PASSIVE REMOVAL OF SELENIUM FROM GRAVEL PIT SEEPAGE USING SELENIUM REDUCING BIOREACTORS[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 goal of this study is to determine: 1) whether a passive selenium-reducing bioreactor can accomplish high-efficiency selenium removal from the basic, saline water typical of the Grand Valley; 2) whether zero-valent iron is beneficial as a bioreactor component; and 3) optimum detention time. To date, bacterial reduction of selenium has been successfully accomplished using power-, and equipment-intensive "active" treatment systems. The passive bioreactors we are testing can function unattended, ideally by a gravity feed (no pumps), and the "fuel" for the bacteria would be agricultural wastes (e.g., wood chips, hay, cow manure inoculum) and other materials (e.g., quarried limestone) collected locally.

Four 208-liter (55 gallon) bioreactors were constructed with varying amounts of cow manure, hay, sawdust, wood chips, limestone, and zero-valent iron. Influent to the reactors is drawn from a dewatering trench in a gravel pit next to the Colorado River near Grand Junction, Colorado. The reactors were operated, with varying detention times, over a six-month period from July through November 2006. The results of this study demonstrate that passive bioreactors can accomplish up to 98% removal of Se from surface and ground waters in the Grand Valley of western Colorado. A bioreactor designed to promote microbial processes functioned as efficiently as reactors incorporating ZVI, in spite of the potential of the ZVI to enhance the biological removal process. The highest removal rates were achieved using a detention time of 12 hours, but circumstances prevented optimization of detention time.

Additional Keywords: Selenium reduction; passive treatment; agricultural runoff

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Introduction

Selenium in surface and ground water has generated concern since 1982, when Se 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 high concentrations of Se in surface waters, causing some areas to be out of compliance with water quality standards.

Although Se forms the active center of certain enzymes and is thus an essential nutrient, in large 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+}), inorganic selenide (Se^{2-}), or organic selenide (organic-Se). Elemental Se has little effect on living organisms. The inorganic forms selenate and selenite are both water soluble and bioavailable, with selenite being the more toxic of the two. Organic selenide is the most bioavailable form of Se, and is taken up by algae 1000 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 recoverable 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 selenium inputs to surface waters. One option is to treat Se-contaminated surface 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 seepage into the pits presents an opportunity for reducing selenium loading to the river.

Various approaches to treatment of Se-contaminated waters have been investigated (Kapoor et al, 1995). Bioremediation is one such approach (Frankenberger and Arshad, 2001). There are several Se removal processes that may take place in typical bioreactors, microbial reduction of soluble selenate and selenite to elemental Se being the most obvious. Reducing conditions created by the depletion of oxygen from aerobic microbial respiration can result in the chemical reduction of selenate and selenite. If sulfur is present in the water, precipitation of a Se sulfide is possible. Certain algae and microorganisms have been shown to converts Se to organo-selenium compounds, some of which are volatilized to the atmosphere. The bacterial-algal removal of Se has been successfully demonstrated at the pilot scale using a power- and equipment-intensive "active" treatment system (Lundquist, 1994).

The goal of this study is to determine: 1) whether a passive Se-reducing bioreactor can accomplish high-efficiency selenium removal from the basic, saline water typical of the Grand Valley; 2) whether zero-valent iron is beneficial as a bioreactor component; and 3) optimum detention time. If effective, the passive Se-reducing bioreactor promises to be a low-cost treatment method with the potential to reduce Se toxicity in waters found throughout western

Colorado and at other high-selenium locations. The passive bioreactors described here can function unattended, potentially by a gravity feed (no pumps), and the reactor components would be agricultural wastes (e.g., wood chips, hay, cow manure inoculum) and other materials (e.g., quarried limestone) that may be collected locally. The passive nature of the system and the use of low-cost, locally-derived substrate (that might require replacement on a decade-plus schedule) should combine to reduce the costs.

Materials and Methods

Site description

The study was performed in a gravel pit on private land adjacent to the Colorado River in western Grand Junction, Colorado. Groundwater seepage into the gravel pit is collected in a trench extending along the pit perimeter, and then pumped into the Colorado River. This site was chosen because of the significant Se concentrations in the dewatering trench, which ranged from 31 to 93 µg/L during the year prior to our study (Kerr, 2006). The site was also within a secure area which prevented theft and vandalism of the equipment.

Materials

Four bioreactors were constructed using 208-liter (55 gallon) polyethylene drums with varying proportions of sawdust, hay, wood chips, agricultural limestone, zero valent iron (ZVI) powder, and manure (Table 1). ZVI (obtained from Connelly Inc., Chicago) was included in varying amounts in order to determine if chemical reduction of Se would be a significant enhancement to the biological reduction of Se. Reactor 1, with no ZVI, served as a baseline. Reactors 2, 3, and 4 had increasing weight percentages of ZVI. The materials were weighed out and homogenized manually before transfer into each bioreactor. The manure, which was collected from cows grazing in areas known to have Se-rich soils, was included as a source of microorganisms acclimated to the presence of Se. The organic materials were chosen to provide substrate for the growth of the microorganisms. Figure 1 shows the bioreactors at the study site.

Table 1. Bioreactor compositions.

Component	Proportion of Each Component by Weight			
	Reactor 1	Reactor 2	Reactor 3	Reactor 4
Sawdust	30%	30%	20%	2.5%
Hay	10%	10%	10%	0%
Wood chips	30%	30%	20%	2.5%
Agricultural limestone	20%	5%	5%	5%
Zero valent iron	0%	15%	35%	85%
Cow manure	10%	10%	10%	5%

Figure 1. Bioreactors at field test site.

Operation

An automatic sampler (Teledyne Isco, Model 6712) was modified to deliver influent from the dewatering trench to the bioreactors. Power was provided to the sampler by three deep-cycle 12-volt marine batteries connected in parallel and recharged by two 40-watt solar panels. The sampler was programmed to deliver specific volumes to each bioreactor at designated time intervals (e.g., 1.25 L every 10 minutes). Upon completion of bioreactor construction on June 27, 2006 the bioreactors were filled with water from the dewatering trench and allowed to sit until July 10, 2006. From July 10 to September 21, 2006 the flow rate was set at 7.5 L/hr to each bioreactor to attain a detention time of 12 hours. Flow sometimes decreased to as low as 6.4 L/hr between site visits; the sampler was recalibrated to bring flow back to the desired 7.5 L/hr. The flow rate was changed to 8.8 L/hr on September 21, 2006 and then to 9.6 L/hr on September 28, 2006 to measure bioreactor performance at a shorter detention time of 9.4 hours. Flow rate was decreased on November 16, 2006 to 7.4 L/hr to return to a 12 hour detention time while temperatures were lower. Equipment problems resulted in downtimes of one to five days, particularly during weeks 10 to 19. Operation of bioreactor 4 was suspended in mid-November in order to reduce demand on the storage batteries. Operation of the remaining bioreactors was suspended on November 27, 2006 (week 20) because of persistent freezing temperatures and malfunctions in the automatic sampler. Routine operation was restored on March 29, 2007 at a flow rate of 7.5 L/hr (12 hour detention time).

Sampling and analysis

Weekly, unfiltered samples were collected manually from the influent and effluent of each bioreactor from July 18, 2006 (week 1) through November 21, 2006 (week 19), except for weeks when the system was down. Whenever operations were re-started following equipment failures, the reactors were run for at least three days before samples were collected. Filtered samples were collected in addition to unfiltered samples on September 19, 2006 (week 10) and November 21, 2006 (week 19). Samples for Se speciation were collected on December 27, 2006 by using a small propane heater to thaw enough of the bioreactor to obtain effluent samples. Samples of

influent, reactor 1 effluent, and reactor 2 effluent were collected on March 30, 2007 in order to compare the results of analysis both with and without sample digestion.

Unfiltered influent and effluent samples were analyzed immediately in the field for temperature, pH, and conductivity using an Oakton pH/CON 10 meter. Dissolved oxygen and oxidation-reduction potential were analyzed immediately using a Hach HQ20 meter. Meters were calibrated and operated according to the manufacturer's instructions.

Analysis for Se and metals was performed by ACZ Laboratories, Inc. (Steamboat Springs, Colorado). Weekly, unfiltered samples were analyzed for total Se using EPA method 200.2 for digestion and method 200.8 for analysis by inductively-coupled plasma (ICP) mass spectroscopy. Duplicate samples for Se analysis were collected on August 8 (reactor 1), September 6 (reactor 3), and October 11 (reactor 1). Once per month, unfiltered samples were digested using method 200.2 and analyzed by ICP-optical emission spectroscopy for total Ca, Fe, and Mn using method 200.7. Unfiltered and filtered sample pairs collected on September 19, 2006 and November 21, 2006 for were analyzed for dissolved Se (no digestion, method 200.8 for analysis by ICP-mass spectroscopy). Samples of influent, reactor 1 effluent, and reactor 2 effluent collected on December 27 were processed using EPA method 3030B then analyzed by atomic absorption-hydride generation for dissolved Se, Se(VI), Se(IV), and organic Se. Samples of influent, reactor 1 effluent, and reactor 2 effluent collected on March 31, 2007 were split, with one portion analyzed directly by method 200.8 without digestion, and the other portion analyzed by method 200.8 following digestion by method 200.2. All samples collected between July 8, 2006 and November 21, 2006 were analyzed for sulfate by ion chromatography at Mesa State College.

Results

Selenium

Selenium (Se) concentrations in bioreactor influent and effluent are shown in Table 2 along with Se removal efficiencies. Reactor 4 had the highest initial Se removal efficiency; reactor 1 had the lowest initial efficiency. During weeks 4 through 10 of operation, there was no significant difference in Se removal efficiency between the four bioreactors, with each bioreactor averaging either 95% or 96% removal. During this time period, the detention time was 12 hours and average daily temperature varied from 24°C to 11°C. Detention time was shortened to 9.4 hours in week 11. Samples taken in weeks 13 and 14 showed a significant decrease in performance in reactors 2, 3, and 4, with removal efficiencies falling to values between 55% and 85%. The removal efficiency of reactor 1 remained high, with values of 94% and 98%. Average daily temperatures decreased during this period from 11 C to a low of 7.8 °C. Although the longer detention time of 12 hours was restored in week 19, removal efficiencies remained low except in reactor 1. The average daily temperature associated with the week 19 sampling event was only 5.2 °C.

Filtered and unfiltered sample pairs were collected in weeks 10 and 19 (Table 3) in order to determine the proportion of Se in the dissolved form. In general, the dissolved analyte concentration determined from the filtered sample should be less than or equal to the total analyte concentration determined from the unfiltered sample. In week 10, this expectation was met only for effluent from reactors 3 and 4, which showed 100% and 95% of Se in the dissolved form, respectively. In week 19, this expectation was met for the influent as well as the effluent

from reactors 2 and 3, with 98%, 93%, and 86% of Se in the dissolved form, respectively. Contrary to expectations, dissolved Se was greater than total Se for influent, reactor 1 effluent, and reactor 2 effluent in week 10, as well as for reactor 1 effluent in week 19.

Table 2. Bioreactor Performance.

Week and Date	Detention Time (hr)	Temperature[1] (°C)	Selenium Concentration (µg/L) and Removal Efficiency[2] Influent	Reactor 1	Reactor 2	Reactor 3	Reactor 4
1 07/18/2006	12	29.6	20.6	9.6 53%	6.1 70%	5.8 72%	0.7 97%
2 07/25/2006	12	30.6	19.4	2.7 86%	1.5 92%	1.4 93%	0.9 95%
3 08/01/2006	12	25.9	27.7	7.9 71%	0.9 97%	0.9 97%	0.8 97%
4 08/08/2006	12	24.4	20.9	1.7, 1.6 92%	1.0 95%	1.3 94%	1.1 95%
5 08/16/2006	12	23.9	24.1	1.4 94%	0.9 96%	1.5 94%	0.8 97%
6 08/24/2006	12	25.6	25.0	0.9 96%	0.9 96%	0.7 97%	0.4 98%
8 09/06/2006	12	22.6	27.2	0.8 97%	0.7 97%	0.7, 0.7 97%	1.2 96%
9 09/13/2006	12	20.6	23.2	0.8 97%	0.7 97%	0.7 97%	1.3 94%
10 09/19/2006	12	11.3	24.8	0.9 96%	0.9 96%	0.6 98%	2 92%
13 10/11/2006	9.4	11.5	42.5	0.8, 0.7 98%	8.4 80%	9.5 78%	6.2 85%
14 10/18/2006	9.4	7.8	68.6	4.0 94%	26.1 62%	30.6 55%	12.7 81%
19 11/21/2006	12	5.2	29.4	0.7 98%	11.2 62%	14.1 52%	-- --

[1]The temperature reported here is the average of the daily high and low temperatures for a 3-day period starting 2 days before the sampling event and ending with the day of the sampling event.
[2]Removal efficiency is calculated as [(influent Se – effluent Se)/(influent Se)]100%.

Table 3. Comparison of Total and Dissolved Selenium in Bioreactor Influent and Effluent.

Week and Date	Detention Time (hr)	Temperature (°C)	Selenium Concentration (µg/L)				
			Influent	Reactor 1	Reactor 2	Reactor 3	Reactor 4
10	12	11.3	24.8 total	0.9 total	0.9 total	0.6 total	2.0 total
9/19/2006			25.3 diss.	30.7 diss.	4.4 diss.	0.6 diss.	1.9 diss.
19	12	5.2	29.4 total	0.7 total	11.2 total	14.1 total	-
11/21/2006			28.7 diss.	3.6 diss.	10.4 diss.	12.1 diss.	-

Samples analyzed for *total* Se are acidified in the field, then digested and analyzed in the laboratory, while samples analyzed for *dissolved* Se are filtered then acidified in the field, and analyzed without digestion. Given that there is no digestion step in the procedure for dissolved Se, we hypothesized that a portion of the Se in the anomalous samples may be occurring in a volatile form that is driven off during digestion, resulting in a *lower* concentration for a digested sample (total Se) relative to the companion undigested sample (dissolved Se). We tested this hypothesis by having the laboratory analyze the same, unfiltered samples both with and without digestion. The results in Table 4 show that the digested samples have Se concentrations that are *higher* than in the undigested samples, thus disproving our hypothesis. At this time we have no explanation for the anomalous results in Table 3, but expect to pursue this problem in a future investigation.

The variation in toxicity among the different forms of Se (Amweg et al, 2003) provided motivation for determining the speciation of Se in bioreactor effluent. From a toxicity standpoint, the most desirable form of Se in the reactor effluent is Se(0). If the effluent Se has a greater proportion of Se(IV) or organic-Se than the influent Se, there is a possibility that the effluent will be more toxic than the influent even if the total Se is less. Samples collected on December 27, 2006 were analyzed for Se(VI), Se(IV), and organic-Se. The influent had 28 µg/L of dissolved Se, of which 57% was Se(VI), 14% Se(IV), and 29% organic-Se. Unfortunately, all forms of Se in the effluent samples were less than the practical quantization limit or the method detection limit, and results were inconclusive. Speciation will be re-attempted in future work.

Table 4. Comparison of Selenium in Split Samples, Analyzed With and Without Sample Digestion.

Sample Preparation	Selenium Concentration (µg/L)			
	Influent	Reactor 1	Reactor 2	Reactor 3
Without digestion	21.9	2.8	3.5	6.5
With digestion	25.1	4.1	3.8	7.0

Other parameters

Results of dissolved oxygen (DO) measurements are shown in Table 5. DO in the influent ranged from 7.0 mg/L to 10.4 mg/L over the period of operation. DO in the bioreactor effluents ranged from 0.1 to 1.7 mg/L, with 91% of the measured values less than 1.0 mg/L. These results support our expectation that aerobic microbial respiration is consuming DO in the reactors.

The oxidation-reduction potential (ORP) was monitored to confirm that reducing conditions occurred within the bioreactors (Table 5). The ORPs of the effluents ranged from -393 mV to -79 mV, with 93% of these values being more negative than -200 mV. The ORP of the influent ranged from -185 mV to +143 mV. On every date the effluent ORPs were more negative than the influent ORPs, as expected.

Table 5. Dissolved Oxygen and Oxidation-Reduction Potentials for Influent and Effluent

Week and Date	Detention Time (hr)	Temperature[1] (°C)	DO concentration (mg/L) and ORP (mV) Influent	Reactor 1	Reactor 2	Reactor 3	Reactor 4
2 07/25/2006	12	30.6	NM -50.1	NM -356.3	NM -195.9	NM -213.9	NM -253.1
3 08/01/2006	12	25.9	NM -102.0	NM -366.1	NM -243.1	NM -270.1	NM -291.8
4 08/08/2006	12	24.4	10.1 -21.7	0.2 -379.6	0.1 -315.8	0.1 -310.8	0.6 -289.7
5 08/16/2006	12	23.9	9.3 -185.1	0.4 -371.2	0.4 -292.6	0.2 -307.6	0.2 -289.6
6 08/24/2006	12	25.6	8.3 -154.8	0.1 -393.1	0.2 -311.3	0.2 -315.9	0.7 -277.7
8 09/06/2006	12	22.6	10.4 -152.1	0.1 -373.7	0.3 -296.8	0.8 -288.6	0.9 -272.9
9 09/13/2006	12	20.6	8.6 -150.0	0.1 -386.2	0.5 -295.6	0.6 -287.2	1.0 -289.5
10 09/19/2006	12	11.3	7.7 79.5	1.0 -350.8	0.7 -320.0	0.9 -316.7	0.8 -280.4
13 10/11/2006	9.4	11.5	9.6 6.1	0.7 -264.6	0.5 -254.0	0.5 -280.7	0.9 -216.6
14 10/18/2006	9.4	7.8	7.9 143	1.7 -78.8	0.8 -197.5	0.8 -228.1	0.7 -238.2
19 11/21/2006	12	5.2	7.0 -75	0.5 -226.0	0.2 -251.0	0.1 -272.0	-- --

[1]The temperature reported here is the average of the daily high and low temperatures for a 3-day period starting 2 days before the sampling event and ending with the day of the sampling event.

With one exception, the pH of the influent ranged from 7.61 to 8.17 (Table 6). The pH of effluent from reactor 1 ranged from 6.53 to 7.22 from weeks 1 through 10, and then ranged from 7.39 to 7.69 during weeks 13 through 19. The pH of effluent from reactor 2 ranged from 6.64 to 7.20 from weeks 1 through 3, and then ranged from 7.52 to 8.12 from during weeks 4 through 19. The pH of effluent from reactor 3 ranged from 6.73 to 7.24 in weeks 1 and 3, but ranged from 7.66 to 8.21 in week 2 and during weeks 4 through 19. The pH of effluent from reactor 4

was generally more basic than that of the other reactors, ranging from 7.78 to 8.79 from weeks 2 through 19.

The conductivity of the influent ranged from 3.4 mS/cm to 5.8 mS/cm (Table 6). During weeks 2 through 4, the conductivities of the effluent of all bioreactors were between 5.26 mS/cm and 5.93 mS/cm, which were greater than influent conductivity, which ranged from 3.46 mS/cm to 3.69 mS/cm in that period. Thereafter, the effluent conductivities were generally much more similar to the influent conductivities, ranging from 0.94 mS/cm below the influent conductivity to 0.34 mS/cm above.

In weeks 2 through 4, the sulfate concentrations in the influent ranged from 1,132 mg/L to 1,239 mg/L (Table 6). During that same period, sulfate concentrations in effluent from reactors 1 through 4 were greater, ranging from 1,356 mg/L to 2,293 mg/L, with reactor 4 effluent always showing the highest concentration. Thereafter, the sulfate concentrations in the effluents were always less than the influent sulfate concentration, which ranged from 1,105 mg/L to 1,980 mg/L.

Calcium and Fe concentrations were measured in order to monitor the depletion of bioreactor components (Table 7). The concentration of calcium in the influent ranged from 180 mg/L to 207 mg/L from July through September. With the exception of reactor 1, effluent Ca concentrations were always less than influent concentrations. The effluent from reactor 1 showed Ca concentrations ranging from roughly equal to influent to 30% higher than influent. Influent Fe concentrations ranged from 0.19 mg/L to 0.43 mg/L. Effluent concentrations in reactors 2, 3, and 4 were all much higher, ranging from 4.5 mg/L to 96 mg/L, 8.6 mg/L to 116 mg/L, and 5.4 mg/L to 13.5 mg/L, respectively. Two of the three iron concentrations measured in reactor 1 effluent were lower than the influent concentrations. Manganese was monitored to determine if this element was being leached from the bioreactor bed materials. In July, all four bioreactor effluents were greater in Mn (0.61 mg/L to 1.7 mg/L) than the influent (0.31 mg/L). Subsequently all four effluent manganese concentrations were less than the influent concentrations.

Table 6. Sulfate Concentration, Conductivity, and pH for Influent and Effluent

Week and Date	Detention Time (hr)	Temperature[1] (°C)	Sulfate Concentration (mg/L), Conductivity (mS/cm) and pH				
			Influent	Reactor 1	Reactor 2	Reactor 3	Reactor 4
1	12	29.6	1116	1042	1024	1008	1145
07/18/2006			0.90	0.98	0.81	1.12	1.86
			7.70	6.57	6.64	6.73	7.15
2	12	30.6	1132	1806	1626	1356	2180
07/25/2006			3.50	5.93	5.70	5.55	5.33
			8.90	7.06	6.97	7.82	8.26
3	12	25.9	1239	2011	1861	1910	2200
08/01/2006			3.69	5.68	5.46	5.47	5.26
			7.83	6.56	7.20	7.24	8.02
4	12	24.4	1162	1674	1779	2012	2293
08/08/2006			3.46	5.77	5.56	5.68	5.52
			7.99	6.62	7.93	7.77	8.43
5	12	23.9	1105	596	940	968	1063
08/16/2006			3.43	3.75	3.36	3.39	3.14
			8.17	6.53	7.90	7.79	8.58
6	12	25.6	1218	873	912	972	1098
08/24/2006			4.05	4.10	3.78	3.88	3.62
			7.82	6.86	8.09	7.90	8.79
8	12	22.6	1407	1193	1073	1094	1164
09/06/2006			4.26	4.26	3.94	4.02	3.77
			7.89	6.93	7.99	7.92	8.56
9	12	20.6	1208	1050	1036	1069	1104
09/13/2006			4.23	4.31	4.05	4.08	3.88
			7.69	7.05	7.99	7.99	8.54
10	12	11.3	1295	1185	1134	1211	1253
09/19/2006			4.39	4.34	4.10	4.08	3.92
			7.87	7.22	8.00	8.21	8.29
13	9.4	11.5	1607	1228	1247	1230	1225
10/11/2006			5.12	4.50	4.24	4.29	4.18
			7.61	7.39	7.72	7.94	8.26
14	9.4	7.8	1980	1830	1681	1607	1598
10/18/2006			5.76	5.56	5.26	5.32	5.06
			7.62	7.54	7.52	7.66	7.78
19	12	5.2	--	--	--	--	--
11/21/2006			4.21	4.14	4.09	4.05	--
			7.68	7.69	8.12	8.15	

Table 7. Calcium, Iron, and Manganese Concentration for Influent and Effluent

Week and Date	Detention Time (hr)	Temperature (°C)	- - - - Calcium (mg/L), Iron (mg/L), and Manganese (mg/L) - - - Influent	Reactor 1	Reactor 2	Reactor 3	Reactor 4
1	12	29.6	180	234	156	161	148
7/18/06			0.43	1.54	95.8	115	13.5
			0.312	0.606	1.120	0.970	1.720
6	12	25.6	183	185	131	143	85.7
8/24/06			0.19	0.09	4.47	9.19	5.39
			0.407	0.195	0.258	0.233	0.271
10	12	11.3	207	206	153	172	107
9/19/06			0.25	0.08	10.1	8.56	0.255
			0.446	0.039	0.221	0.255	0.247

Discussion

During weeks 4 through 10, all four bioreactors achieved selenium removals of at least 92%. These results demonstrate that for a detention time of 12 hours and average daily temperatures between 11 °C and 26 °C, passive bioreactors of the compositions tested here are effective at removing selenium from ground water in the Grand Valley. The reactor with 0% ZVI maintained this high removal efficiency at temperatures down to 5 °C.

The first two sampling events showed a difference in removal efficiencies between the reactors, with reactor 1 having the lowest and reactor 4 having the highest. This suggests that initially the ZVI was responsible for most of the Se removal. The removal efficiencies of the bioreactors increased as the proportion of ZVI in the reactors increased. By the fourth sampling event, all bioreactors achieved a Se removal efficiency of 95% to 96%, suggesting that microorganism populations were well developed and that Se removal through reduction by ZVI was not providing a significant enhancement to removal by microbial processes.

Average daily temperature appeared to have no effect on the efficiency of the reactors through week 10. During this period, while the detention time was 12 hr and average daily temperature decreased from 31°C to 11°C, all four reactors maintained over 90% removal efficiency. Detention time was shortened to 9.4 hr in week 11. Shortly thereafter, the temperature dropped from 11°C to 8°C and influent Se concentration increased from 24.8 mg/L to 68.6 mg/L. These uncontrollable, simultaneous changes in two other factors affecting performance made it impossible to assess the effect of decreased detention time alone. Under these new conditions, the performance of reactors 2, 3, and 4 decreased significantly. Reactor 1 was the only reactor to maintain a removal efficiency over 90%. The detention time was returned to 12 hr prior to the last sampling event in week 19. The influent concentration (29.4 mg/L) simultaneously returned to roughly its value during the original period of high removal efficiency, while the temperature dropped further to 5°C. Removal efficiencies of reactors 2 and 3 remained low (62% and 52% respectively), while the efficiency of reactor 1 remained high (98%). It is surprising that reactor 1 continued to perform so well at the lower temperature even though reactors 2 and 3 performed poorly.

DO and ORP measurements confirm that aerobic microbial respiration is taking place and that conditions within the reactors are reducing. Conductivity and sulfate results support the expectation that during the initial period of operation, salts were leached from the reactor materials. Calcium concentrations that are lower in effluent than influent for reactors 2, 3, and 4 indicate that dissolved Ca is being precipitated as $CaCO_3$ within these reactors. In contrast, Ca results for reactor 1 suggest that Ca from the agricultural limestone is being lost initially, but is unaffected subsequently. As expected, Fe results show that soluble Fe (II) was being removed from the reactors by oxidation of the ZVI in reactors 2, 3, and 4. In two out of the three effluent samples from reactor 1 that were analyzed for Fe, the Fe in the effluent was much less than the Fe in the influent. This result is consistent with the absence of ZVI in this reactor, and suggests that Fe in the influent may be reduced to an insoluble form and retained within the reactor.

Conclusion

The results of this study demonstrate that passive bioreactors can accomplish up to 98% removal of Se from surface and ground waters in the Grand Valley of western Colorado. A bioreactor designed to promote microbial processes functioned as efficiently as reactors incorporating ZVI, in spite of the potential of the ZVI to enhance the biological removal process. The highest removal rates were achieved using a detention time of 12 hours, but circumstances prevented optimization of detention time. Selenium speciation and the effects of detention time, influent concentration, and ambient temperature will be explored more fully in future work.

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