PILOT-SCALE TREATMENT OF SELENIUM IN GRAVEL PIT SEEPAGE WATER USING BIOCHEMICAL REACTOR TECHNOLOGY[1]

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Abstract. Water quality in the lower Colorado and Gunnison Rivers in western Colorado, and many of their tributaries, is impaired by selenium, which originates from the local Mancos shale. Because of the diffuse and widespread nature of this source, there are limited opportunities to reduce selenium inputs. One option is to treat selenium-contaminated surface water at strategic locations, such as point-source discharges. Gravel extraction is common along these rivers, and treatment of discharges from pit dewatering presents an opportunity for reducing selenium loading. The pilot test goals were: 1) demonstrate that a passive BCR can accomplish high-efficiency selenium removal at the pilot scale 2) determine the relationship between selenium removal efficiency and detention time 3) assesses the influence of seasonal temperature fluctuations on treatment performance 4) determine design parameters for a full-scale system (*i.e.*, one with a footprint on the scale of up to a few acres). A single 4,380 cubic foot pilot BCR was constructed to treat flows ranging from 2 to 24 gallons per minute. The vertical-flow reactor media contains cow manure, hay, sawdust, wood chips, and limestone. Influent was drawn from a dewatering trench in a gravel pit next to the Colorado River near Grand Junction, Colorado. The pilot operated, with varying detention times, over a thirteen-month period from September 2008 until October 2009. The pilot achieved maximum selenium removal rates of 98% with a hydraulic retention time of 2.4 days and a minimum effluent concentration of 0.0005 mg/L (0.5 µg/L). The highest mass removal rate achieved by the BCR was 73 mg/day/m^3 and the cumulative mass of total selenium removal was 600 grams. The BCR treatment process was effective throughout the cold winter months during which total selenium removal rates remained greater than 90%. The total capital cost for the pilot BCR was $39,200 or $0.50 per 1,000 gallons treated. The operations and maintenance costs for a passive BCR system are minimal. Based on the successful operation of the pilot, including high rates of selenium removal and consistent year-round operation, the BCR technology appears to be an effective, low-cost selenium treatment option. This project was funded by the US Bureau of Reclamation Science and Technology Program, Project #4414.

Additional Key Words: BCR, biological treatment

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Introduction

Selenium in surface and groundwater has generated concern since 1982, when selenium was found responsible for mortality of fish and birds inhabiting the Kesterson National Wildlife Refuge in California (National Research Council, 1989). The western United States is susceptible to Se contamination of ground and surface water due to a combination of geology, climate, and irrigated agriculture. Over 777,000 km^2 (17%) of the total land area in the western U.S. is composed of seleniferous bedrock, much of which is irrigated (Seiler et al, 2003). Selenium is mobilized as irrigation drainage waters leach it from the bedrock and soils. The arid and semi-arid climates promote high rates of evaporation, which can lead to elevated concentrations of Se in surface waters, causing some areas to exceed water quality standards.

Although Se forms the active center of certain enzymes and is thus an essential nutrient, at elevated concentrations it is toxic to invertebrates, fish, birds, and mammals. The oxidation state of Se determines its bioavailability and toxicity (Amweg et al, 2003). Selenium can occur in its elemental form (Se^0), as selenate (SeO_4^{2-}, Se^{6+}), selenite (SeO_3^{2-}, Se^{4+}), and inorganic selenide (Se^{2-}). Elemental Se is insoluble and has little effect on living organisms. The inorganic forms, selenate and selenite, are both soluble and bioavailable, with selenite being the more toxic of the two. Organic selenide is the most bioavailable form of Se, and is utilized by algae 1,000 times more easily than the inorganic forms. Selenium is also bioaccumulative; its concentration may increase in organisms at successively higher levels in the food chain.

The Grand Valley in western Colorado is underlain by the highly seleniferous Mancos shale. Selenium in surface waters here has been measured at concentrations exceeding 100 μg/L (Spahr et al, 2000), which is well above the U.S. Environmental Protection Agency's criterion of 5.0 μg/L as a maximum continuous concentration of total Se for protection of freshwater aquatic life (EPA). Because of the diffuse and widespread occurrence of the Mancos shale, there are limited opportunities to reduce Se inputs to surface waters. One option is to treat selenium-contaminated water at strategic locations, such as point-source discharges (Bureau of Reclamation, 2006). Gravel extraction is common along the Colorado River, and treatment of discharges created by dewatering of groundwater into the pits presents an opportunity for reducing selenium loading to the river.

Selenium-contaminated water can be treated by physical, chemical, and biological treatment methods (Frankenberger *et al.* 2004). Recently, biological treatment has emerged as a leading technology for Se treatment (Microbial Technologies 2005). Biological treatment of Se is accomplished through microbial reduction of oxidized Se species such as selenate and selenite to insoluble elemental Se. In the generalized reactions below, Se serves as an electron acceptor and organic carbon (e.g., BCR substrate, molasses) serves as an electron donor (Fujita et al. 2002).

$$\mathrm{SeO_4^{2-}} + \text{Org. Carbon} \longrightarrow \mathrm{SeO_3^{2-}} + \text{Org. Carbon} \longrightarrow$$

$$\mathrm{Se^0} + \mathrm{CO_2} + \mathrm{H_20}$$

Common electron acceptors that must be removed prior to Se include dissolved oxygen and nitrate.

Biological treatment offers a low cost alternative to more expensive physical and chemical treatment methods and is effective in cold climates (Microbial Technologies 2005). Additionally, it has the proven ability to meet regulatory selenium limits (MSE 2001, Sonstegar 2008). Passive biological treatment systems have been tested extensively at the bench and pilot scale, but have yet to be implemented at full-scale.

Golder Associates Inc. (Golder) and Mesa State College (Mesa State) received U.S. Bureau of Reclamation Science and Technology funding in 2006 to conduct a bench-scale study on biochemical reactor (BCR) treatment of Se. The bench BCR test cells consistently reduced selenium concentrations in the influent water to values below the EPA maximum continuous concentration for protection of aquatic life (Pahler *et al.* 2007, Mesa State College and Golder 2007).

Based on the successful bench results, additional funding was secured to conduct a pilot with the following goals:

1. demonstrate that a passive BCR can accomplish high-efficiency Se removal at the pilot scale
2. determine the relationship between Se removal efficiency and detention time
3. assesses the influence of seasonal temperature fluctuations on treatment performance

4. determine design parameters for a full-scale system (*i.e.*, one with a footprint on the scale of up to a few acres).

Materials and Methods

Site Description

The study was conducted in a gravel pit operation in Grand Junction, Colorado. Groundwater seeps into a dewatering trench along three sides of the gravel pit perimeter and is pumped from this trench into an adjacent agricultural drain, which flows into the Colorado River approximately 45 m (50 yd) away. Selenium concentrations in the groundwater seepage that is discharged to the agricultural drain range from approximately 30 µg/L to 90 µg/L (Kerr 2006).

Materials and Design

The BCR consisted of an above-ground cell contained within an earthen berm (photo 1). The berm slope was 3H:1V from grade to an elevation of 6 ft above grade on both the inside and outside of the structure, with a three-foot wide level crest. The at-grade "floor" within the bermed area measured 7 ft by 7 ft. The overall footprint of the bermed area was 85 ft by 85 ft. The volume of the BCR interior was 4,380 cu ft.

Photo 1. Inside of pilot cell with berms prior to liner placement.

To provide hydraulic control, the inside of the cell was covered by a 6-ounce polypropylene geotextile; overlain by an impermeable 20-mil high-density cross-laminated polyethylene liner (photo 2). The liner and geotextile were Permalon in products from Reef Industries, Inc. of Houston, Texas. Above the liner, 2-inch diameter perforated PVC pipes were placed diagonally from each corner of the level floor to the center of the cell, where they connect with a below-grade 2-inch diameter PVC pipe that drains treated water from the cell. The drain pipe was connected to a water-level control structure consisting of vertical 2-inch diameter PVC pipes bridged by a horizontal 4-inch diameter PVC pipe (photo 3). The horizontal pipe was initially positioned to establish a water level in the cell 5 feet above the cell floor. Water drained from the level control structure through a 2-inch diameter PVC pipe buried approximately 1-foot below grade to discharge into the dewatering trench approximately 90 ft downstream from intake point for the cell.

Photo 2. Geomembrane liner.

Photo 3. Effluent water level control structure.

The BCR cell was filled with organic substrate which serves as a long-term carbon source for microbial activity. The substrate was a mixture by as-received weight of 30% sawdust, 30% wood chips, 10% grass-alfalfa hay, 10% cow manure, and 20% limestone screener fines. All materials were obtained from local suppliers. Substrate mixing and placement are shown in photos 4 and 5. Perforated, two-inch PVC standpipes were placed in the BCR substrate during construction to serve as substrate sampling ports. Substrate samples were packed into panty hose baggies and inserted into the PVC standpipes. Each baggie was tied off with string that could be retrieved from the top of the standpipe to allow sample removal during pilot operation.

Photo 4. Substrate mixing.

Photo 5. Substrate placement completed. Vertical standpipes are substrate sample ports.

Water was pumped from the dewatering trench to the top of the cell. A pump was placed into a sump created by setting a perforated plastic garbage can on the bottom of the trench (photos 6 and 7). The pump was connected to PVC piping, which ran just below the water level into the side of the trench, then about 1 foot underground from the edge of the trench to the top of the berm. The water was delivered to the cell through a perforated PVC pipe running from the cell edge to the cell center (photo 8).

Photo 6. Influent pumps in pump container.

Photo 7. Influent pump container in the seepage trench with influent pipes.

Photo 8. Influent pipe (white) extends to middle of cell. Drainage pipe cleanout in foreground (white end cap).

In order to insulate the BCR, wood chips were added to the top of the substrate in the cell to create a mound about 2 ft high at the center sloping down to the top of the berm along the sides. A 10-mil high-density cross-laminated polyethylene liner (Permalon™, Reef Industries) was installed on top of the wood chips for insulation and to prevent precipitation from infiltrating into the cell (photo 9).

Photo 9. Influent hose on top of liner cover.

Operation

After filling the cell with water from the trench for the first time, this water was retained in the cell for three weeks to incubate the microorganisms. At the end of this period, the pump was turned on and the study commenced. The first sampling event occurred on 11 September 2008.

Routine operation of the BCR consisted of periodic sampling and analysis (described in the next section), measurement of flow through the cell, and flow rate adjustments. From 11 September 2008 to 27 March 2009, flow was measured as it exited the cell at the water level control structure. Outflow was diverted through a valve in the horizontal pipe (bridging the two vertical pipes) into a calibrated bucket. From 27 March 2009 until the end of data collection on 5 October 2009, flow was measured as it entered the cell using a calibrated bucket and stopwatch.

As the study progressed, Se concentrations in the trench dropped to unacceptably low concentrations (typically less than 20 µg/L). Investigation showed that a separate branch of the dewatering trench draining the west side of the pit had higher Se concentrations. From 11 May 2009 until the end of data collection, water was pumped from this trench through approximately 325 ft of 1.5-inch diameter PVC non-rigid tubing to discharge into a depression excavated in the wood chips at the center top of the cell. A ball valve was used to control the flow rate of the discharge.

Sampling and Analysis

Samples were collected samples and field parameters measured at roughly 10-day intervals (except when the water delivery system was not operating properly) for a total of 32 events. A list of field parameters is provided in Table 1. From 30 September 2008 to 8 June 2009, grab samples of influent were collected and field measurements were performed *in situ* on water in the trench. From 8 June 2009 to the end of the project, influent water was sampled and measured as it pooled and infiltrated at the top of the cell. Grab samples of effluent were collected from the water-level control structure; field parameters were measured here *in situ* as well. All samples were collected into bottles provided by ACZ Laboratories (Steamboat Springs, Colorado) and pre-filled with appropriate preservatives.

Table 1. Field Parameters and Instrumentation

Field Parameter	Instrument
pH	Hach Sension 1 pH meter with automatic temperature compensation; calibrated at beginning of each sampling event
Conductivity	Hach Sension 5 conductivity meter with automatic temperature compensation; calibrated at beginning of each sampling event
Dissolved oxygen	Hach HQ20 oxygen meter with luminescence probe; factory calibrated
Oxidation-reduction potential	Hach HQ20 with platinum combination electrode; calibration verified before each sampling event
Temperature	Each of the three meters listed above; factory calibrated

Samples collected at 10-day intervals were analyzed for total Se and dissolved Se. Samples were collected and analyzed for an extended sampling suite (Table 3) on ten occasions. Substrate samples were collected on four occasions (17 March 2009, 6 August 2009, 16 September 2009, 5 October 2009) and submitted for Toxicity Characteristic Leaching Procedure (TCLP) testing. ACZ Laboratories (Steamboat Springs, Colorado) performed all sample analysis.

Table 2. List of Analytes and Standard Methods

Analyte	Analytical Method
Selenium, total	200.2, 200.8 ICP-MS
Selenium, dissolved	200.2, 200.8 ICP-MS
Selenium (IV)	3114 B, AA-hydride
Selenium (IV) and (VI)	3114 B, AA-hydride
Selenium (VI)	Calculated
Selenium, dissolved	3114 B, AA-hydride
Selenium, organic	calculated
Calcium, total	200.7 ICP
Iron, total	200.7 ICP
Magnesium, total	200.7 ICP
Manganese, total	200.7 ICP
Biochemical oxygen demand (5 day)	5210 B
Total organic carbon	5310 B
Nitrate/nitrite as N	353.2
Nitrogen, total Kjeldahl	351.2
Phosphorous, total	365.1
Sulfate	375.4
Sulfide	376.2
TCLP selenium	1311 extraction 3010A digestion 6010B analysis

Samples to be analyzed for total Se were collected without filtration into laboratory-provided bottles containing enough concentrated HNO_3 acid to lower the sample pH to a value < 2 for preservation. These unfiltered samples are prepared for analysis by digestion, which involves refluxing with HNO_3 and HCl acids to dissolve any Se that may be present in the solid phase within the sample (*e.g.*, sorbed to particulate matter, or in a form that is insoluble under ambient conditions). Samples to be analyzed for dissolved Se were filtered at the time of collection and preserved in a similar manner. The normal laboratory procedure is to analyze the filtered sample directly for Se without digestion.

On some occasions, dissolved Se concentrations were greater than total Se concentrations. A strategy for mitigating the occurrence of dissolved Se exceeding total Se is to digest the filtered samples in the same manner as the unfiltered samples for analysis of total Se. One possible explanation for the success of this modified method is the presence of volatile Se species in effluent samples. The dissolved digestion method is less vigorous and removes a lesser amount of the volatile Se; the total digestion is more vigorous and removes more volatile Se. Within the first month of sampling, three occurrences of the problem were observed: effluent samples on 11 September 2008 (total Se of 1.5 µg/L, dissolved Se of 14 µg/L); effluent samples on 23 September 2008 (total Se of 1.1 µg/L, dissolved Se of 4 µg/L); and influent samples on 9 October 2008 (total Se of 19.5 µg/L, dissolved Se of 26.6 µg/L). Re-analysis of the filtered samples, following digestion, yielded results that better met expectations. For 11 September 2008, the revised result was 1.1 µg/L (<1.5 µg/L); for 23 September 2008, the revised result was 1.2 µg/L (~1.1 µg/L); and for 9 October 2008, the revised result was 20.8 µg/L (~19.5 µg/L). We adopted the practice of digesting filtered samples for the remainder of the study. Consequently, the problem only occurred in an additional three samples (influent samples on 21 October 2008, 4 April 2009, and 5 May 2009) over 28 remaining sampling events.

BCR treatment results and discussion

Field Parameters

pH. Influent pH ranged from 7.0 to 8.1 s.u. and effluent pH ranged from 6.8 to 7.5 s.u.

Temperature. Influent field temperature ranged from 0.8 to 20.3 degrees Celsius (^{o}C) with an average of 13.6 ^{o}C (Fig. 1). Effluent field temperature ranged from 8.1 to 21.0^{o}C with an average of 14.9^{o}C. During winter months, the influent temperatures are significantly higher than ambient temperatures because the influent water is groundwater seepage. The relatively warm winter-time influent temperatures were likely beneficial in maintaining biological treatment activity.

Oxidation Reduction Potential (ORP).ORP values measured with an Ag/AgCl electrode were corrected to standard hydrogen electrode (SHE) values (Fig. 2). The influent ORP values averaged 261 millivolts (mv); effluent measurements were consistently reducing, with an average of -106 mv. Negative ORP values indicate anaerobic conditions conducive to Se reduction.

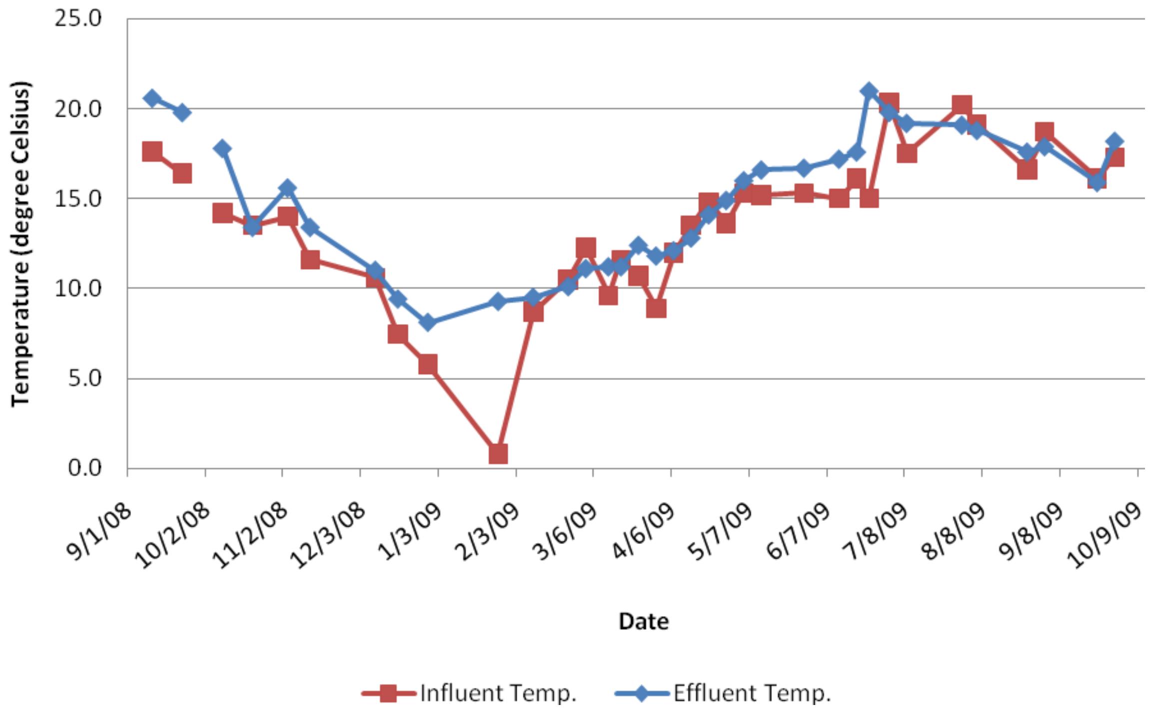

Figure 1. Pilot temperature values.

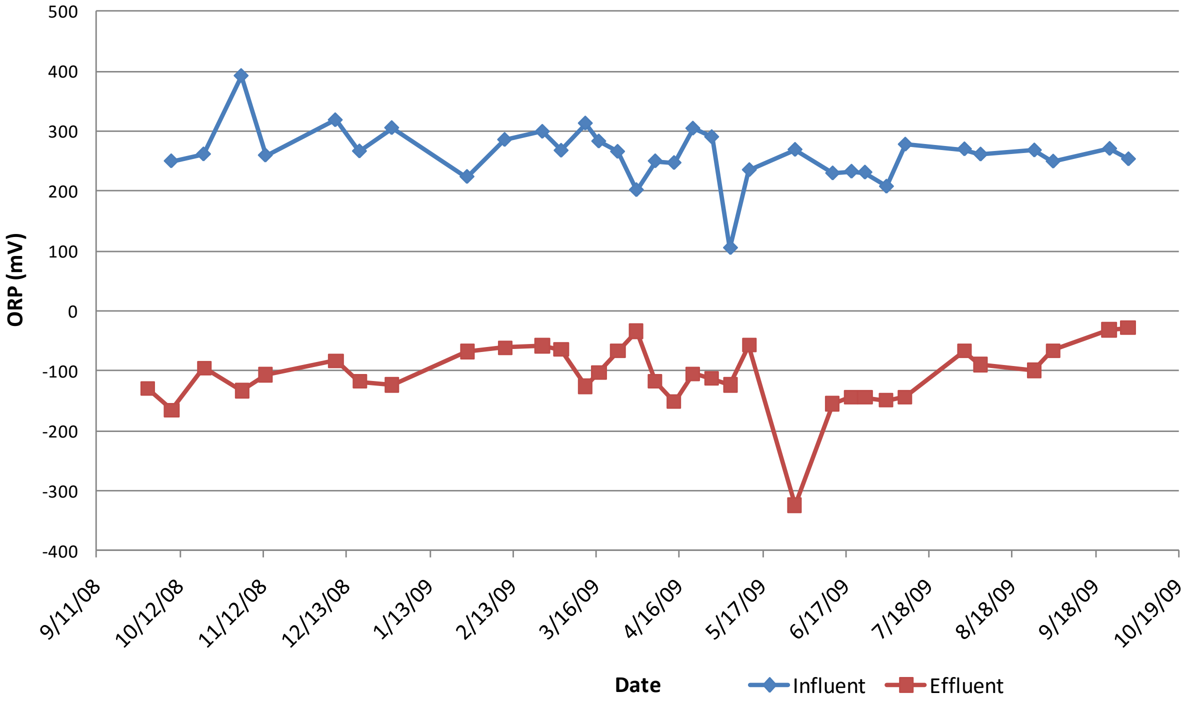

Figure 2. Pilot oxidation reduction potential values.

Dissolved Oxygen. Influent dissolved oxygen ranged from 1.2 to 13 mg/L with an average of 5.0 mg/L. BCR effluent dissolved oxygen ranged from 0.0 to 1.3 mg/L with an average of 0.3 mg/L. The consistently low effluent dissolved oxygen values are consistent with the negative ORP values and indicate that the BCR effluent was consistently anaerobic.

Flow and Hydraulic Retention Time. The pilot flow rate ranged from 1.7 gallons per minute (gpm) to 24 gpm (7 to 91 Liters per minute). Hydraulic retention time (HRT) was calculated based on flow rate and an estimated BCR pore space volume of 57 cubic yards. HRT ranged from 0.4 days (10 hours) to 6.1 days. Flow rate and HRT values, which are inversely related, are shown on Fig. 3. One goal of the pilot study was to optimize performance by varying Se loading rates. As such, the influent flow rate was continually increased during the last three months of the study in order to gauge Se treatment performance under different loading rates.

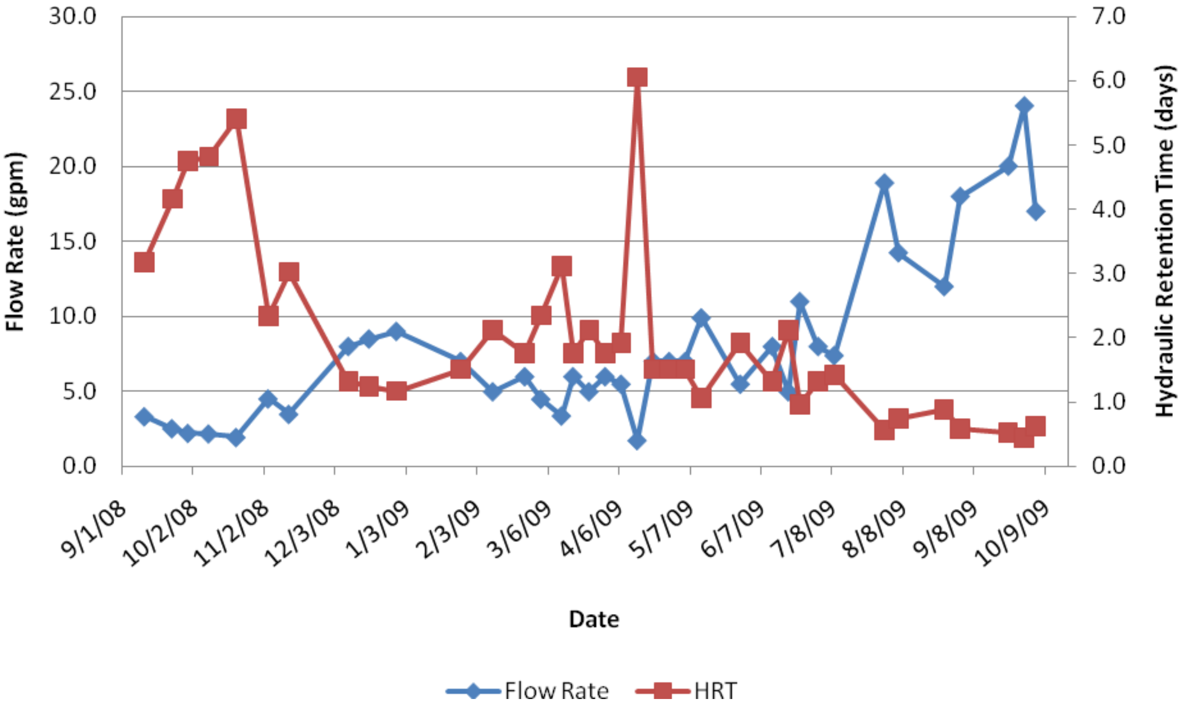

Figure 3. Pilot flow rate and hydraulic retention time (hrt).

Alternate Electron Acceptors

The rate of microbial reduction of Se can be affected by the presence of alternate electron acceptors such as nitrate and sulfate (Masschelyn and Patrick 1993). Nitrate is a more favorable electron acceptor than selenate and typically must be completely removed before significant Se reduction can occur. Sulfate, on the other hand, is a less favorable electron acceptor than selenate. In theory, sulfate reduction should be minimized in a Se-reducing BCR to minimize carbon (*i.e.*, substrate) utilization and sulfide generation.

Nitrate/nitrite. Influent nitrate/nitrite values were variable, ranging from 0.4 to 17.1 mg/L as N with an average of 7.1 mg/L as N. Effluent nitrate/nitrite values ranged from 0.1 to 9.7 mg/L as N with an average of 3.1 mg/L as N. Nitrate/nitrite removal occurs via denitrification which reduces nitrate/nitrite to nitrogen gas. Percent nitrate/nitrite removal values are shown on Fig. 4, which provides a comparison of nitrate/nitrite, Se, and sulfate removal.

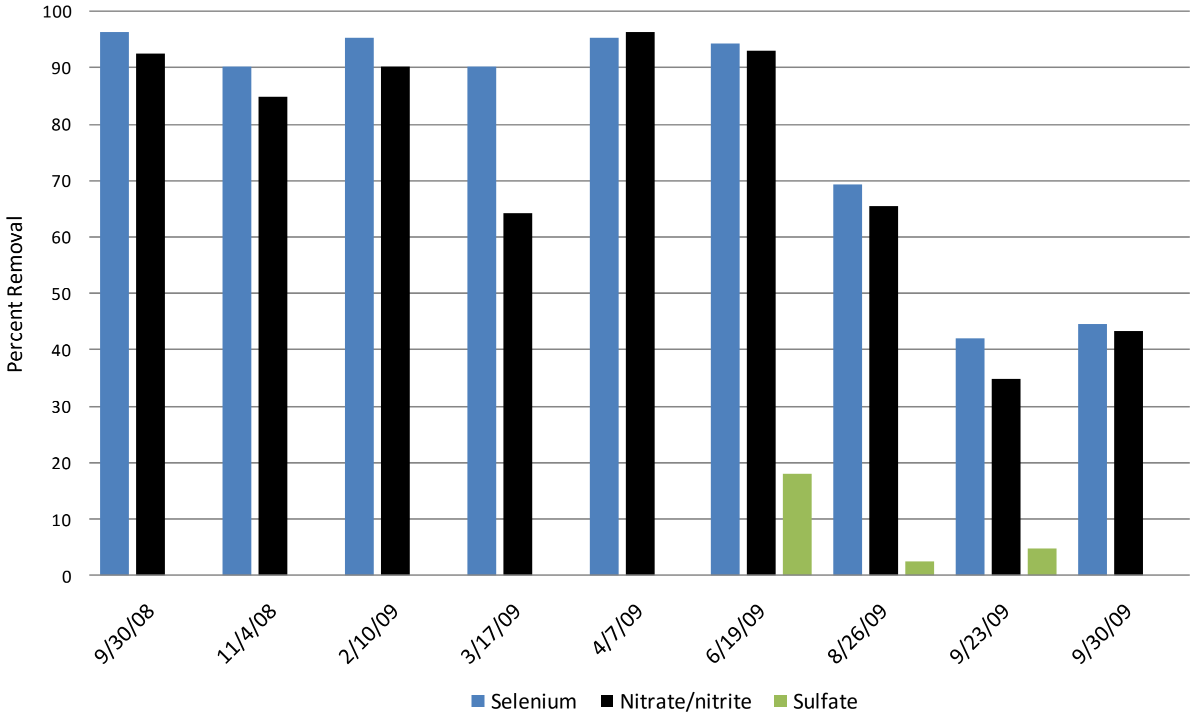

Figure 4. Selenium, Nitrate/Nitrite, and Sulfate Percent Removals.

Sulfate and sulfide. Influent sulfate ranged from 410 to 2700 mg/L with an average of 1495 mg/L. Initial effluent concentrations (30 September 2008 through 28 April 2009), analyzed by gravimetric method (SM 4500), were higher than influent concentrations which is unlikely given anaerobic conditions demonstrated by negative ORP values and the observed increase in sulfide concentrations in the BCR effluent. Influent sulfide concentrations were consistently below the laboratory detection limit of 0.01 mg/L; effluent sulfide concentrations averaged 18.7 mg/L. Beginning with samples collected on 19 June 2008, sulfate samples were analyzed by two additional methods: turbidimetry (EPA 375.4) and ion chromatography (EPA 300.0). The turbidimetry and ion chromatography methods provided more consistent results indicating varying levels of sulfate removal.

Selenium

Total Selenium. Influent total Se concentrations varied considerably from 0.005 to 0.080 mg/L with an average of 0.034 mg/L (Fig. 5). Effluent concentrations ranged from 0.001 to 0.031 mg/L with an average of 0.005 mg/L. The percent removal for total Se ranged from 32 to 98% as shown on Fig. 5. Removal rates equal to or greater than 98% were achieved with a hydraulic retention times ranging from 12 hours to 2.4 days (Fig. 6). This large range in performance is discussed below in the Se loading section. A consistent Se removal rate greater than 90% was typically achieved with a HRT greater than 2 days. Total Se concentrations and percent removal values are provided in Table 4. The percent removal rate was consistently above 90% during winter months; Se removal was not adversely affected by cold winter-time temperatures.

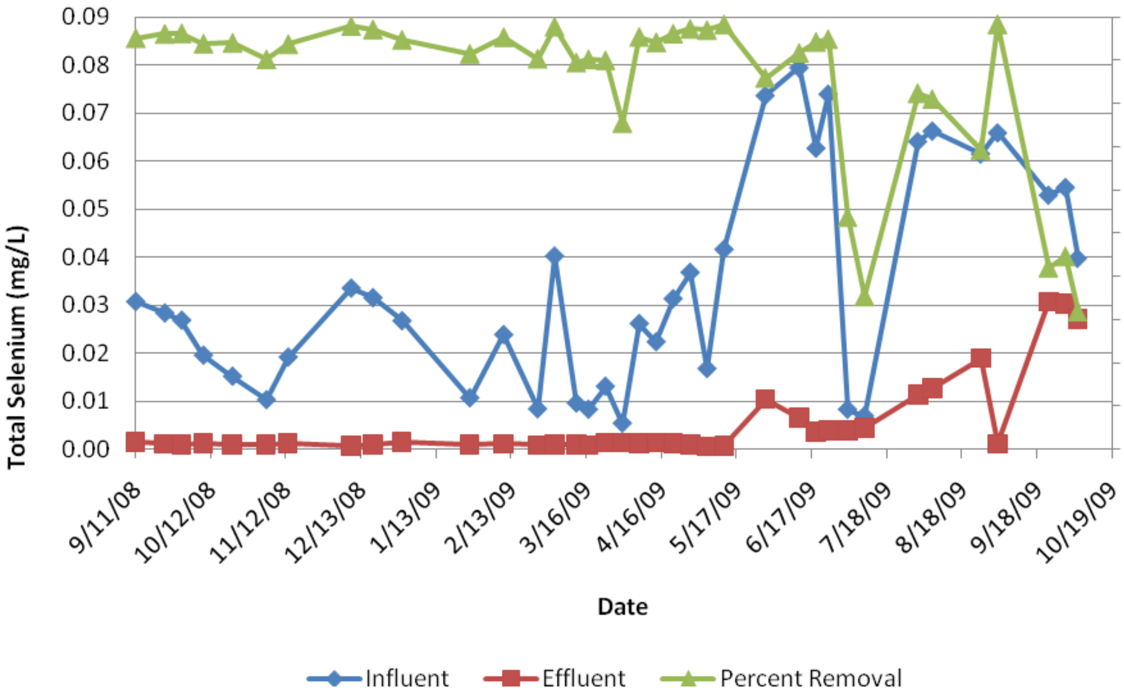

Figure 5. Total selenium concentrations and percent removal.

Table 4. Total Selenium Concentrations by ICP-MS Method

Date	Laboratory Detection Limit mg/L	Influent mg/L	Effluent mg/L	Removal Efficiency
9/11/2008	0.0005	0.0307	0.0015	95%
9/23/2008	0.0005	0.0283	0.0011	96%
9/30/2008	0.0001	0.0268	0.0010	96%
10/9/2008	0.0001	0.0195	0.0012	94%
10/21/2008	0.0001	0.0151	0.0009	94%
11/4/2008	0.0001	0.0102	0.0010	90%
11/13/2008	0.0001	0.0191	0.0012	94%
12/9/2008	0.0001	0.0335	0.0007	98%
12/18/2008	0.0001	0.0315	0.0009	97%
12/30/2008	0.0001	0.0267	0.0014	95%
1/27/2009	0.0001	0.0106	0.0009	92%
2/10/2009	0.0001	0.0238	0.0011	95%
2/24/2009	0.0001	0.0083	0.0008	90%
3/3/2009	0.0001	0.0402	0.0009	98%
3/12/2009	0.0001	0.0095	0.0010	89%
3/17/2009	0.0001	0.0082	0.0008	90%
3/24/2009	0.0001	0.0130	0.0013	90%
3/31/2009	0.0001	0.0053	0.0013	75%
4/7/2009	0.0001	0.0261	0.0012	95%
4/14/2009	0.0001	0.0223	0.0013	94%
4/21/2009	0.0001	0.0313	0.0012	96%
4/28/2009	0.0001	0.0368	0.0010	97%
5/5/2009	0.0001	0.0167	0.0005	97%
5/12/2009	0.0001	0.0416	0.0007	98%
5/29/2009	0.0001	0.0737	0.0104	86%
6/12/2009	0.0001	0.0795	0.0066	92%
6/19/2009	0.0001	0.0627	0.0036	94%
6/24/2009	0.0001	0.0740	0.0038	95%
7/2/2009	0.0001	0.0082	0.0038	54%
7/9/2009	0.0001	0.0068	0.0044	35%
7/31/2009	0.0001	0.0641	0.0113	82%
8/6/2009	0.0001	0.0663	0.0126	81%
8/26/2009	0.0001	0.0615	0.0189	69%
9/2/2009	0.0001	0.0659	0.0011	98%
9/23/2009	0.0001	0.0529	0.0307	42%
9/30/2009	0.0001	0.0545	0.0302	45%
10/5/2009	0.0001	0.0397	0.0271	32%

Dissolved Selenium. Influent dissolved Se concentrations ranged from 0.005 to 0.077 mg/L with an average of 0.036 mg/L (Fig. 6). The similarity between dissolved and total concentrations indicates that nearly all influent Se was present as dissolved. Effluent concentrations ranged from 0.0004 to 0.030 mg/L with an average of 0.006 mg/L. The percent removal for dissolved Se ranged from 36.7 to 98.7% as shown on Fig. 6. Dissolved Se concentrations and percent removal values are provided in Table 5.

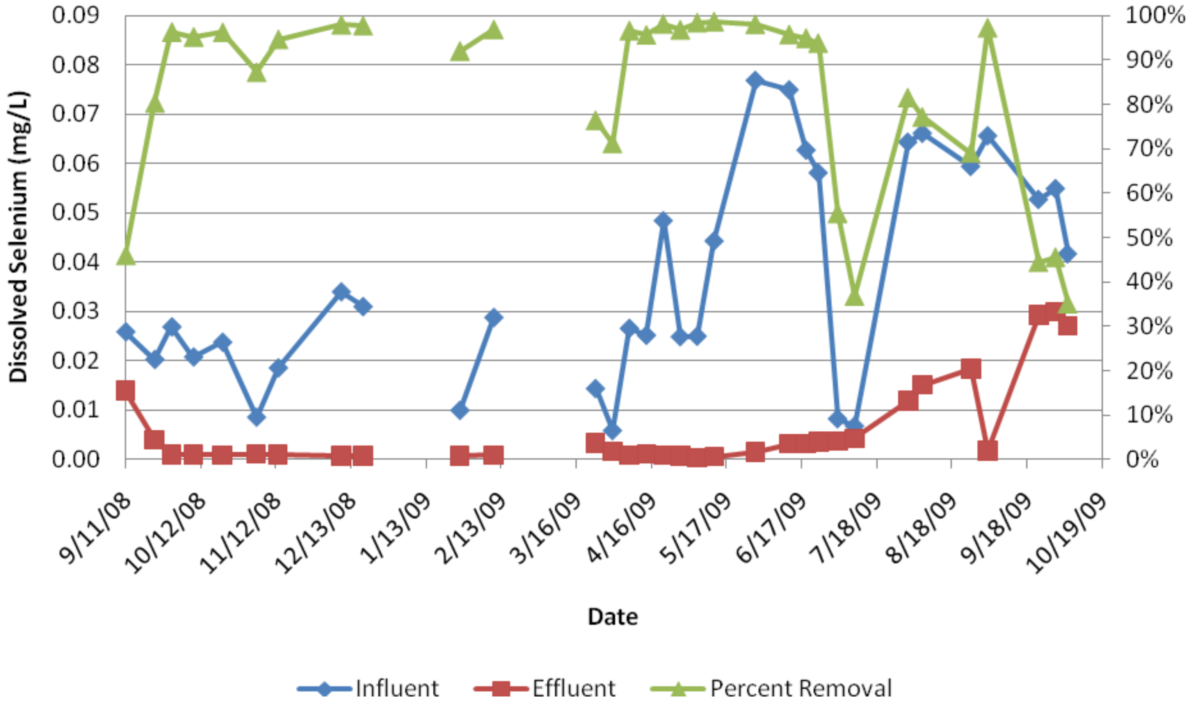

Figure 6. Dissolved selenium concentrations and percent removal.

Selenium Speciation. Influent and effluent speciation results are provided on Tables 6 and 7, respectively. The dissolved Se results by method SM3114B (Tables 6 and 7) differ somewhat from the dissolved Se results by ICP-MS (Table 5). Selenate was the predominant influent species with consistently low concentrations of selenite. The influent selenide concentrations were elevated and also varied considerably between sampling events. Although the data are limited, the BCR process does not appear to increase the more toxic concentrations of reduced Se species (*i.e.*, selenite, selenide); effluent selenite and selenide concentrations were lower than influent concentrations and the majority of effluent selenide concentrations were below the detection limit. Furthermore, the effluent concentrations show consistent selenide removal

Table 5. Dissolved Selenium Concentrations by ICP-MS Method

Date	Laboratory Detection Limit	Influent Dissolved Selenium Concentration (mg/L)	Effluent Dissolved Selenium Concentration (mg/L)	Removal Efficiency
9/11/2008	0.002	0.0259	0.014	45.9%
9/23/2008	0.001	0.0203	0.004	80.3%
9/30/2008	0.002	0.0269	*<0.002*	96.3%
10/9/2008	0.002	0.0208	*<0.002*	95.2%
10/21/2008	0.0001	0.0238	0.0009	96.2%
11/4/2008	0.0001	0.0086	0.0011	87.2%
11/13/2008	0.0001	0.0186	0.0010	94.6%
12/9/2008	0.0001	0.0340	0.0007	97.9%
12/18/2008	0.0001	0.0310	0.0007	97.7%
12/30/2008	NS	NS	NS	NS
1/27/2009	0.0001	0.0100	0.0008	92.0%
2/10/2009	0.0001	0.0288	0.0009	96.9%
2/24/2009	NS	NS	NS	NS
3/3/2009	NS	NS	NS	NS
3/12/2009	NS	NS	NS	NS
3/17/2009	NS	NS	NS	NS
3/24/2009	0.0001	0.0144	0.0034	76.4%
3/31/2009	0.0001	0.0059	0.0017	71.2%
4/7/2009	0.0001	0.0266	0.0009	96.6%
4/14/2009	0.0001	0.0252	0.0011	95.6%
4/21/2009	0.0001	0.0484	0.0009	98.1%
4/28/2009	0.0001	0.0249	0.0008	96.8%
5/5/2009	0.0001	0.025	0.0004	98.4%
5/12/2009	0.0001	0.0443	0.0006	98.6%
5/29/2009	0.0001	0.0768	0.0015	98.0%
6/12/2009	0.0001	0.0749	0.0032	95.7%
6/19/2009	0.0001	0.0627	0.0032	94.9%
6/24/2009	0.0001	0.0581	0.0036	93.8%
7/2/2009	0.0001	0.0083	0.0037	55.4%
7/9/2009	0.0001	0.0068	0.0043	36.8%
7/31/2009	0.0001	0.0643	0.0119	81.5%
8/6/2009	0.0001	0.0661	0.0151	77.2%
8/26/2009	0.0001	0.0594	0.0184	69.0%
9/2/2009	0.0001	0.0656	0.0018	97.3%
9/23/2009	0.0001	0.0527	0.0293	44.4%
9/30/2009	0.0001	0.0549	0.0299	45.5%
10/5/2009	0.0001	0.0417	0.0271	35.0%
10/5/2009	0.0001	0.0417	0.0271	35.0%

Note:

NS - Dissolved Se was not sampled.

Values below the detection limit are shown as preceded with a less than symbol (<). Percent removal calculations for these values below the detection limit were made with a value of one-half the detection limit.

within the BCR when appreciable levels of influent selenide are present (*i.e.*, 7 April 2009, 28 April 2009, 19 June 2009, 26 August 2009). One potential selenide removal mechanism is precipitation of metal selenides such as iron selenide.

Table 6. Influent Selenium Speciation Data based on SM3114B, AA-Hydride Method.

Date	Dissolved Selenium, (µg/L)	Selenate (+VI), (µg/L)	Selenate as percent of dissolved selenium	Selenite (+IV), (µg/L)	Selenite as percent of dissolved selenium	Selenide (-II), (µg/L)	Selenide as percent of dissolved selenium	Sum of selenium species as percent of dissolved selenium
9/30/2008	19.0	8.0	42%	5	26%	6.0	32%	100%
11/4/2008	8	4	50%	2	25%	2.0	25%	100%
2/10/2009	14	12	86%	2	14%	<1	NA	100%
3/17/2009	4	<1	NA	4	100%	<1	NA	100%
4/7/2009	24	7	29%	6	25%	11.0	46%	100%
4/28/2009	21	10	48%	4	19%	7.0	33%	100%
6/19/2009	51	34	67%	3	6%	14.0	27%	100%
8/26/2009	46	27	59%	3	7%	16.0	35%	100%
9/23/2009	41	36	88%	3	7%	2.0	5%	100%
9/30/2009	44	39	89%	3	7%	2.0	5%	100%

Table 7. Effluent Selenium Speciation Data based on SM3114B, AA-Hydride Method

Date	Dissolved Selenium (μg/L)	Selenate (+VI) (μg/L)	Selenate as percent of dissolved selenium	Selenite (+IV) (μg/L)	Selenite as percent of dissolved selenium	Selenide (-II) (μg/L)	Selenide as percent of dissolved selenium	Sum of selenium species as percent of dissolved selenium[1]
9/30/2008	<1	<1	NA	3	NA	<1	NA	NA
11/4/2008	<1	<1	NA	1	NA	<1	NA	NA
2/10/2009	<1	2	NA	<1	NA	<1	NA	NA
3/17/2009	<1	<1	NA	2	NA	<1	NA	NA
4/7/2009	1	<1	NA	3	300%	<1	NA	300%
4/28/2009	1	1	100%	1	100%	<1	NA	200%
6/19/2009	3	<1	NA	3	100%	1.0	33%	133%
8/26/2009	15	9	60%	2	13%	4.0	27%	100%
9/23/2009	23	20	87%	2	9%	1.0	4%	100%
9/30/2009	25	22	NA	1	4%	2.0	8%	100%

Note:

1 - The Se species as a percent of the dissolved Se are greater than 100% when dissolved Se concentrations are very low (*i.e.*, < 5 μg/L) and the analytical precision is insufficient to a detect the various Se species.

Selenium Mass Removal. Selenium mass removal varied from 0.097 grams per day (g/day) to 6.4 g/d and the cumulative Se removal (Fig. 7) over the 13-month operating period was about 600 grams.

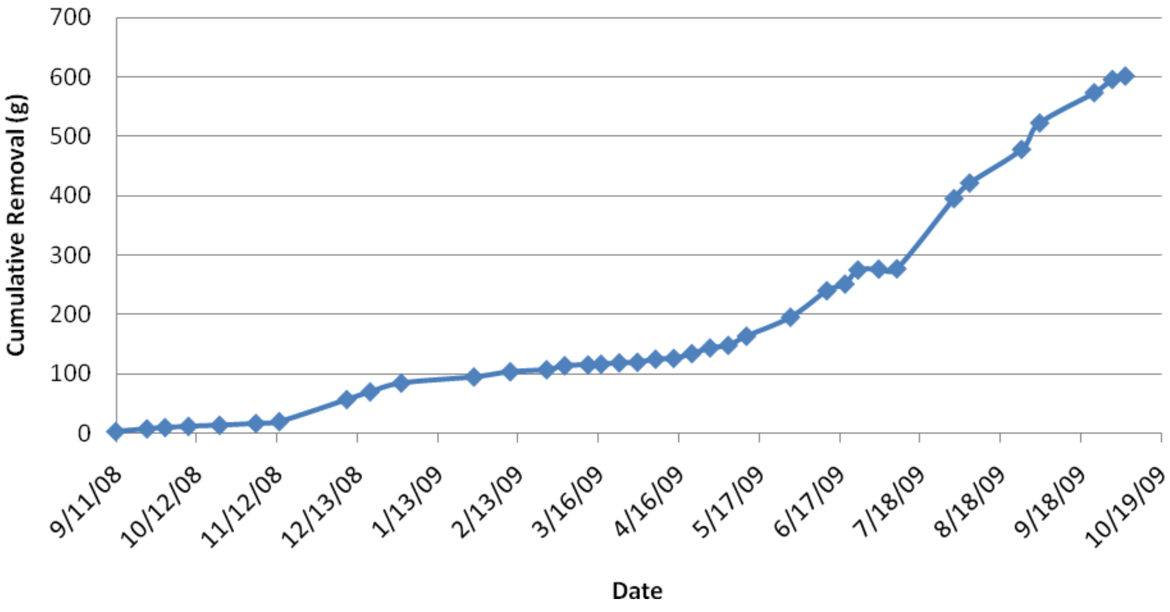

Figure 7. Cumulative total selenium removal.

Selenium Loading. Selenium loading and removal (milligrams per day per cubic meter of substrate) is shown on Fig. 8. The loading graph values are calculated based on influent and effluent Se concentrations and flow rate only. In general, the majority of data points follow a linear trend with a slight decrease in slope at higher loading rates. The maximum removal rate was 73 milligrams per day per cubic meter of BCR media (mg/d/m^3) and the average rate was 16 mg/d/m^3. The three data points that do not fit the trend are circled on the figure. These three points correspond to high influent nitrate concentrations which likely partially explain the decrease in treatment performance. The relative scatter of the loading graph values is likely due to other factors which can affect the removal rate, including temperature and presence of alternate electron acceptors (*i.e.*, nitrate), which are not included in the calculated values. A nitrate/nitrite loading graph was also developed and is shown in Fig. 9. Although nitrate/nitrite data are somewhat limited, the highest calculated nitrate removal rate is about 10 g/d/m^3. The design of future BCR systems should consider both Se and nitrate/nitrite loading criteria.

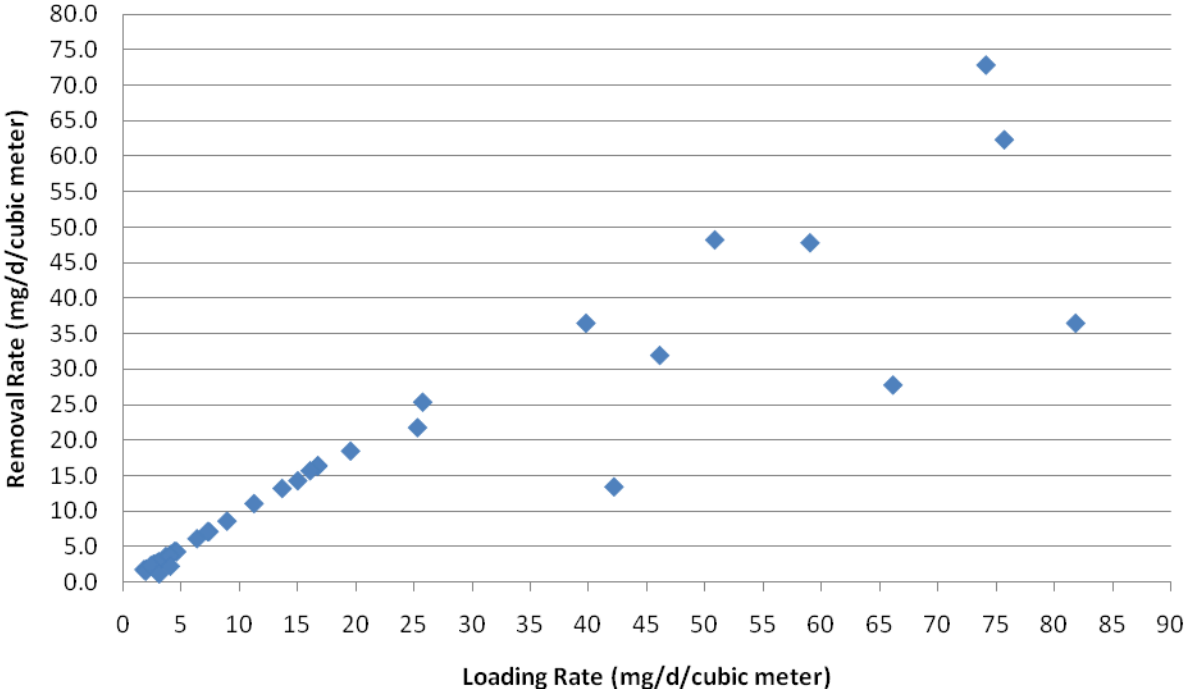

Figure 8. Selenium loading.

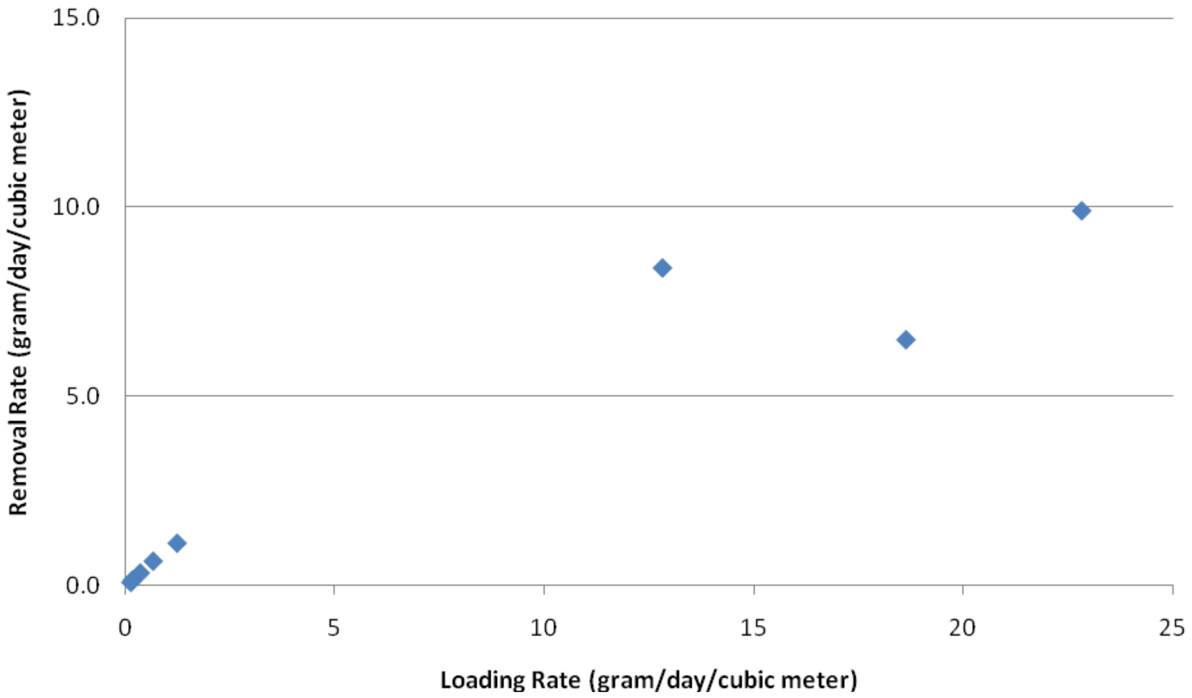

Figure 9. Nitrate + Nitrite Loading

<u>Residual Nutrients.</u> Initial effluent concentrations (9 September 2008) of total organic carbon (TOC), total kjedhal nitrogen (TKN), and phosphorus were 437 mg/L, 11.1 mg/L as N, and 6.4 mg/L, respectively; after thirteen months of operation (30 September 2009), effluent concentrations decreased to 13 mg/L, 1.6 mg/L as N, and 0.05 mg/L, respectively. This large decrease is likely due to flushing of easily degradable organic matter (i.e., manure) and nutrients from the cell.

<u>Fecal coliform.</u> Fecal coliform bacteria are an indicator of fecal contamination. Since animal manure was used as a BCR substrate ingredient, two BCR effluent samples (30 September 2009, 5 October 2009) were collected near the end of the study and analyzed for fecal coliform concentrations. During both sampling events, the effluent fecal coliforms were less than influent concentrations; the effluent concentration on 5 October 2009 was 0 colony forming units per 100 mL. Similar to the concentration trends of the residual nutrients discussed above, the fecal coliform concentrations were likely elevated during startup and decreased throughout the pilot test.

Toxicity Characteristic Leaching Procedure (TCLP) Testing

TCLP testing was performed in order to evaluate disposal options for BCR substrate. All substrate TCLP samples were below the method detection limit for Se. The method detection limit (0.1 mg/L) is well below the hazardous waste regulatory limit (1.0 mg/l) for TCLP Se concentrations (40 CFR 261, Appendix II, 1993 ed., as amended by 58 FR 46040, August 31, 1993). The selenium-negative TCLP results occurred after only 1 year of operation which does not provide a conclusive indication of TCLP results from a system which operates for the lifetime of the carbon substrate (approx. 10 to 20 years). However, given the trace concentrations of Se in the influent water and the buffering capacity of the BCR limestone content, it is likely that a BCR could operate for multiple years prior to exceeding the TCLP Se limit.

Treatment Costs

The capital costs for the pilot cell include materials (*e.g.*, geomembrane liner, piping, pumps, wood chips, and hay), engineering, and construction labor. A significant portion of the construction effort included heavy equipment operation for berm construction and substrate mixing and placement and was provided in-kind by United Sand and Gravel Operations. This portion of the construction cost has been estimated and is included in the capital costs. The total capital cost estimate for the pilot was $39,200 and can roughly be divided into $15,000 for engineering, $8,000 for materials, and $15,700 for labor. Assuming a flow rate of 10 gpm and an operating life of 15 years, the capital cost is equivalent to $0.50 per 1,000 gallons of water treated. Assuming 600 grams of Se removal per year, the pilot BCR would remove 9 kilograms of Se over a 15 year operating life which equates to a mass removal cost of $4,400 per kilogram of Se. The operating costs consisted of electricity for the influent pump, laboratory analysis of water quality samples, and the labor required maintaining flow to the cell. At sites where BCR systems do not require any pumping and operate via gravity flow, operational costs are minimal. The disadvantages of a BCR are the large area required and uncertainty regarding long-term performance.

Conclusions

The 13-month pilot BCR study test was successful in removing Se on a consistent year-round basis. The BCR achieved a maximum total Se removal rate of 98% and a minimum effluent concentration of 0.0005 mg/L (0.5 µg/L). The maximum percent removal rate of 98% was achieved with a range of hydraulic retention times of 12 hours to 2.4 days. The variability in Se removal as a function of HRT is likely due to varying concentrations of Se and nitrate and temperature. In general, a HRT of 2 days is recommended to consistently achieve removal rates greater than 90% for the site. A HRT of at least two days is recommended for future treatment efforts at the site. Other sites would require testing to determine an appropriate HRT; a reasonable estimate of HRT can be made based on dissolved oxygen, nitrate, and Se concentrations. In terms of Se mass removal, the highest mass removal rate achieved by the BCR was 73 mg/day/m3 and the cumulative mass of total Se removal was 600 grams.

In order for significant Se removal to occur, nitrate/nitrite must first be removed. The highest measured nitrate/nitrite removal rate was approximately 10 g/d/m^3. The treatment or nitrate is an ancillary benefit to biological treatment of Se. The BCR treatment process was effective throughout the cold winter months during which total Se removal rates remained greater than 90%.

Based on the TCLP results, the BCR substrate is not toxic with respect to Se and passive treatment residues can be disposed of in a non-hazardous waste landfill. The BCR effluent contains residual nutrients and bacteria that must be considered in the design of a full-scale treatment system. These parameters can be removed in a polishing process such as an aerobic lagoon or wetland. The total capital cost for the pilot BCR was $39,200 or $0.50 per 1,000 gallons treated. The operations and maintenance costs for a passive BCR system are minimal. Based on the successful operation of the pilot, including high rates of Se removal and consistent year-round operation, the BCR technology appears to be an effective, low-cost Se treatment option. The disadvantages of a BCR are the large area required and uncertainty regarding long-term performance.

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