UCRL-JRNL-208346

Containerized Wetland Bioreactor Evaluated for Perchlorate and Nitrate Degradation

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December 2, 2004

Technology News and Trends (An EPA Periodical)

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The U.S. Department of Energy (DOE) and Lawrence Livermore Laboratory (LLNL) designed and constructed an innovative containerized wetlands (bioreactor) system that began operation in November 2000 to biologically degrade perchlorate and nitrate under relatively low-flow conditions at a remote location at Site 300 known as Building 854. Since initial start-up, the system has processed over 3,463,000 liters of ground water and treated over 38 grams of perchlorate and 148 kilograms of nitrate.

Site 300 is operated by the University of California as a high-explosives and materials testing facility supporting nuclear weapons research. The 11square mile site located in northern California was added to the NPL in 1990 primarily due to the presence of elevated concentrations of volatile organic compounds (VOCs) in ground water. At the urging of the regulatory agencies, perchlorate was looked for and detected in the ground water in 1999. VOCs, nitrate and perchlorate were released into the soil and ground water in the Building 854 area as the result of accidental leaks during stability testing of weapons or from waste discharge practices that are no longer permitted at Site 300

Design of the wetland bioreactors was based on earlier studies showing that indigenous chlorate-respiring bacteria could effectively degrade perchlorate into nontoxic concentrations of chlorate, chlorite, oxygen, and chloride. Studies also showed that the addition of organic carbon would enhance microbial denitrification. Early onsite testing showed acetic acid to be a more effective carbon source than dried leaf matter, dried algae, or milk replacement starter; a nutrient and carbon source used in a Department of Defense phytoremediation demonstration. No inocula were added to the system. Groundwater was allowed to circulate through the bioreactor for three weeks to acclimate the wetland plants and to build a biofilm from indigenous flora.

Using solar energy, ground water is pumped into granular activated carbon canisters to remove VOCs (Figure x). Following solar treatment, ground water containing approximately 46 mg/L of nitrate and 13 µg/L of perchlorate is gravity-fed continuously into two parallel series of two-1,900 liter tank bioreactors. Each bioreactor contains coarse, aquarium-grade gravel and locally-obtained plant species such as cattails *(Typha* spp.), sedges (*Cyperus* spp.), and indigenous denitrifing microorganisms. No inocula were added to the system. Groundwater was allowed to circulate through the bioreactor for three weeks to acclimate the wetland plants and to build a biofilm from indigenous flora. Sodium acetate is added to the first bioreactor in each of the two series to promote growth and metabolic activity of rhizome microorganisms. The split flow from each series is combined, and flows through two back-up ion exchange columns to assure complete perchlorate removal. Effluent from the ground water treatment system is monitored and discharged an infiltration trench in accordance with the Substantive Requirements for Waste Discharge issued by the California Regional Water Quality Control Board.

The solar-powered facility operates 10-15 hr/day, depending on cloud cover, sunlight hours, and battery storage capacity. An active flow rate of 3.8 L/min is set to provide a minimum reactor hydraulic retention time (HRT) of 17 to 20 hours. As plants mature, the HRT requirement will increase due to accumulation of organic debris and rootlets that will decrease the available pore water space in the tank. Test data showed that degradation of perchlorate and nitrate, without an added carbon source, required an HRT of four days and 20 hours, respectively. In the presence of a 0.25 g/L solution of sodium acetate, the HRT decreased to 0.5 days.

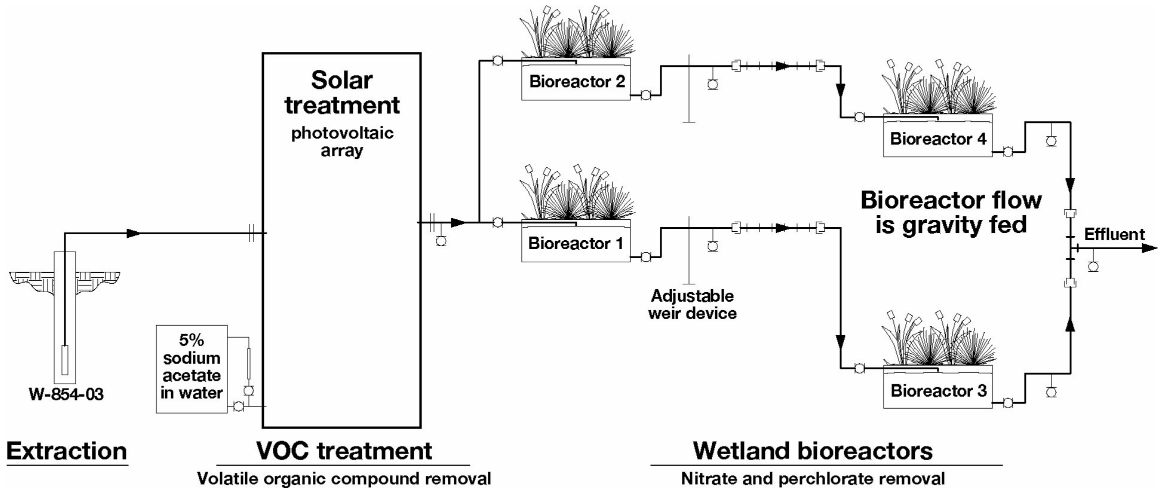

Figure x. Constructed ecosystems at Site 300 employ sun, wetland plants, gravel, microorganisms, and water to trap and degrade perchlorate and nitrate in ground water.

Treatment system samples are collected quarterly from the influent and monthly from the effluent and analyzed in a laboratory for VOCs, nitrate, and perchlorate. Laboratory analysis for perchlorate in influent and effluent ground water uses ion chromatography in accordance with EPA methods 300.0 and 314.0. Analytical results indicate that the contained wetlands reduce perchlorate concentrations from 14-27 µg/L to less than 4 µg/L, which is the analytical reporting limit. The state's current Public Health Goal is 6 ppb. In addition, nitrate concentrations are decreased from 48 mg/L to below the 45mg/L discharge requirement. Portable field instruments are used to collect and analyze samples for pH, electrical conductivity, and temperature. In addition, treatment-system optimization samples are collected quarterly from the solar unit effluent and the bioreactor effluent for analysis of VOCs, nitrate, perchlorate, and DOC. Over the course of operation, perchlorate has been periodically detected in the bioreactor effluent. Initial breakthroughs coincided with acetic acid injection system problems, which were corrected by replacing a venturi-type pump with a peristaltic pump. More recent breakthroughs were corrected by performing maintenance on the bioreactor by removing plant material.

Operation of the wetland bioreactor for more than four years resulted in a stable ecosystem of indigenous microorganisms. Dominant organisms were identified through use of gradient gel electrophoresis conducted on sediment samples taken from noncontinuous, vertical coring of the bioreactor. The bacteria species identified from reactor gravel closely affiliated with species commonly distributed in soils, mud layers, and fresh water. Most of the bacteria (*Pseudomonas, Acinetobacter, Halomonas*, and *Nitrospira*) respire aerobically or anaerobically with nitrate as the terminal electron acceptor. Several identified genera (*Rhizobium, Acinetobacter*, and *Xanthomonas*) are capable of fixing atmospheric nitrogen into a combined form (ammonia) utilizable by host plants. Isolates from the *Proteobacteria* class, known for its ability to reduce perchlorate, were also identified.

Environmental conditions in the wetland bioreactor fluctuated with seasonal changes, even in California's temperate climate. Seasonal average ambient air temperature ranged between 7 to 11°C during the cold season, and between 17 and 26°C during the warm season. Depending on the time of day, wetland plants moderated water temperature variations from 1 to 5°C. The influent water pH was about 7.5, and the effluent was about 7.1, well within regulatory discharge limits (6.5 to 8.5 units). The pH was potentially moderated during the growing season by biological carbon dioxide consumption (aquatic photosynthesis). Bioreactor reduction–oxidation potential ranged from –100 to –150 mV within a few weeks of operation and establishment of the microbial community and native plants. Measurements show that active bacterial growth is consuming oxygen within the bioreactor, generally causing reduction–oxidation values to be in an anaerobic range (<0.5 mg/L for dissolved oxygen). DOC in the effluent water fluctuates with seasonal effects of the plant growth cycle, metabolic activity in the bioreactor, and acetic acid injection rate.

Results demonstrate that the wetland bioreactor system can successfully remove commingled perchlorate and nitrate from ground water in a relatively short time (hours versus days) when continuously provided with a carbon source. In addition, the bioreactor degrades nitrate and perchorate to non-toxic byproducts, eliminating the need for costly waste disposal of ion-exchange resin. Above-ground containerized wetlands are easy to maintain and can be moved when clean-up is complete without impacting the natural habitat.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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