Engineered Bioretention for Treatment of Storm Water Runoff

A Final Report Submitted to

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Submitted by

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Abstract

Bioretention, a “Low Impact Development” urban storm water best management practice consisting of a porous media was developed in the early 1990’s. Although bioretention has been used at many areas in the United States, the impact of this technology on ground and surface water quality, as well as the optimal design of bioretention media for pollutant removal, has not been systematically investigated. The objectives of this study are to investigate the effectiveness of this technology for storm water runoff treatment and give recommendations for future design. The methods include developing pollutant removal performance information for a variety of bioretention media mixes and evaluating the effectiveness of existing bioretention facilities. Synthetic runoff, which contains oil and grease (O/G), suspended solids (SS), lead (Pb), phosphorus (P), nitrate, and ammonium, was employed in laboratory experiments and 6 on-site bioretention evaluations. Two more on-site experiments were conducted during a rainfall event to compare with the laboratory investigations.

Overall, all bioretention columns and on-site facilities demonstrated excellent removal for O/G and Pb. TSS removal was good in columns, but leaching of media particles was noted in field facilities, mostly from new installations. For nutrients treatment during a 6-hr experiment, the removal efficiency of TP ranged widely and appears to be related to both the chemical properties of the media and the flow behavior of runoff through the media. Results from batch sorption tests and continuous and repetitive 6-hr bioretention columns showed that the medium with a higher P sorption capacity can retain more P from the infiltrating runoff. However, the sorption data alone is not adequate to predict the P retention through a bioretention column for a short-term experiment due to the complicated processes occurring between the runoff and media. Unless special provision were made, all media employed in this study were ineffective in removing nitrate and ammonium efficiently. Through specific media configurations, nitrification and denitrification processes could be encouraged in bioretention columns.

Based on the results of this study, two schematic profiles of bioretention media are presented. The first employs a single media layer. The second separates a treatment layer from the vegetation layer.

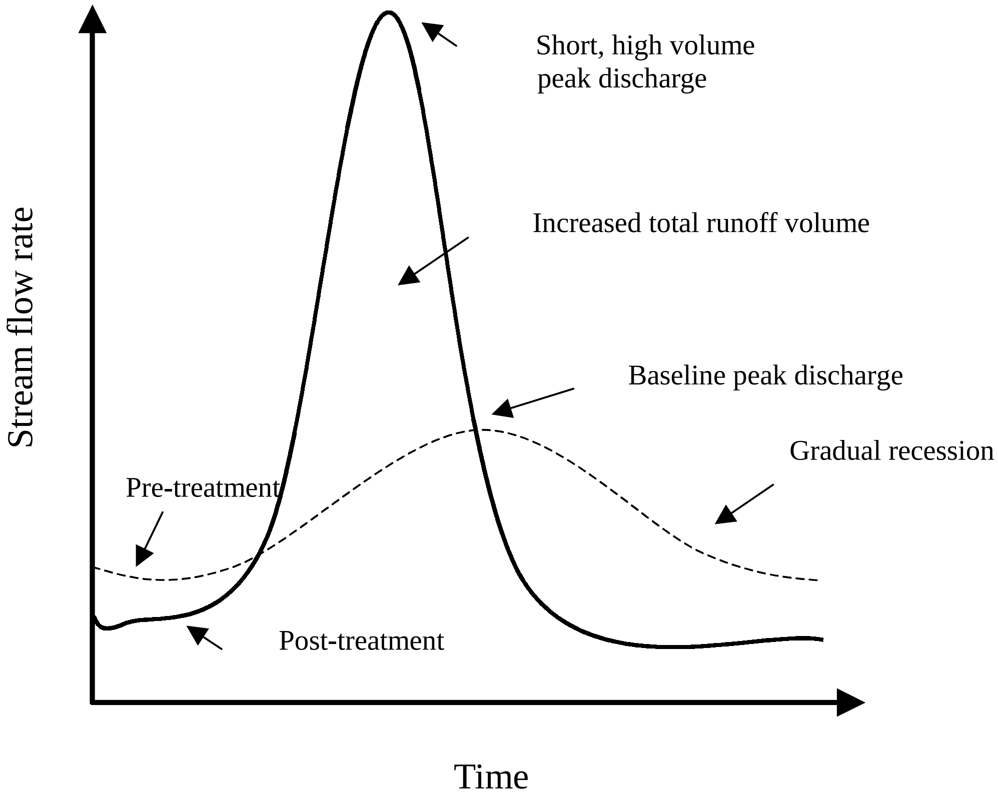
Keywords: Bioretention, Low Impact Development, Media, Best Management Practice, Storm water runoff

Introduction

Ground water and surface water, which account for only 1% of the world's water, are the most important water resources for human beings. Without proper recharge of ground water, the ground water level will continually lower, endangering drinking water resources. The average precipitation in the United States (U.S.) during 1998 was 76 cm. However, only 0.3 cm of the total precipitation infiltrated into the ground water zone, whereas 53 cm returned to the atmosphere through evaporation processes. The other 22.7 cm of precipitation just became runoff and flowed into the ocean (U.S. EPA, 1999a).

Storm water is a very important water resource because of its abundant volume. However, without proper drainage, a large volume of storm water runoff is produced from the growth of impervious surfaces (such as roads, parking lots, and rooftops) created during urbanization. As shown in Figure 1, peak discharge with a high volume and relatively short delay occurs during storms in urban areas, increasing the risk of flooding. Various pollutants (such as oil/grease (O/G), suspended solids (SS), nutrients, and heavy metals) are then washed out from potential storm water hotspots (such as commercial parking lots, construction sites, fueling stations, commercial nurseries, and vehicle washing facilities) located in urban areas, mobilizing them into the runoff. The resulting problem usually includes an increase in the rate and volume of runoff and increase in the variety and concentration of pollutants contained in the runoff. From a physical standpoint, the increase in the rate and volume of runoff results in higher risk of erosion and flooding during storms. From a chemical viewpoint, the increase in the variety and concentration of pollutants contained in the runoff damages the water resource quality and increases subsequent treatment costs. As a result of the large areas of impervious surfaces and various pollutants, these two problems are usually more prominent in urbanized locations.

Figure 1. Impact of Urbanization on Stream Flow (Schueler, 1987)



In 1978, the U.S. Environmental Protection Agency (EPA) initiated the Nationwide Urban Runoff Program (NURP) to quantify the characteristics of urban runoff, assess the impacts of urban runoff on the water quality of receiving waters, and examine the effectiveness of control practices in removing pollutants found in urban runoff. An average of 28 storms for each of the 81 representative outfalls in 28 metropolitan areas was monitored from 1978 to 1983 (U.S. EPA, 1999b). Based on the results, NURP reinforced the findings of Statewide Water Quality Inventory and Assessments (required by CWA Section 305 b) in which contaminated storm water was identified as one of the primary water quality impairments. More recently, urban runoff is rapidly becoming a major source of nonpoint pollution (U.S. EPA, 1996) and is a leading impairment source for surface waters (including rivers, lakes, reservoirs, ponds, estuaries, great lake and ocean shorelines) and ground water (http://www.epa.gov/305b/98report/98brochure.pdf).

Ten pollutants, including total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (TP), soluble phosphorus (SP), total Kjeldahl nitrogen (TKN), nitrate/nitrite, total copper, total lead, and total zinc, were selected being monitored by NURP. The water quality of untreated urban runoff and domestic wastewater were compared and summarized in Table 1 (U.S. EPA, 1999b). Again, it showed the loadings of pollutants from urban runoff can be much higher than the ones from treated domestic wastewater.

Best management practices (BMPs) for storm water runoff are technologies or combinations of practices that provide treatment for storm water runoff. BMPs have been grouped into three categories: pollution prevention practices, source controls, and treatment controls (www.txnpsbook.org/BMPs/URBMPS.htm). Pollution prevention practices serve to keep chemicals away from rainfall and/or runoff. Through source controls, the regulation of the amount and rate of runoff will minimize total runoff from directly- connected impervious areas, in addition to the management of the amount of pollution. Treatment control approaches are designed to remove pollutants from the runoff. Based on the National Storm Water BMP Database (2001), the total number of BMPs for runoff treatment is 198. Due to the variety of urban land uses and storm water runoff characteristics, one or more BMPs which are appropriate to the location and climate are generally applied to an area.

Table 1. Comparison of Water Quality Parameters in Urban Runoff with Domestic Wastewater (U.S. EPA, 1999b)

Pollutant	Urban Runoff		Domestic Wastewater
	Separate Sewers		After Secondary
	Range (mg/L)	Typical (mg/L)	Typical (mg/L)
COD	200-275	75	80
TSS	20-2890	150	20
TP	0.02-4.3	0.36	2
TN	0.4-20	2	30
Lead	0.01-1.2	0.18	0.05
Copper	0.01-0.4	0.05	0.03
Zinc	0.01-2.9	0.02	0.08

Bioretention is an urban storm water BMP developed in the early 1990's to address runoff pollutants in an aesthetically pleasing manner. By employing integrated and distributed micro-scale storm water retention areas, this approach causes less land disturbance, therefore, creating flexibility for different sites and runoff prevention plans. Runoff enters the bioretention facilities through runoff collecting pipes (Figure 2) or curb cut (Figure 3). Following by the treatment of bioretention media, contaminants in the runoff are removed and water quality is improved. In a conventional configuration, as shown in Figure 4, bioretention generally consists of a porous media, supporting a vegetative layer, with a topping layer of hardwood mulch. During storms when the runoff loading is higher than the infiltration rate into the bioretention, the ponding area can serve as storage space, providing more time for both the precipitation and the runoff to infiltrate into the media. The design concept of bioretention is based on several considerations. First, by employing highly permeable media, runoff is expected to quickly infiltrate into the media once flowing into the bioretention facility. Thus, the total amount of runoff for downstream water bodies is reduced. Second, the bioretention media are usually composed of natural soil, sand, and/or organic matter. They remove pollutants from storm water runoff through a variety of mechanisms, including sedimentation, filtration, sorption, ion exchange, biological uptake, and precipitation. Since the incoming runoff is collected near the sources and is expected to contain fewer pollutants than the runoff farther from the source, bioretention can treat larger amounts of runoff than conventional end-pipe treatment facilities before reaching the loading capacity (Figure 5). Consequently by the treatment of bioretention media, the runoff quality is improved.

Figure 2. Collected Runoff through Pipe during a Rain Event

Figure 3. Collected Runoff through Curb-Cut during a Rain Event

Figure 4. Typical Bioretention System (http://www.ence.umd.edu/~apdavis)

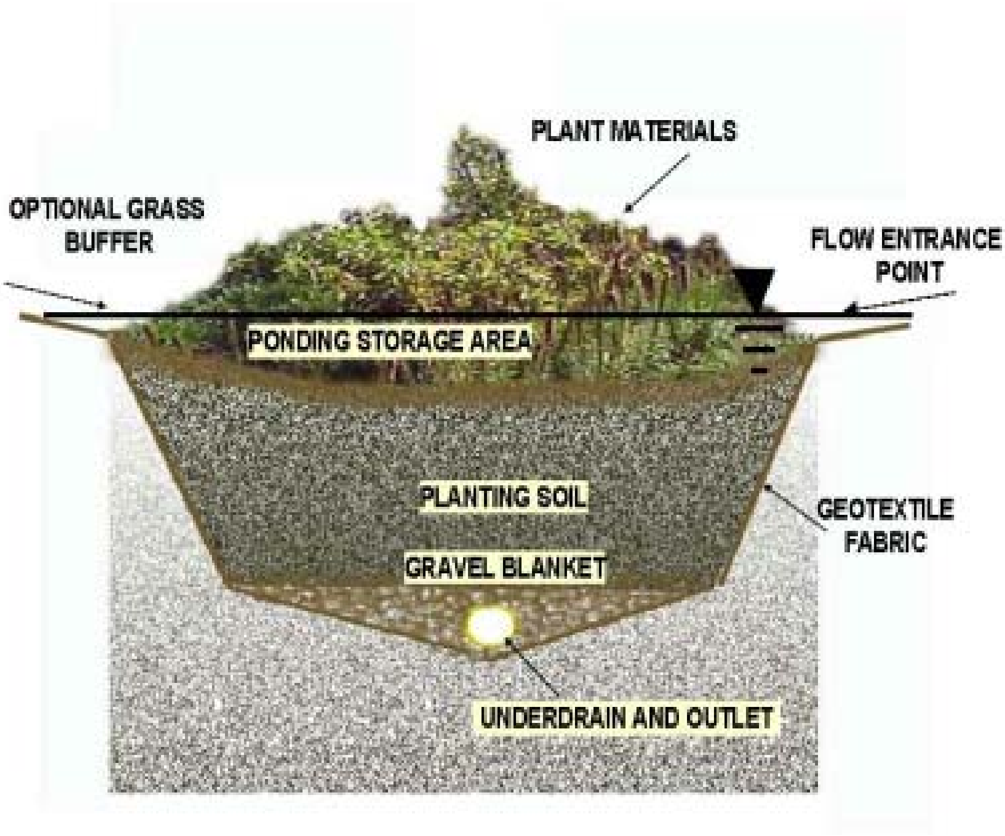


Figure 5a. The Conventional End-Pipe BMPs for Storm Water Runoff Treatment

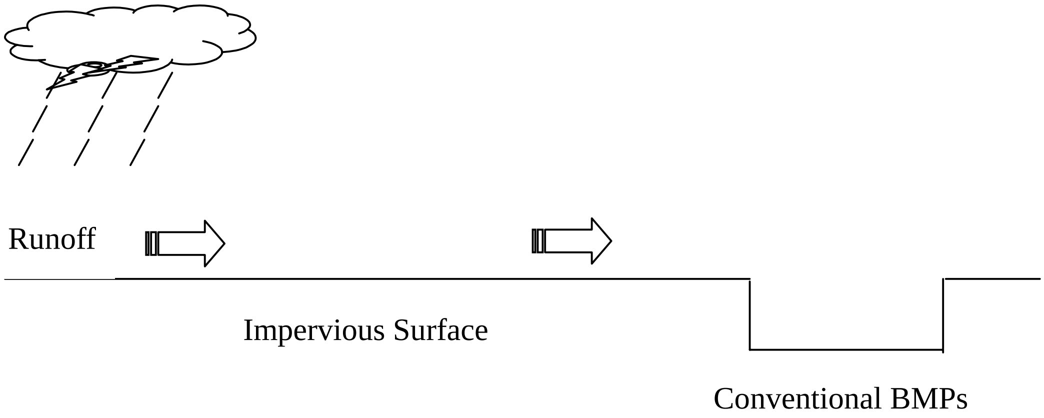
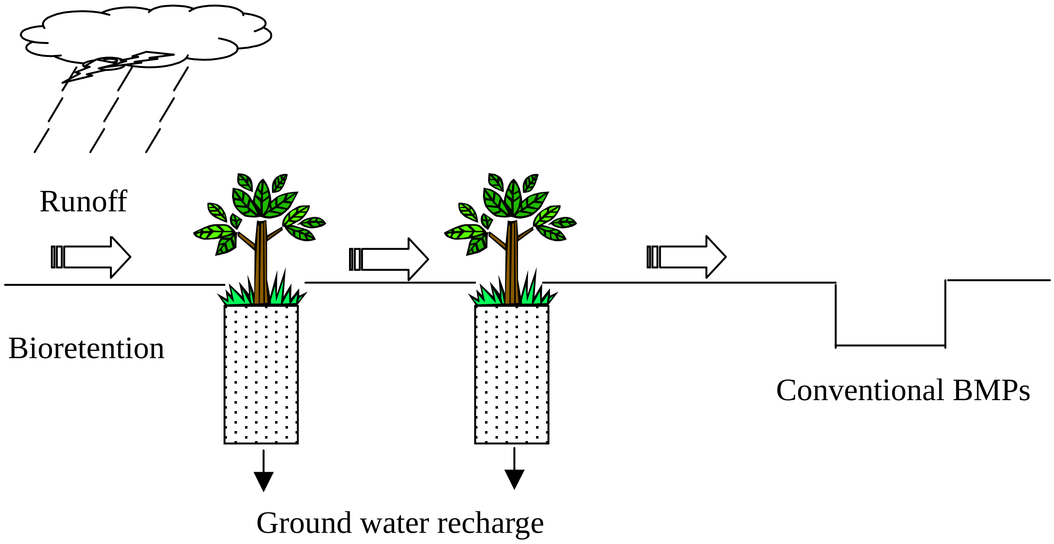


Figure 5b. The Bioretention System for Storm Water Runoff Treatment



I. Role of Bioretention Media for Treatment of Urban Storm Water Runoff

Bioretention and other Low Impact Development (LID) techniques are receiving increasing attention as municipalities struggle with ecological effects of urban growth. Although bioretention has been used at several urban and suburban areas in the United States, a limited amount of research data is available to assess its impact on ground and surface water quality (Claytor and Schueler, 1996). Currently, specifications for bioretention media are only based on the media texture (sand/silt/clay contents). However, characteristics of media (such as particle sizes and silt+ clay contents) and configurations of media profile (layered or homogeneous) could affect runoff infiltration rate and pollutant removals. If bioretention is to be employed as an urban BMP, it must have a high hydraulic conductivity to handle large water volumes directed from impervious areas. Fine fractions in soils tend to be the most chemically active, but high clay contents can be detrimental to infiltration; expanding clays tend to swell markedly after absorbing water and shrink while drying (Brady and Weil, 2002). Therefore, a balance needs to be developed between the permeability of the media and pollutant removal characteristics.

As the experiments conducted in our laboratory previously, the effectiveness of bioretention with certain media for O/G, lead, TP, nitrate, and ammonium removals was tested. However, the influence of media characteristics during runoff treatment processes has not been investigated. In this work, bioretention is assumed to be effective for improving both quantity (runoff infiltration rate) and quality aspects (O/G, TSS, Pb as a representative heavy metal, TP, nitrate, and ammonium removals) of urban runoff. The characteristics of the bioretention media profile, including media texture, chemical property, and media configuration, are hypothesized to be critical to this performance.

II. Long-Term Issues for Bioretention in the Treatment of Urban Storm Water Runoff

As mentioned, biological uptake is one of pollutant removal mechanisms of bioretention media. Under conditions of high runoff infiltration rate, microorganisms do not have sufficient time to degrade pollutants in infiltrating runoff. Alternatively, microorganisms may degrade the retained pollutants during the dormant period, especially P and N, which serve as nutrients for their growth. For runoff infiltrating into bioretention facilities, SS accumulation in the media will decrease the hydraulic conductivity, finally leading to media clogging. Therefore, appropriate media to filter SS without clogging is critical for bioretention operation.

In this work, through several repetitive experiments, the significance of biological processes on bioretention performance was tested. The removal efficiency of TP and N (including nitrate and ammonium) from runoff is hypothesized being affected after dormant periods. In addition, runoff infiltration rate is expected to decrease along with the accumulation of incoming SS.

Objectives

Three primary objectives make up this study:

1) To provide insight on media characteristics in controlling bioretention behavior.
2) To evaluate long-term effectiveness of bioretention for runoff infiltration and pollutant removals.
3) To confirm the performance of existing bioretention facilities and compare field and laboratory results.

By employing 6-hr bioretention columns, the effect of media properties and configurations on bioretention performance was investigated. Through a moderate long-term period, two bioretention columns were tested for runoff infiltration under repetitive SS inputs and pollutant removals with several dormant periods. Also, 6-hr on-site experiments were conducted on six existing bioretention facilities to evaluate their performances with respect to pollutant removal. In order to exclude effects resulting from variation in incoming runoff chemistry and flow, a synthetic runoff solution was made up and used in these experiments. Two additional on-site experiments were conducted during an actual rainfall event for comparison with the simulated-runoff laboratory and field studies.

Overall, the optimal design of bioretention media for increasing pollutant removal by promoting certain physical, chemical, or biological processes, while maximizing infiltration characteristics through making up an appropriate media configuration is the primary benefit of this research. By doing the field tests, existing systems can be evaluated and compared with the column tests to determine improved ways for future design.

Methods

In order to fully investigate bioretention media performance, several different types of tests were completed. Six-hr bioretention column tests were employed to investigate the performance of bioretention systems with different media compositions and configurations during a simulated 6-hr rainfall event. Long-term performance of bioretention systems was tested using repetitive bioretention column tests. Continuous column tests were conducted to measure the maximum P loading for different ratios of sand to soil. The effectiveness of existing bioretention systems was confirmed by 6-hr on-site tests.

Materials

Source of Storm Water Runoff

Experiments for 6 hr-bioretention column tests, repetitive bioretention column tests, and six on-site bioretention confirmation tests used synthetic storm water runoff that was made up in the Environmental Engineering Laboratory, University of Maryland, College Park. Tap water with adding a stoichiometric $NaHSO_3$ for dechlorination (Eq. 1) was employed in this study.

$$HOCl + HSO_3^- \rightarrow Cl^- + SO_4^{2-} + 2H^+ \qquad (1)$$

The target pollutants for the experiments are O/G, TP, Pb, nitrate, ammonium, and TSS. Based on information from Prince George’s County, Maryland, and other references on urban storm water runoff chemistry, a synthetic storm water runoff was produced. The characteristics of this water are presented in Table 2 (Davis et al., 2001). For continuous column tests, synthetic runoff contained only 3 mg-P/L and 120 mg/L of TDS. The pH was controlled at 7.

Table 2. Makeup of Synthetic Runoff Used in this Study (Davis et al., 2001)

	Value (mg/L, except pH)	Source
pH	7.0	HCl or NaOH
Total dissolved solids	120	$CaCl_2$
TP	3 (as P)	Na_2HPO_4
Nitrate	2 (as N)	$NaNO_3$
Ammonium	2 (as N)	NH_4Cl
Pb	0.1	$PbCl_2$
SS	150	Local soil sieved through a 0.0232 inch opening
Motor oil	20	Used oil from local garage

Sources and Characteristics of Media

Two sands, four soils, and a compost mulch that varied in their physical and chemical properties were used in this study to evaluate their pollutant-removal performances. Both sands, with very different particle sizes, were obtained from a local home supply store. Before the experiment started, sands were washed using the Silica Sand Washing Procedure (Kunze and Dixon, 1989). After washing several times using tap water, hydrogen peroxide is consequently applied under 75^{o}C to oxide organic matter contained in the sand.

Three different soils were obtained from the Prince George County (MD) Department of Public Works and Transportation, while the other one was obtained from the Low Impact Development Center (Beltsville, MD). Mulch used in the experiments was obtained from the College Park City Department of Public Works. It was produced from locally-collected municipal leaves and grass clippings that were piled into long rows for composting.

Before the experiments, the soil, sand, and mulch samples were sent to the Soil Testing

Laboratory of the Department of Agronomy, University of Maryland, College Park for analysis. Also, the particle-size distribution of all media on a mass basis was analyzed using dry-sieving techniques in the Geotechnological Engineering Laboratory, University of Maryland, College Park. The uniformity of the particle-size distribution (the uniformity coefficient) was calculated as the ratio between d_{60} (60% of the medium by mass is smaller than d_{60}) and d_{10} (10% of the medium by mass is smaller than d_{10}). All the results are presented in Table 3.

Table 3a. Bioretention Media Chemical and Mechanical Analyses

	d_{10} mm	d_{60} mm	d_{60} / d_{10}	pH	Mg mg/100 g media	P mg/100 g media	K mg/100 g media	Ca mg/100 g media	O.M. %
Sand (I)	0.17	0.30	1.8	7.1	9.5	5	3	2.8	0.15
Sand (II)	0.30	0.84	2.8	5.0	2.5	4	0.8	0.8	0.10
Soil (I)	0.09	0.20	2.2	7.8	29	12	21	> 44	2.20
Soil (II)	0.13	0.81	6.2	6.9	25	17	27	22	2.60
Soil (III)	0.09	0.29	3.2	6.7	28	7.5	35	*	4.40
Soil (IV)	0.10	0.32	3.2	7.1	27	9.9	18	68	3.50
Mulch	0.15	2.31	15.4	7.1	28	56	35	> 44	29.8

* no data collected

Table 3b. Bioretention Media Chemical and Mechanical Analyses

	CEC meq/100 g media	Sand %	Clay %	Silt %	Classification
Sand (I)	1.1	95	3	2	Sand
Sand (II)	0.4	92	5	3	Sand
Soil (I)	19	66	19	15	Sandy Loam
Soil (II)	6.3	79	12	9	Sandy Loam
Soil (III)	*	71	17	12	Sandy Loam
Soil (IV)	15	71	14	15	Sandy Loam
Mulch	34				

The experimental facility for 6-hr and repetitive bioretention experiments consists of a column and media. Two different Plexiglas column sizes were employed. The inner diameter of the large Plexiglas column is 19.1 cm and the height is 110 cm (Figure 6). Different mixtures of media were evaluated for their pollutant removal efficiencies and the resulting runoff infiltration rate. Media employed in these tests contained mulch, sand and soil. In addition, several different fractions of media were mixed homogeneously to yield a new mixed-medium for testing (Table 4). For continuous bioretention experiments, the inner diameter of the Plexiglas column is 6.4 cm with a height of 40 cm. Three homogeneous media mixtures with different soil/sand ratios were employed (soil III/ sand II: 70/30, 50/50, and 30/70 mass basis).

Table 4. Makeup of Synthetic Media

Synthetic media	Components	Component ratio in mass basis
I	mulch/soil I/sand I	1:2:2
II	soil III/sand II	4:1
III	soil III/sand II	1:1

Figure 6. Bioretention Laboratory Column with Different Media Layers

Methods

Pollutants Sorption by SS

To determine the pollutant adsorption portion by SS in simulated runoff, 15 mg soil sieved through a 0.0232 inch sieve were suspended in 100 ml solution containing 100 μg/L Pb standard solution, 3 mg-P/L TP, 2 mg/L NO_3^--N, 2 mg/L NH_4^+-N, 20 mg/L O/G and 120 mg/L $CaCl_2$. The suspension was equilibrated by shaking at laboratory temperature (22^{o}C) for 24 hours. A similar solution without SS was used as the blank.

6-hr Bioretention Column Experiments

A total of eighteen 6-hr column tests, using various media to investigate the effects of media characteristics (including size distribution, chemical properties, and configurations) on the water infiltration rate and pollutant removal, were performed. The media used in these types of experiments included not only layers of the native media (e.g., sand, soil, and mulch), but also some synthetic media made up by mixing several media homogeneously (Table 4).

During the testing period, the simulated runoff was made and mixed in a 200-L container with a large mixer. At the start of the experiment, runoff was pumped into the column from the top and the first sample was collected. Over a six-hr time period, effluent samples were collected every hour from the bottom of the column and taken to calculate the flow rate and measure the pollutant concentration. The water head was maintained constant at 15 cm by an overflow and controlling the pumping rate during the experiment.

Repetitive Bioretention Column Experiments

Two different columns were used and three media layers were employed in each column. The first column included a top mulch layer (5 cm, 0.82 kg), a middle porous soil I layer (15 cm, 8.17 kg), and a bottom sand I layer (75 cm, 30.9 kg). In general, sand is more permeable than mulch or soil. Therefore, less-permeable mulch and soil layer were designed to overlay the high-permeability sand layer in this testing column, which is also a typical configuration used in surface, organic and pocket sand filters. The media for the second column was composed of 3.06 kg mulch, 3.06 kg soil IV, and 6.13 kg sand II homogeneously mix (30 cm) in the top layer, 23.2 kg sand I (55 cm) in the middle layer, and 5.9 kg soil IV (10 cm) in the bottom layer. Usually, mulch and soil contain abundant organic matter and can serve as the media for plant growth. Also, organic matter content can serve as the carbon source for microorganism growth. Both of these are helpful to the operation of bioretention. In addition, because of the bigger media particle size, sand I can treat a larger volume of runoff before clogging. Therefore, mixing mulch and soil with sand I seem to be a good mixture for the upper media. Twelve repetitions for the first repetitive column and sixteen for the second were completed. Runoff was applied into the bioretention column after a 4-14 day dormant period. The testing procedure for each run was similar to the 6-hr bioretention column experiments. The samples were analyzed for flow rate and the concentrations of the six pollutants. The objective of this series of experiments was to evaluate the system performance under repetitive loadings and investigate processes that may occur during the dormant period between rainfall events.

Media samples were collected from different depths in the second repetitive column before and after testing. The media P investigations included environmental soil tests (Water soluble P (WSP) and calcium extractable P ($CaCl_2$-P)) and agronomic soil tests (Mehlich I extractable P and Mehlich III extractable P tests). WSP was determined by mixing 2.5 g of soil with 25 mL of deionized water for 1 hr. Calcium extractable P was analyzed by shaking 5 g of soil with 20 mL of 0.01 M $CaCl_2$ for 24 hrs. Mehlich I extractable P was determined by shaking 2.5 g of each media with 10 mL of Mehlich III reagent (0.05 M HCl+ 0.0125 M H_2SO_4) for 5 mins (Sims and Heckendorn, 1991). Mehlich III extractable P was determined by shaking 2.5 g of each media with 25 mL of Mehlich III reagent (0.2 N CH_3COOH+ 0.25 N NH_4NO_3+ 0.015 N NH_4F+ 0.013 N HNO_3+ 0.001 M EDTA) for 15 mins (Mehlich, 1984). Finally, P in all extractants was analyzed using Murphy and Riley method (1962). The absorbance of molybdophosphate complex was measured on spectrophotometer at 712 nm.

Continuous Bioretention Column Experiments

Three small columns (Plexiglas, 40 cm long by 6.4 cm inner diameter) with different ratios of sand/soil were employed to investigate maximum P loadings for the media. The media compositions (soil III/sand II % in mass basis, total mass= 1350 g) for these three columns were 30/70, 50/50 and 70/30. The flow rate was controlled as constant at 3.1 mL/min (5.9 cm/hr) employing a peristaltic pump. As mentioned, the influent only contained 120 mg/L $CaCl_2$ and 3 mg-P/L Na_2HPO_4, maintained at pH 7. During the experiment, influent was pumped from the top of the column continually and effluent was collected from the bottom of the column every day for a total of 29 days. The samples were analyzed for P concentration.

P Adsorption Capacity

To determine the P adsorption capacity of different media, different masses of each medium were shaken in 100 ml deionized water solution containing 3 mg-P/L Na_2HPO_4 and 120 mg/L $CaCl_2$. Solution without any media served as the control. The suspension was equilibrated by shaking at laboratory temperature (22^oC) for 24 hours. The objective of this study was to determine the P adsorption isotherm for every medium at pH 7.

Evaluation of On-site Bioretention Facilities

A total of six field experiments (Figures 7 to 12), one in Greenbelt, MD (GB), two in Hyattsville, MD (HV1 and HV2), and three in Landover, MD (LO1, LO2, and LO3), were completed. GB site was constructed in 1993, whereas HV1, HV2 were built in 1998; LO1, LO2, and LO3 were finished in 2001. The synthetic runoff was stored in six 200-L containers and transported to each site. An area about 5.3 m^2 (2.3 m x 2.3 m) within each bioretention facility was selected adjacent to a manhole. During the experiment, runoff was mixed and pumped into the selected area at 2.8 L/min (3.2 cm/hr loading). Over a six-hr time period, samples were collected from the facility underdrain outlet pipe in the manhole every half-hour using acid-washed amber glass bottles, along with selected influent samples. All collected samples were transported to the Environmental Engineering Laboratory, University of Maryland, for measuring pollutant concentrations. Additionally, media samples were collected from each facility using a core sampler and were divided into two layers, 10 to 15 cm and 15 to 40 cm depth. Each layer sample was mixed homogeneously and sent to the Soil Testing Laboratory for characterization.

Two additional evaluations of bioretention facilities (Figures 13 and 14) were conducted in College Park, MD (CP1 and CP2) during a rainfall event on February 3, 2003. These are two adjacent, lined cells constructed for research and monitoring. CP1 was constructed according to the design modification of Kim et al. (2003), which includes a bottom sand media layer with shredded newspaper that serves as an electron donor. A raised underdrain pipe maintains anoxic conditions to promote denitrification. During rainfall events, runoff from the adjacent parking lot is split into two separate concrete inlet channels leading to the bioretention cells. Effluent is discharged from the underlying pipes into the adjacent creek. Influent runoff and effluent for both facilities were collected every half hour for 1.5 hours.

Figure 7. Bioretention Field Study (GB) -- Greenbelt, MD (08/22/01)

Figure 8. Bioretention Field Study (LO1) -- Largo, MD (09/19/01)

Figure 9. Bioretention Field Study (HV1) – Hyattsville, MD (06/12/02)

Figure 10. Bioretention Field Study (LO2) – Landover, MD (06/25/02)

Figure 11. Bioretention Field Study (HV2) – Hyattsville, MD (07/09/02)

Figure 12. Bioretention Field Study (LO3) – Landover, MD (07/23/02)

Figure 13. Bioretention Field Study (CP1) – College Park, MD (02/04/03)

Figure 14. Bioretention Field Study (CP2) – College Park, MD (02/04/03)

Analytical Methods

Analytical methods include analysis for TSS, O/G, TP/DP, Pb, nitrate-N, and ammonia-N.

O/G Analysis (Lau and Stenstrom, 1997)

1,000 mg C18 columns (obtained from Analytichem Corp., Folsom, CA) were first conditioned with 5 mL isopropanol, followed by 5 mL deionized water. A 500 mL runoff sample was pretreated by adding 25 mL isopropanol and 1 mL concentrated HCl. The sample was then passed through the column at a flow rate of 5 mL/min using a peristaltic pump. To remove O/G from the wall of the sample container, 5 mL isopropanol and 100 mL deionized water containing 0.1% concentrated HCl were added and the mixture was passed through the column as before. The column was then dried for 25 mins.

A tarred collection vial was placed under the column after it was dried. The column was eluted with 3 mL methylene chloride followed by 2 mL hexane. Each elution fraction in the collection tube was evaporated to dryness. The tube then was weighed to determine the mass of O/G eluted from the C18 column.

TSS Analysis

This test follows Section 2540D of Standard Methods (APHA et al., 1995). A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C for 1 h. The increase in weight of the filter represents the TSS.

Pb Analysis

Total Pb was analyzed by digesting samples at 95 °C, using 2 mL of concentrated nitric acid per 50 mL sample. An aliquot of the digested suspension was then centrifuged and filtered through a 0.2 µm syringe filter (cellulose acetate membrane). This test follows Section 3500-Pb of Standard Methods (APHA et al., 1995). Pb was analyzed on the furnace module of a Perkin Elmer Model 5100ZC atomic absorption spectrophotometer. Pb standards of 2, 5, 10, and 15 µg/L were prepared from 1000 mg/L Pb-reference solution (Fisher Scientific). A VWR Scientific hollow cathode lamp was used at a wavelength of 283.3 nm, slit width of 0.7 nm and an average lamp current of 8 milliamps. The detection limit for Pb was 2 µg/L. To analyze for dissolved Pb, samples were acidified, filtered, and then analyzed directly.

TP Analysis

A P analysis is divided into two general procedural steps: (a) conversion of P to dissolved orthophosphate, and (b) colorimetric determination of dissolved orthophosphate. Filtration through Pall Gelman GF/C filters (0.2 µm) separates dissolved from suspended forms of P. Because P may occur in combination with organic matter, a persulfate digestion method is used to oxidize organic matter effectively to release P as orthophosphate.

After digestion, an aliquot of the suspension was centrifuged and filtered through Pall Gelman GF/C filters (0.2 µm). This test follows Section 4500-P of Standard Methods (APHA et al., 1995). A 50 mL sample was placed into an Erlenmeyer flask and one drop of phenolphthalein was added. If red color appeared, enough H_2SO_4 solution was added to discharge the color. Otherwise, 20 drops of H_2SO_4 solution were added to each flask. Along with 0.5 g $K_2S_2O_8$ (J.T.Baker), the flasks were then boiled on a hot plate until about 10 mL of liquid remained. Followed by, the flasks were removed from the heat and allowed to cool. In addition to another drop of phenolphthalein, 20 mL of distilled water was filled to each flask. Finally, the liquid was neutralized to a faint pink color with NaOH.

Total volume of the solution in each flask was diluted to 100 mL with distilled water. Another drop of phenolphthalein was added to each flask. Once faint pink color appeared, enough H_2SO_4 solution was added to discharge this coloring. Then 4 mL of ammonium molybdate reagent I, and 10 drops of stannous chloride reagent I were added to each flask. The samples were allowed to sit for 10 minutes. Finally, the samples were placed into a spectrophotometer (Bausch and Lomb, Spectronic 21) to measure the color at 690 nm.

Nitrate Analysis

Nitrate-N was analyzed using Dionex DX-100 ion chromatograph instrument with a Dionex AS4 column. Before measuring, an aliquot of the suspension was centrifuged and filtered through a 0.2 µm syringe filter. A solution of 1.2 mM sodium carbonate/2.8 mM sodium bicarbonate (J.T.Baker) was employed as the eluent. During analysis, the flow rate was adjusted to 1.4 mL/min to clearly differentiate nitrate and chloride. The concentration of nitrate in the samples was determined against standards prepared with sodium nitrate (Fisher Scientific) in deionized water. Detection limit for nitrate-N was 0.1 mg/L.

Ammonium Analysis

An aliquot of the suspension was centrifuged and filtered through a 0.2 µm syringe filter. Ammonium-N analysis was carried out using a Dionex DX-100 ion chromatograph instrument with a CS12 column. 1.1 mN sulfuric acid (Fisher Scientific) was employed as the eluent and the flow rate was controlled at 0.4 mL/min to differentiate ammonium and sodium peaks. The ammonium concentrations in the samples were determined against standards prepared by dissolving required amounts of ammonium chloride (J.T.Baker) in deionized water. Detection limit for ammonium-N was 0.05 mg/L.

Results

I. Evaluation and Optimization of Bioretention Media for Treatment of Urban Storm Water Runoff

Bioretention media remove pollutants from storm water through a variety of mechanisms, including sedimentation, filtration, sorption, and precipitation. Accordingly, different media compositions are expected to demonstrate different pollutant removal efficiencies because of the respective effects on pollutant capture mechanisms. For example, Pb, Cu, Ni, and Zn adsorption by and desorption from several soils were affected by the pH of the soil (Harter, 1983). P retention and movement in soils is influenced by both influent and soil characteristics (Nagpal, 1985). Sands with different Ca, Fe, and Al contents resulted in about 3-fold differences in P removals in constructed reed bases (Arias et al., 2001).

Nonetheless, the hydraulic characteristics of bioretention media cannot be ignored. If bioretention is to be employed as an urban BMP, it must have a high hydraulic conductivity to infiltrate large water volumes directed from impervious areas. The hydraulic conductivity of the media depends primarily on the size of conducting pores and, generally, larger pores conduct water more rapidly (Hillel, 1998). Therefore, a sandy media is favored and high clay contents can be detrimental to infiltration; expanding clays tend to swell markedly after absorbing water and shrink as drying (Brady and Weil, 2002). Since fine fractions in soils tend to be the most chemically active, however, a balance needs to be developed between the permeability of the media and pollutant removal characteristics. Consequently, design of the media profile is critical to determining bioretention performance characteristics.

Thus, three bioretention media issues are addressed in this manuscript. Currently, specifications for bioretention media are only based on the media texture (sand/silt/clay contents). While this represents improvement over older designs, media particle sizes (d_{10}, d_{60}) and chemical properties can vary greatly within these three texture designations. Small variations in media sizes or media heterogeneity can result in very different runoff infiltration rates. Similarly, media components with different chemical properties will attenuate pollutants via different efficiencies and mechanisms. Therefore, the runoff infiltration rate and pollutant removal efficiencies can be very different among different media components, even if simple texture designations are similar.

Second, the configuration of the media can also influence bioretention performance. A thin silt/clay media layer with a low permeability could limit the infiltration rate of runoff through an entire bioretention facility. Because of different water heads, the infiltration rate through a facility with a less-permeable layer near the surface would be slower than one with this same layer at the bottom. Also, infiltration rates through a facility employing several media layers would be different from one employing the same media, but mixed homogeneously (Hillel, 1998). Layering and homogeneity may also lead to different pollutant removal efficiencies.

Finally, although bioretention has been implemented at several urban and suburban areas throughout the United States, only a limited amount of research and performance data are available to assess the impact of this technology on ground and surface water quality. Evaluation of the performances of existing bioretention facilities will support findings from laboratory investigations and can serve as the basis for future design improvement, with a focus on media characteristics.

Bioretention is assumed to be effective for improving both quantity and quality aspects of urban runoff. However, the bioretention media profile is critical to this performance. The objective of this study is to provide insight on media characteristics in controlling bioretention behavior.

Eighteen 6-hr bioretention columns with different media mixtures and configurations were employed to compare results on runoff infiltration rate and pollutant removal efficiencies. Also, 6-hr on-site experiments were conducted on six existing bioretention facilities to evaluate their performances with respect to pollutant removal. In order to exclude effects resulting from variation in incoming runoff chemistry and flow, a synthetic runoff solution was made up and used in these experiments. Two additional on-site experiments were conducted during an actual rainfall event for comparison with the simulated-runoff laboratory and field studies.

6-hr Bioretention Column Experiments

Current design specifications for bioretention are based on simple texture composition for the media (limits on clay/silt/sand contents). Nonetheless, it is clear that various types of sands and soils result in different runoff infiltration rates in 6-hr bioretention column experiments because of their wide range of particle sizes and textures (Table 5). Pollutant removal results are also summarized in Table 5. Clearly, different characteristics of the media components promote variation in removal performance for several pollutants.

Table 5a. Characteristics and Results of 6-hr Bioretention Column Tests

Exp. No.	Mass Ratio (%)			Experimental Set	Infil. Rate
	Mulch	Soil	Sand		cm/min
1[a]	0	0	100(I)	A, B	0.84±0.01
2[a]	0	0	100(II)	A	8.15±0.18
3[a]	2	93(I)	5(I)	A, B	0.28±0.04
4[a]	2	93(II)	5(I)	A	0.95±0.01
5[a]	2	93(III)	5(II)	A	0.40±0.02
6[a]	91	0	9(I)	A	0.28±0.01
7[a]	0	0	100(I)	-	0.81±0.02
8	3	0	97(I)	B	0.77±0.01
9[b]	2	21(I)	77(I)	C-1	0.32±0.02
10[b]	8	26(I)	66(I)	C-1	0.31±0.01
11[b]	6	32(I)	62(I)	C-1	0.30±0.01
12[b]	0	24(I)	76(I)	C-1	0.30±0.01
13[c]	3	43(I)	54(I)	B, C-2	0.48±0.02
14[c]	3	24(I)	73(I)	B, C-2	0.66±0.01
15[c]	11	19(I)	70(I)	B, C-2	0.71±0.02
16[d]	2	17(II)	81(II)	D	5.40±0.15
17[d]	2	72(III)	26(II)	D	1.15±0.02
18[d]	2	49(III)	49(II)	D	1.93±0.01

a: native media; b: column with upper soil I layer; c: column with synthetic media I (mixture of soil I/ mulch/ sand I); d: column with upper soil II or soil III layer; e: influent w/o suspended solids; (I), (II), (III): different types of sands and soils- see Table 3.1

Table 5b. Characteristics and Results of 6-hr Bioretention Column Tests

	Removal Efficiency (%)					
Exp. No.	TSS	O/G	Lead	TP	Nitrate	Ammonium
1[a]	>96	>96	>98	85±1.5	11±16.7	8±3.4
2[a]	>96	>96	96±0.7	10±3.1	1±0.7	15±0.8
3[a]	29±2.9	>96	>98	47±3.4	1±0.6	6±2.2
4[a]	88±0.9	>96	>98	41±4.5	14±2.2	24±0.8
5[a]	91±0.3	>96	>98	48±4.0	8±0.7	16±1.1
6[a]	86±1.0	>96	75±2.0	4±4.5	43±3.2	16±1.9
7[a]	-[e]	>96	66±7.0	84±1.3	13±6.4	5±1.7
8	>96	>96	>98	61±4.5	9±0.4	9±2.0
9[b]	66±2.5	>96	>98	47±4.6	3±0.8	2±1.1
10[b]	94±0.6	>96	>98	50±3.8	4±0.7	7±1.0
11[b]	93±0.9	>96	>98	39±4.0	4±0.5	7±0.8
12[b]	93±0.5	>96	>98	39±3.5	2±0.5	5±2.2
13[c]	>96	>96	>98	83±1.4	13±59	26±2.6
14[c]	>96	>96	>98	57±2.7	24±2.9	17±2.1
15[c]	>96	>96	>98	54±2.7	27±1.1	20±1.2
16[d]	>96	>96	97±0.2	24±3.8	6±1.5	11±0.6
17[d]	92±0.3	>96	>98	72±0.8	9±0.9	19±0.6
18[d]	93±0.3	>96	>98	74±0.9	8±0.5	20±0.5

Performance of Different Media Components

The infiltration results for the six native media columns (Exps. 1 to 6- - Set A) demonstrate that the rate through sand II (8.15± 0.18 cm/min) was nearly an order of magnitude faster than that through sand I (0.84± 0.01 cm/min) at 15-cm head. This is readily explained by the larger particle size of sand II (d_{10}= 0.30 mm) compared to sand I (d_{10}= 0.17 mm). Similarly, the infiltration rate using soil II as the dominant medium is much higher (0.95± 0.01 cm/min) than that for soil I (0.28± 0.04 cm/min) or soil III (0.40± 0.02 cm/min). Soil II has larger d_{10} and d_{60} (Table 2), and contains lower fractions of silt (9%) and clay (12%) than soil I (silt + clay= 34%) or soil III (silt + clay= 29%). In addition, visual examination of soil II shows large particles of organic material and sand. The d_{60}/d_{10} ratio is 6.2 for soil II, much larger than for soil I (2.2) and soil III (3.2). Larger pore sizes among media particles can result in a higher media permeability. All of these properties allow soil II to be the most permeable soil among the three employed.

Compared with other media, particle sizes of mulch components are quite heterogeneous (d_{60}/d_{10}= 15.4). Very high values of d_{60}/d_{10} may increase the risk of clogging (Arias et al., 2001) and can reduce permeability. The runoff infiltration rate through the mulch column is low at 0.28± 0.01 cm/min. Therefore, not only d_{10} but also uniformity is important in controlling runoff infiltration rate.

Turning to pollutant removals, both sands and all soils demonstrated excellent removal efficiencies for O/G and total Pb (Table 4.1). With mulch, O/G was removed > 96% (Exp. 6), however, less Pb (75± 2%) was removed using this medium as compared with the others. Very good TSS removal (> 86%) was noted in most of the native-media bioretention columns, except in the column in which soil I (29± 2.9%) was the dominant medium. Visually, it was apparent that some of the soil particulate matter leached out from the soil I column during the testing period. This problem should disappear with subsequent runoff applications.

As the results form the batch experiment, 56% of the influent Pb is sorbed onto the TSS. Thus, this fraction of Pb can be removed via efficient filtration of TSS by the bioretention media. Removals greater than 56%, however, are found in all native media, indicating that some sorption of lead occurred onto the media. Results of sand I columns (Exps. 1 and 7) demonstrate that the removal efficiency of total Pb was > 98% for influent runoff with TSS and only 66± 7% without TSS. Therefore, it is evident that sorption of Pb occurred within the sand I layer and that TSS filtration contributed to Pb removal.
Sand I removed TP from the synthetic storm water runoff at 85± 1.5%, while sand II removed just 10± 3.1%. In addition to physical filtration, TP removal by sand columns may relate not only to simple adsorption, but also to complex sorption/precipitation processes (Arias et al., 2001). All three soils removed just 41 to 48% of TP. In the column with 91% mulch, only 4± 4.5% TP removal was found, indicating that mulch does not play an important role in TP removal. Although mulch is expected to retain P through complexation processes, these organic matter complexes may be in dissolved forms and can leach out.

The removal efficiency of nitrate by the native media ranged from 1 to 43%. The sands were mostly ineffective. The native media removal efficiencies for ammonium were low, ranging from 6 to 24%. Both types of sand produced similar low removal (8 to 15%). Soil I removed about 6± 2.2% ammonium, and soil II removed 24± 0.8%. Soil III and mulch removals were about 16%.

Since fixing the applied water head resulted in different flow rates for different media, the pollutant removals were also evaluated on a mass basis. Input, output, and removed mass of pollutants for different media during 6-hr testing periods are calculated as:

$$M = \sum_{i=1}^{t_d} QC\Delta t \tag{2}$$

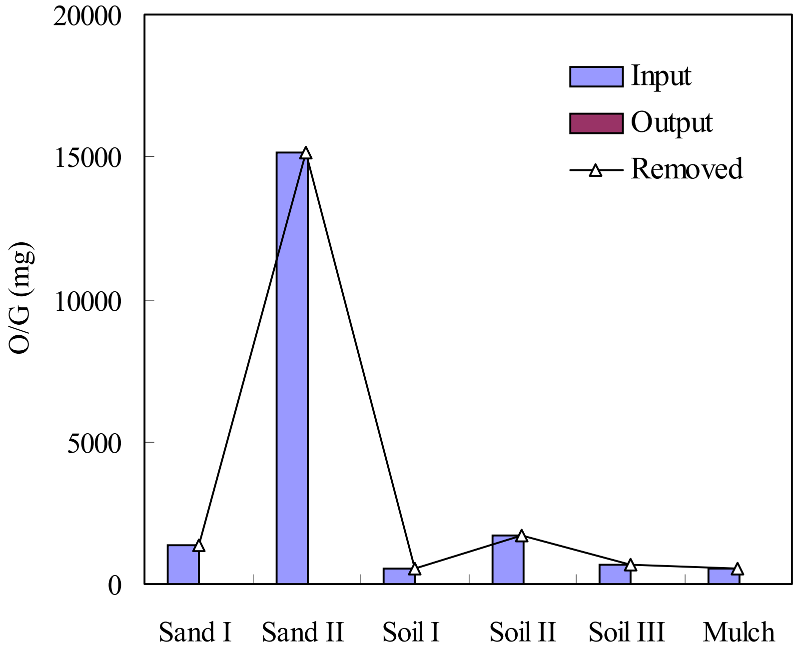
Where M is the pollutant mass, Q is the infiltration flow rate, C is the pollutant concentration, and Δt is the measurement time increment. Both input and output pollutant masses are calculated using appropriate parameters, with the mass removal being the difference between input and output.

The results are summarized in Figure 15. O/G, TSS, and Pb were all removed effectively for all media and the plots for each look similar. On a mass basis, sand II removed much more of these three pollutants from the runoff than the other media because of the resulting high loading coupled with low output concentrations. Sand II therefore appears to be the best performer among these six media for TSS, Pb, and O/G removal. This analysis underscores the importance of particulate removal from urban storm water and the benefits of utilizing a sand filter as a BMP (Pell and Nyberg, 1989; Schueler and Holland, 2000), which is essentially what this single-media sand column represents. Sand filters, however, do not have a number of water quality and ecological advantages, as do bioretention facilities.

Sand I appears to be the better choice for TP treatment since significant mass was removed and a lower output TP concentration was obtained as compared with other media. For nitrate and ammonium, none of the media performed exceptionally well and generally demonstrated minimal removal ability.

Overall, these results emphasize the importance of a high infiltration rate. When employing sand in bioretention media, a high permeability is recommended, with d_{10} near 0.30 mm (such as sand II). Because silt and clay generally contain more nutrient and water holding capacity than sands, soil is necessary for plant growth in the top media layer. The best performance with soils was also noted for that with high d_{10} and a value greater than 0.1 mm is recommended for bioretention soils. High d_{60}/d_{10} can result in high runoff infiltration rate and is desired. However, once the value of d_{60}/d_{10} is too high (such as the mulch used in this study, $d_{60}/d_{10} = 15.4$), the small components among the media may disperse and be transported into media pores; consequently, the risk of clogging and reduction in runoff infiltration rate is increased. A d_{60}/d_{10} value less than 4 has been recommended (Arias et al., 2001).

Figure 15a. Input, Output, and Removed Mass of Pollutants among Different Native Media for 6-hr Runoff Treatment



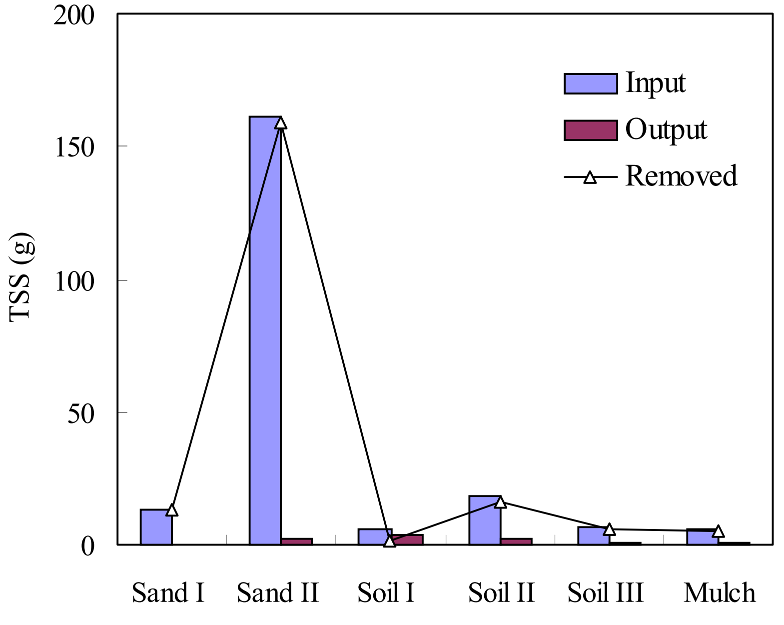
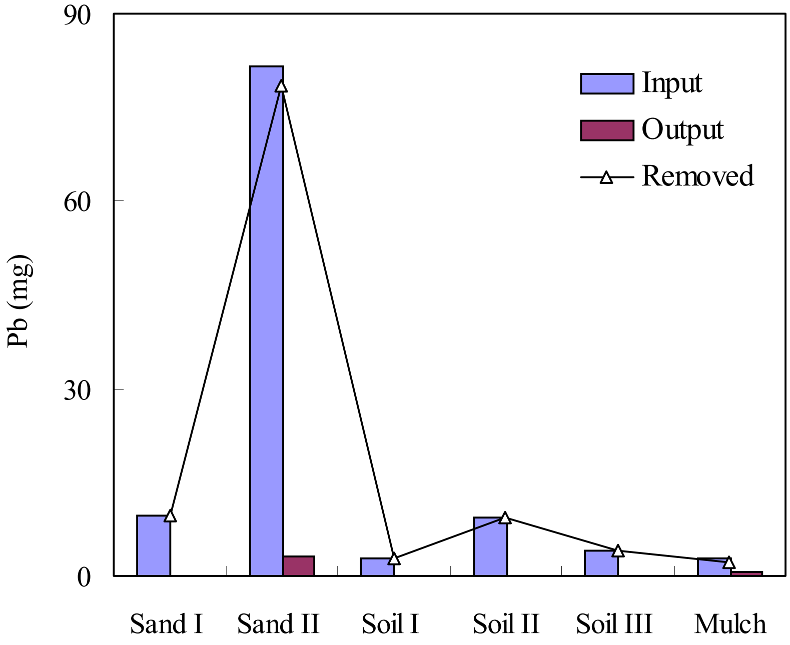


Figure 15b. Input, Output, and Removed Mass of Pollutants among Different Native Media for 6-hr Runoff Treatment



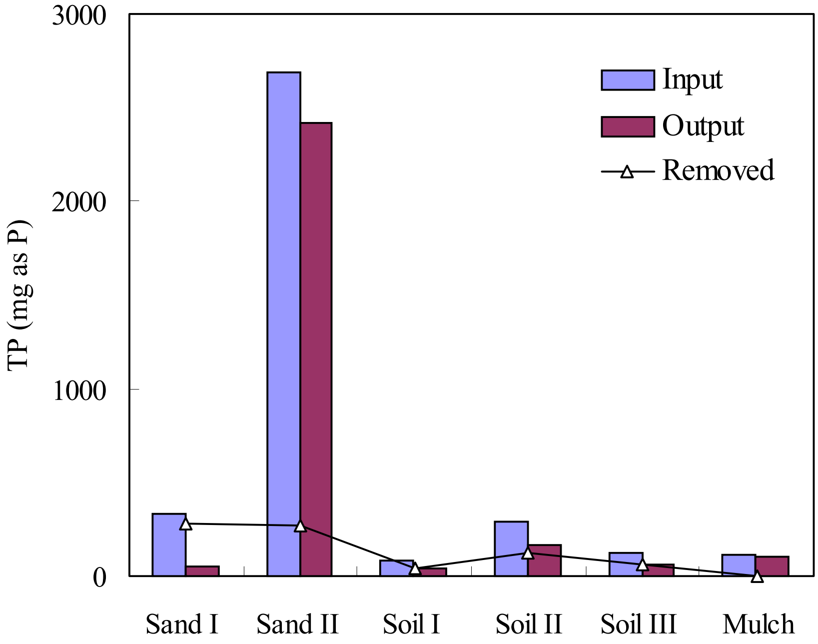
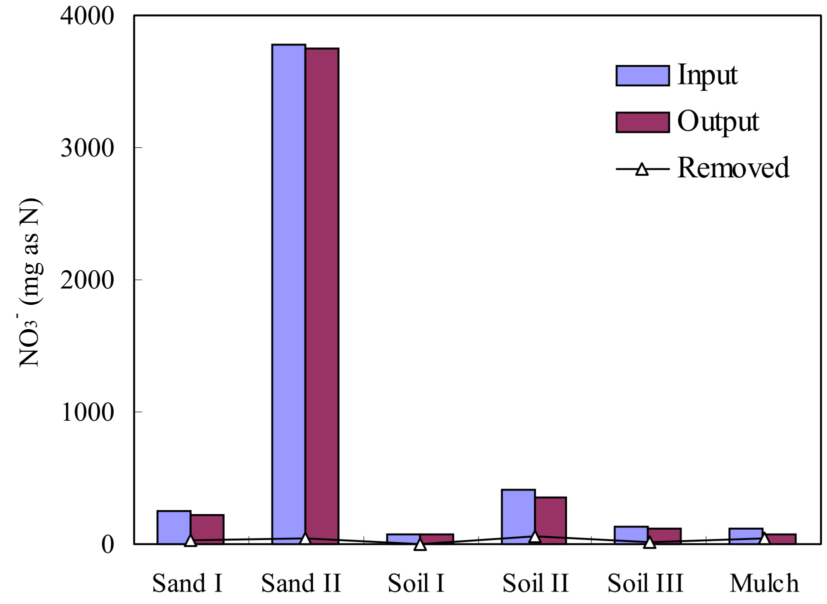
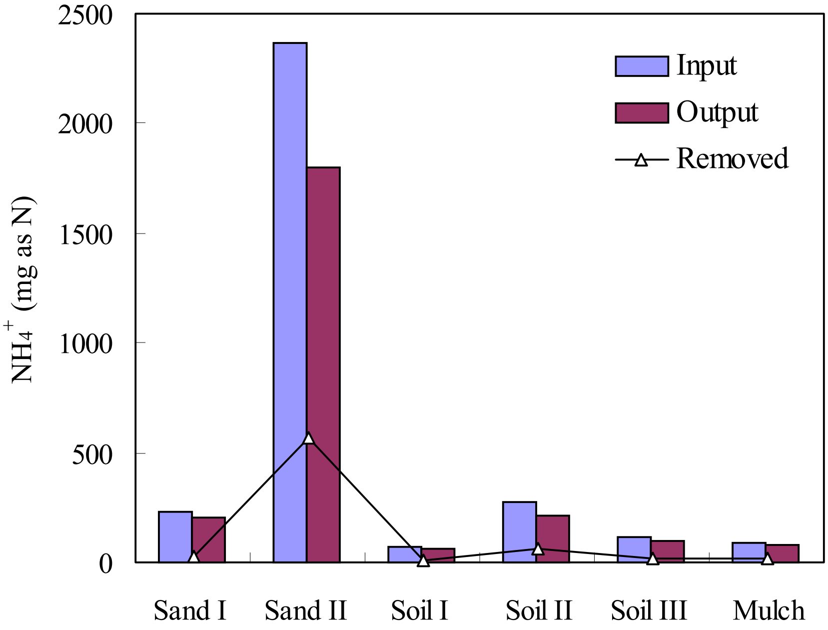


Figure 15c. Input, Output, and Removed Mass of Pollutants among Different Native Media for 6-hr Runoff Treatment





The Effect of Media Properties on the Performance of Bioretention

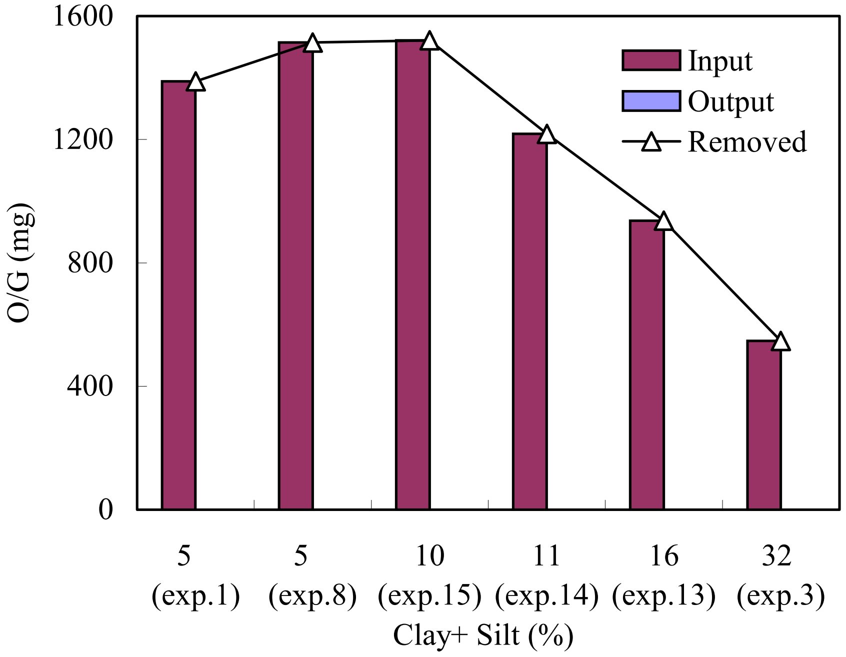
Since details on media properties are available, correlations of properties with pollutant removals by the six native media are examined. First, increased fractions of silt/clay in the medium lowered the runoff infiltration rate, as discussed above. From Table 3, it is seen that the soils composed of higher silt/clay contents had higher cation (Mg/Ca/K) contents, OM, and CEC, which are expected to improve runoff pollutant removal efficiencies. Since both sand (for high infiltration) and soil (for pollutant uptake) are desired, mixtures of these media are evaluated. Columns employing different media (sand I, soil I, or sand I/ soil I/mulch mixtures) with various clay+ silt contents were studied (Exps. 1, 3, 8, 13, 14, and 15- - Set B). The media layering of Exps. 13, 14, and 15 was: top mulch (5 cm), synthetic media I (25 to 82 cm), sand I (8 to 65 cm).

Again, excellent removal of input O/G, TSS, and Pb were found with all media (Table 5). Because these three pollutants are primarily removed through physical filtration, the treatment efficiency does not show any correlation with media chemical properties. Therefore, lower silt/clay contents produced higher infiltration rates, resulting in higher mass removal (Figure 15).

The media with the smaller silt+ clay fractions produced the higher runoff infiltration rates and greater TP mass removals during the 6-hr testing period (Figure 16); percent TP removal efficiency, however, varied. TP retention by bioretention media is expected to depend on media constituents. For example, TP removal by soil was positively correlated with soil OM content (Brejda, 1998). Fe-bound P was positively correlated with soil CEC (Samadi and Gilkes, 1999). Therefore, K+ Mg, P, OM, and CEC of the soil (Table 3) all were individually correlated with TP removal efficiency of these six column tests using linear regression; no correlation, however, was found (R^2 ranged from 0.0681 to 0.1925). The runoff flow path in the column can affect the fate of dissolved substances. Some degree of preferential flow may be allowing TP to bypass the bulk soil media (Kung et al., 2000). Therefore, even though media with higher silt/clay contents have higher OM and cation levels that could help to complex phosphorus from infiltrating runoff, dynamic processes apparently prevent the TP removal efficiency from correlating with OM content or CEC.

Nitrate and ammonium removals also did not correlate with silt/clay contents in the media. Generally, nitrate compounds are quite soluble and primarily removed through biological degradation (Hook, 1983). Ammonium can be adsorbed on exchange sites of contacting media or fixed within the clay or organic matrix (Hook, 1983; Brady and Weil, 2002). Adsorption and desorption of ammonium have also been related to the contents of Ca and Mg in several sandy soils (Wang and Alva, 2000). The removal efficiency of nitrate and ammonium for all column tests was moderate-to-poor (Table 5) and was not significantly affected by media properties in this study.

Figure 16a. Input, Output, and Removed Mass of Pollutants among Different Mixtures of Sand I and Soil I for 6-hr Runoff Treatment Columns



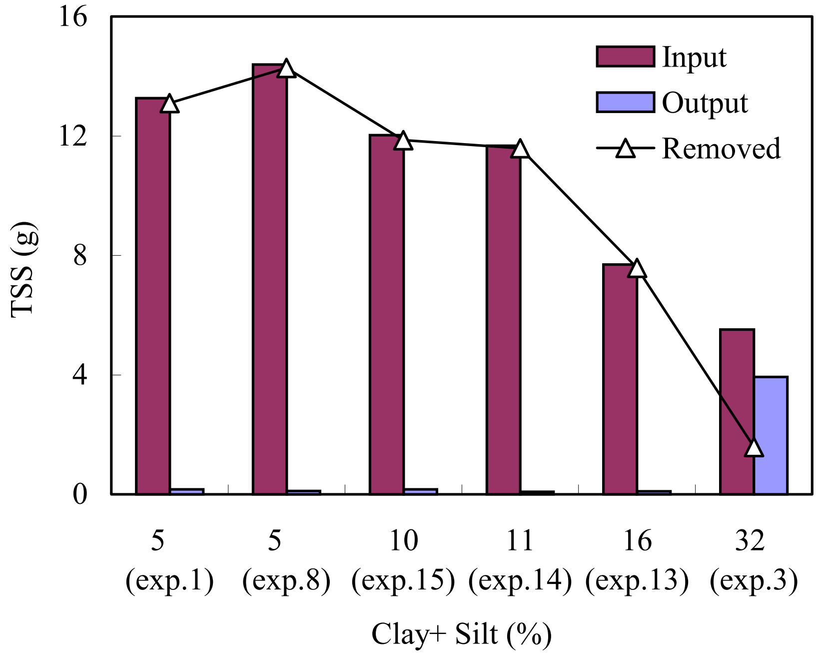
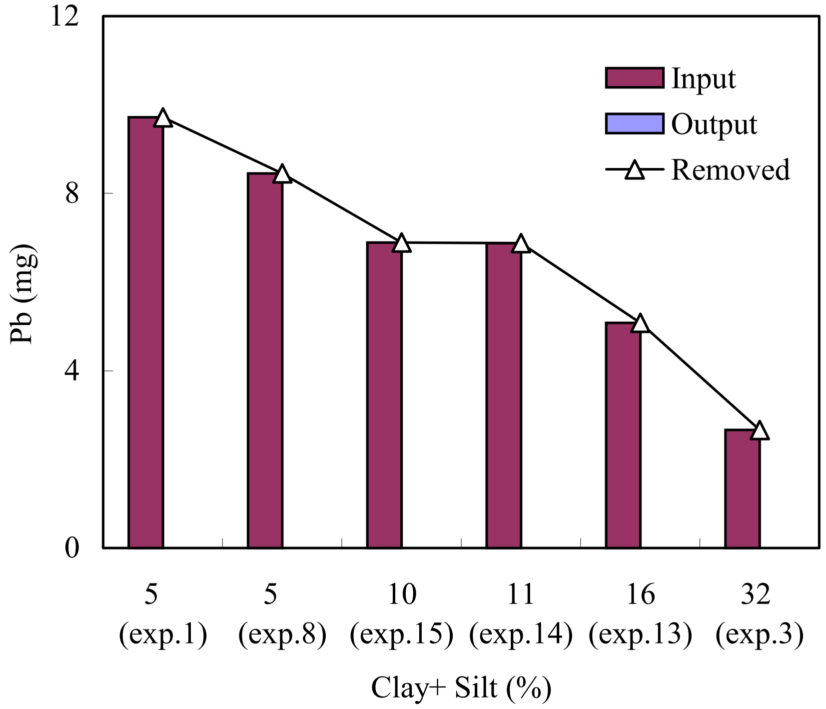


Figure 16b. Input, Output, and Removed Mass of Pollutants among Different Mixtures of Sand I and Soil I for 6-hr Runoff Treatment Columns



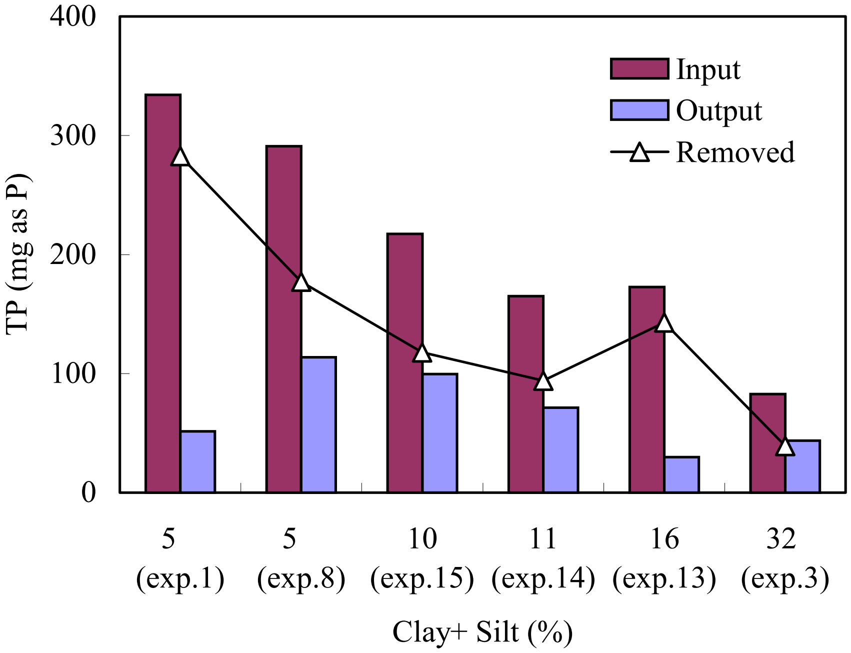
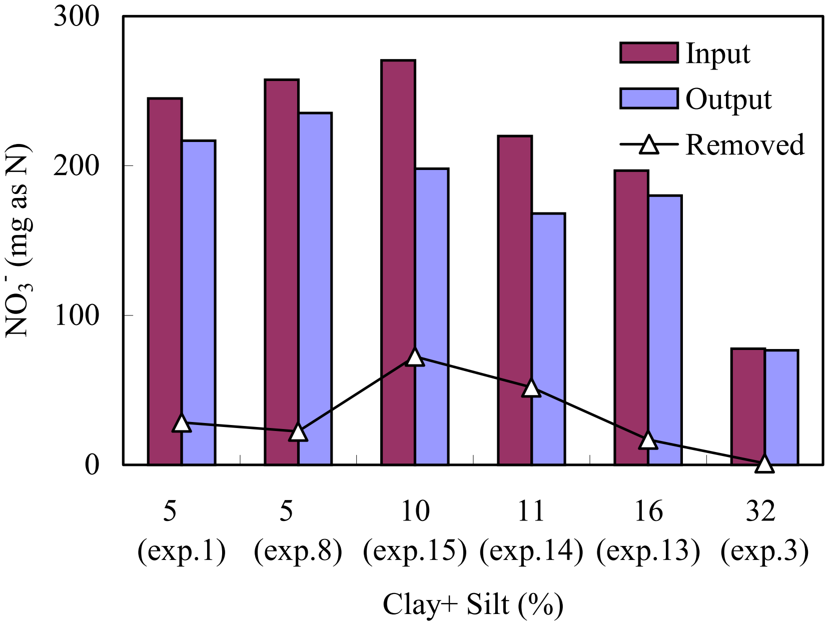
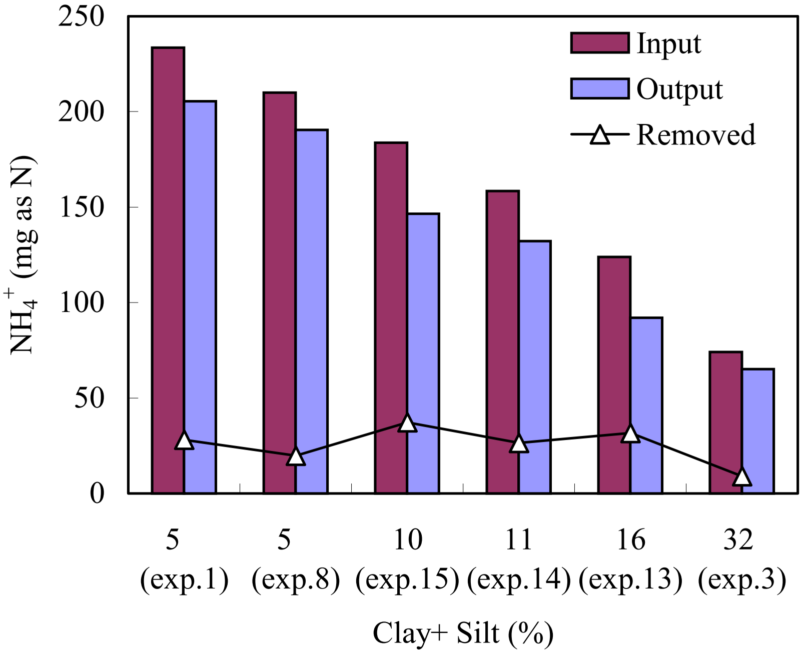


Figure 16c. Input, Output, and Removed Mass of Pollutants among Different Mixtures of Sand I and Soil I for 6-hr Runoff Treatment Columns





The Effect of Media Configuration on the Performance of Bioretention

Different media configurations (uniform vis-à-vis various layering) are expected to result in varied infiltration rates (Hillel, 1998) and pollutant removal efficiencies from infiltrating runoff. Uniform coarse-textured sand, as demonstrated above, is very efficient in promoting a high runoff infiltration rate and pollutant mass removal. Considering the vegetative and ecological aspects of bioretention, however, a certain depth of soil is necessary at the surface for plant growth. Also, coarse media may not be able to sustain pollutant removals over repetitive loadings and have less opportunity to support biological processes. Therefore, two series of layered columns are compared. In the first series of columns (Exps. 9, 10, 11, and 12- - Set C-1), an upper soil I layer (10 to 20 cm) sits on top of either 65 to 75 cm of sand I layer or 15 cm of synthetic media I, with a layer of sand I at the bottom. For the second group of columns (Exps. 13, 14, and 15- - Set C-2), the layer was: top mulch (5 cm), synthetic media I (25 to 82 cm), sand I (8 to 65 cm).

In Set C-1, it was apparent that the runoff infiltration rate was limited by the less-permeable soil I surface layer. All columns had identical rates of 0.30 to 0.32 cm/min. This rate was improved by mixing the soil I surface layer with a fraction (19 to 43%) of sand I, creating the C-2 series with infiltration rates from 0.48 to 0.71 cm/min. For O/G and Pb, both sets of layered columns resulted in excellent treatment (> 96% for O/G and > 98% for Pb). Some TSS (66% removal) leached from Exp. No. 9, which had a deeper (15 cm) soil I layer. Overall, columns with an upper soil I layer (C-1) demonstrated lower removal efficiency for nutrients (39 to 50% for TP, 2 to 4% for nitrate, and 2 to 7% for ammonium) than the ones with the more-permeable synthetic media I surface layer (C-2; 54 to 83% for TP, 13 to 27% for nitrate, and 17 to 26% for ammonium). In less-permeable media, infiltrating water streams usually break in the sublayer and through preferential flow paths, concentrate at certain points rather than the entire layer (Hillel, 1998). This channeling reduces the total contacting surfaces between infiltrating runoff and media, leading to less pollutant removal.

Pollutant mass removals for both types of layered columns are presented in Figure 17. Because of the high permeability, combined with better pollutant removal, a permeable synthetic mixture layer performed better than the soil I surface layer. All of these results are also supported by Exps. 16 to 18 (Set D), which employ layers of mulch (5 cm), synthetic media II or III (85 cm) and sand II (5 cm), which combine a high permeability sand with a sandy soil. Therefore, a layered medium with a permeable sand/soil mixture layer appears to provide the best treatment efficiency for bioretention.

Figure 17a. Input, Output, and Removed Mass of Pollutants among Different Media Configurations for 6-hr Runoff Treatment

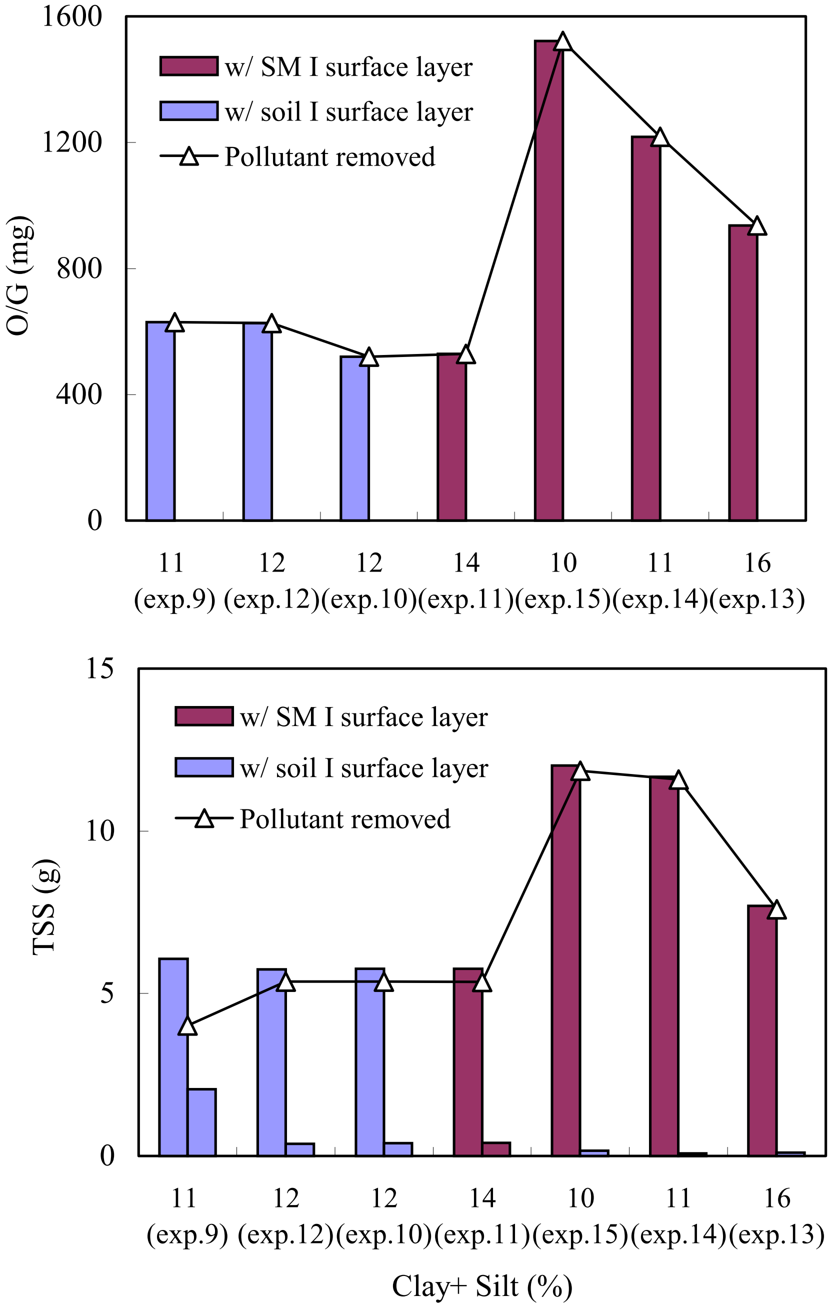


Figure 17b. Input, Output, and Removed Mass of Pollutants among Different Media Configurations for 6-hr Runoff Treatment

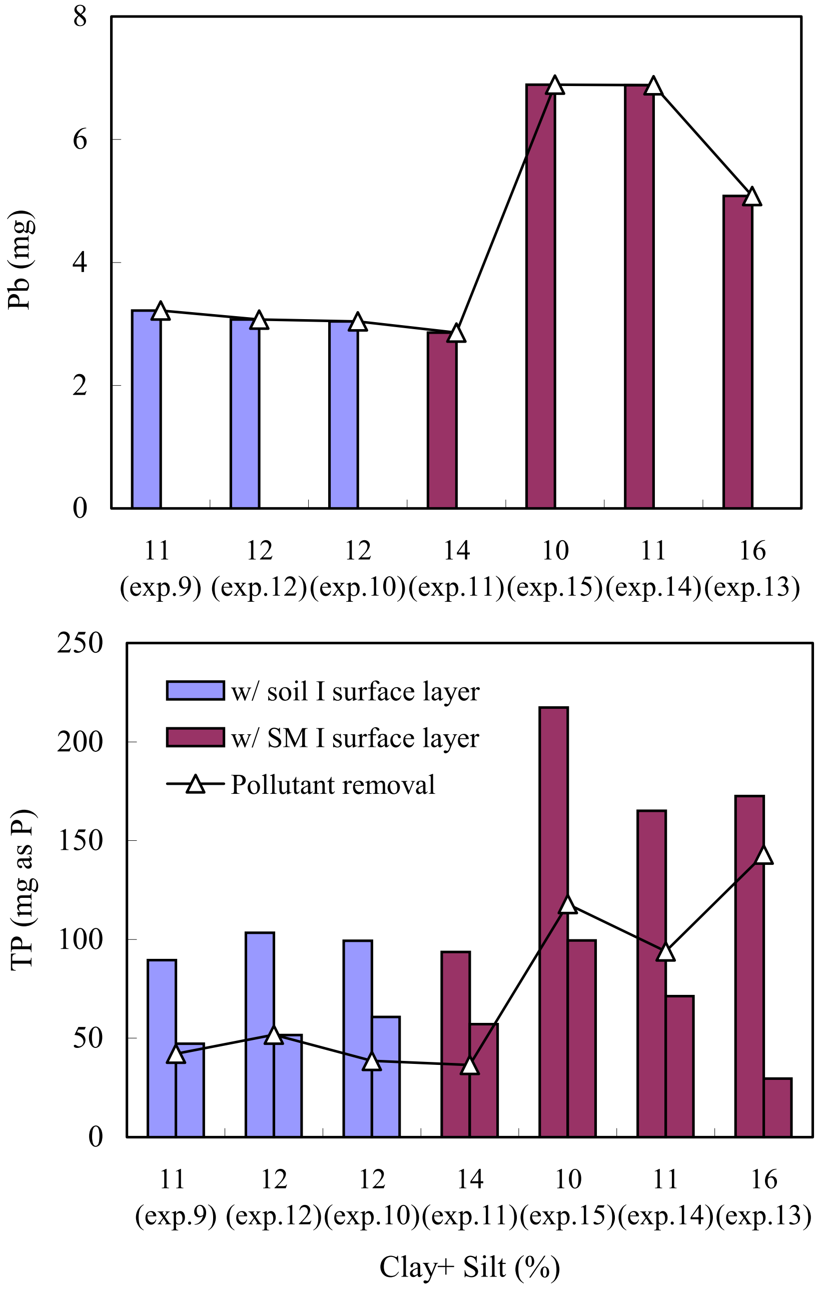
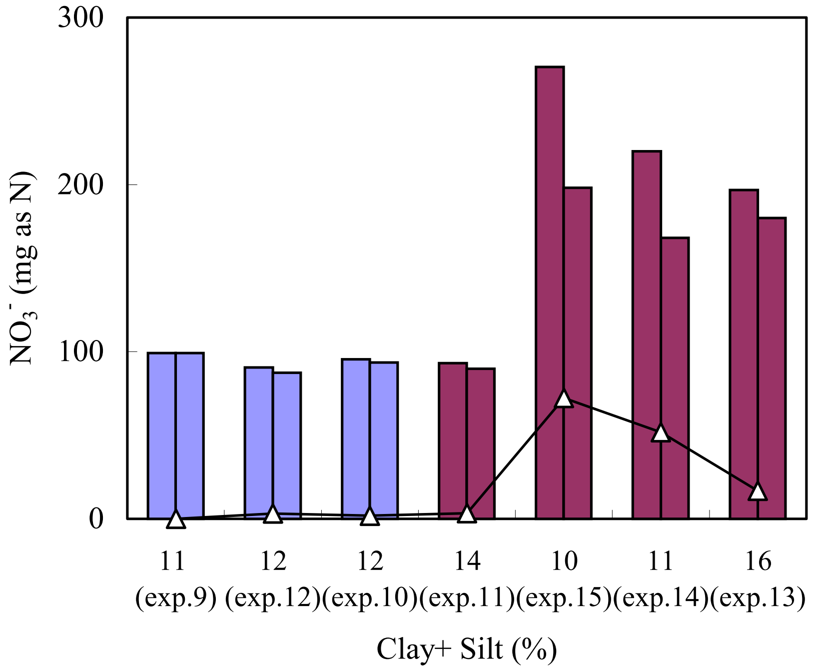
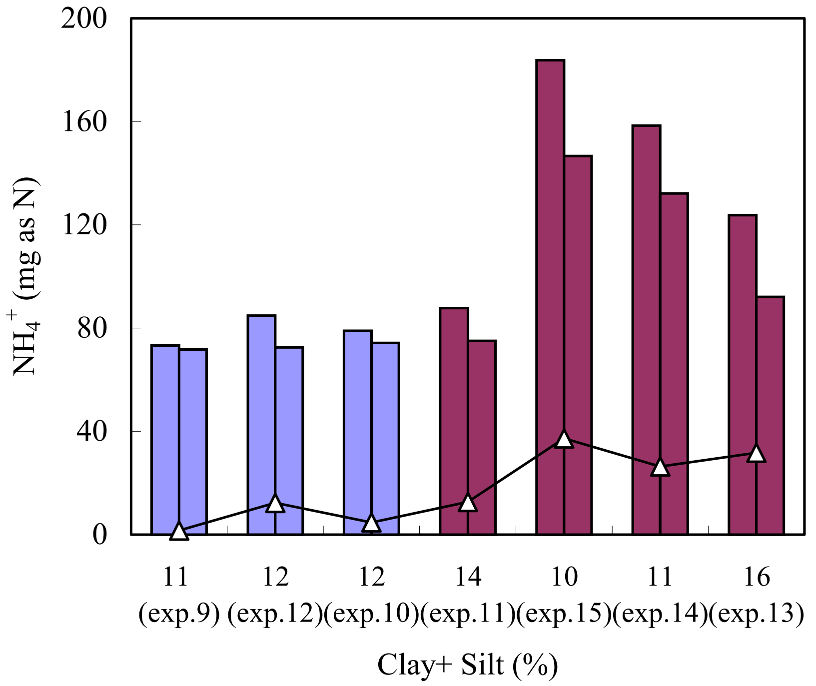


Figure 17c. Input, Output, and Removed Mass of Pollutants among Different Media Configurations for 6-hr Runoff Treatment





Evaluation of Existing Bioretention Facilities

Six existing bioretention sites were evaluated using synthetic runoff. Another two bioretention evaluations were conducted during a rainfall event. The performances of the bioretention facilities are discussed with respect to infiltration and water quality.

Infiltration Aspects

The infiltration rate of runoff through a bioretention cell should relate directly to the textures of the media, as was demonstrated in the column studies. As shown in Table 6, the silt/clay content in the upper media layer is higher than that in the bottom for three of the six sites, either because of the initial design or subsequent TSS accumulation from incoming storm water runoff. Therefore, the less-permeable upper layer of these sites would limit the infiltration rate. Because of the low water loading (3.2 cm/hr), pooling occurred only on two sites. Less than 5 cm pooling occurred at site HV1 after 35 minutes of pumping, and after 28 minutes for the LO3 site. Of the six, these two sites have the highest silt/clay contents in the upper media.

Table 6a. Results of Field Bioretention Media Chemical and Mechanical Analysis

Site		pH	Mg	P	K	Ca	S.S	O. M	CEC
(Media Depth)			mg/100g soil					%	meq/100g soil
GB (109 cm)	10-15 cm	7.1	29	16	16	*	*	3.4	*
	15-40 cm	7.3	29	17	14	*	*	2.5	*
LO1 (51 cm)	10-15 cm	7.3	29	18	13	> 44	38	6.2	17
	15-40 cm	6.8	23	9	7	> 44	17	3.8	12
LO2 (51 cm)	10-15 cm	7.0	29	28	43	37	17	2.1	10
	15-40 cm	7.0	24	5	16	148	96	1.4	30
LO3 (51 cm)	10-15 cm	5.4	16	5	13	11	17	1.8	4
	15-40 cm	5.4	18	5	10	11	17	2.0	5
HV1 (76 cm)	10-15 cm	6.8	24	9	14	37	17	3.3	9
	15-40 cm	7.6	25	7	9	67	17	1.0	14
HV2 (64 cm)	10-15 cm	7.0	25	8	12	44	17	2.3	10
	15-40 cm	7.7	18	10	2	15	17	0.1	4

S.S: soluble salts

* no data collected

Table 6b. Results of Field Bioretention Media Chemical and Mechanical Analysis

Site (Media Depth)		Sand %	Clay %	Silt %	Classification
GB (109 cm)	10-15 cm	66	21	13	Sandy Clay Loam
	15-40 cm	70	17	13	Sandy Loam
LO1 (51 cm)	10-15 cm	83	8	9	Loamy Sand
	15-40 cm	83	10	7	Loamy Sand
LO2 (51 cm)	10-15 cm	89	9	2	Loamy Sand
	15-40 cm	42	26	32	Loam
LO3 (51 cm)	10-15 cm	58	22	20	Sandy Clay Loam
	15-40 cm	48	28	24	Sandy Clay Loam
HV1 (76 cm)	10-15 cm	62	19	19	Sandy Loam
	15-40 cm	78	14	8	Sandy Loam
HV2 (64 cm)	10-15 cm	69	17	14	Sandy Loam
	15-40 cm	93	6	1	Sand

Water Quality Aspects

The water quality results from the first six field studies are presented in Figure 18. Unlike the laboratory column experiments, no or minimal water head existed. In addition, lateral flow is expected within the media. Similar to all laboratory studies, O/G was removed effectively (> 97%) in all six bioretention facilities. In addition, TSS removal ranged from 72 to 99%, and 80 to >98% total Pb removal was found. Pb removal efficiency positively correlated with that of TSS ($r^2 = 0.927$), clearly indicating a significant relationship and the importance of adsorbed Pb, which also was found in the column studies. Because of color differences, it was apparent that most of the leaching TSS was part of the bioretention media instead of the incoming TSS. Therefore, although input TSS was filtered by the media, some media particles leached out. The two facilities with the lowest TSS removal are also two of the newest.

The most variability in the field sites was found in TP removal efficiencies, which ranged from 37 to 99%. Media depth and texture were correlated with TP removal, but no significant relationship was found. For example, although site GB is much deeper than the others, the removal efficiency of TP was not the best among these facilities. A good correlation between TP removal and OM content appears, which was not noted in laboratory studies. The highest OM was found at LO1, which demonstrated 93% TP removal. LO2 and HV2 have the lowest OM content and, correspondingly, the lowest TP removal.

For nitrate and ammonium, all six facilities produced similar low removal (2 to 7% for nitrate-N and 5 to 10% for ammonium-N at 5 sites), as was found with column experiments. The exception was site LO1, in which 49% ammonium-N was removed. The reason for this remains unclear.

The results for two additional tests conducted during a rainfall event are summarized in Table 7. Because sample collection began 4-hr after the beginning of the rain event, the water quality of inlet runoff samples should be better than those from first flush samples. Also, some pollutant loading from the parking lots was removed during transport through channels to the bioretention cells. Overall, TP was not found above the detection limit in all inlet and effluent samples, whereas TSS, Pb, nitrate and ammonium input concentrations were smaller than in the synthetic runoff employed in this study. High concentrations of O/G appeared in the inlet samples, which should be attributed high vehicle activity to the parking lot being drained. In agreement with both laboratory and field studies, over 99% of O/G and 94% of Pb were removed by both bioretention facilities. Because these two sites had been just installed 3 months prior, the soil medium was still not stabilized and some TSS leached out, thus, negative removals were typically found.

More nitrate was removed by CP1 (31± 12%) than by CP2 (10± 10%), supporting the effectiveness of the CP1 denitrification layer. However, using the Hypothesis Test of Two Means with a 20% level of significance does not conclude that the means of these two sets of samples are statistically different. Ammonium was removed to below the detection limit at both sites, but the input was relatively low.

Figure 18. Results of Field Studies for 6-hr Synthetic Runoff Treatment

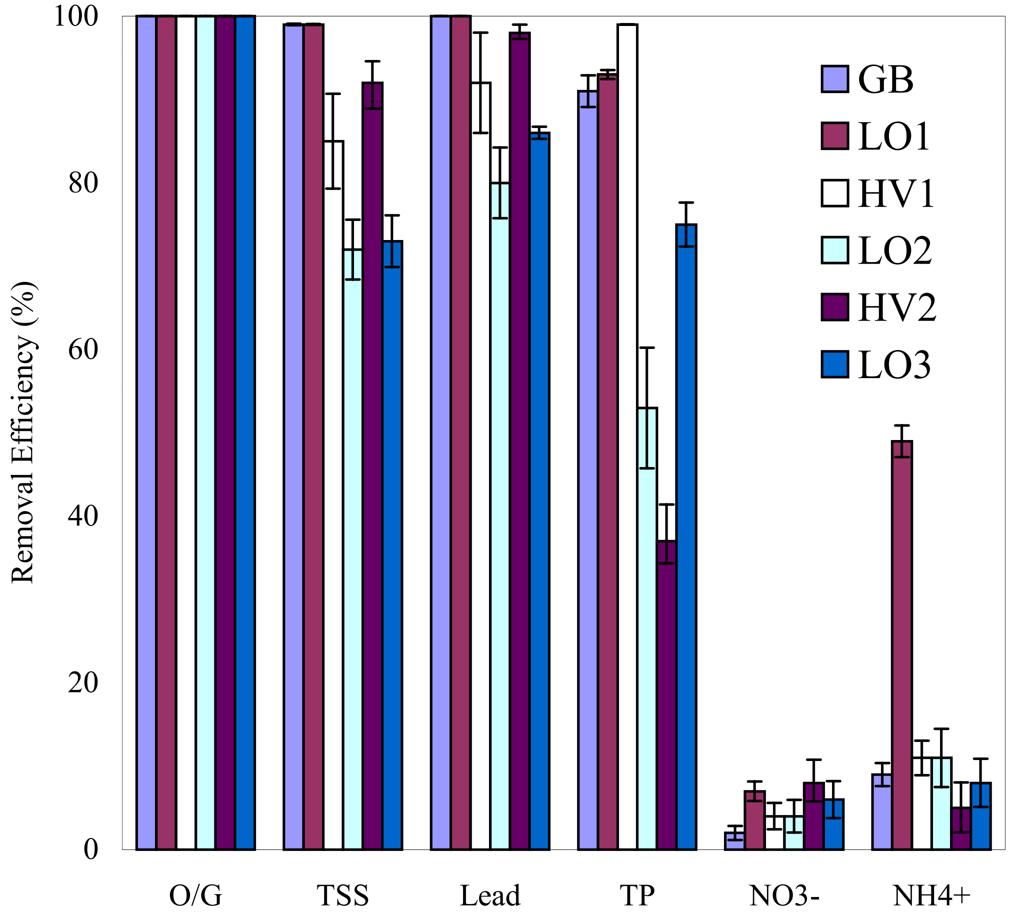


Table 7a. Results of On-Site Bioretention Evaluation during a Rainfall Event

CP1

Sample	Time hr	O/G mg/L	TSS mg/L	Pb µg/L	NO_3^- mg-N/L	NH_4^+ mg-N/L	TP mg-P/L
Input	0	68± 4	17± 3	32± 0	0.13± 0.01	0.09± 0.01	< 0.05
Output		< 0.5	46± 5	< 2	0.08± 0.01	< 0.05	< 0.05
Removal (%)		> 99	-174± 43	> 93	40± 5	> 44	-
Input	0.5	53± 0	19± 5	41± 2	0.13± 0.01	0.08± 0.00	< 0.05
Output		< 0.5	33± 0	< 2	0.08± 0.00	< 0.05	< 0.05
Removal (%)		> 99	-78± 37	> 95	38± 6	> 37	-
Input	1	56± 1	17± 3	32± 2	0.11± 0.01	0.09± 0.01	< 0.05
Output		< 0.5	41± 4	< 2	0.09± 0.00	< 0.05	< 0.05
Removal (%)		> 99	-145± 39	> 93	14± 5	> 44	
Input	1.5	67± 3	23± 4	28± 0	0.13± 0.00	0.09± 0.01	< 0.05
Output		< 0.5	27± 0	< 2	0.09± 0.00	< 0.05	< 0.05
Removal (%)		> 99	-15± 13	> 92	31± 0	> 44	-
Mean							
Input		61± 7	19± 4	33± 5	0.12± 0.01	0.08± 0.01	< 0.05
Output		< 0.5	37± 8	< 2	0.08± 0.01	< 0.05	< 0.05
Removal (%)		> 99	-103± 71	> 94	31± 12	> 37	-

Table 7b. Results of On-Site Bioretention Evaluation during a Rainfall Event

CP2							
Sample	Time hr	O/G mg/L	TSS mg/L	Pb μg/L	NO_3^- mg-N/L	NH_4^+ mg-N/L	TP mg-P/L
Input	0	65± 2	20± 0	36± 0	0.12± 0.01	0.08± 0.00	< 0.05
Output		< 0.5	14± 1	< 2	0.12± 0.00	< 0.05	< 0.05
Removal (%)		> 99	34± 3	> 94	-5± 5	> 37	-
Input	0.5	58± 0	21± 1	52± 2	0.12± 0.00	0.08± 0.01	< 0.05
Output		< 0.5	15± 3	< 2	0.10± 0.01	< 0.05	< 0.05
Removal (%)		> 99	27± 11	> 96	17± 10	> 37	-
Input	1	56± 4	16± 1	36± 2	0.09± 0.00	0.09± 0.01	< 0.05
Output		< 0.5	18± 2	< 2	0.08± 0.00	< 0.05	< 0.05
Removal (%)		> 99	-12± 11	> 93	11± 0	> 44	-
Input	1.5	67± 3	23± 4	28± 0	0.13± 0.00	0.09± 0.01	< 0.05
Output		< 0.5	27± 0	< 2	0.09± 0.00	< 0.05	< 0.05
Removal (%)		> 99	-7± 12	> 92	17± 16	> 44	-
Mean							
Input		63± 7	18± 2	39± 8	0.11± 0.01	0.09± 0.01	< 0.05
Output		< 0.5	16± 2	< 2	0.10± 0.02	< 0.05	< 0.05
Removal (%)		> 99	10± 23	> 95	10± 10	> 44	-

II. Multiple-Loading Evaluation of Bioretention for Treatment of Urban Storm Water Runoff- Runoff Infiltration and Phosphorus Removal

Phosphorus (P) inputs to water bodies are under close scrutiny due to P contribution to water eutrophication and algal blooms, which results in the depletion of dissolved oxygen and high turbidity levels in aquatic ecosystems. These impairments, ultimately, can lead to poor water quality and the loss of biodiversity in the water bodies. P is an essential macronutrient for plant growth. Through leaching processes, however, excess P will endanger the quality of ground and surface waters. In urbanized areas, because impervious surface can result in a significant fraction of impinging rainfall becoming runoff, urban runoff is rapidly becoming a major source of nonpoint pollution (U.S. EPA, 1996), transporting abundant P into waterways. According to recent surveys (http://www.epa.gov/305b/98report/98brochure.pdf), P is becoming a leading pollutant for impaired surface waters (including rivers, lakes, reservoirs, ponds, estuaries, lake shorelines, and ocean shorelines) and ground water.

P found in urban runoff generally comes from lawn fertilizers, atmospheric deposition, automobile exhaust, soil erosion, animal waste, or detergents (U.S. EPA, 1999b). In runoff, P is distributed as both dissolved (DP, particle size < 0.45 μm) and particulate (PP, which was sorbed onto the solids before or after transporting in the runoff (Sharpley, 1985) with particle size > 0.45 μm). Retention mechanisms of P in soils combine biological, chemical, and physical processes. Under vertical flow, PP that was mostly transported through macropore flow in media could be removed through media filtration processes (Heathwaite and Dils, 2000). Through vegetative uptake, microorganism degradation, sorption, exchange reactions, precipitation, sedimentation and entrainment, DP can be retained in soils (Reddy et al., 1999; Van Cuyk et al., 2001).

After being retained, P appears either in organic or inorganic forms in soils. For vegetative purposes, dissolved inorganic P is usually considered as bioavailable and can be used as for plant nutrition (Rechcigl, 1995; Reddy et al., 1999). For environmental concerns, mobility of P compounds in soils determines the potential of retained P to hold detrimental risk to ground and surface water quality. In summary, high plant availability and low mobility is preferred for P management.

Retention of P in bioretention facilities decreases the P load to downstream waterways.

Meanwhile, captured P could be employed as a nutrient for biological growth in bioretention facilities, which would allow a removal pathway via harvesting the vegetation. Previous work has shown that about 80% of DP was removed by a sandy loam soil in two laboratory-scale pilot bioretention facilities (Davis et al., 2001). Similar studies have demonstrated 70-85% of P removal, correlated exponentially with media depth in pilot-scale and full-scale bioretention facilities applying a nonlinear, least-squares regression (Davis et al., submitted).

Three issues regarding P removal in bioretention are addressed in this study. In general, soils possess different P sorption capacities. For example, sorption capacities varied more than 3-fold, from 9 mg/100 g for Merrimac soil to 29 mg/100 g for Paxon soil (Sawhney and Hill, 1975). Sands with a high content metal content (Ca, Al, or Fe) had much higher P-removal capacity than those with lower concentrations of these metals (Arias et al., 2001). However, although the P sorption characteristics of soil media affect P removal in bioretention facilities, the chemical properties of a soil may not accurately predict the mobility of P through media with macroporosity (Cox et al., 2000;) since P removal in columns may not occur by simple sorption processes alone (Van Cuyk et al., 2001). The first objective of this work is to investigate correlations between media P sorption characteristics and TP removal through bioretention columns. As such, P sorption capacity for sands, soils, and mulch, along with three continuous-flow bioretention columns with media consisting of different soil/sand ratios were examined. Media with higher sorption capacity are expected to capture greater total mass of TP from high P loadings to the bioretention column.

Second, two bioretention columns (RP1 and RP2) were tested for P removal and accumulation over a moderate long-term period (80-120 days). Runoff was applied to the columns were operated for 6-hr during each repetition with several days between repetitions, for a total of 12 repetitions for RP1 and 16 repetitions for RP2. The study objectives are to investigate the effect of two inverse configurations (RP1: media with low hydraulic conductivity overlaying one with high hydraulic conductivity; RP2: media with high hydraulic conductivity overlaying one with low hydraulic conductivity) on runoff infiltration rate, and to evaluate long-term effectiveness of these two columns for P removal. Three-layer media with different media components and configurations were employed in each column to maximize the infiltration rate of runoff and P removal efficiency. A capillary barrier between two media layers is hypothesized to form in RP1 to restrict runoff infiltration, thus, demonstrating the RP2 configuration to perform better. Also, P removal efficiency is assumed to decrease with time due to the consumption of P sorption capacity of the media.

Finally, environmental and agronomic soil tests were conducted on the bioretention media before and after repetitive experiments (RP2). The objective is to test the potential for P leaching from the bioretention media and to quantify available P for future plant growth after repetitive experiments.

Overall, long-term effectiveness of alternative bioretention media and media configurations for P removal were evaluated. The significance of sorption processes in P removal through bioretention column was confirmed.

P Sorption

P sorption isotherms were completed with all media employed in this study at pH 7. Apparent P sorption capacity for each medium was calculated using the Langmuir equation (Sparks, 1995).

$$q = \frac{bKC}{1 + KC} \tag{3}$$

Where C is the equilibrium aqueous P concentration, q is the amount of P adsorbed (absorbate per unit mass of adsorbent), b is the P adsorption capacity of the media, and K is a constant related to P binding strength.

The isotherms of TP for all employed media are shown in Figure 19. Except for mulch, the Langmuir equation provides a good fit to all data. Based on the results, P sorption capacities of sands varied from 20 µg/g for sand II to 89 µg/g for sand I. The sorption capacity of soil I was 130 µg/g, 128 µg/g for soil III, and 137 µg/g for soil IV. Mulch adsorbed little P. In summary, the soils employed in this study had higher capacity than sands and mulch for removing P from solution. Sand I has higher sorption capacity than sand II, which is probably related to the higher Ca+ Mg content in sand I (12.3 mg/100g sand for sand I and 3.3 mg/100g sand for sand II, Arias et al., 2001) regarding to the formation of surface precipitation (Sparks, 1995). The sorption capacity of P among the three soils is nearly the same.

When evaluating column studies, however, P removal depends not only on the P sorption capacity of the soil but also on the geometry of the system (Sawhney and Hill, 1975). Such complex processes proceeding at the soil-water surface as well as diffusion processes in the soil matrix have been suggested to affect P retention through a wetland soil (Reddy et al., 1999). Media with higher P sorption capacity should capture greater amounts of TP than others with lower capacity. In order to understand the dynamic trend of P removal, three continuous flow columns with different media compositions were further tested. Three small columns (Plexiglas, 40 cm long by 6.4 cm inner diameter) with different ratios of sand/soil were employed to investigate P uptake.

The media compositions (soil III/sand II %) for these three columns were 30/70, 50/50 and 70/30. The results are shown in Figure 20. During the first 6 days, all columns demonstrated essentially the same P removal efficiency, which ranged from 72 to 77%. After this period, larger amounts of P gradually leached out from the columns with smaller amounts of soil III. Finally, media containing more soil prevented P from leaching longer than the media containing more sand.

Furthermore, the significance of sorption processes on TP removal in the bioretention media was identified by calculating the total TP sorption capacity of each continuous column and comparing with the actual accumulated TP. Based on the results of batch P sorption data, TP adsorption capacity for all three continuous columns was calculated as:

$$m = \sum q_i \times m_i \tag{4}$$

Where m is the adsorptive mass of TP by each continuous column, q_i is the TP adsorption capacity of each media, m_i is each employed media mass at initial 2.85 mg-P/L, and the summation includes both the soil and sand in the column.

Figure 19. P Sorption Isotherms for Different Media (pH= 7, Initial P= 2.85 mg/L, $CaCl_2$= 120 mg/L, Media Concentration= 2 to 700 g/L, Line is equal to Langmuir isotherm fit to data.)

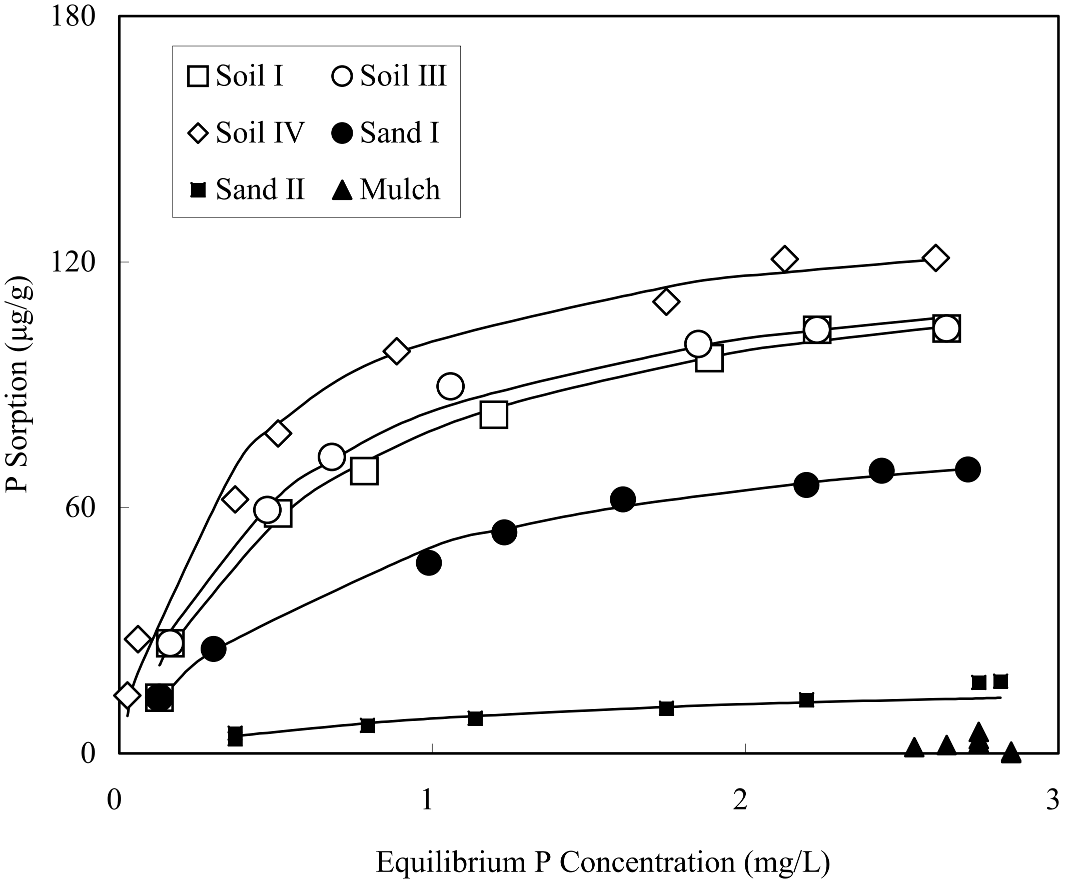
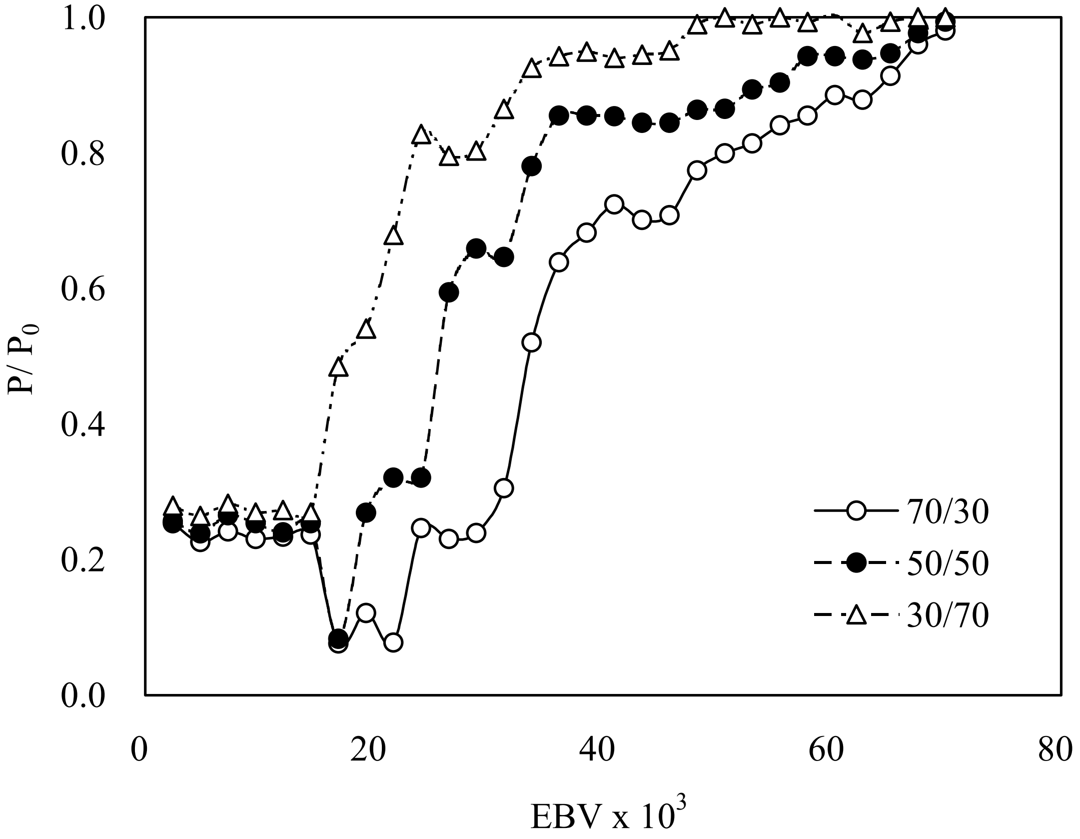


Figure 20. P Effluent from Continuous Flow Columns at Different Soil/Sand Mass Ratios (pH= 7, Input P= 3 mg/L, $CaCl_2$= 120 mg/L)



Additionally, total accumulated mass of TP by each continuous column was calculated as:

$$m_a = \int_{t=0}^{t=29} (C_{in} - C_{out})\, Q\, dt \qquad (5)$$

Where m_a is the accumulated mass of TP by each continuous column, C_{in} and C_{out} are the input and output TP concentrations, Q is runoff flow rate, and t is the experimental period expressed in days. Total input of TP for each column during the testing period is 391 mg.

As calculated from Eq. 4, total sorbable TP is 129 mg TP for the column with 70% of soil III, which actually resulted in 184 mg of TP removal throughout the testing period as calculated from Eq. 5. For the column with 50% of soil III, 100 mg of TP adsorption was expected, whereas actual 139 mg of TP was retained in the column. For the column with only 30% of soil III, the TP adsorption capacity was 71 mg and 92 mg-TP was finally accumulated in the media. As shown, the medium with a higher P sorption capacity can retain more P from the infiltrating runoff after a high P loading.

Overall, the TP sorption capacity of each medium calculated from both studies can not accurately predict the dynamic trend of TP removal efficiency in a vertical column. However, greater amounts of P (92 mg-TP more after 391 mg-TP input) from the infiltrating runoff can be retained by the medium with a higher P sorption capacity after a high P loading.

Repetitive Bioretention Column Tests

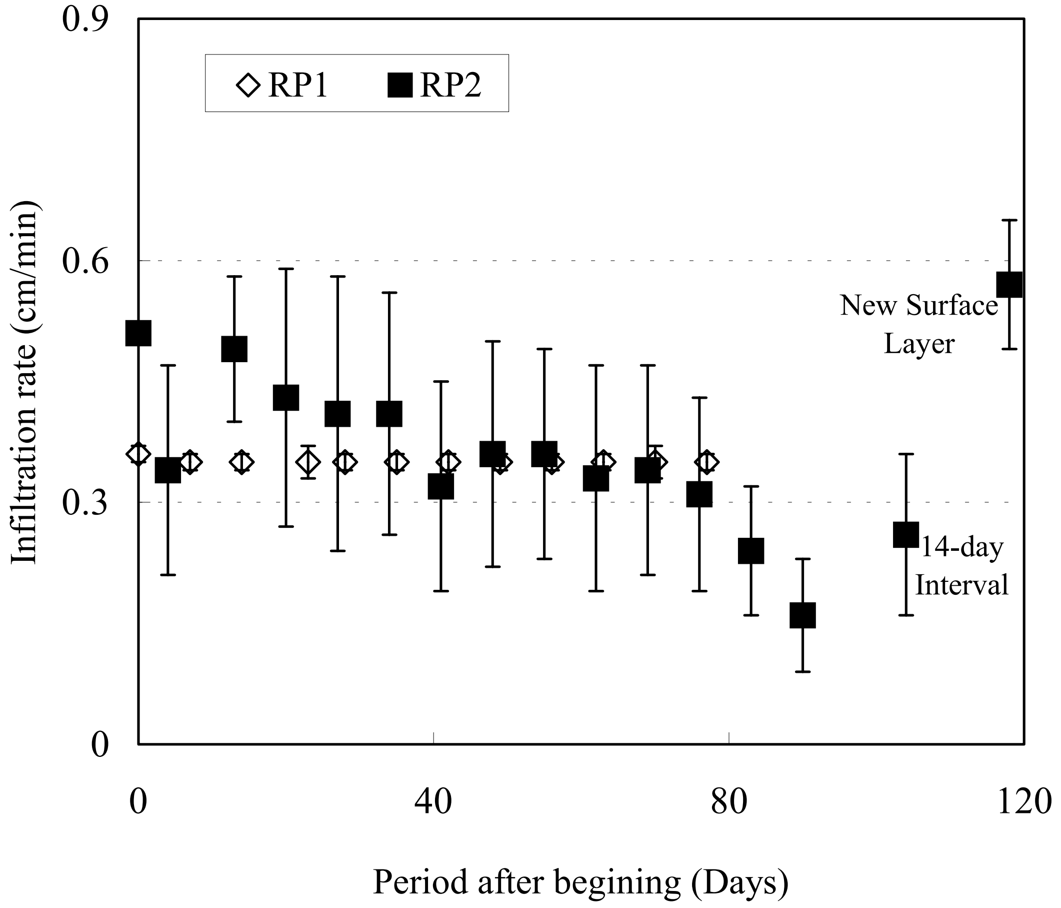
Infiltration Rate

A total of twelve (RP1) and sixteen (RP2) repetitions were completed to test the long-term performance of bioretention, including the infiltration rate and P removals. The results for runoff infiltration rate at a 15 cm head are presented in Figure 21. Based on the results, the infiltration rate of runoff throughout all twelve repetitions in RP1 remained constant at 0.35 cm/min, which is close to that when runoff flows through mulch (0.28 cm/min) or soil I (0.28 cm/min) only. As noticed during the experiments, runoff did not enter the sand layer until the head was built up sufficiently to overcome the capillary tension between layers (Stormont and Anderson, 1999). It was apparent that infiltration of runoff was controlled by the top mulch and soil layers.

For RP2, another three-layer media with a configuration of high hydraulic conductivity overlain one with low hydraulic conductivity was employed. A mixture medium (mulch/soil/coarse sand) with certain amounts of organic matter and soil for vegetating purpose and coarse sand for promoting runoff infiltration was designated being the surface layer. Below this layer, sand I can efficiently remove pollutants and is a better choice among other media with respect to pollutant removal. The top two layers can serve as the bioretention media for the quick infiltration of first flush runoff with efficient pollutant removal. Finally, soil with high pollutant removal capacity in the bottom can increase pollutant contact time with bioretention media.

As expected, runoff infiltrated into RP2 faster than into RP1 during the first few repetitions. However, based on the results (Figure 21), the runoff infiltration rate gradually decreased from 0.51 to 0.16 cm/min throughout the first fourteen tests. Suspended solids (SS) appeared to clog the bioretention surface throughout the 14 repetitions. The 15th repetition was started 14 days after the 14th repetition, which was twice as long as the period between the first 14 repetitions, to simulate a field condition without rain for a longer period. The infiltration rate increased from 0.16 to 0.26 cm/min after the longer dry period. Since the moisture of the surface layer tended to diminish more during the longer interval period, runoff could be absorbed more readily during the 15th repetition (Hillel, 1998). Also, in order to test a remediation method for addressing surface clogging, the top 5 cm of medium (mixture medium) was removed and replaced with new original material. In response, the runoff infiltration rate recovered to the same level as the initial (~ 0.5 cm/min). To summarize this part of the work, bioretention clogging primarily appeared on the surface media and could be improved by simply replacing this surface layer.

Figure 21. Results of Runoff Infiltration Rate for Repetitive Columns (RP1 and RP2)



Comparing RP1 and RP2, the runoff infiltration rate almost remained constant (0.35 cm/min) in RP1, but decreased in RP2 (from 0.51 to 0.16 cm/min) during repetitive experiments. The reason for the difference between the two columns could be due to the various distributions of accumulated SS. Because the mulch layer employed in RP1 has a relatively high uniformity coefficient (d_{60}/d_{10}= 15.6) with many large pores among particles, input SS can move into the surface layer instead being strained on the surface, forming a mat, which restricted liquid flow (Vinten et al., 1983) as occurred in RP2.

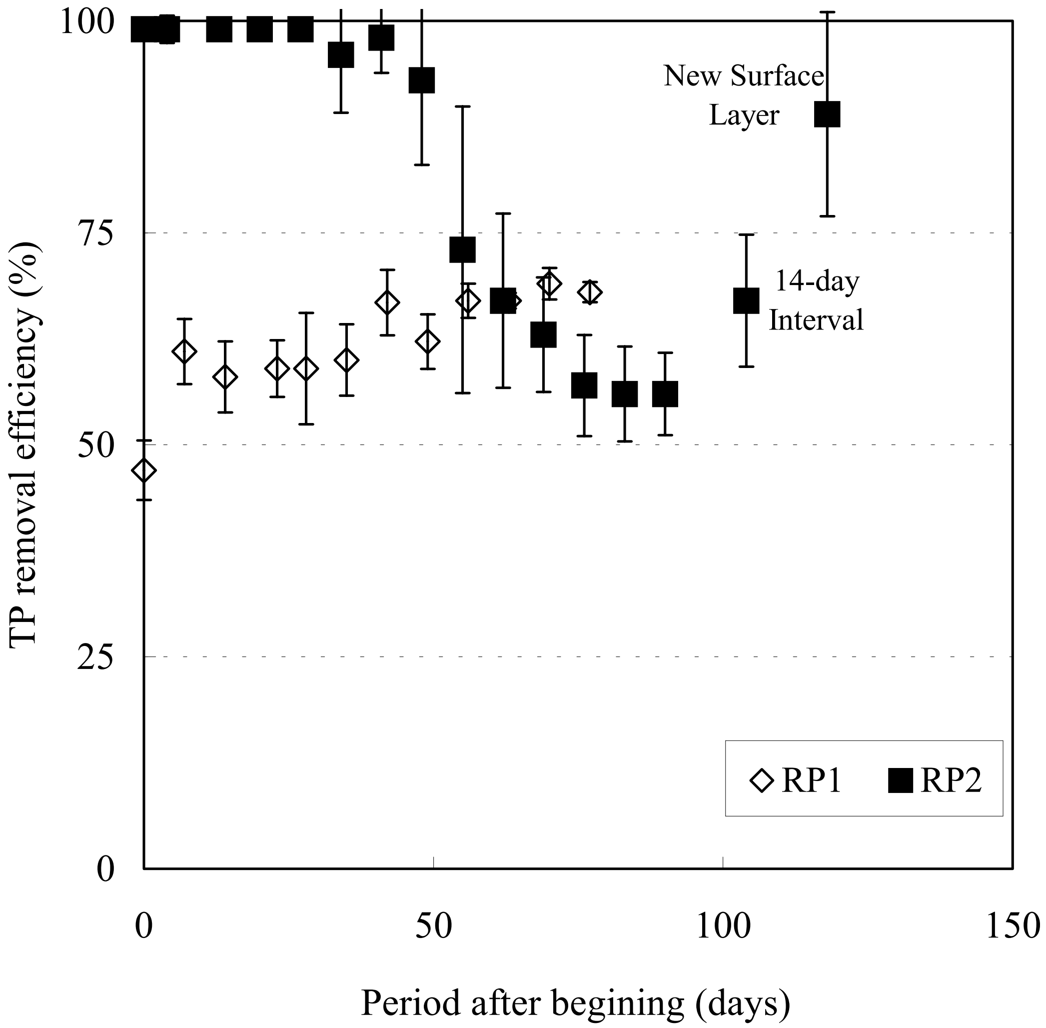
TP Removal

Removal results of TP from RP1 and RP2 are presented in Figure 22. For RP1, the TP removal efficiency ranged from 47 to 68%, with an average of 62± 6.2%. For RP2, TP was nearly all removed in the first 7 repetitions (41 days of operation). After this period, the TP removal efficiency gradually decreased and finally reached only 56% in the 14th repetition.

Similar to the runoff infiltration rate, TP removal efficiency recovered, increasing from 56 to 67% after 14 days drying. As reported by Sawhney and Hill (1975), soils that had been successively treated with P solution showed reduced P sorption capacity, but regained the capacity to adsorb P after drying and wetting cycles. Therefore, this change can be attributed to P being initially adsorbed on the media surface and finally diffusing into the media matrix, releasing new surface for more P to adsorb.

Additionally, the removal efficiency of TP was further increased to 89% after replacing the top 5-cm medium. Because of the effectiveness of this newly-restored top 5-cm medium for TP removal, the importance of surface bioretention media was confirmed. The average removal efficiency of P for RP2 was 82± 18%. In summary, RP2 performed better for P removal.

Figure 22. Results of TP Removal for Repetitive Columns (RP1 and RP2)



Furthermore, the sorption capacity of TP for RP1 and RP2 was calculated using equation 4 and the isotherm data. Overall, 3.8 g-TP can be sorbed by RP1 and 3.4 g-TP by RP2. Although RP1 has higher TP sorption capacity, the average removal efficiency of TP is lower than RP2. As mentioned, sorption capacity of TP is not the only factor affecting TP removal efficiency from runoff. RP2, which employed a bottom less-permeable soil layer can either increase the contacting surfaces between runoff and media or average pollutant contacting time. As such, preferential effects on pollutant removal were decreased and RP2 showed a better TP removal than RP1 employing the conventional bioretention profiles.

P Distribution in Bioretention Media Profile

Understanding the distribution of P in the bioretention column helps to interpret P movement with media depth. The P distribution was investigated by determining the P concentration of media at different depths before and after column experiments. The amounts of TP captured by each layer are calculated as:

$$M_r = S \times m_p \tag{6}$$

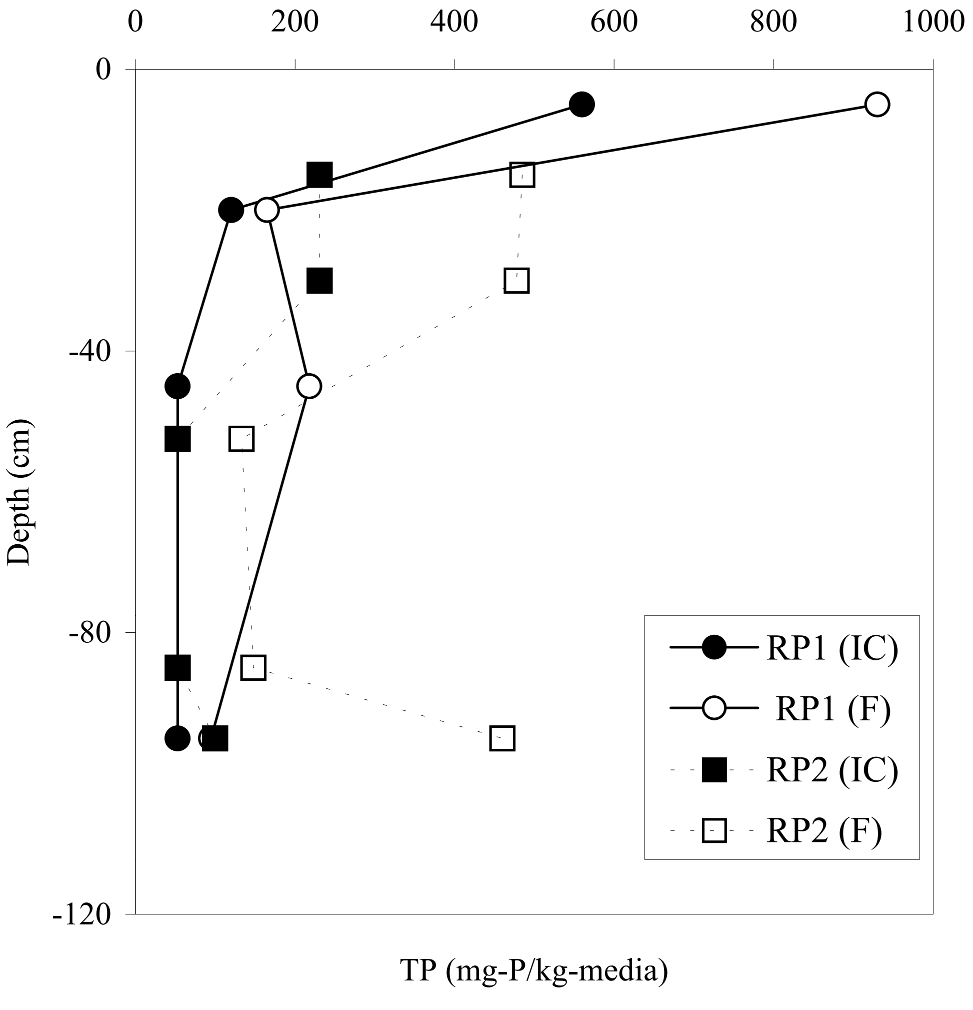
Where M_r is the mass of TP retained in each media layer, S is the employed media mass, and m_p is the TP retained per unit mass of each media. Dividing M_r by the total TP retained in the column, the fraction of retained TP by each layer is determined. All results are summarized in Table 8 and Figure 23.

Table 8. P Retained by Different Media Layers in Bioretention Columns RP1 and RP2

Medium	Layer	Media Mass		P Retained					
		RP1	RP2	RP1	RP2	RP1	RP2	RP1	RP2
		kg		mg-removed P/kg-media		mg-removed P		%	
Top (RP1: Mulch, RP2: Mixture)	U	0.8	6.1	370	254	303	1554	9	22
	L				247		1512		21
Middle (RP1: Soil, RP2: Sand)	U	8.2	12	45	80	368	928	11	13
	L				95		1102		15
Bottom (RP1: Sand, RP2: Soil)	U	10	5.9	165	360	1700	2124	53	29
	L	21		42		865		27	

U: upper, L: lower

Figure 23. P Distribution in the Columns Media before and after Repetitive Experiments



In both columns, the P concentration in all media layers increased after repetitive applications, indicating that the applied P moved through the whole column instead staying only on the surface layer. Every media layer through the column contributed to P removal from runoff (retained P ratio for RP1: 9% for the top mulch, 11% for the middle soil I, and 80% for the bottom sand I; RP2: 43% for the top mixture, 28% for the middle sand I, and 29% for the bottom soil IV).

Because of the higher permeability, RP2 treated more water and greater input mass of P. The P retention of different media layers should be discussed under the same media mass and TP input. First, input mass of P for each column during repetitive periods is calculated as:

$$M_{in} = \sum_{1}^{n} \sum_{i=1}^{t_d} Q\ C_{in}\ \Delta t \tag{7}$$

Where M_{in} is the input TP mass, Q is the input rate of runoff, C_{in} is the input TP concentration, Δt is the measurement time increment over a single trial, and n the number of trails, is 12 for RP1 and 16 for RP2.

Based on equation 7, total input TP was calculated as 1.62 g for RP1 and 2 g for RP2. Furthermore, removal TP per unit mass of different media per input TP, m, is defined as:

$$m = \frac{M_r}{S \times M_{in}} \tag{8}$$

Where M_r is the mass of TP removed, S is the employed media mass, and M_{in} is the total input TP. The results are summarized in Table 9.

Table 9. P Removal from Runoff by Different Media

Medium	RP1 (IC)	RP1 (F)	RP2 (IC)	RP2 (F)	RP1	RP2	RP1	RP2
	mg-P/kg-media				mg-removed P/ kg-media		mg-removed P/ kg-media/mg-input P	
Mulch	560	930	-	-	370	-	228	-
Media mixture	-	-	231	478-485	-	247-254	-	123-127
Sand I	53	95-218	53	133-148	42-165	80-95	26-102	40-48
Soil II	120	165	-	-	45	-	28	-
Soil IV	-	-	100	460	-	360	-	180

IC: before repetitions, F: after 12 repetitions for RP1 and 16 repetitions for RP2

In the repetitive bioretention columns, not only sorption and precipitation processes, but also biological uptake, anion exchange and filtration processes will all account for P removal. Although mulch only sorbed little P from runoff according to the P sorption tests, the surface mulch layer in RP1 still removed 9% of TP from the runoff (Table 8). Visually, it was seen that most of the input SS was filtered by this mulch layer. Because surface mulch filtered most of the input SS (containing 38.5 mg-P/100g SS), abundant P sorbed on SS was collected in this mulch layer (370 mg-removed P/kg-media, expected removal is 329 mg-removed P/kg-media).

Other than surface mulch, physical filtration also dominated in the upper sand I of RP1. Upper sand I in RP1 removed about 4-fold more P (102 mg-removed

P/kg-media/mg-input P) than lower sand I (26 mg-removed P/kg-media/mg-input P). Similar to the result of , TSS removal efficiency of column 3 with 93% of soil I is 29± 2.9%. Leaching of soil particles from middle soil I to sand layer was occurred (silt+ clay contents increased from 5 to 6% in the sand layer). By filtering these leaching particles, upper sand I in RP1 was finally in the high P level.

With RP2, the level of retained P within the same medium was more uniform (123 to 127 mg-removed P/kg-media/mg-input P for upper and lower layers of media mixture, 40 to 48 mg-removed P/kg-media/mg-input P for layers of upper and lower sand I). For soil layers in RP1 and RP2, the bottom layer in RP2 (soil IV) accumulated much more P (180 mg-removed P/kg-media/mg-input P) than the middle layer in RP1 (soil I) (28 mg-removed P/kg-media/mg-input P). Because of the low hydraulic conductivity of soil IV, a lot of water stayed above this bottom layer and continually leached downward through RP2 during the dormant period. Therefore, soil IV always maintained a high water content; carbon and nitrogen can migrate from the upper media mixture layer and it was likely that an anaerobic zone was formed in this area. This anaerobic zone could incubate diverse anaerobic microorganisms, which would contribute to P accumulation.

In conclusion, the surface mulch layer and middle fine sand can capture SS from the runoff or upper media, increasing TP removals. Different configurations of media affected P movement in the media; consequently, different P removal efficiencies resulted.

Media P Affiliations

In addition to total accumulation of P, the affiliation of P with the media of RP2 was evaluated. All results are summarized in Table 10.

Environmental P Soil Tests

Four extraction solutions were employed to predict the leaching potential of retained P from five different layers in RP2. WSP and $CaCl_2$-P were developed to simulate the ionic strength of the soil solution, predicting the potential of easily desorbable P leaching from the soil. Both Melich-I P and Mehlich-III P extractants are strong acid mixtures, and also have relevance to P leaching potential (Maguire and Sims, 2002). The level of

WSP increased from < 0.05 mg-P/kg media for all testing media after 16 repetitions, and the distribution of WSP through the media depth is relatively uniform (2.7 to 7.2 mg WSP/kg-media). For $CaCl_2$-P, only the top medium increased (from 0.2 to 2.6 mg $CaCl_2$-P/kg-media for the upper top-medium and from 0.2 to 0.8 mg $CaCl_2$-P/kg-media for the lower top-medium).

Turning to Melich-I P, the level for both layers in the top-medium did not have significant differences and the average increase is 30 mg Mehlich-I P/kg-media. Similarly, the average increase in Melich-I P was 11.5 mg P/kg-media for the middle-medium. A 24.3 mg Mehlich-I P/kg-media increase was shown in the bottom layer. As expected, larger amounts of P were extracted by Melich-III extractant for all media. The average increase for each layer was 43.5 mg Mehlich-III P/kg-media for the top-medium, 19.4 mg Mehlich-III P/kg-media for middle medium, and 66.9 mg Mehlich-III P/kg-media for the bottom layer. Overall, contributions of retained P to each P forms are shown in Figure 24.

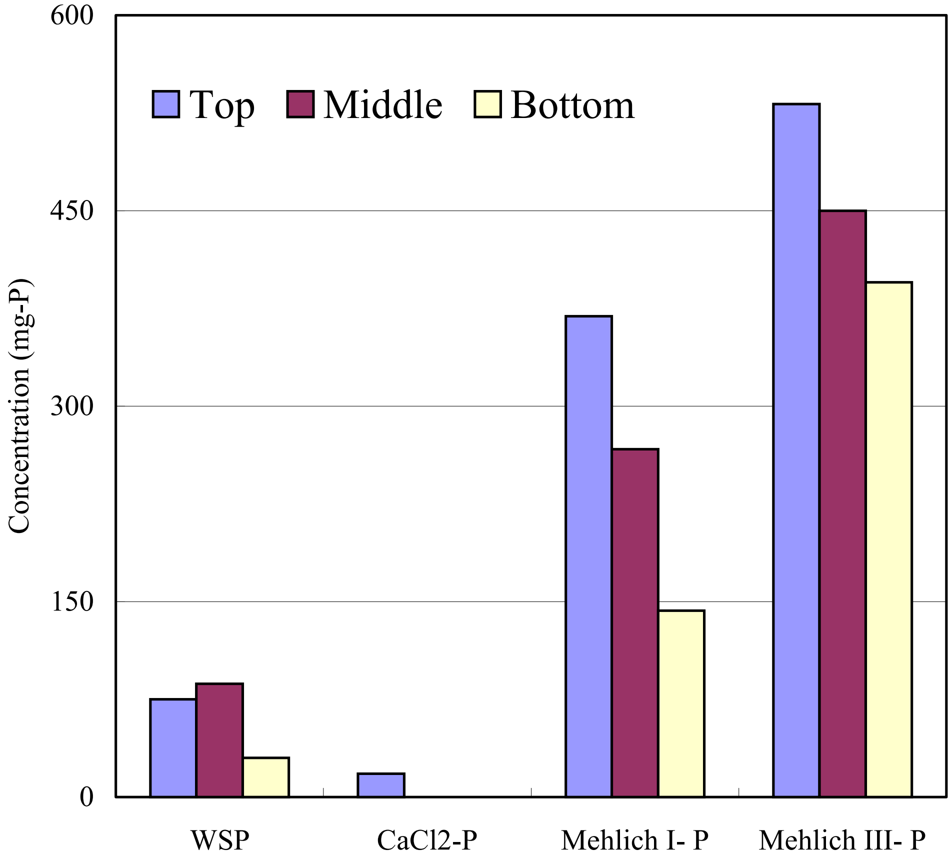
Several studies investigating the correlations between these P extractions and P leaching potential are also summarized in Table 10. Above the change point, which was identified from a quadratic linear regression, the potential for P release from soil to water increases (Kleinman et al., 2000). Comparing with the results of this study, the WSP levels for all media were below the suggested value (8.6 mg WSP/kg soil). $CaCl_2$-P in the upper top-medium (2.6 mg $CaCl_2$-P/kg soil) was higher than the change point (1.59 mg $CaCl_2$-P/kg soil) and leaching probably caused the increase in the lower top-medium $CaCl_2$-P level (0.8 mg $CaCl_2$-P/kg soil). All media were below the change points of P leaching while using Mehlich-I (81 mg Mehlich-I P/kg soil) and Mehlich-III (181 mg Mehlich-III P/kg soil) extractants. In summary, the leaching potential of bioretention media after treating a total of 2 g P in 16 runoff applications was still under the proposed change point.

Table 10. Soil Tests for Bioretention Media after 16 Runoff Applications (RP2) and Recommend Values of Soil P Leaching Potential and Soil P Fertility

Medium	Medium Depth	WSP	$CaCl_2$-P	Mehlich I- P	Mehlich III- P	TP
	cm	mg-P/kg-media				
Top	IC	< 0.05	0.2	20.8	48.1	231
	0-15	7.2	2.6	54.7	95.5	485
	15-30	5.0	0.8	47.2	87.5	478
Middle	IC	< 0.05	< 0.05	3.6	5.1	53
	30-53	2.7	< 0.05	14.4	24.0	133
	53-85	4.8	< 0.05	15.8	25.0	148
Bottom	IC	< 0.05	< 0.05	17.7	51.3	100
	85-95	5.1	< 0.05	42.0	118.2	460
Change Point (Maguire and Sims, 2002)		8.6	1.59	81	181	
Optimum for Nutrient Management (Sims et al., 2001)				25-50	50-100	

IC: Initial Condition, before runoff application

Figure 24. Contributions of Retained P to Each P Forms (RP2)

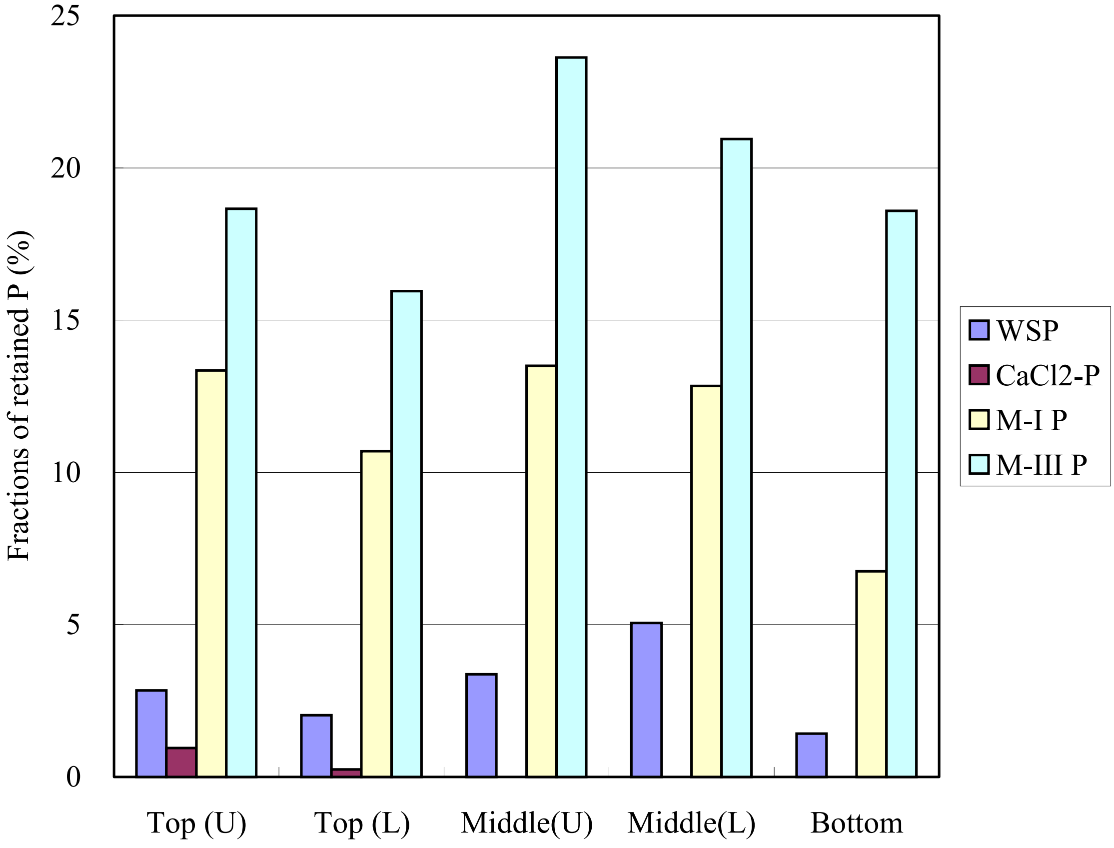


Agronomic P Soil Tests

Vegetation plays an important role (but not well understood) in bioretention facilities. Vegetation in bioretention facilities can enhance water evaporation from the media. For nutrient cycling, P can be stored in plants through assimilation processes. Concurrently, surfaces of the media for P sorption can be regained, promoting the P removal from subsequent runoff events (Reddy et al., 1999). Mehlich-I and Mehlich-III extractants are usually employed for assessing the fertility status of soils. Here, they were applied to show the media fertility for future vegetation in bioretention facilities. The optimum P range suggested by Sims et al. (2001) is 25 to 50 mg Mehlich-I P/kg soil and 50 to 100 mg Mehlich-III P/kg soil. Comparing values from Table 10, P fertility for all testing media was increased, but located under the excess range. Therefore, the contribution of retained P to bioretention media fertility was confirmed.

Fractions among different P forms of retained P in each media layer are compared and the results are shown in Figure 25. Without exceeding the change point for each test, most of the retained P in all layers stays in the forms extractable by Mehlich-I and Mehlich-III solutions, which is optimum for future vegetation utilization through nutrient cycling.

Figure 25. Fractions among Different P Forms of Retained P in Each Media Layer (RP2)



III. Multiple-Loading Evaluation of Bioretention for Treatment of Urban Storm Water Runoff- Oil/Grease, Lead, TSS, Ammonium, and Nitrate Removals

Urban storm water runoff can contain significant concentration of harmful pollutants. Generally, the degree of contaminants found in runoff related to degree of urban development. Due to emissions or leakage from vehicles, the runoff from the areas including parking lots, streets/highways, vehicle service/fuel stations, and recycling centers, is usually concerned for high levels of lead (Pb) and oil/grease (O/G). As reported (Claytor and Schueler, 1996), the concentration of Pb and O/G in the runoff from commercial and industrial sites ranged from 80 to 182 μg/L (national average: 18 μg/L) and 14 to 25 mg/L (national average: 1 to 2 mg/L). A considerable increase of total suspended solids (TSS) is usually appeared in urban storm water runoff (Characklis and Wiesner, 1997). Since abundant pollutants such as Pb are associated with TSS (Sansalone and Buchberger, 1997), TSS is also a frequently reported parameter for runoff quality. Another problems with nitrogen (N), excess inputs of N into the waterways through leaching processes often lead to eutrophication problems, consequently, the depletion in oxygen and biodiversity. To date, nutrients (including N and phosphorus) are becoming leading pollutants for impaired surface waters (including rivers, lakes, reservoirs, ponds, estuaries, lake shorelines, and ocean shorelines) and ground water (http://www.epa.gov/305b/98report/98brochure.pdf). Table 11 summaries the sources of TSS, metals, O/G, and N in urban runoff (U.S. EPA, 1999b).

Table 11. Sources of Contaminants in Urban Storm Water Runoff (U.S. EPA, 1999b)

Contaminant	Sources
TSS	Streets, lawns, driveways, roads, construction activities, atmospheric deposition, drainage channel erosion
Metals	Automobiles, bridges, atmospheric deposition, industrial areas, soil erosion, corroding metal surfaces, combustion processes
O/G	Roads, driveways, parking lots, vehicle maintenance areas, gas stations, illicit dumping to storm drains
N	Lawn fertilizers, atmospheric deposition, automobile exhaust, soil erosion, animal waste, or detergents

Bioretention is a relatively new BMP for runoff treatment. In a typical configuration, bioretention includes a porous medium, supporting a vegetative layer. Generally, the bioretention medium is composed of soil, sand, and organic matter. Through processes such as filtration, sorption, ion exchange, and biological uptake, the media immobilizes pollutants from the infiltrating runoff. For example, organic matter and clay in the soil can serve as the sorbent for O/G. The presence of certain functional groups, such as –OH, $-NH_2$, -NHR (R represents hydrocarbon group), $-CONH_2$, -COOR, and $-^{+}NR_3$, hydrogen bonding, and protonation can promote the adsorption of O/G onto the soil (Brady and Weil, 2002). Ammonium, which carries a positive charge, is usually immobilized by negatively charged clay and humus in soils (ASA and SSSA, 1983; Brady and Weil, 2002; Juang et al., 2001). Through aerobic nitrification processes, captured ammonium ions in soil are further oxidized by *Nitrosomonas* and *Nitrobacter species* and finally become nitrate.

$$NH_4^{+} \xrightarrow{Nitrosomonas} NO_2^{-} \xrightarrow{Nitrobacter} NO_3^{-} \qquad (9)$$

In well-drained soils, most negatively-charged nitrate ions in runoff generally just leach from the soil to the ground water. Within poorly-drained soils, however, the held water will impede diffusion of oxygen and may thereby create an anoxic zone, which is a precondition suitable for denitrification processes (Meyer et al., 2002; Brady and Weil, 2002). Nitrate existing in the soil solution then can return to the atmosphere through denitrification processes.

$$NO_3^{-} \rightarrow NO_2^{-} \rightarrow NO\uparrow \rightarrow N_2O\uparrow \rightarrow N_2\uparrow \qquad (10)$$

Proof-of-concept pilot-scale bioretention box studies with sandy-loam soil have demonstrated 60 to 80% removal of TKN and ammonium, but < 20% removal of nitrate by the media (Davis et al., 2001; Davis et al., submitted). Nitrate and ammonium were both poorly removed in 18 columns and 6 field tests.

For Pb, over 90% of input Pb was captured by laboratory sandy-loam bioretention pilot-plant facilities under different pH, duration, intensity, and pollutant concentrations, supported by field-scale confirmation studies (Davis et al., 2003). Total Pb removal decreased when the TSS level in the effluent increased due to the leach-out of sorbed-Pb on SS. Regarding O/G and TSS, all bioretention columns and on-site facilities demonstrated excellent removal for O/G (> 96%). TSS removal was good in columns, but leaching of media particles was noted in field facilities, mostly from new installations before forming high degree of soil aggregation.

Two issues based on multiple-loading bioretention column experiments are tested in this study. In previous work, effectiveness of 6-hr bioretention columns and on-site facilities for O/G, Pb, and TSS removals were evaluated, showing excellent removal for these pollutants, except for the newly installed facilities. However, the removal performance of bioretention for these pollutants during a long-term period still has not been investigated. Along with accumulations, these pollutants may leach out from the media under excess inputs. Additionally, SS might clog the bioretention media after operation for a certain period. In this study, a total of 28 repetitive experiments were further conducted on two bioretention columns to evaluate the effectiveness of bioretention for O/G, TSS, and Pb removals.

Second, since nitrogen is a essential nutrient of microorganisms, biological uptake is assumed to be a significant process for long-term nitrogen fate in bioretention systems, especially during the wetting-drying cycles, providing enough retention time for microorganism accumulation after the microbial populations are allowed to build up. Alternative designs to keep bioretention media submerged to promote microbial denitrification reactions has been reported to improve nitrate removal (Kim et al., 2003; Hunt et al., 2002). In this study, two separate three-layer bioretention columns were employed to evaluate long-term bioretention behavior. Also, these columns were allowed to develop an anaerobic zone at the interface of a high permeable sand and a less permeable soil layer during total 28 wetting-drying cycles. A sequential combination system of nitrification and denitrification was hypothesized to form in the bioretention media. The objectives are to evaluate the long-term performance of bioretention on O/G, Pb, and TSS removals, and to evaluate and enhance the removal efficiency of ammonium and nitrate in the runoff.

O/G, Pb, and TSS Removal

After all repetitions, 9.8 g of O/G, 51 mg of Pb, and 87 g of TSS were applied into RP1, as well as 10.2 g of O/G, 57 mg of Pb, and 88 g of TSS for RP2.The results of O/G, Pb, and TSS removals by RP1 and RP2 are presented in Figure 26. O/G and Pb were both well removed (> 97% for O/G and > 98% for Pb) during each 6-hr experimental period throughout 12 repetitions for RP1 and 16 for RP2 (Figures 26a and b). As expected, sorption processes might account for the primary removal mechanism for O/G, whereas adsorption, ion exchange, and reaction with organic chelating reagents may responsible for Pb removal (Harrison and Laxen, 1981). For TSS, except for the first repetition of RP1 and the first two repetitions of RP2, over 91% of TSS were filtered by the bioretention media. Similar to the results conducting in newly constructed bioretention facilities, some SS leached from the soil media and resulted in low TSS removal efficiency during the first two repetitions (91 and 57%, Figure 26c) before forming high degree of soil aggregates. Afterward, the media stabilized and most of the input SS were removed from the runoff (> 94%) throughout the experiments. As shown in Chapter 5, clogging appeared only in RP2 without a surface mulch layer. This problem was improved by simply replacing the top 5-cm media. Overall, the effectiveness of bioretention for O/G, Pb, and TSS removals under multiple-loading was confirmed.

The influence of TSS accumulation in runoff infiltration rate is further investigated. By comparing TSS removal efficiency (Figure 26) with runoff infiltration rate (Figure 17), it clearly shows that the infiltration rate throughout all twelve repetitions in RP1 remained constant at 0.35 cm/min, whereas the runoff infiltration rate gradually decreased from 0.51 to 0.16 cm/min throughout the first fourteen tests of RP2. Suspended solids (SS) appeared to clog the bioretention surface of RP2 after completing 14 repetitions. As mentioned, the reason producing the difference between the two columns could be the various distributions of accumulated SS in the surface media (Vinten et al., 1983), which confirmed the contribution of surface mulch layer in RP1 to filter SS (Figure 27).

Figure 26a. O/G Removal during Repetitive Experiments

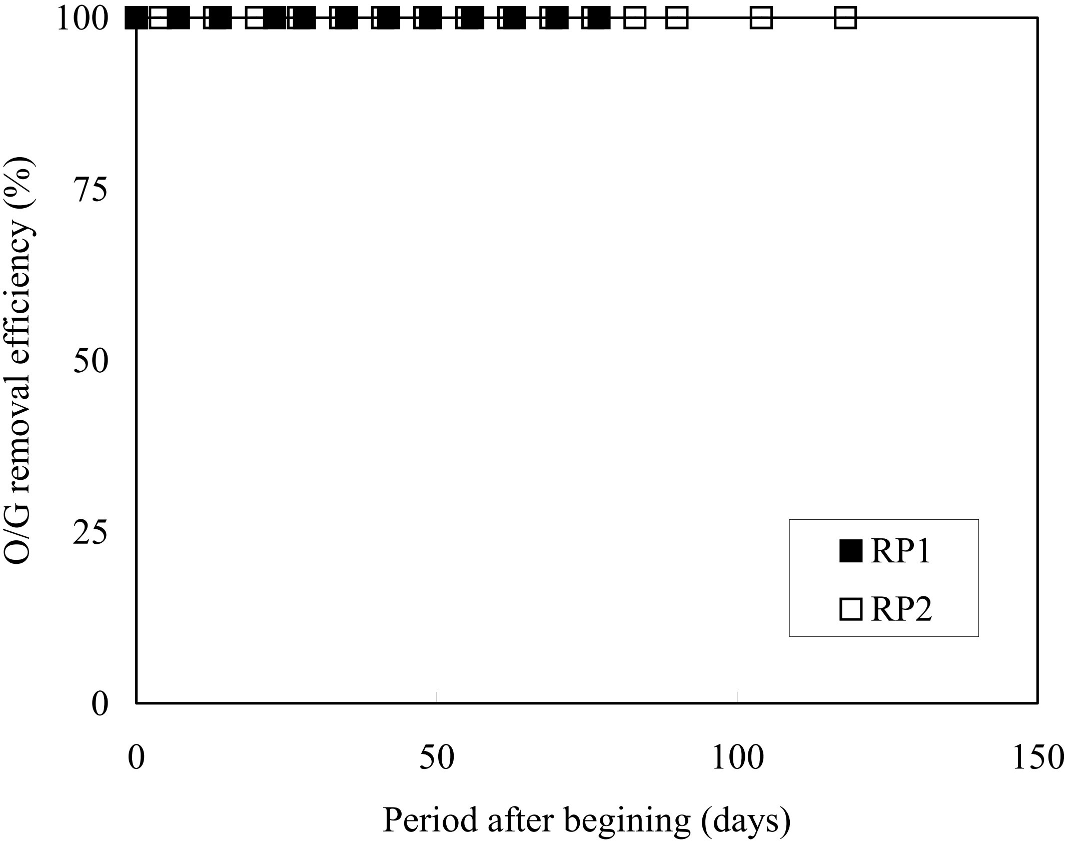


Figure 26b. Pb Removal during Repetitive Experiments

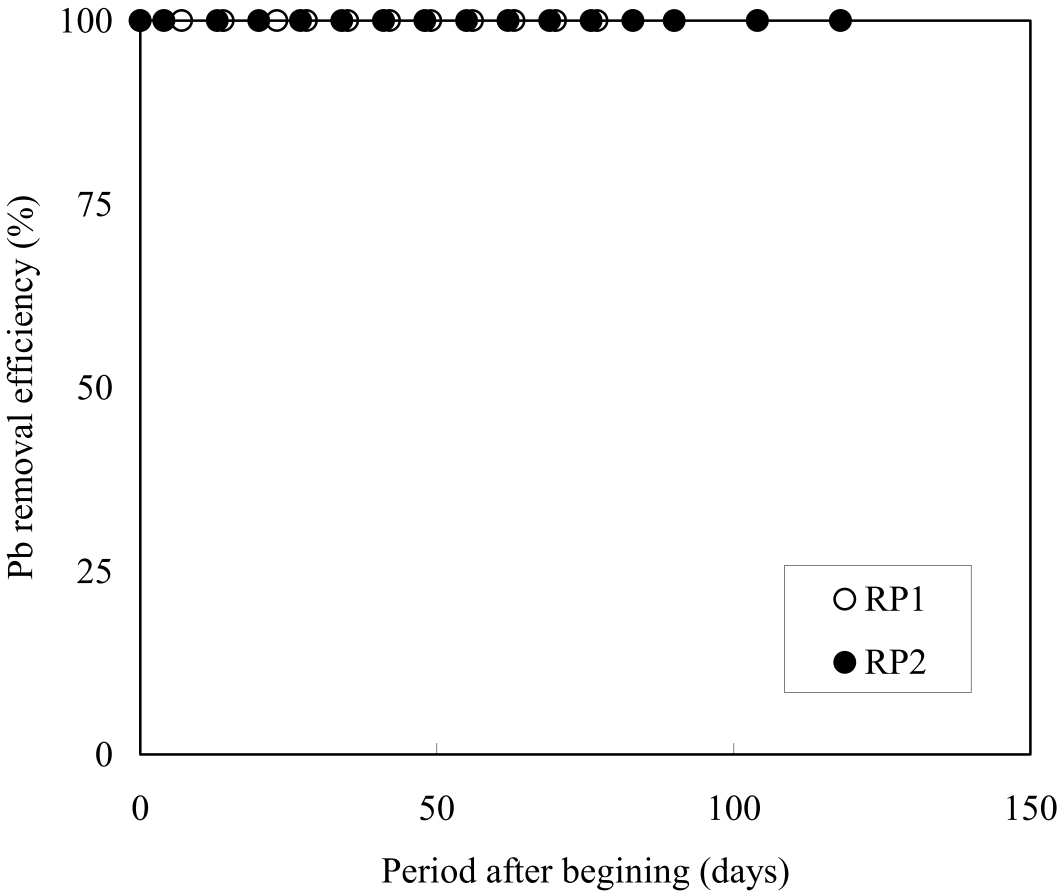


Figure 26c. TSS Removal during Repetitive Experiments

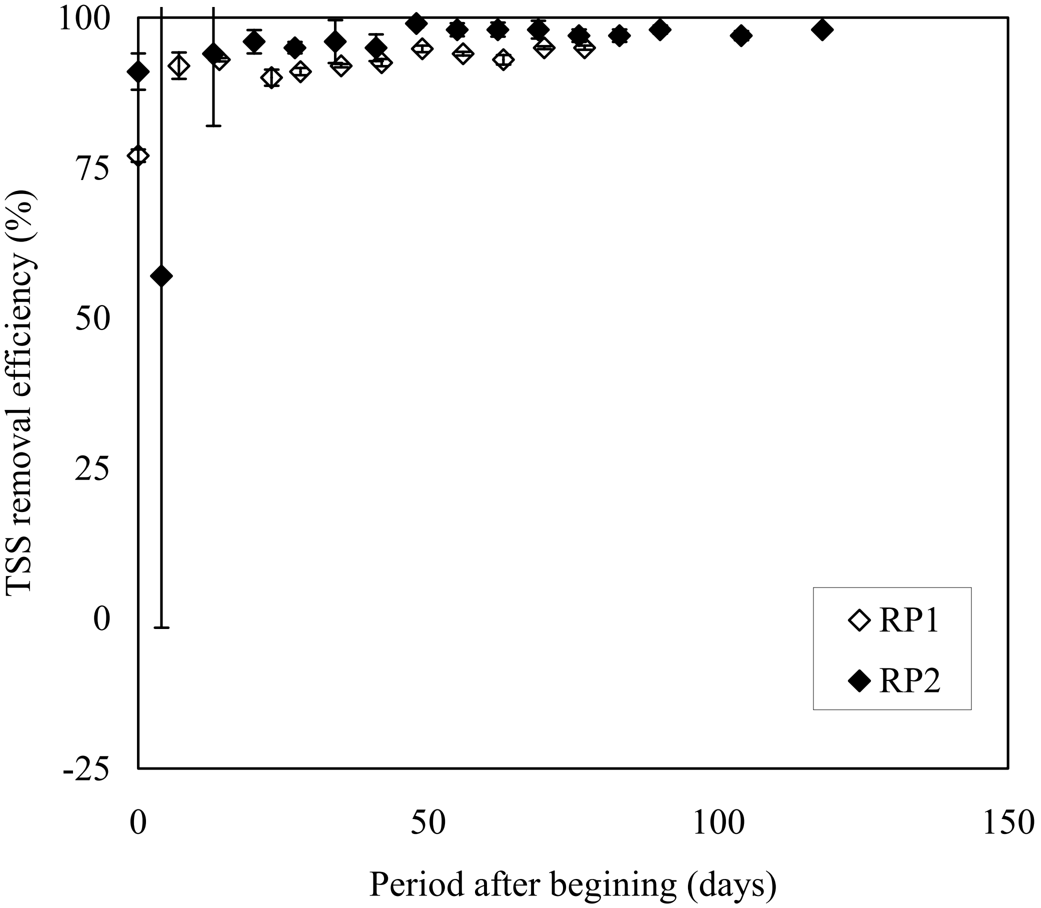


Figure 27. SS Filtered by Surface Mulch Layer

Ammonium and Nitrate Removal

The removal efficiency (mean± standard deviation) of ammonium for each-hour sample throughout the twelve repetitions of RP1 and sixteen repetitions of RP2 is compared in Figure 28. In previous experiment, all eighteen 6-hr columns did not show good removal efficiency for ammonium (8 to 24% removal). In this study, during each 6-hr repetition, a low variability of ammonium removal efficiency in RP1 was shown (standard deviation ranged from 0.7 to 2%) whereas a significant variability always occurred in RP2 for ammonium removal (standard deviation ranged from 7 to 31%). Surprisingly, efficient removal of ammonium was noticed during the first 2 hours (90± 2% for the 1st hour and 92± 2% for the 2nd hour), and then the removal efficiency was gradually decreased to 51± 16%. Overall, greater amounts of ammonium were immobilized in RP2 (68± 16%) than in RP1 (12± 6%) (Figure 29).

Figure 28. Ammonium Removal (mean± standard deviation) for each-hour Sample during the 1st to 12th Repetitive Experiments (RP1) the 2nd to 16th Repetitive Experiments (RP2)

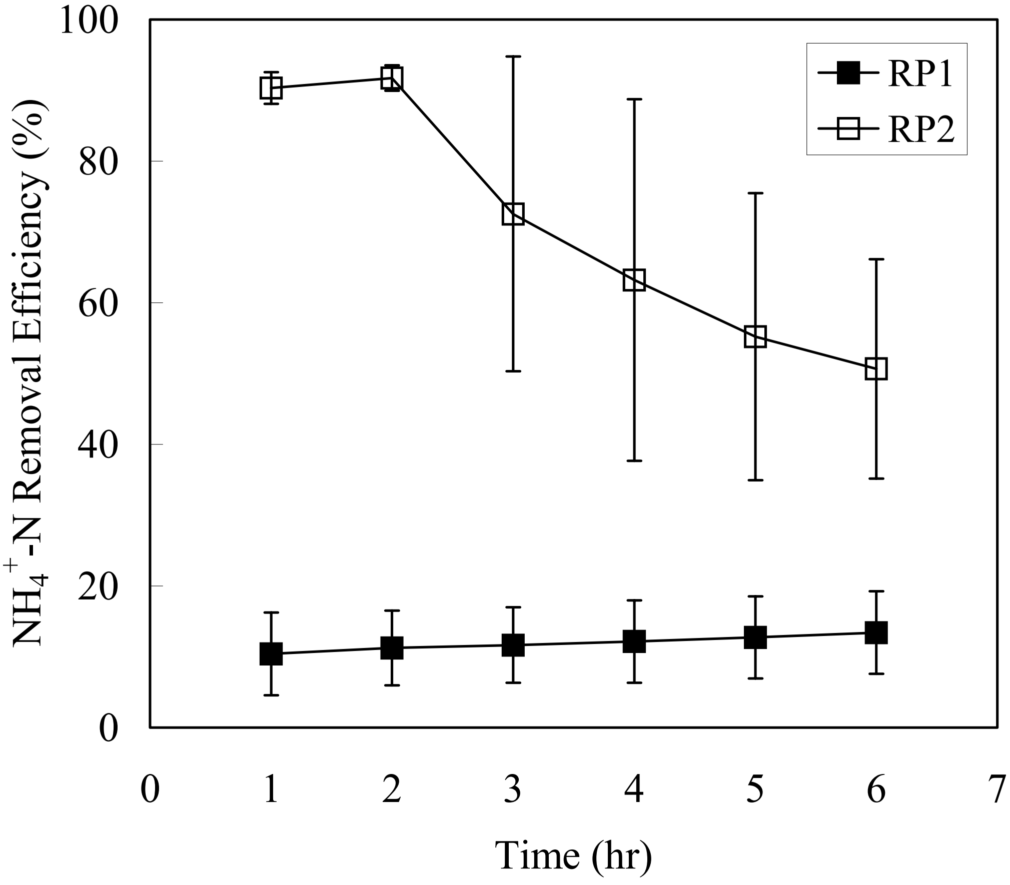
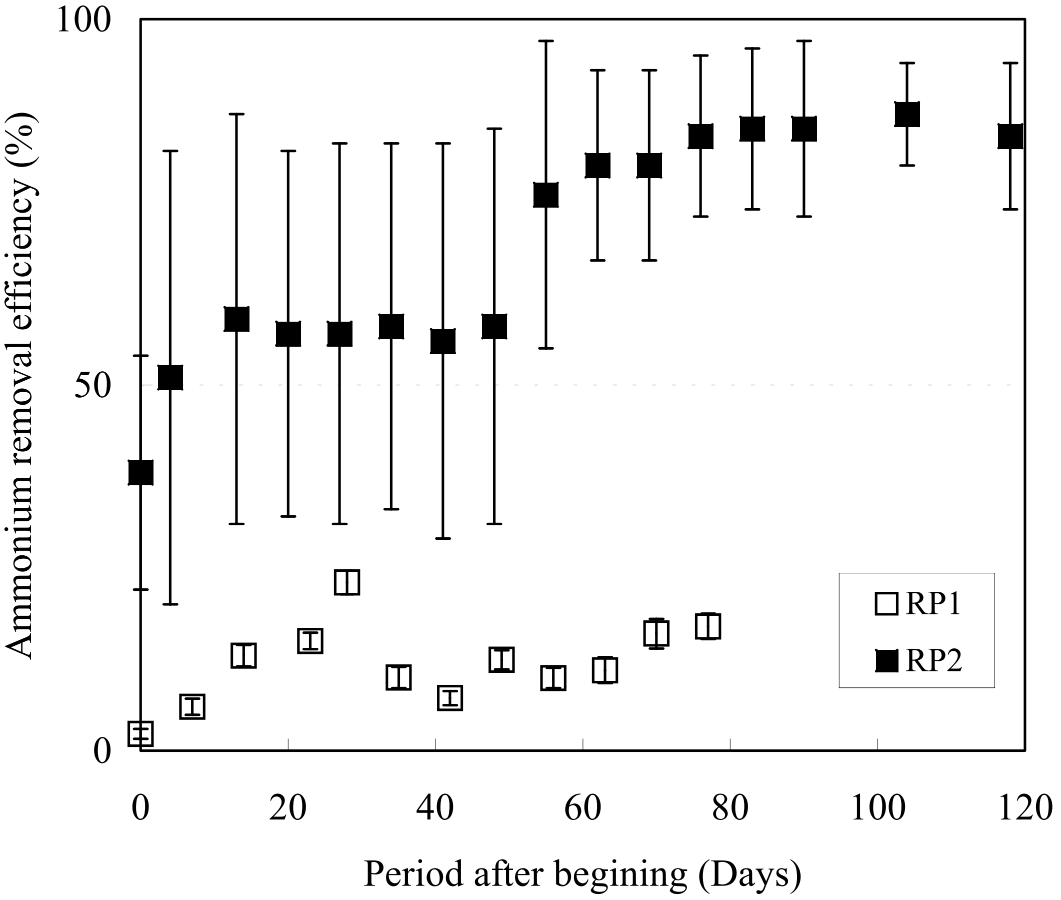


Figure 29. Ammonium Removal Efficiency (mean± standard deviation) during Repetitive Experiments (RP1 and RP2)



For nitrate removal, the previous eighteen 6-hr columns demonstrated 1 to 43% removal efficiency. Apparently, physical and chemical processes account for most of nitrate removal since there is insufficient time for microbial degradation. In this study, looking into each repetition (Figure 29), nitrate removal efficiency in RP1was quite uniform after the initial leaching (standard deviation ranged from 0.7 to 2%). In contrast, the removal efficiency of nitrate in RP2 ranged widely, especially for the first six repetitions (removal efficiency range from -102± 216% to -17± 37%). Washout of nitrate originally containing in the media, combined with the buildup of the corresponding microbial population might result in these fluctuations. Figure 30 shows the nitrate level in each-hour effluent. After the 6th repetition, high nitrate removal efficiency (75± 22%) consistently appeared in the first-hour sample of RP2 during each 6-hr experiment. Subsequently, a large amount of nitrate started to leach out from the column and nitrate removal efficiency was -204± 37% in the second-hour sample. Afterward, the removal efficiency of nitrate increased gradually from -125± 31% to -18± 6% in the 6th-hr sample. The summary results of nitrate removal throughout the entire experimental program are presented in Figure 31. Overall, the media of RP1 and RP2 did not show good removal efficiency for nitrate (-9± 32% for RP1 and -54± 22% for RP2). For RP1, significant nitrate-N leached out from the column during the second to fifth repetitions (range from -21 to –64% removal). Here, most of the leaching nitrate was probably originally in the media. After this period, the average removal efficiency for nitrate-N ranged from 8± 1% to 19± 1%. Similar to RP1, abundant nitrate either originally in the media or from the input of runoff leached out from RP2 (range from -17 to –102% removal).

Figure 30. Nitrate Removal Efficiency (mean± standard deviation) for Each-hour Sample during Repetitive Experiments (RP1 and RP2)

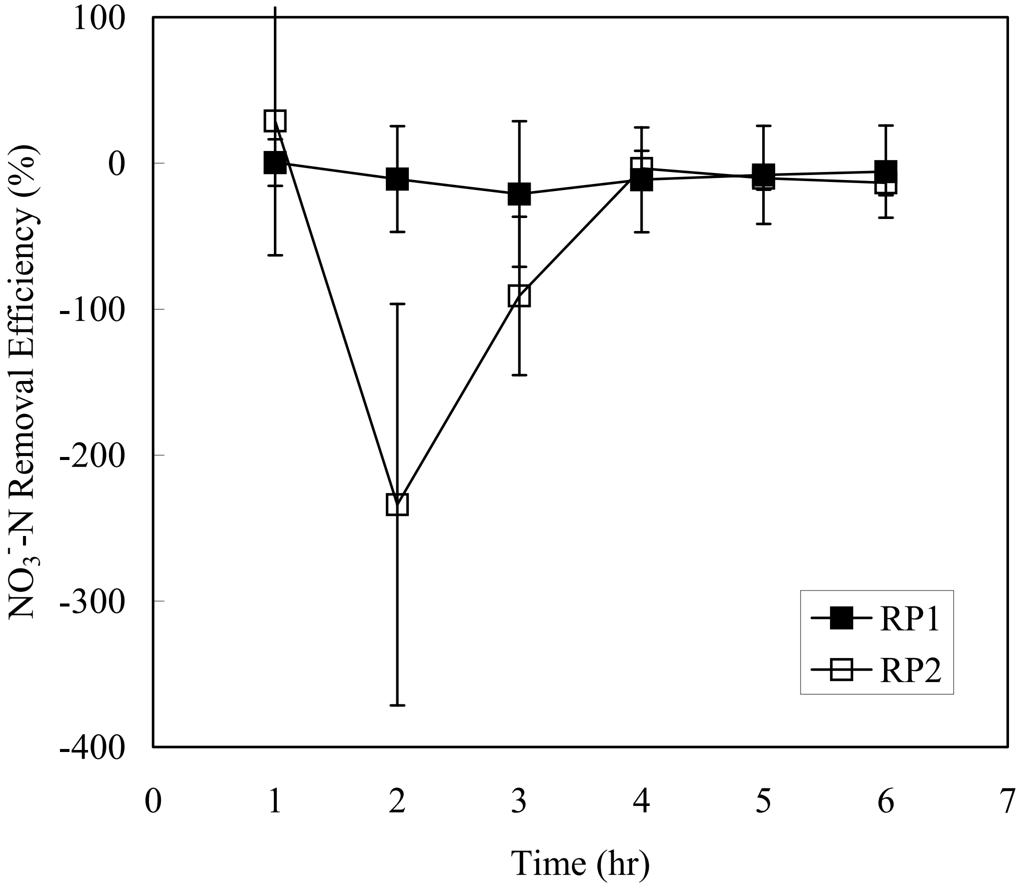
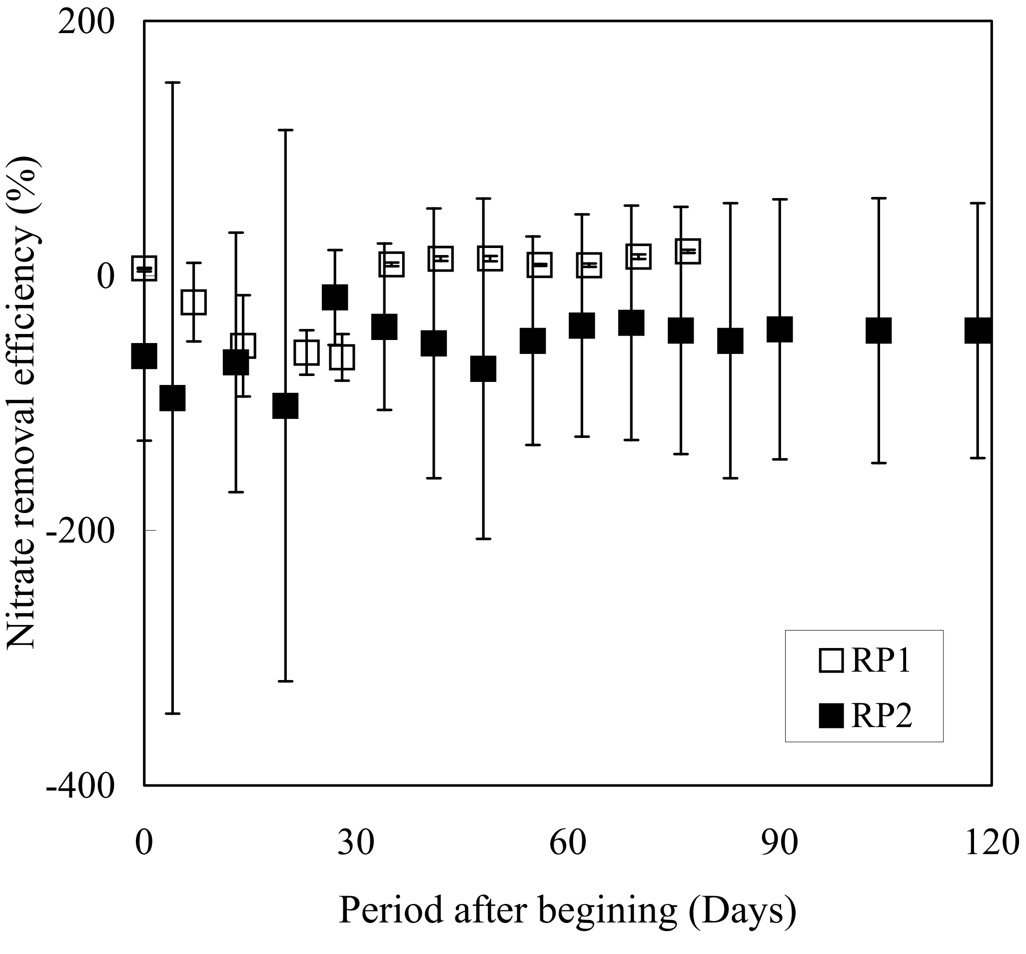


Figure 31. Nitrate Removal Efficiency (mean± standard deviation) during Repetitive Experiments (RP1 and RP2)



In RP1, the less permeable mulch and soil II made up the upper media layer (0-25 cm deep). Most of the runoff leached out from RP1 after each repetition because bottom sand II had only 5% silt+ clay content to hold runoff. Therefore, little water stayed in the upper mulch and soil layers during the dormant period. As a result, all of the effluent of RP1 throughout each 6-hr repetition resulted primary from the runoff input during experiments. In contrast to RP1, a less permeable soil was located in the bottom layer of RP2 (85- 95 cm deep). Without sufficient head for drainage, some runoff water was held in RP2 after each experimental repetition. As such, in the subsequent repetition, most of the initial effluent of RP2 was from the residual water instead of the newly input runoff, and the effect of microbial degradation on ammonium and nitrate removals for these effluent samples was significant.

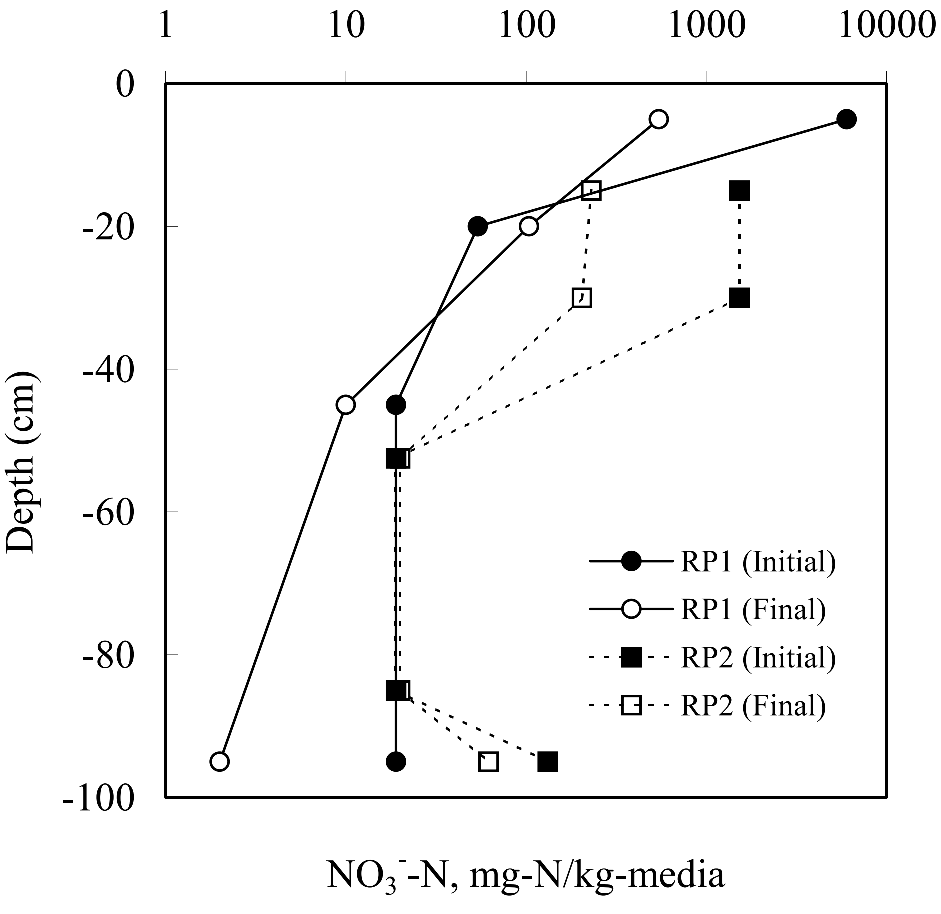
The variable removal efficiencies of ammonium and nitrate in RP2 are postulated to be occurring from biological uptake mechanisms operating during dormant periods. As mentioned, only small volumes of runoff stayed in the RP1column after each repetitive experiment and most of the effluent sample resulted from the input runoff. Due to the short retention time, microorganisms present in the media did not have sufficient time to metabolize ammonium and nitrate during each 6-hr repetition. Therefore, the removal efficiency of both pollutants was controlled by the rapid chemical or physical processes with a less variability resulting. Similar low ammonium and nitrate removals were also shown in eighteen 6-hr bioretention columns with different media. However, high nitrate removal (75± 22%) regularly occurred in the first sample of RP2. Based on the runoff infiltration rate data, this sample was composed of mostly residual water in the lower media (2 to 25 cm away from the bottom). Nitrate in this water was depleted by the microorganisms through denitrification processes in this poorly-drained layer (Meyer et al., 2002). Subsequently, a nitrate flux appeared in the second sample (-204± 37%), which mostly composed by the holding water in the upper media (11 to 60 cm away from the bottom). Combining these data with the efficient ammonium removal results occurring in the first two effluent samples (90± 2% for the 1st hour and 92± 2% for the 2nd hour), it was evident that ammonium in the residual water of upper media was transformed to nitrate through nitrification processes during the wetting-drying cycles (Lance et al., 1976). Along with the inputs of nitrogen in the subsequent repetitions, abundant nitrate leached out and appeared in the second effluent sample. Owing to a short retention period (< 10 hrs), most of nitrate contained in the latter input runoff just leached out along with the residual nitrate (removal efficiency ranged from -125± 31% to

-18± 6%).

Nitrate Distribution in Bioretention Media Profile

The distribution of nitrate in the media was investigated to assist in understanding the retaining/leaching potential of nitrate in the media after wetting-drying cycles. The results are summarized in Figure 32. It appears that significant nitrate was lost from the surface media in both columns, which should cause the large nitrate flux in the effluent samples of the first few repetitions.

Figure 32. Nitrate-N Distribution in RP1 and RP2 before and after Repetitive Experiments



Due to different runoff infiltration rates and nitrate inputs in RP1 and RP2, nitrate retaining/leaching potential of different media layers was compared. First, input and output mass of nitrate (M) for each column during repetitive periods is calculated as:

$$M = \sum_{1}^{n} \sum_{i=1}^{t_d} QC \, \Delta t \tag{11}$$

Where Q is the runoff flow rate, C is the input or output nitrate concentration, Δt is the measurement time increment, and n is the number of repetitions, 12 for RP1 and 16 for RP2. Based on these calculations, total input and output nitrate-N were 1.60 g and 1.85 g for RP1 and 1.42 g and 2.22g for RP2. Accordingly, 0.25 g of nitrate-N was exported from RP1, whereas 0.8 g from RP2.

In addition, removal/leached nitrate-N per unit mass of different media per input nitrate-N is defined as:

$$m = \frac{M_r}{M_{in}} \tag{12}$$

Where m is removed/leached nitrate-N per unit mass of different media per input nitrate-N, M_r is the mass of removed/leached nitrate-N per unit media mass, and M_{in} is the total mass of input nitrate-N. All of the results are summarized in Table 12.

Table 12. Nitrate-N Retaining/Leaching Potential in Different Media

Medium	RP1		RP2		RP1	RP2	RP1	RP2
	IC	F	IC	F	Difference			
	mg NO_3^--N/kg-media						mg NO_3^--N/kg-media/g-input NO_3^--N	
Mulch	1355	123			-1232		-770	
Media mixture			345	46~51		-299~-294		-210~-207
Sand I	4	0.2-2	4.3	4.5	-3.5~-2	0.2	-2.2~-1.3	0.14
Soil I	12	23			11		7	
Soil IV			30	14		-16		-11

Apparently, significant nitrate leached out from the mulch layer in RP1 (770 mg-N/kg-media/g-input NO_3^--N), which originally containing high concentration of nitrate (1355 mg-N/kg-mulch). Similar leaching of nitrate occurred in the surface mixture medium of RP2 (207 to 210 mg-N/kg-media/g-input NO_3^--N), which also was composed of 50% mulch on a mass basis. In short, high concentrations of desorbable nitrate in the mulch proved detriment to the performance of bioretention for nitrate removal.

Comparing soil layers in RP1 and RP2, the nitrate concentration of soil II in RP1 increased (7 mg-N/kg-media/g-input NO_3^--N), whereas the nitrate level of Soil III layer in the bottom layer of RP2 decreased (-11 mg-N/kg-media/g-input NO_3^--N). As discussed, nitrate entered both soil layers either from the input runoff or the upper media layer. During the dormant period, ammonium in the media can be transformed to nitrate through nitrification processes (Lance et al., 1976), contributing to the increase of nitrate in soil II of RP1. Instead of nitrification processes, denitrification could occur in the bottom soil III layer of RP2 (Meyer et al., 2002) because of its anaerobic condition. Therefore, nitrate in the soil was degraded by the denitrifying bacteria to gaseous nitrogen species, resulting in the decrease of nitrate. Due to a small microbial population, retaining/leaching potential of nitrate in both sand II layers did not show significant difference (–1.3 to –2.2 mg-N/kg-media/g-input NO_3^--N for RP1 and 0.14 mg-N/kg-media/g-input NO_3^--N for RP2).

Mass Balance of Nitrate-N/Ammonium-N

Mass balances of nitrate and ammonium are calculated as:

$$M_{added} = M_{in} + \sum M_i L_{ii} \qquad (13)$$

$$M_{leached} = M_{out} + \sum M_i L_{if} \qquad (14)$$

Where M_i is the mass of media employed, and L_{ii} and L_{if} are the nitrate-N concentration in the original media and in the media after the runoff applications. There is no data about the ammonium level in the media. The results are shown in Table 13.

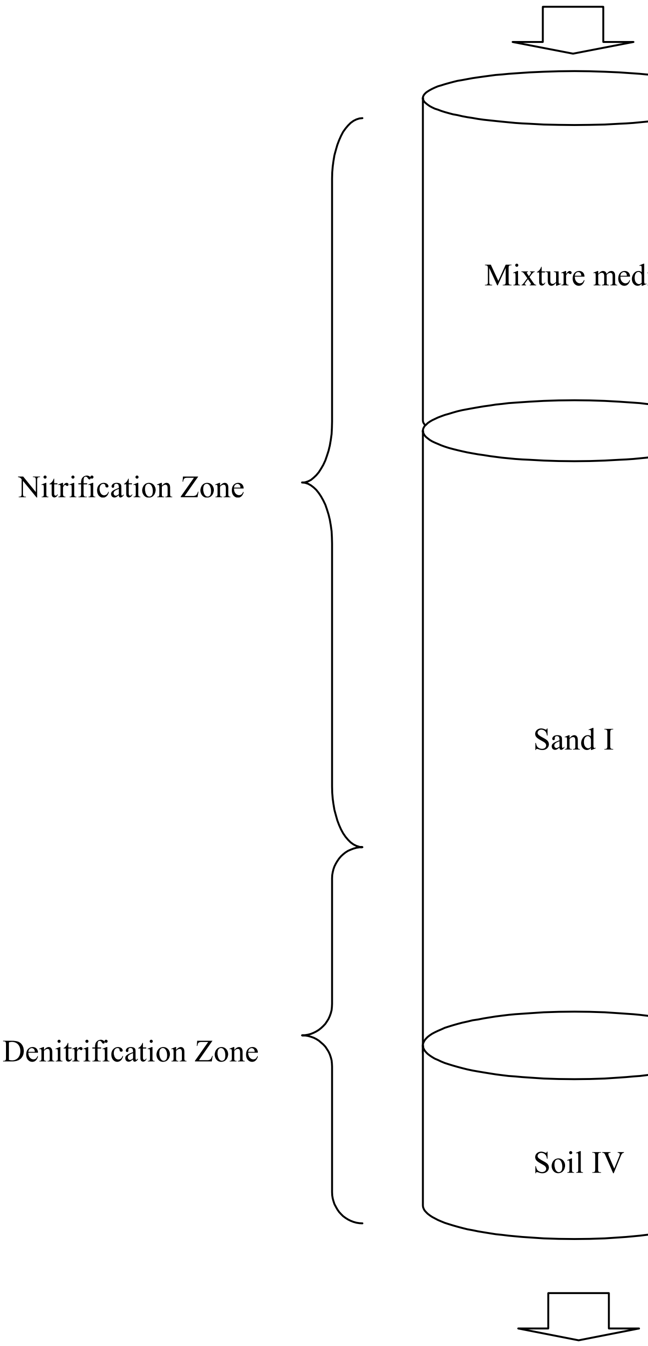
The recovery of total nitrate-N in the effluent RP1 and RP2 was 71% and 43%, respectively. Totally, 0.8 g of nitrate-N was lost from RP1, whereas 2.9 g loss from RP2, which was due to denitrification processes. In addition, 0.16 g of ammonium-N was removed by RP1 and 0.86 g by RP2.

Table 13. Mass Balance Analysis of Nitrate-N from Sequential Events (RP1 and RP2)

Column	RP1		RP2	
	NH_4^+	NO_3^-	NH_4^+	NO_3^-
	g-N			
Input from runoff (A)	1.26	1.60	1.46	1.42
Loss from media (B)		1.02		3.72
Output from effluent (C)	1.10	1.85	0.6	2.22
Removal by media (A+B-C)	0.16	0.77	0.86	2.92

Overall, it was evident that nitrification processes proceeded in the upper media of RP2 because of the efficient ammonium removal of the first two-hour samples and the accumulation of nitrate in the middle soil layer as well. In addition, high nitrate flux in the second hour sample, which mostly was composed of the residual water in the upper media, also supported the occurrence of nitrification processes in this area. Meanwhile, since nitrate was regularly well removed from the first-hour sample, which mostly came from the holding water in the bottom soil layer of RP2, denitrification processes obviously took place in this area, which was also supported by the loss of nitrate-N in the media of RP2 according to the mass balance analysis. The relative appearance of nitrification and denitrification processes in RP2 is shown in Figure 33.

Figure 33. Relative Appearance of Nitrification/Denitrification Processes in RP2



Discussion

Results from eighteen 6-hr bioretention columns with different media mixtures, six on-site bioretention facilities employing synthetic runoff, and two others conducted during a rainfall event provide a comprehensive picture on bioretention behavior during periods when runoff infiltrates into bioretention media. Overall, all bioretention columns and on-site facilities demonstrated excellent removal for O/G and Pb. TSS removal was good in columns, but leaching of media particles was noted in field facilities, mostly from new installations before forming high degree of soil aggregation. Mulch with large pore sizes can be effective in preventing media from clogging longer under SS input. For nutrients treatment, the removal efficiency of TP ranged widely and appears to be related not only to chemical properties of the media, but also to the flow behavior of runoff through the media. Unless special provision were made, all media employed in this study were mostly ineffective in removing nitrate and ammonium efficiently.

Results from repetitive 6-hr bioretention columns and investigation of P and NO_3^--N distribution in the media before and after repetitive experiments provide a comprehensive information of bioretention behavior on runoff infiltration, as well as pollutant removals during a long-term period including several wetting-drying cycles. A series of environmental and agronomic P tests conducted on the media of repetitive columns show the distribution of retained P. In addition, experiments of batch P sorption tests on six media and three continuous column studies help to understand the importance of sorption processes in P removal in bioretention facilities. Overall, the medium with a higher P sorption capacity can retain more P from the infiltrating runoff after a high P loading. However, the sorption data alone are not adequate to predict the P retention through a bioretention column for a short-term experiment due to the complicated processes occurring between the runoff and media. A specially-designed column, RP2 (media profile with high hydraulic conductivity media overlaying one with low hydraulic conductivity) resulted in a higher runoff infiltration rate (from 0.51 to 0.16 cm/min) and was more efficient in P (82± 18%) and NH_4^+-N (68± 16%) removals than RP1 (P: 62± 6.2%, NH_4^+-N: 12± 6%), which employed more traditional media design. Without exceeding the change point for each test (which indicates high risk for P leaching), most of the retained P in all media layers is optimum for future vegetation through nutrient cycling.

The removal efficiency of ammonium was low in RP1 (12± 6%) and was improved in RP2 (68± 16%). By combining the level of ammonium and nitrate in the subsequent effluent samples, as well as the nitrate mass balance analysis, the development of nitrification and denitrification processes in RP2 was strongly supported. Generally, the mulch, with high nitrate-leaching potential, resulted in poor removal efficiency in both bioretention columns. The media established in various configurations performed different efficiencies for ammonium and nitrate removals. The upper media in aerobic conditions allowed microorganisms to conduct nitrification processes. Through nitrification processes proceeding during wetting-drying cycles, captured ammonium levels were decreased and high ammonium removal efficiency from runoff. Via transformation by denitrifying bacteria in the bottom anoxic/anaerobic soil layer, nitrate was consumed and apparently became nitrogen gas. In both columns, O/G, Pb, and TSS were removed well under multiple-loading.

Recommendations

Based on the results of this study, two schematic profiles of bioretention media are presented in Figures 34 and 35 as design recommendations. The permeability of the composted mulch used in this study was low and could limit runoff infiltration. However, a top mulch layer can filter incoming TSS and prevent the underlying media from clogging. In addition, a mulch layer can assist in maintaining soil moisture during dry weather and can provide nutrients for future vegetation. Therefore, mulch with TSS filtering ability and high permeability (d_{10}> 0.1 mm), with appropriate uniformity (a d_{60}/d_{10} value less than 4) is recommended as the top media layer in both designs. In addition to uniformity, a low desorbable nitrate level is also desired for mulch employed.

Figure 34. Proposed Profile of Bioretention Media (Single Filter Media)

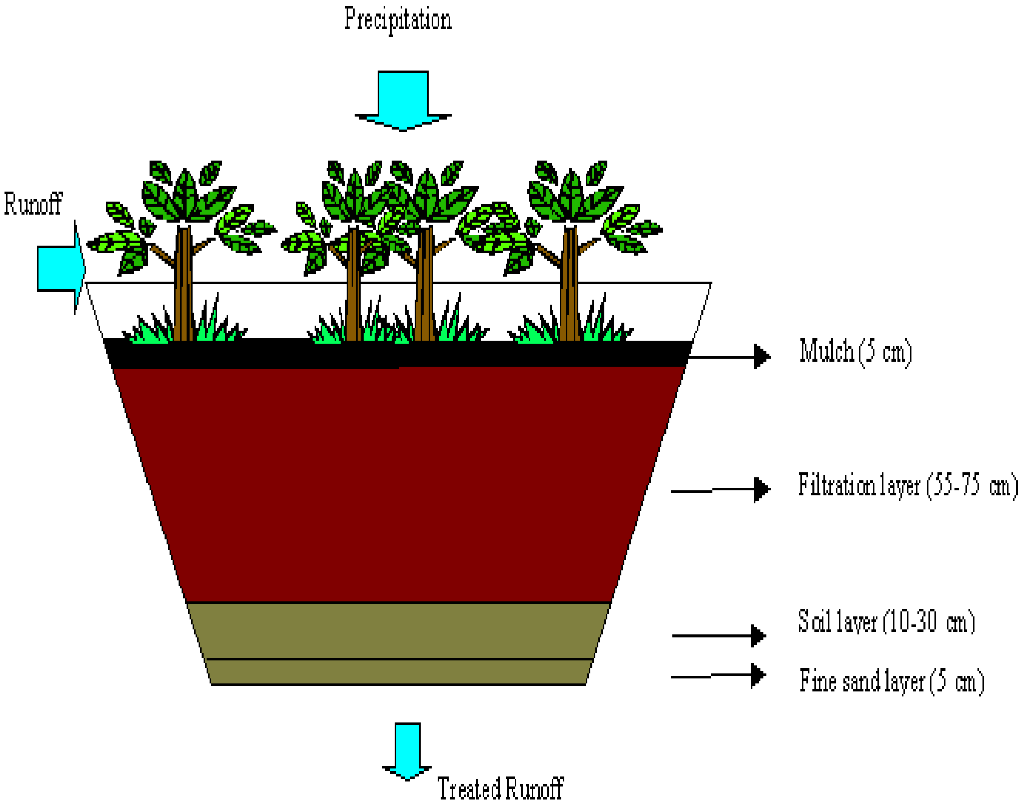
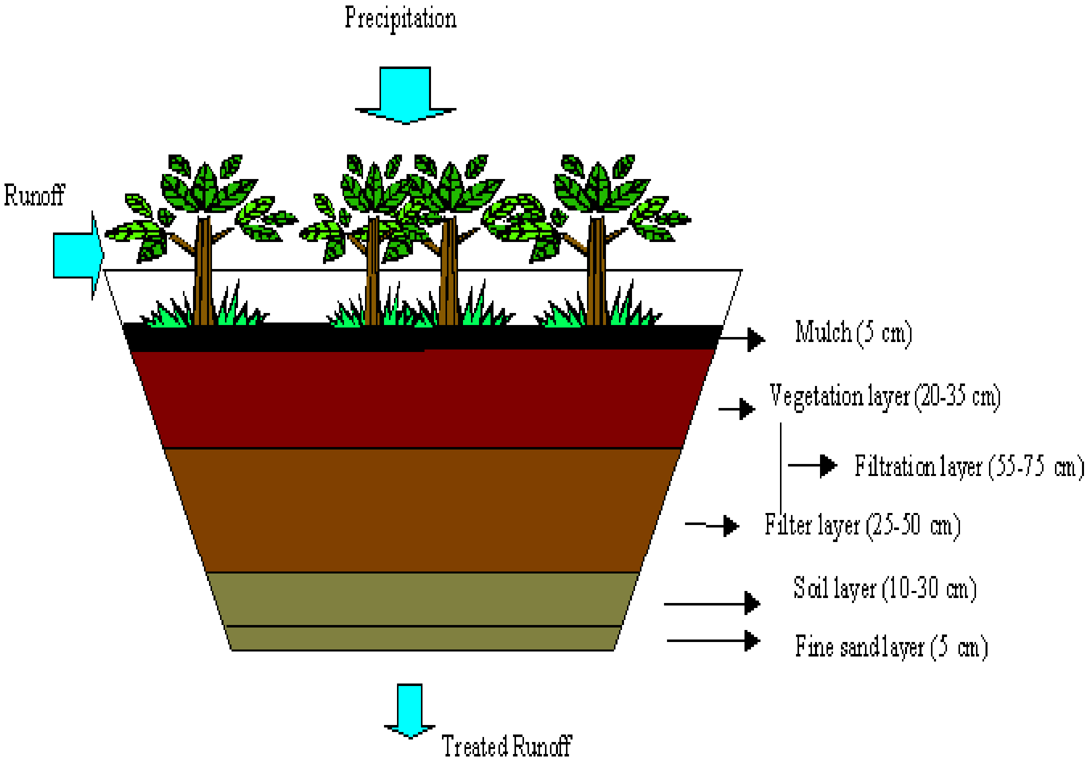


Figure 35. Proposed Profile of Bioretention Media (Dual Filter Media)



The differences between the two design recommendations are the components of the bulk filtration layers. From the perspectives of construction and maintenance, a uniform profile is a more cost-effect alternative than multi-layer media. Therefore, Figure 34 is proposed which includes a combined filtration and vegetative layer. As mentioned, this upper media layer is critical to bioretention performance because runoff will begin to pond on the bioretention surface once the runoff loading is higher than the infiltration rate into the top media layer. An impervious upper layer would limit the overall infiltration rate (e.g., Exps. 9, 10, 11, and 12- Table 5), even though lower layers may be highly permeable. In all cases, the hydraulic conductivity of the upper filtration layer should be higher than the lower soil layer to prevent the formation of a capillary barrier restricting infiltrating runoff.

With respect to pollutant removal, storing runoff temporally in upper media layers is better than having it pond on the surface. In this manner, pollutants contained in the runoff can be sorbed onto the media or assimilated by microorganisms present in the media. Column studies showed that a sand II/soil III mixture produced a high runoff infiltration rate (Exps. 16 to 18- Table 5) and very good pollutant mass removal. Therefore, a media layer created by mixing coarse sand (e.g., d_{10}> 0.30 mm) with a sandy soil (sandy loam texture), where the soil ratio (20 to 70% by mass) depends on the requirements for the plant species to be employed is recommended. The suggested depth is 55 to 75 cm. With this design, the initial runoff infiltration rate is expected at 1.2 to 5.4 cm/min at 15 cm water head (Exps. 16, 17, and 18- Table 5), which is 4 to 6 times faster than that through a sandy loam soil (Exp. 3, 0.28 cm/min). For pollutant removal, > 96% of TSS, > 96% of O/G, > 98% of Pb, 24 to > 70% of TP, 6 to 9% of nitrate and 11 to 20% of ammonium are expected to be removed from the infiltrating runoff.

The second design contains separate vegetation and filter layers. The vegetation layer is employed to optimize vegetation survival, whereas the filter layer is optimized for pollutant removal. Bioretention plants provide several natural functions to the facility and can also uptake some nutrients and heavy metals from the media. The advantage of this design is that it allows the filter layer to back up the deficiency of the vegetation layer in pollutant removal. Since supporting plant growth is not necessary, the same components are employed, coarse sand (e.g., d_{10}> 0.30 mm) with sandy loam soil, but at a greater sand/soil ratio of 50/50 (Exp. 18), which produced the best pollutant removal noted in column studies. The vegetation layer depth recommendation is 25 to 30 cm with the media tailored to meet the needs of the plants. The filter layer depth is recommended at 25 to 50 cm. Under this design, > 96% of TSS, > 96% of O/G, > 98% of Pb, >82% of TP, ~ 9% of nitrate and > 68% of ammonium are expected to be removed from the infiltrating runoff.

If nitrate removal is desired, an additional layer is required. Nitrate was poorly removed in all column and most field tests. As shown in RP2, both single and dual layers of bioretention media with a less-permeable soil bottom layer could form an aerobic or anoxic/anaerobic zone for promoting nitrification/denitrification processes. Under these designs, over 68% of ammonium could be removed. Without washout of nitrate from the surface mulch layer, nitrate removal efficiency could be improved through the denitrification processes occurring during the dormant periods. A bottom fine sand layer (5 cm, as used in the column experiments) is included to prevent soil particles from leaching and clogging. The total media depth is 65 to 115 cm.

Bioretention has potential for significant improvement in storm water runoff quality as well as slowing flows. Careful design is necessary to optimize water flow and quality characteristics. Establishment of a process to evaluate the media suitability in target pollutant removal, as well as runoff infiltration is recommended for future research. Followed by, apply the appropriate media into these designs to advance the environmental effectiveness of bioretention.

Technology Transfer and Management Application

Several modes of technology transfer have been completed thus far. The first is through the Chesapeake NERR. In March 2002, a presentation was made on this work to Maryland NERR personal, through interaction with Carol Towle, Maryland NERR Director. Ms. Towle has been kept up to date with work results throughout the project and has been very supportive of the work.

The second mode of technology transfer has been via presentation at scientific meetings. As described in the **Scientific and Academic Achievement** section, Portions of this work were presented at *Watershed 2002*, Ft. Lauderdale, FL, February 2002 (sponsored by the Water Environment Federation), *World Water and Environmental Resource Congress 2003*, Philadelphia, PA, June 22, 2003 (sponsored by the American Society of Civil Engineers), and the *7th International Conference- Diffuse Pollution and Basin Management*, in Dublin, Ireland, August 17 to 23, 2003 (sponsored by the International Water Association).

Additionally, information on this project and other bioretention research is presented at www.ence.umd.edu/~apdavis/Bioret.htm. Specific information on this project is listed at www.ence.umd.edu/~apdavis/bio-columns-ciceet.htm. Researchers, government agencies, and practitioners throughout the world visit these sites.

The PI also maintains ongoing contact with the Prince George's County Government, Maryland State Highway Administration, the Low Impact Development Center and several other agencies. Although results from this work have not yet made it into practice, new bioretention specifications are being evaluated in the State of Maryland and results from this work on bioretention media effects will be considered.

Finally, one manuscript has been submitted and two others are in preparation for submission for publication in referred journals. Referred journal publications are necessary for this work to be considered credible in the academic research community and for eventual inclusion in educational programs.

Technology Commercialization

No intellectual property rights, patents, copyrights, or licensing agreements have resulted from the project. No private sector partnerships or commercial production have been created.

Scientific and Academic Achievement

Three presentations based on parts of this work were presented at national and international conferences; an abstract for a fourth presentation was just submitted:

1. Hsieh, C.-h. and Davis, A.P. "Engineering Bioretention for Treatment of Urban Storm Water Runoff," *Watersheds 2002*, *Proceedings on CDROM Research Symposium,* Session 15, Ft. Lauderdale, FL, Feb. 2002.
2. Hsieh, C.-h. and Davis, A.P. "Evaluation of Bioretention for Treatment of Urban Storm Water Runoff," *World Water and Environmental Resource Congress 2003*, Session 11 Sustainable Urban Drainage Systems, Philadelphia, PA, June 22, 2003.
3. Hsieh, C.-h. and Davis, A.P. "Multiple-Event Study of Bioretention for Treatment of Urban Storm Water Runoff," *7th International Conference- Diffuse Pollution and Basin Management*, Dublin, Ireland, August 17 to 23, 2003.
4. Hsieh, C.-h. and Davis, A.P "Multiple-Event Studies of Bioretention for Treatment of Urban Storm Water Runoff" *Putting the LID on Stormwater,* Conference to be held in College Park, MD, September 2004

One manuscript is under review for possible publication in *Journal of Environmental Engineering, ASCE*:

Hsieh, C.-h. and Davis, A.P. "Evaluation and Optimization of Bioretention Media for Treatment of Urban Storm Water Runoff," submitted to *J. Environ. Engg., ASCE,* September 2003.

Two other manuscripts for publication are currently in preparation for submission to a referred journal. (Tentative titles)

1. Hsieh, C.-h. and Davis, A.P. "Multiple-Loading Evaluation of Bioretention for Treatment of Urban Storm Water Runoff: Runoff Infiltration and Phosphorus Removal," in preparation.
2. Hsieh, C.-h. and Davis, A.P. "Multiple-Loading Evaluation of Bioretention for Treatment of Urban Storm Water Runoff: Oil/Grease, Lead, TSS, Ammonium, and Nitrate Removals," in preparation.

One Ph.D. student worked full time on this project. His Ph.D. defense is scheduled for December 2003:

Chu-hsu Hsieh, "Engineering Bioretention for the Improvement of Storm Water Quality," (degree award expected, May 2004).

Also two undergraduate civil and environmental engineering students assisted with this project:

Sophia Zarembski, BSCE 2001
Daniel Baer, BSCE 2003

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