Quick Start BMP Program

Evaluation of a Low-Tech Selenium Removal Best Management Practice

Final Report

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Prepared for the:
NPDES TAC and
Nitrogen and Selenium Management Program
Working Group

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Glossary of specific terms, acronyms and symbol used in this report:

AF; Acre-Feet

Bioavailable; The relative ease that a chemical is acquired by organisms. Some forms of selenium are more bioavailable than others. If two different forms of selenium are present at the same concentration, the more bioavailable form will be taken up faster by plants and animals.

Biotransformation; The act of living organisms changing the chemical form of selenium. The two most common biotransformations of concern in this context are the conversion of selenate to selenite in reducing environments, and the conversion of inorganic selenium to organoselenium within organisms.

Bioaccumulation; Consumption of a pollutant through food that results in an increase in the body burden of the pollutant in the consuming organism.

CALTRANS; California Department of Transportation, a member of the working group

Cutter method; an analytical method for determining selenium **speciation.** Named for Dr. Greg Cutter, who developed the method as part of his doctoral research at the University of California, Santa Cruz.

Difference method; an analytical method that determines a particular selenium **species** (e.g., organoselenium) as the difference between the analytical results of two different analyses (e.g., total selenium – inorganic selenium = organoselenium). The uncertainty of results by difference methods can be relatively large if the result is a small difference.

Elemental selenium; Se^0. An insoluble reddish precipitate, readily removed from water by precipitation. Low solubility and bioavailability lessen ecological risk compared to selenite and selenate. This form is more reduced than selenite, but not as reduced as selenide or organoselenium.

IRWD; Irvine Ranch Water District, a member of the working group.

gpm; gallons per minute

Hydride generation; a technique for measuring selenium. Hydride generation, combined with a series of chemical transformations, can be used to determine selenium **speciation**. This is known as the **Cutter method**.

ICP/MS; Inductively coupled plasma mass spectrometry. An analytical method for determining total and dissolved selenium. In contrast to **hydride generation**, ICP/MS does not provide information on selenium **speciation** unless some additional front-end chemical separations are performed.

Mesocosm; a small scale study, in between a bench-scale study (microcosm) and a scaled up pilot test (macrocosm). Microcosms, mesocosms, and macrocosms all refer to study areas that are essentially isolated from the surrounding environment**.**

NSMP; Nitrogen Selenium Management Program. The program funded by a cooperative agreement of public and private parties covered by the general permit for discharge of extracted groundwater. The five year program is intended to develop watershed management tools to ensure attainment of water quality standards for nutrients and selenium.

Organoselenium; Reduced selenium (selenide) that has at least one carbon bonded to selenium. Produced through biotransformation of selenite and selenate. Most common form is selenium substituted for sulfur in amino acids (e.g. selenomethionine). Accumulation of selenium-substituted amino acids through the diet is the major cause of reproductive problems in birds and fish.

ORP; Oxidation reduction potential - the degree of completion of a chemical reaction by detecting the ratio of ions in the reduced form to those in the oxidized form as a variation in electrical potential measured by an ORP electrode assembly. In this study, the ORP electrode assembly used is a standard platinum electrode. In general, higher ORP values (> 100 millivolts) indicate less reducing power, lower ORP values <0) indicate more reducing power. It should be noted that field measurements of ORP are very qualitative.

Reduce / reducing / reduction; In this report, the term "reduce" is only used to indicate chemical reduction, i.e., the addition electrons to reduce the oxidation state of selenium.

Selenate; ($SeO4^{2-}$) An extremely soluble selenium salt, with a very low affinity for sorption to particles. Purported to be the main form in groundwater extracted from the San Diego Creek watershed (Meixner et al, 2004). Very low bioaccumulation and/or biotransformation by microorganisms and algae. This is the most oxidized (least reduced) form of selenium.

Selenite; ($SeO3^{2-}$) A moderately soluble selenium salt with a much greater affinity for sorption to particles than selenate. This is a reduced form of selenium, though not as reduced as elemental selenium. Principal form of concern as it accumulates in phytoplankton ~10-fold more readily than selenate; Uptake is not inhibited by sulfate.

Species; In this context, a particular chemical form of selenium (e.g., **selenate, selenite, organoselenium, elemental selenium**)

Speciation; The distribution of selenium in a sample among all it's species. Saying "determine selenium speciation" means that in addition to quantifying the total amount of selenium in a sample, the relative amounts of each selenium **species** are also quantified.

µg/L; micrograms per liter, a.k.a parts per billion, or ppb

Working group; At least 16 public agencies and private entities that have entered into a funding agreement to support the Nitrogen Selenium Management Program.

EXECUTIVE SUMMARY

Managing selenium-laden extracted groundwater is an emerging issue for coastal watersheds. The San Diego Creek – Newport Bay watershed in Orange County is one of the first regions in the nation confronted with the impact of selenium water quality standards on activities such as construction site dewatering and dewatering of subterranean seepage that occur in urban watersheds. In December 2004, the Santa Ana Regional Water Quality Control Board issued a General NPDES Permit regulating certain groundwater-related discharges that provides dischargers with two options: (1) comply with a numeric effluent limit of 4 parts per billion selenium (monthly average) or (2) participate in the implementation of a work plan focused on developing treatment technologies and BMPs as well as a watershed management program for both selenium and nitrogen. A Working Group of at least 16 public agencies and private entities is funding and implementing this work plan over the next five years.

One of the early commitments in the work plan is the evaluation of a low-cost, low-tech Best Management Practice to decrease selenium concentrations in extracted groundwater. Existing contract resources available to the Countywide NPDES Stormwater Permit program were made available. Information gained from this BMP evaluation provides countywide benefits, because many groundwater dischargers throughout the County face the need to reduce nitrogen and selenium in short-term, small-scale discharges of extracted groundwater.

A structural BMP was designed and constructed at a location of known high selenium concentration in extracted groundwater. Measurements of selenium concentrations and chemical forms, as well as other constituents, were made to evaluate the BMP's effectiveness and feasibility. This report presents the results of that BMP evaluation.

The structural BMP selected was a bioreactor. The bioreactor is essentially a small-scale treatment wetland that utilizes anaerobic bacteria to set up chemically reducing conditions. The bioreactor removes selenium from water by chemically reducing highly soluble selenate to less soluble selenite and elemental selenium. This BMP was deemed the best fit for the Quick Start Program goal of developing and evaluating a BMP quickly and cost effectively.

The bioreactor design was based on a smaller scale prototype developed in 2003 by the Irvine Ranch Water District. (IRWD) Native soil, perlite, hay and straw provided the bioreactor media that was contained in a rollaway debris box. Extracted groundwater known to be high in selenium flowed through the bioreactor medium at flow rates ranging from 0.5 – 1.5 gpm over a period of two weeks. Total recoverable selenium, selenate, and selenite concentrations were measured in the inflow and outflow water. Additional measurements provided important information about the conditions in the bioreactor and ancillary benefits and drawbacks of this BMP design. Nitrate and nitrite measurements demonstrated the capacity of the system to remove nitrogen, which could be important for nutrient load management in the San Diego Creek Watershed. Nitrate reduction is also a good indicator of reducing potential necessary to achieve reductions in selenium concentrations. Sulfate measurements provided additional information about the reducing capacity of the bioreactor. Bacteria measurements (fecal

coliforms, total coliforms, enterococci, and E. coli) evaluated the potential for negative unintended consequences.

This BMP removed as much as 10-20 µg/L selenium from waters having 50-80 µg/L selenium. While this amount of removal is not adequate to attain the effluent limits of 4 µg/L, recommendations from this BMP evaluation may lead to more effective designs. The bioreactor BMP was nearly 100% effective at removing nitrogen from 29-30 mg/L down below the limit of detection (0.02 mg/L). Indicator bacteria flourished within the bioreactor, resulting in bacteria concentrations in the effluent that consistently exceeded water quality objectives. Overall, this particular BMP design is not projected to be a feasible or cost-effective way to reduce selenium concentrations in extracted groundwater. However, lessons learned from the BMP evaluation form the basis for recommendations to improve the design of similar, small-scale BMPs, as well as recommendations for the development of larger scale treatment wetlands.

According to success criteria defined for this BMP evaluation, the BMP is not a feasible way to reduce selenium or nitrogen concentrations in extracted groundwater:

- The BMP was partly successful at removing selenium.
- The BMP was successful at removing nitrogen.
- The BMP was unsuccessful in that it produced unwanted indicator bacteria that exceeded water quality objectives.
- The BMP was unsuccessful in terms of nuisance factors (e.g., the mass caused it to sink into the concrete, it produced odors).
- The BMP was unsuccessful in terms of feasibility. The design is at the limit of feasibility in terms of size and mass. The cost and level of effort are beyond feasible compared to the relatively small flow rates and moderate selenium reductions achieved.

Information gained from this BMP evaluation has produced many recommendations for next steps in the design of small scale and large scale selenium-removing BMPs.

1.0 INTRODUCTION

1.1 Purpose of this BMP evaluation

Selenium is a potential water quality problem throughout the arid west (Harris, 1991). Although it is a naturally occurring element, human activities can mobilize selenium into surface waters, where it can bio-transform to harmful chemical forms and accumulate in the food chain. In California, problems at Kesterson Reservoir led to a general recognition that precautions are needed when managing selenium-laden waters to avoid impacts to beneficial uses. At Kesterson, disposal of large quantities (~ 8000 AF) of agricultural drainage water with extremely high selenium concentrations (~ 300 µg/L) led to biotransformation and bioaccumulation with severe ecological consequences**,** such as widespread mortality and developmental abnormality in birds nesting and foraging around the Reservoir (Ohlendorf, 2002).

Because of the Kesterson experience, the discovery of elevated selenium concentrations in extracted groundwater and surface water of developed California coastal watersheds has triggered concerns that management actions may be needed to avoid impacts to beneficial uses. In the San Diego Creek / Newport Bay Watershed, surface water concentrations consistently exceed the California Toxics Rule chronic criterion of 5 µg/L. The source for most of the selenium in the surface water of the watershed is groundwater. As a result, the Santa Ana Regional Water Quality Control Board (Regional Board) determined that discharges of groundwater extracted from construction dewatering, dewatering wastes from subterranean seepage, and other activities posed a potential threat to water quality. Therefore, in December 2004, the Regional Board adopted Order No. R8-2004-0021 (Order), a general National Pollutant Discharge Elimination System (NPDES) permit for the watershed. This Order specifies waste discharge requirements for certain short-term (i.e. one year or less) groundwater-related discharges and other *de minimus* activities. The Order requires immediate compliance with the provision that "neither the treatment nor the discharge of waste shall create, or threaten to create, a nuisance or pollution." For selenium, the permit defines compliance with this provision as either

1) Comply with a maximum monthly average concentration of 4 µg/L and daily maximum of 8 µg/L selenium in discharges of extracted groundwater; or
2) Demonstrate that compliance with the selenium limits is infeasible, and propose and offset for discharges above the effluent limits; or
3) Participate in a Working Group responsible for timely delivery of specific work products needed to develop a watershed management strategy for groundwater sources of selenium and nitrogen. Certain dischargers in the watershed, both public agencies and private entities, have formed the Working Group and have launched the Nitrogen and Selenium Management Program (NSMP).

During the development of the Order, the Working Group made a commitment to the Regional Board to conduct a "quick start" Best Management Practice (BMP) program, which included the evaluation of a low-cost, low-tech BMP designed to decrease selenium concentrations from groundwater discharge. This report presents the results of this Quick Start BMP evaluation. During the implementation of the Work Plan, other BMP evaluations will be conducted.

The goals of this BMP evaluation were to:

1) Evaluate the feasibility of a low-cost, low-tech BMP to remove selenium from water;
2) Build on previous selenium BMP investigations;
3) Evaluate the potential for multiple benefits, such as nutrient removal;

1.3 Rationale for BMP design

The BMP design (Larry Walker Associates, 2005) proposed to the working group evolved as a result of several constraints and opportunities. The physical and chemical properties of selenium, the short-term nature of the discharges being addressed, and the experiences of previous BMP evaluations led to the design, construction, and evaluation presented in this study. Those factors are summarized briefly below.

Selenium's physical and chemical properties (Table 1) are what make its treatment such a challenge. The most common form of selenium in groundwater of the San Diego Creek watershed is selenate. Selenate is a highly soluble salt, preventing effective removal by simple filtration, coagulation, or settling. Selenate is also one of the least bioavailable forms of selenium, compared to forms such as selenite and organoselenium (Luoma et al. 1992). The potential for chemical reduction[1] of selenate to more bioavailable forms and uptake by plants and prey organisms is the principle reason for concern over potential wildlife impacts resulting from discharges to surface waters.

However, reduced forms of selenium are easier to remove from solution, so selenium-removal BMPs often rely upon biochemical processes that reduce selenium. Selenite has a greater tendency to adsorb to particles than selenate. Further reduction of selenite to elemental selenium yields even more effective removal, as elemental selenium is extremely insoluble. The selenium-decreasing BMPs reviewed in the development phase of this study all relied upon some kind of biologically-mediated reduction of selenate.

A bioreactor that cultures native microorganisms from native soils was selected as the best fit for the project constraints. The IRWD mesocosm study **(**IRWD, 2003**)** provided a blueprint for a low-cost bioreactor that has been shown to decrease both selenium and nitrogen concentrations. In that study, small scale chambers (the mesocosms) were filled with a bioreactor media that had three principle components: native soils to provide an inoculant of native bacteria and a substrate for them to live on, chopped cattails as a source of carbon for the native bacteria, and quartz sand to facilitate the flow of water through the media. The resulting "miniature marsh" provided the strongly reducing conditions needed to convert selenate to selenite and elemental

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[1] In this report, the term "reduce" is only used to indicate chemical reduction, i.e., the addition electrons to reduce the oxidation state of selenium.

selenium, thereby trapping selenium in the bioreactor media and decreasing selenium concentrations in the effluent.

The IRWD mesocosm study used small (3 ‘W x 4’L x 3’D) cells packed with the bioreactor media and connected in series to treat flows of 1 – 2 gallons per hour. The study concluded with the recommendation to evaluate the feasibility of treating higher flows using larger cells. Cells sized at 10’L x 10’W x 3’ deep were projected to be able to treat 10 – 20 gallons per hour using horizontal flow through the cell. This Quick-Start BMP evaluation is based on the recommendations of the IRWD mesocosm study, aiming to evaluate the performance of a wetland cell approximately 15 times larger than the IRWD mesocosms.

Through discussions with the Working Group, several modifications were made to improve on the design approach from the IRWD mesocosm study and other new considerations:

- Perlite was substituted for quartz sand to decrease the overall mass of the scaled up bioreactor.
- A mixture of mulched hay and straw was substituted for chopped cattails to develop a bioreactor media based on readily purchased materials.
- The bioreactor was designed for vertical flow, because at larger scales horizontal flow is constrained by the hydraulic conductivity of the media. This is a natural consequence of Darcy’s Law[2].
- Selenium speciation (analysis of the chemical form of selenium) and indicator bacteria (coliforms, enterococci) were added to the analyte list to assess the potential for negative unintended consequences.

Details of these design features are presented in Section 2.1.

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[2] Darcy’s Law: $\frac{V(ft^3)}{D_t(hr)} = K(\frac{ft}{hr}) \times \frac{A(ft^2) \times H(ft)}{L(ft)}$,

where V/D_t = maximum flow rate, K = hydraulic conductivity of the media, A = surface area of the media; H = hydraulic head, and L = length of travel through the media. In a box 8’ W x 6’H x 23’ L,, the horizontal flow configuration would result in a path length L of 23’, and H would be limited to about 1-2’ maximum. In the vertical flow configuration, L decreases to the depth of the media (about 3’) and H increases to about 4.5’ (3’ of media plus 1.5’ of water above the media).

Table 1. Chemistry and Significance of Selenium forms in Natural Waters.

Shading indicates forms with the relatively greater ecological risk.

Oxidation State	Selenium form	KEY CHARACTERISTICS	Importance to Selenium Cycling
Se^{+6}	Selenate ($\mathrm{SeO4}^{2-}$)	Extremely soluble, with a very low affinity for sorption to particles.	Reported to be the main form in groundwater in the San Diego Creek watershed (Meixner and Hibbs, 2004). Very low bioaccumulation and/or biotransformation by microorganisms and algae. Uptake is inhibited by sulfate.
Se^{+4}	Selenite ($\mathrm{SeO3}^{2-}$)	Moderately soluble with a much greater affinity for sorption to particles than selenate.	Principal form of concern as it accumulates in phytoplankton ~10-fold more readily than selenate; Uptake is not inhibited by sulfate.
Se^{0}	Elemental Selenium	Insoluble reddish precipitate.	Removed from water by precipitation. Low solubility and bioavailability lessen ecological risk compared to selenite and selenate.
Se^{-2}	Inorganic selenide (Se^{2-})	Forms insoluble precipitates with metals in the same way that sulfide does	Removed from water by precipitation
	Cellular Organoselenium (a.k.a., particulate)	Most common is selenium substituted for sulfur in amino acids (e.g. selenomethionine)	Accumulation of selenium-substituted amino acids through the diet is the major cause of reproductive problems in birds and fish.
	Dissolved Organoselenium (a.k.a., organoselenide)	Dissolved organic compounds (e.g. selenomethionine) released from decaying cellular tissues.	Decay of cells creates a regenerative pool of bioavailable selenium that can be acquired by other microorganisms. Lower ecological risk than particulate organoselenium, because diet is more important than direct uptake from water column.
	Dimethylselenide, dimethyldiselenide	Produced by microbes, plants, and animals.	Provides gaseous escape from sediments and surface waters into the atmosphere.

2.0 BMP DESIGN

2.1 Location selected

The BMP evaluation was conducted at the CALTRANS Denitrification Facility located at 3210-1/2 Walnut Avenue in Irvine (Figure 1). This location was selected because:

- It is owned and controlled by CALTRANS, a Working Group member;
- It has a dewatering pump that continuously dischargers approximately 500 GPM of high selenium (50 – 80 µg/L) water through the sanitary sewer to the Orange County Sanitation District (OCSD);
- The location is secured behind locked gates and reasonably out of sight;
- The site has access to power; and
- Effluent water from the BMP could be returned to the flow sent to OCSD. OCSD granted permission to discharge flows from the BMP evaluation into their sewer.

Important features on the location are shown in Figure 2 and Figure 3, including an underground vault, a wet well, and a pump house. A monitoring port outlet in the underground vault served as the groundwater source for the BMP evaluation. Effluent from the bioreactor was discharged to the wet well adjacent to the pump house. Power came from 110V AC power supplies located in the pump house.

Other existing features at the denitrification facility included a stormwater detention basin and two other buildings. These features were not used or impacted by the BMP evaluation

2.2 BMP construction

A large (8′ W x 23′L x 6′H) rollaway debris box was rented and transported to the site. A back wall constructed of plywood and two-by-fours was constructed inside the debris box. A rubber liner was laid down inside the interior space formed by the container and constructed back wall. In the bottom of the box, inside the rubber liner, a French drain was constructed using 3″ diameter PVC piping, which was sealed with silicon as it passed through the rubber sheet and back wall. An 8″ layer of pea gravel covered the French drain, and a filter fabric cover was placed on top of the pea gravel (Figure 4). The resulting volume of the soil media layer was 430- ft^3, or 3,200 gallons, calculated according to the dimensions and formula shown in Figure 5.

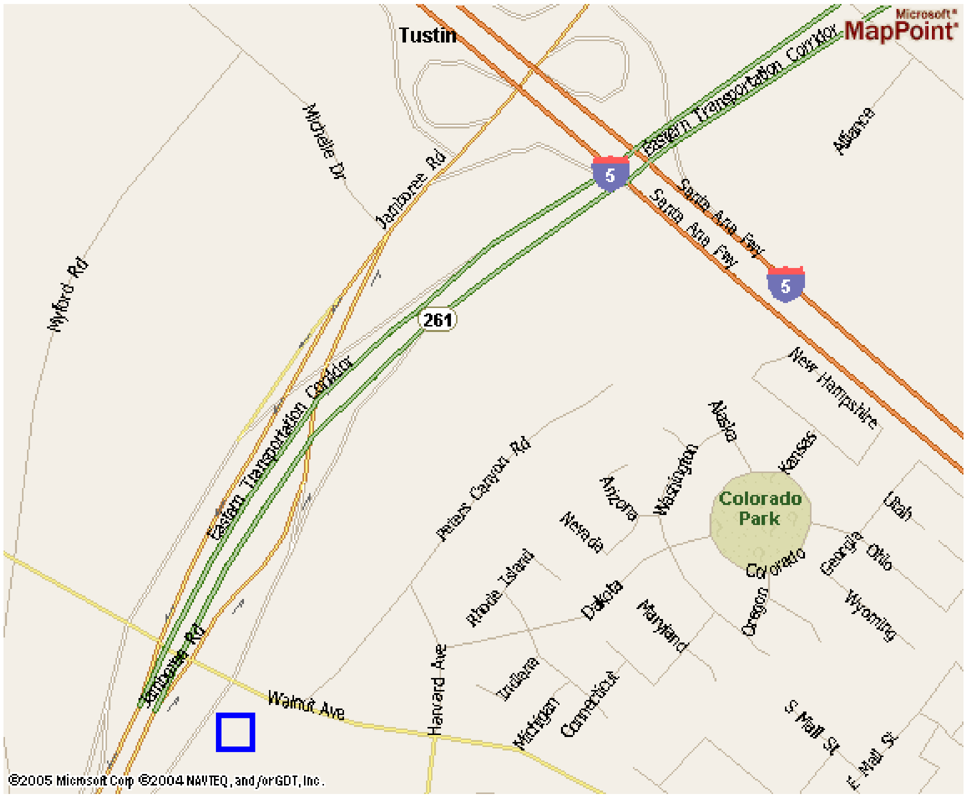


Figure 1. Location of selenium BMP site
(blue square in lower left corner of map).

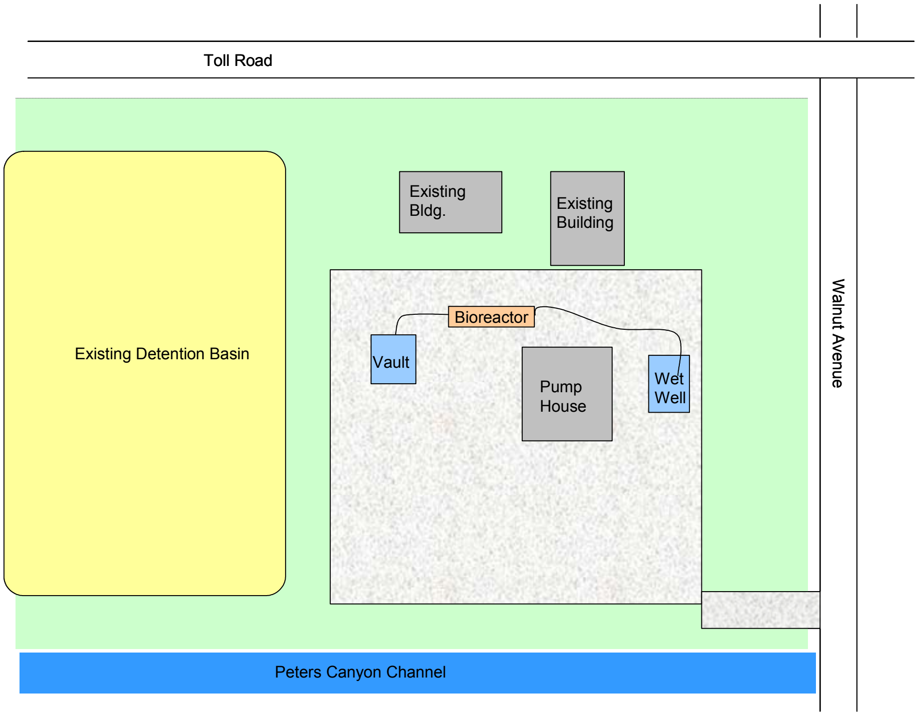


Figure 2. Plan view of the selenium BMP site.

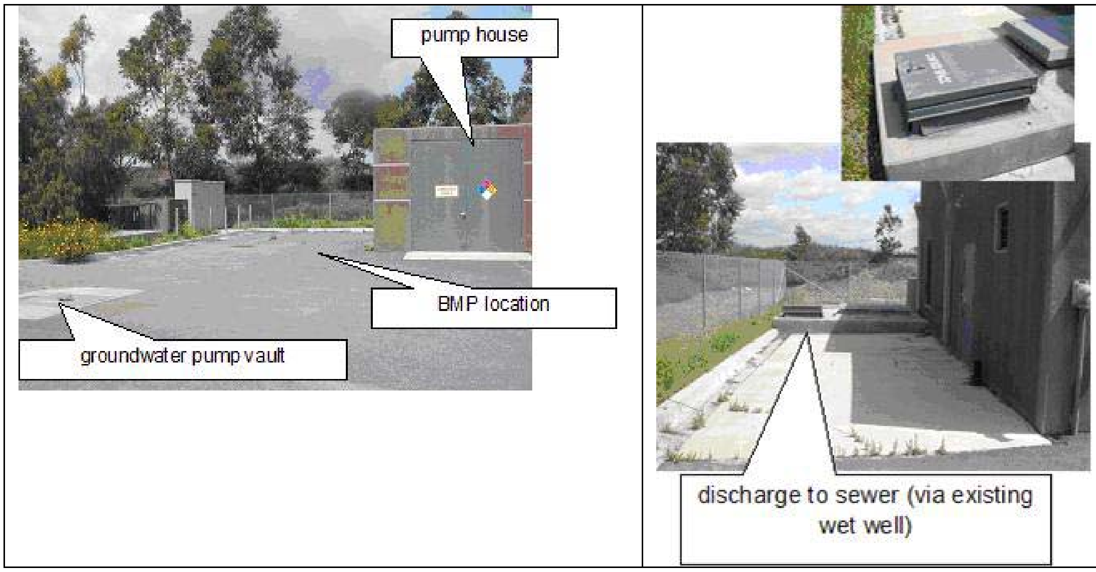


Figure 3: Ground-view photo of BMP location.

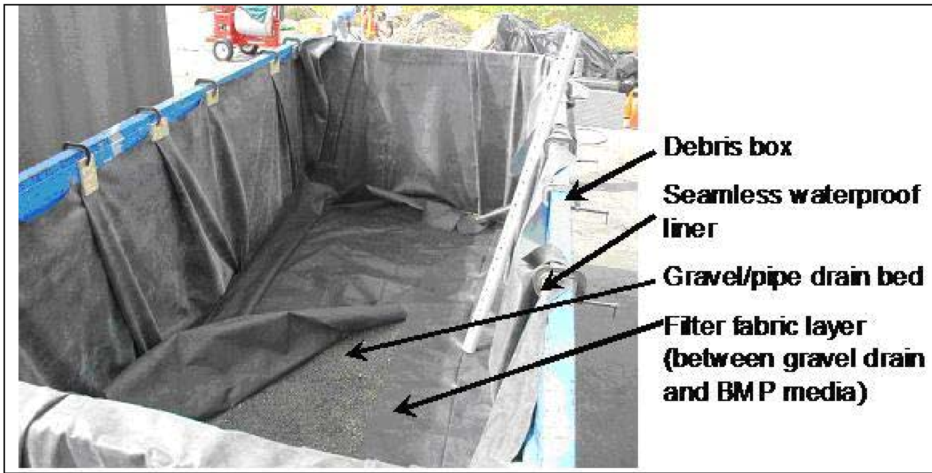
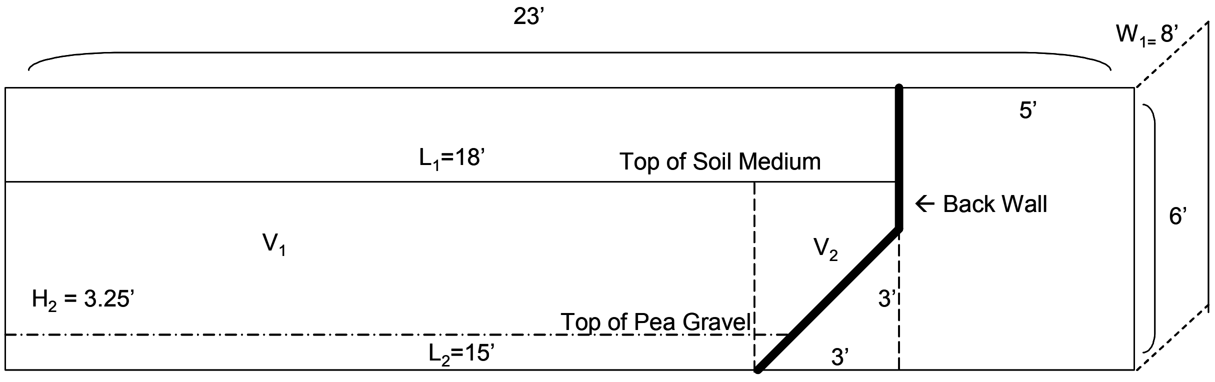


Figure 4: Bioreactor BMP under construction.



$V_1 = L_2 \times H_2 \times W_1$

$V_2 \cong [(L_1 - L_2) \times H_2 - (3' \times 3' \times \tfrac{1}{2})] \times W_1$

Figure 5: Side view schematic of the bioreactor BMP evaluated.

Important dimensions and resulting volume calculations are shown (L = Length, H = Height, W = Width, V = Volume).

2.3 Bioreactor media preparation

The bioreactor media was prepared and loaded into the BMP at the CALTRANs denitrification facility. Dredged sediments were obtained directly from the IRWD spoils area. Pea gravel, perlite, hay and straw were purchased from nearby suppliers. These materials, shown in Figure 6, were mixed together in the proportions shown in Table 2.

Table 2: Mixing volumes of the components of the bioreactor media.

(expressed as parts, or number of 5 gallon buckets)

Component	Parts	% by Volume
Native soils	6	55%
Perlite	3	27%
Hay	1	9%
Straw	1	9%

A Whiteman mortar mixer (Figure 7) was used to blend the soil mixture materials together. The mixer was loaded in the 6:3:1:1 proportion described above, and then turned on. Steel paddlewheels inside the machine mixed the medium for 3 minutes. This both thoroughly blended the materials and also broke up the hay and straw matter into smaller pieces than found in the bales (most individual strands of hay were not longer than about 6-9″ inches after mixing). A bobcat was used to move the soil mixture into the bioreactor, where it was carefully spread and lightly compacted as uniformly as possible (Figure 8). A small probe well, slotted at the lower 6″ but capped at the very bottom end, was inserted into the media to allow measurement of oxidation-reduction potential (ORP) and other parameters at depth. The bottom of the probe well rested in the media at least 6″ above the gravel layer, and the top extended above the water surface in order to avoid creating a "short circuit" through the media to the gravel drainage.

Figure 6. Materials used to make the bioreactor media.

From upper left, clockwise: dredged soils obtained from IRWD, hay, pea gravel, and perlite.

Figure 7. Whiteman Mortar Mixer.

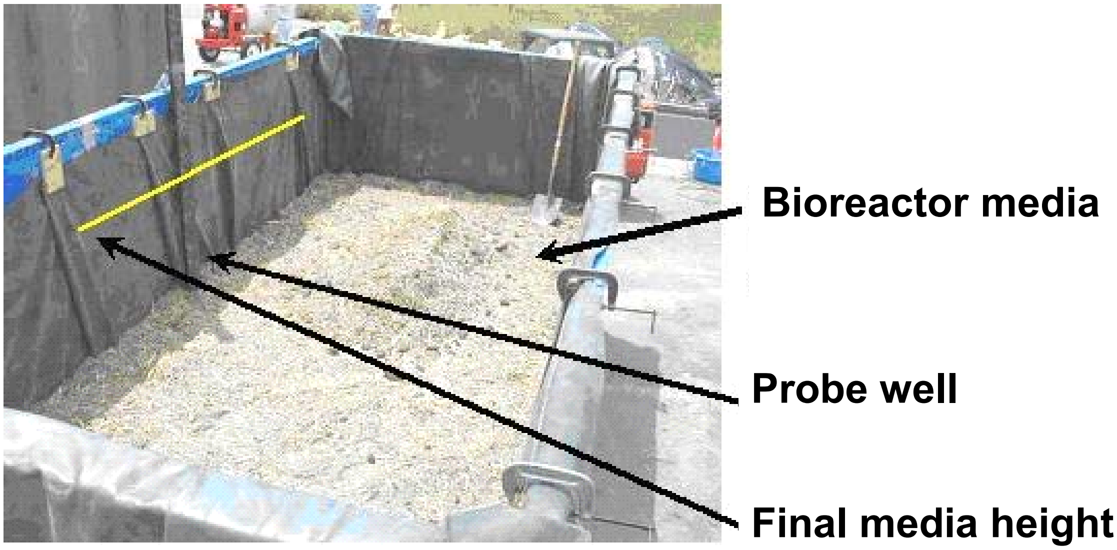


Figure 8: Filling the bioreactor BMP with media.

2.4 Inlet and outlet pumps

Water from the monitoring port outlet tapped into the main groundwater pump line flowed into a holding bucket on the ground (Figure 9). A submersible pump (Pump 1) lifted the flow from the holding bucket to a metering tank mounted above the bioreactor (Figure 10). This was necessary because the pressure available at the monitoring port outlet was not sufficient to deliver water to the top of the BMP. The metering tank had a second submersible pump (Pump 2) activated by a float valve mounted above the soil medium. Pump 1 operated continuously to keep the water supply tank full. When Pump 2 was not activated by the float valve, water from the elevated bucket was diverted through an overflow outlet pipe directly to the sanitary sewer (Figure 11). Flow through the BMP was set by means of a ball valve at the outlet. The float-activated inlet pump allowed inlet flow to be matched to outlet flow, and a constant 18" head of water maintained over the bioreactor. Effluent flow was collected in a large, flat plastic trough and sent to the sanitary sewer with a third submersible pump (Pump 3) (Figure 12).

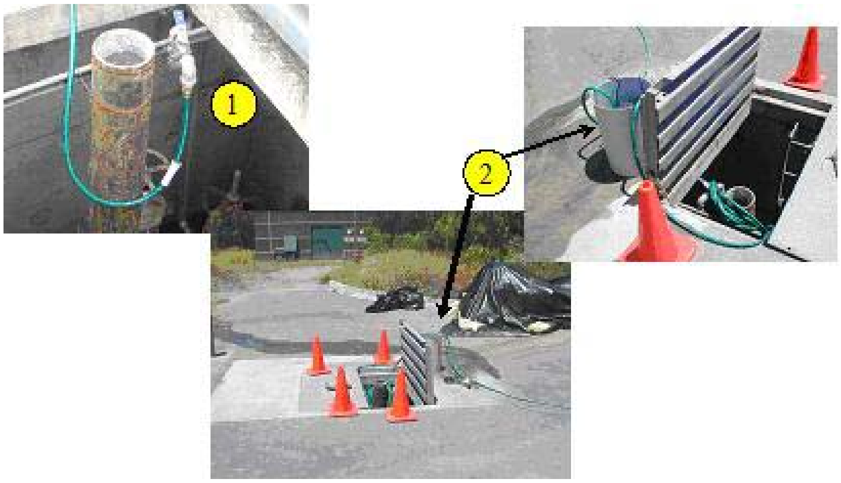


Figure 9: Water supply (1) from the monitoring port outlet filled a bucket with a submersible pump (2).

Figure 10: Source water (1) was pumped into a metering tank above the BMP (2).

Figure 11: The metering tank had a submersible pump connected to a float valve.

The float valve directed water to the BMP through a spreader pipe

(1). When the float valve was all the way up, overflows bypassed the BMP via a bypass pipe (2) that was connected to the sewer wet well.

Figure 12: Bypass source water (1) was directed to the wet well.

Water introduced to the BMP flowed vertically downward and exited via a 2" ball valve at the back of the BMP (2), and the pumped through a meter (3) to the wet well.

2.5 Bioreactor hydraulic characteristics

The porosity of the soil mixture was tested by filling a container with 16 gallons of soil mixture and then adding water to saturate the soil medium. When 5.5 gallons of water were added the water level reached the top of the soil medium. The soil mixture is therefore estimated to have a porosity of 5.5/16 = 34%. This is comparable to the estimated 33% - 45% porosity of the soil medium used in the IRWD mesocosm study.

The porosity is needed to calculate detention time in the bioreactor at different flow rates. As discussed in the findings sections, detention time within the reducing media is an important parameter to track for optimizing BMP performance. The volume of the bioreactor medium is 3,200 gallons. With an effective porosity of 34%, this means the volume of water within the bioreactor is 3,200 gallons x 34% = 1,099 gallons (rounded to 1,100).

The BMP was evaluated at three different flow rates: 1.5 ± 0.1 GPM, 0.8 ± 0.1 GPM, and 0.4 ± 0.1 GPM. The corresponding detention times (D_t's) are 0.51 ± 0.03, 1.0 ± 0.1, and 1 .9 ± 0.6 days, respectively. For comparison, the IRWD mesocosm study concluded that a detention time of 3 – 6 days was needed to achieve desired selenium reductions in waters containing 20 – 60 µg/L selenium. This BMP evaluation targeted higher flow rates initially in order to find the balance point between removal effectiveness and sufficient flow. Given that the source water at the CALTRANS denitrification facility is pumped at about 500 GPM, a BMP of this size that cannot process flows greater than 0.5 GPM may not be feasible.

3.0 BMP EVALUATION

3.1 Success criteria

The following criteria were used to evaluate the BMP:

- Selenium removal effectiveness – The BMP would be considered successful if selenium concentrations in the effluent meet or are below the monthly average effluent limitation in the general permit (4 µg/L). The BMP would be considered partially successful if selenium concentrations decrease from the influent to the effluent, but are not decreased enough to attain 4 µg/L.

- Nitrogen removal effectiveness – The BMP would be considered successful by this criterion if it also decreases nitrate concentrations below 1 mg/L. The BMP would be considered partially successful by this criterion if it lowers nitrate and nitrite concentrations compared to influent concentrations, but still exceeds 1 mg/L.

- Bacteria indicators – The BMP would be considered successful if the effluent does not exceed [or counts do not increase from influent] water quality objectives for total coliforms, fecal coliforms, and enterococcus as specified in regulations established through AB-411.

- Nuisance factors – The BMP will be considered successful if the effluent does not threaten to cause nuisances such as odor, color, or low dissolved oxygen in receiving waters.

- Feasibility – The BMP will be considered successful if it can process a reasonable flow rate (e.g. 1 gpm) using readily available, low-cost materials and a design that provides minimum site disturbance.

Most of the criteria above were introduced to the Working Group through the BMP design report. Nuisance factors and feasibility were added in as success criteria based on experience gained though evaluating the BMP. The measurements used to evaluate water quality success criteria (selenium, nitrogen, bacteria) are summarized in Table 3.

3.2 Flow rates evaluated

The BMP was operated at different flow rates to evaluate removal efficiency at different hydraulic residence times. The bioreactor was filled with water on May 18, 2005 and allowed to condition overnight with no flow, to give the bacteria time to multiply, and the reducing potential time to develop. By the next day, the ORP in the probe well had dropped to -100 mV or less. The flow was set initially at a relatively high rate (1.5 GPM) to assess system performance under relatively short detention times (D_t = 0.5 days). The desired condition was to effect complete nitrate removal, but only slight or no sulfate removal. The reducing potential needs to be sufficient to effect complete nitrate removal to reduce selenate to selenite and organoselenium. Too much sulfate reduction generates excess sulfide, which can cause odor nuisances and increase the chemical oxygen demand (COD) in receiving waters.

The condition of nitrate reduction with little or no sulfate reduction was attained throughout the BMP evaluation. Rapid analysis (24-hour turnaround) of selenium by ICP-MS provided feedback on selenium removal. If sufficient removal was not attained, the flow was decreased in order to increase the detention time. After initial assessment at 1.5 GPM (D_t = 0.5 days), the flow was decreased to 0.8 GPM (D_t = 1 day).

Table 3: Constituents, Methods, Laboratory Reporting Limits (RL), and Holding Times.

Constituent	Analytical Method	RL	Bottle/Preservation	Holding Time
Water samples				
Total Selenium (filtered and unfiltered)	BR[3]-0020	0.03 µg/L	2 x 250 ml HPDE, ship to lab next-day to ensure samples are filtered w/in 48 hrs of collection; lab will preserved with HCl to pH <2.	6 months
Selenium speciation (selenate, selenite)	Method BR-0023	0.03 µg/L	2 x 125 mL Glass with Teflon-lined lids. Ship to lab next-day to ensure samples are filtered and preserved with HCl to pH 1.8 by lab w/in 48 hrs of collection.	28 days
Total selenium (filtered and unfiltered) Rush	EPA 200.8	0.5 µg/L	250 ml HDPE plastic, preserved by laboratory	48 hours
Organoselenium	Calculated by difference between BR-020 and BR-023			
Nitrate, Nitrite	EPA 300.0	0.01 mg/L	500 mL HDPE	48 hours
Sulfate	EPA 300	0.05 mg/L	500 mL HDPE	48 hours
Total Suspended Solids	EPA 160.2	1 mg/l	500 mL HDPE	7 days
Fecal and total coliform	SM9221[4]	20-1,600,000 MPN / 100 ml	125 mL $Na_2S_2O_3$	6 hours
E. Coli	SM9223	10-24,196 MPN / 100 ml	125 mL $Na_2S_2O_3$	6 hours
Enterococcus	SM9230	10-24,196 MPN / 100 ml	125 mL $Na_2S_2O_3$	6 hours
pH	Field measurement	0.1 unit	None	NA
Temperature	Field measurement	0.1°C	None	NA
EC	Field measurement	1 µS/cm	None	NA
Bioreactor media samples				
Selenium, total (solid)	EPA 6020	0.05 µg/g	4 oz glass, 4° C	6 months

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[3] BR = Brooks Rand methods; these have been reviewed for consistency with Cutter (1989) by the TAC

[4] SM = Standard methods

4.0 RESULTS

4.1 Selenium removal effectiveness

Over the course of the evaluation, outflow from the bioreactor consistently had lower selenium concentrations than the inflow[5] (Figure 13). Overall, the bioreactor BMP was able to decrease selenium concentrations by about 10 – 20 µg/L in groundwater samples having 50 – 80 µg/L selenium. While this still falls short of attaining the monthly average effluent limit of 4 µg/L, this constitutes a partial success by the criterion of selenium removal.

In general, most of the selenium in both influent and effluent was present as dissolved selenium. On one occasion, dissolved selenium measurements by ICP/MS were greater than total selenium measurements by ICP/MS. The difference between the dissolved and total selenium was within the known precision of the analytical method, i.e., <10%, so this could be simply an analytical artifact. Similarly, in two of the events measured by hydride generation dissolved concentrations exceeded total concentrations, again within the overall precision of the method[6].

Selenium removal effectiveness increased at lower flow rates. At the highest flow rate, 1.5 GPM, removal of dissolved selenium ranged from 8 – 10 µg/L (7% – 13% removal compared to source waters). At lower flow rates (0.4 – 0.8 GPM), removal of dissolved selenium ranged from 8 – 19 µg/L (15% – 39% removal compared to source waters). Lower flow rates lead to longer contact time of water within the reducing zone of the bioreactor. It is possible that the reducing zone was getting smaller as the BMP evaluation progressed: note that ORP in the probe well rose to as high as 340 mV toward the end of the run, although ORP in the effluent remained around -45 mV (Table 6, Table 7 in Appendix A). Thus, at the same time as removal effectiveness was increasing due to longer contact time, the loss of reducing potential within the bioreactor may have worked against that, resulting in only moderate selenium removal.

Direct measurements of selenite by hydride generation showed that the BMP removed selenite (Figure 15). Selenite is a chemical form of selenium that poses greater direct bioaccumulation risk than selenate (Luoma et al., 1992, and see summary in Table 1). Previous studies (Hibbs and Lee, 2000; Meixner and Hibbs, 2004) suggests that the majority of selenium in groundwater of the San Diego Creek watershed is selenate, with trace (<10%) amounts of selenite, consistent with the results of this BMP evaluation. Over time, the concentration of selenite in the BMP effluent increased somewhat, but there isn't enough information to determine what that represents in terms of biogeochemical cycling of selenium, or its ecological risk.

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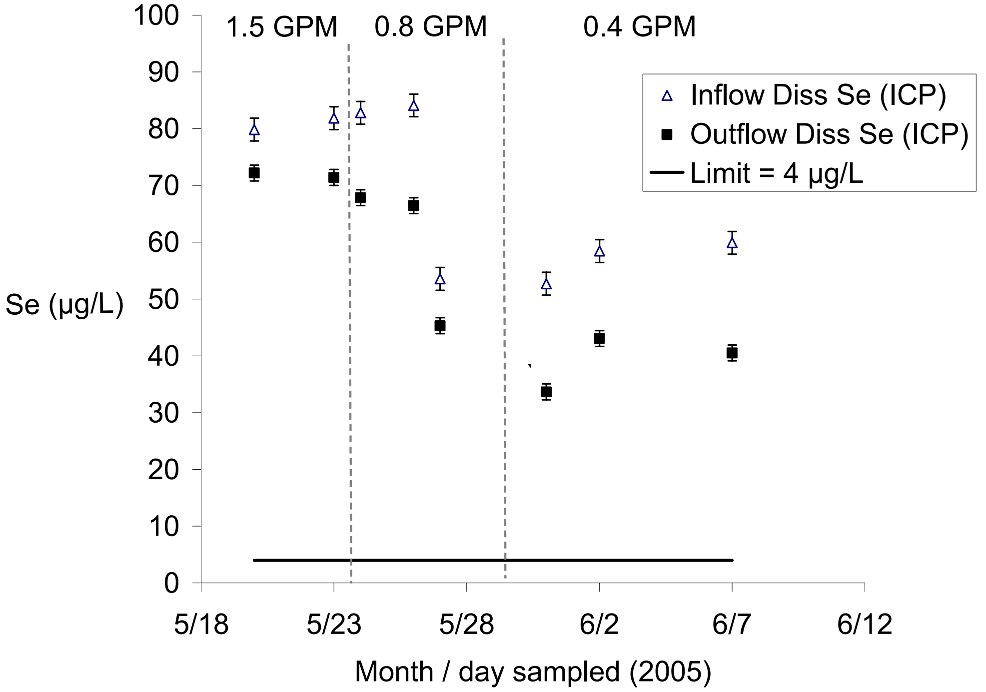
[5] The single exception to this was total selenium on 5/24/2005. The outflow water in that sample is believed to contain relatively high concentrations of colloidal or organic matter, which would elevate the total selenium concentrations, Note that the detection limit for TSS on this sample was <29 mg/L, compared to < 0.5 mg/L for all other samples. Discussions with the laboratory indicated that this was caused by the limited filtration volume that resulted from clogged filters.

[6] Through additional discussions with both laboratories, CRG and BRL, it was determined that dissolved selenium measurements occasionally and, as yet, inexplicably do exceed total selenium measurements.

In general, selenium measurements by ICP/MS were always higher than measurements by hydride generation. Both methods, however, showed overall removal of selenium from inflow to outflow. A more detailed discussion of the analytical issues appears in Appendix B.



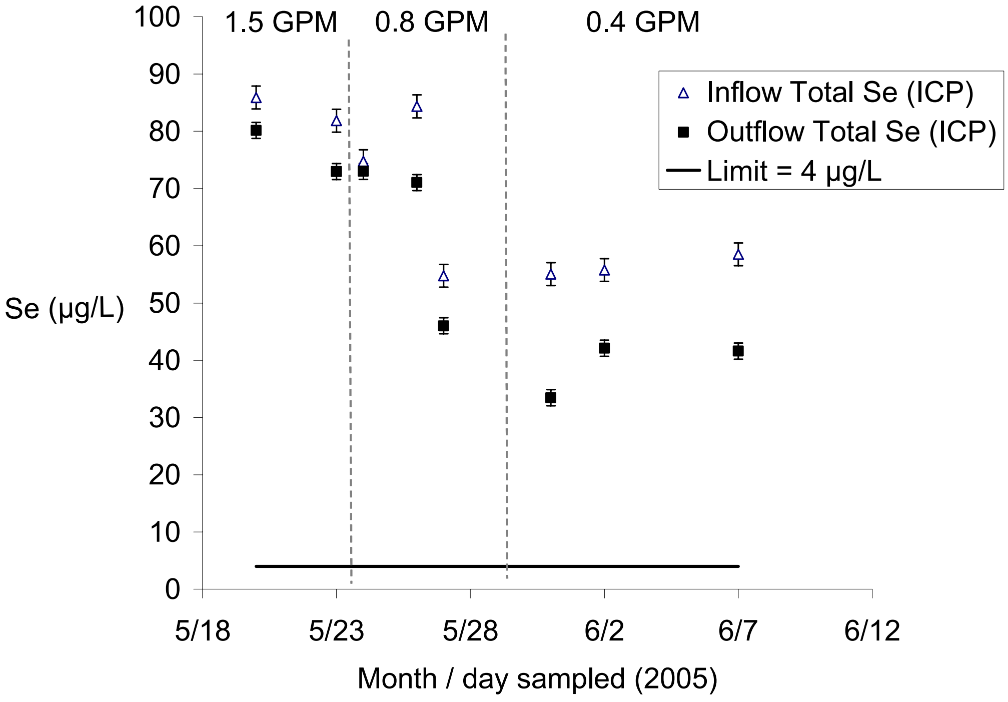


Figure 13: Concentrations of unfiltered (upper plot) and filtered selenium (lower plot) measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines. The horizontal line along the bottom shows the monthly average effluent limit of 4 µg/L. Error bars show one standard deviation of pooled analytical replicates.

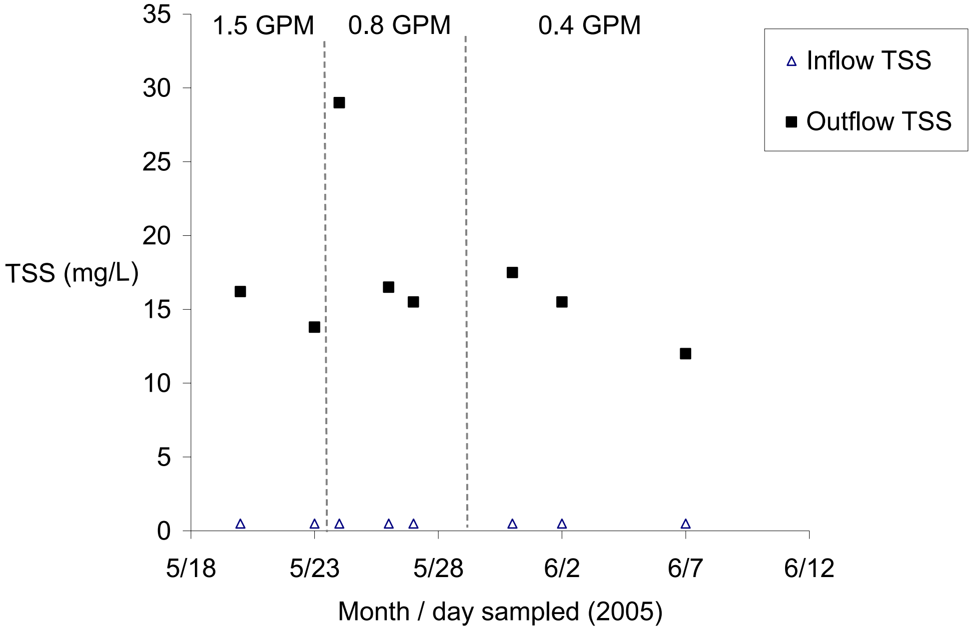


Figure 14: Concentrations of total suspended solids (TSS) measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines.

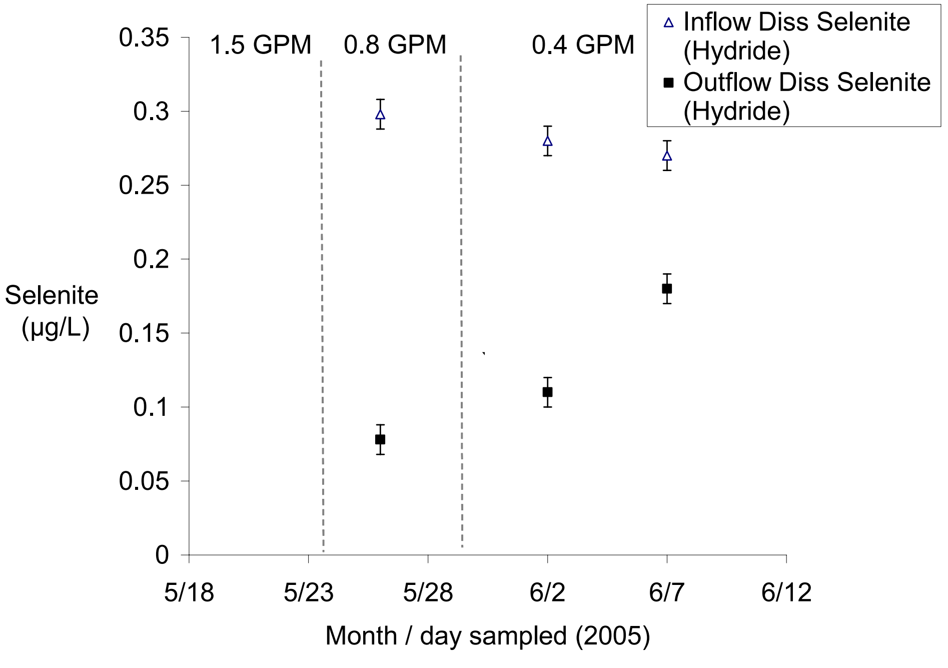


Figure 15: Concentrations of dissolved selenite measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines. The vertical error bars indicate one standard deviation.

4.2 Changes in selenium speciation due to biotransformation

For a selenium-removing BMP to be protective of water quality, it will need to avoid biotransformations which result in a net overall increase in the risk of selenium bioaccumulation. One important aspect of this is determining whether the BMP produces significant quantities of organoselenium, because organoselenium is more easily bioaccumulated than other selenium forms (Luoma et al., 1992).

The Cutter method of selenium analysis allows the determination of organoselenium by the difference between total selenium measurements and inorganic selenium measurements. Unfortunately, in this study, analytical interferences called into question the measurements of total selenium by hydride generation (See Appendix B for discussion), so calculation of organoselenium is not possible. This is the basis for the recommendation in section 5.3.1 below.

4.3 Nitrogen removal effectiveness

The bioreactor consistently lowered nitrate concentrations from the ~30 mg/L found in the inflow. On four events the nitrate concentration of the outflow was < 1 mg/L, and on four others it ranged from 7 – 20 mg/L (Figure 16). Nitrate concentrations are decreased by reducing conditions in a similar manner to selenate. This was also observed in the IRWD mesocosm study.

A selenium-removing BMP needs to develop enough reducing power to remove nitrate in order for selenium removal to occur. Therefore, this type of selenium-reducing BMPs can provide nitrogen-reducing benefits as well.

4.4 Introduction of unwanted bacteria

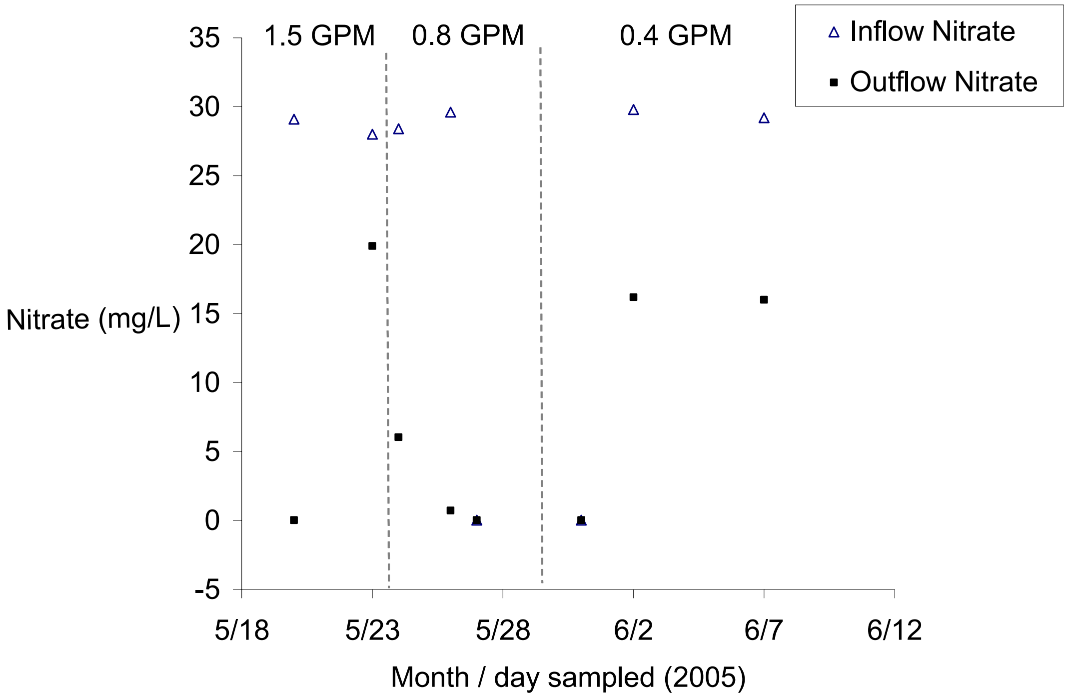
The bioreactor BMP relies on bacteria to set up the reducing conditions necessary to remove selenium from water. The native soils used to inoculate the bioreactor provided the necessary microbial populations needed to create the reducing conditions. Unfortunately, the bioreactor also causes unwanted species of bacteria to flourish, including fecal coliforms, total coliforms, *E. coli*, and enterococci (Figure 17, Figure 18). Outflow concentrations consistently exceeded water quality standards established by AB-411.

This may diminish the feasibility of using a bioreactor inoculated using native soils. A recommendation to investigate pure culture techniques is discussed in Section 5 of this study. However, it is worth noting that detectable levels of nuisance bacteria were occasionally found in the inflow to the bioreactor. Even a pure culture bioreactor is at risk of contamination by unwanted bacteria, though it may remain uncontaminated by nuisance bacteria longer than a bioreactor inoculated with native soils.

4.5 Suitability of media for conventional disposal

Selenium analysis of six random subsamples of the bioreactor media prior to disposal showed that the material was suitable for disposal in a conventional landfill. The threshold for hazardous waste disposal is 100 ppm selenium. If the solid-phase selenium concentration is below this, but above 10 ppm, static leaching testing procedures may be required. The selenium concentration of the six samples was 0.8 ± 0.2 ppm, so the bioreactor medium was disposed in a conventional landfill.

A reasonable question would be where selenium removed from groundwater ends up in this kind of BMP. It likely ends up in the soils of the bioreactor, though volatilization is another possible pathway. As discussed in the study design report, complete removal of 100 µg/L selenium from 5000 gallons of water would increase the selenium concentration of the bioreactor medium by 0.08 ppm over its starting condition. Larger scale BMPs, or BMPs that run longer, may need to consider the impacts of accumulation of solid phase selenium.



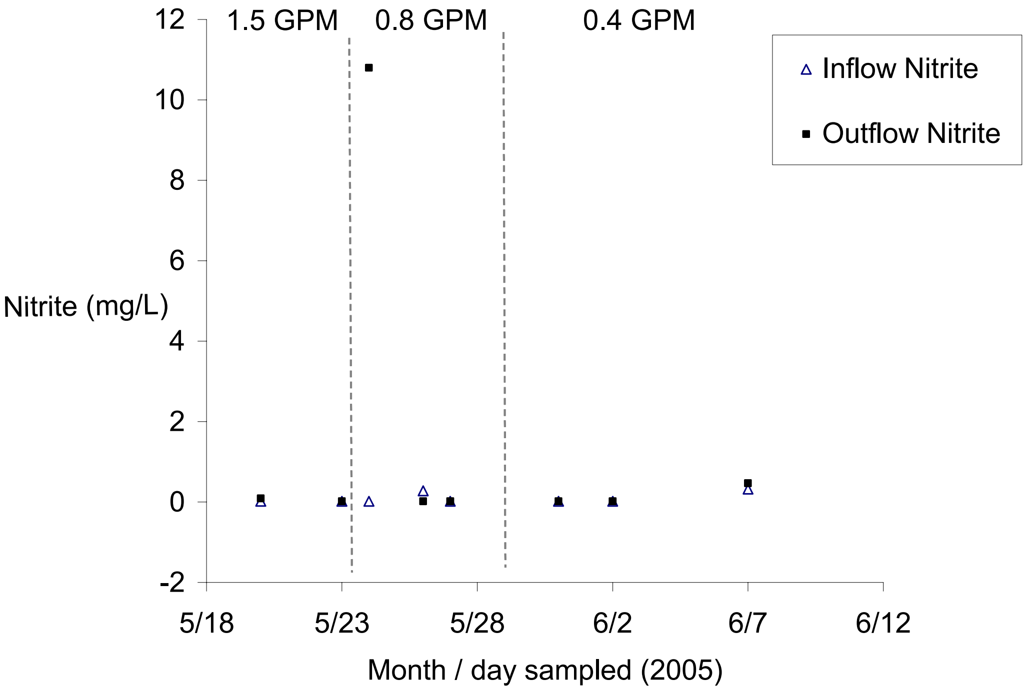
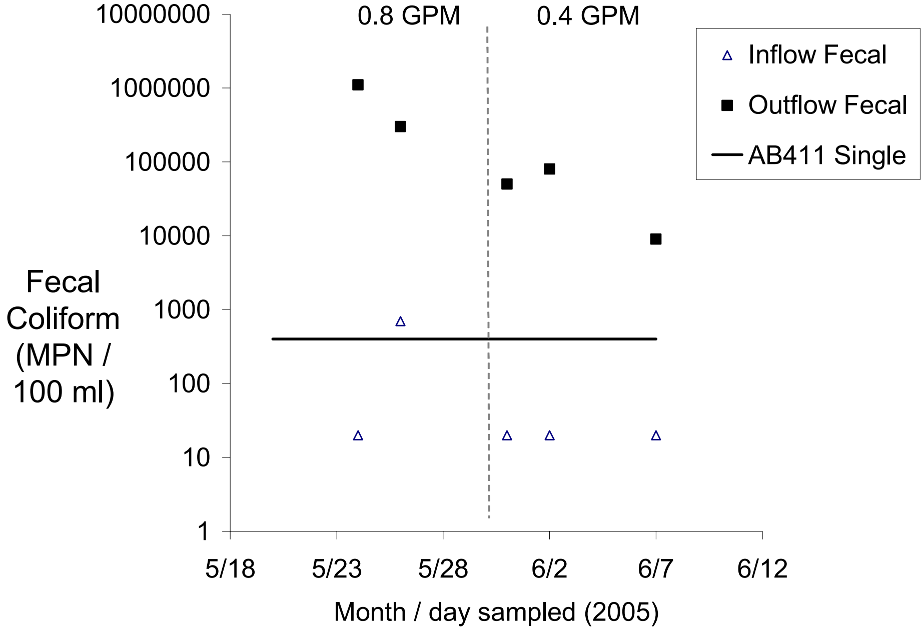


Figure 16: Concentrations of nitrate (upper plot) and nitrite (lower plot) measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines. Note the Y axis is extended slightly into the negative to make non-detect (<0.02 mg/L) symbols more visible.



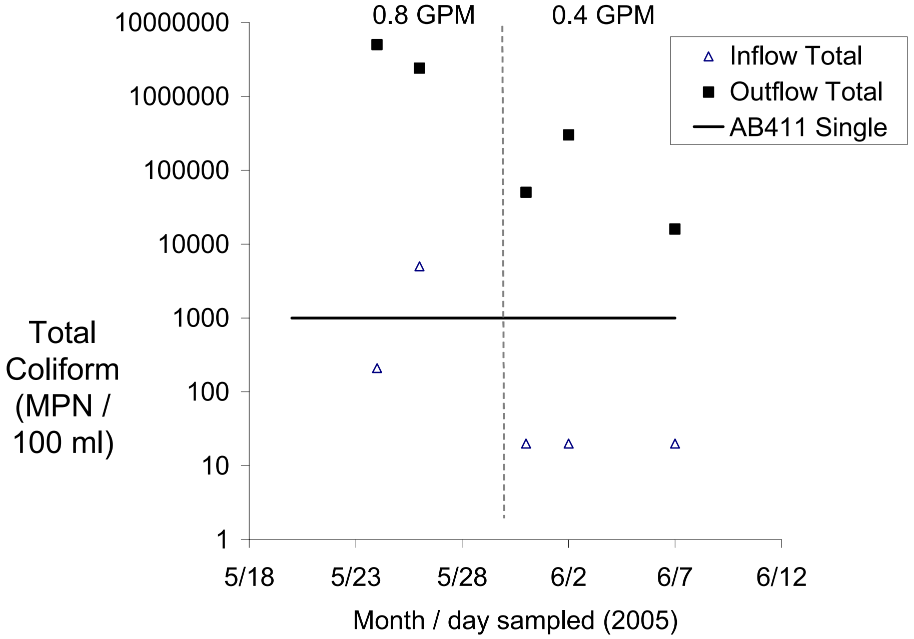


Figure 17: Concentrations of fecal (upper plot) and total coliforms measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines. The solid line shows the AB411 standard for a single grab sample (fecal / total ratios exceed 0.1 in all samples).

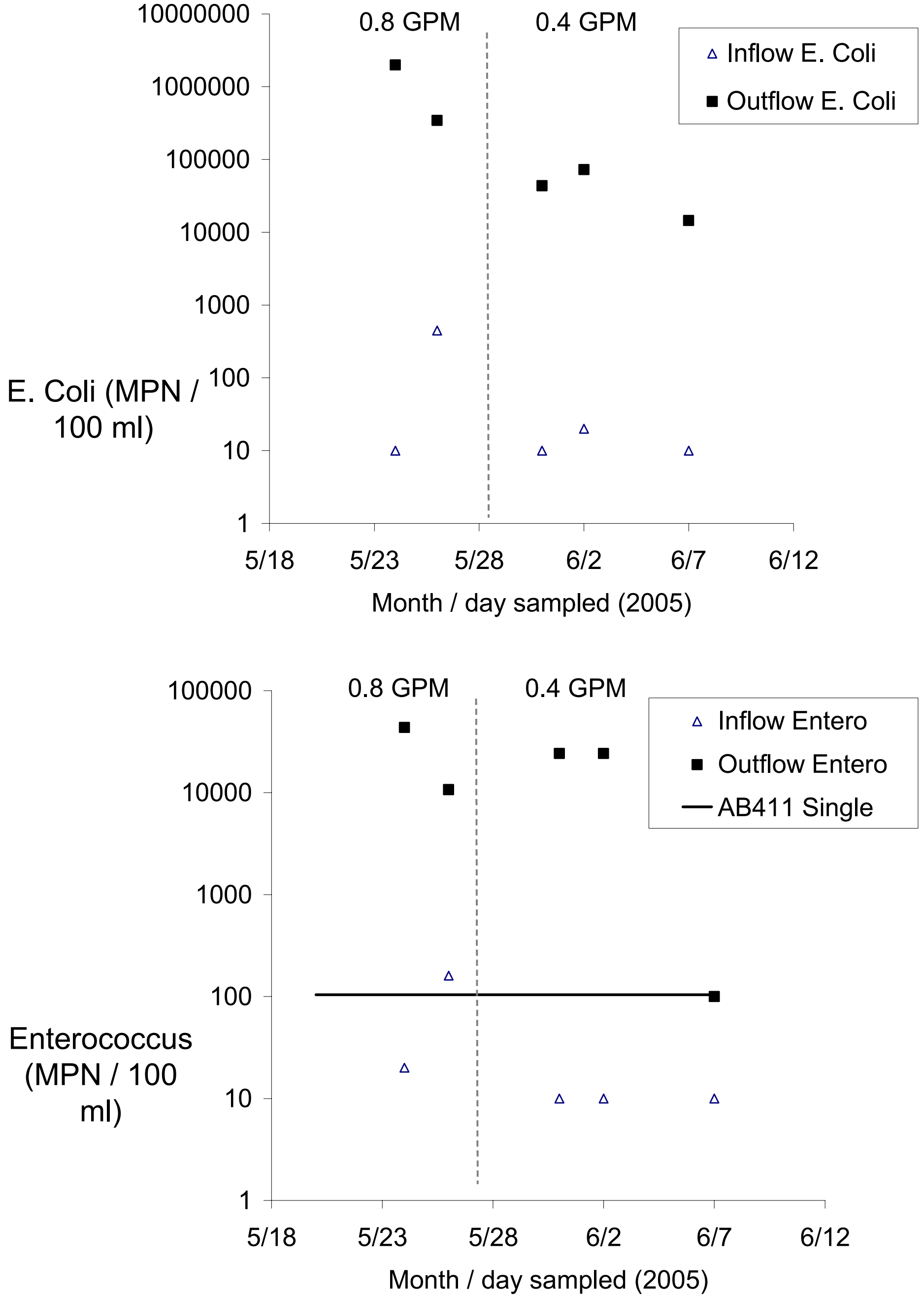


Figure 18: Concentrations of *E. Coli* (upper plot) and *Enterococci* measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines. The solid line shows the AB411 standard for a single grab sample.

4.6 Reducing conditions indicated by sulfate

Nutrient measurements provide important feedback on system performance. In this kind of BMP approach, the system needs to have enough reducing power to reduce nitrate. Complete reduction of selenate and selenite to elemental selenium occurs under conditions where nitrate is completely reduced and sulfate is partly reduced (IRWD 2003, Oremland et al. 1989). Complete reduction of sulfate would likely produce unwanted excess sulfide, increasing the chemical oxygen demand (COD) of the outflow water and causing odor nuisances. But some amount of sulfate reduction assists selenate reduction by producing sulfide, which increases the bioreactor's reducing power (Twidwell, 1999).

Sulfate concentrations did not change much from inflow to outflow. This suggests that the performance of the bioreactor could have been improved by increasing its reducing power. ORP measurements in the BMP outflow were consistently low, remaining between -40 and – 50 mV through most of the BMP evaluation (see Table 6 and Table 7 in Appendix A). In contrast, ORP measurements inside the probe well were more variable, and reached as high as 440 mV during the course of the BMP evaluation. Reducing conditions developed in the bioreactor, but the size of the reducing zone was probably not very big, perhaps just the bottom few inches of the bioreactor media. Recommendations in the next section discuss how this can be improved in future BMP evaluations.

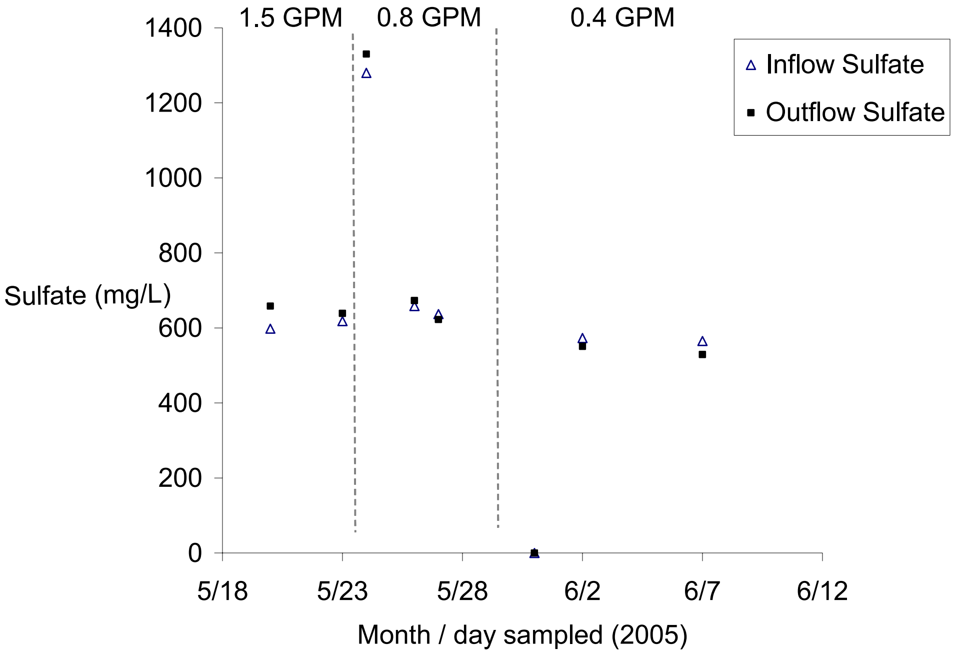


Figure 19: Sulfate Concentrations measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines.

4.7 Variability of groundwater sources

The data from the above findings show that groundwater characteristics at this location can vary considerably over time. Inflow concentrations of selenium, nitrate, and sulfate varied considerably, indicating that the groundwater sources at the BMP location were not constant. The variability in the source water did not prevent this evaluation from successfully identifying the strengths and weaknesses of the bioreactor approach. However, future monitoring for BMP evaluation, loads assessments, and other work will need to plan for the variability inherent to the composition of groundwater.

The variable selenium concentrations are particularly intriguing, as selenium is known to be spatially heterogeneous in the watershed. The changing concentrations of the inflow water shown in Figure 13 are typical of variability reported by CALTRANS at this location. The variability raises the question of whether identifiable factors, such as pumping to clean up aquifers at the nearby Tustin Naval Air Station, other dewatering operations, or the rise and fall of groundwater levels with rain events can be correlated to variations in the selenium concentrations of groundwater observed at this location near Peters Canyon Wash.

This type of variability is common in the confined upper aquifer throughout this watershed, as shown by other studies (e.g.,Meixner et al., 2004). A proposition-13 grant has recently funded a project to develop a groundwater-surface water interaction model that will help characterize factors causing this variability.

4.8 Tradeoff between residence time and removal efficiency

Effective removal of selenium by this approach is a product of the reducing power of the bioreactor and the detention time of water within the bioreactor. From the foregoing findings, it is fairly clear that future assessments will need to attain more reducing power. But detention time is also important, as selenium-reducing chemical reactions take time.

The detention time of the bioreactor is defined as its water volume divided by the flow rate. Thus, once the optimum reducing power is attained and the needed detention time is determined, the limiting factor on flow rate becomes the water volume of the bioreactor. This bioreactor BMP is already at the limit of feasibility in terms of size and mass, so the most feasible way to increase the water volume would be to increase the effective porosity of the bioreactor media. An effective porosity of 70% instead of 35% could double the flows possible.

The combined ideas of pure culture inoculations, augmented reducing power, and increased porosity lead to specific design recommendations for future evaluations that are discussed in Section 5.

5.0 RECOMMENDATIONS FOR FUTURE BMP EVALUATIONS

The results discussed in Section 4.0 above lead to specific recommendations to the Working Group for next steps in the implementation of the nitrogen selenium management plan. The recommendations are organized into three categories:

1) Recommendations for future studies of similar small, low-flow, low-cost BMPs;
2) Recommendations for future BMP studies on a larger scale; and
3) General recommendations.

5.1 Recommendations for future studies of small scale, low-cost BMPs

5.1.1 Maximize the pore volume of the bioreactor

As discussed in Finding 4.3, the detention time is a limiting factor for selenium and nitrogen removal, once the optimum reducing potential is attained. Once the minimum required detention time of the bioreactor is established, the only way to increase its flow rates is to increase its volume. To increase volume and keep the size and mass of the overall system reasonable, future designs should increase the effective pore volume of the bioreactor media.

Increasing the pore volume can be achieved by using more porous materials. Pure, coarse perlite has a porosity of about 70%, so if bacteria could be cultured in such a media, it could double maximum flow rates for a BMP with the same footprint. Using pure perlite would require supplying the bacteria with a carbon source, such as molasses, and adding a top layer of sand or a screen to hold down the perlite, which is less dense than water.

5.1.2 Consider using pure culture inoculations of desired microorganisms

Rather than relying upon native soils, which can contain unwanted bacteria, a bioreactor BMP should start with pure culture inoculums of the desired microorganisms. There are patents for selenium-reducing bacteria systems, (Oremland, 1991; Oremland, 1993), and evaluations of recent applications have been reviewed by Twidwell et. al (1999). These were developed for treating acidic mining wastes, and so the microorganisms from those applications may not be directly useful in this watershed. If researchers can identify and isolate local, culturable selenium-reducing microorganisms that can reduce selenium, a pure culture Bioreactor BMP could be considered. Without pure culture approaches, mitigating factors such as UV irradiation may be needed to attain effluent limits for bacteria from a bioreactor discharge.

5.1.3 Develop more reducing power in the bioreactor

The BMP evaluation underscored the importance of ensuring that the bioreactor is reducing enough to get some sulfate reduction. This could mean allowing the bioreactor to condition longer before initiating flow, adding a readily available carbon source such as molasses to accelerate development of microbial populations, or decreasing dissolved oxygen concentrations of the source water.

The bioreactor BMP evaluated used a vertical flow system, because it was determined that horizontal flow through the medium would be restricted to less than 0.2 gpm. This may have had the effect of bringing excess oxygen into the bioreactor, moving the strongly reducing layer downward in the bioreactor media. Thus, even though the volume of the water in the bioreactor was 1,100 gallons, the volume of water in the reducing zone may have been much less. One way to overcome this would be to consider a hybrid system that reduces the dissolved oxygen of inflow water.

Monitoring ORP within the bioreactor gave important information. It would be better to be able to sample a suite of indicators of reducing power at discreet depths: nitrate, nitrite, ammonia, sulfate, sulfides, manganese, etc. To allow this, future designs should replace the probe well with small water sampling tubes, i.e. sediment porewater "peepers," placed at fixed depths within the bioreactor. This would allow collection of sufficient sample volumes for analysis of nutrient profiles without risking introduction of excess oxygen.

5.1.4 Consider hybrid systems

This BMP evaluation focused on a single approach, a bioreactor to remove selenium by bioechemically mediated reduction. Hybrid systems can enhance performance and mitigate unwanted effects.

For example, systems have been investigated which reduce selenium using ferrous ion (chemically reduced iron). Production of large amounts of iron sludge decreases the feasibility of such an approach (Twidwell et al., 1999), so the effect of iron or mineral additions on the suitability of material for disposal would need to be determined. A hybrid system that relies primarily on biological reduction, but uses a smaller amount of ferrous iron to decrease dissolved oxygen concentrations of influent water, could be useful. This could mean adding a layer of solid material containing ferrous ion (e.g., magnetite, pyrite) to the top of the bioreactor. Nitrate is known to interfere with direct reduction of selenium by ferrous ion (Twidell, 1999). However, the reduced iron in a hybrid application could be used simply as an oxygen scavenger, leaving it to the microorganisms to produce the needed selenium reducing power.

Another important feature to incorporate in a hybrid system would be filtration media to remove particles. Selenium is regulated based on total recoverable concentrations. In the one event where the bioreactor showed no removal of total selenium, it still showed removal of dissolved selenium (see Figure 13). This event also had relatively high TSS in the outflow water (See Figure 14). Ensuring that the outflow water has the lowest possible TSS, by inclusion of sand or mixed media filters, can likely enhance overall selenium removal.

Dissolved and total measurements in this study are very close to each other in this study. To assess BMP effects on particulate selenium concentrations, particulate selenium species need to be analyzed directly, not by difference between dissolved and total measurements. This is important, because particulate organoselenium is a key food chain linkage (Luoma et al 1992).

Finally, hybrid systems could be designed to mitigate nuisance bacteria. Flow through shallow, sunlit reaches or other means of UV irradiation could potentially be incorporated into larger designs to bring bacteria counts into compliance with water quality standards.

All hybrid systems, in addition to optimizing for selenium removal, will need to be integrated into site-specific features of the landscape, from scales such as settling basins and natural treatment systems down to the smaller footprint type of BMP evaluated in this study. The design features of hybrid systems will need to account for local conditions and the need to comply with all applicable water quality standards.

5.1.5 Recognize size limitations on flow

It should be recognized that no matter how well the system is optimized, a bioreactor of the size tested here will likely never be able to process flows higher than 5-10 gpm, and 1-5 gpm is a more reasonable expectation. This is simply a consequence of the need for a sufficient contact time of selenium in the reducing conditions. As the working group plans for future implementation, it should keep this in mind when considering the feasibility of such small scale approaches. To treat the desired amount of groundwater from small, short-term discharges, throughout the watershed, how many such bioreactors would have to be deployed? What would the cost be, and what additional problems or challenges would be created? Developing answers to those questions may be one of the highest priorities, before putting any additional resources into testing small scale BMPs. If costs and feasibility mean that development of large, centralized treatment systems or restoration of natural function within the watercourses are more cost effective ways to deal with discharges, it would be good to know that before evaluating any more small scale projects.

5.1.6 Design for easy deployment

The BMP evaluated had several features which decreased its practicality. It was extremely heavy, damaging the asphalt it was sitting on. The mass prevented it from being moved around as a unit – the media had to be loaded into the box onsite, and then unloaded for disposal. If small scale BMPs are determined to be useful for short-term discharges, the BMP will need to be designed for easy deployment. This means cutting the mass at least in half. A pure perlite media could help this. Another feature to optimize for ease of deployment includes the box housing the BMP (have it sit on steel runners or reinforced concrete pavement to spread the weight around).

Additional considerations include the overall visual impact and degree of expertise needed to successfully implement the BMP. For example, standing water from leakage through the pond liner (where the drain line was inserted through, but not sealed properly – near back wall) necessitated application of "mosquito donuts". Flies and slimy/foamy surface growth on the leakage water ponding on the floor of the roll-off was a constant maintenance problem and contributed to blowing out one of the pumps. For this to work, it has to be an approach that is acceptable to and usable by the average construction contractor, and approvable by Regional Board staff.

5.1.7 *Improve the plumbing*

The use of three pumps to keep water flowing through the BMP tripled the chances of pump failure causing problems. A better approach would be to rely as much as possible on gravity flow and passive systems to achieve the desired balance between inflow and outflow. A suggested configuration to achieve this is shown in Figure 20. Key features include:

1) A single pump continuously fills the elevated supply tank, with overflow diverted directly to the sanitary sewer, as with the original design.
2) Instead of a float valve activating a second pump, water flows from the supply tank through a Hudson valve[7]. Hudson valves can operate at low water pressures to shut off water supply when a threshold water level is reached.
3) An overflow hole is drilled in the top of the bioreactor wall, and connected directly to the sanitary sewer, as a fail-safe to prevent overflow and spillage in the event the Hudson Valve fails.
4) The vertical flow configuration puts a fair amount of water pressure on the exit valve. To allow fine-tuning of outflow rates, two PVC ball valves can be connected in series.

With this configuration, if the single pump were to fail, it would not cause overflow or spillage of water.

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[7] Information on the Hudson Valve can be found at http://hudsonvalve.com/home.html

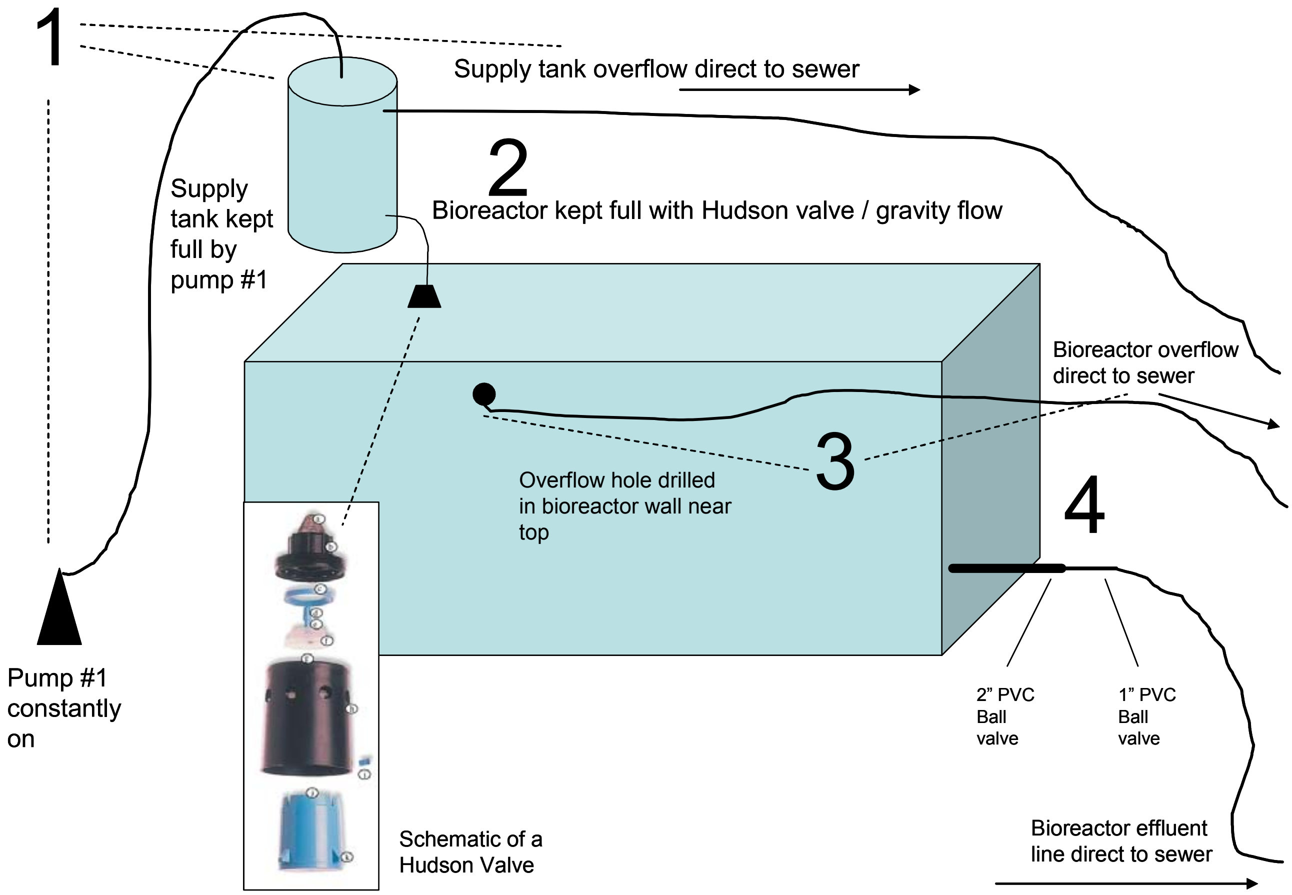

Figure 20: Improved plumbing configuration for a similar BMP evaluation.

5.1.8 Exclude wildlife

During the course of the BMP evaluation, three dead crows were found floating in the top of the bioreactor. Crow mortality is a common occurrence in Orange County this time of year, most likely because of West Nile Virus[8]. However, it did point out the need for a wildlife exclusion plan, to ensure that any BMPs deployed do not become attractive nuisances to birds seeking water and a place to rest. In this case, a simple net or cover over the BMP would ensure that birds stay out of the BMP.

5.2 Recommendations for future studies on a larger scale

The Working Group can consider the following lessons learned from this smaller scale BMP when contemplating larger scale wetlands and natural treatment systems.

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[8] Orange County Vector Control was notified, and Orange County Animal Control came to dispose the crows. Field Crews were advised on precautions against West Nile Virus, including application of mosquito repellant and keeping skin covered as much as possible.

5.2.1 *Vertical flow has benefits and drawbacks*

The French drain system employed to allow vertical flow greatly increases the flow capacity of the system, compared to horizontal flow through a soil medium of the same size and shape. This is a natural consequence of Darcy's law: hydraulic head increases flow, whereas horizontal path length through a resistant media decreases flow. This should be kept in mind when designing larger wetland treatment systems.

For smaller scale BMPs, a more vertical design, e.g., shaped like a silo, could be considered. This was described by researchers from UC-Riverside and Agrarian in a presentation attended by Regional Board staff (Schiedlinger et al., 2003; Agrarian, 2005).

It should be noted that vertical flow can have its drawbacks as well. In this BMP evaluation, vertical flow is thought to have limited the reducing power of the bioreactor by enhancing the transport of dissolved oxygen into the system.

5.2.2 *Design for bacteria control in effluent*

Large wetlands and natural treatment systems cannot be expected to maintain pure cultures of bacteria, so steps would have to be taken to mitigate discharge of unwanted bacteria. Inclusion of vegetation can help retain bacteria within root systems. Also, allowing the effluent water to flow through a shallow, shade-free reach after discharge could allow sunlight to kill off unwanted bacteria.

5.2.3 *Seek added benefits of phytoremediation*

A natural treatment system should probably include selenium-accumulating plants to derive added benefits of phytoremediation. Many selenium-accumulating plants can convert selenium to volatile forms, such as dimethylselenide. This provides a removal pathway for selenium, which can prolong the life of the treatment system and avoid accumulation of selenium in soils to hazardous levels. Selenium-accumulating plants also can sequester selenium, making it possible to remove selenium from the treatment system by harvesting. And of course, the presence of plants typically improves the visual appearance of an area, depending on the plants and community aesthetics.

Wildlife also find plants attractive, so a selenium treatment system involving plants will have to avoid or mitigate impacts to wildlife. This could mean exclusion through nets, hazing with propane cannons, or other measures. It could also mean monitoring plants and foragers to determine if an ecological risk is present.

5.3 General Recommendations to the Working Group

5.3.1 *Standardize Se analytical methodologies*

Local groundwater appears to have interferences which can frustrate the use of the hydride generation method. A standardized method for detecting organoselenium is needed in order to evaluate ecological risk. It is preferable, if possible, to avoid difference methods[9], as they tend to be less precise when measuring small differences between large numbers.

The principal forms of ecological concern are selenite and organoselenium. If the ICP-MS method is validated for determination of total selenium, than the only remaining needs are methods for selenite and organoselenium. Hydride generation for just selenite may be feasible, as it does not rely on any antecedent chemical reactions (see discussion in Appendix B for more detail)

If so, then the main effort needs to be on the development of a method for direct detection of organoselenium. Some basic research has been accomplished by the UC-Riverside Department of Soil Sciences on column chromatography methods to isolate organoselenium, but this application has not been validated for use in water.

The ultimate endpoint is protection of wildlife. The concern over organoselenium and selenite is availability for uptake by the prey and food of wildlife species. Therefore, until acceptable methods for measuring selenium species are validated, the next best approach in terms of monitoring is to measure selenium in food items, such as fish, invertebrates, and plant seeds favored by birds.

For task 1.6 of the Work Plan, the following steps are recommended:

- Validate ICP/MS (EPA 200.8) as a method for determining total selenium;
- Validate hydride generation (The Cutter Method) as a method for determining selenite;
- If hydride generation is not acceptable for determination of selenite, develop and validate an alternative;
- Develop and validate a direct method for determination of organoselenium in water and sediments;
- If a direct method for determination of organoselenium cannot be developed or validated, consider validating the modified hydride generation method of Zhang et al. (1999);
- The methods of subsampling and homogenizing sediments and tissues will also need to be standardized.

5.3.2 Include West Nile Virus awareness in health and safety plans for all field work.

As discussed in Section 5.1.8, three dead crows were discovered in the BP during the course of the evaluation. This raised concerns because of the spread of West Nile Virus incidents in Orange County. In the future, any health and safety plans for field work undertaken as part of the NSMP should include information for field teams to take precautions against exposure. This means providing any literature available from the County Department of Health or Vector Control, providing mosquito repellent in field equipment, and covering exposed skin as much

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[9] Difference method means an analytical method that determines a particular selenium species (e.g., organoselenium) as the difference between the analytical results of two different analyses (e.g., total selenium – inorganic selenium = organoselenium). The uncertainty of results by difference methods can be relatively large if the result is a small difference

as possible. BMP designs will also need to avoid conditions that breed mosquitoes (standing water), and include larvicide's if necessary and appropriate.

5.3.3 Continue to take advantage of existing landscape features and infrastructure

The BMP evaluation took advantage of existing infrastructure available through the CALTRANS denitrification facility. The Working Group should continue to seek opportunities to make use of existing sites, infrastructure, and landscape features. For example, detention basins such as the one next to the denitrification facility could provide land necessary for treatment wetlands, if flood control and stormwater detention benefits could be maintained. The CALTRANS denitrification facility may provide useful infrastructure for investigation of pure culture bioreactor systems, since the denitrification system was itself a bioreactor for nitrogen removal.

Finally, it was noted that Peters Canyon Wash, adjacent to the BMP evaluation site, is full of cattails and bulrush plants. The working group should consider whether monitoring in this area could provide insights into the risks and benefits of natural treatment systems.

6.0 CONCLUSIONS

The BMP evaluation overall was a success, in that measurable progress was made towards development of solutions for small, short-term groundwater discharges. Lessons learned from the BMP evaluation help advance important tasks required in the NSMP, including the evaluation of selenium analytical methods in development of innovative BMPs.

According to the success criteria defined in Section 3.2, the feasibility and effectiveness of the bioreactor BMP was evaluated as follows:

- The BMP was partly successful at removing selenium.
- The BMP was successful at removing nitrogen.
- The BMP was unsuccessful in that it produced unwanted indicator bacteria that exceeded water quality objectives.
- The BMP was unsuccessful in terms of nuisance factors (e.g., the mass caused it to sink into the asphalt, it produced odors, standing water attracted flies and mosquito larvae).
- The BMP was unsuccessful in terms of feasibility. The design is at the limit of feasibility in terms of size and mass. The cost and level of effort are beyond feasible compared to the relatively small flow rates and moderate selenium reductions achieved.

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APPENDIX A SUMMARY OF ANALYTICAL RESULTS

Table 4: Summary of selenium, nutrient, and bacteria analyses.

BRL = Brooks Rands Laboratories (Seattle, Washington); CRG = CRG Labs (Torrance, California).

		Event		1	2	3	4	5	6	7	8	9	10	11
		Date		5/20/2005	5/23/2005	5/24/2005	5/26/2005	5/26/2005	5/27/2005	5/31/2005	6/2/2005	6/2/2005	6/7/2005	6/7/2005
		Time (Se)		15:45	14:40	12:00	9:30	14:45	8:30	11:00	11:00	14:30	10:00	12:00
Inflow	**CRG**	Total Se	µg/L	86.3	79.5	76.0	85.4		53.5	56.3	57.9		58.1	
		Total Se Rep	µg/L	85.5	84.2	73.5	83.3		56.0	53.8	53.6		58.9	
		Diss Se	µg/L	80.2	79.5	84.1	84.2		53.4	55.0	58.5		59.7	
		Diss Se Rep	µg/L	79.5	84.2	81.5	84.0		53.7	50.4	58.4		60.1	
	BRL	Total Se	µg/L			48.6	42.2				47.6		53.8	
		Diss ToSe	µg/L			57.4	56.6				49.7		27.2	
		Inorganic se	µg/L					41.6				39.6		40.8
		Diss Inorganic Se	µg/L					42.4				42.7		38.7
		selenite	µg/L					0.3				0.33		0.27
		Diss selenite	µg/L					0.3				0.28		0.27
		selenate	µg/L					41.3				39.3		40.5
		Diss selenate	µg/L					42.1				42.5		38.5
	CRG	Inflow Nitrate	mg/L	29.1	28	28.4	29.6		<0.02	<0.02	29.8		29.2	
		Inflow Nitrite	mg/L	<0.02	<0.02	<0.02	0.3		<0.02	<0.02	<0.02		0.32	
		Inflow Sulfate	mg/L	598	618	1280	658		637	<0.01	573		565	
		Inflow TSS	mg/L	<0.50	<0.50	<0.50	<0.50		<0.50	<0.50	<0.50		<0.50	
		Inflow Fecal	MPN/100mL			<20	700			<20.0	<20.0		<20	
		Inflow Total	MPN/100mL			210	5000			<20.0	<20.0		<20	
		Inflow E. Coli	MPN/100mL			<10	448			<10.0	20		10	
		Inflow Entero	MPN/100mL			<20	160			<10.0	<10.0		<10	
Outflow	**CRG**	Total Se	µg/L	79.3	73.2	75.4	69.9		45.9	33.1	41.9		41.1	
		Total Se Rep	µg/L	81.0	72.7	70.6	72.2		46.1	33.8	42.3		42.1	
		Diss Se	µg/L	71.6	70.7	68.2	65.5		43.6	33.4	43.4		40.4	
		Diss Se Rep	µg/L	72.8	72.1	67.5	67.4		47.0	33.9	42.7		40.6	
	BRL	Total Se	µg/L			42.4	30.5	***Pending***			22.0		37.1	
		Total Se Dup1						***Pending***						
		Total Se Dup2						***Pending***						
		Diss ToSe	µg/L			44.2	23.6	***Pending***			25.3		20.9	
		Diss ToSe Dup1						***Pending***						
		Diss ToSe Dup2						***Pending***						
		Inorganic Se	µg/L					30.4				27.9		17.8
		Inorganic Se Dup1	µg/L					27.6						
		Inorganic Se Dup2	µg/L					31.0						
		Diss Inorganic Se	µg/L					31.0				30.0		14.8
		Diss Inorganic Se Dup1	µg/L					29.7						
		Diss Inorganic Se Dup2	µg/L					29.3						
		selenite	µg/L					0.09				0.17		0.13
		selenite Dup1	µg/L					0.14						
		selenite Dup2	µg/L					0.18						
		Diss selenite	µg/L					0.07				0.11		0.18
		Diss selenite Dup1	µg/L					0.08						
		Diss selenite Dup2	µg/L					0.09						
		selenate	µg/L					30.4				27.7		17.7
		selenate Dup1	µg/L					27.5						
		selenate Dup2	µg/L					30.8						
		Diss selenate	µg/L					30.9				29.9		14.6
		Diss selenate Dup1	µg/L					29.7						
		Diss selenate Dup2	µg/L					29.2						
	CRG	Outflow Nitrate	mg/L	<0.02	19.9	6.0	0.7		<0.02	<0.02	16.2		16	
		Outflow Nitrite	mg/L	0.09	<0.02	10.8	<0.02		<0.02	<0.02	<0.02		0.47	
		Outflow Sulfate	mg/L	658	639	1330	673		622	<0.01	551		529	
		Outflow TSS	mg/L	16.2	13.8	<29	16.5		15.5	17.5	15.5		12.0	
		Outflow Fecal	MPN/100mL			1100000	300000			50000	80000		9000	
		Outflow Total	MPN/100mL			5000000	2400000			50000	300000		16000	
		Outflow E. Coli	MPN/100mL			1986300	344100			43520	72700		14500	
		Outflow Entero	MPN/100mL			43600	10710			> 24192	> 24192		100	

Table 5: Field measurements of BMP inflow

(Temperature, conductivity, dissolved oxygen, pH, and ORP).

DateTime	Temp	SpCond	DO Conc	pH	ORP
M/D/Y	C	mS/cm	mg/L		mV
5/19/2005 11:23	22.1	2.29	6.4	7.2	171
5/19/2005 18:27	21.9	2.29	6.1	7.1	66
5/20/2005 11:21	22.0	2.29	5.9	7.2	59
5/24/2005 15:11	22.7	2.32	9.0	7.8	156
5/26/2005 8:56	21.9	2.28	5.6	7.2	110
5/26/2005 13:43	21.9	2.28	5.5	7.2	95
5/27/2005 8:56	21.9	2.28	5.5	7.2	147
5/31/2005 11:43	22.7	2.29	5.8	7.2	373
6/2/2005 11:26	22.0	2.28	6.1	7.1	328
6/4/2005 14:16	22.3	2.29	5.1	7.1	234
6/7/2005 12:10	22.8	2.29	5.5	7.2	340

Table 6: Field measurements of BMP outflow

(Temperature, conductivity, dissolved oxygen, pH, and ORP).

DateTime	Temp	SpCond	DO Conc	pH	ORP
M/D/Y	C	mS/cm	mg/L		mV
5/19/2005 11:27	23.0	4.89	4.2	6.3	59
5/19/2005 18:28	26.0	3.48	3.4	6.4	30
5/20/2005 11:23	22.5	2.61	4.0	6.9	12
5/20/2005 13:06	23.9	2.62	4.1	6.9	17
5/24/2005 15:13	24.2	2.55	5.2	7.0	-43
5/26/2005 9:04	20.6	2.68	3.4	6.6	-50
5/26/2005 13:59	24.6	2.46	6.0	7.0	-57
5/27/2005 9:08	20.2	2.47	4.2	6.8	-39
5/31/2005 11:45	21.2	2.52	3.3	6.7	-49
6/2/2005 11:31	20.1	2.37	5.7	6.7	-46
6/4/2005 14:20	21.5	2.34	4.5	6.8	-47
6/7/2005 12:13	21.2	2.34	2.9	6.8	-51

Table 7: Field measurements of BMP conditions inside the probe well

(Temperature, conductivity, dissolved oxygen, pH, and ORP).

Date Time	Temp	SpCond	DO Conc	pH	pHmV	ORP
M/D/Y	C	mS/cm	mg/L		mV	mV
5/19/2005 11:56	24.1	4.04	2.0	6.37	27.3	-114
5/19/2005 11:57	24.5	2.86	2.9	6.85	-0.4	-85
5/19/2005 18:24	23.1	2.31	6.5	7.34	-28	-5
5/19/2005 18:25	22.8	0.03	8.9	7.55	-39.8	42
5/19/2005 18:28	23.1	0.04	8.9	6.76	5	21
5/20/2005 11:24	22.3	2.32	5.0	7.29	-24.9	23
5/24/2005 13:36	21.9	2.3	3.6	7.3	-24.0	190.0
5/26/2005 13:31	22.0	2.3	5.4	7.2	-17.8	201.0
5/27/2005 13:38	21.0	2.3	4.1	7.0	-10.5	134.0
5/31/2005 11:08	28.0	4.7	8.7	7.1	-11.6	440.0
6/2/2005 11:34	20.7	2.27	11.6	7.38	-34.4	61
6/2/2005 11:35	20.6	2.27	11.6	7.40	-35.3	76
6/2/2005 14:50	21.1	2.28	12.3	7.53	-43.1	201

APPENDIX B COMPARISON OF SELENIUM ANALYTICAL RESULTS BY TWO DIFFERENT METHODS

The study plan called for analysis by "hydride generation" to determine total selenium concentrations, as well as selenium forms of concern (organoselenium, selenite, selenate). This has been discussed with the working group as the "Cutter Method" (Cutter, 1978). In order to provide rapid feedback on system performance, the study plan also called for total selenium analysis by ICP/MS. This method is the standard, USEPA method 200.8 that is being used by CALTRANS for its regular monitoring program at the BMP location, as well as other selenium monitoring projects in the watershed. As it turns out, including ICP/MS analysis was a fortunate decision. Both total (i.e., unfiltered) and dissolved (i.e., filtered) selenium analyses by the hydride generation method were consistently lower than analyses of the same samples by ICP/MS (Figure 21).

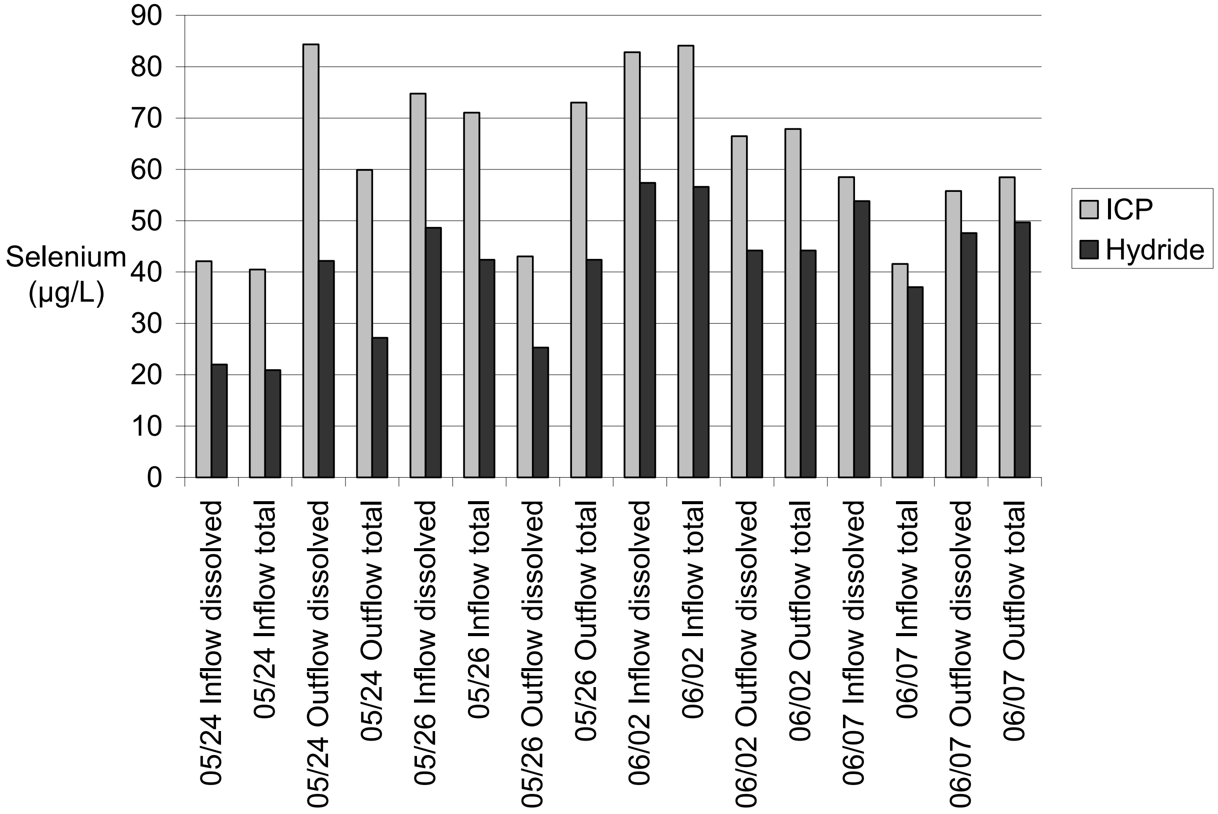

Figure 21: Comparison of paired results for selenium analyses by ICP/MS and Hydride generation.

While the exact reason for this discrepancy needs to be determined, difficulties reported with poor and inconsistent spike recoveries suggest that something is interfering with the Cutter method in this instance. Brooks Rands Laboratory has performed extensive methods development to try and resolve the causes of this.

From discussions with Brooks Rand staff, it appears a possible issue is that chemicals such as nitrite, iron, or organic carbon can interfere with the chemical transformations the Cutter method relies upon. The analysis of selenite concentrations to produce the data shown in Figure 15 relies upon a single step – reaction of selenite with hydride to form a volatile compound that can be purged from the sample and trapped on a column. This is why the method is referred to as "hydride generation."

Analysis of other chemical forms, such as selenate and organoselenium[10], requires stepwise transformations by chemical reduction and chemical oxidation. Anything that interferes with the chemical oxidation or chemical reduction steps directed at selenium can result in artificially low total selenium measurements (Figure 22).

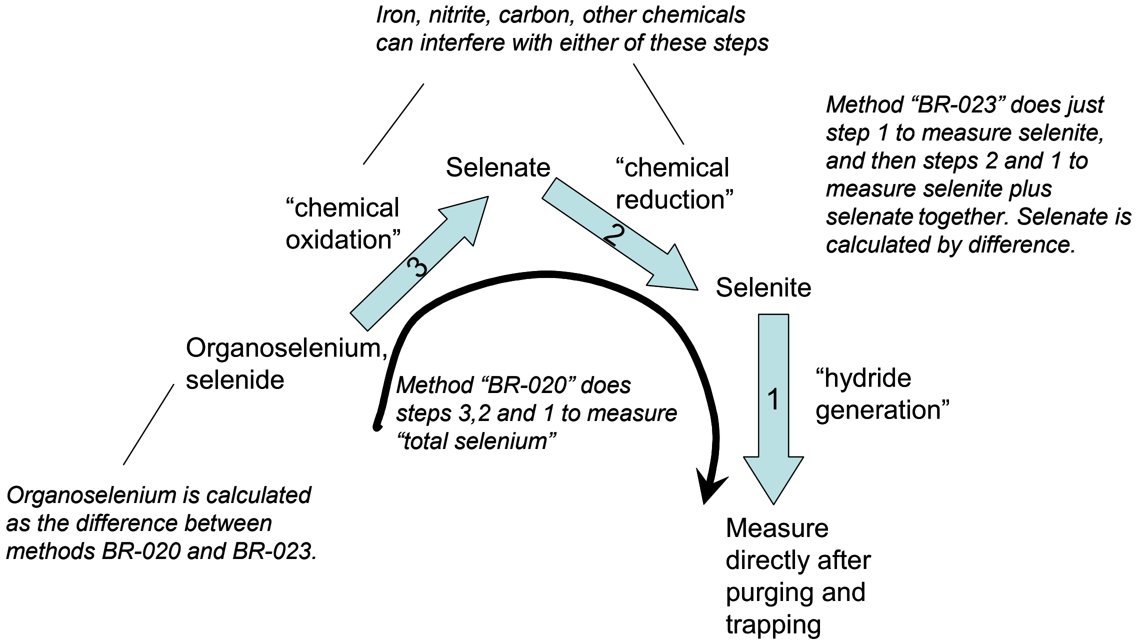

Figure 22: Conceptual illustration of the chemical steps involved in the Cutter method, and the potential for interference.

By comparison, the ICP/MS method takes all chemical forms of selenium shown in Figure 22 and blasts them in a plasma torch at thousands of degrees, forming the same selenium ions no matter what form they started out as in solution. ICP/MS is also subject to interferences, such as substances that inhibit formation of aerosol droplets when sample water is sprayed into the plasma torch, and ions with masses similar to the selenium ions being measured.

This matter is still under investigation, and may or may not be completely resolved between the submission of this review draft to the working group and its final revision. It should be

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[10] Organoselenium assessment was tried at sampling even #5 on 5/26/2005, by requesting triplicate analyses by method BR-023, and later BR-020. Results are still pending on method BR-020, but uncertainties that have arisen because of poor spike recoveries and interferences make it doubtful that low levels of organoselenium could be quantified. This is another methods development need.

emphasized, however, that both laboratories supporting this project have provided excellent service. The challenges described in this finding reflect basic research needs for selenium analysis methods that can be used in local monitoring projects.

It is not known for sure which of the two methods employed gave the more accurate measurements of total selenium. All that is known is that there are more potential chemical reactions steps involved in the hydride generation method where another compound could interfere. By either method, the bioreactor outflow selenium was lower than the inflow. In fact, measurements by hydride generation show outflow concentrations as low as 24 µg/L, even closer to attainment of the 4 µg/L monthly average effluent limit than results by ICP/MS suggest (Figure 23). Clearly, resolving this through Task 1.6 of the Work Plan is a high priority.

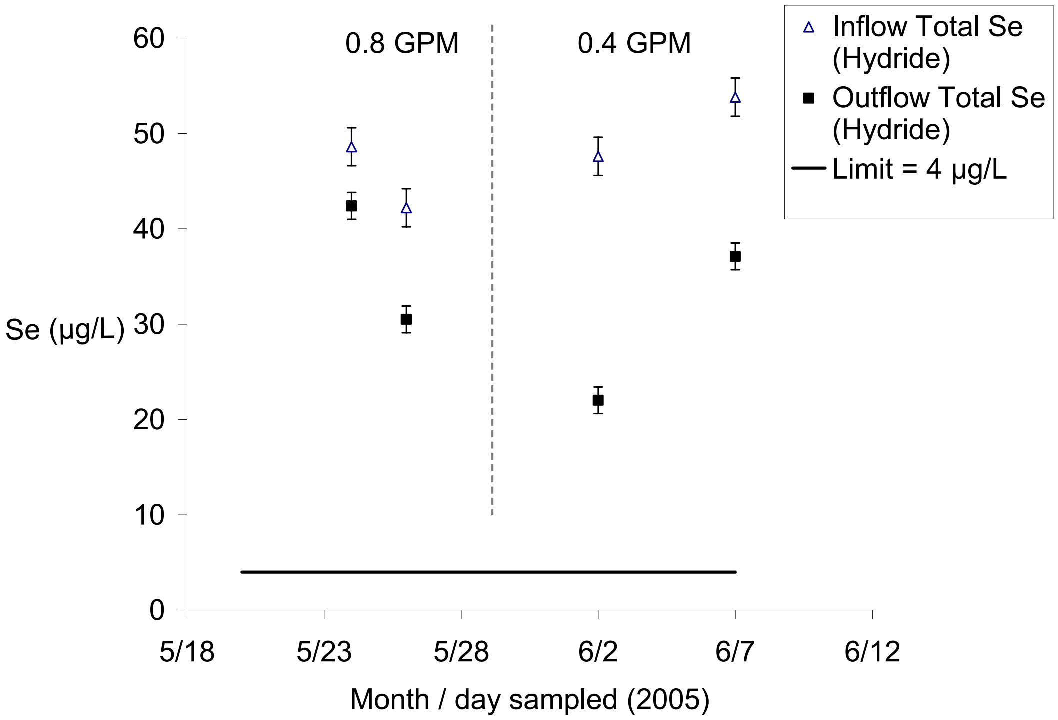

Figure 23: Concentrations of total (unfiltered) selenium measured in the inflow and outflow of the bioreactor BMP over time.

The different daily average flow rates tested (gallons per minute) are shown in upper axis, divided by vertical dashed lines. The horizontal line along the bottom shows the monthly average effluent limit of 4 µg/L. Error bars show one standard deviation of pooled analytical replicates. All measurements are by hydride generation.