

Adsorptive Media Investigations and Testing for Improved Performance of Stormwater Treatment Systems in the Tahoe Basin

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Executive Summary

Retrofit activities, such as improving hydrology and incorporating more advanced treatment methods into systems where feasible, may improve phosphorus (P) removal performance of current Best Management Practices (BMPs). In the recent past, chemical treatment systems such as chemical dosing and the use of adsorptive media have become more prevalent for treating stormwater and hold promise for improving the P removal performance of stormwater treatment BMPs (Bachand et al., 2005; Patel et al., 2005). Our primary objective for this project has been to investigate whether adsorptive media hold any promise for improving P removal performance of stormwater basins and treatment wetlands at Lake Tahoe. In meeting this objective, we have taken a number of steps:

- Conducted a literature review of currently available adsorptive media and assessed their promise for application in the Tahoe Basin;
- Initially assessed the potential of these different adsorptive media for improving P removal performance using laboratory studies;
- Implemented laboratory column studies to understand P uptake characteristics of selected media; and
- Implemented field column studies to better understand P uptake characteristics of media under conditions when real stormwater is applied.

In the literature review for this project, we identified a number of substrates that we believed were worthy of investigation during this project for application in the Tahoe Basin. These substrates were generally iron-, calcium- or aluminum-rich materials that were locally available and were not expected to be sources of heavy metals or other pollutants. Many had high specific surface area, which was expected to improve porosity and provide a greater number of adsorptive sites. The substrates selected for further studies included bauxite, lightweight aggregates (LWAs) and expanded shales/clays, iron-rich sands, activated alumina, marble and dolomite, and natural and lanthanum-activated diatomaceous earth.

Laboratory isotherm studies have been completed, laboratory column studies are ongoing, and field column studies will begin in the spring. All studies are expected to be completed by May 2005 with an amendment to this report planned for August 2005. Though these studies are not complete, a number of findings have resulted from this work:

- There appear to be opportunities to improve the performance of stormwater treatment basins and wetlands through utilizing adsorptive media. A number of possible media choices exist that would seem good candidates to improve the performance of stormwater basin and wetland BMPs with regard to P removal. The most promising medias that we have tested to date are activated alumina and lanthanum coated diatomaceous earth. These media do affect pH concentrations in the outflow, however, and activated alumina has resulted in the leaching of aluminum (Dipen et al., 2005). Both the potentially positive and negative water

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quality effects need to be further tested. Additionally, other media that have not been tested may also prove effective at P removal.

- Compared to other naturally occurring materials, the Tahoe Basin soils tested have relatively poor phosphorus uptake capacity because of their chemical and physical characteristics. Soil amendments to infiltration areas and use of adsorptive media in stormwater basins would be expected to improve phosphorus removal performance and retard the development and movement of any subsurface P plumes.
- For synthetic stormwaters, retardation rates predicted from the isotherm studies have been in general agreement with those determined from column studies and thus isotherms appear to be a good first step in estimating phosphorus front velocity and the time it will take for phosphorus breakthrough to occur within a defined soil unit. For real stormwaters, the complex chemistry will likely affect P-uptake performance of the different media, so these estimates should be seen as indicators at this time that identify order-of-magnitude differences in performance between different media. In developing retardation factors, careful determination of the key soil parameters (e.g. adsorption constant, porosity, dry bulk density) will help provide a better prediction of retardation rates.
- Reaction and mass transfer kinetics are important considerations for chemical and biological retention of nutrients extracted from soil waters. Retention efficiency is reduced if water moves through the soils or media at a rate faster than the dominant removal processes. Determining appropriate flow rates for system design in specific soil types is necessary to assure long-term phosphorus removal by these systems. These kinetics are a consideration when developing retardation rates from isotherm studies.

These studies have not addressed the implementation issues associated with retrofitting basins or applying these media in infiltration areas. Associated issues include the method of application, the development of design criteria and specifications, and the predicted performance goals. If these studies ultimately show that adsorptive media can improve P removal, these other issues should be investigated. Larger-scale experimental pilot systems in coordination with small-scale laboratory studies will likely be needed to address these questions before large-scale implementation around the Basin can be implemented. Some of these issues are being partially addressed in current OWP pilot-scale studies (Dipen et al., 2005) though these experiments are mainly focusing on highway runoff.

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Acronyms

Technical Terms

BMP	Best Management Practice
CEBMP	Chemically Enhanced Best Management Practice
LWA	Light Weight Aggregates
mg/L	milligrams per liter (ppm)
P	Phosphorus
ppm	parts per million (mg/L)
ppb	parts per billion ($\mu\text{g/L}$)
Peq	Equilibrium phosphorus concentration
SOP	Standard Operation Procedure
$\mu\text{g/L}$	micrograms per liter (ppb)

Organizations

OWP	Office of Water Programs, California State University Sacramento
TRG	Tahoe Research Group
TRPA	Tahoe Regional Planning Agency
UCDCEE	University of California Davis Civil and Environmental Engineering
USDA	U.S. Department of Agriculture

1 Introduction

Lake water clarity has been decreasing at a long-term rate of about one foot per year since the late 1960s. This decrease is most likely from increased nutrient and fine sediment particle loading. Phosphorus is of particular importance because it is the macronutrient limiting algae growth in the lake. Approximately 75% of annual load of bioavailable P, soluble reactive P, is mobilized by rain events (Strecker and Howell, 2003). Because of the importance of stormwater in delivering phosphorus to the Lake, the Lahontan Regional Water Quality Control Board and the Tahoe Regional Planning Agency (TRPA) have established discharge standards and local agencies around the Lake are implementing a number of Best Management Practices (BMPs) to help reduce stormwater loading of these pollutants.

A number of BMPs have been implemented in the Tahoe Basin to reduce fine particle and nutrient loading to the Lake. Dry detention basins, infiltration basins, bioretention basins, and water quality swales are relatively numerous around the Lake and vegetated filter strips, wet ponds and stormwater wetlands can also be found (Bachand et al., 2005). We have reviewed the performance of different BMPs and concluded that for these types of BMPs, a total P load reduction between 15 and 45% may be realistic (Bachand et al., 2005). These BMPs are expected to achieve very similar total P outflow concentrations, approaching 0.1 mg/L, and Bachand et al. (2005) concluded that these BMPs will have difficulty meeting the surface discharge standard of 0.1 mg/L unless inflow concentrations are near or at the surface water discharge standard.

Retrofit activities, such as improving hydrology and incorporating more advanced treatment methods in systems in which it is feasible, may improve the P removal performance of current BMPs. In the recent past, chemical treatment systems such as chemical dosing and the use of adsorptive media have become more prevalent for treating stormwater and hold promise for improving the P removal performance of stormwater treatment BMPs (Bachand et al., 2005; Patel et al., 2005). These systems have also begun to be tested in the Tahoe Basin. The City of South Lake Tahoe with funding from the U.S.D.A. Forest Service and CALTRANS have supported work by a research team that includes the University of California Davis (Civil and Environmental Engineering – UCDCOE, and the Tahoe Research Group - TRG), the USGS, and Bachand & Associates to investigate chemical dosing retrofit opportunities and applications in the Tahoe Basin. Another research team headed by California State University Sacramento Office of Water Programs (OWP) and funded by CALTRANS has been investigating chemical dosing and adsorption technologies to treat highway runoff around the Basin. Meanwhile the project discussed in this report, funded by the U.S.D.A. Forest Service and the California Tahoe Conservancy, has been supporting an investigation of adsorptive media to improve the performance of stormwater basins and treatment wetlands. All of these teams have been working cooperatively with funding from a variety of sources to investigate the opportunities and applications of chemically enhanced BMPs to improve stormwater treatment throughout the Tahoe Basin.

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1.1 Project Objective

Our primary objective for this project has been to investigate if adsorptive media hold any promise for improving P removal performance of stormwater basins and treatment wetlands. In meeting this objective, we have taken a number of steps:

- Conducted a literature review of currently available adsorptive media and assessed their promise for application in the Tahoe Basin;
- Initially assessed the potential of these different adsorptive media for improving P removal performance using laboratory studies;
- Implemented laboratory column studies to understand P uptake characteristics of selected media; and
- Implemented field column studies to better understand P uptake characteristics of media under conditions when real stormwater is applied.

These studies have been conducted in coordination with efforts by OWP, in the context of the different efforts listed above, to investigate the different chemically enhanced BMPs (CEBMPs) such that data from these different efforts are complimentary.

1.2 Report Layout

This report summarizes the efforts that were conducted during each of these steps and provides a schedule for completion of the remaining efforts. These efforts will be documented and provided as amendments to this document as described in the schedule. Much of the details on the different efforts are provided in the Appendix.

2 Literature Review Summary

The literature review for this project is in Appendix 1. As discussed in Appendix 1, phosphorus removal by wetlands and basins in Lake Tahoe may be improved through designing these systems to filter stormwater through media having higher phosphorus removal capabilities than local parent material.

2.1 Phosphorus Removal Model

Phosphorus enters these BMPs as dissolved P and particulate P. Several sinks exist for phosphorus in wetlands and other aquatic systems. For dissolved P, these sinks include short-term sinks such as plant uptake, adsorption and algal uptake as well as long-term sinks such as burial of plant material and sediments to which P adsorption has occurred (Figure 2-1). For particulate P, settling and filtration are the primary removal processes and once the particulate P is integrated into the sediments, sinks for dissolved P in the soils, such as soil adsorption and plant uptake and burial help control P from recycling back into the surface waters. How well an aquatic system removes and retains P depends upon the characteristics of that system.

Because of the importance of adsorption and burial, the type of media used in the construction of a treatment BMP and how it is utilized is expected to have a large effect on the P removal efficiency of that system. Both chemical and physical characteristics of different media should affect the short-term storage of P from adsorption as well as the stability of long-term storage through burial.

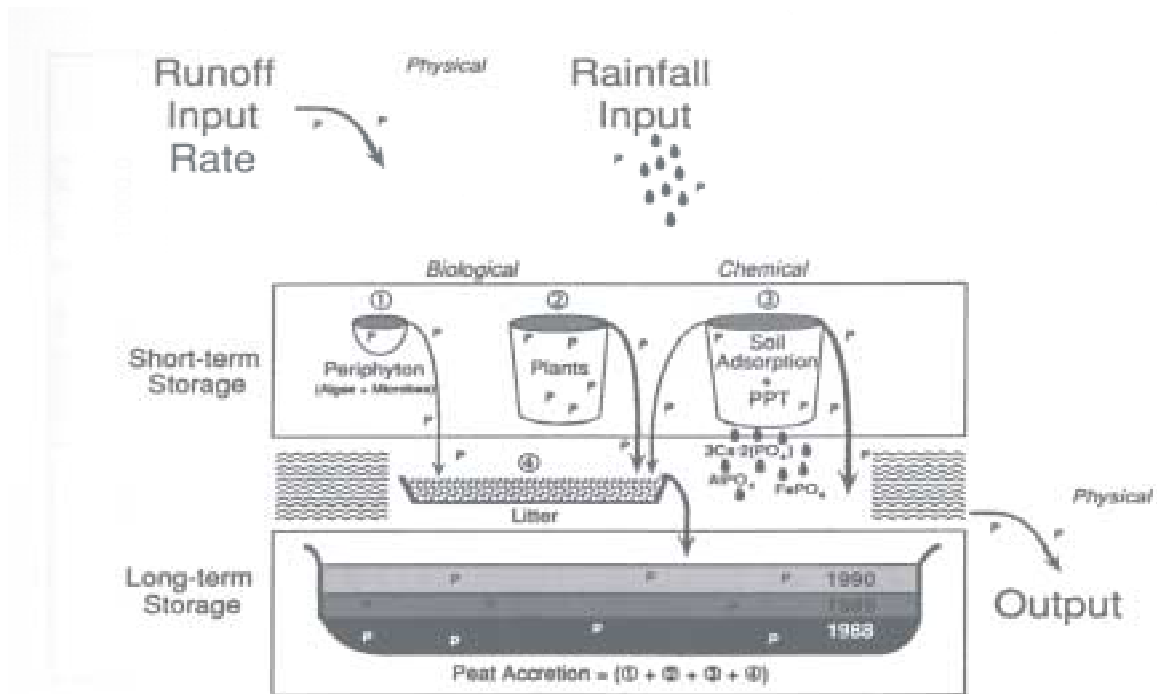


Figure 2-1. Wetland Phosphorus Uptake Model (Richardson et al., 1997)

2.2 An Overview of Media Characteristics that Affect Performance

Substrates rich in iron, aluminum and calcium oftentimes have enhanced phosphorus removal. These substrates can be naturally occurring, byproducts of industrial or water treatment processes, or engineered. Naturally occurring materials that have been tested by others for their ability to improve P removal include zeolite, bauxite, laterite, dolomite, shale, limestone, calcite, vermiculite and iron-rich sands. Some of these are iron and/or aluminum rich and some of these are calcium rich. Industrial materials tested with regard to their potential to improve P removal include blast furnace slag, steel furnace slag, red mud, Lightweight Aggregates (LWA) of which Light Expanded Clay Aggregates (LECA) is a subset, Fly ash, HiClay Alumina (HCA), and aluminum and iron based water treatment residuals (WTR). All these materials are either rich in aluminum, iron and/or calcium. Finally, some substrates have been engineered for phosphorus removal and are proprietary. Some of these substrates are based upon the principle that iron and aluminum rich materials enhance P uptake. Examples of these are activated alumina, Phoslock™, and lanthanum-coated diatomaceous earth. Many of these materials have been tested for their ability to remove P. Appendix 1 provides an in depth review of these different studies that show how many of these media which are rich in iron, aluminum or calcium have enhanced P removal capabilities.

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In Appendix 1 we list all the different media considered for use at Lake Tahoe, provide chemical data on many of these media, review different studies that assess these different media, and discuss other issues that affect the selection of media for application in the Tahoe Basin. In reviewing the studies, we found discrepancies in the data. This result may be due to the fact that depending upon where a material is found, it may have different P uptake characteristics because of its natural chemical characteristics. For instance, limestone is found through the United States. Some limestone is less chemically structured and more amorphous in nature, while other forms are more crystalline such as the metamorphic limestone found throughout much of California. Differences in methods used may also result in differences in P adsorption results.

Based upon our review, we found a number of substrates seem to effectively remove P in case studies. Based upon these studies, promising substrates include water treatment residuals, blast furnace slag, steel furnace slag, OPC, calcite, marble, Uelite and other LWAs, zeolite and shale. However, other nonperformance factors such as environmental considerations, application logistics, costs, and potential for cementification narrowed our list of possible media for application at Tahoe. Industrial byproducts such as slags risk possible leaching of heavy metals and this potential cannot be easily predicted. Fly ash and other fine particle substrates would be more difficult to apply because they would need to be blended, making them less desirable and more costly to apply than larger diameter media. High transportation costs rule out non-local products. Finally, amorphous calcium products will eventually cementify reducing their effectiveness in filtration systems. Based upon these considerations, bauxite, LWAs and expanded shales/clays, iron-rich sands, activated alumina, marble and dolomite, and natural and lanthanum activated diatomaceous earth were selected for testing by this project. These materials are typically iron, calcium or aluminum based; many have a high specific surface area; and all have low transportation costs.

A number of physical and chemical characteristics affect phosphorus uptake potential and rates including specific surface charge, likelihood to form precipitates, and pH. This literature review discusses the different substrates studied for phosphorus removal and their removal mechanisms. This literature review also discusses the logistics of using different media at Lake Tahoe and recommends media to test at Lake Tahoe.

3 Experimental Methodology

Three experiments have been conducted for this project:

1. Isotherm studies to describe and quantify P uptake capacity of different tested adsorptive media;
2. Laboratory breakthrough column studies to develop retardation rates for different adsorptive media and local soils; and
3. Field column studies to quantify the confounding effects of stormwater on adsorptive media and quantify the uptake capacity of these different media when treating the more complex chemistry of stormwater.

This section provides an overview of the experimental design of the laboratory studies. Appendices 2, 3 and 4 are referenced in this section. Appendix 2 summarizes the experimental design that was conceived and generally followed for these studies. Appendices 3 and 4 provide the standard operating procedures (SOPs) that were developed for the laboratory and field column studies.

3.1 Isotherm Studies

Isotherm studies are laboratory experiments in which a mass of substrate is mixed in a solution that is spiked with a solution of specific phosphorus concentration. After a period of mixing on a shaker-table, usually 24 to 48 hours, the concentration in the solution is measured, and uptake by the tested substrate is calculated by difference. Substrates are tested in a number of solutions, each with a different initial P concentration. These treatments are replicated. For each treatment, the final P concentration in solution and the calculated P concentration in the substrate are recorded, and these values describe the equilibrium uptake characteristics of that tested substrate.

A number of equations have been found that model these equilibrium relationships:

1. Langmuir isotherm
2. Freundlich isotherm
3. Linear isotherm

Each of these was fitted to the data, and the constants used to describe the data were calculated. These constants allow us to compare the uptake characteristics of these media not only for the different media tested in this study but also with the results of other studies in which other media were tested.

These studies thus characterize the *equilibrium* uptake characteristics of the different media and allow us a means to predict which media are more likely to be effective for use in the Tahoe Basin. From these isotherms we are able to also calculate retardation coefficients for different media, which can then be used to predict how these media will retard the flow of phosphorus when water is flowing through the media. This prediction is useful in assessing the utility of these different media for filtration applications.

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Media tested in these isotherm experiments were based upon the results of the literature review and included activated alumina, iron and/or lanthanum coated diatomaceous earth, bauxite, dolomite, expanded shales and other lightweight aggregates, and native Tahoe soils. Some of these media were tested on the recommendations of OWP, since OWP was considering a number of different substrates and felt these tests would be useful in assessing the different media being considered. Each media was mixed for 24 hours with a number of water solutions containing different concentrations of P, ranging from 0.01 mg/L to 5000 mg/L. These concentrations were selected so that we could characterize P uptake at P concentrations typical of stormwater (0.01 to approximately 0.2 mg/L), as well as to test the media at P concentrations where we expect to see saturation. The results from these tests allow us to then effectively fit the data with one of the isotherm models.

3.2 Laboratory Breakthrough Column Studies

Laboratory column studies were planned for three or four of the most promising media based upon the isotherm results. The goal of these studies is to determine the P uptake and retention characteristics of different tested adsorptive media. Additionally local soils were tested so that a comparison could be made between adsorptive media and local soils.

Adsorption column tests go beyond isotherm studies in that they integrate physical characteristics and properties such as cementification, diffusion and hydraulic conductivity with phosphorus removal by adsorption and precipitation. Furthermore, they integrate the phosphorus removal by adsorptive processes with removal by filtration processes. Thus, adsorption columns allow a monitoring of steady state and perhaps non steady-state water quality under continuous P loading conditions. Finally, they provide a good estimate of media uptake capacity and modeled breakthrough characteristics of the adsorptive media when it reaches saturation.

Adsorption column studies were conducted using 3" PVC columns and fairly standardized methods. These column studies were conducted under conditions in which the media were flooded in order to minimize short-circuiting of flow paths through the media. During these tests, P dosed and non-dosed DI water was fed into the columns, traveled upward through the media and then flowed out from the top. Water quality samples were taken at the inflows and outflows of the columns and flow rates were monitored.

Column studies were conducted in three sequential phases:

1. Initial P leaching phase in which columns are loaded with DI water to leach out any P associated with the media. Columns are operated in this phase until P concentrations in the outflow show that leaching is no longer occurring.
2. P adsorption phase in which the columns are loaded with DI water spiked with P to a concentration of around 1 to 2 mg/L. Columns are operated in this phase until P concentrations in the outflow increase signifying that the P front has traveled through the media and breakthrough is occurring.

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3. P desorption phase in which the columns were loaded with DI water. Columns are operated in this phase until P concentrations in the outflow show that no P is desorbing from the adsorptive media.

For the column tests, adsorptive media and local soils were compared against sand. Sand has essentially no P uptake capacity and is thus used as a control. For each phase, flow and the P concentration in the inflow and outflow were measured. Data were put into a database such that the time to and volume required for breakthrough could be calculated. Because these columns used DI water dosed and not dosed with P, they measured the P uptake characteristics of these different media isolated from other stormwater effects.

Appendix 2 provides a detailed description of the experimental design of this study. Appendix 3 provides the standard operation procedures (SOP) developed for this study, which includes a layout of the equipment. These studies are currently ongoing. Local soils and sand have been tested and four adsorptive media (e.g. Utelite, dolomite, activated aluminum and lanthanum-activated diatomaceous earth) are currently being tested. Breakthrough of the P front has not occurred in the activated aluminum or lanthanum-activated diatomaceous earth columns.

3.3 Field Column Studies

Field Column Studies are being conducted on a selected subset of candidate adsorptive media to experimentally determine levels of phosphorus removal that can be achieved under real stormwater conditions and for a variety of runoff. These tests are the final step in assessing the chemical and physical characteristics of these media for P removal. The subset of media tested in this study was selected after assessment of data from the literature review, isotherm tests and breakthrough studies.

Appendix 2 presents the initially planned experimental design for these studies as well as sketches describing the initially planned field equipment and its layout. These tests were initially planned for deployment in the field directly at a basin. But we have decided that we could achieve very similar results by deploying these columns at the TRG lab in Tahoe City and use real stormwater collected from stormwater basins in Placer County. Thus, this design has changed such that each column is setup on a common manifold through which the collected stormwater is pumped. This provides greater control of exogenous variables and more replication with the test media.

For these field tests, several replicated media treatments are being conducted:

- Sand is used as a control as sand has essentially no uptake capacity,
- Dolomite, Utelite, activated alumina and lanthanum-coated diatomaceous earth are being tested as the different adsorptive media treatments.

As in the laboratory columns, flow and water quality measurements are planned and data will be put into the same database as has been used for the laboratory column studies. This will enable us to determine the P-uptake capacity of the different media under real stormwater conditions and to compare that data with the data from the laboratory column studies in which the media are loaded with only P-spiked laboratory water. The water

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quality data collected in these experiments will include concentration analysis for total dissolved P and orthophosphorus, dissolved organic carbon, dissolved iron and aluminum, and the measurement of pH.

The column setup has been installed at the TRG lab and the SOP for this work has been written (Appendix 4). These experiments are planned for April and May 2005.

4 Results and Discussion

With the various studies and experiments, we are at several levels of data collection and analyses. The literature review is complete. The isotherm studies and their data analyses are complete. The laboratory column studies are ongoing. Local soils have been tested for those studies, and the adsorptive media tests are ongoing (we are still waiting for breakthrough to occur). These studies are planned for completion by May 2005 with data analyses occurring in June and July 2005. The field column studies have not begun and are planned for completion by May 2005 with data analyses following in June and July 2005. The final report amendments are planned for August 2005. The schedule for completing this study is shown in Figure 4-1. This following sections detail results to date.

Project Component	2005						
	Mar	Apr	May	Jun	Jul	Aug	
Laboratory Column Studies							
Experiments	Ongoing						
Data Analyses							
Field Column Studies							
Experiments							
Data Analyses							
Final Report Amendment							

Figure 4-1. Schedule to Complete Adsorption Column Study

4.1 Isotherm Studies

Table 4-1 shows the different media that were tested during the isotherm analyses. Wollosthanite, iron-lanthanum coated diatomaceous earth and a limestone from outside of California were selected beyond those substrates recommended from our literature review in order to provide OWP with information that would aid them in their assessment of adsorptive media for highway applications. Figure 4-2 shows isotherm data for two of the substrates tested to which Langmuir isotherm models were applied:

- Dolomite which has relatively low uptake capacity and
- Lanthanum-coated diatomaceous earth which has relatively high uptake capacity.

Appendix 5 provides an in depth analysis of the data from these experiments. What follows is a summary of that report.

4.1.1 Isotherm models

Media tested during these experiments were fitted with three isotherm models: Freundlich, Langmuir and linear isotherms. For the tests we conducted, Langmuir isotherms generally provided the best fit for the data over the full range of phosphorus adsorption. This range was typically from 10 ppb to up to 5,000 ppm and for this range

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the R² was generally between 0.88 and 1.00, except for two media. Based upon the Langmuir isotherms, performance for the different media vary greatly with maximum uptake rates varying over nearly two orders of magnitude. More engineered substrates like activated alumina and lanthanum-coated diatomaceous earth perform much better than any of the naturally occurring media or local soils.

However, for low phosphorus concentrations typical of Lake Tahoe stormwater, these results are somewhat misleading. Tahoe stormwater typically has a phosphorus concentration in the range of 10 to 1,000 ppb, and for these low concentrations, neither the Langmuir nor Freundlich isotherm is a particularly good predictor. This poor relationship is shown in residual analyses, in which residuals for low uptake concentrations are often of a similar or greater magnitude than the predicted value itself. Thus, at these low phosphorus concentrations, linear isotherms are often the best predictor (Figure 4-3). In an analysis of slopes, the differences between the media are much smaller than in the Langmuir analyses. As with the Langmuir analysis, activated alumina and lanthanum coated diatomaceous earth are the better performers. However, unlike the Langmuir analyses, other media such as Utelite (an expanded shale) and Dolomite sometimes perform at a similar level, depending upon the method of analyses. This similarity in performance is shown again when measuring uptake rates for different phosphorus loading rates.

4.1.2 Direct analyses of data at low P loading rates

To better understand the performance of these media, we looked at the data only for low loading rates between 100 and 10,000 ppb. At those loading rates, the best performing media only perform slightly better than the average performing media.

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Table 4-1. Tested Media

Tested Media	Code
<i>Native soils</i>	
Elois Basin	ELOIS
Coon Street Basin	COONS
Round Hill Basin	ROUND
<i>Placer County Study Selected Media</i>¹	
Activated Alumina DD2 ⁴	ALDD2
Activated Alumina CD714 ⁴	CD714
Bauxite, 16 - 20 mesh	BXTLG
Dolomite, 20-mesh	DOL20
Riverside Expanded Shale	XSHAL
Utelite Expanded Shale	UTILT
Lanthanum coated silica ²	LANSI
Diatomaceous Earth, MP79	MP79D
Lanthanum coated MP79	MP79L
<i>OWP CSUS Media</i>	
Wollostanite	WOLLO
Iron-Lanthanum coated MP79	MP79F
Limestone ³	CALIM

1. Media selected based upon screening study done as part of Placer County Kings Beach study.

2. Laboratory product from University of Nevada Reno.

3. Limestone supplied from outside California. Previously tested limestone was metamorphic limestone from California

4. Activated alumina products from Alcoa

4.1.3 Ranking Media

Based upon these analyses, we developed an overall ranking for the media, which included results from the isotherm analyses and measured uptake rates. Media were ranked in several ways to select media appropriate to the Tahoe Basin for further testing:

- Maximum adsorption capacity as determined from Langmuir isotherm model;
- Phosphorus uptake characteristics at low water phase P concentrations as predicted by linear isotherm models;
- Phosphorus uptake at an equilibrium water phase concentrations at the surface water standard ($P_{eq} = 100$ ppb); and
- Phosphorus uptake characteristics near typical stormwater loading rates (100 ppb to 10 ppm).

This ranking was developed to better assess media performance in a way that considered performance at low concentrations but also performance at higher loadings. From this analysis we recommended that activated alumina, lanthanum coated diatomaceous earth, dolomite and Utelite be considered for further testing (Table 4-2). We believe that these media will all have greater uptake capacities than the locally available soils.

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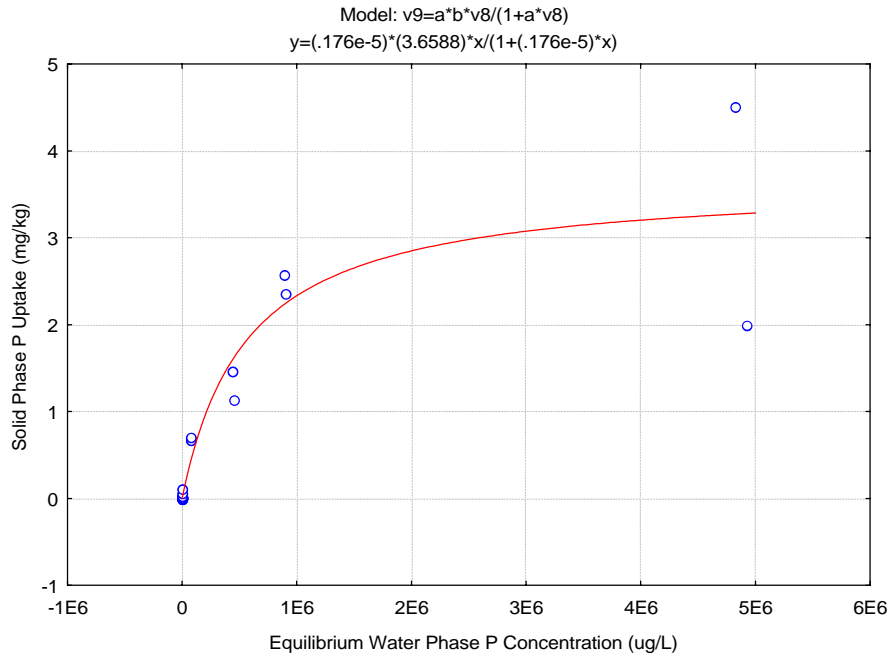
Table 4-2. Media selected for further testing

	Performance at High P Conc	Performance at Low Dosing Concentrations			Summary		Notes
	Maximum adsorptive capacity	Ranking based upon slopes of Linear and Langmuir Isotherms	Ranking based up Cs calculated for Peq = 100 using all isotherms	Cs measured at typical stormw ater concentrations (100, 1000, 10000 ppb)	Total	Final Rank	
ALDD2	2	1	2	3	6	1	3
BXTLG	10	10	9	11	30	10	
CD714	3	3	3	4	10	3	1
COONS	11	15	11	8	34	11	
DOL20	8	6	6	4	16	5	3
ELOIS	14	13	14	10	37	13	
LANSI	4	7	8	1	16	5	2
MP79D	15	11	12	12	35	12	
MP79F	7	4	4	13	21	7	
MP79L	1	1	1	6	8	2	3
ROUND	13	14	15	13	42	15	
UTILT	6	5	4	2	11	4	3
WOLLO	12	9	13	15	37	13	
XSHAL	9	7	7	7	21	7	
CALIM	5	11	10	8	29	9	
Notes							
1. CD714 not selected for future testing as it is very similar to ALDD2.							
2. LANSI not selected for future testing as it is similar to lanthanum coated MP79L and is only available from a UNR lab.							
3. Selected for recommendation for further testing.							

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Figure 4-2. Isotherm data fitted with the Langmuir model.

a. Coon Street Basin Soil



b. Lanthanum coated MP79

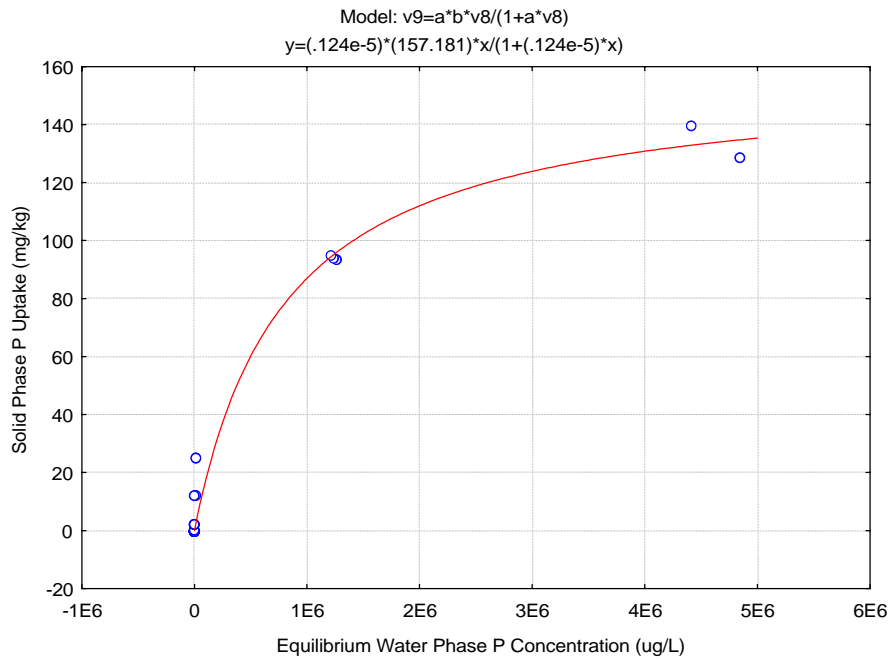
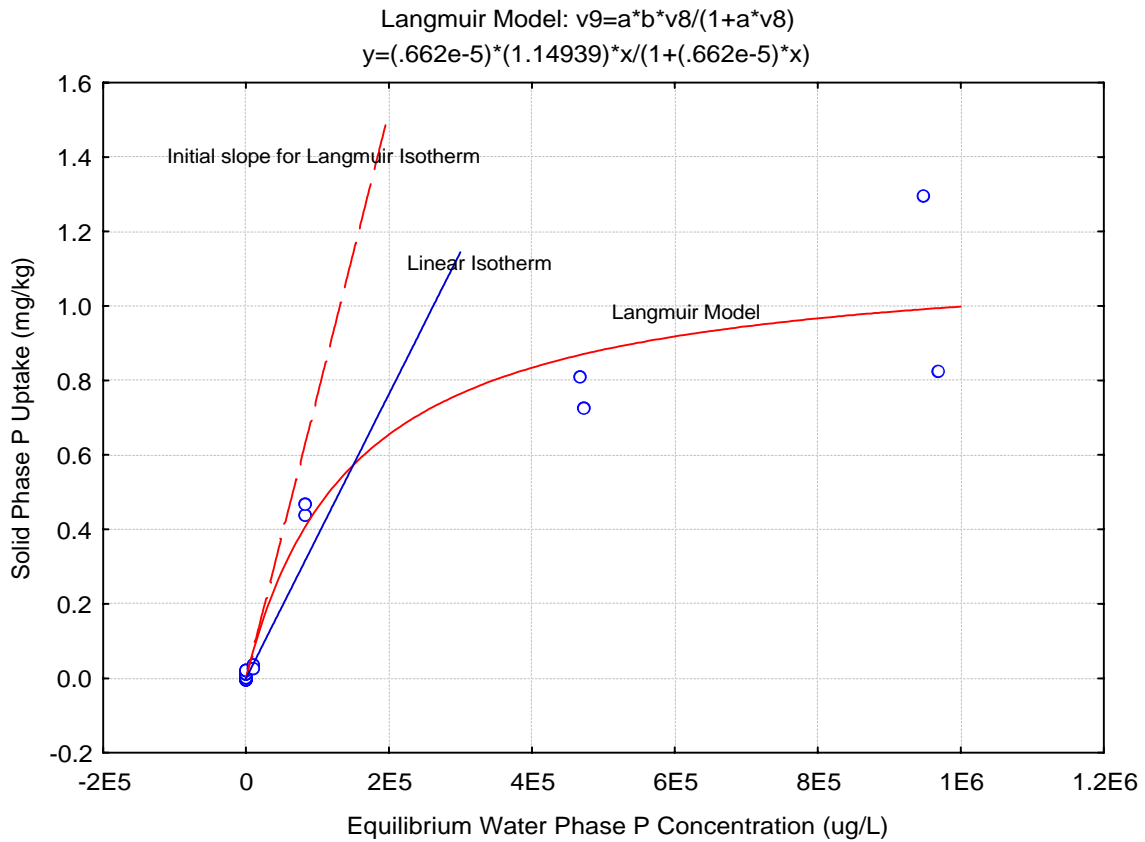


Figure 4-3. Langmuir and Linear isotherms fit to data from Round Hill soils



4.1.4 Retardation Factors

Finally, in assessing the data, we considered if we could predict the retardation of phosphorus movement through these different substrates. Soils with greater adsorptive capacity are predicted to retard phosphorus movement through soils based upon the following relationship:

$$R \equiv 1 + \frac{\rho_b K_d}{n}$$

where

n is the porosity,

ρ_b is the dry bulk density.

K_d is the adsorption coefficient determined from a linear isotherm model

and

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R = the retardation coefficient that is defined as the ratio of the water velocity to the contaminant velocity:

From this relationship, we can see that the adsorption coefficient that depends upon the chemical nature of the media and physical characteristics of porosity and bulk density should affect how much the application of a specific media should retard the movement of phosphorus under ideal flow conditions. This has applications not only in regards to retrofitting stormwater treatment BMPs but also with regard to applying adsorptive media to infiltration areas to help prevent the movement of a P plume into the subsurface zones.

Using this expression, preliminary retardation factors have been calculated for the three Basin soils as well as for the Martis Valley sands and dolomite (Table 4-3). These calculations are based upon standard porosity and dry bulk density values for mixed grain or fine sands. These results show that Tahoe soils are expected to retard P at a similar rate. In comparison, two media selected for further testing, activated alumina and lanthanum-coated diatomaceous earth are predicted to retard P movement by an order of magnitude or better. These numbers are only preliminary at this time and will be verified during the adsorption column studies. Nonetheless, they show the potential promise of utilization adsorptive media to improve P removal in retrofitted basins and to help retard P movement through soils in infiltration zones.

Table 4-3. Preliminary Retardation Factors for Selected Soils and Adsorptive

Soil/Media	Retardation Factor R_d^c
Activated Alumina	1117
Lanthanum Coated DE	888
Coon St. Basin	81
Round Hill Basin	25
Eloise Basin	125
Fine Truckee Sand ^b	23
Course Truckee Sand ^b	6

Notes

- a. Based upon equilibrium phosphorus concentrations in the water of < 10 ppm.
- b. From Martis Valley, Truckee, CA.
- c. Assumed porosity of 30% and a dry bulk density of 1.86 g/cm³ based upon dense mixed-grain sand (Terzaghi and Peck, 1967) or fine gravel and sand (Garde and Rau, 1987)

4.2 Laboratory Column Studies

Column leaching, adsorption and desorption studies are being conducted on four adsorptive media: dolomite, the expanded shale Utelite, lanthanum coated diatomaceous

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earth and activated alumina, as well as on a control of sand. These studies are similar to studies on local soils that were conducted for the TRPA (Heyvaert et al., 2004). In the TRPA studies, soils were collected from three Tahoe Basins: Coon Street, Eloise, Round Hill.

The TRPA report describes the water quality from these flows through column studies during the three phases. For these studies, the hydraulic residence time for the columns was just over one hour. Thus, each hour of operation represented the complete exchange of pore water volume. For ease of understanding, we describe each period of time during which all the pore water volume in the column has been exchanged as a *cycle*.

During the leaching phase, most P leaching occurred during the first four to five hours. During the following adsorption phase, P concentration breakthrough occurred between 20 and 60 hours after P dosing began depending upon the soil. Measured breakthrough was in fairly good agreement with those predicted by the retardation calculations utilizing the isotherm data. In general, the predicted retardation factors and the measured retardation factors were off by less than a factor of two. Finally, during the desorption phase, most desorption occurred relatively quickly as occurred during the leaching phase, though desorption of P occurred over an extended period of time and P concentrations in the outflow waters were higher than they had been during the leaching phase. More detailed analyses of these data can be found in the TRPA report (Heyvaert et al., 2004).

For this project, the laboratory column studies are ongoing. Preliminary data shows that activated alumina and lanthanum coated diatomaceous earth have continued to retain P over several hundred cycles, thus improving P adsorption by at least one to two orders of magnitude than the local soils. This analysis is very preliminary. We are currently putting data from these studies into a Microsoft Access database to better evaluate the uptake characteristics through a more comprehensive mass balance analysis (Appendix 6). Data from the TRPA study will also be put in the same database such that the same statistics and analyses can be conducted on both. These experiments have not shown breakthrough of P so far, and we expect to run the columns through March and April. Data analyses will follow in May and June.

4.3 Field Column Studies

Data collection has not yet begun on this study. Data will be collected during April and May, with data analyses subsequently following in June and July. Data for this study will be put into the same database designed for the laboratory column studies (Appendix 6).

5 Conclusions

We have several main conclusions from the adsorptive media studies conducted to date:

- There appear to be opportunities to improve the performance of stormwater treatment basins and wetlands through utilizing adsorptive media. A number of possible media choices exist that would seem good candidates to improve the performance of stormwater basin and wetland BMPs with regard to P removal. The most promising medias that we have tested are activated alumina and lanthanum coated diatomaceous earth. These media do affect pH concentrations in the outflow, and activated alumina has resulted in the leaching of aluminum (Dipen et al., 2005). Both the potentially positive and negative water quality effects need to be further tested. Additionally, other media that have not been tested may also prove effective at P removal.
- Compared to other naturally occurring materials, the Tahoe Basin soils tested have relatively poor phosphorus uptake capacity because of their chemical and physical characteristics. Soil amendments to infiltration areas and use of adsorptive media in stormwater basins would be expected to improve phosphorus removal performance and retard the development and movement of any subsurface P plumes. In both conventional and amended BMPs, periodic adsorptive media replacement may be needed to prevent infiltrated water from becoming sources for subsurface P plumes.
- For synthetic stormwaters, retardation rates predicted from the isotherm studies have been in general agreement with those determined from column studies and thus isotherms appear to be a good first step in estimating phosphorus front velocity and the time it will take for phosphorus breakthrough to occur within a defined soil unit. For real stormwaters, the complex chemistry will likely affect P-uptake performance of the different media, so these estimates should be seen as indicators at this time, identifying order-of-magnitude differences in performance between different media. In developing retardation factors, careful determination of the key soil parameters (e.g. adsorption constant, porosity, dry bulk density) will help provide a better prediction of retardation rates
- Reaction and mass transfer kinetics are important considerations for chemical and biological retention of nutrients extracted from soil waters. Retention efficiency is reduced if water moves through the soils at a rate faster than the dominant removal processes. Determining appropriate flow rates for system design in specific soil types is necessary to assure long-term phosphorus removal by these systems. These kinetics are a consideration when developing retardation rates from isotherm studies.
- These studies have not addressed the implementation issues associated with retrofitting basins or applying these media in infiltration areas. Associated issues include the method of application, the development of design criteria and

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specifications, and the predicted performance goals. If these studies show that adsorptive media can improve P removal, these other issues should be investigated. Larger-scale experimental pilot systems in coordination with small-scale laboratory studies will likely be needed to address these questions before large-scale implementation around the Basin can be implemented. Some of these issues are being partially addressed in current OWP pilot-scale studies (Dipen et al., 2005) though these experiments are mainly focusing on highway runoff.

These studies are expected to address a number of issues more completely:

- The development of more accurate retardation factors for the different media currently being tested in the laboratory columns and a comparison of those factors to local soils.
- A better understanding of the effects on P removal performance that can occur when real stormwater is being treated by the different media.
- The effects of the different media on a number of other water quality parameters, including dissolved organic carbon, pH and dissolved aluminum, iron and calcium. These results will provide insight on the processes retaining P in the media and potential secondary water quality effects.

From these studies, we plan to develop recommendations, which are expected to include a discussion of potential designs and application strategies to improve the performance of existing and new stormwater treatment BMPs.

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Appendices

ADSORPTIVE MEDIA INVESTIGATION

Appendix 1 – Adsorptive Media Literature Review

2003.01

Literature Review

**Potential Application of Adsorptive Media to Enhance Phosphorus
Uptake in Stormwater Basins and Wetlands at Lake Tahoe**

Final Revision

**By Philip A.M. Bachand, Ph.D.
Bachand & Associate**

**submitted to the
University of California Davis
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Abstract

Phosphorus removal by wetlands and basins in Lake Tahoe may be improved through designing these systems to filter stormwater through media having higher phosphorus removal capabilities than local parent material. Substrates rich in iron, aluminum and calcium oftentimes have enhanced phosphorus removal. These substrates can be naturally occurring, byproducts of industrial or water treatment processes, or engineered. Phosphorus removal fundamentally occurs through chemical adsorption and/or precipitation and much of the phosphorus can be irreversibly bound. In addition to these standard media, other engineered substrates are available to enhance P removal. One such substrate is locally available in Reno and uses lanthanum coated diatomaceous earth for arsenate removal. This material, which has a high positive surface charge, can also irreversibly remove phosphorus. Physical factors also affect P removal. Specifically, specific surface area and particle shape affect filtration capacity, contact area between water and the surface area, and likelihood of clogging and blinding. A number of substrates have been shown to effectively remove P in case studies. Based upon these studies, promising substrates include WTRs, blast furnace slag, steel furnace slag, OPC, calcite, marble, Utelite and other LWAs, zeolite and shale. However, other nonperformance factors such as environmental considerations, application logistics, costs, and potential for cementification narrow the list of possible media for application at Tahoe. Industrial byproducts such as slags risk possible leaching of heavy metals and this potential cannot be easily predicted. Fly ash and other fine particle substrates would be more difficult to apply because they would need to be blended, making them less desirable and more costly to apply than larger diameter media. High transportation costs rule out non-local products. Finally, amorphous calcium products will eventually cementify reducing their effectiveness in filtration systems. Based upon these considerations, bauxite, LWAs and expanded shales/clays, iron-rich sands, activated alumina, marble and dolomite, and natural and lanthanum activated diatomaceous earth are the products most likely to be tested for application at Tahoe. These materials are typically iron, calcium or aluminum based; many have a high specific surface area; and all have low transportation costs.

1. Introduction

Phosphorus removal by wetlands and basins in Lake Tahoe may be improved through designing these systems to filter stormwater through certain types of media having high phosphorus removal capabilities than local parent material. Studies have shown using substrate rich in iron (Fe), aluminum (Al) or calcium (Ca) concentrations enhances phosphate removal in experimental subsurface wetlands beyond that which can be achieved by using native soils (Arias *et al.* 2001; Pant *et al.* 2001; Grüneberg and Kern 2001; Mæhlum and Stålnacke 1999; Cerezo *et al.* 2001; Comeau *et al.* 2001). Substrates studied include fly ash, steel furnace slag, blast furnace slag, red mud, limestone, zeolite, iron-rich sands, laterite, bauxite, burnt oil shale, shale, light expanded clay aggregate (LECA), crushed marble, vermiculite and calcite (Comeau *et al.* 2001; Sakadevan and Bavor 1998; López *et al.* 1998; Ugurlu and Salman 1998; Wood and McAtamney 1996; Drizo *et al.* 1999; Brix *et al.* 2001). Thus, utilizing media with higher P uptake potential may make these basins more effective at P removal.

A number of physical and chemical characteristics affect phosphorus uptake potential and rates including specific surface charge, likelihood to form precipitates, and pH. This literature review discusses different substrates studied for phosphorus removal and their removal mechanisms. This literature review also discusses the logistics of using different media at Lake Tahoe and recommends media to test at Lake Tahoe.

2. Examples of Different Substrates Used for Phosphorus Removal

Typically, substrates studied for enhanced phosphorus removal have elevated aluminum (Al), iron (Fe) or calcium (Ca) concentrations. Aluminum, iron and calcium rich materials have been shown to enhance P removal as previously discussed and the mechanisms for removal are discussed in Section 2. Different substrates have been studied in different parts of the country and world. One major reason for this different testing preference by region is transportation costs. Transportation costs can be the highest costs associated with these different media, especially in the case of natural materials and industrial byproducts. Thus, source location of the substrate is very important in determining which material to consider for an application and this issue is reflected in the studies that have been done to date by others.

Many of the substrates tested are naturally occurring. Others are byproducts of industrial or wastewater processes. Finally, some are engineered. Of these different substrates, most are based upon the principal that aluminum, iron and calcium enhance dissolved phosphorus removal through precipitation or adsorption of dissolved phosphorus species. Table 1 shows the chemical characteristics of selected substrates for which there was published data. For many of the substrates discussed here, data in the form shown in Table 1 were not available.

2.1 Natural and local mineral soils.

Zeolite, bauxite, laterite, dolomite, shale, limestone, calcite, vermiculite and iron-rich sands are naturally occurring minerals tested for phosphorus removal. Some of these are iron and/or aluminum rich and some of these are calcium rich.

Zeolite, bauxite, laterite and shale are aluminum- and/or iron-rich. Zeolite is a hydrous aluminum silicate. It is composed primarily of silica oxides and secondarily of aluminum oxides (Sakadevan and Bavor 1998). Calcium, ferric, magnesium and titanium oxides are also found in zeolite at much lower concentrations. Bauxite, a naturally occurring mixture of hydrous aluminum oxides and aluminum hydroxides, is the principle source of aluminum and is also high in ferric oxides. Laterite, a low grade bauxite (Wood and McAtamney 1996), is red in color and high in iron oxides and aluminum hydroxides. Shale is a fissile rock formed by the consolidation of clay, mud, or silt. It has a laminated structure, and is composed of minerals essentially unaltered since deposition. Shale has high concentrations of iron and aluminum (Pant *et al.* 2001).

Limestone, marble, wallastonite and dolomite are calcium-rich. Limestone is a rock formed primarily by the accumulation of shells, coral and other calcium rich organic matter and consists mainly of calcium carbonate. Marble is essentially crystallized limestone. Dolomite is mineral consisting of calcium magnesium carbonate. Wollastonite is a native calcium silicate.

2.2 Industrial or wastewater byproducts

Several industrial and wastewater byproducts have also been tested by others. These include blast furnace slag, steel furnace slag, red mud, Lightweight Aggregates (LWA) of which Light Expanded Clay Aggregates (LECA) is a subset, Fly ash, HiClay Alumina (HCA), and aluminum and iron based water treatment residuals (WTR). All these materials are either rich in aluminum, iron and/or calcium.

Blast furnace slag has tested in several studies (Johansson 1999; Agyei *et al.* 2002; Grüneberg and Kern 2001; Sakadevan and Bavor 1998) and is an industrial by-product of iron ore processing. Its composition varies with the ore used. Blast furnace slag is rich in calcium oxide (33 – 43%) and is also relatively high in aluminum oxide (9 – 16%; Table 1). Blast furnace slag can be granulated by rapid quenching (Sakadevan and Bavor 1998). It has been tested for use in wastewater treatment and in constructed wetlands.

Sakadevan and Bavor (1998) tested steel furnace slag, which is rich in both iron and calcium (Table 1). Steel furnace slag results from the conversion of pig-iron to steel and consists of iron, aluminum and calcium oxides.

Lopez *et al.* (1998) investigated using red mud to remove phosphorus from secondary effluent for the removal of phosphorus and heavy metals. Red mud is a byproduct of bauxite refining and composed primarily of iron, calcium and titanium oxides, though also having nearly 5% of calcium oxide as well (Table 1; Lopez *et al.* 1998). It has a high initial pH and forms stable suspensions in water. When pretreated with 8% anhydrite, it forms aggregates stable in aqueous media and has a lower pH, just above neutral (Lopez *et al.* 1998).

HiClay Alumina is a byproduct of the commercial alum production, consisting of bauxite impurities that did not react with sulfuric acid used to produce alum. It has a similar elemental composition to that of highly weathered soils (Haustein *et al.* 2000) and is approximately 1.5% aluminum.

Water Treatment Residuals (WTR) are byproducts of potable water treatment. Haustein *et al.* (2000) investigated WTR produced from water treatment with alum. It is typically composed of coagulated aluminum compounds and other materials like sand, silt, clay, bacteria and color-forming compounds found in raw water. WTR are typically similar to natural soils in both the metal concentrations, like Al, as well as in trace element concentrations unless the source water is grossly contaminated (Haustein *et al.* 2000). Aluminum concentrations are approximately three times higher than in HiClay Alumina at roughly 5%.

WTR can also be iron based. Brown (1999) studied blending iron-rich WTR with sand to improve fertilizer uptake and retention for use on golf greens. This iron-rich WTR results from using ferric sulfate to treat drinking water. The Ferric Sulfate reacts with the natural organic material (NOM) in colored surface waters to form Iron Humate®, a registered product of Kemiron.

Fly ash has been the subject of many studies including those focusing on wastewater treatment (Agyei *et al.* 2002; Ugurlu and Salman), constructed wetlands (Sakadevan and Bavor 1998;

Drizo *et al.* 1999, Mann 1997) and infiltration (Cheung and Venkitachalam 2000). Fly ash is a residue of combustion from coal power plants (Ugurlu and Salman 1998). Fly ash is categorized as Type F which is produced when either anthracite, bituminous or sub-bituminous coal is burned or Type C which normally comes from lignite or sub-bituminous (Rinker Materials 2003). The amount of calcium, silica, alumina and iron content in the ash differentiates these two classes. Type F fly ash, typically has total calcium ranging from 1 – 12% with it in the form of calcium hydroxide, calcium sulfate and glassy components combined with silica and alumina (Turner-Fairbank 2003). Type C can have calcium oxide as high as 30 – 40% and has higher sulfate concentrations. Silica and aluminum oxide concentrations are higher in Type F fly ash, and calcium oxide concentrations are higher in Type C (Grubb *et al.* 2000). Type F fly ash are more acidic. Approximately sixty million tons of fly ash are produced annually in the United States and only 25 – 30% of the material is reused (Grubb *et al.* 2000).

Lightweight aggregates (LWAs) are factory made filter media used mainly for construction material such as building blocks but recently tested for phosphorus removal (Zhu *et al.* 1999). Some LWAs are clay-based and some are shale-based; thus their chemical composition varies according to the parent material. LECA is one such material, produced in Norway. It is clay aggregate formed by expanding clay minerals at high temperatures (Drizo *et al.* 1999).

2.3 Engineered Substrate

Some substrates have been engineered for phosphorus removal and are proprietary. Some of these substrates are based upon the principle that iron and aluminum rich materials enhance P uptake. One such substrate is activated alumina. Activated alumina is used commercially from several manufacturers and is used for removal of phosphorus and other pollutants. Activated alumina is characterized by high aluminum content, high specific surface area and high macroporosity. LWAs can also be considered engineered substrates in some respects. These substrates are engineered for other purposes but because of their relatively high specific surface area and high aluminum content some of these substrates are also good for phosphorus removal.

Other engineered substrates rely on other technologies. Phoslock™ is a modified clay developed by CSIRO Land and Water. Laboratory batch studies by CSIRO have shown that Phoslock™ effectively reduces filterable reactive phosphorus and in field mesocosm studies this removal has been shown to be approximately 90% (Douglas *et al.*, unpublished). There is very little information on the mechanisms for phosphorus removal by Phoslock™ as the product is pending patents.

Another such proprietary product is modified or activated diatomaceous earth (DE). Modified diatomaceous earth (MDE) utilizes lanthanum oxide and lanthanum-alumina oxide to remove phosphorus. This technology was first developed for arsenic and arsenate removal (Misra and Lenz, 2003) but has been recently been shown to effectively remove phosphorus as well (Misra, unpublished data). The mechanisms for phosphorus removal are discussed in Section 2. This technology was developed at the University of Nevada Reno Lackey School of Mines and products based on this technology are available locally to Lake Tahoe from Eagle-Picher Minerals, Inc., located outside of Reno, Nevada.

3. Chemical Mechanisms for P removal

Two mechanisms lead to phosphorus removal, adsorption and precipitation. Under appropriate pH conditions, all the above media have been tested and found to have some success in phosphorus removal. However, pH is an important consideration when predicting which substrate is likely to be among the more effective and the associated mechanisms controlling phosphorus removal. In general, alkaline environments favor phosphorus (P) removal by calcium through adsorption and precipitation whereas low pH and acidic environments favor removal by iron and aluminum (Ugurlu and Salman 1998).

3.1 Iron and aluminum rich minerals

In acidic to neutral environments, phosphate ions are chemically adsorbed onto Fe and Al oxide surfaces through ligand exchange (Wood and McAtamney 1996). In many substrates, P adsorption correlates better with the amount of oxalate extractable aluminum and iron than with other independent factors such as total aluminum or iron, or specific surface area (Sakadevan and Bavor 1998; Reddy *et al.* 1995). Oxalate extractable iron or aluminum represents amorphous and poorly crystalline oxides of Al and Fe. This fraction, rather than the crystalline phases, is often more critical for P removal in iron and aluminum rich minerals. This explains why Baskaran *et al.* (1994) found that allophanic soil adsorbed 7 times more phosphate than non-allophanic soil. As pH rises above 7 – 8, P adsorption by amorphous iron and aluminum decreases (Grubb *et al.* 2000).

However, this fraction may also not be thermodynamically stable (Misra, personal communications). As the amorphous structure of these substrates evolves into more ordered and crystalline structures, P may be released.

Hongshao and Stanforth (2001) use a two-phase model to describe P uptake onto iron oxides. They propose in their model that adsorption initially occurs rapidly through formation of a surface precipitate. This precipitate is non-exchangeable. These sites then act as sorption sites for dissolved iron, which in turn sorbs more phosphate slowly from solution, forming an amorphous iron phosphate precipitate. This model is only one model used to describe this process and is not the definitive model describing this process.

During P uptake, other ions compete with phosphate for adsorption. Arsenate (AsO_4) competes with phosphate for uptake onto the iron hydrogen oxide goethite (Hongshae and Stanforth 2001). Sulfate, arsenate and silicic acid compete with phosphate for uptake by both allophane, an amorphous aluminum crystal, and gibbsite, an amorphous iron oxide (Gustafsson 2001). This competitive adsorption may be caused by either direct competition for adsorption sites or through changes in surface charge upon adsorption (Geelhoed *et al.* 1997). Regardless, this competitive adsorption is likely a factor in why red mud, laterite and other iron and aluminum rich substrates can effectively removal heavy metals like manganese, chrome, lead, cadmium, copper, nickel and zinc in addition to P (Lopez *et al.* 1998; Wood and McAtamney 1996).

For iron and aluminum substrates, P uptake rate will decrease over time as the P concentrations increase in the substrate (Ugurlu and Salman 1998; Haustein *et al.* 2000). The rate of decrease is dependent upon the P loading rate and at low loading rates may be negligible over time (Grüneberg and Kern 2001). Much of the bound P is likely to be irreversibly bound. Mann

(1997) showed in laboratory desorption studies that about 85% of the adsorbed phosphate remained adsorbed to both blast furnace and steel furnace slags during the desorption studies. However, some of the P will likely be adsorbed reversibly and as substrate are used and become more saturated with respect to P, higher phosphate concentrations are to be expected in the outflow under equilibrium conditions (Pant *et al.* 2001). The increase in equilibrium phosphate concentration in the outflow will depend upon the chemistry of the media and its P loading history.

Finally, uptake will be pH dependent. Oh *et al.* (1999) found that optimum pH for iron and aluminum based materials were at about 5.4 and decreased with increasing pH.

3.2 Calcium rich minerals

Ugurlu and Salman (1998) conclude that at higher pH, phosphate removal occurs through calcium phosphate precipitation. This is supported by a decrease in Ca^{2+} ions and a decrease in pH values found by Ugurlu and Salman (1998) during adsorption studies on fly ash as well as the formation of a white-looking precipitate at the top of the fly ash bed in column studies. Precipitates were originally amorphous calcium phosphate as shown in XRD studies. Johansson and Gustafsson (2000) also found that precipitation was the primary mechanism removing P from solution but calcium and P speciation data ruled out formation of amorphous calcium phosphates. Instead evidence existed that precipitation to hydroxyapatite was the primary mechanism. Hydroxyapatite has low solubility and may tightly bind P.

Regardless of the exact mechanism, Johansson and Gustafsson (2000) concluded the strongest P removal is obtained from substrate from which calcium easily leach to supersaturate solutions with regard to calcium, and for substrate that already contain seeds for hydroxyapatite or other apatite which can act as seeds for precipitation. The rate of calcium desorption may be a primary factor in sorption experiments which show that there is an initially rapid removal of P followed by a lower but more sustained P removal rate. The initially high removal rate is attributed to rapid desorption of calcium from the substrate leading to precipitation (Cheung and Venkitachalam 2000).

For these calcium rich substrates, calcium content and its form is the primary factor determining P sorption capacity (Brix *et al.* 2001, Johansson 1999). Johansson (1999) found that amorphous forms of calcium outperformed crystalline forms.

P removed initially by calcium-rich minerals appears to be relatively insoluble. Mann (1997) tested sandstone, blast furnace slag, granulated blast furnace slag, steel slag, fly ash bottom ash, coal wash and two local gravels. He found P removal was significantly related to Ca, Mg, S and Si concentrations as well as pH. He concluded that high and stable P removal of the slags occurred because stable calcium-P complexes occurred at elevated pH. Effluent pH levels were found to range from 8.5 – 9.5. Slags removed 4 – 8 times as much P as local gravels and desorbed less. O'Reilly and Sims (1995) found similarly that as the percentage of fly ash amended to soils increased, the soils had higher P uptake rates and desorbed less P. O'Reilly and Sims (1995) found that over time the adsorbed and precipitated P removed by fly ash became more stable and was less likely to desorb.

However, P removed by these materials may also later become bound to iron or aluminum complexes or hydroxides. Johansson (1999) found in P fractionation experiments that 50-63% of P removed by blast furnace slag, a substrate high in calcium, was loosely bound while another 34-46% was iron bound even though iron makes up less than 1% of the substrate. Thus, there may not be such a clean break between calcium based processes and iron and aluminum based processes as once P is adsorbed or precipitated onto a substrate, it may migrate to another mineral that might more tightly bind to it.

3.3 Lanthanum based substrates

The University of Nevada Reno and Eagle-Picher Minerals, Inc. have developed a new technology to remove arsenic from drinking water. Naturally occurring DE is coated with nanocrystals of lanthanum (Misra and Lenz 2003). DE is a naturally occurring siliceous sedimentary material resulting from the accumulation of an enormous number of fossil diatoms. Its microscopic structure traps sub-micron particles while maintaining its permeability. Lanthanum is coated onto the DE in a crystalline hydroxy-gel. The hydroxy-gel has a high positive surface charge up to a pH of 11 and this enables negatively charged arsenate to be tightly bonded to the substrate (Misra and Lenz 2003). Arsenate and phosphate compete for adsorption sites. Thus, data shows that the modified DE (MDE) also removes phosphate (Misra, unpublished data).

4. Other factors affecting performance: Specific surface Area, Porosity, pH, hydraulic conductivity

A number of other factors may affect P uptake by different substrates and this includes specific surface area, porosity, cation exchange capacity (CEC), pH and hydraulic conductivity (Drizo *et al.* 1999). Drizo *et al.* (1999) in a study of several different substrates which included bauxite, shale, burnt oil shale, limestone, zeolite, LWA and fly ash found that none of these factors significantly affected phosphate adsorption capacity as determined through the Langmuir equation. This represents the results of laboratory adsorption isotherm batch studies and not that of an adsorption column. In systems in which adsorption and filtration is occurring through columns of some sort, such as in sand filters or subsurface wetlands, these other characteristics can affect P uptake.

4.1 Physical factors: Size distribution, Specific Surface Area, Porosity and Hydraulic Conductivity

Physical factors that compromise water flow and cause short-circuiting and blinding can reduce P removal efficiencies. Hydraulic conductivity, size distribution, porosity and specific surface area are different variables quantifying the physical characteristics of the media. Hydraulic conductivity is dependent upon size distribution, porosity and specific surface area. Porosity is a function of size distribution, specific surface area and particle shape. Thus, size distribution and specific surface area are the key variables defining these physical factors and these two characteristics are discussed below.

Size distribution. Size distribution is expected to affect both physical filtration and adsorption efficiency. In specifying size distribution, a balance exists between too small of particles that will cause clogging and blinding, and too large of particles providing inefficient filtering.

Danish EPA guidelines recommend an effective grain size d_{10} in the range of 0.3 – 2.0 mm, a d_{60} between 0.5 and 8.0 mm, and a uniformity coefficient (d_{60}/d_{10}) less than four (Arias *et al.* 2001). These recommendations are to help ensure adequate hydrologic conductivity and to reduce blinding during filtration. Substrates with smaller particle size distribution are expected to increase the potential for direct reaction between the water and the substrate because these substrates are expected to have the highest surface area. Drizo *et al.* (1999) showed P removal data supporting this expectation with substrates with smaller particles size distribution typically having higher P adsorption capacity as derived from a Langmuir equation. Stevik *et al.* (1999) support these recommendations finding that finer grain media enabled stable unsaturated flow through a greater area of a filter because of the higher capillary forces in finer particles. This reduces diffusion limitations and improves the exchange between mobile and less mobile water.

Specific surface area. Specific surface area is the surface area of the substrate normalized against its mass. It is a function of both the size of the particles but also the structure of the particles and is expressed as m^2/g . Porous or fractured media will have a higher specific surface area than solid media. Thus, porous media such as activated alumina ($>300 m^2/g$), diatomaceous earth ($> 2 m^2/g$), modified diatomaceous earth (lanthanum coated; up to $90 m^2/g$) and LWA have higher specific surface area than solid media such as sands. Stevik *et al.* (1999) showed that specific surface area can enhance pollutant uptake (e.g. bacteria) because of an increased surface area available for adsorption sites. However, the density of charged adsorption sites on the available specific surface area will also affect pollutant uptake. Drizo *et al.* (1999) show an example of this in which zeolite has poor P uptake capacities despite a high specific surface area because of the low density of adsorption sites. Conversely, Misra and Lenz (2003) show MDE with a high arsenate removal capacity because of both its high specific surface area and high charge density.

4.2 pH

During chemical precipitation or adsorption of P by iron, aluminum and calcium, the process affects pH. P removal by iron and aluminum lowers pH and has an optimum of around 5.4 (Oh *et al.* 1999). For P removal by calcium-based substrates in which P is removed by precipitation, pH increases. pH can be increased to as high as 10, as is shown when P is removed by Utelite, an expanded shale. For more crystalline calcium substrate, such as marble or metamorphic limestone such as found in California, pH changes are smaller though the P removal is also less effective. Thus, under acidic conditions, iron and aluminum based substrates tend to be more effective than calcium based substrates. Under basic conditions, the reverse is true. Lanthanum based substrates do not affect pH and P removal with lanthanum based substrates is effective over a wide range of pH, showing similar P removal rates up to a pH of 10.

5. Case Studies and Comparisons Between Substrates

Case studies have shown that adsorptive media can be used successfully as a substrate to improve P removal in subsurface flow wetlands. Grüneberg and Kern (2001) showed blast furnace slag removed P in a subsurface constructed wetland mesocosm under both aerobic and anaerobic conditions. In these systems, most P was removed by the substrate rather than by plant uptake. Under aerobic conditions, the P fraction removed was attributed to loosely bound P or P

associated with Ca or Mg carbonates. This mechanism is very pH dependent. Under anaerobic conditions, slag also stored P but more as a fraction associated with the formation of amorphous iron oxides. This compartment appeared redox-insensitive, forming under both aerobic and anaerobic conditions.

Wood And McAtamney conducted pilot scale constructed wetland tests (5m long x 1 m wide x 0.5 m deep) in systems with *Phragmites spp.* planted in crushed granite gravel with laterite strips. These systems were operated under detention times of 4 – 8 days and achieved 95% P removal, achieving P concentrations of 0.1 mg/L from an inflow of 1.46 mg/L. Cadmium, chrome and lead were also removed.

Several studies have compared substrates:

- Haustein *et al.* (2000) found that Water Treatment Residuals (WTRs) removed 20 times more P than does HiClay Alumina and attributed the higher removal rates primarily to the WTR having aluminum concentrations three times higher. Runoff for WTRs contained higher aluminum concentrations than for HiClay Alumina.
- Johansson and Gustafsson (2000) found blast furnace slag more efficient at retaining P than opoka, a mineral with a high calcium content and not insignificant iron and aluminum concentrations. Though opoka has high calcium concentrations, it was ineffective at P retention and this was attributed to opoka not being able to supersaturate the solution with calcium ions and thus not enable the initiation of precipitation.
- Mann (1997) compared 2 gravels, hawkesbury sandstone, granulated blast furnace slag, blast furnace slag, steel slag, fly ash, bottom ash, and coal wash. He found calcium and magnesium concentrations in the substrates best correlated with P removal performance.
- Agyei *et al.* (2002) compared OTC (ordinary Portland cement), steel slag, and fly ash and found OPC the most effective and fly ash the least effective. CaO concentrations best predicted performance.
- Sakadevan and Bavor (1998) compared six soils, blast furnace slag, steel furnace slag and zeolite. Blast furnace slag was found to have the highest P adsorption capacity and this factor best correlated with the oxalate extractable iron and aluminum concentrations.
- Arias *et al.* (2001) compared different sands and found that calcium content best predicted P removal performance.
- Brix *et al.* (2001) compared 13 sands as well as LECA, crushed marble, diatomaceous earth, vermiculite and calcite. Calcium content was the most important criteria determining performance. Order of performance were calcite, marble, diatomaceous earth, LECA, vermiculite and quartz sand.
- Drizo *et al.* (1999) compared a suite of natural and industrial products, which included bauxite, shale, burnt oil shale, limestone, zeolite, LECA and fly ash. Fly ash and shale had the highest P adsorption values, with bauxite, limestone and LECA with the next highest values. In column studies, the order of effectiveness for adsorbing P was shale, fly ash, bauxite and LECA.
- Zhu *et al.* (1997) compared several LWAs which included LECA with iron-rich sands. They found P removal capacity of the different LWAs varied greatly with higher uptake rates by those LWAs with a higher total metal concentration (i.e. iron, aluminum,

calcium). Poor performing LWAs removed about one order of magnitude less P than iron rich sands. Good performing LWAs removed about one order of magnitude more.

- Oh *et al.* (1999) compared synthetic hematite, goethite and allophane with alumina. Alumina had the second highest adsorption capacity of the four tested compounds and is commercially available.
- Pant *et al.* (2001) found that over time media performance decreased for dolomite, sand and shale. Shale had the highest adsorptive capacity after a period of extended use and thus had the highest capacity of media tested. Over the time period tested, shale had taken up between 71 and 88% loaded P as compared to 56 – 68% with dolomite.
- Phillips (1998) compared zeolite, red mud and calcium phosphate as soil amendments and found when red mud and zeolite were added to sandy soil at a 10% (w/w) ratio, phosphate uptake improvements were negligible. This was attributed to the high pH and predominantly negative charge of the red mud and lack of sorption sites of zeolite.

Tables 2 and 3 summarize these findings. Based upon these comparisons, a number of substrates would seem more promising and just as importantly a number seem not very promising. LECA, vermiculite, uncoated sands, gravels, coal wash bottom ash, Opoka, and HiClay alumina are not promising being either the worst or poorer performers in one of the reported studies (Table 2). More promising substrates are WTRs (iron or aluminum based), blast furnace slag, steel furnace slag, OPC, calcite, marble, UTELITE, and shale. In general, these were either best performers in a reported study (e.g. WTR, blast furnace slag, fly ash, OPC, calcite, UTELITE, shale) or in another study outperformed a substrate that was the best in one study (e.g. steel furnace slag).

Table 4 presents Langmuir isotherm data for the various media. There is great variation in these results. For instance, blast furnace slag has S_{max} values that vary by several orders of magnitude. This variation could be due to several factors including chemical differences in the tested substrate or laboratory methodology differences. Nonetheless, based upon these results, activated alumina is a commercially available substrate that should be added to the list of more promising substrates.

6. Other issues when considering substrates

Several other issues should be considered when selecting coagulants to test. These include potential to environmental considerations, application logistics, transportation costs and cementification.

6.1 Environmental considerations

Heavy metals. Industrial byproducts such as blast furnace slags and steel furnace slags and fly ash have inherently high concentrations of metals. Thus, there may be a higher likelihood with these products than with more natural products or less processed products to leach heavy metals into the environment (Misra, personal communications; Patel, personal communications).

Conversely, several substrates may actually remove heavy metals. Lopez *et al.* (1998) found that red mud removed nickel, copper and zinc. Ugurlu and Salman (1998) reported that fly ash has been found to removal cadmium, chromium, arsenic and can be substituted for activated carbon when blended with coal in the removal of chrome dye. Wood and McAtamney (1996) showed that laterite can reduce cadmium, chromium and lead concentrations to undetectable

levels. Notably, red mud and fly ash are high in calcium whereas laterite is high in aluminum and iron, suggesting that both classes of adsorptive media, iron and aluminum rich media vs. calcium rich media, can effectively remove heavy metals.

Thus, heavy metal leaching and uptake are both possible and may not be easily predicted. For instance fly ash is an industrial byproduct and would be expected to leach heavy metals but has also been shown to remove cadmium, chromium and arsenic. This issue needs to be considered when initially selecting substrates for consideration and at some point tested for when finalizing substrate selection.

Aluminum and iron content in runoff. Several aluminum based material can result in elevating aluminum concentrations above background levels. Haustein *et al.* (2000) found that WTRs removed P more effectively than HiClay Alumina but also resulted in more greatly elevating aluminum concentrations in runoff. Patel (personal communications) found higher aluminum concentrations in waters experimentally treated with Utelite and with activated alumina than in non-treated waters. These increases may be incidental or negligible under many situations but still should be considered when deciding upon and testing different substrates for P removal.

6.2 Application logistics

Depending upon the selected site, the expected design, and available expertise and budget, certain substrates may be eliminated. For instance, if P removal is expected to occur in a system with subsurface flow, the ideal substrate will have a good hydraulic conductivity, not blind easily and require minimal replacement and maintenance. Thus, substrates will have a specific size distribution typical of substrates such as fine sand, but also have high uptake P uptake capabilities. Several of the substrates discussed would not be ideal for this application. For instance, more fine substrate such as fly ash would need to be blended with sand or other media as it is likely too fine for good filtration. Blending adds additional costs and expertise. Under such an application, porous media such as DE, activated alumina, LWA and expanded shales would seem more ideal than non-porous media such as sands.

6.3 Costs

Costs standardized against performance is an important consideration. Activated alumina is very effective at P removal and is widely used in water treatment systems, but it is also very expensive as compared to natural products and industrial and wastewater treatment byproducts. Thus costs is a very important consideration.

For many products, there will be costs associated with their manufacturing or mining, and costs associated with their transportation. For many products, such as aggregates (e.g. sand, limestone), transportation cost will be the major factor determining cost to the customer. Transportation costs is a major factor in determining what substrates have been tested where.

For an application at Lake Tahoe, transportation costs can be minimized by considering substrate local to California and Nevada. Metamorphic (not amorphous) limestone and dolomite; iron-rich sands; sands; diatomaceous earth and modified diatomaceous earth; bauxite; and expanded shale are natural substrates found in either or both California and Nevada. Local producers of

industrial byproducts such as fly ash, blast furnace slag and steel furnace slag are not easily found in California or Nevada. Utelite can be found relatively locally in Utah. We have not been able to find local producers of other promising substrate discussed in this literature review.

6.4 Cementification

Cementification is an issue for amorphous calcium based substrates. In these substrates, P removal occurs through precipitation. This eventually results in cementification of the substrate (Misra, personal communication). Cementification will eventually reduce hydraulic conductivity in filtration or subsurface flow applications.

7. Conclusion

Substrates rich in iron, aluminum and calcium oftentimes have enhanced phosphorus removal. P removal by iron and aluminum is more prevalent under pH conditions below neutral and removal by calcium is more prevalent under more alkaline pH conditions. These substrates can be naturally occurring, byproducts of industrial or water treatment processes, or engineered. Phosphorus removal fundamentally occurs through chemical adsorption and/or precipitation. Phosphorus removal is typically greater for amorphous materials because of the greater number of adsorption sites. However, this removal process may not be thermodynamically stable and could release phosphorus as the structure becomes less amorphous and more crystalline. Nonetheless, in many substrates, most the P removed is irreversibly bound.

Other options have become available for P removal and these are engineered substrates. One such substrate is locally available in Reno and uses lanthanum impregnated diatomaceous earth for arsenate removal. This material, which has a high positive surface charge, can also irreversibly remove phosphorus.

Other factors affect P removal and these are mainly physical. Specific surface area and particle shape are the likely key variables. These variables affect filtering capacity, contact area between water and the surface area, and likelihood of clogging and blinding.

A number of substrates have been shown to effectively remove P in case studies. Based upon these studies, promising substrates include WTRs, blast furnace slag, steel furnace slag, OPC, calcite, marble, Utelite and other LWAs, zeolite and shale. However, other nonperformance factors such as environmental considerations, application logistics, costs, and potential for cementification further narrow the list of possible media for application at Tahoe. Industrial byproducts such as slags risk possible leaching of heavy metals and this potential cannot be easily predicted. Fly ash and other fine particle substrates would be more difficult to apply because they would need to be blended, making them less desirable and more costly to apply than larger diameter media. High transportation costs rule out non-local products. Finally, amorphous calcium products will eventually cementify reducing their effectiveness in filtration systems. Based upon these considerations, bauxite, LWAs and expanded shales/clays, iron-rich sands, activated alumina, marble and dolomite, and natural and lanthanum activated diatomaceous earth are the products most likely to be tested for application at Tahoe. These materials are typically iron, calcium or aluminum based; many have a high specific surface area; and all have low transportation costs.

Table 1. Chemical characteristics selected substrates. Shaded region shows aluminum, iron and calcium based materials.

Substrate	Reference		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	CaCO ₃	MnO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	LOI ²
Natural and local minerals															
zeolite	Ash Meadows 2001.	Natural Clinoptilolite	66.9	10.5	0.9		1.2		< 0.1	0.6		3.0	4.1	0.1	9
bauxite	IMPASCO 2003	Depends upon grade	>12 - 22	57 - 71	2 - 35		< 1			< 1				3 - 3.8	13 - 15
laterite	Wood and McAtamney 1996		0.7	39.8	26.7									3.6	
shale	Krishisworld		58.9	15.6	4.1	2.5	3.2			2.5		1.3	3.3	0.7	
wollastonite	Dada 2003		42.1	6.4	2.6					3.1					6.3
dolomite - magnesium limestone	Dada 2003		0.6	<0.1	<0.1		30.3		Nil	20.7		1.6		Nil	46.2
opoka	Johansson and Gustafsson 2000		34.1	8.8		5.2		50.7							
calcium carbonate (marble, limestone) ¹	CMC SRL 2003	Typical	1.7	0.6	0.3		53.4			0.7					
Industrial and Wastewater Byproducts															
blast furnace slag	Sakadevan and Bavor 1998		32-37	13-16		<1.3	38-43		<1	5-8		<0.5	<1		
	Johansson and Gustafsson 2000		35	9.6-11.4		0.3-0.5	33.4-35.0		0.4-0.5	13.7-14.3					
steel furnace slag	Sakadevan and Bavor 1998		10-15	1-5		20-30	35-45		2-5	7-12		<0.5	<1		
red mud				20.1	31.8		4.8							22.6	
Fly ash	Turner-Fairbanks 2003	Bituminous	20-60	5-35	10-40		1-12			0-5	0-4	0-4	0-3		0-15
		Subbituminous	40-60	20-30	4-10		5-30			1-6	0-2	0-2	0-4		0-3
		Lignite	15-45	10-25	4-15		15-40			3-10	0-10	0-6	0-4		0-5
	Ugurlu and Salman 1998		26.4	10.0	3.4		33.8			1.7		0.2	1.0	0.4	
1. Marble is approximately 97% calcium carbonate and limestone ranges from about 93 - 97% calcium carbonate															
2. Loss on ignition															

Table 2. Qualitative comparison of adsorptive media used for phosphorus removal.

Citation	Substrate in order of performance (best to worst)					Comment	
Haustein et al. 2000	WTR	HiClay Alumina				Depended upon aluminum content.	
Johansson and Gustafsson 20001	FC and CC Blast Furnace Slag	FA Blast Furnace Slag	CA Blast furnace slag	Opoka		Opoka not supersaturate Ca in solution	
Mann 19972	Fly ash	G. Blast Furnace Slag	steel slag, blast furnace slag	Hawkesbury sandstone	coal wash bottom ash	gravels.	Correlated primarily to Ca and Mg concentration
Agyei et al. 20023	OPC	steel slag	fly ash				Correlated with CaO concentration in substrate
Sakadevan and Bavor 19984	Blast Furnace Slag	Some soils, steel furnace slag, zeolite	Some soils				Phosphorus removal best correlated with oxalate extractable iron and aluminum
Brix et al 2001	Calcite	Marble	Diatomaceous earth	LECA, vermiculite			Calcium content best predictor of performance.
Brown 1999	Iron Humate	Iron rich sands	Uncoated sands				Iron Humate is a WTR. pH was not depressed as much with iron rich sands.
Zhu et al. 1997	UTELITE	Other LWAs	Iron rich sands	LECA			Performance depend upon total metal content.
Drizo et al 1999	Shale	Fly ash	Bauxite	LECA			No specific property best predict performance

1. FC = Fine crystalline, FA = Fine amorphous; CC = Course Crystalline; CA = Course Amorphous

2. G=Granulated

3. Ordinary Portland Cement

4. No clear rating given

Table 3. Phosphorus removal in subsurface flow experimental systems

media	Size	Influent mg/L	Effluent mg/L	Removal %	HRT days	Length of study months	Comment	Citation
Blast furnace slag	Buckets	>40	1	98	20	3	w/o aeration	Gruneberg and Kern 2001
Blast furnace slag	Buckets	>40	0.6	98	20	3	w/aeration	Gruneberg and Kern 2001
laterite	pilot scale reed bed	5 - 10	<1	96	3	10		Wood and McAtamney 1996
Shale	wetland mesocosm	10	~0.2	98	5	10		Drizo et al 1997
Marble	Column	10	~2.5	75	0.5	3		Brix et al 2001
Vermiculite	Column	10	~7.0	30	0.5	3		Brix et al 2001
LECA	Column	10	~7.0	30	0.5	3		Brix et al 2001
Diatomaceous earth	Column	10	~3.5	65	0.5	3		Brix et al 2001
Dolomite	wetland mesocosm			56		45		Pant et al 2001
Queenstone shale	wetland mesocosm			88		40		Pant et al 2001
Fonthill sand	wetland mesocosm			77 - 82		33		Pant et al 2001
Fly ash	wetland mesocosm	20	0.8 - 4.0	80 - 96	0.04	0.1		Ugurlu and Salmon 1998
15-30% Fly ash in spearwood sand	Column		ND			3		Cheung and Venkitachalam 2000
Blast furnace slag	Column	10	~0.5	>95		2		Johansson 1999
Red mud	Column	5.2	~3.4	38	0.13	2		Lopez et al. 1998

Table 4. Langmuir Isotherm results for various adsorptive media.

Adsorption Media	Sorption maxima S_{max} mg kg ⁻¹	Binding strength k l mg ⁻¹	Equilibrium P concentration(b) EPCo mg L ⁻¹	Shaking time hr	Notes	Citations
LWA - Arkansas Lightweight Corp	37(a)			24		Zhu et al 1997
LWA - Chandler, OK	39(a)			24		Zhu et al 1997
LECA	46 - 565(a)			24	Varies with type	Zhu et al 1997
Queenston shale	192	0.07	0.48	24		Pant et al. 2001
Evesboro Loamy sand + 10% fly ash	203	0.55		24		O'Reilly and Sims 1995
FILTRALITE	209 - 2210(a)			24		Zhu et al 1997
Evesboro loamy sand	213	0.49		24		O'Reilly and Sims 1995
Evesboro Loamy sand + 20% fly ash	242	0.44		24		O'Reilly and Sims 1995
Evesboro Loamy sand + 30% fly ash	280	0.28		24		O'Reilly and Sims 1995
Lockport dolomite	303	0.16	0.05	24		Pant et al. 2001
Steel Furnace Slag	380			30		Mann 1997
Blast Furnace Slag	400			30		Mann 1997
Foothill sand	417	0.07	0.02	24		Pant et al. 2001
LECA	420	0.1		24		Drizo et al 1999
Sand	439-443(a)			24		Zhu et al 1997
Zeolite	460	0.03		24		Drizo et al 1999
Burnt Oil Shale	580	0.06		24		Drizo et al 1999
Bauxite	610	0.26		24		Drizo et al 1999
Fly Ash	625			30		Mann 1997
Shale	650	0.61		24		Drizo et al 1999
Limestone	680	0.1		24		Drizo et al 1999
Lagoon fly ash	860	0.07		24	Aged	Drizo et al 1999
Steel Furnace Slag	1430	0.046		48		Sakadevan and Bavor 1998
Zeolite	2150	0.0442		48		Sakadevan and Bavor 1998
hematite	2200				Synthesized	Oh et al 1999
UTELITE	3496(a)			24		Zhu et al 1997
Red mud	7027			24		Lopez et al 1998
Precipitator Fly ash	13766	0.28		24		Cheung and Venkitachalam 2000
goethite	16400				Synthesized	Oh et al 1999
alumina	17100					Oh et al 1999
Blast Furnace Slag	44247	0.367		48		Sakadevan and Bavor 1998
Allophane	51000				Synthesized	Oh et al 1999

Notes

- a. At equilibrium with P concentration of 320 mg/L, below level required for Langmuir calculation of Smax
- b. Solution P concentration in equilibrium with media.

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ADSORPTIVE MEDIA INVESTIGATION

Appendix 2 – Experimental Design of Laboratory and in situ Studies

2003.01

**Experimental Design Summary for Laboratory and *In situ* Adsorption
Studies**

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Bachand & Associates**

**Submitted to the
University of California Davis
Tahoe Research Group
In fulfillment of Contract No. 02-00700ICR**

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Introduction

The following document presents the experimental design for the laboratory and *in situ* studies to test and assess various adsorptive media for this project. The laboratory and *in situ* studies are the basis of media selection for this project. Media tested and selected in these studies will be further tested in the field-column studies, though those studies will focus more on the logistical aspects of media application, implementation and integration with stormwater wetlands and basins. The experimental designs of the laboratory and *in situ* studies are presented together because together they provide the basis for evaluating the performance characteristics of the different adsorptive media.

Analysis of adsorptive media for laboratory study with recommendation on sources

Based upon the literature review (Bachand, 2003), various media were investigated for initial screening. As discussed in the literature review (Bachand 2003), iron, aluminum and calcium media are good candidates for having enhanced phosphorus removal. These media can be natural, engineered or byproducts of industrial processes. Based upon the studies cited in the literature review, promising substrates include wastewater treatment residuals, blast furnace slag, steel furnace slag, OPC, calcite, marble, lightweight aggregates (LWA, i.e., Utelite), zeolite and shale. However, other factors such as environmental considerations, application logistics, costs, and potential for cementification need also be considered because of their implications on cost or long-term performance potential. For instance, transportation cost is very important in determining whether a media will be cost effective, and for that reason media tested in various studies are largely restricted to those locally available (see Bachand 2003 for review and relevant citations). Additionally, in discussions with Dr. Alan Heyvaert of the University of California at Davis Tahoe Research Group, we expect that the adsorptive media will need to be applied to provide both adsorption and filtering for removal of both dissolved and particulate phosphorus, and fine particles. Thus, fine substrates such as fly ash, which will need to be blended with other larger size particles such as sand, are considered too difficult to apply.

We initially reviewed two publications to determine mineral supplies in California and to develop leads for suppliers:

- The Mineral Industry of California (USGS 2000)
- Mineral Industry Surveys (USGS 2001)

We also searched the internet for local suppliers of various industrial and natural products. From these two efforts, we contacted a number of scientist and suppliers to understand the availability of different media. Some of these contacts are listed in Table 1.

In reviewing the different media options, we sought to select media that would provide good phosphorus adsorptive capacity based upon various physical and chemical specifications (i.e., surface area; iron, calcium or aluminum content; particle size distribution). We also decided to test locally available sands. Sands are commonly used for filtration and thus this enabled us to quantify the adsorptive capacity of the different sands in case there was a need to blend sands with other media.. Finally, we wanted to test adsorptive media that would complement work currently done to date by CSUS Office of Water Programs. That office has been testing various adsorptive/filtration media for turbidity and phosphorus removal from stormwater in an effort to develop systems to treat highway and roadside runoff in the Tahoe Basin.

From these efforts and our literature review (Bachand 2003), we considered and subsequently selected a number of media to test at the laboratory scale and these are listed in Table 2.

Table 1. Contacts for investigating adsorptive media locally available to Lake Tahoe

Contact	University/Company/Agency
Dipen Patel	CSUS Office of Water Programs
Jeff Barrick	Supplier, Utelite Corporation, Utah
Jeff Hauser	Principal, Ecologic, Roseville, CA
Steve Clement	Supplier, Teichert Aggregates
Peter Lenz	Eagle Picher Minerals, NV
Dr. Misra	University of Nevada Lackey School of Mines
Ron Appleton	Engineer, Brown and Caldwell, Walnut Creek, CA
Bob Hill	California Geological Survey
Bob Zierenberg	UCD Geologist
Bob Zasoski	UCD Soil Scientist
John Clinkenbeard	California Geological Survey
Mike Nannini	Eagle Picher Minerals, NV
Hugh Walker	Alcoa

Table 2. Media considered for testing in laboratory studies.

Material Class	Name	Justification
Materials considered and recommended for testing		
Activated Alumina	Alcoa F 200	Alumina products are engineered for good removal of phosphorus (high surface area, high charge density) and also provide good filtration. Compared different activated alumina including one product (DD2) for which CSUS OWP has developed one year of performance data for stormwater treatment. Though these products are expected to be relatively expensive, they are also expected to provide above average performance.
	Alcoa DD2 14X28	
	Alcoa Selexsorb CDX 7X14	
	Alcoa Selexsorb CD 7X14	
Bauxite	Bauxite Large	Bauxite is high in iron and aluminum and been shown to have above average phosphorus removal. Bauxite is locally available in California.
	Bauxite Small	
Sand	Coarse Truckee Sand	Sand is locally available and an effective and cost-effective filtration media. Truckee sand represents typical sand for the Tahoe Basin and thus potentially provides a control for all media tested. High iron sand is a byproduct of gold mining in California and could potentially provide enhanced P removal. Lanthanum coated silica is an engineered sand. Any sand could be coated with lanthanum. Thus, lanthanum coated sand tests the effectiveness of this technology that could be used with any locally available sand.
	High Fe Sand	
	Local Sand	
	Truckee (Fine) Morter Sand	
	La-Si (Lanthanum silica blend)	
LWA	Expanded Shale	Expanded shales and lightweight aggregates (LWA) have been shown to have enhanced P removal. A high surface area that is also charged is expected to provide elevate initial and longterm phosphorus removal. Utilite is a LWA from Utah. An expanded shale from Riverside was also tested and considered as a local LWA/expanded-shale alternative.
	Utilite	
	Acid Washed Utilite	
DE	Diatomaceous Earth	Diatomaceous earth (DE) is locally available and effective and cost-effective filtration media. Lanthanum coating represents a technology to enable DE to also become a good adsorption media for removal of arsenate and phosphate. This technology has been developed by Eagle Picher and the University of Nevada Lackey School of Mines.
	Lanthanum Diatomaceous Earth (2 sizes)	
Dolomite	Dolomite 11	Dolomite is locally available. Dolomite is high in magnesium and calcium and thus expected to have above average phosphorus removal. Locally available dolomite is metamorphic and not amorphous so it is expected to less affect pH but also to be less effective at phosphorus removal than amorphous dolomite
	Dolomite 20	
Limestone	Limestone	Metamorphic limestone is locally available. Limestone is high in calcium and thus expected to have above average phosphorus removal. Locally available limestone is metamorphic and not amorphous so it is expected to less affect pH but also to be less effective at phosphorus removal than amorphous limestone
Wastewater residual	Waste Water Residuals	Wastewater residuals are common to all high population areas and are high in amorphous aluminum and iron. Thus, these materials potentially offer a cost-effective and effective media for dissolved P removal. High organic content may provide other mechanisms besides precipitation and adsorption, such as complexation, for P removal and thus may perform well over a broad range of conditions.
Materials considered but not recommended for testing		
Fly ash		Too fine for good filtration. Not able to find local source. Concerns over cementification
Slag	Blast furnace slag	Not able to find local source. Concerns over cementification and leaching of heavy metals.

Experimental design of adsorption and desorption laboratory studies

Laboratory studies for this project have been broadened to include both Langmuir Isotherm studies and adsorption columns. This replaces the original intention for this project of characterizing the different media only with adsorption and desorption isotherm studies.

Langmuir isotherm studies

The Langmuir isotherm studies will be conducted to initially screen adsorptive media based upon physicochemical uptake characteristics and performance. In the isotherm studies, the adsorptive capacity of different media will be determined by putting solutions with different phosphate concentrations in centrifuge tubes, adding to each tube a predetermined mass of media, shaking for 24 hours, and then measuring phosphate concentrations in the solution. From that measurement, phosphate uptake by the tested media can be determined. From this information in which each media is placed in a series of tubes with different initial phosphate concentrations, Langmuir isotherm constants can be determined which can be used to model the phosphate uptake trends and capacity for the different media.

These studies will be done in two phases, a screening phase and a selection phase. The screening phase will be used to narrow the media initially considered (Table 2). The second or selection phase will be used

1. to develop Langmuir constants for the remaining media,
2. to better understand phosphate uptake over a broader range of phosphate concentrations for each media, and
3. to select three or four media for further testing using using adsorption columns.

Table 3 shows the experimental design for these tests. It shows the methods used for conducting the isotherms (i.e., shaking time, mass of substrate), the media to be tested, analyses and quality assurance/quality control (QAQC) planned, and phosphate dosing levels. These tests are being conducted using standard procedures (Drizo et al 1999, Oh 1999, Zhu 1997, Arias 2001).

Additionally, we plan to determine particle size distribution through published data or dry sieving and porosity. These two physical characteristics will provide a basis for evaluating the appropriateness of these different media for filtration.

Adsorption column studies

After selecting three or four adsorptive media based upon the above isotherm studies and physical characterization, adsorption column studies will be conducted.

Adsorption column tests go beyond isotherm studies in that they integrate physical characteristics and properties such as cementification, diffusion and hydraulic conductivity with phosphorus removal by adsorption and precipitation. Further they integrate together phosphorus removal by adsorptive processes with removal by filtration processes. Thus, adsorption columns allow a monitoring of steady-state and perhaps non steady-state water quality under continuous loading conditions. Finally, they provide a good estimate of media uptake capacity and will model breakthrough characteristics of the adsorptive media when it reaches saturation.

Adsorption column studies will be conducted using 3” PVC columns and fairly standardized methods (Ugurlu and Salman 1998, Brooks et al 2000, Cheung and Venkitaachalom 2000). Adsorption tests will be conducted under conditions of saturated flow in order to prevent short-circuiting of flow paths through the media.

The column studies will be done in two phases. The first phase will be to assess adsorption characteristics of the selected media under flow-thru conditions:

- The long-term P uptake capacity,
- P concentrations achievable in the outflow, and
- P desorption after periods of high P and hydrologic loading.

Results using media will be compared to results using native Tahoe soils in order to assess the improvement in P adsorption achievable using imported media in the construction of stormwater wetlands and basins.

Table 3. Experimental Design for Adsorption Isotherms

Goals				Media to be Tested in Screening Isotherms. Four will be selected for Validation Isotherms.			
Screening Isotherm Studies							
	Screen media for further testing and narrow to 4 media						1 Activated Alumina, 4 different products
							2 Utelite Expanded Shale, acid and non-acid washed
							3 Expanded Shale, local product
Validation Isotherm Studies							4 Lanthanum coated silica
	Narrow media to top 1 or 2						5 Metamorphic crushed Limestone/marble
	Develop isotherm constants						6 Monterey sand (~16 mesh)
							7 Truckee Sand, concrete sand (~16 mesh)
Adsorption Isotherm Methodology							8 Truckee Sand, mortar sand
	Shaking Time		24 hours				9 Bauxite, 2 sizes
	Sampling Time		24 hours				10 Dolomite, 2 sizes
	Replicates		2				11 iron-rich sand, black sand
	Substrate weight		1 g				12 Water Treatment Residual (Iron Humate)
	Solution volume		50 ml				13 Diatomaceous Earth (DE)
	Centrifuge or filter before SRP analyses						14 Lanthanum coated DE
Dosing Levels				Units			
			0 ppb				
			10 ppb				
			50 ppb		Selection Only		
			100 ppb				
			500 ppb		Selection Only		
			1 ppm				
			10 ppm				
			100 ppm		Selection Only		
			500 ppm		Selection Only		
			1000 ppm				
			5000 ppm		Selection Only		
			10000 ppm		Selection Only		
QAQC							
	Experiment Blanks - blanks on experimental equipment						
	Method blanks - blanks on analytical equipment						
	Water Blanks						
Analyses of Water							
	pH						
	ortho-P						
Analyses of Media - By others							
	pH				See Sakadevan and Bavor		
	Total Fe, Al, Mg, Ca				Danr		
	Total N, P, K				Danr		
	Oxate Fe, Al				Danr		
	Exchangeable Ca, Mg, K				Danr		

The second phase will be to test these columns using either real or synthetic stormwater. These tests will be conducted in order to not only validate the uptake P capacity under circumstances with other dissolved constituents are present in the water but also determine the removal of particulate phosphorus and fine particles through filtration in these systems.

Table 4 shows the experimental design planned for the adsorptive column studies. In these studies, water quality characteristics besides phosphorus such as aluminum concentrations and turbidity will be measured as well. Columns will be designed to operate under a range of flow and hydraulic residence times to accommodate different column designs, media porosity and experimental goals.

Table 4. Adsorption Column Experimental Design

Experimental Design					
Media and Packing Material¹					
Packing material at base	glass beads or glass wool				
Media	Media to be selected from screening isotherms				
Number of Media	3 or 4				
Number of replicates	3				
Packing material at top	None				
Packing material at bottom	washed glass beads				
Column specifications					
Column Material	Clear PVC Sch 40				
Nom dia	3 cm		← Enter Pipe Size Here		
Column ID	7.7 cm				
Height of media	2 ft				
	61 cm				
Volume of column in which media is packed	2858 cc				
	2.86 L				
	0.76 gallons				
	0.10 cu ft				
Pump and Flow Specifications and Range¹					
Scenario	Expected duration	Contact Cycle	HRT (days)	Notes	
Maximum Flows	4	200	0.48	Rapid experimental assessments	
Minimum Flows	4	8	12	Simulates field conditions	
Planned First Experiment	4	200	0.48		
Dosing Range^{1,2}					
Maximum Planned dosing level	1000 ppb				
Minimum planned dosing level	100 ppb				
Notes					
1. Media will be experience saturated flow such that no short-circuiting occurs.					
2. Water initially used will be DI or Lake Water with desired phosphate concentrations in order to determine phosphorus levels.					
Real or synthetic stormwater will be later used to determine filtering for particulate P and small particle removal in addition to adsorption for dissolved P removal.					

Experimental design for *in situ* adsorption tests with recommended protocols for media deployment

In situ adsorption tests are being conducted on a select few media to experimentally determine levels of phosphorus and fine particle removal that can be achieved under real stormwater conditions and for a variety of runoff. These tests are the final step in assessing the chemical and physical characteristics of these media for P and fine particle removal. These tests do not address the logistics of this application.

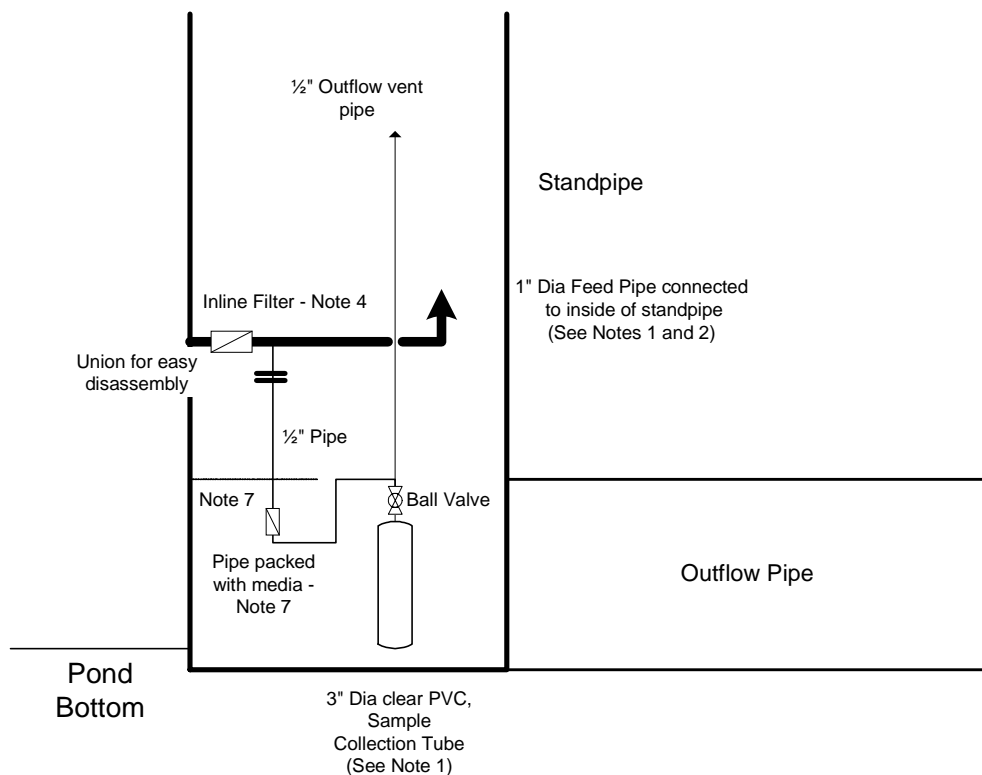
For this test, adsorptive columns will be placed at the Coon or Fox Street Basin before storm events and during runoff events (i.e., snow melt). In discussions with Dr. Alan Heyvaert of the University of California Tahoe Research Group (TRG), we are currently planning to deploy these columns a minimum of three times during the upcoming 2003/2004 wet season.

Figure 1 presents the conceptual sketch for this deployment. Figures 2 through 5, found in Appendix A, present greater details on the design of individual components. For this design, a feed line will be threaded to the inside of the outflow standpipe. When the basin fills to that level, water will flow into the feed line, through an adsorption column by gravity flow and then into a collection tube. In all there will be five collection systems such that five different treatments can be tested simultaneously. Currently, we expect four of the five collection systems will have an inline adsorption column and one will have a throttling valve in its place. During each deployment, the different collection systems will be adjusted such that they fill at a similar rate. This adjustment is expected to be minimal for the different systems with an inline adsorption column but will need to be a valve adjustment for the collection system without an inline adsorption column. Thus at the end of each deployment, five collection bottles will be filled with approximately equal volumes with water collected at approximately equal times.

Under this scenario, for each deployment the collection system without an inline adsorption column will provide an unfiltered control. For one of the collection systems, sand will be used in the adsorption column and the resulting sample will be considered a filtered control, having removal of fine particles but relatively negligible adsorptive uptake of dissolved constituents. The remaining three treatments will have media selected based upon previous studies. Table 5 presents the experimental design for this study, describing the expected minimum deployment times, expected analyses and suggested media for testing.

Figure 1. Overview of in situ sample collection system.

Shown below is conceptual drawing of the sample collection system designed to integrate with the outflow standpipe on the Fox or Coon St. basins. Only one collection tube is shown though five collection tubes off the same feed pipe are anticipated such that various media can be tested simultaneously. Collection tube volume represents over 100 times the pore space volume of the inline adsorption column.



Notes

1. One collection tube per media. Up to 5 treatments per deployment. See Figure 4 for more details on sample collection system components. Only one collection tube shown in this sketch.
2. Slight upturn on 1" feed pipe ensures that pipe is always full. See Figure 5 for more details on feed pipe.
3. Vent tubes need to be above outflow level of 1" feed pipe.
4. Inline filter for removal of large particles and leaves (Figure 5)
5. Drawings are not too scale. Layout is conceptual and will need to be finalized with implementation in the field.
6. Most fittings are threaded for easy assembly and disassembly.
7. Top of media to be below EI such that media is submerged and has saturated flow. See Figure 3 for details on media column.

Table 5. Preliminary Experimental Design for *In Situ* Adsorption Column Tests
 Table describes the planned number of deployments, chambers and tested media as well as planned water analyses. These systems would be deployed at different storm and runoff events.

Suggested in situ adsorption column experimental design		
Total No. of chambers	5	
Total No. of media tested	4	
Suggested Media Tested	Mesh 16 sand Activated Alumina DE MDE None	Filtered Control OWP Comparison Sand alternative Lanthanum coated DE Unfiltered Control
Number of Deployments	3 minimum	rainfall and snow-melt runoff events
Water Analyses for each chamber	Dissolved phosphorus Total phosphorus ortho-phosphate turbidity Dissolved aluminum Volume/mass of collected water	

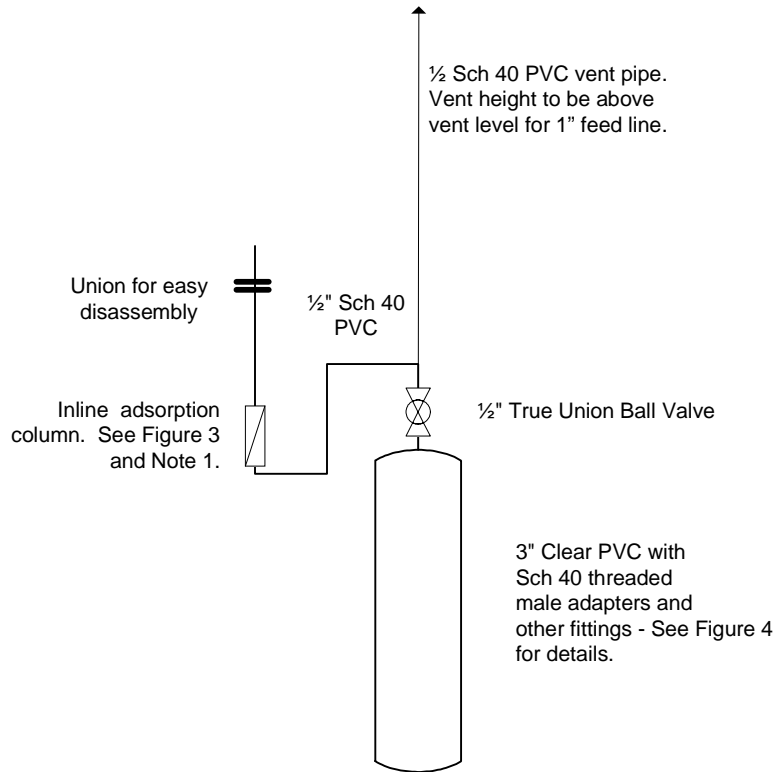
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Appendix A. Design and Layout Sketches for In situ Adsorption Study

Figure 2. Conceptual drawing of collection system.

Five collection systems are planned. See Figures 3 through 5 for details on components.



Notes

1. For treatment with no media, replace with needle valve
2. Not to scale.

Figure 3. Inline Adsorption Column

Inline adsorption column will operate under submerged conditions such that it experiences saturated flow. This will help minimize short-circuiting through the column. Media height is expected to be 2 inches but that can be adjusted. Initially, media volume will be designed such that the collection bottle volume is approximately 100 times greater than the pore space volume in the inline column. This will enable an approximation of long-term capacity and long-term P concentrations that can be achieved. An upstream strainer in the feed line will remove large debris and particles. See Table 6 for parts lists.

Notes

1. Parts are glued together.
2. Screen is fit snug between male adapter and pipe.
3. Not to scale.

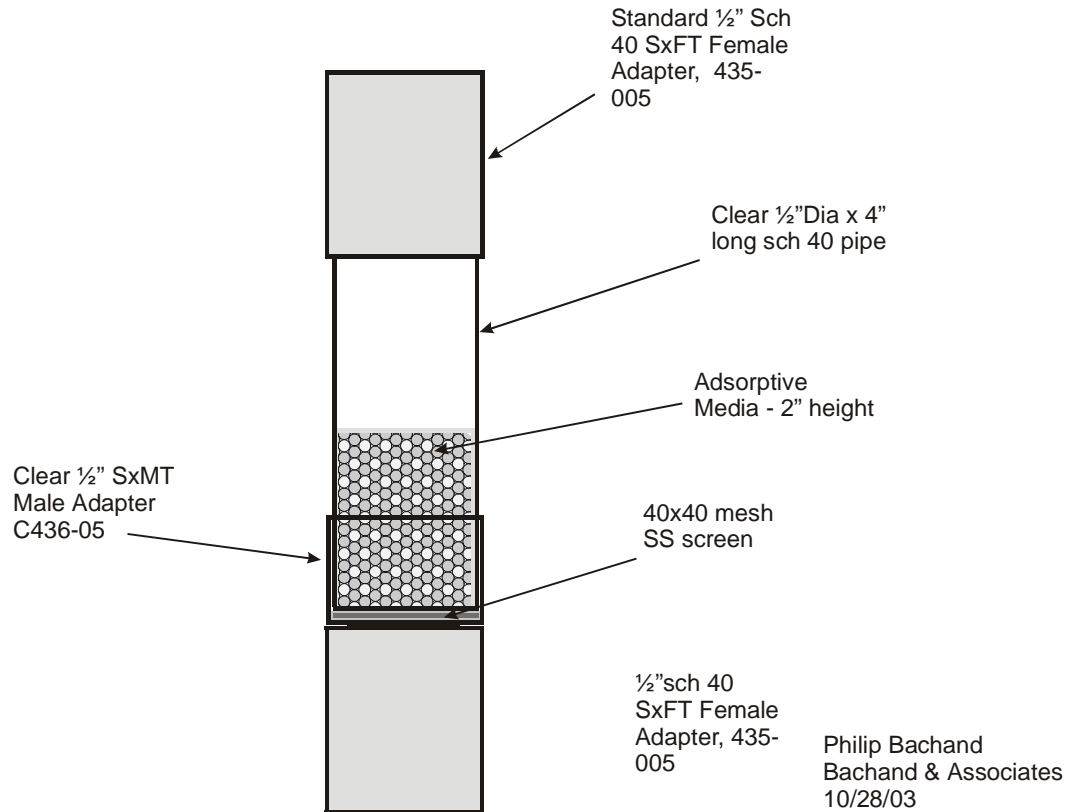
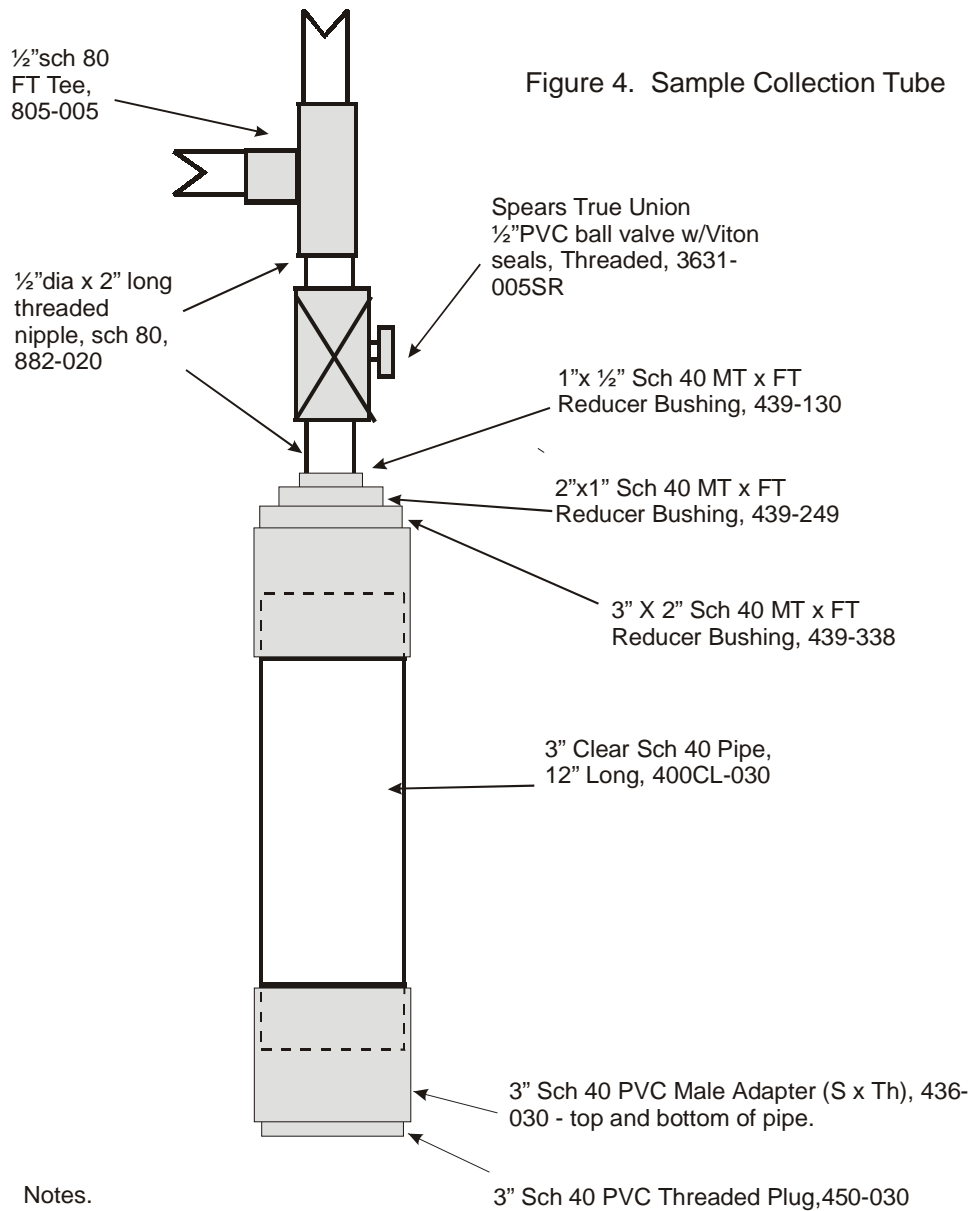


Figure 4. Collection Tube.

Tube is designed to collect approximately 100 times the volume of the inline adsorption column pore space (Figure 3). Collection Tube is clear such that an initial field assessment can be made on the collected system and whether there were failures. Ball valve allows the sample to be sealed and isolated from disturbance before moving the collection system from the field. See Table 6 for parts lists.

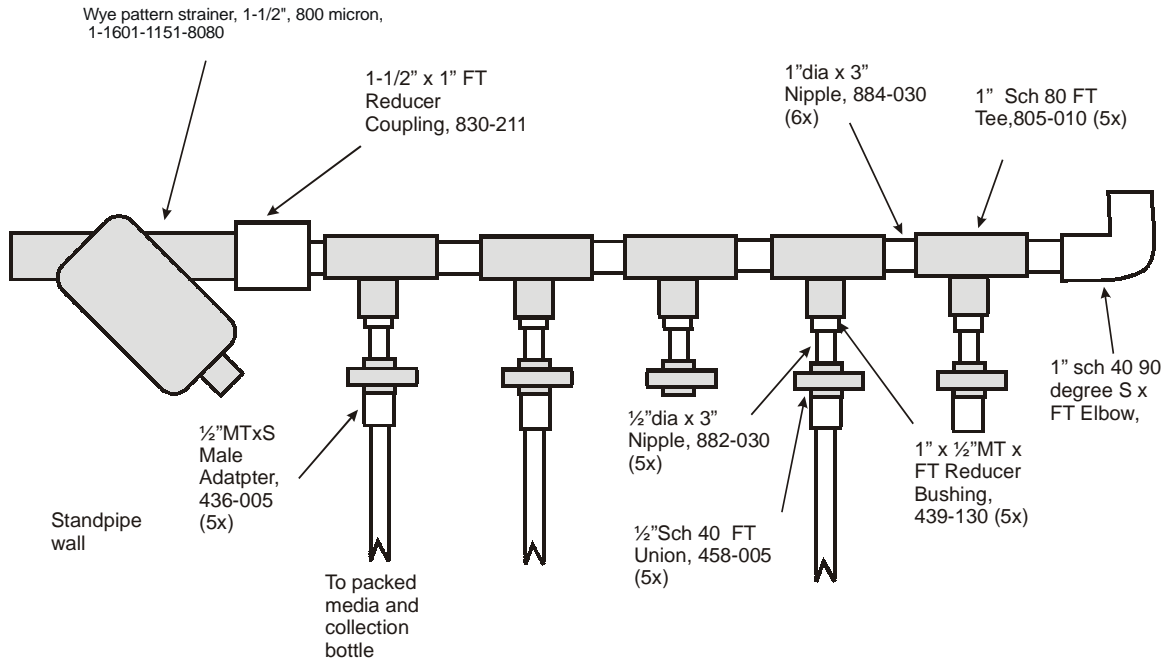


- Notes.
1. Not to scale.
 2. All components are threaded unless otherwise indicated.
 3. Component catalog numbers are shown for ordering from Harrington Plastics.

Philip Bachand
 Bachand & Associates
 10/28/03

Figure 5. Collection System Feed Line.

System is designed to allow connection of five sample collection systems. Upturned el ensures that feed line is filled and ensures equal head to all collection systems. An inline filter removes large debris and particles. Feed line is threaded to the inside of the outflow standpipe. See Table 6 for parts lists.



- Notes.
1. Not to scale.
 2. All components are threaded unless otherwise indicated.
 3. Component catalog numbers are shown for ordering from Harrington Plastics.
 4. Tees and els may need to be integrated into feed line if there is insufficient room in the standpipe .

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Table 6. Suggested parts and components for in situ adsorption tests.

Prices shown are based upon Harrington Plastics catalog prices. UCD will receive a discount on these prices. See Figures 1 through 5 for information on assembly.

Referenced Figure	Item	Description	Part No	No.	Unit	Catalog Cost	Extended	Vendor
Figure 3	1	Clear ½" SxMT Male Adapter	C436-05	5	ea	3.62	18.10	Harrington
Figure 3	2	40 mesh SS screen		5	ea			Not determined
Figure 3	3	Clear ½"Dia sch 40 pipe`	400CL-005H	5	ft	1.35	6.75	Harrington
Figure 3	4	Standard ½" Sch 40 SxFT Female Adapter	435-005	5	ea	0.44	2.20	Harrington
Figure 3	5	½"sch 40 SxFT Female Adapter	435-005	6	ea	0.42	2.52	Harrington
Figure 4	6	Clear 3" Dia x 12" Long Sch 40 PVC	400CL-030	10	ft	13.94	139.40	Harrington
Figure 4	7	3" Sch 40 PVC Male Adapter (S x Th)	436-030	10	ea	6.20	62.00	Harrington
Figure 4	8	3" Sch 40 PVC Threaded Plug	450-030	5	ea	5.43	27.15	Harrington
Figure 4	9	3" X 2" Sch 40 MT x FT Reducer Bushing	439-338	5	ea	12.22	61.10	Harrington
Figure 4	10	1"x ½" Sch 40 MT x FT Reducer Bushing	439-130	5	ea	1.54	7.70	Harrington
Figure 4	11	2"x1" Sch 40 MT x FT Reducer Bushing	439-249	5	ea	2.96	14.80	Harrington
Figure 4	12	Spears True Union ½"PVC ball valve w/Viton seals, Threaded	3631-005SR	5	ea	27.99	139.95	Harrington
Figure 4	13	½"dia x 2" long threaded nipple, sch 80,	882-020	10	ea	1.12	11.20	Harrington
Figure 5	14	Wye pattern strainer, 1-1/2", 800 micron	1-1601-1151-8080	1	ea	129.50	129.50	Harrington
Figure 5	15	1" Sch 80 FT Tee	805-010	5	ea	15.39	76.95	Harrington
Figure 5	16	½"Sch 40 FT Union	458-005	5	ea	4.11	20.55	Harrington
Figure 5	17	1" x ½"MT x FT Sch 40 Reducer Bushing	439-130	5	ea	1.54	7.70	Harrington
Figure 5	18	½"dia x 3" Nipple	882-030	5	ea	1.26	6.30	Harrington
Figure 5	19	1"dia x 3" Nipple	884-030	6	ea	1.96	11.76	Harrington
Figure 5	20	1-1/2" x 1" sch 80 FT Reducer Coupling	830-211	1	ea	22.01	22.01	Harrington
Figure 5	21	1" sch 40 90 degree S x FT Elbow	407-010	1	ea	1.00	1.00	Harrington
Figures 2,5	22	½"MTxS sch 40 Male Adatpter	436-005	20	ea	0.35	7.00	Harrington
Figures 1, 2	23	1/2" Sch 40 PVC pipe	400-005	40	ft	0.55	22.00	Harrington
Figure 4	24	½"sch 80 FT Tee	805-005	5	ea	6.26	31.30	Harrington
Figure 1, 2	25	1/2" sch 40 90 deg S Els	406-005	15	ea	0.38	5.70	Harrington
Figure 2	26	1/2" Asahi Globe Valve	1261005	1	ea	27.60	27.60	Harrington
Total							862.24	

ADSORPTIVE MEDIA INVESTIGATION

Appendix 3 – Standard Operating Procedure for Laboratory Column Study

Standard Operating Procedure

Breakthrough Column Study, Version 1.0

July 28, 2004

Philip Bachand and Ron Weyand

Supplies

- Scale for weighing substrate
- 800 ml graduated beaker
- 25 ml graduated cylinders
- Timer
- Sample containers

Clean Columns and Tubing

1. Disconnect columns from hydraulics (pump, tubing, etc...) and clean columns with DI water. Do not save glass beads or glass wool.
2. Run DI water through inflow tubing for one hour.

Check and Adjust Flow Rates

Flow rates need to be check and adjusted to allow calculations of nutrient release and uptake using a mass balance approach.

1. See BreakThru worksheet for experiment being run.
2. Determine number of channels needed for experimental run. For most studies from 9 to 11 columns will be needed for feeding water to the columns. Assuming two channels are used for each column, this corresponds to 18 to 22 channels. Additionally, one channel will be needed to feed chemicals.
3. Identify on worksheet tubing used for each channel in the Watson-Marlow pump and check tubing to ensure proper tubing is being used for the experiment.
4. Identify on worksheet flow rates for tubing being used. Flow rates will be the same during all three phases of the study (e.g. leaching, adsorption, desorption).
5. Measure flow using a 25 ml beaker and a timer for recording times. For convenience, use workbook sheet "HydrologyCheck ..." can be used for recording data, calculating flow rates, and comparing measured flow rates to flow rates predicted for the tube size and motor speed.
6. Adjust peristaltic pump channels such that measured flow is within 1% of predicted flows.
7. Do not need to measure for chemical feed. Adjust lever so similar to other channels.

Load Sediment and Adsorptive Media into Columns

Columns need to be loaded similar to allow calculations of nutrient uptake and release using mass balance approaches.

1. Mix blends for 50% Ace Sand and 50% Local Tahoe Soils.
2. Load glass beads in bottom of column so that are level with the top of the PVC cap at the bottom of the column.
3. Determine beaker size for which we can determine corresponding mass.
4. Determine mass on that volume. Note in worksheet (Local – MediaData).
5. Add 1500 ml of selected blends or sediment into each column using selected size beaker. Tap side of beaker to settle media for more accurate volumetric measurements.
6. Weigh and record media weight if possible. Record data in worksheet “Local – MediaData”.
7. Pour media into column and lightly tap column sides to settle media.
8. Pack glass wool to a height of approximately 4 inches above the media or sediment.
9. Label column to identify media or sediment within the column.
10. Place column on rack.
11. Enter data into appropriate worksheet (Local – MediaData).

Sediment and Media Chemical Determination

Media will be analyzed for moisture content and organic content to determine nutrient uptake and release on a mass basis (e.g. mg/kg).

1. Collect approximately 10 g of each media
2. Weigh wet weight and record in workbook (Local-MediaData).
3. Dry in oven at 105 degrees C for 72 hrs.
4. Weigh dry weight and record in workbook.
5. Combust in oven at 550 degrees C for 2 hours.
6. Weigh post-combustion weight and record in workbook.
7. Collect sample of media and send to DANR for chemical analyses. Contact Alan Heyvaert for necessary chemical analyses and replicates needed.

System Start-up and Preparation of Chemical Dosing Solution

System operates under leaching, adsorption and desorption phases. Only adsorption phases require chemical dosing.

1. Before hooking up columns, make sure flow rates calibrated as described above.
2. Check that all tubing, pumps and tanks are correctly set-up according to piping and instrument diagram.
3. Check that chemical feed system is ready when adsorption phase begins. For adsorption phase operate chemical feed (Manostat pump). During other phases,

make sure that tubing is disconnected so that water does not backflow into chemical feed tank.

4. Prepare chemical feed for concentration as defined in workbook.

Column Operation and Maintenance

Columns should be operated continuously once operation begins. Columns should not be drained and should not be tapped to promote compaction because such actions can cause blinding, short-circuiting and clogging.

1. Make sure that tank and drain overflows are draining to sink and are not kinked or clogged.
2. Check all tube connections for leaks.
3. Check to make sure all tubes are drawing liquids from tanks and that none are floating on top of water and not pulling water, or kinked or clogged.
4. Qualitatively check outflows from all columns.
5. After tubing has been checked, make sure all tube outflows are in drains to prevent overflow onto floor.
6. Make sure that all columns are not building up head above column outflow. If outflows are clogged, clear outflows by blowing through outflow tube.
7. Operate column system for each of the different phases. During leaching and desorption phase, do not operate chemical feed system and hydrologically disconnect chemical feed pump to ensure that backflow does not occur from the system into the chemical feed tank. During adsorption phase, hook-up chemical feed system.

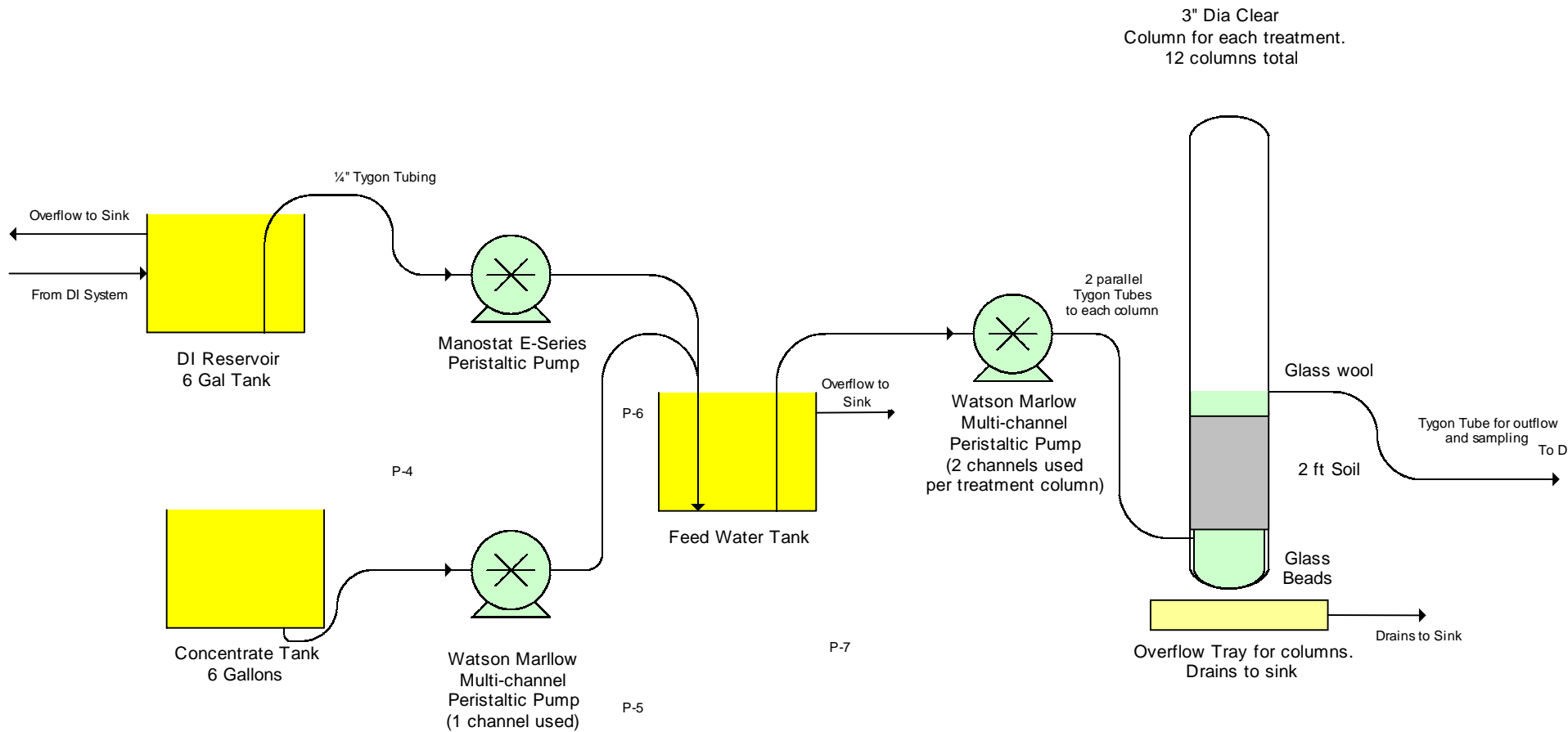
Water Quality and Flow Sampling

Water quality sampling focuses on nutrient uptake and release by measuring concentrations and using flow rate measurements to determine nutrient loads uptake and release.

1. Check column operation as defined above to ensure that no leaks are occurring and that the system is operating correctly. Make notes of any maintenance actions required.
2. Collect water quality and flow sample as defined in the experimental design. Collect adequate water sample volumes for analyses defined. Make note of column and outflow characteristics. Preserve as required. Record data in worksheet "Local -Sampling ddmmyy". For each sample event, create and date a new worksheet page.
3. Measure flow rates as defined in the experimental design. Measure flow with a timer and a 25 ml graduated cylinder. Record any comments.

Operational Strategy

1. Run Leaching phase until you have SRP concentration in outflow < 20 ppb or a similarly low and steady state condition. May need to confer with Alan Heyvaert to determine last day for leaching phase.
2. Run Adsorption phase until you have SRP concentration in outflow at steady state that meets one of the following criteria:
 - Outflow is at 1 ppm
 - Outflow shows sudden or great increase over previous steady state condition. For instance, if outflow has been near say 200 ppb, then it quickly (within a day or two) increases to 700 ppb. After that event, run for a couple more days until it reaches another steady state condition.
3. Run Desorption phase until you have SRP concentration at steady state that is different than the initial steady state condition when desorption was begun. For instance, initially, SRP concentrations may be say 800 ppb, but show a decline to a steady state of say 100 ppb.



Piping and Instrument Diagram

ADSORPTIVE MEDIA INVESTIGATION

Appendix 4 – Standard Operating Procedure for Field Column Studies

DRAFT - Standard Operating Procedure

Field Column Study, Version 2.0

February 18, 2005

Tim Delaney and Philip Bachand

Column Setup

Clean Columns and Tubing

1. Fill storm water holding tank with adequate volume of DI water.
2. Disallow return of unused DI water. Let drain to floor.
3. Disconnect columns from manifold, and clean columns with DI water. Run DI water through inflow tubing for one hour.

Check and Adjust Manifold Pressure

Manifold gate valves need to be adjusted to achieve the proper head pressure or simulated head pressure.

1. Adjust inflow gate valve so that the inflow pressure is XX psi.
2. Adjust outflow gate valve so that manifold pressure is XX psi

Load Sediment and Adsorptive Media into Columns

Columns need to be loaded similar to allow calculations of nutrient uptake and release using mass balance approaches.

1. Media filter columns are fitted with 40 mesh screens.
2. Add XX ml up to the 2" mark of selected media into column.
3. Tap side of column to settle media for more accurate volumetric measurements.
4. Label column to identify media or sediment within the column.
5. Place column in manifold.
6. Enter data into appropriate workbook.

System Start-up and Preparation of Chemical Dosing Solution

System tests operates under adsorption. Check that all tubing, pumps and tanks are correctly set-up according to piping and instrument diagram.

1. Check that storm water delivery system is ready when adsorption phase begins.
Column Operations

Column Maintenance

1. Make sure that tank and drain overflows are draining to the ground and are not kinked or clogged.
2. Check all tube connections for leaks.

3. Qualitatively check outflows from all columns.

Column Operation and Phase Changes

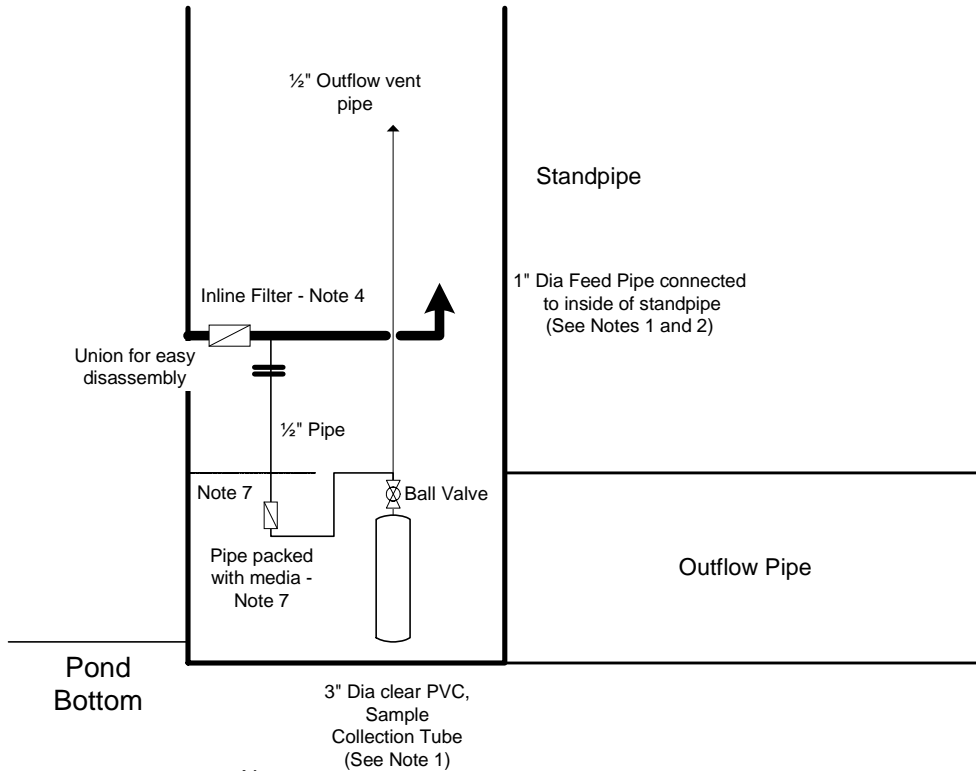
1. Columns will be operated, alternating between sample collection and chemical analysis once operation begins. Columns should not be drained and should not be tapped during operation as such actions cause blinding, short-circuiting and clogging.

Water Quality and Flow Sampling

1. Ensure you have adequate sampling containers for collecting all analytes.
2. Collect water quality and flow sample as defined in the experimental design. Collect adequate water sample volumes for analyses defined. Make note of column and outflow characteristics. Preserve as required.
3. Collect sample when collection vessel is full. Record time. Label bottles with time, your initials, date and treatment name
4. Collect daily source water sample.
5. The first sample will be analyzed for SRP, every fourth sample will be analyzed. Once breakthrough is achieved in a column, back collected samples will be analyzed for SRP to draw the breakthrough curve.
6. On selected samples, analyze for total dissolved P, total P, dis Al, dis Mg, dis Ca, pH, DOC, turbidity.

Figure 1. Overview of in situ sample collection system.

Shown below is conceptual drawing of the sample collection system designed to integrate with the outflow standpipe on the Fox or Coon St. basins. Only one collection tube is shown though five collection tubes off the same feed pipe are anticipated such that various media can be tested simultaneously. Collection tube volume represents over 100 times the pore space volume of the inline adsorption column.

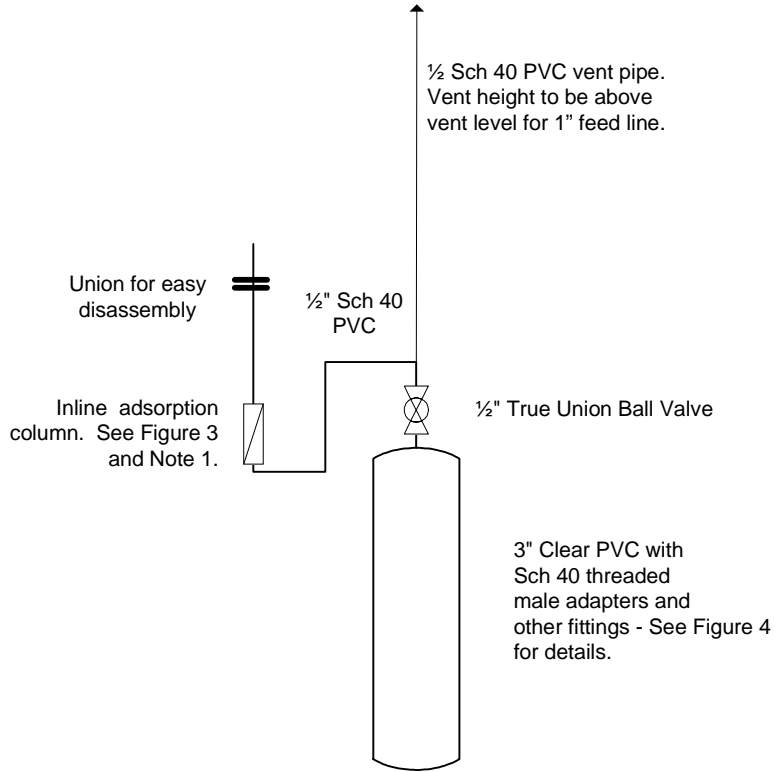


Notes

1. One collection tube per media. Up to 5 treatments per deployment. See Figure 4 for more details on sample collection system components. Only one collection tube shown in this sketch.
2. Slight upturn on 1" feed pipe ensures that pipe is always full. See Figure 5 for more details on feed pipe.
3. Vent tubes need to be above outflow level of 1" feed pipe.
4. Inline filter for removal of large particles and leaves (Figure 5)
5. Drawings are not too scale. Layout is conceptual and will need to be finalized with implementation in the field.
6. Most fittings are threaded for easy assembly and disassembly.
7. Top of media to be below EI such that media is submerged and has saturated flow. See Figure 3 for details on media column.

Figure 2. Conceptual drawing of collection system.

Five collection systems are planned. See Figures 3 through 5 for details on components.



Notes

1. For treatment with no media, replace with needle valve
2. Not to scale.

Figure 3. Inline Adsorption Column

Inline adsorption column will operate under submerged conditions such that it experiences saturated flow. This will help minimize short-circuiting through the column. Media height is expected to be 2 inches but that can be adjusted. Initially, media volume will be designed such that the collection bottle volume is approximately 100 times greater than the pore space volume in the inline column. This will enable an approximation of long-term capacity and long-term P concentrations that can be achieved. An upstream strainer in the feed line will remove large debris and particles. See Table 6 for parts lists.

Notes

1. Parts are glued together.
2. Screen is fit snug between male adapter and pipe.
3. Not to scale.

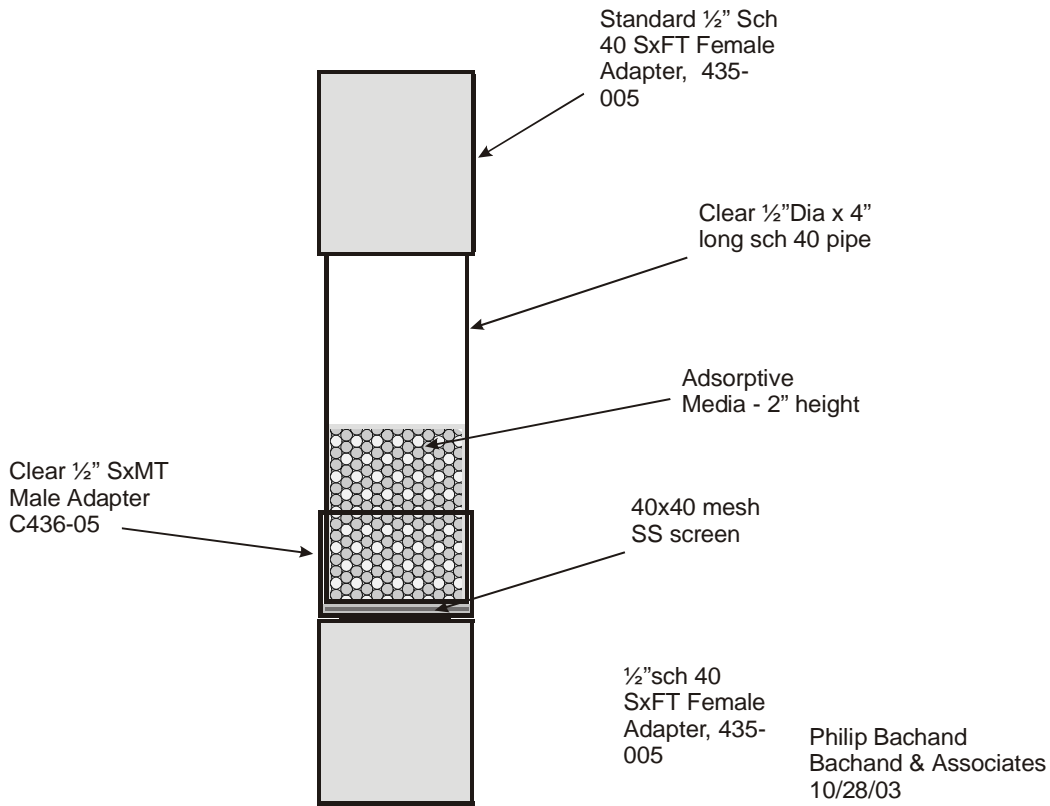
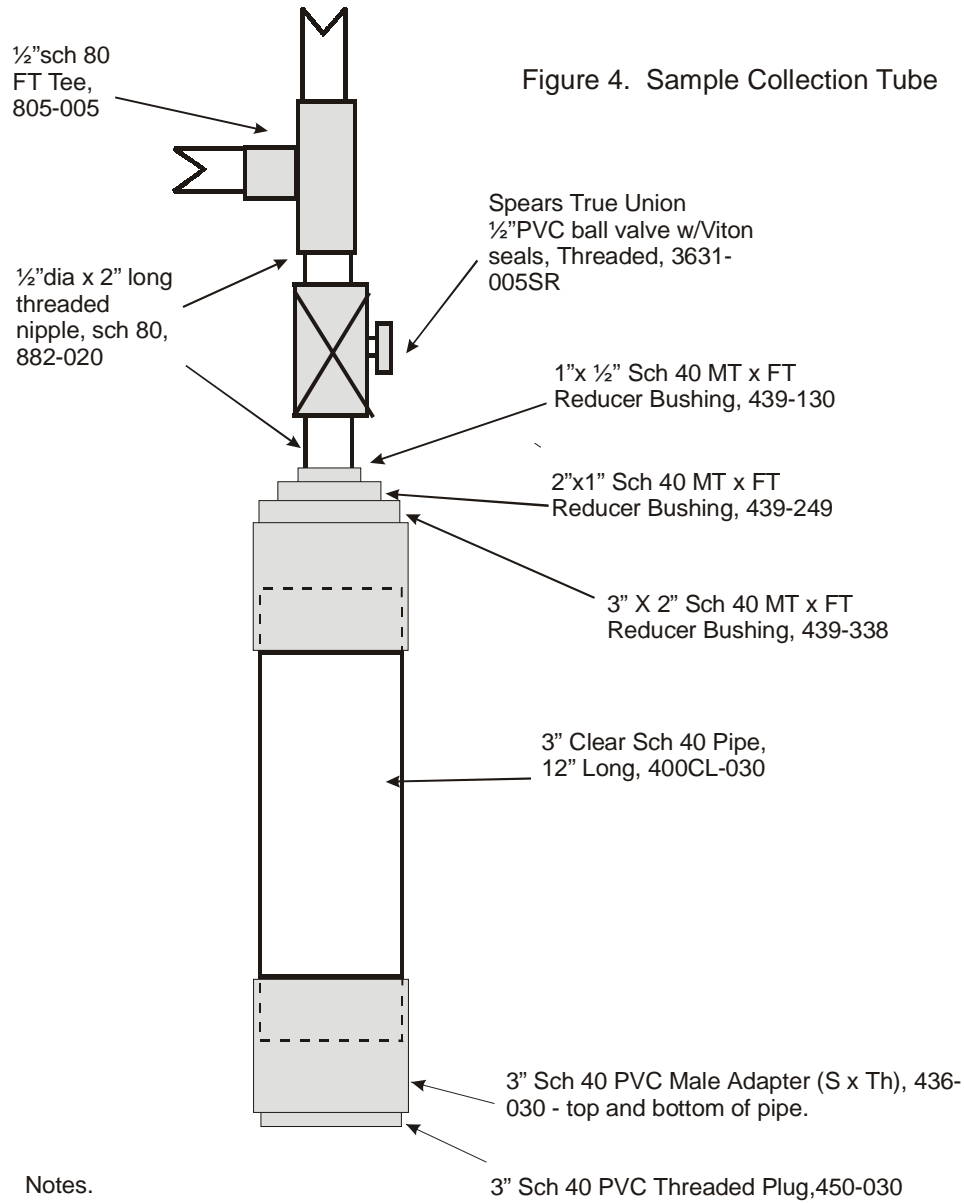


Figure 4. Collection Tube.

Tube is designed to collect approximately 100 times the volume of the inline adsorption column pore space (Figure 3). Collection Tube is clear such that an initial field assessment can be made on the collected system and whether there were failures. Ball valve allows the sample to be sealed and isolated from disturbance before moving the collection system from the field. See Table 6 for parts lists.

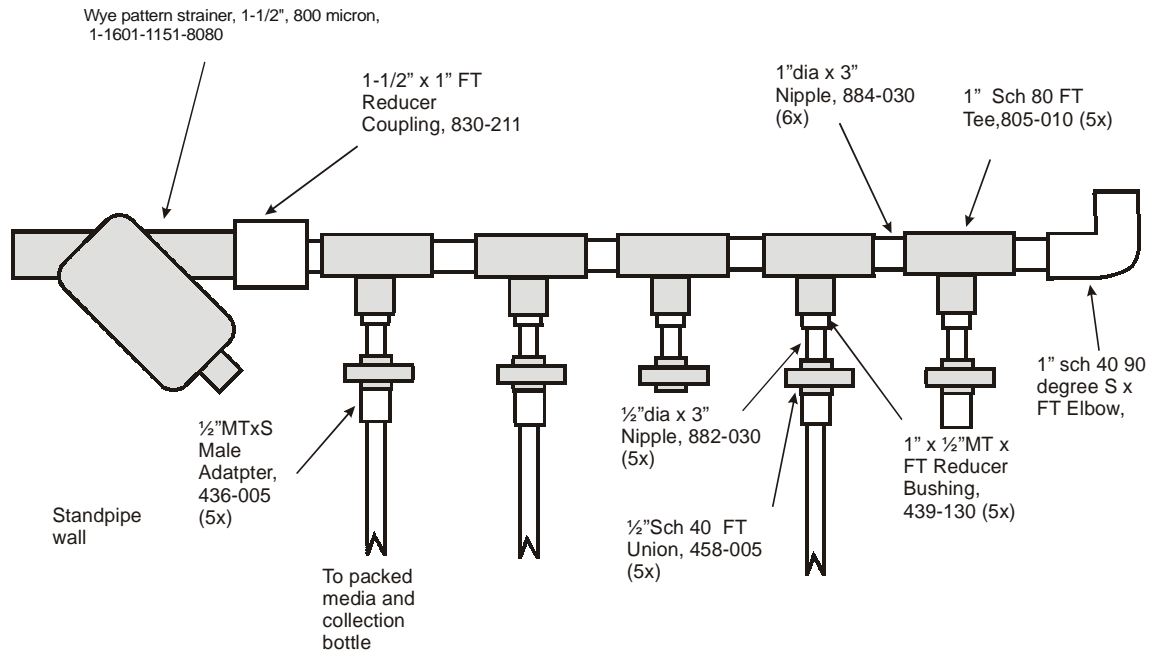


- Notes.
1. Not to scale.
 2. All components are threaded unless otherwise indicated.
 3. Component catalog numbers are shown for ordering from Harrington Plastics.

Philip Bachand
 Bachand & Associates
 10/28/03

Figure 5. Collection System Feed Line.

System is designed to allow connection of five sample collection systems. Uprturned el ensures that feed line is filled and ensures equal head to all collection systems. An inline filter removes large debris and particles. Feed line is threaded to the inside of the outflow standpipe. See Table 6 for parts lists.



- Notes.
1. Not to scale.
 2. All components are threaded unless otherwise indicated.
 3. Component catalog numbers are shown for ordering from Harrington Plastics.
 4. Tees and els may need to be integrated into feed line if there is insufficient room in the standpipe .

Philip Bachand
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10/28/03

Appendix 5 – Analyses of Isotherm Data

2003.01

**Ranking adsorptive media for phosphorus uptake in the Tahoe Basin based upon
Isotherm Analyses**

**By Philip A. M. Bachand, Ph.D.
Bachand & Associates**

**Submitted to the
University of California Davis
Tahoe Research Group
In fulfillment of Contract No. 02-00700ICR**

and

**Alan L. Heyvaert
UC Davis Tahoe Research Group**

October 11, 2004

Ranking Adsorptive Media

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Abstract

A variety of isotherms are typically used to rate the phosphorus uptake characteristics of soils and different media. Media considered in this analysis included activated alumina, iron and/or lanthanum coated diatomaceous earth, bauxite, dolomite, expanded shales and other light weight aggregates, and locally available Tahoe soils. These media were analysed using freundlich, langmuir and linear isotherms. For the tests we conducted, langmuir isotherms generally provided the best fit for the data over the full range of phosphorus adsorption. This range was typically from 10 ppb to up to 5,000 ppm and for this range the R^2 was generally between 0.88 and 1.00, except for two media. Based upon the langmuir isotherms, performance for the different media vary greatly with maximum uptake rates varying over nearly two orders of magnitude. More engineered substrates like activated alumina and lanthanum coated diatomaceous earth perform much better than any of the naturally occurring media or local soils. However, for low phosphorus concentrations typical of Lake Tahoe stormwater, these results are somewhat misleading. Tahoe stormwater typically has a phosphorus concentration in the range of 10 to 1,000 ppb, and for these low concentrations, neither the Langmuir nor Freundlich isotherm is a particularly good predictor. This poor relationship is shown in residual analyses, in which residuals for low uptake concentrations are often of a similar or greater magnitude than the predicted value itself. Thus, at these low phosphorus concentrations, linear isotherms are often the best predictor. In an analysis of slopes, the differences between the media are much smaller than in the langmuir analyses. As with the langmuir analysis, activated alumina and lanthanum coated diatomaceous earth are the better performers. However, unlike the langmuir analyses, other media such as Utelite (an expanded shale) and Dolomite sometimes perform at a similar level, depending upon the method of analyses. This similarity in performance is shown again when measuring uptake rates for different phosphorus loading rates. At loading rates between 100 and 10,000 ppb, the best performing media only perform slightly better than the average performing media. Based upon these analyses, we developed an overall ranking for the media which included results from the isotherm analyses and measured uptake rates. We recommend that further testing be conducted on activated alumina, lanthanum coated diatomaceous earth, dolomite and Utelite. We believe that these media will all have greater uptake capacities than the locally available soils.

Introduction

Adsorptive isotherm studies were run on fifteen different adsorptive media. Media tested comprised three different groups: native soils used as a standard of comparison, media selected as part of the Placer County Kings Beach study based upon an earlier literature review and screening isotherm studies, and media selected by CSUS Office of Water Programs. The goals of these adsorptive isotherms was to determine the phosphate uptake capacity and trends for these different adsorptive media and from understanding those trends select adsorptive media for further testing in break-through columns. The different media tested here are listed in Table 1.

Table 1. Tested Media

Tested Media	Code
<i>Native soils</i>	
Elois Basin	ELOIS
Coon Street Basin	COONS
Round Hill Basin	ROUND
<i>Placer County Study Selected Media</i> ¹	
Activated Alumina DD2 ⁴	ALDD2
Activated Alumina CD714 ⁴	CD714
Bauxite, 16 - 20 mesh	BXTLG
Dolomite, 20-mesh	DOL20
Riverside Expanded Shale	XSHAL
Utelite Expanded Shale	UTILT
Lanthanum coated silica ²	LANSI
Diatomaceous Earth, MP79	MP79D
Lanthanum coated MP79	MP79L
<i>OWP CSUS Media</i>	
Wollstonite	WOLLO
Iron-Lanthanum coated MP79	MP79F
Limestone ³	CALIM

1. Media selected based upon screening study done as part of Placer County Kings Beach study.

2. Laboratory product from University of Nevada Reno.

3. Limestone supplied from outside California. Previously tested limestone was metamorphic limestone from California

4. Activated alumina products from Alcoa

Isotherm Models

Isotherms are commonly used to model the phosphorus adsorption capacity and trends of different media. The most commonly used isotherms are the langmuir isotherm, the freundlich isotherm and linear isotherms.

The langmuir isotherm is described by the following equation:

$$C_s = \frac{abC}{1 + aC}$$

Ranking Adsorptive Media

where

a is a constant related to binding strength,

b is the P adsorption maximum,

C_s is the P concentration on the solid media, and

C is the equilibrium P concentration in solution.

The freudlich isotherm is described by

$$C_s = K_f \bullet C^n$$

where

K_f = Freundlich adsorption constant

n = Freundlich exponent

If n = 1, the Freundlich isotherm reduces to a linear isotherm:

$$C_s = MC$$

where M is the linear constant or slope.

If the isotherms present a reasonable approximation of the phosphorus adsorption characteristics, then performance of the media can be predicted. The maximum P adsorption can be predicted by using the P adsorption maximum (b) from the langmuir isotherm. This approximation predicts the maximum uptake that can be achieved. However, greater solid phase concentrations correlate with greater liquid phase concentrations. In a situation like the Tahoe Basin, where background phosphorus concentrations in the water are often less than 1 ppm and the desired standard is 100 ppb, maximum adsorption capacity may not be the best indicator for selecting adsorption media. In this case, characteristics such as initial rapid uptake of phosphorus as defined by the initial slope may be more important. Two of these isotherms provide an estimate of initial slope. For the linear isotherm, M defines slope. For the langmuir isotherm, taking the derivative of the expression defines the slope:

$$m_L = \left(\frac{ab}{1+aC} \right) - \frac{a^2bC}{(1+aC)^2}$$

Setting the water phase concentration C to zero defines the initial slope:

$$m_{L,0} = ab .$$

This is then the product of the binding energy and the maximum uptake capacity.

Results

Media were ranked in several ways to select media appropriate to the Tahoe Basin for further testing:

- Maximum adsorption capacity
- Phosphorus uptake at low water phase P concentrations

Ranking Adsorptive Media

- Phosphorus uptake at an equilibrium water phase concentrations at the surface water standard ($P_{eq} = 100$ ppb)
- Phosphorus uptake characteristics near typical stormwater loading rates.

Rankings were developed using a combination of isotherm results and phosphorus uptake from an analysis of raw data.

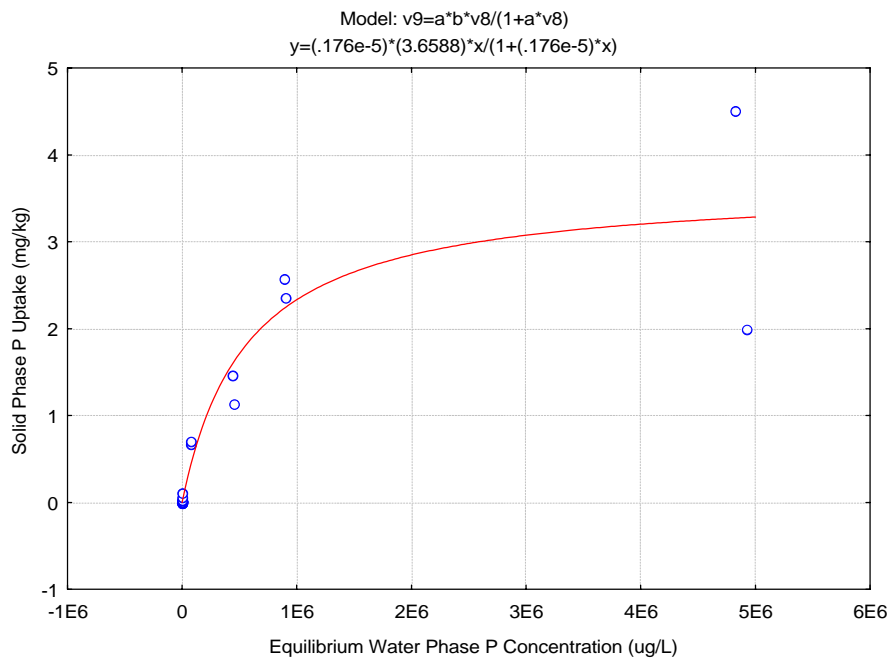
Ranking media on maximum adsorption capacity

A prediction of maximum adsorption capacity was based upon the langmuir b constant (Table 2). For most media, the langmuir isotherm fit the data well. For nearly all media, the fit explained over 80% of the variance in the data. Figure 1 presents the langmuir fits for soil from the Coon Street Basin, a relatively poor substrate for adsorbing phosphorus, and lanthanum coated MP79, the media with the highest phosphorus adsorption capacity. The curve from the Coon Street Basin data shows typical problems with achieving a good fit of the data. At equilibrium P concentrations in the area where the curve begins to flatten out, saturation and dilution are two contributing factors to increased variance in the data. A high amount of variance can also be found at very low concentrations. At very low concentrations (< 100 ppb), there is often much noise in the data and this is likely do to heterogeneity in the media affecting phosphorus uptake. For media less likely to be saturated, such as the lanthanum coated MP79, the curve better fits the data as the data is more robust.

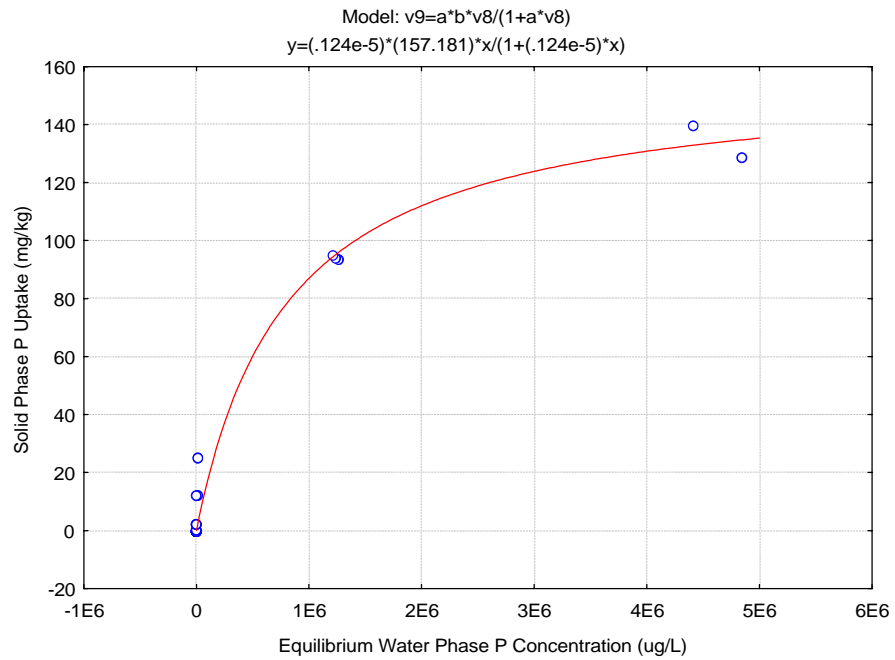
Ranking Adsorptive Media

Figure 1. Langmuir Curves for Isotherm Data.

a. Coon Street Basin Soil



b. Lanthanum coated MP79



Ranking Adsorptive Media

The highest ranked media based upon this criteria was the lanthanum coated MP79 with a predicted maximum P adsorption capacity of 95,095 mg/kg. Both activated alumina products (ALDD2 and CD714) were ranked two and three with predicted capacities of about 42,000 mg/kg. The top six media are shown in green in Table 2. Three of the lowest five media for maximum P adsorption capacity were native soils (e.g. COONS, ELOIS, ROUND).

Table 2. Langmuir Isotherm Results

Media	Langmuir Constants		R ²	Ranking	Notes
	a	b			
	L/mg	mg/kg			
ALDD2	0.01012	42,967	0.9484	2	1
BXTLG	0.00201	6,263	0.9261	10	1
CD714	0.00444	41,006	0.9781	3	1
COONS	0.00176	3,659	0.8820	11	1
DOL20	0.03601	7,976	0.8816	8	1
ELOIS	0.00910	796	0.6870	14	1
LANSI	0.00053	22,070	0.9943	4	1
MP79D	0.06531	653	0.4666	15	1
MP79F	0.11019	8,393	0.9422	7	1
MP79L	0.08691	95,095	0.9930	1	1
ROUND	0.00662	1,149	0.9452	13	1, 2
UTILT	0.02016	8,719	0.7571	6	1
WOLLO	0.02566	2,168	0.9784	12	1
XSHAL	0.00931	7,455	0.9565	9	1
CALIM	0.00424	9,296	0.8997	5	1, 2
Notes					
1. Calculated from replicated data for dosing levels of 0,10 50 100, 500 and 1000 ppb and 10, 100, 500, 1000 and 5000 ppm unless noted otherwise.					
2. Did not include dosing level of 5000 ppm in calculation as data considered outliers.					

Ranking based upon predicted solid phase P uptake at low water phase P concentrations

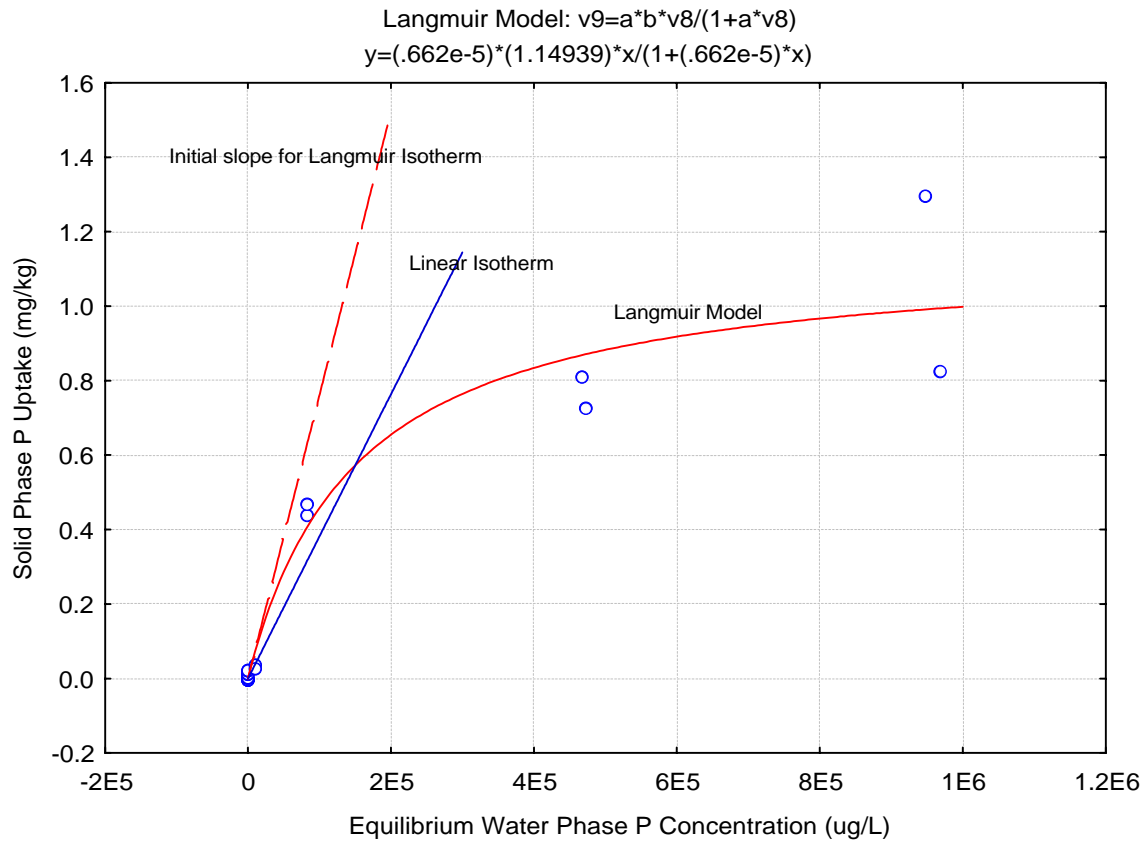
To predict uptake effectiveness at low water phase P concentrations, isotherm curve slope was used as an indicator. With both the langmuir and linear isotherms, an initial slope can be estimated. (The initial slope for the freundlich isotherm is infinity.) Figure 2 demonstrates calculations of the slopes. The solid red line is the langmuir isotherm and the dashed line represents the initial slope for the isotherm. Langmuir constants were developed for dosing concentrations up to 5,000 ppm unless otherwise noted (Table 2).

Linear isotherms were developed for the low range of phosphorus concentrations in the liquid stage. We tried to develop isotherms for equilibrium phosphorus concentrations less than 1,000 ppb. For media with low phosphorus uptake capacity, such as the native soils, the curves were developed for dosing concentrations less than 1,000 ppb. For media with higher uptake capacity, dosing concentrations up to 10,000 ppb were used. The dosing range used in developing the isotherms are shown in Table 3. In Figure 2, the solid blue line represents the linear fit for the low equilibrium phosphorus concentrations. For the Round Hill soils, this predicted slope is less

Ranking Adsorptive Media

than the slope calculated from the langmuir curve. However, that relationship is not always the same as shown in Table 3.

Figure 2. Slopes shown for adsorption data for Round Hill soils



These calculated slopes thus represent estimates of the initial slope for the phosphorus uptake and are indicators of uptake characteristics of media at low water column concentrations typical of that found in the Tahoe Basin. The greater the slope then the greater phosphorus uptake at low dosing water column phosphorus concentrations.

Ranking differs slightly based upon which isotherm approach is used. In Table 3, the top six for each method are shaded. Activated aluminas, Utelite and lanthanum coated DE rank high under both approaches. We totaled the points for the two approaches and developed a cumulative rank based upon that total sum. Under that approach, the media that were most effective at initial phosphorus uptake are the lanthanum coated DE, the two activated aluminas, the iron coated MP79, Utelite and Dolomite. The poorest performers were the locally collected soils.

Table 3. Ranking media based upon initial slopes.

Media	Init. Langmuir slope (a*b)		Linear slope, Peq < 1000 ppb		Final Rank		Notes
	Slope kL/g	Rank	Slope kL/g	Rank	Total Points	Cum. Rank	
ALDD2	0.00043	3	0.00115	3	6	1	2
BXTLG	0.00001	11	0.00025	9	20	10	2
CD714	0.00018	5	0.00136	2	7	3	2
COONS	0.00001	15	0.00001	14	29	15	1
DOL20	0.00029	4	0.00026	8	12	6	2
ELOIS	0.00001	14	0.00002	13	27	13	1
LANSI	0.00001	12	0.00194	1	13	7	2
MP79D	0.00004	9	0.00003	12	21	11	1
MP79F	0.00092	2	0.00033	7	9	4	2
MP79L	0.00826	1	0.00087	5	6	1	2
ROUND	0.00001	13	0.00000	15	28	14	1
UTILT	0.00018	6	0.00091	4	10	5	2
WOLLO	0.00006	8	0.00010	10	18	9	1
XSHAL	0.00007	7	0.00053	6	13	7	2
CALIM	0.00004	10	0.00009	11	21	11	1
Notes							
1. Linear fit based upon dosing up to 1,000 ppb.							
2. Linear fit based upon dosing up to 10,000 ppb							

Ranking based upon predicted phosphorus uptake at Tahoe Basin phosphorus standard

Another approach we used in ranking media was to rank them based upon expected media uptake at the Tahoe Basin phosphorus discharge standard for surface waters. The current discharge standard is 100 ppb. Thus, we estimated phosphorus uptake based upon the isotherm analyses of the data. For this estimate, we used all three isotherms (langmuir, freundlich, linear; Table 4). In general, the langmuir isotherm gave better results though all the isotherms are only estimates. Table 5 highlights this point by showing the measured, predicted and residual C_s using both the langmuir and freundlich isotherms. Essentially, the models are only estimates and oftentimes the greatest inaccuracies in the model occur at the very lowest concentrations, where there is a high variance associated with working at those low levels, and at the highest values, where dilution and saturation introduce variance.

Based upon this approach, the activated aluminas, Utelite and the lanthanum coated MP79 were ranked highly for all isotherms in which constants could be calculated. And as in the previous analysis in which ranking was based upon slope, the local soils ranked the poorest. For each isotherm, an uptake rate is estimated for an equilibrium water concentration for phosphorus of 100 ppb. These calculated uptake rates range over two orders of magnitude. This clearly shows that calculating phosphorus uptake rates based using isotherm constants introduces much uncertainty, especially at lower phosphorus concentrations, and thus the isotherm results may be most useful for relative comparisons instead of absolute predictions. Table 5 shows this clearly as in many cases the residuals are greater than the predicted uptake rates. This is especially true

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at the lower solid phase uptake concentrations. At these lower levels, prediction errors from the isotherms can result in great variance from actual values.

Table 4. Ranking media performance based upon predicted uptake at $P_{eq} = 100$ ppb.

	Langmuir			Freundlich			Linear			Summary			
	R2	Cs	Rank	R2	Cs	Rank	R2	Cs	Rank	Rank Ave.	Cum. Rank	Estimated Cs	
												Upper	Lower
ALDD2	0.948	0.043	3	0.963	2.506	1	0.959	0.057	3	7.0	2	2.506	0.043
BXTLG	0.926	0.001	11	0.881	0.140	7	0.389	0.013	10	28.0	9	0.140	0.001
CD714	0.978	0.018	5	0.992	1.273	3	0.951	0.068	2	10.0	3	1.273	0.018
COONS	0.882	0.001	15				0.000	0.000	15	30.0	11	0.001	0.000
DOL20	0.882	0.029	4	0.709	1.402	2	0.956	0.013	9	15.0	6	1.402	0.013
ELOIS	0.687	0.001	14	0.587	0.088	11	0.760	0.014	8	33.0	14	0.088	0.001
LANSI	0.994	0.001	12	0.994	0.068	12	0.994	0.097	1	25.0	8	0.097	0.001
MP79D	0.467	0.004	9	0.340	0.115	9	0.274	0.005	13	31.0	12	0.115	0.004
MP79F	0.942	0.091	2	0.785	0.953	5	0.368	0.016	7	14.0	4	0.953	0.016
MP79L	0.993	0.819	1				0.881	0.043	5	6.0	1	0.819	0.043
ROUND	0.945	0.001	13	0.850	0.001	13	0.000	0.007	12	38.0	15	0.007	0.001
UTILT	0.757	0.018	6	0.696	1.181	4	0.991	0.046	4	14.0	4	1.181	0.018
WOLLO	0.978	0.006	8	0.952	0.109	10	0.499	0.001	14	32.0	13	0.109	0.001
XSHAL	0.956	0.007	7	0.848	0.696	6	0.275	0.026	6	19.0	7	0.696	0.007
CALIM	0.900	0.004	10	0.935	0.116	8	0.863	0.012	11	29.0	10	0.116	0.004

Table 5. Model Residuals for Cs for iron-lanthanum coated MP79.

Datapoint	Model	Freundlich		Langmuir	
	R ²	0.785		0.942	
	Measured Cs	Predicted Cs	Residual Cs	Predicted Cs	Residual Cs
1	-0.003	0.995	-0.998	0.111	-0.114
2	-0.004	1.053	-1.056	0.143	-0.147
3	-0.003	0.977	-0.979	0.102	-0.105
4	-0.003	0.983	-0.986	0.105	-0.108
5	-0.002	0.992	-0.993	0.110	-0.111
6	-0.002	0.989	-0.991	0.108	-0.110
7	-0.001	0.994	-0.994	0.111	-0.111
8	-0.001	0.999	-0.999	0.113	-0.114
9	0.008	1.075	-1.067	0.157	-0.149
10	0.008	1.081	-1.073	0.161	-0.153
11	0.019	1.152	-1.133	0.214	-0.195
12	0.019	1.151	-1.132	0.213	-0.194
13	0.242	1.239	-0.997	0.294	-0.053
14	0.242	1.239	-0.997	0.294	-0.053
15	2.429	1.993	0.436	2.006	0.423
16	2.408	2.111	0.297	2.431	-0.023
17	6.988	5.196	1.791	8.061	-1.074
18	6.756	5.244	1.513	8.074	-1.318
19	9.875	6.491	3.384	8.269	1.606
20	10.075	6.472	3.603	8.267	1.808
21	9.750	10.155	-0.405	8.377	1.373
22	5.875	10.229	-4.354	8.377	-2.502
Average	2.485	2.855	-0.370	2.550	-0.065

Ranking based upon phosphorus dosing concentrations typical of Tahoe Basin stormwater

The final approach we used to rank media was to use data measured directly from the isotherm studies, and not utilizing a model for interpretation. Typical stormwater in the Tahoe Basin has phosphorus concentrations ranging from less than 100 to over 1,000 ppb. So for this analysis we used data from the isotherm experiments for P dosing concentrations of 100, 1,000 and 10,000 ppb. We did not use data from lower dosing concentrations because of the noise in the data at those dosing concentrations.

Under this approach, we calculated C_s for each media at each of the three dosing concentrations ($N=2$), ranked each media at each concentration, totaled the rankings across dosing concentrations, and then ranked the cumulative total. This approach focuses on load reduction at each dosing concentration and differs from the previous approach in that it does not focus on meeting a 100 ppb phosphorus standard. Thus, this approach is more consistent with ranking media based upon their performance after TMDLs have been implemented for phosphorus in the Tahoe Basin.

Many of the same media that have been highly ranked before continue to perform well. The activated aluminas and utelite perform well at all dosing levels. Surprisingly, the local soils do not perform as poorly as previous rankings would suggest. They are generally below average performers, though not performing as poorly as some other tested media such as wollostonite or iron-lanthanum coated MP79. However, at the higher dosing concentration (10,000 ppb), all the native soils perform very poorly. This is in contrast to the media such as activated aluminas, utelite and lanthanum coated MP79, which continue to perform well at the higher dosing concentration. This suggests that the native soils are less robust performers with regard to phosphorus adsorption, oftentimes performing reasonably well at low phosphorus concentrations but become much less effectively if those phosphorus concentrations in the stormwater should increase.

One striking result from this analysis is the similarity in performance for most the media tested when being dosed by stormwater at these low concentrations (< 10 ppm). At all dosing levels, the best performing media only perform 13 to 30% better than the average. And the median C_s value is only 4 to 11% below the maximum C_s . Thus, for all dosing levels, the media ranked in the top eight are very close in performance.

Table 6. Ranking based upon measured Cs from isotherm studies for phosphorus dosing concentrations typical of stormwater.

Media	Pdose						Summary	
	100 ppb		1000 ppb		10,000 ppb		Rank total	Cum. Rank
	Cs	Rank	Cs	Rank	Cs	Rank		
ALDD2	0.0023	5	0.0242	5	0.2449	4	14	3
BXTLG	0.0019	10	0.0139	14	0.2370	8	32	11
CD714	0.0023	6	0.0238	8	0.2458	2	16	4
COONS	0.0022	8	0.0244	4	0.0883	14	26	8
DOL20	0.0024	1	0.0241	6	0.2283	9	16	4
ELOIS	0.0019	9	0.0235	9	0.1108	13	31	10
LANSI	0.0024	3	0.0247	2	0.2469	1	6	1
MP79D	0.0015	12	0.0228	10	0.1433	12	34	12
MP79F	-0.0006	15	0.0191	13	0.2418	7	35	13
MP79L	0.0018	11	0.0247	1	0.2436	5	17	6
ROUND	0.0014	13	0.0239	7	0.0330	15	35	13
UTILT	0.0024	2	0.0245	3	0.2434	6	11	2
WOLLO	0.0009	14	0.0113	15	0.2084	10	39	15
XSHAL	0.0022	7	0.0191	12	0.2458	2	21	7
CALIM	0.0023	4	0.0226	11	0.1961	11	26	8
Average	0.0018		0.0218		0.1971			
Median	0.0022		0.0238		0.2370			
Min	-0.0006		0.0113		0.0330			
Max	0.0024		0.0247		0.2469			
St Dev	0.0008		0.0041		0.0695			

Summary

For a final ranking, we have taken the ranking results for the four previous analyses, totaled those rankings and selected media for further testing based upon ranking those totals. This approach considers the maximum adsorptive performance but weights the ranking based upon performance at low phosphorus concentrations. Under this approach, the top six media tested were the two activated aluminas (ALDD2, CD714), the lanthanum coated diatomaceous earth (MP79L), the lanthanum coated silica, an expanded shale (Utelite) and dolomite. Of these, CD714 is not recommended for further testing as it is very similar to the ALDD2. LANSI is also not recommended for further testing as it is only available in very small quantities from a research lab at University of Nevada Reno.

Generally, the local soils do not rank well based upon the four different approaches used in this analysis. This is primarily do to their poorer performance at dosing concentrations above 1,000 ppb. That poor performance is reflected in the models that are the basis for many of these ranking approaches used here.

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Table 7. Media selected for further testing

	Performance at High P Conc	Performance at Low Dosing Concentrations			Summary		Notes
	Maximum adsorptive capacity	Ranking based upon slopes of Linear and Langmuir Isotherms	Ranking based up Cs calculated for Peq = 100 using all isotherms	Cs measured at typical stormwater concentrations (100, 1000, 10000 ppb)	Total	Final Rank	
ALDD2	2	1	2	3	6	1	3
BXTLG	10	10	9	11	30	10	
CD714	3	3	3	4	10	3	1
COONS	11	15	11	8	34	11	
DOL20	8	6	6	4	16	5	3
ELOIS	14	13	14	10	37	13	
LANSI	4	7	8	1	16	5	2
MP79D	15	11	12	12	35	12	
MP79F	7	4	4	13	21	7	
MP79L	1	1	1	6	8	2	3
ROUND	13	14	15	13	42	15	
UTILT	6	5	4	2	11	4	3
WOLLO	12	9	13	15	37	13	
XSHAL	9	7	7	7	21	7	
CALIM	5	11	10	8	29	9	
Notes							
1. CD714 not selected for future testing as it is very similar to ALDD2.							
2. LANSI not selected for future testing as it is similar to lanthanum coated MP79L and is only available from a UNR lab.							
3. Selected for recommendation for further testing.							

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ADSORPTIVE MEDIA INVESTIGATION

Appendix 6 – Column Study Database Structure

