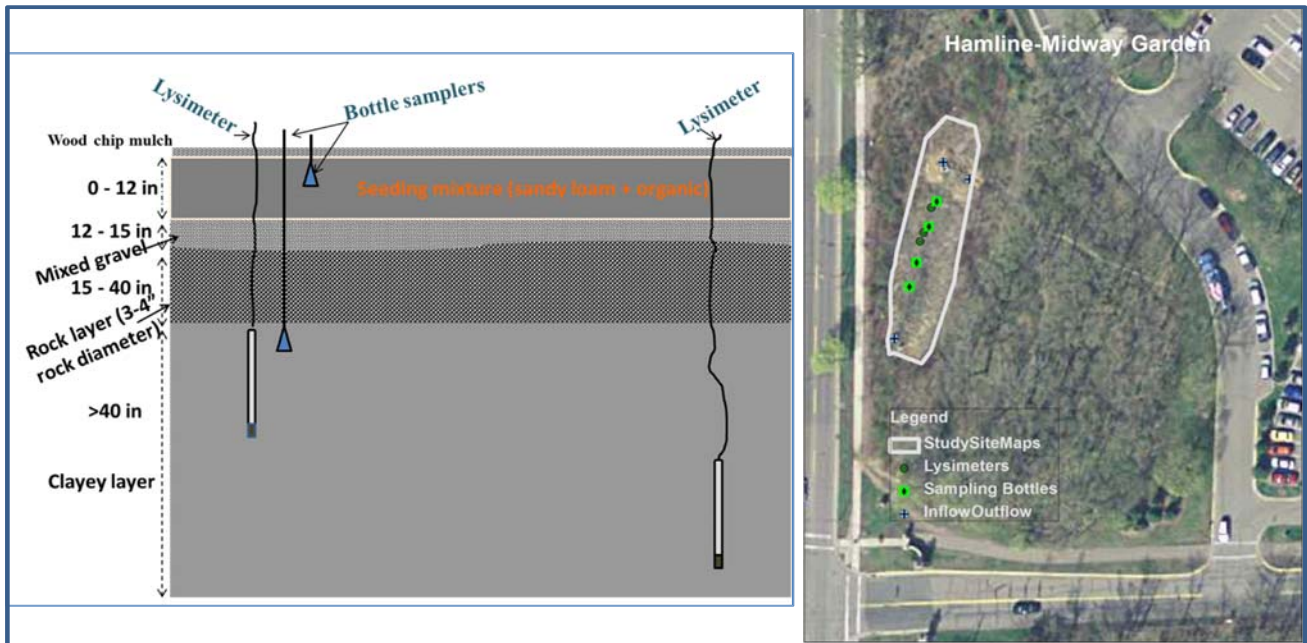


THE IMPACT OF STORMWATER INFILTRATION PRACTICES ON GROUNDWATER QUALITY



The Impact of Stormwater Infiltration Practices on Groundwater Quality

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Executive Summary

Establishing enhanced infiltration sites for the control of stormwater runoff in developed areas is becoming a common practice among municipalities, departments of transportation, other government entities, and private entities. One of the purposes of enhanced infiltration is to control the volume and rate of runoff from developed areas in order to keep the level of runoff close to that of undeveloped conditions. Another purpose is to capture the stormwater so that contaminants contained in the stormwater will be treated through the process of water infiltrating and flowing through the soil profile. With the increasing adoption of enhanced infiltration practices there is a growing concern that these practices might be putting the quality of the groundwater resources underlying some of these practices in jeopardy. In recent years there have been some efforts to quantify the potential for degradation of groundwater resources by infiltrated stormwater.

The study described in this report is an effort to quantify the potential for contaminants to reach the groundwater resources in the Twin Cities Metropolitan Area, Minnesota. A literature review was first conducted to identify concerns with regard to groundwater contamination and the extent of the research that has been completed with regard to these issues. The field study was then conducted over a period of 18 months in which three sites containing enhanced infiltration practices were monitored to quantify the amount of contaminants reaching depths large enough to infer that the contaminants would eventually reach the underlying surficial aquifer. The sites investigated included an infiltration basin near the St. Paul campus of the University of Minnesota (referred to as the Sheep Pasture, SP), a large infiltrating rain garden located within Como Park (referred to as the Hamline-Midway Ave. site, HM), and an infiltration gallery constructed in a formerly industrial area located at Beacon Bluff (referred to as BB) in the eastern side of St. Paul. These sites were selected from a number of potential sites based the criteria: 1) should have been functioning long enough contain contaminants; (2) be local for convenience of access; and (3) represent one of the infiltration practices that are of primary concern with regard to groundwater pollution.

Contaminants of concern at these infiltration sites included chloride, nitrate, phosphorus, a suite of heavy metals (iron, lead, nickel, copper, cadmium, and chromium), and petroleum hydrocarbons. Site monitoring at the SP and HM sites included lysimeters to extract water from the soil at various depths, and surface water collectors to capture samples of runoff entering the infiltration areas. The lysimeters were constructed with a PE-nylon membrane that makes the samplers suitable for sampling for a range of contaminants including organics, heavy metals, as well as conventional macro- and micro-nutrients. Surface water samples were collected using hard nylon plastic cups installed flush with the soil surface. The monitoring system for the BB was in place already prior to the initiation of this study. It consisted of barrel lysimeters placed at two locations and five different depths within the infiltration gallery. The barrels were essentially the bottom parts of 50-gallon drums cut off from the top, filled with gravel, and with a PVC pipe protruding from the upright barrel and connected to the land surface. Percolating water entering a barrel lysimeter from above and temporarily stored there could then be pumped from the depth of the barrel to the surface. Surface water flows into the infiltration gallery was monitored by a consultant, and water samples for the inflow were also analyzed by that consultant for relevant

water quality parameters. Representative weather data for each of these sites were available from weather stations installed previously.

Sampling of the lysimeters and surface water collectors at the sites was conducted from mid-summer of 2012 through the end of the summer of 2013. The protocol for sampling was that samples would be collected whenever there was an occurrence of a rainfall event producing significant stormwater volume. The number of sampling dates varied a slight amount between the study sites because of the different conditions for the contributing areas, but essentially the total number of sample dates ranged from eight to ten among the sites. The total number of water samples collected for all sites at all locations and depths was 145.

Water samples from the subsurface and surface collectors were analyzed for the various contaminants by different labs. The chloride, nitrate and phosphorus samples were analyzed by the Research Analytics Lab located in the Department of Soil, Water and Climate at the University of Minnesota, and the metals were all analyzed by the geochemistry lab at the Department of Earth Sciences at the University of Minnesota. The analysis for petroleum hydrocarbons was conducted in one of the chemistry labs of the Department of Bioproducts and Biosystems Engineering at the University of Minnesota.

The literature research indicates that a surface-oriented practice, such as a bioinfiltration facility, swale, filter strip, infiltration basin, etc. has the capacity to capture groundwater contaminants on the soil or infiltration media. These contaminants include dissolved toxic metals and petroleum hydrocarbons. There is evidence that captured petroleum hydrocarbons will be degraded by the bacteria surrounding plant roots. Toxic metals will need to be eventually harvested. The soil or media through which they are infiltrated generally filters infiltrated pathogens and suspended solids. This may not be true of viruses, which are currently a concern in drinking water aquifers due to leakage from sanitary sewers and septic tanks. This is currently dealt with through disinfection of drinking water.

Evidence from the literature and the three study sites herein indicates that nitrate contamination of infiltrating stormwater is not a big concern. Nitrate in urban runoff is typically at fairly low concentrations (median of 0.6 mg/L, Maestre and Pitt, 2005) relative to the drinking water MCL of 10 mg/L, such that it is unlikely that stormwater could be the cause of high nitrate concentration in drinking water. At the three study sites, only 4% of the measured nitrate concentrations were above the drinking water MCL of 10 mg/L. At the three study sites, a seasonal trend in nitrate concentration was observed, decreasing from a high in mid-fall to a low value in late summer, with isolated high values throughout. There was no indication of attenuation as the water moved through the soil towards the groundwater table, however, probably due to the high uncertainty in the individual measurements and the fact that water extracted from different levels in the unsaturated zone represent different temporal portions of a storm or different storms altogether.

Chloride is a contaminant that has no known sinks in natural systems. Chloride is a concern for both groundwater (secondary MCL of 250 mg/L) and surface water (chronic toxicity for aquatic biota of 300 mg/L). One sample from the Hamline-Midway site in the fall of 2012 had a measured chloride concentration above 1,500 mg/L, and measurements throughout the year were above the MCL 15% of the time. In addition, Novotny et al. (2009) found that 77% of the chloride that is placed on surfaces remains in the Twin Cities Metropolitan watershed, and does

not leave by river flow. A reduced use of salt during winter is recommended for MnDOT (where low salt practices have been implemented), city streets (where low salt practices currently are sometimes implemented), and commercial parking (where low salt practices are rarely implemented). Low salt practices are a temporary measure, and eventually the Twin Cities Metro region will need to come up with an alternative for using salt on their streets, because the alternative will be salt-water aquifers and reverse osmosis for drinking water taken from groundwater sources.

Sub-surface infiltration systems store water underground and allow the infiltration process to begin beneath the soil surface. This means that the retention of contaminants by organic compounds in the soil may not occur. Thus, metals and petroleum hydrocarbons are more likely to enter into groundwater from these infiltration systems. The attenuation of petroleum hydrocarbons at the Beacon Bluff site was inconclusive, as are many monitoring studies, and the impact of sub-surface infiltration systems needs further study.

It is evident that there remain areas in which the understanding of stormwater, its contaminants, and their fate and treatment is limited or non-existent. Further research into these areas, or knowledge gaps, is key to the continued and increased protection of groundwater.

Introduction

To keep surface waters clean and mitigate negative environmental impacts of stormwater runoff, a variety of Stormwater Control Measures (SCMs) have been developed and installed throughout the Minneapolis-St. Paul Metro area. Infiltration practices such as bioinfiltration rain gardens, swales, infiltration basins and trenches have proven especially effective in reducing total runoff volume, thereby reducing stormwater contaminant loads. There are, however, concerns that the relative short residence time of the contaminant laden stormwater runoff infiltrated by these practices could impact the quality of groundwater, especially those aquifers which provide residents with drinking water.

Regional maps compiled by Minnesota Geological Survey from available information indicate that infiltrated water in the northeast metro area has a 100 to 500 year residence time in the surface glacial aquifer compared to a short residence time (less than 1 year) for the southeast metropolitan area. Davis (2012) describes portions of the southeast metropolitan area as having a relatively quick connection between the surface and drinking water aquifers. A quick connection between surface and groundwater would imply potential increase in transport of untreated contaminants with the infiltrating water into the groundwater aquifers. Monitoring infiltration and testing for presence and concentration of contaminants though the sub-stratum in the Twin Cities Metropolitan area is therefore necessary.

The original design and installation of infiltration practices were intended to be tools to reduce runoff caused by impervious surfaces and improve the quality of infiltrated water through filtration in the soil. The systems have also demonstrated benefits of including extending time of concentration and recharging groundwater. These benefits help maintain or restore aquatic ecosystem health, reduce peak storm flows, and reduce runoff volume to constrain channel

erosion and sedimentation (Austin, 2012). However, not all contaminants are filtered by the soil, and some infiltration practices infiltrate below the root zone, where soil is limited. These are the reasons for this study.

Various studies have reported that infiltration practices are effective in improving both water quality and drainage area hydrology (Davis et al. 2001, 2003; Hunt et al. 2006; Davis 2007, 2008; Hunt et al. 2008). There however, are gaps in our knowledge on the water quality performance of the practices for many contaminants as well as details on contaminant fate and transport characteristics (Li and Davis, 2009). The study culminating in this report has been conducted to investigate potential impacts of stormwater infiltration practices on the quality of infiltrating stormwater in select sites in a northeast metro location (Ramsey County). Fieldwork and experimentation involved installation of sampling devices and collecting water samples from three select sites. The analysis of samples was aimed at detection and quantifying concentrations of specific contaminants, including nitrate, chloride, volatile and total petroleum hydrocarbons, and metals including lead, zinc, chromium, cadmium, iron, copper, and nickel.

Tasks implemented in the study included:

- Conducting a literature review on studies pertaining to the impacts of enhanced infiltrating stormwater on groundwater quality.
- Determining the presence and concentrations of contaminants in stormwater beneath selected infiltration practices.

The findings of the study will enhance our understanding of contaminants that are candidates for posing a threat to groundwater quality in urban areas where infiltration practices are used to mitigate stormwater runoff. Relationships between soil properties, climate and the contaminants reaching the groundwater aquifers with infiltrating stormwater may be inferred.

Literature Review

Non-point source pollution from stormwater runoff is well documented as a leading cause of impairment of freshwater lakes, rivers, and estuaries (U.S. EPA, 2000; U.S. EPA, 2005). When impervious surfaces such as roads, parking lots, and rooftops replace areas that previously allowed infiltration of stormwater, the resulting stormwater runoff is typically conveyed to storm or sanitary sewers which may act as conduits that carry contaminants (e.g., sediments, nutrients, metals, petrochemicals) to receiving water bodies. Stormwater management is an issue of importance to the health of the general public and the environment; thus municipalities throughout the nation have been seeking improved methods of managing stormwater. One increasingly popular technique is Low Impact Development (LID), of which a large component is the infiltration of stormwater instead of conveyance to receiving waters through sewers. LID is gaining popularity because it promotes more sustainable water resources management while recognizing the needs of economic growth within local communities (Coffman, 2002). Additionally, LID may also benefit air quality and the quality of life (Coffman, 2002). Several

modeling experiments have shown that LID—when properly implemented—is capable of nearly restoring the predevelopment hydrologic regime (Brander et al., 2004; Holman-Dodds et al., 2003).

Historically, stormwater management has consisted of reducing the peak flow of runoff from developed watersheds with little or no thought given to water quality. Methods used to accomplish this goal have often involved the construction of detention ponds, which, although they reduce peak flows and can remove a fraction of solid particles, have been shown to be inadequate at addressing ecological stream degradation (Booth et al., 2002). With greater attention now being given to water quality issues, alternative stormwater management approaches within the framework of LID are being implemented. LID seeks to reduce the volume of runoff from developed sites while focusing on both water quantity and water quality. Alternative stormwater management utilizes small, decentralized infiltration structures to mimic the predevelopment hydrologic regime (US EPA, 2005). Examples of alternative stormwater management techniques being implemented include green roofs, infiltration chambers, constructed wetlands, and bioinfiltration systems (rain gardens). Green roofs are planted atop buildings and slow runoff flows while enabling evapo-transpiration (Teemusk and Mander, 2007). Infiltration chambers are underground chambers that store runoff and allow it to infiltrate into the existing soil. Initially, constructed wetlands had been utilized to treat municipal wastewater, but more recently they have also been used to treat stormwater (Walker and Hurl, 2002; Schutes et al., 1997). Rain gardens are shallow vegetated depressions into which stormwater is directed for recharge (US EPA, 2000). These techniques, among others, are collectively known as stormwater Best Management Practices (BMPs) in protecting water quality (Clary et al., 2002).

Many alternative stormwater management techniques rely on infiltration of stormwater into the soil where sub-surface flow and groundwater recharge may occur. This provides a reduction in runoff quantity and may promote contaminant removal through physical, chemical, and biological means. Current infiltration practices include bioinfiltration systems, infiltration basins, infiltration trenches, and underground infiltration chambers. Other stormwater management techniques may not use infiltration as their primary treatment method but do infiltrate stormwater. For example, a standard detention pond relies primarily on sedimentation to remove contaminants but infiltration usually occurs through the bottom and sides of the pond.

With the rise in popularity of stormwater management techniques that infiltrate polluted runoff, concern has arisen regarding potential groundwater contamination. After a summary of common stormwater infiltration practices and contaminants typically found in urban stormwater, this paper provides a literature review of existing work that has investigated the fate of stormwater contaminants once infiltration has occurred and the potential for groundwater contamination.

Stormwater Infiltration Practices

As previously discussed, in an attempt to reduce runoff volumes, many stormwater management practices seek to infiltrate stormwater runoff into the soil where it can be transported by sub-surface flow and/or recharge groundwater aquifers. For example,

bioinfiltration systems, rain gardens, and infiltration trenches are all designed based on a desired volume of infiltration. Other practices, such as detention ponds, have typically been designed based on the desired reduction in the peak runoff flow rate and, when considering only water quantity, are often assumed to have no infiltration capacity. While this is an acceptable and conservative assumption when considering peak flows and flood control, pond infiltration cannot be ignored when considering the fate of contaminants and potential groundwater contamination. Thus, this paper reviews information on stormwater management techniques that rely primarily on infiltration as well as other techniques, such as detention ponds, whose primary function or processes are not infiltration but that have the capacity to infiltrate stormwater. A summary of such practices is given below.

Infiltration Basins

Infiltration basins are constructed with the intent of storing and infiltrating stormwater runoff up to a targeted design volume. As defined in the “Assessment of Stormwater Best Management Practices” manual (UM, 2007):

“An infiltration basin is a natural or constructed impoundment that captures, temporarily stores, and infiltrates the design volume within an acceptable time period. Infiltration basins contain a flat, densely vegetated floor situated over naturally permeable soils. Nutrients and contaminants are removed from the infiltrated stormwater through chemical, biological, and physical processes. Infiltration basins are well suited for drainage areas of 5 to 50 acres (2.03–20.25 hectares) with land slopes that are less than 20%, with typical depths in the basin ranging from 2 to 12 feet (0.61–3.66 meters).”

Infiltration basins often require relatively large land areas and, with well-chosen vegetation, are often aesthetically pleasing.

Infiltration Trenches

The primary purpose of infiltration trenches is to collect stormwater and reduce runoff volumes by allowing the water to infiltrate into the surrounding soil. The “Assessment of Stormwater Best Management Practices” manual defines infiltration trenches as follows:

“An infiltration trench is a shallow excavated trench, typically 3 to 12 feet deep (0.91–3.66 meters), that is backfilled with a coarse stone aggregate allowing for the temporary storage of runoff in the void space of the material. Discharge of this stored runoff occurs through infiltration into the surrounding naturally permeable soil. Infiltration trenches are well suited for drainage areas of 5 acres (2.03 hectares) or less.”

Infiltration Chambers

Infiltration chambers are long (> 8 ft) chambers, typically of pervious pipe, set underground below the root zone of most plants, with the exception of trees. The chambers are surrounded by material of high hydraulic conductivity to increase the infiltration surface and avoid clogging of porous surfaces on the chambers. Drainage areas are typically greater than 20 acres (8.12 hectares).

Pervious Pavements

The primary purpose of pervious pavements is to reduce runoff volumes by allowing stormwater to pass through the pavement structure and infiltrate into the underlying soil. While pervious asphalt and concrete are the most obvious varieties of these pavements, Ferguson (2005) lists a total of nine categories with this classification. These include pervious aggregate, pervious turf, plastic geocells, open-jointed paving blocks, open-celled paving grids, pervious concrete, pervious asphalt, soft pervious surfacing, and decks. For the case where the pervious pavement is either asphalt or concrete, the pavement system is designed such that stormwater infiltrates through the pervious upper pavement layer and then into a reservoir of stone or rock below. Water from the reservoir then either percolates into the underlying soil or is collected by a perforated pipe underdrain system and carried to a surface discharge location.

Pervious pavements are gaining in popularity; however, their use is sometimes met with (not necessarily valid) concerns of increased maintenance costs and decreased durability.

Bioinfiltration systems

Bioinfiltration systems (rain gardens) are low areas, natural or excavated, that are planted with vegetation and receive stormwater runoff from nearby impervious surfaces via stormwater conveyances, such as curb cuts. The collected stormwater exits the rain garden primarily via infiltration, reducing runoff volume and potentially recharging groundwater. Alternatively, some rain gardens are equipped with underdrains that are typically used when the underlying soil has a low infiltration capacity. Such rain gardens are constructed by excavating the soil, placing a drain tile or perforated pipe collection system at the bottom, backfilling with high permeability soil, and then planting with vegetation. In these systems the collection pipe discharges the water out of the rain garden and groundwater contamination is most likely of little concern.

Swales and Filter Strips

Swales are vegetated canals or trenches that convey stormwater, filter and/or settle solids, and infiltrate a portion of the runoff. Other names for swales are ditches, grassed channels, dry swales, vegetated swales, wet swales, biofilters, or bioswales. Permeable structures (e.g., check dams) are sometimes installed in the flow path to reduce flow velocities and increases infiltration volumes.

Filter strips are vegetated areas specifically designed and positioned for overland sheet flow of stormwater runoff. The vegetation filters particulate contaminants and reduces runoff velocities, which increases infiltration. Filter strips may also be called buffer strips or buffers. Sheet flow is required for filter strips to effectively treat stormwater runoff.

Detention Ponds

Detention ponds are depressions in the soil surface that are designed to collect and store stormwater runoff. Dry detention ponds have their main outlet elevation at the pond bottom and are typically designed to discharge all stormwater within 48 hours of the end of a runoff event. Historically, dry detention ponds have been designed solely on the basis of peak flow reduction. More recently, however, dry detention ponds, which can settle an appreciable amount of solids, have been designed with water quality as a driving factor. In both cases, significant infiltration can occur if the pond is not lined with an impermeable membrane or clay barrier.

Wet detention ponds have their main outlet above the pond bottom and are designed to store a portion of the runoff volume long after the runoff event ends with the intent of infiltrating a portion of the runoff volume.

Stormwater Contaminants and their Fate in Infiltration Systems

Urban stormwater runoff can originate from roads, buildings, houses, lawns, industrial parks, and a host of other human-made structures. Many studies on the contaminants and the concentration ranges common to urban runoff have been performed (Moxness, 1986, 1987, 1988; Driscoll et al., 1990; Oberts, 1994; Barrett et al., 1995; Stanley, 1996; Wu et al., 1996; Sansalone and Buchberger, 1997; Barrett et al., 1998; Anderle, 1999; Legret and Colandini, 1999; Waschbusch et al., 1999; Carleton et al., 2000; Drapper et al., 2000; Brezonik and Stadelmann, 2002; Harper et al., 1999; Maestre and Pitt, 2005). Typical urban runoff contaminants include nutrients (i.e., phosphorus and nitrogen), metals, suspended solids, petroleum hydrocarbons, pathogens (i.e., bacteria and viruses), and chloride. Studies have shown that contaminant concentrations in urban runoff can vary widely by season, location, traffic volumes, and rainfall volumes and intensity. If infiltrated into the soil, these contaminants have the potential to degrade soil and impact groundwater quality and, therefore, are of concern. A study by Maestre and Pitt (2005) analyzed hundreds of stormwater samples across the United States to determine concentrations of contaminants in stormwater. The analysis revealed differences in contaminant concentrations that varied by watershed land use and also a wide range of values for a single land use. Overall median concentrations of some common contaminants are listed in Table 1 along with the coefficient of variation. The coefficient of variation, which is the standard deviation divided by the average, is a measure of the spread of the data.

Nutrients

The most common and influential forms of nutrient pollution to stormwater are phosphorus and nitrogen, the latter of which may be in many forms. Nutrients are of concern because of their ability to cause algal blooms and consequential eutrophication in receiving water bodies. Nitrate is a common contaminant in groundwater but phosphorus contamination has not been as common or as severe. Nutrient contamination of groundwater is, however, not always caused by stormwater infiltration. For example, in areas of some sedimentary deposits, ammonium in the soil can be oxidized to nitrate (Pitt et al., 1999). Some common nutrient sources include animal waste, septic leakage, fertilizers, and atmospheric deposition (U.S. EPA, 1999). Zinc and

phosphorus is found in motor oil where it forms a film that helps to prevent the wearing of metal parts. While typical stormwater nutrient loadings are significantly less than that of treated wastewater they can be higher under some wet weather conditions (U.S. EPA, 1999). Event mean concentrations vary seasonally and by land use. Correlations between these parameters and nutrient flux have been ascertained but are weak because of the complexity inherent in non-point source pollution (Brezonik and Stadelmann, 2002).

Table 1. Summary of contaminant concentrations in stormwater runoff (Maestre and Pitt, 2005).

Contaminant	Total Suspended Solids mg/L	Total Phosphorus mg/L	Dissolved Phosphorus mg/L	Ammonia (NH ₃) mg/L	Nitrite & Nitrate (NO ₂ /NO ₃) mg/L	Oil/Grease mg/L
Median	59	0.27	0.13	0.44	0.6	4.3
Coefficient of Variation	1.8	1.5	1.6	1.4	0.97	9.7
Contaminant	Total Cadmium µg/L	Dissolved Cadmium µg/L	Total Copper µg/L	Dissolved Copper µg/L	Total Nickel µg/L	Dissolved Nickel µg/L
Median	1.0	0.5	16	8	8	4
Coefficient of Variation	3.7	1.1	2.2	1.6	1.2	1.5
Contaminant	Total Lead µg/L	Dissolved Lead µg/L	Total Zinc µg/L	Dissolved Zinc µg/L	Fecal Coliform mpn/100 mL	E. Coli mpn/100 mL
Median	17	3	116	52	5091	1750
Coefficient of Variation	1.8	1.5	3.3	3.9	4.6	2.3

Phosphorus

Phosphorus is of concern because it can cause algal blooms and subsequent eutrophication to receiving water bodies where P is the limiting nutrient (Mihelcic, 1999). Sources of phosphorus include motor oil (Pitt et al., 1999), animal wastes and remains, plant material, and fertilizers. Orthophosphate (PO₄⁻³) is the form of P most readily available to aquatic life (U.S. EPA, 1999) and is the most common form occurring in stormwater. It has been found that phosphorus loading is correlated to intensity of urban land use. Phosphorus was found to increase logarithmically with impervious surface area in construction using curb-and-gutter style stormwater management. No such trend was observed for a comparable LID development (Dietz and Clausen, 2008). In this study, traditional development produced a phosphorus export rate of 2 kg/ha/yr, while 0.4 kg/ha/yr was observed in the LID development.

Typical average total phosphorus concentrations reported in stormwater runoff are approximately 0.30 mg/L as P (Erickson et al., 2007) but the actual concentration in a single runoff event can vary widely depending on watershed land use, rainfall intensity, traffic volumes, elapsed time since the previous rainfall event, etc. In an analysis of runoff samples throughout the Twin Cities metropolitan area in Minnesota, it was determined that approximately 44% of total phosphorus, on average, is in dissolved form. By definition, dissolved phosphorus is any phosphorus that can pass through a filter with openings of 0.45 µm. Although an average of 44% was reported, the percent of total phosphorus in dissolved form ranged from near zero to 100% (Erickson et al., 2007).

Once in the soil media, orthophosphate can be removed from infiltrated stormwater via precipitation or chemical adsorption onto soil particle surfaces through reactions with iron, calcium, or aluminum. The dominant precipitation reactions are pH dependent and typically form iron and aluminum phosphates under low pH conditions and calcium phosphates under high pH conditions. In neutral conditions the reactions are rate-limited, thus the solubility appears to be higher than the solubility in basic or acidic conditions (Pitt et al., 1999). As discussed later, Erickson et al. (2007) found that the addition of elemental iron to stormwater sand filter media significantly increases dissolved phosphorus removal rates.

Wu et al. (1996) conducted a study of stormwater contaminants in urban wet-detention ponds, and found removal rates ranging from -55% (phosphorus was released) to 100%. Dietz and Claussen (2005, 2006) also found negative phosphorus removal rates. In this study, a rain garden field site was constructed in a residential area of Connecticut with roof runoff directed to it and an underdrain included for effluent sample collection (Dietz and Clausen, 2005, 2006). It was found that instead of retaining phosphorus, the rain garden was a source of phosphorus. One possible cause was partial breakdown of new plant materials in the new rain garden, resulting in a short term P release. When monitored over time, however, the investigators found the influent-effluent differential to decay over time and expected steady state equilibrium to be reached. It was found that the highest phosphorus retention occurred in the mulch of the rain garden while the soil media retained the nutrients at much lower concentrations. Plants assimilated only 3% of the total P entering the test cell. Overall, due to leaching of phosphorus, it was concluded that long-term phosphorus retention would be minimal.

One column study found reductions in phosphorus equaling approximately 70% when synthetic stormwater was fed to a column of media designed to mimic a rain garden (Davis et al., 2001). Subsequent studies, however, revealed much lower P retention rates, 41 to 48% (Hsieh and Davis, 2005). Hsieh and Davis (2005) predicted that addition of mulch would aid in removal by retaining P complexes, but found that this was largely not the case. Different media compositions were tested because it was hypothesized that silt/clay complexes would increase phosphorus sorption. It was found, however, that P removal did not correlate to media composition. It was also determined that adsorbed phosphorus leached out the bottom of the columns.

In contrast, other studies have found media composition to be influential on P retention (Arias et al., 2001). After studying a subsurface flow constructed wetland for phosphorus retention, it was determined that chemical properties of the granular media can have a large impact on removal efficiencies. Under neutral and slightly basic conditions, higher calcium content increased P removal via precipitation. Under more acidic conditions, iron and aluminum composition in the sand may be influential. Phosphorus was also found to be incorporated into biofilms and plants in addition to being adsorbed to solids.

Erickson et al. (2007) found that adding chopped granular steel wool to soil media can increase the removal of dissolved phosphorus without negatively impacting the quality of effluent. When the steel wool rusts elemental iron is oxidized and the oxidized iron, which has a positive charge, chemically binds with the negatively charged phosphate ions. More recently, filter sand media has been mixed with iron shavings, which are cheaper than steel wool. Analysis of these filters indicate that iron mixed with sand at 5% by weight can remove near 90% of the

dissolved phosphorus that enters the filter in stormwater runoff while maintaining the capacity to do so for years (Erickson and Gulliver, 2010; Erickson et al., 2012).

Nitrogen

Nitrogen in stormwater may be present in many forms with ammonia (NH_3) being most toxic to aquatic life. Nitrate (NO_3^-) and nitrite (NO_2^-) are other common inorganic forms. Although nitrite is highly soluble (Pitt et al., 1999), very little nitrite is usually found in urban stormwater (U.S. EPA, 1999) because it is oxidized to nitrate. Nitrate, due to its high solubility, can leach from decaying plant material and other organics in the soil to infiltrating stormwater and eventually contaminate groundwater aquifers. High nitrate concentrations may also be found in heavily industrialized areas and groundwater contamination due to stormwater infiltration in these areas has been documented (Pitt et al., 1999).

Nitrate is the most common nonpoint-source groundwater contaminant in the world (Gurdak and Qi, 2012). Naturally occurring ammonium in soils can be oxidized to nitrite and nitrate and cause groundwater contamination. Areas in the United States with the most nitrate groundwater contamination are those with large farm animal populations that have dairy and poultry industries and irrigated agricultural areas. In urban areas, the major source of groundwater nitrogen contamination is from road runoff, which is contaminated by nitrate in vehicle exhaust and the soil brought onto the roadway by vehicle traffic.

The maximum contaminant concentration (MCL) of nitrate for drinking water as set by the U.S. EPA is 10 mg/L (as N), primarily due to negative health impacts upon fetuses/infants (U.S. EPA, 2008). Because of the health effects and solubility in groundwater, nitrate is often the most studied form of nitrogen groundwater pollution. According to Pitt et al. (1996) nitrate, due to its typically low concentrations in urban runoff, has low to moderate groundwater contamination potential for both surface infiltration (bioinfiltration practices, infiltration basins, filter strips, swales, pervious pavement, etc.) and subsurface infiltration/injection systems (infiltration chambers, infiltration trenches, etc.). If nitrate concentrations are high, however, the groundwater contamination potential would also be high. Carlson et al. (2011) studied urban runoff in Arizona and found that nitrate from non-point source pollution was contaminating groundwater aquifers. Although nitrate concentrations were lower than regulatory limits, the authors suggested that, unless nitrate loading was reduced, nitrate concentrations in the groundwater would continue to increase.

In areas with traditional development (i.e., no LID), nitrate export from the watershed was found to increase logarithmically with increased impervious area. In LID areas, nitrate export did not correlate with impervious surface area (Dietz and Clausen, 2008). Nitrate concentrations in stormwater were found to be lower in LID developments compared to non-LID developments. Total N export from traditional developments averaged 10 kg/ha/yr and 2 kg/ha/yr for LID developments.

Gurdak and Qi (2012) investigated the vulnerability of 17 aquifers to contamination by nitrate. All selected aquifers were fully recharged within the last 60 years and, altogether, include parts of all 48 contiguous states in the US. Eighty-seven variables were tested for their impact on aquifer contamination by nitrate and 25 were determined to be statistically significant. Individual

aquifers were modeled, as was the nation as a whole. In both cases dissolved oxygen concentration was identified as a major factor in determining if nitrate concentrations would exceed background concentrations. At low DO concentrations denitrification occurs, which results in the reduction of nitrate. These results support the recommendation that DO should always be included in water monitoring programs when an objective is to determine the vulnerability of an aquifer to nitrate contamination. Other important factors include the presence of agricultural crops and if those crops are irrigated, fertilizer application, depth to water table, and soil properties that affect infiltration and denitrification. As a result of their study, Gurdak and Qi developed the map shown in Figure 1 that shows the probability of detecting nitrate in groundwater at concentrations greater than background concentrations.

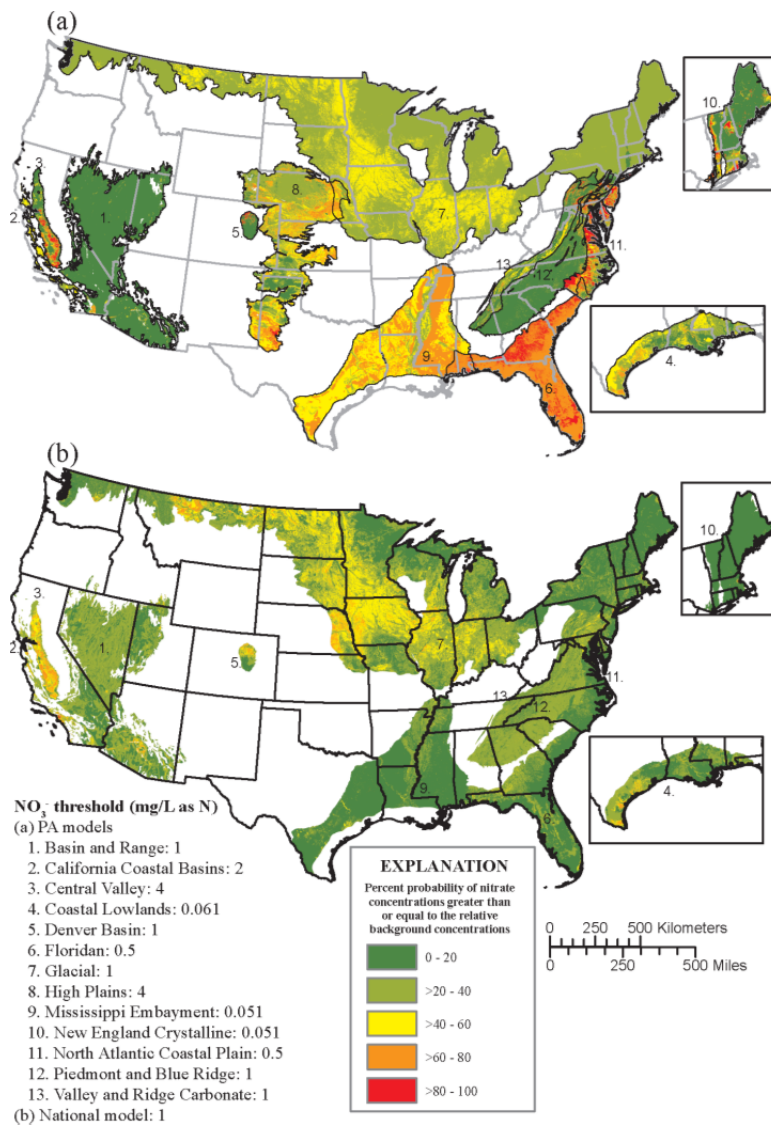


Figure 1. Probability of detecting nitrate concentrations above background concentrations; (a) is for logistic regression models developed using data from principal aquifers in given regions, while (b) is based on logistic regression models on a national scale. (Gurdak and Qi, 2012).

Detailed column studies have determined the capacity of media to retain nitrogen species. One column study in which stormwater was allowed to pass through a soil media found that total Kjeldahl nitrogen (TKN), or the organic nitrogen, ammonia (NH_3), and ammonium (NH_4^+), was reduced 65% to 75% and that ammonia was reduced 60 to 80% (Davis et al., 2001). However, nitrate concentrations within the column media and in the effluent increased. This increase was determined to be most likely attributable to biological activity. In subsequent studies, material was added to serve as organic and inorganic electron donors, forming saturated layers and creating an anaerobic environment to biologically remove nitrate via denitrification (Kim et al., 2003). Of the material tested, it was found that newspaper clippings were most successful at increasing denitrification. Other materials tested included sawdust, elemental sulfur, alfalfa, straw, and woodchips. Pilot scale studies indicated overall nitrate-nitrite retention of 70 to 80%.

Another study examined the influence of media upon nitrate removal (Hsieh and Davis, 2005). Nitrate removal in columns was found to range from 1 to 43% with ammonia removal rates of 2 to 26%. Mulch was found to be most effective at removing nitrate and ammonia, followed by native soil. Sand was determined to be least effective. Removal efficiency was not found to correlate with clay or silt composition. During a field component of this study, six rain gardens were examined for nitrogen retention with all having less than 10% removal.

Good et al. (2012) investigated the performance of laboratory scale rain gardens for their effectiveness with respect to metal removal. Three different rain garden medias were tested: 1) sand, 2) sand and topsoil mix, and 3) topsoil only. Although their studies were primarily to determine the retention of metals, nitrate concentrations in the influent and effluent were determined and compared. Average values of nitrate in the effluent increased by 409% to 516% as compared to the 883 $\mu\text{g/L}$ value in the influent.

Other researchers have measured similar results. At a field rain garden constructed for a contaminant removal study, less than 36% retention of total nitrogen, TKN, organic nitrogen, and nitrate was observed (Dietz and Clausen, 2005). Ammonia, however, was retained at 85%. Another study examined the use of a saturated mulch layer in an attempt to increase denitrification (Dietz and Clausen, 2006). With the added saturated layer in the rain garden, nitrate effluent concentrations were significantly reduced, as was the ammonia concentration in the rain garden. During the entire study period, 51% of TN was retained (33% by mulch and 0.3% by plants). Mulch TN increased, while soil TN decreased throughout the study period. Ammonia was found to have the highest retention rate (86% in the unsaturated layer and 69% in the saturated material), with nitrification and adsorption being the primary mechanisms. Hunt et al. (2006) similarly found total nitrogen mass removal rates of 40%, with nitrate removal being highly variable (13 to 75%). Sharkey and Hunt (2005) also experimented with a saturated layer for nitrate removal and observed a 77% decrease; however, TKN and ammonia concentrations increased.

Efforts have been made to engineer bioretention facilities to improve nitrate removal via denitrification; some results show some improvement when a carbon source was added (Kim et al., 2003), while others had no statistically significant improvement (Dietz and Clausen, 2006).

Toxic Metals

In a nationwide study of stormwater runoff, Pitt et al. (1995) found metals (including metals in the dissolved form) in almost all stormwater samples analyzed. Due to frequency of occurrence and toxicity, cadmium, copper, lead, and zinc are the primary metals of concern in urban stormwater runoff (Weiss et al., 2006); each is discussed below. At sufficiently high concentrations, all metals are considered a threat to human health and the environment; different organisms have different tolerances to different metals. Metals are present in stormwater in dissolved phases, but a large fraction of most metals are usually bound to suspended solids (Davis and McCuen, 2005; Marsalek et al., 2001). Of the metals typically found in stormwater, lead has largest tendency to adsorb to solids. The ranking of adsorption potential for some common metals to soil particles is, with lead having the highest potential, as shown below (Pitt et al., 1995).

lead > copper > nickel > cobalt > zinc > cadmium

Other metal removal mechanisms include precipitation, occlusion with other precipitates, diffusion into solid particles, and biological uptake. Dissolved metals are typically removed through adsorption to soil particles in the vadose zone, while metals associated with the particulate phase are usually removed via physical straining at the soil surface (Pitt et al., 1999).

Since metals are often bound to solid particles, removal of suspended solids can be an effective method of reducing metal concentrations in stormwater. Metals do not generally degrade to another element in the environment, however, and stormwater loading into rain gardens (or other stormwater structures) with subsequent detention will result in metal accumulation. Using typical stormwater contaminant loading and soil capacity estimates for bioretention practices, Davis et al. (2003) estimated that, after 20 years, concentrations of cadmium, lead, and zinc would reach or exceed concentrations permitted by EPA biosolids land application regulations.

Assuming that all metals are retained in a soil layer, the soil metal concentration, C_s (metal mass/soil mass) can be estimated by (Marsalek et al., 2001):

$$C_s = C_w \cdot \frac{A_r}{A_i} \cdot \frac{MAR}{d \cdot \rho} \cdot t$$

where C_w is the concentration of metal in the runoff water, A_r/A_i is the ratio of runoff area catchment to infiltration area, MAR is the mean annual rainfall, d is the thickness of the soil layer, ρ is the soil bulk density, and t is time in years. Consistent units must be used when applying this equation.

Once adsorbed to the surface of a soil particle, metals may not necessarily remain stationary. Depending on soil conditions such as pH and Eh, metals may be released from the solid surface. The relative mobility of divalent (i.e., +2 charge) stormwater metals in soil is (Harter 1983):

nickel > zinc > copper > lead

Harden and Pitt (2011) evaluated the impact of soil amendments on the immobilization or retardation of copper, chromium, and arsenic leaching from a soil/CCA wood ash mixture. CCA, or chromated copper arsenate, wood has been pressure treated with CCA to prevent it from rotting. Soil amendments evaluated were agricultural lime, gypsum soil softener, and iron sulfate. The gypsum soil softener reduced leaching of chromium and arsenic by over 70% and was the most effective amendment. Copper leaching increased in the presence of all three amendments.

Some metals are also micronutrients needed by plants and may be accumulated into plant biomass as plants grow. Some plants uptake metals at a much higher rate than others (known as hyperaccumulators) and/or have greater tolerances to high metal concentrations. Ideally, if used for removal of a metal from stormwater or soils, a plant would have a high uptake rate and a tolerance to high metal concentrations within the plant material. Sun and Davis (2007) ranked the general tendency of metals to accumulate in plants (Sun and Davis, 2007), with zinc having the highest tendency, as:

zinc > copper > lead > cadmium

According to Pitt et al. (1996), nickel and zinc would have high groundwater contamination potential in infiltration/injection systems and chromium and lead, moderate potential. Pitt et al. (1996) assert that if sedimentation pretreatment were used, all metals would probably have low groundwater contamination potential.

In most of the reviewed articles, most metals were removed in the upper 50 cm or less of soil as stormwater infiltrates through the soil. While soil often removes metals through the physical straining of particulate-bound metal and the adsorption of dissolved metal ions, increased metal concentrations have been detected in the groundwater beneath infiltration practices when the groundwater is acidic (Pitt et al., 1996). Also, O'Connor et al. (2012) showed that maintenance activities that disturbed sediment of a constructed wetland caused a temporary (<9 month) increase in the mobile fraction of some metals and a corresponding increase in metal concentrations in the tissues of macroinvertebrates.

Cadmium

Cadmium is of concern due to human health implications; although it is commonly detected, concentrations in stormwater are typically very low (Pitt et al., 1995). In a French study on an existing infiltration practice, cadmium concentrations in stormwater from a heavily used roadway were found to average less than 5 µg/L (Barraud et al., 1999). Concentrations detected from highway runoff at three sites near Charlotte, North Carolina averaged 2.5 µg/L average for ten storms (Wu et al., 1998); for reference, the U.S. EPA MCL for cadmium in drinking water is 5 µg/L (U.S. EPA website). In contrast to the other studies, a correlation between impervious surface cover or vehicle use intensity and cadmium concentration in runoff was not found. This finding supports the suggestion that the main source of cadmium is wet deposition (Davis et al., 2001). Pitt et al. (1995), however, found the highest median cadmium concentrations (8 µg/L) in

vehicle service runoff, and samples from one street that was examined contained 220 $\mu\text{g/L}$, which was the highest of all samples collected (Pitt et al., 1995).

Because the main removal mechanisms for cadmium are ion exchange, sorption, and precipitation (Pitt et al., 1996), soil media may retain cadmium. Laboratory column studies conducted thus far have shown removal rates of up to 95% or higher (Sun and Davis, 2007).

In filter column experiments with media consisting of 95% anthracite sand and 5% hydrous ferric oxide by weight, Mohammed et al. (2012) observed 21% to 50% removal of dissolved cadmium cations. The initial cadmium concentration was 0.1 mg/L and the pH of the synthetic stormwater was adjusted to be between 6 and 8.

Due to the typically low concentrations of cadmium found in stormwater, many studies to date have neglected cadmium.

Copper

Copper was found in virtually all stormwater samples analyzed by Pitt et al. (1995); the highest median copper concentrations were from urban stream samples (160 $\mu\text{g/L}$) and street runoff had the highest single concentration (1250 $\mu\text{g/L}$). Wu et al. (1998) found copper concentrations in highway runoff to be between 2.5 and 15 $\mu\text{g/L}$ for ten storms in North Carolina. Copper loading correlated well to increased impervious cover and vehicle usage intensity. In a groundwater contamination study in France, stormwater from a mostly industrial area was found to have copper concentrations between 7 and 49 $\mu\text{g/L}$ (Bardin et al., 2001). The chief copper removal mechanisms in soil are sorption, complex ion formation, and ion exchange (Pitt et al., 1996). The U.S. EPA MCL for drinking water is 1.5 mg/L (U.S. EPA, 2008)

In one laboratory column study, 93% of copper in a synthetic stormwater influent was removed (Davis et al., 2001). A subsequent laboratory study found copper removal efficiencies of between 88 and 93% (Sun and Davis, 2007).

In filter column experiments with media consisting of 95% anthracite sand and 5% hydrous ferric oxide by weight, Mohammed et al. (2012) observed 36% to 56% removal of dissolved copper cations. The initial copper concentration was 1.2 mg/L and the pH of the synthetic stormwater was adjusted to be between 6 and 8.

Good et al. (2012) investigated the performance of laboratory scale rain gardens for their effectiveness with respect to metal removal. Three different rain garden media were tested: 1) sand, 2) sand and topsoil mix, and 3) topsoil only. The influent copper concentration was 17.1 $\mu\text{g/L}$ (16% dissolved and the remainder particulate) and removal was found to range from 37% to an increase of 221% (i.e., negative removal) in the top soil-only rain garden.

Field studies indicate lower removal efficiencies than laboratory studies. 43% (standard deviation of 11%) of copper was removed in one field study (Davis et al., 2003); another subsequent study indicated between 50 and 60% removal (Davis, 2007). The results of a study that examined the fate of copper within bioretention cells found 98% of the influent copper was retained in a mulch layer, with 0.1% uptake by plants (Dietz and Clausen, 2006). Backstrom (2003) studied field sites with grassed swales and found that the swale provided a total reduction of 34% for copper. Higher reductions have been observed; Hunt et al. (2006) observed a 99% reduction in mass loading for copper in a rain garden field study.

Lead

Lead can originate from a variety of sources. Davis and Burns (1999) studied lead contribution of buildings to stormwater by spraying synthetic rainwater on buildings of various ages. The lead concentrations in the runoff were several orders of magnitude higher than drinking water standards. The study reported that the major source of lead was older weathered paints and that most lead was in the particulate form and could potentially be removed by filtration. The U.S. EPA MCL for lead in drinking water is 15 µg/L (U.S. EPA, 2008).

Wu et al. (1998) examined the presence of lead in highway runoff in Charlotte, NC and found that the event mean concentration for each of the 10 storms monitored ranged from 6 mg/L to 15 mg/L. Increases in lead concentrations at the study sites correlated to increases in the percentage of impervious surface area and traffic intensity (number of average daily trips). Pitt et al. (1996) stated that lead concentrations are generally highest in runoff from streets and parking areas.

In a groundwater contamination study in France, stormwater from a mostly industrial area was found to have lead concentrations between less than 5 and 90 µg/L (Bardin et al., 2001). In another French study on infiltration practices, lead concentrations in stormwater from a heavily used roadway prior to recharge were found to average 98 µg/L (Barraud et al., 1999).

The main removal mechanisms of lead from stormwater are sorption to solids, ion exchange, and precipitation (Pitt et al., 1995). In three different studies, synthetic runoff (containing a suite of metals including lead) was added to rain garden column reactors. Lead removal rates were found to be from 62% to more than 99% (Hsieh and Davis, 2005); greater than 98% (Davis et al., 2001); and 95% to 97% (Sun and Davis, 2007). It was noted that 56% of the lead in the synthetic stormwater was adsorbed to the suspended solids of the synthetic stormwater and that lead retention directly correlated to the suspended solids retention rate. Davis et al. (2003) observed a 94-99% lead removal rate. With respect to lead, the study found sand to be a more effective media than mulch. As a field component of the study, four test sites were dosed with synthetic stormwater; removal rates of 80% to 98% were observed. Event mean contaminant concentrations of actual rainstorms were monitored, and similar removal rates were found. Dietz and Clausen (2006) found that mulch was less effective at retaining lead as it retained only 36% in their study. Plants in the rain garden (chokeberry [*Aronia prunifolia*], winterberry [*Ilex verticillata*], and compact inkberry [*Ilex glabra compacta*]) were found to accumulate none of the lead.

Good et al. (2012) investigated the performance of laboratory scale rain gardens for their effectiveness with respect to metal removal. Three different rain garden media were tested: 1) sand, 2) sand and topsoil mix, and 3) topsoil only. The influent lead concentration was 35.1 µg/L (4% dissolved) and removal was found to range from 71% to 85%.

Most field studies have yielded lower lead removal efficiencies than laboratory studies; however, in some cases, higher removal rates have been observed. For example, Hunt et al. (2006) observed an 81% reduction in mass loading for lead in a rain garden field study and Davis (2007) observed a lead removal rate of 83% in a field study. One study suggested that the lead-soil adsorption bonds were weakened when sediment was allowed to dry and that this impacted lead removal (Pitt et al., 1999).

Nickel

Sources of nickel include fuels, oils, metal plating, bushing wear, asphalt, brakes, and leaching from rooftops (Clark et al. 2006). Nickel is often found in stormwater runoff and, compared to other metals; the particulate bound fraction is low. Pitt et al. (1995) found that runoff from parking lots and storage areas had the highest concentrations, with nickel being detected in 90% of the samples and the dissolved fraction being relatively low. Although others have ranked nickel high in terms of mobility, Clark et al. (2006) give nickel a low rating in this category. The U.S. EPA (1983) reported that nickel was found in 43% of the stormwater samples analyzed with a range of concentrations from 1 $\mu\text{g/L}$ to 182 $\mu\text{g/L}$, though no US E.P.A regulations for nickel exist. Primary removal mechanisms for nickel include surface adsorption, ion exchange, and chelation (Pitt et al., 1996).

Bardin et al. (2001) examined the soil and water beneath an infiltration basin in Lyon, France for over a year, analyzing samples for many metals, including nickel. Although nickel was found in the particulate form in the soil, it was not detected in the water. Aryal et al. (2006) investigated the nickel concentration on road dust, the sediment near the inlet of an infiltration basin, and the soil of an infiltration basin in Japan and found concentrations ranging from 41 to 62 $\mu\text{g/kg}$, 8.2 to 84 $\mu\text{g/kg}$, and 25 to 26 $\mu\text{g/kg}$, respectively. Mikkelsen et al. (1997) investigated the soil and groundwater beneath an infiltration basin for contamination by many compounds, including nickel. It was determined that the concentrations of nickel were insignificant or low compared to background concentrations.

In filter column experiments with media consisting of 95% anthracite sand and 5% hydrous ferric oxide by weight, Mohammed et al. (2012) observed 11% to 23% removal of dissolved nickel cations. The initial nickel concentration was 0.1 mg/L and the pH of the synthetic stormwater was adjusted to be between 6 and 8.

Zinc

Zinc is a common stormwater metal contaminant (Davis et al., 2001; Dietz and Clausen, 2006). Concentrations of zinc are typically greatest in parking lot and street runoff (Pitt et al., 1996). In an analysis of stormwater samples by Pitt et al. (1995), zinc was found to occur mostly in dissolved form with roof runoff containing the highest concentrations. In a groundwater contamination study in France, stormwater from a mostly industrial area was found to have zinc concentrations between 126 and 681 $\mu\text{g/L}$ (Bardin et al., 2001). In another French study, zinc concentrations in stormwater from a heavily used roadway prior to recharge were found to average 802 $\mu\text{g/L}$; zinc also had the highest variability among all contaminants studied (Barraud et al., 1999). The U.S. EPA has not established a MCL for zinc but has established a non-enforceable secondary drinking water regulation of 5 mg/L (U.S. EPA website). Secondary regulations are guidelines for contaminants that can cause cosmetic or aesthetic effects. The principle removal mechanisms of zinc from stormwater are precipitation, sorption, and ion exchange (Pitt et al., 1996).

In both laboratory and field studies, zinc has been found to be removed from stormwater via infiltration devices. Zinc retention was found to be similar to lead in a laboratory column study (>98%), and was removed more effectively than copper (Davis et al., 2001). Another column laboratory study found zinc removal efficiencies to be 94 to 97% (Sun and Davis, 2007).

In filter column experiments with media consisting of 95% anthracite sand and 5% hydrous ferric oxide by weight, Mohammed et al. (2012) observed 44% to 63% removal of dissolved zinc cations. The initial zinc concentration was 4.0 mg/L and the pH of the synthetic stormwater was adjusted to be between 6 and 8.

Good et al. (2012) investigated the performance of laboratory scale rain gardens for their effectiveness with respect to metal removal. Three different rain garden media were tested: 1) sand, 2) sand and topsoil mix, and 3) topsoil only. The influent zinc concentration was 168 $\mu\text{g/L}$ (51% dissolved) and removal was found to range from 8% to 69%.

Field studies, in general, have shown lower zinc removal efficiencies than laboratory studies. For a field site in Maryland dosed with synthetic stormwater, 64% of zinc was removed (with a standard deviation of 42%) (Davis et al., 2003). A subsequent performance study revealed 50% to 70% removal of zinc (Davis, 2007). Another field study examined the fate of zinc loading in rain gardens, and found only 16% to be retained in a mulch layer with another 0.2% being assimilated into plant material. Most of the remaining zinc was assumed to be adsorbed to sediment because zinc was not detected in the effluent (Dietz and Clausen, 2006). Backstrom (2003) studied grassed swale field sites and found a total reduction of 66% for zinc. However, higher reductions have been also been observed; Hunt et al. (2006) observed 98% of the influent mass loading of zinc retained by a rain garden.

Suspended Solids

Suspended solids, which are almost always found in stormwater runoff samples, can degrade water quality (U.S. EPA, 1999). Construction and land-disturbing activities are the leading source of suspended solids in stormwater (U.S. EPA, 1999). Because metals, pesticides, and petroleum hydrocarbons often are sorbed to solid surfaces, suspended solids provide a means of transport and accumulation of contaminants (U.S. EPA, 1999). Additionally, suspended solids can degrade aquatic ecosystems by covering fish spawning areas (U.S. EPA, 1999) and blocking sunlight.

In a study on the cost and effectiveness of stormwater BMPs, Weiss et al. (2007) collected stormwater suspended solids data from existing literature. Data was gathered from study sites located across the United States and the average suspended solids concentration was found to be 143 mg/L (± 77 mg/L, 67% confidence interval).

The primary removal mechanisms of suspended solids are physical filtration and sedimentation. Infiltration systems provide filtration of runoff but the percent removal of solids depends on, among other variables, particle size and the size of the pore opening between soil particles. Hsieh and Davis (2005) conducted both laboratory column tests and field studies. Column percent removal of suspended solids ranged from 29% to greater than 96% and removal at six field sites ranged from 77% to 99%. However, Davis (2007) found that only 43% and 47% of the suspended solids were removed (on average) from two bioretention cells monitored for twelve storm events (Davis, 2007). Hunt et al. (2006) observed an increase in suspended solids concentrations in a rain garden field study, which may be due to the uncertainties involved in monitoring research. Backstrom (2003) observed a 70% TSS removal efficiency at a roadside

grassed swale field site, and the International Stormwater Best Management Practices Database (1999 to 2007) reports a median removal value of 66% for biofilters (ASCE, 2007).

Organic Compounds

Organic compounds can be naturally occurring (e.g., animal waste, vegetation, soil organisms) or anthropogenic in origin (e.g., petroleum hydrocarbons, automobile tire particles). A measurement of oil and grease reflects the amount of total petroleum hydrocarbons present (one form of organic compounds). As applied to groundwater contamination, the focus has been mainly on anthropogenic organic compounds including petroleum hydrocarbons. For a complete list of U.S. EPA drinking water standards for organic compounds see: <http://water.epa.gov/drink/contaminants/index.cfm#7>. Organic compound removal may occur through volatilization, sorption, and degradation (Pitt et al., 1999).

In a study to characterize stormwater contaminants, Pitt et al. (1995) found that a large fraction of the organic contaminants for which stormwater samples were analyzed were not frequently detected. 1, 3-dichlorobenzene and fluoranthene were detected in 23% of the samples analyzed, which was the highest detection rate for all organic compounds. Pitt et al. (1996) report that 1,3-dichlorobenzene, pyrene, and fluoranthene may have high groundwater contamination potential in subsurface infiltration/injection systems without pretreatment, but would probably have lower contamination potential in surface infiltration systems. A series of other organics (benzo (a) anthracene, bis (2-ethylhexyl) phthalate, butyl benzyl phthalate, pentachlorophenol, phenanthrene) are listed as having moderate groundwater contamination potential for subsurface injection when no pretreatment system is used. Anthracene, fluorine, and naphthalene are listed as having low potential for groundwater contamination for subsurface injection with minimal pretreatment. All organics are listed as having low or moderate contamination potential for subsurface infiltration with sedimentation as a pretreatment mechanism.

In a Florida study reviewed by Pitt et al. (1999) the fate of organic compounds that were infiltrated with stormwater was investigated. Most organic hydrocarbons were found to be attenuated in the soil but one compound, bis(2-ethylhexyl)phthalate, was detected in the groundwater. In an Arizona study reviewed by Pitt et al. (1999), base and neutral compounds from residential areas were found in the groundwater and phenol, ethylbenzene, and toluene contaminated groundwater was found near commercial sites. In this same study, toluene, xylene, and phenol were detected in perched groundwater from residential sites.

Five stormwater recharge basins that were in watersheds comprised of expressways or commercial and/or residential areas in Long Island, New York were investigated by Ku and Simmons (1986). Groundwater samples were analyzed for 113 USEPA priority contaminants. Concentrations exceeding New York drinking water guidelines were found in groundwater at highway infiltration basins (p-chloro-m-cresol, 79 pg/L; 2,4-dimethylphenol, 96 pg/L; methylene chloride, 230 µg/L) and in a parking lot infiltration basin (4-nitrophenol, 58 µg/L). Organic compounds (benzene, bis(2-ethylhexyl)phthalate, chloroform, toluene, 1,1,1-trichloroethane, p-chloro-m-cresol, 2,4-dimethyl phenol, 4-nitrophenol) were also found in groundwater samples.

Three infiltration practices were investigated in Maryland with benzene, trichlorofluoromethane, 1,2-dichloroethane, 1,2-dibromoethylene, toluene, and methylene blue

active substances (MBAS) being detected in stormwater runoff entering the infiltration practices. Only MBASs were detected consistently in elevated concentrations in groundwater beneath the infiltration practices. The other compounds were either retained by the practice or removed in the vadose zone (Wilde, 1994). The authors noted that although most organic compounds were not detected in the groundwater, the dissolved organic content of the stormwater beneath and down gradient of the practice was higher than in control groundwater samples.

Sources of petroleum hydrocarbons include leaky storage tanks, parking lot and roadway runoff, automotive emissions, illicit dumping, and spills (U.S. EPA, 1999). Petroleum hydrocarbons are classified as priority contaminants; some are at least somewhat water soluble, making them a common groundwater contaminant (Płaza et al., 2007). Petroleum hydrocarbons are known for their acute and chronic toxicity (U.S. EPA, 1999); thus small concentrations can be of concern. Despite their toxicity and presence in stormwater runoff, existing literature on the fate of hydrocarbons in infiltration systems is much less than for metals and nutrients.

A study from the Washington, DC metropolitan area found petroleum hydrocarbon median concentrations of 0.7 to 6.6 mg/L; the concentrations used for protection of fisheries is 0.01 to 0.1 mg/L (Shepp, 1996). The work by Shepp (1996) did not measure individual hydrocarbon concentrations, only total hydrocarbons. Oil and grease concentrations found in highway runoff ranged between 1.3 and 3.3 $\mu\text{g/L}$ (Kim et al., 2007; Wu et al., 1998). Other studies, however, have found higher concentrations of oils/grease. Kim et al. (2005) observed 5.23 $\mu\text{g/L}$, Zanoni et al. (1986) observed 2 to 79 $\mu\text{g/L}$, and Barraud et al. (1999) observed 110 $\mu\text{g/L}$ in stormwater.

Hsieh and Davis (2005) tested laboratory column rain gardens with sandy and sandy loam media and found greater than 96% removal of oils and grease (introduced as used motor oil through synthetic stormwater). The results of their field study found that removal efficiency of oils and greases from a synthetic stormwater was nearly 100% and 99% removal was observed during a natural rain event.

LeFevre et al. (2012a) investigated the removal of naphthalene in laboratory column studies and found 73% removal in non-vegetated columns and 93% removal for columns planted with vegetation. Removal of added naphthalene occurred due to adsorption to soil (56 to 73%), mineralization (12 to 18%), and plant uptake (2 to 23%). Volatilization of naphthalene was negligible. The authors concluded that bioretention can be suitable for hydrocarbon removal and that vegetation can increase removal rates and stimulate biodegradation.

LeFevre et al. (2012b) analyzed 78 soil samples from 58 rain gardens and 4 upland areas (control sites) and found that total petroleum hydrocarbon concentrations were greater in rain garden soils than in the upland soils but that rain garden concentrations were orders of magnitude below regulatory limits. Total petroleum hydrocarbon (TPH) concentrations in rain gardens were much lower than would be expected based on mass loading rates, suggesting that significant biodegradation occurred in the rain gardens. Vegetation in the rain gardens also appeared to increase biodegradation rates. Finally, TPH concentrations in the rain garden soils were significantly lower than what is typically found in stormwater pond sediments, suggesting that rain gardens may be more effective in treating TPH.

Foulquier et al. (2010) examined dissolved organic carbon (DOC) concentrations and dissolved oxygen (DO) concentrations in groundwater beneath stormwater infiltration sites in France and compared them to control sites. At the infiltration sites, the groundwater had higher

concentrations of DOC, which is not uncommon because organic compounds can leach from the vadose zone into the infiltrating stormwater. DO in the groundwater below infiltration sites was lower than the control sites, a tendency that is not uncommon and is often attributed to increased microbial activity. Foulquier et al. (2010), however, attributed the changes in the groundwater DOC and DO concentrations to only the physical mixing of the infiltrated water and groundwater, not to microorganisms.

Pathogens

For residential and light commercial developments, pathogens (i.e., bacteria and viruses) in stormwater are a primary contaminant of concern. They may be present in high concentrations and not retained well in the soil (Pitt, 1999). The highest bacteria and virus concentrations in groundwater are found to occur when the water table is near the land surface (Pitt et al., 1999). By analyzing data in the National Stormwater Quality Database, Clark and Pitt (2007) found that *Fecal streptococci* and *E. coli* were found in 94% and 95.5%, respectively, of municipal separate storm sewer system (MS4) outfalls monitored.

Pitt et al. (1996) state that enteroviruses have high groundwater contamination potential for all surface and subsurface infiltration/injection systems and that a variety of other pathogens would have high groundwater contamination potential for subsurface infiltration/injection systems.

Bacteria may be removed by straining at the soil surface and sorption to solid particles. Once removed from the water, the ability of bacteria to survive is a function of factors such as temperature, pH, presence of metals, etc. Bacteria survive longer in acidic soils and in soils with large amounts of organic matter. Bacteria survival may be between two and three months but survival for up to five years has been documented (Pitt et al., 1999).

As part of the National Urban Runoff Program, fecal coliform was evaluated at 17 sites for 156 storm events and, based on the results, it was concluded that coliform bacteria are present at high concentrations in urban runoff and may exceed EPA water quality criteria during and after storm events (U.S. EPA, 1999). There exists a high degree of variability within the data but land use did not appear to correlate with coliform concentration. During warmer months, concentrations were approximately 20 times higher than cold months because of a higher rate of coliform growth during warm months.

Groundwater contamination potential by bacteria and viruses depends on the soil chemical properties, adsorption capability, the ability of the soil to physically strain the pathogens, and pathogen survival characteristics. Bacteria and viruses can move through soil media and may be transported to aquifers by infiltrating stormwater. The transport distance of bacteria seems to be partially a function of bacteria density and water velocity through the soil (Camesano and Logan 1998; Unice and Logan, 2000).

Large volumes of stormwater runoff can ultimately causes receiving streams and rivers to flood. The risk of groundwater contamination by river water can increase during these periods. During these events, river water can contain higher concentrations of pathogens and the increased turbulence and sheer stresses can lead to increased infiltration (Page et al., 2012). Because testing for the presence of pathogens in water requires time to grow colonies of the

pathogens (typically ~1 day), Page et al. investigated the possibility of using other water parameters to indicate the presence of pathogens in infiltrated river water. The aquifer studied had media of mostly carbonate gravel along with variably sorted sediment with layers of silts and clays, and received recharge from river infiltration, lateral inflow from a nearby watershed, and periodic artificial recharge. Samples of river and well water were analyzed and values of temperature, electrical conductivity, turbidity, spectral absorption coefficient, and particle density were continuously recorded and compared to the counts of *E. coli* and *Enterococcus* sp. Although all of the monitored parameters were affected by infiltration of river water, none of the parameters matched the response of the bacteria closely enough to be used as a proxy indicator. Instead, the authors suggested using a combined set of proxy parameters.

Documented virus contamination of groundwater due to infiltration practices has occurred at sites on Long Island where the water table was less than thirty-five feet below the infiltration practice. The highest bacteria and virus concentrations in groundwater samples were found at locations where the groundwater table was close to the ground surface (Clark et al., 2006).

E. coli and enterococci have been shown to pass through stormwater sand filters (Clark 2000). Clark (2000) used various media to conduct pilot scale tests on filters receiving stormwater runoff from medium density residential areas. Pilot scale filters were constructed from 55 gallon drums with a filter surface area of 2.33 ft². The drums contained a gravel base with six inches of sand above the gravel and one foot of filter media on top of the sand. Stormwater entered the top of the drum, filtered through the media, the sand layer, and finally through the gravel base and out a spigot on the side of the drum. Influent and effluent samples were collected and analyzed for *E. coli* and enterococci. Results indicated that sand filters could reduce concentrations but *E. coli* and enterococci were not reduced to below detection limits. Ranges of removal efficiencies for a 100% sand media ranged from 0 to 88% for *E. coli* and 16 to 89% for enterococci. Media consisting of a peat-sand mixed retained 35 to 96% of *E. coli* and 0 to 94% of enterococci.

Dietz and Clausen (2005) found fecal coliform concentrations to be less than 10 colony forming units (CFU) per 100 mL in both the influent (from roof runoff) and the effluent from a rain garden. Rusciano and Obropta (2007) created a bioretention column in which horse manure was fed to the column to simulate a bacterial contaminant source. Results indicated the median reduction in fecal coliform was 98.6%.

Chloride

Because chloride is soluble, easily transported in surface and sub-surface flow, non-filterable, and does not readily sorb to solids, it has a high potential for groundwater contamination (Pitt et al., 2002). Rather than being reduced, chloride concentrations typically increase as water moves through soil due to leaching of salts into the water (Pitt et al., 1999). The U.S. EPA secondary drinking water regulation for chloride is 250 mg/L.

Research has shown that concentrations of chloride have been increasing in local waterways in New England (Kaushal et al., 2005), and if current trends continue, chloride concentrations in streams will reach concentrations that will threaten aquatic life.

Ostendorf et al. (2009) investigated the presence of de-icing agents in groundwater plume beneath an infiltration basin by measuring the specific conductance in the plume. Through a mass balance on the de-icing agent, it was determined that more dissolved de-icing agent left through infiltration than entered through runoff. This was attributed to solid de-icing agent being washed from roadways into the basin where it dissolved more slowly over time. Also supporting this notion was the fact that the minimum specific conductance of the groundwater plume during the autumn was an order of magnitude higher than the specific conductance of the runoff entering the basin.

Novotny et al. (2008) found that in the Twin Cities Metropolitan Area of Minnesota, chloride from winter road salt application was washed to nearby lakes where it significantly increased chloride concentrations at the bottom of the lakes. Due to the increased density of the high chloride concentration water, fingers of salt water moved further into the sediment through advection and dispersion. High chloride concentrations can cause the release of metals that are fixed to soil particles. Once released, the metals are free to diffuse upwards towards the interface between the sediment and lake water or to move with the salt water farther into the sediment below the interface. Similar transport of chloride into the sediment of a detention pond that received runoff from a highway was observed by Mayer et al. (1999).

Anticaking agents are usually used to prevent road salt from forming clumps (i.e., caking). Paschka et al. (1999) investigated the potential effects of anticaking agents used in road salt on water quality. The major contaminant of concern in anticaking agents is cyanide, which may occur as HCN. Although HCN is usually assumed to volatilize quickly, there is insufficient data in the literature to confirm this assumption. In addition, HCN is a weak acid, and it partially dissociates into H^+ and CN^- , and these ions do not volatilize. The literature reviewed contained studies on the influence of anticaking agents on surface water quality but none, however, addressed the issue of groundwater contamination.

Groundwater Contamination and Removal of Contaminants in Soil

The previous section focused on the most common contaminants found in urban stormwater runoff and the capability of infiltration systems to retain them. Most of those studies monitored influent and effluent contaminant concentrations or mass loads and, by comparing the difference between them, calculated a percent removal. Other studies have investigated whether or not stormwater runoff contaminants have the ability and/or potential to travel to aquifers and pollute groundwater. Other investigations have focused on the soil (or other media) contaminant concentration that result from infiltration of polluted stormwater. Groundwater and soil protection from stormwater contamination are legitimate concerns for protecting human and environmental health and merit further investigation (Lind and Karro, 1995).

This section first provides a literature review of studies that directly investigated the potential of stormwater infiltration to contaminate groundwater. After a summary of articles that investigated the potential for groundwater contamination, a review of articles that investigated the removal of contaminants by soil media through which groundwater infiltrates is presented. The latter is important because removal of contaminants by soil can protect groundwater from

contamination but all soils have a finite capacity with regards to contaminant retention. Also, removal of contaminants by soil is, in some cases, a reversible process, which may result in the release of contaminants so that the soil because of source of contamination. Finally, the section ends with a review of published literature that compiled results and presented summaries of these two topics or that involved model simulations of contaminant transport related to infiltration systems.

Groundwater Contamination

Appleyard (1993) investigated the impact of three infiltration basins on adjacent groundwater quality. In total, twelve sampling wells were drilled adjacent to the infiltration basins and water concentrations and quality were monitored after runoff/infiltration events. It was noted that groundwater concentrations responded quickly to infiltration with peak increases of up to 2.5 m observed within 6 to 24 hours. The largest impact on groundwater was an increase in dissolved oxygen (DO) concentrations and a decrease in salinity in the upper part of the aquifer. Salinity was reduced from 250 to 500 mg/L to 20 to 140 mg/L and DO concentrations increased in some cases to near saturation. Concentrations of metals, nutrients, pesticides, and phenolic compounds did not increase due to infiltration and no fecal coliforms, streptococci, or *Salmonella* were found in the groundwater samples. Phthalates were detected in all wells except one but this compound could have originated from the plastic casing used in the wells or plastic trash that had accumulated in the basins.

Stephenson et al. (1999) performed a monitoring and die tracer study on highway runoff entering a sinkhole in Knoxville, Tennessee and a spring located 420 feet away from the sinkhole. Total zinc, dissolved lead, total lead, total petroleum hydrocarbons, polycyclic aromatic hydrocarbons, total dissolved solids, total suspended solids, and total volatile solids concentrations at the sinkhole and spring were monitored for only one runoff event. For most contaminants, the peak contaminant concentrations at the spring lagged behind that at the sinkhole by about one hour. The peak concentration of TDS, however, lagged by only 20 minutes. The peak concentrations were higher at the spring than at the sinkhole for TDS and dissolved zinc, but lower for all other contaminants. The authors concluded that groundwater is more susceptible to contamination by highway runoff in karst aquifers because these aquifers can transport runoff and contaminants with little or no attenuation or filtration.

Fischer et al. (2003) compared groundwater beneath 16 detention basins in developed areas with groundwater from monitoring wells in undeveloped areas. Results showed that some pesticide concentrations were higher in the undeveloped areas but in some cases the opposite was true. The authors suggested that with some pesticides the water from the monitoring well was diluted by the infiltration of detention basin water. That is, the existing groundwater concentration of some contaminants was higher than the concentration in the infiltrating water such that the infiltrating water diluted the groundwater. Other contaminants, however, had higher concentrations in the infiltrating water than the groundwater. In these situations, the infiltrating water increased groundwater concentrations. The most noticeable difference was that the water beneath the detention basins had much lower DO concentrations than the monitoring wells in undeveloped areas. Also, concentrations of nitrite and nitrate were typically higher in the high

DO monitoring well water. This was probably due to the fact that nitrification occurs more readily under aerobic conditions. Concentrations of ammonia and organic nitrogen, however, were found to be higher in the water beneath the detention basins (i.e., low DO water). Chloride concentrations were found to be roughly the same; however, the study was conducted in a year with low snowfall and consequently lesser quantities of salts were applied to the roadways during the course of the study.

Datry et al. (2004) investigated the effects of infiltration on water quality beneath an infiltration basin on the campus of University Claude Bernard in Lyon, France. The basin, which had been in operation for over 30 years at the time of the study, had a surface area of over 750 m² and a storage volume of approximately 4000 m³. Organic stormwater sediment contaminated with hydrocarbons and metals had accumulated on the bottom of the basin with no mention of dredging or contaminant removal performed during the history of the basin. Six sampling wells were located within the basin, which allowed groundwater samples to be collected at various depths. The water table was 1.2 m below the ground surface during dry periods but, due to infiltration, was closer to the surface during wet periods. The authors found that groundwater at a depth of 1 meter below the water table consisted almost entirely of stormwater and that stormwater did not penetrate to depths greater than 3 meters below the water table. Dissolved phosphate in the groundwater was higher in concentration than the stormwater influent indicating that it was produced or added in the infiltration bed; the authors concluded that mineralization of organic sediments was the most likely cause. There was also evidence that organic sediments increased the dissolved organic content of the water.

Within the water samples collected from the infiltration bed, ammonium was the dominant nitrogen species during dry weather but it was not found in the groundwater. This indicates that ammonium was oxidized to nitrate within the infiltration bed. Also metals and hydrocarbons were not detected in the groundwater. The authors found that stormwater infiltration during cold rains raised the groundwater DO slightly and decreased the DO during warm rains. This is most likely due to the fact that oxygen becomes more soluble in water as the temperature drops.

Kwiatkowski et al. (2007) investigated the impact on groundwater from a pervious concrete infiltration basin. The infiltration basin was on the campus of Villanova University and the watershed consisted of grassed areas (36%), asphalt/concrete (30%), and building/roofs (30%) that were directly connected to the infiltration basin. Seventeen runoff events were investigated by taking water samples from the vadose zone and analyzing the samples for suspended solids, dissolved solids, chloride, copper, and total nitrogen, although chloride and copper were the contaminants of primary concern. The average infiltration rate was 9 cm/day. Copper was not found below 0.30 m and chloride was not significant enough to negatively impact the groundwater. The authors concluded that with proper siting, infiltration stormwater BMPs would not adversely affect groundwater aquifers.

O'Reilly et al. (2012) analyzed dissolved oxygen (DO) and nitrate (NO₃⁻) concentrations in the soil below two infiltration basins in northern Florida over a two year span. The soil beneath one basin contained 41% silts and clays while the soil beneath the second basin consisted of only 2% silts and clays. The water in the clayey soil exhibited decreases in DO with depth from 3.8 mg/L to 0.1 mg/L and decreases in nitrate from 2.7 mg/L to less than 0.016 mg/L as N. The DO in the sandy soil did not drop and remained between 5.0 and 7.8 mg/L. Also, nitrate

concentrations below the infiltration basin in the sandy soil (i.e., in the high DO water) were 1.3 mg/L to 3.3 mg/L as N. Vertical profiles as a function of depth below the soil surface for each basin are shown in Figure 2. It was concluded that the fines in the clayey soil impeded the diffusion and/or transport of oxygen into the soil. This lack of oxygen created anaerobic conditions and denitrification, which is a microbial process that converts nitrite and nitrate to nitrogen gas. Thus, denitrification led to the drop in nitrate concentration in the clayey soil. The presence of oxygen in the water in the sandy soil prevented denitrification from occurring and lead to the conservative transport of nitrate farther beneath the soil surface.

Whittemore (2012) investigated the impact on groundwater of stormwater runoff that entered five pits in Wichita, Kansas. The pits were mined for sand and the surrounding land was later developed for residential use. An additional pit, surround by agricultural land, was used as a control. With the groundwater table higher than the bottom of the pits, the pits filled with water and now also receive stormwater runoff during and after rainfall events. Pit water surface elevations (i.e., groundwater) ranged from 2.0 to 5.6 meters below the ground surface. Three monitoring wells were installed around each of the six pits and groundwater samples were collected and analyzed for inorganic compounds, bacteria, and 252 organic compounds. Pit sediments were also analyzed for inorganic compounds and 32 organic chemicals. Concentrations of iron, manganese, ammonia, as well as pesticides and other organics indicated that the groundwater was being contaminated by stormwater runoff that had infiltrated. No contaminant concentrations were above health regulatory limits but the authors concluded that the potential exists if stormwater becomes more polluted.

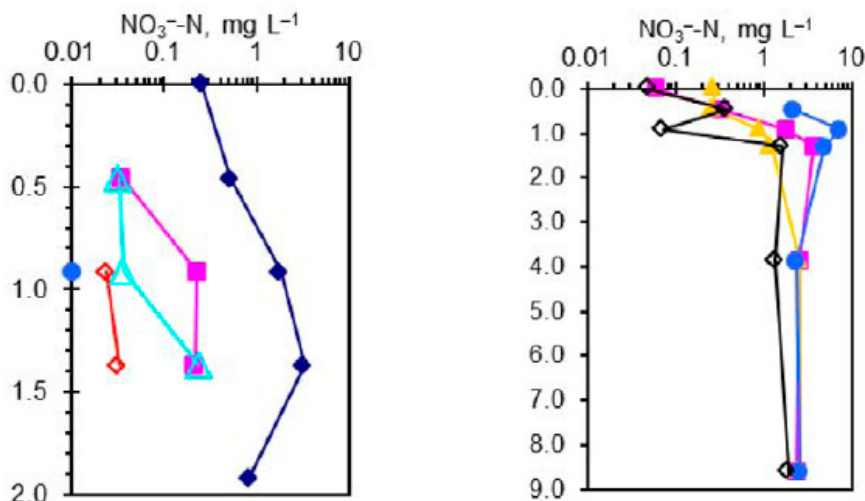


Figure 2. Nitrate concentrations as a function of depth (meters) below soil surfaces of infiltration basins. The left graph shows the profile in a clayey soil and the right graph the profile in a sandy soil. Each color (or line) represents a different storm event (O'Reilly et al., 2012).

Removal of Contaminants by Soil/Media

Natural soils typically have the ability to remove or retain some concentration of dissolved contaminants. The capacity, however, is finite and depends on a host of variables including soil,

water, and contaminant properties. Contact time between the water and soil is also an important variable that impacts overall retention performance. Clark and Pitt (2011) reviewed the following six primary soil properties that affect contaminant retention:

1. Permanent cation exchange capacity,
2. Variable (pH dependent) cation exchange capacity,
3. Point of zero charge (the pH at which the net surface charge is zero),
4. Strong surface complexes,
5. The potential of the soil to adsorb water, and
6. Buffering capacity of the soil (i.e., its ability to resist pH change).

Studies have found that most hydrocarbons are trapped in the first few centimeters of soil in infiltration basins (Barraud et al., 1999; Dierkes and Geiger, 1999). The type of hydrocarbon appears to affect the fate; Dierkes and Geiger (1999) found that ‘mineral oil’ type hydrocarbons (MOTHs) were more likely to be captured in soil and degraded than polycyclic aromatic hydrocarbons (PAHs). Mikkelsen et al. (1997) researched soil and groundwater contamination of infiltration sites due to stormwater contaminated with PAHs and found that they readily sorb to soil particles. The authors concluded that these contaminants posed little risk to groundwater contamination. Bardin et al. (2001) studied the performance of various pretreatment facilities just upstream of infiltration basins and found simple sand filters to be ineffective at capturing hydrocarbons. LeFevre et al. (2012a, 2012b) found that rain gardens are effective in retaining naphthalene and that naphthalene is biodegraded in rain gardens. The studies concluded that rooted vegetation in the soil increased biodegradation rates and suggested that rain gardens are an effective means of promoting biodegradation of naphthalene and TPHs.

Hathorn and Yonge (1995) performed laboratory column studies and field studies on metal retention by soils from infiltrating stormwater. The authors concluded that cation exchange capacity (CEC) and the presence of silts and clays are indicators of a soil’s ability to retain metals. In order to insure hydraulic capacity, upper limits on silt and clay composition were recommended to be 20% and 10%, respectively. It was also concluded that organic matter is largely responsible for removal of copper and zinc and cation exchange is primarily responsible for the retention of cadmium and lead. The authors suggested that organic carbon content exceed 0.3% to provide metal retention but not exceed 1.5%. With organic carbon content higher than 1.5% the hydraulic capacity (i.e., permeability) of the soil could be significantly reduced. By reviewing literature, the authors found that under low pH conditions, lead, cadmium, and copper can leach into water. It was also noted that dissolved organic matter could increase the mobility of metals by forming metal complexes. Finally, the authors observed that the organics leached from soil, the metals removed, and the hydraulics of the infiltration system can change significantly within five runoff events.

Hong et al. (2006) examined the fate and biodegradation potential of oils and greases (dissolved and particulate-associated naphthalene, dissolved toluene, and dissolved motor oil hydrocarbons) within infiltration systems. Based upon the work of Hsieh and Davis (2005), which found that the majority of oils and greases were trapped (but not degraded) in a top mulch layer in a column study, Hong et al. (2006) created a reactor in which a 3 cm deep mulch layer

was fed synthetic stormwater containing, among other contaminants, naphthalene, toluene, motor oil, and particulate associated naphthalene. Mulch, having high lignin content, has a strong affinity for nonionic organic compounds and will retain hydrocarbons. Filtration may also be a significant removal process because 74% to 90% of hydrocarbons in urban runoff are associated with particulate matter. For biodegradation to occur, the mulch layer must support a large enough population of hydrocarbon degrading microbes and allow for a long enough contact time.

Naphthalene was removed from the stormwater at approximately 90%, toluene and motor oil removal was 80%, and particulate associated naphthalene removal was 97%. By observing the decrease in concentrations of contaminants in the mulch layer and the increase of the microbial population after the contaminant was captured, it was determined that biodegradation was occurring in the mulch.

Mikkelsen et al. (1997) investigated the contaminant concentrations of several contaminants in the soil of an infiltration system in Switzerland. Soil characteristics and contaminant concentrations were determined at two sites and calcareous gravel deposits dominated soil conditions at both sites. One site (Site A) received runoff from a watershed that included agricultural, residential, and light industrial land uses. The road near the test section had an average traffic density of 37,000 vehicles per day. The second site (Site B) was located near a city with heavy traffic and a waste incineration plant. Results of soil properties and contaminant concentrations at each site are shown in Figure 3.

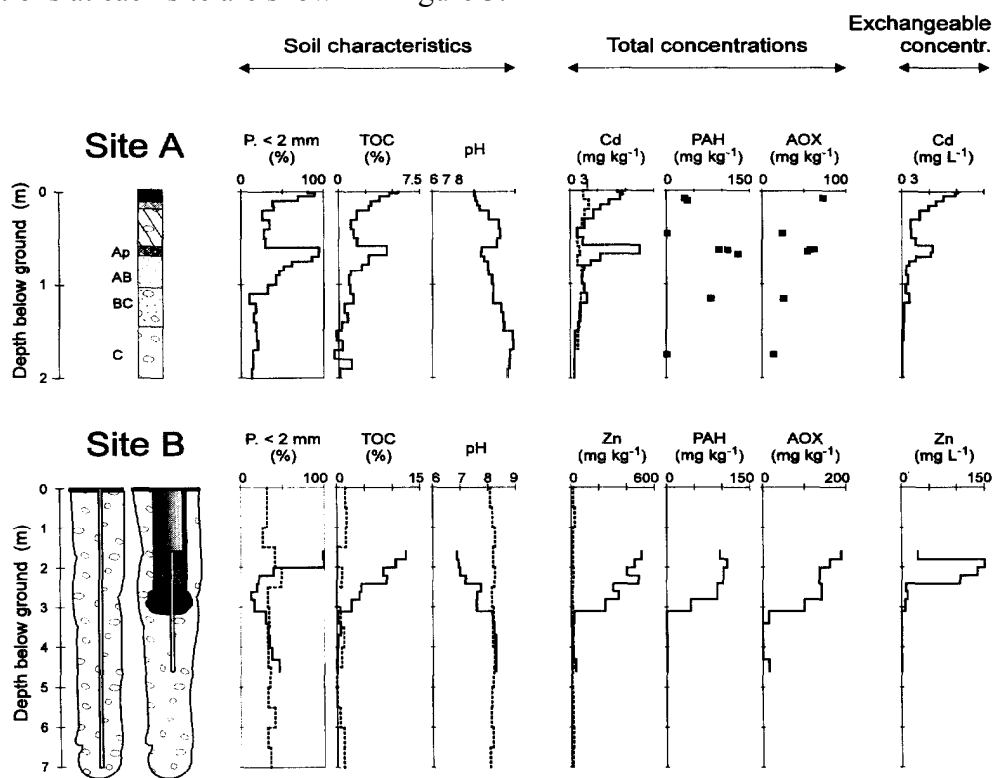


Figure 3. Vertical profiles of soil properties and contaminant concentrations (Mikkelsen et al., 1997).

It was concluded that the solids deposited by the runoff were a source of contaminants but also were capable of some contaminant retention through sorption. A topsoil layer was found to

contain high concentrations of contaminants, but concentrations decreased rapidly with increasing depth. Thus the authors suggest groundwater contamination is not a threat for the foreseeable future. Also, contaminants that do not sorb to soil solids (e.g., salts) may have passed through the media to the groundwater. The results are dependent on the site geology and should not be assumed to hold true in other areas.

Bucheli et al. (1998) investigated pesticides in rainwater, roof runoff, and artificially infiltrated runoff. Pesticide concentrations in infiltrating water at different depths and at different infiltration rates were found to be very similar to those in the runoff. Figure 4 shows this trend and the data suggest very quick infiltration of runoff and that pesticides were not retained by the soil media. As defined in the legend, the black dots indicate roof runoff samples and the lines are data from three different samplers. If not retained by the soil, these contaminants could potentially contaminant groundwater supplies.

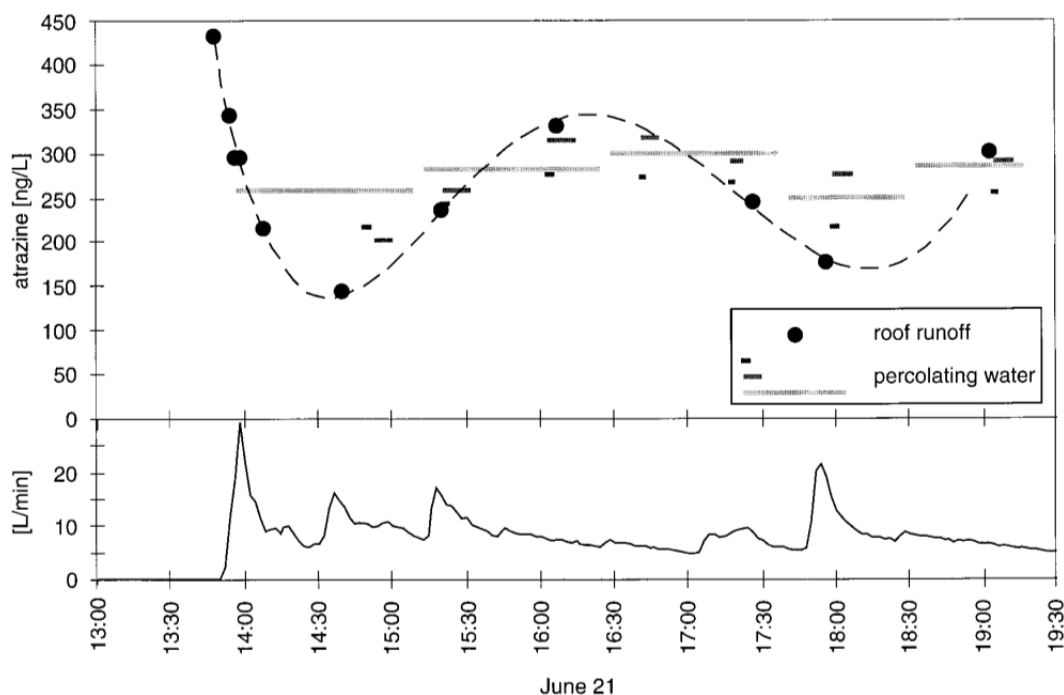


Figure 4. Atrazine concentrations in roof runoff and infiltrated water (upper graph) and runoff flow rate (lower graph) as a function of time (Bucheli et al., 1998).

Legret et al. (1999) investigated the infiltration of stormwater containing copper, cadmium, lead, and zinc into a porous pavement and underlying soil. Laboratory studies and mathematical modeling were conducted with concurrent field verification at the site (in France). The concentrations in rainwater for lead, copper, cadmium, and zinc were 28 to 50 $\mu\text{g/L}$, 17 to 24 $\mu\text{g/L}$, 0.4 to 0.8 $\mu\text{g/L}$, and 250 to 370 $\mu\text{g/L}$, respectively. In general, results from the model simulations concluded that most metals were retained in the upper 30 cm of soil with cadmium migration extending beyond 30 cm (to 50 cm or more). The increase in lead, copper, and zinc in the soil appears slight after 50 years and remains well below regulation threshold values.

Dierkes and Geiger (1999) investigated the concentrations of zinc, copper, cadmium, polycyclic aromatic hydrocarbons, and mineral oil-type hydrocarbons along the side of five

major highways near Essen, Germany. Soil cores were taken and the soil was analyzed at depths of 0 to 5 cm, 5 to 10 cm, and 10 to 30 cm. They found that contaminant concentrations in the soil were a function of traffic density and the length of time the soil had been infiltrating runoff. Highest concentrations were found in the upper 5 cm of soil within a distance of 2 meters from the road. Dierkes and Geiger (1999) also found that concentrations of contaminants decreased rapidly with depth. Between 10 and 30 cm, in most cases, only 7% to 25% of the metal concentrations found in the upper 5 cm were detected. The decrease in metal concentration with depth was most pronounced for lead and copper and weakest for cadmium. At a distance of 10 m from the road, the concentrations of copper decreased to 7% of that found close to the road. For lead, zinc, and cadmium the decreases were 30%, 30%, and 45%, respectively. The results of this portion of the study are summarized in Table 2. Although some contaminants were detected in the groundwater, concentrations were low and the impact on groundwater was deemed minimal. For example, zinc and copper were detected in the groundwater but concentrations did not exceed German and European drinking water standards. It was suggested that a minimum of 40 cm of unsaturated soil be in place to protect groundwater. The mobility of these metals once deposited, however, is unknown (Perez et al., 2008).

Table 2. Concentrations of contaminants at five sites as a function of leachate sampling depth and distance from road (Dierkes and Gieger, 1999).

Highway	Depth	Dis- tance	Pb	Zn	Cu	Cd	PAH	MOTH
	[cm]	[m]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
A 2	0-5	0.5	239	527	413	3.9	6.7	150
	5-10	0.5	202	361	78	3.5	11.3	110
	10-30	0.5	34	99	31	2.7	5.3	57
	0-5	0.3	213	398	121	3.4	16.6	190
	0-5	2	220	336	95	3.0	9.4	74
	0.5	5	141	231	42	2.0	9.4	62
	0-5	10	65	155	27	1.8	2.1	36
A 3	0-5	2	81	174	25	2.0	5.3	200
	5-10	2	69	141	20	1.9	7.0	73
	10-30	2	67	114	11	1.1	5.0	23
A 31	0-5	0.75	276	759	268	4.3	< 2.1	28
	5-10	0.75	130	303	69	2.6	< 2.1	23
	10-30	0.75	54	112	24	2.5	< 1.6	12
A 42	0-5	2	290	1580	167	5.6	23.0	510
	5-10	2	348	1630	155	8.5	16.9	220
	10-30	2	27	138	23	3.1	< 1.6	60
B 224	0-5	0.75	71	187	40	2.2	2.5	160
	5-10	0.75	53	120	42	2.5	< 1.9	25
	10-30	0.75	18	69	24	-	< 1.7	21

To characterize the concentrations of contaminants in the runoff water Dierkes and Geiger (1999) sampled runoff water at three of the sites and a detention pond (additional site, A43). Results of the chemical analysis of the runoff water are given in Table 3. Samples of the water were used in laboratory tests on lysimeters of soil collected from the field sites. The sampled

water was infiltrated into the lysimeters and resulting leachate collected over a six-month period. Results of the chemical analysis of the runoff water and the leachate are summarized in Table 4.

The authors concluded that cadmium exhibited the most significant downward mobility but that breakthrough of all metals (i.e., contamination of groundwater) is not expected in the near future. There is a limitation on the amount of contaminants the soil can retain, however, and at some point in the future soil capacity will be exhausted and the soil will have to be removed. PAH's, which biodegrade slowly, accumulated in the upper 10 cm of the soil whereas MOTH's decreased more rapidly with depth due to faster degradation.

Table 3. Runoff quality as found by Dierkes and Gieger (1999).

	Total metals				Dissolved metals			
	Zn (mg/l)	Cu (µg/l)	Pb (µg/l)	Cd (µg/l)	Zn (mg/l)	Cu (µg/l)	Pb (µg/l)	Cd (µg/l)
A 43	0.8-3.0	80-130	10-20	0.8-3.6	0.3-1.3	17-56	n.d.-10	n.d.-0.7
A 31	-	40-150	4-60	0.5-1.0	-	20-80	n.d.	n.d.-0.6
A 42	0.7-41.0	60-70	10-40	1.7-3.3	0.2-23.1	30-60	n.d.	n.d.-2.4
B 224	0.2-0.8	60-160	n.d.-4	0.7-7.6	0.1-0.6	20-50	n.d.	n.d.-1.8

n.d. = not detectable

Table 4. Mean concentrations of source water (i.e., runoff) and effluent from soil samples (Dierkes and Gieger, 1999).

	runoff	B 224	A 2	A 3	A 31	A 42
pH	7.3	7.7	7.4	7.5	7.6	7.6
Pb [µg/l]	17	< 5	< 5	< 5	11	8
Zn [µg/l]	1250	44	101	69	274	107
Cu [µg/l]	140	31	50	38	40	50
Cd [µg/l]	1.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4

Barraud et al. (1999) investigated the effectiveness of two different infiltration chambers and the potential impact on soil and groundwater. One infiltration chamber was two years old and the other was 30 years old. Both received similar qualities of runoff and the bottoms of both structures were 40 cm above the water table. Both soil solids and groundwater samples were analyzed for various contaminants. Table 5 shows the quality of runoff water that entered the two-year old infiltration chamber (i.e., soakway) and the groundwater quality below the chamber during dry and rainfall conditions.

Perforated PVC pipe 50 cm high and 100 mm wide was filled with fine sand and installed into the bottom of each chamber. The mass of contaminants that entered each chamber was estimated by multiplying contaminant concentrations by runoff volumes. After ten months the mass of contaminants retained by the sand cores were analyzed. Results for the new and old chambers are provided in Table 6 and Table 7, respectively.

For some contaminants, the mass of contaminant input into the chamber was less than that retained. Possible explanations provided by the authors include variable concentrations in runoff that were not fully captured by the sampling method, samples taken were not representative of the runoff (e.g., floating mineral oils not present at sampler intake), or uncontrolled discharges into the chambers.

Table 5. Runoff and groundwater quality at 2-year-old infiltration chamber (Barraud et al., 1999).

	Runoff-water at soakway entry (01/10/96)	Groundwater under dry weather conditions (mean value)	Groundwater during the rainfall downstream from newer soakway	
			1.15 pm	3.20 pm
Conductivity ($\mu\text{S}/\text{cm}$)	54	675	179	123
pH	7	7.4	7.4	8.2
Nitrates NO ₃ (mg/l)	3	59	13	4
TKN (mg/l)	1.2	<1	1.2	1.4
Zn ($\mu\text{g}/\text{l}$)	5700	0 to 8	90	50
Pb ($\mu\text{g}/\text{l}$)	45	0 to 6	8	13
Cd ($\mu\text{g}/\text{l}$)	<5	<5	<5	<5
COD (mg/l)	63	0	42	27
TOC (mg/l)	8.7	0.9	21.2	3.5

Table 6. Contaminant loads and retention in 2-year-old infiltration chamber (Barraud et al. 1999).

element	concentration in sand-cores (mg/kg)			trapped mass (g)	input mass (g)	% retention
	0/5 cm	5/10 cm	mean			
Zn	857	917	887	70	80-130	54-88
Pb	197	212	204.5	16	10-16.3	98- ?
Cd	2.2	2.5	2.35	0.18	<	?
Aromatic hydrocarbons	0.29	0.1	0.19	0.02	<	?
Mineral oils	1290	1600	1445	113	10	?
					< : not calculable (concentration below the threshold level of detection)	? : not calculable

The authors concluded that metal and hydrocarbon concentrations were very high in the first few centimeters of soil but decreased rapidly with depth. Even though metal and hydrocarbon concentrations decreased rapidly with depth into the soil, groundwater contamination after extended time periods is possible because all soils have a finite capacity to retain contaminants. As the total contaminant load entering the soil increases over time, soil capacity near the surface will become exhausted and contaminant transport will continue deeper below the surface. As this process continues, the layer of soil that has become exhausted with respect to contaminant retention will increase in thickness, which will allow contaminants to travel farther below the

surface. Eventually, contaminants will travel all the way to the groundwater table but, the authors note, the concentrations of contaminants could remain lower than Dutch standards. The impact on groundwater was classified as “low” although metal contamination in the groundwater was detected. The impact could be reduced by providing more than 40 cm of separation between the bottom of the infiltration chambers and the water table.

Table 7. Contaminant loads and retention in 30-year-old infiltration chamber (Barraud et al., 1999).

element	concentration in sand-cores (mg/kg) 0/10 cm	trapped mass (g)	input mass (g)	% retention
Zn	143	118	380	31
Pb	82	67	46	?
Cd	0.9	0.7	2.37	29.5
Aromatic hydrocarbons	0	0	<	?
Mineral oils	866	710	55	?

< : not calculable (concentration below the threshold level of detection) ? : not calculable

The performance of a sand trap, pre-settling basin, infiltration basins, and oil separator system with regards to contaminant retention was investigated by Bardin et al. (2001) in a heavy industrial area in France. Although not defined in the paper, a sand trap is a pre-treatment device designed to remove larger solids (i.e., sand) typically by sedimentation and/or filtration. The pre-settling basin provides additional pre-treatment of stormwater runoff upstream of the infiltration basin by allowing additional solids to settle. The intent of pre-treatment (i.e., the sand trap and pre-settling basin) is to remove larger solids and prolong the life (and maintenance intervals) of the infiltration basin. The system had been in operation as a stormwater infiltration device since 1975 and had undergone some modifications since it was first constructed. Since 1988, however, it had consisted of two sand traps, a settling basin, an infiltration basin, and an oil separator. At the time of the study, the land use in the 380 ha watershed was 77% industrial, 20% agricultural, and 3% residential. The infiltration basin had a volume of 80,000 m³ and an area of over 2 hectares. Total event mean concentrations for the pre-settling basin influent and effluent along with the infiltration basin influent are given in Table 8. Results from the analysis of solids in the sand trap, settling basin, and oil separator are given in Table 9.

Based upon full results (Bardin et al., 2001), the authors concluded that the sediment in the infiltration basin tends to sorb contaminants and increase the removal efficiency of contaminants from the runoff and that removal is more of a biological and/or chemical process than it is physical filtration. The authors also concluded that the gravel and geotextile have a significant filtration effect but could not make any conclusions with respect to the quantity of contaminants that passed through to the underlying groundwater. It was also concluded that metal retention was not very high (25% to 60%, depending on the metal).

Indiati and Diana (2004) investigated the capacity of acidic soils to sorb phosphorus. Sorption capacities were found to range from 19.1 mmol P/kg soil to 284.3 mmol P/kg soil, with

the degree of phosphorus saturation being time dependent. Time to full phosphorus saturation ranged from 10 to 100 days. The phosphorus sorption capacity was determined to have a strong correlation with the sum of aluminum and iron oxides/hydroxides (Figure 5).

Table 8. Event mean concentrations for the pre-settling basin inlet (I), pre-settling basin outlet (SB), and infiltration inlet (IB) (Bardin et al., 2001).

	Event no. 1			Event no. 2			Event no. 3			Event no. 4			Event no. 5			Event no. 6			Event no. 7		
	I	SB	IB	I	SB	IB	I	SB	IB	I	SB	IB	I	SB	IB	I	SB	IB	I	SB	IB
SS mg/l	39	21	21	64	57	71	64	47	38	51	23	21	128	35	50	37	15	13	135	43	/
Zn µg/l	177	<5	162	327	329	294	262	282	256	267	266	209	681	433	451	303	266	265	126	160	/
Cu µg/l	16	11	13	36	27	29	21	15	14	15	13	12	49	23	23	9	9	10	7	8	/
Pb µg/l	17	13	11	34	17	0.0	24	14	12	<5	<5	65	90	36	42	9	<5	<5	<5	5	/
COD mg/l	41	22	24	28	43	13	101	52	36	43	40	42	126	63	63	47	45	41	/	28	/
oils µg/l	294	664	692	53	262	276	<50	63	<50	<50	<50	<50	1497	1060	858	597	1413	1257	92	92	/

I: settling basin inlet; /: not analyzed; SB: settling basin outlet (separator inlet); IB: infiltration basin inlet (separator outlet)

Table 9. Concentrations of sorbed contaminants on solids in sand traps, settling basin, and oil separator (Bardin et al., 2001).

		T200 sand-trap	C1200 sand-trap	Settling basin		Oil separator
		13/10/95	13/10/95	23/11/94	13/10/95	23/02/95
Operation period of the system		6 months	6 months	12 months	11 months	4 months
Zn	(g/t dry matter)	288	224	1148	1836	168
Cu	(g/t dry matter)	39	219.5	188	230	237
Ni	(g/t dry matter)	111.6	14.2	25	42.8	27.9
Cr	(g/t dry matter)	96	41.6	57	88	61.9
Cd	(g/t dry matter)	1.9	1.95	5	5.6	5.83
Pb	(g/t dry matter)	38.5	120.8	286	338.5	342
Hg	(g/t dry matter)	0.083	0.1	/	0.45	/
Mineral oils	(g/t dry matter)	624	768	10000	6583	37660

An infiltration basin in France that had been operating for 14 years was investigated by Dechesne et al. (2004). The 2,616 m³ basin infiltrated water from a 7 hectare truck parking lot and existed above highly permeable soils of calcareous sand, pebbles, and rocks. The water table was 4 meters below the basin and hydraulic conductivity values in the area ranged from 10⁻⁴ to 10⁻² m/s. At ten locations, soil samples were taken at the surface, at 30 to 40 cm, 60 to 70 cm, and 100 to 110 cm below the surface and analyzed for a host of contaminants. Data for all ten sampling locations and all four depths are shown in Table 10.

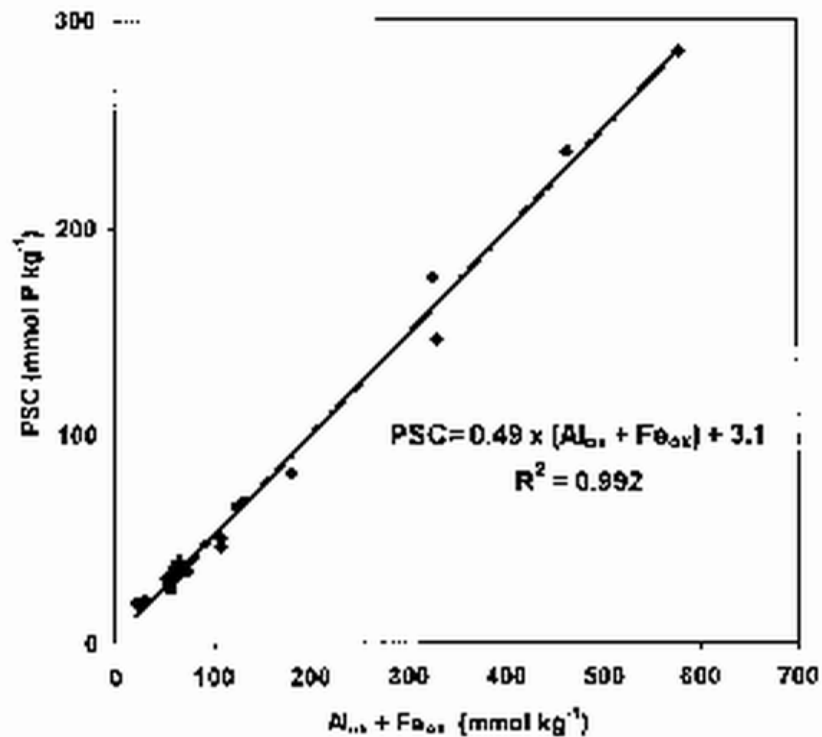


Figure 5. Phosphorus sorption capacity as a function of the sum of extracted aluminum and iron oxides/hydroxides (Indiati and Diana, 2004).

The authors concluded that contaminant concentrations decreased rapidly with depth while pH, mineral content, and grain size increased. Metals were concentrated in the top 30 cm of soil except for zinc, which exhibited more mobility. Also, hydrocarbon contamination was found to be deeper than most metals, although no hypothesis explaining this finding was offered. Finally, the highest hydrocarbon concentrations were found near the influent location but the highest metal concentrations were found at the low point of the basin. The authors also proposed a methodology for reducing the number of required samples while still adequately characterizing the soil.

In a study previously described, Datry et al. (2004) also investigated sediment samples. Sediment samples were withdrawn from six monitoring wells installed within an infiltration basin that had been in operation for more than 30 years. Organic sediment contaminated with hydrocarbons and metals had accumulated and partially clogged the basin. The sediment samples revealed that nitrogen was mostly in organic form (not ammonium) and that zinc, lead, and copper comprised 95% of the metals. The concentrations of metals, nutrients, and hydrocarbons dropped significantly at a depth of 0.5 m below the bottom of the basin and concentrations in the sediment below the groundwater table were not statistically higher than sediment samples from a control site.

Zimmerman et al. (2005) used the results of batch and column studies performed to model soil metal (zinc, copper, lead) concentration profiles resulting from the infiltration of contaminated stormwater. Runoff metal concentrations used in the computer model were obtained from a literature review and were chosen to represent runoff from four different roof types (e.g., green roof, roof without zinc, roof with zinc gutters/sheets, copper sheets). Soil

properties used in the model were chosen to represent a low permeable soil, high permeable sand, and two types of trench backfill (one sand and one gravel). The soils differed in the content of organic carbon, clay, carbonate, and cation exchange capacity. Breakthrough curves of a laboratory column experiment were modeled and compared to experimental results (Figure 6).

Table 10. Soil contaminant concentrations under an infiltration basin in France. Samples taken at ten points and four depths: A (surface), B (30 to 40 cm), C (60 to 70 cm), D (100 to 110 cm). (Dechesne et al., 2004).

	pH	CEC meq/kg	Mineral matter %	TOC %	TN %	TP %	Cd mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg	Hg mg/kg	As mg/kg	THC mg/kg
1A	7.9	98.8	86	10.78	0.33	0.27	4.00	60.94	142.4	29.97	222.3	1414	0.11	7.99	1565
1B	9.3	11.0	99.1	1.07	0.02	0.07	0.51	13.69	7.61	7.61	8.62	65.9	<0.1	3.04	29.75
1C	9.3	9.0	99.2	0.73	0.02	0.07	0.51	14.68	8.10	8.10	7.08	56.2	<0.1	3.04	22.48
1D	9.4	12.8	99.2	1.08	0.01	0.07	0.49	11.37	6.43	7.42	4.94	38.1	<0.1	2.47	13.29
2A	8.1	76.5	87.6	10.67	0.24	0.32	3.53	49.42	110.4	23.20	147.8	1145	<0.1	6.56	1745
2B	8.9	16.0	98.7	1.3	0.03	0.09	0.94	18.24	14.03	10.29	28.07	182.0	<0.1	4.21	138.1
2C	9.3	9.0	99.3	1.02	0.02	0.09	0.47	14.46	7.47	7.47	6.53	71.9	<0.1	3.27	18.87
2D	9.3	9.6	99.3	0.89	0.02	0.07	0.45	13.59	7.25	9.06	4.98	66.1	<0.1	3.62	9.97
3A	9.0	25.8	97.8	2.45	0.04	0.09	0.97	22.74	24.68	11.61	67.73	255.5	<0.1	4.84	151.1
3B	9.4	6.8	99.4	1.05	0.03	0.07	0.50	10.53	2.51	6.52	5.01	19.0	<0.1	3.01	<10
3C	9.4	6.6	99	1.05	0.01	0.05	0.49	12.76	3.93	7.36	4.91	23.6	<0.1	3.44	<10
3D	9.5	7.9	99.2	1.11	0.01	0.05	0.53	20.82	3.20	9.07	5.34	21.9	<0.1	4.27	<10
4A	8.2	83.9	86.7	11.13	0.25	0.25	3.55	56.33	121.8	27.40	176.6	1269	0.107	8.12	538
4B	9.0	18.6	98.2	1.8	0.03	0.07	1.04	23.85	20.74	11.41	52.89	247.8	<0.1	4.15	72.82
4C	9.3	13.5	98.9	1.24	0.02	0.07	0.51	19.54	13.37	11.83	10.29	85.9	<0.1	4.11	<10
4D	9.4	13.2	98.9	1.11	0.02	0.07	0.52	19.22	10.91	12.99	6.75	52.0	<0.1	3.64	<10
5A	8.7	37.6	95.7	2.78	0.09	0.11	1.54	29.32	38.06	14.40	84.87	458	0.1	4.63	95.17
5B	8.9	28.0	97.3	1.72	0.04	0.09	1.01	29.91	29.40	14.19	83.13	371.0	0.1	4.06	151.5
5C	9.3	11.1	98.9	0.74	0.02	0.05	0.51	13.24	7.64	7.64	17.82	73.3	0.1	3.56	63.26
5D	9.4	27.5	98.5	0.74	0.02	0.11	0.51	22.87	14.23	19.31	7.11	54.4	0.1	5.59	<10
6A	7.9	75.8	91.5	6.26	0.19	0.18	2.45	38.17	75.36	21.53	111.1	837	<0.1	8.81	811
6B	9.2	15.9	99.1	0.59	0.02	0.07	0.46	16.59	5.99	10.14	4.61	27.6	<0.1	5.53	<10
6C	9.5	7.4	99.3	0.5	0.01	0.07	0.46	16.03	5.04	8.70	4.58	22.4	<0.1	5.04	<10
6D	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7A	7.8	129.3	79	14.8	0.41	0.34	4.75	66.92	175.6	33.22	223.1	1827	0.1	12.34	1054
7B	9.2	7.6	99.3	0.46	0.01	0.05	0.48	21.59	7.68	9.60	4.80	45.6	<0.1	4.80	<10
7C	9.2	7.6	99.3	0.69	0.01	0.07	0.46	19.49	8.35	9.75	4.64	41.8	<0.1	5.11	<10
7D	9.2	11.0	99.2	0.3	0.02	0.07	0.48	17.82	8.67	9.63	4.82	55.4	<0.1	5.30	<10
8A	8.1	83.8	89.3	7.61	0.23	0.23	3.67	50.43	97.20	24.30	155.9	1151	<0.1	9.17	346.5
8B	8.8	15.4	98.6	0.84	0.03	0.09	0.96	22.03	17.72	10.54	28.73	197.3	<0.1	4.79	105.7
8C	9.2	8.7	99.2	0.54	0.02	0.07	0.48	15.43	9.16	8.68	8.20	89.7	<0.1	3.86	36.68
8D	9.3	9.5	99.2	0.43	0.02	0.07	0.49	14.62	9.26	8.77	6.33	75.0	<0.1	3.90	21.78
9A	8.0	103.8	85.2	9.97	0.31	0.27	4.11	66.64	152.0	31.04	224.6	1566	0.1	11.41	399.2
9B	8.8	12.8	98.8	0.65	0.03	0.07	0.93	17.28	14.01	8.87	19.14	142.0	<0.1	4.67	30.68
9C	9.1	8.7	99.3	0.35	0.02	0.07	0.52	28.32	9.97	9.44	8.92	89.7	<0.1	3.67	28.63
9D	9.2	12.8	99.1	0.36	0.02	0.07	0.48	21.28	13.54	12.09	5.80	83.2	<0.1	8.71	<10
10A	7.9	72.8	90.5	6.37	0.2	0.18	2.96	48.84	88.81	22.70	143.6	1066	<0.1	8.88	447.0
10B	8.9	15.5	98.7	0.7	0.03	0.07	0.52	21.78	14.52	10.37	19.70	156.1	<0.1	5.19	42.41
10C	9.2	9.7	99.2	0.48	0.02	0.07	0.52	14.95	9.28	9.28	7.73	67.0	<0.1	3.09	19.34
10D	9.3	8.7	99.1	0.37	0.02	0.05	0.48	17.43	8.71	9.20	4.84	49.4	<0.1	3.39	<10
Reference ^a	8.2	–	–	–	–	–	<0.5	35	10	13.5	6.5	51	<0.1	6.7	–
c _v ^b	2.5%	–	–	–	–	–	20.28%	24.14%	31.44%	–	19.11%	3.38%	–	–	–
DSt ^c	–	–	–	–	–	–	0.5	43	19	15	57	68	0.2	18	50
DSi ^d	–	–	–	–	–	–	7	162	100	90	354	347	7	34	5000

^a (Winiarski et al., 2001).

^b c_v stands for coefficient of variation (calculated from Bedell et al., 2001).

^c DSt stands for Dutch Standards target values (NMHSPE, 2000).

^d DSi stands for Dutch Standards intervention values (NMHSPE, 2000).

Next, Zimmerman et al. (2005) modeled the infiltration of contaminated stormwater into the soil beneath swales (over a 50 year time span) and developed the soil metal concentration profiles beneath the swales. To prevent soil concentrations from exceeding German critical values, the authors recommended replacing the first 20 cm of soil after two or three years for highly adsorbing soil and after three or four years for low-adsorbing material, depending on the

metal. Also, according to the authors, metals may migrate down to the water table over several years or decades.

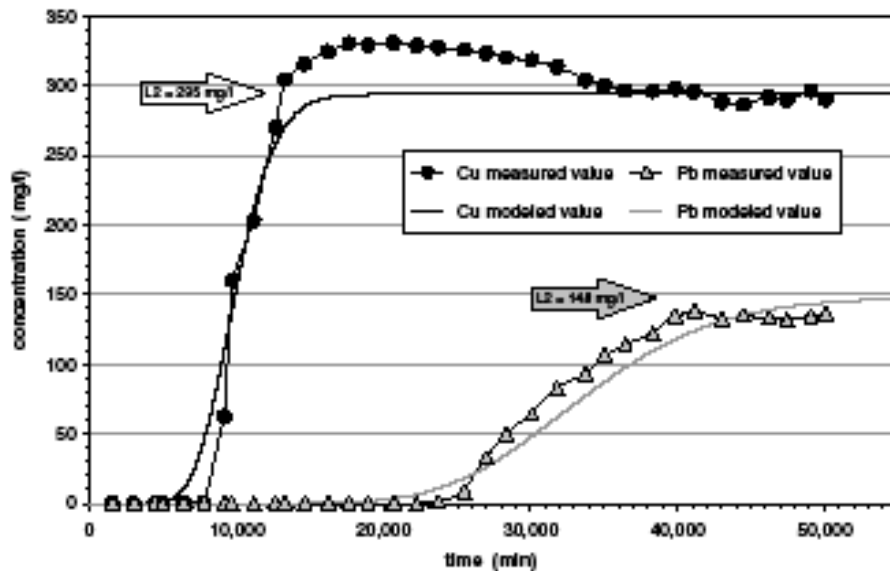


Figure 6. Comparison of model and experimental breakthrough curves (Zimmerman et al., 2005).

Winiarski et al. (2006) investigated the effect of about 20 years of stormwater infiltration on the receiving soil of an infiltration basin. The basin had a surface area of over 7,400 m², a volume of over 30,800 m³, and a depth of about 5.5 m. Soils samples were taken so as to obtain a vertical profile of soil characteristics and contaminant concentrations at three different locations: 1) near the basin inlet, 2) in the middle of the basin, and 3) at the southern end of the basin. Results are shown in Figure 7 to Figure 12.

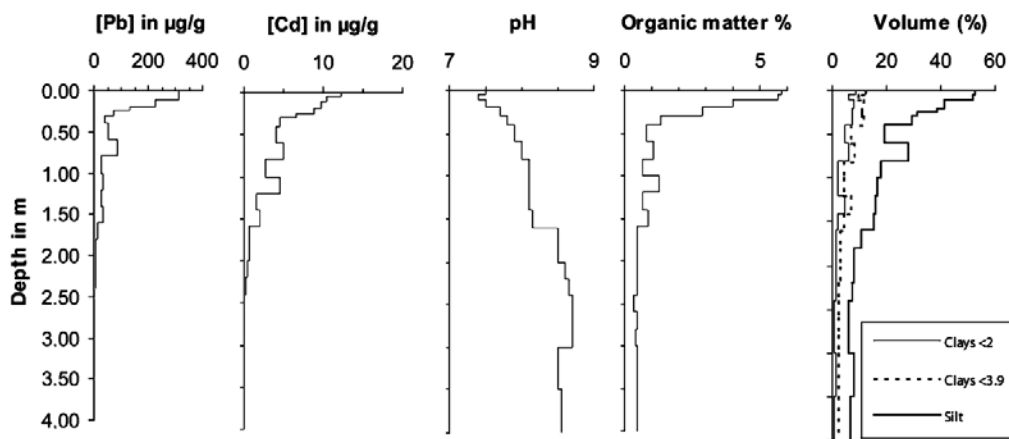


Figure 7. Concentrations of metals, pH, organics, clays and silts at point 1 (Winiarski et al., 2006).

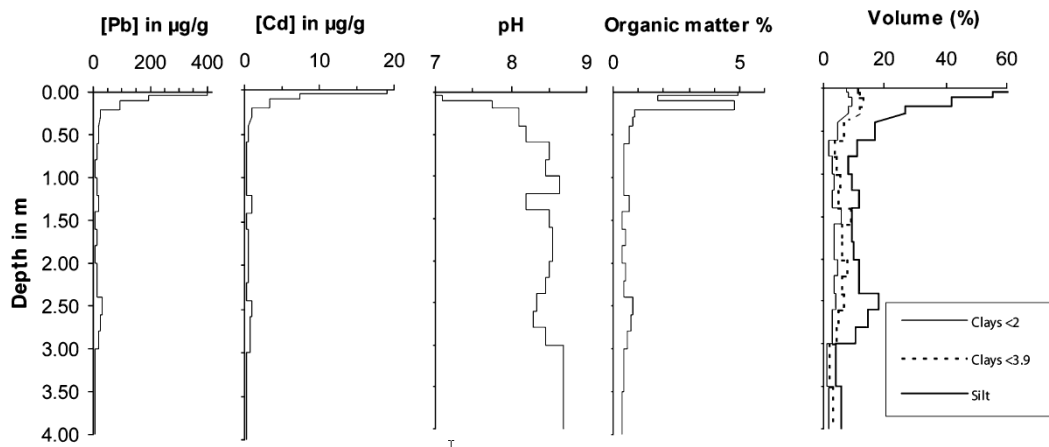


Figure 8. Concentrations of metals, pH, organics, clays and silts at point 2 (Winiarski et al., 2006).

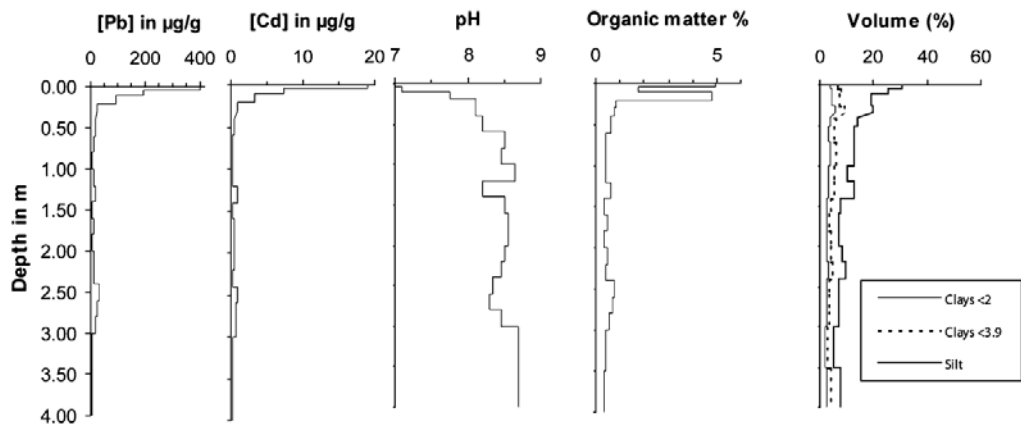


Figure 9. Concentrations of metals, pH, organics, clays and silts at point 3 (Winiarski et al., 2006).

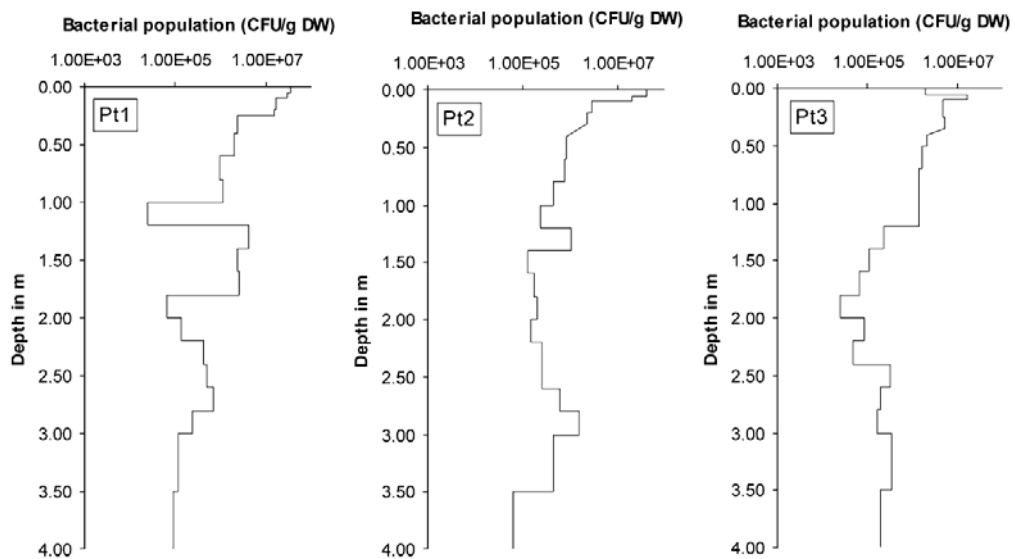


Figure 10. Density of viable heterotrophic bacteria along vertical profiles at points 1, 2, and 3 (Winiarski et al., 2006).

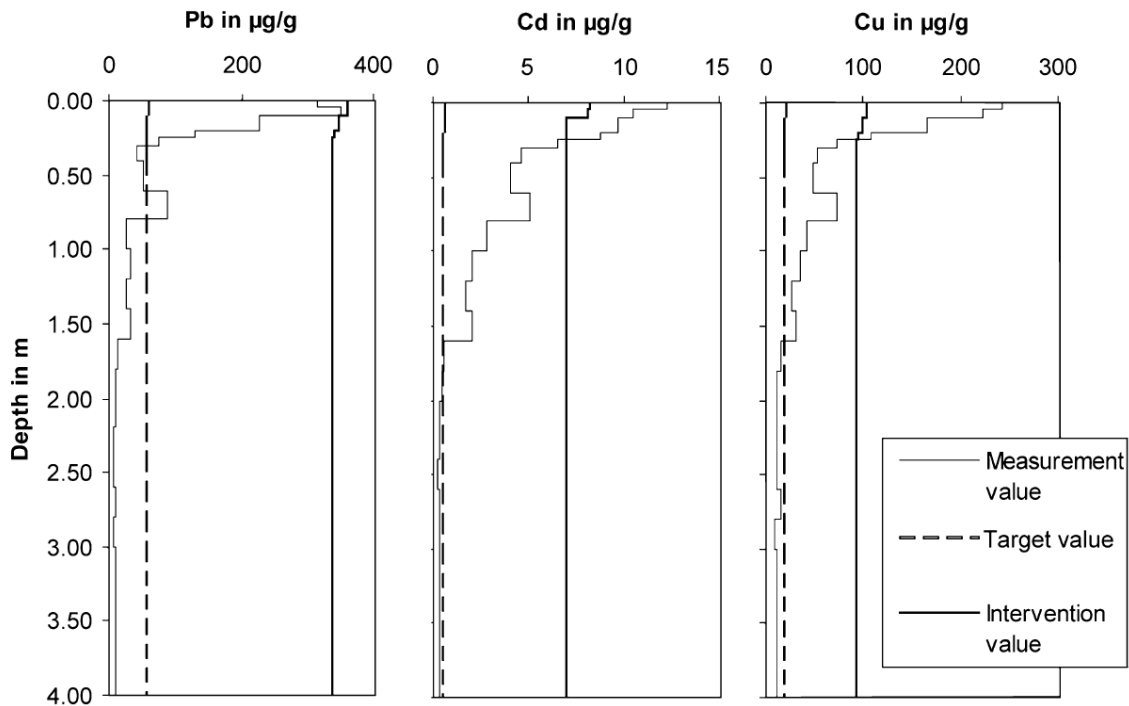


Figure 11. Metal concentrations at point 1 (Winiarski et al., 2006).

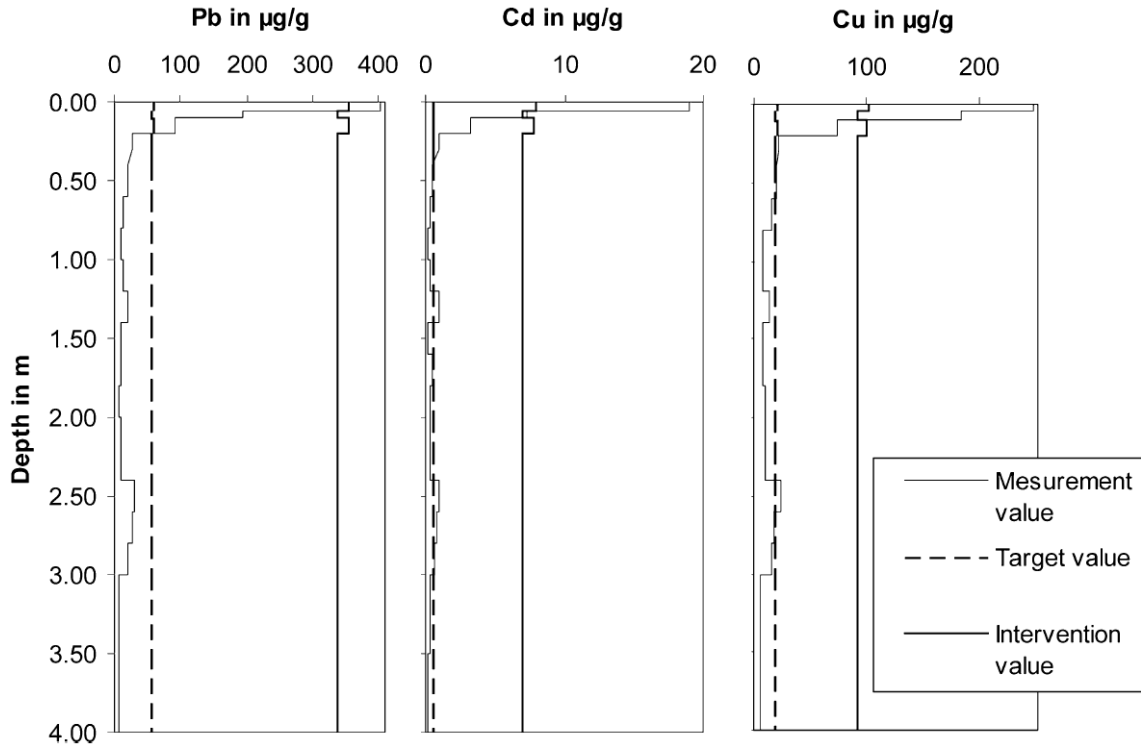


Figure 12. Metal concentrations at point 2 (Winiarski et al., 2006).

The concentrations of metals in the upper soil layers were much higher than control soils. Possible reasons include the presence of carbonates that can retain metals through cation exchange, chemical precipitation with carbonates, or the filtration of particles to which metals are sorbed. The soils also exhibited low pH in the top 1.5 meters, which could be due to microorganisms and organic matter. The authors speculate that at point 2 there may be preferential flow paths because the soil has a large capacity to retain contaminants and yet contaminant concentrations increase at a depth of 2.4 to 3.0 meters. If so, preferential flow paths could lead to contamination of groundwater. Also, the relatively high contaminant concentrations down to a depth of 1.5 meters indicate that the practice of removing a thin layer of topsoil during maintenance may need to be expanded to include more soil depth.

An investigation of 20-year old infiltration facilities in Tokyo, Japan was conducted by Aryal et al. (2006). Based on the high metal content of road dust and sediment in the inlets to the infiltration facilities, the authors concluded that road dust was a major source of metals to the infiltration facilities. After determining the metal profile in the sediment, it was concluded that there was probably leaching of metals into the underlying soils. The concentration of metals found were not above values that typically are considered to be a serious threat, but the authors stated that the leaching of metals to the underlying soil could have serious ramifications.

Studies that investigated whether or not plants in a bioretention system uptake metals and, if so, to what extent found that less than 3% of retained metals accumulated in plant tissue, while the rest remained in the soil media (Dietz and Clausen, 2006; Sun and Davis, 2007).

Based upon results of column studies, adsorption capacities of soil and mulch were estimated for lead, copper, and zinc (Davis et al., 2001), and breakthrough characteristics of the soil media were observed. Using stormwater/contaminant loading and soil capacity estimates, it was estimated that after 20 years, concentrations of cadmium, lead, and zinc would reach or exceed concentrations permitted by EPA biosolids land application regulations (Davis et al., 2003).

Using batch and column studies, Morgan et al. (2010) investigated the retention of cadmium, copper, and zinc from synthetic stormwater by compost/sand mixtures. At typical stormwater concentrations, a 70% sand/30% compost mixture was estimated to remove over 90% of the influent metals for more than 95 years. The compost, however, released phosphorus over the course of the study and increased the phosphorus concentration of the effluent to values higher than the 0.13 mg/L concentration of the influent. Initially the release of phosphorus was high but the rate dropped with time and reached a steady value of 0.29 mg/L.

A study by Hatt et al. (2011) used synthetic stormwater to investigate breakthrough of metals (Cd, Cu, Pb, Zn) in a series of columns designed to mimic biofiltration systems. In practice, these are vegetated systems in which infiltrating stormwater passes through a soil media and is collected by an underdrain system. Media length was varied from 30 to 70 cm and three different media types were tested, 1) loamy sand (LS), 2) loamy sand mixed with 10% vermiculite and 10% perlite by volume (LSVP), and 3) loamy sand mixed with 10% leaf mulch and 10% compost by volume (LSC). Zinc was the only metal for which breakthrough was observed. Results were used to predict time to zinc breakthrough for two Australian cities (i.e., Melbourne and Brisbane). Breakthrough times for each city were estimated for filter areas of 1%, 2%, 3%, and 5% of the watershed impervious area and filter depths of 30, 50, and 70 cm. Results are shown in Table 11.

Table 11. Estimated time to zinc breakthrough in a bioretention filter (LS = loamy sand, LSVP = loamy sand with 10% vermiculite and 10% perlite, LSC = loamy sand with 10% leaf mulch and 10% compost) in Melbourne (temperate climate, annual rainfall = 648 mm) and Brisbane (sub-tropical climate, annual rainfall = 1149 mm) (Hatt et al., 2011).

Media	Depth (m)	Years to breakthrough							
		Melbourne				Brisbane			
		% of impervious catchment				% of impervious catchment			
		1	2	3	5	1	2	3	5
LS	0.3	4	9	14	23	2	4	6	10
LS	0.5	7	15	23	39	3	7	10	18
LS	0.7	10	21	32	54	5	10	15	25
LSVP	0.3	3	7	10	17	1	3	4	8
LSVP	0.5	5	11	17	29	2	5	8	13
LSVP	0.7	8	16	24	41	3	7	11	19
LSC	0.3	5	11	17	29	2	5	8	13
LSC	0.5	9	19	29	48	4	9	13	22
LSC	0.7	13	27	41	68	6	12	19	31

The authors concluded that if the filter area is at least 2 to 3% of the watershed area, bioretention filters could be designed so that metal capacity is not exhausted before the filter media needs to be replaced due to clogging. Metal concentrations in the media, however, would be higher than governing health limits and thus, media would have to be handled and disposed of properly.

Model Studies and Literature Reviews

Stephenson and Beck (1995) performed a thorough review of literature related to highway stormwater runoff and the potential threat to groundwater. The literature reviewed in the paper generally agreed that contaminants typically found in highway runoff (and urban runoff, due to similar compositions) can be, but may not always be, removed from infiltrating stormwater by the soil media. The potential for removal is higher in areas with thick layers of soil. The paper goes on to review work that investigated the potential threat of highway runoff to groundwater in karst areas. As may be expected, due to more direct flow paths, groundwater in karst areas is much more susceptible to contamination from runoff, particularly where soils may be very thin or nonexistent. Documented cases of groundwater contamination in karst areas are readily available (Stephenson and Beck, 1995). For example, after a heavy rain event in West Virginia, silt and clay from a construction site was washed into a cavernous aquifer and emerged at a spring. This greatly increased the turbidity of the stream and killed more than 150,000 trout during a single storm event. Spills of diesel fuels at the site killed additional fish.

Paschka et al. (1999) investigated the potential effects of anticaking agents, which are used in road salt, on water quality. Based on the results of a 2004 nationwide survey (CTC & Associates, 2004), the standard anti-caking agent used is sodium ferrocyanide ($\text{Na}_4\text{Fe}(\text{CN})_6$), also known as

Yellow Prussiate of Soda (YPS) or, in some cases, its equivalent, ferric ferrocyanide ($\text{Fe}_4(\text{Fe}_3\text{CN}_6)_3$), is also accepted by regulatory agencies. The major contaminant of concern in anticaking agents is cyanide, which may take the form of HCN or CN^- , both of which are toxic (Paschka et al., 1999). The fate of these cyanide species have not been studied in depth. HCN, for example, is usually assumed to evaporate quickly because of its volatility, but there is not sufficient data in the literature to confirm this assumption. Of all the studies reviewed in this paper, however, none addressed the issue of groundwater contamination by anticaking agents.

Dietz (2007) wrote a review of studies related to stormwater infiltration systems and also discussed the potential for groundwater contamination. This review stated that, for residential and light commercial developments, the common contaminants (i.e., nutrients, petroleum residue, metals, and possibly pesticides) are usually found in low concentrations and are retained by soil so that groundwater contamination is not a concern. Two exceptions to this statement were pathogens and salts. Fecal coliform, it was stated, is often found in high concentrations and may not be retained well by soil media. Also, salts are highly mobile and can easily travel to shallow groundwater. Some studies reviewed by Deitz (2007) indicate that salt concentrations have been increasing in some waterways in the U.S. and, if this trend continues, salt concentrations will reach concentrations that could damage the health of the river. Dietz concluded that certain sites might not be good choices for infiltration or other LID technologies. Areas with high contaminant loads such as gas stations or recycling centers, for example, may not be good candidates for LID. Also, locations with steep slopes, shallow depth (< 3 feet) to bedrock, or seasonal high water tables also may not be appropriate for LID.

Clark and Pitt (2007) discussed factors that can influence groundwater contamination by infiltration practices as well as proposed a means to evaluate contamination potential. The evaluation method contains the following three steps: 1) Determine concentrations and forms of the contaminants entering and leaving the infiltration device, 2) Determine characteristics of the soil that affect water quality, and 3) Determine required pretreatment actions. The paper also reviews previous articles that address groundwater contamination from the infiltration of stormwater. This review found that typical nitrite and nitrate concentrations (unfiltered median value of 0.60 mg/L at MS4 outfalls) are such that their threat to groundwater contamination is low. Pesticides and other organics, however, may contaminate groundwater in agricultural areas with sandy soils if crops are irrigated. Because salts are not removed by soils, groundwater contamination can occur rapidly as soon as salt loading begins.

Documented pathogen contamination of groundwater due to infiltration practices was also reviewed and discussed by Clark and Pitt (2007). Contamination potential depends on the soil chemical properties and adsorption capability and the ability of the soil to physically strain the pathogens.

Metals, as in other studies, were found to be mostly removed in the soil within the infiltration practice or in the vadose zone below the structure. Metal removal may occur by soil surface association (e.g., adsorption, ion exchange, surface complexation), precipitation, inclusion with other precipitates, diffusion into soil solids, biological action, or filtration of particle-bound metals.

Clark and Pitt (2007) further state that important soil parameters that affect contaminant transport are organic content, microorganism activity in the vadose zone, porosity, and

infiltration capacity. Infiltration capacity, which is the maximum rate at which the soil can infiltrate runoff, is a function of soil properties (e.g., hydraulic conductivity, moisture content, etc.) and the amount of water already infiltrated. The authors present two methods for predicting groundwater contamination potential: a simple method which involves reading a series of three tables, and a more complicated computer model with examples given for each model.

Wolf et al. (2007) used a computer model analysis and a Monte Carlo simulation to determine the impact of leaky sewers and urban drainage systems on the city of Rastatt in southwest Germany with respect to boron and chloride contamination. This study used a chain of models to connect water supply, drainage (including leaky sewers), soil vadose zone, and groundwater systems. Thus, it provides a more holistic approach to subsurface water transport and potential groundwater contamination than studies targeting only one specific component. The first model in the system used input parameters such as climate data, water consumption, and land surface type to calculate runoff flows and contaminant loads to discharge points in the drainage system including the groundwater. The results from the first model were used as input into a second model that estimated the amount of water exfiltration to groundwater. Seventy-four different neighborhoods were incorporated and the total urban water balance for Rastatt was calculated over a year's time. The authors concluded that while the native soil system alone is not sufficient to completely protect urban groundwater from contamination. Based on the results of their study, the authors claim that the urban water cycle can be managed in a sustainable manner. The investigators concluded that the urban drainage system in Rastatt was too small to induce systemic groundwater contamination but that local areas could be contaminated if maintenance was inadequate.

Conclusions from Literature Review

Many advances in the understanding and treatment of stormwater runoff have been realized since the U.S. EPA first published results of the National Urban Runoff Program in 1983 (U.S. EPA 1983). Many of these advances with regard to the impact of infiltrated water on groundwater quality are discussed in this literature review. Although there is no guarantee with regard to stormwater, the research to date indicates the following:

1. A surface-oriented practice, such as a bioinfiltration facility, swale, filter strip, infiltration basin, etc. has the capacity to capture some groundwater contaminants on the soil or infiltration media. These contaminants include dissolved toxic metals and petroleum hydrocarbons. There is evidence that captured petroleum hydrocarbons will be degraded by the bacteria surrounding plant roots. Toxic metals will need to be eventually harvested. The capacity of soil organic compounds to retain toxic metals, however, is substantial, such that hundreds of years are required for saturation to occur.
2. Infiltrated pathogens and suspended solids are generally filtered by the soil or media through which they are infiltrated.
3. Nitrate in urban runoff is typically at fairly low concentrations (median of 0.6 mg/L, Maestre and Pitt, 2005) relative to the concentration of concern for drinking water

(10 mg/L), such that it is unlikely that stormwater could be the cause of high nitrate concentration in drinking water.

4. Sub-surface infiltration systems store water underground and allow the infiltration process to begin beneath the soil surface. This means that the retention of contaminants by soil may not occur. Thus, metals and petroleum hydrocarbons are more likely to enter into groundwater from these infiltration systems. The impact of sub-surface infiltration systems needs further study.

5. Chloride is a contaminant that has no known sinks in natural systems. In addition, Novotny and Stefan found that two-thirds of the chloride that is placed on surfaces remains in the Twin Cities Metropolitan watershed, and does not leave by river flow. This is a long-term contaminant of concern for groundwater pollution in northern climates.

Knowledge Gaps

It is evident that there remain areas in which the understanding of stormwater, its contaminants, and their fate and treatment is limited or non-existent. Further research into these areas, or knowledge gaps, is key to the continued and increased protection of groundwater. Knowledge gaps identified are listed below.

1. When stormwater infiltrates into the soil surface from an infiltration practice, metals and other contaminants in stormwater appear to be retained in the upper 50 cm of soil or practice media. The soil, however, has a finite capacity with regards to retaining contaminants and, at some point, contaminant transport will continue farther into the soil. When will this breakthrough occur, how can it be most cost-effectively modeled, and how can maintenance in these situations be performed in the most cost-effective manner?

2. Sub-surface infiltration systems store water underground and allow the infiltration process to begin beneath the soil surface. What impact does this have on the retention of contaminants by the soil, and how much does this increase the risk of groundwater contamination?

3. How much of a threat does chloride, which is applied to roadways as a de-icing agent in cold climates, pose to surface and groundwaters and, correspondingly, how can that threat be optimally managed?

4. What is the fate of numerous infiltrated hydrocarbons and what are the important variables and processes that affect the ultimate fate of these hydrocarbons?

5. Iron cyanide anti-caking agents are often used with de-icing agents applied to roadways. These anti-caking agents lead to the presence of HCN and CN^- in runoff. The fate of each has not been determined with certainty. For example, HCN is assumed to volatilize upon application but no research has confirmed the accuracy of this assumption. What fraction of HCN volatilizes, how quickly, and what are the important variables that affect the fate of HCN? What is the fate of CN^- and what is its impact on water quality?

Materials and Methods

This section provides information on the criteria used in selecting the sites for study of contaminant migration beneath stormwater infiltration practices within the Twin Cities Metro Area, and also provides a full description of each selected site and the methods for sampling for soil water beneath each of the sites.

Site Descriptions

Selection of study sites was based on the following:

- The age of the facility – Preference was given to older sites due to the potential for contaminant accumulation over time.
- Sizes of the infiltration system – Sites with larger sizes were selected to provide sufficient space for installation of the sampling equipment.
- Availability of background hydrologic data, including stormwater flow data (gauging) useful in developing relationships between contaminant concentrations and quantity of inflow to the site
- Accessibility of the site and proximity from/to the researchers' offices were important practical considerations.

Based on the criteria, three sites were selected from the east metro and adopted for the study (Figure 13). These are:

1. The Hamline-Midway rain garden in Como Park located at the northeast quadrant, intersection of Midway Parkway and Hamline Avenue, St. Paul
2. Beacon Bluff, an underground infiltration system located due east of the northeast quadrant, intersection of E. Wells Street and N. Forest Street in St. Paul
3. The Sheep Pasture infiltration basin is located in the University of Minnesota St. Paul Campus, at the northwest quadrant of the intersection of Hoyt Avenue W. and Randall Avenue, adjacent to the Minnesota State Fairgrounds, St. Paul.

Hamline-Midway

The Hamline-Midway rain garden is a bioinfiltration practice constructed at the NE quadrant of the intersection of Hamline Avenue and Midway parkway, St. Paul. The installation replaced a storm sewer pipe previously located at the site. This rain garden was designed to contribute to water quality improvements and volume and rate control for stormwater runoff of a 10.5 acre watershed consisting of predominantly residential development. The garden also increases groundwater recharge, improves aesthetics, and provides wildlife habitat and educational opportunities for the community. This rain garden was constructed between 2005 and 2006 and began operating in 2006. The garden receives runoff from two storm sewer inlets at the south and east ends of the rain garden. It has an outlet structure set at approximately 3 feet above

ground concentration, and a grated emergency overflow opening located above the outlet structure. Emergency outflow starts when water concentration reaches approximately 5 feet above the soil surface, with the overflow entering the storm sewer system and discharging directly into Como Lake.

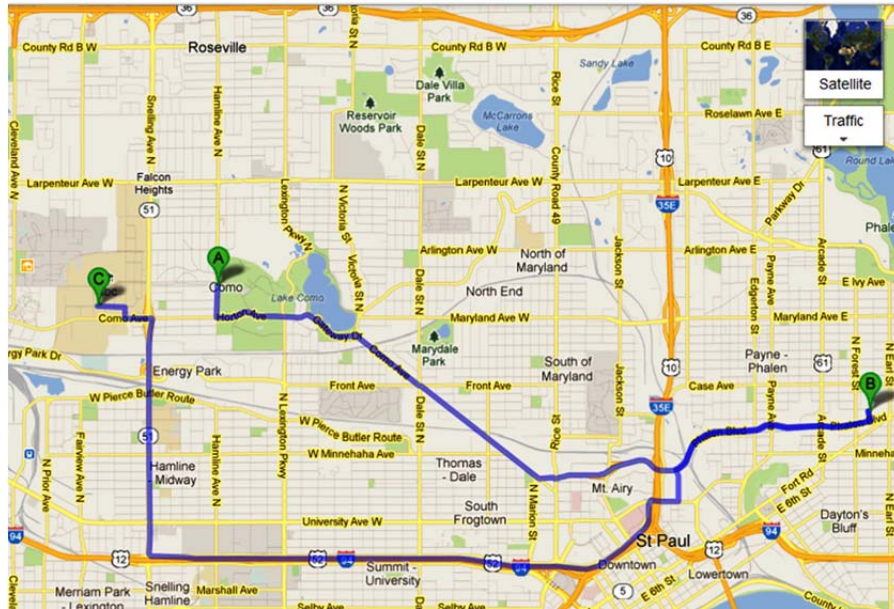


Figure 13. Location of the study sites A = Hamline-Midway rain garden, B= Beacon Bluff underground system, and C = Sheep Pasture infiltration Basin (Source: Google Maps).

The Hamline-Midway Rain Garden has a bottom area of 331 ft², a storage area of 6,364 ft², a water storage volume of 12,576 ft³ and drains an area of 10.5 acres that is 18% impervious (Figure 14). Located adjacent to Como Park and the Como Zoo, the garden plant cover is mainly shrubs and trees, with native forbs and sedges.

Beacon Bluff

The infiltration system at Beacon Bluff is composed of a surface infiltration basin and an underground infiltration gallery directly beneath the basin. The gallery consists of three rows of 10 ft diameter perforated corrugated metal pipes, providing a total of 650 linear feet of piping and a total storage volume of 51,000 ft³ (Figure 15). This system receives stormwater runoff from 163 acres of residential development. Delineation of the watershed contributing runoff to the Beacon Bluff infiltration system is shown in Figure 16. Construction of the Beacon Bluff system was completed in 2010. At least 45% of the area is listed as being under urban development. A one-year monitoring of the system by the City of St. Paul (2012) show stormwater inflow volumes in excess of 2 million cubic feet a year (Figure 17).

The Beacon Bluff site, also known as the Next Generation Storm Sewer Management System, is one of the largest underground infiltration systems in the State of Minnesota. Constructed by the St. Paul Port Authority, it stands on a 61-acre brownfield redevelopment (previously the St. Paul Business Center). The profiles of the material above the underground gallery consist of granular soil material and shredded tire chips (5 inches by 9 inches), as shown

in Figure 15. Subsurface boring by the American Testing Engineering (AET) Company reveal the top 4.5 feet below the underground gallery consists of silty sand and clayey gravel. Deeper soil is coarse alluvium and fine grained, light brown sandy material (AET, 2008). From around 8 feet deep and beyond, a mix of silty sand and gravel till dominate. Initial test results of the performance of the infiltration system show a capture of more than 62% of the stormwater runoff (WSB Project, 2012).

Soils of the watershed contributing runoff to the Beacon bluff infiltration system are as described in Figure 18 and Figure 19. The area in the vicinity of the infiltration system was previously industrial/manufacturing, and is currently under redevelopment.



Ramsey County, Minnesota (MN123)			
Map Unit Symbol	Map Unit Name	Acres in AOI	Percent of AOI
155D	Chetek sandy loam, 12 to 25 percent slopes	0.3	0.4%
298	Richwood silt loam, 0 to 2 percent slopes	6.2	8.0%
298B	Richwood silt loam, 2 to 6 percent slopes	8.7	11.1%
857	Urban land-Waukegan complex, 0 to 3 percent slopes	28.0	36.0%
857C	Urban land-Waukegan complex, 3 to 15 percent slopes	34.5	44.4%
Totals for Area of Interest		77.7	100.0%

Figure 14. Soils of the Hamline-Midway rain garden and surrounding watershed area (Source: NRCS WEB Soil Survey).

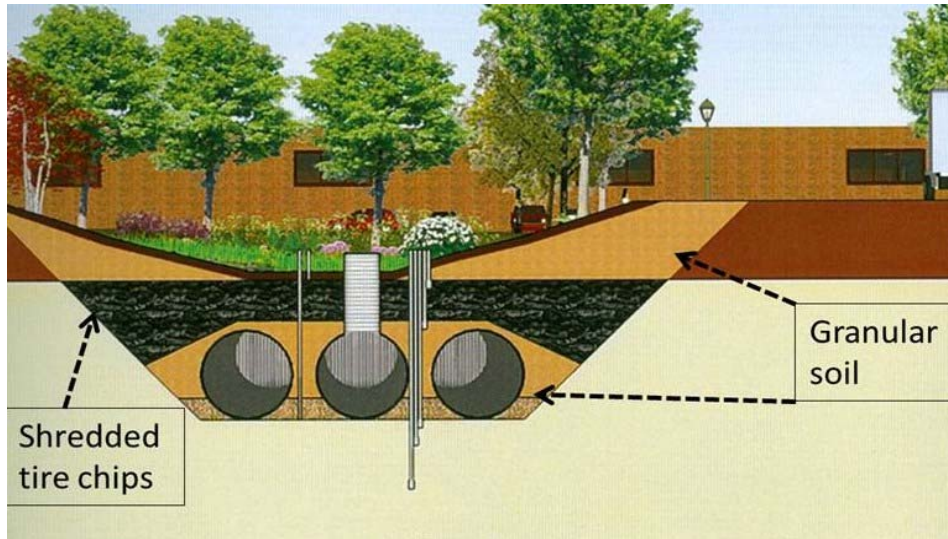


Figure 15. Illustration of the Beacon Bluff Second Generation underground stormwater Management system. (Adapted from Loucks Associates, Beacon Bluff Redevelopment, 2010).

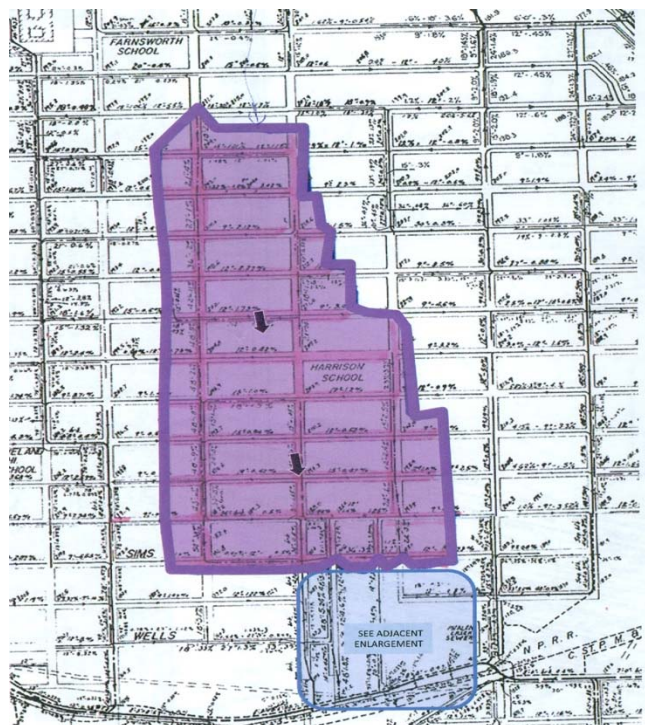


Figure 16. Watershed contributing runoff (purple shaded area) to the Beacon Bluff infiltration system (light blue shaded area). (Adapted from Loucks Associates, Beacon Bluff Redevelopment, 2010).

Monitoring Period	10/17/11 thru 11/08/12	
Total Rainfall	25.2 in.	
Diversion Structure Water Balance		
Runoff Volume:	3,504,574 cu-ft	
Bypassed Volume:	1,413,451 cu-ft	
Volume Diverted into BMP:	2,091,123 cu-ft	
Volume Captured by Underground System		
Inflow Volume from Diversion Structure:	SubWSHD A	2,091,123 cu-ft
Inflow Volume from West Pond:	SubWSHD B	66,417 cu-ft
Inflow Volume from East Pond :	SubWSHD C	165,881 cu-ft
System Outlet		
Total Outflow Volume:	0 cu-ft	
Beacon Bluff System Performance		
Total Runoff Volume:	3,736,872 cu-ft	
Total Runoff Volume Captured:	2,323,421 cu-ft	
Percent of Total Runoff Volume Captured:	62.2 %	
Maximum Percentage of Storage Volume Utilized:	31 %	

Figure 17. Beacon Bluff water quality and quantity monitoring study by the City of St. Paul, 2012. (Source: WSB Project number 1610-10, Todd Hubner, Personal Communication, 2012).

Sheep Pasture Infiltration Basin

Located at the southeast end of the University of Minnesota, St. Paul campus, the Sheep Pasture study area is constructed in the NW quadrant of intersection of Randall and Hoyt Avenues. The structure was installed at a former location of a depressional wetland previously used to store runoff from the St. Paul campus farm fields. This new system was designed to complement the power plant fore basin and Sarita Wetlands which receive and infiltrate stormwater discharge from the remainder of the St. Paul campus watershed. The Sheep Pasture site consists of two sedimentation basins and three infiltration basins all connected in series. The site receives runoff water from the St. Paul campus watershed of the University of Minnesota, comprised of research farm fields and animal housing to the north and west, asphalt roads and parking areas to the east and southern parts, and a compositing area to the north. The system of sedimentation ponds and three infiltration basins handle stormwater runoff from the northern portion of the St. Paul campus and the north and the north western section of the Minnesota State Fair grounds. An aerial view of the system is provided in Figure 20 and Figure 21. The Sheep Pasture system was re-vegetated after construction to create a natural woodland and prairie landscape. The system became operational in 2007. The area is inundated by stormwater several times during the year, each lasting at least a week or more before draining completely.

Potential sources of nutrients and other contaminants in stormwater runoff water received by the Sheep Pasture system include animal housing and pasture used to pasture livestock to the west, crop production fields to the northwest, compost stock pile to the north and roads and parking areas to the south and east sides.

The predominant soil at this site is Waukegan silt loam located over a sandy outwash at 50 to 100 cm depth (Figure 20). Because design installation included re-grading and placement of engineered soil material, soils at the site may be different from that in the rest of the watershed. Fill material in the infiltration basin is dominated by coarse textured material with relative high hydraulic conductivity (Banschbach, 2008)



Ramsey County, Minnesota			
Map Unit Symbol	Map Unit Name	Acres in AOI	Percent of AOI
861C	Urban land-Kingsley Complex, 3 to 15 percent slopes	137.2	79.5%
1039	Urban Land	35.4	20.5%
	Totals for Area of Interest (AOI)	172.6	100.0%

Figure 18. Classification of soils of the Beacon Bluff runoff-contributing watershed. (Source: A visualization of NCSS/USDA soil survey data in Google Earth-<http://casoilresource.lawr.ucdavis.edu/drupal/node/538>]

<p>Ramsey County, Minnesota</p> <p>861C—Urban land-Kingsley complex, 3 to 15 percent slopes.</p>	
<p>Map Unit Setting</p> <ul style="list-style-type: none"> Elevation: 1,000 to 1,300 feet Mean annual precipitation: 27 to 33 inches Mean annual air temperature: 39 to 46 degrees F Frost-free period: 135 to 180 days 	<ul style="list-style-type: none"> Across-slope shape: Convex Parent material: Till
<p>Map Unit Composition</p> <ul style="list-style-type: none"> Urban land: 60 percent Kingsley and similar soils: 35 percent 	<p>Properties and qualities</p> <ul style="list-style-type: none"> Slope: 3 to 15 percent Depth to restrictive feature: More than 80 inches Drainage class: Well drained Capacity of the most limiting layer to transmit water (Ksat): Moderately low to moderately high (0.14 to 0.57 in/hr) Depth to water table: More than 80 inches Frequency of flooding: None Frequency of ponding: None Available water capacity: Moderate (about 8.5 inches)
<p>Description of Urban Land</p> <p>Setting</p> <ul style="list-style-type: none"> Landform: Moraines Landform position (two-dimensional): Shoulder Down-slope shape: Linear Across-slope shape: Linear 	<p>Interpretive groups</p> <p>Farmland classification: Not prime farmland</p> <p>Land capability (nonirrigated): 3e</p> <p>Hydrologic Soil Group: C</p>
<p>Description of Kingsley</p> <p>Setting</p> <ul style="list-style-type: none"> Landform: Moraines Landform position (two-dimensional): Shoulder Down-slope shape: Convex 	<p>Typical profile</p> <ul style="list-style-type: none"> 0 to 8 inches: Sandy loam 8 to 39 inches: Sandy loam 39 to 60 inches: Sandy loam <p>Natural Resources Conservation Service Web Soil Survey, National Cooperative Soil Survey</p>

Figure 19. Map Unit Description of the Urban land-Kingsley complex, that is in the watershed contributing to the Beacon Bluff Infiltration system, Ramsey County, Minnesota.

Climate

Climate data for the study areas was obtained from the University of Minnesota's Climatological Working Group website (<http://climate.umn.edu/hidradius/radius.asp>). The temperature, rainfall and snow data values for the three study sites are as presented in Figure 22 and Figure 23.

Sampler types and installation

The fieldwork and data collection for this project employed three different types of samplers installed at varying depths in the three infiltration practices. The samplers installed include ten (10) lysimeters, fifteen (15) bottle samplers, and ten (10) barrel samplers. These were installed at different depths in the selected sites (see Appendix A – installation protocols) adopted for the study.

The ten SPE20 lysimeters (Figure 24), purchased from Decagon Devices, Inc., have a porous PE-nylon-membrane, which is especially suitable for heavy metals, herbicides, and pesticides, and wherever ceramic porous membranes are inappropriate. The SPE20s used in this project have a 100 cm long shaft and 300 cm long Teflon tubing. Other specifications are given in Table 12. The samplers were installed at different depths at the Hamline-Midway Rain Garden and the Sheep Pasture Infiltration Basin, following the methods and procedures described in the “Installation and Sampling Protocols” in Appendix A. Nalgene bottles 500 ml in volume (Figure 25), were also installed at the two sites with the SP20 samplers. These bottles were installed to sample ponded water at the soil surface, and at one of the sites to sample water perched within the soil profile.

Finally, at the Beacon Bluff site, water samples were collected from the large barrel samplers installed by the system installation contractor during construction of the infiltration system.



Ramsay County, Minnesota (MN123)			
Map Unit Symbol	Map Unit Name	Acres in AOI	Percent of AOI
411	Waukegan silt loam, 0 to 2 percent slopes	153.0	48.2%
411B	Waukegan silt loam, 2 to 6 percent slopes	35.4	11.1%
857	Urban land-Waukegan complex, 0 to 3 percent slopes	11.0	3.5%
857C	Urban land-Waukegan complex, 3 to 15 percent slopes	1.0	0.3%
858C	Urban land-Chetek complex, 3 to 15 percent slopes	31.6	9.9%
861C	Urban land-Kingsley complex, 3 to 15 percent slopes	0.4	0.1%
1039	Urban land	85.1	26.8%
Totals for Area of Interest		317.5	100.0%

Figure 20. Soil Map of University of Minnesota St. Paul Campus (Source: NRCS WEB Soil Survey).



Figure 21. Close-up view of the Sheep Pasture infiltration system.

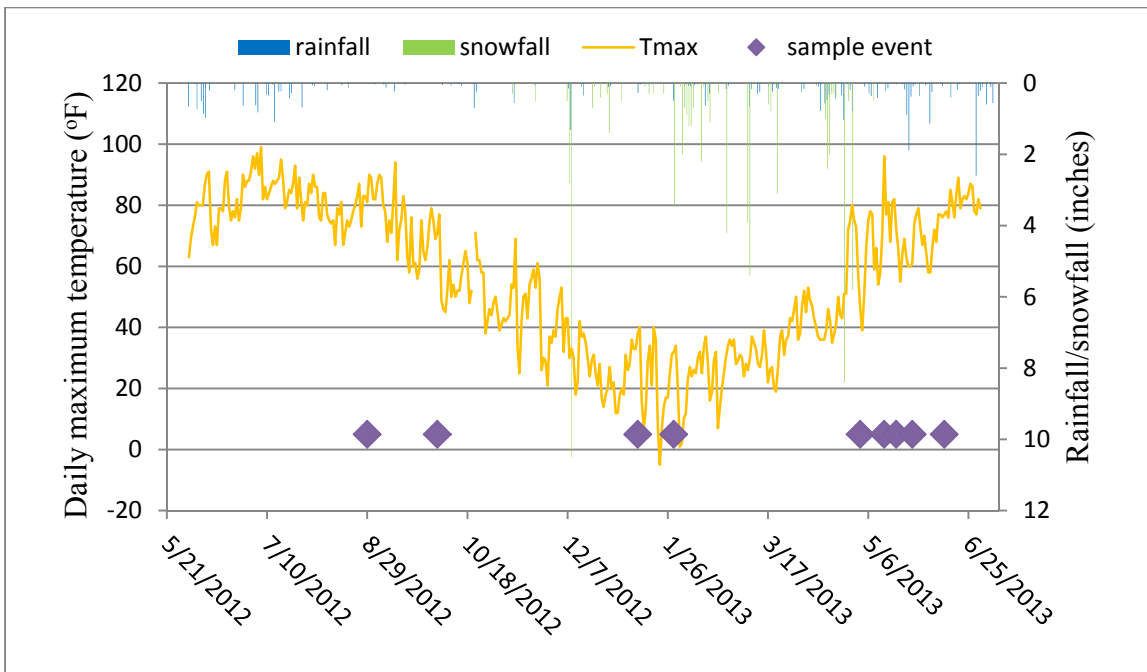


Figure 22. Climatic Data at the Beacon Bluff site, St. Paul (Source: Minnesota Climatology Working Group, <http://climate.umn.edu/HIDradius/radius.asp>).

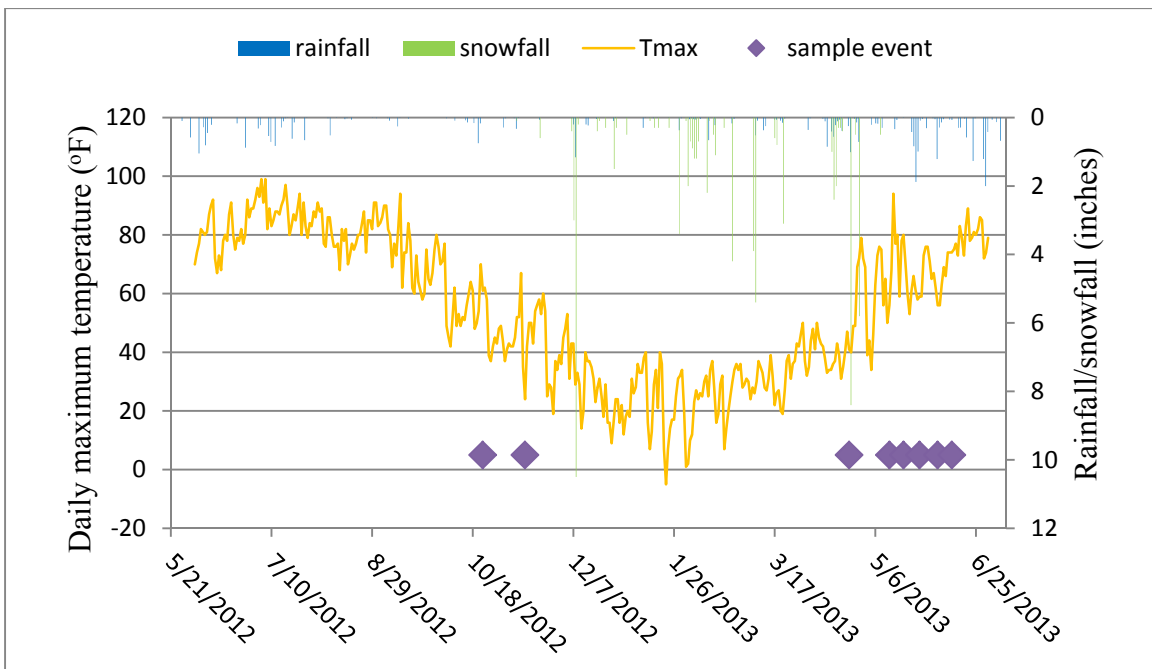


Figure 23. Climatic Data at the Sheep Pasture and Hamline-Midway sites and sampling dates (Source: Minnesota Climatology Working Group, <http://climate.umn.edu/HIDradius/radius.asp>).



Figure 24. Decagon's SPE20 sampler (1 cm shaft) pore water sampler with a porous PE-nylon-membrane, which is especially suitable for heavy metals.

To sample stormwater runoff at the surface, five plastic sample bottles (Figure 25) were installed at the Sheep Pasture and Hamline-Midway sites. Installation procedures are described in the “Installation and Sampling Protocols” in Appendix A. Obtaining water samples from stormwater at the surface before infiltrating provided information on the content and concentrations of the contaminants being investigated in the project.

A suction hand pump was used to apply a vacuum to sample from lysimeters and bottle samplers, while a 12V submersible well pump was used on the barrel samplers located at the Beacon Bluff site. Sampling procedures, the sample process, handling and storage are described in Appendix A. Sampling was scheduled to be conducted following events of significant rainfall and/or snowmelt. At least ten storm and/or snowmelt events were sampled, providing enough data points necessary for significance statistical analysis.

The barrel samplers at the Beacon Bluff infiltration system are made from a section of a 55 gallon plastic oil drum cut laterally. The lower half, about 18 inches tall, is filled with gravel and placed at predetermined depths in the Beacon Bluff underground infiltration system (Figure 27). The barrel samplers were installed to aide sample collection for monitoring the quality of water infiltrating through the system. A four-inch PVC pipe, perforated at the lower end and covered with filtration fabric, was screwed into the bottom of the barrel providing access and purging of water collected in the samplers. Table 13 provides a summary of properties and specifications of sampling devices installed at the three study sites. Table 14 provides the locations and depth of sampler installation in the Sheep Pasture and Hamline-Midway sites. Table 15 and Table 16 provide the characteristics of the soil profile at sampler installation locations for the Sheep Pasture Infiltration Basin and the Hamline-Midway Rain Garden, respectively.

Table 12. Specifications of the Decagon SPE20 sampler.

Shaft	Outer diameter 20 mm; acrylic
PE-nylon cup	Outer diameter 20 mm; length 60 mm
Bubble point	1 bar
Suction tube	PE; Ø 1,6 mm x Ø 2,8 mm
Protective tube	PVC; Ø 11 mm



Figure 25. Illustration of the Nalgene bottle sampler arrangement set up for sampling stormwater and any infiltrated stormwater perched on the clay layer within the Hamline-Midway rain garden site. A similar bottle arrangement without the vertical access tube was used for sampling water on the surface of the basins at the Hamline-Midway and Sheep Pasture sites.

Table 13. Equipment installations at the three sites adopted in the study.

Study Site	Sampling Equipment	Number installed	Installation Depth	Comments
Beacon Bluff	Barrel samplers	10	5 depths (ft): 42.0, 26.8, 24.65, 13.3, and 4.0.	Installed during system construction (Figure 27)
Hamline-Midway (Como)	Lysimeters (Decagon, SPE20)	2	1 installed at 48 inches depth, 1 installed at 91 inches depth	Shallow lysimeters placed about 12 inches below rock layer (Figure 26)
	Surface bottle samplers	5	Installed 1-2 inches below ground surface	Sample surface runoff (Figure 25)
	Subsurface bottle samplers	5	Installed immediately below the rock layer (approx. 3 ft below ground surface)	Sample water ponding in rock layer above underlying clayey layer (Figure 25)
Sheep Pasture (U of Mn)	Lysimeters (Decagon, SPE20)	7	Installed depths ranged from between 3.5 – 3.7 feet, and 8.4 – 9.0 depending on location	Installation depths depended on location in the field.
	Surface bottle samplers	5	Installed with rim of the sample bottle flush with ground surface	Sample surface runoff (Figure 25)

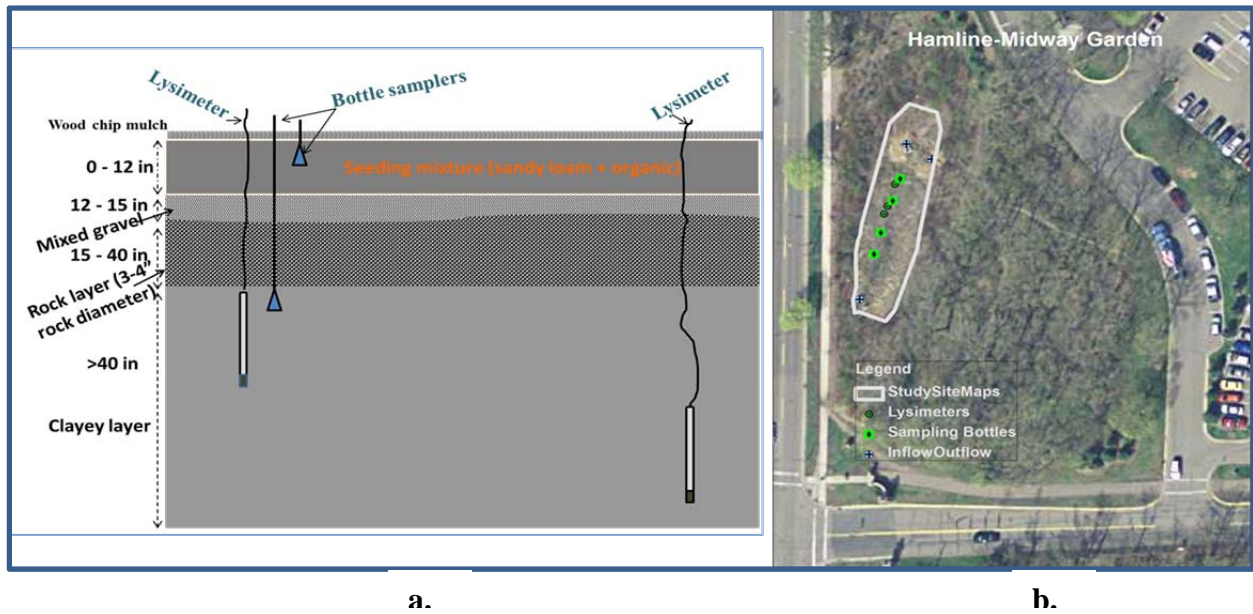


Figure 26. (a) Cross-section of Hamline-Midway rain garden, (b) Aerial view of the garden showing approximate location of installed sampling equipment.

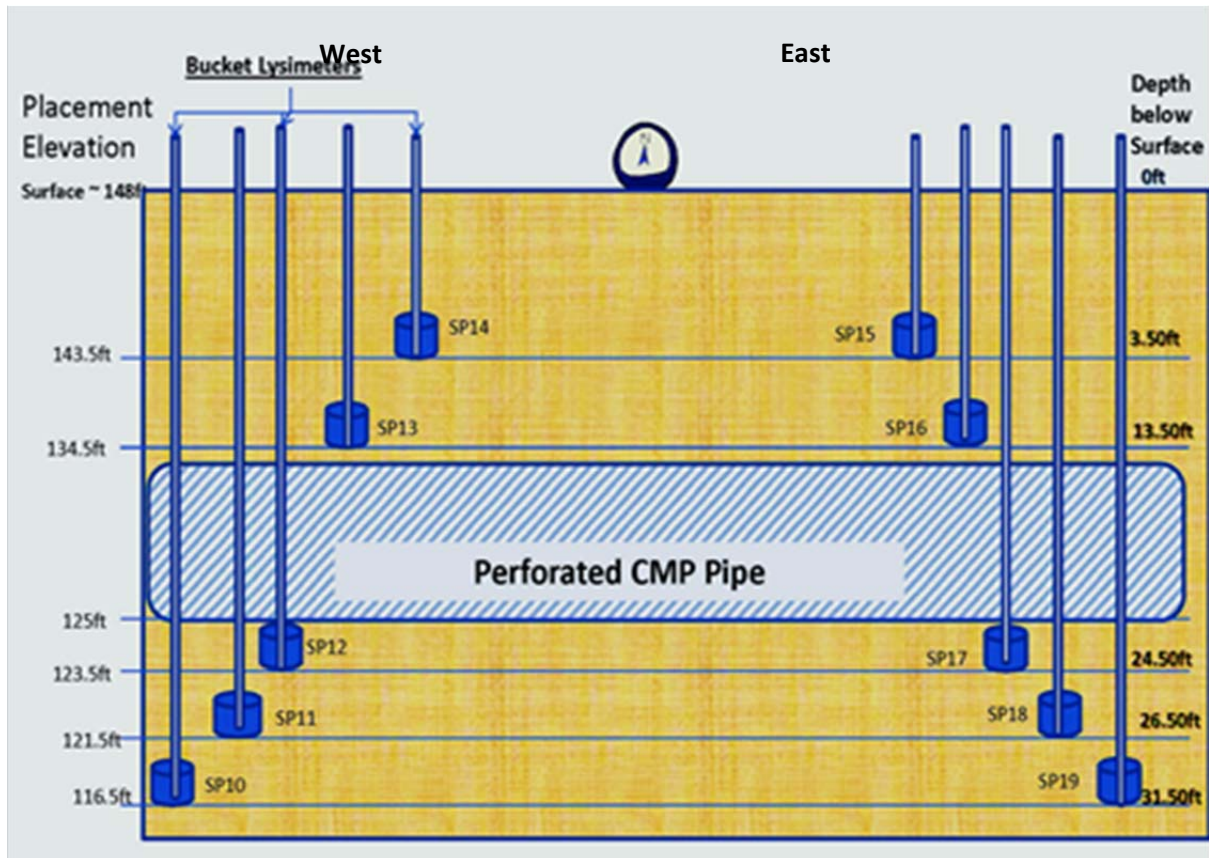


Figure 27. Illustration of the relative location and depth below datum of the perforated corrugated metal pipe and the ten barrel-samplers at the Beacon Bluff infiltration system.

Table 14. Locations and depth of installation of samplers in Sheep Pasture and Hamline-Midway sites.

Sampler ID	Date installed	Depth installed (ft)	Coordinates/Location	Remarks
UL1	9/12/2012	8.67		Northern part of Sheep Pasture site
UL2	11/13/12	3.50		Sheep Pasture site
UL3	9/24/2012	9.00		Sheep Pasture site
UL4	9/4/2012	9.00		Sheep Pasture site
UL5	9/4/2012	8.58		Sheep Pasture site
UL6	11/13/12	3.67		Sheep Pasture site
UL7	9/24/2012	8.42		Southern part Sheep Pasture site
HML1	10/09/2012	8.33		Northern part of the Hamline-Midway garden
HML2	10/08/2012	7.85		Hamline-Midway garden
HML3	10/23/2012	4.00		Hamline-Midway garden

Table 15. Characteristics of soil profile at sampler installation sites: Sheep Pasture Basin.

Sampler ID	Soil Profile	Depth installed (ft)
UL1	0-4' 2": dark clay loam 4' 2" – 6' 8": brown loamy >6' 8": Light brown loamy-sand	8.67
UL2	0-3.0': dark clay loam. 3.0' – 3'6": brown loamy	3.50
UL3	0-4ft: dark sandy loam 4 – 8.5ft: dark brown sandy loam > 8.5ft: Light brown sandy-loam	9.00
UL4	0-2ft: light brown sandy loam > 2ft: Light brown sand	9.00
UL5	0-3'0": dark brown clay loam 3'0" – 8.0': light brown sand	8.58
UL6	0-36": dark clay loam. 36" – 44": brown loamy	3.67
UL7	0-1 ft: dark brown clay loam 1 – 2.5ft: light brown loamy 2.5 – 8.5ft: Light brown sandy-loam	8.42

Table 16. Characteristics of soil profile at sampler installation sites: Hamline-Midway Rain Garden.

Lysimeter ID	Installation Date	Soil Profile descriptions	Depth installed (ft)
HML1	10/09/2012	0-1'3": dark loamy sand/sandy loam 1'3" - 1'6" mixed gravel (1/4" - 1/2" diameter) 1'6"-3'7": stones (2" - 3" diameter) 3'7" - 4' 4": dark brown clay loam 4' 4" - 7'1": light brown clay loam > 7'1": Light brown clay loam with red mottles >7' 1" wet, clayey	8.33
HML2	10/08/2012	0-1ft: dark loamy sand/sandy loam 1' - 1' 3": gravel / pebbles (1/4" - 1/2" diameter) 1'3" - 2' 6": stones (2" - 3" diameter) 2' 6" - 5' 5": dark brown clayey 5' 5" - 7' 2" Light brown silty-clay/clay loam >7' 2" wetness; flowing clay	7.58
HML3	10/12/2012	0-1'3": dark loamy sand/sandy loam 1'3" - 1'6" mixed gravel (1/4" - 1/2" diameter) 1'6"-3'7": stones (2" - 3" diameter) 3'7" - 4' 0": dark brown clay loam	4.0

Procedures for sample extraction

Samples were collected from all three sites following each significant storm event, as described in the sampling procedures in Appendix A (e). Figure A.4 (in Appendix A) shows the sampling bottle of the lysimeter through which vacuum is applied to suction water from the soil through the porous cup walls of the lysimeter to the soil surface.

Sample collection from the installed sampling bottles (surface and sub-surface, Figure 26) did not require use of the suction bottles as used with the lysimeters. In this extraction, a 500 ml bottle plugged with a 2-hole stopper with two tubes was used to connect a hand vacuum pump and the installed sampling bottle. By operating the hand pump, a vacuum is applied in the 500 ml bottle, hence sucking water from the installed surface or sub-surface sampling bottle.

Sampling the barrel samplers at the Beacon Bluff site required use of a 12-volt submersible pump with Teflon tubing of sufficient length. Procedures for sampling the barrel samplers using this pump are described in Appendix A.

Sample processing, storage and submission for laboratory analysis

Water samples were treated following established handling protocols for each of the laboratory analyses to be performed. Samples to be analyzed for metals had nitric acid added (to prevent precipitation of metal hydroxides due to high pH), bringing acidity to pH 2. The samples for total petroleum products (TPH) were treated with hydrochloric acid bringing pH to 2. Samples, which were to be analyzed for chloride and nitrate, were properly sealed then submitted immediately to the laboratory for analysis. All water samples, which could not be submitted to

the laboratories for immediate analyses, were tightly capped before being placed upside down in the refrigerator (to minimize losses through vaporization and/or leakage).

Samples for metals analysis were submitted to the Geochemistry Laboratory, Earth Sciences Department, University of Minnesota, while the Research Analytical Laboratory (RAL) of the Soil, Water and Atmosphere Department, University of Minnesota analyzed those for chloride, phosphorus and nitrate. The samples for total petroleum hydrocarbons were processed in the Bioproducts and Biosystems Engineering laboratory. All laboratories to which samples were submitted were confirmed to have capability for reporting results with detection limits that conform to the Metropolitan Council's specifications.

Results and Discussion

Sampling and data collection was carried out beginning summer 2012 through summer 2013. Fieldwork was not conducted during the winter season because freezing temperatures had an adverse effect upon the sampling tube. However, some samples were collected on a few winter days when temperatures were uncharacteristically warm, causing snowmelt. Generally, sampling was conducted on days following periods of sufficient precipitation resulting in runoff at the study sites.

This study monitored for presence and quantities of chloride, nitrate, phosphorus, metals (Pb, Ni, Cd, Fe, Cu, and Zn) and total petroleum hydrocarbons in samples of stormwater runoff infiltrated in bioretention structures. The results of analysis of water samples collected at different depths from beneath infiltration stormwater control measures (SCMs) are presented in the following sections.

The results will be compared with the maximum contaminant concentration (MCL) set by the U.S. Environmental Protection Agency (EPA) for primary and secondary drinking water standards. National Primary Drinking Water Regulations (primary standards) are legally enforceable standards that apply to public water systems. Primary standards protect public health by limiting the concentrations of contaminants in drinking water. National Secondary Drinking Water Regulations (secondary standards) are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. Where nutrient fluxes to surface waters are of concern, we will cite U.S. EPA Ecoregion Criteria, which are the recommended water quality criteria to reduce problems associated with excess nutrients in water bodies in specific areas of the country.

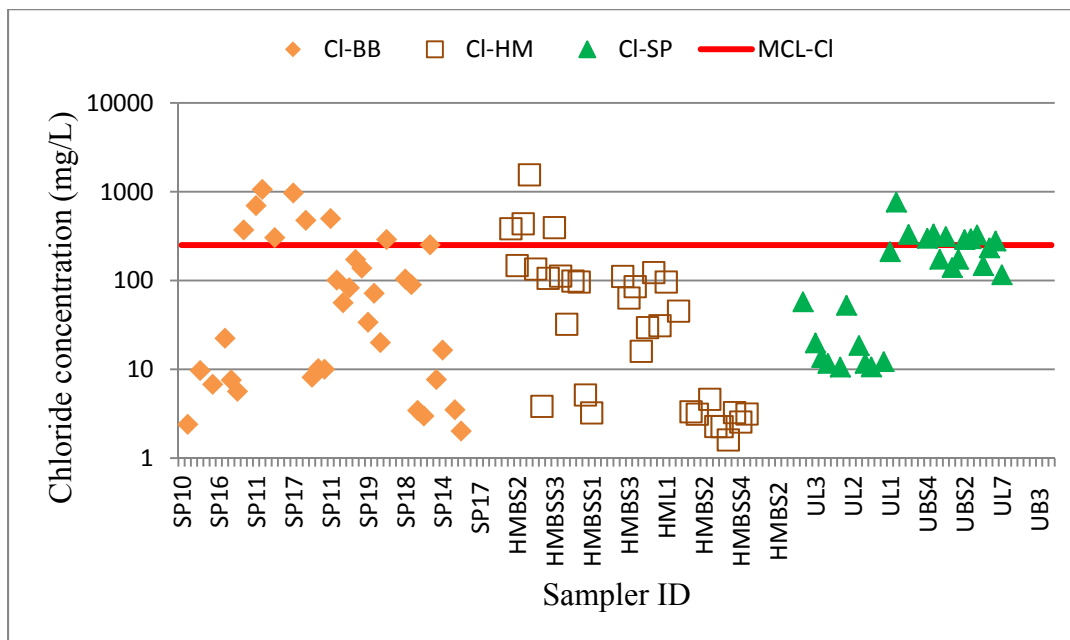
Nitrate, Chloride and Phosphorus

As mentioned in the review, the primary drinking water MCL of nitrate is 10 mg/L (as N), primarily due to negative health impacts upon fetuses/infants (U.S. EPA, 2008). For chloride, the secondary standard is 250 mg/L. There is no drinking water MCL for phosphorus, however there are concerns about groundwater to surface water fluxes of chloride and total phosphorus. The

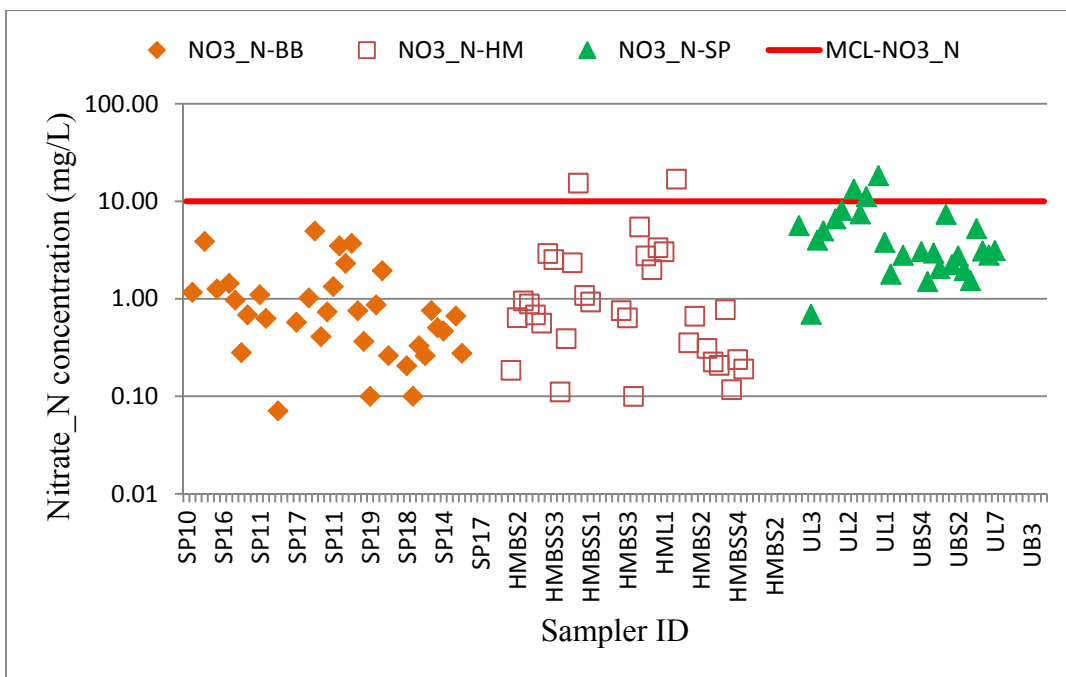
chronic and acute aquatic life criteria for chloride in freshwater systems are 230 and 860 mg/L, respectively. The ecoregion criteria for total phosphorus in surface waters vary by region, and across Minnesota it ranges from 0.037 mg/L (lakes) and 0.076 mg/L (rivers) in Southwestern Minnesota to 0.008 mg/L (lakes) and 0.010 mg/L (rivers) in Northeastern Minnesota. In the Twin Cities metropolitan area it is 0.015 mg/L (lakes) and 0.033 mg/L (rivers).

The results of laboratory analysis of samples from the three study sites are given in Figure 28 illustrating the mean concentrations measured for influent, barrel and lysimeter samplers at the three sites. When nitrate and chloride are compared to the U.S. EPA standards for drinking water, both are noted to exceed the safe concentrations for drinking water at various times during the measurement period. Figure 29 shows that concentrations of chloride, and nitrate exceed the MCL for 15% and 4% of the samples obtained, respectively. Although concentrations of nitrate did exceed the EPA standards for drinking water, this occurred only at the Hamline-Midway and Sheep Pasture locations, but not at the Beacon Bluff site (Figure 28 and Figure 29). The high nitrate concentration at the Sheep Pasture site is not surprising due to runoff generated from the crop farming fields, animal housing and a composting heap, which are channeled into the infiltration system. The same sources could also be contributing to the high total phosphorus at this site. The sources of nitrate at the Hamline-Midway study site have not been identified.

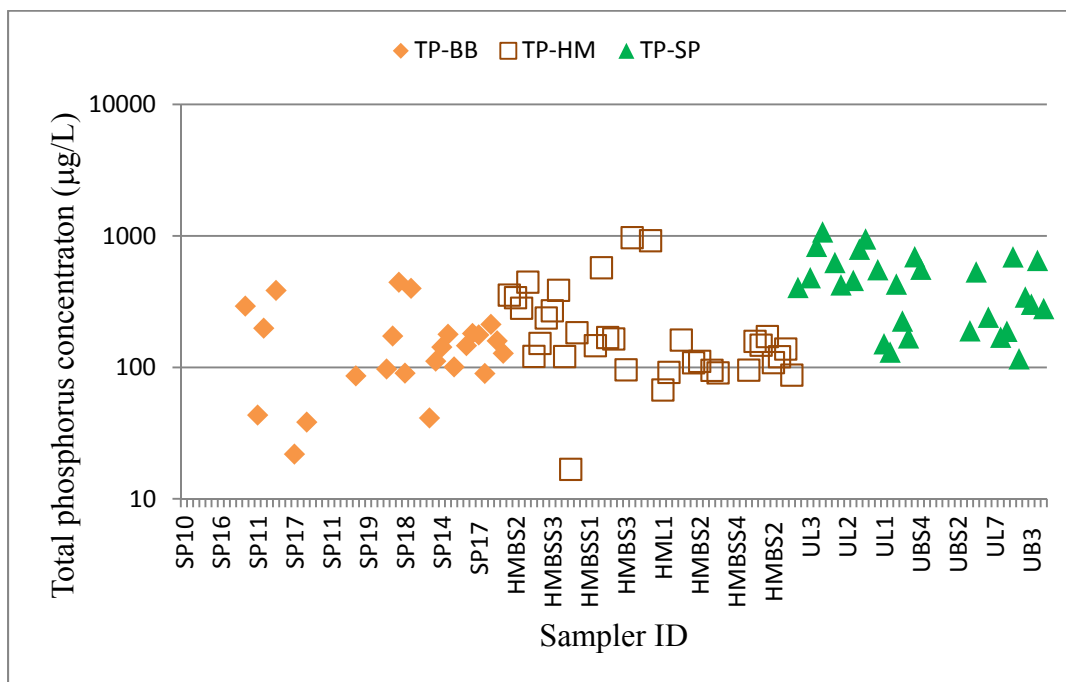
Chloride, nitrate and phosphorus concentrations are plotted versus depth in Figure 30, Figure 31, Figure 32, respectively, for each of the three sites. A linear trend of concentration versus depth is also fit to the data in each figure. The R^2 values for the linear curve fits are generally low, indicating that minimal trend was found. The exception was an increase of nitrate concentration with depth at the Sheep Pasture site. This could be a conversion of ammonium to nitrate by aerobic bacteria. Ammonium, however, was not monitored in this study. Overall, no discernable trend with depth was found for chloride, nitrate or phosphorus concentrations in the monitoring study.



(a)

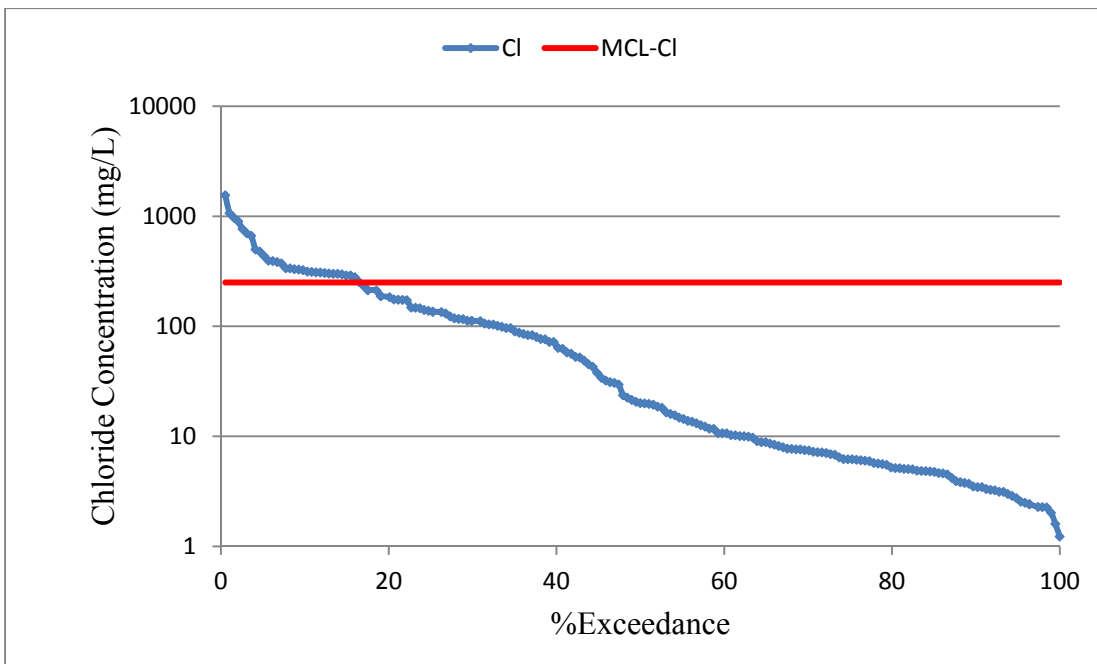


(b)

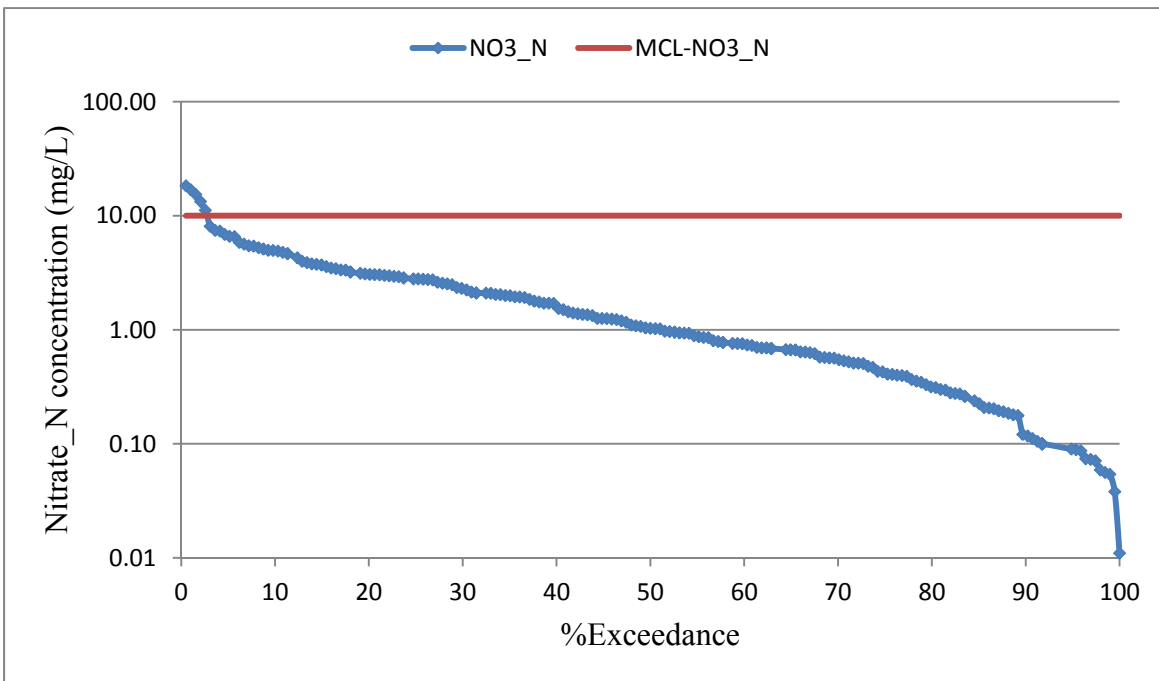


(c)

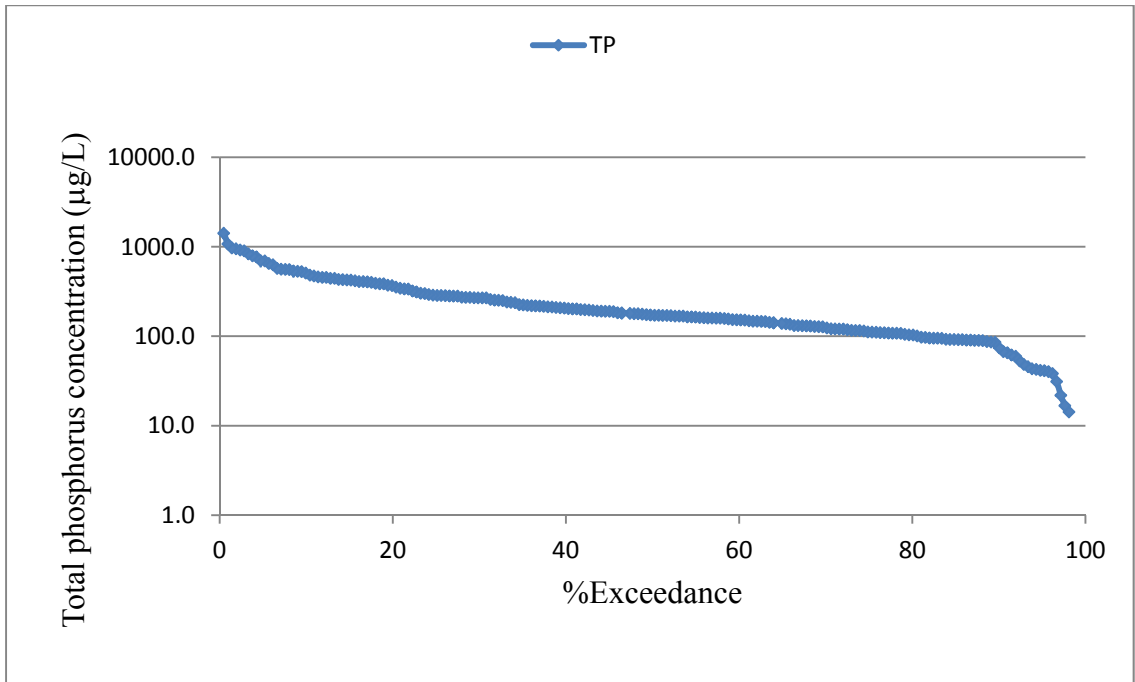
Figure 28. Presence and concentration of (a) chloride, (b) nitrate and (c) total phosphorus at the three study sites in the Twin Cities Metro Area, with the red line showing the U.S. EPA’s MCL for drinking water for chloride and nitrate. The x-axis proceeds from shallow to deep for each site.



(a)

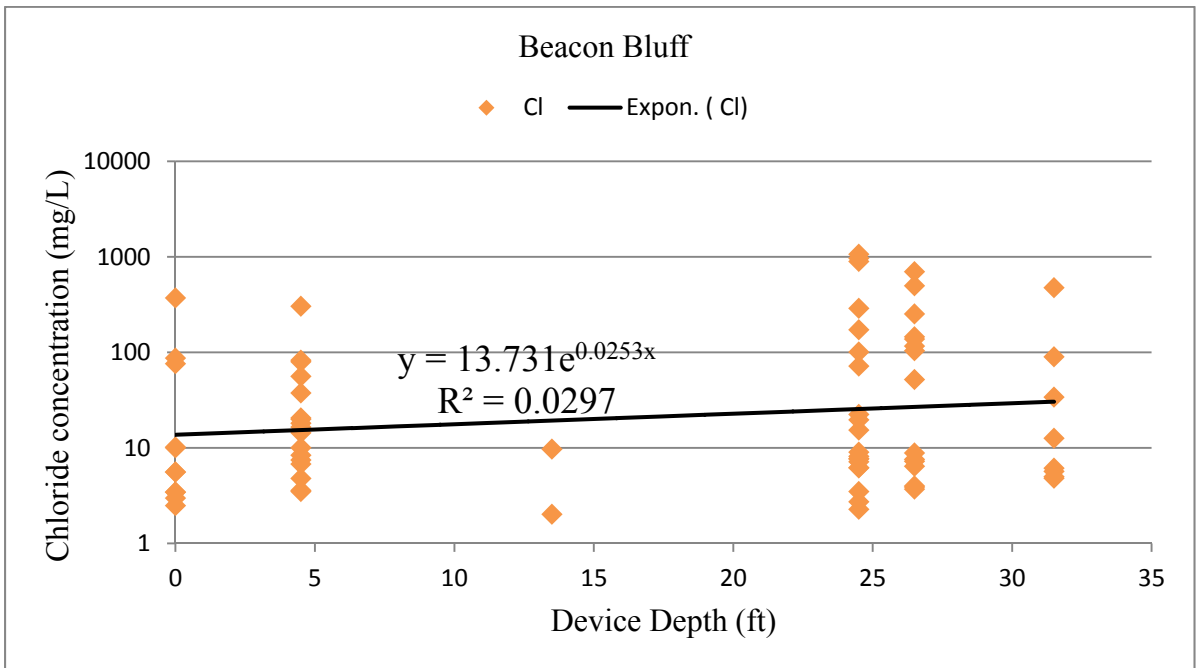


(b)

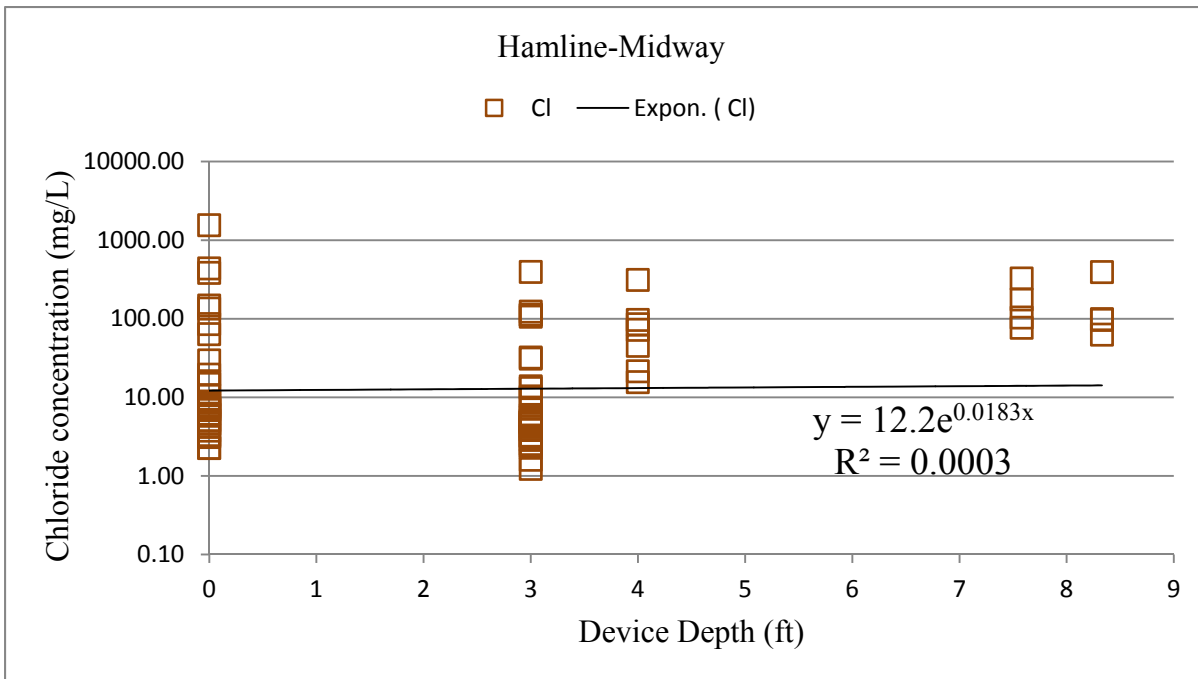


(c)

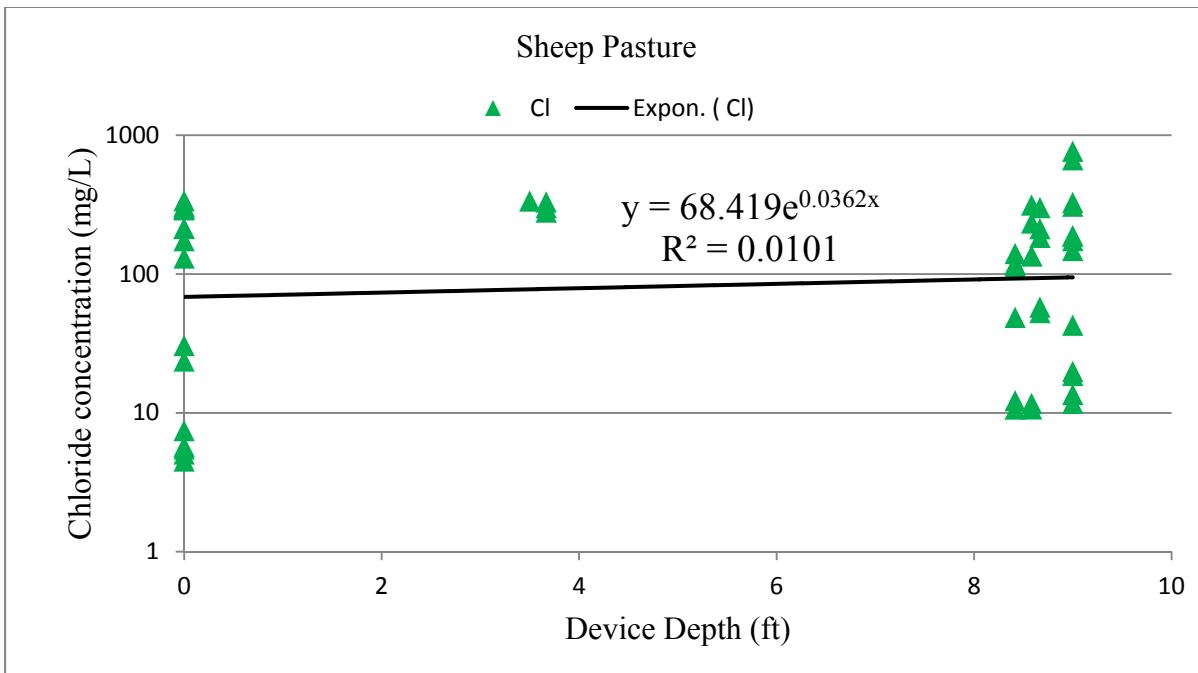
Figure 29. Percent exceedance of concentration for (a) chloride, (b) nitrate-N and (c) total phosphorus at the three study sites in Twin Cities Metro, with the red line showing the U.S. EPA’s MCL for drinking water (chloride and nitrate).



(a)

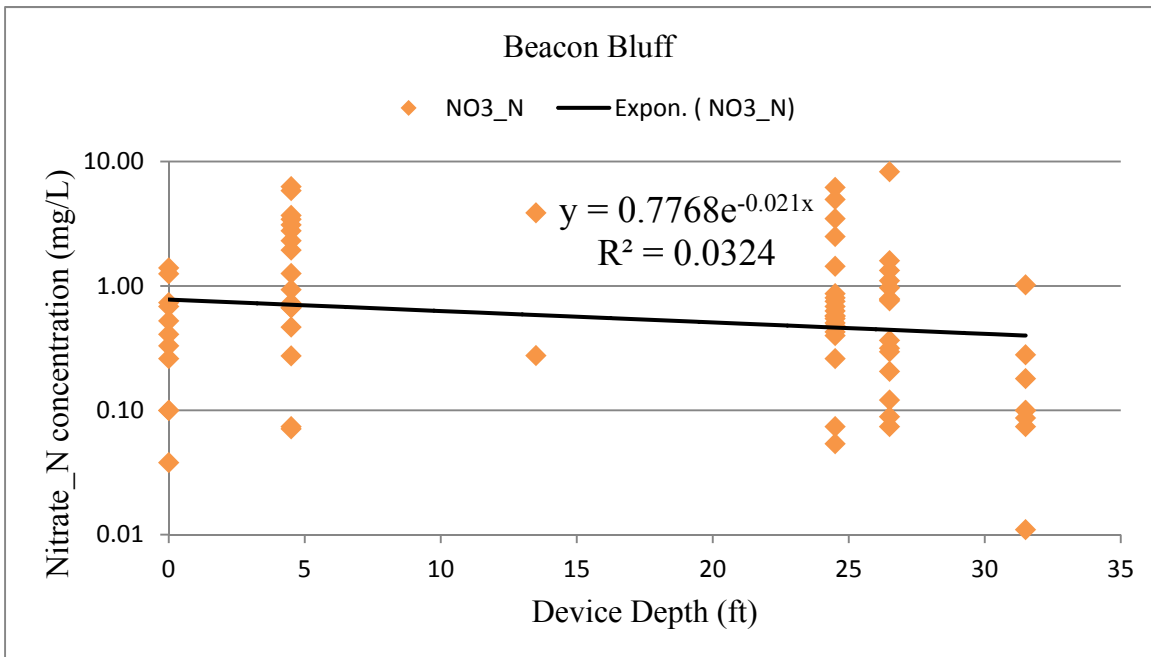


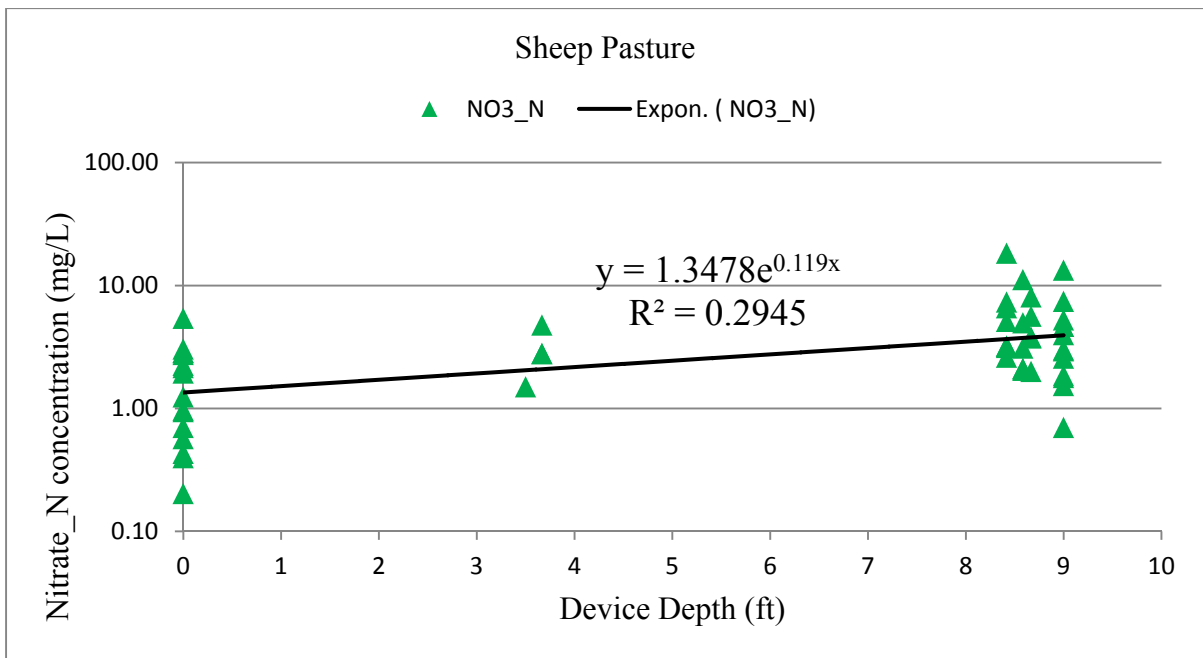
(b)



(c)

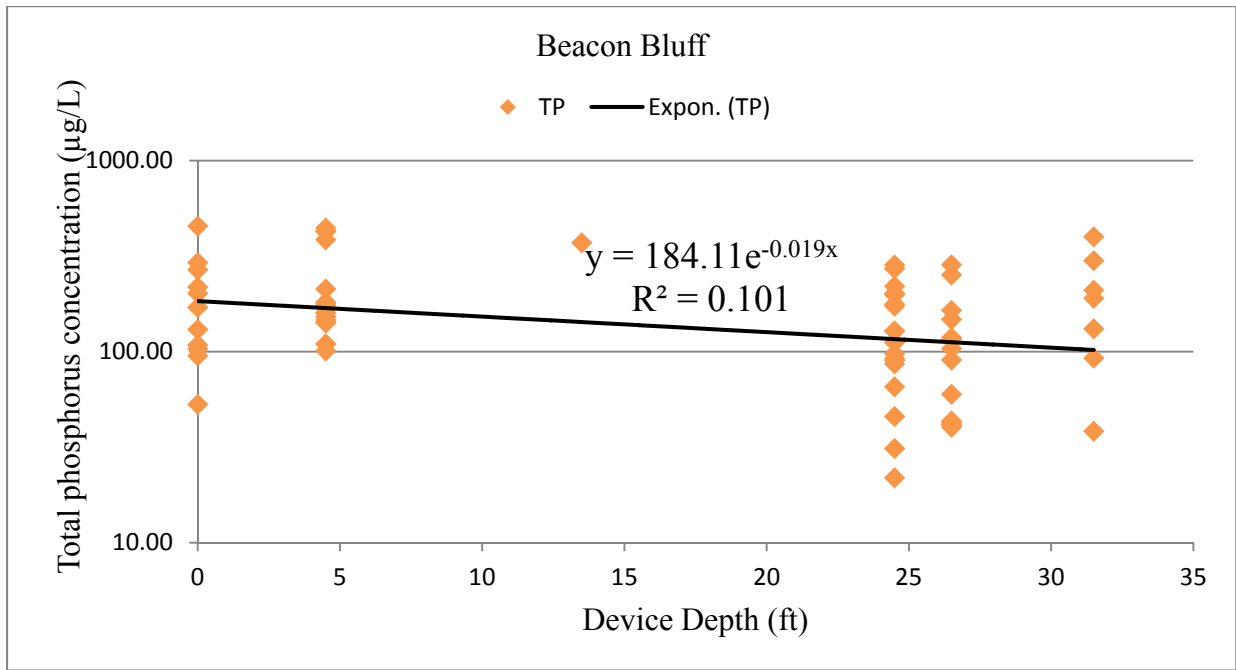
Figure 30. Plot of chloride concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



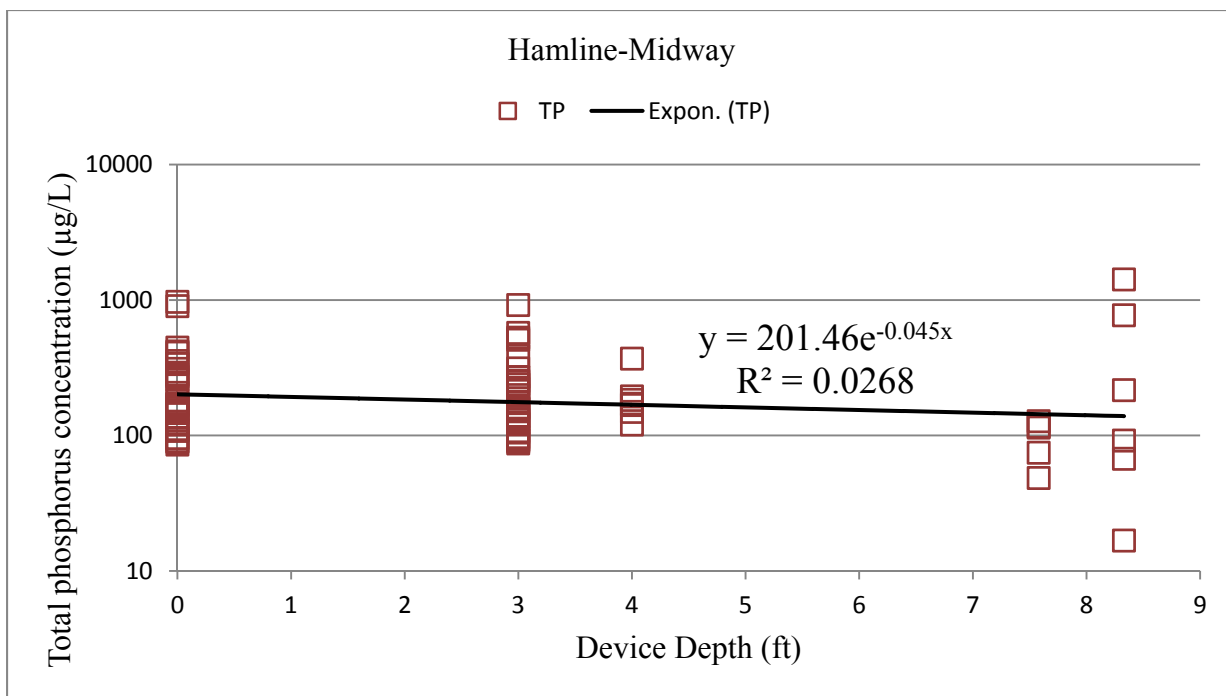


(c)

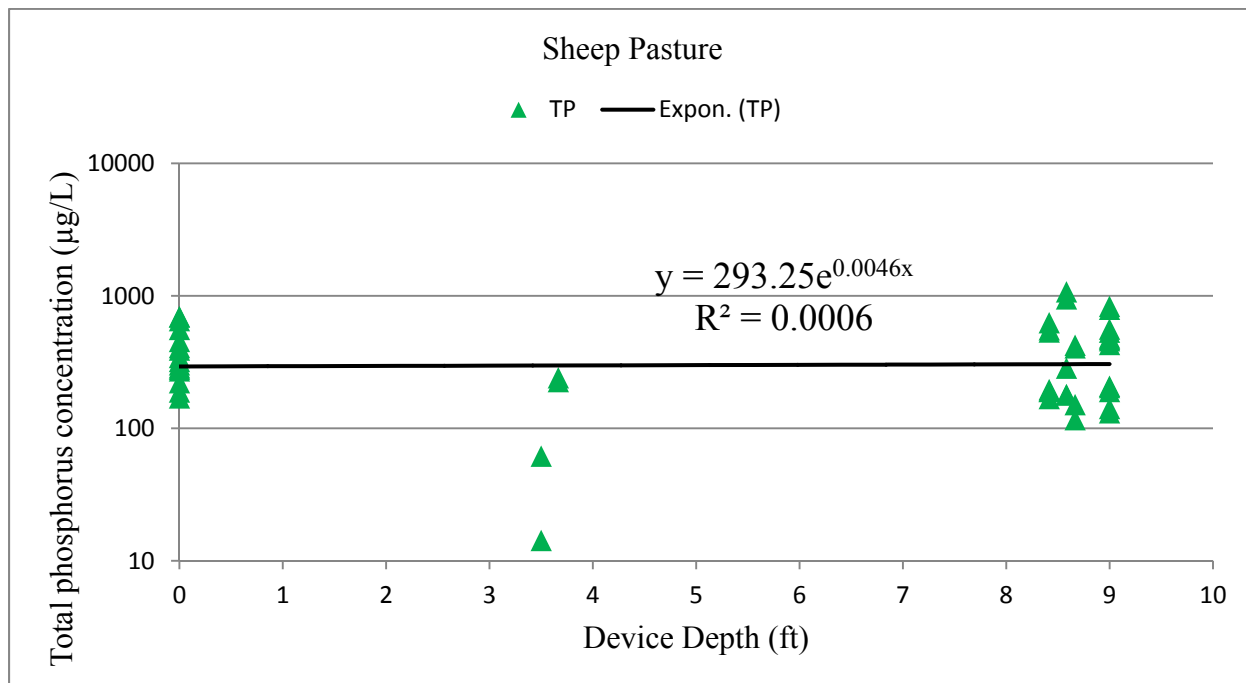
Figure 31. Plot of nitrate concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)



(b)

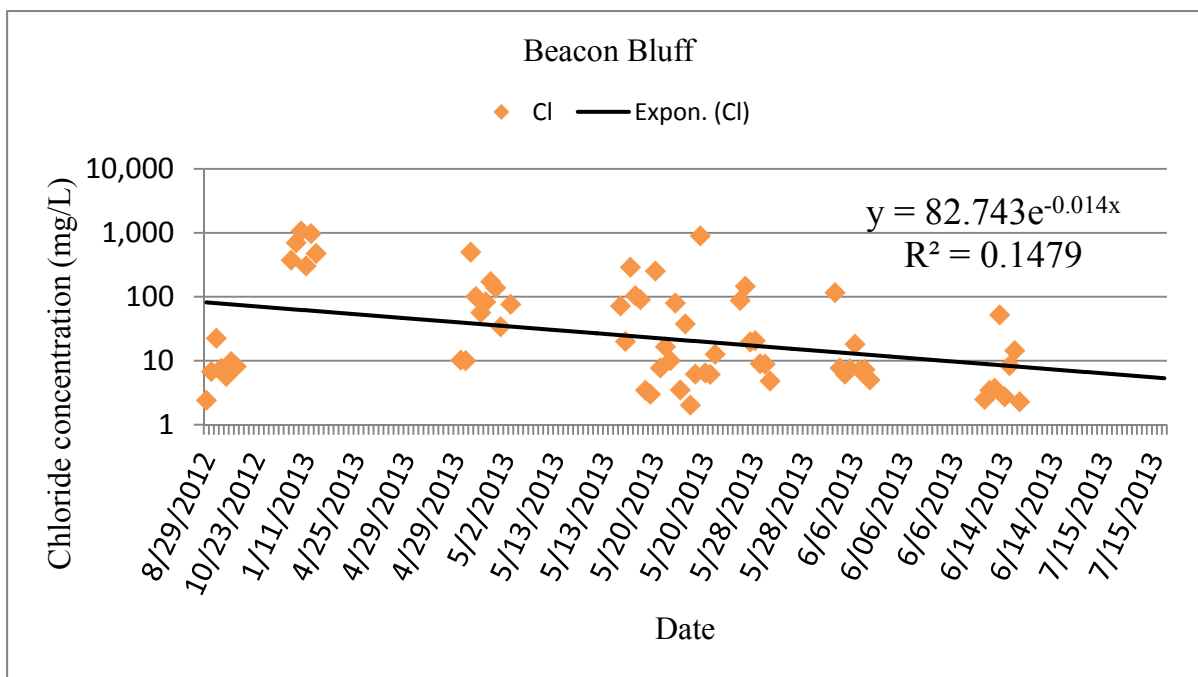


(c)

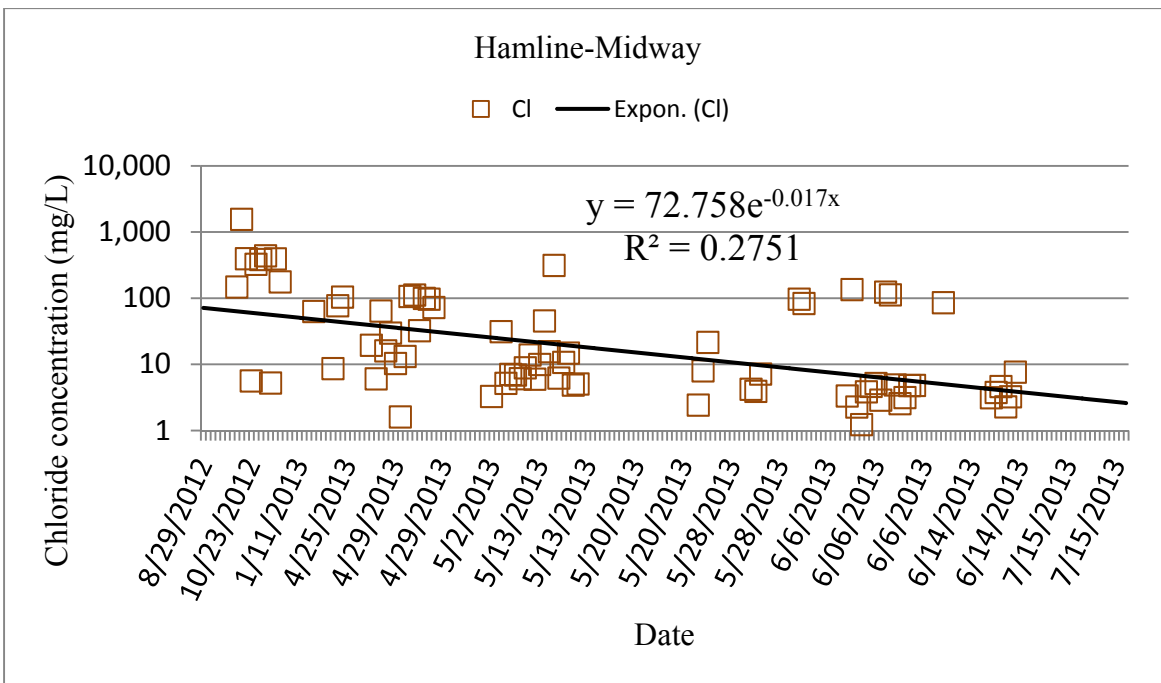
Figure 32. Plot of total phosphorus concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.

Figure 33, Figure 34, and Figure 35 show the temporal variation in concentrations of chloride, nitrate, and total phosphorus at the three monitoring sites, respectively. In each plot an exponential function has been fitted to the data. The equation for the fit along with the correlation coefficient is given on each plot. Observed peaks in chloride concentration occurred in mid-fall and spring at the Hamline-Midway and Beacon Bluff sites, but not at the Sheep Pasture site, possibly because there is less road salt applied to the watershed at the latter site.

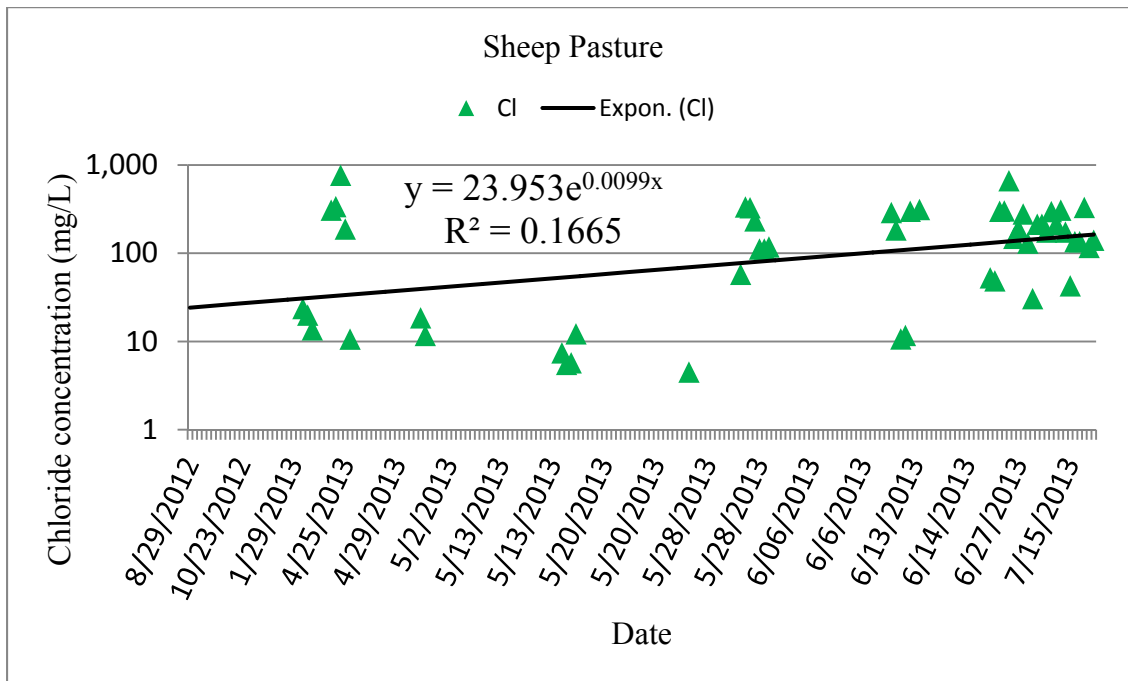
Chloride can be considered a conservative tracer. In addition, it is applied to roads in Minnesota typically during the months of December through March, so one would expect those months to have high chloride concentrations in the ground. However, Figure 33a and Figure 33b indicate that groundwater concentrations of chloride have peaks throughout the summer and fall. The overall trend at these two sites is a sharp increase in mid-fall, followed by a decline through the summer, with isolated peaks throughout. While the December and January samplings of chloride were high, the highest concentration occurred in October, and some samples taken in April, May and June also had high concentrations. It appears that movement of chloride in the unsaturated zone can be slow, possibly because of water caught between the small pores of the media, such that high concentrations at a given depth can be observed at any time of the year. This may be important for the groundwater-supplied baseflow of streams, which will experience a reduction of chloride concentration over that which would be expected in spring at the expense of higher concentrations during the remainder of the year.



(a)



(b)

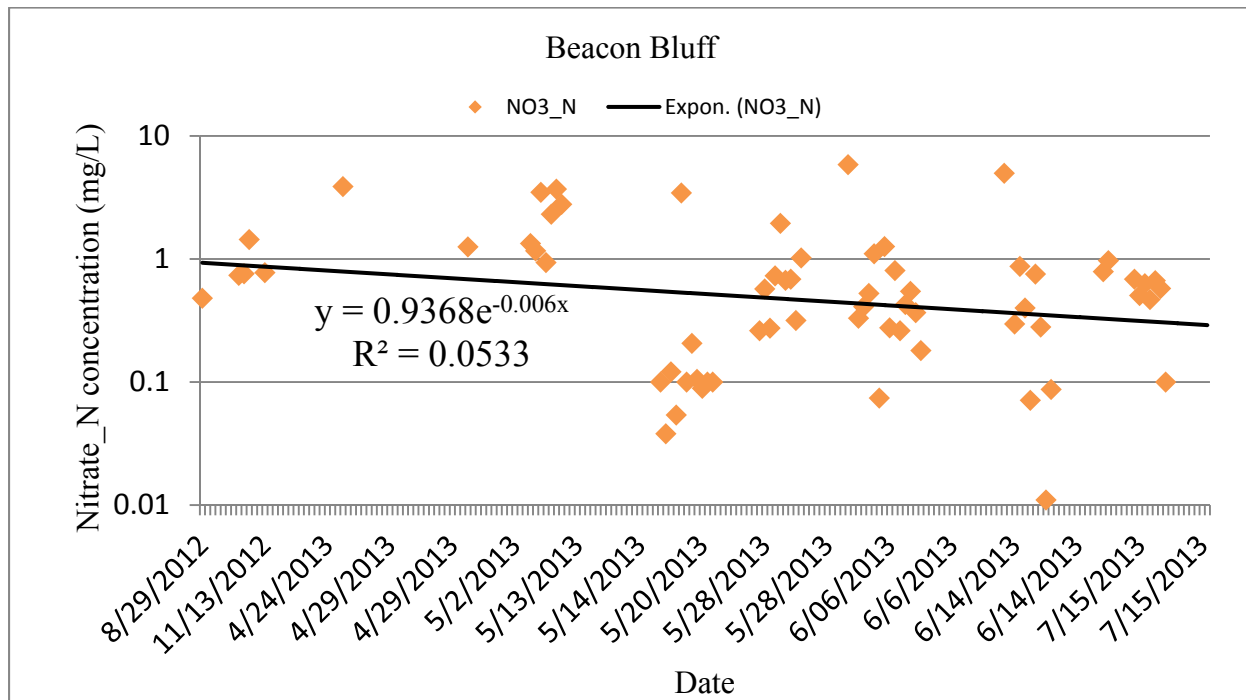


(c)

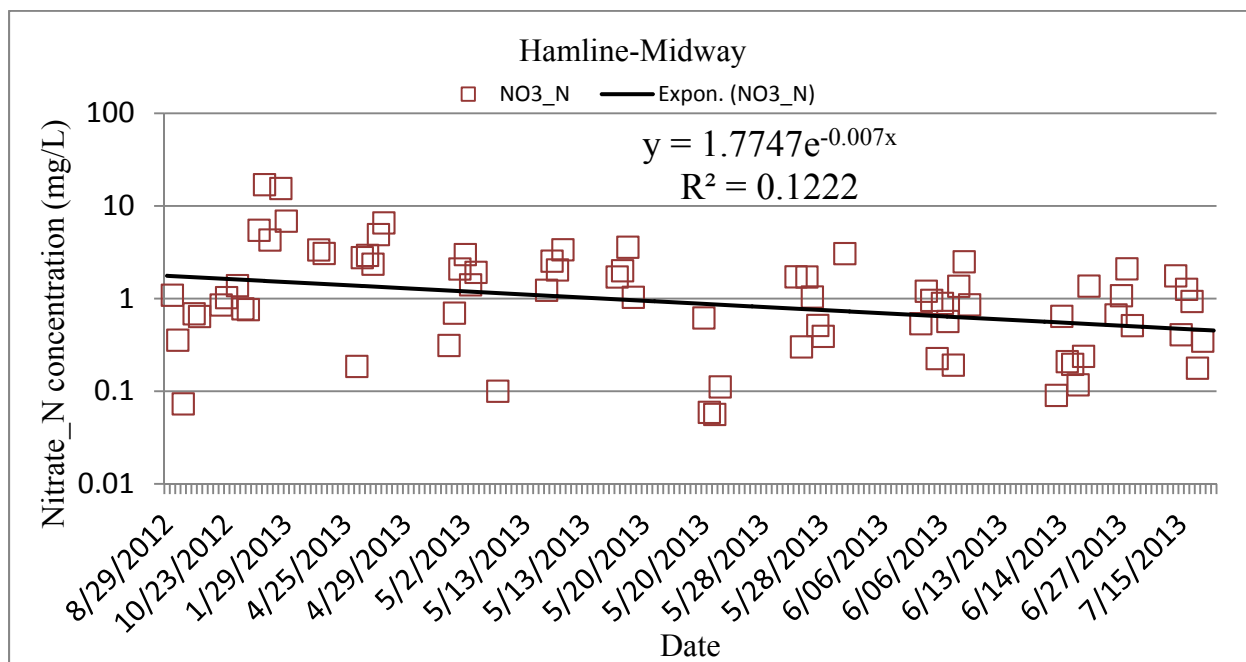
Figure 33. Temporal trends for chloride concentration at the (a) Beacon Bluff, (b) Hamline-Midway and (c) Sheep Pasture sites. An exponential best fit equation to the data is shown for each site.

There are negative seasonal trends from fall to summer, with isolated peaks, in nitrate concentration at all three sites (Figure 34). One possible reason may be the increase of organic particles (from fallen tree leaves and seeds) breaking down to release ammonia, which eventually

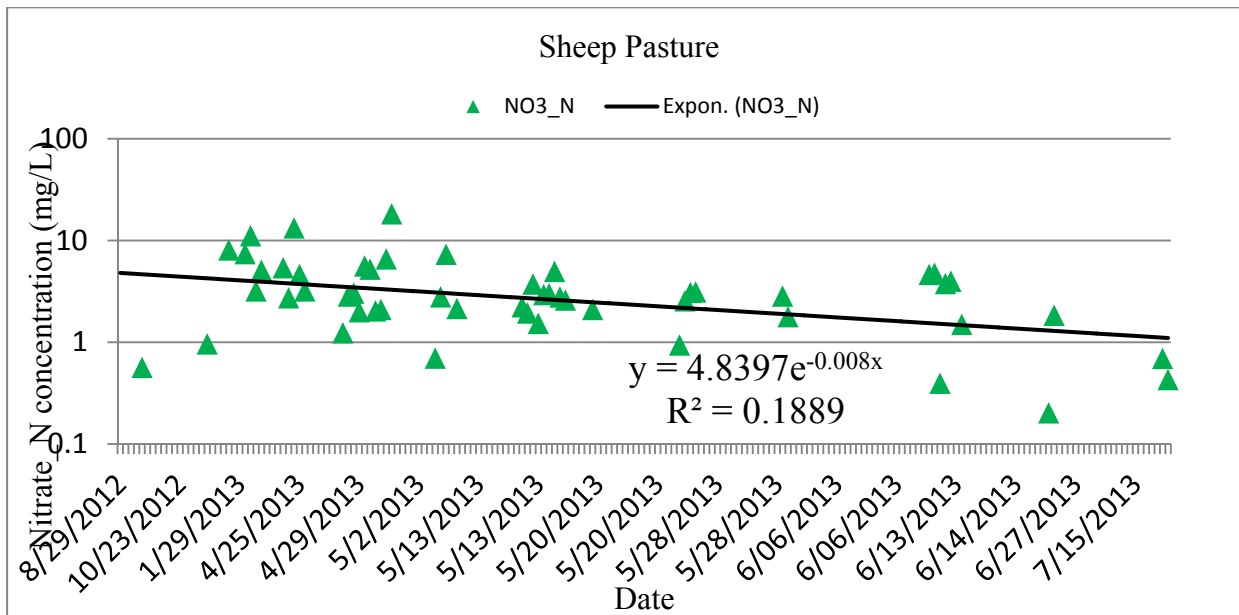
is converted to nitrate. If these observations are combined with the observations of chloride given above, we can speculate that the flushing of nitrate, combined with the ability of the soil to retain some water with nitrate, and the conversion of ammonium to nitrate results in a complex pattern of concentrations in the unsaturated soil beneath an infiltration practice. Hence, although there is some seasonal trend, peaks in nitrate concentration occur throughout the year.



(a)



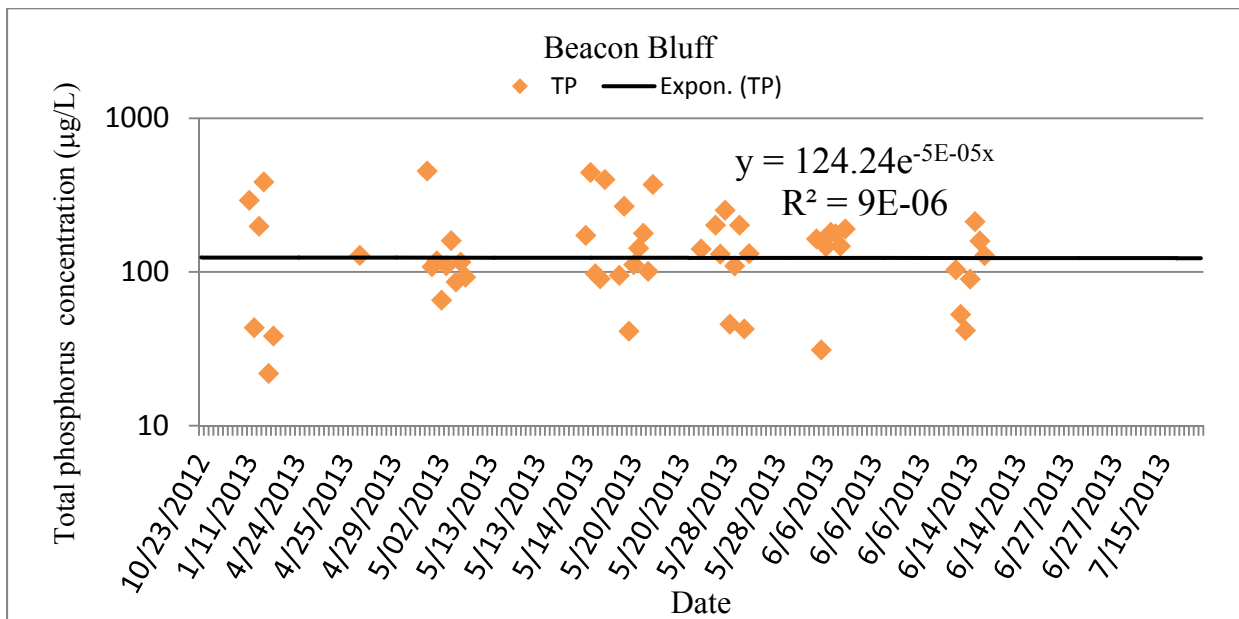
(b)



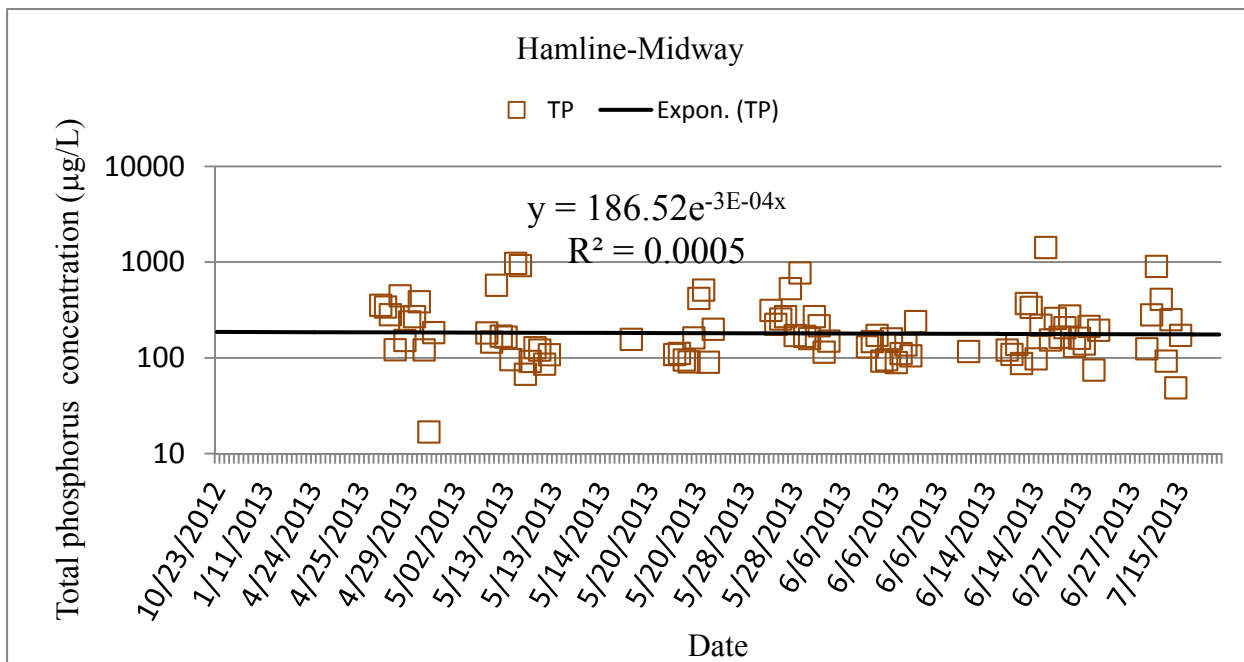
(c)

Figure 34. Temporal trends for nitrate-N concentration at the (a) Beacon Bluff, (b) Hamline-Midway and (c) Sheep Pasture sites. An exponential best fit equation to the data is shown for each site.

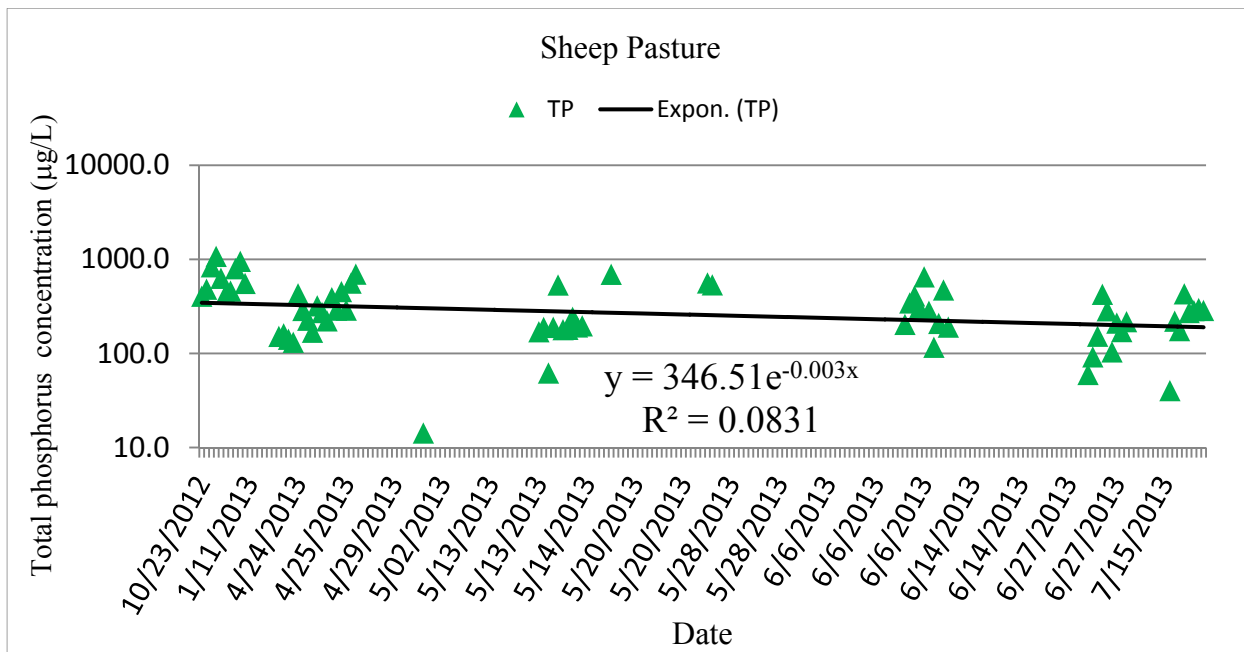
Total phosphorus concentration in the unsaturated zone (Figure 35) tends to vary between low and high relative to the U.S. EPA Ecoregion Criteria throughout the seasons at all sites. The R^2 values of the three curve-fits in Figure 35 were low, indicating that there is minimal seasonal trend of total phosphorus concentration. As with nitrate, higher concentrations were measured at the Sheep Pasture and Hamline-Midway sites than at the Beacon Bluff site.



(a)



(b)



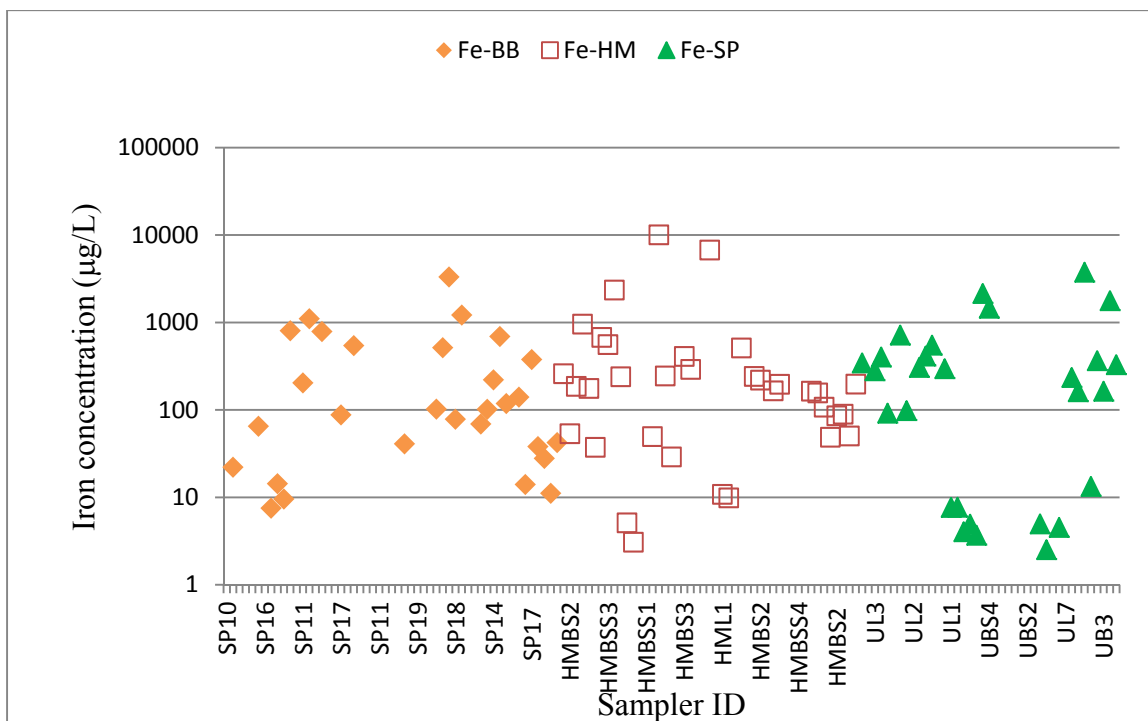
(c)

Figure 35. Temporal trends for total phosphorus concentration at the (a) Beacon Bluff, (b) Hamline-Midway and (c) Sheep Pasture sites. An exponential best fit equation to the data is shown for each site.

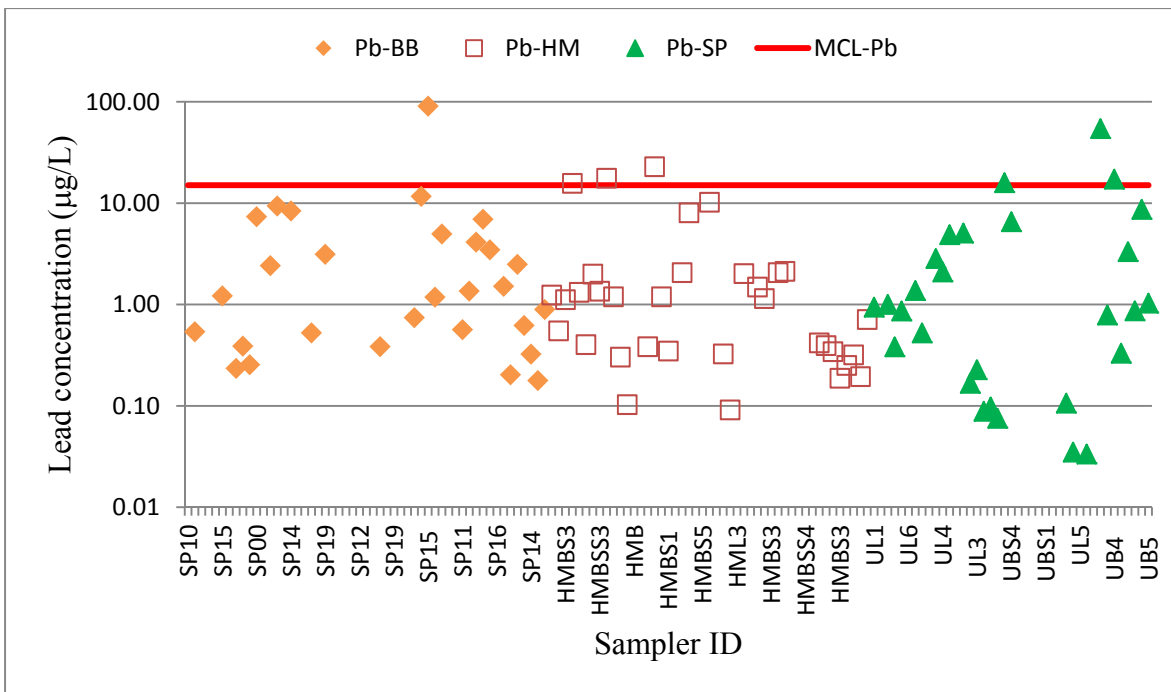
Metals

The concentrations of metals in the water samples collected from soil profiles in the infiltration systems are given in Figure 36. In general, most metals in the stormwater and below the infiltration practices are well below MCLs. The exceptions are iron, which has a secondary MCL of 300 $\mu\text{g/L}$ and lead, which has a primary MCL of 15 $\mu\text{g/L}$. The highest concentrations of iron were found in the unsaturated zone of the Hamline-Midway site. The highest concentration of lead was found at one location and one depth at the Beacon Bluff site. Both Hamline-Midway and Sheep Pasture had three exceedances of the MCL, whereas Beacon Bluff had one. Lead is a legacy contaminant, and concentrations are much lower today than when lead-based gasoline was in use. Lead is also adsorbed by soil, which means that it is possible that the lead from the 1970s is still in the groundwater. Thus, the lead concentrations in groundwater could be confounding.

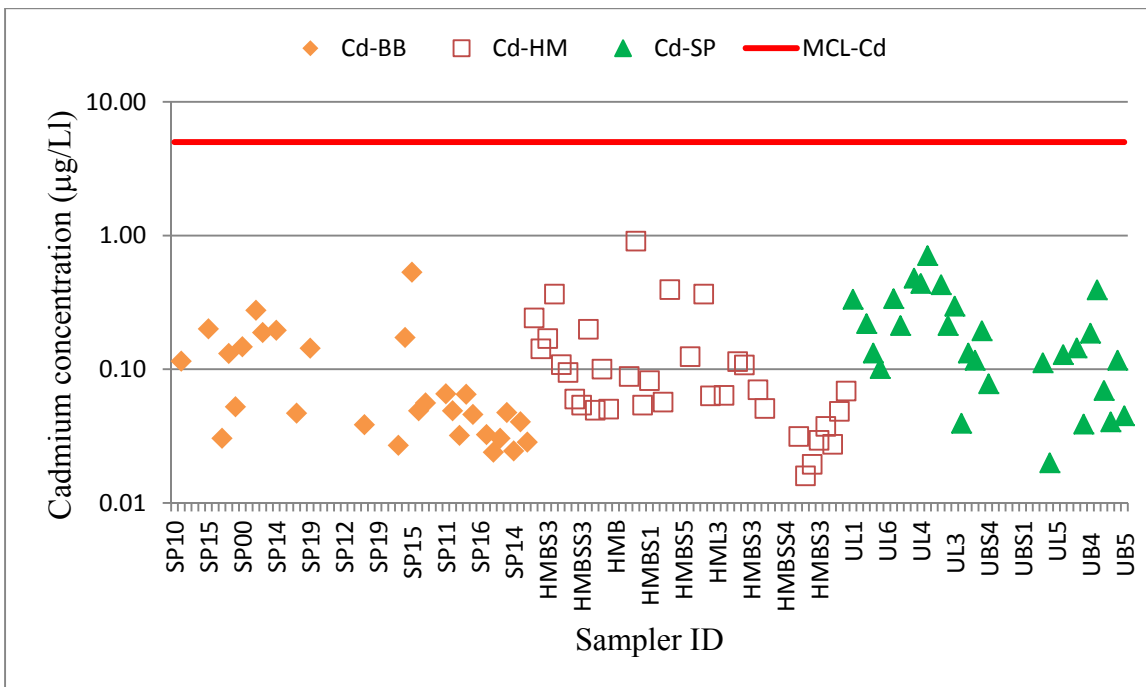
Nickel concentrations recorded at the Sheep Pasture location (Figure 36e) were consistently higher than in samples from Beacon Bluff and Hamline-Midway sites. The source of nickel in the Sheep Pasture study site is not known, but nickel is common in metal plating. There also appears to be more samples with higher copper concentrations recorded at Hamline-Midway study site compared to those at Sheep Pasture and Beacon Bluff sites (Figure 36g). The source of copper at this site was not determined during the study.



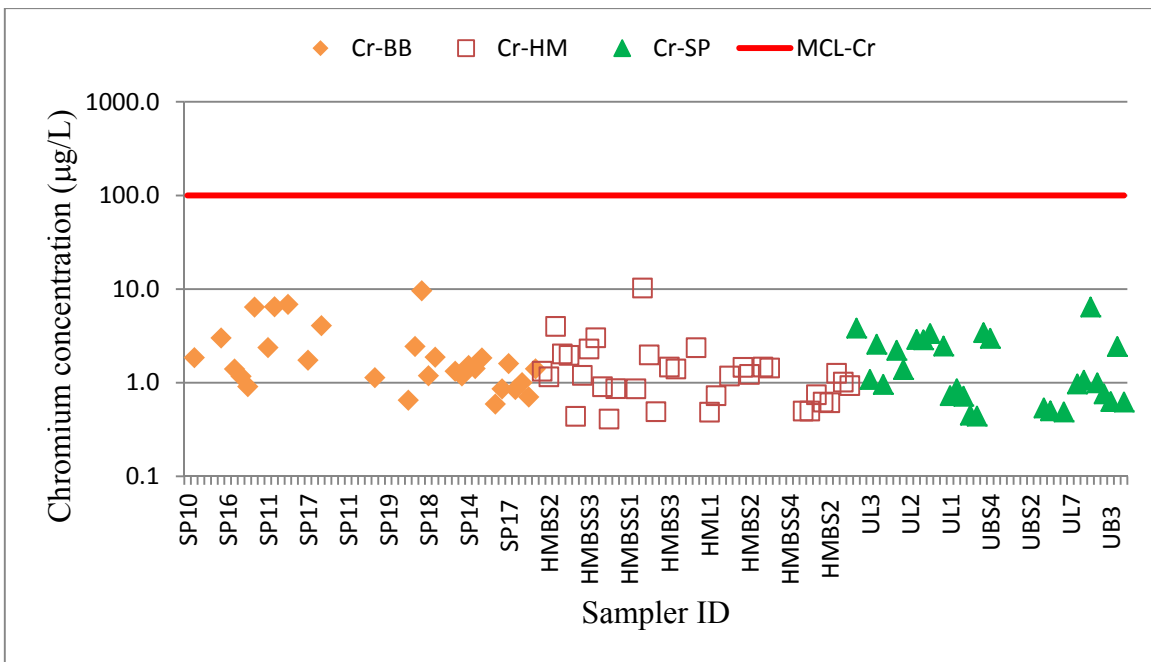
(a)



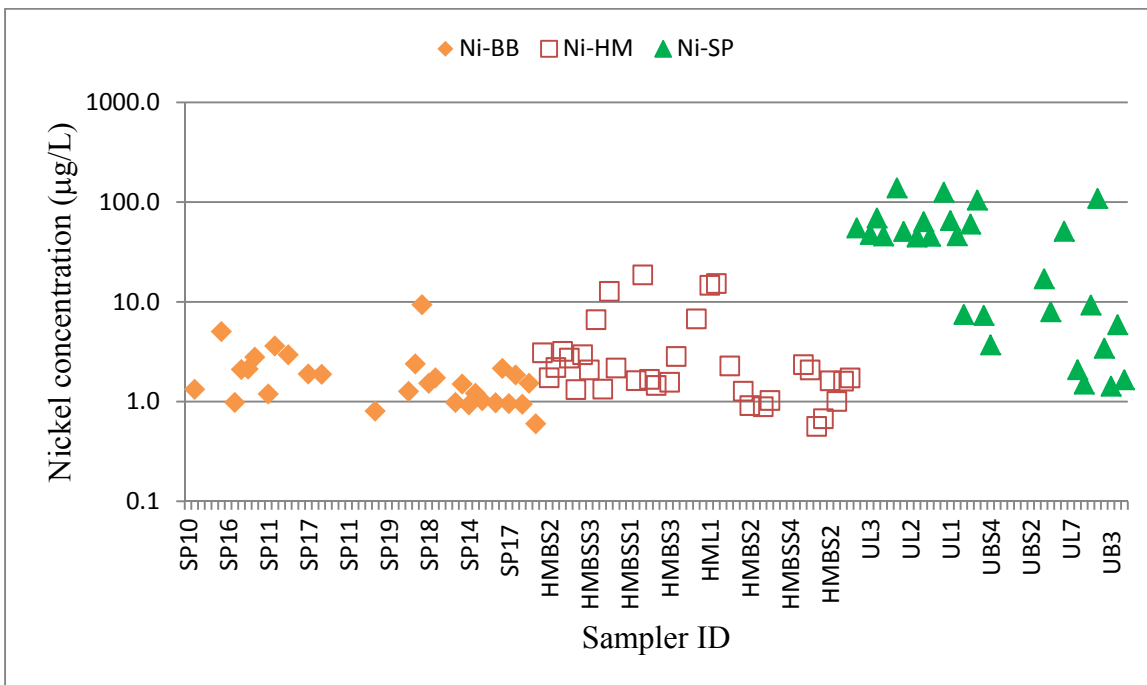
(b)



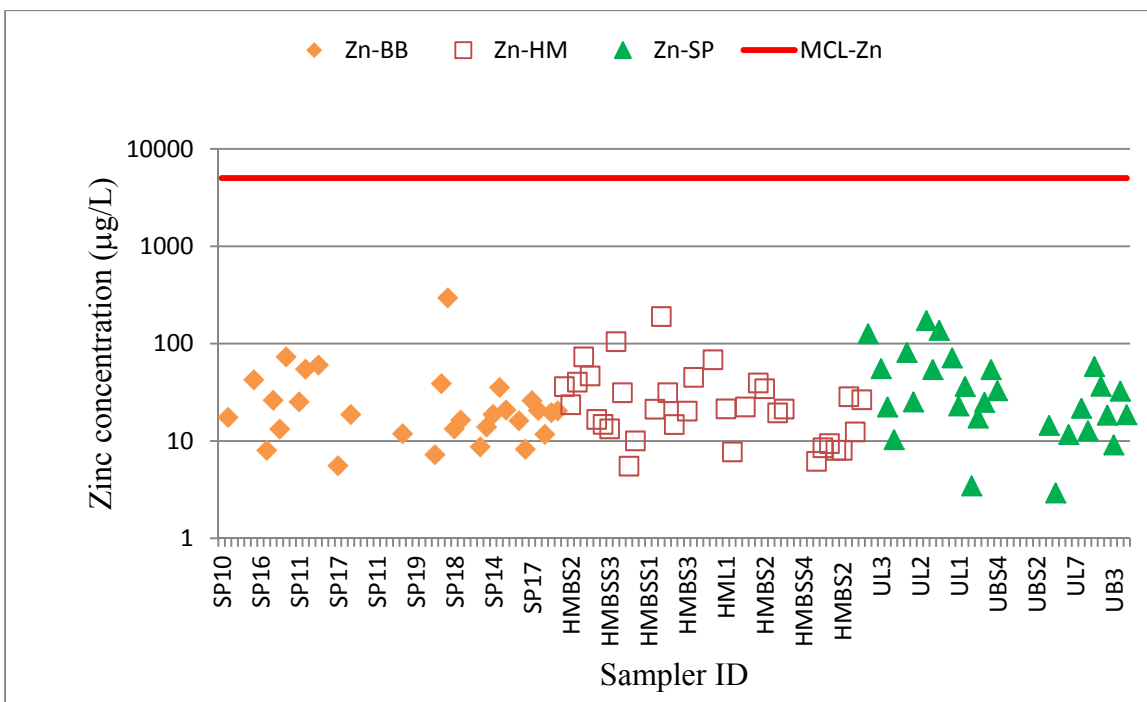
(c)



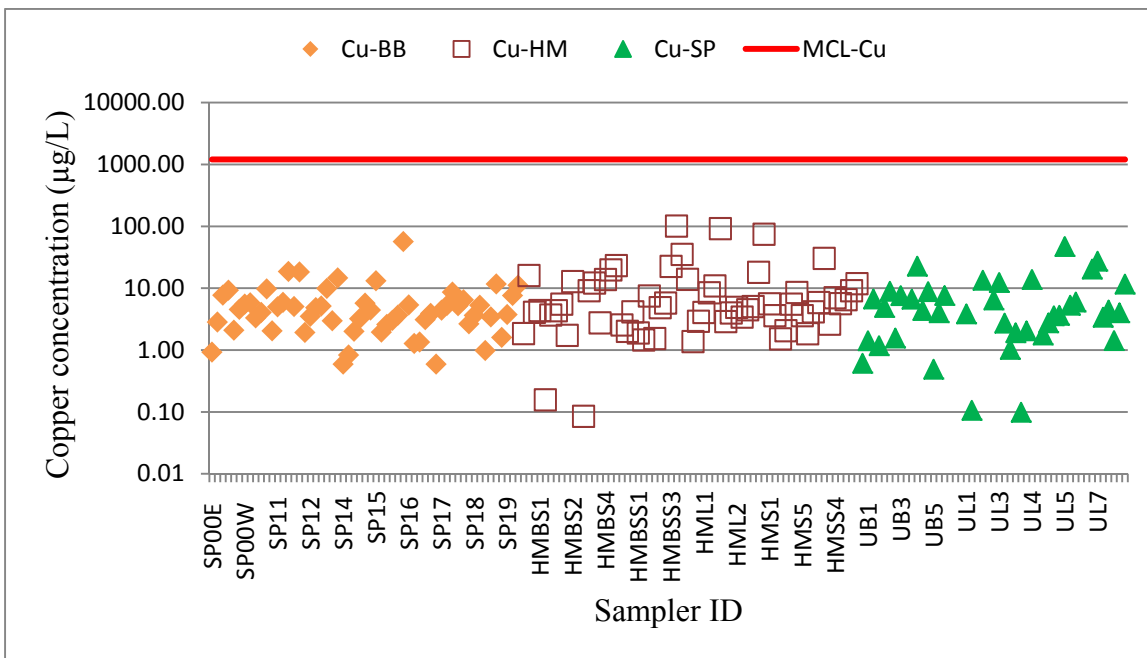
(d)



(e)



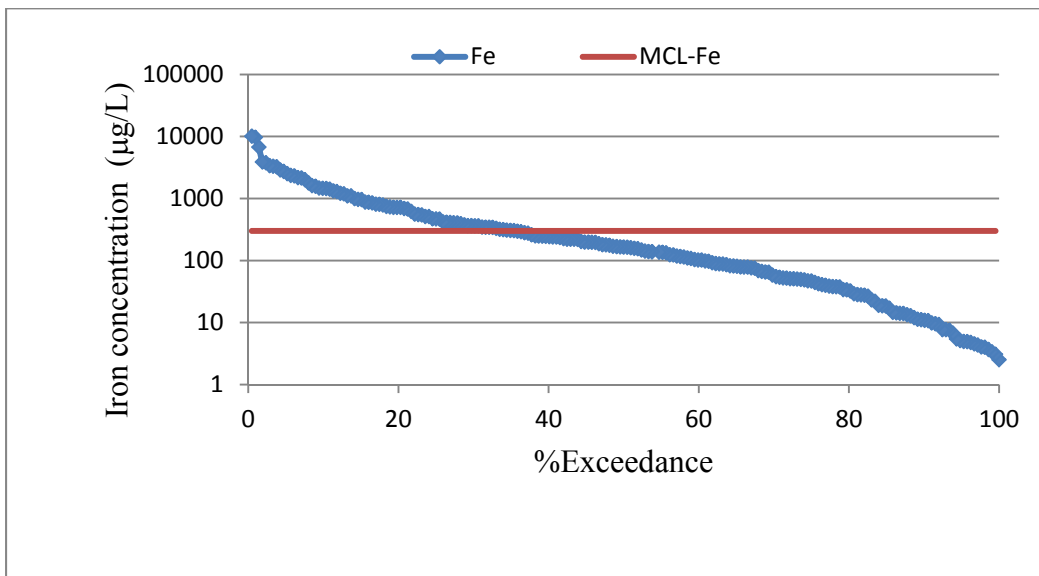
(f)



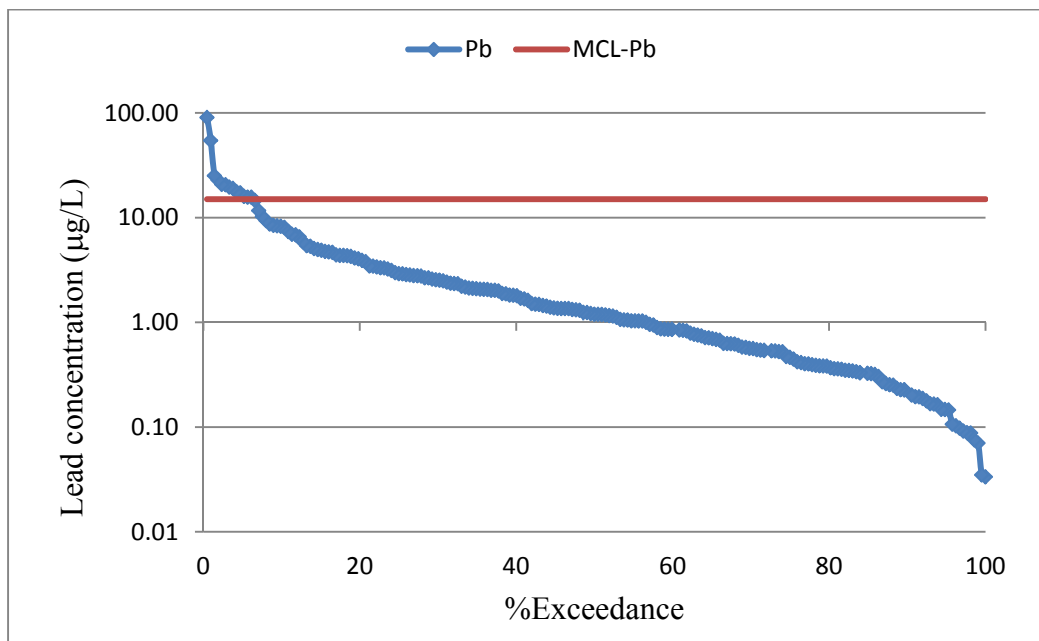
(g)

Figure 36. Concentrations for (a) iron, (b) lead, (c) cadmium, (d) chromium, (e) nickel (e), (f) zinc and (g) copper in water samples from the three study sites. The EPA MCL value is superimposed for each metal except for iron and nickel. For iron, the given MCL is a secondary standard for aesthetic purposes set at 0.3 mg/l. There is no drinking water MCL for nickel.

Exceedance curves for two metals, iron and lead, are plotted in Figure 37. Iron concentrations exceed the EPA’s secondary standards approximately 40% of the time (Figure 37a). Concentrations of lead exceeded the MCL values at least 8% of the time (Figure 37b).



(a)



(b)

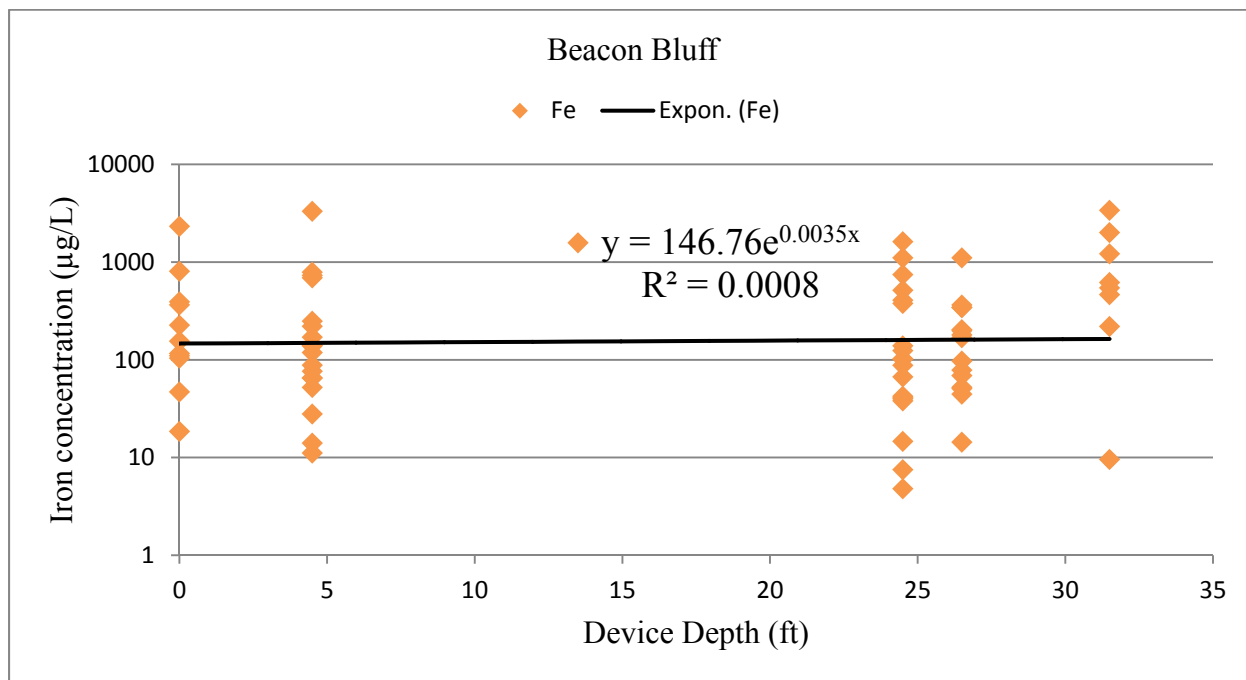
Figure 37. Percent exceedance of concentration for (a) iron and (b) lead at the three study sites, with the red line showing the EPA’s secondary (iron) and primary (lead) MCLs for drinking water.

Iron concentrations versus depth are plotted in Figure 38, with an exponential fit applied to the data. The R^2 values for the three sites are low, such that no trend with depth is apparent,

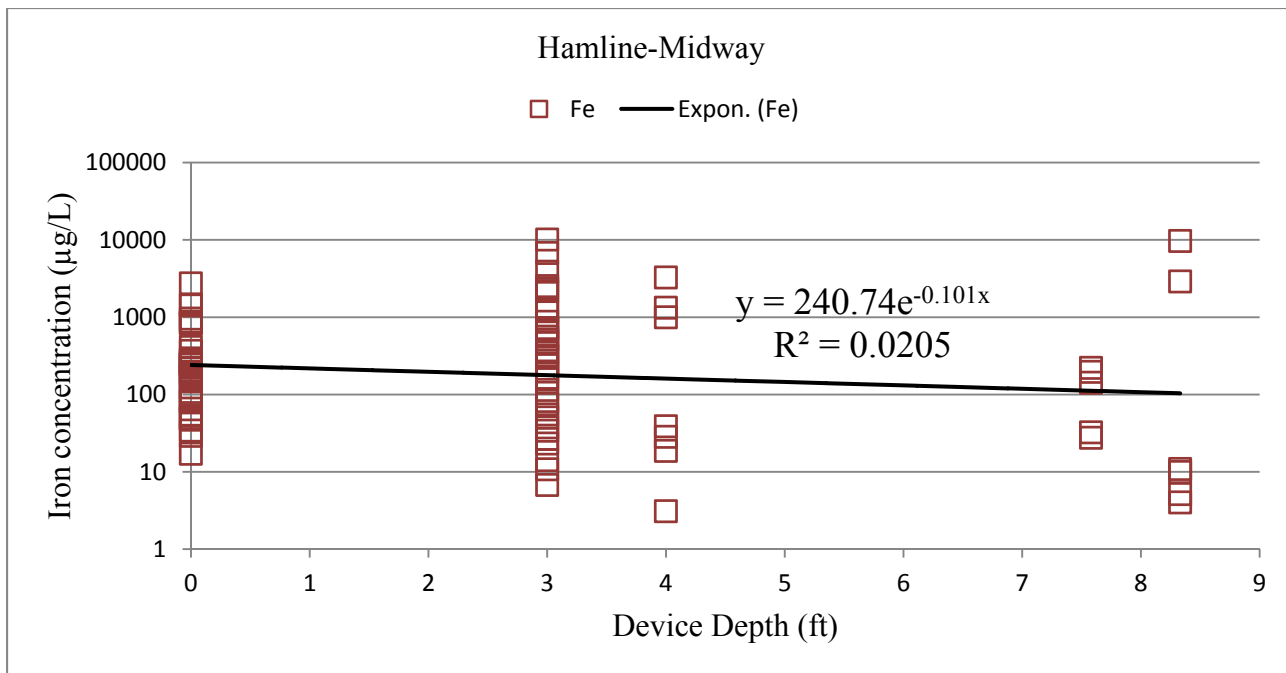
except for the Sheep Pasture. The main reason for this higher R^2 value is the wide range of iron concentrations measured in the surface runoff.

Cadmium, chromium, nickel, zinc and copper concentrations versus depth are plotted in Figure 40, Figure 41, Figure 42, Figure 43, and Figure 44, respectively, with an exponential fit applied to the data. Again, the R^2 values are low, with the exception of cadmium at the Sheep Pasture site and nickel at the Hamline-Midway and Sheep Pasture sites, where the trend is for an increase in concentration with increasing depth. This is counter-intuitive, because one would expect a decrease with depth if the media is retaining the metals. The measurements at different depths, however, are likely quantifying what remains after different pulses of stormwater move through the media. It is possible that the deep measurements represent a storm of higher runoff concentration, while the shallower measurements represent a storm with lower concentrations.

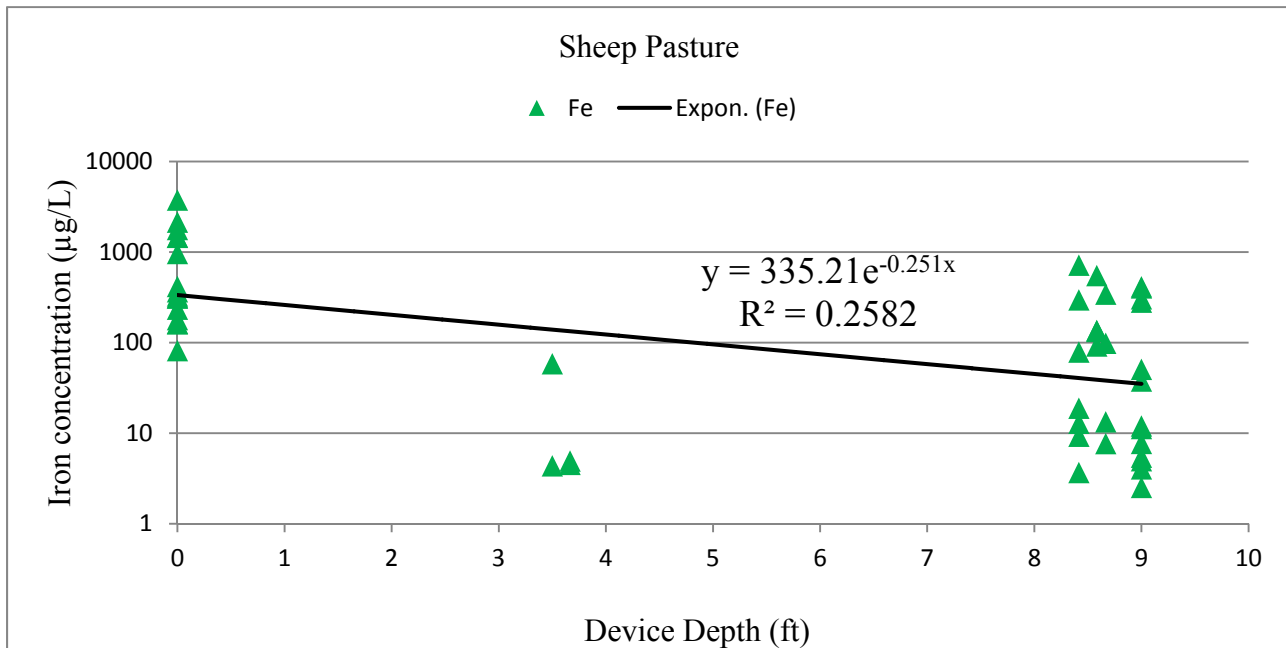
Lead concentrations versus depth are plotted in Figure 39 with an exponential fit applied to the data. Again, the R^2 values are low, with the exception of the Sheep Pasture site. The decrease in lead concentration with depth could indicate that organics in the soil surface are adsorbing the lead, but Beacon Bluff and Hamline-Midway do not show similar trends.



(a)

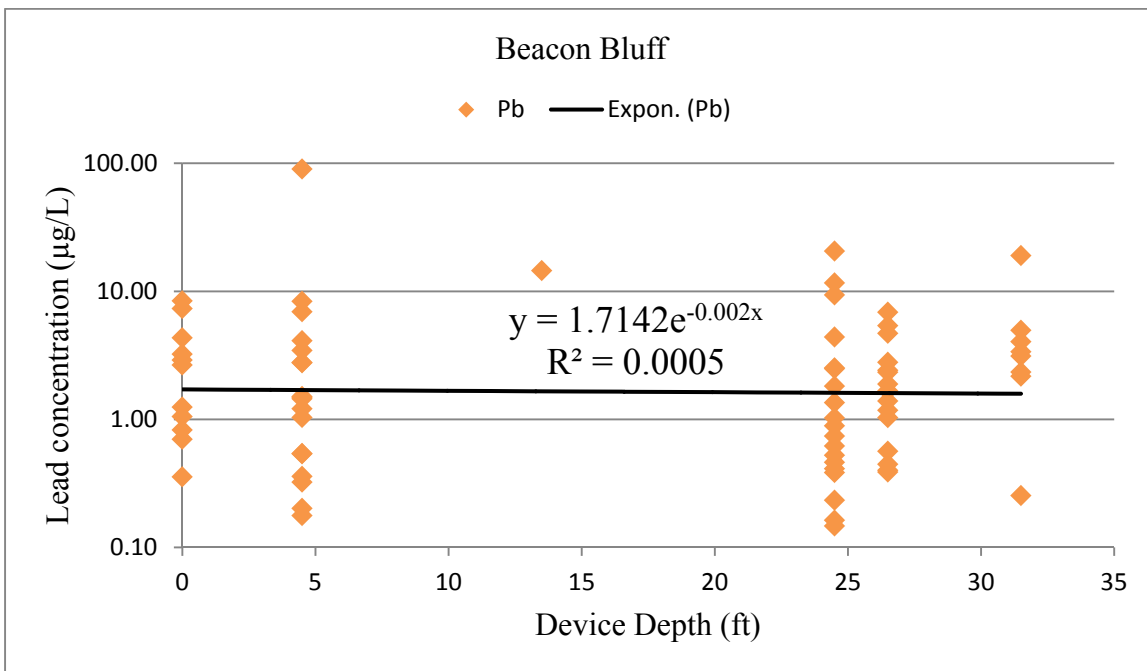


(b)

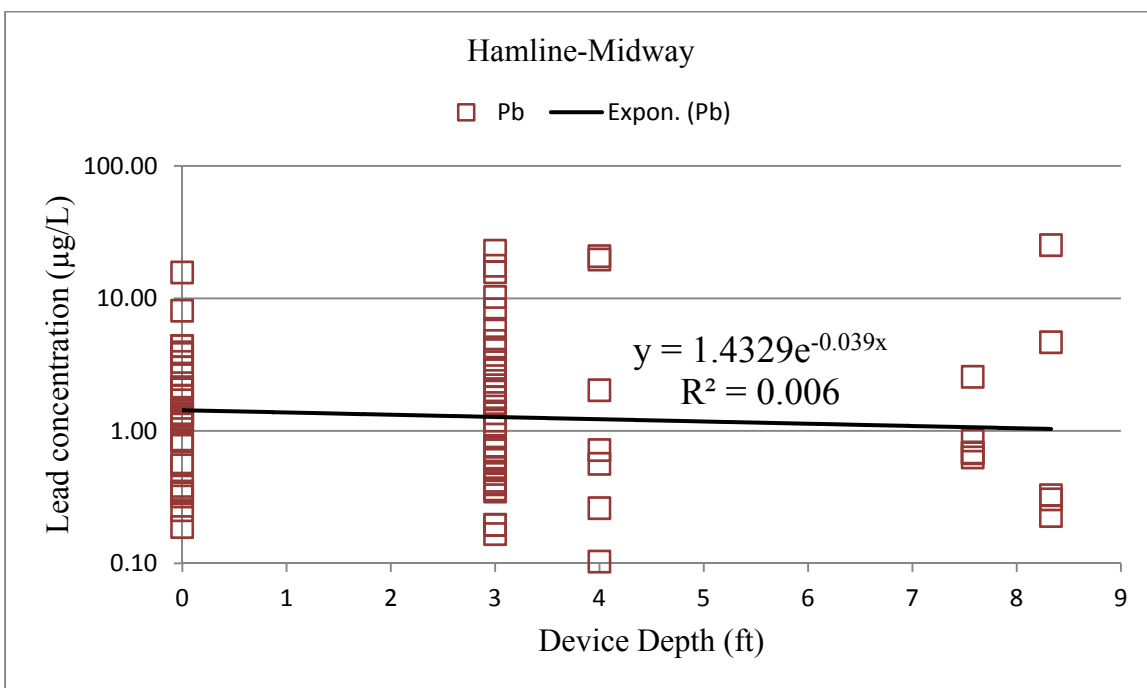


(c)

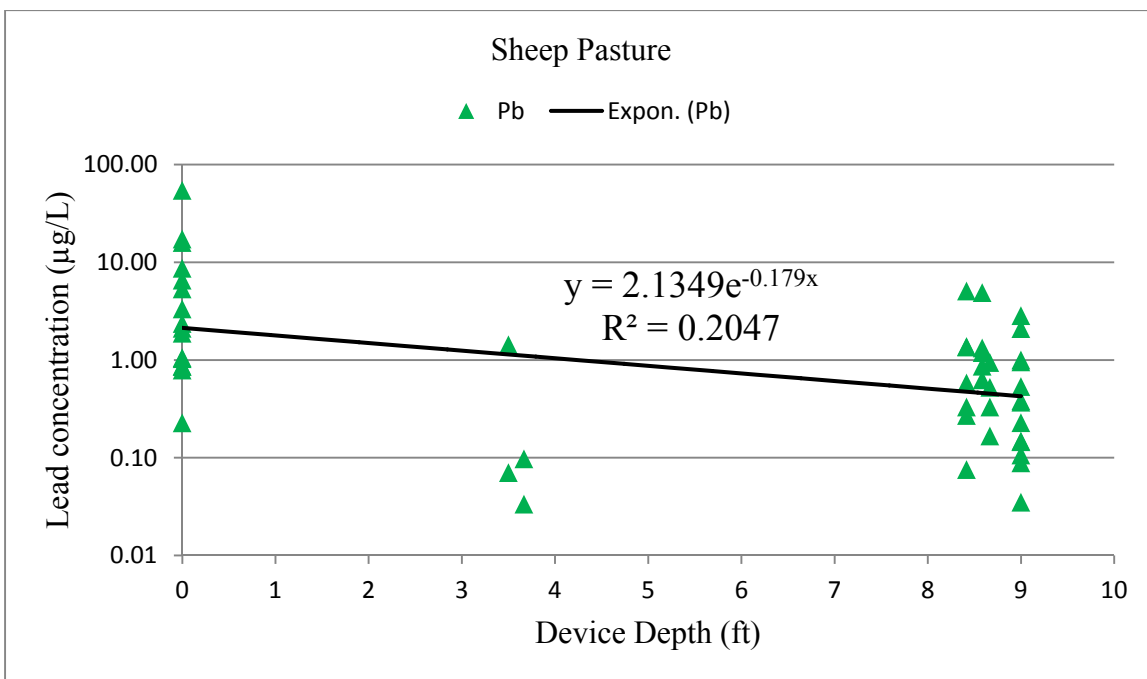
Figure 38. Plot of iron concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)

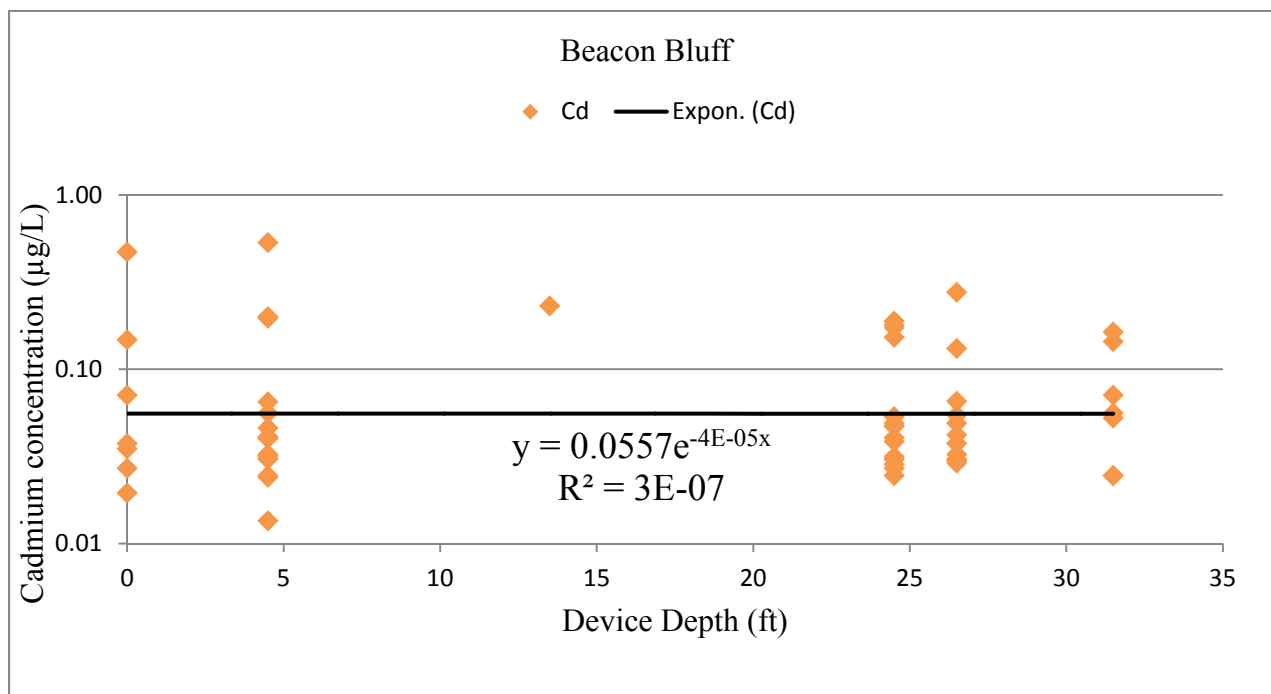


(b)

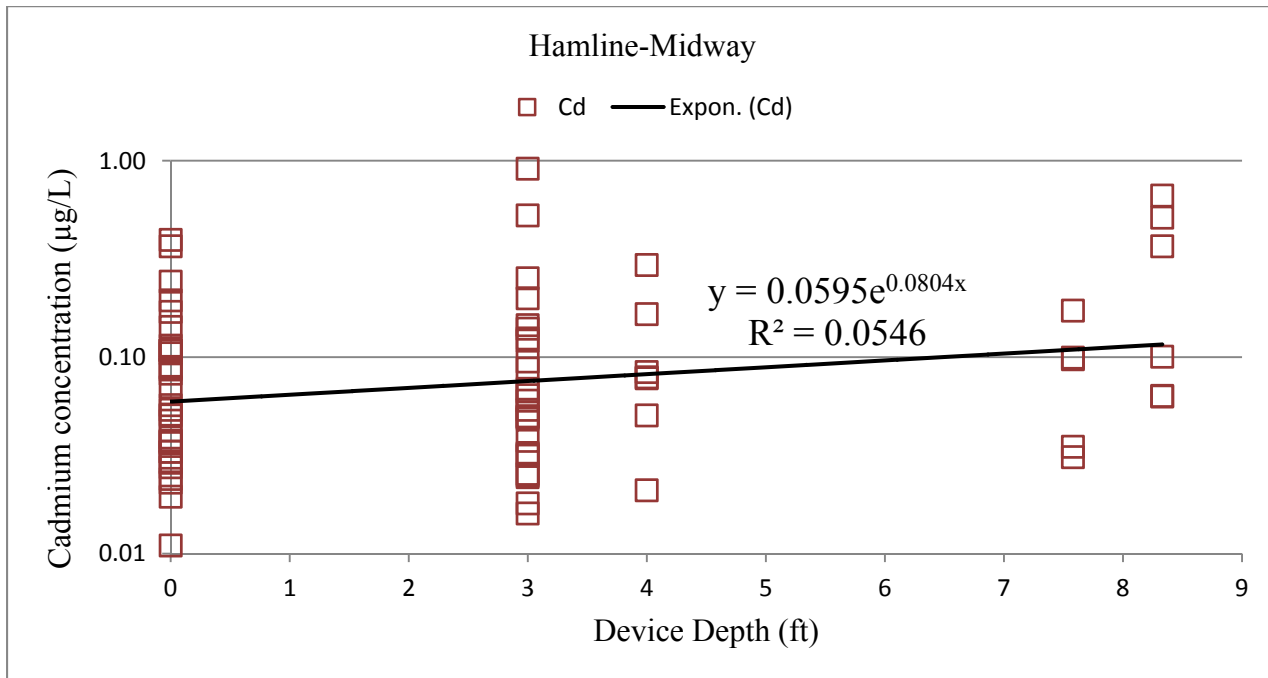


(c)

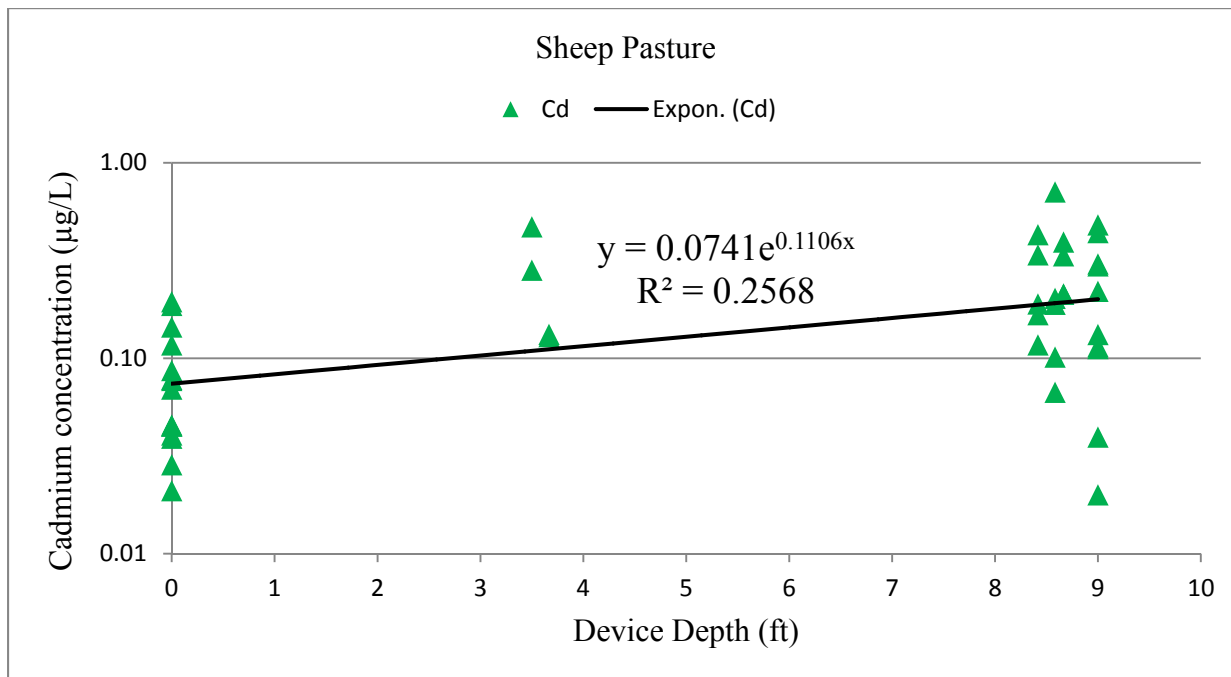
Figure 39. Plot of lead concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)

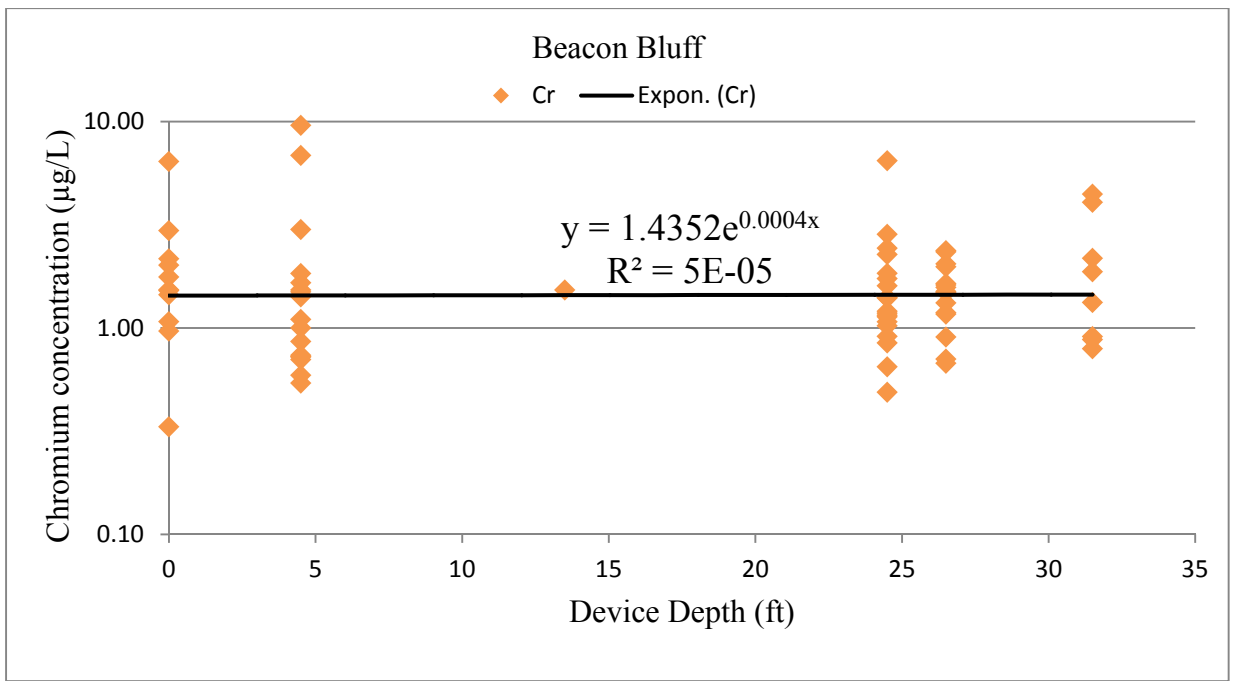


(b)

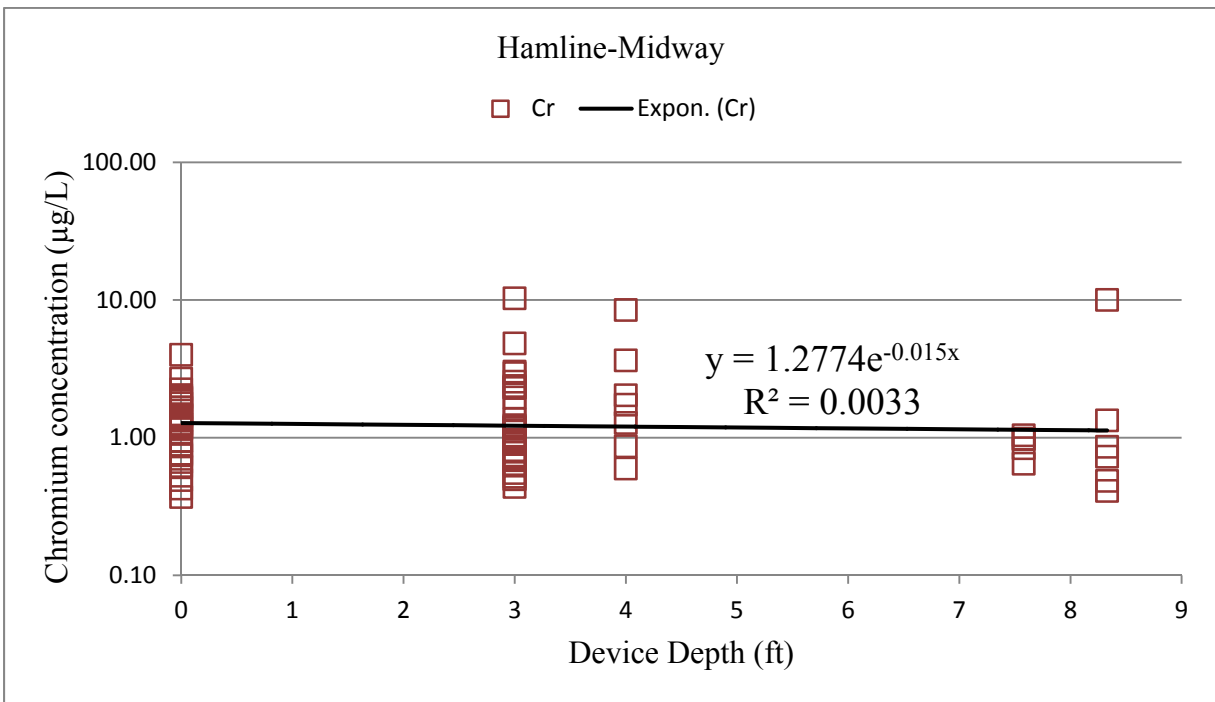


(c)

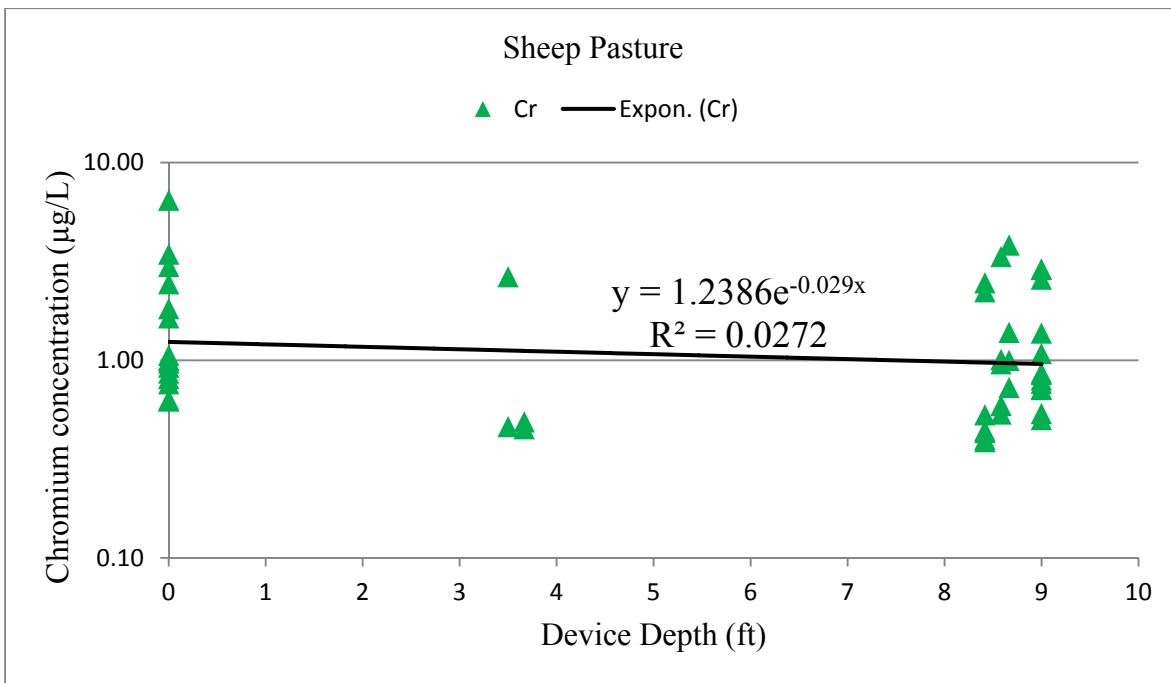
Figure 40. Plot of cadmium concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)

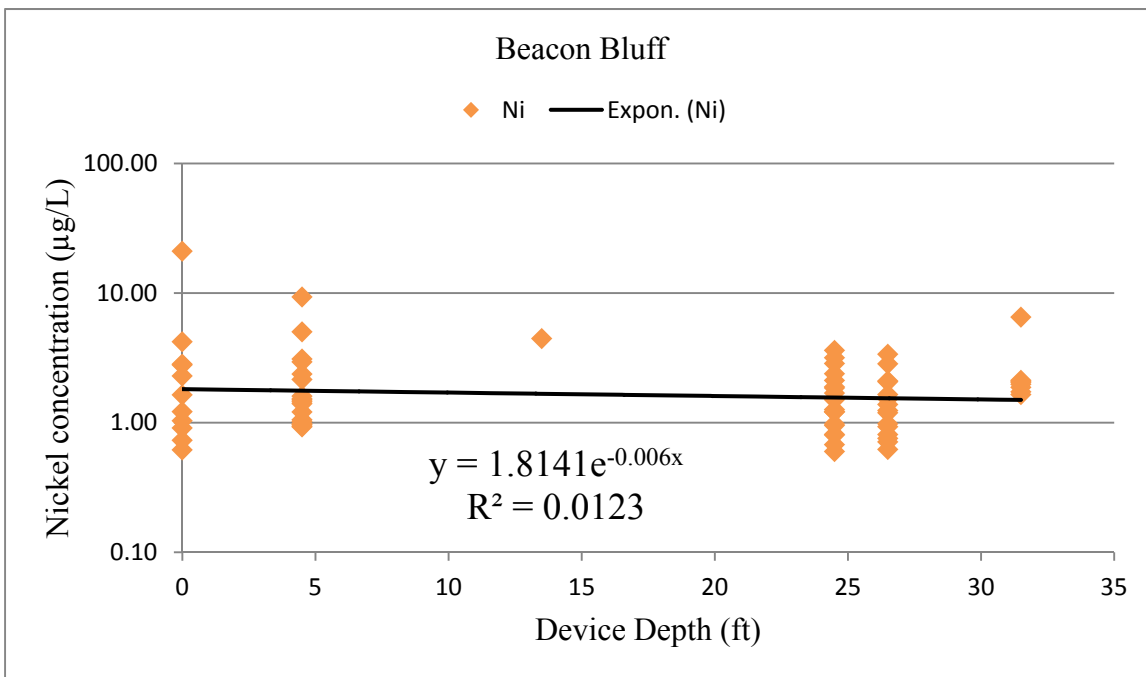


(b)

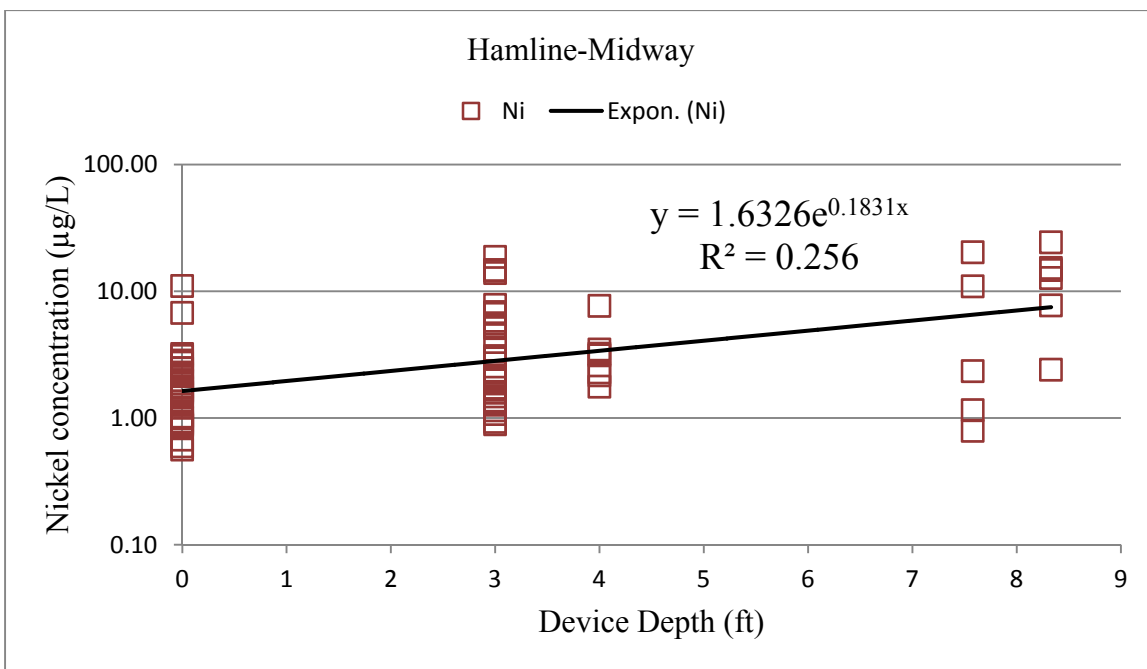


(c)

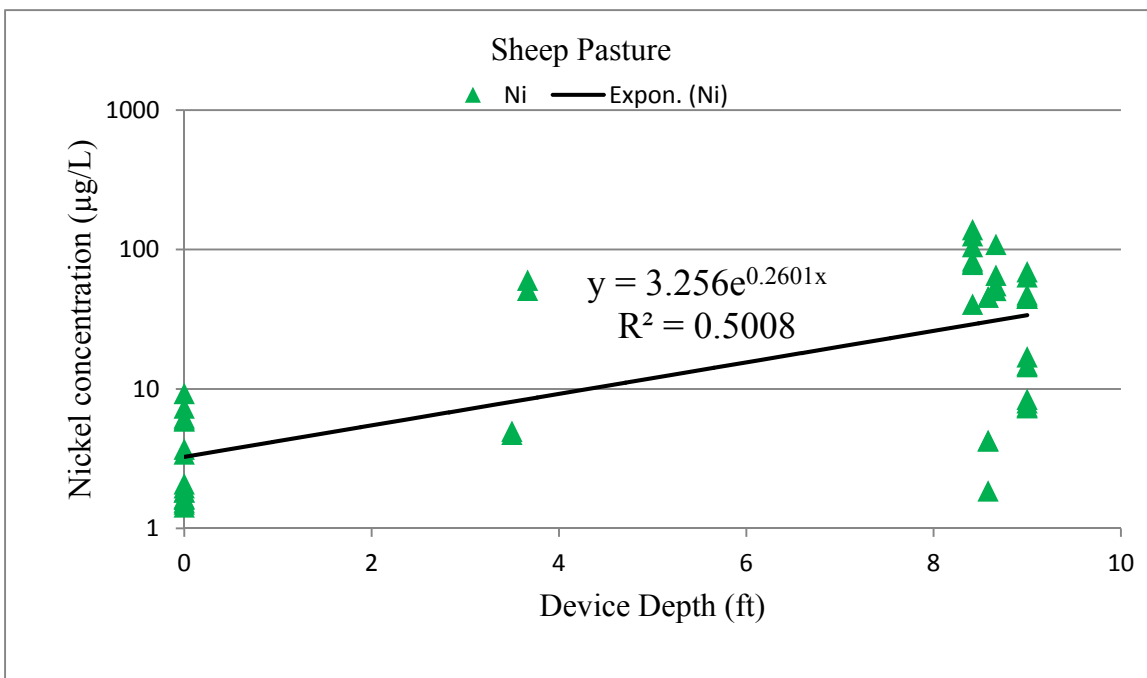
Figure 41. Plot of chromium concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)

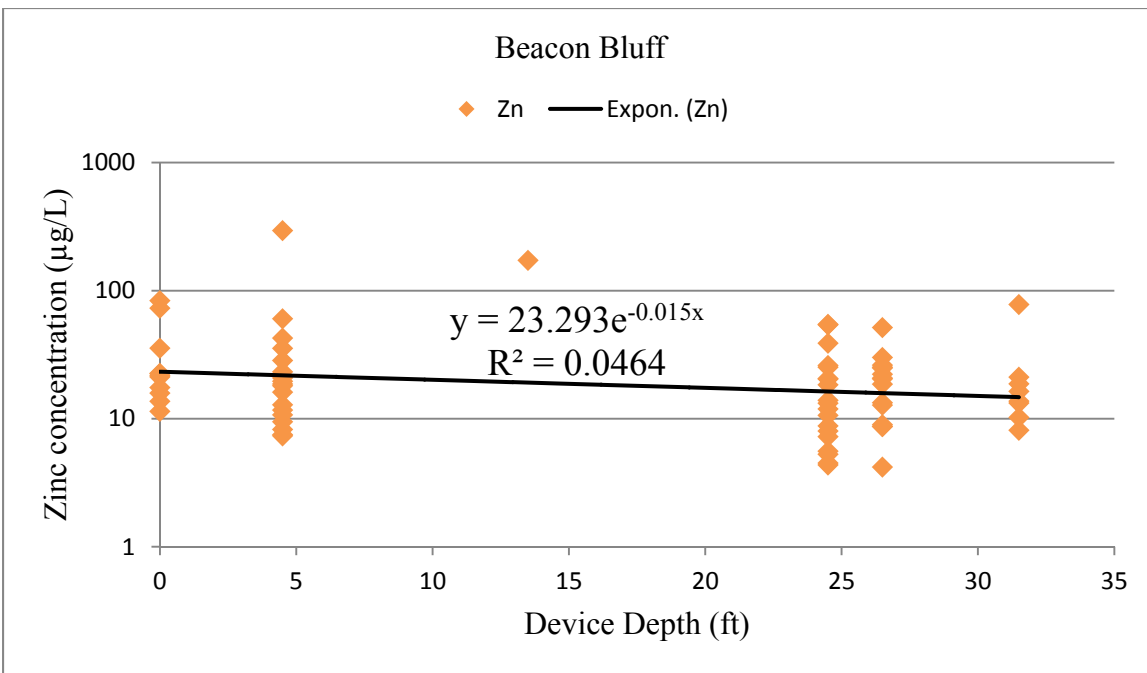


(b)

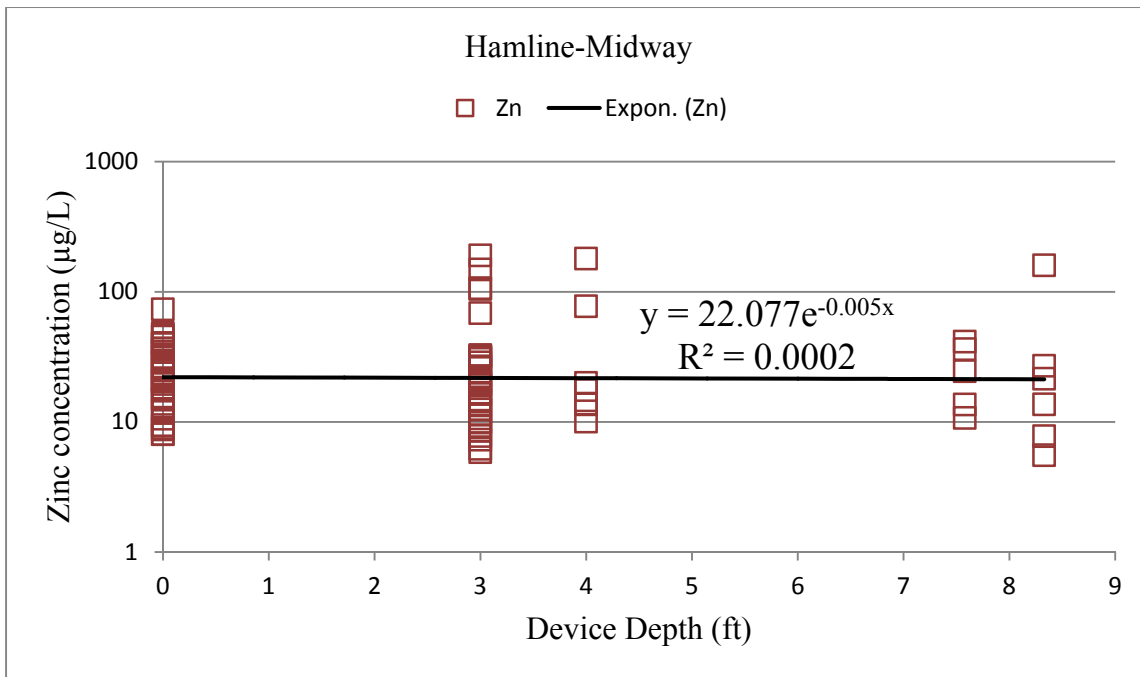


(c)

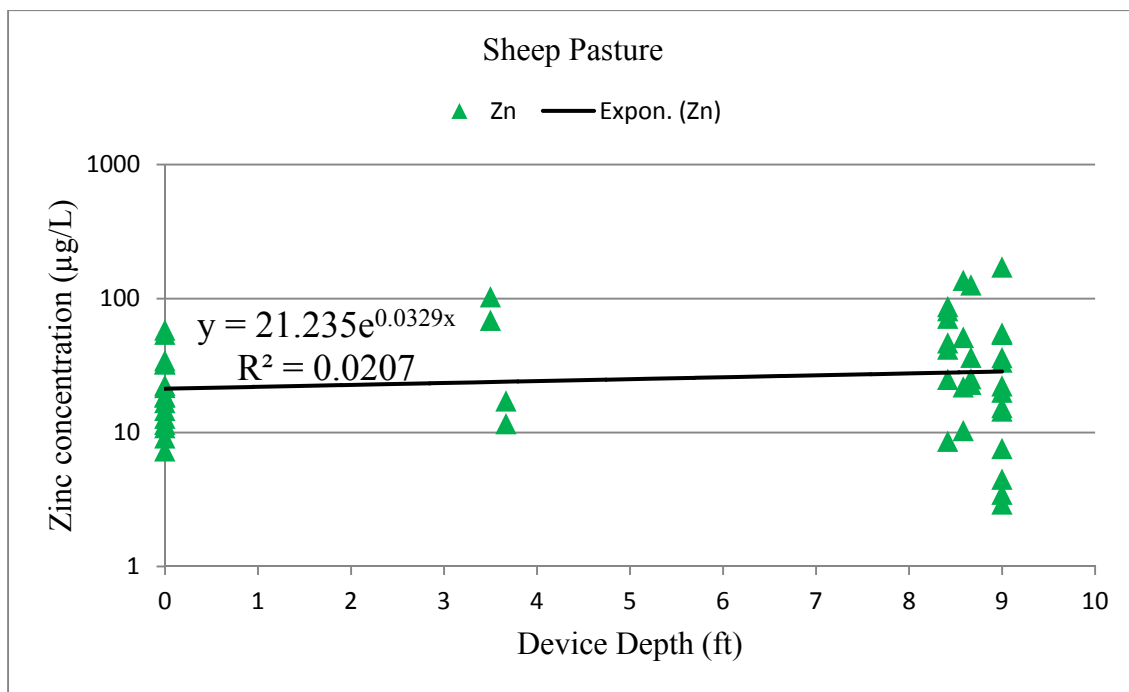
Figure 42. Plot of nickel concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)

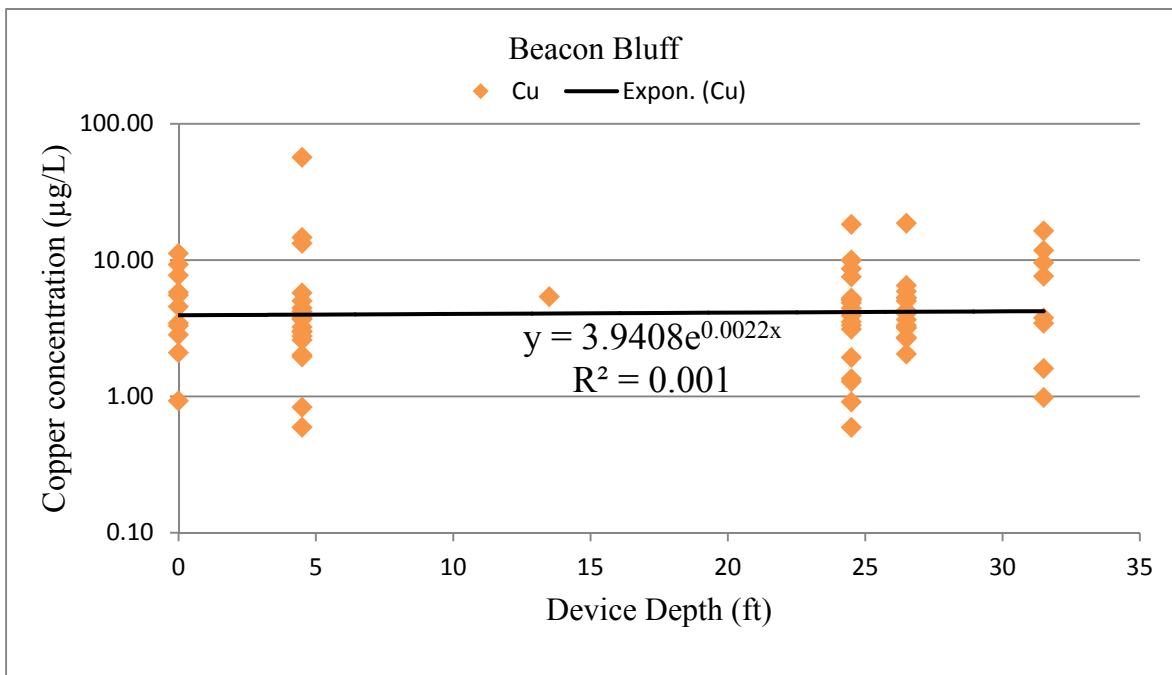


(b)

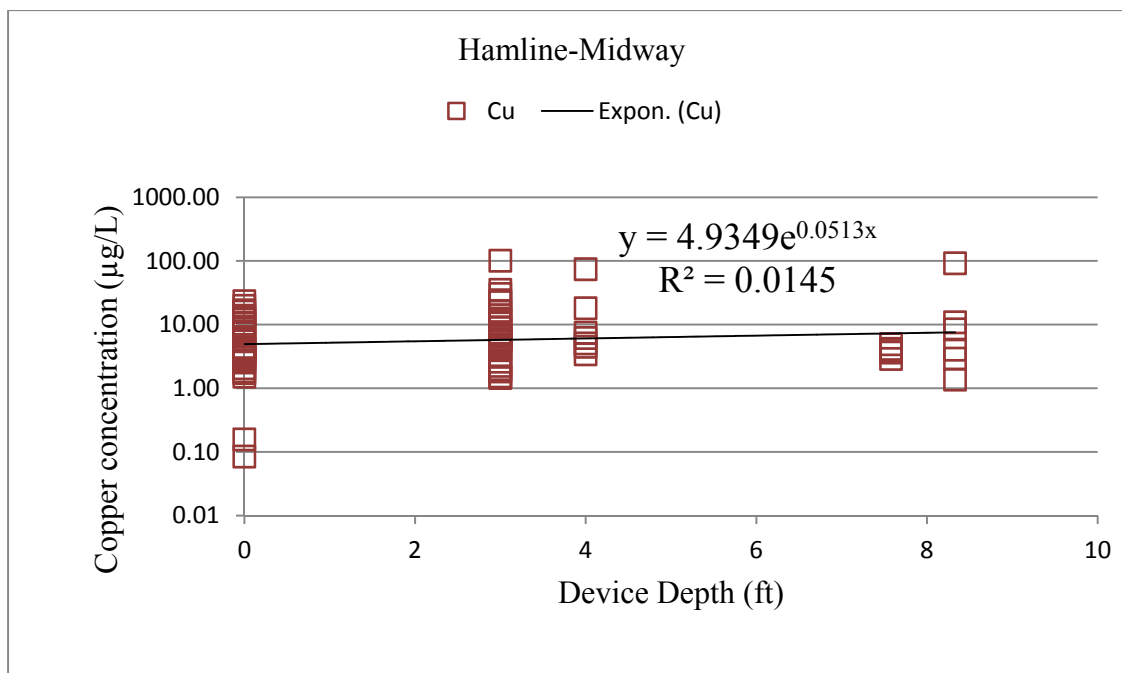


(c)

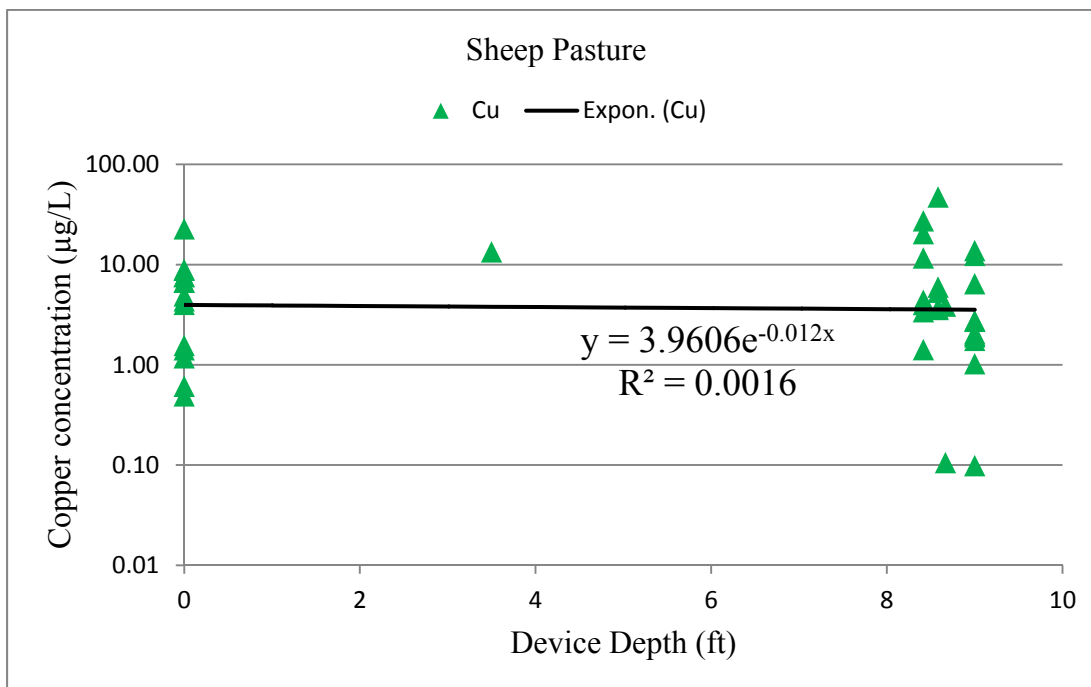
Figure 43. Plot of zinc concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.



(a)



(b)



(c)

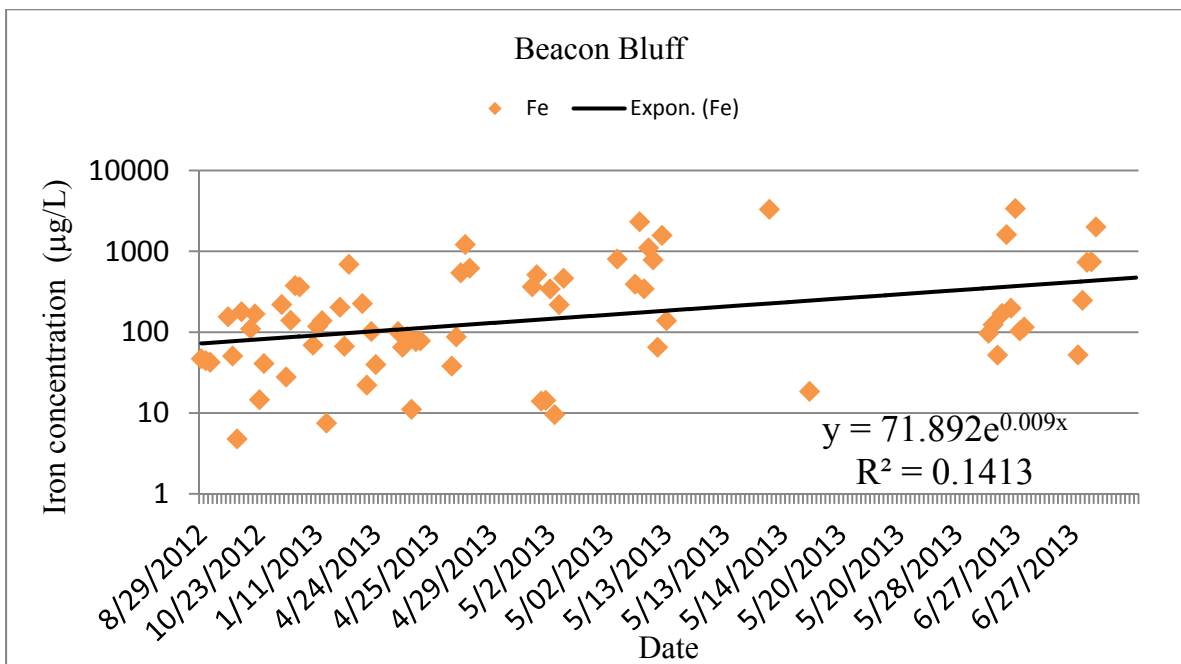
Figure 44. Plot of copper concentration as a function of sampling depth at (a) Beacon Bluff, (b) Hamline-Midway, and (c) Sheep Pasture site. An exponential best fit equation to the data is shown for each site.

The iron and lead concentrations are plotted versus time of the year for all three sites in Figure 45 and Figure 46. There does appear to be a period in mid-May when iron concentration at the three sites was high. A similar trend is not observed for lead concentrations.

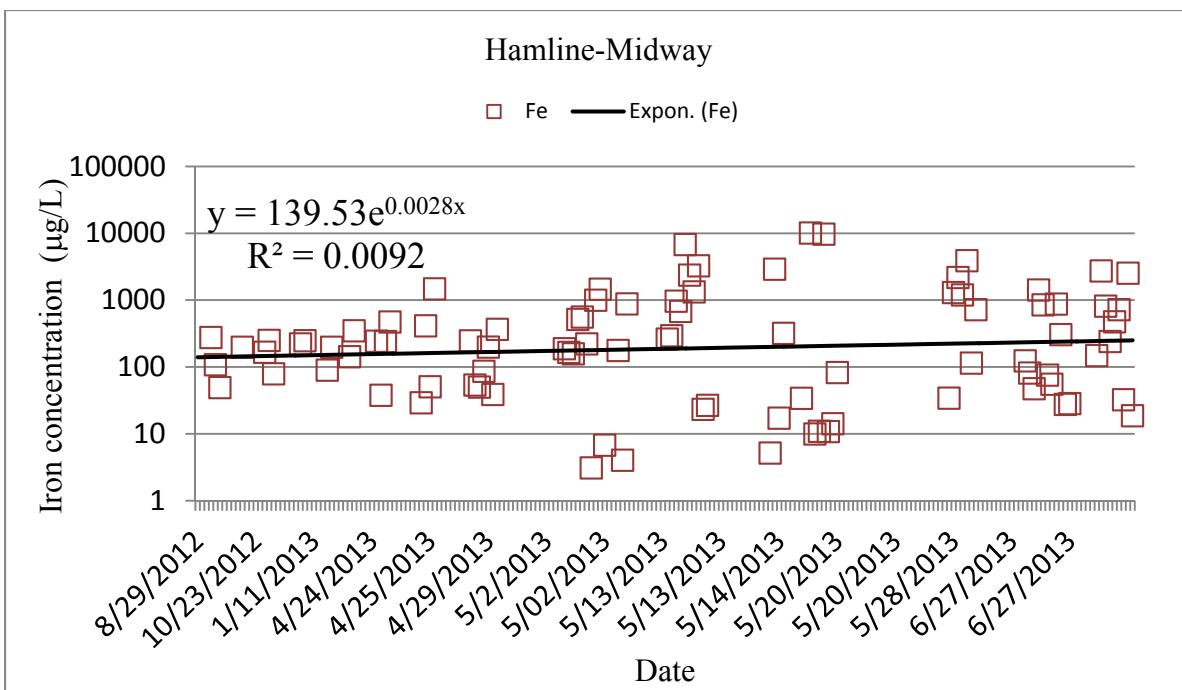
Total Petroleum Hydrocarbons

Water samples from the Beacon Bluff site were analyzed for total petroleum hydrocarbons (TPH). As shown in Figure 47, the measured TPH concentrations range from 0 mg/L to 58 mg/L. The values measured in the surface water samples (SP00E and SP00W) were 2.8 to 3.8 mg/L in the May 2013 sampling event, while they were 24 to 58 mg/L in the June sampling event. Insufficient samples were collected to be able to determine whether there is a seasonal trend in the influent TPH concentrations.

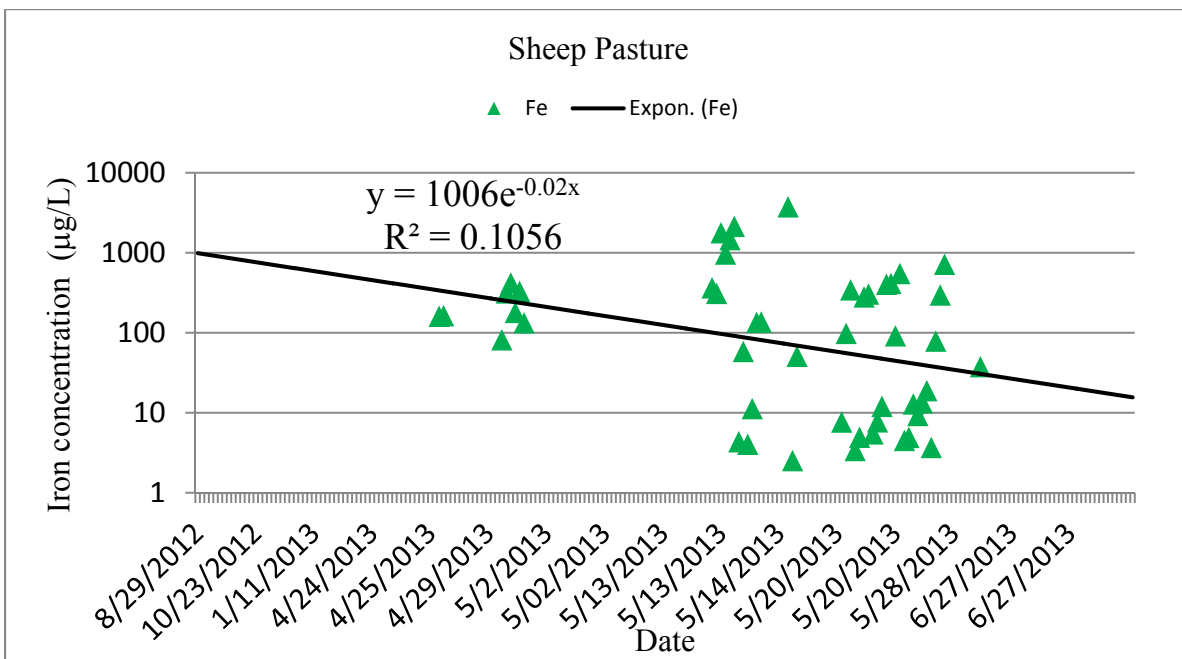
The TPH concentrations in the subsurface were larger than the surface concentrations in many of the cases. It is not possible to determine the relation between the concentrations occurring at the surface and the concentrations at depth. A sequence of measurements over a period of time for the different depths would be necessary to determine the amount of attenuation, if any, that occurs within the treatment system.



(a)

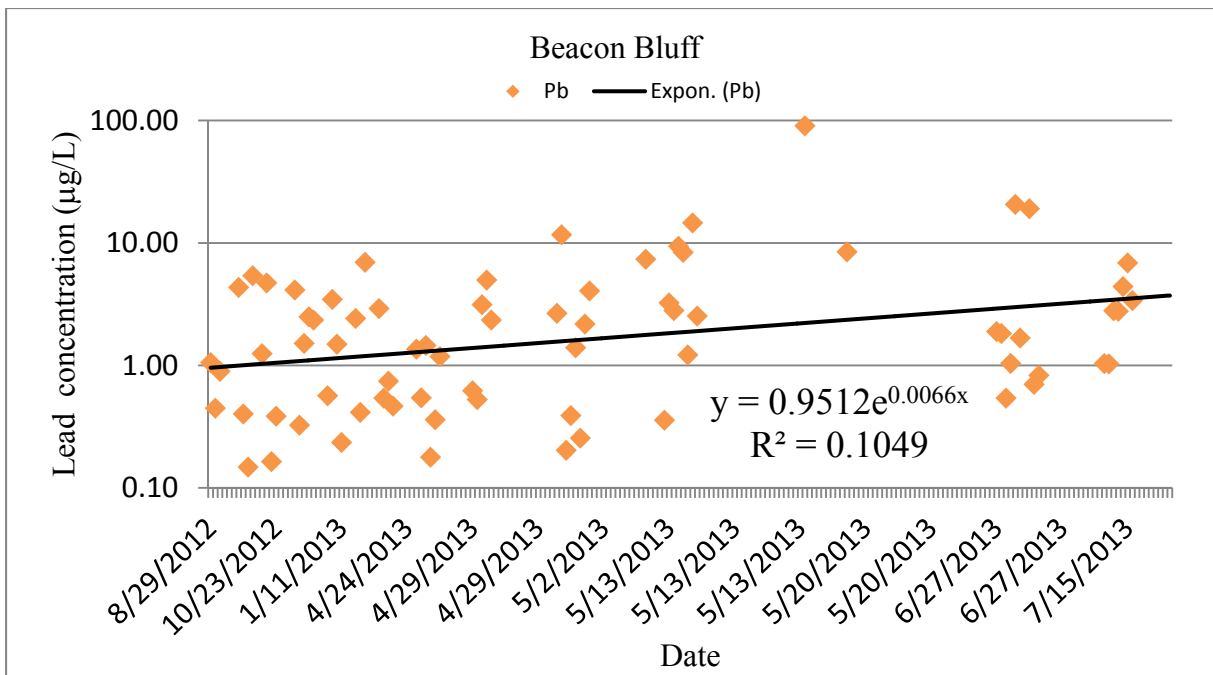


(b)

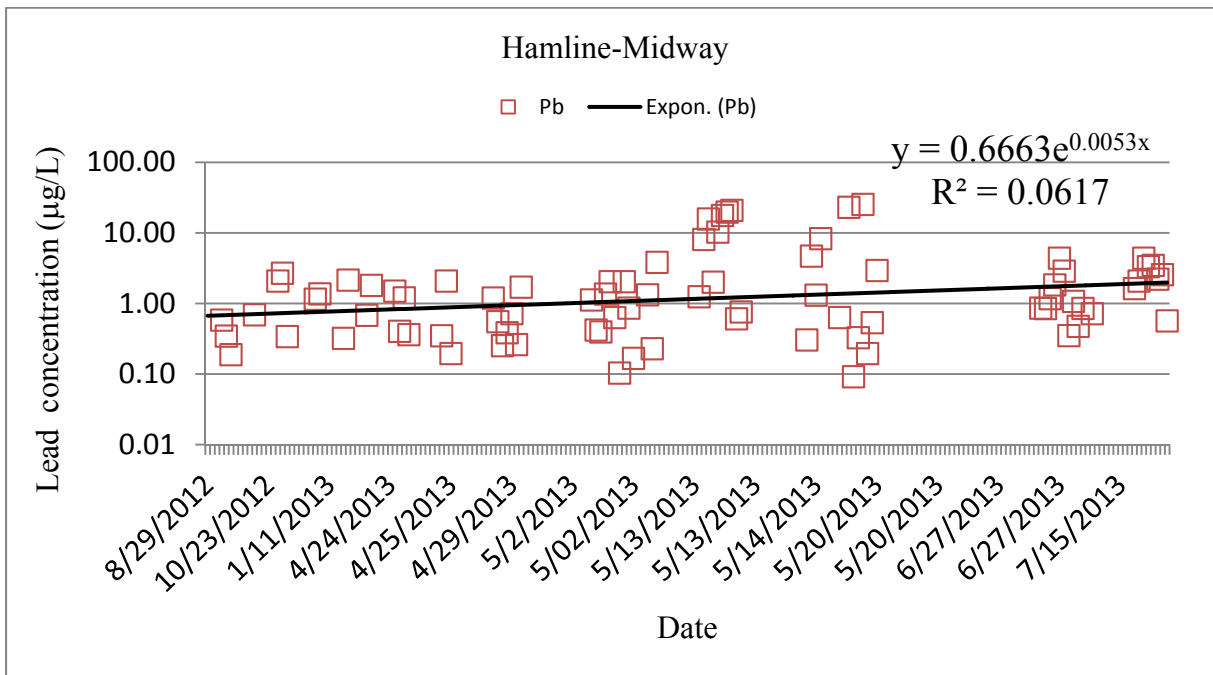


(c)

Figure 45. Temporal trends for iron concentration at the (a) Beacon Bluff, (b) Hamline-Midway and (c) Sheep Pasture sites. An exponential best fit equation to the data is shown for each site.



(a)



(b)

Conclusions

Many advances in the understanding and treatment of stormwater runoff have been realized since the U.S. EPA first published results of the National Urban Runoff Program in 1983 (U.S. EPA 1983). Many of these advances with regard to the impact of infiltrated water on groundwater quality are discussed in the literature review (section 2). Although there is no guarantee with regard to stormwater, the research to date indicates the following:

1. A surface-oriented practice, such as a bioinfiltration facility, swale, filter strip, infiltration basin, etc. has the capacity to capture contaminants on the soil or infiltration media. These contaminants include dissolved metals and petroleum hydrocarbons. There is evidence that captured petroleum hydrocarbons will be degraded by the bacteria surrounding plant roots. Metals will need to be eventually harvested. The capacity of soil organic compounds to retain metals, however, is substantial.
2. The soil or media through which stormwater is infiltrated can filter infiltrated pathogens and suspended solids. This may not be true of viruses, which are currently a concern in drinking water aquifers due to leakage from sanitary sewers and septic tanks.
3. Evidence from the literature and these three study sites is that nitrate and phosphorus contamination of infiltrating stormwater is not of concern. Nitrate in urban runoff is typically at low concentrations (median of 0.6 mg/L, Maestre and Pitt, 2005) relative to the drinking water MCL of 10 mg/L, such that it is unlikely that stormwater could be the cause of high nitrate concentration in drinking water. At the three study sites, only 4% of the measured nitrate concentrations were above the drinking water MCL of 10 mg/L. Phosphorus is only of concern when the groundwater becomes surface water, and the ecoregion criterion is applied.
4. Dissolved metals and petroleum hydrocarbons can be adsorbed to organic compounds in the soil, and metals associated with particulates are filtered by the soil.
5. Sub-surface infiltration systems store water underground and allow the infiltration process to begin beneath the soil surface. This means that the retention of contaminants by soil may not occur. Thus, metals and petroleum hydrocarbons are more likely to enter into groundwater from these infiltration systems. The attenuation of petroleum hydrocarbons at the Beacon Bluff site was inconclusive.
6. Chloride is a contaminant that has no known sinks in natural systems. Chloride is a concern for both groundwater (MCL of 250 mg/L) and surface water (chronic toxicity for aquatic biota of 300 mg/L). One sample from the Hamline-Midway site in the fall of 2012 had a measured chloride concentration above 1,500 mg/L, and measurements throughout the year were above the MCL 15% of the time. In addition, Novotny, et al. (2009) found that 77% of the chloride that is placed on surfaces remains in the Twin Cities Metropolitan watershed, and does not leave by river flow. A reduced use of salt during winter is recommended for MnDOT (where low salt practices have been implemented), city streets (where low salt practices currently are sometimes implemented), and commercial parking (where low salt practices are rarely implemented).

The following conclusions can be made from the monitoring study:

7. The primary source of chloride is salt used for management of snow and ice on streets during the winter season. However, groundwater concentrations of chloride have peaks throughout the summer and fall. While the December and January samplings of chloride were high, the highest concentration occurred in October, and some samples taken in April, May and June also had high concentrations of chloride. It appears that movement of chloride in the unsaturated zone can be slow, possibly because of water caught within the small pores of the media, such that high concentrations at a given depth can be observed at any time of the year. This may be important for the groundwater-supplied baseflow of streams, which will experience a reduction of chloride concentration over that which would be expected in spring at the expense of higher concentrations during the remainder of the year.
8. About 15% of the water samples collected/analyzed had chloride concentrations exceeding the EPA's secondary MCL for chloride in drinking water, 250 mg/L. For the samples analyzed there did not appear to be any attenuation of chloride concentration with depth. This is to be expected since chloride is a conservative chemical, which does not adsorb to soil or precipitate.
9. For the samples collected and analyzed, about 4% showed nitrate concentrations that exceed the EPA's MCL for drinking water, 10 mg/L. There did not appear to be a strong trend of nitrate concentration attenuation with depth. Nitrate is quite mobile in the subsurface, not being adsorbed to negatively charged mineral materials, so this was as expected.
10. High nitrate concentrations were found at the Sheep Pasture. The source of nitrate at this site is likely due to agricultural operations on the St. Paul Campus of the University of Minnesota, which contributes runoff to the infiltration site. For the Hamline-Midway site and the Beacons Bluff site the source of nitrate is probably lawn fertilizers, decaying organic matter on the land surface, and atmospheric deposition.
11. Total phosphorus concentrations in the stormwater runoff at all sites were between 5 and 1,400 $\mu\text{g/L}$. There are no drinking water criteria for phosphorus, but there is concern about groundwater to surface water exchange, where the surface water ecoregion criteria is 18 $\mu\text{g/L}$ for lakes and 33 $\mu\text{g/L}$ for rivers in the Twin Cities metropolitan area. Of course, leaks from water supply systems, where phosphate is used as a corrosion inhibitor, and from sanitary sewer systems also supply phosphorus to the near-surface groundwater. Sources for the phosphorus in runoff include decaying organic matter at the land surface, animal feces, and sediment bound phosphorus. No substantial trend with depth was found at the monitored field sites. Phosphate complexes with iron and aluminum oxides in the soil, so some decrease due to retention was expected with an increase in depth.
12. Concentrations of lead exceeded the EPA's MCL standards for drinking water 8% of the time. Lead is a legacy contaminant, however, slowly decreasing from high concentrations in the 1970s. Copper, nickel, cadmium, and zinc, though present in detectable

concentrations in the water samples, were all far below the EPA MCL standards for drinking water. However, attenuation with depth below the surface was not consistently observed across the sites. This could be due to the randomness inherent in monitoring urban runoff and the unsaturated zone, but it is not what has been found in laboratory column studies. Organics in soil, in particular, have been found to have a large capacity to adsorb metals (Paus, et al 2013, 2014a, 2014b). Beacon Bluff may not have high attenuation because of a lack of organics in the underground infiltration system. If potential metal pollution of groundwater at underground infiltration sites were a concern, one possible remediation would be to place soil of high organic content around the base of the infiltration chambers to capture these metals.

13. The concentrations of TPH in the surface water samples collected from the Beacons Bluff site ranged from 2 mg/L to 59 mg/L. Analysis of samples collected from the barrel samplers as deep as 32 feet showed concentrations as high as 30 mg/L. The number of samples collected at the site for TPH analysis was limited and at the present time it is not possible to determine the degree of TPH attenuation. Studies of hydrocarbons in column studies with rain garden media with a high organic content have shown substantial attenuation (LeFevre, et. al 2012a). However, this might not be the case at the Beacon Bluff site if there is a lack of organic compounds in the treatment system.

Knowledge Gaps

It is evident that there remain areas in which the understanding of stormwater, its contaminants, and their fate and treatment is limited. Further research into these areas, or knowledge gaps, is key to the continued and increased protection of groundwater. Knowledge gaps identified are listed below.

1. Soil has a finite capacity with regards to retaining contaminants and, at some point, contaminant transport will continue farther into the soil. When will this breakthrough occur, how can it be most cost-effectively modeled, and how can maintenance in these situations be performed in the most cost-effective manner?
2. Sub-surface infiltration systems store water underground and allow the infiltration process to begin beneath the soil surface. What impact does this have on the retention of contaminants by the soil, and how much does this increase the risk of groundwater contamination? Column studies with a media of different types of soil and aquifer rock are recommended to establish the attenuation of dissolved metals and petroleum hydrocarbons in these media.
3. How much of a threat does chloride, which is applied to roadways as a de-icing agent in cold climates, pose to surface and groundwaters and, correspondingly, how can that threat be optimally managed?
4. Iron Cyanide anti-caking agents are often used with de-icing agents applied to roadways. These anti-caking agents lead to the presence of HCN and CN^- in runoff. The fate of each has not been determined with certainty. For example, HCN is assumed to volatilize upon

application but no research has confirmed the accuracy of this assumption. What fraction of HCN volatilizes, how quickly, and what are the important variables that affect the fate of HCN? What is the fate of CN^{-1} and what is its impact on water quality?

5. The monitoring of three field sites in the metropolitan area did not find a substantial decrease in the concentration of metals and phosphorus with depth. It is believed that some metals, such as lead, would decrease in concentration as they moved through the soil because they have a high affinity for soils. Our hypothesis is that the soil media stores substantial water and constituents in its pores, and samples taken at different depths are not associated with the same portion of the storm or even the same storm. This hypothesis needs to be tested in the laboratory and the field.

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Appendix A. Installation and Sampling Protocols

This appendix describes the procedures for installation of samplers, collection of samples, sample treatment and storage, and methods of laboratory analyses

Equipment

Materials. The following apparatus/equipment were acquired and applied in collection of critical data for the project: Suction Sampler (Decagon Device Inc., Cat. No. SPE20)

- Silica PowderDistilled water
- Soil Auger
- Rock picker
- Plastic sheeting
- Site marker
- GPS
- Gloves
- Tape measure
- SAKRETE Tube (10 in. x 48 in.) for Concrete – purchased from Home Depot



Figure A.1. Backfilling the hole during installation of the SPE20 sampler (white PVC used to protect the device during backfilling rocks at the Hamline-Midway site).

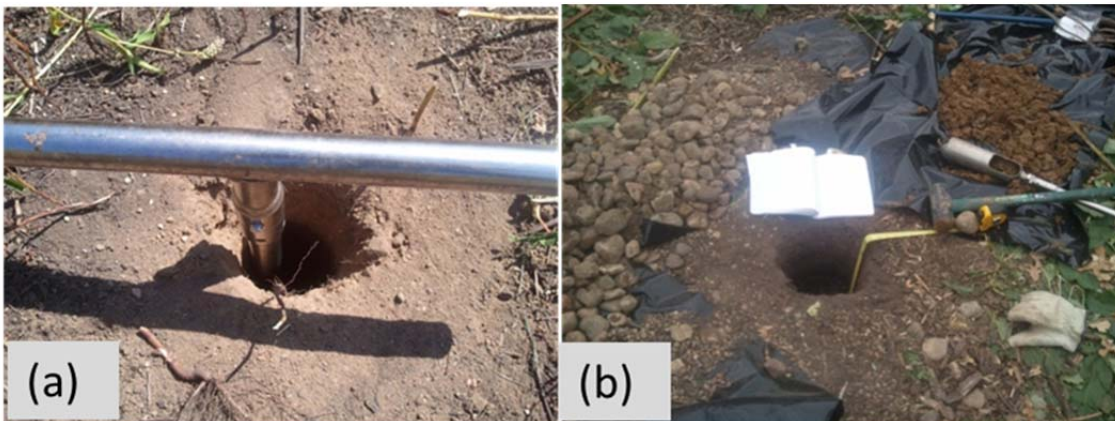


Figure A.2. A completed hole ready for installation of sampler, and (b) Completed auger hole with backfill material placed in separated piles from different depths.

Installing Lysimeters (suction samplers)

Lysimeters used for extraction of samples of seepage water were installed at predetermined depths in the selected study sites (Hamline-Midway rain garden, and the Sheep Pasture infiltration Basin, University of Minnesota), enabling collection of water samples through application of vacuum in the sampler closed system.

1. Using a soil auger or a post hole digger, auger a hole to the desired depth. Arrange the soil material from the hole on a plastic sheet sequentially in the order it was removed. Record notes describing site characteristics including soil color and texture of the profiles (record depths at which changes in the soil profile are observed). Record the final sampler installation depth.

(**Make note of when soil became wet and when/if you hit the water table!)

2. Lower the lysimeters into the borehole with the porous cup end down and the extra length of connecting Teflon tubing extending above the ground surface. Prepare a silica powder slurry to be poured into the

augered hole to a depth sufficient to completely submerge the porous cup section of the sampler. The Silica powder slurry should be prepared by adding distilled water (not regular tap water) in approximately 2:1 (powder: water ratio) then mixing well. Pour the slurry into the borehole, then lower the sampler (with the porous cup first into the hole), working the porous cup section until it is well embedded in the silica slurry at the bottom of the hole. Hold the sampler upright and well centered in the hole for two to three minutes to allow the slurry to settle bottom, then complete the installation by carefully refilling the hole around the sampler with the same soil removed during augering. You may also start backfilling with fine sandy soil for better contact between the porous cup and the silica slurry. Subsequent backfill material should be added in small loose amounts to avoid clogging the hole and leaving unfilled gaps around the sampler casing. Avoid waiting too long before completing backfilling as the slurry dries up breaking established contact between the cup and slurry if moved during backfilling.

3. Protect the sampler tubing extending above the ground housing it in a PVC pipe placed in the installation hole with the tubing inside the pipe, tucking the piping firmly in the ground. This extra length of sampler tubing will be safe in the pvc piping from damage by animals (gnawing), human activity, or equipment. Make enough tubing length can be retracted out of the PVC pipe for connection to the sampling bottle placed on the ground during sampling.
4. Attach a weather proved/resistant label to the PVC pipe for identifying each sampler
5. Using GPS unit, record coordinate locations at each device.
6. Inform land owner (provide map) of device locations.
7. Generate visuals of site cross-sections including depths of each device and soil profiles

Installation of the sub-surface sampling bottles (Hamline-midway site)

1. The site has a 12-inch thick layer of potting material overlying a gravel and rock layer. This rocky layer is underlain, at around 3.5 ft depth, with a clayey layer.
2. Auger a 10-inch hole until you expose the clayey layer; keep material from the different depths separate on a plastic sheet. Using a 2-inch auger, prepare a hole in the exposed clayey layer to 8-inch depth to hold the bottle sampler (Figure 1).
3. Wrap the sampler in permeable fabric, then insert a 1-inch diameter pvc tube which will provide access of water collecting in the bottle sampler. The fabric material over the mouth of the sampler must be sturdy enough to hold soil and rock from tearing and falling into the bottle.
4. Carefully re-fill hole(s), starting with that removed last.

Installing surface cup samplers (Installed both at the Sheep Pasture and Hamline-midway sites)

1. Auger a 2-inch hole to 8-inches depth.
2. Push the bottle sampler (which will fit snugly in this hole); with the top rim of the sampler will be flush with the ground surface.

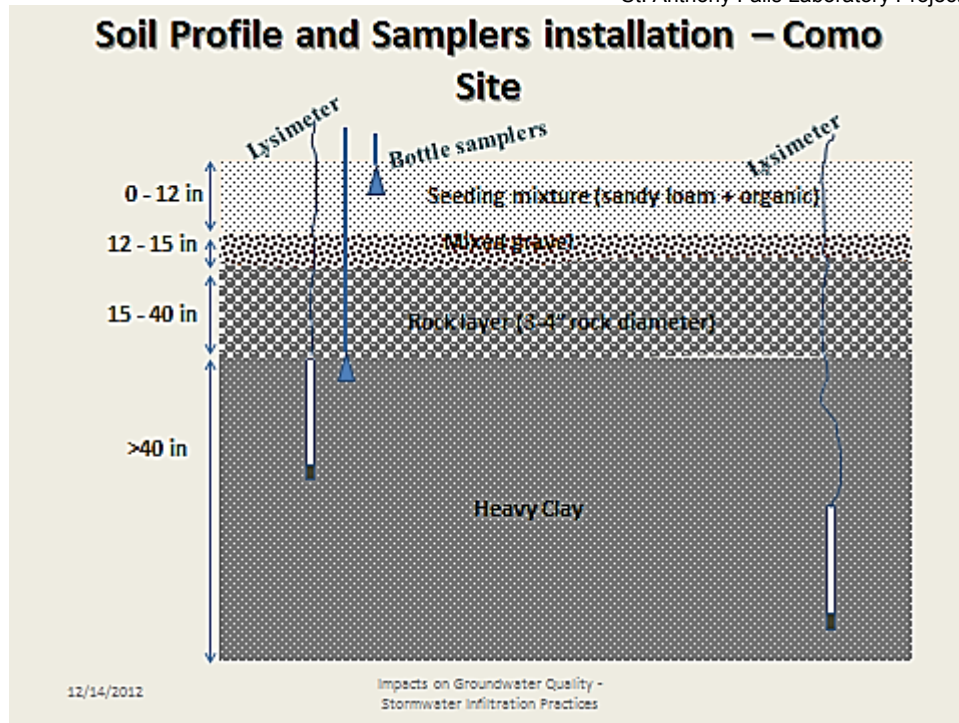


Figure A.3. Cross-section view of the Hamline-Midway rain garden site showing sampling equipment installed

Procedures for sample collection, storage, and submission for analyses

Equipment

- Hand pump
- Submersible pump
- Fully charged car battery (marine type)
- Well water concentration metering tape
- Distilled water (2 gallons each for Beacon Bluff and Hamline-Midway sites)
- 15ml sample bottles and 10 1000ml sample bottles (for hydrocarbons analysis)

Sampling procedures

Preparing for sampling:

- Sample holders (bottles or vials) and sampling equipment need to be cleaned and sterilized prior to going out for sample collection.
- Soak all sampling bottles and sample holding bottles/vials in warm soapy water; wash carefully until visibly clean then thoroughly rinse. Rinse them in hydrochloric acid, then rinse in distilled water.
- Labeling bottles/vials appropriately before leaving for the field minimizes possible sample labeling errors.

Beacon Bluff: (Located at 949 Wells Street, St. Paul MN 55106)

At least one day prior to going to the site, send an email message informing Sewer Maintenance (PW-SewerDispatch@stpaul.gov) and Sewer Design (Aaron Hass to aaron.hass@ci.stpaul.mn.us) of the intended work; include dates and time you will be at the site. It is a good idea to go with a copy of the City of St. Paul permit (Permit #12-214647) to the site incase required to show prove of permission to work at the site.

1. Locate the device to be sampled. Confirm it's ID.
2. Unlock the well caps and record water concentration measurements
3. Introduce the submersible pump into the well powered by a 12-volt car battery. Pump out the appropriate sample (catch mid-stream). After obtaining the sample, continue pumping until you purge all water from the barrel sampler
4. Before introducing the pump into next well, wash it in distilled water; clean the tubes by running the pump immersed in distilled water for a few seconds. Make sure the pump and attached tube is empty before lowering into the next well. Turn on the pump and let it run, discarding the outflow the first 5-10 seconds to further clean the pumping system before obtaining a sample. Collect at least three (3) samples for submission to the three different laboratories for metals (10-15ml), Nitrate & Chloride (10-15ml), and total petroleum hydrocarbons (upto 900ml) analyses.
5. Repeat steps 1 to 4 for all remaining samplers.
6. Caution should be taken while transferring the pump and connecting tubing between wells to avoid contamination by getting in contact with the surrounding ground surface or surface water
7. Label all sample holders (bottles) with at least, the well ID and sampling date.
8. Record descriptive information for the site, including surface condition (is there water on surface), latest precipitation date and amounts, snow melt, vegetation condition; also record water volume (estimated as in each sampler
9. In lab, store samples up-side down in refrigerator. Add a few drops of nitric acid to samples for metals analyses. Add a few drops of concentrated hydrochloric or sulfuric acid to the samples for TPH analyses. (Determine the number of drops of acid to be added to the samples by treating a duplicate sample of similar volume, then measuring its pH with a pH meter).

Sampling from the SPE20 samplers

Sites for these samplers are located at the Sheep Pasture site (North-west quadrant of Randall avenue and Hoyt Avenue, St. Paul, MN 55108), and the Hamline-Midway rain garden (Located at Hamline Ave N & Midway Pkwy St. Paul, MN 55103)

1. Locate the device to be sampled and confirm it's ID.
2. Connect the tubing from one of the two ports of the sampling bottle to the sampler, and the other to a hand-held vacuum pump.
3. Making sure a proper seal is maintained, apply 60 centibars of vacuum. Close the clamp on the tube connected to the pump, then remove the pump for use in the next sampler.
4. Check the system after 2-4 hours depending on the soil ate the site (more time for finer textured material). If collected sample is less than desired amount, connect the pump to the system and check the amount of vacuum still remaining; it should be much less than the 60 centibars; apply

more vacuum to bring it up to the 60 centibars. Sometimes it may be necessary to leave this to stand overnight for full effect.

5. Disconnect the bottle from the sampler tubing. Divide the obtained water sample among the three sample bottles/vials for the metals (10-15ml), nitrate & chloride (10-15ml), and total petroleum
6. Repeat steps 2 to 5 for the rest of the samplers.
7. Label all sample holders (bottles) with at least, the unique sampler ID and sampling date.
8. Record descriptive information for the site, including surface condition (is there water on surface), latest precipitation date and amounts, snow melt, vegetation condition; also record estimated water content in each sampler
9. In the lab, filter sample to be analyzed for metals through a 0.45 μm filter paper; add a few drops of nitric acid to bring pH to about 2.0, then store these up-side down in refrigerator.

Sampling from a surface /sub-surface sampling bottles

1. Locate the device to be sampled, and verify it's ID.
2. Using provided glass bottle with a 2 hole rubber stopper; using suitable tubing, connect the vacuum pump to one of the rubber stopper holes. Introduce an appropriate inert tubing (Teflon) into the installed surface or sub-surface sampler and connect this to the second hole on the stopper.
3. Plug the glass bottle mouth with this 2-hole stopper and apply vacuum in the glass bottle; water which has collected in the installed sampler will flow immediately into the vacuumed glass bottle.
4. Divide the obtained water sample among the three sample bottles/vials for the metals (10-15ml), nitrate & chloride (10-15ml), and total petroleum hydrocarbons (upto 900ml) analyses.
5. Moving to the next sampler, introduce a new Telfon tubing into the next installed sampler (if re-using the same tubing, clean it thoroughly with acid then distilled water to avoid cross contamination). Repeat steps 2 to 4 for the rest of the installed samplers
6. Label all sample holders (bottles) with at least, the unique sampler ID and sampling date.
7. Record descriptive information for the site, including surface condition (is there water on surface), latest precipitation date and amounts, snow melt, vegetation condition; also record estimated volume of water in each sampler. In the lab, filter sample to be analyzed for metals through a 0.45 μm filter paper; add a few drops of nitric acid to bring pH to about 2.0, then store these up-side down in refrigerator.

Sample handling and Storage

1. Cap bottles tightly and transport back on ice for either immediate submission for lab analysis or short term storage on Campus.
2. Samples stored on campus should be stored upside down in the refrigerator in room BBE 11 or in 3rd floor walk-in refrigerator (contact Lucas Stolp <stol0028@umn.edu>).
3. Samples for TPH analysis are treated with hydrochloric or sulfuric acid to bring sample pH to about 2; samples for metal analysis have a few drops of nitric acid added bringing pH to around 2.0. The samples are then stored upside down in the refrigerator while awaiting submission to labs for analysis. Storing

samples upside down effectively traps any evaporating compounds leaving the sample getting trapped in the sealed bottom of the sample bottle/vial.

4. Present the samples to respective laboratories within one week for analysis (or until you have more than 35 samples to avoid setting up fee with RAL laboratories).



Figure A.4. The 500ml bottle for extraction of samples from lysimeter

Sample submission to laboratories for analysis

Samples are submitted to different laboratories for the various samples analyses.

Sample analyses for metals (Geochemistry Lab)

Submit samples to:
RICK A. KNURR
DEPARTMENT OF GEOLOGY & GEOPHYSICS
RM 4 PILLSBURY HALL
310 PILLSBURY DR SE
612-624-8084
knurr001@umn.edu

Laboratory analyses for concentration is conducted the Geochemistry Laboratories at a cost \$25 per sample. This laboratory provides analyses results of metal concentration (ppm) for a suite of 29 metals, including phosphorus, chromium, iron, cobalt, nickel, zinc, lead among others which are contaminants of drinking water which pose serious health risk (US Environmental Pollution Agency, <http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf>).

The Geochem Laboratory does not charge setting up fee, making it possible to submit small numbers of samples immediately after sampling. It is import filter water samples through a 0.45 μ m opening filter paper, then adding 2 or 3 drops of nitric acid to increase sample pH to 2.0. This initiates the process of precipitating metals present in the sample, thus minimizing errors following significant periods of sample storage.

Sample analyses for Chloride and Nitrate (Research Analytical Laboratory, RAL)

Samples submitted to this lab are for Nitrate/Nitrite-N and Chloride analyses. Charges per sample are (rates for U of MN researches) are \$6.00 for 0.02 to 2.00mg/l or \$7.5 for 0.5 to 50.0mg/l, or \$7.50 for Chloride. The laboratory also charges additional set-up fee (\$25.00 for nitrate, or \$35.00 for Chloride) if the submitted sample group is less than 35.

Samples can be dropped off at the laboratory office where relevant paperwork is completed. Once paperwork is completed, the person at the office will forward the samples to the correct laboratory/person. Keith Piotrowski is in charge of analysis of water samples.

Research Analytical Laboratory (RAL)

Room 135 Crops Research Building

1902 Dudley Ave

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GC Analysis for Total Hydrocarbons in Water Samples

Methods:

Methods were based on ASTM D7678-11 and ISO 9377-2 (Mod.) Application note 10170.

Extraction: Samples were brought to room temperature, weighed then added to a separatory funnel. The sample bottles were rinsed with 50 ml of cyclohexane which was then added to the separatory funnel. The funnel was shaken for 30 seconds and the layers were then allowed to separate. If emulsions formed, MgSO₄ was added during the liquid-liquid extraction. The funnel was shaken a second time for 30 seconds. If emulsions still persisted, additional cyclohexane was added. After separation, the bottom layer was drained into a small buchner funnel layered with 2g of Florisil covered with a 2g layer of sodium sulfate. The extract was collected into 50 ml polypropylene tubes and capped. Extracts not immediately analyzed were refrigerated. If evaporation had occurred by the time of analysis, cyclohexane was added to bring extracts up to original concentrations.

GC analysis:

GC analysis was performed on a Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD) equipped with a PTV injector on a high-temperature column (RTX-Biodiesel TG; 15 M, 0.32 mm [inner diameter], 0.10-m df; Restek, Bellefonte, PA). The program utilized a temperature profile of 35°C for 1 min, with a 10°C/min temperature ramp to 360°C for 5 min. A standard TPH mixture obtained from Sigma-Aldrich was used to determine the retention times of C10-C40 linear hydrocarbons. A standard curve was prepared by running a 50:50 mixture of light mineral oil and diesel fuel at 93, 186, 934, 1869, 9345 mg/L. Peak area was plotted against concentration and sample concentrations were determined from this curve using the TREND function in Microsoft Excel. Before analysis, 10 ml of extract was brought down to dryness with a rotary evaporator and then reconstituted in 0.5 ml of cyclohexane. Solvent enrichment and rotovap concentration were corrected for in the final sample concentration value.