THREE-YEAR PILOT CASE STUDY OF BIOCHEMICAL REACTOR TREATMENT OF SELENIUM[1]

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Abstract: A pilot biochemical reactor (BCR) for Se treatment has been operating at a coal mine since 2008. The BCR is an anaerobic reactor comprised of organic and inorganic substrate including woodchips, straw, and limestone. The BCR is considered a passive treatment because it does not require continuous chemical inputs or electricity. Selenium is removed in the BCR by biological reduction of oxidized Se species (i.e., selenite, selenate) to insoluble elemental Se. The pilot influent water contained an average of 195 ug/L of Se.

Average influent dissolved oxygen (DO) and nitrate (as N) concentrations were 9.2 mg/L and 36 mg/L, respectively. The maximum removal rate for total selenium was 93%. The average Se and NO_3 removal rates were 17 $mg/d/m^3$ and 5 $g/d/m^3$, respectively. The decomposition of organic matter in the BCR provides simple carbon molecules that can serve as an electron donor in the anaerobic reduction; however this process is not constant over time. In the pilot test, effluent nutrient concentrations decreased with time but remained sufficiently high to support Se reduction after three years. The Se removal rate did decrease over time indicating that decreasing nutrients in the BCR may be responsible for the decreasing Se removal rates.

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Introduction

Selenium in surface and groundwater has generated concern since at least 1982, when Se was found responsible for mortality of fish and birds inhabiting the Kesterson National Wildlife Refuge in California (National Research Council, 1989). 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. 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 (SeO_4^{2-}) and selenite (SeO_3^{2-}) to insoluble elemental Se.

Passive anaerobic biological treatment systems, (also known as biochemical reactors, vertical flow ponds, or sulfate-reducing bioreactors), require neither continuous nutrient feeds nor electricity. Biochemical reactor (BCR) media is a mixture of limestone and several solid organic materials such as wood chips, sawdust, and hay. In a BCR, a diverse microbial community including cellulose degraders and fermenters is necessary to transform solid organic materials to short chain organic compounds that can be used as electron donors for Se reduction (Pruden et al., 2006). The BCR technology has been developed over the past two decades for treatment of acidity and metals in mining-influenced water. Bench, pilot and demonstration-scale testing of BCR technology for selenium treatment in recent years has demonstrated effective rates of selenium removal (Pahler et al. 2007, Blumenstein et al. 2008, Rutkowski et al. 2010).

To evaluate the performance of a BCR with regard to Se removal, a pilot BCR study was conducted at a coal mine in Canada. The study was performed at a site that is characterized by multiple high flow and high Se concentration discharges. The treatment goal was to reduce Se loading in the site discharge waters, even through the site does not have a Se discharge limit. Goals for the BCR testing were to determine the breakthrough point and maximum removal rate for Se in order to treat as much water as possible.

Pilot Testing

A pilot BCR was constructed and began treating water on November 1, 2008. The pilot BCR is a top to bottom flow reactor with a media volume of 253 m^3. The pilot system included influent and effluent structures designed to capture and control flow through the pilot BCR. A geomembrane cover was constructed over the pilot BCR for insulation and to keep rainfall from entering the system. The BCR media is limestone-buffered organic substrate mixture consisting of (by weight): 55% wood chips, 20% sawdust, 10% limestone fines, 10% silage, 4.5% Dried Distiller's Grain with Solubles (DDGS) and 0.5% cow manure. The organic substrate serves as the inoculum. A BCR construction photo is provided in Fig. 1. Golder Associates Inc. (2011) has been conducting an evaluation of the pilot treatment system since its construction. This paper provides a summary of the pilot results over the past 3 years.

Figure 1. Organic media being placed in a lined cell during construction of the pilot BCR.

Pilot Results

A total of 50 sampling events were conducted between the end of 2008 and December 20, 2011 (12/20/2011). The discussion of pilot results is divided into field parameters and laboratory results which are discussed below.

Field Parameters

Field parameters were obtained during the analytical sampling events. Flow rate was measured with bucket and stopwatch, and other field parameters were measured with portable meters.

Flow Rate and Detention Times Flow rate and Hydraulic Retention Time (HRT) values, which are inversely related, are shown on Fig. 2. The HRT shown was calculated using the total void space in the organic substrate. Flow measurements taken between August 2010 and April 2011 are not provided due to improper valve adjustment during this time. The improper valve adjustment made it impossible to determine the actual flow and resulted in higher than expected flows through the BCR. Overloading of the BCR cell likely caused the poor performance of the BCR from October 2010 through April 2011. This is referred to as the overloading period.

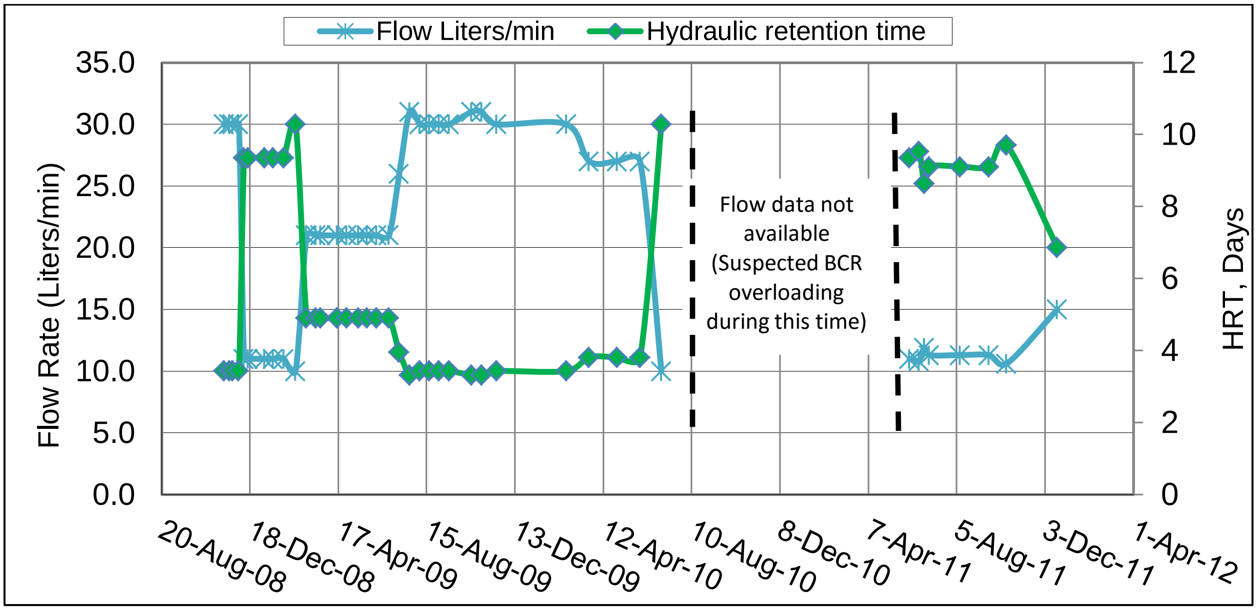

Figure 2. Flow rate and HRT for the BCR.

<u>Oxidation Reduction Potential (ORP)</u> Selenium reduction can occur at ORP values between -50 and -200 millivolts (mv). BCR influent and effluent ORP values are provided in Fig. 3. The influent ORP values for the test period averaged 78 mv; effluent measurements for the same period ranged from 35 mv to -304 mv with an average of -147 mv. After the first few weeks of startup, the effluent ORP values were consistently in the range conducive to Se reduction.

<u>Dissolved Oxygen (DO)</u> Influent DO for the test period ranged from 4.5 to 14.1 mg/L with an average of 9.2 mg/L. Effluent DO ranged from 0.0 mg/L to 4.1 mg/L with an average of 0.8 mg/L. The consistently low effluent DO values are consistent with the low ORP values and indicate that the effluent was consistently anoxic. DO values are shown in Fig. 4.

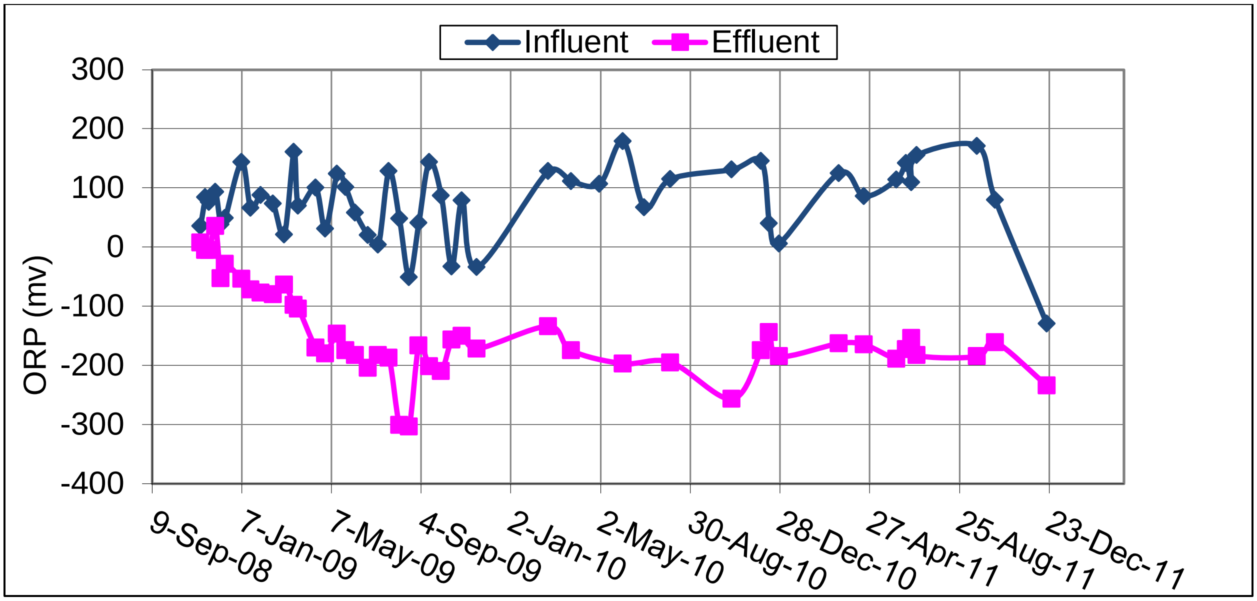

Figure 3. BCR Influent and Effluent ORP Values.

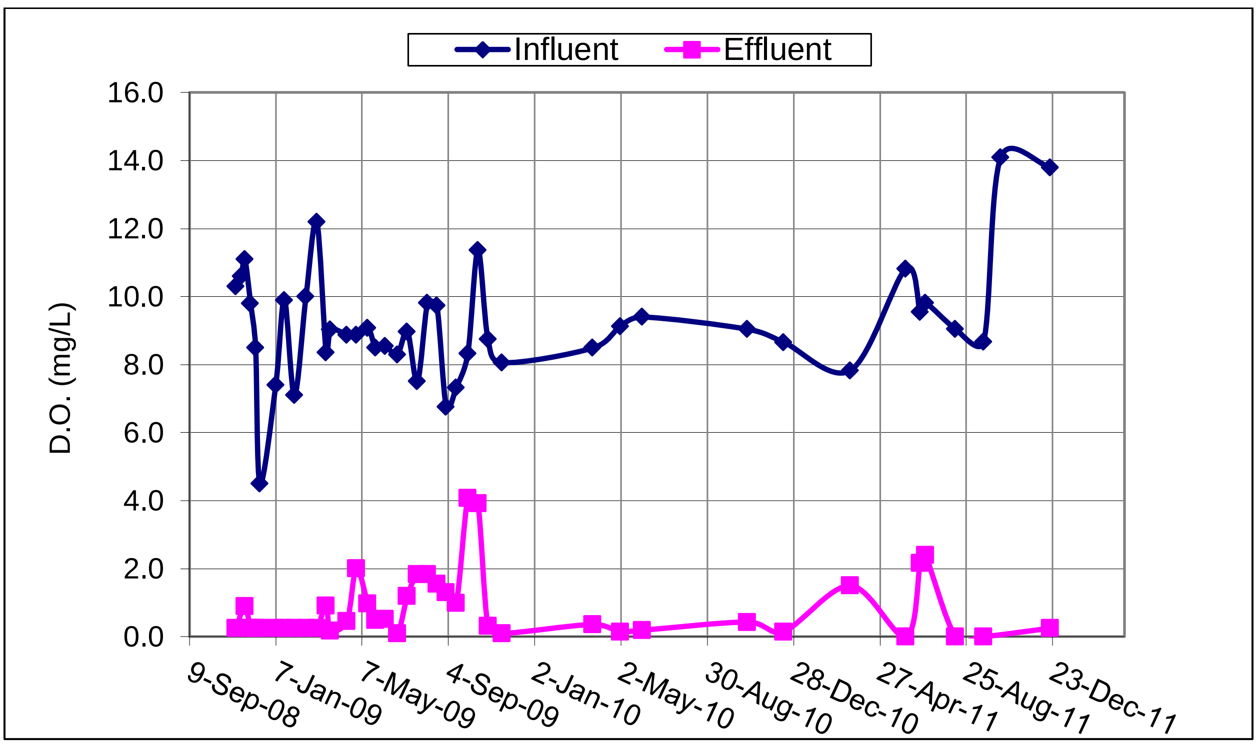

Figure 4. BCR Influent and Effluent DO Concentrations.

<u>Temperature</u> Influent field temperature ranged from 0.7 to 8.3 degrees Celsius (^{o}C) with an average of 3.8 ^{o}C (Fig. 5). Effluent field temperature ranged from 0.7 to 13.6 ^{o}C with an average of 3.5 ^{o}C.

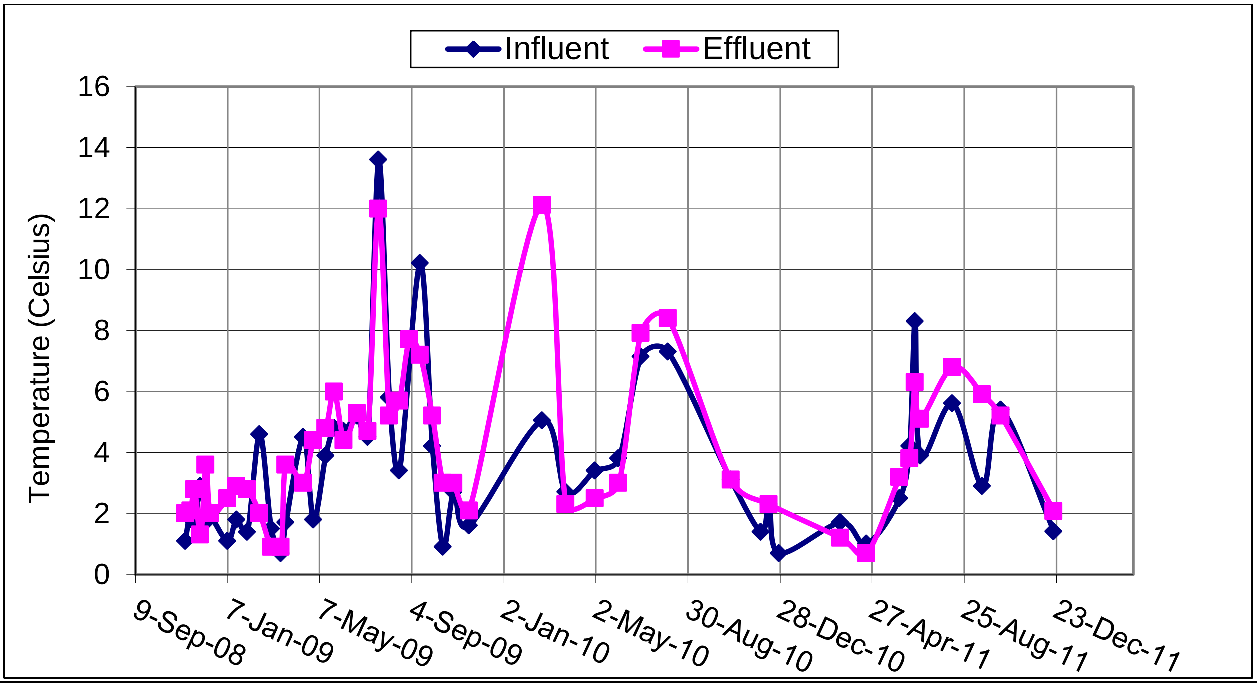

Figure 5. BCR Influent and Effluent Temperatures

Laboratory Results

Total Selenium Total Se analysis was performed by both ICP-MS (Method reference SW 846-6020 ICPMS) (EPA 2007) and hydride analysis (Method reference APHA 3114C) (Eaton 2005). Influent total Se concentrations varied from 0.120 to 0.292 mg/L with an average of 0.195 mg/L. Effluent concentrations ranged from 0.014 to 0.167 mg/L with an average of 0.083 mg/L. The percent removal for total Se ranged from 13 to 93%, with BCR overloading being suspected for lower removal rates. Total Se data are provided in Fig. 6.

Selenium Speciation Influent and effluent samples collected on 2/21/2010 were analyzed for selenate and selenite (Table 1). Selenate was the dominant species at all locations and the BCR effluent selenite concentration was below the detection limit (0.5 µg/L). The results indicate that the BCR is not increasing selenite concentrations, which is a potential concern as selenite is considered more toxic to aquatic life than selenate (Jose 2011).

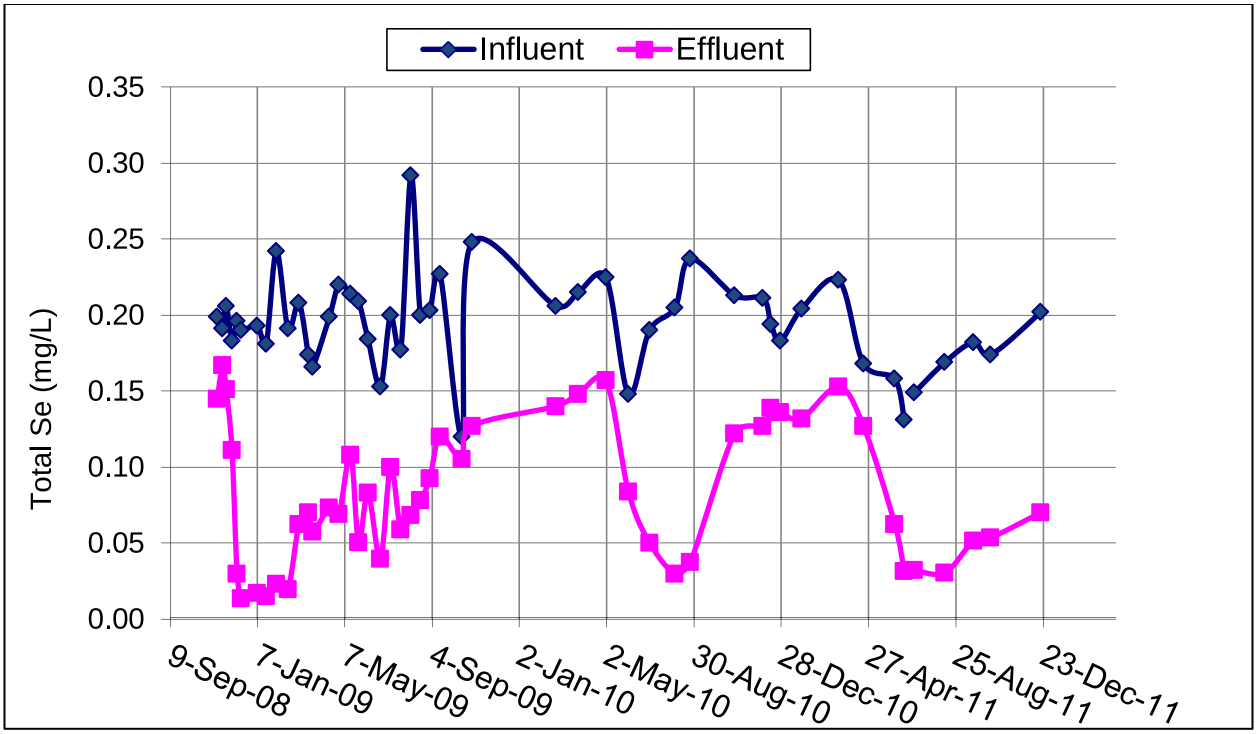

Figure 6. BCR Influent and Effluent Total Selenium Concentrations

Table 1: BCR Influent and Effluent Selenium Speciation Results From the 2/21/2010 Sampling Event.

Sample Location	Selenate (µg/L)	Selenite (µg/L)
BCR Influent	183	0.72
BCR Effluent	127	<0.5

Nitrate Influent nitrate-N (NO_3-N) values ranged from 7.2 to 108 mg/L with an average of 36 mg/L. Effluent nitrate-N values ranged from below the laboratory detection limit (0.05 mg/L) to 28 mg/L with an average of 5.7 mg/L. Nitrate removal was low during suspected BCR overloading, but increased during later sampling events after flow rate issues were resolved. This is consistent with the increasing Se reduction during this time. Data for influent and effluent nitrate values are shown in Fig. 7.

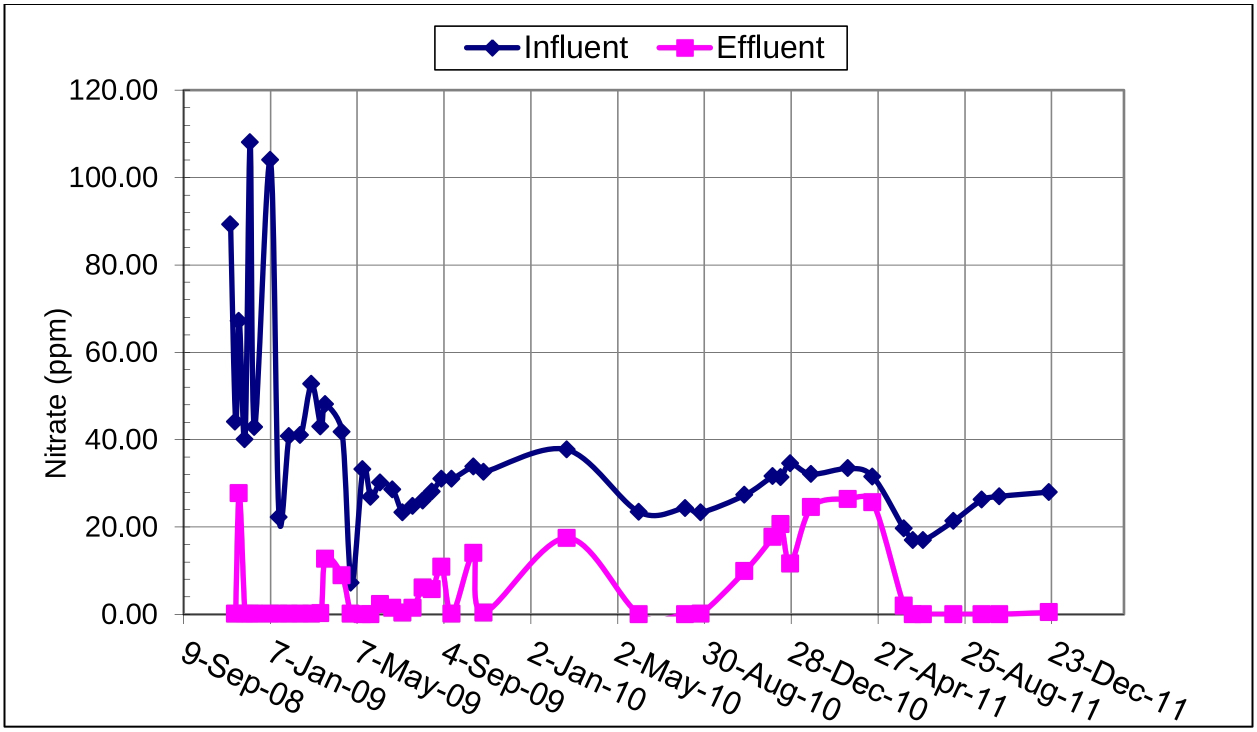

Figure 7. BCR Influent and Effluent Nitrate Concentrations

Residual Nutrients Effluent total organic carbon (TOC) concentrations were elevated during startup and decreased substantially in the latter half of 2009 as shown in Fig. 8. This nutrient decrease is consistent with other BCR systems (Blumenstein and Gusek, 2010). In a BCR, a diverse microbial community including cellulose degraders and fermenters is necessary to transform solid organic materials to short chain organic compounds that can be used as electron donors for Se reduction (Pruden et al., 2006). The initial flush of organic material during the maturation period is due to easily degradable organics, such as manure, being flushed from the cell. Once the initial flush is complete, BCRs should continue to generate organic carbon on a lower, but consistent, basis during steady-state conditions. Steady-state is defined by consistent Se mass removal rates (i.e., mg/d/m^3). During the overloading period, TOC effluent concentrations decreased to the detection limit of 4 mg/L. After the pilot flow rate was adjusted in June 2011, TOC concentrations increased. Nitrogen and P effluent concentrations have also increased, although not as substantially as TOC. A typical target ratio of TOC to N (i.e., total kjeldahl nitrogen) to P for biological treatment is 100 TOC:10 N:1 P (Flathman, et.al., 1994). In 2010, the nutrient ratio was limited by TOC and N and P were not limiting.

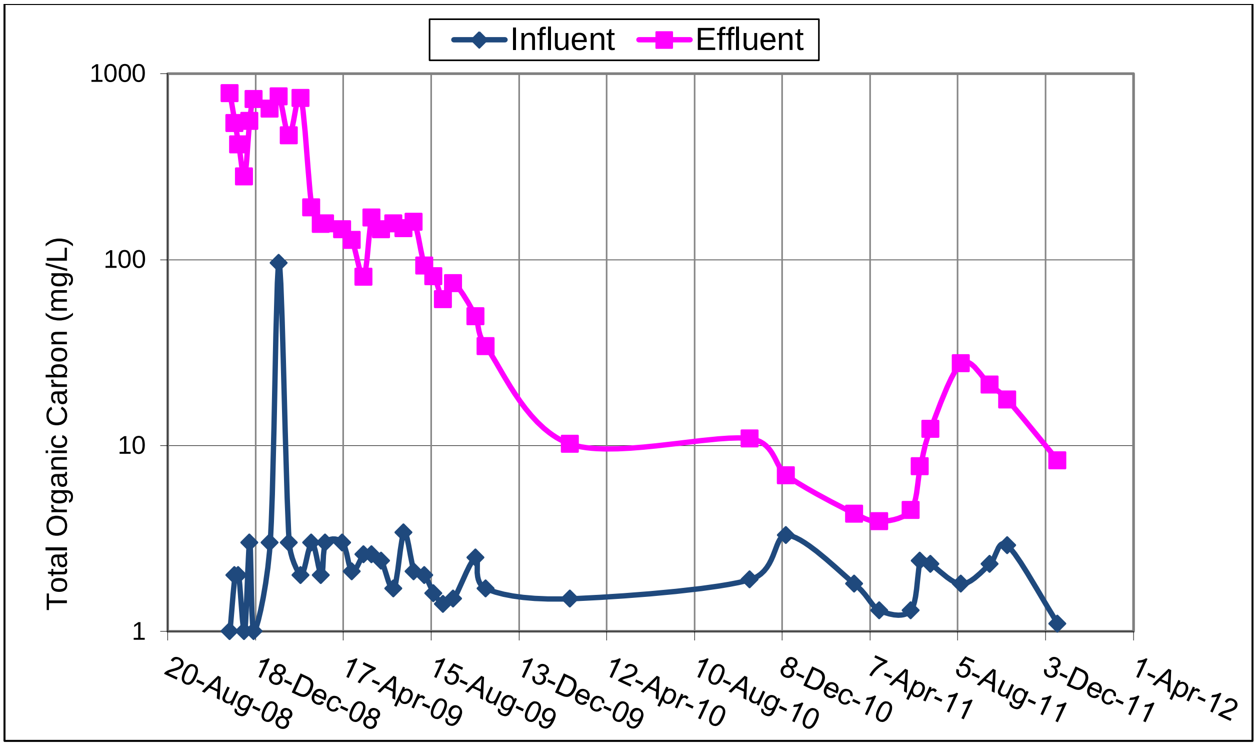

Figure 8. BCR Influent and Effluent Total Organic Carbon Concentrations

Discussion

Mass loading and removal rates (mass per day per cubic meter of substrate,) were calculated for NO_3 and Se for sampling events which included flow measurements. Selenium and NO_3 removal rates are shown in Fig. 9 and 10, respectively. Data from sampling events conducted during the overloading period (October 2010 to April 2011) were excluded due to uncertain flow rates. The diagonal line on each figure represents complete parameter removal.

Typically, loading curves are produced by increasing loading until breakthrough is observed. Breakthrough occurs when additional treatment is not observed although the load is increased. The 2009 Se breakthrough occurred at about 25 mg/d/m3; the 2010 and 2011 Se breakthroughs occurred at about 14 mg/d/m3 (Fig. 9). The pilot Se removal rates were less than the 73 mg/d/m^3 (Rutkowski et al., 2010) observed during another pilot study; the difference is likely due to lower influent nitrate concentrations in the other study. The decrease in the breakthrough level is expected based on the decrease in residual nutrients as discussed in the Residual Nutrients Section. In addition to being a function of media flushing or BCR age, TOC generation has been shown to be a function of HRT. A longer HRT affords the microbial population more opportunity to degrade solid organic matter into TOC. Pilot monitoring should continue for flow and residual nutrients to further understand the relationship between BCR age, HRT, and TOC generation as well as the steady-state Se removal rate. The steady-state removal rate can then be utilized as a design criterion for larger systems. Although TOC generation decreased substantially from 2009 to 2011, effluent TOC values were sufficient (albeit limiting) to maintain consistent anoxic (low DO), reducing (negative ORP) conditions in the effluent. Once the flow rate was adjusted in June 2011, the effluent TOC concentration increased and reached a maximum of 27 mg/L on 8/10/2011.

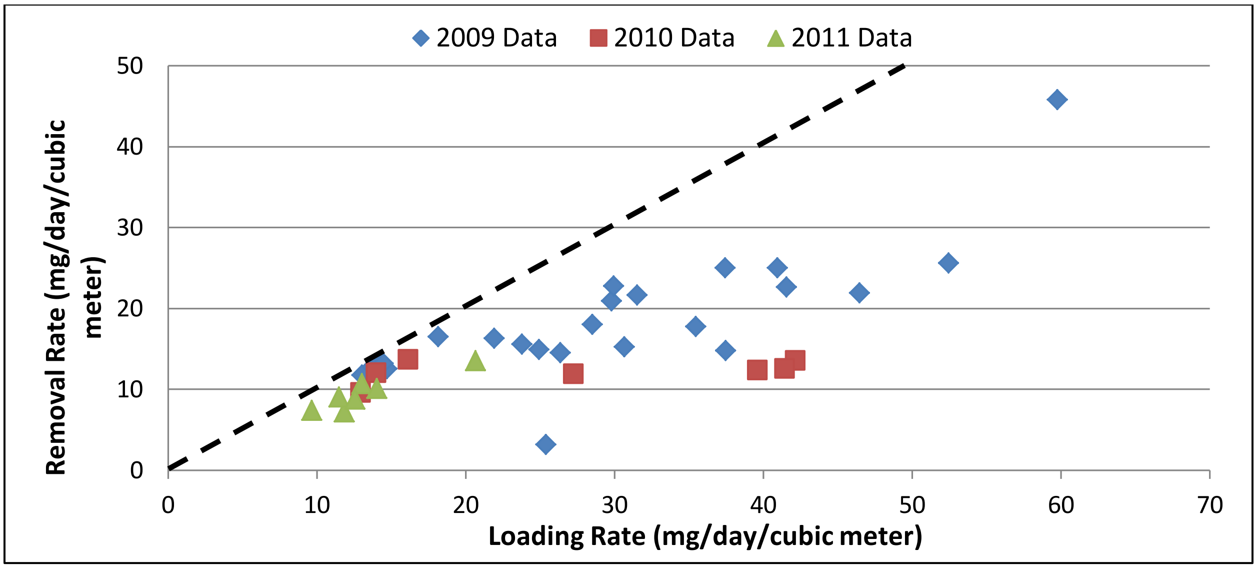

Figure 9. BCR Selenium Loading and Removal

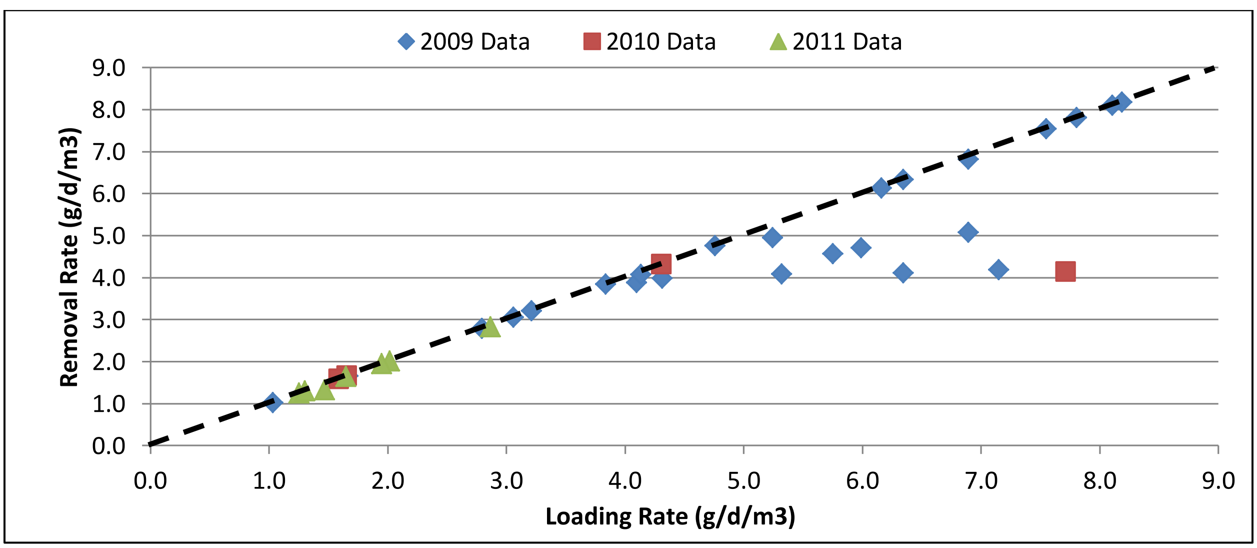

Figure 10. BCR Nitrate Loading and Removal

Nitrate is removed preferentially when compared with Se removal. Nitrate removal rates of 99% or greater were regularly achieved during the first two years of pilot operation and during the sampling events after the flow issues were resolved. The NO_3 loading graph (Fig. 10) exhibits high removal rates during the first year of operation with lower rates in the second and third years.

Conclusions

The 3-year pilot BCR test was successful in removing Se while characterizing a reduction in the performance with diminishing organic substrates. The maximum percent removal for total Se was 93% with a minimum effluent concentration of 14 µg/L. Nitrate removal to below detection was also generally achieved. Given that the goal of the pilot test was Se load reduction rather than achieving a Se discharge limit, the testing emphasis was on developing loading curves and removal rates. The average Se and nitrate-N removal rates were 17 mg/d/m^3 and 5 g/d/m^3, respectively. The Se removal rate did decrease from 25 mg/d/m^3 in the first year to about 14 mg/d/m^3 in both second and third years. The NO_3 removal rate also decreased. Continued evaluation of the pilot test will determine whether this removal rate is sustainable and a proper sizing criterion for full-scale systems. The performance decrease was due to a decrease in available nutrients once the initial flush occurred during the first six to eight months of operation.

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