2004-21

Final Report

Laboratory Measurements of Stormwater Quality Improvement in Detention Ponds

MINNESOTA DEPARTMENT OF TRANSPORTATION

Research

Technical Report Documentation Page

1. Report No.
MN/RC – 2004-21

2.

3. Recipients Accession No.

4. Title and Subtitle
LABORATORY MEASUREMENTS OF STORMWATER QUALITY IMPROVEMENT IN DETENTION PONDS

5. Report Date
March 2004

6.

7. Author(s)
Jeffrey D. Weiss, Miki Hondzo

8. Performing Organization Report No.

9. Performing Organization Name and Address
University of Minnesota
Department of Civil Engineering
500 Pillsbury Drive S.E.
Minneapolis, MN 55455

10. Project/Task/Work Unit No.

11. Contract (C) or Grant (G) No.
(c) 81655 (wo) 17

12. Sponsoring Organization Name and Address
Minnesota Department of Transportation
Office of Research Services
395 John Ireland Boulevard Mail Stop 330
St. Paul, Minnesota 55155

13. Type of Report and Period Covered
Final Report

14. Sponsoring Agency Code

15. Supplementary Notes
http://www.lrrb.org/PDF/200421.pdf

16. Abstract (Limit: 200 words)

Recent interest in detention ponds and constructed wetlands has extended to improving the quality of the runoff by reducing the concentrations of pollutants associated with stormwater runoff. Lead, zinc, copper, cadmium, phosphorus, and chloride are the contaminants of primary concern in the state of Minnesota.

This study examined removal mechanisms in detention ponds. Three wetland graminoids, *Glyceria grandis* (reed manna grass), *Scirpus validus* (soft stem bulrush), and *Spartina pectinata* (prairie cordgrass) were studied for their phytoremediation capabilities for the six target contaminants. The uptake rates of the six target contaminants by the sediments of a detention pond were determined. These two removal processes were incorporated in an analytical model that can be used to determine critical parameters for the design of a detention pond that would produce effluent guidelines that meet requirements set by the Minnesota Pollution Control Agency.

Removal rates for the three species were determined. Uptake rates were dependent on both the contaminant and species. The removal rates of the phytoremediation and the sorption sediment experiments were combined to develop a numerical model to simulate the removal mechanisms in detention ponds. This model can be used to develop design plots for a detention pond.

17. Document Analysis/Descriptors
Heavy metals
Stormwater
Zinc
Copper
Chloride
Detention ponds
Runoff
Lead
Cadmium
Phosphorus

18. Availability Statement
No restrictions. Document available from: National Technical Information Services, Springfield, Virginia 22161

19. Security Class (this report)
Unclassified

20. Security Class (this page)
Unclassified

21. No. of Pages
97

22. Price

LABORATORY MEASUREMENTS OF STORMWATER QUALITY IMPROVEMENT IN DETENTION PONDS

Final Report

Prepared by

Jeffrey D. Weiss, MS
Miki Hondzo, PhD
Department of Civil Engineering
University of Minnesota

March 2004

Published by

Minnesota Department of Transportation
Research Services Section
Mail Stop 330
395 John Ireland Boulevard
St. Paul, Minnesota 55155

Acknowledgements

Researchers

Miki Hondzo
Principal Investigator
Department of Civil Engineering
University of Minnesota

Michael Semmens
Co-Principal Investigator
Department of Civil Engineering
University of Minnesota

John Gulliver
Co-Principal Investigator
Department of Civil Engineering
University of Minnesota

David Biesboer
Co-Principal Investigator
Department of Plant Biology
University of Minnesota

Jeff Weiss
Graduate student
Department of Civil Engineering
University of Minnesota

Technical Advisory Panel

Ann Mclellan
Administrative Liaison
Research Services Section
Minnesota Department of Transportation

Robert Jacobson
Technical Liaison
Office of Environmental Services
Minnesota Department of Transportation

Greg Busacker
Office of Environmental Services
Minnesota Department of Transportation

Marilyn Jordahl-Larson
Office of Environmental Services
Minnesota Department of Transportation

Benjamin Timerson
Office of Environmental Services
Minnesota Department of Transportation

Faruq Faruq
Office of Environmental Services
Minnesota Department of Transportation

Table of Contents

List of Tables

List of Figures

Executive Summary

While effective in reducing the peak runoff volume and flow, recent interest in detention ponds and constructed wetlands has extended to improving the quality of the runoff by reducing the concentrations of pollutants associated with stormwater runoff. Stormwater runoff has been identified as a contributor to the degradation of surface water quality, with an estimated 30% of identified cases of water quality impairment being directly attributable to stormwater discharges (Line et al., 1997; Heitz et al., 2000). Water quality changes resulting from road runoff discharge include the occurrence of surface oil films, deoxygenation of water from increased biological oxygen demand (BOD) and chemical oxygen demand (COD), and increased concentrations of suspended solids and heavy metals (Shutes et al., 1999). A review of stormwater runoff studies indicated that lead, zinc, copper, cadmium, phosphorus, and chloride are the contaminants of primary concern in the state of Minnesota.

This study was conducted to examine removal mechanisms in detention ponds in consultation with the Minnesota Department of Transportation (Mn/DOT). Mn/DOT selected three wetland graminoids, *Glyceria grandis* (reed manna grass), *Scirpus validus* (soft stem bulrush), and *Spartina pectinata* (prairie cordgrass), to be studied for their phytoremediation capabilities for the six target contaminants. In addition, uptake rates of the six target contaminants by the sediments of a detention pond were determined. These two removal processes were incorporated in an analytical model that can be used to determine critical parameters for the design a detention pond that would produce effluent guidelines that meet requirements set by the Minnesota Pollution Control Agency.

Removal rates of the target contaminants by the three selected wetland species were determined. Uptake rates into the plant material were dependent on both the contaminant and species. It was discovered that the root zones of all three species accumulated much higher concentrations of the target contaminants in their biomass than the stems. It was also found that plants grown hydroponically resulted in a higher final concentration of the target contaminants in their biomass than those grown in sand. However, those grown in sand had a much larger increase in biomass, so they removed a greater amount of the target contaminants. Also, it was found that plants grown in flow reactors had a higher final concentration of the target

contaminants than those grown in non-flow reactors. The removal rates found in the phytoremediation experiments were combined with the removal rates found in the sorption sediment experiments to develop a numerical model to simulate the removal mechanisms in detention ponds. This model can be used to develop design plots to determine critical variables when designing a detention pond.

1.0 Introduction and Literature Review

1.1 Highway Drainage and Problem Pollutants

Stormwater runoff from highways has been studied by many researchers (Driscoll et al., 1990; Moxness, 1986, 1987, 1988; Sansalone and Buchberger, 1997; Drapper et al., 2000) in recent decades to determine which pollutants are present in the runoff and what threat they pose to receiving waters. Each study identified phosphorus, lead, zinc, copper, and cadmium as some of the most important pollutants to be monitored. These pollutants either frequently exceeded local and/or national discharge standards or have the potential for significant environmental impact. A summary of the findings from these studies and a comparison to Minnesota Pollution Control Agency (MPCA) standards can be found in Table A1 in the appendix.

Many of the studies also identified a “first flush” phenomenon that is generally described as the occurrence of a disproportionately large concentration of pollutants being found in the first portion of the runoff. Barbosa and Hvitved-Jacobsen (1999) described the first flush as 61% to 69% of the total pollutant load being transported in the first 50% of the runoff volume. Sansalone and Buchberger (1997), on the other hand, described it as the period of time when $m'(t) \geq v'(t)$; where $m'(t) = m(t)/M$; $m(t)$ = mass transported up to time t; M is the total mass of the constituent for the entire event; $v'(t) = v(t)/V$; $v(t)$ is the flow volume up to time t; and V is the total volume of flow for the entire event.

1.1.1. Cadmium

Cadmium tends to be bioaccumulated in mammals, and its effects in humans include erythrocyte destruction, testicular damage, renal degradation, respiratory disorders, emphysema, gastric and intestinal dysfunctions, anemia, osteomalacia, itai-itai, and hypertensive heart disease (Levine, 1975). Automobile brakes and tires are the main sources of cadmium in highway runoff (Sansalone and Buchberger, 1997). Very little of the cadmium is particulate bound and most of it is dissolved in the runoff and is, therefore, more bioavailable (Lundberg et al., 1999; Sansalone and Buchberger, 1997). The highest concentrations of cadmium were measured in snowmelt runoff events, followed by mixed events and rainfall events, and runoff concentrations were highest in the winter, followed by spring, summer and fall (Moxness, 1986). Runoff concentrations ranged from 1.1 to 17 μg L^{-1} (see Table A1). The MPCA discharge limit varies with hardness, and using USGS data for water chemistry of rivers around the Twin Cities area that showed an average hardness of 83.21 mg L^{-1} as $CaCO_3$, the MPCA discharge limits for Critical Standard (CS), Maximum Standard (MS) and Final Acute Value (FAV) are CS, MS, and FAV Standards for discharge of cadmium are 0.98, 27.18, and 54.35 μg L^{-1} respectively.

1.1.2. Chloride

Chloride ions are needed in small quantities by plants for the photolysis of water to release oxygen, for ATP formation, and for certain phosphorylation reactions. However, a high chloride concentration in runoff increases the salinity of receiving waters. For surface waters, the increased salinity can result in the stratification of water in small lakes, which can potentially lead to the prevention of the spring overturn and transport of oxygen to the bottom of the lake, reduced dissolved oxygen (DO) levels, the mobilization of metals from the sediments, and the elimination of benthic species that are especially sensitive to high chloride concentrations (Marsalek et al., 1999). Chloride concentrations in runoff studies vary by season and range from 11.5 to 570 mg L^{-1}. The MPCA CS, MS, and FAV standards are 230, 860, and 1720 mg L^{-1}, respectively.

1.1.3. Copper

Copper is a trace nutrient that functions mainly as a metalloprotein component and is required by enzymes concerned with nitrate transformation. When copper reaches toxic concentrations, it interferes with the activity of enzymes situated on cell membranes of algae. This interference prevents cell division and causes photosynthesis to stop (Levine, 1975). Copper is especially toxic to smaller organisms such as phytoplankton and zooplankton. As little as 0.1 μg L^{-1} of ionic copper can kill some algae in waters with low concentrations of chelating agents. In lakes with normal concentrations of chelating agents, 5 to 10 μg L^{-1} affects blue-green algae while most fish are almost unaffected by copper until the concentration reaches 100 to 500 μg L^{-1} (Horne and Goldman, 1993). In highway runoff, copper is present in both particulate and dissolved forms and also exhibits a strong first flush (Sansalone and Buchberger, 1997). Copper had the same patterns as cadmium with respect to the season and the type of runoff event. Mean copper concentrations in the runoff ranged from 8.2 to 135 $\mu g\ L^{-1}$. MPCA standards for copper discharge also vary with the hardness of the receiving water, and MPCA CS, MS, and FAV standards of 8.77, 14.92, and 29.83 $\mu g\ L^{-1}$, respectively.

1.1.4 Lead

Lead is a well-known pollutant that is toxic to many organisms and is toxic to humans in concentrations as low as 1 mg L^{-1} (Horne and Goldman, 1993). It is mostly particulate bound in highway runoff and exhibits a poor first flush (Sansalone and Buchberger, 1997). Sources of lead in the runoff are primarily from brakes, tires, fuels/oils, and to a smaller extent, de-icing salts (Sansalone and Buchberger, 1997). Lead has the same trends as copper in that the highest concentrations were found in runoff during winter months and snowmelt runoff events. Progressively lower concentrations were found in mixed events and rainfall runoff events, and in spring, summer, and fall months (Moxness, 1986). Mean runoff concentrations in rainfall runoff events ranged from 30 to 450 $\mu g\ L^{-1}$, and the MPCA CS, MS, and FAV discharge standards, based on a hardness value of 83.21 mg L^{-1} as $CaCO_3$, are 2.52, 64.78 and 129.54 $\mu g\ L^{-1}$, respectively.

1.1.5 Phosphorus

Phosphorus is an essential nutrient required by all living organisms. In freshwater aquatic environments, phosphorus is frequently limited and therefore is a limiting factor on the growth of primary organisms such as algae. When phosphorus rich water enters lakes and streams, it can upset the natural limitation on the growth of aquatic plants and cause them to grow in abundance. Such uncontrolled growth can lead to water quality degradation through eutrophication that results in such problems as foul taste and odors, depletion of dissolved oxygen, and aesthetic and recreational impairment (Comings et al., 2000). In lakes and streams, only a small percentage of total phosphorus is in soluble form with the vast majority being held in biologically unavailable forms in particulate matter (Horne and Goldman, 1993). Phosphorus was measured in highest concentrations in runoff from snowmelt events. Runoff from mixed events had the next highest concentrations and the lowest concentrations were measured in rainfall runoff events (Moxness, 1986). Mean concentrations of phosphorus in rainfall runoff events ranged from 0.19 to 0.57 mg L^{-1}. The MPCA standard for phosphorus effluent concentration is 1 mg L^{-1}.

1.1.6 Zinc

Zinc is a trace nutrient for both flora and fauna and has been found to occasionally be a limiting nutrient for phytoplankton growth (Goldman, 1965). It serves as an activator in some enzymatic reactions and is a cofactor for the enzyme carbonic anhydrase. This enzyme catalyzes a critical rate-limiting step for carbon use in photosynthesis (Levine, 1975). However, the addition of zinc into natural waters from urban runoff, mine drainage, and zinc plating of pipes, gutters, and culverts can increase zinc concentrations to toxic levels. The sources of zinc found in highway runoff are automobile brakes, tires, frame, and body (Sansalone and Buchberger, 1997). Zinc is primarily present in dissolved form in highway runoff and exhibits a strong first flush (Lundberg et al., 1999; Sansalone and Buchberger, 1997). The highest concentrations of zinc were measured in snowmelt runoff events, followed by mixed events and rainfall events, and runoff concentrations were highest in the winter, followed by spring, summer and fall (Moxness, 1986). Mean concentrations in runoff ranged from 23 to 4280 μg L^{-1}. The MPCA CS, MS, and FAV standards are 90.72, 100.15, and 200.3 μg L^{-1}, respectively.

1.1.7 Environmental Influences

The effects that the above pollutants have on a receiving environment are controlled or influenced by a variety of factors, including: the inherent buffering capacity, receiving water quality, ecological sensitivity, site protection, and sensitivity of groundwater. The sensitivity of the receiving environment is influenced by factors such as pH, DO and water hardness (Shutes et al., 1999). As pH rises, metals are less soluble and more likely to be specifically bound to the sediments, thus reducing their availability to aquatic organisms. If DO levels become too low, heavy metals can be reduced and become more likely to be found in dissolved forms, which are more bioavailable and toxic (Sansalone and Buchberger, 1997; Carleton et al., 2000). Metals will tend to precipitate in hard waters and may accumulate in sediments. Once they are in the sediments, they can become toxic to macroinvertebrates (Boxall and Maltby, 1995).

1.1.8 Local Conditions

Drapper et al. (2000) stated that local information is very important in order to accurately assess the goals and needs of a detention pond. This is apparent from the summary of the runoff studies in Table A1 in the appendix in which the measured concentrations of the target pollutants in the stormwater runoff were found to be highly variable. This variability can partially be attributed to several parameters that influence the concentrations of the pollutants in a particular area, including average daily traffic volume, the season, the characteristics of the particular stretch of highway, the type of pavement, and drainage area.

Moxness (1986, 1987, and 1988) conducted a series of studies that analyzed the characteristics of highway runoff in the Twin Cities along stretches of I-694, I-494, and I-94. The seasonal variation of the more problematic pollutants was discussed earlier and is summarized in Table 1.1. Moxness (1986) also found correlations between median concentrations and traffic volume between events. Alkalinity, chloride, phosphorus, copper, zinc, cadmium, and lead all had their highest median concentrations when the total traffic volume between events was the highest. All of them except alkalinity also had their lowest concentrations when traffic volume between events was lowest. Similarly, the highest median concentrations of cadmium, chloride, phosphorus, copper, lead, and zinc all correlated to both the highest traffic volume and traffic density during rainfall events. The length of the preceding dry period was also correlated to higher concentrations of total solids and metals in the runoff (Lundberg et al., 1999). Furthermore, the partitioning of metals between dissolved and particulate stages was influenced primarily by the pavement residence time, rainfall pH, the nature and quantity of solids present, and the solubility of the metal element. Events where the rainfall pH was lowest and where the average pavement residence time (APRT) was highest resulted in significantly larger dissolved fractions of the metals (Sansalone and Buchberger, 1997).

Table 1.1. Relationship between season, type of runoff, and the runoff concentration of various pollutants. The numbers indicate the ranking of the runoff concentration in relation to the season or runoff type. For example, a "1" in a box relating winter and Total Suspended Solids (TSS) concentration indicates that TSS runoff concentrations are highest in the winter.

	Rainfall	Mixed	Snow	Winter	Spring	Summer	Fall
TSS	3	2	1	1	2	4	3
Zinc	3	2	1	1	2	3	4
Copper	3	2	1	1	2	3	N/A
Cadmium	3	1/2	1/2	1	2	3	4
Lead	3	2	1	1	2	4	3
Phosphorus	3	2	1	1	2	3	N/A

1.2 Phytoremediation

In recent years, the ability of plants to accumulate pollutants has received a lot of attention and given rise to a new technology called phytoremediation (Black, 1995). Wetland vegetation species are primary candidates for use in phytoremediation because they play a major role in the removal of toxic trace elements from waters passing through the wetland. Wetland plants remove trace elements by several processes. Phytoextraction is the uptake and accumulation of trace elements and toxic metals into the harvestable plant tissues. Phytostabilization occurs when heavy metal tolerant plants immobilize the metals or transforming the element into an unavailable form, thereby preventing them from posing further risk to the environment. Rhizofiltration is the phytostimulation of rhizosphere microorganisms that mineralize, sequester, and stabilize the element. This causes the plant roots to absorb, precipitate and concentrate toxic metals. Lastly, phytovolatilization removes volatile elements (e.g., Se, Hg) into the atmosphere (Berti and Cunningham, 1997; Srivastava and Purnima, 1998). Each of these processes requires the use of plants that have exhibited enhanced abilities to perform these duties (Zhu et al., 1999).

Wetland species differ, however, in their abilities to take up and accumulate various trace elements in their tissues (Rai et al., 1995), and several studies have been conducted that have examined the abilities of some species to accumulate metals in their biomass. Some species have been found to have a great ability to accumulate metals in their biomass and are referred to as "hyperaccumulators." One known zinc hyperaccumulator is *Thlaspi caerulescens*. However, Ebbs and Kochian (1998) found that *Brassica juncea* (Indian mustard grass) removed 4 times more Zn than *T. caerulescens* because *B. juncea* produced 10 times the biomass during that period. A greater shoot biomass can therefore overcome lower shoot concentration, and plant species suitable for phytoremediation may not be limited to hyperaccumulators. Ebbs and Kochian (1998) also found that a balance must be struck between the ability to accumulate high concentrations of the target contaminant and the tolerance to that contaminant in order to find the species that are most appropriate for a given site. A strong accumulator is not necessarily highly tolerant, which can lead to an increase of maintenance at the site.

Translocation of a target contaminant from roots to the stems can be a limiting factor in choosing the appropriate species for a phytoremediation project. Zhu et al., (1999) found that water hyacinth was a good accumulator of Cd and a moderate accumulator of Cu, but Cd and Cu concentrations in the roots were about 10 to 20 times higher than in shoots. High accumulation of trace elements in plant roots is partially due to the binding of the metal cations to the anionic sites in the cell wall and inefficient transport to the shoot (Zhu et al., 1999; Jenatte et al., 1994). In water hyacinth, Cd and Cu are thought to be accumulated in roots by adsorption to charged residues in the Donnan free space and by sequestration by phytochelatins (Jenatte et al., 1994).

A high bioconcentration factor (BCF) for metal elements at low external concentrations is important for phytoremediation because the process is more cost-efficient than other conventional techniques in treating large volumes of wastewater with low-concentrations of pollutants. A good accumulator should have both the ability to take up more than 0.5% dry weight of a given element (Zhu et al., 1999). If a plant has a high BCF and the translocation of the trace elements to the shoots is efficient, then the harvesting of the above ground portion of the biomass can improve phytoremediation efficiency, remove of a greater amount of the target pollutants, and minimize the toxicity of accumulated trace elements to wildlife (Falbo and Weaks, 1990; Qian et al., 1999). The cost of harvesting the plants is very small compared to other forms of remediation, so it proves to be a very cost-effective method to treat runoff.

Another factor affecting the removal efficiency of any given trace element is plant density. Qian et al. (1999) found that plants that grow in dense patches and have a high BCF result in the removal of a greater amount of the target pollutant. Considering all of these factors, a judicious selection of plant species to be planted in a constructed wetland treatment system must be made so that the capacity of wetland to remove potentially toxic trace elements from wastewaters can be maximized.

1.3 Detention Pond Design

The design criteria for a detention pond can vary greatly depending on the intended goals of the pond. If the goal of the detention pond is only to reduce the runoff load to the receiving waters, then the primary concern is the volume of the pond and the release rate from the pond. If the detention pond is also to be used to effectively treat the runoff to reduce pollutant load to receiving waters, then several factors need to be considered, including: local climate, topography, geology, land availability, cost, size and type of receiving water body, water quality classification and objective (including water uses), drainage area, and environmental enhancement value. A detention pond to treat highway runoff should consider the road drainage area and traffic loadings and ideally include the following structures: oil separator, silt trap, spillage containment, settlement pond and associated control structures, constructed wetland and associated control structures, final settlement tank, outfall into receiving water-course, and an access route for maintenance. Oil and phytotoxic chemicals in highway runoff can seriously affect both the efficiency of treatment by detention ponds and constructed wetlands and the viability or performance of the plants. As constructed wetlands require 1-3 years to mature and become capable of efficient wastewater treatment, bypass oil separators, silt traps, and spillage containment facilities must be installed prior to the discharge of highway runoff into the constructed wetland (Shutes et al., 1999).

There are two primary theories concerning the proper size and volume of a detention pond or constructed wetland. One theory is that the pond size should be a certain percentage of the size of the watershed, while the other focuses more on the ability to capture the runoff volume from a certain sized storm event. With either method, detention pond volume determines the fraction of a runoff event that can potentially be captured, and therefore made available for treatment during periods between events. The importance of proper sizing was recognized in early design guidelines published by the MPCA, which recommended that the surface area of a constructed stormwater wetland be between 0.6 and 3% of the contributing watershed area, depending on the land type. Other authors have suggested various ratios between the drainage area and the surface area of the pond or between the runoff volume and storage volume. Ellis (1991) suggested after a review of a number of studies, that the maximum pollutant removal appears to occur when the settlement pond surface area is 2-3% of the drainage area and the retention volumes exceed 100 m^3 per hectare of effective drainage area. Another guideline recommends both a minimum area ratio of 2% (or 1% for wetlands with extended detention), and a treatment volume large enough to capture 90% of all storm events (Carleton et al., 2000). Lawrence et al. (1996) pointed out that stormwater quality impacts are primarily related to the first flush and/or the large number of small-scale storm events. About 85 to 90 percent of storm events are smaller than a 1-year storm event, so pond systems that are capable of treating a 1-year storm event will effectively treat the vast majority of runoff events while keeping the size and cost of the ponds lower than trying to capture larger scale events. Others have been more concerned with accommodating specific storm events such as 2-, 5-, 10-, or 100-year storm events, including Shutes et al., (1999) who determined that a constructed wetland should be designed to treat a 10-year storm event, if the land is available. One optimization scheme for determining pond size finds the point where the slope of the curve for pond size versus volume capture has a gradient of 1 to 1. This is the point of diminishing returns for increasing pond size (Guo, 1993). However, if economics and the removal of pollutants need to be considered when selecting pond size, then the conclusions by Guo (1993) may not hold true (Heitz et al., 2000).

Detention time is one of the most important factors in the treatment performance of detention ponds and constructed wetlands and simply designing a stormwater detention pond to accommodate specific storm events (e.g. 1-, 2- or 100-year storm events) does not guarantee adequate detention time required to remove or reduce the impact of the stormwater runoff on the receiving waters (Guo, 1993). Some of the mechanisms that improve the runoff quality, like sorption to the sediment and the settling of large particles, occur relatively quickly (in a matter of hours). However, some of the other biological and chemical mechanisms, such as plant uptake and settling of finer particles, require detention times of up to a week or more and may be dependent on factors such as plant growth rate, season, etc. Considerations affecting the detention time include the aspect ratio (width: length), the vegetation, substrate porosity, depth of water, and the slope of the bed (Shutes et al., 1999). A detention time of 24 hours was found to provide good levels of treatment (Heitz et al., 2000; Grizzard et al., 1986), but Comings et al. (2000) showed that a longer detention time, up to 7 days, further increased the efficiency of the pond. Tanner et al., (1995) also found increased pond efficiency as the detention time increased from 2 to 3 to 5.5 to 7 days, and Lawrence et al. (1996) showed that TSS and total phosphorus (TP) removal increased as the detention time increased from 10 to 30 days.

In the main treatment area, flow length and path through the pond affects the settling performance. According to the MPCA guidelines, detention ponds with an aspect ratio of at least 3:1 will provide the additional detention time required for settling of suspended solids and for biological and chemical treatment of the runoff. The main treatment area can be designed with baffles or curved flow paths to reduce short-circuiting and increase settling efficiency.

The above guidelines are supported by Comings et al., (2000) who analyzed the performance of two differently designed detention ponds. Their Pond A was primarily designed for water detention with minimal design aimed specifically for water quality improvement. The detention time was 1 day, and flow attenuation was not limited. Meanwhile, Pond C was specifically designed to remove pollutants with limited flow attenuation. It had 2 pools; the first being the inlet/settling basin and the second being horseshoe shaped with wetland vegetation planted throughout the pond. The detention time was 7 days. Table 1.2 compares the removal efficiencies of the two ponds.

Table 1.2. Percent removal results of two detention ponds. Pond A was designed for detention, and not primarily for water treatment. Pond C was specifically designed for water treatment, from Comings et al., 2000.

	Pond A	Pond C
Target Pollutant	% Removal	% Removal
TSS	61	81
Total Phosphorus	19	46
Cadmium	68	52
Copper	37	47
Lead	73	76
Zinc	45	72

The increased detention time in Pond C provided the settling time needed for solid pollutants to be removed and chemical interactions to take place. Short-circuiting took place in Pond A and reduced effective detention time. The conclusions from this study were that pond volume dedicated to water quality improvement is a critical feature and that the flow path should be carefully considered to fully utilize the storage space of a pond and minimize areas of quiescent water (Comings et al., 2000).

A final variable that strongly influences pond performance is the choice of substrate. One of the mechanisms for removal of the dissolved fraction of phosphorus and heavy metals is sorption to the substrate. Each soil has different capacities to adsorb and retain phosphorus and heavy metals, so soils with a higher capacity to bind those pollutants would be preferred. In addition, since sorption reactions are strongly dependent on pH, the ideal sediment would have a high resistance to desorption at low pH (Barbosa and Hvitved-Jacobsen, 1999). The substrate should also be resistant to resuspension (Shutes et al., 1997).

1.3.1 Pollutant Removal Mechanisms

Ponds can remove pollutants in a variety of ways, depending on the type and form of the pollutant. Solid constituents such as TSS, particulate phosphorus, and particulate-bound metals are primarily removed by settling. The dissolved fractions of the heavy metals are can be removed by chemical or biological means. Biological removal of metals is primarily by the uptake of metals into plant tissue and was described in Section 1.2. Chemical removal of metals is primarily by precipitation and sorption onto the substrate. The factors controlling sorption are pH, redox potential, concentrations of the metal, competing ions, and chelating agents, ion exchange capacity of the soils, temperature, and ionic strength (Benjamin, 2002).

Phosphorus has long been a target pollutant, and numerous studies have been done that examine the removal of P from runoff by detention ponds. The major routes of TP removal are through uptake by vegetation, sorption and exchange reactions with sediments, chemical precipitation in the water column, and sedimentation (Reddy et al., 1999). Both pH and redox potential control the mobility of P in the environment. The long-term storage of the P is controlled by sediment reactions, and P storage in the sediments is directly proportional to TP in the water column (Richardson et al., 1997). In fact, at low P loadings, wetland, soil or stream sediments release rather than retain P (Reddy et al., 1999). P removal is greatest during the first 1-3 years of the life of a detention pond when sorption and precipitation of P are the greatest (Craft, 1997; Maristany, 1993). However, as sedimentation decreases and sorption sites become saturated, P retention decreases to levels supported by organic P accumulation (1-2 g P m^{-2} yr^{-1}) and sorption precipitation with incoming aqueous and particulate Fe, Al, and Ca. In fact, the precipitation of phosphorus can be significantly improved with the addition of small amounts of lime (2-4% of the total sediment) (Zurayk et al., 1997). Richardson et al. (1997) found wetland effluent concentrations of P rose exponentially when P loadings were greater than 1 g m^{-2} y^{-1}, so they established the "one gram rule" which states that "Phosphorus loading into freshwater wetlands above 1 g m^{-2} yr^{-1} will result in a significant increase in P concentration above baseline outputs (>40 µg L^{-1}) once short-term uptake process are saturated." This rule does not hold if Fe, Ca or Al is added to the wastewater entering the wetland and continuous precipitation is the removal mechanism (Richardson et al., 1997).

Floating macrophytes usually are present in areas with deep water and absorb P directly from the water column. Although emergent macrophytes effectively store P, very little of the water column P is directly assimilated by these plants. Such plants are rooted in the soil, and the majority of their P requirements are usually met from soil pore water P. Unfortunately, the removal of P by macrophtyes proves to be mostly temporary as up to 80% of the P stored in some aquatic macrophytes detrital tissue is released in to the water column during decomposition (Reddy et al., 1999).

1.3.2 Pollutant Removal Efficiencies

The removal efficiency of the target pollutants in various studies have had mixed results, and a summary is given below in Table 1.3. It must be noted that each detention pond/constructed wetland system used was unique, with unique designs, substrates, vegetation and loading rates. As described earlier, each of those factors can play an important role in the effectiveness of a detention pond system, but when each is variable, it is nearly impossible to make a fair comparison of pond performance. Even though many of the studies reported the percentage removal of their target pollutants, few of them reported what the effluent concentration was. Without knowing the effluent concentration (or the influent concentration coupled with the percent removal), it is impossible to know what pollutants might still be exceeding discharge guidelines and if there will be any impact on the receiving waters by the effluent from a detention pond. In order to gain an idea of the possible expected effluent concentrations, the following will be done. Two average runoff concentrations of each target pollutant will be calculated. One will be from studies that have been conducted only in the Twin Cities, and the other will be the average runoff concentrations from all of the studies. These two values for each pollutant will serve as a theoretical influent concentration. Next, the average percent removal for each pollutant in Table 1.3 will be used to remove that percentage of the runoff concentration from the influent and determine a theoretical effluent concentration. Two removal percentages will be used. The first will be the average percent removal from all of the studies. The second will be the average percent removal only from Comings et al. (2000). That study was the only one to give individual removal efficiencies for each of the heavy metals while other studies simply gave ranges for the percent removal of all heavy metals.

Table 1.3. Percent removal of target pollutants in detention pond/wetland systems.

	TP	**N**	**Zn**	**Cd**	**Cu**	**Pb**	**TSS**
USEPA Wet Pond[1]	48	31	49	49	49	49	67
USEPA SW wetlands[1]	56	19	29	29	29	29	71
Lawrence et al., 1996[1]	50	30	70	70	70	70	90
Shutes et al., 1997[1,2,3]	65	N/A	65	65	65	65	85
Comings et al., 2000 Pond A	19	N/A	45	68	37	73	61
Comings et al., 2000 Pond C	46	N/A	72	52	47	76	81
Carleton et al., 2000	33.3	N/A	23.4	50	0	N/A	N/A
Kantrowitz and Woodham, 1995	40	N/A	N/A	N/A	N/A	N/A	N/A
Gain, 1996[2]	26	N/A	N/A	N/A	N/A	N/A	N/A
Wu et al., 1996 Pond A	45	N/A	N/A	N/A	N/A	N/A	N/A
Wu et al., 1996 Pond B	36	N/A	N/A	N/A	N/A	N/A	N/A
Average	**42**	**27**	**50**	**55**	**42**	**60**	**76**

[1] Ranges were given for heavy metal removal, but not for specific metals. The average value for the range given was used for all of the metals. E.g. for USEPA Wet Pond, removal efficiencies were given as 24-73% for heavy metals. Then 49% removal was used for all metals, even though the actual percent removal of each metal will vary, depending on the dissolved and particulate fractions.

[2] A range was given for total phosphorus removal, so the average value in that range was used, i.e. in Shutes et al. (1997), a range of 60-70% removal was given, so 65% was used.

[3] A range of 80-90% removal for TSS was given, so the average value of 85% was used.

Table 1.4. Theoretical effluent concentrations from a detention pond/wetland system.

	Cu ($\mu g\ L^{-1}$)	Zn ($\mu g\ L^{-1}$)	Cd ($\mu g\ L^{-1}$)	Pb ($\mu g\ L^{-1}$)	TP ($mg\ L^{-1}$)
A	30.4	457.1	2.9	100.9	0.3
B	13.3	60.7	1.1	95.8	0.3
C	30.6	383.1	2.5	64.8	0.3
D	13.4	50.9	1.0	61.6	0.3
MPCA Std. (CS)	8.77	90.72	0.98	2.52	1
MPCA Std. (MS)	14.92	100.15	27.18	64.78	1
MPCA Std. (FAV)	28.84	200.3	54.36	129.56	1

A – Concentrations: averages from all runoff studies;
Removal rates: average percent removal from all detention pond studies.
B – Concentrations: averages from runoff studies in the Twin Cities area;
Removal rates: average percent removal from all detention pond studies
C – Concentrations: averages from all runoff events studied;
Removal rates: average percent removal from all detention pond studies for TP, and average percent removal from Comings et al., (2000) for heavy metals.
D – Concentrations: averages from runoff studies in the Twin Cities area;
Removal rates: average percent removal from all detention pond studies for TP, and average percent removal from Comings et al. (2000) for heavy metals.

1.4 Conclusions

The composition of urban highway runoff is highly variable and largely depends on site-specific characteristics and characteristics of each runoff event, including: local climate, pavement type, average pavement residence time, the duration between runoff events, season, and traffic volume. The pollutants of greatest concern in the runoff are chloride, heavy metals (Pb, Zn, Cu, and Cd), nutrients (P). Of the pollutants of greatest concern, large percentages of lead, copper and phosphorus are particulate-bound and settle out of the runoff in the settling basin of the detention pond. Zinc, chloride, and cadmium are primarily dissolved in the runoff and must be treated through chemical or biological means in the detention pond.

Based on the theoretical effluent concentrations calculated in this progress report, zinc, lead, and copper appear to be the heavy metals that have the greatest potential to cause harm to the receiving waters. Even after treatment in a detention pond, they occasionally exceed MPCA standards. It does not appear that highway runoff is a source of phosphorus that directly results in effluent concentrations that exceed MPCA standards. However, given the sensitivity of the receiving waters to phosphorus loadings and the numerous other sources of phosphorus in an agricultural state such as Minnesota, it is something that should be carefully monitored.

The efficiency of a detention pond can be increased by proper selection of plant species. Certain species have been found to accumulate large concentrations in their biomass, so it is more effective to select plants that are not only tolerant of the pollutants associated with the runoff, but also have the ability to accumulate the pollutants in their biomass. In general, plants with a large biomass tend to accumulate a greater amount of the target pollutants even if the concentrations within the biomass are not as high. It is even more effective if the plants can accumulate the pollutants in the harvestable portion of the biomass. Therefore, the pollutants can be removed from the system, thereby decreasing the toxic effects to both the plants themselves and the wildlife in the pond. It has also been shown that high plant density increases removal efficiency.

2.0 Experiment 1 – Non-flow Reactors

2.1 Introduction

This experiment was conducted to determine pollutant removal rates from non-flow reactors in order to gain a baseline for later experiments. It was decided to model the design of this experiment after those done by Spriggs (1998). Plants were purchased from Hild and Associates nursery in River Falls, WI, in November, 2001. Plants had already senesced for the winter, so they were placed under growth lights in a room at 68^oF until they reached sufficient height for transplanting to reactors.

2.2 Experimental Setup

2.2.1 Nutrient Solutions

Each jar was filled with a modified duckweed nutrient solution described in Standard Methods, 1995. It was modified to have the average runoff concentrations for the 6 target pollutants: Pb, Cu, Cd, Zn, P, and Cl. Stock solutions were made with concentrations according to the following tables:

Table 2.1: Stock Solution A used in Experiment 1.

Compound	Concentration (g/L)
$NaNO_3$	25.5
$NaHCO_3$	15.0
K_2HPO_4	1.04

Table 2.2: Stock Solution B-1 with elevated concentrations of metals for Experiment 1.

Compound	Concentration (g/L)
$CaCl_2 \cdot 2H_2O$	4.41
$MgCl_2$	5.7
$FeCl_3$	0.096
$Na_2EDTA \cdot 2H_2O$	0.3
$MnCl_2$	0.264
$ZnCl_2$	0.104
$CuSO_4$	0.025
$CdCl_2$	0.00163
$Pb(NO_3)_2$	0.079

Table 2.3: Stock Solution B-2 for control reactors for Experiment 1.

Compound	Concentration (g/L)
$CaCl_2 \cdot 2H_2O$	4.41
$MgCl_2$	5.7
$FeCl_3$	0.096
$Na_2EDTA \cdot 2H_2O$	0.3
$MnCl_2$	0.264

Table 2.4: Stock Solution C for use in Experiment 1.

Compound	Concentration (mg/L)
$MgSO_4.7H_2O$	14700
H_3BO_3	186
$Na_2MoO_4.2H_2O$	7.26

To prepare the nutrient solution, 1 mL of each stock solution was added per 100 mL of deionized water. The quart-sized canning jars used in this experiment held 800 mL of water, so 8 mL of each stock solution was added to each jar. The pH was adjusted to 7.5 by adding small aliquots of 6N NaOH and monitoring with a Beckman Φ 32 pH meter until the pH was at the desired value. From here on, "spiked solution" refers to the nutrient solution made by using the Stock Solution B-1 because it results in the desired "spiked" concentration of each heavy metal, and "spiked reactor" refers to a reactor with the spiked solution. "Control solution" refers to the nutrient solution made using Stock Solution B-2 because it results in a nutrient solution without any concentration of heavy metals. For reactors with spiked solutions, the final concentrations of the target pollutants were:

Table 2.5: Final concentrations of target pollutants in spiked solutions.

Element	Cd	Cl	Cu	P	Pb	Zn
Concentration ($\mu g\ L^{-1}$)	10	33000	100	1000	300	250

2.2.2 Plant Selection

After new growth had begun, plants with heights between 15 and 20 cm were selected for the experiment. Each plant height was recorded, and one plant was suspended in a hydroponic solution in each reactor. It was suspended by cutting a slit in a small piece of foam rubber, placing the plant into the slit, and putting the plant and foam rubber into a hole that had been cut in the lid of the canning jar. Please refer to Figures 2.1 and 2.2.

2.2.3 Setup

Plants and nutrient solutions were sampled on the following days after initial planting: 1, 2, 4, 7, 14, 21, and 35. Three reactors with spiked solution but without any plants were made for each sampling day. This combination of solution and plants was labeled Combination 1. Four reactors of each species were set up for each sampling day in both control and spiked reactors. The reactors with spiked solution and plants were labeled Combination 2, and the final combination with control solution and plants was labeled Combination 3.

Table 2.6: Solution and plant combinations used in Experiment 1.

Combination	Description
1	Spiked solution without plants
2	Spiked solution with plants
3	Control solution with plant

Each replicate was labeled 1, 2, 3, or 4, accordingly. Finally, the grass species *G. grandis, S. pectinata, and S. validus* were labeled Species A, B, and C, respectively. Each reactor was labeled first with the solution/plant combination, followed by the sampling day, then the replicate number and lastly the plant species. Therefore, a reactor labeled 2-14-3-C would correspond to a reactor with combination 2, sampled 14 days after it was planted, and the 3rd replicate of *S. validus.* Each plant was suspended into its reactor by the procedure described above. For each sampling day, there were a total of 27 reactors. However, the plugs of plants received from Hild and Associates, Inc. failed to generate the desired number of plants. There were 24 fewer plants than necessary for *S. validus* and 8 plants fewer than necessary for *G. grandis*, so plants and water samples were not taken for *S. validus* for Days 1, 2, and 4, nor for Day 1 for *G. grandis*. Due to time constraints, it was not possible to wait for more plants to arrive before beginning the experiment. Furthermore, there were concerns that the new plants would be from a separate batch and would not have the same baseline conditions as the first batch of plants. Also, had we completed the experiment for the missing sampling days for those two species at a later date, the growing conditions would inevitably be different and the results would not be comparable.

Figures 2.1 and 2.2: The experimental setup for the non-flow reactors in Experiment 1. The picture on the left is of the entire setup with all reactors. The picture on the right is a close-up of one of the reactors. In it, it is possible to see how each plant was suspended in its reactor.

2.2.4 Sampling and analysis

2.2.4.1 Plants

When it was time to sample each reactor, the following procedure was followed: First, each plant was removed from its reactor and its height was measured. The stems and roots were separated and each placed in its own envelope labeled the same way in which the reactors were labeled plus an “S” for stem or “R” for root accordingly. Envelopes were placed in an oven at 105^{o}C for 3 days to allow the plant tissue to dry. The dry weights of each plant were then measured and recorded.

The plant samples were taken to the Research Analytical Labs on the University of Minnesota, St. Paul campus for analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). This method returns results for concentrations of 15 elements, including P, Pb, Cu, Cd, and Zn. Samples had to be resubmitted for Cl analysis.

2.2.4.2 Water

Prior to sampling, 50-mL plastic sampling vials were acid-washed in a 10% HNO_3 acid bath. A 50-mL sample was taken from each reactor. Each sample was acidified to $pH < 2$ by adding 1 mL of concentrated metals grade HNO_3. Samples were then stored at 4°C until analysis.

Phosphorus concentrations were determined by using the Ascorbic Acid Method (Standard Methods, 1985) and using a DR/4000V UV-Vis Spectrophotometer at 880 nm. Chloride concentrations were found by analyzing water samples with an ion chromatograph. Heavy metal analysis was done by using a Perkin-Elmer 5100 Zeeman Graphite Furnace Atomic Adsorption Spectrophotometer.

2.3 Results and Discussion

2.3.1 Growth Rates

There were no distinct trends when comparing growth between species or between plants that were grown in spiked reactors or control reactors. Please see the following table and graphs:

Table 2.7: Total plant growth in centimeters for Experiment 1.

Species	*G. grandis*		*S. pectinata*		*S. validus*	
Day	Spiked	Control	Spiked	Control	Spiked	Control
1	NA	NA	0.075	0.025	NA	NA
2	0.3	0.2	1.4	1	NA	NA
4	3.2	1.1	1.6	1	NA	NA
7	4.3	5.9	7.5	4.9	1	0.6
14	2.8	1.3	1.4	4.9	1.9	3
21	3.1	1.6	6.1	7.3	1.6	4.2
35	3.6	2.0	8.6	5.0	1.3	2.0

Figure 2.3: Total average growth (cm) for *G. grandis* in spiked and control reactors.

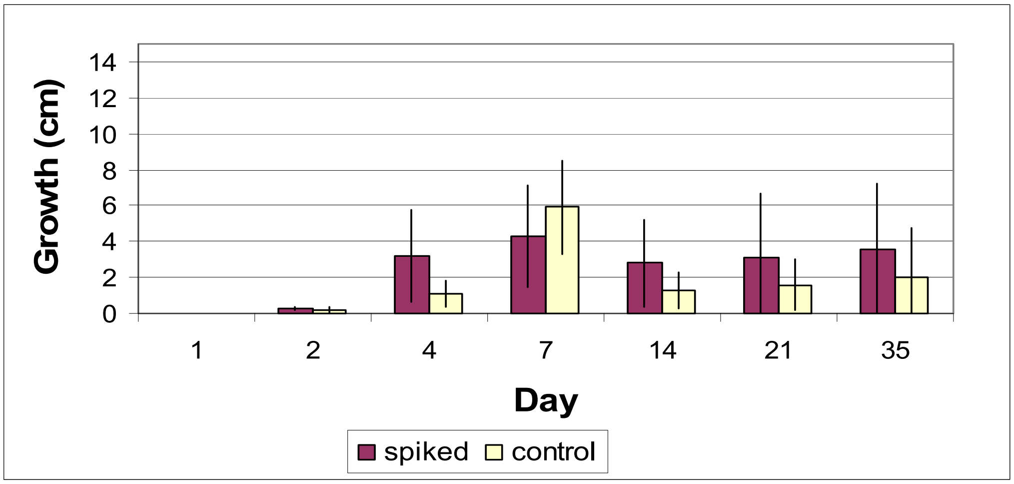


Figure 2.4: Total average growth (cm) for *S. validus* in spiked and control reactors.

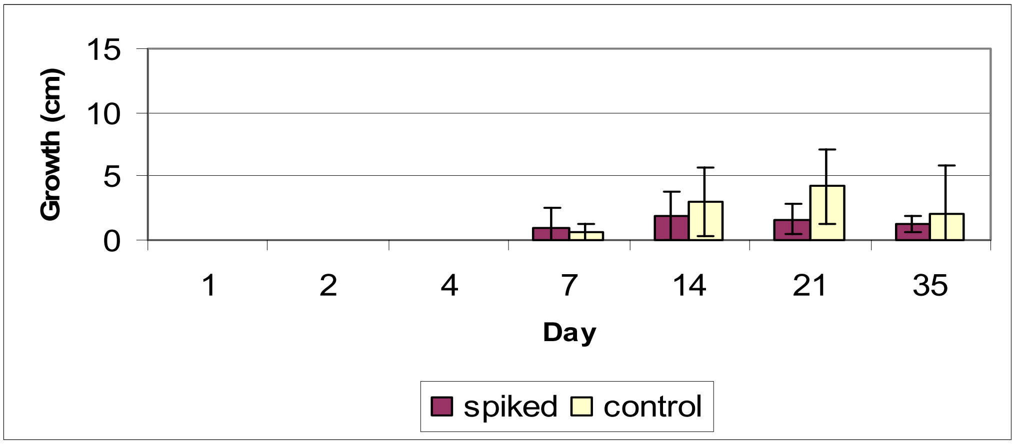


Figure 2.5: Total average growth (cm) for *S. pectinata* in spiked and control reactors.

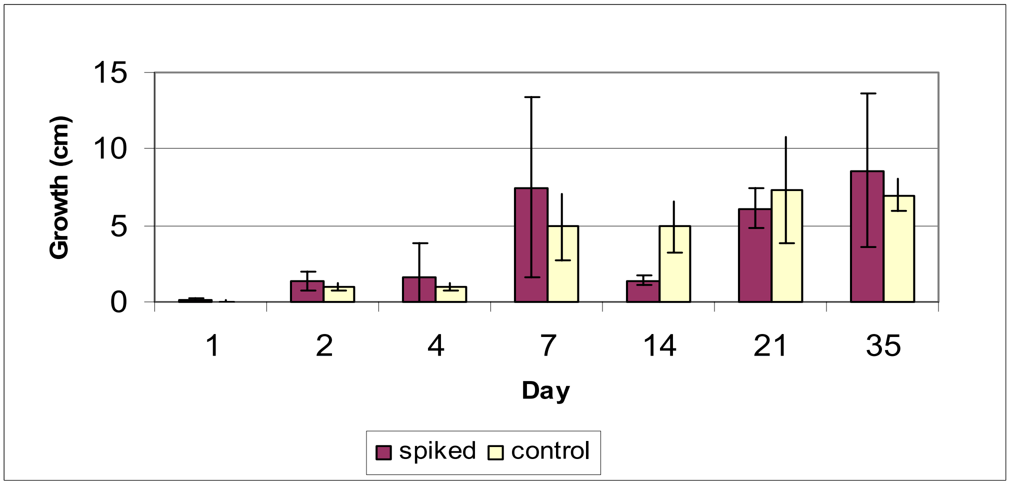


Figure 2.6: Total average growth (cm) for all species in spiked reactors.

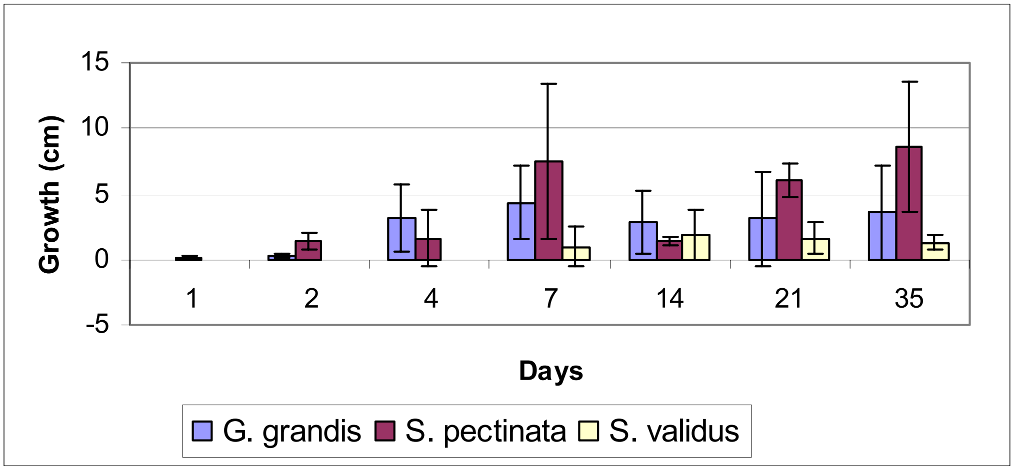
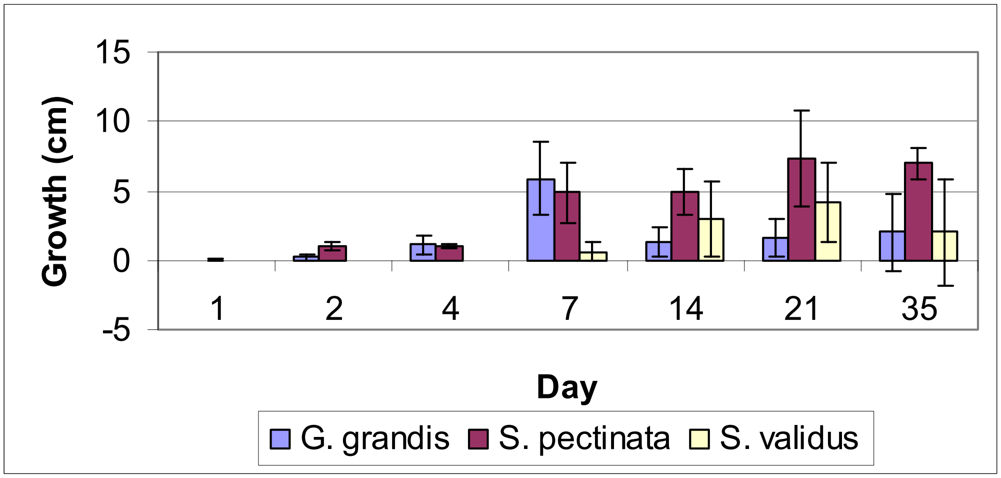


Figure 2.7: Total growth (cm) for all species in control reactors.



Analysis of the growth revealed that there are some general trends present. *S. validus* plants in control reactors had better growth for all days except Day 7, while *G. grandis* plants showed better growth for every day except Day 7. *S. pectinata* showed no general trend. T-tests were performed on the data and revealed that there were no significant differences ($p<0.05$) between the growth in spiked and control reactors for the same species except for Day 14 for *G. grandis*.

When comparing growth between species, the only general trends are that *S. pectinata* grew the best and *S. validus* grew the worst. Again, t-tests were performed, and only isolated days showed a significant difference ($P<0.05$) in growth:

Table 2.8: Days with significant differences in growth ($p<0.05$).

Species compared	Reactor type	Day
S. validus vs. G. grandis	Control	7
S. validus vs. G. grandis	Spiked	21
S. validus vs. S. pectinata	Control	7
S. pectinata vs. G. grandis	Control	14, 35
S. pectinata vs. G. grandis	Spiked	2

Besides the isolated days where there was actually a significant difference in growth between the two species, a few general trends can be noted. First, for all three species, the spiked concentrations of the contaminants seemed to have no harmful effect on growth. All three species had some days when the spiked reactors showed better growth and other days when the control reactors showed better growth. One of the more interesting and surprising results was that there was not a general trend of increased overall growth with time for any of the three species. One would expect that Day 35 would have shown the greatest overall growth for all species, but that was only true for *S. pectinata* and even for that species, there was not a strong trend of increased growth for each sampling day.

Since only isolated days showed significant differences in growth when comparing species, there do not seem to be any strong trends. However, when looking at Figure 2.4, it can be seen that *S. pectinata* had a general trend of having the best overall growth of the three species. *G. grandis* also seemed to grow better than *S. validus*.

In general, the overall growth of the three species was not as great as was expected, which could possibly be attributed to less than optimal growing conditions. The plants were received in November, not long after going into dormancy for the winter. Reviving them out of dormancy proved to be easier said than done. Furthermore, the growth lights used could have been more intense, but even so, it is not always possible to "fool" plants into thinking the days are longer than they actually are (personal communication, Biesboer). Lastly, the experiment was done in February and the temperature where the experiment took place was regulated to between 60-65^{o}F. According to the owner of the nursery where the plants were purchased, these species prefer much warmer temperatures, especially *S. validus* which prefers temperatures in excess of 80^{o}F before it starts to grow with more vigor (personal communication, Hild), which could explain why *S. validus* did not grow as well as the other two species.

2.3.2 Accumulation Rates in Plants

By looking at the increase in concentration (mg kg^{-1}) of the target pollutants in each species, it was possible to determine accumulation rates in the plants. Table 2.9 below presents the rates of increase in the concentration of the target pollutants in each species. Analysis was done to determine if the uptake of the pollutants was a zero-, first-, or second-order process, and results indicated that first-order processes (ln(C) vs. t) had the best linear fit.

Table 2.9 First-order rate constant k-values (t^{-1}) for the increase of concentration for the target pollutants in each of the three selected species and the r^2 values for each regression in parentheses.

Plant Part	Species	Cadmium	Copper	Lead	Phosphorus	Zinc
Stems	*G. grandis*	0.061 (0.56)	0.033 (0.91)	0.023 (0.84)	0.028 (0.43)	0.035 (0.64)
	S. pectinata	0.084 (0.78)	0.032 (0.98)	0.031 (0.76)	0.012 (0.97)	0.057 (0.85)
	S. validus	0.079 (0.56)	0.030 (0.72)	0.018 (0.97)	0.027 (0.91)	0.048 (0.45)
Roots	*G. grandis*	0.063 (0.74)	0.031 (0.49)	0.042 (0.97)	0.036 (0.40)	0.079 (0.81)
	S. pectinata	0.082 (0.81)	0.037 (0.73)	0.037 (0.65)	0.009 (0.91)	0.088 (0.73)
	S. validus	0.010 (0.51)	0.038 (0.85)	0.022 (0.94)	0.002 (0.23)	0.074 (0.56)

Table 2.10 Average rates of increase of concentration (mg kg^{-1} d^{-1}) for the target pollutants in each of the three selected species.

Plant Park	Species	Cadmium	Copper	Lead	Phosphorus	Zinc
Stems	*G. grandis*	0.049	0.554	5.341	83.835	4.371
	S. pectinata	0.284	0.576	2.232	45.002	7.583
	S. validus	0.072	0.734	1.566	163.474	4.683
Roots	*G. grandis*	3.386	7.925	29.432	72.515	75.476
	S. pectinata	3.544	8.214	18.770	28.612	65.814
	S. validus	1.332	12.682	15.983	11.320	29.947

It must be noted once again that because of the problem of low dry weights, all four replicates for each species on each sampling day had to be combined in order to have a sample larger enough to reduce analytical error. Therefore, the values presented would be equivalent to the weighted average of the four replicates. Since there was only one sample analyzed for each day, it was not possible to determine a standard deviation or conduct any statistical tests.

Furthermore, because of the small sample sizes, it was not possible to analyze the plant samples for chloride concentrations. However, rates of depletion of chloride from the nutrient solution in the reactors were analyzed and the results are presented in Section 2.3.3.

It can be seen in Tables 2.9 and 2.10 above that the uptake rate for each element varies between species. One species may have the highest uptake rate for one element, but have the lowest uptake rate for another element. For example, *G. grandis* roots had the highest uptake rate for cadmium but the lowest uptake rate for copper. Also, it can be noted that, except for phosphorus, the uptake rates were much higher for the roots than they were for the stems. This phenomenon has been noted by other researchers (Qian et al., 1999; Zhu et al., 1999), and there a couple of possible explanations. It is possible that the harmful elements like the heavy metals are simply sequestered into waste areas in the roots while beneficial elements, like phosphorus, are readily transferred to the stems where they are needed. Another possibility is that the heavy metals simply sorb onto the outside of the roots and are not incorporated into the biomass at all.

2.3.3 Depletion Rates in Water

Even though we would be able to calculate accumulation rates in the plants, in order to conduct a mass balance of the target pollutants in the reactors, it was necessary to measure the depletion of the concentrations of the target pollutants in the nutrient solutions. As expected, the results indicated a first order relationship for the depletion of the pollutants in the reactors. Once again, zero-order, first-order, and second-order rates were tested, and the first-order resulted in the best correlation. The following table gives the first order rates of depletion in the reactors. Figures showing the reduction in concentration are also presented below.

Table 2.11: First-order depletion rates (t^{-1}; t in days), along with r^2 values.

	G. grandis		*S. pectinata*		*S. validus*	
	k-value (t^{-1})	R^2	k-value (t^{-1})	R^2	k-value (t^{-1})	R^2
Phosphorus	-0.018	0.88	-0.017	0.89	-0.014	0.94
Lead	-0.047	0.69	-0.056	0.76	-0.063	0.81
Copper	-0.039	0.88	-0.088	0.85	-0.047	0.93
Cadmium	-0.031	0.93	-0.029	0.90	-0.027	0.87
Zinc	-0.039	0.82	-0.045	0.90	-0.038	0.82
Chloride	-0.012	0.73	-0.012	0.69	-0.010	0.69

It can be seen in Table 2.11 and the figures below that the greatest rate of reduction of each element from the nutrient solutions depended on the species. No one species had the greatest rate of reduction for all of the elements.

Figure 2.8: Change in P conc. (mg/L) with time. Regression equations: *S. validus*: y = -0.01x + 6.71 (R^2=0.94); *G. grandis*: y = -0.02x+6.66 (R^2=0.88); *S. pectinata*: y = -0.02x + 6.65 (R^2=0.89)

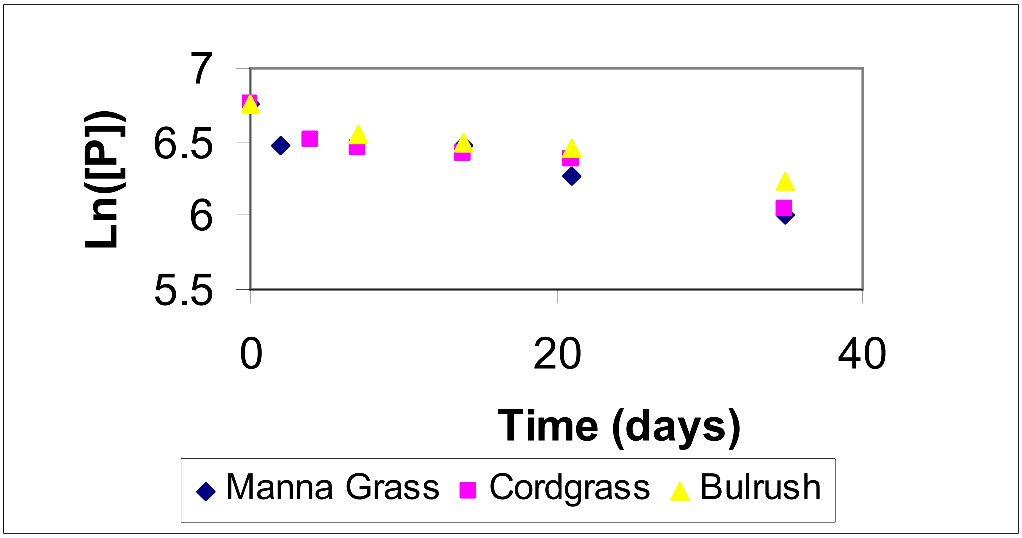


Figure 2.9: Change in Pb conc. (µg/L) with time. Regression equations: *S. validus*: y = -0.06x + 5.25 (R^2=0.81); *G. grandis*: y = -0.05x+4.99 (R^2=0.69); *S. pectinata*: y = -0.06x+4.88 (R^2=0.76).

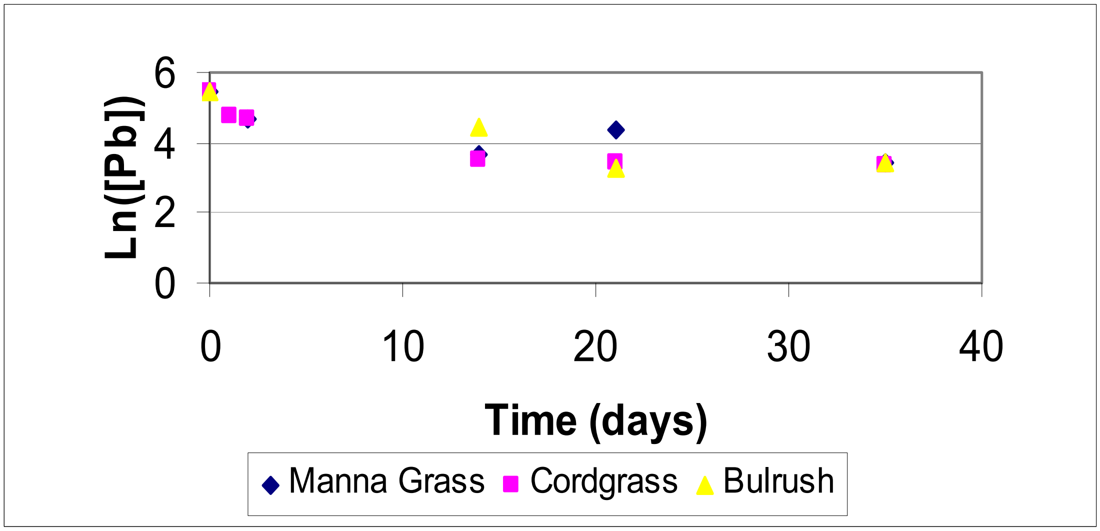


Figure 2.10: Change in Cu conc. (µg/L) with time. Regression equations: *S. validus*: y=-0.05x + 4.31 (R^2=0.93); *G. grandis*: y=-0.04x+4.19 (R^2=0.88); *S. pectinata*: y=-0.09x+4.07 (R^2=0.85).

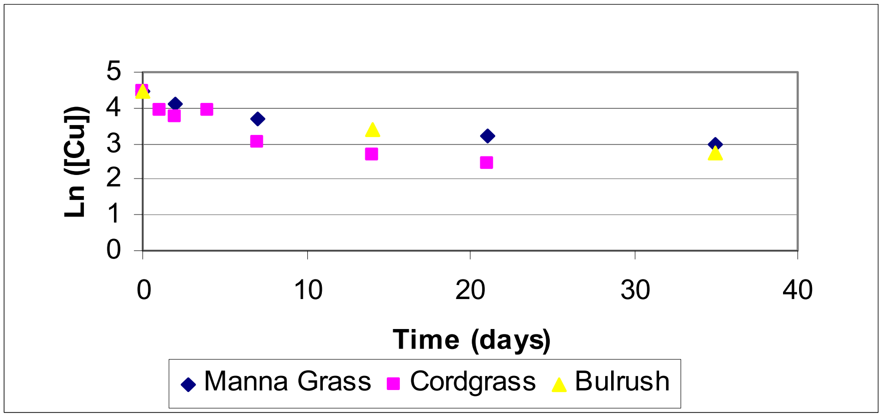


Figure 2.11: Change in Cd conc. (µg/L) with time. Regression equations: *S. validus*: y= -0.027x +2.41 (R^2=0.87); *G. grandis*: y=-0.03x+2.39 (R^2=0.93); *S. pectinata*: y=-0.029x+2.28 (R^2=0.90).

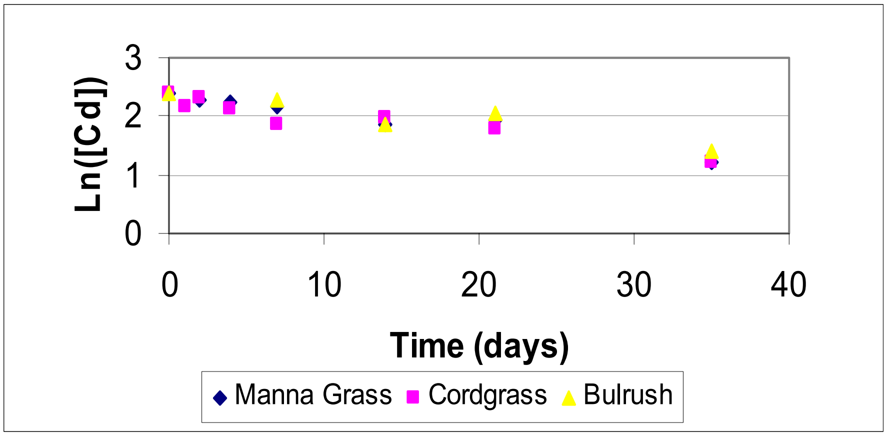


Figure 2.12: Change in Zn conc. (µg/L) with time. Regression equations: *S. validus*: y = -0.04x +4.59 (R^2=0.82); *G. grandis*: y=-0.04x+4.53 (R^2=0.82); *S. pectinata*: y = -0.05x + 4.6 (R^2=0.90).

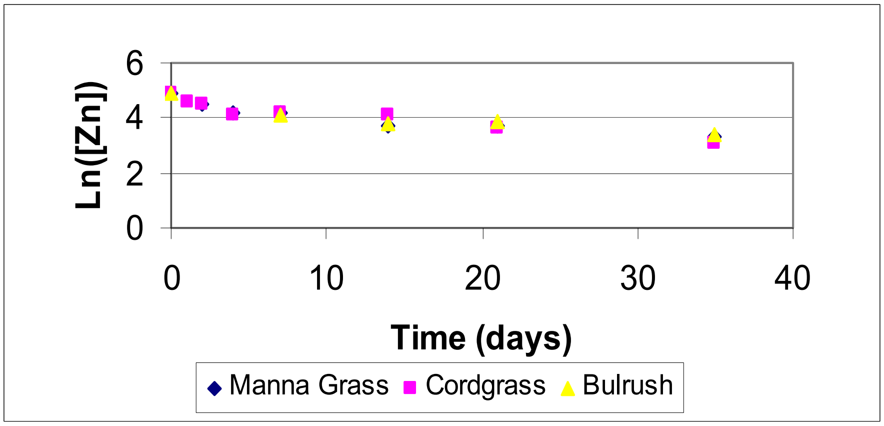
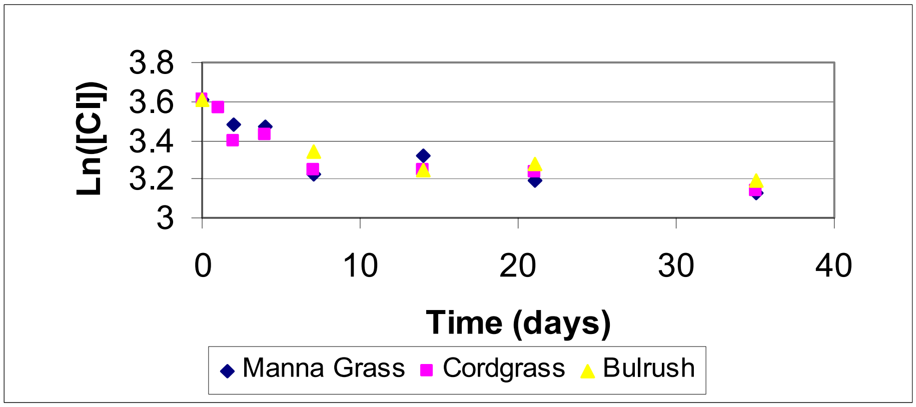


Figure 2.13: Change in Cl conc. (mg/L) with time. Regression equations: *S. validus*: y=-0.01x +3.49 (R^2=0.69); *G. grandis*: y=-0.01x+3.49 (R^2=0.73); *S. pectinata*: y=-0.01x+3.48 (R^2=0.69).



2.4 Conclusions

A few basic conclusions were drawn from this experiment. First, as is consistent with other researchers (Qian et al., 1999; Zhu et al., 1999), all three species accumulate a higher concentration of the target contaminants in their roots than they do in their stems. Next, the depletion rates of the target contaminants from the nutrient solution depended on the contaminant in question and the species accumulating the contaminant. None of the three species was a clear-cut best at removing the target contaminants from the nutrient solution, but *G. grandis* was the best at removing three contaminants (P, Cd, and Cl) while *S. pectinata* was the best at removing two contaminants (Zn and Cu) and *S. validus* was the best at removing Pb.

3.0 Experiment 2 – Flow Reactors

The next phase of the project was to use flow reactors and measure the uptake of target contaminants by the selected species to see if there was a significant difference between the uptake rates in the non-flow reactors in Experiment 1.

3.1 Experimental Materials and Methods

3.1.1Nutrient Solutions

For this experiment, ¼ strength Hoagland's nutrient solution was used as the base nutrient solution for the plants (Hoagland, 1936; Qian et al., 1999; Zhu et al., 1999). The recipe for the stock solutions is as follows:

Table 3.1: Stock Solutions for ¼ strength Hoagland's nutrient solution

Solution	Compound	Concentration (g/L)	Amt. needed for dilution (mL)
A	$MgSO_4 \cdot 7H_2O$	246	1
B	$Ca(NO_3)_2 \cdot 4H_2O$	236	2.3
C	KH_2PO_4	136	0.5
D	KNO_3	101	2.5
E	H_3BO_3	2.86	0.5
	$MnCl_2 \cdot 4H_2O$	1.82	
	$NaMoO_4 \cdot 2H_2O$	0.09	
F	$FeCl_3 \cdot 6H_2O$	0.484	20
	Na-EDTA	1.5	

Table 3.2: Stock solutions for spiked Hoagland's nutrient solution.

Solution	Compound	Target Contam.	Conc. (mg/L)	Amt. needed for dilution (mL)	Final Conc. (µg/L)
G	$CuSO_4 \cdot 5H_2O$	Cu	392.7	1	100
H	$Pb(NO_3)_2$	Pb	479.54	1	300
I	$ZnCl_2$	Zn	521.09	1	250
J	$CdCl_2 \cdot 2.5H_2O$	Cd	20.31	1	10

The column titled "Amount needed for dilution" is the amount of stock solution added per liter of deionized water to form the nutrient solution. As with Experiment 1, "control solution" refers to the solution without any metal concentration, while "spiked solution" refers to the solution with elevated concentrations of metals. For Experiment 2, the control solution was made by using Solutions A-F. The spiked solution consisted of the control solution plus 1 mL each of solutions G-J.

3.1.2 Plant Selection

The same three species were used as in Experiment 1, *S. pectinata*, *S. validus*, and *G. grandis*. This time, an attempt was made to grow the plants from seed in order to minimize any background concentrations of metals in the biomass that could be attributed to the soil the seedlings were grown in. Seeds were ordered from Hild and Associates, Inc., and seeds from all three species were planted in sand in flats and placed in a greenhouse on the University of Minnesota, St. Paul campus. The seeds were watered with deionized water once every 24 to 48 hours, or as frequently as necessary to keep the sand moist. Once the seeds germinated and reached a height of about ¼ inch, the flats were watered with the control nutrient solution described below. They were watered with the control nutrient solution once per week and with deionized water all other times during the week.

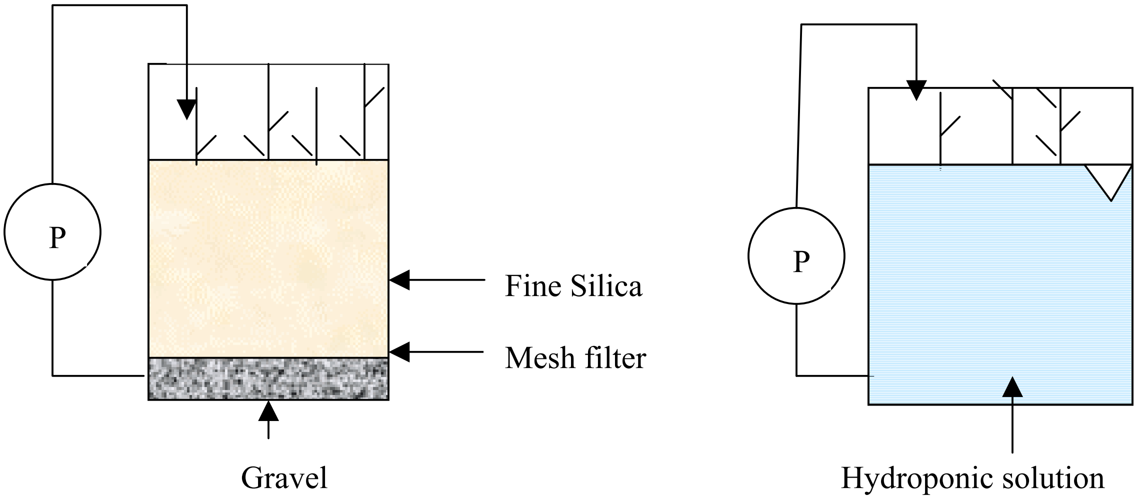
Seeds of *G. grandis* and *S. pectinata* germinated well, however, due to a miscommunication with the nursery, the seeds for *S. validus* were not properly treated before planting, and the germination rate was too poor to have enough plants for this experiment. Flats of *S. validus* then had to be ordered from Hild and Associates, Inc., and arrived at full height. They had been grown in potting soil, and the soil was completely removed from the roots prior to using the plants in the experiment.

Seedlings of *S. pectinata* were carefully removed from the sand in which they were growing and any remaining sand was rinsed off by gently moving the plants through deionized water until all sand particles had been removed. Seedlings were measured from the roots to the end of the stem and those that were between 4 and 4.25 inches tall were selected for this experiment. The same procedure was used for *G. grandis* seedlings except seedlings were selected for a height between 2 and 2.25 inches since growth rate was slower than *S. pectinata*. The difficulty arose for the selection of *S. validus* because we received mature plants and this species is a strongly rhizomic plant, meaning that has multiple stems coming from the same rhizome. Most plants had 4-6 stems per plant, but some had as many as 8 and others as few as 2. Since the design of the flow reactors called for 10 plants per reactor it was decided to have approximately the same number of total stems per reactor. After considering the approximate average number of stems per plant, it was decided to have 50 – 55 total stems per reactor.

3.1.3 Experimental Setup

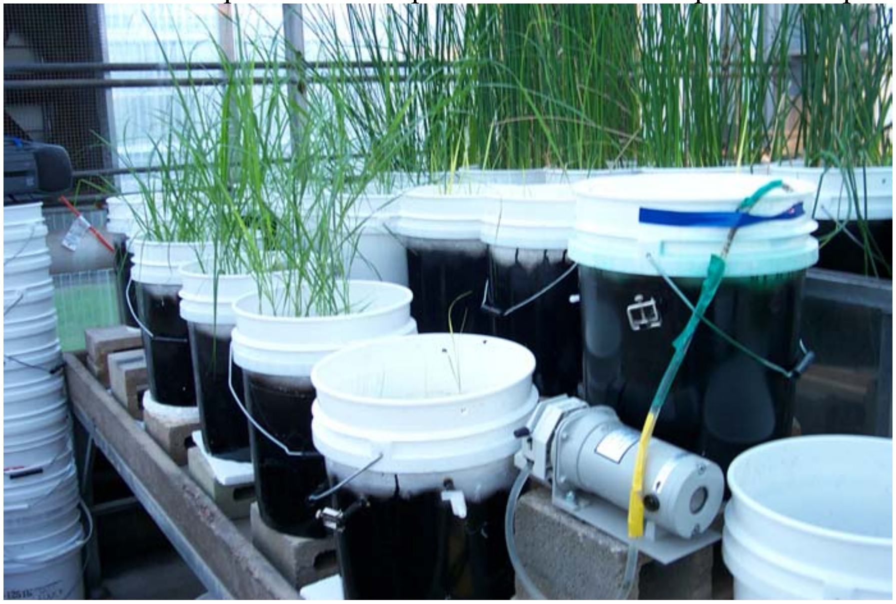
Reactors were constructed out of 5-gallon buckets, with 2 sets of reactors and five subsets of reactors for each species. Set I consisted of hydroponic reactors, and Set II had sand reactors. Subset I had the spiked solution as a nutrient solution and a "fast" flow rate of 12 inches/day. Subset II also used the spiked solution and a "slow" flow rate of 4 inches/day. Subsets III and IV had the same flow rate as subsets I and II, respectively, but used the control solution, and reactors in subset V used the spiked solution but were non-flow reactors. There were 3 reactors in each subset and 10 plants in each reactor. Please refer to Figure 3.1 for a schematic of the hydroponic and sand reactors.

Figure 3.1. Diagram of the silica sand and hydroponic reactors to be used.



For the hydroponic setup, the plants were suspended in the solution with Styrofoam and foam rubber. Styrofoam was cut into a circle to fit into the reactors at the target water level. Next, 10 holes were cut into the Styrofoam and one plant was suspended in each hole with foam rubber plugs in the same manner as in Experiment 1. Hydroponic flow reactors were painted black to prevent algae growth and because root growth is inhibited by light. For sand reactors, the plants were planted directly into the sand, and Styrofoam was cut to cover the exposed areas between the plants to prevent algae growth. Pinch valves were placed on the effluent tubes from each reactor, and the valves were set at the target flow rate. All flow reactors - 3 reactors each for fast/sand, slow/sand, fast/hydroponic, and slow/hydroponic for a total of 12 - for each solution and for each species were tied together in parallel through a peristaltic pump. Therefore, a total of 6 pumps were used to tie together reactors for spiked and control solutions for all three species. The pumps made it possible to keep the flow rates constant and to expose all flow reactors in each setup the same nutrient solution. Flow rates on the reactors and peristaltic pumps were recalibrated once per week. The reactors were arranged randomly within the setup. Water levels were monitored daily and DI water was added as needed to maintain consistent water levels.

Figure 3.2. Photo of *S. pectinata* spiked reactors. There were 6 identical setups like the one in the picture – 2 for each species with a spiked and control setup for each species.



In Figure 3.2, please note that the reactors are set at slightly different heights from each other. Each reactor is connected to its two neighbors at their respective water lines. So, any excess water in the first reactor flows into the second reactor, and so on. The nutrient solution drains at the set flow rate from the bottom of the reactor and a series of tubes is connected to the peristaltic pump. From the pump, the solution goes into a reservoir, which is connected to the first reactor at its water line.

Figure 3.3: Plan view of one setup of flow reactors. Circles are reactors; circle with "R" inside is the reservoir, circle with "P" inside is the peristaltic pump; solid lines are the tubes that connect the reactors at the water level; dashed lines are the tubes that drain the reactors and feed into the peristaltic pump.

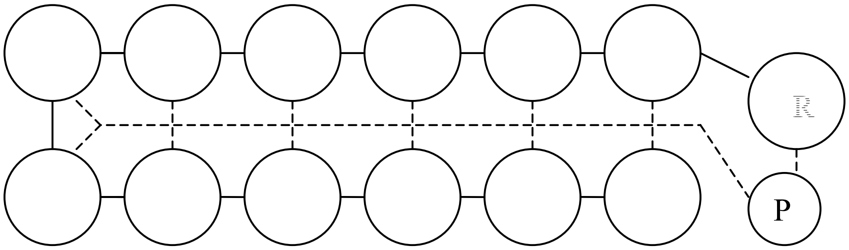
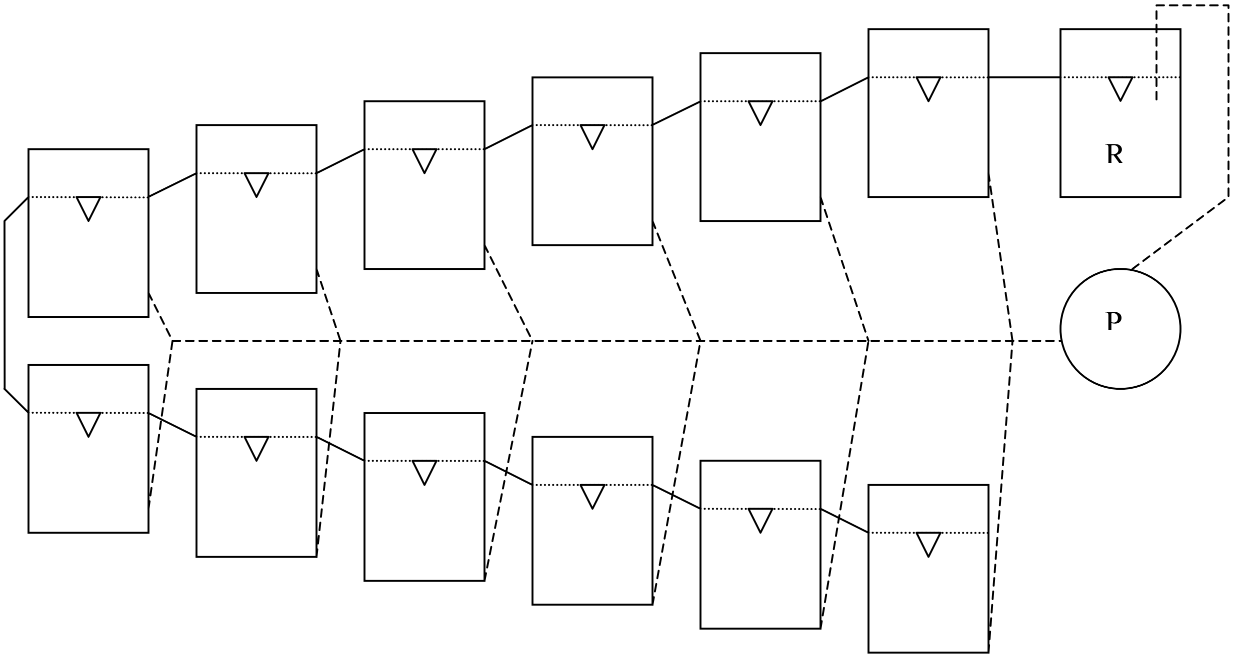


Figure 3.4: Side view of the flow reactor setup. Squares are reactors. Solid lines are the tubes that connect the reactors. Dotted lines and triangles indicate water level. Dashed lines indicate tubes draining the reactors and feeding the peristaltic pump.



Please note that in Figures 3.3 and 3.4, the tubes draining the reactors are leading into the peristaltic pump are not drawn to scale. Care was taken to make sure that the total length of tubing from each reactor to the pump was equal. In addition, the height difference between the two reactors on the left side of the diagram was exactly the same as the height difference between any other two adjacent reactors.

The total number of reactors for this phase was:

(3 species) * (3 replicates) * (5 subsets) * (2 sets) = 90 reactors

Biesboer (personal communication) pointed out that growing plants in silica sand is very similar to growing them in a hydroponic solution since the plants do not gain any nutritional value from the sand, and the sand does not influence the nutrient solution in any significant way. The major difference between the two types of reactors is the fact that the root structure is more natural in the silica sand reactors than they are in the hydroponic reactors. In hydroponic reactors, the roots tend to grow longer and branch out less than they normally do, while the roots structure for those growing in sand is much more similar to that of plants growing in soil. Therefore, the silica sand reactors will more closely simulate the plant behavior in soil.

A third set of reactors that would have plants going in soil was considered but was eliminated for several reasons. Since soils have a relatively high affinity for sorption of all the target pollutants except Cl, it was thought that a vast majority of the P, Pb, Cd, Cu, and Zn in solution would sorb to the soil, leaving a very low concentration of these pollutants in the nutrient solution. It is also more than likely that the soil would contain some levels of Cu, Zn, and P since they are nutrients that the plants require. Because of both of these issues, it would be very difficult to do a mass balance of the pollutants in the reactors. Furthermore, it would be very difficult to analyze the plants at the end of the experiment since it will be difficult to separate the roots from the soil for analysis. We would almost surely lose some of the root tissue in the process of separating the soil from the roots, and it could be possible that trace amounts of the soil would remain on the roots and skew the results. Finally, each type of soil has a different sorption affinity for each of the target pollutants, so conducting an experiment in one type of soil will not provide sufficient information to make general statements. However, analysis of sorption onto detention pond sediment was examined and will be discussed in Chapter 4.

3.1.4 Analysis

3.1.4.1 Water

Once per week, 50 mL water samples were taken from the reservoir of each recirculating setup, and 50 mL composite samples were taken from the non-flow reactors. Samples were acidified to $pH < 2$ with metals grade HNO_3, filtered through a 0.45 micron filter, and stored at 4^oC until analysis. The analysis was done in the same way as it was for Experiment 1. The metals were analyzed with a Perkin-Elmer 5100 graphite furnace atomic adsorption spectrophotometer. Phosphorus concentrations were determined by a Hach UV/Vis Spectrophotometer, and chloride concentrations were determined by a Metrohm ion chromatograph.

3.1.4.2 Plants

At the end of the experiment, the plants were removed from the reactors and each individual plant height was measured to determine overall growth. Roots were separated from stems and root volume was measured by immersing the roots into a graduated cylinder and measuring the displacement. All of the stems from each reactor were then placed in a labeled, paper bag and placed in a drying oven at 105^oC for 3 days. The same was done for all of the roots from each reactor. Dry weights were measured and the plant samples were ground using plant grinders located at the Soil Analytical Labs. Once plants had been ground, samples were submitted for ICP analysis at the Soil Analytical Labs for determination of all target pollutants.

3.2 Results and Discussion

3.2.1 Growth, Dry Weight, and Root Volume

Graphs from the growth, dry weight and root volume for each species in the flow reactors are presented in the appendix at the end of this chapter. Statistical tests using a Z-distribution were done and found that there was a significant difference ($p<0.05$) for the following comparisons of growth:

S. validus: sand/spiked – slow flow vs. no flow; fast flow vs. no flow;
spiked/fast flow – sand vs. hydroponic;
spiked/slow flow – sand vs. hydroponic.

S. pectinata: spiked vs. control – hydroponic/slow flow; hydroponic/fast flow;
sand/spiked – slow flow vs. fast flow; slow flow vs. no flow
sand vs. hydroponic – all combinations.

G. grandis: spiked vs. control – sand/slow flow; hydroponic/slow flow;
sand vs. hydroponic (spiked) – no flow; slow flow; fast flow;
sand/spiked – slow flow vs. no flow;
hydroponic/spiked – fast flow vs. no flow; slow flow vs. no flow

It is interesting to note that by looking at the graphs below, the spiked solution actually seemed to increase growth in all three species, including those cases listed above where there was a significant increase in growth. It is acknowledged that the levels of contamination present in the reactors are generally not sufficiently high to cause noticeable toxicity to the species involved. For example, Zayed et al. (1998) did not see an effect on growth or chlorosis in duckweed until concentrations of Cd and Pb reached 5 mg L^{-1}. Even though each species will have different toxicity thresholds to different contaminants, 5 mg L^{-1} is approximately 500 and 15 times more concentrated for Cd and Pb, respectively, than were used in this experiment.

It was necessary to compare the difference in the increase in dry weight because the *S. validus* plants were much more mature and nearer to full height at the start of the experiment than the other two species. Furthermore, since all three species are strongly rhizomic, multiple new shoots sprouted from the base roots for all plants during the experiment. Therefore, it was thought that comparing the increase in dry weight would be another way to compare the growth of all three species. Comparisons of the increase in dry weight (final dry weight – initial dry weight) reveal significant differences between the following comparisons:

G. grandis
Stems: spiked vs. control – sand/slow flow; hydroponic/slow flow
sand vs. hydroponic – all comparisons
Roots: spiked vs. control – sand/slow flow; hydroponic/slow flow
fast flow vs. slow flow – spiked/sand
flow vs. no flow – sand/spiked/fast flow
sand vs. hydroponic – all comparisons

S. pectinata
Stems: spiked vs. control – sand/slow flow; hydroponic/fast flow
flow vs. no flow – sand/spiked/slow flow
sand vs. hydroponic – all comparisons
Roots: spiked vs. control – sand/slow flow; hydroponic/fast flow
fast flow vs. slow flow – sand/spiked
flow vs. no flow – fast flow/sand
sand vs. hydroponic – all comparisons

S. validus
Stems: spiked vs. control – sand/slow flow
fast flow vs. slow flow – sand/spiked
flow vs. no flow – sand/slow flow; sand/fast flow
sand vs. hydroponic – all comparisons
Roots: spiked vs. control – sand/slow flow; sand/fast flow; hydroponic/fast flow
fast flow vs. slow flow – hydroponic/spiked;
flow vs. no flow – hydroponic/fast flow/spiked;
sand vs. hydroponic – all comparisons.

The information is summarized in the following tables and figures that compare the number of times the total dry weight increased. In other words, M/M_o is presented, with M = the final dry weight (g) and M_o = the initial dry weight (g).

Table 3.3 Average M/M_o (final dry weight/initial dry weight) for all three tested species.

M/M_o		Control Reactors				Spiked Reactors					
		Slow flow		Fast flow		Slow flow		Fast flow		No Flow	
		Stem	Root	Stem	Root	Stem	Root	Stem	Root	Stem	Root
G. grandis	Sand	11.58	3.21	30.76	8.56	64.89	27.27	41.11	12.89	0.36	0.24
	Hydro	3.55	0.62	5.73	1.16	13.35	1.94	17.51	1.80	22.75	10.99
S. pectinata	Sand	4.45	3.59	3.53	3.06	6.12	5.47	4.40	5.37	2.73	8.42
	Hydro	2.71	2.73	2.29	2.00	3.59	3.10	2.09	2.25	2.42	4.81
S. validus	Sand	58.50	57.83	37.06	34.85	27.50	10.83	27.73	21.86	20.51	27.95
	Hydro	33.93	1.70	44.50	1.76	24.38	0.88	4.28	0.48	3.05	0.38

Figure 3.5: Comparison of M/M_o for *G. grandis*.

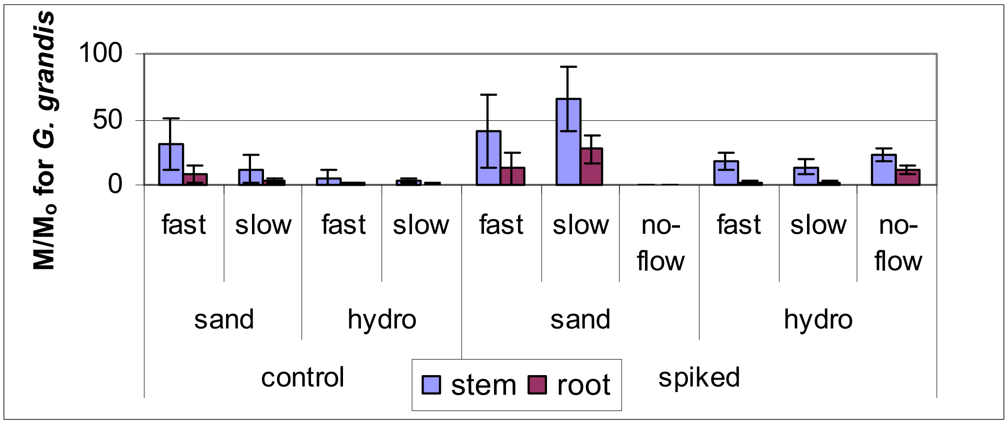


Figure 3.6: Comparison of M/M_o for *S. validus*.

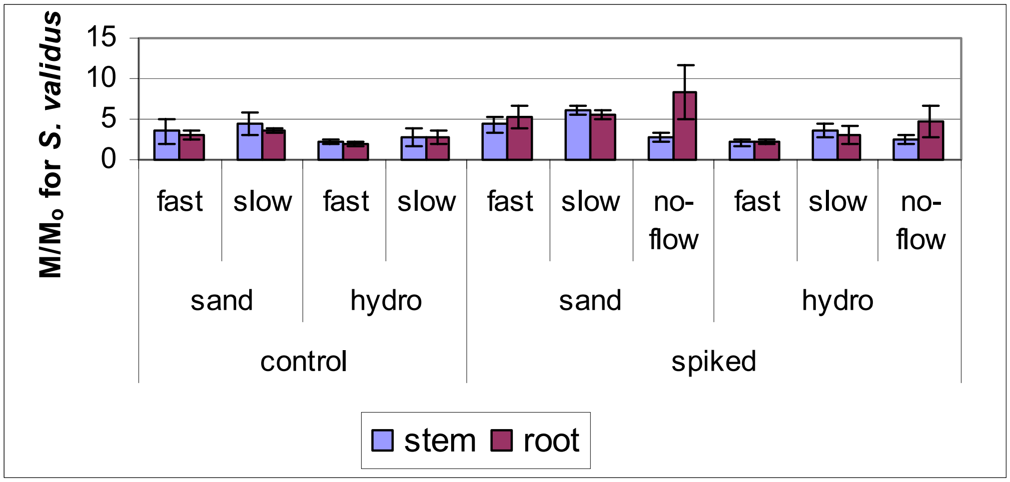
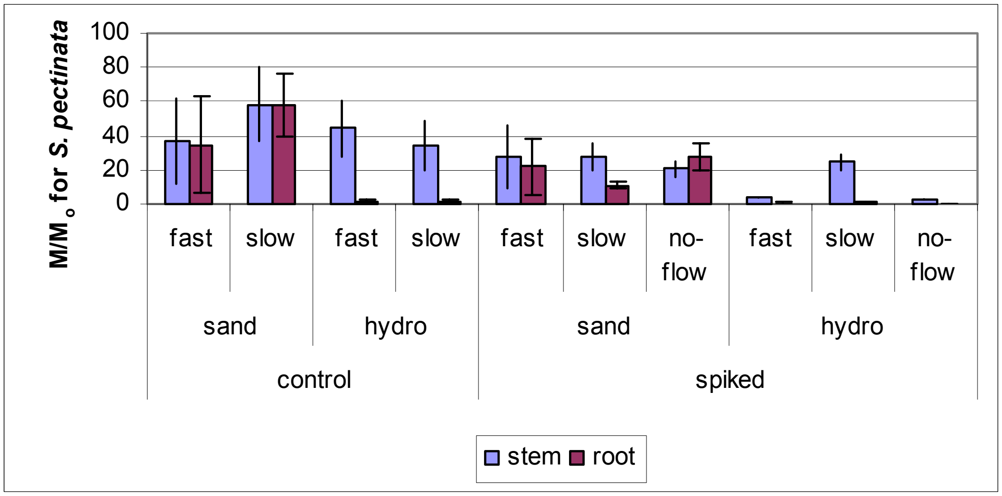


Figure 3.7: Comparison of M/M_o for *S. pectinata*.



The results from the increase in dry weight accentuate the differences seen between growth rates. *G. grandis* and *S. validus* seemed to handle the spiked solution quite well and showed a marked increase in dry weight over the control reactors. Meanwhile, *S. pectinata* in spiked reactors had a smaller increase in dry weight compared to the control reactors. Also, those plants grown in sand reactors had a much greater increase in dry weight than those grown in hydroponic reactors, and that difference was much more evident for *S. pectinata* and *G. grandis* than it was for *S. validus*.

We also compared the increases in root volume and those comparisons revealed significant differences between the following reactors:

S. validus: spiked vs. control – sand/slow flow; sand/fast flow; hydroponic/slow flow
fast flow vs. slow flow – sand/spiked; hydroponic/spiked
flow vs. no flow – sand/fast flow; sand/slow flow; hydroponic/fast flow
sand vs. hydroponic – spiked/fast flow; spiked/no flow

G. grandis: spiked vs. control – sand/slow flow; hydroponic/slow flow;
sand vs. hydroponic – spiked/no flow; spiked/slow flow; spiked/fast flow; control/slow flow;
slow flow vs. no flow – spiked/sand;

S. pectinata: sand vs. control – hydroponic/slow flow;
spiked/sand – fast vs. slow flow; fast vs. no flow; slow vs. no flow;
sand vs. hydroponic – all combinations

The increase in root volume is important because the roots are where contaminants are initially taken into the plant. So a greater root volume would theoretically lead to a greater uptake of contaminants into the plant.

3.2.2 Accumulation in Plants

As was done in the Experiment 1, the rates of accumulation in the plants were determined. However, unlike Experiment 1 in which plant and water samples were taken on the same days, plant samples were only taken on the final day of the experiment. This was done because of the problem in Experiment 1 where individual plant samples were too small and all replicates had to be combined. If that had been done, then the reduction in the number of plants in each reactor could have affected the depletion rates of the target contaminants in the water.

The following tables present normalized increase in contaminant concentration (C/C_o), in which C is the final concentration and C_o is the initial concentration.

Table 3.4: Normalized increase in concentration of cadmium in all three species.

Cd		*G. grandis*		*S. pectinata*		*S. validus*	
		stem	Root	Stem	root	Stem	Root
sand	Fast	0.866	2.614	1.156	6.673	0.959	1.987
	Slow	0.782	1.701	0.937	8.486	1.034	2.254
	no-flow	0.440	0.885	0.392	0.997	1.129	0.973
hydro	Fast	1.820	8.553	2.621	29.390	2.108	8.940
	Slow	1.527	9.074	2.653	35.314	2.825	8.687
	no-flow	4.409	10.725	5.508	36.976	1.940	5.406

Figure 3.8: Normalized increase in concentration of cadmium in all three species.

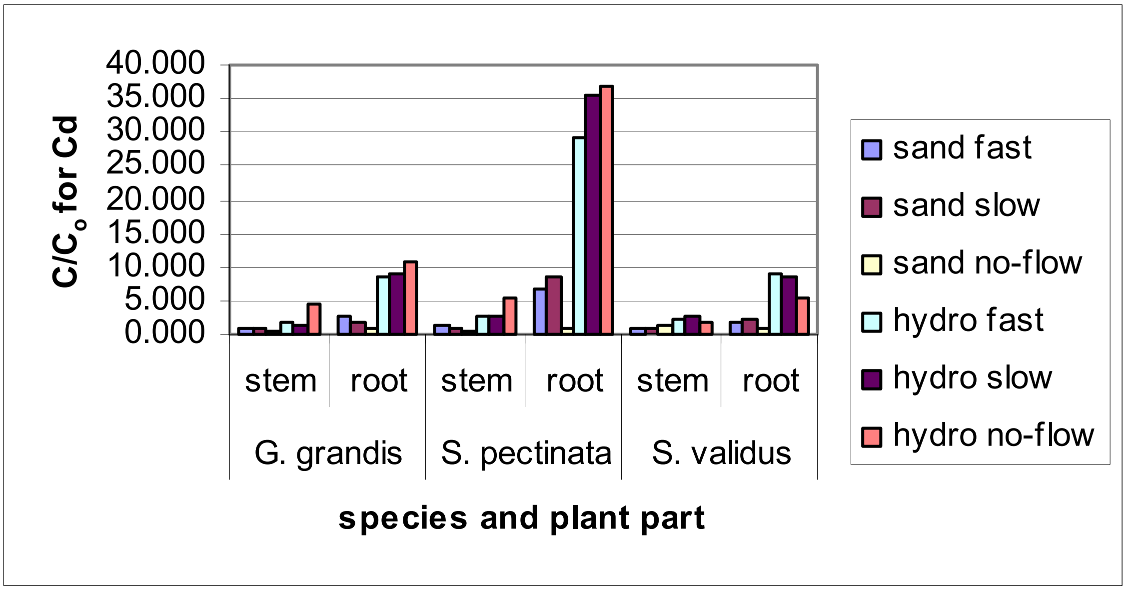


Table 3.5: Normalized increase in concentration of copper in all three species.

Cu		*G. grandis*		*S. pectinata*		*S. validus*	
		stem	Root	Stem	root	Stem	Root
Sand	Fast	2.537	9.212	0.832	2.395	2.635	2.571
	Slow	2.824	9.159	0.785	2.118	2.895	2.431
	no-flow	2.999	6.600	0.518	1.376	1.120	1.737
Hydro	Fast	2.613	19.494	1.020	4.049	4.260	7.089
	Slow	2.707	18.669	1.024	4.593	4.340	5.298
	no-flow	3.919	9.665	1.096	3.877	1.824	1.607

Figure 3.9: Normalized increase in concentration of copper in all three species.

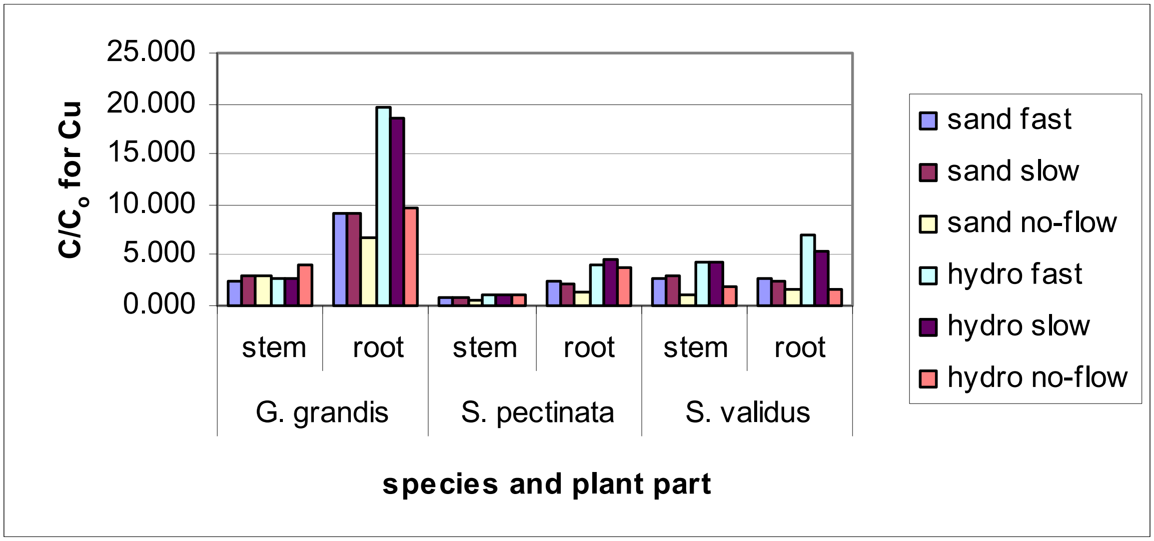


Table 3.6: Normalized increase in concentration of phosphorus in all three species.

P		*G. grandis*		*S. pectinata*		*S. validus*	
		stem	root	Stem	root	stem	Root
Sand	Fast	9.434	6.946	4.103	3.655	0.902	0.685
	Slow	15.035	7.906	3.469	3.702	0.950	0.638
	no-flow	4.110	3.535	1.073	1.164	0.413	0.447
hydro	Fast	13.669	13.214	5.650	8.287	1.078	1.279
	Slow	12.727	13.502	6.295	7.562	1.123	1.072
	no-flow	19.392	32.274	5.256	14.712	0.706	1.050

Figure 3.10: Normalized increase in concentration of phosphorus in all three species.

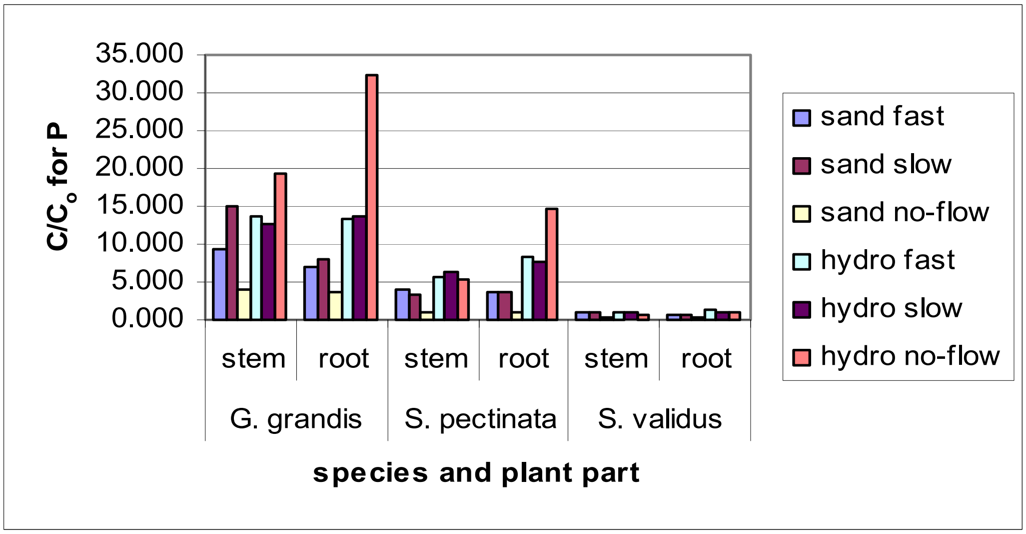


Table 3.7: Normalized increase in concentration of lead in all three species.

Pb		*G. grandis*		*S. pectinata*		*S. validus*	
		stem	root	Stem	root	stem	Root
Sand	Fast	1.759	2.170	1.448	0.773	2.017	1.503
	Slow	1.634	2.024	1.561	0.804	1.632	1.648
	no-flow	1.029	2.917	1.003	0.571	1.817	1.912
Hydro	Fast	2.322	8.568	2.332	3.689	3.896	7.112
	Slow	2.208	7.214	2.335	3.159	4.058	7.713
	no-flow	4.175	7.926	3.317	16.691	4.494	5.405

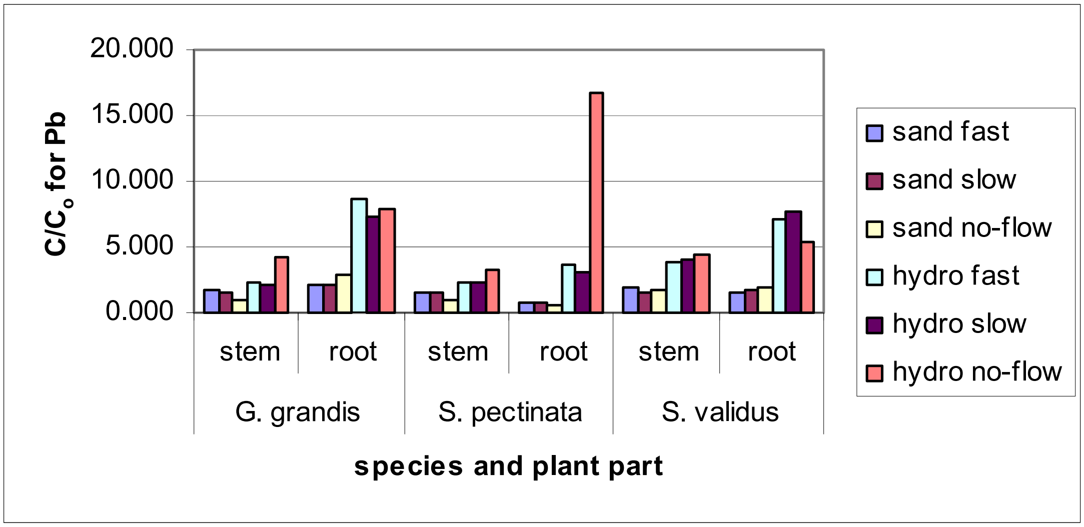


Figure 3.11: Normalized increase in concentration of lead in all three species.

Table 3.8: Normalized increase in concentration of zinc in all three species.

Zn		*G. grandis*		*S. pectinata*		*S. validus*	
		stem	Root	Stem	root	stem	Root
Sand	Fast	0.566	4.997	1.523	2.897	1.563	3.205
	Slow	0.964	7.536	1.310	2.392	1.717	3.745
	no-flow	0.153	2.087	0.629	0.532	0.435	1.585
Hydro	Fast	1.469	18.869	7.830	11.211	10.624	28.450
	Slow	1.775	14.412	7.593	8.830	5.406	15.415
	no-flow	6.528	11.396	7.267	6.276	8.268	14.111

Figure 3.12: Normalized increase in concentration of zinc in all three species.

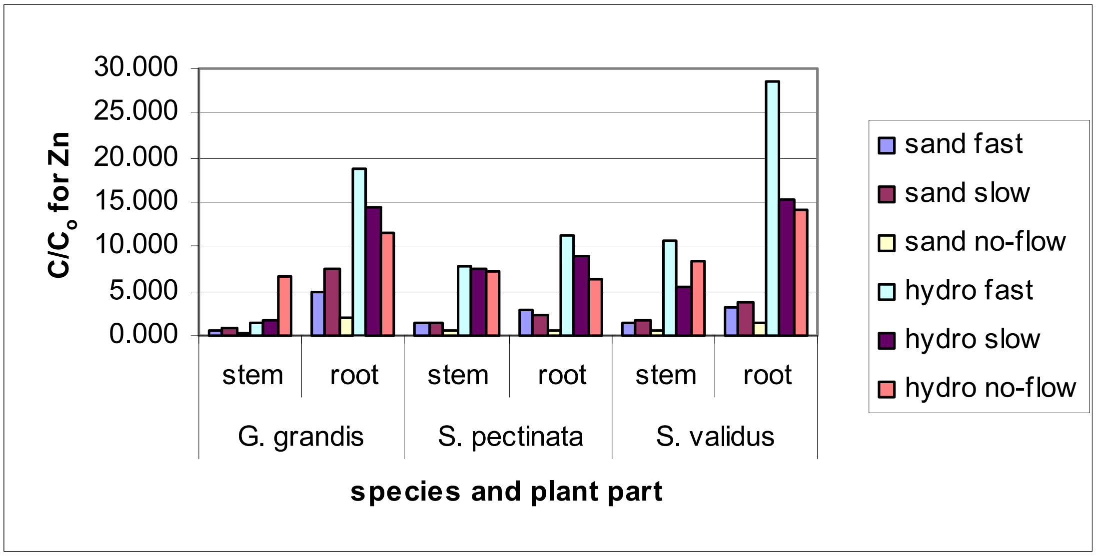
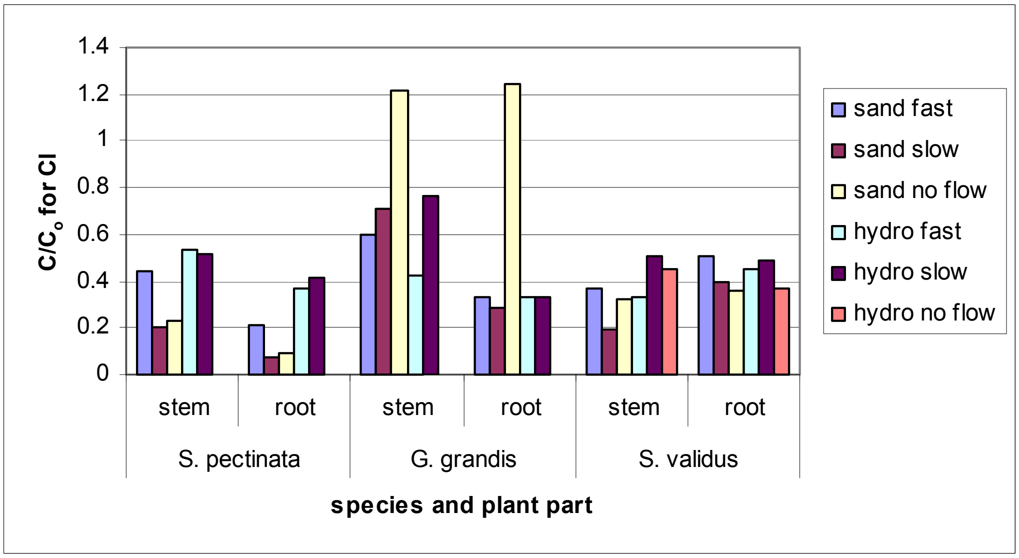


Table 3.9: Normalized increase in concentration of chloride in all three species.

Cl		*G. grandis*		*S. pectinata*		*S. validus*	
		stem	Root	Stem	root	stem	Root
Sand	Fast	0.329	0.210	0.533	0.330	0.369	0.138
	Slow	0.791	0.509	0.688	0.305	0.286	0.155
	no-flow	1.218	1.242	0.231	0.088	0.322	0.360
Hydro	Fast	0.325	0.322	NA	NA	0.372	0.377
	Slow	0.301	0.206	0.859	0.398	0.382	0.353
	no-flow	NA	NA	NA	NA	0.450	0.365

Figure 3.13. Normalized change in concentration of chloride in all three species.



Analysis of the data for the increase on concentration of the contaminants in the plants reveals that for the heavy metals, the roots resulted in a much greater increase in concentration than the stems. This was very similar to the results in Experiment 2 and to the result from several researchers, including Zayed et al. (1998) and Zhu et al. (1999). The opposite was true for Cl as the stems had a greater increase in concentration, and there were mixed results for P. One interesting note is that there was actually in decreased concentration of P in *S. validus*; however, as can be seen below in the analysis of the depletion of concentrations in the water, the reactors with *S. validus* resulted in the greatest overall decrease in P. So, while the analysis of the increase in concentration in the plants is interesting, it is obvious that it does not paint the entire picture.

3.2.3 Depletion Rates in Water

As in Experiment 1, the rates of depletion of the target contaminants from the nutrient solutions were determined. Since all reactors for each species with either the spiked or control nutrient solutions were tied together in parallel, they were exposed to the same solution and only one water sample was taken from each set of reactors. Therefore, on each sampling day, one sample was taken from the *S. pectinata* spiked set of reactors and one from the *S. pectinata* control set of reactors. The same was done for *G. grandis* and *S. validus*. The sand and hydroponic non-flow reactors for each species stood independently and were not tied together in any way. However, when samples were taken, an equal amount of sample was taken from each reactor and the samples were combined to form one composite sample from the three reactors in each combination. The following table presents first-order reaction rates for the uptake of the target contaminants from the spiked nutrient solutions. More data and figures are available in the appendix.

Table 3.10: Reaction rates for the depletion of the target contaminants from the spiked flow reactors for each of the three tested species ($V\ t^{-1}\ plant^{-1}$; V in liters and t in days).

	Cd	Cl	Cu	P	Pb	Zn
S. pectinata	-0.029	-0.012	-0.088	-0.017	-0.056	-0.045
G. grandis	-0.031	-0.012	-0.039	-0.018	-0.047	-0.039
S. validus	-0.027	-0.010	-0.047	-0.014	-0.063	-0.038

3.3 Conclusions

There are five main conclusions that were drawn from this experiment. First, all three species successfully removed contaminants from the spiked nutrient solutions. The depletion rates were measured and will be used in a conceptual model in Chapter 5. Second, the removal rate from the spiked nutrient solution depends on both the contaminant in question and the species involved. Third, roots accumulate a higher concentration of heavy metals than do the stems for all three species. Meanwhile, the stems had a greater increase in concentration of Cl than the roots did, and there were no general trends for P accumulation. Fourth, plants grown hydroponically had a higher concentration than those grown in sand. Lastly, plants grown in flow reactors removed a greater mass of contaminants than those grown in non-flow reactors.

4.0 Sorption

Another major component of the removal of contaminants from water is sorption onto the pond sediment. Several researchers have mentioned that for young detention ponds (< 10 years), sorption plays a significant role in the removal of contaminants. However, as sorption sites are filled up, the rate of removal can decrease or essentially stop. Nonetheless, it is necessary to examine sorption rates in an established detention pond. In this chapter, sorption refers to both the processes of adsorption and absorption. There was not an effort made to differentiate between the two processes.

4.1 Experimental Materials and Methods

A series of experiments were performed to determine rates of pollutant concentration depletion due to sorption onto the sediments. Two sets of experiments were completed: 1) one to measure the rate of sorption, and 2) one to measure the equilibrium concentrations. Sediment samples were taken from a detention pond at the intersection of TH-13 and Pilot Knob Road in Mendota, MN. Several sediment cores were taken using a sediment corer. Four cores were left intact in the sediment cores. Four other cores were taken and mixed together stored. Also, several samples of the top two inches of sediment were taken from the center of the detention pond. All cores and samples were brought back to St. Anthony Falls Laboratory and frozen until experiments began, except for two undisturbed cores and a few samples of disturbed, mixed sediment. The two undisturbed cores were sliced, and the slices and the mixed samples were placed in an oven at 105^{o}C for 3 days until completely dry. All samples were sent to the Soil Analytical Labs on the University of Minnesota, St. Paul campus for analysis to determine what background concentrations of our target pollutants were already present in the sediment and to find the concentration profile with depth in the sediment cores.

4.1.1 Rate of Sorption

For the experiments to determine the rate of sorption, the disturbed and undisturbed sediment cores were used. A recirculating pump was attached to the top of each core. All of the pumps were connected to the same power supply and therefore had the same flow rate through each of the pumps. The intake pipe of each pump was set up to be approximately 1 inch above the sediments in the bottom of each tube. The outlet of each pump was set to be just above the water level in each tube. The purpose of this was to entrain oxygen as the outlet from the pump entered the bulk solution and, therefore, keep the water oxygenated to prevent the release of heavy metals and nutrients from the sediment due to anoxic and reducing conditions. The exact rate of flow was not important as long as the outlet was above the water level and flow rate was not too high to disturb the sediments.

For the undisturbed sediment cores, the sediment levels were left as they were when the samples were taken. The levels ranged from 14 to 18 cm above the bottom of the sediment core tube. For the disturbed sediment cores, 200 grams of mixed sediment was added to each core. This amount was chosen because it resulted in approximately the same height of sediment as the average for the undisturbed cores. However, the exact amount of sediment in each tube was not considered to be especially important since only the top 3-4 cm of sediment were expected to react with the solution in sorption processes. The parameters of most importance were the volume of solution in each core, the initial concentrations of the target contaminants, and the area of sediments exposed to the solution, and care was taken to make sure those parameters were consistent. There were also 3 tubes without any sediment to serve as a control and gain an understanding of any sinks that may have been associated with the system.

The solution added to each core was identical to the spiked ¼ strength Hoagland's solution used in Experiment 2, except Na-EDTA was eliminated. One large batch of the nutrient solution was made and then 1.5 liters was added to each sediment core system. An initial water sample was taken from the initial batch of solution. While adding solution to each core system, care was taken to minimize any suspension of the sediment. After solution was added to each core, any disturbed sediment was allowed to settle for 1 hour, after which another 15 mL water sample was taken. Immediately after this sample was taken, the pumps were turned on. Samples of 15 mL were taken from each core system on the following schedule:

Number of hours after starting pumps: 0.5, 1, 2, 4, 8, 12, 24, 36, 48, 72, 96, 120.

After each sample was taken, it was filtered through a 0.45 micron filter, acidified with metals grade HNO_3 to pH < 2, and stored at 4^oC until analysis. Water samples were analyzed in the same method as was done in Experiments 1 and 2.

4.1.2 Equilibrium Experiments

This set of experiments was conducted by using the sediment sampled from the first 2 inches of sediment in the detention pond and some clear, glass BOD bottles. Various amounts of sediment (¼, ½, and 1 gram) were added to 200 mL of the control ¼ strength Hoagland's solution, with various concentrations of the target pollutants. The concentrations of the target pollutants are listed in Table 4.1 below.

Table 4.1. Concentrations of the target pollutants in the solutions used for the equilibrium experiments.

Solution	Cd (µg/L)	Cl (mg/L)	Cu (µg/L)	P (mg/L)	Pb (µg/L)	Zn (µg/L)
1	5	15	50	0.5	100	125
2	7.5	22.5	75	0.75	200	188
3	10	30	100	1	300	250
4	15	45	150	1.5	400	375
5	20	60	200	2	500	500

Once each solution was added to each BOD bottle, an initial 25 mL sample was taken. The BOD bottles were placed on a shaker table and shaken for 24 hours. After 24 hours, the table was turned off and the solution was allowed to settle for 3-4 hours and 50 mL samples were taken. As soon as all samples were taken, they were filtered through a 0.45 micron filter, acidified with metals grade HNO_3 to pH < 2 and stored at 4^oC until analysis. Due to a malfunction of the analytical machinery, these samples had to be analyzed at the Soil Analytical Labs on the St. Paul campus by using the ICP method of analysis.

4.2 Results

4.2.1 Background Concentrations in the Sediments

The following data and graphs show what the concentration profile in the sediments taken from the TH-13 detention pond.

Figure 4.1. Concentration profile for cadmium in sediment cores.

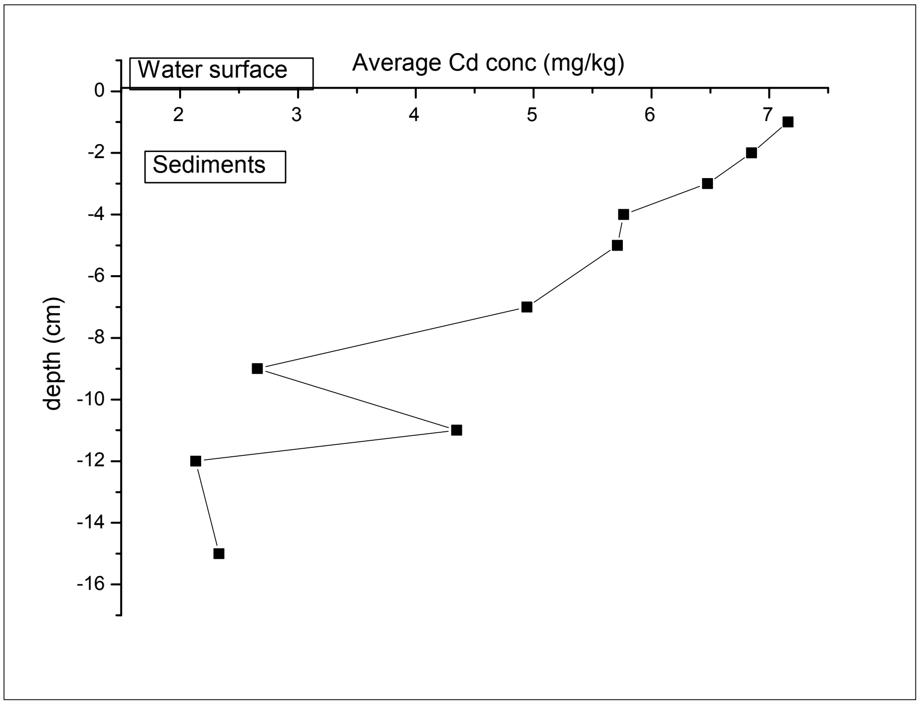


Figure 4.2. Concentration profile for copper in sediment cores.

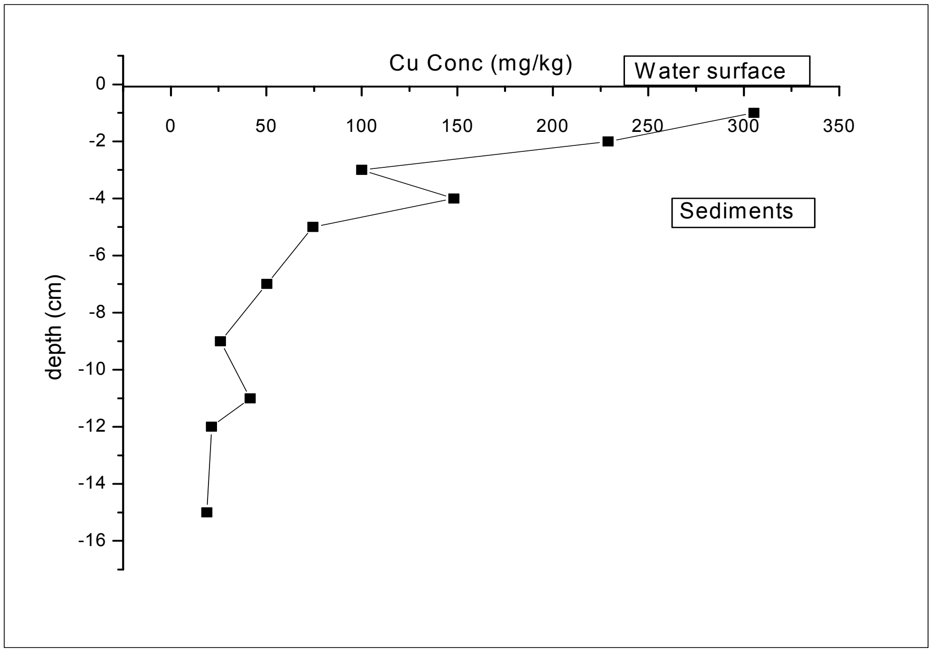


Figure 4.3. Concentration profile for lead in sediment cores.

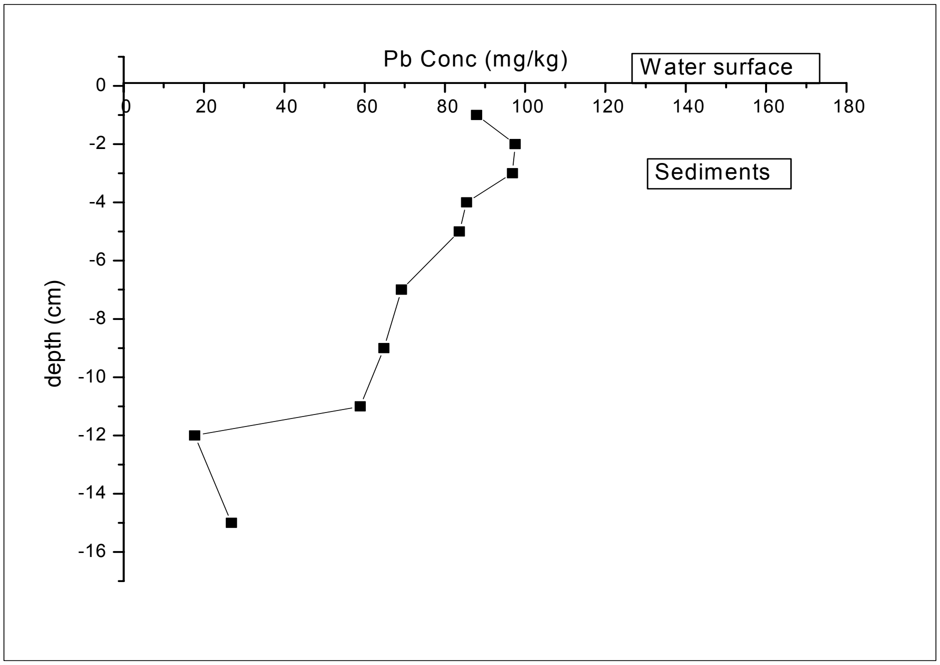


Figure 4.4. Concentration profile for phosphorus in sediment cores.

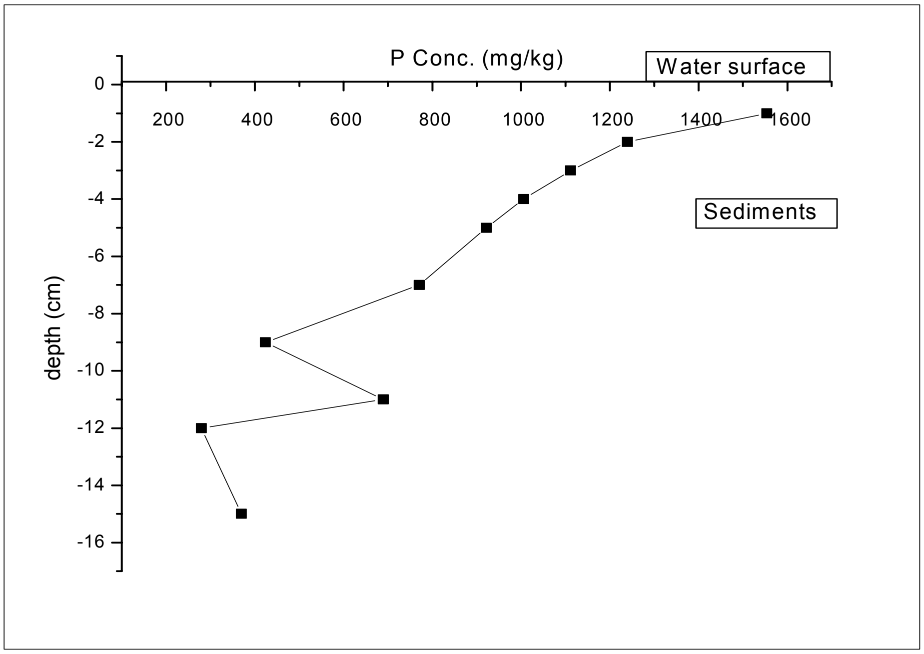


Figure 4.5. Concentration profile for zinc in sediment cores.

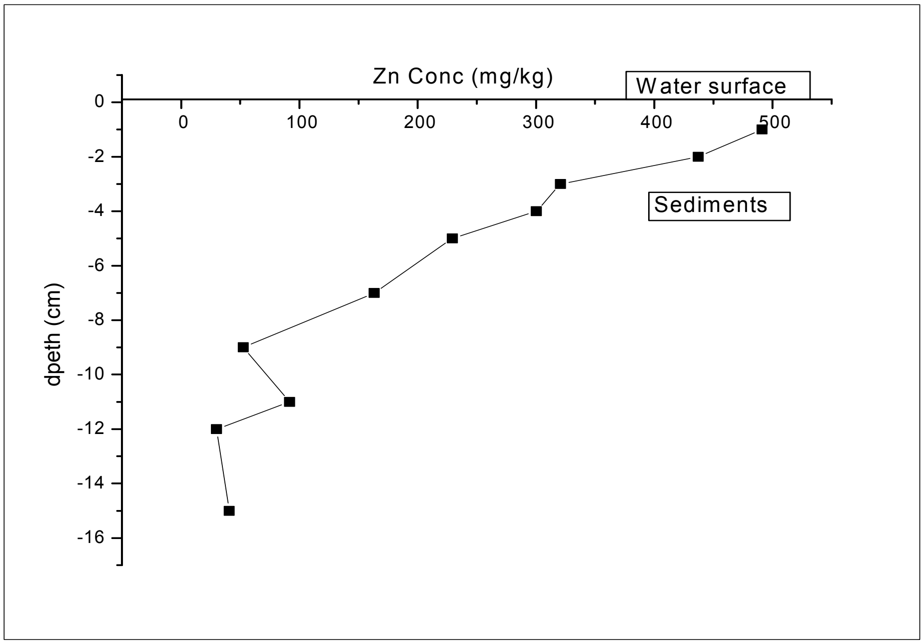


Table 4.2. Average concentrations (mg kg^{-1}) of five contaminants in sediment cores taken from TH-13 detention pond.

Depth (cm)	Cadmium	Copper	Lead	Phosphorus	Zinc
Bulk sample	6.916	239.265	93.393	1349.238	440.235
-1	7.160	305.271	87.889	1553.650	491.155
-2	6.850	228.995	97.506	1239.800	437.160
-3	6.476	99.929	96.872	1111.800	320.625
-4	5.765	148.180	85.434	1006.310	300.405
-5	5.711	74.405	83.588	921.975	229.215
-7	4.945	50.287	69.189	770.825	163.137
-9	2.655	26.057	164.860	423.600	52.558
-11	4.347	41.560	58.962	689.750	91.618
-12	2.132	21.321	17.680	279.520	30.020
-15	2.330	18.955	26.830	369.990	40.629

It was expected that the concentrations would decrease with depth, as was the case, because contaminants in the water in the pond would sorb to the shallower sediments before they would have a chance to diffuse to deeper depths.

4.2.2 Rates of Depletion From Water

Results from the sorption experiments showed some mixed results, as can be seen in the following figures. In each figure, the concentrations presented represent the net concentration in the solution due to the presence of the sediments in the sediment core. These numbers were generated from best fits from three different tests. The first test was to look at the depletion of the concentrations of the target contaminants in spiked nutrient solutions without sediments. This represents the sinks inherent to the system. The concentrations were found and best fit regression lines were applied to try to model the behavior of each contaminant in the reactor core. These regression lines were labeled C1. Secondly, potential sources of the target contaminants were tested by finding the concentrations generated by having deionized water and sediments present in the sediment cores. In all cases, we found that a constant value resulted and we concluded that this represents a source of the contaminant from the sediments. The constant value was labeled C2. Lastly, we tested the change in concentrations of the target contaminants in spiked solutions with sediment present on the bottom of the cores. Just as when finding equations for C1, best fit regression lines were found for the data sets. These regression lines were labeled C3. Then, the sink due to the sediments was determined by subtracting equations C1 and C2 from C3. This combination of equations was labeled C4, and this is presented in the figures below. It could be said that it is necessary to look at the data from the figures below from the perspective of the water. A negative value in the figures represents a reduction in the aqueous concentration, and therefore, a net sink associated with the sediments. A positive value in the figures represents an increase in the aqueous concentration, and, therefore, a net source of the contaminant from the sediments. The effective rate of decrease for the target contaminants from the water are summarized below in Table 3.13. Figures 4.6 through 4.11 show the change in concentration attributable to the sediments. The rates on the regression lines may not agree with those displayed in Table 4.3 because the extreme variability, or "noise", often present during the first couple of hours of the experiment was removed prior to finding the rates shown in Table 4.3.

Table 4.3. Effective rate of change (C4 model) of the target contaminants in the nutrient solution attributable to sorption onto the sediments ($L^3\ t^{-1}\ m^{-2}$).

Target contaminant and units	Rate of change of concentration in nutrient solution
Cd	0.0189
Cl	-0.0081
Cu	-0.2717
P	-0.0013
Pb	-0.3752
Zn	-0.0104

Figure 4.6. Net change in cadmium concentration (C4 model) in the nutrient solution due to sorption onto the sediments.

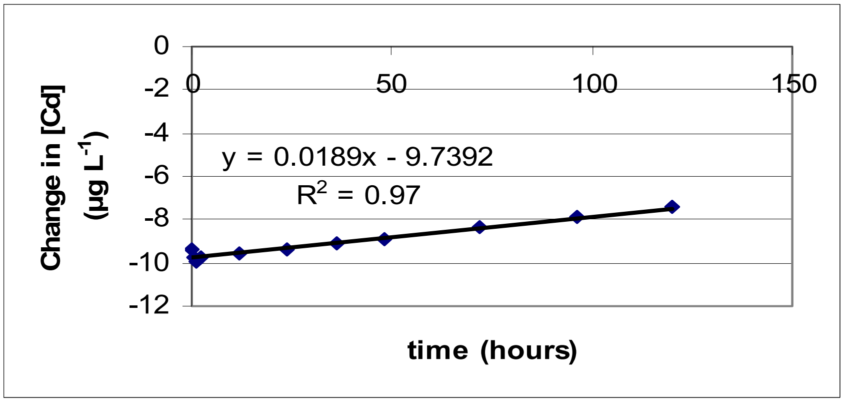


Figure 4.7. Net change in chloride concentration (C4 model) in the nutrient solution due to sorption onto the sediments.

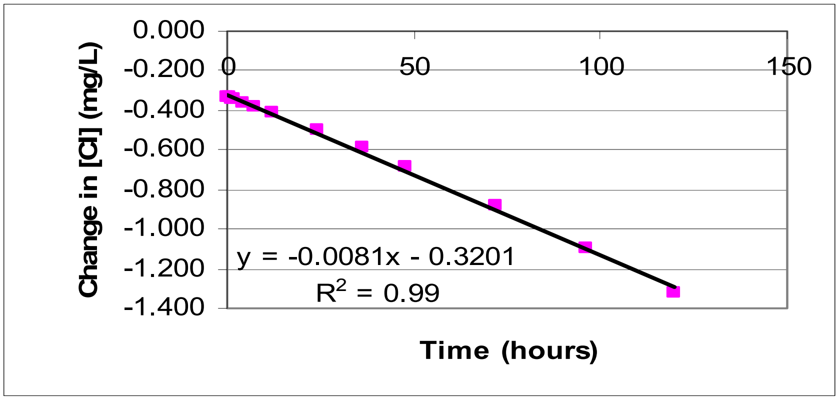


Figure 4.8. Net change in copper concentration (C4 model) in the nutrient solution due to sorption onto the sediments.

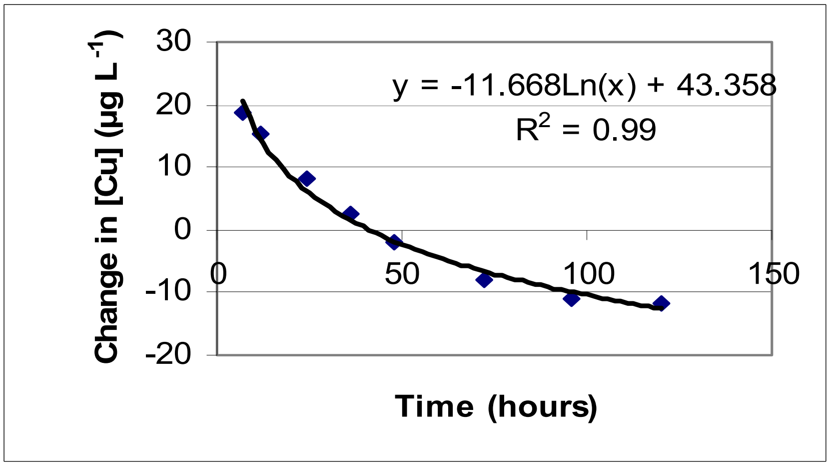


Figure 4.9. Net change in phosphorus concentration (C4 model) in the nutrient solution due to sorption onto the sediments.

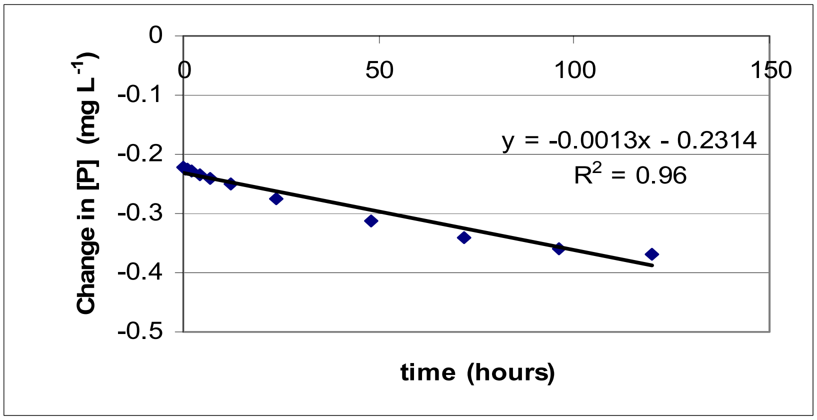


Figure 4.10. Net change in lead concentration (C4 model) in the nutrient solution due to sorption onto the sediments.

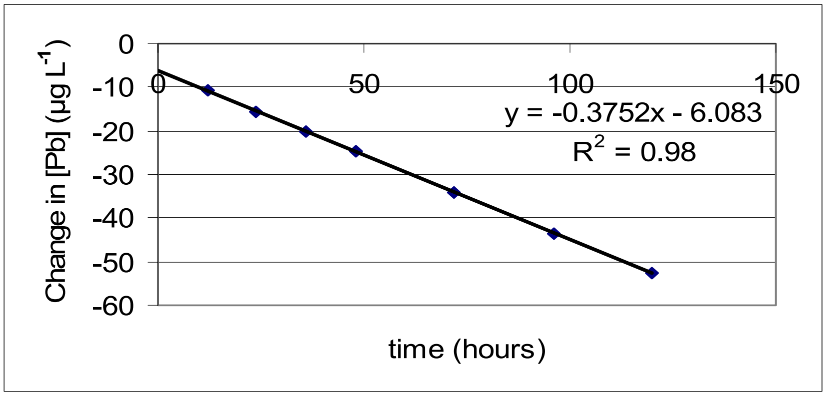
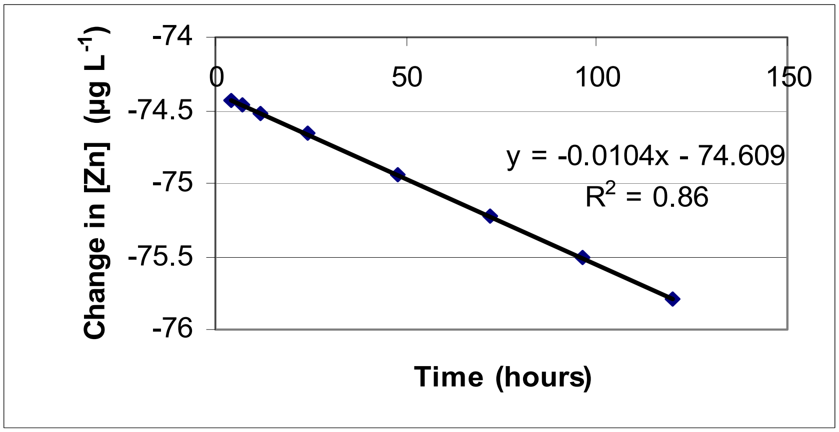


Figure 4.11. Net change in zinc concentration (C4 model) in the nutrient solution due to sorption onto the sediments.



As expected, each target contaminant had a vastly different rate of change of concentration that could be attributable to the sediments. Different elements have different affinities for a given sediment type. In addition, there is a certain competition between the different ions for the sorption sites present in the sediments. However, there were some surprising results with this experiment. Cadmium showed a net decrease in concentration with the sediments in the cores, and that can be seen in Figure 4.6. However, over time, that decrease in concentration became smaller and smaller which implies that cadmium was slowly being released by the sediments back into the solution. The most likely explanation for this phenomenon is that competition from other metal ions pushed the cadmium out of the sorption sites and back into solution.

4.2.3 Equilibrium Experiments

Results from the equilibrium experiments indicated that the final equilibrium concentration for each of the target contaminants is a function of the initial concentration. The result and regression lines are presented in the figures below.

Figure 4.12. Amount sorbed (mg/g) vs. the equilibrium concentration (µg/L) for Cd.

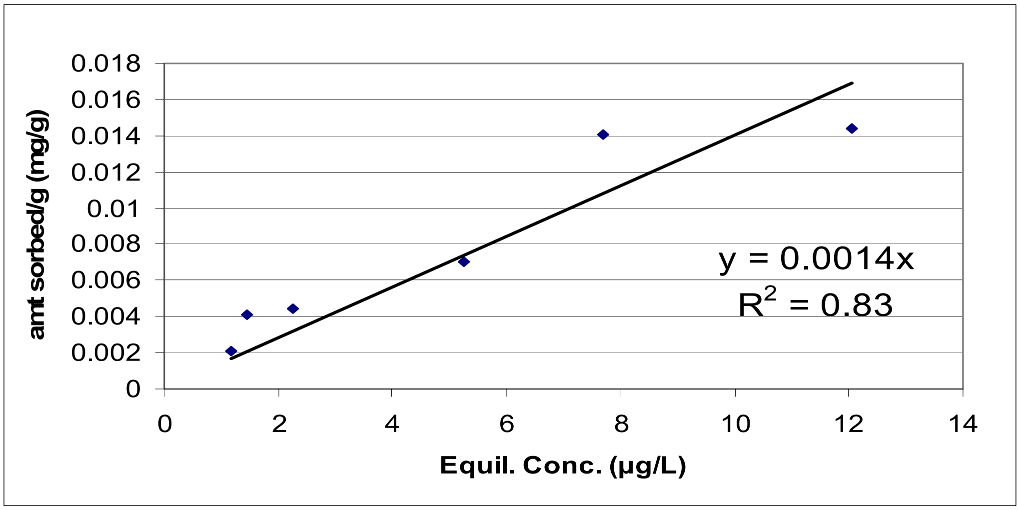


Figure 4.13. Amount sorbed (mg/g) vs. the equilibrium concentration (µg/L) for Cu.

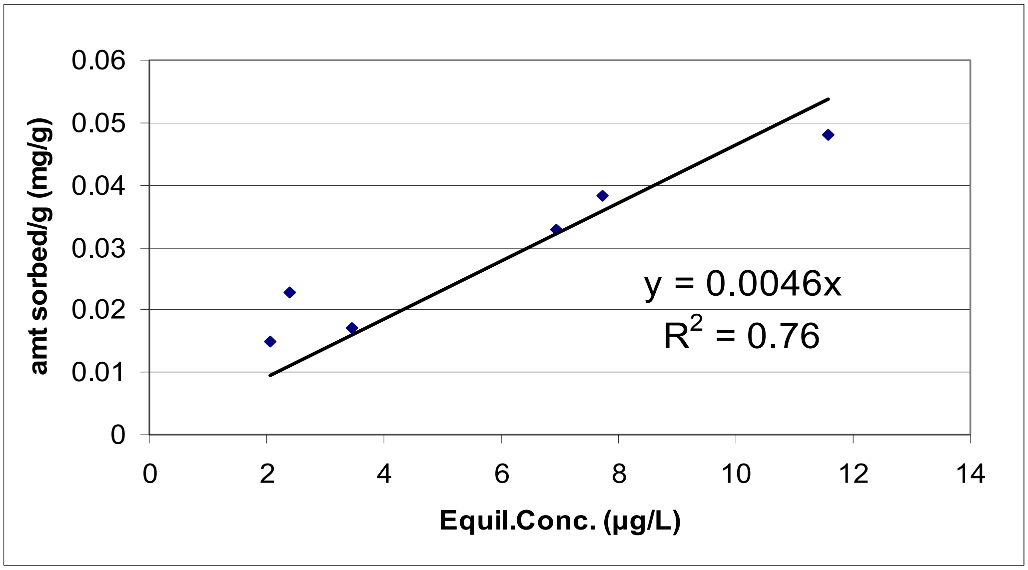


Figure 4.14. Amount sorbed (mg/g) vs. the equilibrium concentration (µg/L) for Pb.

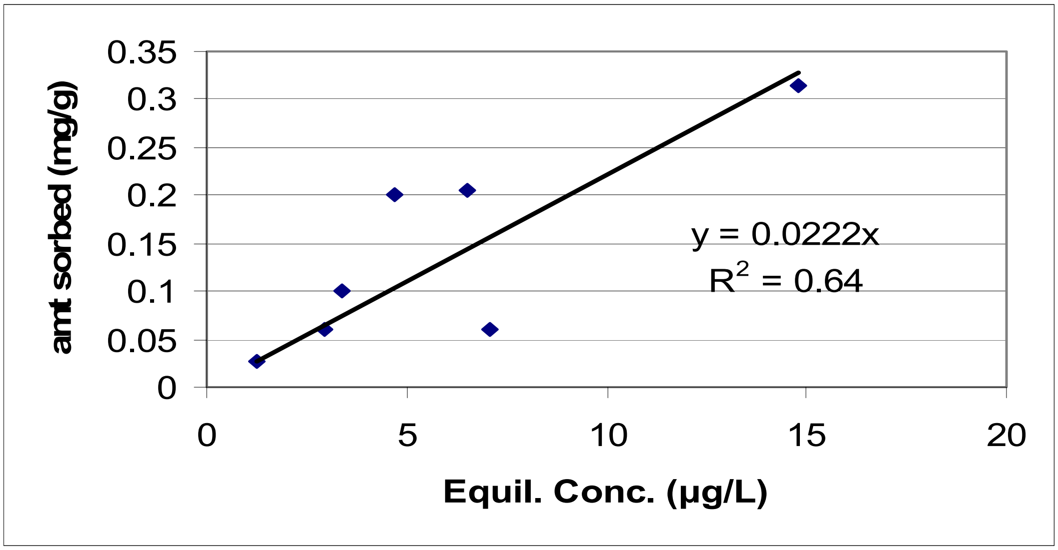


Figure 4.15. Amount sorbed (mg/g) vs. the equilibrium concentration (mg/L) for P.

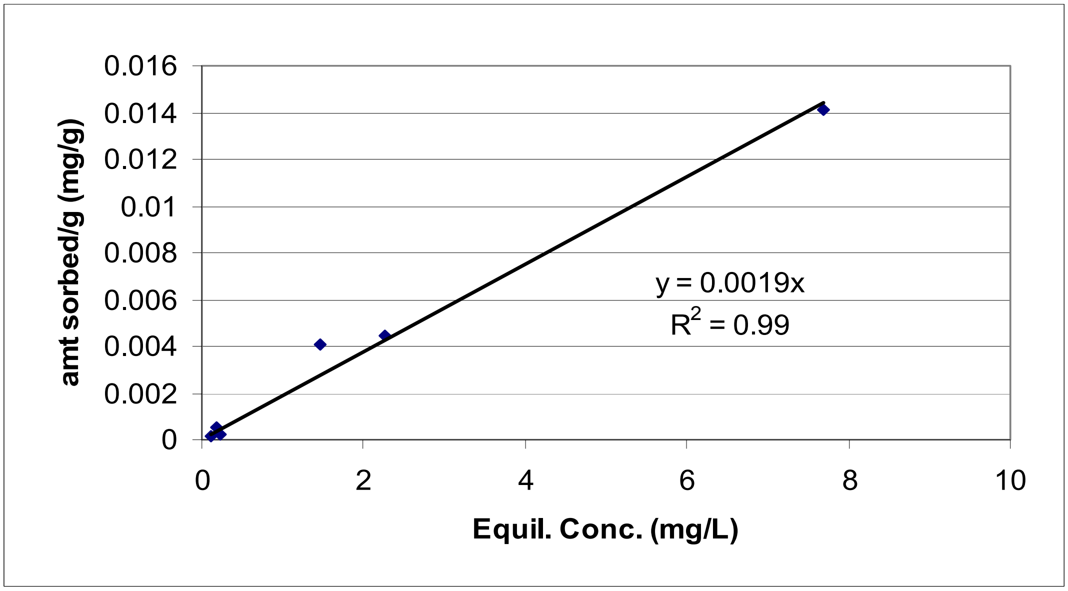
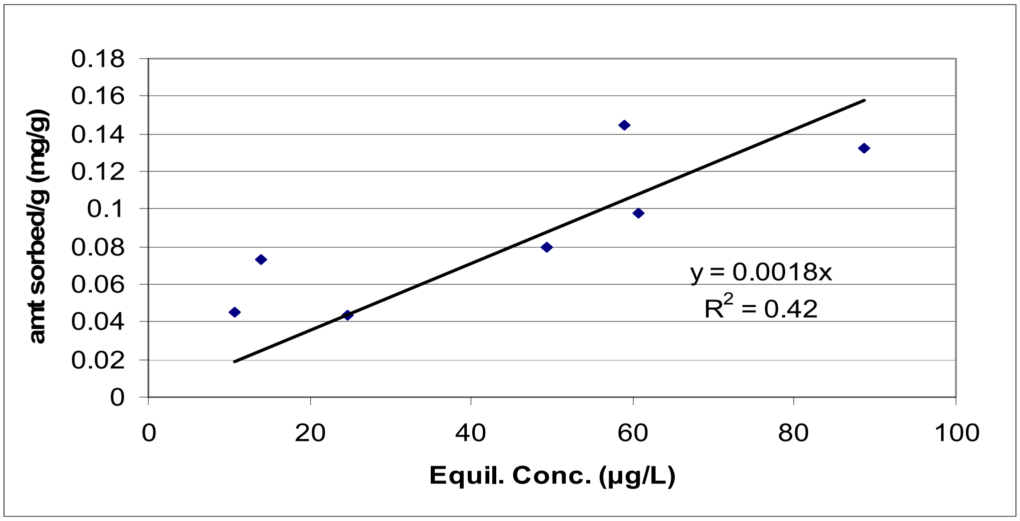


Figure 4.16. Amount sorbed (mg/g) vs. the equilibrium concentration (µg/L) for Zn.



4.3 Conclusions

Sorption rates of the target contaminants were determined, as were the equilibrium concentrations between spiked solutions and detention pond sediments. As was expected, each target contaminant sorbed at different rates and had different equilibrium concentrations. The sorption rates and equilibrium relationships can be implemented into a model to determine expected effluent concentrations for a detention pond.

5.0 Numerical Model

The final step of this project was to use the rates of change found in the first three sets of experiments and incorporate them into a model that would aid in the determination of required detention times in stormwater detention ponds to meet water quality standards. The analytical solution is presented in Equation 1 and the derivation is presented in Section 5.1. The analytical solution is as follows:

$$C(t) = C_e + \left(C_o - C_e\right)\exp\left[-\left(\frac{\sum Q_{out}}{V} + \frac{DK_pA_p}{V} + \frac{K_sA_s}{V}\right)t\right] \qquad (1)$$

Where: C(t) = the concentration at time = t; C_e = the equilibrium concentration (M L^{-3}); C_o = the initial concentration in the pond (M L^{-3}); ΣQ_{out} = the summation of the flow out of the pond (L^3 t^{-1}); V = the volume in the pond (L^3); D = pond diameter (L); A_p = the area of the plants (L^2); K_p = the uptake rate (L^3 t^{-1} $plant^{-1}$) by the plants of the target contaminant; A_s = the area of the sediments in the pond (L^2); K_s = the uptake rate (L^3 t^{-1} L^{-2}) by the sediments of the target contaminant; and t = time.

5.1 Derivation of Analytical Solution

First consider the mass balance of the pond system:

$$\underset{1}{\int \frac{\partial}{\partial t} C dV} = -\underset{2}{\int J\ \hat{u} dA} \pm \underset{3}{\int r_p dV} \pm \underset{4}{\int r_s\, dV} \qquad (2)$$

where C = concentration (M t^{-1}); V = volume (L^3) and is assumed to be constant; J = flux (M t^{-1}); û = unit vector; A = cross-sectional area of the flow (L^2); r_p = rate of generation or degradation due to the plants; and r_s = rate of generation and degradation due to the plants.

First consider term 2 in equation 2 for the advective flux for the control volume seen in Figure 5.1.

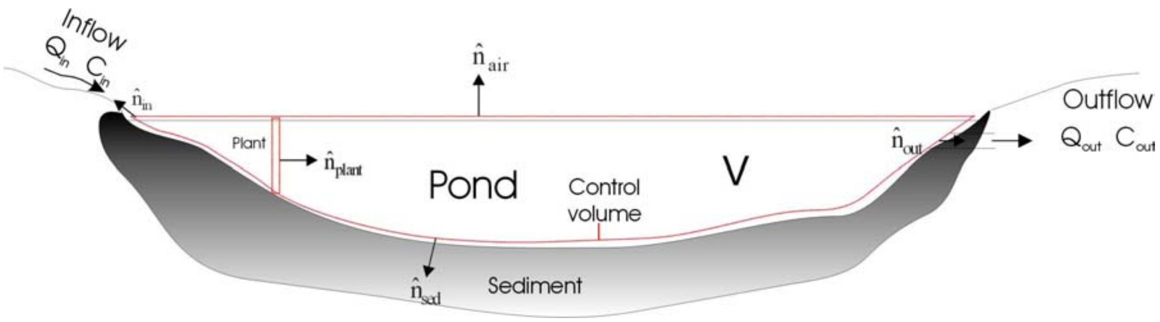


Figure 5.1: Advective flux through a detention pond. Q = flow ($L^3\ t^{-1}$); û = unit vector; and C = concentration ($M\ L^{-3}$).

The formula for advective flux can be written as:

$$J = UC \tag{3}$$

where J = the advective flux per unit area ($M\ L^{-2}\ t^{-1}$); U = velocity ($L\ t^{-1}$); and C = concentration ($M\ L^{-3}$). Therefore,

$$J_{in}\hat{u} = UC_{in}\hat{u}_{in} = C_{in}|U||\hat{u}_{in}|\cos(180) = -\ UC_{in} \tag{4}$$

and

$$J_{out}\hat{u} = UC_{out}\hat{u}_{out} = C_{out}|U||\hat{u}_{out}|\cos(0) = U_{out}C \tag{5}$$

where, C_{in} = concentration ($M\ L^{-3}$) entering the pond with the inflow and C_{out} = C = concentration ($M\ L^{-3}$) in the pond. Then, combining Equations 4 and 5 with Equation 2,

$$-\int_{C.V.} J\hat{u}dA = -\ (-UC_{in}A_{in} + U_{out}CA_{out}) = UC_{in}A_{in} - U_{out}CA_{out}$$

$$= QC_{in} - Q_{out}C = \sum_{i=1}^{n} Q_i C_{in\,i} - \sum_{i=1}^{n} Q_{out\,i} C \tag{6}$$

Therefore, by temporarily ignoring the terms 3 and 4, Equation 1 becomes

$$\frac{dC}{dt}V = \sum_{i=1}^{n} Q_i C_{in\,i} - \sum_{i=1}^{n} Q_{out\,i} C \tag{7}$$

Next, consider term 3 in Equation 2 for the degradation and generation due to plants. The flux into the plants is assumed to be a first order reaction. Uptake rates per plant were determined experimentally. The flux into the plants can be written as:

$$\int J A_p = UC = DK_pA_pC \tag{8}$$

where J = flux of the contaminant into the plants (M t^{-1}); D = plant density (number of plants L^{-2}); K_p = the uptake rate of the target contaminant (L^3 t^{-1} $plant^{-1}$); A_p = the area of the plants in the pond (L^2); and C = concentration (M L^{-3}) of the contaminant in the pond. Therefore, by still ignoring term 4, Equation 7 becomes:

$$\frac{dC}{dt}V = \sum_{i=1}^{n} Q_i C_{in\,i} - \sum_{i=1}^{n} Q_{out\,i} C \pm DK_pA_pC \tag{9}$$

Lastly, consider term 4, or the effect of the sediments on the concentration of the contaminant in question. Once again the uptake rate by the sediments is assumed to be a first-order reaction. Therefore the flux into the sediments can be written as:

$$\int J A_s = U(C - C^*) = K_sA_s (C - C^*) \tag{10}$$

where A_s = the area of the sediments in the pond (L^2); K_s = the uptake rate of the target contaminant by the sediments (L^3 L^{-2} t^{-1}); C = concentration (M L^{-3}) of the target contaminant in the pond; and C* = sorption equilibrium concentration (M L^{-3}) of the target contaminant between the sediments and the water in the pond. Therefore, Equation 9 becomes

$$\frac{dC}{dt}V = \sum_{i=1}^{n} Q_i C_{in\,i} - \sum_{i=1}^{n} Q_{out\,i} C - DK_pA_p\mathrm{C} - K_sA_s(\mathrm{C} - \mathrm{C}^*) \tag{11}$$

To solve Equation 11, follow the following steps:

1) $$\frac{\frac{dC}{dt}V}{V} = \frac{\sum_{i=1}^{n} Q_i C_{in\,i} - \sum_{i=1}^{n} Q_{out\,i} C - DK_pA_p\mathrm{C} - K_sA_s\mathrm{C} + K_sA_sC^*}{V}$$

2) $$\frac{dC}{dt} = \frac{\sum Q_{in}C_{in}}{V} - \frac{\sum Q_{out}C}{V} - \frac{DK_pA_pC}{V} - \frac{K_sA_sC}{V} + \frac{K_sA_sC^*}{V}$$

3) $$\frac{dC}{dt} + \frac{\sum Q_{out}C}{V} + \frac{DK_pA_pC}{V} + \frac{K_sA_sC}{V} = \frac{\sum Q_{in}C_{in}}{V} + \frac{K_sA_sC^*}{V}$$

Assume that $\sum Q_{out}C = C\sum Q_{out}$. Then,

4) $$\frac{dC}{dt} + C\left(\frac{\sum Q_{out}}{V} + \frac{DK_pA_p}{V} + \frac{K_sA_s}{V}\right) = \frac{\sum Q_{in}C_{in}}{V} + \frac{K_sA_sC^*}{V}$$

For $\frac{dC}{dt} = 0$,

$$C\left(\frac{\sum Q_{out}}{V} + \frac{DK_pA_p}{V} + \frac{K_sA_s}{V}\right) = \frac{\sum Q_{in}C_{in}}{V} + \frac{K_sA_sC^*}{V}$$

and

$$C_e = \frac{\frac{\sum Q_{in}C_{in}}{V} + \frac{K_sA_sC^*}{V}}{\frac{\sum Q_{out}}{V} + \frac{DK_pA_p}{V} + \frac{K_sA_s}{V}} = \frac{\sum Q_{in}C_{in} + K_sA_sC^*}{\sum Q_{out} + DK_pA_p + K_sA_s} \tag{12}$$

where C_e is the equilibrium concentration. By integrating with the boundary conditions of $C = C_o$ at $t = 0$ and solving for $C(t)$,

$$C(t) = C_e + (C_o - C_e)\exp\left[-\left(\frac{\sum Q_{out}}{V} + \frac{DA_pK_p}{V} + \frac{K_sA_s}{V}\right)t\right] \tag{13}$$

Then, (13) can be used to determine the detention time needed to decrease the target contaminant to a maximum concentration. For example, that concentration could be set to the maximum allowable discharge concentration set by the Minnesota Pollution Control Agency (MPCA). In that case, set $C(t) = C = C_{MPCA}$. Solving for t, (13) becomes

$$t_{pol} = -\frac{1}{\frac{\sum Q_{out}}{V} + \frac{DK_p A_p}{V} + \frac{K_s A_s}{V}} \ln\left(\frac{C_{MPCA} - C_e}{C_o - C_e}\right) \qquad (14)$$

5.2 Application of Model

The model and analytical solution can be used to determine the critical variables for a proposed detention pond. By keeping some variables constant, it is possible to estimate the required hydraulic retention time in order for the average effluent concentration of the target pollutants to be below a specified concentration. A few of these design plots are presented below:

Figure 5.2: Proposed design plot for Cd. Necessary pollutant residence time vs. percent cover of plants for Cd. $C_o = 35$ µg/L; $C_e = 10$ µg/L; Q = 30 m^3/day; and $A_s = 8300$ m^2

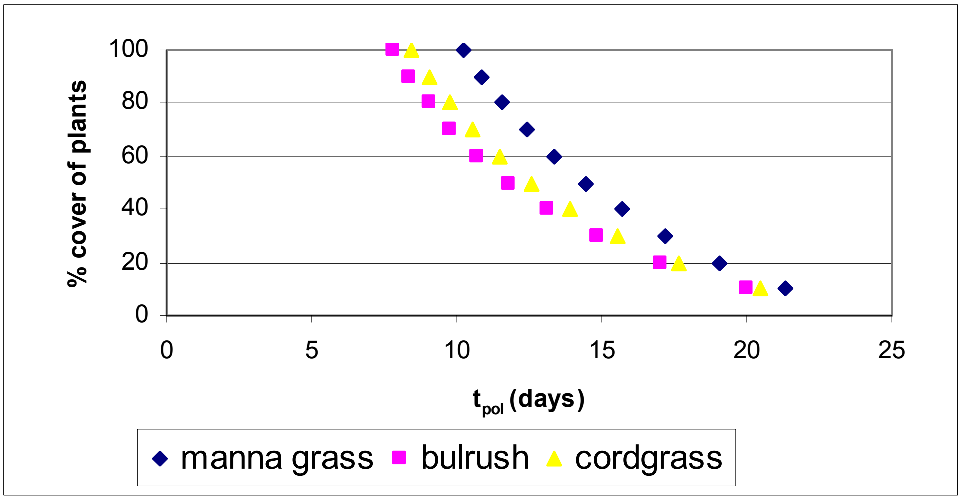


Figure 5.2 provides a relationship between the percent of the surface area of the pond covered by plants to the amount of time it would take for the concentration of the target contaminant (in this case, Cd) to be reduced to the desired level. If the average concentration of Cd in runoff is known to be 30 µg/L, the effluent concentration is desired to be 10 µg/L, the outflow rate from the pond is 30 m^3/day, the area of exposed sediments in the pond is equal to 8300 m^2, and there is a desire to have a pollutant residence time of 5 days or less, then the Figure 5.2 indicates that there needs to be at least 50% cover by the plants to meet that goal. Design plots similar to the one in Figure 5.2 with the similar constant conditions are presented below.

Figure 5.3: Proposed design plot for Cl. Necessary pollutant residence time vs. percent cover of plants for Cl. $C_o = 900$ mg/L; $C_e = 800$ mg/L; $Q = 30\ m^3/day$; and $A_s = 8300\ m^2$

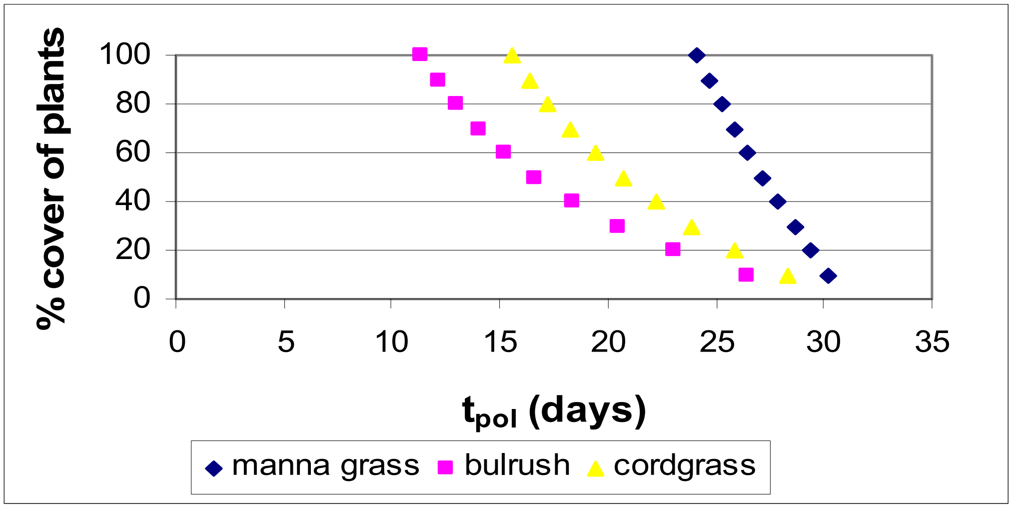


Figure 5.4: Proposed design plot for Cu. Necessary pollutant residence time vs. percent cover of plants for Cu. $C_o = 40\ \mu g/L$; $C_e = 30\ \mu g/L$; $Q = 30\ m^3/day$; and $A_s = 8300\ m^2$

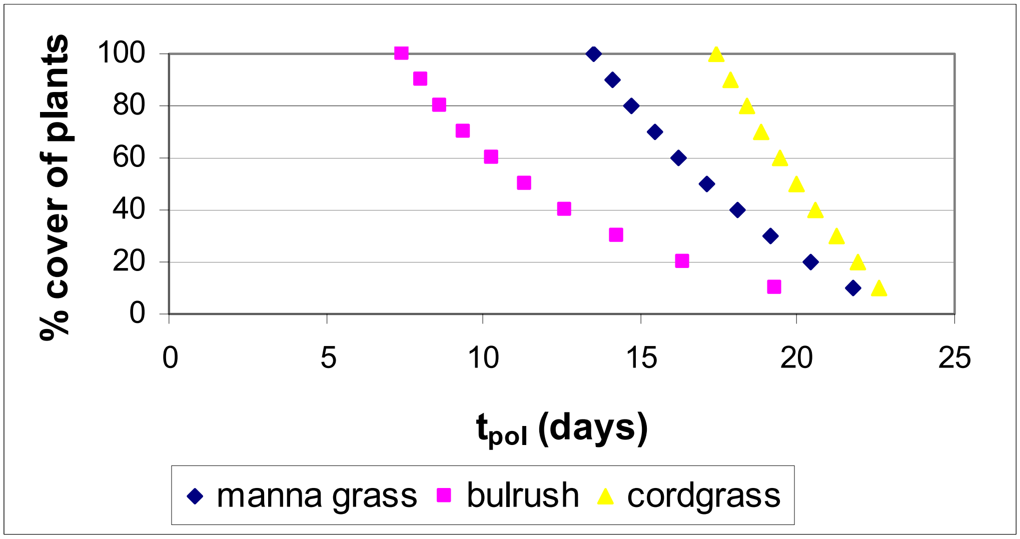


Figure 5.5: Proposed design plot for P. Necessary pollutant residence time vs. percent cover of plants for P. $C_o = 1.25$ mg/L; $C_e = 1.0$ mg/L; $Q = 30\ m^3$/day; and $A_s = 8300\ m^2$

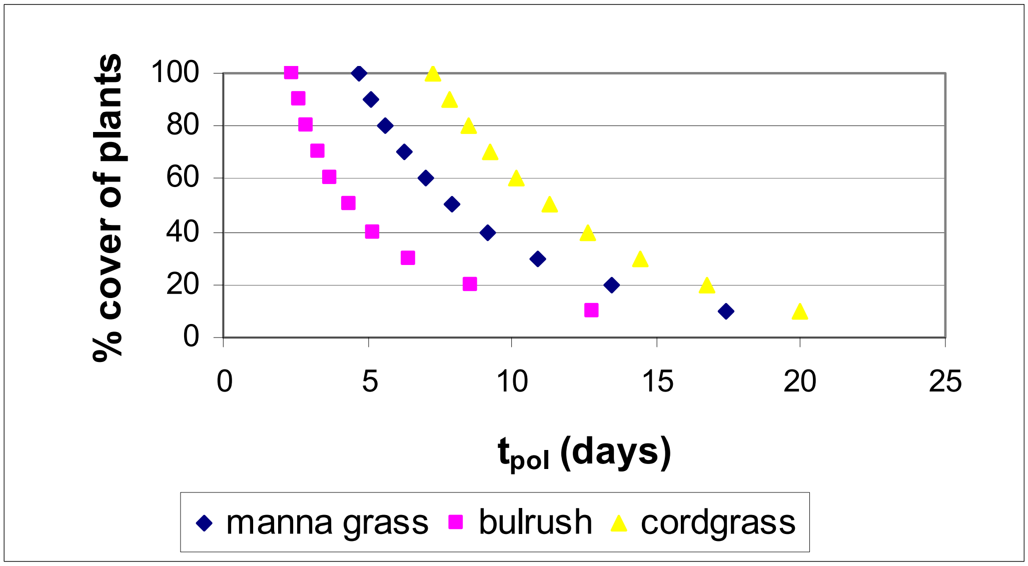


Figure 5.6: Proposed design plot for Pb. Necessary pollutant residence time vs. percent cover of plants for Pb. $C_o = 175$ µg/L; $C_e = 130$ µg/L; $Q = 30\ m^3$/day; and $A_s = 8300\ m^2$

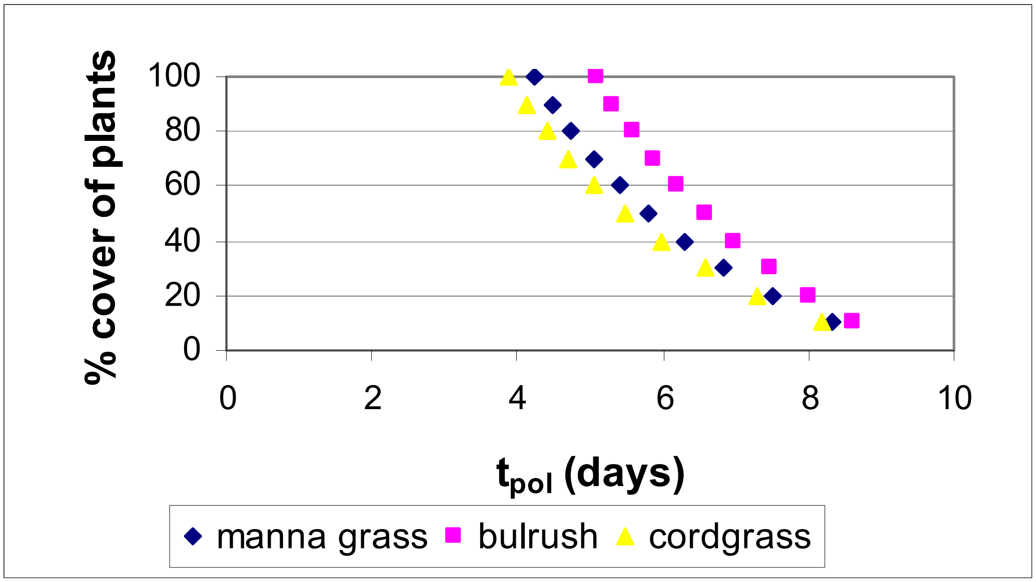
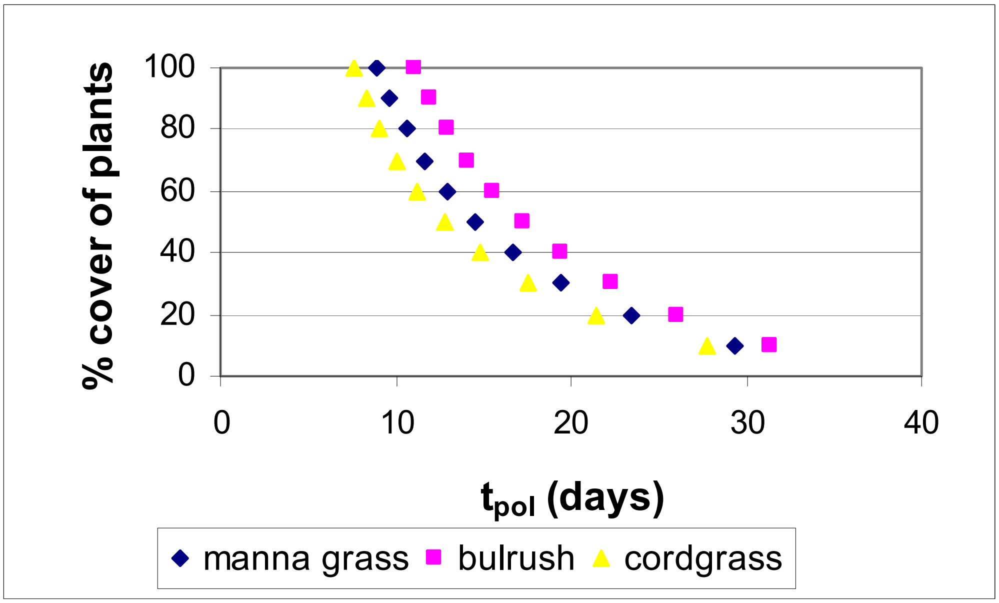


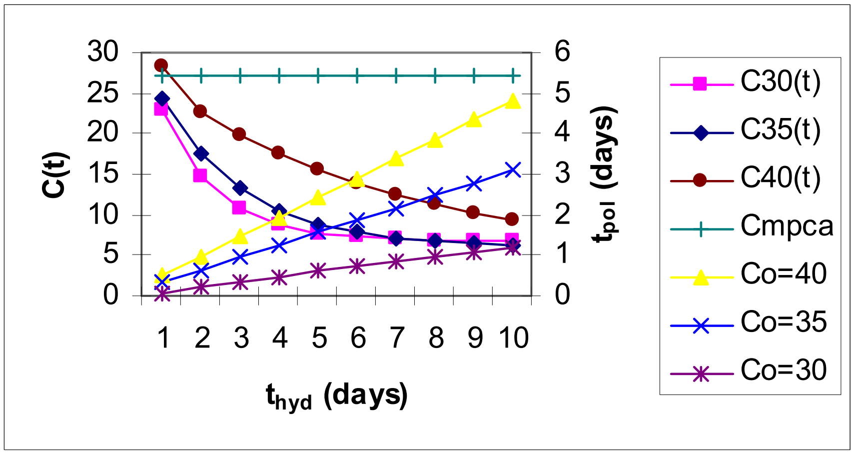
Figure 5.7: Proposed design plot for Zn. Necessary pollutant residence time vs. percent cover of plants for Zn. $C_o = 250$ µg/L; $C_e = 200$ µg/L; $Q = 30\ m^3$/day; and $A_s = 8300\ m^2$



By using design plots for all of the target pollutants, it is possible to determine the percent cover of plants or the necessary pollutant residence time of the most problematic pollutant so that desired reductions of all other target concentrations are automatically met.

Another approach to this problem is to look at the relationship between the hydraulic residence time in the pond and the pollutant residence time. For clarity, the pollutant residence time (t_{pol}) is the average amount of time an individual atom or molecule of a pollutant will spend in the dissolved phase in the pond. The hydraulic residence time (t_{hyd}) is the average amount of time an individual water molecule will spend in the pond. The value for t_{pol} is a function of t_{hyd}. Comparing the two different residence times may help in determining the necessary hydraulic residence time in order to help the concentration of the pollutant to be reduced to target levels.

Figure 5.8. t_{pol} and C(t) vs. t_{hyd} for Cd and *S. validus* with 70% plant cover.



As can be seen in Figure 5.8, as the value for t_{hyd} increases, the value for t_{pol} increases, and the concentration of Cd vs. time (C(t)) decreases. The point of this figure is to illustrate that a longer detention time will allow for a longer pollutant residence time which will allow for more time for the target pollutant to be taken up by the plants or the sediment.

5.3 Example of Model Application

Problem

A new detention pond is proposed and the following input data must be considered. Due to space restrictions, the pond surface area will be limited to 8300 m^2. Analysis of the runoff that would be entering the pond indicates that there will be the following average input concentrations of the six target pollutants: C_{Cd} = 30 µg/L; C_{Cl} = 500 mg/L; C_{Cu} = 40 µg/L; C_P = 1.5 mg/L; C_{Pb} = 175 µg/L; and C_{Zn} = 150 µg/L. Desired hydraulic residence time for proposed detention pond: 10 days. In order to satisfy MPCA pollution discharge limits, determine the percent plant cover needed to reduce the most problematic contaminant concentrations.

Solution:

Consultation with MPCA guidelines indicate that Zn and Cl are already below discharge limits, so those two contaminants do not need to be considered for design purposes. After consulting the uptake rates for the remaining four target contaminants, it is decided that *S.*

validus (Soft-stem bulrush) would be the most appropriate species for this detention pond. Based on the design plots (Figures 5.2-5.7), it is determined that 70% of the surface area must be covered by plants in order to reduce the Cd concentration to target levels (Table A1) within the 10 day hydraulic residence time. This percent plant cover will be more than sufficient to reduce all of the other target contaminants. Consulting Figure 5.8 reveals that the effluent concentration will be below MPCA discharge guidelines after only one day. Therefore, the 10 day hydraulic residence time will be more than enough to sufficiently remediate the stormwater runoff prior to release to receiving waters.

5.4. Limitations of the Model

Limitations of the applicability of this model have to do with some of the assumptions that were made. First, the uptake rates used are constant values, but in the field, many parameters may affect the actual uptake rate, including temperature, light availability, and exact chemistry of the water.

5.5. Conclusions

This model estimates effluent concentrations of target pollutants based on various input parameters. A variety of design charts can be used to determine which variable is the most important so a detention pond can be designed to adequately remove the target contaminants.

The analytical solution indicates that the reduction of concentrations of some target pollutants to target concentrations require an excessive detention time if the only means of removal is by uptake by plants and sorption onto the sediments. Therefore, other means of removal may be required for those contaminants.

This model can be improved upon by determining seasonal variation of uptake rates for both the target plant species and for sediment. It is acknowledged that uptake rates are not constant, but at this point data does not exist that sufficiently relates the uptake rates to the important variables as season and other environmental factors.

6.0 Conclusions

Recent studies have examined contaminant concentrations in stormwater runoff (Moxness, 1986, 1987, and 1988; Sansalone and Buchberger, 1997; Driscoll et al., 1990), the ability of detention ponds to remediate stormwater runoff (Comings et al., 2000), and the phytoremediation capabilities of various wetland macrophytes (Qian et al., 1999 and Zhu et al., 1999), but none have made any attempt to try to combine these variables to develop a system that would be able to design a detention pond based on the hydraulic residence time needed to reduce contaminant concentrations to desired levels. An attempt has been made to do that with this study.

Several runoff studies from both the Twin Cities area and from around the United States indicate that urban highway runoff composition is highly variable and largely depends on site-specific characteristics and characteristics of each runoff event, including: local climate, pavement type, average pavement residence time, the duration between runoff events, season, and traffic volume. On a national scale the pollutants of greatest concern are heavy metals (Pb, Zn, Cu, and Cd), nutrients (P), and on a local scale in a northern climate like that of the Twin Cities, chloride is also a major concern. Theoretical effluent concentrations of these target contaminants were generated using average concentrations in the runoff and average percent removal from the detention pond studies. This exercise indicated that Pb, Zn, Cu, and Cd have the greatest chance of exceeding Minnesota Pollution Control Agency guidelines for discharge into receiving waters.

The Minnesota Department of Transportation selected three species (*G. grandis*, *S. validus*, and *S. pectinata*) to be studies for their phytoremediation capabilities. In flow and non-flow reactor experiments, uptake rate constants were found for each species for each of the target contaminants. The depletion rates of the target contaminants from the nutrient solution depended on the contaminant in question and the species accumulating the contaminant. None of the three species was a clear-cut best at removing the target contaminants from the nutrient solution. In the non-flow reactor experiments, *G. grandis* appeared to be the best overall for removing the target contaminants. In the flow reactor experiments, *S. validus* was the best at removing target contaminants. These experiments also showed that, as is consistent with other researchers (Qian et al., 1999; Zhu et al., 1999), all three species accumulate a higher concentration of the target contaminants in their roots than they do in their stems. Chloride and phosphorus were exceptions as they were found in higher concentrations in the stems than in the roots. It was also found that plants grown hydroponically had a higher concentration than those grown in sand, and plants grown in flow reactors removed a greater mass of contaminants than those grown in non-flow reactors.

Sorption rates of the target contaminants were also determined. As was expected, each target contaminant sorbed at different rates and had different equilibrium concentrations.

Lastly, a model was developed that determines theoretical effluent concentrations of target pollutants based on various input parameters. A variety of design charts can be used to determine which variable is the most important so a detention pond can be designed to adequately remove the target contaminants.

The analytical solution indicates that some target pollutants require an excessive detention time if they are to be reduced to target concentration levels in the only means of removal is by uptake by plants and sorption onto the sediments. Therefore, other means of removal may be required for those contaminants.

This model can be improved upon by determining seasonal variation of uptake rates for both the target plant species and for sediment. It is acknowledged that uptake rates are not constant, but at this point data does not exist that sufficiently relates the uptake rates to the important variables as season and other environmental factors.

References

Barbosa, A. E. and T. Hvitved-Jacobsen, 1999. "Highway runoff and potential for removal of heavy metals in an infiltration pond in Portugal." *The Science of the Total Environment* 235:151-159.

Benjamin, M. M., *Water Chemistry*. New York: McGraw-Hill, Inc. 2002. pp. 362-627.

Berti, W.R. and S. D. Cunningham. 1997. "In-place inactivation of Pb in Pb-contaminated soils." *Environmental Science Technology*. 31:1359-1364.

Biesboer, David D. Professor of Plant Biology, University of Minnesota. Personal communication.

Black, J. 1995. "Absorbing possibilities: Phytoremediation." *Environmental Health Perspectives* 103:1106-1108.

Boxall, A.B.A. and L. Maltby, 1995. "The characterization and toxicity of sediment contaminated with road runoff." *Water Research* 29(9):2043-2050.

Carleton, J. N., T. J. Grizzard, A. N. Godrej, J. E. Post, L. Lampe, P. P. Kenel, 2000. "Performance of a Constructed Wetlands in Treating Urban Stormwater Runoff*." Water Environment Research*. 72(3):295-304.

Comings, K. J., D. B. Booth, and R. R. Horner. 2000. "Stormwater Pollutant Removal by Two Wet Ponds in Bellevue, Washington." *Journal of Environmental Engineering* 126(4):321-330.

Craft, C. B. 1997. "Dynamics of nitrogen and phosphorus retention during wetland ecosystem succession." *Wetlands Ecology and Management* 4(3): 177-187.

Drapper, D., R. Tomlinson, and P. Williams. 2000. "Pollutant concentrations in road runoff: southeast Queensland case study." *Journal of Environmental Engineering* 126(4):313-320.

Driscoll, E. D., P. E. Shelley, and E. W. Strecker. 1990. "Pollutant loadings and impacts from highway stormwater runoff, Volume 1-IV." *Federal Highway Administration FHWA-RD-88-006.*

Ebbs, S.D. and L.V. Kochian. 1998. "Phytoextraction of Zinc by Oat (*Avena sativa*), Barley (*Hordeum vulgare*), and Indian Mustard (*Brassica juncea*)" *Environmental Science and Technology*, 32(6):802-806.

Ellis, J. B., 1991. "The design and operation of vegetation systems for urban source runoff quality control." In: *Proc. 3rd Standing Conf. Stormwater Science Control*. Coventry Polytechnic, 1991.

Falbo, M. B. and T. E. Weaks, 1990. "A comparison of *Eichhornia crasspes* (Pontederiaceae) and *Sphagnum quinquefarium* (Sphagnaceae) in treatment of acid mine water." *Econ. Bot*. 44:40-49.

Gain, S. W. 1996. "The effects of flow-path modification on water-quality retention in an urban stormwater detention pond and wetland system, Orlando, Florida." *Water-Res. Investigations Rep. 95-4297*, USGS, Tallahassee, FL.

Goldman, C. R. 1965. "Micronutrient limiting factors and their detection in natural phytoplankton populations." In: *Primary Productivity in Aquatic Environments*, C. R. Goldman (Ed.) pp121-135.

Grizzard, T. J., C. W. Randall, B. L. Weand, and K. L. Ellis, 1986. "Effectiveness of Extended Detention Ponds." *Urban runoff Quality – Impacts and Quality Enhancement Technology*, ASCE, New York, New York.

Guo, J. C. Y., 1993. "Optimization of runoff volume capture rate for detention basins." Department of Civil Engineering, University of Colorado, Denver, Colorado.

Heitz, L. F., S. Khosrowpanah, and J. Nelson, 2000. "Sizing of surface water runoff detention ponds for water quality improvement." *Journal of the American Water Resources Association*. 36(3):541-548

Hild, George. Owner of Hild and Associate, River Falls, WI. Personal Communication.

Hoagland, D., and D.I. Arnon. 1938. "The water culture method for growing plants without soil." *California Agriculture State Bulletin*. 346.

Horne, A. J., and C. R. Goldman (Eds.), 1993. *Limnology*, McGraw-Hill, Inc, New York, New York. pp 133-192.

Jenatte, P. F., J. Canbraia, M. A.Oliver, and C. P. Jordao, 1994. "Absorption and distribution of cadmium in water hyacinth plants." *Journal of Plant Nutrition* 17:1219-1230.

Kantrowitz, I. H. and W. M. Woodham 1995. "Efficiency of a stormwater-detention pond in reducing loads of chemical and physical constituents in urban streamflow, Pinellas County, Florida." *Water-Res. Investigations Rep. 94-4217*, USGS Tallahassee, FL.

Lawrence, A.I., J. Marsalek, J. B. Ellis, and B. Urbonas, 1996. "Stormwater detention and BMPs." *Journal of Hydraulic Research* 34(6):799-813.

Levine, P. E., 1975. "Sorption of zinc, lead, and cadmium on glacial outwash soil." MS Thesis, University of Washington.

Line, D. E., J. Wu, J. A. Arnold, G. D, Jennings, and A. R. Rubin, 1997. "Water quality of first flush runoff from 20 industrial sites." *Water Environment Research* 69(3): 305-310.

Lundberg, K., M. Carling, P. Lindmark, 1999. "Treatment of highway runoff: a study of three detention ponds." *The Science of the Total Environment* 235:363-365.

Maristany, A. E., 1993. "Evaluation of pollutant loads from urban non-point sources." *Water Science and Technology* 22(10-11):23-30.

Marsalek, J., Q. Rochfort, B. Brownlee, T. Mayer, and M. Servos. 1999. "An exploratory study of urban runoff toxicity." *Water and Science Technology* (12):33-39.

Moxness, K. L., 1986. "Characteristics of urban freeway runoff, Phase I." Water Quality Unit, Environmental Services Section, Office of Technical Support, Minnesota Department of Transportation.

Moxness, K. L., 1987. "Characteristics of urban freeway runoff, Phase II." Water Quality Unit, Environmental Services Section, Office of Technical Support, Minnesota Department of Transportation.

Moxness, K. L., 1988. "Characteristics of urban freeway runoff, Phase III." Water Quality Unit, Environmental Services Section, Office of Technical Support, Minnesota Department of Transportation.

Qian, JH., A. Zayed, Y. L. Zhu, M. Yu, and N. Terry, 1999. "Phytoaccumulation of trace elements by wetland plants: III. Uptake and accumulation of ten trace elements by twelve plant species." *Journal of Environmental Quality* 28(5):1448-1455.

Rai, U.N., S. Sinha, and P. Chandra, 1995. "Wastewater treatability potential of some aquatic macrophytes: removal of heavy metals." *Ecological Eng.* 5(1):5-12.

Reddy, K. R., R. H. Kadlec, E. Flaig, and P. M. Gale, 1999. "Phosphorus retention in streams and wetlands: a review." *Critical Review in Environmental Science and Technology* 29(1):83-146.

Richardson, C. J, S. Qian, C. B. Craft, and R. G. Qualls. 1997. "Predictive models for phosphorus retention in wetlands." *Wetlands Ecology & Management* 4:159-175.

Sansalone, J. J and S. G. Buchberger. 1997. "Partitioning of first flush of metals in urban roadway stormwater." *Journal of Environmental Engineering* 123(2):134-143.

Shutes, R. B. E., D. M. Revitt, I. M Lagerberg, and V. C. E. Barraud. 1999. “The design of vegetative constructed wetlands for the treatment of highway runoff.” *The Science of the Total Environment* 235:189-197.

Shutes, R. B. E., D. M. Revitt, A. S. Numgur, and L. N. L. Scholes. 1997. "The design of wetland systems for the treatment of urban run off." *Water Science and Technology* 35(5):19-25.

Spriggs, T.A. 1998. “Phytoremediation of Copper from a Contaminated Solution using Wetland Macrophytes” MS Thesis, Purdue University.

Srivastava, A. K. and Purnima, 1998. "Phytoremediation for heavy metals - a land plant based sustainable strategy for environmental decontamination." *Proceedings of the National Academy of Sciences, India*. 68(3/4):199-215.

Standard Methods for the Examination of Water and Wastewater. 1995. A.D. Eaton, L.S. Clesceri, and A.E. Greenberg (Eds). American Public Health Association.

Tanner, C. C., J. S. Clayton, and M. P. Upsdell. 1995. “Effect of loading rate and planting on treatment of dairy farm wastewaters in constructed wetlands – II. Removal of nitrogen and phosphorus.” *Water Research* 29(1):27-34.

USEPA. 2001. “Stormwater Wetlands” Stormwater Phase II Menu of BMPs and Model Permits.

USEPA. 2001. “Wet Pond” Stormwater Phase II Menu of BMPs and Model Permits.

Wu, J. S., R. E. Holman, and J. R. Dorney, 1996. “Systematic evaluation of pollutant removal by urban wet detention ponds.” *J. of Envir. Eng.* 122(11):983-988.

Zayed A., S. Gowthaman, and N. Terry. 1998. “Phytoaccumulation of trace elements by wetland plants: I. Duckweed.” *Journal of Environmental Quality* 27(3):715-721.

Zhu, Y. L., A. M. Zayed, J. H. Qian, M. De Souza, and N. Terry, 1999. “Phytoremediation of trace elements by wetland plants: II. Water Hyacinth.” *Journal of Environmental Quality*, 28(1):339-344.

Zurayk, R., M. Nimah, Y. Geha, and C. Rizk. 1997. “Phosphorus retention in the soil matrix of constructed wetlands.” *Communications in Soil Science and Plant Analysis* 28(6-8):521-535.

Appendix A

Additional Tables and Figures

Table A1. Pollutant concentrations found in highway stormwater runoff in various studies.

	MPCA Standards[a]			Moxness, 1986		Moxness, 1987		Moxness, 1988		Drapper et al., 2000		Sansalone and Buchberger, 1997		Driscoll et al., 1990 (Mpls/St.P.)		Driscoll et al., 1990 (nationwide)	
	CS[b]	MS[c]	FAV[d]	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
Hardness (as $CaCO_3$) (mg/L)	83.21[e]	83.21[e]	83.21[e]	34	79	128	410	56	86	N/A	N/A	67.6	92	N/A	N/A	N/A	N/A
Copper (µg/L)	8.77	14.92	29.83	33.9	330	25	71	8.2	17	90	340	135	325	25	N/A	52	N/A
Zinc (µg/L)	90.72	100.15	200.30	147	960	200	560	21	33	523	1850	4280	15244	N/A	N/A	368	N/A
Cadmium (µg/L)	0.98	27.18	54.35	1.1	7.1	2.5	17	3.9	18	N/A	N/A	7	11	N/A	N/A	17	N/A
Lead (µg/L)	2.52	64.78	129.55	225	1700	450	1300	30	100	224	620	64.4	97	261.5	N/A	525	N/A
Phosphorus (mg/L)	1	1	1	0.333	2.43	0.57	0.988	0.5	1.1	0.7	1.8	N/A	N/A	0.328	N/A	0.435	N/A
Chloride (mg/L)	230	860	1720	31	570	63	200	49	304	N/A	N/A	N/A	N/A	11.5	N/A	33	N/A

[a] The MPCA Standard values given above for the metals were calculated from formulas given in Chapter 7050.0222 Waters of the State, Class 2B waters. The values for phosphorus are set discharge standards.

[b] The CS (Chronic standard) values are those that correspond to the highest water concentration of a pollutant to which organisms can be exposed indefinitely without causing chronic toxicity.

[c] The MS (Maximum standard) values are those that correspond to the highest concentration of a pollutant in water to which aquatic organisms can be exposed for a brief time with zero to slight mortality.

[d] The FAV (Final Acute Value) values are those that correspond to the estimate of the concentration of a pollutant that results in a 0.05 probability that the pollutant is at a toxic level.

[e] Not an MPCA guideline, but is the average hardness of waters in rivers and creeks in the Twin Cities area. This value was used to calculate the MPCA standards for zinc, copper, cadmium, and lead because those standards are dependent on hardness.

Table A2. Summary of mean concentrations found in highway runoff and a comparison between the concentrations found in the Twin Cities area and that found in all of the studies across the United States.

	Cu (µg/L)	Zn (µg/L)	Cd (µg/L)	Pb (µg/L)	Total P (mg/L)	Total N (mg/L)	TSS (mg/L)
Moxness, 1986	33.9	147	1.1	225	0.333	0.37	246
Moxness, 1987	25	200	2.5	450	0.57	1.6	140
Moxness, 1988	8.2	21	3.9	30	0.5	0.344	11
Driscoll et al., 1990 (TC)	25	N/A	N/A	261.5	0.328	N/A	68
Driscoll et al., 1990 (nationwide)	52	368	17	525	0.435	0.84	143
Drapper et al., 2000	90	523	N/A	224	0.7	N/A	336
Sansalone and Buchberger, 1997	135	4280	7	64.4	N/A	N/A	N/A
Average (TC Area)	**23.0**	**122.7**	**2.5**	**241.6**	**0.43**	**0.77**	**116.3**
Average (nationwide)	**52.7**	**923.2**	**6.3**	**254.3**	**0.48**	**0.79**	**157.3**

Figure A1. Average growth in centimeters for *S. validus* in Experiment 2.

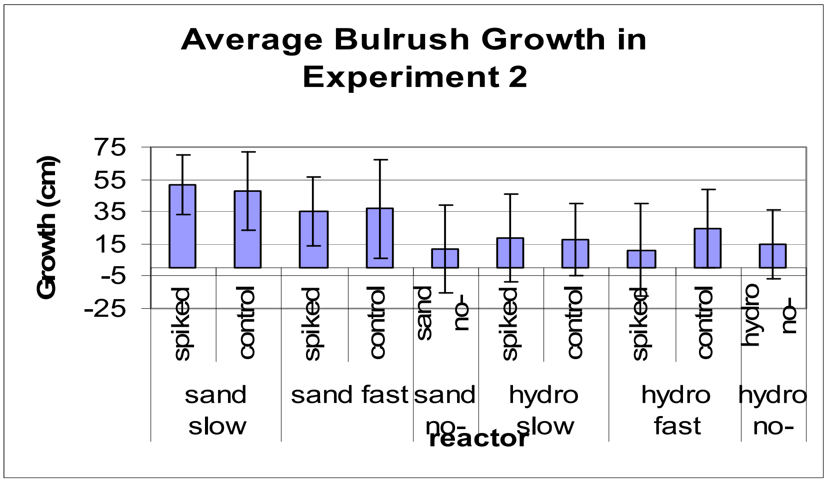


Figure A2. Average growth in centimeters for *G. grandis* in Experiment 2.

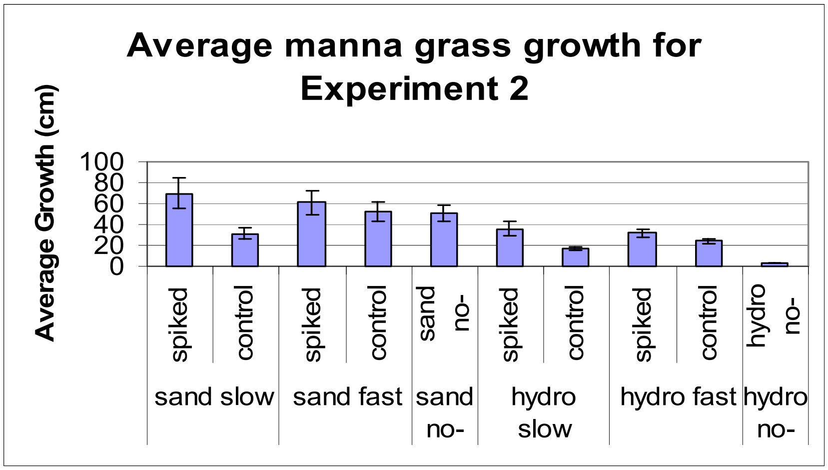


Figure A3. Average growth in centimeters for *S. pectinata* in Experiment 2.

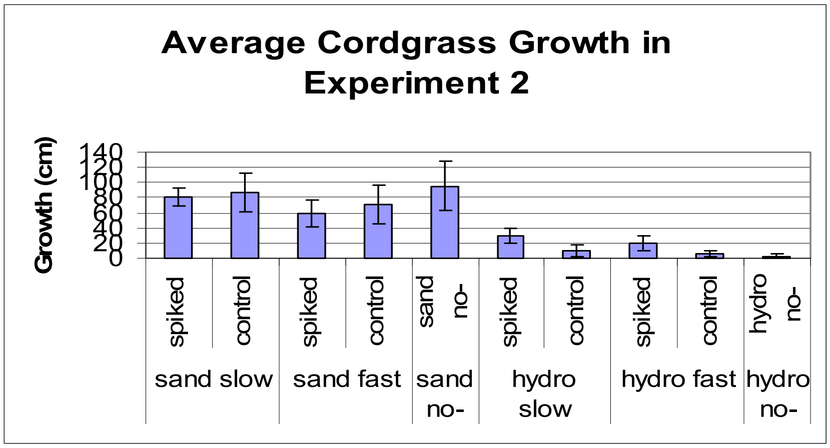


Figure A4. Change in phosphorus concentration versus time for all three tested species in Experiment 2. The regression equations for *S. pectinata*, *S. validus*, and *G. grandis*, are in the lower left, upper right, and lower right corner, respectively.

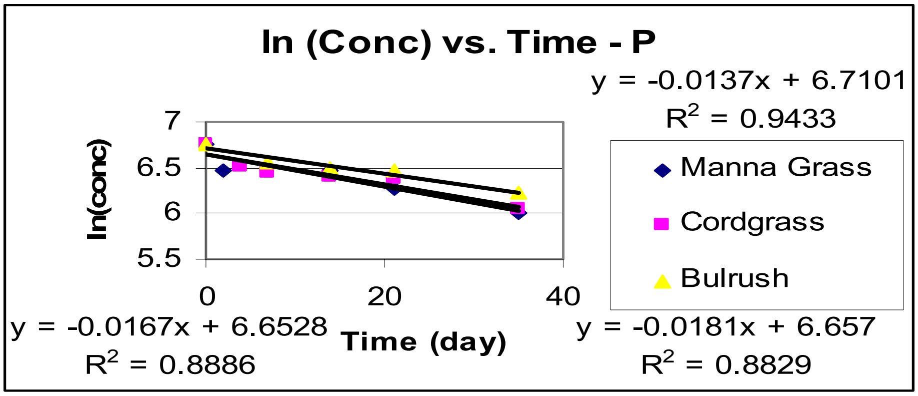


Figure A5. Change in lead concentration versus time for all three tested species in Experiment 2. The regression equations for *S. pectinata*, *S. validus*, and *G. grandis*, are in the lower left, upper right, and lower right corner, respectively.

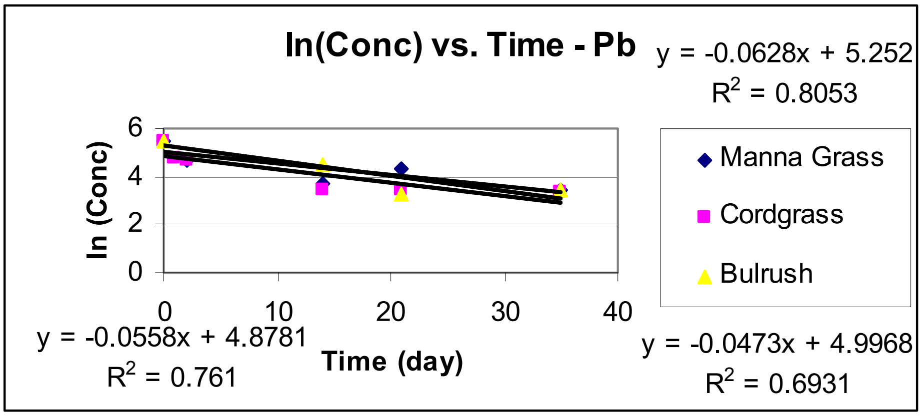


Figure A6. Change in copper concentration versus time for all three tested species in Experiment 2. The regression equations for *S. pectinata*, *S. validus*, and *G. grandis*, are in the lower left, upper right, and lower right corner, respectively.

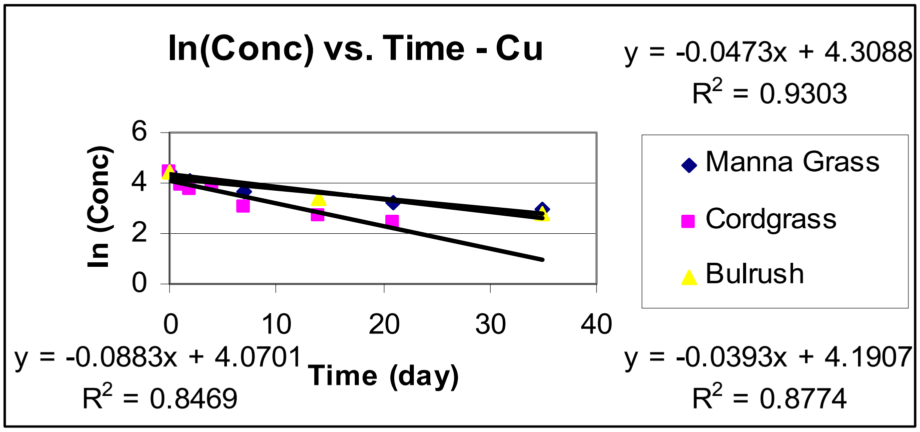


Figure A7. Change in zinc concentration versus time for all three tested species in Experiment 2. The regression equations for *S. pectinata*, *S. validus*, and *G. grandis*, are in the lower left, upper right, and lower right corner, respectively.

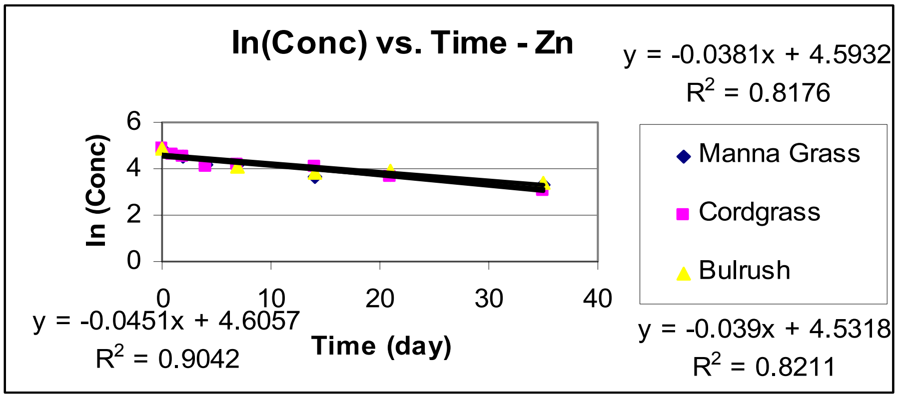


Figure A8. Change in cadmium concentration versus time for all three tested species in Experiment 2. The regression equations for *S. pectinata*, *S. validus*, and *G. grandis*, are in the lower left, upper right, and lower right corner, respectively.

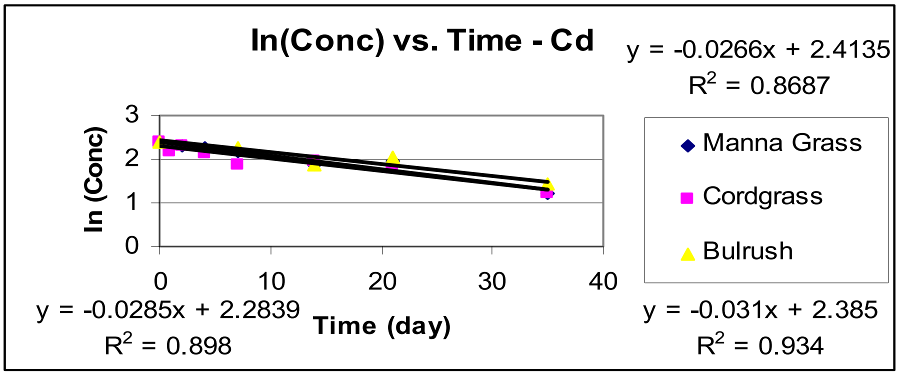


Figure A9. Change in chloride concentration versus time for all three tested species in Experiment 2. The regression equations for *S. pectinata*, *S. validus*, and *G. grandis*, are in the lower left, upper right, and lower right corner, respectively.

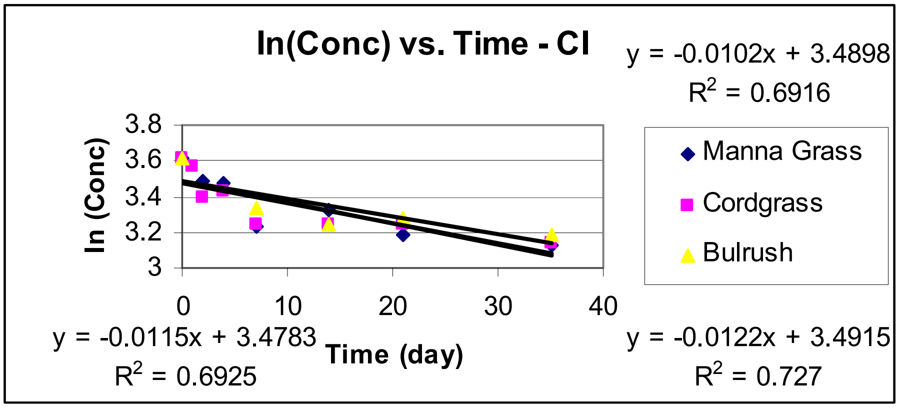


Figure A10. Change in Cadmium concentration in the flow and non-flow reactors in Experiment 2. C = *S. pectinata*; B = *S. validus*; M = *G. grandis*; SS = sand, non-flow; S = spiked, flow; H = hydroponic, non-flow

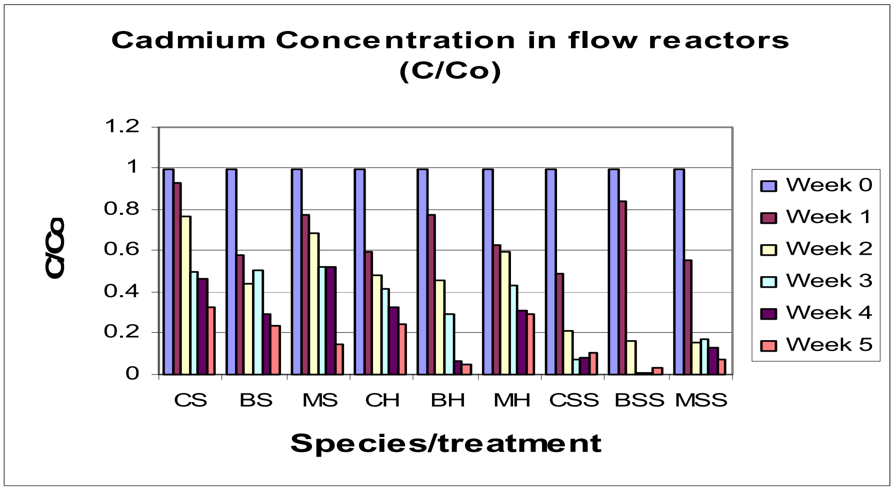


Table A3. Raw data for the change in cadmium concentration in the spiked flow and non-flow reactors in Experiment 2. Concentration is in units of $\mu g\ L^{-1}$.

	Day 0	7	14	21	28	35
CS	5.88	5.46	4.5	2.91	2.74	1.94
BS	6.39	3.68	2.82	3.25	1.9	1.49
MS	5.87	4.53	4.03	3.06	3.07	0.86
CH	6.26	3.71	3.01	2.62	2.05	1.54
BH	6.47	5.03	2.94	1.9	0.41	0.33
MH	6.5	4.11	3.86	2.82	2.03	1.91
CSS	5.9	2.88	1.23	0.45	0.46	0.61
BSS	6.19	5.2	1.02	0.07	0.06	0.19
MSS	6.33	3.51	0.97	1.11	0.82	0.45

Figure A11. Change in normalized concentration of chloride in the flow and non-flow reactors in Experiment 2. The legend is the same as for Figure A10.

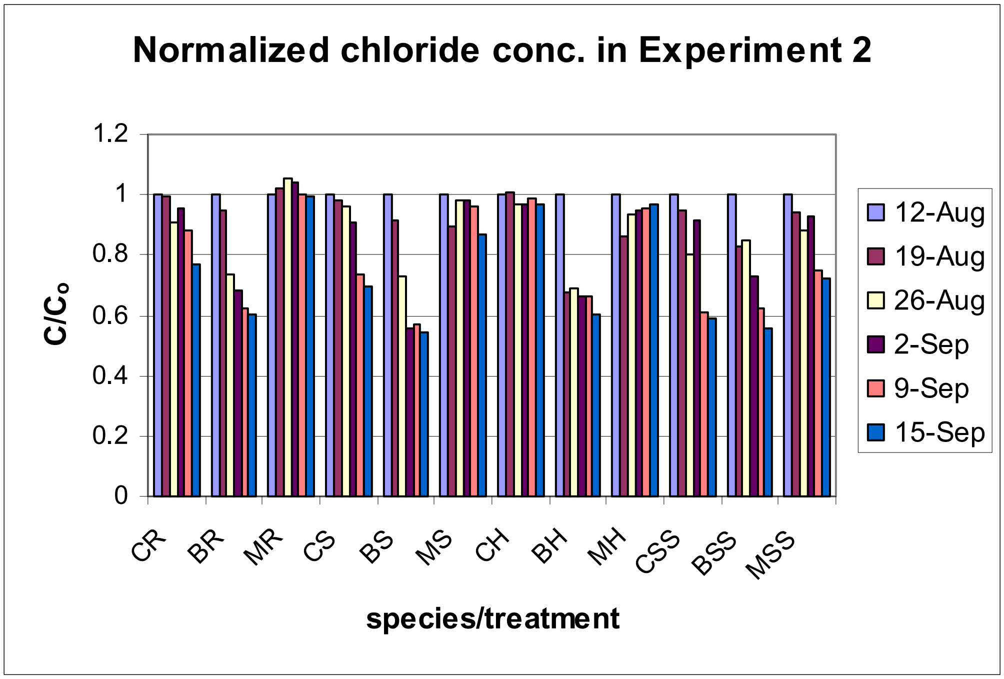


Table A4. Raw data for the change in chloride concentrations in the spiked flow and non-flow reactors in Experiment 2. Concentration is in units of mg L^{-1}.

Day	0	7	14	21	28	35
CS	9.088	8.931	8.753	8.277	6.694	6.327
BS	9.572	8.747	6.978	5.317	5.447	5.229
MS	9.67	8.655	9.478	9.489	9.328	8.428
CH	8.647	8.717	8.369	8.352	8.57	8.397
BH	8.65	5.833	5.963	5.715	5.707	5.219
MH	9.423	8.141	8.836	8.946	8.976	9.103
CSS	9.67	9.16	7.774	8.844	5.898	5.711
BSS	9.67	8.027	8.216	7.056	6.027	5.394
MSS	9.67	9.088	8.549	8.977	7.243	7.007

Figure A12. Change in normalized concentration of copper in the flow and non-flow reactors in Experiment 2. The legend is the same as for Figure A10.

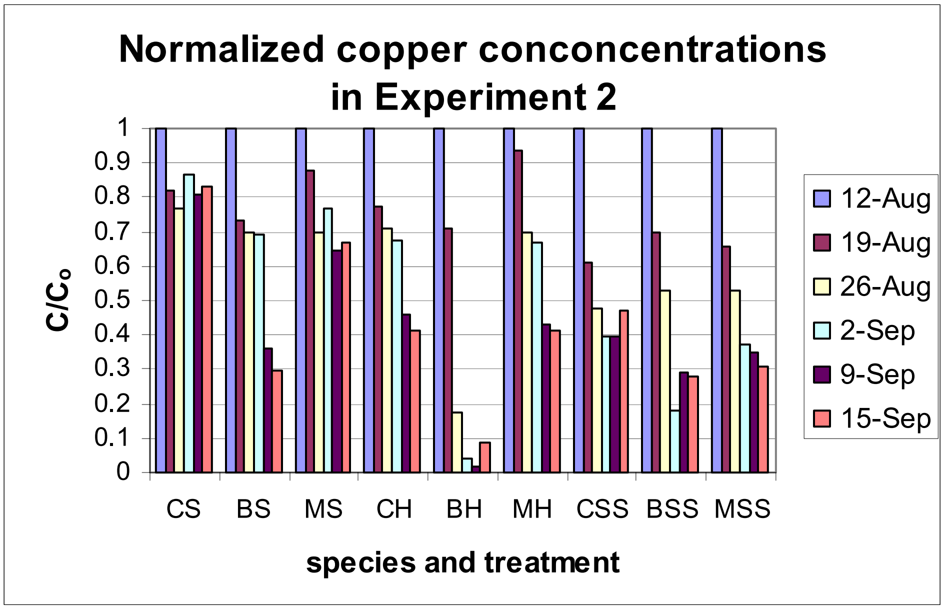


Table A5. Raw data for the change in copper concentrations in the spiked flow and non-flow reactors in Experiment 2. Concentration is in units of $\mu g\ L^{-1}$.

Day	0	7	14	21	28	35
CS	188	148	144	159	149	153
BS	194	166	143	115	60	49
MS	203	207	144	159	134	129
CH	186	140	82	78	53	148
BH	186	132	70	55	52	60
MH	214	157	116	154	103	64
CSS	191	198	94	78	78	93
BSS	193	136	65	22	36	34
MSS	191	184	97	69	64	37

Figure A13. Change in normalized concentration of phosphorus in the flow and non-flow reactors in Experiment 2. The legend is the same as for Figure A10.

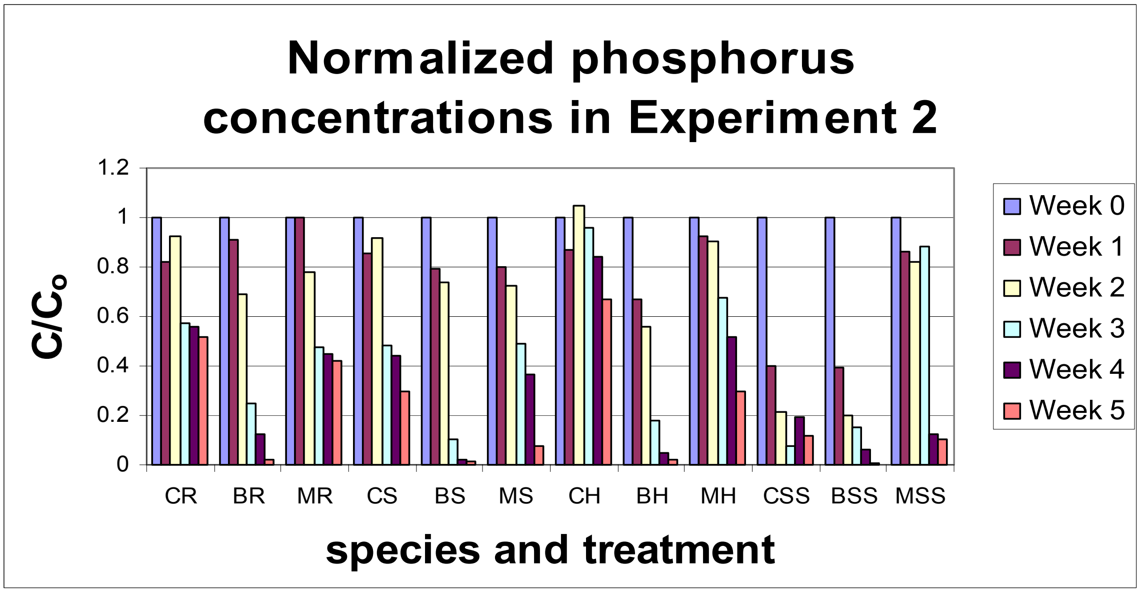


Table A6. Raw data for the change in phosphorus concentrations in the spiked flow and non-flow reactors in Experiment 2. Concentration is in units of μg L^{-1}.

Day	0	7	14	21	28	35
CS	2.431	2.075	2.237	1.165	1.071	0.721
BS	2.567	2.027	1.885	0.261	0.051	0.037
MS	2.604	2.077	1.891	1.274	0.955	0.206
CH	2.574	2.241	2.701	2.462	2.169	1.714
BH	2.515	1.688	1.407	0.454	0.117	0.055
MH	2.486	2.298	2.252	1.679	1.285	0.736
CSS	2.661	1.071	0.576	0.207	0.522	0.305
BSS	2.611	1.025	0.517	0.388	0.158	0.027
MSS	2.733	2.359	2.237	2.407	0.344	0.287

Figure A14. Change in normalized concentration of lead in the flow and non-flow reactors in Experiment 2. The legend is the same as for Figure A10.

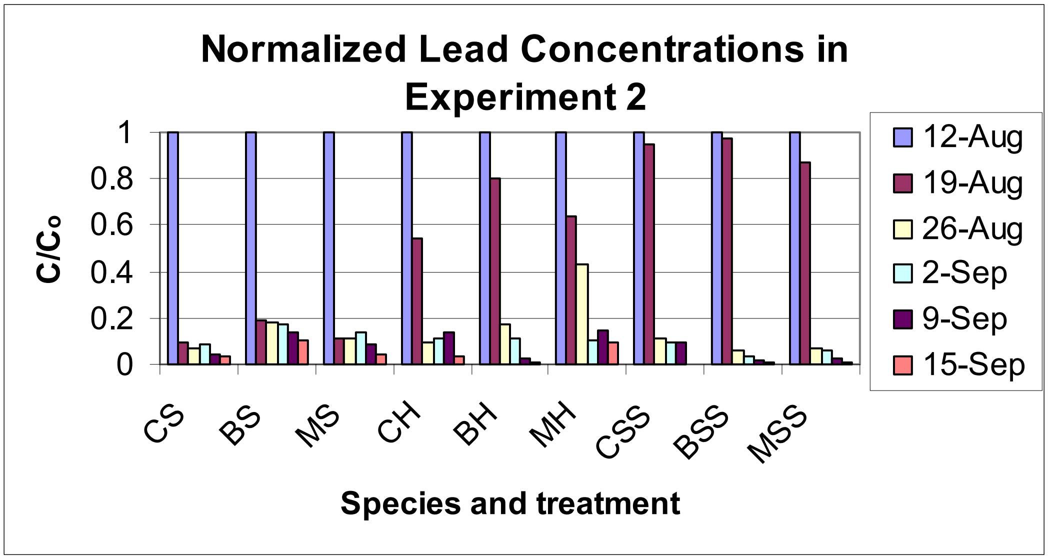


Table A7. Raw data for the change in lead concentrations in the spiked flow and non-flow reactors in Experiment 2. Concentration is in units of $\mu g\ L^{-1}$.

Day	0	7	14	21	28	35
CS	360	35	24	30	16	12
BS	380	72	69	66	51	39
MS	382	44	43	54	32	17
CH	364	199	33	40	50	11
BH	377	302	65	41	9	4
MH	355	226	154	37	52	35
CSS	319	102	61	30	30	1
BSS	324	316	94	11	5	3
MSS	375	325	78	22	10	4

Figure A15. Change in normalized concentration of zinc in the flow and non-flow reactors in Experiment 2. The legend is the same as for Figure A7.

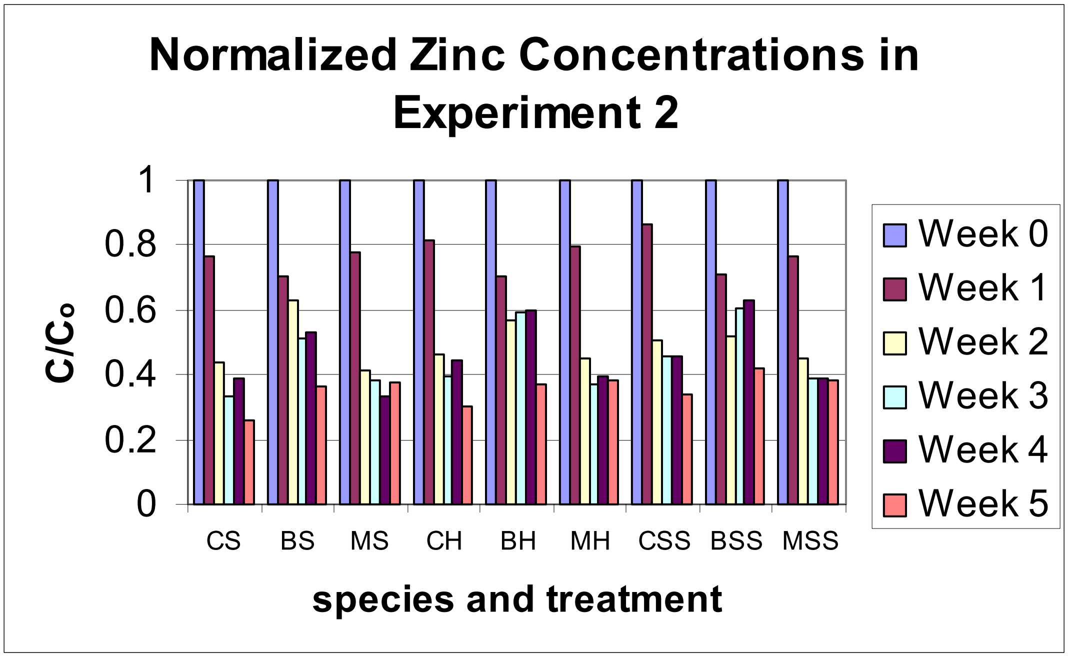


Table A8. Raw data for the change in zinc concentrations in the spiked flow and non-flow reactors in Experiment 2. Concentration is in units of μg L^{-1}.

Day	0	7	14	21	28	35
CS	257	197	112	86	100	66
BS	242	170	153	124	128	88
MS	253	196	105	97	85	96
CH	263	214	121	104	117	79
BH	242	170	138	143	145	90
MH	265	211	120	98	104	102
CSS	266	229	135	121	121	91
BSS	250	178	130	152	157	106
MSS	278	213	125	108	108	106