOM. Having a greater membrane SA enables higher flow rates at lower osmotic pressures (Pressman et al. 2010). However, at low influent flow rates, larger membranes experience less salt recovery, or more loss of constituents to the permeate flow than the same membrane with less SA.

Filmtech brackish water membranes are designed to achieve approximately 99.5% NaCl rejection, which has a molar weight of 58.44 g/mol, at 15% recovery. Typical organic compounds range in size from 16 g/mol for the simple n-alkane group to 390 g/mol for the highly complex phthalate group chemical. Thus, large, complex organic compounds should not permeate through the resin regardless of the operating parameters. This conjecture is supported by Speth et al. (2008) and Namjesnik-Dejanovic (2004). It should be noted that several simple organic compounds found in the branched and n-alkane, aldehyde, alicylic hydrocarbon, and aliphatic amine groups are smaller than sodium chloride and may permeate the membrane at a rate proportional to the operating conditions as observed above. All of these groups have been found to be present in stormwater runoff but, as discussed previously, compositions vary widely over both the spatial and time domains.

The reverse osmosis system is capable of achieving concentration factors for the organic matter of approximately 150X. This material may be used in this form, further purified through electro-dialysis, or freeze-dried and stored for future use. If the material is to be freeze-dried, then sulfate must be

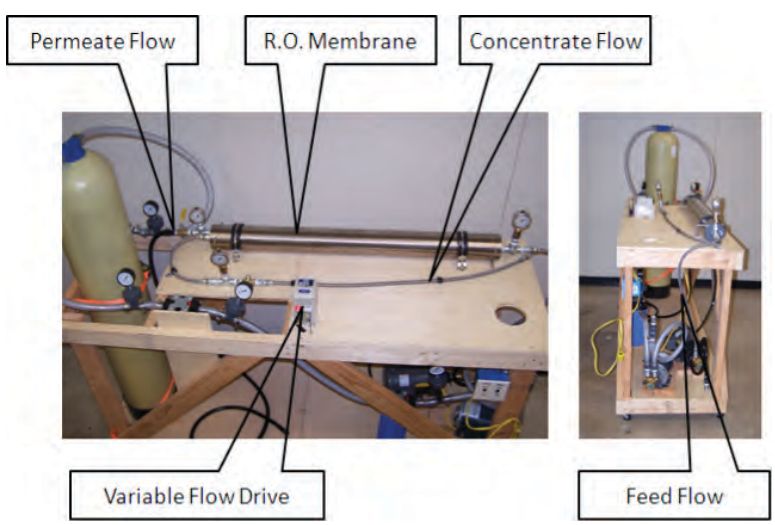


Figure 5-9. Photograph of a reverse osmosis process.

removed from the system. Because sulfate is an anion, it is not removed during the cation ion exchange process and is concentrated through reverse osmosis proportionally to the DOM (Serkiz and Perdue 1990; Pressman et al. 2010). The preferred method for removing sulfate from the concentrated sample is precipitation using barium chloride. The reaction that takes place is as follows:

$$SO_4^{2-}{}_{(aq)} + BaCl_2 \rightleftharpoons BaSO_{4(s)} + 2Cl^-$$

Precipitation works better at higher concentrations. It is for this reason that the sulfate is not removed until after it has been concentrated.

The goal of the concentration process is to minimize losses of organic matter throughout the pretreatment, concentration, sulfate precipitation, and freeze drying process. Previous research has shown that this is achievable with recoveries of organic matter of over 85% (Pressman 2012). In tests with highway runoff collected in Austin, TX the initial TOC concentration of the raw water was 8.86 mg/L and the average concentration of our reconstituted organic matter was 8.60 mg/L. This is similar to the median value of 12.6 mg/L in the FHWA database. Thus, it appears that the process was successful in recovering the organic matter. However, reconstitution of the organic matter presented several challenges including relatively high concentrations of Ba in the reconstituted water (approximately 30 mg/L), and it was difficult to re-dissolve the organic matter to create a concentrated solution for use in the column experiments. While the high barium concentration did not appear to interfere with the experiments, it was a significantly higher concentration than was observed in the raw water (9 µg/L). The challenge of re-dissolving the organic matter was resolved by implementing a sonicating step into the reconstitution procedure.

The process for reconstituting the organic matter is a topic discussed in depth by McCurry et al. (2011), where they recommend continuously mixing a concentrated solution containing the dried (NOM) for 72 hours at a pH of 10 (achieved by adding NaOH). However, original efforts to implement this procedure did not dissolve all of the organic matter. Addition of a 1 hour sonication step after adding the solid material to water was more successful. Moreover, in the trials the pH of reconstitution had no effect on the TOC as demonstrated when equal portions of freeze-dried organic matter were added to a series of five separate beakers. After 1 hour of sonication, 200 ml samples were drawn from the beakers and passed through 0.45 µm filters into precleaned/treated TOC vials at dilutions of 1:10 (30 mL total).

Figure 5-10 shows the results of two separate TOC measurements from the same experiment, and these results suggest that the pH of the solution into which NOM was dissolved had little to no effect on the reconstitution of the organic material.

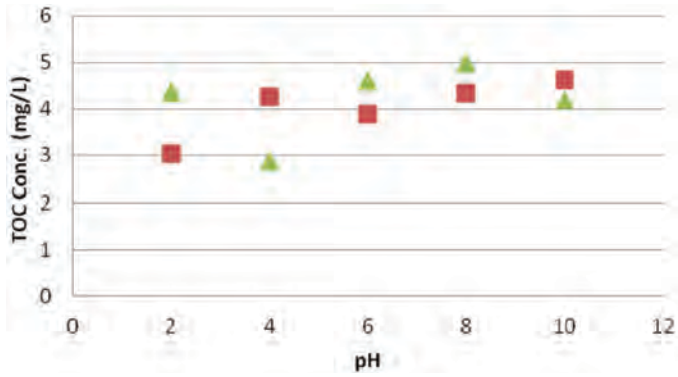


Figure 5-10. Effect of pH on TOC concentrations achieved by dissolving freeze-dried highway runoff organic matter into 200 ml vials.

Since determining that pH of the dissolution water does not influence the reconstitution of the organic matter, the pH adjustment step was removed from the procedure; however, to aid in solids separation post sonication, the reconstituted super-concentrated solution was centrifuged at 10,000 RPM for 15 minutes. The centrifugation helped to separate out any of the inorganics and insoluble components of the freeze-dried NOM material.

5.3.2 Composition of the Inorganic Constituents in the Synthetic Runoff

The organic matter represents only one component of the highway runoff composition. The inorganic composition of the water to be used in experimental evaluation must also be selected to match conditions anticipated in the field. Ideally, the composition is based on measured concentrations of the regional highway runoff collected over a range of conditions and sampling events. Alternatively, literature values can be used. For this set of experiments the concentrations provided in Table 5-2 were used to create the synthetic runoff. Values for chloride and hydrogen ion were varied to match the ionic strength.

The four main cations identified were magnesium (Mg), calcium (Ca), potassium (K), and sodium (Na). None of these ions is expected to substantially interfere with heavy metal adsorption onto most media except with respect to their impact on ionic strength and precipitation. In addition to matching the ion concentrations, the overall ionic strength was considered as well. This was done by calculating the ionic strength of the water from the composition in Table 5-3 and matching it to the ionic strength obtained through addition of a series of chemicals that match both the ionic content and ionic strength. Geochemical codes such as Visual MINTEQ can be useful in evaluating the composition. The stormwater recipe created to match the composition and ionic strength of literature values is detailed in

Table 5-2. Literature values for ions/anion concentrations.

Constituents	g/mol	mg/L {Req'd}	mol/L
Na	23	50	0.002174
K	39	50	0.001282
Ca	40	50	0.00125
Mg	24	10	0.000417
NO3	62	110	0.001774
Cl	35.5	110	0.003099
SO4	96	10	0.000104
HCO3	61	100	0.001639
HCl	36.5	30	0.000822

Table 5-3. The ionic strength of the water was calculated to be 0.009 M. Moreover, use of a program such as Visual MINTEQ can also provide saturation indices that assess whether any solid phases are likely to form in the system. An example of a saturation index for this water is shown in Table 5-4. Note that the saturation indices are all negative, which indicates that all potential precipitates are below saturation.

5.3.3 Media Selection and Preparation

Media selection is a key step in developing a treatment system for removing metal ions from highway runoff or other waters. However, the protocol described in this report is meant to be generic for a range of media. For this study, two iron oxides and two MO were obtained commercially and the two waste products, crab shell and concrete, were obtained locally. The basis for selecting the oxide minerals included previous use as an adsorbent for metal and oxyanion sorption, commercial availability, and availability in particle diameters suitable for the experimental column and field conditions. The mineralogy of each of the iron and MO were similar; however, they were purchased through two different sources.

Granular iron oxides are produced from several different forms of iron oxide including: granular ferric hydroxide (GFH), which is a poorly crystallized akaganeite (β-FeOOH) distributed by companies including US Filter, a goethite based Bayoxide (E33) distributed by AdEdge or Severn Trent, and hematite (α-Fe_2O_3) based iron oxide (e.g., ARM 200 distributed by Engelhard Inc.). The reported SAs of 250 m^2/g and 142 m2/g for GFH and E33, respectively, suggest that GFH provides more surface sites for adsorption; however, previous research has demonstrated that for arsenic removal both of these granular materials, GFH and E33, perform similarly in batch and column experiments. Two sources of goethite based oxide mineral [granular ferric oxide (GFO) and E33] used in the work were obtained from Bulk Reef Supply and AdEdge Inc., respectively. X-ray diffraction confirmed that that Bulk Reef Supply Material was primarily goethite.

The manganese oxide minerals were MTM (Northern Media Company), which contains a granular core with a coating of manganese dioxide and a similar product provided by Pureflow PM-200 manganese dioxide. Analysis of the material indicated that the manganese dioxide was amorphous in nature and as such did not exhibit an x-ray diffraction signal. The SA of the MnO_2 was determined to be 23.6 m^2/g.

The PCC used in the experiments was obtained from a recycling facility in the Austin area and the crab shell was purchased from DirtWorks (www.dirtworks.net), where it is sold as a soil amendment/fertilizer. The crab shell waste was chosen because crab shell is known to contain calcite and chitin. Calcite can be used to increase the pH of the stormwater and chitin exhibits adsorptive properties for metal ions. The

Table 5-3. Synthetic stormwater composition.

Lab Salts	g/mol	{Conc} mg/L	Measured Mass (mg) / 40L Batch Solution
MgSO4·7H2O	246	55	2,200
KCl	74.5	25	1,000
KNO3	101	90	3,600
NaNO3	85	90	3,600
CaCl2	111	200	8,000
CuSO4·5H2O	249.5	0.196 (0.050 Cu)	From Concentrate
ZnSO4·7H2O	287.6	0.440 (0.100 Zn)	From Concentrate

Table 5-4. MINTEQ saturation indices output @ pH = 6.3.

Mineral	log IAP	Sat. index	Stoichiometry							
Antlerite	2.124	-6.664	3	Cu+2	4	H2O	-4	H+1	1	SO4-2
Aragonite	-10.238	-1.902	1	Ca+2	1	CO3-2				
Artinite	-2.379	-11.979	-2	H+1	2	Mg+2	1	CO3-2	5	H2O
Atacamite	3.67	-3.721	2	Cu+2	3	H2O	-3	H+1	1	Cl-1
Azurite	-21.181	-3.781	3	Cu+2	2	H2O	-2	H+1	2	CO3-2
Brochantite	8.334	-6.888	4	Cu+2	6	H2O	-6	H+1	1	SO4-2
Brucite	8.763	-8.337	1	Mg+2	2	H2O	-2	H+1		
CaCO3xH2O(s)	-10.238	-3.094	1	Ca+2	1	CO3-2	1	H2O		
Calcite	-10.238	-1.758	1	Ca+2	1	CO3-2				
Chalcanthite	-10.296	-7.656	1	Cu+2	1	SO4-2	5	H2O		
Cu(OH)2(s)	6.21	-3.08	1	Cu+2	2	H2O	-2	H+1		
Cu2(OH)3NO3(s)	3.365	-5.886	2	Cu+2	3	H2O	-3	H+1	1	NO3-1
CuCO3(s)	-13.695	-2.195	1	Cu+2	1	CO3-2				
CuOCuSO4(s)	-4.086	-14.39	-2	H+1	2	Cu+2	1	H2O	1	SO4-2
CuSO4(s)	-10.296	-13.236	1	Cu+2	1	SO4-2				
Dolomite (ordered)	-21.38	-4.29	1	Ca+2	1	Mg+2	2	CO3-2		
Epsomite	-7.743	-5.617	1	Mg+2	1	SO4-2	7	H2O		
Gypsum	-6.839	-2.229	1	Ca+2	1	SO4-2	2	H2O		
Halite	-5.143	-6.693	1	Na+1	1	Cl-1				
Huntite	-43.665	-13.697	3	Mg+2	1	Ca+2	4	CO3-2		
Hydromagnesite	-35.806	-27.04	5	Mg+2	4	CO3-2	-2	H+1	6	H2O
KCl(s)	-5.406	-6.306	1	K+1	1	Cl-1				
Langite	8.334	-9.155	-6	H+1	4	Cu+2	7	H2O	1	SO4-2
Lime	9.667	-23.032	-2	H+1	1	Ca+2	1	H2O		
Magnesite	-11.142	-3.682	1	Mg+2	1	CO3-2				
Malachite	-7.485	-2.016	2	Cu+2	2	H2O	-2	H+1	1	CO3-2
Melanothallite	-11.29	-17.547	1	Cu+2	2	Cl-1				
Mg(OH)2 (active)	8.763	-10.031	1	Mg+2	2	H2O	-2	H+1		
Mg2(OH)3Cl:4H2O(s)	8.776	-17.224	2	Mg+2	1	Cl-1	-3	H+1	7	H2O
MgCO3:5H2O(s)	-11.142	-6.602	1	Mg+2	1	CO3-2	5	H2O		
Mirabilite	-9.292	-8.178	2	Na+1	1	SO4-2	10	H2O		
Natron	-12.691	-11.38	2	Na+1	1	CO3-2	10	H2O		
Nesquehonite	-11.142	-6.472	1	Mg+2	1	CO3-2	3	H2O		
Periclase	8.763	-12.821	-2	H+1	1	Mg+2	1	H2O		
Portlandite	9.667	-13.037	1	Ca+2	2	H2O	-2	H+1		
Tenorite(am)	6.21	-2.28	1	Cu+2	1	H2O	-2	H+1		
Tenorite(c)	6.21	-1.43	1	Cu+2	-2	H+1	1	H2O		
Thenardite	-9.292	-9.614	2	Na+1	1	SO4-2				
Thermonatrite	-12.691	-13.328	2	Na+1	1	CO3-2	1	H2O		
Vaterite	-10.238	-2.325	1	Ca+2	1	CO3-2				

The ratio of the ion activity product (IAP) to the reaction equilibrium constant is the saturation index.

SA of the crab-shell waste was determined to be 13.3 m^2/g and the XRD spectra verified the presence of calcite.

All media must be sized to meet the hydrodynamic considerations of the experimental column system. Specifically, in order to prevent channeling and inhibit wall effects in columns, the column diameter should be at least 30 times that of the particle diameter (Chellam and Wiesner 1993). All filtration media used were sieved to particle diameters between 0.25 mm to 0.40 mm (sieve sizes 60 and 40), which meet the criteria that the diameter of the particles be at least 30 particle diameters smaller than the column internal diameter. Media diameter can be controlled either by crushing the media to the appropriate size or sieving the material to the appropriate diameter.

5.4 Batch Reactor Studies

Preliminary assessment of the capacity of the iron oxide media was conducted to estimate the equilibration times for sorption of copper and zinc and obtain an estimate of the sorption capacity of the media to ensure that the column

design was appropriate and that experimental runs would be conducted within a reasonable time frame.

A preliminary rate study was performed to verify that 48 hours of equilibration time was sufficient. VWR Polypropylene 15 mL centrifuge tubes were used as batch reactors. Inside a CO_2-free glove box (Labcono Catalog No. 50700009147), a solids slurry stock solution was prepared using 1000 mg/L of the iron oxide fines in CO_2-free Millipore water. An inorganic stormwater stock solution containing an ionic composition similar to the feed used in the column experiments (with MES buffer added to control pH) was also prepared in the glove box using CO_2-free Millipore water. Both solutions were adjusted to a pH of approximately three.

To assemble the reactors, first 5 mL of Fe oxide slurry and 5 mL of inorganic stormwater salts stock solution were added to the reactor. The reactor was then spiked with Cu and Zn stock solutions to achieve the desired metal concentrations of 1250 μg Cu/L and 2500 μg Zn/L. Visual MINTEQ was used to confirm that the resulting reactors would not be oversaturated and lead to precipitation. The reactors were mixed well before the pH was adjusted using CO_2-free 0.1M NaOH to a pH of 6 ± 0.02. To verify the final solids concentration, gravimetric analysis of three 2.5 mL aliquots of solids stock solution, spaced evenly throughout reactor preparation, was performed. In addition, control reactors with either Fe oxide or Cu and Zn excluded were prepared to check for other metals sources and losses. The sealed caps were wrapped in Parafilm before the reactors were moved from the glove box to tumble end-over-end at ambient temperature (20–25°C). The equilibration times evaluated ranged from 0 to 98.5 hours, as presented in Figure 5-11.

At the time of sampling, the final pH of each reactor was measured in the glove box. After pH measurement, the reactors were centrifuged at 3000 rpm for 10 minutes. A 4-inch Air-Tight disposable hypodermic syringe needle was used to remove the supernatant, which was then filtered through a disposable VWR 0.2 μm polyethersulfone membrane filter. The first 1 mL that passed through the filter was wasted. The filtered supernatant was then acidified to 1.5% HNO_3 to avoid sorption to container walls or precipitation. The prepared supernatant was analyzed by inductively coupled plasma (ICP) optical spectroscopy on the Varian 710-ES ICP Optical Spectrometer to determine the final amount of metal remaining in solution. The amount of metal adsorbed was determined from a mass balance by subtracting the final concentration in solution from the initial solute concentration.

Batch equilibrium reactors were also used to generate single points on adsorption isotherms (fixed pH and varying adsorbate concentration). VWR Polypropylene 15 mL centrifuge tubes were used as the batch reactors. Inside a CO_2-free glove box (Labcono Catalog No. 50700009147), a solids slurry stock solution was prepared using 1000 mg/L of iron oxide in CO_2-free Millipore H_2O. The inorganic stormwater salts stock solution with MES buffer was also prepared as described for the rate study. All three of these solutions were adjusted to a pH of approximately 3.

To assemble the reactors, first 2.5 mL of pH 3 CO_2-free Millipore water was added to a 15 mL centrifuge tube. The volume of Cu and Zn stock solution to be added was then removed to minimize dilution of the metals. Next, 2.5 mL of Fe oxide slurry and 5 mL of inorganic stormwater salts stock solution were added. The reactor was then spiked with varying Cu and Zn stock solutions to achieve the desired metal concentrations.

5.5 Experimental Column System

The experimental column system can be constructed using a variety of materials and in a variety of configurations. The essential components include an influent storage tank; a pump or system configuration that provides constant flow; a means of maintaining constant pH and water chemistry of the influent; and influent and effluent sampling ports for analysis of flow rate, pH, metal ion concentrations, and TOC as required. It is often desirable to run columns in parallel so as to allow evaluation of different media using the same influent water composition. In addition, it is important to use inert materials that do not adsorb or leach metals or background organic matter from the system during the experiment. For these reasons, the experimental columns used in this research were constructed from Teflon components. Specific details of the system used in this research serve as an example of the type of experimental reactor system that can be used to evaluate media.

Experimental Flow Path

The apparatus constructed for this experiment was made up of three series (A,B,C) of fixed bed reactors (FBR), each containing three individual columns connected with tubes and fittings made from Teflon®. The columns were aligned vertically, with the feed solution entering the lowest column in each series (Column 1) from the bottom, and flowing through the top into the bottom of Column 2. This flow path continued through the top of Column 2 and into the bottom of Column 3. After passing through the final column (Column 3), the solution passed a ball valve used for sampling, and was then discharged.

Cocktail Feed Tank Setup

The feed solution was kept in a 50L Nalgene tank (Tank 1) with a constant volume of 40L, providing a consistent positive head. A tube connected to the bottom of Tank 1 had a ball valve port attached which was used for sampling. Past the ball valve, the line was split into three separate streams leading

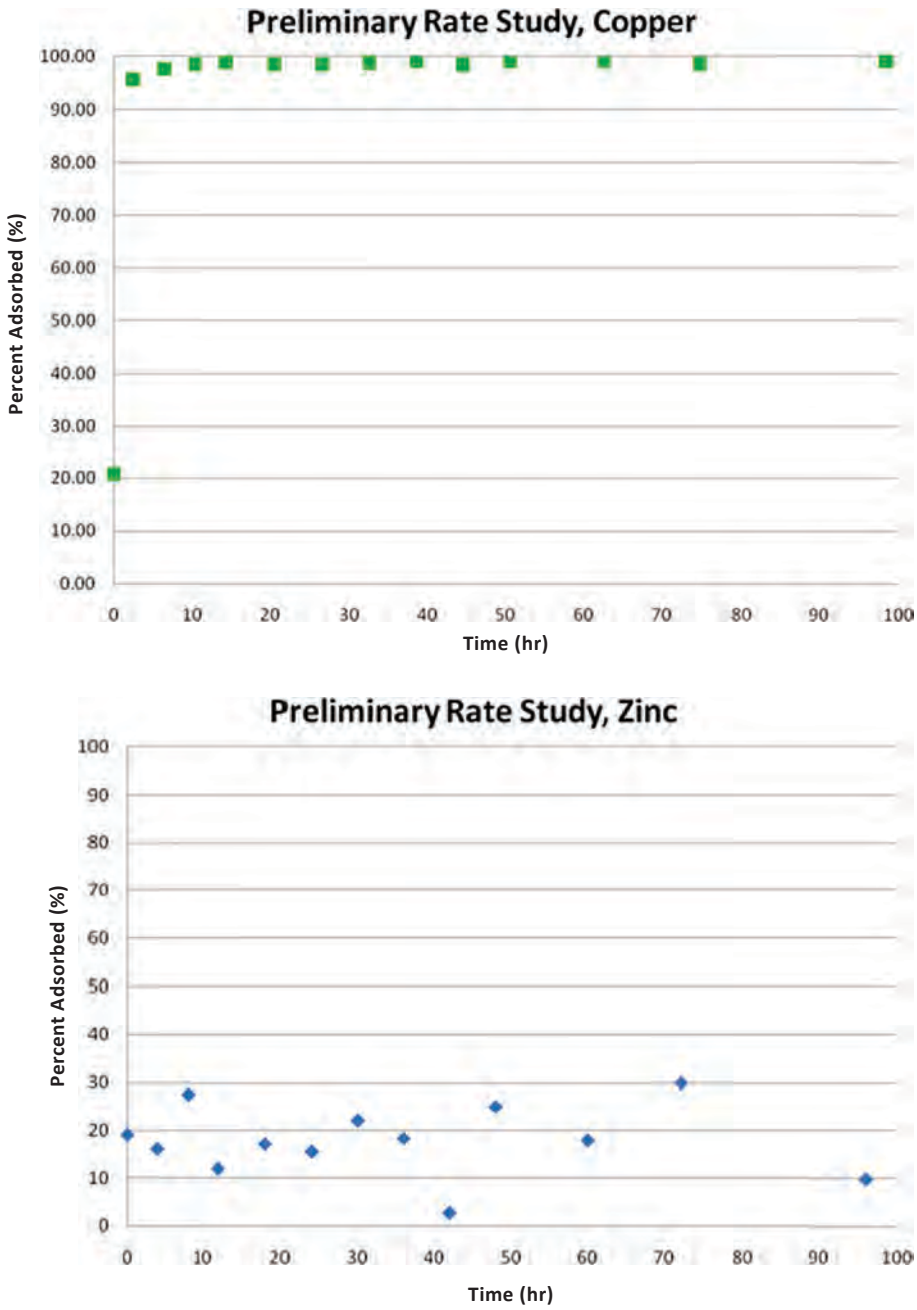


Figure 5-11. Equilibration of copper (*top*) and zinc (*bottom*) onto GFO at pH 6.0.

into a peristaltic pump. The three separate lines were fed to the bottoms of each of the column series (A,B,C). See Figure 5-12 for a detailed diagram of the apparatus.

System Rinse

In order to rinse out tubing and newly packed columns, Tank 1 was filled with Millipore water, which was pumped through the tubes for at least 24 hours prior to starting the trial. Once the system had been flushed for at least a day, the synthetic stormwater solution was pumped into an empty Tank 1, brought to the constant 40L head mark, and the pumps were initiated.

Nitrogen Blanket

In most experiments, the alkalinity was negligible in order to eliminate potential complexation by copper. A N_2 tank was used to prevent CO_2 exchange and maintain a constant influent pH throughout the run. A regulator was connected to an N_2 gas cylinder, and two gas lines delivered a low flow of N_2 into the headspace of both the filling tank (Tank 2) and Tank 1. The

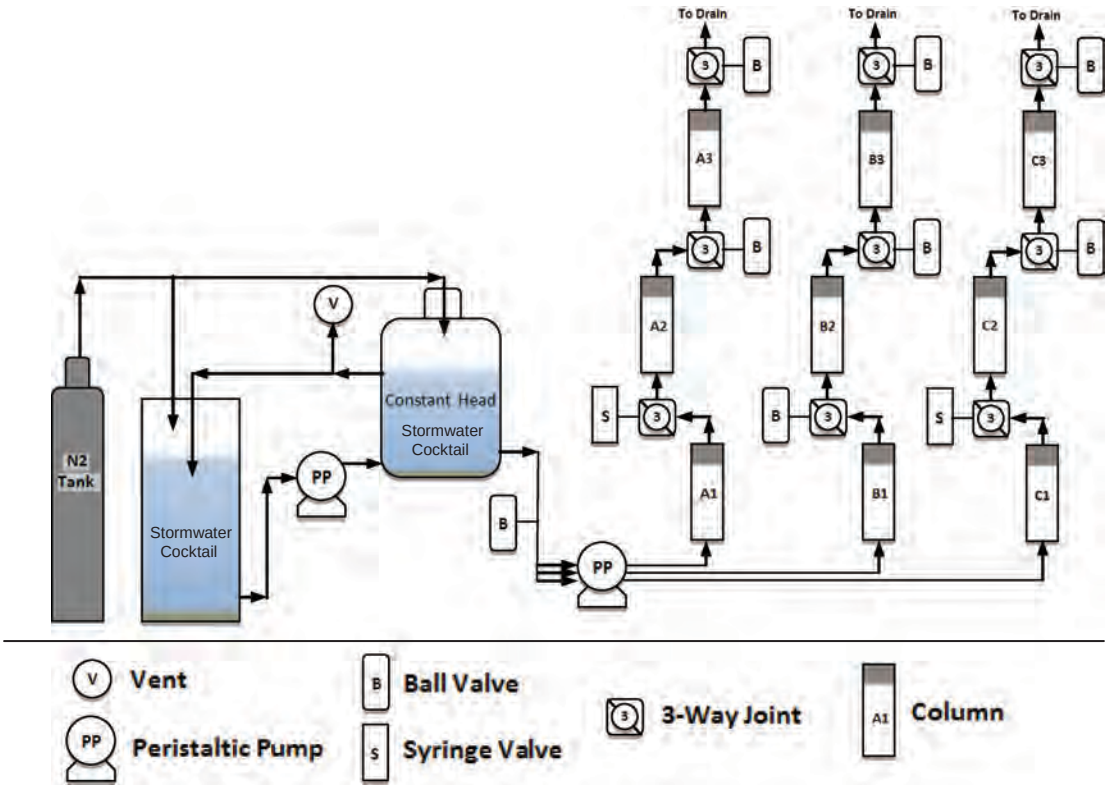


Figure 5-12. Experimental column setup (not to scale).

tops of the tanks were covered with Parafilm® to minimize gas exchange between the tanks and the atmosphere.

Solution Refill Setup

A filling tank (Tank 2) was the main storage basin which fed influent water directly into the constant head tank (Tank 1). Tank 1 was set up with an overflow line to feed back into Tank 2 when the volume reached 40L. Tank 2 was filled on a daily basis by syphoning stormwater solution from a mixing tank (Tank 3, not shown). The influent water was prepared in Tank 3, and like the other two tanks, it was acid washed prior to use in the experiments.

Column Assembly

The columns consisted of an 8cm long Teflon tube with an ID of 0.9cm and OD of 1.3cm, with Teflon joints on both ends to allow connection to the next column in series. All individual parts on the column were made of Teflon, and acid washed prior to use. A ball valve was installed at the effluent end of each of the columns so that the effluent from each column could be sampled immediately after passing through the media. The columns were filled with Teflon® beads (Polytetrafluoroethylene with > 40mm particle size) and a known mass of media as shown in Figure 5-13.

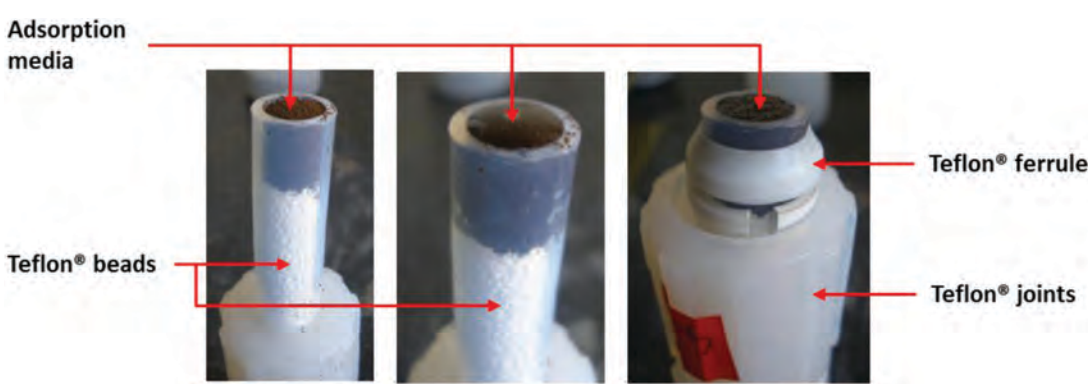


Figure 5-13. Example of a packed column surrounded by Teflon® beads.

5.6 Experimental Results

5.6.1 Batch Reactor Studies of Cu Adsorption Capacity and Equilibration Times

The evaluation of zinc and copper adsorption to GFO suggests that equilibration is achieved within several hours at pH 6 as shown in Figure 5-11. The data also suggests that adsorption of copper is significantly greater than zinc as nearly all of the copper is removed from solution and only approximately 20% of the zinc added to the system is removed from the solution. The capacity of the GFO for copper and zinc at the influent concentrations of 1,250 mg/L and 2,500 mg/L, respectively, were 2.45 µg/mg and 1 µg/mg. Assuming a linear isotherm equation for the low end of the isotherm:

$$q_e = K_D C_e$$

in which q_e represents the mass adsorbed per mass of adsorbent in mg/mg, C_e is the equilibrium concentration of the metal ion in mg/L, and K_D is the linear partitioning coefficient in L/kg, the value of log K_D for each metal ion is 4.99 and 2.7, respectively.

A complete isotherm developed for adsorption of copper onto GFO is presented in Figure 5-14 and suggests that the adsorption of copper onto GFO is non-linear, which is consistent with previous research examining sorption of metal ions onto oxide minerals at fixed pH. Indeed, the data can be described by a Langmuir isotherm:

$$q_e = \frac{Q_{max} K C_e}{1 + K C_e}$$

where Q_{max} is the maximum adsorption capacity and K is a constant that is related to the energy of adsorption. Isotherm parameters determined from the data are Q_{max} = 20 µg/mg, K = 0.01 L/µg. It is also evident that the concentrations of interest for stormwater appear within the linear portion of the isotherm below 20 µg/L. In fact, within a flow-through treatment system the equilibrium concentration is equal to the desired effluent concentration which is below 3 µg/L for copper. Using a value of 3 µg/L and 0.01 for C_e yields a value of 0.03 for the second term in the denominator, which is significantly less than 1. Thus, the denominator is approximately one and the isotherm becomes linear in which K_D is the product of Q_{max} and K or 0.2 L/mg (200,000 L/kg) corresponding to a log K_D of 5.3. Linear regression of the q_e versus Ce data yields a slope (or K_D value) of 0.18 L/mg. These results are consistent with the value of K_D estimated from the rate study. Estimates of breakthrough in the flow-through columns systems can be made using these values of K_D.

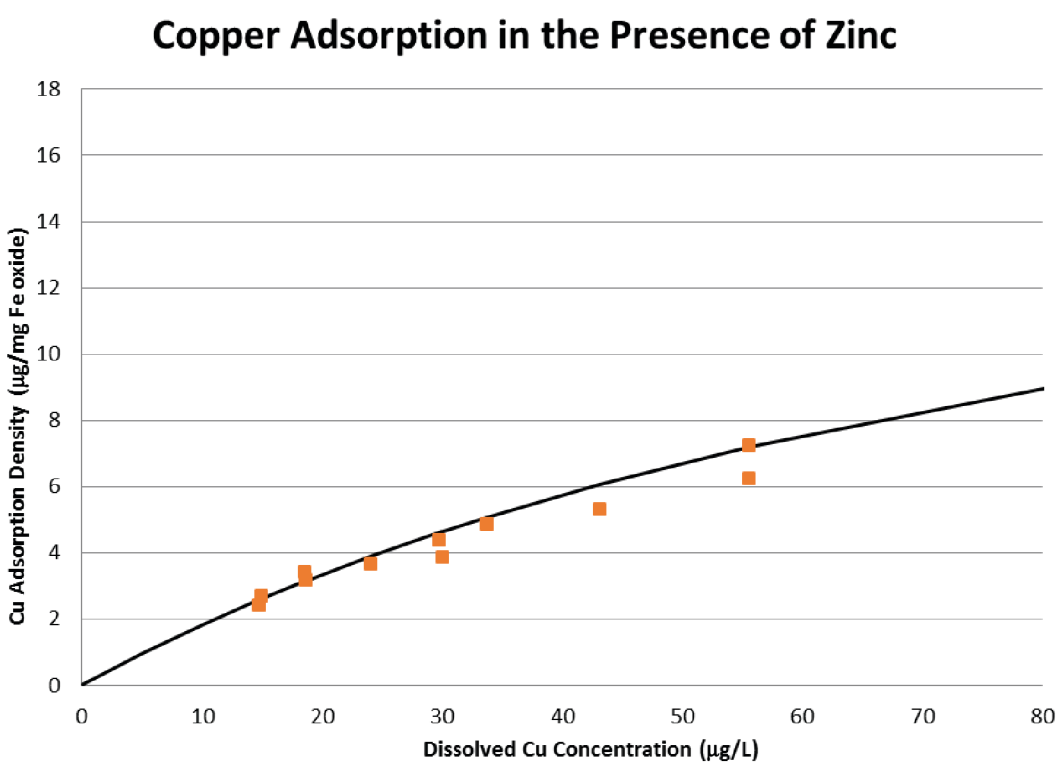


*Figure 5-14. Adsorption isotherm data (*symbols*) and Langmuir model fit (*solid line*) for copper sorption onto GFO at pH 6 with an initial zinc concentration of 3,300 µg/L.*

5.6.2 Column Protocol Verification

Selected results from column experiments conducted in this research are presented to highlight several different key issues including the ability to distinguish performance of different media for different metal ions, sensitivity of removal to changes in pH, the role of organic matter, the role of ionic strength, and the potential benefits of dual media systems. A summary of the results from all of the experiments is presented in Table 5-5. The table contains the adsorption capacity values and log K_D values calculated from the column data.

The capacity of each type of media to adsorb copper or zinc was determined by measuring the difference in influent and effluent concentrations over the course of each run (until breakthrough or a plateau was observed). By the principle of mass balance, the metal not accounted for in the effluent stream was attributed to sorption by the media or precipitation within the column. In addition to influent and effluent metal concentrations, the masses of media packed into each column at setup and the flow rates through each column over time were measured. Measurement of the flow rates allowed for an accurate determination of the cumulative volume output from each column. Essentially, a numerical integration utilizing the trapezoid rule was performed on the difference between influent and effluent concentration as a function of cumulative volume output, yielding the total mass of metal adsorbed onto each column. This value was then divided by the recorded mass of media for each column, resulting in the adsorptive capacity in μg metal per mg media. Modifications to this procedure were required for breakthrough profiles that did not reach complete breakthrough (C/Co = 1). In those cases, the mass removed was only determined up to the point that a plateau in the breakthrough profile was achieved.

As there were three beds per column, measurements of effluent taken at each bed incorporated the adsorptive capacity of that bed and any bed upstream. That is, while the influent of Column 1 was indeed the measured influent to the column, the influent to Column 2 was the effluent from Column 1 and would differ from the original effluent. Hence, in calculating capacity the bed masses were combined in order to characterize the cumulative adsorptive capacity of one, two, or three columns in series. In most cases Columns 1, 2, and 3 were the same type of media, so this approach was appropriate. In cases where the beds were mixed (i.e., utilizing crab shell or concrete to boost influent pH prior to a metal oxide bed), the calculated capacities apply to the overall behavior of the combination of media within the column and not only to the oxide media in question. This distinction is significant because the crab media, and to a lesser extent the concrete, were observed to adsorb metal from solution, hence altering the composition of the influent to the metal oxide media bed.

The coefficients of adsorption, K_D, were calculated by dividing the mass capacity of each bed (calculated as described earlier) by the concentration of solution in equilibrium with the media. In cases where the column achieved breakthrough, this calculation was straightforward since the equilibrium concentration was simply the influent concentration to the column. However, in cases where a plateau was observed at lower-than-influent concentrations, the equilibrium concentration of the solution was assumed to be the average between the true influent concentration and the effluent concentration of the observed plateau. This assumption stems from the hypothesis that the observed plateaus are a result of precipitation processes occurring within the column, hence lowering the apparent effluent concentration while potentially maintaining higher metal concentrations within the column itself. That this impact was only seen with the iron oxide media and Cu may represent an advantage for iron oxide media and copper removal in real systems.

Values of log K_D for sorption of copper on GFO are lower than the log K_D value estimated from the batch reactor data, demonstrating the importance of conducting experiments in flow-through systems which more closely capture the dynamics of the field systems. The results also verify that the values of log K_D are dependent on pH. To determine whether there is a linear relationship between log K_D and pH as suggested by Langmuir (1997) for sorption on hydrous ferric oxide, log K_D values from Trials 1 through 4 and Trial 11 without organic matter were grouped according to the influent pH. A plot of log K_D versus pH is shown in Figure 5-15 along with the linear regression of the data that shows that the log K_D increases over an order of magnitude for each unit change in pH. This is consistent with the results obtained by Langmuir (1997) in which he derived the equation $\log K_D = -5.48 + 1.77\text{pH}$ for sorption of zinc to hydrous ferric oxide.

The summary table also shows that zinc log K_D values are approximately an order of magnitude lower than the values for copper for all of the media. This is consistent with the batch reactor experiments; however, the batch reactor experiments showed an even greater reduction in zinc sorption. The estimate of the log K_D for zinc sorption from the batch reactor studies was not representative of the column system because it was obtained from a single isotherm point at an equilibrium zinc concentration of approximately 2,000 μg/L; a concentration that is well above the linear range of the isotherm. Using a log K_D derived from data collected in the non-linear region of the isotherm will underestimate the value at lower equilibrium concentrations.

5.6.3 Contrasting Performance of Different Media and Different Metal Ions

Figure 5-16 and Figure 5-17 show the results for sorption of copper and zinc in column trains A1-A3 and B1-B3 using

Table 5-5. Summary of results from column experiments including average sorption capacity and estimated log K_D values.

Experimental Conditions									Experimental Results				
Trial	Influent Conc.	Media			pH	Ionic Strength	Matrix	Flow Rate (mL/min)	Bed pH (average)	Avg. Capacity (μg/mg)		log Avg. K_D (K_D in L/kg)	
	Cu / Zn μg/mg (average)	Bed 1	Bed 2	Bed 3						Cu	Zn	Cu	Zn
1	25.3 Cu (No Zinc)	GFO	GFO	GFO	6.26	0.009 M	Inorganic Only	6.8	6.35	2.00	N/A	5.11	N/A
		MnO2	MnO2	MnO2				6.9	6.66	0.26	N/A	4.01	N/A
		Crab	Crab	GFO				6.9	6.73	0.36	N/A	4.33	N/A
2	38.8 / 101	GFO	GFO	GFO	6.30	0.009 M	Inorganic incl. NaHCO3	7.7	6.39	1.80	0.486	4.76	3.62
		MnO2	MnO2	MnO2				7.7	6.5	0.142	0.0029	3.57	1.02
		Crab	Crab	E33				8.5	6.54	0.909	0.419	4.37	3.59
3	39.7 / 95.3	GFO	GFO	GFO	6.02	0.009 M	Inorganic only	7.8	6.07	0.788	0.417	4.38	3.64
		MnO2	MnO2	MnO2				7.9	6.03	0.098	0.0179	3.38	2.25
		Crab	Crab	MnO2				7.8	6.52	1.00	1.05	4.42	4.01
4	40.2 / 118.5	E33	E33	E33	6.14	0.011 M	Inorganic only	8	6.01	2.01	0.754	4.87	3.8
		GFO	GFO	GFO				8	5.94	2.15	0.616	4.93	3.72
		Crab	Crab	E33				8	6.2	1.67	1.39	4.76	4.03
5	47.2 / 113.6	E33	E33	E33	5.03	0.011 M	Inorganic only	8	5.22	0.0286	N/A	2.78	N/A
		GFO	GFO	GFO				8	5.24	0.120	N/A	3.37	N/A
		Crab	Crab	E33				8	5.79	0.472	N/A	3.79	N/A
6	40.7 / 114.7	E33	E33	E33	5.91	0.011 M	Inorganic only	8	5.73	1.54	0.258	4.70	3.24
		GFO	GFO	GFO				8	5.68	1.65	0.304	4.72	3.38
		Crab	Crab	E33				8	6.09	0.345	N/A	3.63	N/A
7	43.1 / 109.7	E33	E33	E33	5.90	0.009 M	Inorganic only	8	5.82	0.875	N/A	4.43	N/A
		GFO	GFO	GFO				8	5.84	1.04	N/A	4.53	N/A
		Concrete	Concrete	E33				8	6.85	1.50	1.28	4.61	4.03
8	37.3 Cu (No Zinc)	GFO	GFO	GFO	6.14	Low	Inorganic and NOM (8.9)	7.2	6.29	0.98	N/A	4.61	N/A
		MnO2	MnO2	MnO2				6.8	6.217	0.07	N/A	3.25	N/A
		Crab	Crab	GFO				6.5	6.496	1.26	N/A	4.65	N/A
9	49.8 / 150.4	GFO	GFO	GFO	5.88	0.009 M	Inorganic and NOM (16.2)	7.6	5.95	1.13	0.516	4.40	3.53
		MnO2	MnO2	MnO2				7.8	5.83	0.063	0.012	3.10	1.87
		Crab	Crab	MnO2				8.5	6.39	2.03	2.44	4.56	4.16
10	58.9 / 183.4	GFO	GFO	GFO	6.01	0.009 M	Inorganic and NOM (19.7)	9.9	6.04	1.28	0.736	4.27	3.73
		E33	E33	E33				9.9	6.08	2.06	1.70	4.67	3.98
		Concrete	Concrete	E33				10	6.69	0.371	0.697	3.60	3.78
11	32.8 / 105.1	GFO	GFO	GFO	6.91	0.009 M	Inorganic Only	8	6.86	5.71	2.16	5.31	4.31
		MnO2	MnO2	MnO2				8	6.86	0.305	0.100	4.00	2.97
		Crab	Crab	GFO				8	7.06	2.38	2.27	4.92	4.31
12	42.8 / 102.6	E33	E33	N/A	5.92	0.100 M	Inorganic Only	7.7	5.90	1.50	0.447	4.88	3.64
		Concrete	E33	N/A				7.7	6.61	1.36	1.29	4.59	4.10
		Bone Meal	E33	N/A				7.7	6.08	0.561	0.273	4.17	3.42
13	36.7 / 43.6	GFO	Bone Meal	GFO 2cm	GFO 2cm	7.41	N/A	Actual Stormwater	8	7.5	0.25	0.59	3.89	4.29
14	8.89 / 28.5	GFO	Concrete	GFO 2cm	GFO 2cm	7.52	0.010 M	Inorganic and High CO3	7.8	7.6	0.235	1.31	4.51	4.79

GFO is granular ferric oxide, E33 is an iron oxide, MnO_2 is manganese oxide, Crab is crushed crab shell waste, Concrete is crushed concrete, NOM is natural organic matter. Trials 4-7 refer to experiments run in series conducted without changing media.

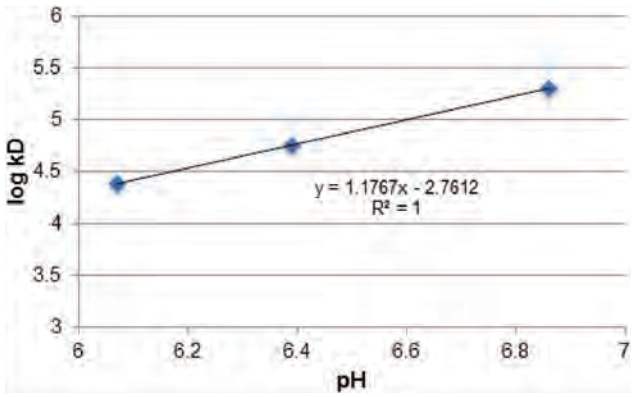


Figure 5-15. Relationship between pH and log K_D for sorption of copper onto GFO (Trials 2, 3, and 11).

GFO obtained from Bulk Reef Supply in Column Train A and MTM granular manganese dioxide from Northern Media Company (Muscatine, IA) in Column Train B. It is readily apparent that the iron oxide media performs significantly better than the manganese dioxide media. Complete breakthrough of copper occurs in the manganese dioxide columns at approximately 20,000 bed volumes. In contrast, copper breakthrough profiles plateau at 80, 60, and 40% in the three sequential columns, A1-A3. This behavior suggests that adsorption is not the only removal mechanism in the iron columns and suggests that copper precipitation is occurring within the bed. In contrast, zinc adsorption reaches complete breakthrough for both media. Since copper is significantly more insoluble than Zn, the dramatic differences in the results are not surprising.

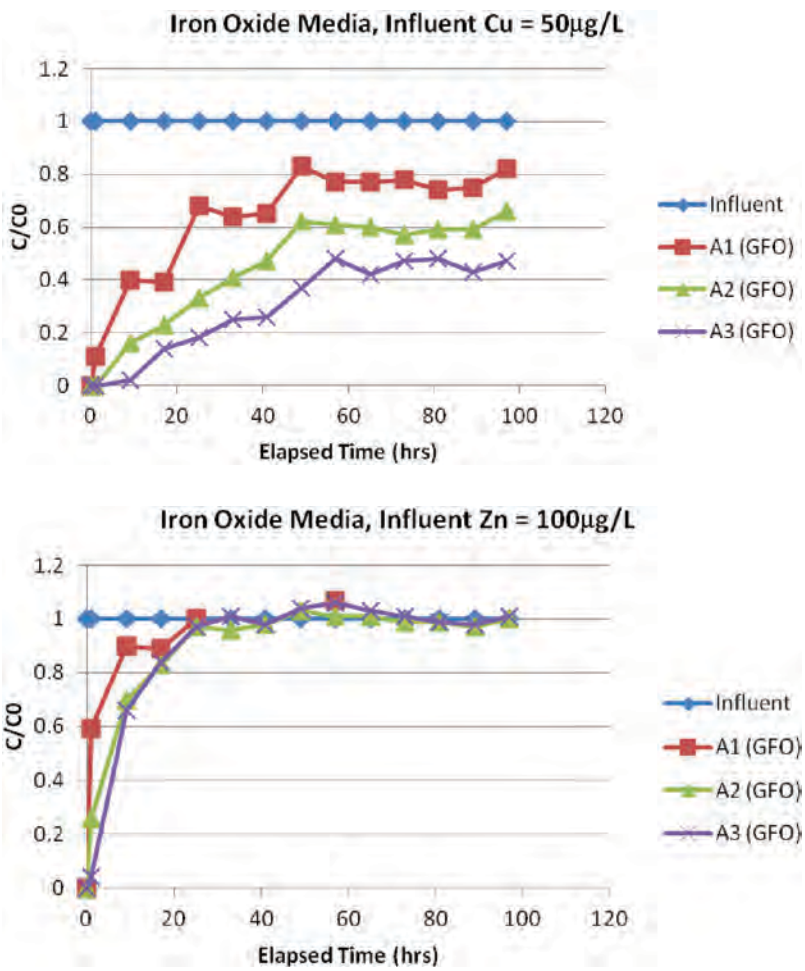


Figure 5-16. FBR breakthrough profiles for Cu (top) and Zn (bottom) from a synthetic stormwater solution onto granular iron hydroxide (Columns A1-A3 in series). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 µg/L, and the influent Zn(II) concentration was 100 µg/L. The influent ionic strength was 0.01M. Three columns were connected in series with A1 being the first bed in the series.

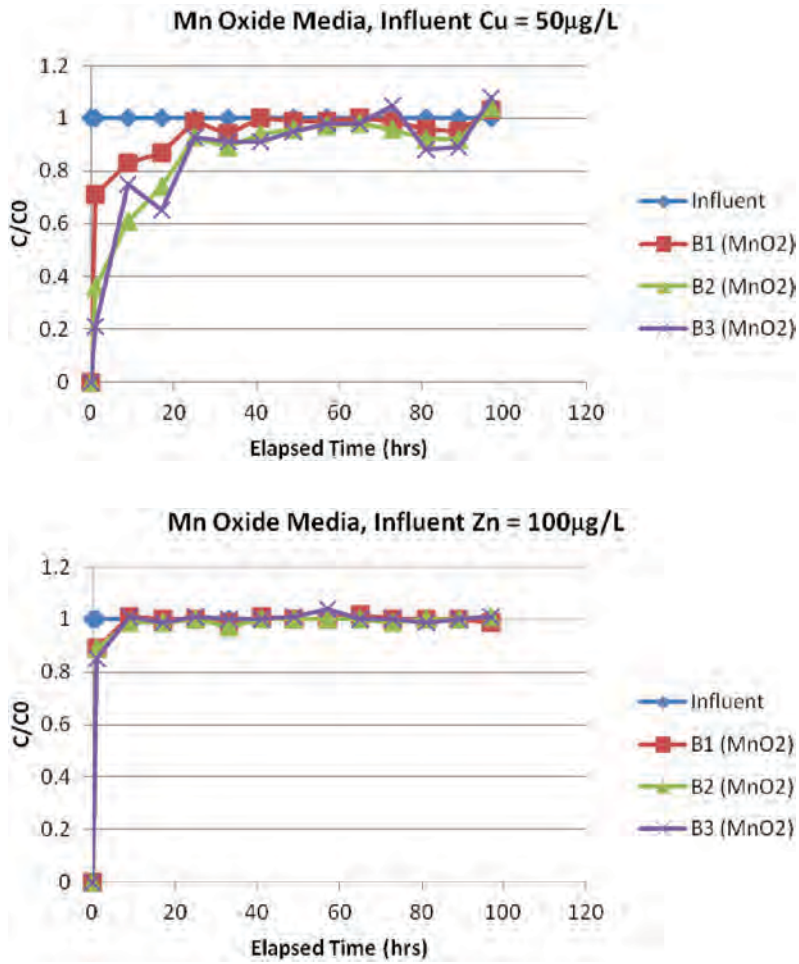


Figure 5-17. FBR breakthrough profiles for Cu (*top*) and Zn (*bottom*) from a synthetic stormwater solution onto granular manganese oxide (Columns B1-B3 in series). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 µg/L, and the influent Zn(II) concentration was 100 µg/L. The influent ionic strength was 0.01M. Three columns were connected in series with B1 being the first bed in the series.

5.6.4 Impact of Highway Organic Matter

In a separate experiment (Trial 9), reconstituted organic matter was added to the synthetic stormwater solution containing salts and adjusted to a pH of approximately 6. The average influent pH to the columns containing organic matter was 5.9, within 0.1 pH unit of the experiments without organic matter. The column experiments captured the impact of the organic matter for both oxide minerals. Results from these experiments for the iron oxide media are shown in Figure 5-18 for the three columns, A1-A3. For all three columns in series the initial breakthrough in columns with and without organic matter appears similar; however, the plateau obtained as breakthrough occurs in each case is at a higher value of C/Co indicating lower Cu removals. In fact, in the presence of organic matter, almost complete breakthrough is achieved for column A1, the first column in the treatment train.

The reduced removal of copper could be due to the presence of organic matter complexation with the copper that reduces the extent of copper precipitation. Reductions in copper removal were also observed for the manganese oxide media as seen for Column B2 in Figure 5-19. In both cases, complete copper breakthrough occurred; however, the presence of the organic matter led to more rapid breakthrough again suggesting that Cu-organic complexation reduced the extent of adsorption.

These results serve to emphasize that organic matter is an essential component of a representative synthetic stormwater solution. While synthetic inorganic stormwater solutions allow

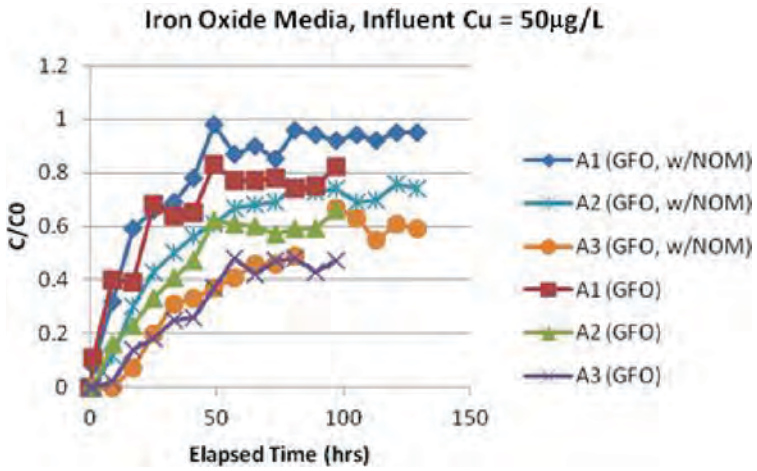


Figure 5-18. Comparison of FBR breakthrough profiles for Cu from synthetic stormwater solution with and without reconstituted NOM. The columns were packed with granular iron oxide (Columns A1–A3 in series). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L. The influent ionic strength was 0.01M and the TOC of the experiments with NOM was 17 mg/L.

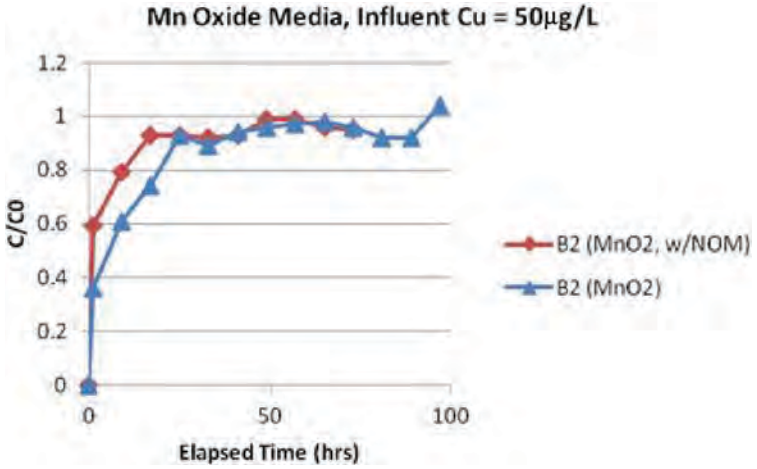


Figure 5-19. Comparison of FBR breakthrough profiles for Cu from synthetic stormwater solution with and without reconstituted NOM. The columns were packed with granular manganese oxide (Columns B1–B3 in series) but only data from Column B2 is shown for clarity. The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L. The influent ionic strength was 0.01M and the TOC of the experiments with NOM was 17 mg/L.

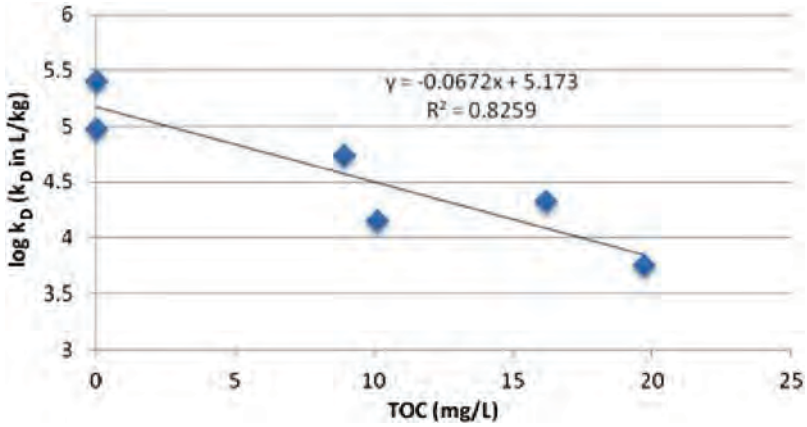


Figure 5-20. Relationship between log K_D and TOC for sorption of copper onto GFO (Trials 4, 8–11, and 13).

for the isolation and study of mechanisms affecting adsorptive behavior (i.e., pH, ionic strength, alkalinity), to accurately capture the performance of the media systems under real conditions organic matter is indispensable. A plot of log K_D vs. TOC for Trials 4, 8–11, and 13 is shown in Figure 5-20. Despite scattering due to differences in pH between runs, the relationship between log K_D and TOC is clear.

5.6.5 Effects of pH and Ionic Strength on Cu(II) and Zn(II) Sorption

The effects of pH were investigated in an iron oxide column experiment in which the ionic strength was increased slightly to 0.011M through addition of 500 mg/L NaCl to the synthetic stormwater solution at the start of the experiment, and the pH was set to approximately pH 6 (stage 1). In stage 2, the influent pH was reduced from approximately pH 6 to pH 5 after the columns had achieved breakthrough or steady-state operation. The pH was then increased again to pH 6 in Stage 3, and then the influent ionic strength was reduced to 0.009M in Stage 4 of the experiment by omitting the additional 500 mg/L NaCl. The results from this experiment for the first column (A1) are presented in Figure 5-21, which shows the four different operating stages. As expected, the reduction in pH led to a decrease in copper removal. Moreover, as the pH was decreased, desorption of copper (and to a lesser extent Zn) led to C/Co values in excess of one. This dramatic increase in copper concentrations above

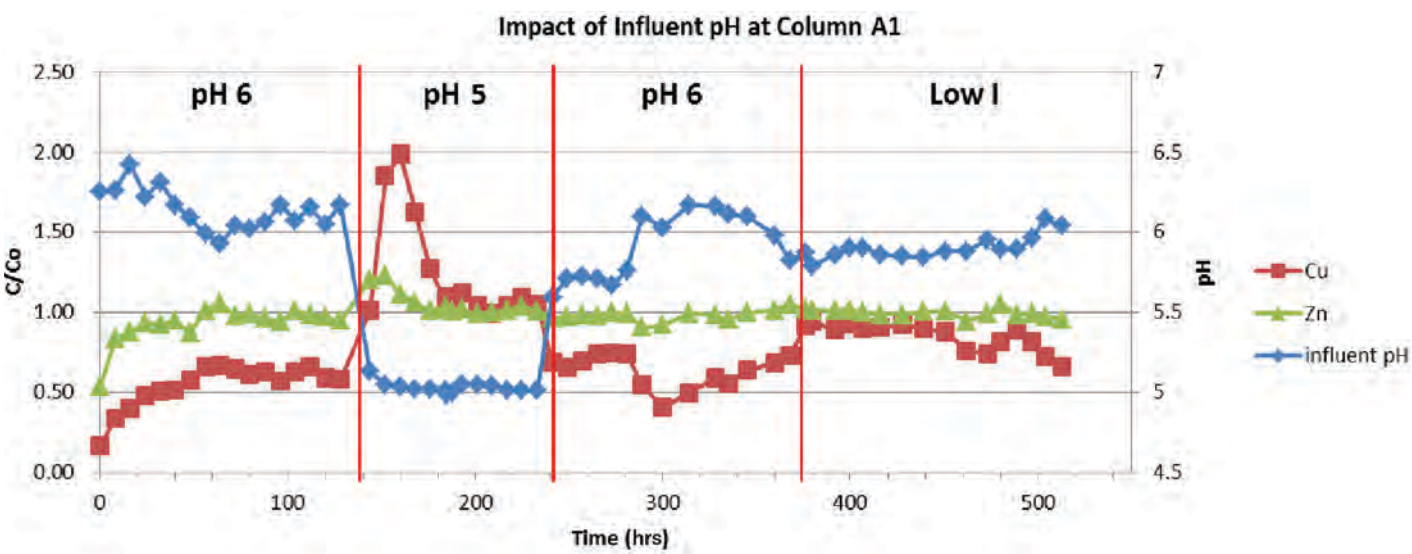


Figure 5-21. Effect of changes in pH and chloride concentration in FBR breakthrough profiles for removal of Cu and Zn in the first column in series (A1). The columns were packed with granular iron oxide (Columns A1–A3 in series). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L.

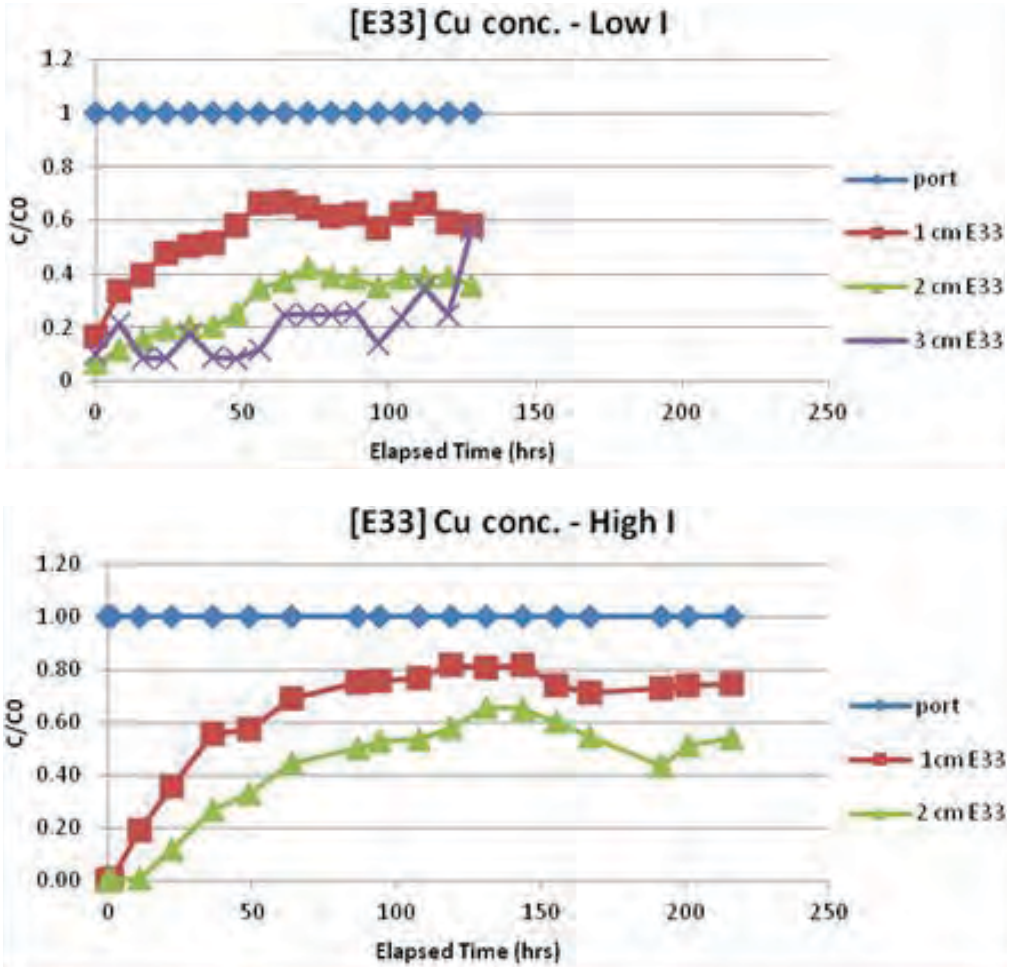


Figure 5-22. Effect of changes in ionic strength in FBR breakthrough profiles for removal of copper on granular iron hydroxide media. High I represents an ionic strength of 0.1M. Low I represents an ionic strength of 0.009M. The column diameter was 1 cm ID, flowrate = 8 ml/min, and the influent copper concentration was 50 μg/L.

the influent concentration highlights the need to control pH in metal ion sorption treatment systems.

In order to assess the effect of high ionic strength, an additional test was conducted with synthetic stormwater of ionic strength on an order of magnitude higher (0.1M) than typical highway runoff (0.009M). To obtain the higher ionic strength, 5340 mg/L of NaCl were added to the synthetic stormwater solution in order to raise the ionic strength to 0.1M while the concentrations of other cations and anions were maintained consistent with previous tests. The test results, as shown in Figures 5-22 and 5-23, show that metal removal capacity appears to be somewhat lower in high ionic strength water. However, this small difference also can be attributed to the higher overall pH during the low ionic strength test as compared to the high ionic strength test (see Figure 5-24), and hence the difference is not necessarily a direct result of ionic strength differences. Considering the fact that the high ionic strength used in this test is highly unlikely in real conditions, it can be concluded that the impact of ionic strength is not as significant as the impact of pH or other variables in the design of heavy metal removal systems for stormwater.

5.6.6 Evaluation of pH Stabilizing Media

The strong effect of pH on column performance suggests that a media that both increases and stabilizes column pH would yield improved performance in the field. Two different media were tested in this research to assess whether performance could be improved by adding pH stabilizing media to the front of the treatment system. Experiments were conducted by adding either crushed crab shell or concrete to the first two columns in the treatment train (Columns C1 and

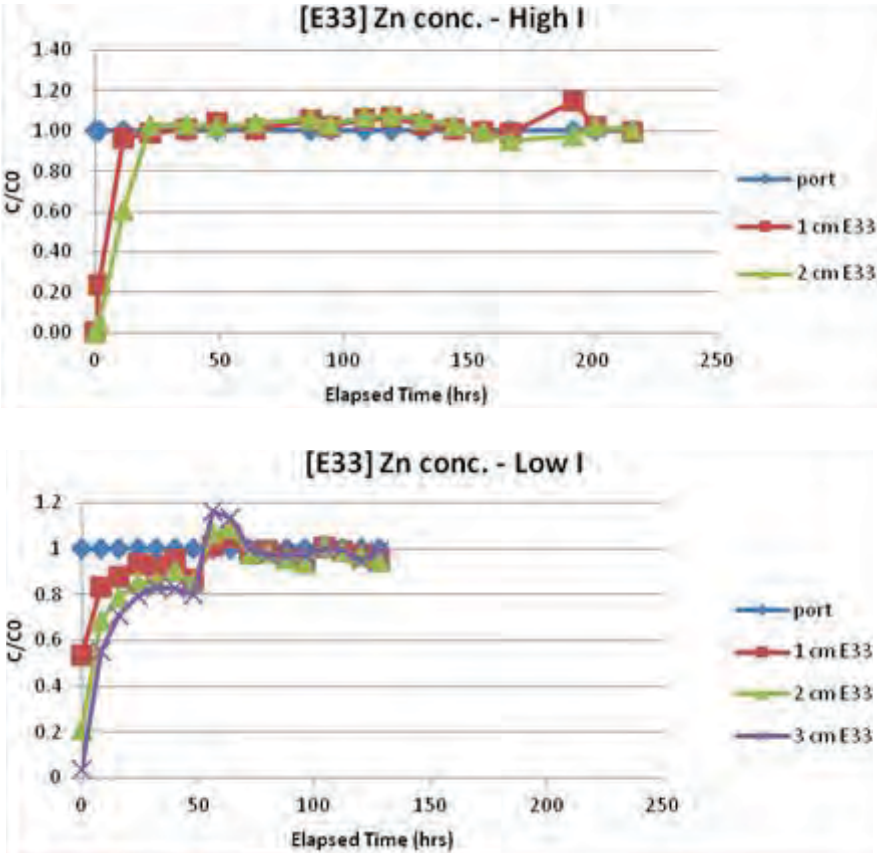


Figure 5-23. Effect of changes in ionic strength in FBR breakthrough profiles for removal of zinc on granular iron hydroxide media. High I represents an ionic strength of 0.1M. Low I represents an ionic strength of 0.009M. The column diameter was 1 cm ID, flowrate = 8 ml/min, and the influent Zn(II) concentration was 100 µg/L.

C2). In the first set of experiments shown in Figures 5-25 and 5-26, crushed crab shell was placed in Columns C1 and C2, and granular manganese oxide was placed in Column C3 in the series. The addition of the crab shell particles initially had a dramatic impact on increasing pH (Figure 5-25) and removal of zinc (Figure 5-26). In fact, the crab shell itself appears to outperform the manganese dioxide as no additional removal is observed in Column 3. Similar results were observed in experiments conducted in the absence of organic matter as shown by comparing the log K_D values in Table 5-5.

The addition of crab shell waste had less impact on copper removal in the column experiments. In the four stage experiment, described previously, in which the pH was varied during the course of the experiment, the presence of crushed crab shell in Phase I showed comparable removal of copper (see C2 in Figure 5-27) compared to the single iron oxide column (A1). These results are evident in Table 5-5, by comparison of the log K_D values of 4.91 for the column packed only with GFO to the log K_D of 4.75 for the series of columns packed with crushed crab shell followed by GFO. Moreover, when the pH was decreased to pH 5, the impact of desorption was minimized in the C column train compared to column trains packed entirely with iron oxide. Indeed, the average pH in the columns over the duration of the pH 5 stage remained over pH 6. In the final stage of this experiment, the crab shell waste was replaced with concrete waste. While this led to an initial increase in pH (Figure 5-28) in all of the columns, which was accompanied by increased removal, over time the pH dropped and removal decreased to levels consistent with the crab shell packed columns. The spike in pH was likely due to the fact that the material was not washed prior to use. Regardless, it appears that the presence of a pH stabilizing material is beneficial in the design of a passive treatment system for metal ion removal. Another important point of interest is that the pH of the system increased for a short period of time after the flow was interrupted for more than 24 hours. This type of behavior may have significant impacts in field scenarios and should be evaluated further.

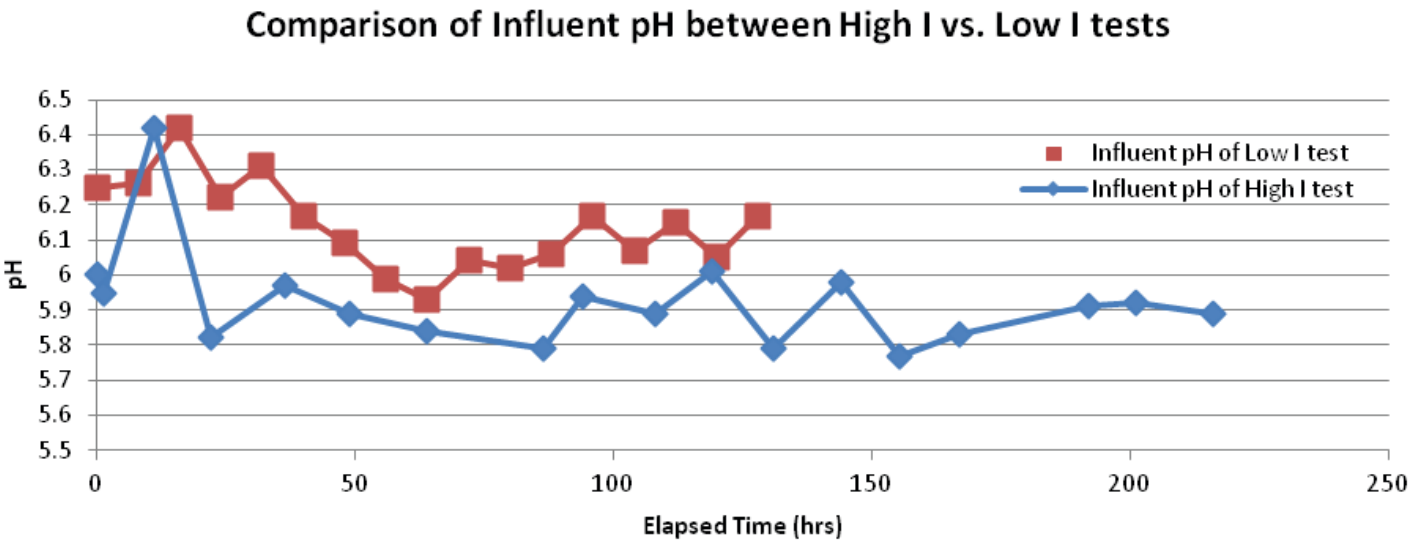


Figure 5-24. FBR pH data for Cu and Zn sorption onto granular iron hydroxide in two tests varying in the ionic strength of the synthetic stormwater solution. High I represents an ionic strength of 0.1M. Low I represents an ionic strength of 0.009M. A nitrogen blanket was used to control the influent pH during this experiment.

5.6.7 Experiments Conducted at pH Representative of Stormwater

Experiments conducted at higher pH (between 6.8 and 7.0) demonstrate the potential of the iron oxide media for achieving the effluent criteria of 3.0 µg/L copper for a sustained period of time. The columns were operated in this pH range for 130,000 bed volumes. However, after approximately 40,000 bed volumes the influent pH began dropping due to the loss of the nitrogen blanket used to maintain the storage tank CO_2 free. Nevertheless, the data in Figure 5-29 show that the effluent concentration from GFO Column C remains consistently low, suggesting that this media is capable of achieving effluent Cu concentrations that meet the water quality criteria under the low alkalinity conditions used in this research. While removal of Cu from the column packed

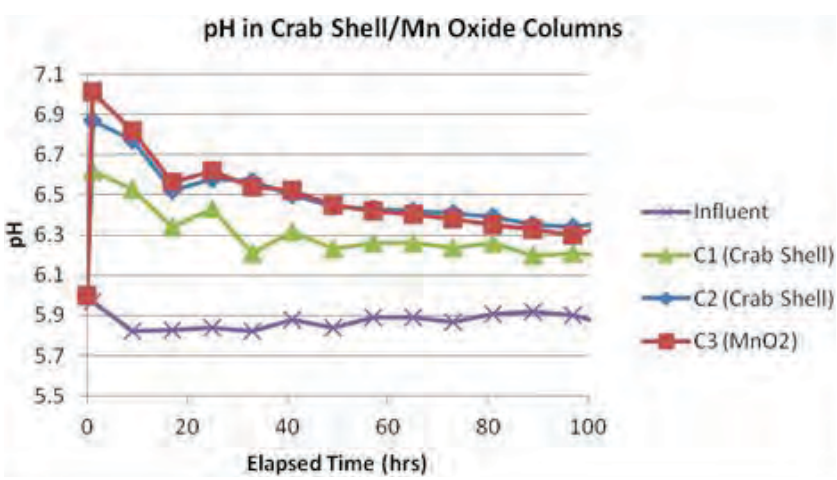


Figure 5-25. pH profiles from FBR experiments with crushed crab shell placed in the first two columns (C1 and C2) and in final column (C3) packed with manganese dioxide. The column diameter was 1 cm ID, flowrate = 8 ml/min, influent copper concentration was 50 µg/L, and the influent Zn(II) concentration was 100 µg/L. The influent ionic strength was 0.01M and the TOC was 17 mg/L.

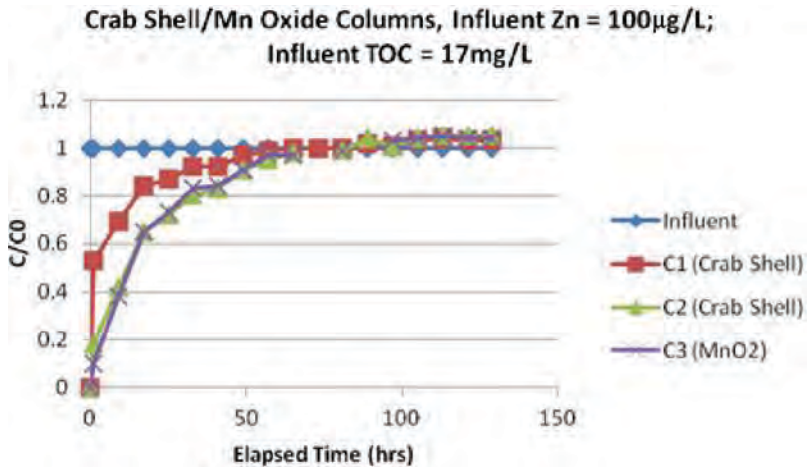


Figure 5-26. Zn(II) breakthrough profiles from FBR experiments with crushed crab shell placed in the first two columns (C1 and C2) in the final column in series (C3) packed with MnO_2. The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 µg/L, and the influent Zn(II) concentration was 100 µg/L. The influent ionic strength was 0.01M and the TOC was 17 mg/L.

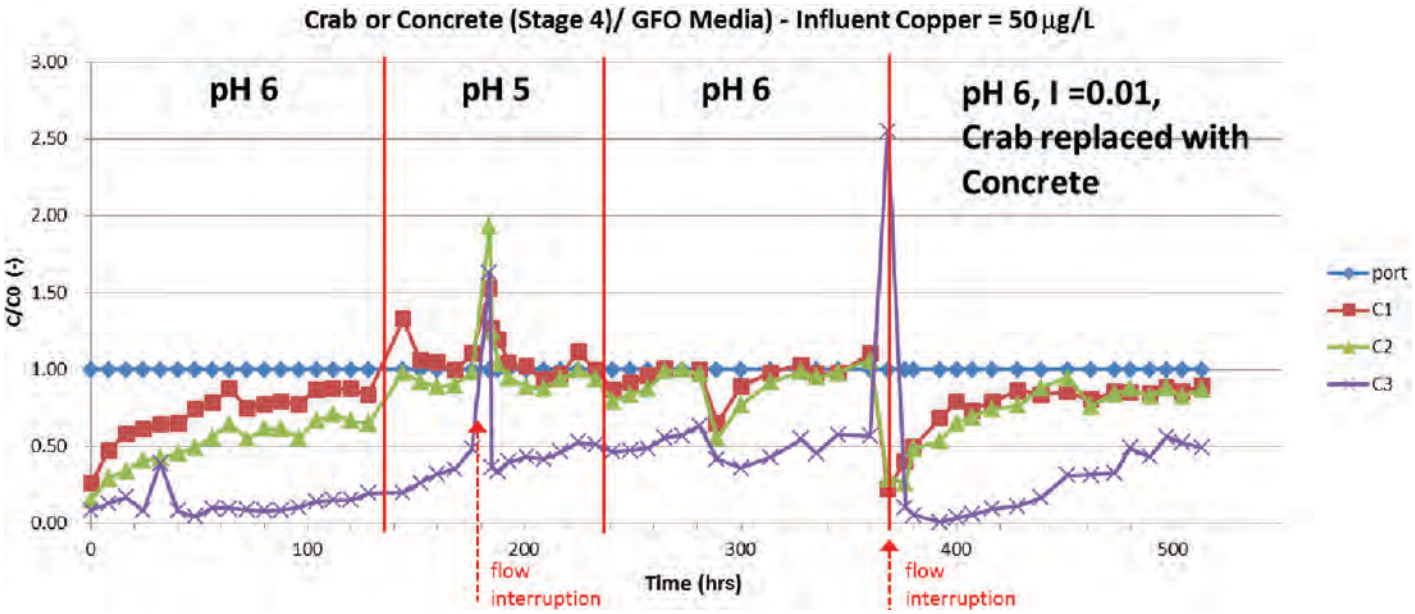


Figure 5-27. Effect of changes in pH and ionic strength in FBR breakthrough profiles for removal of Cu in a series of columns packed with crushed crab shell (C1 and C2) and granular iron oxide (C3). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 µg/L, and the influent Zn(II) concentration was 100 µg/L. The crab shell was replaced with unwashed concrete in the last stage of the experiment. Two periods of flow interruption are displayed in the plot.

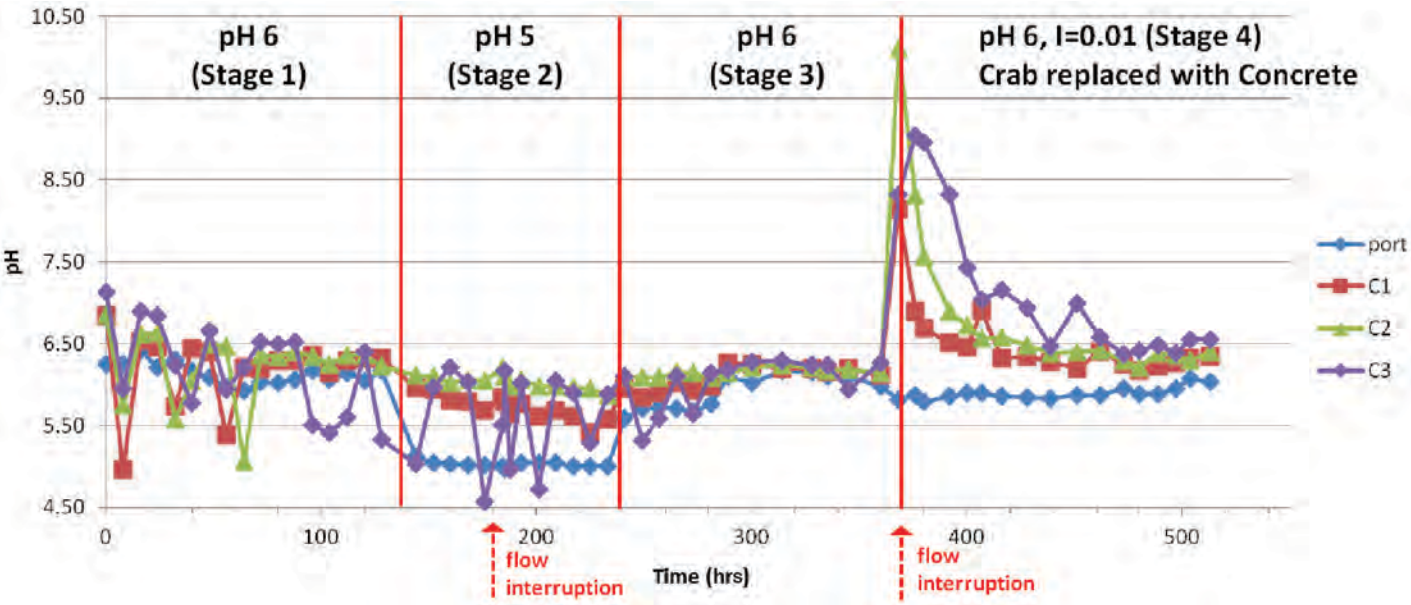


Figure 5-28. pH profile in FBR breakthrough profiles for removal of Cu in a series of columns packed with crushed crab shell (C1 and C2) and granular iron oxide (C3). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L. The crab shell was replaced with unwashed concrete in the last stage of the experiment.

with manganese dioxide also shows dramatic improvement at the higher pH, the results are still not as promising as the iron oxide media. In fact, the waste crab material outperforms this particular manganese dioxide in part because the average pH in the column is higher in the crab-shell/GFO columns.

Performance of the media for zinc removal also improves at pH 7. Log K_D values for zinc removal from the GFO column series and the waste crab/GFO column series were similar at pH 7 whereas at lower pH, zinc removal was significantly better in the columns packed with crab/GFO or crab/MnO_2. Thus, the presence of the crab shell mainly contributes to zinc removal in lower pH systems.

5.6.8 Experiments Conducted with Real Stormwater

Experiments were conducted utilizing actual stormwater in place of synthetic stormwater in order to evaluate performance under conditions closer to those that would be seen in the field. Highway runoff was collected immediately after a rain event from a site on Loop 360 in Austin, TX and was pre-filtered in order to remove particulate matter that would clog the FBR. The filtration process consisted of circulating the runoff through a nominal 0.45 μm cartridge filter (Pentek model 155403-75) for 12 hours. The pH, alkalinity, TSS, TOC, and heavy metal content of the highway runoff were characterized after filtration (Table 5-6).

In this test, GFO was used as the sole sorbent media in conjunction with crab shell and bone meal as pH stabilizers. No attempt to control the influent pH was made so to more closely simulate field conditions. The results indicate that copper removal was not as successful when compared to the tests conducted previously with synthetic stormwater (Figure 5-30). This is likely attributable to the high alkalinity and pH of the runoff, since in this environment much of the copper is present in a relatively inert form. By simulation with Visual MINTEQ, it was determined that under the conditions found in the actual stormwater, over 80% of total copper exists as dissolved copper carbonate, which does not sorb to iron oxide to the same as free copper, and less than 3% of total copper is present in the form of cupric ion. Conversely, zinc removal was relatively more successful as compared to the tests utilizing synthetic stormwater (Figure 5-30). This can be explained by the high pH of the stormwater, which increases the tendency of zinc ion to sorb onto the surface of the oxide media.

Figure 5-31 shows the relative effects of crab shell and bone meal on Cu and Zn adsorption from real stormwater onto GFO media. As can be seen in the plots, the breakthrough profiles are almost identical in both cases, suggesting that there is no significant difference between them in terms of improving heavy metal removal.

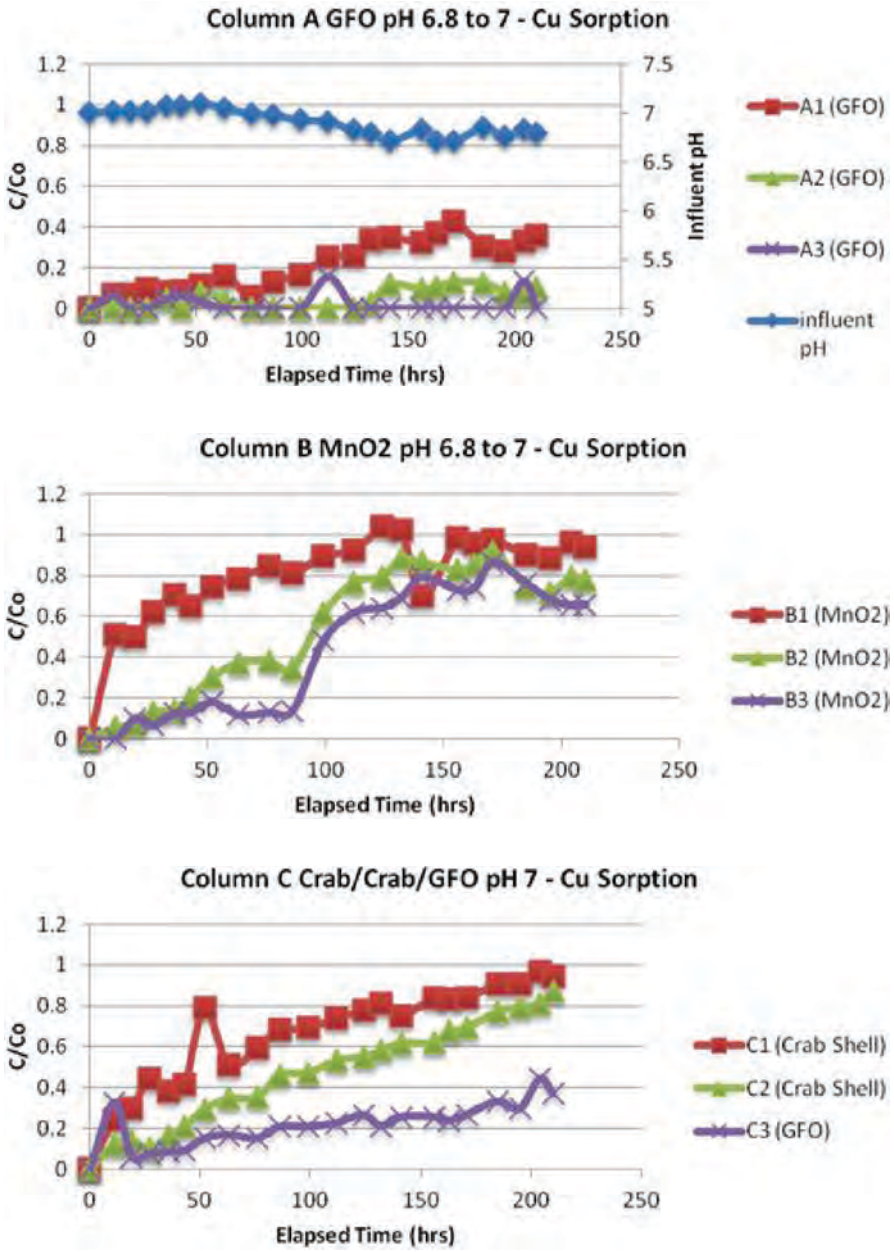


Figure 5-29. FBR breakthrough profiles for Cu from a synthetic stormwater solution onto granular iron hydroxide (Columns A1–A3 in series), MnO2 (Columns B1–B3 in series), and waste crab shell/waste crab shell/GFO columns in series (Columns C1–C3 in series, respectively). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L. The influent ionic strength was 0.01M. Three columns were connected in series with A1 being the first bed in the series.

Table 5-6. Characterization of collected stormwater used in FBR study (post-filtration).

pH	7.78
Alkalinity (meq/L)	2.4
TSS (mg/L)	0.8
TOC (mg/L)	10.1
Cu conc. (µg/L)	36.0
Zn conc. (µg/L)	49.8
Fe conc. (µg/L)	129.4
Cr conc. (µg/L)	2.0

5.6.9 Experiments Conducted at Alkalinity Representative of Stormwater

Experiments were conducted with a synthetic runoff solution formulated to have an alkalinity similar to that observed in real stormwater in order to understand the breakthrough behavior observed with real stormwater. The alkalinity of the solution was raised to 2.15 meq/L by addition of $NaHCO_3$ so to be comparable to the alkalinity of the real stormwater (2.4 meq/L). Otherwise, the solution was identical in composition to the synthetic inorganic runoff solutions used in previous experiments. The amounts of copper and zinc added in order to achieve 50 and 100 µg/L, respectively, in the influent were also the same as those used previously. In this test, as in the real stormwater test, GFO was used as the sole sorbent media in conjunction with crushed concrete. Since attempts to set the solution to a lower pH via addition of acid would simply have titrated away the desired alkalinity, the pH was left uncontrolled and rose steadily from 7.25 at the beginning of the run to about 7.65 at completion.

Analysis revealed that influent copper and zinc concentrations were about five times lower than expected: 8.9 µg/L Cu and 28.5 µg/L Zn. A possible explanation for the apparent disappearance of copper and zinc from the influent solution is that mixed calcium carbonate precipitates of copper and zinc formed due to elevated levels of calcium in the system, removing the metals from solution before they could

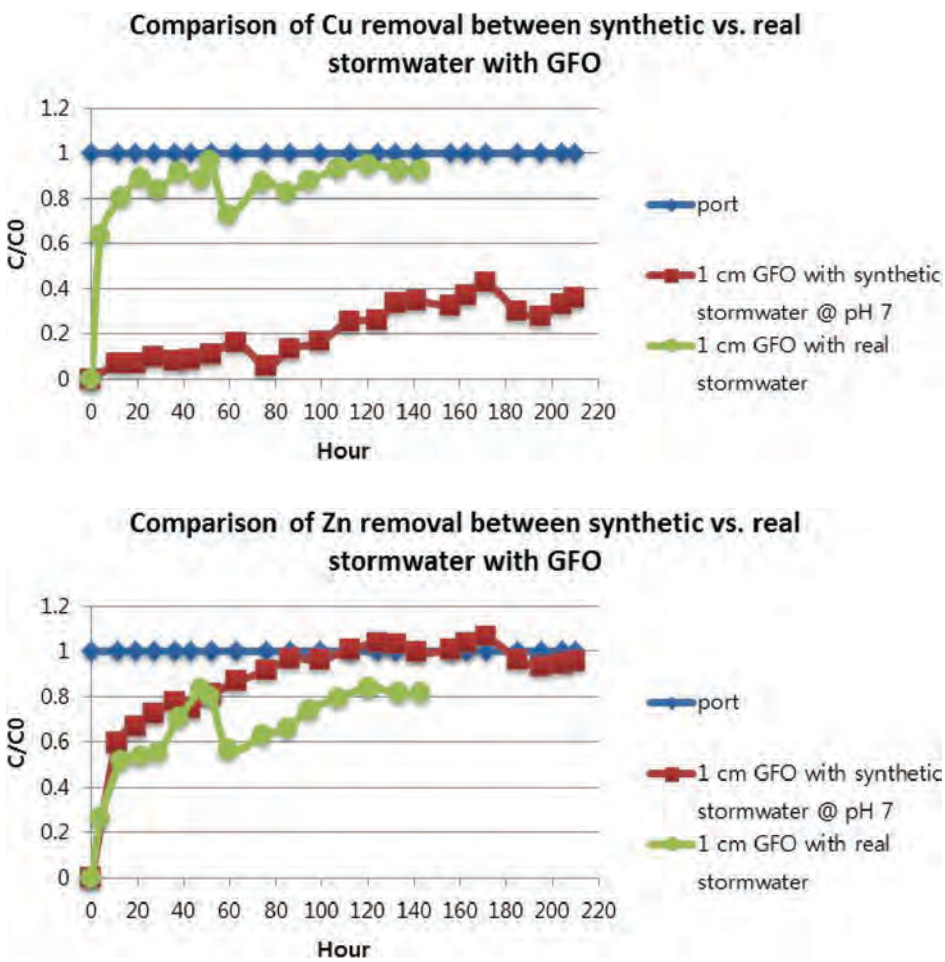


Figure 5-30. Comparing FBR breakthrough profiles for copper and zinc removal between tests utilizing synthetic stormwater and actual stormwater.

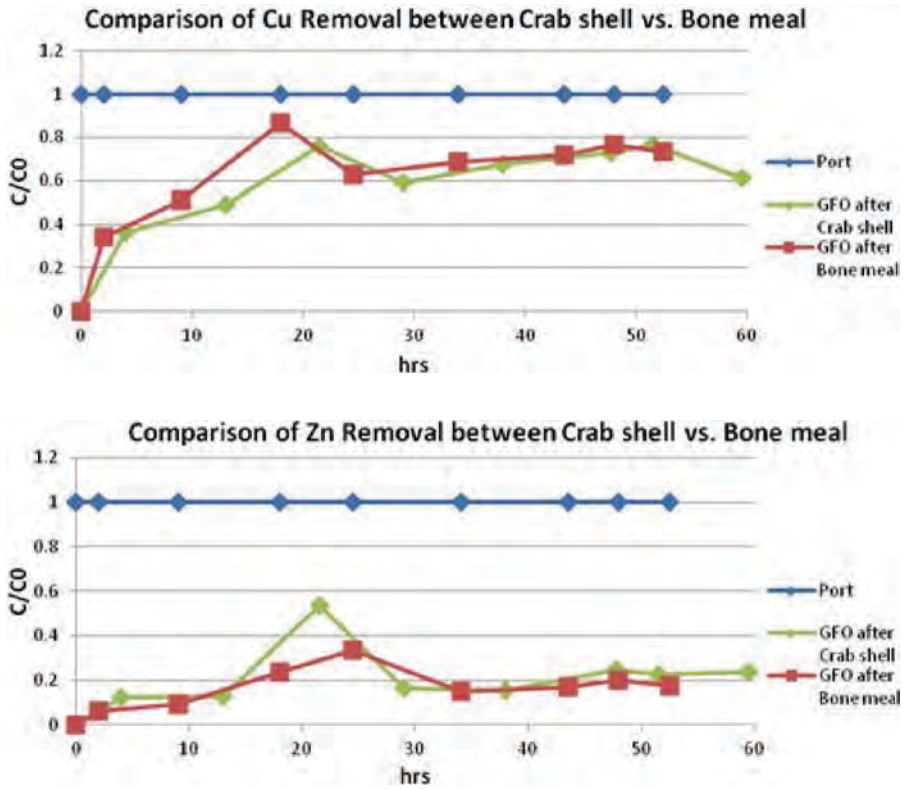


Figure 5-31. Comparing the effects of crab shell and bone meal on copper and zinc removal in a FBR.

even enter the columns. Indeed, precipitates were visually observable in the feed tank. This explanation is supported by a column experiment performed subsequently in which magnesium chloride was substituted for calcium chloride in the synthetic runoff cocktail, allowing the same alkalinity and ionic strength to be achieved without the presence of calcium. In this case, the expected influent concentrations of 50 µg/L Cu and 100 µg/L Zn were measured, and no precipitates were visually observable in the solution.

Despite low influent concentrations, sufficient data were collected in order to evaluate removal efficacy and capacity under these conditions. Comparing log K_D values for copper between Trials 11, 13, and 14 (low CO_3 at pH 7, real stormwater, and high CO_3 at pH 7.5, respectively) and Trials 8-10 (with organic matter) suggests a relationship between copper removal, organic matter, and carbonate concentration. Namely, log K_D values for copper decrease both in the presence of organic matter and in the presence of high carbonate concentrations as compared to the inorganic, low carbonate case (Trial 11 vs. Trials 8–10 and Trial 14). Moreover, log K_D values for copper are lower than any of the above trials in the case of real highway runoff, which contained elevated concentrations of both organic matter and carbonate. Hence, the inhibitory effects that NOM and carbonate each exert on adsorptive copper removal are additive. The effect of NOM can be attributed to complexation of copper ions from solution, and the effect of carbonate can be attributed to the complexation and potential formation of mixed copper precipitates, as seen in this experiment. Indeed, the copper breakthrough profile (Figure 5-32) shows essentially immediate development of plateaus, suggesting that precipitation was a significant controlling process in this system.

For zinc, slightly higher log K_D values were observed with high carbonate solutions as compared to the low carbonate case (Trial 11). This relationship, where zinc removal outperforms copper removal, mirrors the behavior observed in the real highway runoff experiment, suggesting that high carbonate concentrations may not be inhibitory to zinc removal. As noted before, this may be explained simply by the fact that high pH increases the tendency of zinc to sorb to the media surface (Trial 14 pH was 7.5 while Trial 11 pH was 6.9) and the formation of aqueous zinc carbonate complexes is not as thermodynamically favorable as copper carbonate complexes.

In conjunction, the results of Trials 8–10 and 13–14 indicate that synthetic stormwater experiments incorporating both NOM and carbonate most accurately represent the behavior of real stormwater. While an experiment incorporating all of these factors simultaneously was not performed, based on the data at hand this extrapolation is not unreasonable. A linear relationship exists between log K_D and TOC, and although slightly weaker, relationship exists between log K_D and alkalinity (Figure 5-33). The additive manner by which organic matter

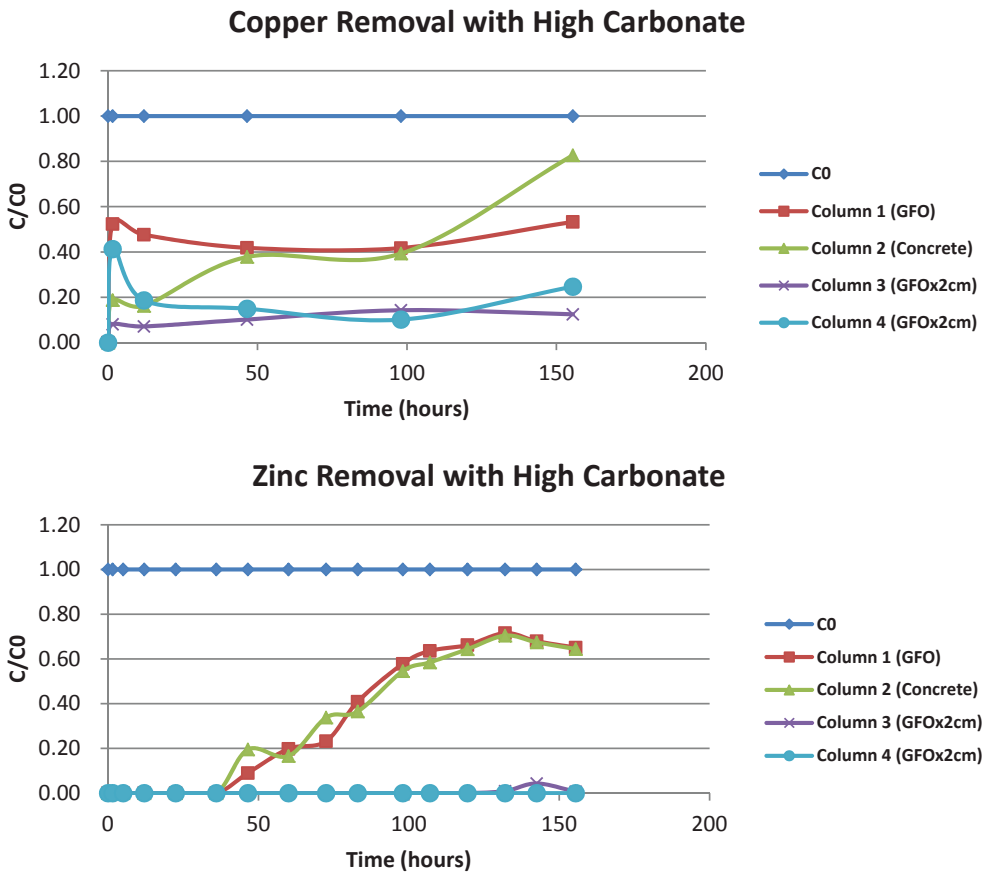


Figure 5-32. FBR breakthrough profiles for copper and zinc from a synthetic stormwater solution high in carbonate concentration (Trial 14).

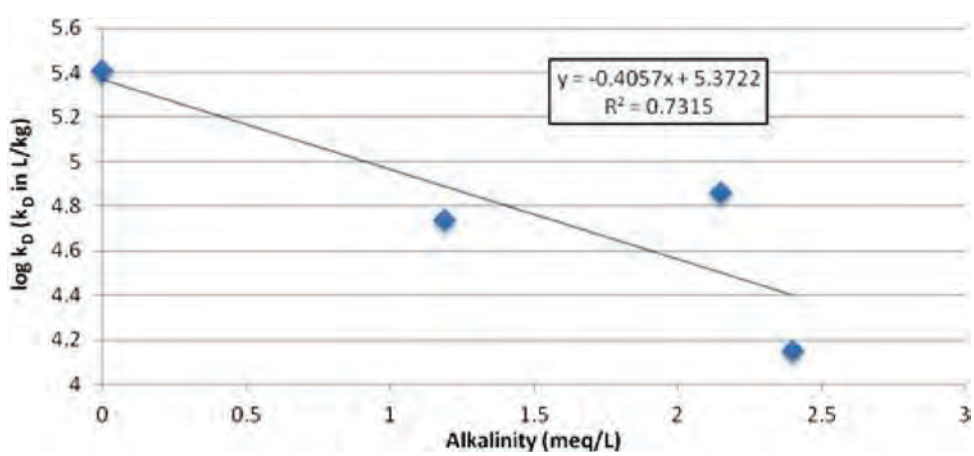


Figure 5-33. Relationship between log K_D and alkalinity for sorption of copper onto GFO (Trials 2, 11, 13, and 14).

and carbonate were observed to affect copper sorption onto GFO (as in Trial 13) follows from the demonstrated linearity of the individual relationships. Based on these results, it is our recommendation that both NOM and carbonate be included as components in future synthetic stormwater solutions to accurately simulate dissolved metal sorption in the laboratory.

5.7 Application of Results for Field Scale Design

Most highway runoff waters are characterized by relatively low alkalinity and pH between 6.5 and 8.0. The results of the experimental testing suggest that iron oxide media is capable of achieving copper effluent concentrations of 3 µg/L or less for extended periods of time in the column reactors. The results also indicate that the use of a mixed oxide system containing concrete or crab shell can achieve similar, if not better, results for copper without raising the pH of the effluent. The mixed media system with iron oxide also provided better removal of zinc. The data from experiments conducted using the protocol described earlier can be used to guide the design of field scale treatment systems by assisting in selecting appropriate media and by estimating the capacity of the media. In addition, modeling approaches can be used to assist in scaling from the bench scale system to the field.

In this research, iron oxide was identified as the most promising media. The adsorption capacity of the iron oxides tested in this work was evaluated from batch and column data. The batch reactor experiments suggested that at the low effluent concentrations desired for the field system, the adsorption isotherms were linear. For copper and zinc, log K_D values obtained from the column experiments for GFO at circumneutral pH were 5.2 and 4.3, respectively. At this pH, the use of a mixed media system in which the first two columns in the series contained crab shell waste (containing calcite or chitosan) did not improve removal of either copper or manganese. The impact of organic matter may reduce the capacity of the system, but as shown in this research the impact may be minimal if pH is controlled near circumneutral values. Finally, the results also suggest that adsorption to the oxide media is rapid, and at flow rates typical of a highway runoff filtration system rates of adsorption should not limit the adsorption process.

The K_D values obtained at pH 7 can be used to provide an estimate of the capacity of the full-scale system for copper removal from highway runoff of similar composition and to assess the economic feasibility of the material. K_D represents the mass of contaminant removed per mass of adsorbent. Therefore, for a given amount of copper to be removed from the stormwater, the required mass of media can be calculated. This process is described for copper removal by the GFO iron oxide media used in this research.

At pH 7, the estimated log K_D for this system is conservatively assumed to be 5. In addition, the assumption of 30 in./yr of rainfall over a one acre drainage area yields a volume of stormwater runoff of approximately 3,000 m^3 per year. For an influent copper concentration in the stormwater runoff of 10 µg/L and desired effluent concentration of 3 µg/L, the required mass of copper adsorbed per year is approximately 22 g. Using the linear isotherm equation:

$$q_e = K_D C_e$$

and a value of 3 µg/L for C_e and a K_D of 10^5 L/kg, yields a required adsorption capacity of 300 mg removed/kg of GFO. Dividing the mg of copper adsorbed per year by 300 mg removed/kg of GFO yields a GFO demand of 72 kg/yr (150 lbs/yr) or 1,600 lbs over a 10-year design period. The reported bulk density of GFO and E33 are 0.45 g/cm^3, which means that 720 kg of media 1.5 m^3 of volume. Assuming a design depth of 45 cm indicates that 1.5 m^3 of media are required for the 10-year design period. The cost for oxide media ranges from $4 to $10/lb with GFH at the lower end of the price range compared to E33 or GFO media. Thus, the media costs for the 10-year design period range between $6,400 to $16,000/acre.

This research also highlighted the benefits of adding a media to help control pH and increase removal of zinc. Both of the materials used in this research are waste materials. Either waste concrete or crab shell added to the system would provide pH control as well as adsorptive capacity. For example, the design of a system containing crushed crab shell could be conducted by using one-third of the bed for the waste material. As shown in Figure 5-29 this would not impact copper removal significantly. The bulk density of the crushed concrete (0.54 g/cm^3) is comparable to the bulk density of the E33, so the bed design would be similar. In addition, the cost of crushed concrete is significantly lower than the cost of iron oxide media and would represent a significant savings.

More detailed design of the full-scale system can be determined through modeling exercises. Based on the results of this research, the application of site-specific models that incorporate the retardation factors observed in the experiments conducted using the protocol described in this report may be most appropriate. More complex models such as SCMs and ligand binding models can be incorporated into transport codes and are useful for evaluating the impact of various parameters on adsorption; however, the results of this research suggested that pH control and assessment of organic matter and carbonate complexation are the most important operating parameter for stable operation of a treatment system.

One model that is relatively simplistic and user-friendly is CXTFIT/EXCEL (Tang et al. 2010). The original form of the

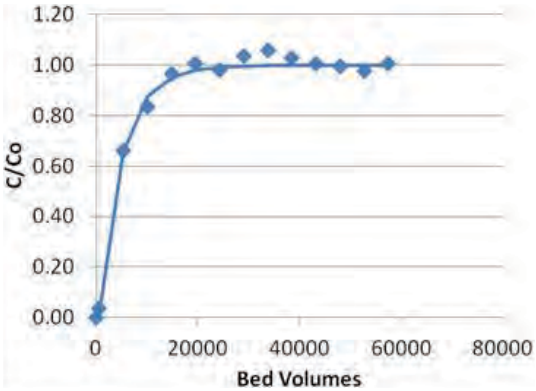


Figure 5-34. Example CXTFIT/EXCEL equilibrium advection-dispersion-retardation model calibration of zinc breakthrough profile of column A3 in a bed packed with granular iron oxide (Columns A1–A3 in series). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L. The influent ionic strength was 0.01M.

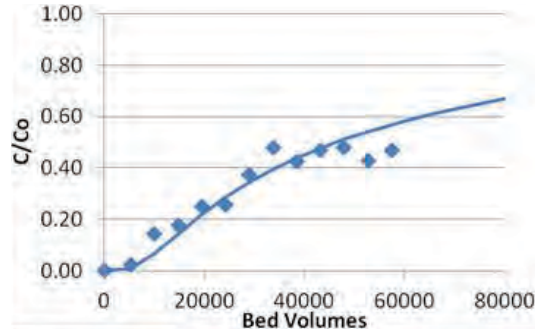


Figure 5-35. Example CXTFIT/EXCEL equilibrium advection-dispersion-retardation model calibration of copper breakthrough profile of column A3 in a bed packed with granular iron oxide (Columns A1–A3 in series). The column diameter was 1 cm ID, flowrate = 8 ml/min, the influent copper concentration was 50 μg/L, and the influent Zn(II) concentration was 100 μg/L. The influent ionic strength was 0.01M.

model was developed for tracer experimental data analysis to investigate transport of solutes in the groundwater systems. The model optimizes parameters for equilibrium or non-equilibrium advection-dispersion-reaction models. It uses an ordinary non-linear least squares method based on the assumption of normally distributed error and equal variance. Figure 5-34 provides an example of the model output for the removal of zinc from column A3 in which Columns A1, A2, and A3 were packed with iron oxide and the influent zinc concentration was 100 μg/L. The dispersion coefficient and retardation factor were the only fitting parameters in the model. The same dispersion coefficient was used for copper removal and then data for copper were fit by optimizing the value of the retardation coefficient as shown in Figure 5-35. More sophisticated analysis would include a reaction term to account for precipitation in the column. This model can be used in a predictive mode by adjusting the hydrodynamic parameters associated with the field scale conditions which will be evaluated in future phases of research.

SCMs can also be used to adapt the design sorption capacities to changing water quality conditions. Visual MINTEQ is a geochemistry code that incorporates ligand binding, surface complexation, and aqueous complexation using standard models. Moreover, Visual MINTEQ includes databases for surface complexation using the DLM for hydrous ferric oxide and hydrous manganese oxide. Thus, water quality conditions can be input to the model and the inherent database can be used to assess changes in sorption capacities for the specific metal ions.

CHAPTER 6

Conceptual BMP Designs

6.1 Basis of BMP Design Concepts

Design of treatment BMPs for highways has received considerable investigation for the past 25 years. Accordingly, there exist designs that are relatively proven in operation and can be constructed and maintained with common methods and equipment. Elements of these proven designs were used in the development of the concepts for the GFO media BMP. For example, the Austin Sand Filter has been designed and proven to operate passively in a highway environment and provide good particle removal with a reasonable maintenance interval. The proposed GFO BMP will operate using a similar horizontal bed configuration with a pretreatment chamber.

The prototype designs can operate passively and with deferred maintenance in the highway environment. The basic design constraints used to guide the development of the concept configurations (Caltrans 2004) included:

- Obstructions (above-ground obstacles and slopes greater than 4:1) within the clear recovery zone (30 feet from edge of traveled way) were avoided.
- Maintenance access with adequate room for maintenance vehicles and equipment must be available outside of the traveled way and shoulder areas.
- Passive operation required (no mechanical or powered components).
- Inspection is non-destructive, requiring minimum time and training of personnel.
- Maintenance intervals are reasonable (actual interval to be refined during prototype testing).
- The prototype design is compatible with typical highway drainage systems and requires a minimum amount of physical space.

Pretreatment of influent will be highly desirable to remove solids prior to introducing runoff to the GFO media. The typical suspended solids concentration in highway runoff nationally is 132 mg/l (Granato and Cazenas 2009). Pretreatment will extend the life of the filter media by reducing particles that would otherwise occlude the system. The prototype designs include a basic pretreatment layer to protect the GFO media but treatment prior to the BMP remains highly recommended. Various pretreatment strategies will be discussed.

Three configurations have been developed to accommodate the majority of the design scenarios that DOTs will need: highly urban areas, more rural locations with vegetated shoulders or embankments up to a 2:1 slope ratio, and on bridges. The urban area design was developed for highway cross sections that are largely impervious within the ROW. These locations will typically include a paved shoulder between the edge of traveled way and the curb, and pavement between the curb and the ROW. In the urban configuration, runoff is conveyed along the curb to a drain inlet that discharges to a longitudinal drainage system. The drainage system will typically discharge to a cross culvert (transverse to the highway centerline) at a location joining the adjacent municipal storm drain system. A below-grade vault design has been developed for urban locations that are compatible with the longitudinal drainage system, to preserve surface use, and avoid above-ground obstructions.

The second design was developed for locations with vegetated shoulders, with embankments up to a 2:1 slope ratio. Vegetated shoulders may also have a curbed section and a longitudinal drainage system, but in many cases the paved shoulder abuts a vegetated buffer strip that discharges to a longitudinal vegetated swale. The advantage of this type of design is that runoff may be intercepted in a sheet flow condition and vegetated strips are effective for pretreatment to remove solids in runoff. The prototype design is configured to work either with a vegetated swale system or with the media filter drain developed by Washington State DOT (WSDOT). The media filter drain (MFD) is constructed along the edge of shoulder usually following a gravel then vegetated strip, accepting sheet flow from the pavement surface. Both the swale and the MFD designs have the advantage of a relatively low hydraulic loading rate with an expected

advantage in an extended maintenance interval. The sub-drain system from the MFD is connected to the GFO vault for treatment. For the vegetated swale configuration, a drain inlet or culvert entrance is used to connect to the treatment vault. The vault spacing is generally dictated by cross-culvert locations to discharge treated effluent.

A third configuration has been developed for bridge decks. There may be some instances where dissolved metals removal from bridge deck runoff is desirable. Piping water to the bridge abutment is costly and introduces aesthetic and maintenance issues. The conceptual design integrates the media into the bridge scupper to treat bridge deck runoff.

6.1.1 Site-Specific Constraints and Design Considerations

Each of the three BMP concept configurations has been developed to provide the engineer with flexibility to integrate the units into existing and new highway drainage systems. General considerations for prototype design will include pretreatment of runoff, pH buffering, physical retention of the media, hydraulic design, and system maintenance.

6.1.1.1 General Constraints and Design Considerations—Pretreatment

- Pretreatment of runoff will be desirable upstream of the GFO media to extend the maintenance interval of the unit. The unit is configured as a vault for the urban and rural applications for the reasons discussed earlier, and to minimize the amount of media used since it is relatively expensive. Pretreatment strategies will reflect the configuration of the highway cross section, whether a longitudinal storm drain system is used, and the availability of ROW.
- One of the most flexible pretreatment approaches will be the use of a permeable friction course (PFC) overlay. Eck et al. (2012) have demonstrated that PFC overlays can reduce TSS concentrations in highway runoff to values less than 10 mg/l. PFC has the advantage that it can be placed as an overlay on most pavement sections and is compatible with either new construction or retrofit. PFC also has ancillary advantages such as reduced noise, improved visibility during rain events, and improved vehicle stopping. If the use of PFC is not desirable or feasible, pretreatment may be omitted if TSS concentration is relatively low (less than 100 mg/L). Alternatively, a pretreatment vault for TSS removal could be used.
- Vegetated filter strips may also be a suitable pretreatment strategy where discharge will be collected in open swales prior to treatment or as a part of a system using the WSDOT MFD. *NCHRP Report 565* notes that vegetated filter strips can routinely reduce TSS in typical highway runoff to less than 60 mg/l and routinely below 30 mg/l (third quartile). Vegetated strips may only be used in the absence of a curb and gutter system where runoff sheet flows from the paved shoulder.
- An alternative to filter strips is the MFD developed by the WSDOT. The MFD has a proven track record for both operation and maintenance and is documented to routinely reduce TSS from typical highway values to less than 20 mg/l (WSDOT 2006). The 'rural' area configuration for the concept BMP design was developed to be compatible with the MFD design, with vaults located at intervals governed by the desired maximum inflow along the system. The MFD system has the additional advantage of reducing runoff volume through exfiltration from the system. WSDOT limits the use of the MFD to 3:1 slopes. Prototype testing should include a configuration with the MFD on a 2:1 slope. Alternatively, flow can either be collected by a vegetated swale at the base of the slope, or collected and conveyed in a storm drain system to the treatment vault (with PFC as pretreatment).
- In highly urbanized areas there may not be sufficient space to install filter strips or MFDs and PFC may not be an option acceptable to the DOT. In these cases, the DOT may wish to consider a proprietary, below-grade device for pretreatment. The most effective of these devices for reducing sediment loads include a filtration process, either using a granular media or membrane.
- The conceptual BMP designs include a layer of sand and crushed concrete to cover the GFO media. The purpose of this layer is three-fold: first, the unit weight and the specific gravity of the media is less than water (40 lbs/cf vs. 100 lbs/cf) so the sand/crushed concrete mix is used to dissipate energy of the influent and prevent the GFO from becoming fluidized and/or experiencing media loss. The sand/crushed concrete layer may also modestly increase the pH of acidic runoff to enhance the performance of the media where acid rain conditions are present. The efficacy of this approach can be validated during prototype testing. Finally, the sand/crushed concrete layer also serves as a filter to reduce TSS loading to the media to ensure that it does not fail through occlusion prior to the laboratory estimated breakthrough volume for dissolved metals.

Pretreatment for some installations may be optional, if solids loading is expected to be relatively low or if a more frequent 'minor' maintenance of the sand layer is acceptable.

6.1.1.2 General Constraints and Design Considerations—Runoff Interception and Overflow

The conceptual designs for urban and rural areas were developed to accept runoff from a closed conduit system. Highway runoff that is collected in a longitudinal drainage

system (storm drain, or vegetated open channel) is introduced to the treatment vault through a flow splitter. The purpose of the flow splitter is to maintain a constant head on the filter media in the treatment vault, bypassing flows that would exceed the hydraulic capacity of the unit. The flow splitter is not necessary in the configuration using a MFD for collection.

A conceptual design has not been provided for the flow splitter. There are various public domain systems available that have been developed to facilitate the off-line operation of end of pipe BMPs. The practitioner is free to use an appropriate splitter design consistent with local practices and preferences. The splitter should discharge to the site storm drain system for bypass level flows, and to the treatment vault for flows at or below the hydraulic capacity of the media. Care should be taken to ensure that the treatment vault does not surcharge during high flow events. This can be accomplished by designing a splitter system that has a maximum operating water surface for the range of expected inflow.

6.1.1.3 General Constraints and Design Considerations—Maintenance and Estimated Service Life

Routine and major maintenance of the treatment vault will be required depending on the volume of inflow, effectiveness or presence of pretreatment, the TSS loading, and the dissolved metal loading. Routine maintenance tasks will include the following:

- Check operation of the flow splitter to ensure the diversion conduit and overflow weir are free of obstructions or solids buildup.
- Check the sand/crushed concrete filter layer for excessive solids buildup/occlusion. Occlusion is indicated when there is little to no effluent from the vault outlet pipe, indicating that most flow is bypassing.
- Remove trash/debris from the sedimentation chamber or area above the sand/crushed concrete layer for bridge scuppers.

Major maintenance tasks will include the following:

- Replace the sand/crushed concrete layer and top layer of geotextile
- Replace the GFO media and filter fabric.

6.1.1.4 Configuration #1: Urban Highways

The first configuration was developed for urban highway cross sections with a curb and gutter section served by a longitudinal drainage system. The media is held in a cast-in-place vault in a horizontal bed. Flow enters from the top of the media from a weir downstream of a debris chamber and exits through an underdrain below the media bed. The vault is intended to be placed near a discharge point for the highway longitudinal drainage system, such as at a cross culvert. However, the vaults may be placed at any location along the drainage system and the size of the filter bed is based on the desired flow rate. Figure 6-1 shows the basic configuration from a section view of the urban vault system.

The vault must be preceded by a splitter structure to ensure a constant head in the unit during operation. Flow enters the debris/sedimentation chamber in the treatment vault and ponds until it exceeds the height of the filter chamber inlet weir. The purpose of the gravel infiltration area is to eliminate standing water between storm events in the debris chamber. At the option of the designer, a concrete invert may be substituted, but standing water in the unit will result, and treatment for vectors in the debris chamber may be required. Influent then flows onto the crushed concrete/sand mixture. The concrete should be the same size as the sand and conform to the ASTM C-33 standards for fine aggregate. The crushed/concrete sand mixture is underlain by a woven filter fabric acting as a separation barrier between the crushed concrete/sand mixture and the filter media. The filter fabric should have an apparent opening size of 50 US sieve or smaller, and a flow rate of at least 10 gal/min/sf. Prototype testing should verify the use of a filter fabric as performance has been poor in some biofiltration designs due to clogging. The pretreatment specified for the GFO should reduce this potential, but field studies are required for verification of the final design configuration.

6.1.1.5 Configuration #2: Rural Highways

Figure 6-2 shows the vault configuration for rural highways. The configuration is very similar to an urban area, except that the vault is designed to accept input from the WSDOT MFD system or an open swale system transitioned to a closed conduit either through a culvert entrance or a drop inlet. Similar to the urban area, the vault is placed at intervals coincident with cross culvert or other discharge locations for the MFD.

Flow into the vault can be limited by an orifice plate at the vault entrance consistent with the capacity of the filter bed. A splitter structure is not needed with the MFD since the system will not accept discharges that exceed the capacity of the integral sub-drain system. The rural vault configuration can also be used with an open vegetated swale system. Flow from the open system can be directed to the vault via a short length of pipe. A diversion structure must be designed if an open ditch system is used to divert flow that exceeds the capacity of the vault. The vault will generally be placed at the base of the roadway embankment. Embankment slopes of any ratio can be accommodated, since the vault is designed to collect flow from a standard longitudinal drainage system (either open or

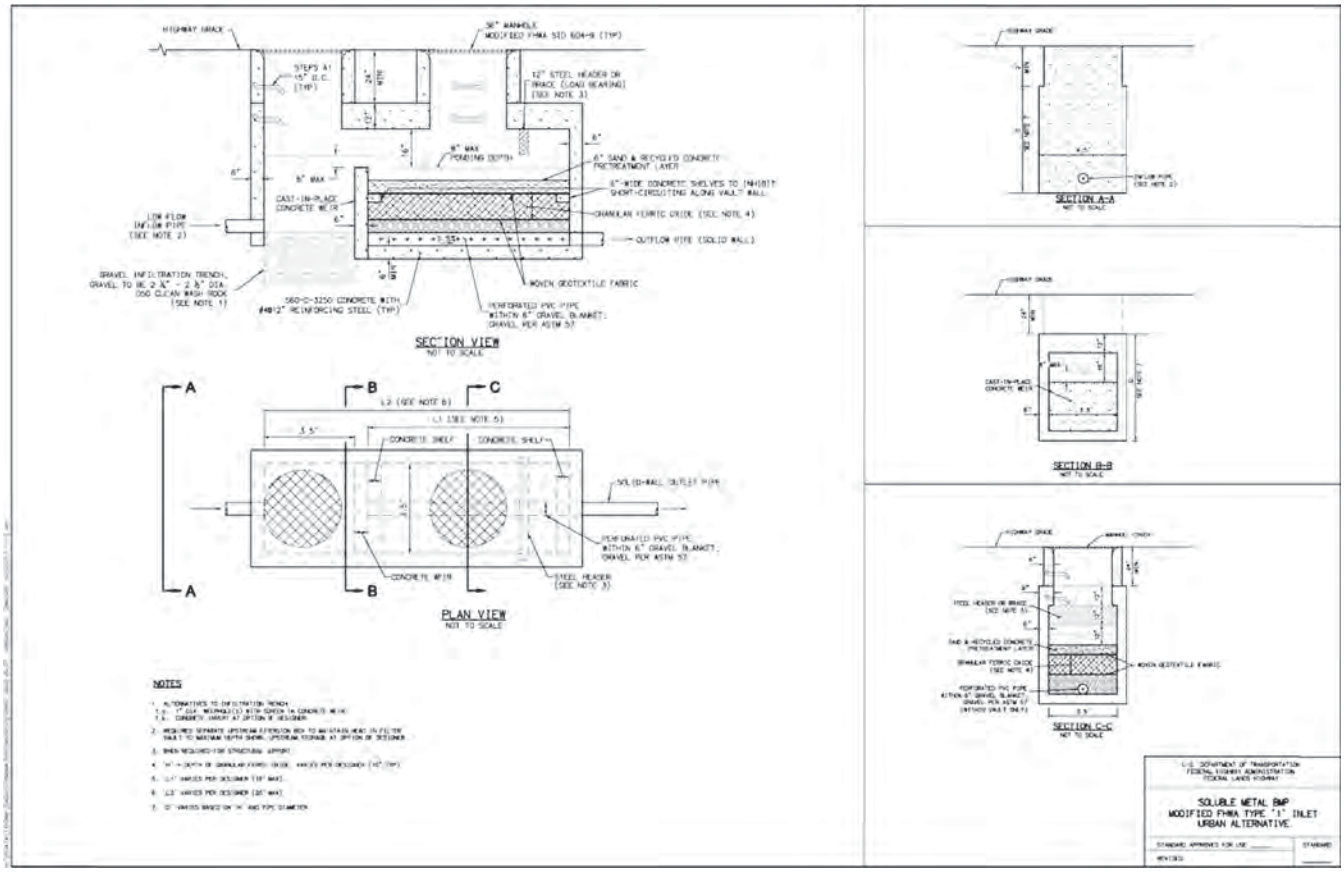


Figure 6-1. Urban vault system.

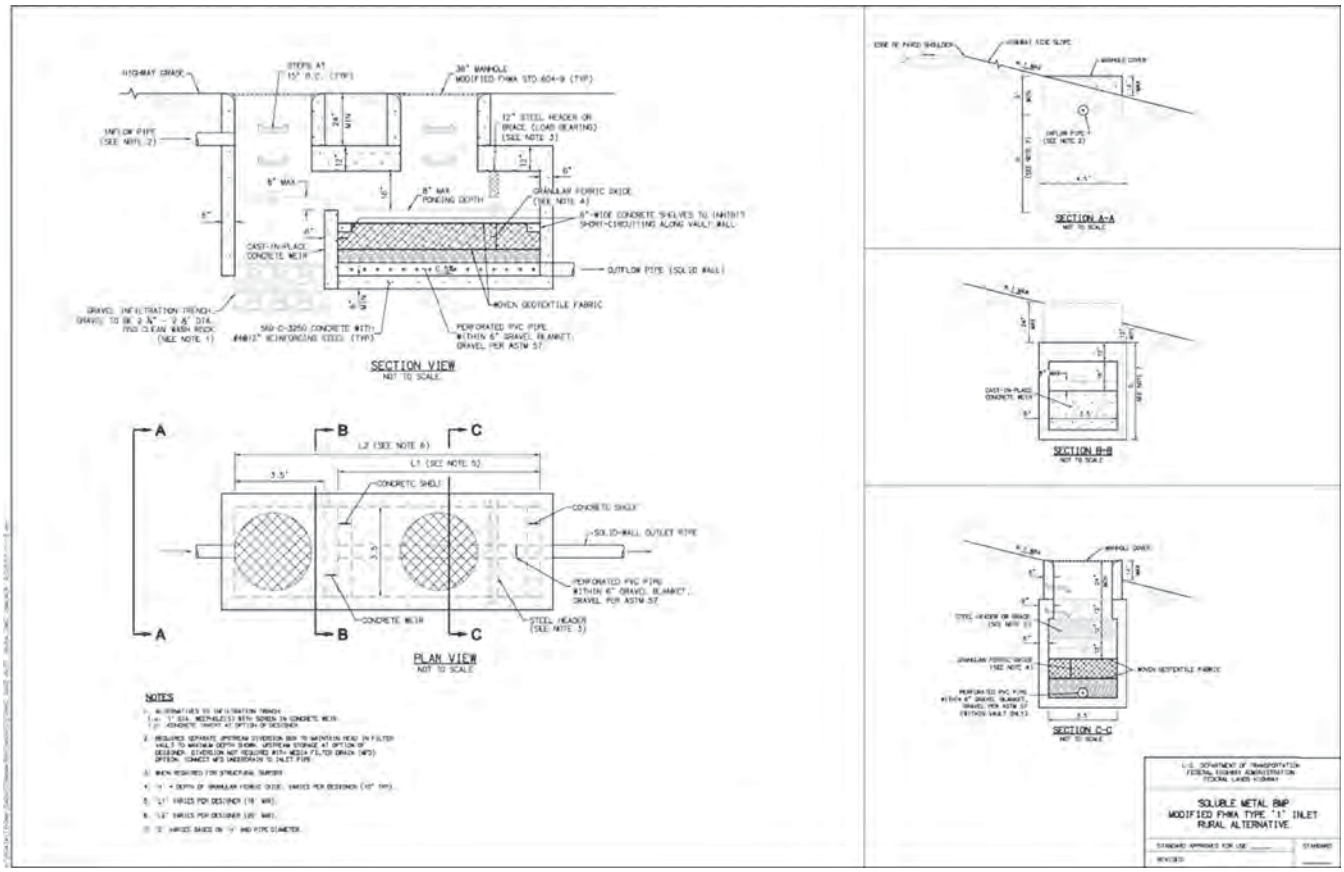


Figure 6-2. Rural vault configuration.

closed conduit). The GFO treatment vault used downstream of a WSDOT MFD is viewed as a 'polishing' step to further reduce the dissolved fraction of metals that are untreated by the MFD.

6.1.1.6 Configuration #3: Bridge Decks

The third configuration is designed for bridge deck drainage systems. The media is housed in a modified bridge scupper to serve a designated portion of the bridge deck area. Figure 6-3 shows a section of the bridge scupper. The scupper is designed for interception of the 'water quality' design flow only, and must be followed downgrade by a scupper designed to intercept the remaining drainage flow to maintain flooded width criteria. The scupper can be fabricated from concrete or steel, or cast integrally with the bridge deck.

6.1.2 Design Procedure

The design procedure for the vault or inlet scupper is based on laboratory column tests. A spreadsheet has been developed to assist in sizing the filter bed in the vaults and the bridge deck inlet scupper. The media depth is fixed at a minimum value (10 inches) in the spreadsheet, to achieve a minimum contact time with the media consistent with that obtained during the column testing (3 minutes). Thicker media depths may be used, but the required head should be computed using Darcy's Law. The permeability of the media (K) was determined to be 0.24 cm/s. Caution should be used in developing designs with head requirements that are relatively large since the effective solids loading rate of the media will be higher, resulting in shorter runs between maintenance intervals due to possible media occlusion.

User input cells on the spreadsheet are shaded in blue. Output cells are shaded in green. The user inputs the area of the tributary highway cross section, the trial vault dimensions, and the spreadsheet computes an estimated vault spacing. Hydraulic sizing computations in the spreadsheet are based on a media loading rate of 2 gpm/ft^2, a media thickness of 10 inches, and a required head of 8 inches.

The media breakthrough time is estimated based on the laboratory testing. At a pH 7, the estimated log Kd for the system was determined to be 5. Using the linear isotherm equation:

$$qe = KdCe$$

and a value of 3 μg/L for Ce and a Kd of 10^5 L/kg, yields a required adsorption capacity of 300 mg removed/kg of GFO. For example, assuming 30 in./yr of rainfall over a one

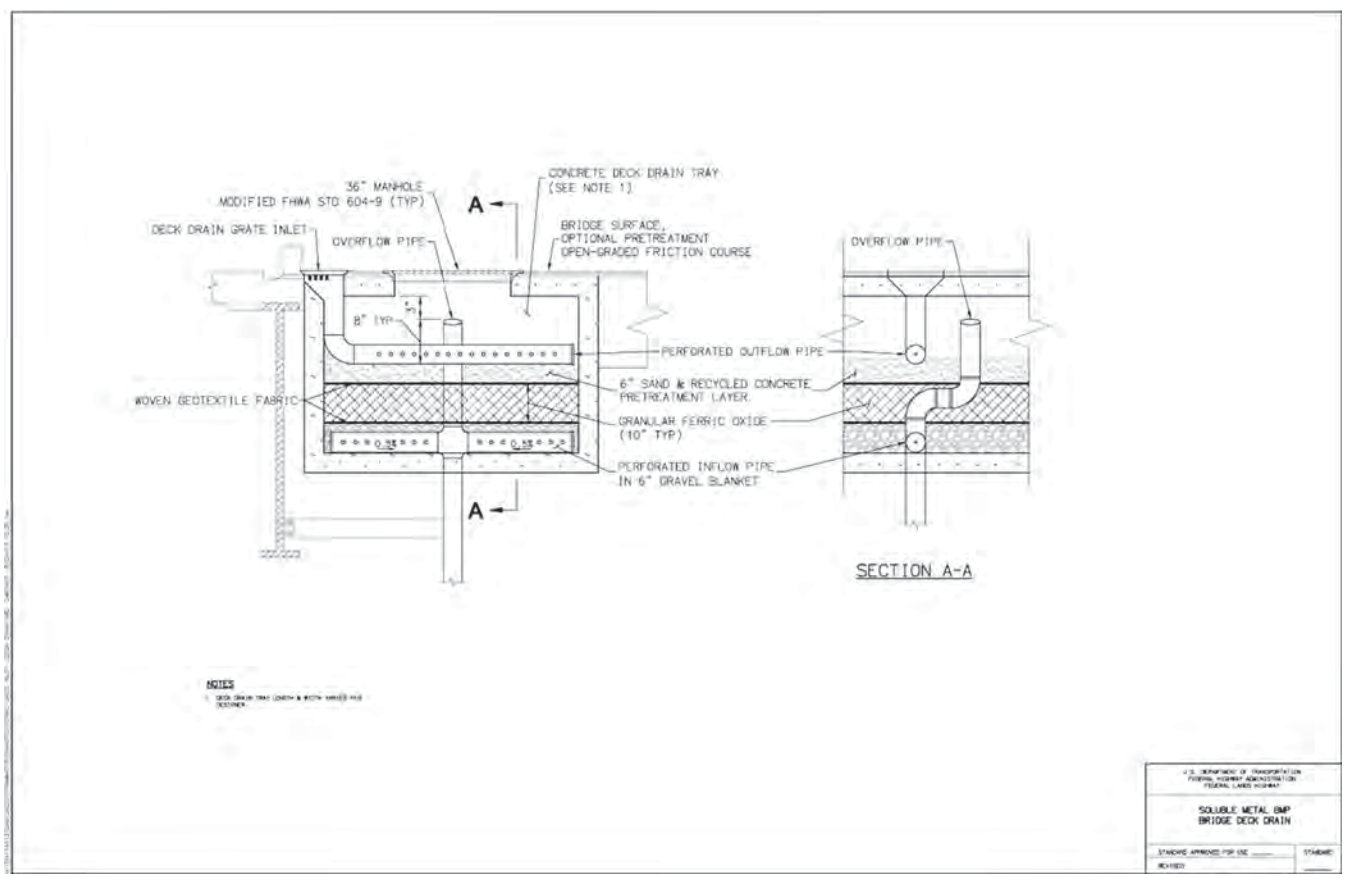


Figure 6-3. Inlet scupper with media.

acre drainage area yields a volume of stormwater runoff of approximately 3,000 m^3 per year. For an influent copper concentration in the stormwater runoff of 10 μg/L and desired effluent concentration of 3 μg/L, the required mass of copper adsorbed per year is approximately 22 g. Dividing the copper adsorbed per year by 300 mg removed/kg of GFO yields a GFO demand of 72 kg/yr. The unit weight of GFO was measured as 40 lb/ft^3 or 640.74 kg/m^3.

The spreadsheet also provides capital and O&M and whole life cost estimates using user provided unit prices. The unit cost of GFO provided in the spreadsheet as a default is $15/lb. This cost is likely to decrease for GFO purchased in bulk quantity, and represents the cost of the material obtained for the laboratory trials. The user can overwrite the default unit prices for GFO, poured in place concrete, and the cost to remove and dispose of spent filter media on a per vault basis.

6.1.2.1 General Sizing and Hydraulic Loading

The laboratory testing was completed using columns with a cross sectional area of less than a square centimeter. Consequently, the hydraulic sizing procedure provided in the spreadsheet must be validated during prototype testing. It is likely that the field permeability of the media will vary from that tested in the laboratory, and the permeability will change over time as solids accumulate. The crushed concrete/sand filter layer is used to reduce the solids loading to the media and extend the media life. Therefore, the anticipated change in permeability for the media over the operating life of the filter should be relatively small.

The crushed concrete/sand layer and geotextile must be removed and replaced whenever the head requirements for the design flow become unacceptably high. Pretreatment of flow is recommended to maximize the maintenance interval of the top layer and geotextile fabric. Oversizing the vault will also increase the maintenance interval, but the cost of the GFO media likely makes this option less desirable than a more effective pretreatment system. In summary, the prototype testing program should assess a range of filter bed sizes based on the variables of solids loading, copper loading, flow, media thickness and contact time, hydraulic loading rate, and time to breakthrough. The initial values for these parameters in the spreadsheet tool that can also be used to develop the prototype designs (measured data where appropriate is preferable) are:

- Solids loading: 100 mg/l
- Copper loading: 10 μg/l
- Media thickness: 10 inches
- Media contact time: 3 minutes
- Hydraulic loading rage: 2 gpm/ft^2 (based on laboratory testing)
- Adsorption: 300 mg (copper in influent)/kg (GFO media)

The study team found that there are a variety of grain sizes commercially available for GFO. The study team recommends that the prototype testing evaluate the efficiency of the media for metals removal as well as the time to breakthrough and hydraulic performance.

6.1.2.2 Regional Considerations for General Sizing Criteria

Locations with high metals loading rates and high average annual rainfall will require larger amounts of media and more frequent maintenance intervals than those areas with lower metals loading and lower annual rainfall. Annual loading rates for TSS and metals will be the most important considerations when sizing the vault or bridge scupper. Retention of metals on the media in areas with acid rain may vary compared to those areas with more pH neutral rainfall. Ultimately, regional testing of the design to assess variability in performance and operation will be desirable.

The design is likely optimized by providing storage upstream of the vault to reduce the filter bed size. The design water quality volume or flow rate will be dictated in most cases by state criteria. In absence of a required flow or volume design standard, the guidelines published in the ASCE Manual of Practice No. 87, *Design of Urban Stormwater Controls*, is recommended. This publication provides a method to compute a localized treatment volume based on a maximized detention volume concept to capture the average annual volume whereby beyond this value relatively larger increases in incremental storage volume are required for diminishing increases in average annual percent capture. This type of procedure is recommended as one approach to normalize BMP sizing based on local rainfall and approximate a maximum extent practicable (MEP) standard.

6.1.3 Description of Construction Details of Preferred Concept Alternatives

The prototype design was developed to be simple to construct using locally available components such as standard manhole rings and covers. Cast-in-place concrete is recommended to allow vaults and bridge scuppers of various sizes to be used, though precast components are a viable option. Structural design may be optimized from that shown based on soil unit weight and expected lateral earth pressure and location of the water table for the design depth though a single standard will likely be sufficient for the vast majority of installations.

Manhole access is recommended to be 36″ without a taper to allow extra room for vactor operations to remove spent media and place new media. Confined space procedures will be required. The perforated outflow pipe should be connected to a receiving storm drain system for discharge. Access should be provided at the connection location, and the length of the

discharge pipe should be limited to about 100 feet without intermediate access.

6.1.3.1 Configurations #1 and #2: Urban and Rural Highways

The concept prototype design shown in Figure 6-1 accepts flow from a splitter structure and introduces it to a storage chamber. The primary purpose of the storage chamber is to reduce the size of the filter bed. The dimensions of this chamber can be optimized based on the estimated maintenance interval of the filter bed using the spreadsheet tool. The storage can also be varied to meet physical constraints of the longitudinal drainage system such as available discharge locations. The structure should be designed with the minimum depth possible for ease of construction. The dimensions of the filter chamber will be based on the hydraulic loading rate. The chamber may be constructed to any dimension, though in the concept prototype design, the width has been shown as 3.5 feet to be compatible with the manhole access and limit the sub-drain to a single outlet pipe. Wider filter chambers would require multiple outlet pipes and a manifold. The designer may want to consider sloping the filter chamber invert slab for designs that become longer or wider than about 5 feet to improve drainage of the media. The outlet pipe should rest on the invert slab with perforations along the entire circumference. The outlet pipe should not be raised off of the invert, since positive drainage is needed to completely drain the filter chamber of the vault.

6.1.3.2 Configuration #3: Bridge Decks

The scupper prototype configuration will be cast integrally with the bridge deck for concrete box girder and slab designs. Other design configurations will be required for steel bridges. Solids loading on bridge decks is generally consistent with at grade roadways. Due to the relatively confined dimensions of the scupper inlet, pretreatment for solids removal on a bridge deck would be a prerequisite. To reduce solids loading to the bridge scupper, a PFC overlay is recommended. As previously indicated, PFC overlays have been shown to be effective in reducing TSS in highway runoff. A PFC overlay can be used on a bridge deck to achieve solids reduction. Specific design will be based on local conditions, but the overlay should probably be discontinued at a distance from the bridge railing coincident with the edge of the scupper inlet to allow the flow within the overlay to collect in an effective 'gutter' area. It is also recommended that a second scupper inlet is provided downstream of the treatment inlet in the event that the treatment inlet becomes blocked with solids.

CHAPTER 7

Recommendations for Future Work

7.1 Introduction

During the course of this work, a number of items related to the removal of dissolved heavy metals in stormwater were identified that deserve additional research. These include:

- Field testing of GFO
- Characterization of highway runoff
- Modification of PFC

7.2 Field Testing of GFO Conceptual BMPs

The highest priority for future work should be to verify the results of this research through a field verification program. There are a number of reasons why the laboratory results may not be directly transferable to the highway environment. First of all, the synthetic stormwater used in the laboratory experiments did not include any solids. This was necessary in the lab because sediment would have clogged the small diameter columns used in the experiments, likely before the adsorption capacity of the media was exhausted. The solids present in actual runoff will need to be reduced in a pretreatment step to avoid rapid clogging and blinding of the adsorptive media. Nevertheless, some solids will remain, so the adsorptive media will still be subject to some degree of solids loading, which will have a significant impact on both performance and maintenance requirements. These items can only be investigated through a prototype field testing program.

The laboratory work also demonstrated that the amount of organic matter and alkalinity have a very strong impact on the ability to remove dissolved copper from runoff. A field evaluation is critical for determining the precise levels at which adsorption becomes ineffective for dissolved copper removal.

Although this work was focused on the removal of dissolved heavy metals, field testing may identify other water quality benefits as well. GFO is frequently used in aquarium filters to reduce phosphate levels in the water to prevent algal growth and the original material used in these tests was actually acquired from a business that sells aquarium supplies. It is very likely that this reduction in phosphorus will also occur when stormwater is treated. Phosphorus is generally the controlling nutrient in fresh water systems for eutrophication, and the tools available for reducing dissolved phosphorus concentrations are limited. Consequently, quantifying nutrient reduction in the field setting is also a priority.

7.3 Additional Characterization of Highway Runoff

Many highway runoff characterization projects involve only a limited suite of constituents, typically those thought of as constituents of concern. These include solids, nutrients, and selected heavy metals. What this research has demonstrated is that many of the secondary constituents, normally not regarded as pollutants, have a very strong impact on the effectiveness of adsorption for removing dissolved metals. These other constituents include species such as carbonate (a component of alkalinity), NOM, and others. In order to determine whether GFO can be effective and used widely, a better characterization of stormwater from selected locations across the country should be encouraged. This characterization must include pH, TOC, and a full suite of inorganic ions, such as typically used by the U.S. Geological Survey when sampling natural systems. The results of this monitoring program can then be input into chemical speciation and adsorption computer models to predict the effectiveness of GFO for dissolved metals removal for various regions of the country.

7.4 Incorporation of GFO in the PFC

A PFC, which is also known as open graded friction course (OGFC), is a porous asphalt overlay increasingly used by DOTs as a wearing course that improves safety during wet

weather. Recent research in the United States and Europe has demonstrated that pollutant concentrations in runoff are substantially lower than conventional asphalt or concrete surfaces (e.g., Eck et al. 2012). The primary pollutant reduction process appears to be removal of solids and associated pollutants through sedimentation and filtration. PFC appears to be one of the better options for stormwater treatment for highways in that it provides treatment within the pavement itself, rather than requiring additional ROW, construction of structural treatment controls, and their continued maintenance. One drawback is the lack of effectiveness for dissolved constituents.

A back of the envelope calculation suggests that there is sufficient porosity in PFC that GFO could be incorporated into the pavement after it is installed, which potentially increases the removal of both dissolved heavy metals and dissolved phosphorus. The initial evaluation could be carried out at the laboratory scale to determine the effectiveness for pollutant removal as well as the impacts on permeability and porosity of the PFC. Should the results be promising, a follow-up field study could then be conducted to determine the best method for placement on an actual highway and verification of the pollutant removal performance.

7.5 Incorporation of GFO in Filtration Systems

GFO could also be incorporated into BMPs that include a filtration component as a unit process. One example is the MFD developed by WSDOT. The MFD mix is a mixture of crushed rock, dolomite, gypsum, and perlite. The crushed rock provides the support matrix of the medium; the dolomite and gypsum add alkalinity and ion exchange capacity to promote the precipitation and exchange of heavy metals; and the perlite improves moisture retention to promote the formation of biomass within the MFD mix. GFO could be incorporated uniformly throughout the mix or installed just above the underdrain, with the media filter providing a level of pretreatment.

There are also a variety of proprietary, below-grade systems that include a filtration component. Many times these filters include a special mix of zeolites, perlite, activated carbon, and other constituents. GFO could be included as one of the components to improve dissolved metals removal. Whether the MFD or modification of a proprietary device is of interest, field testing would be needed to verify the pollutant removal prior to widespread implementation.

CHAPTER 8

Summary and Conclusions

8.1 Introduction

The objective of this chapter is to provide a brief summary of the results achieved during this research project. Various topics have been investigated including:

- Characterization of highway runoff
- Environmental chemistry of dissolved metals in natural surface waters
- Previous work on the removal of dissolved metals in runoff
- A laboratory evaluation of the dissolved metals removal for selected materials
- Development of conceptual BMP designs for the most promising materials
- Identification of future research needs

Each of these topics is discussed in more detail below.

8.2 Characterization of Highway Runoff

The concentrations of metals in highway runoff are generally higher than observed in natural water bodies, which leads to concerns about potential toxicity. In fact, several studies have demonstrated acute and chronic toxicity to aquatic ecosystems, and metals are commonly listed as a cause of impairments in receiving waters in the United States. A fact that is often overlooked is that the distinction between dissolved and particulate associated metals is operational rather than chemically based. Laboratory methods for determining the fraction of a metal in the "dissolved" phase are based on the mass passing through a 0.45 μm filter. Clearly, this is a rather arbitrary division, since many particles can be smaller than this threshold. In addition, metal ions can be associated with organic and inorganic ligands rather than existing as free ions. Consequently, dissolved is not synonymous with ionic. A study of metal transport in the Sacramento River indicates that up to 70% of the metals characterized as "dissolved" according to standard protocols are actually associated with colloidal particles and may not be bioavailable.

Organic constituents in highway runoff also have an important role in determining the bioavailability of dissolved metals and the effectiveness of various treatment processes. These constituents include oil, grease, humic acids, plastics, tire rubber, fecal material, PAH's, phthalates, pesticides, and herbicides, which are derived from a variety of natural and anthropogenic sources.

Stormwater runoff also transports significant loads of dissolved, colloidal, and suspended particles in a complex mixture that includes metals and inorganic and organic compounds. Knowledge of the PSD and the association of metals with the various size fractions is required to design an effective system for reducing the concentrations of metals in highway runoff. Although small particles have a relatively high SA, the majority of the mass of sorbed metals is often found associated with larger particles because of their substantially greater mass.

In order to accurately characterize dissolved metals characteristics in stormwater, a rigorous protocol is required for both sampling and analysis due to the very low concentrations at which these species impact aquatic life. A protocol was developed as part of this effort and is included as a standalone document in Appendix A that can be used directly by DOTs and their consultants to assess dissolved metals concentrations.

8.3 Environmental Chemistry of Metals in Natural Waters

Chemical speciation in natural waters has significant implications for controlling the mobility, toxicity, and bioavailability of metals in water. Metal ion properties and solution chemistry dictate the speciation and determine the extent of sorption to inorganic, organic, and biological particulate matter. The key processes that must be considered for predicting metal ion speciation are acid/base chemistry, complexation with simple inorganic ligands (CO_3, SO_4, etc.),

complexation with NOM, oxidation/reduction reactions, precipitation, and sorption.

This literature review presented a brief description of each of these processes and identified their impact on speciation of commonly identified metal ions. The review has identified state-of-the-art approaches used to predict metal ion speciation for each of these processes, and has highlighted interactions among these processes that affect metal ion speciation. The complexity of natural water chemistry was emphasized throughout the review, especially with respect to the heterogeneity of NOM and approaches for incorporating NOM into predictive speciation models.

Finally, the impact of metal ion speciation on bioavailability was addressed, and a description of the BLM was presented. The BLM represents an approach to incorporate all processes affecting metal ion speciation into a toxicity model for predicting the impact of metal ions on target organisms (the biotic ligand). The bioavailability of metal ions is dependent on the speciation in solution, the affinity of metal species for surfaces on organisms, the modes of transport through biological membranes, and metal ion toxicity. The BLM predicts complexation of the metal ion with a specific receptor site within an organism where metal complexation leads to acute toxicity. This model represents the state-of-the-art with respect to predicting metal ion toxicity in natural waters and has significant potential as a regulatory tool.

Water quality standards for dissolved metals in many receiving waters are based solely on the hardness of the water, which is a function of calcium and magnesium concentrations. These other metal ions compete for sorption sites on aquatic organisms and reduce the toxicity of heavy metals that may be present. This review has indicated that there are many other factors that affect dissolved metals bioavailability and that need to be considered when developing water quality standards. Consequently, many current standards may be overly conservative and need to be reconsidered in light of this information.

8.4 Previous Studies of the Treatment of Dissolved Metals

Previous studies concerning the removal of dissolved metals, identification of candidate materials for evaluation, and how these materials could be included in conceptual designs for stormwater treatment systems were reviewed. Treatment of runoff transporting particulate-bound metals generally requires sedimentation, coagulation/flocculation, filtration, or combinations thereof. In contrast, dissolved metal complexes and metal ions can be more effectively removed using adsorption, ion exchange, or surface complexation mechanisms.

A variety of in situ structural BMPs that are designed for infiltration to surrounding soil have been developed that remove metals. Infiltration systems are adaptable and potentially can remove dissolved and particle-bound constituents. Benefits of these infiltration BMPs are increased mean residence times relative to pre-BMP conditions, and promotion of high discharges to surrounding soils, even for soils with low saturated hydraulic conductivity. Infiltration BMPs in soils of lower hydraulic conductivity (typically clayey materials of higher SA and surface charge) have a reduced risk for soil and groundwater contamination resulting from increased loadings of pollution in urban and highway runoff, especially heavy metals.

Metal adsorption onto natural and engineered media, such as sand, soils, activated carbon, and oxide-coated media, has been studied by many researchers. Results from this previous work demonstrated that plain sand or gravel media has insignificant SA and is ineffective for removal of dissolved stormwater metals. Consequently, researchers have often augmented the sand filter media with organic matter, perlite, and zeolite, all of which have shown only modest effectiveness for dissolved metals removal.

Oxide-coated metals have long been used for dissolved metal adsorption. These mineral surfaces are amphoteric (net surface charge is a function of pH). This leads to the idea that engineered amphoteric oxide-coated surfaces on stormwater filter media can have large SAs for adsorption and precipitation processes in a chosen pH range. Therefore, engineered media such as the oxide-coated filter substrates or cementitious media with high SA can be utilized to remove dissolved metals in a variety of treatment configurations.

A common choice for sorption of dissolved metals is iron oxide coated media. Previous research with respect to performance of iron oxide-coated media for sorptive-filtration of stormwater has demonstrated proof-of-concept for oxide-coated media in stormwater treatment systems. Engineered media also include manganese oxide-coated polymeric and cementitious media. MO have a PZC below the typical pH range of runoff resulting, allowing their use as adsorbents without pH control.

Cementitious media such as graded concrete, masonry, rubble, or brick, when coated, sprayed, or synthesized with oxides or oxide-admixture, can be effective for metal removal. The idea of using cementitious infrastructure material or recycled cementitious material is based on three advantages beyond the inherent economy of the substrate. First, cementitious material increases the alkalinity. This alkaline environment will not only improve the metal removal efficiency by precipitation of dissolved metals, but also benefit from the electrostatic interaction between the oxide and dissolved cationic metal, because MO have larger negative surface charge in higher pH solutions.

A number of recent studies have evaluated low cost adsorbents for metal ion removal from stormwater. While many of these have little potential for widespread application due

to impacts on pH, headloss, and clogging, one particular material that has demonstrated potential for application to stormwater treatment is crab-shell waste. The combination of chitin and calcium carbonate has been proposed as an ideal media combination because the calcium carbonate promotes the formation of metal carbonate microprecipitates and chitin is a good adsorbent for these microprecipitates.

Based on this review of the literature, the following materials were recommended for further evaluation for the removal of dissolved metals in highway runoff.

- Iron and MO have demonstrated the highest potential for adsorbing the range of metals observed in highway runoff. Therefore, commercially available forms of these oxide metals should be evaluated as well as mixtures containing both types of media. The pH of the PZC is different for these two oxides. Therefore, both types of media should be tested over a range of pH values for a variety of metals that exhibit varying affinity for the oxides. Concentration ranges to be tested should be consistent with the concentrations observed in stormwater.
- Concrete materials and calcite offer the possibility of providing adsorptive capacity as well as pH buffering. Both of these materials should be assessed for their potential for adsorption of metal ions. While calcite represents a well-characterized and less variable material, concrete provides the opportunity to recycle waste materials. Preliminary experiments with concrete should include evaluating differences among different concrete sources including concrete rubble, crushed concrete, or recycled concrete.
- Crab shell has also been shown to have potential for removal of metal ions from stormwater due to the presence of chitin and calcium carbonate. Thus, these sorbents should be evaluated for their potential to synergistically promote adsorption of metal ions.

8.5 Laboratory Evaluation of Dissolved Metals Removal

The goal of this effort was to develop and verify laboratory testing and modeling methods to determine the effectiveness of adsorption for reducing the dissolved metals concentration in stormwater. One of the major challenges of this project was in selecting the composition and sources of the synthetic stormwater to be used during the experimental testing phase. Previous research has employed both natural stormwater that has been obtained from actual field highway runoff sites (natural stormwater) as well as synthetic stormwater compositions that have attempted to mimic the major components of natural stormwater.

A compromise between using natural and synthetic stormwater was made by recognizing the importance of capturing the organic matter from natural stormwater, but adding the flexibility of using synthetic stormwater to provide the ionic composition. To alleviate concerns associated with storing large volumes and aging of organic solutions, the stormwater was concentrated within 24 hours of collection using reverse osmosis and then the organic matter freeze-dried. The freeze-dried organic matter was reconstituted as needed at concentrations that mimic the initial total organic concentration of the stormwater when it was collected.

Two types of experiments were conducted to evaluate dissolved metal behavior: batch experiments and column experiments. Batch experiments were used to evaluate sorption equilibria over several orders of magnitude in initial metal ion concentration at a fixed pH. Experiments were conducted with each metal ion individually in single solute systems as well as in multi-solute systems. The data from these models were then used to calibrate and verify surface complexation model parameters that can be used to predict the extent of sorption over a range of solution conditions such as pH, ionic strength, and solution compositions. Upon completion of the batch equilibrium experiments, bench scale flow-through columns packed with the selected media were used to assess the rates of adsorption and to verify the equilibrium studies. These data will be used to calibrate dynamic models or used in scaling approaches to predict performance at field scale.

A number of issues were identified and addressed while conducting the laboratory experiments that will be incorporated in the recommended protocol for future testing. An example of one of these issues is the difficulty in controlling pH during each experiment. pH is by far the largest factor affecting the solubility, adsorption, and precipitation of dissolved metals in runoff, so it is of paramount importance that it be maintained at a constant level during the column experiments. It was observed that even exposure to the atmosphere will cause the pH to drift as carbon dioxide is absorbed. Consequently, a nitrogen blanket over the synthetic stormwater to manage the pH level had to be provided.

The experimental work evaluated two metal oxides, iron and manganese, both of which are available commercially. The results indicate that the iron oxide provided substantially better removal of dissolved metals under the aerobic conditions of this study than manganese oxide. The high removals reported for manganese dioxide in previous experiments were likely the result of the cementitious substrate on which the manganese was deposited.

The two metal oxides in conjunction with crab shell waste and recycled concrete were also evaluated. Both materials raised the pH at least briefly at the start of an experimental run, which increased zinc removal, but had little effect on copper adsorption. The crab shell and recycled concrete also tended to stabilize the pH, which would be beneficial in the design of a passive treatment system for metal ion removal,

since the pH of rainfall can vary substantially. Another important point of interest is that the pH of the system increased for a short period of time after the flow was interrupted for more than 24 hours. This type of behavior may result in significantly better removal in field scenarios and should be evaluated further.

The research also found that DOM significantly reduces dissolved metal sorption and should be included in any synthetic stormwater cocktail. In this study, we first concentrated DOM in highway runoff and then had it freeze-dried to reduce the potential changes in form that might occur over time. Re-dissolving the organic matter was not as straightforward as just adding water, however. This difficulty was addressed by including a sonication step, but in the future, it is recommended that freeze drying this material be avoided, since the changes that might occur during this process could easily be as large as those caused by aging.

It was also demonstrated that the laboratory results were in good agreement with model predictions. There are complex models such as SCMs and ligand binding models that can be incorporated into transport codes and are useful for evaluating the impact of various parameters on adsorption; however, the results of this research suggested that pH control is the most important operating parameter for stable operation of a treatment system. Consequently, a relatively simplistic and user-friendly model, CXTFIT/EXCEL, was used to model these experimental results. This model can be used in a predictive mode by adjusting the hydrodynamic parameters associated with the field scale conditions that should be evaluated in future phases of research.

Runs were also conducted using actual stormwater runoff collected from a highway in the Austin, TX area. Removal of dissolved copper was much worse than expected. This is likely attributable to the high alkalinity and pH of the runoff, since in this environment much of the copper is present in a relatively inert form. By simulation with Visual MINTEQ, it was determined that under the conditions found in our actual stormwater, over 80% of total copper exists as dissolved copper carbonate, which does not directly sorb to GFO, and less than 3% of total copper is present in the form of cupric ion. Consequently, adsorption of dissolved copper will not be a very effective process in runoff with substantial carbonate concentrations. Conversely, zinc removal was relatively more successful as compared to the tests utilizing synthetic stormwater. This can be explained by the high pH of the stormwater, which increases the tendency of zinc ion to sorb on to the surface of the oxide media. Processes that increase precipitation of carbonates could reduce the carbonate concentration to levels that would substantially increase Cu sorption.

Finally, some calculations to determine the amount of iron oxide media that would be required for a system with an operational life (the period over which a dissolved copper concentration of less than 3 μg/L is achieved) of 10 years were made. The calculations indicate that the footprint of the system would not be excessive (approximately 30 square feet) and the cost of media to provide 10 years of treatment for the runoff from one acre of pavement getting 30 inches of rain/year could be as little as $6,400/acre.

8.6 Stormwater Treatment Conceptual Designs

The conceptual designs for the treatment devices were based on the opportunities and constraints identified in the literature review for candidate material selection. The candidate materials have a variety of preferred operating conditions that were accommodated in the prototype designs. The designs targeted compliance with the most restrictive receiving water standards for dissolved metals.

The prototype designs are passive, practical, and able to operate with deferred maintenance within the constraints of a highway environment. Some of the practical constraints identified in previous treatment BMP studies for highways (Caltrans 2004) that were used include:

- No obstructions (above-ground obstacles and slopes greater than 4:1) within the clear recovery zone (30 feet from edge of traveled way) should be avoided.
- Maintenance access with adequate room for maintenance vehicles and equipment must be available outside of the traveled way and shoulder areas.
- Passive operation required (a minimum of mechanical and powered components).
- Inspection should be non-destructive and require minimum time and training of personnel.
- Maintenance intervals should be reasonable (annual is a preferred minimum).
- The prototype design should be compatible with highway drainage systems and require a minimum amount of physical space.

Three configurations have been developed to accommodate the majority of the design scenarios that DOTs will need: highly urban areas, more rural locations with vegetated shoulders, and on bridges. The urban area design was developed for highway cross sections that are largely impervious within the ROW. In the urban configuration, runoff is conveyed along the curb to a drain inlet that discharges to a longitudinal drainage system. The drainage system will typically discharge to a cross culvert (transverse to the highway centerline) at a location joining the adjacent municipal storm drain system. A below-grade vault design has been developed for urban locations that are compatible with the longitudinal drainage system, to preserve surface use and avoid above-ground obstructions.

Locations in rural areas with vegetated shoulders may also have a curbed section and a longitudinal drainage system, but in many cases the paved shoulder abuts a vegetated buffer strip that discharges to a longitudinal vegetated swale. The advantage of this type of design is that runoff may be intercepted in a sheet flow condition and vegetated strips are effective for pretreatment to remove solids in runoff. The prototype design is also configured to work with the MFD developed by WSDOT.

A third configuration has been developed for bridge decks. There may be some instances where metals removal from bridge deck runoff is desirable. Piping water to the bridge abutment is costly and introduces aesthetic and maintenance issues. The conceptual design integrates the media into the bridge scupper to treat bridge deck runoff.

One of the major needs when installing systems for dissolved metals removal was identified as the need to provide pretreatment to reduce solids loadings on the systems. Potential pretreatment options were identified as vegetated filter strips, MFDs, and the PFC. The feasibility of each of these options is to a large extent a function of the available ROW.

A sizing spreadsheet was also developed that provides capital, O&M, and whole life cost estimates using user–provided unit prices. The user can overwrite the default unit prices for GFO, poured in place concrete, and the cost to remove and dispose of spent filter media on a per vault basis. Locations with high metals loading rates, and high average annual rainfall will require larger amounts of media and more frequent maintenance intervals than those areas with lower metals loading and lower annual rainfall. Annual loading rates for TSS and metals will be the most important considerations when sizing the vault or bridge scupper.

8.7 Recommendations for Future Research

Finally, a number of items were identified for future research. These include:

- Field testing of GFO conceptual BMP designs
- Characterization of highway runoff
- Modification of PFC

The most obvious need is a field testing program for the conceptual BMP designs. There are two primary objectives. One is to validate the laboratory evaluation protocol to verify that the results are applicable in the field setting. The second objective is to determine the efficiency of pretreatment process for reducing the solids load on the adsorptive media and how the presence of the remaining solids impacts the adsorption of dissolved metals.

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APPENDIX A

Practical Guidance for Measurement of Dissolved Metals in Stormwater Runoff

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CHAPTER 1
Introduction

One major challenge associated with characterization of receiving waters and stormwater runoff, as well as assessment of BMP effectiveness are the low concentrations that must be achieved to meet water quality standards (Table 1). When hardness is depressed in a freshwater receiving water body, the water quality standards for dissolved copper, lead and cadmium can approach the detection limits that can reasonably be achieved by most laboratories. The difficulties in measuring trace metals in ambient waters became readily apparent in the late 80s and early 90s when surveys using ultraclean, reliable sampling and analytical methods (Shiller 1987; Horowitz et al. 1994; Windom et al. 1991) first demonstrated the lack of reliability of previous metals data. Contamination resulting from cumulative effects of sampling equipment and processing techniques used prior to 1990 were found to bias the concentrations of cadmium, copper, lead, and zinc that had been reported in surface waters.

Each aspect of sampling, processing, and analyzing water quality becomes increasing critical as lower project reporting limits are required to evaluate concentrations of dissolved metal in environmental samples. Methods and materials used in sample collection, processing, and analysis may introduce contamination or artificially reduce measured concentrations of dissolved metals in the samples. An extensive suite of quality control measures is necessary to address potential contamination and adsorptive losses. This starts with assuring that all parts of the sampling system that come into contact with the water are comprised of appropriate materials, proper cleaning procedures are employed, and systems are in place to document cleanliness of all system components.

Over the past 15 years, a number of documents have been developed to provide guidance for monitoring of stormwater discharges. Three of these documents are comprehensive in scope and should be considered when developing any stormwater monitoring effort. The Caltrans Stormwater Monitoring Protocols (Caltrans 2003) were initially developed in 2000 and later updated and expanded in 2003. This set of protocols was developed to provide comprehensive guidance to Caltrans management, staff, and contractors for use in the planning and implementation of stormwater monitoring programs. Step-by-step descriptions are provided to guide the user through the processes used to plan and implement a successful water quality monitoring program specific to runoff from transportation-related facilities. Soon after the first edition of the Caltrans manual, another manual was developed for the FHWA (Strecker, Mayo et al. 2001). The FHWA stormwater monitoring manual included monitoring strategies for five different objectives common to stormwater programs, equipment selection, installation and applicable QA/QC requirements. In the same time frame, U.S. Geological Survey and the FHWA (Granato, Zenone and Cazenos, eds, 2003) compiled another significant resource consisting of a series of chapters written by experts in each field. The individual chapters address a wide range of topics directly related to monitoring stormwater. These chapters included basic information requirements and data quality; quality assurance and quality control practices; measurement of precipitation and runoff flow; the geochemistry of runoff; measurement of sediments, trace elements, and organic chemicals in runoff; assessment of the potential ecological effects of runoff; monitoring atmospheric deposition; and interpreting runoff data using appropriate statistical techniques.

Many additional resources are available that provide specific information on cleaning procedures, sampling methods, general water quality testing, and documentation necessary to support and validate monitoring data. Horowitz et al. (1994), Keith (1996) and the most current version of the USGS National Field Manual (NFM) for Collection of Water Quality Data (various dates) are essential sources of information on cleaning, sampling and processing water samples. The USGS NFM is maintained online at http://pubs.water.usgs.gov/twri9A/ in order to provide easy access to periodic modifications and improvements. These documents should be considered central to most any water quality monitoring effort. A

Table 1. Water quality criteria for metals.

		Freshwater[1]				Marine[2]	
		Total		Dissolved		Total	Total
Metal	Hardness	CMC	CCC	CMC	CCC	Acute	Chronic
As	25	340	150	340	150	69	36
Cd	25	0.52	0.10	0.52	0.09	40	8.8
Cr(III)	25	580	28	180	24		
Cr(VI)	25	16	11	16	11	1100	50
Cu	25	3.8	2.9	3.6[3]	2.7[3]	4.8	3.1
Pb	25	14	0.5	14	0.5	210	8.1
Ni	25	140	16	140	16	74	8.2
Ag	25	0.4		0.3		0.95[4]	
Zn	25	37	37	36	36	90	81

[1] Freshwater criteria are based upon hardness with the exception of arsenic (As) and trivalent chromium (Cr+3). CMC (Criteria Maximum Concentration) is the highest level for a 1-hour average exposure not to be exceeded more than once every three years. CCC (Criteria Continuous Concentration) is for a 4-day exposure not to be exceeded more than once every three years.

[2] Criteria for marine waters based upon unfiltered samples.

[3] Based upon CTR (2000) hardness-based calculation. Lower criteria can result from use of the EPA (2007) biotic ligand model when pH is depressed (6.0-6.5) and dissolved organic carbon content is low (<2 mg/L).

[4] Criterion is halved for consistency with 1985 guideline derivation.

number of other resources have been developed in recent years that contain useful information for planning and implementing stormwater monitoring efforts that focus on dissolved metals at concentrations relevant to water quality criteria. Many of the more valuable guidance documents and areas addressed by these documents are summarized in Table 2.

This manual is intended to provide specific monitoring guidance for sampling, processing, and analyzing dissolved metals in highway and urban runoff. Clean sampling techniques are required whenever low-level analytical reporting limits are necessary for analysis of metals. It is well recognized that measurement of dissolved metals at levels relevant to water quality criteria can be extremely challenging. Extreme care is required to avoid contamination during the collection, processing, transport, and analysis of samples.

The validity of the data is dependent upon implementation of quality assurance measures to demonstrate that all materials contacting the samples are free of contamination and that sampling handling processes do not introduce contamination. Monitoring guidelines emphasize the steps necessary to collect, process, and analyze stormwater samples while providing the documentation necessary to demonstrate that the data are reliable and repeatable. Access to supporting documentation allows other researchers to independently validate the monitoring data and to make informed decisions regarding appropriate use of the data for other purposes.

Although this manual focuses on assessment of dissolved metals, monitoring protocol are intended to provide representative and accurate measurement for all phases of metals associated with runoff from small, highly impervious drainages as well as supplementary information necessary to evaluate the metals data. Recommended protocols are provided for development of a monitoring program designed for assessment of loads and concentrations of dissolved trace metals. This requires representative rainfall, flow, and water quality information.

These are intended to provide insight as the strategies, approaches, and techniques useful for monitoring highway or urban stormwater runoff. Specific objectives and site conditions must be considered when establishing a sampling program. The overall objectives of monitoring programs for dissolved metals will be quite varied and may necessitate different monitoring strategies. This manual is intended to address all considerations necessary to assure that sampling and analytical processes are well documented and provide the necessary sensitivity to address water quality objectives.

The manual was designed to be used by both field and laboratory staff. The intent was to produce a document that serves as a practical working document. Protocols are presented to assist staff in all phases of the process starting with designing a successful study and the preparations necessary for successful implementation.

1.1 The Issues

The National Highway Runoff Water-Quality Data and Methodology Synthesis (Granato, Zenone et al. 2003) provided a comprehensive look at technical issues associated

Table 2. Summary of key resources for the design and implementation of a sampling program for dissolved metals at low levels.

Reference	Preparation and Planning	Site and Equipment Selection	Cleaning and Blanking Procedures	Field Sampling – Equipment & Strategies	Field Sampling – Sample Handling	Analytical Methods and Quality Assurance	Data Management
Caltrans (2003). *Caltrans Comprehensive Protocols Guidance Manual.*	●	●	●	●	●	●	●
Granato, G. E., C. Zenone (2003). *National Highway Runoff Water-Quality Data and Methodology Synthesis, Volume I: Technical Issues for Monitoring Highway Runoff and Urban Stormwater.*	●	●	●	●	●	●	●
Strecker, E., Mayo, J. (2001). *Guidance Manual for Monitoring Highway Runoff Water Quality*.	●	●	●	●	●	●	●
Keith, L. H., ed (1996*). Principles of Environmental Sampling, Second Edition.*	●		●	●	●	●	
Horowitz, A.J., et al. (1994). U.S. Geological Survey Protocol for the Collection and Processing of Surface Water Samples for the Subsequent Determination of Inorganic Constituents in Filtered Water.			●	●	●	●	
U.S. EPA (1996). Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.			●		●	●	
U.S. EPA (1996). Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring			●			●	
Burton, G. A. and R. Pitt (2002) Stormwater effects handbook: a toolbox for watershed managers, scientists, and engineers.							
U.S. Department of Agriculture-National Resources Conservation Services. (2003). *National Handbook of Water Quality Monitoring*.		●	●	●	●	●	●
Shaver, E. R., R. Horner, J. Skupien, C. May, and G. Ridley (2007). Fundamentals of Urban Runoff Management: Technical and Institutional Issues	●	●	●	●	●	●	●
Law, Neely L., L. Fraley-McNeal, K. Cappiella, and R. Pitt (2008). Monitoring to Demonstrate Environmental Results: Guidance to Develop Local Stormwater Monitoring Studies Using Six Example Study Designs	●	●	●	●	●	●	●
Florida Department of Environmental Protection 2008. Standard Operating Procedures for Field Activities, Surface Water Sampling and General Sampling			●	●	●	●	
U.S. Geological Survey (Various Dates). *Techniques of Water Resources Investigations*, *Book 9, Handbook for Water Resources Investigations, National Field Manual for Collection of Water Quality Data.* http://pubs.water.usgs.gov/twri9A/			●		●	●	
Geosyntec Consultants and Wright Water Engineers, Inc. (2009). *Urban Stormwater BMP Performance Monitoring*.	●	●	●	●	●	●	●

with sampling, processing, and analyzing dissolved metals in highway and urban runoff. Runoff from highly impervious pavements and roadways transports dissolved, colloidal, and suspended solids in a heterogeneous mixture and, along with pH, alkalinity, traffic levels, and residence time, influences the partitioning of heavy metals. Water quality characteristics such as low alkalinity, low hardness, and short pavement residence times can cause a majority of the heavy-metal mass to remain in solution at the edge of the pavement, with partitioning coefficients approaching equilibrium conditions only toward the end of the event, as heavy metals partition to entrained solids (Sansalone and Buchberger 1997; Sansalone and Glenn 2000; Glenn, Liu et al. 2001; Magnuson, Kelty et al. 2001; Dean, Sansalone et al. 2005; Barber, Brown et al. 2006). The rate at which these geochemical processes occur may be an important consideration when considering the application of typical best management practices (BMPs) for highway runoff within the right-of-way. BMPs such as a detention basin or roadside swale may be necessary to detain runoff and produce sufficient residence time so that partitioning to the entrained solids occurs. This calls for an improved understanding of the concentrations of dissolved metals in stormwater at the point of entry into a BMP or receiving water body as well as better geochemical and hydrological information to assess factors that will contribute to modification of the dissolved fraction (f_d) of trace metals.

The numerous hydrologic and geochemical factors controlling speciation of metals and the varying rates at which metals partition between dissolved and particulate forms presents a significant problem with respect to the quantification of the dissolved fraction. All research conducted to investigate the transformational processes that occur in stormwater runoff from highways has been based upon grab samples that received filtration within one to six hours. The current criteria used for flow-weighted composites necessitates filtration after completion of all flow from a storm event, a process that can extend from less than one hour to days. The EPA method for analysis of dissolved metals specifies that samples should be filtered within 15 minutes or as soon as possible after completion of sampling. Caltrans guidelines (Caltrans 2003) called for filtration to occur within 48 hours of the time the last aliquot is sampled, but did identify the basis for this specification. The time that geochemical and hydrologic factors are expected to result in the partitioning process to near equilibrium is estimated to take 2–12 hours. Given the uncertainties in the duration of storm events and the many factors that could influence partitioning, none of the existing guidelines for holding times would be expected to provide consistent data that would be considered useful or even comparable among storm events at a given location. Current stormwater practices that delay filtration until samples reach the laboratory are likely to be more representative of equilibrium conditions than conditions during the storm at the monitoring point.

Without modification of current commercial stormwater monitoring systems to enable real-time filtration, it is unlikely that concentrations of dissolved metals during the storm event can be adequately characterized at the sampling point with flow-weighted composites. EPA's Engineering and Analysis Division (U.S. EPA 1998) experimented with adaptation of in-line filtration procedures to automated compositing devices at a wastewater treatment facility with the objective of assembling a system from commercially available parts in a cost-effective manner capable of obtaining clean field blanks and uncontaminated samples. Using an equipment configuration similar to that proposed in this guidance document, they were able to achieve the objective of clean field blanks and uncontaminated samples but were not successful in assembling a system that provided immediate filtration. Development of an automated sampling system with the capabilities of providing immediate, real-time filtration for dissolved metals should remain an important goal for programs using flow-weighted composite methods to characterize dissolved metals.

For purposes of this document, we utilize the commonly accepted operational definition for "dissolved" metals that is based upon the concentration of metals in whole-water samples after passing through a 0.45 μm membrane filter. Depending upon the particular metal of concern and geochemical factors associated with the sample, it is recognized that "dissolved" fraction is not comprised solely of ionic species but can contain a substantial proportion of colloidal metals (Horowitz 1994; Bricker 1999; Tucillo 2006). In actuality, only a small proportion of some metals in a filtered water sample may be in the dissolved state as the majority are adsorbed to colloids or bound to humic or fulvic compounds. The importance of colloids will depend upon specific site conditions and project objectives. Studies suggest that transport of metals associated with colloids can be enhanced in cold climates where roads are salted with NaCl (Amrhein, Mosher and Strong 1993; Amrhein et. al 1994). Tucillo (2006) found that copper and zinc were primarily in the dissolved concentrations (less than 10Kda or 0.003 micron) or fractions greater than 20 microns. This was thought to explain high variability in performance of BMPs that relied upon settling.

Artifacts of the filtration process influence whether colloidal metals are captured in the filtrate or on the filter. The volume filtered, amounts of sediment present, the effective surface area of the filter, and the type of membrane material used to manufacture the filter can all influence what passes through the filter (Horowitz, Lum et al. 1996). As such, this simple definition for dissolved chemical constituents must be applied with some caution. Despite the known flaws in

using filtration pore size to distinguish between particulate and dissolved metal species, monitoring typically requires assessment of dissolved metals since they serve as the basis for both interpretation of biological effects and current water quality criteria. It becomes more important to standardize and document the actual filtration techniques used as well as control factors such as filter packing, which is known to increase variability.

This guidance manual provides guidance for the design and implementation of stormwater monitoring for dissolved metals. These protocols include (1) batch cleaning of sampling equipment, bottles, hoses; (2) quality checks necessary to verify that each batch of components subjected to cleaning meet project objectives; (3) tracking the use of all system components by batch so that they can be linked to the field samples; (4) establish requirements and guidelines for representative samples; (5) detailed sample handling and transportation procedures; (6) sample processing in the laboratory; (7) laboratory accreditation and participation in inter-laboratory calibration studies; and (8) the basic level of documentation necessary for final reports to allow others to assess the validity of the data set. This guidance also includes important ancillary data and standardized explanatory variables recommended to both provide a common basis for comparison among studies and to account for some of the variability in the data.

CHAPTER 2

Preparation and Planning

Developing a stormwater monitoring program that is capable of obtaining environmental data that are representative, accurate, and provide the supporting information needed to be used by other programs requires careful preparation and planning. A monitoring program designed to obtain environmental data for decision making purposes should be conducted in three phases: planning, implementation, and assessment. Jones (1999) provides a detailed outline of the necessary elements to be addressed as part of the project planning process. In addition, EPA provides a set of extensive guidelines (http://www.epa.gov/quality/qa_docs.html) for the design and implementation of monitoring programs to enable validated data with minimized total error that can be used to support decision-making processes. These guidelines provide a basis for development of the major components of a SAP with emphasis on use of clean sampling methods and providing the documentation necessary to support use of the data by others.

The preparation and planning stage includes development of a SAP that will serve as the roadmap for all phases of the program. An example of the contents and structure of a typical SAP for stormwater monitoring is shown in Figure 1. The SAP includes an overview of the monitoring objectives, project organization, sampling site locations, monitoring constituents and detection limits, analytical methods, sampling frequency, field equipment operation, sample collection methods, QA/QC protocols, and logistical details for the project. The SAP incorporates Data Quality Objectives (DQOs) developed to meet the goals of the program and expected use of the data.

The SAP should provide information on data management and reporting which is an important element of assuring that basic data generated by the program are (1) available for public use as original data, (2) supported by sufficient quality assurance information (to indicate the validity, reliability, and compatibility of data from different sources), and (3) available in electronic files in database formats that are universally available. These factors were among the important issues cited by Granato, Bank et al. (2003) as primary requirements for assuring data that are both accessible and useful for incorporation into larger data sets for larger scale comparison.

The SAP should provide details on the data validation process to describe how the data will be validated to determine if DQOs were met. The data quality assessment report should identify any data quality issues that were encountered, correction action taken and any necessary qualifications applied to the data. This report should provide an overall assessment of the uncertainty of data based upon project QA/QC activities and any limitations on interpretation of the study results that might result from data quality issues.

Preparation and planning is especially critical to measurement of dissolved metals. Collection of high quality samples that are free of external contaminants and representative of actual field conditions will require an extensive expenditure of effort in the planning stages. A large proportion of the effort necessary to obtain representative stormwater samples is expended well before the actual sampling events.

SAMPLING AND ANALYSIS PLAN

1.0 PROJECT OVERVIEW/DESCRIPTION

- 1.1 Description of why the project is being conducted
- 1.2 Description of who is conducting the project
- 1.3 General scope of monitoring activities
- 1.4 Project organization/roles and responsibilities

2.0 MONITORING SITE(S)

- 2.1 Site location (map)
- 2.2 Written driving directions
- 2.3 Site access instructions (gates, locks, keys, combinations)
- 2.4 Notification procedures

3.0 ANALYTICAL CONSTITUENTS

List of constituents for sampling and analysis (including sample collection method, bottle type, volume required, preservation, and laboratory performing analysis)

4.0 DATA QUALITY OBJECTIVES (DQOs)

- 4.1 Analytical reporting limits
- 4.2 Analytical precision, accuracy, and completeness

5.0 FIELD EQUIPMENT MAINTENANCE

- 5.1 Equipment calibration
- 5.2 Equipment maintenance
- 5.3 Equipment cleaning (bottles/lids/tubing)

6.0 MONITORING PREPARATION AND LOGISTICS

- 6.1 Weather tracking
- 6.2 Storm selection criteria
- 6.3 Storm action levels
- 6.4 Communications/notification procedures
- 6.5 Sample bottle ordering
- 6.6 Sample bottle labeling
- 6.7 Field equipment preparation

7.0 SAMPLE COLLECTION, PRESERVATION, AND DELIVERY

- 7.1 Sample collection methods
- 7.2 Field measurement methods
- 7.3 Field equipment list

Figure 1. Outline of typical sampling and analysis plan for stormwater monitoring.

CHAPTER 3

Constituent Selection

A substantial amount of research has been conducted on the characterization, speciation, and removal of dissolved metals in highway runoff. This research has demonstrated that metal partitioning between the dissolved and particulate-bound fractions in stormwater is a dynamic process that is influenced by a number of different factors (Doner 1978; Bauske and Goetz 1993; Granato, Church, and Stone 1995; Breault et al. 1996; Sansalone and Buchberger 1997). Monitoring of dissolved metals in runoff should incorporate measurement of the major constituents known to influence partitioning. This includes geochemical data such as sediment, pH, alkalinity, major ions, hardness, and dissolved organic compounds (DOC). Use of geochemical or biotic ligand models to examine conditions that may mobilize metals and make them more available has been suggested as an alternative to direct measurement of dissolved metals (Geosyntec Consultants and Wright Water Engineers 2009).

3.1 Conventional Parameters

Conventional parameters should include total dissolved solids (TDS), total suspended solids (TSS) or suspended solids concentration (SSC), total organic carbon (TOC), and DOC. Specific conductance and pH should be measured during both the subsampling process and immediately upon arrival at the laboratory since values can be subject to change over relatively brief periods. Field values should be used for purposes of a geochemical model. Laboratory data should be considered as backup if field measurements experience QA problems.

Accurate measurement of pH will require use of a probe designed specifically to measure pH in waters with low ionic strength (less than 200 µmho conductivity). The USGS NFM (Chapter 6, Section 6.4 pH) provides specific guidance for measurement of waters with low ionic strength. Waters with low ionic strength tend to cause sluggish, drifting responses that fail to stabilize. A variety of manufacturers make pH probes that are specifically designed for low-ionic strength waters. These sensors normally provide higher bleed rates at the reference junction that result in faster stabilization and increase accuracy and reproducibility. Low ionic strength buffers are also available that help response time and accuracy even when used with standard pH probes. Temperature will also be an issue when measuring pH in stormwater samples. Stormwater composite samples should be maintained at temperatures of 4–6°C due to refrigeration of icing of the samplers. The temperature of the subsample taken for pH measurements should be maintained at the composite sample temperature and the temperature recorded with the measurement.

Measurement of solids in stormwater or receiving water has received a substantial amount of discussion with respect to both sampling and analytical methods. Peristaltic pumps have been shown to be limited sediment size fractions of 250 µm or less (Clark, Siu et al. 2009). Furthermore, the SSC method is generally recommended for more accurate quantification of suspended particulates but method is not strictly suited for composite sampling. The SSC method requires the whole sample be processed. Although the method is used, it is based upon processing a complete subsample from the composite. Selection of a method of measuring solids should consider overall objectives of the program and the known limitations of peristaltic sampling methods. Additional measures such as particle size distributions may be necessary if the objectives include the need to understand partitioning among available sediment particles.

Total alkalinity should be measured along with the three major components: carbonate alkalinity, bicarbonate alkalinity, and hydroxide alkalinity. Hardness as CaCO3 is another critical parameter since water quality criteria for many of the dissolved metals are a function of hardness. The most accurate measurement of hardness is based upon individual analysis of calcium (Ca) and magnesium (Mg), the two major cations comprising hardness, and then calculating total hardness.

Temperature can be an important factor especially in regions that receive summer storm events and where thermal effects are important to measure. Temperature can also be important when using a geochemical model to determine speciation of dissolved metals. This would normally be measured with use of a thermistor attached near the intake.

3.2 Major Ions

As a minimum, selected constituents should include the major cations and anions. Recommended cations include calcium (Ca) and magnesium (Mg), typically measured to calculate hardness, and both sodium (Na) and potassium (K). In addition, concentrations of iron (Fe) and aluminum (Al) will be useful to support geochemical speciation and adsorption modeling. Major anions should include sulfate (SO_4) and chloride (Cl).

The quality of the chemical analyses should be checked by calculation of the ion balance. Ion balance is calculated as the total cation concentration minus the total anion concentration divided by the total concentration of ions in the solution. Concentrations are based upon the milliequivalents of each ion.

3.3 Organic Composition

TOC measurements provide a surrogate measure of the organic matter content in water; however, its utility for estimating the extent of metal binding to solid organic matter or dissolved organic matter is questionable. Geochemical computer models such as model VI (Tipping, 1998) and the NICA-Donnan model (Kinniburgh et al., 1999) require estimation of the concentration of binding sites and the metal-ligand equilibrium constant. Ideally, these model constants are obtained by calibrating the model to data obtained by titrating concentrated organic matter into a solution containing the metal ion and measuring free metal concentration as a function of organic matter concentration DOC. However, these types of measurements are not routinely conducted.

As a result, modelers often assume a range of assumptions regarding the fraction of humic and fulvic acids and the fraction of inert organic matter present in a water. Recent data (Amery et al. 2008) suggests that one easily measurable parameter, SUVA, correlates well with the available fraction of organic matter. Therefore, we suggest that specific UV at 254 nm be measured to provide an assessment of the active fraction of fulvic acid in the sample.

CHAPTER 4

Equipment

This guidance is based on use of automated stormwater monitoring equipment to collect flow-weighted composite samples of runoff for analysis of dissolved metals at levels relevant to receiving water quality criteria. Stormwater monitoring systems are commercially available from several sources. The two most common systems are manufactured by American Sigma and Isco. These systems were originally designed for waste water treatment plants where conditions are relatively constant. Manufacturers of these systems started modifying the design of the equipment in the 90s to provide functionality for delivering fixed volumes of water even when water levels were changing quickly. They then were integrated with a variety of datalogger/flow modules that provided better flow quantification and the ability to pace the samplers in response to changing flows. Monitoring equipment has continued to be improved by improved software, integration with rain gauges, and in situ water quality instrumentation and telecommunications. Providing reliable telecommunications for real-time access to data and to provide command and control functionality has greatly improved efficiency and contributed to improved stormwater data.

Most automated stormwater sampling stations incorporate peristaltic pumping systems for sample collection. Alternative systems (e.g. Manning Environmental, Sirco, etc.) are also available that utilize vacuum pumps to draw water into a measuring chamber. These vacuum systems have some distinct advantages when it comes to sampling water containing high loads of suspended particulates and sampling situations requiring high vertical lift. Although the measuring chambers allow collection of very repeatable sample volumes, they are generally considered difficult to configure for ultraclean sampling and have not been extensively used for stormwater monitoring applications. The two most common stormwater monitoring systems both use peristaltic pumping systems. When appropriate measures are taken, it has been demonstrated that these systems are capable of collecting blanks that are uncontaminated and high quality, reproducible data using detection limits appropriate to water quality criteria. In order to accomplish this, extreme care must be taken to avoid introduction of contaminants.

Requirements include:

- Assurance that all materials coming into contact with the samples are intrinsically low in trace metals and do not adsorb/absorb metals (Table 3);
- Material coming into contact with the sample water are subjected to intensive cleaning using standardized protocol and subjected to systematic blanking to demonstrate and document that blanking standards are met;
- All cleaned sampling equipment and bottles are appropriately tracked so that blanking data can be associated with all components deployed in the field;
- Samples are collected, processed, and transported, taking extraordinary care to avoid contamination from field personnel or their gear; and
- Laboratory analysis is conducted in a filtered air environment using ultrapure reagents.

Although the technical limitations of autosamplers are often cited, they still provide the most practical method for collecting representative samples of stormwater runoff for characterization of water quality and have been heavily utilized for this purpose for the past 20 years. The alternative, manual sampling, is generally not practical for collection of flow-weighted composite samples from a large number of sites or for sampling events that occur over an extended period of time. Despite the known drawbacks, autosamplers combined with accurate flow metering remain the most common and appropriate tool for monitoring stormwater runoff. Understanding the limitations of autosamplers allows the user to minimize and compensate for those limitations. Among the most common limitations cited are the following:

- Lack of ability to collect isokinetic samples
- Poor representation of suspended particles and particle size distributions

Table 3. Appropriate materials for environmental samples.

(From USGS NFM, Table 2-1)

Construction material for sampling equipment (does not apply to well casing)		Target analyte(s)	
Material	**Description**	**Inorganic**	**Organic**
Plastics[1]			
Fluorocarbon polymers[2] (other varieties available for differing applications)	Chemically inert for most analytes.	(potential source of Fl)	(Sorption of some organics.)
Polypropylene	Relatively inert for inorganic analytes.	*	Do not use.
Polyethylene (linear)	Relatively inert for inorganic analytes.	*	Do not use.
Polyvinyl chloride (PVC)	Relatively inert for inorganic analytes.	*	Do not use.
Silicone	Very porous. Relatively inert for most inorganic analytes.	(potential source of Si)	Do not use.
Nylon	Relatively inert for inorganic analytes.	*	Do not use. Exception: CFCs
Metals[3]			
Stainless steel, 316-grade (SS 316)	SS 316—metal having the greatest corrosion resistance. Comes in various grades. Used for submersible pump casing.[3]	* (potential source of Cr, Ni, Fe, and possibly Mn and Mo, if corroded4) Do not use for surface-water sampling: equipment must have a plastic coating (does not apply to submersible pumps).	* Do not use if corroded.[4]
Stainless steel, 304-grade (SS 304)	Similar to SS 316, but less corrosion resistant.	Do not use.	* Do not use if corroded.[4]
Other metals: brass, iron, copper, aluminum, and galvanized and carbon steels	Refrigeration-grade copper or aluminum tubing are used routinely for collection of $^{3}H/^{3}He$, CFC, and SF-6 samples.	**Do not use** (except as noted for isotopes).	* Routinely used for CFCs. Do not use if corroded.
Glass			
Glass, borosilicate (laboratory grade) Ceramic	Relatively inert. Potential sorption of analytes.	(glass is potential source of B and Si)	*

* Generally appropriate for use shown; Fl, fluoride; Si, silica; Cr, chromium; Ni, nickel; Fe, iron; Mn, manganese; Mo, molybdenum; 3H/3He, tritium/helium-3; CFC, chlorofluorocarbon; SF-6, sulfur hexafluoride; B, boron]

[1] Plastics used in connection with inorganic trace-element sampling must be uncolored or white (Horowitz and others, 1994).

[2] Fluorocarbon polymers include materials such as Teflon®, Kynar®, and Tefzel® that are relatively inert for sampling inorganic or organic analytes.

[3] Most submersible sampling pumps have stainless steel components. One can minimize effects on inorganics samples by using fluorocarbon polymers in construction of sample-wetted components (for example, for a bladder, stator, impeller) to the extent possible.

[4] Corroded/weathered surfaces are active sorption sites for organic compounds and can leach trace elements.

Reproduced from USGS NFM -Table 2-1. General guidelines for selecting equipment on the basis of construction material and target analyte(s)

- Sample line velocities that decrease with head differentials (ability to meet minimum recommended line velocity of 2.0 ft/s diminishes) without the use of auxiliary pumps
- 100-foot line limitation
- Sample volume repeatability

Most of these limitations can be minimized by incorporation of these considerations in the site selection process and when installing the equipment. In small drainages, a primary control device such as a flume or weir is necessary to obtain accurate measurement of flow. Flumes are generally preferred since they are not as prone to trapping sediments as weirs. Conditions necessary for collecting accurate flow measurements are not conducive to collection of representative water samplers. When designing the installation, consideration should be given to providing a hydraulic jump near the primary control device so that turbulent mixing is encouraged. This can be accomplished by installing a sampling port downstream of the flume. The intake should be set on the bottom of the sampling port. The sampling port should provide a minimal retention volume (depth of approximately one inch) to allow for the intake to be covered during very low flow conditions but minimize potential trapping of particulates. In most cases, the intake can and should be placed on the bottom of the sampling point.

The sampling equipment should be placed as close as possible to the sampling point without creating a safety issue. Safety should always be the primary consideration but sites are preferred that provide safe access combined with the ability to minimize lengths of the intake hose and head differentials. Whenever possible, intake hose should be limited to 10 to 20 feet in total length with a head differential of no more than 4 to 6 feet. Laboratory tests with common autosamplers (Clark, Siu et al. 2009) concluded that the peristaltic pumps used in these systems can provide accurate measures of solids that are less than 250 microns in diameter with a specific gravity of 2.65. The ability to effectively represent particles less than 250 microns started to degrade when head differentials exceeded 2.5 meters (~8.3 feet).

4.1 Sampler Intake Strainer, Intake Tubing and Flexible Pump Tubing

Intake strainers are used to prevent small rocks and debris from being drawn into the intake tubing and causing blockages or damage to the pump and peristaltic pump tubing. Strainers typically come in a limited number of sizes and are constructed of a combination of Teflon® and 316 stainless or simply stainless steel. The low profile version is typically preferred to provide greater ability to sample shallow flows. Intake strainers constructed of stainless steel should be coated with a fluoropolymer coating if they are to be used for sampling dissolved metals. If the stainless steel intake is not coated, the strainer should never be subjected to cleaning with acids. Cleaning should be limited to warm tap water, laboratory detergents and MilliQ water rinses.

Tubing comprised of 100% fluorinated ethylene propylene (FEP) should be used for the intake tubing. Several alternative fluoropolymer products are available but 3/8″ ID solid FEP tubing has the chemical characteristics suitable for sampling metals (and organics) at low levels and appropriate physical characteristics. The rigidity of FEP tubing provides resistance to collapse at high head differentials but still is manageable for tight configurations.

The rigidity of the tubing can also be a problem if not installed correctly. The length of the tubing should be tailored to the site to minimize the overall length and provide a smooth path to the pump. Anti-kink should be used whenever the tubing passes through a point where it would be susceptible to bend. If the tubing develops a kink, the entire intake line will require replacement (at a substantial cost!).

Tubing constructed of polyethylene with a Teflon® liner is available and was at one time recommended by companies supplying stormwater monitoring equipment, but these products should strictly be avoided. Zinc contamination can occur if water gets between the liner and the polyethylene tubing. The liner also can be uneven leading to collapse of the lightweight liner and will often compress and distort when attaching fittings.

The peristaltic hose used in autosamplers is a medical-grade silicon product. The specifications for the peristaltic pump hoses used in these samplers are unique to the samplers. It is very important that the hose specified and provided by the manufacturers of the autosamplers be used. Minor differences in the peristaltic hose can cause major deterioration in performance of the samplers. Use of generic peristaltic pump hose from other sources can lead to problems with the ability to calibrate the samplers and maintain intake velocities of greater than 2.5 feet per second with higher lift requirements.

The peristaltic hose is connected to the FEP tubing and fed through the pump head leaving the minimum amount necessary to feed the peristaltic pump hose into the top of the composite bottle. The composite container should always have a lid to prevent dust from settling in the container.

A number of issues must be considered when installing the intake strainer and hose. Many of the key issues are addressed in the Caltrans Stormwater Monitoring Guidance and the National Highway Runoff Data and Methodology Synthesis (Breault and Granato 2000; Granato, Zenone et al. 2003). Use of autosamplers with a relatively constant intake flow rate and a fixed input point have inherent problems with regards to collecting samples with particle size distributions that are truly representative of the discharge (Edwards and Glysson

1999; Smith and Granato 2010). A number of approaches have been suggested for minimizing the bias introduced by autosamplers but each requires special consideration of site specific conditions. Edwards and Glysson (1999; p. 27) provide a list of important factors that should be addressed when positioning an intake when using autosamplers. Intake strainer are often located near the invert of small pipes or channels but this can often lead to biasing the samples towards coarser sediment, burial of the intake within bedload material, or clogging by large particles.

In general, intakes should be oriented in a downstream direction since field testing (Edwards and Glysson 1999) suggests that this allows for more representative collection of coarser particles and limits the tendency for debris to foul the intake. Whenever possible, the intake should be located in a position where active mixing occurs to enhance suspension of the full range of particles being transported. Other options have been proposed for improving representativeness of samples collected with autosamplers. These include installation of static mixers (Figure 2) such as developed by USGS (Smith 2002; Smith and Granato 2010), mechanical float devices to allow sampling at a depth of roughly 0.6 times the depth of the flow (Eads and Thomas 1983; Gettel et al. 2011), or the Depth-Integrated Sample Arm (DISA) recently tested by Selbig and Bannerman (2011). The extensive efforts made to develop intake systems that provide more representative samples illustrate the importance of this issue. Although some of these proposed solutions are complex, they all share a common goal of seeking to improve the ability of autosamplers to obtain representative samples. The ultimate approach to mounting the intake should be based upon site conditions and the simplest, most reliable method to optimize representative sampling.

If trash and debris are common at the site, a stainless steel cage may need to be manufactured to deflect plastic bags or heavy objects moving through the channel. If such protection is required, the cage should be constructed with 316 grade stainless steel (Table 3) and preferably coated with fluoropolymer coating. The intake hose and strainer must be attached in a manner that provides a high probability of remaining in place during high flows. Use of conduit to protect the intake hose and allow it to be securely attached to the channel is recommended for most sites. The intake hose also must be installed without low points or loops so that water is not retained.

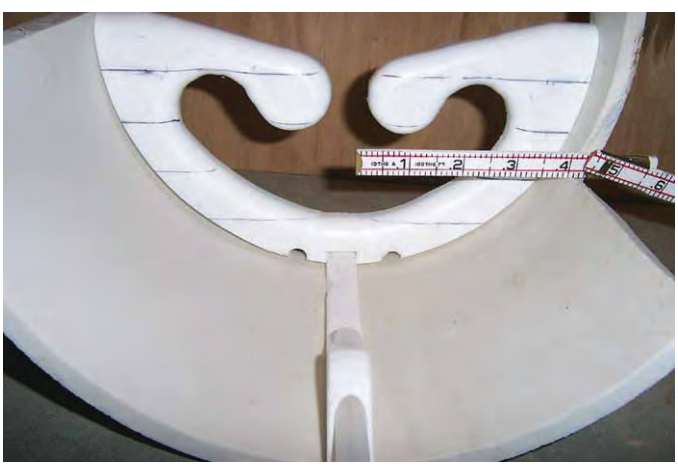

Figure 2. Static mixer (from Smith and Granato (2010).

4.2 Composite Containers

A composite container should be used that can be demonstrated to be free of metals of interest at the desired levels (U.S. EPA 1996). Containers constructed of fluoropolymers (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz are considered optimal but borosilicate glass has been shown to meet sampling objectives for trace metals measured at limits appropriate to EPA water quality criteria. High capacity borosilicate media bottles (20 liters or 5 gallons) are preferred for storm monitoring since they can be cleaned and suitably blanked for analysis of both metals and organic compounds. The transparency of the bottles is also a useful feature when subsampling and cleaning the containers for reuse.

These large media bottles are designed for stoppers and thus do not come with lids. Suitable closure mechanisms must be fabricated for use during sampling, transport, and storage of clean bottles. The preferred closure mechanism is a Teflon® stopper fitted with a Viton O-ring ($2^3/_8''$ - ID × $2^3/_4''$- OD) that seals the lid against the media bottle. A polypropylene clamp (Figure 3) is used to seal the Teflon® stopper and O-ring to the rim of the composite sample bottle. Two polypropylene bolts with wing-nuts are used to maintain pressure on the seal or to assist in removal of the lid.

Every composite bottle requires one solid lid for use in protecting the bottle during storage and transport. A minimum

Figure 3. Composite bottle with label and installed tubing.

of one Teflon® stopper should be available for each monitoring site during storm events. Each field sampling crew should have additional stoppers with holes ("sampling stopper") that would be available if a sampling stopper is accidentally contaminated during bottle changes or original installations.

The holes in the sampling stoppers should be minimally larger than the external diameter of the peristaltic hose. If a tight fit exists, the pressure created when water is pumped into the bottle will cause the hose to be ejected and the sampling event will need to be abandoned.

Transporting composite bottles is best accomplished by use of 10-gallon Brute® containers to both protect them from breakage and simplify handling. They also provide additional capacity for ice while transporting full bottles to the laboratory or subsampling site.

Bottle bags (Figure 4) are also useful in allowing full bottles to be handled easier and reduce the need to contact the bottles near the neck. They are important for both minimizing the need to handle the neck of the bottle and are also an important health and safety issue. The empty bottles weigh 15 pounds and they hold another 40 pounds of water when full. These can be very slippery and difficult to handle when removing them from the autosamplers. Bags can be easily fabricated out of square-mesh nylon netting with nylon straps for handles. Use of bottle bags allows two people to lift a full bottle out of the ice in the autosampler and place it in a Brute® container. Whether empty or full, suitable restraints should be provided whenever the 20-L composite bottles and Brute® containers are being transported.

Figure 4. Composite bottle showing bottle bag used for transport and lifting.

4.3 Flow Monitoring

Collection of flow-weighted stormwater samplers requires the ability to accurately measure flow over the full range of conditions that occur at the monitoring site. The ability to accurately measure flow should be an important aspect of site selection. Hydraulic characteristics necessary to allow for accurate flow measurement include a relatively straight and uniform length of pipe or channel without major confluences or other features that would disrupt establishment of uniform flow conditions. The actual measurement site should be located sufficiently downstream from inflows to the drainage system to achieve well-mixed conditions across the channel. The flow sensor and sample collection inlet should be placed a minimum of five pipe diameters upstream and 10 pipe diameters downstream of any confluence to minimize turbulence and ensure well-mixed flow. The *Isco Open Channel Flow Measurement Handbook* (Walkowiak 2008) is an invaluable resource to assist in selection of the most appropriate approach for flow measurements and information on the constraints of each method.

Use of a primary control device is recommended for most sites. Flumes are generally preferable to weirs as they tend to be self-cleaning and are less subject to the errors due to approach velocities. When properly sized and installed, they can provide accuracy of +/-3%. Flumes generally require a stilling well and communication port connecting to the flume at the measurement point. Bubblers are recommended for measurement of water levels within the stilling wells as they provide stable, accurate stage measurements for calculation of flow.

Calibration checks are essential to assure that flow measurements are accurate (Maheepala et al. 2001; Church, Granato and Owens 2003; Smith and Granato 2010). This is particularly important if flow measurements do not utilize a primary control device. Calibration of flow meters in small pipes (less than 12-16 inches) can typically be performed by using a portable water tank and then pumping water through the system with centrifugal pumps over a range of conditions expected. Flow data from the meter being calibrated are compared with paired flow measurements taken at a downstream location using a volumetric weir or secondary flow meter. For larger pipes, a nearby fire hydrant fitted with a certified flow meter and totalizer may be used as a water source, preferably in association with routine servicing of the hydrant. Before conducting any calibration checks involving discharges to the storm drain, one should consult with local authorities. If discharges are not permitted, calibrations may need to be performed during an actual storm event using dilute solutions of fluorescent dyes such as Rhodamine WT and a fluorometer.

4.4 Rainfall Gauges

Installation of electronic tipping bucket rain gauges is highly recommended for monitoring of smaller drainages. Use of a localized rain gauge provides better representation of conditions at the site. This is less important at larger watersheds best characterized by a network of rain gauges. The basic requirements for collecting, documenting, and reporting precipitation data are summarized in work conducted under the National Highway Runoff Data and Methodology Synthesis (Church, Granato et al. 2003).

A variety of quality instruments are available but all require substantial maintenance to ensure maintenance of high data quality. Typical gauges will have 8-inch diameter cones, provide 1 tip per 0.01″ of rain and have an accuracy of ± 2% up to 2″/hr. The accuracy of tipping bucket rain gauges can be impacted by very intense rainfall events but errors are more commonly due to poor installations. Proper installation and maintenance of the rain gauge is as important as gauge proximity to the monitoring site. Proper installation requires that the equipment is level, clear of trees and other major obstructions, and mounted firmly to avoid introduction of artifacts due to vibration. Monthly maintenance should be conducted to assure that no obstructions have developed due to birds, insects and spiders, or other debris.

Supporting data are necessary to document the accuracy and representativeness of the precipitation data. Basic information needs include:

- Location relative to the monitored drainage area
- Length of record
- Recording frequency
- Equipment (model, specifications, and measuring methods)
- Records of maintenance visits and calibration records
- A data quality assessment
- Availability and access to final data records

Continuous data records should be maintained throughout the wet season with data being output and recorded for each tip of the bucket. Data for storm events should include total precipitation, hyetographs, maximum 5-minute intensity, the length of the antecedent dry period, and total precipitation associated with the antecedent event.

4.5 In Situ Sensors

Both standard commercial stormwater monitoring equipment and custom systems designed around datalogger/control modules such as those made by Campbell Scientific are now capable of incorporating an array of additional water quality sensors using an SDI-12 interface. The wide variety of SDI-12 compatible stage, flow, and water quality probes that are available can allow collection of important ancillary data such as temperature and conductivity. Continuous records of temperature and conductivity can provide important information for general characterization or as input for modeling equilibrium conditions between particulate and dissolved forms. Most monitoring equipment has the ability to trigger sampling based upon specified water quality conditions.

4.6 Power

Stormwater monitoring equipment can generally be powered by battery or standard 120VAC. Standard systems come with built-in batteries but use of external, sealed deep-cycle marine batteries are recommended if the equipment must run under battery power. Even systems with access to 120VAC should be equipped with batteries that can provide backup power in case of power outages during an event. All batteries should be placed in plastic marine battery cases to isolate the terminals and wiring. Systems equipped with telecommunication packages should have a second battery that is obligated to telecommunications equipment and, if conditions are suitable, equipped with a solar panel to assure that a full charge is available when needed for a storm event.

4.7 Telecommunication for System Command/Control and Data Access

The ability to remotely communicate with the monitoring equipment allows for more efficient and representative sampling. Remote communication facilitates preparation of stations for storm events and making last minute adjustments to sampling criteria based upon the most recent forecasts. Communication with the sites also reduces the number of field visits by monitoring personnel. Remote two-way communication with monitoring sites allows the project manager (storm control) to make informed decisions during the storm as to the best allocations of human resources among sampling sites. By remotely monitoring the status of each monitoring site, the manager can more accurately estimate when composite bottles will fill and direct field crews to the site to avoid disruptions in the sampling. Real time access to flow, sampling, and rainfall data also provides important information for determining when sampling should be terminated and crews directed to collect and process the samples. Increases in both efficiency and sample quality make two-way communication with monitoring stations a necessity for most monitoring programs.

CHAPTER 5

Sample Collection and Handling Procedures

Monitoring stations typically include a flow monitoring component that incorporates instrumentation and software for measuring and recording flow. The flow meters are comprised of a datalogger/control module to allow storage and processing of the flow data and communication with a composite sampling device.

When collecting flow-weighted composite samples, the flow meter is programmed to send a pulse to the sampler each time a specified volume of water has passed the site. Upon receiving a pulse from the flow meter, the autosampler initiates a process designed to collect a fixed volume of water (aliquot) and discharge it into a composite bottle. Autosamplers are often programmed to go through a purge cycle before and after collecting a sample aliquot. This helps assure that the line remains clear and water does not get trapped in the line and incorporated into the sample aliquot. It also assists in clearing debris that might collect around or within the intake strainer. The time required to complete this cycle under worst case conditions (maximum head differentials) plays a critical role in determining sampling rates. Elimination of the post purge process is recommended to reduce cycling time and improve the overall ability to obtain representative samples of runoff from smaller drainages.

Cycling times will increase with increasing lengths of intake hose, higher head differentials, and as sampling volumes are increased for the sampling aliquot. The cycling time defines the minimum time interval that can be maintained between sampling pulses and still maintain a flow-weighted composite sample. If pulses exceed this rate for a substantial period of time, the sampling pulses become "stacked" in the autosampler's memory and sampling will continue at this maximum rate until such time that the sampler catches up with declining storm volumes.

Unfortunately, stacking of sampling pulses is a common but rarely recognized occurrence in many stormwater monitoring studies that utilize flow-weighted composited sampling strategies. Furthermore, the impacts of stacking on the data are often impossible to assess. Brief occurrences of stacking that recover within a few cycles would not be expected to bias the data but extended periods of stacked sampling commands that continue to execute well after major flows have subsided most certainly impact the data. This latter condition is most common when multiple (four bottle) composite bottles are used to sample runoff in small drainages.

This sampling configuration has been used as a strategy to provide field duplicates and/or additional water samples for QA/QC. Cycling times associated with this sampling configuration can easily run up to five minutes when the full purge-sample-purge cycle is performed for each bottle. Although samplers may be programmed to eliminate purges between bottles, this modification further impairs the effectiveness in sampling suspended sediments and flow conditions may still change radically by completion of the sampling routine. It is extremely common for sites using this configuration to exhibit "stacking" and miss aliquots intended for the third or fourth bottles due to rapidly changing water levels.

Small, highly impervious drainages associated with highway and ultra-urban areas are particularly challenging. These types of sites tend to have "flashy" flows that are highly responsive to changes in rainfall intensity. Monitoring strategies for these types of sites must take into consideration the range of flow conditions and the rates at which changes occur at these types of sites. Monitoring under these types of conditions can often benefit from use of smaller, more frequent sample aliquots. This improves the chances of sample aliquots being taken near the time and under the flow conditions responsible for initiating the sampling sequence. However, there is a point of diminishing returns as the size of the aliquot decreases; decreases in the system cycling time become less significant and controlled primarily by the length of the intake hose and the head differential. With the exception of extremely small drainages, it is generally recommended that 200 ml be used as the lower limit for aliquot volumes. A volume of 1,000 ml is recommended as the upper limit for aliquot size in most situations. Sampling of discharges from a pump is an exception since water is often discharged

at very high rates for brief periods of time. More frequently, aliquot volumes are set around 500 ml. With aliquot volumes set to 500 ml, a 20-liter composite bottle provides capacity for 40 aliquots without changing bottles.

5.1 Pacing the Sampler

Designing a sampling strategy for obtaining a representative composite sample from any given storm event requires consideration of the following key factors:

- Total sample volume required - fixed
- Capacity of the composite bottle - fixed
- Volume of individual aliquots - fixed
- Quantitative precipitation forecast (QPF) for the event
- Maximum sustained rainfall intensity - fixed
- Drainage area - fixed
- Cycling Time - fixed

A sampling program designed to focus on assessment of metals and ancillary parameters will require less than four liters of water. The composite containers provide a total capacity of 20 liters. Given these parameters, the sampling strategy would be based upon providing twice the required sample volume for the forecasted storm event and would still provide capacity for effectively sampling runoff that was up to 2.5 times greater than expected.

The flow volume per sample (the amount of flow that passes the sampling point between each aliquot collected) must be programmed into the flow meter in proportion to the predicted rainfall amount for each storm event, to set the sample pacing so as to fill the composite bottle(s) at an appropriate rate.

Calculation of the flow volume per sample *(Vs)* is performed using the predicted rainfall amount (*QPF*), the known or estimated drainage area (*A)*, and the composite runoff coefficient (*C)* for the area monitored to calculate the expected runoff flow volume for the storm event. The runoff coefficient for a specific drainage area is defined as the fraction of total precipitation volume delivered to the area that ends up as runoff at the point of discharge. Flow volume per sample can be determined using the formulas presented below:

$$Vr(cf) = QPF(\text{inches}) \times \frac{1\text{ ft}}{12\text{ inches}} \times A(\text{acres}) \times C \times \frac{43{,}560\text{ sq. ft}}{1\text{ acre}} \quad Vs(cf) = \frac{Vr(cf)}{CSA}$$

$$Qm(cf/\text{min}) = PIm\left(\frac{\text{inches}}{\text{hr}}\right) \times \frac{1\text{ hr}}{60\text{ min}} \times \frac{1\text{ ft}}{12\text{ inches}} \times A(\text{acres}) \times \frac{43{,}560\text{ sq. ft}}{1\text{ acre}}$$

Vr = estimated runoff volume in cubic feet
QPF = Quantitative Precipitation Forecast in inches
A = drainage area in acres
C = runoff coefficient
Vs = flow volume per aliquot in cubic feet
CSA = number of composite sample aliquots required for complete composite
PIm = maximum 5-minute precipitation intensity
Qm = maximum flow rate in cubic feet per minute

Successful collection of representative samples from a small, highly impervious drainage requires a sampling strategy that optimizes the probability of obtaining the necessary sample volumes and aliquot counts even when actual rainfall is found to substantially differ from predictions. Use of high capacity composite containers is an important part of the sampling strategy that enables effective sampling even when monitoring events that significantly differ from weather forecasts. Determination of appropriate settings requires knowledge of the maximum time for the autosampler to go through a full sampling cycle (*Ts*), the minimum volumes necessary to complete all analyses (*Va*), and the volume of each aliquot produced by the aliquot. The following calculations illustrate an iterative approach used to determine initial setting.

Example:

QPF = 0.55 inches = QPF (quantity of precipitation forecast)
A (drainage area) = 4.5 acres
C (runoff coefficient) = 0.9
CSA (target number of composite sample aliquots for sample composite) = 20
Va = 4,000 ml = minimum volume necessary for all analyses
Vc = 20,000 ml = composite bottle capacity
Ts = 0.36 minutes based upon a Vq of 400 ml
PIm = 2.2 inches/hour (based upon 5-minute rainfall intensity)

$$Vr = 0.55\text{ inches} \times \frac{1\text{ft}}{12\text{ inches}} \times 4.5\text{ acres} \times 0.9 \times \frac{43{,}560\text{ sq. ft}}{1\text{ acre}} = 8086\text{ cf}$$

$$Vq = \frac{(4{,}000 \times 2)\text{ml}}{20} = 400\text{ ml per aliquot}$$

$$Vs = \frac{8086\text{ cf}}{20\text{ aliquots}} = 404\text{ cf per aliquot}$$

$$Qm = \frac{2.2\text{ inches}}{1\text{ hr}} \times \frac{1\text{ hr}}{60\text{ min}} \times \frac{1\text{ ft}}{12\text{ inches}} \times 4.5\text{ (acres)} \times \frac{43{,}560\text{ sq. ft}}{1\text{ acre}} \times 0.9 = 540\text{ cf per min}$$

Ts = Maximum time (minutes) for sampler to go through the full sampling cycle.
Va = Minimum volume (milliliters) necessary to complete all analyses.
Vq = Aliquot volumes (milliliters), 200 to 1000 ml

In this example, we have applied a margin of safety by doubling the total volume required for conducting all analyses. Doubling of the aliquot volume (*Vq*) provides the ability to successfully capture storm events ranging from ½ to nearly 2½ times the predicted rainfall volumes without a bottle change. A margin of safety can be applied in several different ways but one must always consider impacts on other sampling constraints. Any adjustments in the volume used for sampling aliquots (*Vq*) will require examination of impacts on cycling time (*Ts*) for the autosampler.

A rough estimate of the potential maximum sustained flow rate (*Qm*) from the drainage area will help to reduce the possibility of setting sampling rates (*Vs*) that commonly exceed the time required for the monitoring system to go through the full sampling process (*Ts*) before receiving a pulse to trigger initiation of another sample aliquot. This example uses a maximum sustained rainfall intensity of 2.2 inches/hour. This was based upon rainfall records from Long Beach, California. In this region, 97.5% of the storm events monitored over a 10-year period had maximum 5-minute rainfall intensities that were less than this level. If it is assumed that the site is established with an 8-foot length of FEP tubing and the required head is 40 inches, a sampling cycle (*Ts*) could be completed every 0.36 minutes (22 seconds) if a post purge is not used (Figure 5). The sampling flow volume (*Vs*) used for this hypothetical site should always be greater than 200 cubic feet in order to handle the estimated maximum sustained flow (*Qm*) of 540 cubic feet per minute. This is roughly half of the proposed flow volume (*Vs*) of 404 cf and thus would provide ample cushion to increase the *CSA* without the risk of stacking sample pulses.

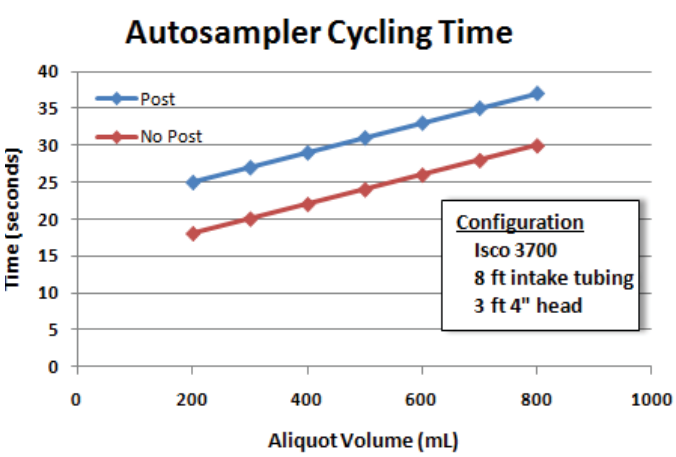

Figure 5. Example of autosampler cycling time with and without a post purge.

Based upon these initial calculations, the total number of aliquots (*CSA*) could be increased to 30. Adjusting the volume of each aliquot (*Vq*) to 300 ml would maintain the same projected sample volumes. This would have a minor effect of reducing cycling time (*Ts*) from 22 to 20 seconds and the flow volume per aliquot (*Vs*) would 270 cubic feet per aliquot. Reducing the volume of each aliquot to 300 ml would reduce the lower limit for *Vs* to 180 cubic feet. This adjustment would still allow a comfortable margin of safety to handle unexpected high intensity rainfall and provide for approximately 15 aliquots if the storm yielded half of the expected runoff.

Once a sampling strategy is established, most parameters such as the volumes used for each aliquot (*Vq*) and target number of aliquots (*CSA*) should remain constant. The only adjustments would be based upon predicted rainfall (*QPF*) for each event. After monitoring the first few storm events, the calculations for predicted runoff volume should be reviewed and adjusted as necessary to provide the optimal settings for assuring representative samples. This review should include an assessment of measured rainfall intensity and resulting flows to verify that settings used for the monitoring station are within the capacity of the equipment to maintain flow-weighted pacing.

5.2 Percent Capture

Percent storm capture (Percent Capture) is the percentage of the total event flow effectively represented in a composite sample. This is determined by the following formula:

$$\text{Percent Capture} = \frac{Vr \times \text{total \# of aliquots}}{\text{Total Run of } f \text{ Volume}} \times 100$$

This calculation assumes that the storm volume represented by each aliquot is constant and not impacted by stacking of sampling pulses. The actual data should be reviewed to verify that this assumption is correct.

Percent Capture will rarely equal 100%. A number of factors contribute to small reductions in Percent Capture. Frequent periods of low flows can lead to reductions in percent capture since autosamplers require suspension of sampling when water levels go below a minimum level. Flow measurements with primary control devices allow flow to be monitored below typical sampling limits. With small, highly responsive watersheds, water levels may frequently drop below levels that can be sampled. This condition also occurs at the end of the event as flows subside.

The most significant losses in percent capture tend to occur when sampling requires that composite bottles be replaced during a storm event. This can happen due to the need for high sample volumes for other analytical or toxicological purposes or as the result of substantial deviations

from predicted rainfall. Minimizing these losses requires the ability to remotely monitor progress at the site so that sampling crews can be alerted and directed to the site before the last aliquot is pumped. Crews should remove the composite bottle immediately after the last sample is taken and place a new bottle in the sampler before another sample is initiated. At high flows, this can be a matter of just a few minutes. In the real world, factors that contribute to the need for composite bottles to be changed at one site typically have comparable impacts at other monitoring sites. Intense shower activity also limits the ability of field crews to safely get through traffic to service the site. If a program typically requires use of multiple composite bottles, one should plan on using more field crews to avoid this problem.

5.3 Peak Capture

Successful sampling conducted throughout periods of high flows is considered important for sampling to be considered representative. This is generally reported as a "yes" or "no" situation, but minor loss of sampling efficacy around periods of peak flow should not be considered important if all other quality measures are met. Periods of high flows cause elevated sampling frequency, which may cause composite bottle capacities to be exceeded faster than anticipated. Maintaining effective sampling through these time periods will generally result in the capture of high percentages of the total storm flows. If the monitoring station was not effectively sampling during peak flow, the sampling data should be examined and professional judgment applied to determine whether data should be qualified.

5.4 Evaluation of Representative Sampling

A sample is considered representative if (1) the sampling aliquots were taken in direct proportion to the flow, (2) a minimum number of aliquots are obtained, and (3) the sample represents runoff for the entire duration of the event. Each of these issues requires careful examination and documentation in order to assess representativeness of samples collected by the autosampler. Although some guidelines (Table 4) have been suggested for addressing representativeness (Strecker, Mayo et al. 2001; Caltrans 2003), standards have not been clearly established to determine acceptance or rejection of the data set. Documentation included with the reports should include the standards used to assess representativeness of the samples and include a discussion of the potential impacts of any excursions on use of the data. Recommended criteria are discussed below.

The representativeness of sampling tends to improve with increased sampling density. Using overly aggressive sampler settings with the intent of providing high sampling density also increases the chances of sample pulses becoming backed up. Evidence of possible stacking of sampling pulses is evaluated by examining the times that each aliquot is taken, the volume represented by that aliquot, and the total volume of stormwater runoff that has occurred up to the point that the sample was taken. Stacking becomes evident when the timing between samples becomes constant despite changing flow rates. This will occur if flows exceed the ability of the equipment to complete the sampling cycle before receiving a pulse indicating that another sampling sequence should be initiated. If flow exceeds this limit for an extended time, the sampler will just continue to take samples until the system catches up with the total volume of stormwater runoff. Brief and limited excursions do not typically have a severe impact on representativeness. When three to five sampling pulses become backed up on the autosampler, there is a substantial increase in the potential to introduce bias. Such cases must be critically examined and evaluated to determine whether the data warrant rejection or qualification based upon the magnitude of these excursions.

Overly conservative setting can result in an insufficient number of aliquots being collected over the duration of the storm event for the composite sample to be considered representative of the storm event. Guidance as to the minimum number of aliquots needed to be considered representative

Table 4. Criteria used to evaluate representativeness of stormwater runoff samples.

Total Event Precipitation	Strecker et al. (2001)[1]		Caltrans (2003)[2]	
	Minimum Acceptable Number of Aliquots	Percent Capture Requirement	Minimum Acceptable Number of Aliquots	Percent Capture Requirement
0-0.25"	12-16 (10-20% of the mean)	>60% (note events with <80%)	6	85
0.25-0.5"			8	80
0.5-1"			10	80
>1"			12	75

[1] Strecker et al. (2001). Guidance Manual for Monitoring Highway Runoff Water Quality. FHWA-EP-01-022

[2] Caltrans (2003). Comprehensive Protocols Guidance Manual: Stormwater Quality Monitoring Protocols. CTSW-RT-03-105.51.42

is limited. Strecker, Mayo et al. (2001) conducted a sampling exercise that suggested that 12–16 aliquots were necessary for samples to be considered representative. Twelve aliquots provided resulted in estimates within 20% of the mean. Increasing the aliquot count to 16 samples provided estimates within 10% of the mean. Caltrans (2003) took a different approach suggesting that the minimum acceptable number of aliquots should be considered to vary with the magnitude of the storm event. Acceptable aliquot counts ranged from six for an event with under 0.25 inches of rainfall to 12 for an event exceeding 1 inch of rain.

Given the variability that can exist within a single storm event, we recommend using a lower limit of 12 aliquots. Unusual circumstances such as a monitoring event associated with extremely small rainfall events (lower than 0.15 inches) may warrant acceptance of lower numbers of aliquots if all other criteria are acceptable.

A ***Percent Capture*** of greater than 70 to 80% is generally considered the minimum to be considered as an acceptable sample (Table 4). Opinions differ as to what levels represent a significant loss of storm coverage. If a sampling event results in a ***Percent Capture*** of less than 70%, the specific circumstances causing the reduced coverage should be examined to determine the cause of the reduction. Professional judgment should be used to determine whether the data from the event can be used to address the project objectives. Data should be appropriately qualified in cases where storm coverage is less than this limit and it is determined that data are still useful for the purposes of the program. The average ***Percent Capture*** for events at most sites should be at least 85–90%.

5.5 Sample Splitting

The process of sample splitting can be a major source of error. Errors are more likely to be introduced when whole stormwater samples contain suspended sediments with particles larger than 250 µm. In addition it is unlikely that particle sizes greater than 250 µm will be effectively represented in samples taken with autosamplers (Clark et al. 2009).

The two methods recommended in the USGS National Field Manual for Collection of Water-Quality Data (http://pubs.water.usgs.gov/twri9A) include 14-L churns (plastic or fluoropolymer) and Dekaport cone splitters (Figure 6 and Figure 7). Each method has advantages and disadvantages as noted in Table 5. Many of the most significant disadvantages can be mitigated by having pre-cleaned and packaged splitting equipment available for each site. This may be practical for some programs if metals are the only key analytes and the 14-L plastic USGS modified churns (~$600–$800) can be utilized; however, few programs can bear the cost of 14-L fluoropolymer churns, which currently cost approximately $6000 each with disposable supplies. The Dekaport fluoropolymer cone splitter can be used to (1) split samples that are to be analyzed for both organic and inorganic compounds and (2) is not constrained by an upper limit on volume. The price point of the Dekaport splitter (~$1200) also makes it more reasonable to have precleaned equipment for each site, but field cleaning procedures specified by USGS (1997) have been shown to be effective in producing blanks at appropriate levels. Proper use

A. 14 L Plastic Churn **B. 14 L Fluoropolymer Churn**

(From USGS NFM, Chapter A2. Selection of Sampling Equipment)

Figure 6. Churns used for splitting whole stormwater samples.

(From USGS NFM and Capel and Larsen 1996)

Figure 7. Cone splitter.

Table 5. Advantages and disadvantages of splitting equipment and procedures.

(Based upon and modified from USGS NFM Table 2-6)

Splitter	Advantages	Limitations
Fluoropolymer churn splitter	Suitable for both inorganic and non-volatile organic analyses. Simple to operate. Easy to clean. No modification of the splitter design is necessary.	Can be used to split samples with particle sizes 250 µm and suspended-sediment concentrations 1,000 mg/L, but splitting accuracy becomes unacceptable for particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. Sample volumes less than 4 L or greater than 13 L cannot be split for whole-water subsamples from this 14-L churn. If pre-cleaned equipment is not available for each site, the churn requires field decontamination and additional blanking.
Plastic (non-fluorocarbon polymer) churn splitter	Simple to operate. Easy to clean.	Plastic (nonfluorocarbon polymer) churn splitters must not be used to composite samples for determination of organic compounds. Can be used to split samples with particle sizes 250 µm and suspended-sediment concentrations 1,000 mg/L, but splitting accuracy becomes unacceptable for particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. When using the 14-L churn, sample volumes that total less than 4 L or greater than 13 L cannot be split for whole-water subsamples. Requires a modified spigot and construction of a funnel assembly. If pre-cleaned equipment is not available for each site, the churn requires field decontamination and additional blanking.
Fluorocarbon-polymer cone splitter	Can be used on samples with suspended-sediment concentrations from 0 to 10,000 mg/L. Samples containing sediment particles ranging in size from very fine clay and silt (1 to 10 µm) to sand-size particles (250 µm) can be split. Samples as small as 250 mL can be split into 10 equal subsamples. Samples greater than 13 L can be processed. Suitable for samples to be analyzed for both inorganic and non-volatile organic analyses. The FEP distributor tubes can be pre-cleaned and replaced for each sample to reduce field decontamination efforts.	Accuracy of the volume equivalents must be verified before using a new or modified cone splitter. Splitter is awkward to operate and clean in the field. If pre-cleaned equipment is not available for each site, the cone splitter requires field decontamination and additional blanking. Sample is vulnerable to contamination from atmospheric sources or from improper operation. Splitting accuracy for sediment particles >250 µm or sediment concentrations >10,000 mg/L must be quantified by the user. The cone splitter must be level for proper operation.
Magnetic Stir Bar and Autosampler Pump	All equipment can be pre-cleaned, no field decontamination needed. Minimizes contact with additional surfaces and secondary containers. Very adaptable to processing large numbers of samples in limited time. Wet sieving of whole storm samples through 64 µm prior to splitting would make reproducibility acceptable.	Ineffective with coarse sediments (>150-200 µm). Accuracy and reproducibility with significant sediment loads must be verified. Accuracy and reproducibility when performed by different personnel must be verified.

[L, liter; mg/L, µm, micrometer; milligrams per liter; mL, milliliters; >, greater than; ≤, less than or equal to.]

of churns and cone splitters are well described in the USGS National Field Manual (various dates).

Selbig, Bannerman, and Bowman (2007) tested an alternative approach to processing samples. Whole storm samples were initially filtered through 63 µm nylon filters to remove all particles in the sand fraction. The remaining storm samples were then split and subsampled into standard 250 ml containers for analysis of trace metals. They further modified the procedure by digesting the entire 250 ml sample rather than using the standard procedure of withdrawing an aliquot of the 250 ml sample for digestion.

With only the silt and clay fraction remaining in the stormwater composite sample, alternative splitting methods such as used by Gossett and Schiff (2010) for developing subsamples for a large interlaboratory comparison study. Sample splitting was accomplished by the use of a large-capacity stirrer and a 2- to 3-inch, pre-cleaned, Teflon-coated stir bar (larger stirbars can be used for larger volume containers) placed in the bottom of 20-L borosilicate media bottle containing the stormwater composite. Stirring speed was controlled to avoid creation of a large vortex within the composite bottle that can actually concentrate heavier particles. The final speed setting was based on a visual assessment of the most even mixing throughout the composite bottle. Sub-sampling from the homogenized composite bottle was accomplished using a peristaltic pump and pre-cleaned (inside and outside) sub-sampling hose. The sub-sampling hoses consisted of a short piece of silicone hose with FEP tubing attached to both ends. The rigid FEP tubing was long enough to reach the bottom of the 20-L composite bottle and extend at least 6 inches to allow space for manual manipulation of the tube.

Filling sample containers by pumping from the composite bottle was performed by two people. One person was responsible for filling individual sample containers and one person was responsible for constantly moving the intake tubing up and down in the water column of the composite sample. Based on experimental evidence, this up and down movement of the intake is a procedure that helps obtain a more representative sub-sample since some stratification of heavier particles in the composite sample despite the mixing created by the stirrer. (Note that these samples were whole storm composites that included suspended material greater than 63 µm in diameter.) They recommend limiting the up and down movement of the intake tubing should to approximately 80 to 90% of the depth of the water column and never touch the bottom of the composite bottle.

Regardless of the methods and approach selected to split large composite samples, initial testing is essential to demonstrate that the process can be performed without introducing contamination and assure that subsamples can be obtained that consistently meet project requirements for precision, accuracy, and representativeness.

5.6 Filtration Issues

A number of important questions remain unanswered with respect to the magnitude and importance of changes in the partitioning of dissolved and particulate metals during the process of collecting and handling the composite samples. The sampling process may occur over the period of just a couple of hours to a couple of days. Once storm discharges are complete, the composite sample is removed and subjected to strong mixing in order to obtain uniformly mixed subsamples for analysis. The federal guidelines indicate that filtration should occur within 15 minutes of splitting the composite sample. These guidelines are not considered practical for most stormwater programs. The Caltrans stormwater monitoring guidelines (Caltrans 2003) established a holding time of 48 hours for filtration of flow-weighted composite samples to allow samples to be transported and filtered in the laboratory.

The time required to attain an equilibrium distribution of constituents between the dissolved and particulate fractions in stormwater merits further research investigation. If there is a significant trend toward increased particulate phase metals during storage, then this trend could be useful in BMP selection. BMPs that can store the runoff can provide time for increased particulate phase concentrations and therefore greater metals removal, because metal removal by BMPs is primarily due to suspended solids removal. The hydraulic detention time for many BMPs, such as detention basins, is quite small compared to the time typically allowed for equilibrium to be reached in most samples collected as part of monitoring programs.

Holding times for both filtration and analyses are measured from the time the last aliquot is taken to the time when samples are filtered in the laboratory. By any measure, this is a highly arbitrary starting point. The extent to which geochemical and physical partitioning processes may have progressed by the end of the storm event cannot be established. Ultimately, the issue becomes a question of how rapidly these partitioning processes occur and whether exposure times in a BMP are sufficient to accelerate precipitate and sequester metals. It is estimated that partitioning processes can approach equilibrium within 1 to 12 hours depending largely on the sediment content and size composition.

The National Highway Runoff Water-Quality Data and Methodology Synthesis (Breault and Granato 2000) identified the existence of dissolved matrix sampling artifacts associated with historical water quality data that could be classified as either environmental or procedural. Environmental factors were defined as geochemical composition, suspended solids, concentrations of colloids, and the amount of organic material in the samples. All of these factors varied substantially between storm events and contributed to variability. Procedural artifacts were identified as those introduced by use

of different filter types, pore sizes, filter surface areas, and methods of filtration. They also demonstrated how filter packing could alter the size classes of sediment that pass through the filter. Even though the filter was designed to let size classes of 0.45 µm or less to pass through the filter, it is evident that the filter packing set up a finer filter that limited many smaller particles from crossing the filter.

In an attempt to overcome some of these issues, Breault and Granato (2000) suggested three potential options:

- Large surface area stainless steel, Teflon filter holders with 0.45 µm filters; or
- Use of pre-centrifugation to remove sediment and colloid that might clog the membrane. This eluate would then be filtered through a standard 0.45 µm; or
- "Exhaustive filtration" with the more complex techniques that are designed to remove colloids and thus leave only metals that are truly "dissolved."

Since these volumes were published in 2003, few changes have been made in the manner in which stormwater samples have been collected and tested for dissolved and total trace metals. The majority of stormwater monitoring has been conducted with autosamplers taking flow-weighted composites for the full duration of an event. Two recent studies based upon intensive grab sampling (Dean, Sansalone et al. 2005; Lau, Han et al. 2009) and filtration within 2–4 hours of collection both illustrate a substantial degree of variability in the dissolved fraction (f_d) of metals and generally higher proportions of dissolved metals compared to flow-weighted composite samples filtered up to 48 hours after the end of an event. Work conducted in Baton Rouge, Louisiana (Dean, Sansalone et al. 2005) showed that metal partitioning and speciation was influenced by hydrologic conditions. High intensity rainfall was noted to result in increased f_d values that was attributed to shortened residence times. During high flow rates, cadmium, copper and zinc tended to exhibit low f_d values due to a more pronounced diluting effect on dissolved metal concentrations and a more pronounced delivery of particulate-bound metals. Another study (Lau, Han et al. 2009) conducted in southern California also primarily used grab sampling to characterize highway runoff at three sites with average daily traffic (ADT) volume greater than 260,000. The study was conducted over a period of three storm seasons from 2000 to 2003. Samples were transported to the nearby UCLA campus laboratory and filtered within a few hours of the collection. Lau, Han et al. (2009) provided tables comparing calculated dissolved and total recoverable metals EMC results for the Los Angeles highway sites with stormwater composite data from six years of monitoring at Caltrans sites throughout the state. These data were restructured by Minervini (2010) to compare the average percentages of metals present in the dissolved form (Table 6). The UCLA study found that cadmium, copper, nickel and zinc were predominantly in the dissolved fractions (71 to 82% dissolved). It was suggested that the much shorter holding times used for completing the filtration process was a likely factor in the higher percentages of the metals in the dissolved fraction. Another contributing factor may have been the low concentrations of suspended solids available in the samples relative to those reported in the flow-weighted composite samples from other Caltrans monitoring efforts.

5.6.1 Filtration Methods

Filtration is best conducted in the laboratory where the environment can be better controlled. Given the lack of comparability and potential for introduction of contaminants, it is recommended that samples be transported to the laboratory as soon as practical and filtered immediately. Filtration methods should be consistent with those outlined in EPA Method 1669. When necessary, these filtration methods can be utilized in a range of environments. If filtration is required to be conducted in a field situation, it would best be performed in

Table 6. Average percent dissolved metals.

Parameter	Lau et al. 2009	Caltrans (1997-2003)		
	Los Angeles (>260,000 ADT)	Statewide	Nonurban (<30,000 ADT)	Urban (>30,000 ADT)
TSS (mg/L)	68	175	232	152
Cd	72	38	40	33
Cr	28	32	29	33
Cu	71	34	35	33
Ni	79	40	34	42
Pb	15	10	12	10
Zn	82	37	35	37

(Lau, Han et al. 2009; Minervini 2010.)

a mobile laboratory or walk-in shelter that provides a clean, dry, and well lit location for handling the samples. Use of a glovebox is recommended for maintaining clean conditions. The glovebox should be set up in a protected area that has been set up with the intent of filtering water.

Capsule filters are recommended for use in filtering stormwater samples since they minimize potential for introduction of contaminants and studies have demonstrated that they are capable of producing suitable blanks at levels appropriate to EPA water quality criteria. Pall AquaPrep 600 Capsules 0.45 µm tortuous-path capsule filters (Catalog #12175) provide a 600 cm^2 effective filtration area (EFT) that can be sufficient for filtration of less than 1 liter of stormwater with relatively low quantities of suspended solids. This capsule filter uses Pall Supor membrane made of polyester-reinforced polysulfone (PES). The Pall GWV High Capacity Groundwater Sampling Capsules (Catalog #12178) are often a better filtration capsule for stormwater due to their ability to handle larger sediment loads before clogging. The GWV capsule provides 0.45 µm filtration but has an EFT of 700 cm^2 and uses Pall's Versapor® membrane (acrylic copolymer on a nonwoven support). Comparable alternative capsule filters are available with similar specifications. Regardless of the selected brand and membrane type, blanking studies are necessary to assure that the filters can produce blanks that are below target detection limits for the program.

The Pall capsule filters are intended for pressure filtration. A small, portable peristaltic pump is used to pump the sample water through the capsule filters. Cole Parmer sells a Masterflex L/S drive (Catalog No. H-07570-10) equipped with a quick load pump head that is commonly used for this purpose due to the range of pumping rates, working pressure, and flexibility to operate off AC or DC power. C-Flex™ peristaltic pump tubing (3/8 in. ID by approximately 3 feet) is the preferred tubing for use with this pump. C-Flex ™ is a thermoplastic elastomer made from styrene-ethylene, butylene-styrene (SEBS) resins. SEBS resintubing can be subjected to more aggressive cleaning with acids and does not tend to sorb metals. Unfortunately, this material will not hold up to the forces of the high-volume peristaltic pumps used for wastewater and stormwater sampling. The C-Flex™ peristaltic hose is connected to short 6-8 inch lengths of FEP tubing at both ends. Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors that have been subject to protocol cleaning procedures can be used to connect segments of tubing.

Tubing is cleaned by soaking in a nitric acid solution for 8–24 hours, rinsed with reagent water and air-dried. After drying, the ends are capped, tubing is bagged in clear polyethylene bags, serialized with a unique number associated with that cleaning batch, and stored until use.

The capsule filters and tubing should be pre-rinsed and conditioned by pumping approximately 1 liter of Type 1 laboratory water (Milli-Q or equivalent) through the capsule filters and discarded. This filter rinse is recommended even though Pall now indicates that each capsule filter is now certified to have been rinsed in this manner. Water from a minimum of 1 out of every 20 filters or one in every batch should be analyzed for metals to verify that quality standards are being maintained.

After the pre-rinse is complete, the intake is placed in the 1-liter HDPE bottle that was designated for dissolved metals and an initial portion of the sample (~50–100 ml) is pumped into a waste container. The remainder of the filtered water is directed into the final sample container and fixed with an ultrapure nitric acid such as Seastar Chemicals BASELINE nitric acid. Five milliliters of 10% Seastar Chemicals BASELINE nitric acid is typically sufficient to fix a 1-liter sample. If samples are fixed in the field, polypropylene or Teflon® vials of 50% Ultrex-grade nitric acid should be used (USGS 1998). A minimum of one (2 ml each) vial should be used for each 250 ml of sample in order to adjust pH to less than 2.

The filtration process is best performed with two personnel with one assigned to be "clean hands (CH)" and the other "dirty hands (DH)". The following is a summary of the process used to obtain a filtered composite sample for analysis of dissolved metals.

1. Set up the filtration system and supplies in a comfortable, convenient, and well-lit working location. DH opens the plastic bag and CH removes a section of C-Flex™/FEP tubing.
2. DH closes the bag and then assists CH in loading the peristaltic hose into the pump.
3. DH opens the storage bag containing the sample to be filtered and CH removes the water sample from the inner storage bag and places the bottle on the counter.
4. CH also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.
5. CH removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.
6. DH starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle.
7. CH then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. DH stops the pump.
8. CH removes the lid of the sample bottle and places the intake end of the tubing in the bottle.
9. DH starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. CH uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

10. DH starts the pump and the remaining sample is processed through the filter and collected in the sample bottle (final volume 500 mL). If preservation is required, the sample is acidified at this point.
11. CH replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag.
12. CH then places the zipped bag into the outer bag held by DH.
13. DH zips the outer bag and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

5.6.2 Real-time Filtration

A conceptual approach has been developed for performing real-time filtration (Figure 8) that would enable collection of flow-weighted composite samples for dissolved metals that represent actual conditions at the sampling point. This approach also avoids the additional handling of the composite sample to obtain subsamples for filtration thus providing less potential for introduction of contaminants. This approach would require some experience with electronics and the knowledge of the autosamplers. Minor fabrication would also

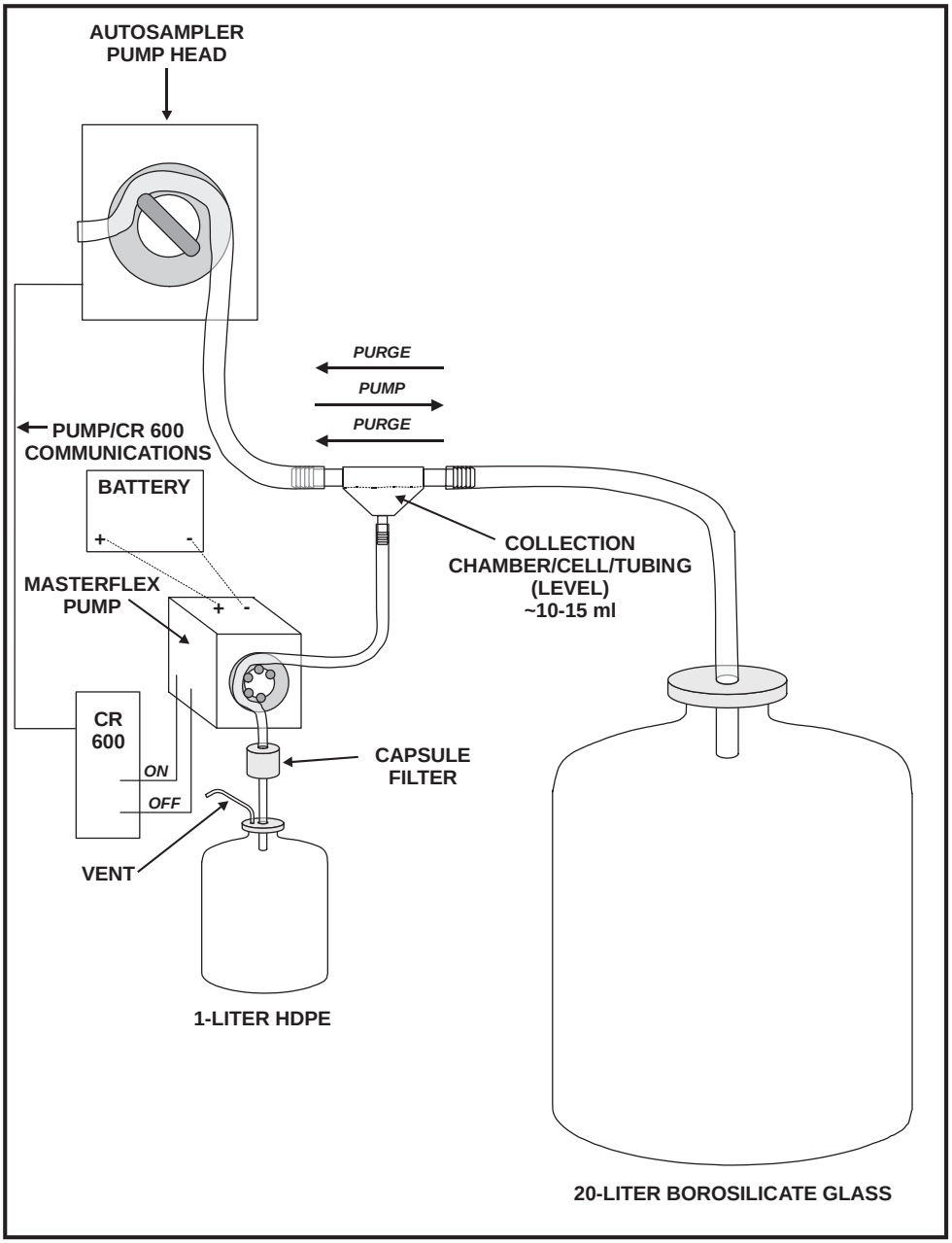

Figure 8. Diagram showing conceptual real-time filtration system for dissolved metals.

be required to construct the sampling capsule from appropriate materials.

A small, inline capsule could be used to trap a small quantity (~20ml) of water from each aliquot. Water would enter and exit near the top of the capsule. The bulk of the aliquot sample (typically 200 to 500 ml) would pass through and get discharged into a large, standard composite container that would be used for measurement to total metals, sediment, major ions, etc. A third port would be located at the bottom of the capsule. The filtration system would be connected at this point. The capsule would need a mounted level such that a consistent quantity of water would be subsampled during the pumping process, and the volume remaining in the cell would not be impacted by the purge cycle.

Most modern autosamplers have a range of potential for outputting information to a port indicating that a successful aliquot has been taken. The signal can be read by any basic data logger/control module such as a Campbell Scientific CR200X. The logger would be connected to a control switch or relay that allows switching a connection between two terminals (3 and 4) that control whether the Masterflex Pump is running or not. A closure of the remote switch contacts will turn the pump system on. Opening the contact will turn the pump system off. The datalogger would be programmed to run for a fixed time of roughly 10-20 seconds at 200/ml per minute to pump all of the water out of the bottom of the capsule and through a 0.45 micron capsule filter into a container. Tubing coming from the exit of the capsule filter would enter through the lid of the sample container and a second small hose would exit the lid and be vented through another small hose fitted with a PTFE vent filter. Use of small subsamples on the order of 20 ml would allow 50 aliquots to be sampled before filling a 1-liter bottle. If the high volume capsule filters are used, filter clogging should not be an issue for samples of this size.

CHAPTER 6

Analytical Methods and Quality Assurance/ Quality Control

The sampling and analysis plan (SAP) should incorporate a quality assurance and quality control (QA/QC) plan. This plan should detail activities that will be conducted to assure that both chemical and physical measurements meet the standard of quality needed to evaluate dissolved and particulate metals at levels relevant to EPA water quality criteria. Data comparability is an important consideration when developing these project plans. Intergovernmental Task Force on Monitoring Water Quality (ITFM 1995) defines comparability as the "characteristics that allow information from many sources to be of definable or equivalent quality so that it can be used to address program objectives not necessarily related to those for which the data were collected."

One important aspect of comparability is the use of analytical laboratories that are accredited under a program such as the National Environmental Laboratory Accreditation Program (NELAP) or a well-qualified research laboratory. In addition, the laboratory should be a participant in a laboratory proficiency and intercalibration program.

The online National Environment Methods Index (2011; http://acwi.gov/methods/index.html) is a key resource for selection of analytical methods that meet detection limits needed for the project and help insure that data are comparable. The SAP should incorporate all protocols that will be used to validate the analytical data. Protocols provided in the *National Functional Guidelines for Inorganic Superfund Data Review (USEPA540-R-10-011)* (U.S. EPA 2010) and the *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring (EPA/821/B/95/002)* (U.S. EPA 1996) are recommended.

The sections that follow address activities associated with both field sampling and laboratory analyses. Quality assurance activities start with procedures designed to assure that errors introduced in the field sampling and subsampling processes are minimized. Field QA/QC samples are collected and used to evaluate potential contamination and sampling error introduced into a sample prior to its submittal to the analytical laboratory. Laboratory QA/QC activities are used to provide information needed to assess potential laboratory contamination, analytical precision and accuracy, and representativeness.

6.1 Detection Limits, Data Quality Objectives, and Measurement Quality Objectives

There are a great number of definitions related to detection and quantification limits. A basic understanding of the derivation of these various limits is essential when data from the monitoring effort are being reported and assessed. The Method Detection Limit (MDL) for any test is currently defined in Title 40 of the Code of Federal Regulations Part 136 as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte." (40 CFR 136, Appendix B, revision 1.11). The MDL is derived from seven analyses conducted on a sample containing concentrations of the analyte of concern. The MDL is calculated by multiplying the standard deviation of the seven replicates by the appropriate 1-tailed Student's T value for 6 degrees of freedom (n-1) and a probability of 0.01 (3.143). Therefore the MDL is actually a distribution with the limit established at the mean or 50% percentile value. The Limit of Quantification (LOQ) is defined as the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated operational conditions of the method. The LOQ, which here considered the Reporting Limit, is approximately 10 times the standard deviation of the seven replicates analyzed in the MDL study. A reporting limit (or LOQ) is a "threshold based on a measure of the variability or noise inherent in the laboratory process, while a detection limit is a threshold below which measured

values are not considered statistically different from a blank signal" (Helsel 2005).

Reporting limits for the metals and many of the other proposed constituents are often near the practical limits of modern instrumentation with use of implementation of methods that require extraction and concentration of the metals. These suggested reporting limits were established based upon the need to evaluate the data at levels appropriate to receiving water quality standards. The relative accuracy of most laboratory methods decreases as concentrations approach the detection limits. For this reason it is recommended that, where possible, reporting limits should be established at levels that are 0.1 to 0.5 times the level of concern. These lower reporting limits are necessary in order to minimize analytical variability so that data can be used to effectively assess water quality relative to the established standards.

Data that are below reporting limits should be identified as <RL. For purposes of calculating descriptive statistics, one of three methods for handling left-censored data with single or multiple detection limits (Helsel 2005, 2009). These three methods [maximum likelihood estimation (MLE); regression on order statistics (ROS); and Kaplan-Meier (K-M)] are summarized and compared in Geosyntec and Wright Water Engineers (2009; http://bmpdatabase.org). The ROS method is recommended by the International Stormwater Best Management Practices (BMP) Database project and is currently used by Caltrans studies in California. A Microsoft Excel add-in macro and instructions for the ROS method can be accessed from the Caltrans Stormwater website (http://www.dot.ca.gov/hq/env/stormwater/pdf/DAT.zip).

Performance acceptance criteria, also known as Data Quality Objectives (DQOs), should be specified for the project, to help ensure that the data produced by the monitoring program will be useful in addressing program objectives. DQOs are intended to limit the probability of making decision errors by considering the purpose for collecting the data, defining the appropriate data needed, and defining the tolerable probabilities of making decision errors. Measurement Quality Objectives (MQOs) provide specific acceptance criteria (constituent reporting limits, analytical precision, accuracy, completeness, and representativeness) for each analytical method.

MQOs, as defined for this guidance document, specify the quality of data required to support the specific objectives of the monitoring program. Table 7 and Table 8 provide suggested MQOs for measurement of dissolved metals at levels of ecological concern and provide the ancillary data that are useful in the interpretation of the data. The MQOs for ancillary data were selected to provide the ability to run various geochemical models that can improve assessment of bioavailability and mobility of metals in stormwater runoff.

6.2 Precision, Bias, Accuracy, Representativeness, Completeness, and Comparability

The overall quality of analytical measurements is assessed through evaluation of precision, accuracy/bias, representativeness, comparability, and completeness. Precision and accuracy/bias are measured quantitatively. Representativeness and comparability are both assessed qualitatively. Completeness is assessed in both quantitative and qualitative terms. The following sections examine how these measures are typically applied.

6.2.1 Precision

Precision provides an assessment of mutual agreement between repeated measurements. These measurements apply to field duplicates, laboratory duplicates, matrix spike duplicates, and laboratory control sample duplicates. Monitoring of precision through the process allows for the evaluation of the consistency of field sampling and laboratory analyses.

The Relative Percent Difference (RPD) will be used to evaluate precision based upon duplicate samples. The RPD is calculated for each pair of data and is calculated as:

$$RPD = [(x_1 - x_2) * 100] / [(x_1 + x_2)/2)$$

Where:

x_1 = concentration or value of sample 1 of the pair
x_2 = concentration or value of sample 2 of the pair

In the case of matrix spike/spike duplicate, RPDs are compared with MQOs established for the program. Suggested MQOs are provided in Table 8 but final objectives should be established based upon the objectives of the monitoring program and in consultation with the laboratory. In the case of laboratory or field duplicates, values can often be near or below the established reporting limits. Calculation of RPDs is not appropriate if one or both values are below reporting limits. When both values are near the detection limits RPDs may exceed established limits but the absolute difference between the two samples should not exceed the reporting limit.

6.2.2 Bias

Bias is the systematic inherent in a method or caused by some artifact or idiosyncrasy of the measurement system. Bias may be either positive or negative and can emanate from a number of different points in the process. Although both positive and negative biases may exist concurrently in the same sample, the net bias is all that can be reasonably addressed in this project. Bias is preferably measured through analysis of spiked samples so that matrix effects are incorporated.

Table 7. Recommended constituents, analytical methods, and specifications for sample handling.

Analyte	Method Type	EPA Method Number	Holding Time	Container Type	Preservation	Detection[1,2] Limit/ Resolution	Units
			Conventionals				
pH	electrometric	150.1	15 minutes	glass or PE	none	+/- 0.1	std. units
Alkalinity	titrimetric;	SM 2320B	Filter ASAP, 14 days	PE	none	1	mg/L
Carbonate	titrimetric;	SM 2320B	Filter ASAP, 14 days	PE	none	1	mg/L
Bicarbonate	titrimetric;	SM 2320B	Filter ASAP, 14 days	PE	none	1	mg/L
Hydroxide	titrimetric;	SM 2320B	Filter ASAP, 14 days	PE	none	1	mg/L
Conductivity	conductivity meter	SM 2510	28 days	glass or PE	4°C; filter if hold time >24 hours	+/- 1	µmho/cm
Hardness	titrimetric; colorimetric; calculation; ICP-AES	130.2; 130.1; SM 2340B; 200.7	6 months	glass or PE	4°C and HNO_3 or H_2SO_4 to pH<2	1	mg/L
Calcium	ICP-AES	SM 2340B; **200.7**	6 months	glass or PE	4°C and HNO_3 or H_2SO_4 to pH<2	0.01	mg/L
Magnesium	ICP-AES	SM 2340B; **200.7**	6 months	glass or PE	4°C and HNO_3 or H_2SO_4 to pH<2	0.02	mg/L
TOC; DOC	oxidation or combustion	415.1	28 days	glass or PE	4°C and HCl or H_2SO_4 to pH<2	1	mg/L
TDS	dried filtrate weight	160.1	7 days	glass or PE	4°C	1	mg/L
TSS	dried filter weight	160.2	7 days	glass or PE	4°C	4	mg/L
SSC	dried filter weight	ASTMD3977B	7 days	glass or PE	4°C	4	mg/L
Ca, Mg, Na, K	ICP-AES	**200.7**; 6010B	6 months	glass or PE	4°C and HNO_3 or H_2SO_4 to pH<2	0.01-0.3	mg/L
SO_4, Cl^-	Ion chromatography	300	28 days	glass or PE	4°C	0.02	mg/L

(continued on next page)

6.2.3 Accuracy

Accuracy is a measure of the closeness of a measurement or the average of a number of measurements to the true value. Accuracy includes a combination of random error as measured by precision and systematic error as measured by bias. An assessment of the accuracy of measurements is based on determining the percent difference between measured values and known or "true" values applied to surrogates, matrix spikes (MS), laboratory control samples (LCS) and standard reference materials (SRM). Surrogates and matrix spikes evaluate matrix interferences on analytical performance, while laboratory control samples, standard reference materials, and blank spikes (BS) evaluate analytical performance in the absence of matrix effects.

Assessment of the accuracy of measurements is based upon determining the difference between measured values and the true value. This is assessed primarily through analysis of spike recoveries or certified value ranges for SRMs. Spike recoveries are calculated as percent recovery according to the following formula:

$$\text{Percent Recovery} = [(t - x)/\alpha] * 100\%$$

Table 7. (Continued).

Analyte	Method Type	EPA Method Number	Holding Time	Container Type	Preservation	Detection[1,2] Limit/ Resolution	Units
			Metals				
Aluminum	GF-AA; ICP-MS	200.9; **200.8**	filter for dissolved fraction and preserve within 24 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2	1	µg/L
Arsenic	ICP-MS	**200.8**; 1632				1.4	µg/L
Cadmium	ICP-MS	**200.8**; 1638				0.5	µg/L
Chromium	GF-AA; ICP-MS	**200.8**				0.9	µg/L
Copper	GF-AA; ICP-MS	**200.8**; 1638				0.5	µg/L
Iron	GF-AA; colorimetric	200.7; 200.9; **SM 3500-Fe B**				10	µg/L
Lead	GF-AA; ICP-MS	200.8;1638				0.6	µg/L
Nickel	GF-AA; ICP-MS	200.8; 1638				0.5	µg/L
Selenium	GF-AA; GH-AA; ICP-MS	**200.9**; 200.8; 1638; 1639				0.6	µg/L
Silver	GF-AA; ICP-MS	**200.8**; 1638				01	µg/L
Zinc	GF-AA; ICP-MS	**200.8**; 1638				1.8	µg/L

[1] When multiple analytical methods are stated, the analytical method associated with the detection limit was bolded.

[2] Suggested detection limits are based upon the National Environmental Methods Index (https://www.nemi.gov/apex/f?p=237:1:175271955775976), accessed September 30, 2011.

Where:

t = total concentration found in the spiked sample
x = original concentration in sample prior to spiking, and
α = actual spike concentration added to the sample

6.2.4 Representativeness, Comparability, and Completeness

Representativeness is the degree to which data accurately and precisely represent the natural environment. For stormwater runoff, representativeness is first evaluated based upon the automated flow-composite sample and the associated hydrograph. To be considered as representative, the autosampler must have effectively triggered to capture initial runoff from the pavement and the composite sample should (1) be comprised of a minimum number of aliquots over the course of the storm event, (2) effectively represent the period of peak flow, (3) contain flow-weighted aliquots from over 80% of the total runoff volume, and (4) demonstrate little or no evidence of "stacking." Stacking occurs when the sampling volume is set too low and commands back up in the memory of an autosampler causing it to continuously cycle until it catches up with the accumulation of total flow measured by the stormwater monitoring station.

Representativeness is also assessed through the process of splitting or subsampling 20 L composite bottles into individual sample containers being sent to the laboratory. The first subsamples removed from the composite bottle should have the same composition as the last. Subsampling standard operation procedures (SOPs) should be established and closely followed to minimize variability in this process. As noted in Section 5.5, sample splitting can introduce a substantial amount of error especially if significant quantities of coarse sediments (greater than 250 µm) represent a significant fraction of the suspended sediments. Wet sieving of the whole storm sample with a 63 µm mesh prior to splitting the sample (Selbig and Bannerman 2008) and subsequent digestion of the entire unfiltered and filtered subsample containers has shown some promise of providing better assessments of the particulate and dissolved loads of metals in stormwater. The sand fraction can be analyzed independently as a single sample or further fractionated to assess partitioning within the sand fractions. Removal of the sand fraction from the whole stormwater material greatly reduces variability among split samples regardless of the method used.

Comparability is the measure of confidence with which one dataset can be compared to another. The use of standardized methods of chemical analysis and field sampling and processing are ways of insuring comparability. Application of

Table 8. Suggested measurement quality objectives.

Analyte	Target[5] Detection Limit	Holding Times	Accuracy		Precision		Completeness
			Spike Recovery	SRM[2] Recovery	Matrix Spike RPDs	Laboratory Duplicate RPDs	
Conventionals							
pH	0.1 units	Immediately[1]	—	—	—	±20%	95%
Alkalinity	1 mg/L	Filter ASAP, 14 days	—	—	—	±20%	95%
Carbonate	1 mg/L	Filter ASAP, 14 days	—	—	—	±20%	95%
Bicarbonate	1 mg/L	Filter ASAP, 14 days	—	—	—	±20%	95%
Hydroxide Alkalinity	1 mg/L	Filter ASAP, 14 days	—	—	—	±20%	95%
Spec. Conductance	1 μmhos/cm	28 days [1]	—	80-120%	—	±25%	95%
Hardness as $CaCO_3$	1 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
Calcium	0.01 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
Magnesium	0.02 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
TDS	1 mg/L	7 days[3]	80-120%	80-120%	±25%	±20%	95%
TSS	1 mg/L	7 days[3]	80-120%	80-120%	±25%	±20%	95%
SSC	1 mg/L	7 days[3]	80-120%	80-120%	±25%	±20%	95%
TOC	1 mg/L	28 days	85-115%	85-115%	±25%	±15%	95%
DOC	1 mg/L	28 days	85-115%	85-115%	±25%	±15%	95%
Major Ions							
Sulfate	0.02 mg/L	28 days	80-120%	80-120%	±25%	±20%	95%
Chloride	0.02 mg/L	28 days	80-120%	80-120%	±25%	±20%	95%
Calcium	0.01 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
Magnesium	0.02 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
Potassium	0.30 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
Sodium	0.03 mg/L	6 months	80-120%	80-120%	±25%	±20%	95%
Metals (dissolved[4] and total)							
Aluminum	1.0	6 months	75-125%	80-120%	±20%	±20%	95%
Arsenic	1.4 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Cadmium	0.5 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Chromium	0.9 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Copper	0.5 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Iron	10 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Lead	0.6 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Nickel	0.5 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%
Zinc	1.8 μg/L	6 months	75-125%	80-120%	±20%	±20%	95%

[1] Performed in field if possible

[2] SRM recovery values based upon values provided with each specific SRM

[3] 7 days based upon limit for measuring TSS/no regulatory limit.

[4] Filter within 24 hours of end of storm

[5] Suggested detection limits are based upon the National Environmental Methods Index (https://www.nemi.gov/apex/f?p=237:1:175271955775976), accessed September 30, 2011.

consistent sampling and processing procedures is necessary for assuring comparability among data sets. Thorough documentation of these procedures, quality assurance activities, and a written assessment of data validation and quality are necessary to provide others with the basic elements to evaluate comparability.

Completeness is a measure of the percentage of the data judged valid after comparison with specific validation criteria. This includes data lost through accidental breakage of sample containers or other activities that result in irreparable loss of samples. Implementation of standardized chain-of-custody procedures which track samples as they are transferred between custodians is one method of maintaining a high level of completeness.

A high level of completeness is essential to all phases of this study due to the limited number of samples. Of course, the overall goal is to obtain completeness of 100%; however, a realistic data quality indicator of 95% insures an adequate level of data return.

6.3 Laboratory Quality Assurance/ Quality Control

The quality of analytical data is dependent on the ways in which samples are collected, handled, and analyzed. DQOs provide the standards against which the data are compared to determine if they meet the quality necessary to be used to address program objectives. Data should be subjected to a thorough verification and validation process designed to evaluate project data quality and determine whether data require qualification.

The three major categories of QA/QC checks, accuracy, precision, and contamination, were discussed in the previous section. As a minimum, the laboratory should incorporate analysis of duplicate samples, method blanks, and matrix spike/spike duplicates with each analytical batch. Use of a certified reference material (CRM) or standard reference material (SRM) is also recommended as these allow assessment of long term performance of the analytical methods so that representativeness can be assessed. Laboratories often use an internal CRM that is analyzed with each batch to evaluate any potential long-term shift in performance of the analytical procedures. Recommended minimum quality control samples are provided in Table 9.

6.4 Field QA/QC

6.4.1 Blanks

A thorough system of blanking is an essential element of monitoring. Much of the blanking processes are performed well in advance of the actual monitoring in order to demonstrate that all equipment expected to contact water is free of contaminants at the detection limits established for the program. Equipment components are cleaned in batches.

Table 9. Laboratory quality control samples by analyte.

Analyte	Equipment/ Container Blanks	Filter Blanks	Method Blanks	Field and Laboratory Duplicates	MS/ MSDs[1]	LCSs[2] or SRMs[3]
pH	—	—	—	●	—	—
Alkalinity	—	—	●	●	—	●
Carbonate	—	—	●	●	—	●
Bicarbonate	—	—	●	●	—	●
Hydroxide	—	—	●	●	—	●
Spec. Conductance	—	—	—	●	—	●
Hardness as $CaCO_3$	—	—	●	●	●	●
TDS	●	—	●	●	—	●
TSS	—	—	●	●	—	●
TOC	●		●	●	●	●
DOC	●	●	●	●	●	●
Cations (Ca, Mg, K…)	—	—	●	●	●	●
Anions (Cl, SO_4…)	—	●	●	●	●	●
Metals	●	●	●	●	●	●

[1] Matrix Spike and Matrix Spike Duplicate

[2] Laboratory Control Samples

[3] Standard Reference Materials

Table 10. Summary of blanking requirements for field equipment.

System Component	Blanking Frequency
Intake Hose	One per batch
Peristaltic Pump Hose	One per batch[1] or 10% for batches greater than 10
Composite Bottles	One per batch or 10% for batches greater than 10
Subsampling Pump Hose	One per batch or 10% for batches greater than 10
Laboratory Sample Containers	2% of the lot[2] or batch, minimum of one
Capsule Filter Blank[3]	One per batch or 10% for batches greater than 10
Churn/Cone Splitter	When field cleaning is performed, process one blank per session

[1] A batch is a group of samples that are cleaned at the same time and in the same manner.

[2] If decontaminated bottles are sent directly from the manufacturer, the batch would be the lot designated by the manufacturer in their testing of the bottles.

[3] If filtration is performed in the laboratory, the capsule filter blanks would be considered part of laboratory QA/QC.

Subsamples from each cleaning batch are rinsed with Type 1 laboratory blank water and submitted to the laboratory for analysis. If hits are encountered in any cleaning batch, the entire batch is put back through the cleaning and blanking process until satisfactory results are obtained. If contaminants are measured in the blanks, it is often prudent to reexamine the cleaning processes and equipment or materials used in the cleaning process. Equipment requiring blanks and the frequency of blanks is summarized below and in Table 10.

6.4.2 Field Duplicates

Composite subsampling duplicates associated with flow-weighted composite samples are often referred to as field duplicates but, in fact, they are subsampling replicates. These replicates help assess combined variability associated with subsampling from the composite container and variability associated with the analytical process. They are evaluated against the same criteria as used for laboratory duplicates.

CHAPTER 7

Equipment Cleaning, Blanking, and Tracking

Sample collection, handling, and processing materials can contribute and/or sorb trace elements within the time scales typical for collection, processing, and analysis of runoff samples. The relative effect of potential contamination and/or attenuation of trace elements in runoff samples is a function of the concentrations of major and trace elements, organic chemicals, and sediment in solution. Sampling artifacts are especially important when measured concentrations that are at or near analytical detection limits (Horowitz 1997). Therefore, great care is required to collect and process samples in a manner that will minimize potential contamination and variability in the sampling process (Breault and Granato 2000).

Sampling conducted to measure dissolved metals at levels relevant to EPA water quality criteria requires documentation that all sampling equipment is free of contamination and that the processes used to obtain and handle samples do not introduce contamination. This requires documentation that methods used to collect, process, and analyze the samples do not introduce contamination. Documentation should include establishing detailed written procedures for cleaning all components of the sampling system, blanking processes necessary to verify that system components and sample handling are not introducing contamination, and a system of tracking deployment of protocol-cleaned equipment in the field.

All sample containers and equipment used for sample collection in the field and/or sample storage in the laboratory must be decontaminated and cleaned prior to use. These include the FEP tubing, Teflon® lids, strainers, and hoses/fittings that are used in the subsampling process (USGS 1993). It is important that personnel assigned to clean and handle the equipment are thoroughly trained and familiar with the cleaning, blanking, and tracking procedures. All field sampling staff should be familiar with these processes so that they have a better understanding of the importance of using clean sampling procedures and the effort required to eliminate sources of contamination.

Cleaning procedures require use of correct equipment, protective gear, and proper handling of waste products. Work should be conducted in a well-ventilated area using appropriate protective garments and goggles for eye protection whenever cleaning the sampling equipment with the acid.

Cleaning protocols should also be consistent with ASTM (2008) standard D5088–02 that covers cleaning of sampling equipment and sample bottles. The generalized cleaning process is based upon a series of washings that typically start with tap water with a phosphate-free detergent, a tap water rinse, soaking in a 10% solution of reagent grade nitric acid, and a final series of rinses with laboratory Type 1 water.

SOPs for cleaning sampling equipment are provided in Appendix B. The Florida State Department of Environmental Protection (DEP) also maintains a list of SOPs that contain detailed cleaning procedures for equipment to be used for ultra-trace metals sampling and general water quality sampling. These SOPs are available on-line at http://www.dep.state.fl.us/water/sas/sop/sops.htm.

The SOPs include guidelines for packaging and labeling cleaned equipment by batches, blanking each batch, and tracking deployment of each system component in order to link site data with blanking data for all bottles and tubing. These are intended as general guidelines that can be modified to fit specific project requirements. Ultimately, application of the final cleaning protocols should be tested to verify that blanks can consistently be obtained that meet the project objectives before implementation of the field sampling program. If contamination is routinely encountered, the procedures and materials used in the cleaning process should be reexamined and modified as necessary to eliminate possible sources of contamination.

Sample contamination has long been considered one of the most significant problems associated with measurement of dissolved metals. One of the major elements of QA/QC documentation is establishing that clean sampling procedures are used throughout the process and that all

equipment used to collect and process the water samples are free of contamination.

7.1 Laboratory Sample Bottles

In order to account for any contamination introduced by sampling containers, blanks must be collected for composite bottles and laboratory bottles used for sample storage for metals analysis. A sampling container blank is prepared by filling a clean container with blank water and measuring the concentrations of selected constituents (typically metals and other trace contaminants for composite bottles and metals analysis only for metals storage bottles). These blanks may be submitted "blind" to the laboratory by field personnel or prepared internally by the laboratory.

Certified pre-cleaned QC-grade bottles can be used. These bottles are cleaned using acceptable protocol for analysis of dissolved metals and tracked by lots. They come with standard certification forms that document the concentration to which the bottles are considered "contaminant-free," but these concentrations are not typically suitable for program reporting limits required for measurement of dissolved metals. Manufacturers may provide an option of certification to specific limits required by a project but it is preferable to purchase the QC bottles that are tracked by lot and conduct internal blanking studies. Lots not meeting project requirements should be returned to the manufacturer and exchanged for containers from another lot. At least 2% of the bottles in any lot or batch should be blanked at the program detection limits with a minimum frequency of one bottle per batch. A batch is a group of samples that are cleaned at the same time and in the same manner; or, if decontaminated bottles are sent directly from the manufacturer, the batch would be the lot designated by the manufacturer in their testing of the bottles.

After cleaning, sample bottles and laboratory-cleaned sampling equipment are handled only while wearing clean, powder-free nitrile gloves. All laboratory-cleaned sampling equipment and metals analysis storage bottles are double bagged in clean zip-lock plastic bags for storage or shipment. Clean bottles are stored in a clean area with lids properly secured.

Immediately prior to the filling of laboratory sample bottles, the bottle labels should be checked, and date and time added using a waterproof pen. Attempting to label grab sample bottles after sample collection may be difficult because of wet labels. The remainder of the information on the labels is prepared in advance to minimize handling requirements during the field effort.

CHAPTER 8

Reporting and Documentation

The National Highway Runoff Data and Methodology Synthesis project (Granato, Zenone et al. 2003) involved an extensive review of available monitoring data and provided a number of key recommendations for improving the information and data generated by runoff monitoring programs would be valuable for local, regional, and national needs. In an effort to improve data comparability, increase data sharing, and allow use of data for secondary purposes, the Methods and Data Comparability Board of the National Water Monitoring Council (2006) developed a set of standardized data elements that should be incorporated in any program. Additional information is provided by Geosyntec Consultants and Wright Water Engineers (2009). This document provides specific guidance on data structures and metadata necessary to submit data to the International Stormwater BMP database. A data entry file is provided on the www.bmpdatabase.org web site that identifies all required and recommended data elements needed for submission of stormwater BMP monitoring data.

Among the most important issues cited was a lack of basic information necessary to determine the uncertainty of data sets and documentation of QA/QC practices. This information was considered critical for evaluating the potential utility of available water quality information for any given purpose (Church, Granato et al. 2003). They indicated that all studies should provide certain basic data that would eventually lead to the ability of other researchers to independently review the information and make informed decisions as to the utility of the data for other purposes. Without the ready availability of the basic data and the necessary information to evaluate the supporting quality assurance information, studies are often considered to be of limited value.

Ideally, all data and reports should be archived on an internet site where the information can be readily accessed. Consideration should be given to making data available through regional data centers that are becoming more common for consolidating and accessing research and monitoring information to improve distribution and documentation. These centers may have specific requirements for data formats which should be a consideration when designing the monitoring program. Full access to data along with appropriate documentation generated from these types of investigations will promote better science and help speed progress towards more effective BMPs. This allows data to be used with confidence in other studies, encourages improved sampling designs, and will contribute to an improved understanding of the complex processes involved as metals are mobilized from impervious surfaces and transported to the storm drains and receiving waters. Understanding major factors controlling the rates of these processes and the state of metals in the runoff at different locations along the discharge pathway will lead to better BMPs.

Table 11 provides a summary of major elements needed to improve acceptance and usability of stormwater runoff data. The Methods and Data Comparability Board (2006) also provides a summary and structure for water quality data that is considered the minimum for assuring that appropriate information is provided to assure that data can be shared and used by others. Copies of the SAP, Data Assessment and Validation Report, and any final reports summarizing and interpreting the results should be available as PDF documents.

The Data Assessment and Validation Report should provide a thorough review of QA/QC activities and summarize the results. This report should provide a systematic assessment of the data and quality assurance measurements against the MQOs established in the SAP. This report is often included as an appendix to main body of the report. Information should include:

- Tabular summaries of all quality assurance measures,
- Identify cases where MQOs may not have been met,
- Discuss the potential cause of these excursions,
- Identify corrective actions taken,
- Discuss impacts of any data quality issues, and
- Apply qualifiers based upon criteria established in the SAP.

Electronic data files should be included that contain information on the monitoring sites; rainfall, runoff, sampling data and water quality data associated with each monitoring event; and time series data for seasonal flow and precipitation information. If possible, this information should be provided in a standardized format such as that used by the Caltrans stormwater monitoring program in California (Caltrans 2003). If data are not provided in one of several established data base formats, metadata should be included with the files to describe the overall structure and contents of each field.

Table 11. Summary of recommended information and data needed to improve use of the data in addressing regional and national issues.

Written Documents		• SAP • Project Report(s) • Data Assessment and Validation Report
ELECTRONIC DATA FILES (Excel, Access or Other Database Formats)	**SITE DATA**	**Monitoring Site Information** • Location • Size of drainage area • Average slope • Soil type • Percent impervious • Estimate runoff coefficient • Average Annual Daily Traffic (AADT) • Type of pavement or land use • BMPs applicable to site
	EVENT DATA (Include metadata identifying database structure and fields)	**Rainfall** • Total rainfall • Seasonal rainfall to date • Antecedent rainfall (inches) • Antecedent dry weather (days) • Maximum rainfall intensity • Date/time of start and end of rainfall • Duration of rainfall **Runoff** • Total runoff volume • Peak flow rate • Date/time of start and end of runoff • Duration of runoff **Sampling Data** • # of aliquots • Time of each aliquot • % storm capture • Peak flow capture? **Water Quality Data** • Validated field and laboratory measurements
	TIME SERIES DATA (Seasonal or Event Data)	**Flow** • Site data only **Precipitation** • Site or regional data • If regional, include location, site ID and agency responsible for site

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APPENDIX B

Detailed Cleaning Protocol for Equipment to be Used for Collection of Stormwater Samples for Measurement of Dissolved Metals

CLEANING PROTOCOL FOR:

FEP intake sampling hoses, silicon peristaltic pump tubing, and sub-sampling hose setups.

1.0 SCOPE

This Standard Operating Procedure (SOP) describes the procedures required to properly clean hoses and tubing involved in non-point source (NPS) sampling. These include: The purpose of these procedures is to ensure contaminant-free sampling hoses and to ensure the safety of the personnel performing these procedures.

2.0 APPLICATION

This SOP applies to all activities pertaining to the cleaning of NPS sampling hoses.

3.0 HEALTH AND SAFETY CONSIDERATIONS

The cleaning of sampling hoses may subject personnel performing this task to contact with hazardous materials. Skin contact with all materials and solutions should be minimized by wearing appropriate personal protective equipment (PPE) including: chemically-resistant protective gloves, laboratory coats, chemically-resistant aprons and goggles. In addition, the material safety data sheets (MSDSs) for nitric acid and laboratory detergents should be reviewed prior to beginning this task to ensure that you are aware of the hazards involved with handling the respective chemicals as well as being informed of any revisions to the data sheets.

When introducing soap or acid through a series of hose with a peristaltic pump, it is safest to “Pull” the fluids through vs. “Push”. Pushing the fluids through may over-pressurize the connections and blow out (particularly if there is an obstruction, e.g., twisted hose, kink, etc.). Pulling the fluids through the series creates a negative pressure inside the tubing and reduces the potential for accidents.

4.0 DEFINITIONS

4.1 Tubing - either sample intake hose, sub-sample hose, or peristaltic pump tubing.

4.2 Intake sampling hose - 3/8" I.D. x 1/2" O.D. FEP tubing.

4.3 Sub-sampling hose setup - two 3-4 foot sections of 3/8-inch I.D. x 1/2-inch O.D. FEP hose connected with a section of silicon peristaltic pump tubing.

4.4 Peristaltic pump tubing - 3/8" I.D. x 5/8" O.D. silicon tubing.

4.5 DI water - commercial de-ionized water.

4.6 Laboratory Detergent - 2% solution of Contrad 70® or Micro-90® detergent.

5.0 EQUIPMENT

5.1 Instrumentation:

1) Peristaltic pump

5.2 Reagents:

1) ACS Reagent Grade nitric acid in a 2 Normal solution (2N HNO_3)

2) Contrad 70® non-phosphate laboratory detergent

3) Micro-90® non-phosphate laboratory detergent

4) Baking soda or equivalent to neutralize acid

5) pH paper

5.3 Apparatus:

1) Numerous 4-inch sections of protocol-cleaned silicon tubing.

2) Numerous 4-inch sections of protocol-cleaned Teflon® tubing.

3) Protocol-cleaned polyethylene bucket with lid (with hole in top).

4) Neutralization tank.

5.4 Documentation: Label each hose as to the date each was cleaned and the initials of the cleaning technician.

6.0 CLEANING PROCEDURES.

Care must be taken to ensure that no contaminants are introduced at any point during these procedures. If the wash is not performed with this in mind, the possibility for the introduction of contaminants (i.e., from dirty floors, dirty counter tops, dirty fingers/gloves, dirty hose ends, etc.) is increased significantly.

6.1 Sub-sampling Hose Setup:

6.1.0 This is used with a peristaltic pump to sub-sample from a 20 liter composite sample bottle **and** to facilitate pumping and/or circulation of laboratory detergent and nitric acid. A sub-sampling hose setup consists of two lengths of FEP hose (one approximately 3 feet and the other 4 feet) connected by a 24-inch section of silicon tubing. Numerous sub-sampling hose setups should be cleaned simultaneously by connecting them by 4-inch

sections of silicon peristaltic tubing. Important: Check for kinks or twists along the series that would inhibit the flow in and out.

6.1.1 **48 Hour Soak:** Place the series of hoses to be cleaned into a secondary container until the entire washing process is completed. Prepare a 2% solution of laboratory detergent in a protocol-cleaned bucket. Install one sub-sampling hose setup into a peristaltic pump. Connect this with the series of sub-sampling hose setups using a 4-inch section of silicon peristaltic tubing. Pump the detergent solution into the series of sub-sampling hose setups. It is recommended that the fluids be "pulled" through vs. "pushed". Circulate the solution through the hoses and bucket until there are no air bubbles left in the hoses. Separate both ends of the hose series from the pump setup and cap them with protocol-cleaned orange caps OR connect both ends using a protocol-cleaned 4-inch section of silicon. Let the hose soak for 48 hours. Pump out detergent solution and dispose of used solution down a sanitary drain.

6.1.2 **Tap Water Rinse:** Rinse by pumping tap water for 5 minutes from a protocol-cleaned HDPE bucket through the hose/hoses and into a neutralization tank and dispose of the rinsate in a sanitary drain. Important: In order to avoid contaminating the rinse water always be sure to clean the outside of the hose end that will be immersed in the rinse water: wash with laboratory detergent and a plastic brush, rinse with tap water and rinse three times with DI water.

6.1.3 **DI Water Rinse:** Rinse by pumping DI water for 5 minutes from a protocol-cleaned HDPE bucket through the hose/hoses and into a neutralization tank and dispose of the rinsate in a sanitary drain.

6.1.4 **2N (10%) Nitric Acid (2N HNO_3) Wash**: Wash with 2N (10%) nitric acid solution by pumping in a circular cycle for 10 minutes from the 2N (10%) nitric acid carboy. **Do not exceed 10 minutes.** Pump all the acid back into the acid carboy.

6.1.5 **DI Water Rinse:** Rinse by pumping DI water through the hose into the neutralization tank for 7 minutes. Neutralize and dispose of rinsate in accordance with all federal, state, and local regulations

6.1.6 **FEP Hose and Peristaltic Tubing Storage:** To store FEP hose put protocol-cleaned orange polypropylene caps on each end. To secure the silicon peristaltic tubing, attach both ends with a small protocol cleaned piece of FEP hose. Store the hose or tubing in a new garbage bag to

prevent contamination before use. **Label as clean, the date cleaned, and your initials**.

6.1.7 **Sub-Sampling Hose Exterior Cleaning and Storage:** NPS sub-sampling hoses require an additional cleaning procedure for the exterior portions of the hose (approximately 2 feet on one end) using protocol-cleaned squirt bottles as follows:

1) Place a protocol-cleaned orange cap on one end of the sub-sampling hose and wash the remaining end with a 2% solution of laboratory detergent using a plastic brush. Hold the hose in a way that prevents interior contamination from the exterior cleaning procedure.

2) Rinse end three times with tap water.

3) Rinse end three times with DI water.

4) Wash end three times with 2N nitric acid squirt bottle.

5) Rinse end three times again with DI water. Dispose of rinsate in accordance with all federal, state, and local regulations.

6) Place a protocol-cleaned orange cap on the end and cover with a long plastic bag. Secure bag with a rubber band. Store the tubing in a new large plastic bag to prevent contamination before use. **Label as clean, the date cleaned, and your initials**.

CLEANING PROTOCOL FOR:

Miscellaneous Laboratory Equipment used for Cleaning and Blanking

1.0 SCOPE

This Standard Operating Procedure describes the procedures for cleaning the miscellaneous items necessary to complete the tasks of cleaning 20-liter composite sample bottles and hoses. The purpose of these procedures is to ensure that the items are contaminant free and to ensure the safety of the personnel performing this procedure.

2.0 APPLICATION

This SOP applies to all laboratory activities that comprise the cleaning of ancillary items necessary to complete the tasks of cleaning 20 liter composite sample bottles and NPS hoses.

3.0 HEALTH AND SAFETY CONSIDERATIONS

The cleaning of the following items may involve contact with hazardous materials. Skin contact with all materials and solutions should be minimized by wearing appropriate personal protective equipment (PPE) including: chemically-resistant protective gloves, laboratory coats, chemically-resistant aprons, and goggles. In addition, to ensure that you are aware of the hazards involved and of any new revisions to the procedure, the material safety data sheets (MSDSs) for nitric acid and the laboratory detergent should be reviewed before beginning any of these procedures.

4.0 DEFINITIONS

4.1 Polyethylene Squirt Bottles - ½ and 1 liter squirt bottles for washing and/or rinsing with DI water or nitric acid.

4.2 Polycarbonate and Polyethylene De-ionized Water Jugs - For holding DI water.

4.3 Polyethylene Bucket - For holding tap water, DI water or detergent solutions during hose washing procedures.

4.4 Four-inch Teflon® Connector - For connecting two lengths of silicon peristaltic tubing together.

4.5 Four-inch Silicon Connector - For connecting two lengths of Teflon® hose together.

4.6 Orange Polypropylene Hose Caps - For placing over the ends of clean Teflon® hose to prevent contamination.

4.7 De-ionized (DI) water - Commercial de-ionized water.

4.8 Laboratory Detergent - 2% solution of Contrad 70® or Micro-90® detergent.

5.0 EQUIPMENT

5.1 Instrumentation: Not applicable.

5.2 Reagents:

1) ACS Reagent Grade nitric acid as a 2 Normal solution (2N HNO_3).

2) Micro-90® non-phosphate laboratory detergent.

3) Contrad 70® non-phosphate laboratory detergent.

4) Contrad 70® anti-foaming agent.

5) pH paper or pH meter.

6) Baking soda ($NaHCO_3$), marble chips or equivalent to neutralize acid

5.3 Apparatus:

1) Clean polyethylene squirt bottles.

2) Clean polyethylene trays or 2000 ml glass beakers.

3) Neutralization Tank.

5.4 Documentation:

Label each squirt bottle, DI jug, storage container holding clean items, etc., as to the date each was cleaned and the initials of the cleaning technician.

6.0 CLEANING PROCEDURES

Care must be taken to ensure that no contaminants are introduced at any point during these procedures. If the wash is not performed with this in mind, the possibility for the introduction of contaminants (i.e., from dirty sinks, dirty counter tops, dirty fingers/gloves, dirty hose ends, etc.) is increased significantly.

Rinsing properly is essential to ensure proper cleaning. This is done by squirting the liquid over the item to be cleaned in a top-down fashion, letting the water flow off completely **before** applying the next rinse. Rinse the item in this fashion **a minimum** of three times. **Numerous rinses of relatively small volumes are much better than one or two rinses of higher volume.** Be aware of handling: use clean gloves (it is best if they have gone through the same prior wash as the item to be rinsed) and rinse off the fingers prior to grasping the item to be cleaned. Try to

grasp the item in a slightly different place between rinses so one's fingers do not cover a portion of the item throughout the rinses.

6.1 Polyethylene squirt bottles:

1) Soak in a 2% solution of laboratory detergent in a protocol-cleaned bucket for 48 hours.

2) Rinse thoroughly (minimum of three times) with tap water.

3) Rinse thoroughly (minimum of three times) with DI water.

4) Wash three times with 2N (10%) nitric acid.

5) Rinse thoroughly (minimum of three times) with DI water. Neutralize and dispose of rinsate in accordance with all federal, state, and local regulations.

6.2 Polycarbonate and Polyethylene DI Water Jugs:

1) Fill to the rim with a 2% solution of laboratory detergent, cap the jug, and let soak for 48 hours. Wash cap with an all-plastic scrub brush after soak.

2) Rinse thoroughly (minimum of three times) with tap water.

3) Rinse thoroughly (minimum of three times) with DI water.

4) Wash three times with 2N (10%) nitric acid.

5) Rinse thoroughly (minimum of three times) with DI water. Neutralize and dispose of rinsate in accordance with all federal, state, and local regulations.

6.3 Polyethylene Bucket:

1) Fill to the rim with a 2% solution of laboratory detergent and let soak for 48 hours.

2) Rinse thoroughly (minimum of three times) with tap water.

3) Rinse thoroughly (minimum of three times) with DI water.

4) Wash three times with 2N (10%) nitric acid squirt bottle.

5) Rinse thoroughly (minimum of three times) with DI water. Neutralize and dispose of rinsate in accordance with all federal, state, and local regulations. **Label as to the date cleaned and initial**.

6.4 Four-inch Teflon® and Silicon Hose Connectors and Orange Polypropylene Hose Caps. The purpose of the four-inch sections of Teflon® and silicon hose is to connect longer lengths of each type of hose together during the hose cleaning procedures. The orange polypropylene hose caps are for the ends of cleaned FEP hoses to prevent contamination prior to use in the field or laboratory.

1) Using a 2% solution of laboratory detergent, soak the four-inch sections of FEP hose, silicon tubing, and orange caps for 48 hours.

2) Rinse thoroughly with tap water (minimum of three rinses).

3) Rinse thoroughly with DI water (minimum of three rinses).

4) Using a squirt bottle filled with 2N (10%) HNO3, thoroughly rinse the interior and exterior of the connectors and caps thoroughly OR, roll/agitate them in a shallow layer of 2N (10%) HNO3 in a laboratory detergent cleaned glass beaker or other appropriate, clean container for a more thorough washing.

5) Thoroughly rinse connectors and caps with DI water (minimum of three rinses). Neutralize and dispose of rinsate in accordance with all federal, state, and local regulations. Keep clean connectors and caps in a similarly cleaned (or certified clean) widemouth glass jar or detergent-cleaned resealable bag and **label as clean, date cleaned, and initial**.

CLEANING PROTOCOL FOR:

20-L Borosilicate Glass Composite Bottles (Media Bottles) and Closures

1.0 SCOPE

This Standard Operating Procedure (SOP) describes the procedures for the cleaning of 20-liter composite sample bottles and the related equipment necessary to complete the task. The purpose of these procedures is to ensure that the sample bottles are contaminant-free and to ensure the safety of the personnel performing this procedure.

2.0 APPLICATION

This SOP applies to all laboratory activities that comprise the cleaning of 20-liter composite sample bottles and stoppers.

3.0 HEALTH AND SAFETY CONSIDERATIONS

The cleaning of 20-liter composite-sample bottles and associated equipment involves hazardous materials. Skin contact with all materials and solutions should be minimized by wearing appropriate personal protective equipment (PPE) including: chemical-resistant gloves, laboratory coats, chemical-resistant aprons, and goggles. To ensure that you are aware of the hazards involved, the material safety data sheets (MSDSs) for nitric acid and laboratory detergents should be reviewed before beginning any of these procedures.

Note: Preparations should be made to contain and neutralize any spillage of acid. Be aware of the location of absorbent, neutralizing, and containment materials in the bottle cleaning area.

4.0 DEFINITIONS

4.1 Composite sample bottle - 20 liter borosilicate glass bottle that is used with autosamplers to collect a stormwater composite sample.

4.2 Stopper - a Teflon® cap used to seal the composite sample bottle (either solid or drilled with holes for the silicon inlet tubing).

4.3 O-Ring - Viton O-ring 23/8"- I.D. x 23/4"- O.D. that is located around the base of stopper.

4.4 Clamp - Polypropylene clamp, 2 bolts, and wing nuts specifically designed to fasten the stopper and the O-ring to the rim of the composite sample bottle.

4.5 De-ionized (DI) water - commercial de-ionized water (12-13 Megohm/cm).

4.6 Laboratory Detergent - 2% solution of Contrad 70® or Micro-90® detergent.

5.0 EQUIPMENT

5.1 Instrumentation:

1) Peristaltic pump with a protocol-cleaned sub-sampling hose setup.

5.2 Reagents:

1) ACS Reagent Grade nitric acid in a 2 Normal solution (2N HNO_3)

2) Contrad 70® non-phosphate laboratory detergent

3) Contrad 70® anti-foaming agent

4) Micro-90® non-phosphate laboratory detergent

5) Baking soda or equivalent to neutralize acid

6) pH paper

5.3 Apparatus:

1) Bottle Rolling Rack

2) DI Rinse Rack

3) Yellow Neutralization Drip Bucket

4) Neutralization Tank

5.4 Documentation:

The status of each composite sample bottle must be tracked. Bottles should be washed in batches of 10, 20, or 30 and the status of each batch must be made apparent to all personnel by posting a large status label (including the start date) with each batch. This will ensure that all required soak times have been attained and that each bottle was subjected to the proper cleaning procedures. Information on each batch of bottles cleaned (including bottle number, QA batch, date cleaning started, date finished, date blanked, and cleaning technicians) should be entered in the **Bottle Cleaning Log Sheet**.

6.0 CLEANING PROCEDURES

Care must be taken to ensure that no contaminants are introduced at any point during this procedure. If the wash is not performed with this in mind, the possibility for the

introduction of contaminants (i.e., from dust, dirty sub-sampling tubing tips, dirty fingers/gloves, automobile emissions, etc.) is increased significantly.

6.1 **Teflon® Bottle Stoppers with/without Holes and Field Extras:**

To be performed whenever required for field use.

1) Wash with laboratory detergent using a clean all-plastic brush.

2) Rinse thoroughly (minimum of three times) with tap water.

3) Rinse thoroughly (minimum of three times) with DI water.

4) Wash three times with 2N nitric acid squirt bottle.

5) Rinse thoroughly (minimum of three times) with DI water.

6) Allow to dry in a dust-free environment.

7) Store in two sealed clean Ziploc® bags.

6.2 **NPS 20-Liter Composite Sample Bottle Cleaning:**

6.2.1 Preliminary Bottle Cleaning:

Bottles should undergo a preliminary rinse with tap water as soon as possible after they are available. This includes dumping any remaining stormwater into a sanitary drain and rinsing the bottles and stoppers. This prevents material from adhering to the interior surface of the bottle.

6.2.2 48 Hour Soak: Place the bottle to be cleaned into a secondary containment bucket. Prepare a 2% solution of laboratory detergent with tap water directly in the bottle. Note: Since laboratory detergent is a foaming solution, add 3/4 of the tap water first, add the detergent, then add the rest of the water. Should excessive foam be generated, a few drops of Contrad 70® anti-foaming agent may be added. **Make sure that the bottle is filled to the rim and scrub the rim with an all-plastic scrub brush.** Scrub a Teflon® stopper with 2% solution of laboratory detergent and place stopper over the full bottle so overflowing happens. This will allow both the stopper and the bottle to soak for 48 hours. After the 48 hour soak, this solution may be may be retained for reuse (i.e., siphoned into other dirty bottles) or it can be poured off into a sanitary drain.

6.2.3 Tap-Water Rinse: Tap water rinses detergent better than DI water. Flush upside down bottle with tap water for 20 sec. Rinse each bottle 3 times with tap water being careful not to contaminate the clean surfaces.

6.2.4 DI Rinse: Rinse the top and neck of the bottles with DI water using a squirt bottle and then rinse upside down for three minutes on the DI rinse rack for bottles. Make sure to tip bottles from side to side for a more thorough rinsing. Allow 1-2 minutes for the bottles to drain as much as possible. Rinse each stopper with DI water squirt bottle 3 times (being careful not to touch the clean surfaces).

6.2.5 Acid Wash: Note that it is important to wash the bottle with 2N nitric acid according to the following procedure:

1) Place the empty bottle near the 2N nitric acid carboy and peristaltic pump. The location should be able to safely contain a spill if the 20-liter bottle breaks.

2) Pump acid into the bottle using the peristaltic pump fitted with a protocol-cleaned sub-sampling hose setup.

3) Fill the bottle slightly more than half full.

4) Place a protocol-cleaned solid Teflon® stopper (with a properly seated O-ring) (refer to Section 6.2.3 above) on the bottle and clamp it securely.

5) **Carefully** lift and place the bottle on the roller rack and check for leakage from the stopper. Neutralize any spillage. Often small leaks can be corrected by a slight tightening of the clamp. Roll the bottles for twenty minutes.

6) Pump the acid into another bottle for rolling or back into the 2N nitric acid carboy.

6.2.6 DI Rinse for Bottles: Allow the bottles to drain into a yellow neutralization bucket for at least 1 minute. Place four bottles at a time on the DI rinse rack and rinse for 5 minutes. Move bottles around to ensure complete and thorough rinsing. Rinse the outside of the bottle with tap water. Allow bottles to drain for 2 minutes.

6.3 Storage: Clamp a stopper (one that went through the entire cleaning procedure) on the bottle. Properly label the bottle as to the date cleaned and by whom and place on the bottle storage rack or in a secondary containment bucket in a safe area. Also, fill out the **Bottle Cleaning Log Sheet**.

7.0 QUALITY ASSURANCE REQUIREMENTS

7.1 The 20-liter composite sample bottles must be evaluated ("blanked") for contaminants after they have completed the decontamination procedure. The analytical laboratory performing the evaluation should supply Milli-Q® water that is used as a blanking rinsate, and sample bottles for the appropriate constituents of

concern. This evaluation will be accomplished by randomly blanking 10% of the washed bottles, or 1 bottle per batch (whichever is greater) and having the blanking rinsate analyzed by the laboratory for the appropriate constituents.

7.2 If any of the bottles fail the analyses (concentration of any analytes are at or above the limit of detection), all of the bottles from that batch must be decontaminated. Again, 10% of these bottles must be subjected to the blanking process as described above.

7.3 If results of the evaluation process show that the bottles are not contaminant-free, the cleaning procedure must be re-evaluated. Consult with the Quality Assurance/Quality Control Officer to determine the source of contamination.

Abbreviations and acronyms used without definitions in TRB publications:

A4A	Airlines for America
AAAE	American Association of Airport Executives
AASHO	American Association of State Highway Officials
AASHTO	American Association of State Highway and Transportation Officials
ACI–NA	Airports Council International–North America
ACRP	Airport Cooperative Research Program
ADA	Americans with Disabilities Act
APTA	American Public Transportation Association
ASCE	American Society of Civil Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATA	American Trucking Associations
CTAA	Community Transportation Association of America
CTBSSP	Commercial Truck and Bus Safety Synthesis Program
DHS	Department of Homeland Security
DOE	Department of Energy
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FHWA	Federal Highway Administration
FMCSA	Federal Motor Carrier Safety Administration
FRA	Federal Railroad Administration
FTA	Federal Transit Administration
HMCRP	Hazardous Materials Cooperative Research Program
IEEE	Institute of Electrical and Electronics Engineers
ISTEA	Intermodal Surface Transportation Efficiency Act of 1991
ITE	Institute of Transportation Engineers
MAP-21	Moving Ahead for Progress in the 21st Century Act (2012)
NASA	National Aeronautics and Space Administration
NASAO	National Association of State Aviation Officials
NCFRP	National Cooperative Freight Research Program
NCHRP	National Cooperative Highway Research Program
NHTSA	National Highway Traffic Safety Administration
NTSB	National Transportation Safety Board
PHMSA	Pipeline and Hazardous Materials Safety Administration
RITA	Research and Innovative Technology Administration
SAE	Society of Automotive Engineers
SAFETEA-LU	Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (2005)
TCRP	Transit Cooperative Research Program
TEA-21	Transportation Equity Act for the 21st Century (1998)
TRB	Transportation Research Board
TSA	Transportation Security Administration
U.S.DOT	United States Department of Transportation