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

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Placer County
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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

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.

Table of Contents

List of Figures

List of Tables

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 (μg/L)
Peq	Equilibrium phosphorus concentration
SOP	Standard Operation Procedure
μg/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 – UCDCEE, 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.

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.

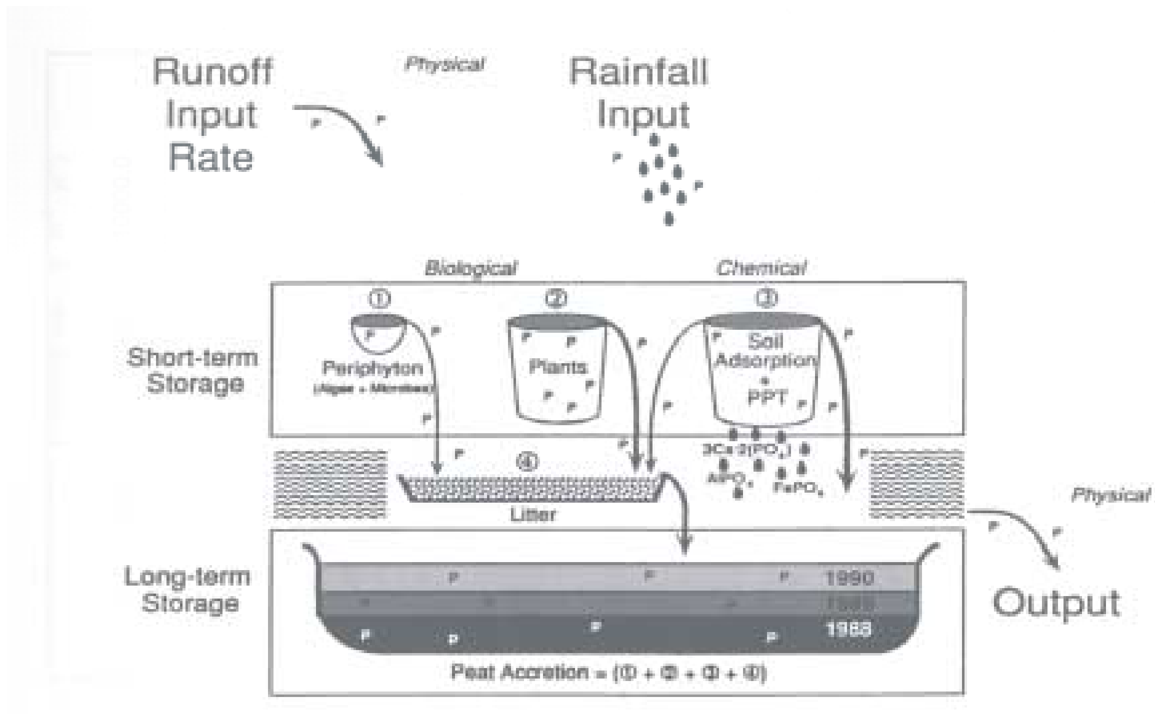


Figure 2-1. Wetland Phosphorus Uptake Model (Richardson et al., 1997)

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.

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, Utelite 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.

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 is 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.

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 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.

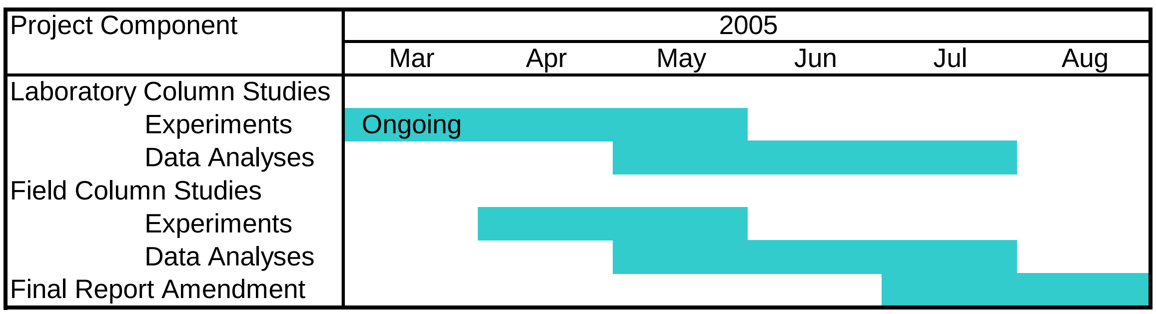


Figure 4-1. Schedule to Complete Adsorption Column Study

4.1 Isotherm Studies

Table 4-1 shows the different media that were tested during the isotherm analyses. Wollostanite, 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 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.

Table 4-1. Tested Media

Tested Media	Code
Native soils	
Elois Basin	ELOIS
Coon Street Basin	COONS
Round Hill Basin	ROUND
Placer County Study Selected Media [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
OWP CSUS Media	
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 (Peq = 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.

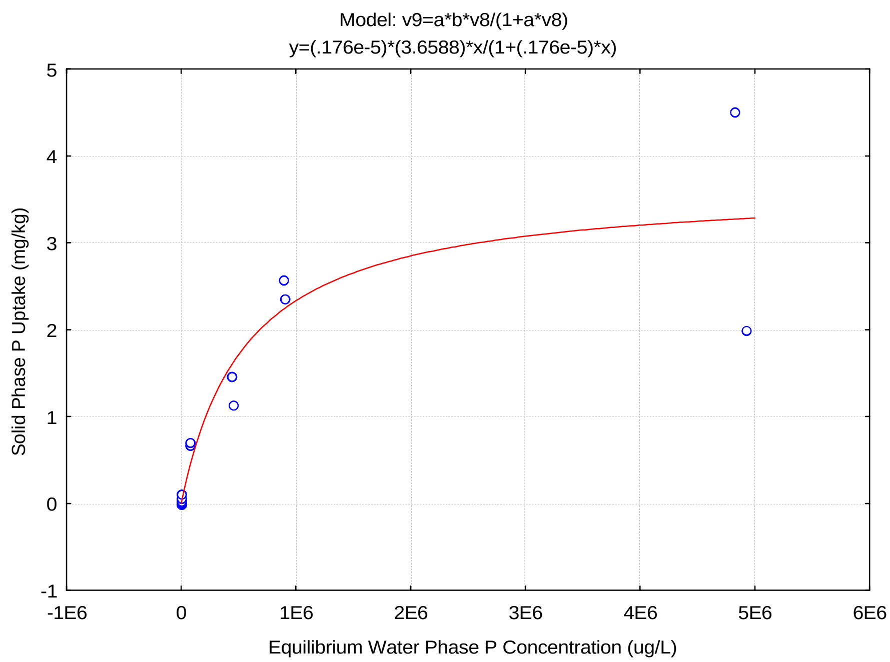
Table 4-2. Media selected for further testing

	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 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.

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

a. Coon Street Basin Soil



b. Lanthanum coated MP79

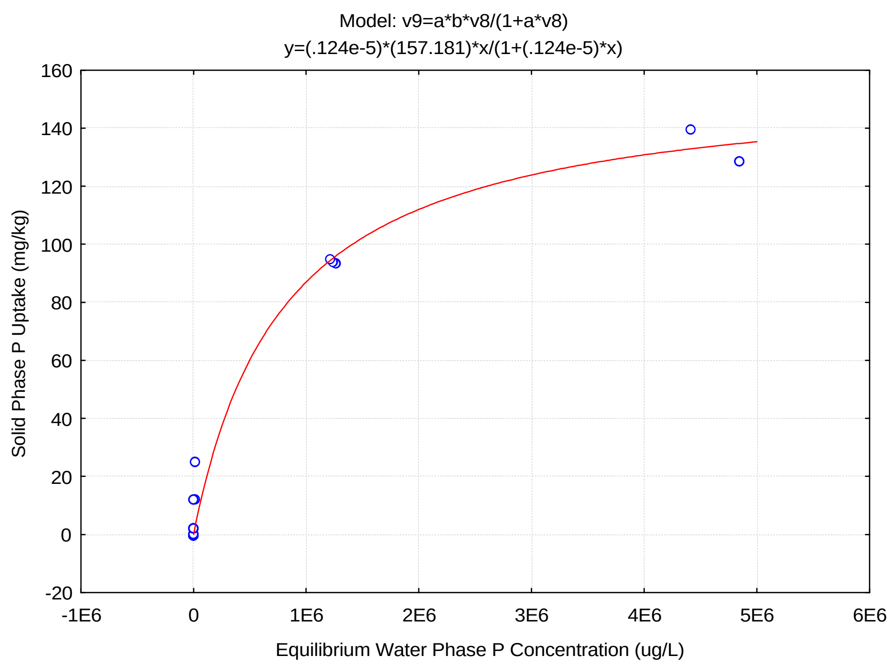
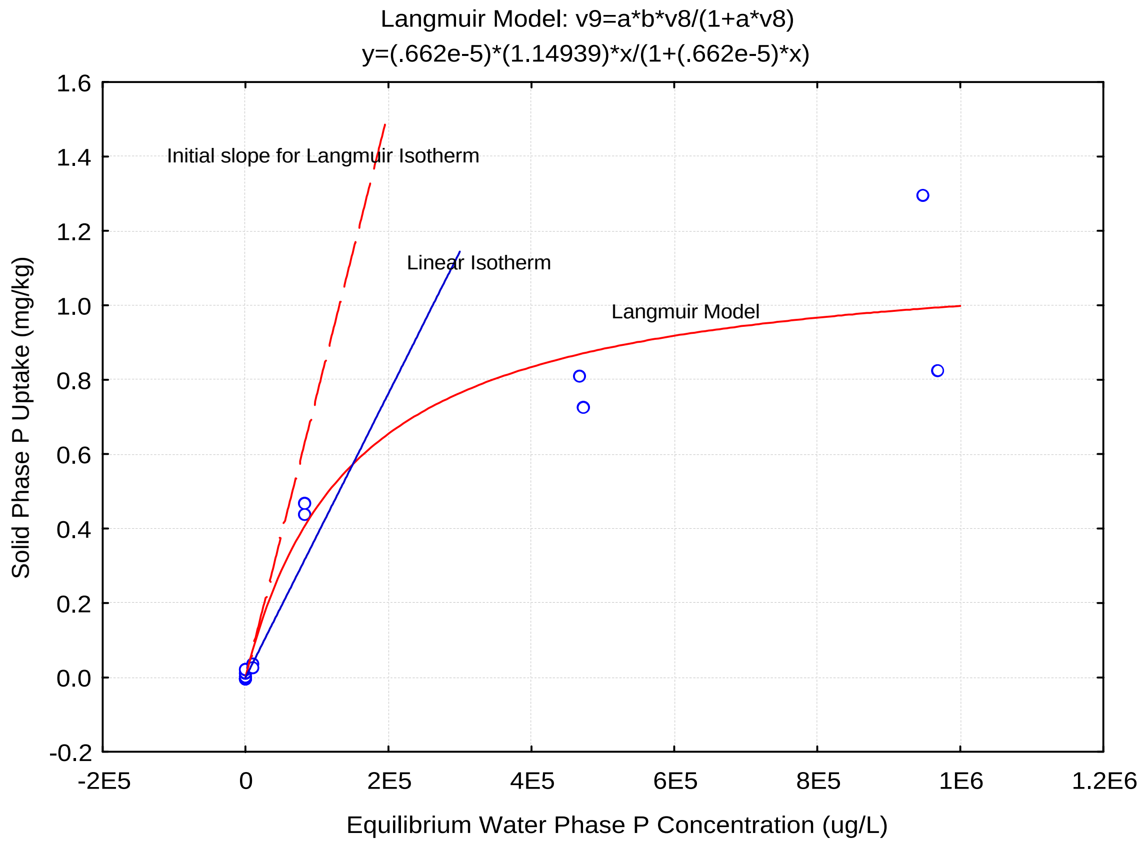


Figure 4-3. Langmuir and Linear isotherms fit to data from Round Hill soils



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

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/cm^3 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 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 then 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 then 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 then 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 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

Appendix 1 – Adsorptive Media Literature Review

Appendix 2 – Experimental Design of Laboratory and in situ Studies

Appendix 3 – Standard Operating Procedure for Laboratory Column Study

Appendix 4 – Standard Operating Procedure for Field Column Studies

Appendix 5 – Analyses of Isotherm Data

Appendix 6 – Column Study Database Structure