Column Studies to Evaluate EVO for Nitrate Removal in Permeable Reactive Barriers on Cape Cod, MA

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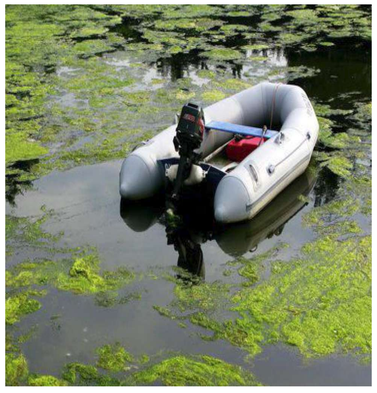
Abstract. Column studies are underway using soil and ground water from a Falmouth, MA site contaminated with nitrate from septic systems. The tests are designed to evaluate the effectiveness of biological nitrate reduction using two loadings of Terra Systems, Inc. emulsified oil product, SRS, and SRS-Z, a combination of SRS and zero-valent iron (ZVI). The emulsion no longer appeared in the effluent after 1.3 to 2.4 pore volumes in columns 1 and 2. Complete removal of nitrate-nitrogen was observed shortly after column start-up and continued to be observed for all columns over 317 days from SRS injection, equivalent to 83 to 93 column pore volumes. Sulfate was completely consumed until about 62 to 64 pore volumes. TOC levels in the effluent from the column reached as high as 3,900 mg/L as the emulsion was washed out of the columns for 3 pore volumes for columns 1 and 2 and about 11 pore volumes for column 3 with the SRS-Z. TOC levels have fallen to between 1.1 and 1.3 mg/L after day 340. The column studies have shown that EVO can be effectively applied to stimulate naturally occurring denitrifying bacteria in Cape Cod soil and groundwater and PRBs show promise for nitrate removal. Between 1,301 to 1,398 mg of nitrate-nitrogen have been consumed by the additions of 15,400 to 30,800 mg of EVO. Data generated from the column study will aid in the design of the next proposed step, a field PRB demonstration on Cape Cod.

Backgound. Septic systems, lawn fertilizer, and road runoff on Cape Cod have lead to widespread nitrate contamination of the groundwater. Large dilute plumes of nitrate move into estuaries causing eutrophication. Municipalities are looking for ways to address the nitrate plumes. Potential management actions include new and updated wastewater treatment facilities along with innovative and sustainable green infrastructure approaches. Permeable reactive barriers (PRB) are one potential solution.



Salt Water Pond Impacted By Eutrophication

Column Studies

Three 117 cm, 5 cm PVC columns were each packed with 5.2 kg sand from the Falmouth, MA site. The pore volumes were estimated to be 592 mL. Groundwater or tap water spiked with 20 mg/L Nitrate-N were pumped up through the columns at the representative groundwater flow rate of 0.37 m/day or about 0.13-0.19 mL/min. The residence times were about 2.2 to 3.2 days. Column 1 received 30.8 g SRS (Terra Systems, Inc. emulsified vegetable oil) diluted with 277 mL groundwater sufficient to fill the column to 53 cm. Column 2 received 61 g SRS diluted with 555 mL groundwater sufficient to fill the column to 69 cm. Column 3 received 61 g SRS, 24.6 Ferox Flow Zero Valent Iron and stabilizer, and chased with 513 mL groundwater sufficient to fill the column to 69 cm. Flow to columns was stopped for 1-2 days to allow the SRS to coat the soil. The columns and influent were sampled for the following:

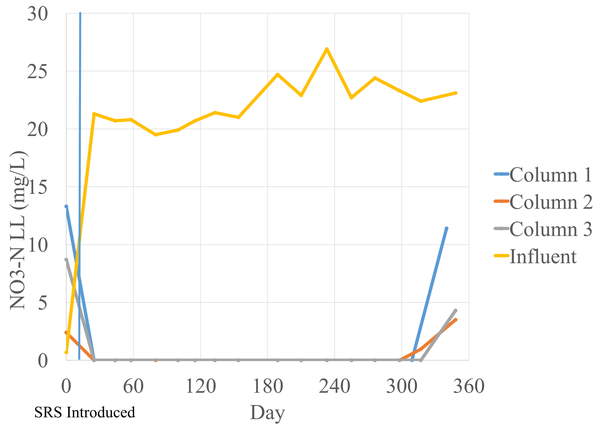
One to three times per week
- Flow
- pH
- Redox potential
- Dissolved oxygen
- Hach nitrate

About every three weeks
- Nitrate-N by Ion Chromatography
- Sulfate by Ion Chromatography
- Total Organic Carbon (TOC)

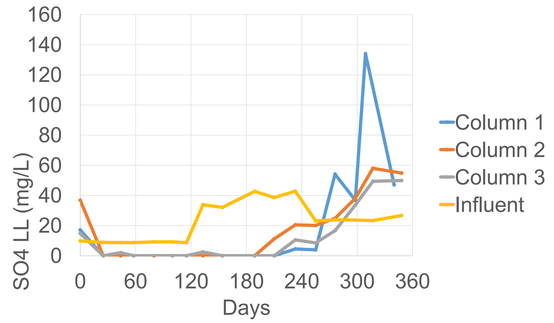
Column 1 Day 130 Showing Ferrous Sulfide Bands

Results

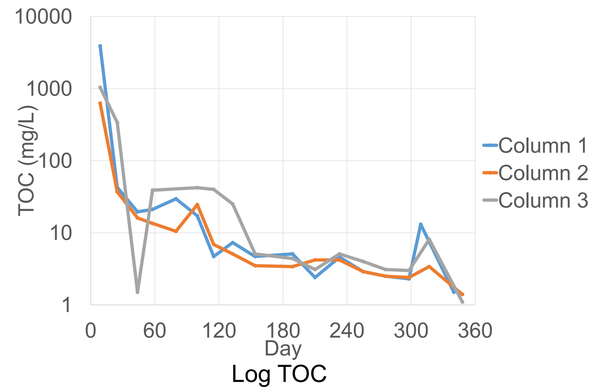
- Flow rates generally ranged from 0.09 to 0.19 mL/min
- pH became mildly acidic (<5.0) in column 3 for several weeks. Over the last 300 days, the pH has generally been above 7.0 with no discernible trend between the columns and influent.
- Redox potentials have almost always been positive as the effluents are collected in open containers exposed to the atmosphere and the measured are likely higher than the water existing within the columns.
- Dissolved oxygen measurements are also likely biased high due to the exposure to air. Dissolved oxygen levels in the influent are almost always higher than the column effluents suggesting that there is oxygen reduction within the column due to an oxygen demand from the substrate.
- Hach nitrate-N measurements, taken one to three times per week, show a similar trend to the ion chromatography measurements taken about every three weeks. The Hach nitrate-N measurements show between 6.25 and 22.5 mg/L nitrate in the influent and 0.05 mg/L or less in the effluent until Day 305. Nitrate-N levels measured by the Hach method began to increase after Day 305 as the TOC was consumed.



Nitrate-N by Ion Chromatograph



Sulfate by Ion Chromatography



Log TOC

Conclusions

- Complete continuous removal of between 19.5 to 26.9 mg/L of nitrate-nitrogen in influent for over 317 days or equivalent to 83 to 93 column pore volumes by the naturally occurring bacteria.
- After injection, TOC reached 626 to 3,900 mg/L in effluents. The emulsion no longer appeared in effluent after 1.3 to 2.4 pore volumes in columns 1 and 2. This demonstrates the limited potential for migration of EVO in the groundwater.
- Consumption of an estimated 1,301 to 1,398 mg of nitrate-N has been supported by the 15,400 to 30,800 mg of SRS initially applied to the columns.
- TOC concentrations in the effluent of the columns has fallen to between 1.1 and 1.5 mg/L. TOC levels above 2.3 mg/L supported complete denitrification.
- The continued effectiveness of an EVO barrier to completely remove nitrate even at low residual EVO concentrations, demonstrating the longevity an EVO barrier will have in mitigating nitrate in groundwater and eliminate its impact to surface waters even in Cape Cod soils with high groundwater flowrates.

Recommendations

- A field scale permeable reactive barrier pilot be conducted to evaluate SRS transport and denitrification. We recommend the SRS-NR formulation with a larger droplet size and stickier, anionic surfactant mixture for maximum retention and longevity.