REMOVAL OF DIOXINS FROM GROUNDWATER USING HiPOx ADVANCED OXIDATION

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Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (dioxins and furans) are recalcitrant compounds in environmental media. Few remediation options exist for dioxins and furans in soil, sediment or water. Typically, dioxins and furans in soil or sediment requiring remediation are either managed in place using institutional controls, disposed of in a landfill, or incinerated. These approaches lead to long-term land use restrictions and/or substantial costs. The removal of dioxins and furans from groundwater or surface water presents an even greater challenge as off-site transport and disposal is not typically feasible and mechanisms for in situ or on-site destruction of dioxins and furans are not well established. The objective of this study was to evaluate the destruction of dioxins and furans in groundwater using the HiPOx® advanced oxidation process, developed by APTwater, Inc. The water used in this study was collected from groundwater monitoring wells at a former sawmill and plywood mill in Northern California that historically used pentachlorophenol (PCP)-containing solution for wood surface protection. To evaluate advanced oxidation as a treatment alternative for groundwater containing dioxins and furans prior to discharge of treated water to surface water, the treatment goal was established as 0.013 picograms/liter (pg/L) total toxic equivalence (TEQ), which is the U.S. EPA ambient water quality criterion for surface water in California.[1]

This study is a continuation of previous work which indicated that, depending on site-specific dioxin and furan congener profiles and the treatment goal, the HiPOx® advanced oxidation process can be successful at destroying dioxins and furans in water. The previous work also preliminarily indicated that certain dioxin and furan congeners are resistant to destruction using advanced oxidation. Consequently, groundwater samples with varying congener profiles, including samples both with and without the potentially recalcitrant congeners, and with varying total TEQ concentrations, were used in the current study. In addition, selected samples were spiked with polychlorinated biphenyls (PCBs) in order to evaluate the potential for creation of dioxins or, especially, furans, from PCBs during the oxidation process.

Materials and Methods

Groundwater samples were collected using low flow sampling techniques to minimize the occurrence of suspended solids, including colloidal particles, in the samples. The samples were collected from six monitoring wells in March 2011 .The wells were selected so that samples of varying dioxin and furan congener profiles and varying total TEQ concentrations would be evaluated in the study.

The samples were shipped to APTwater to perform the HiPOx advanced oxidation bench tests. The HiPOx process is an ozone-based plug flow reactor technology that can be used as either an advanced oxidation reactor or a highly efficient ozone dissolution/contacting system. In the advanced oxidation mode, HiPOx maximizes the production of hydroxyl radicals with efficient injection and mixing of ozone and hydrogen peroxide while minimizing bromate formation. In the ozone-only mode, HiPOx maximizes the benefits of ozone with high mass-transfer efficiency to ensure ozone is not wasted and reacts completely with the water. The advanced oxidation mode was used for all the samples in this study.

All pre-test samples were analyzed by third party laboratories for dioxins and furans and total suspended solids. Selected samples were filtered prior to analysis. Selected samples were also analyzed for polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons, PCBs, and chlorinated phenols. Frontier Analytical Laboratory, Inc. of El Dorado Hills, California, performed the dioxin and furan and PCB analyses using U.S.

EPA Method 8290 and U.S. EPA Method 1668, respectively. Alpha Analytical, Inc. of Sparks, Nevada, performed the total suspended solids analysis using Standard Method SM 2540D, PAH and chlorinated phenol analyses using U.S. EPA Method 8270 SIM, and, total petroleum hydrocarbons analyses using U.S. EPA Method 8015. In addition, prior to treatment, APTwater personnel measured the alkalinity, pH, turbidity, ultraviolet transmittance, temperature, and chemical oxygen demand (COD) of the untreated water.

APTwater's semi-continuous bench-scale test unit includes an ozone generator, ozone analyzer, ozone injector, static mixer, tubular reactor, recirculation pump, gas-liquid separator, and thermocatalytic ozone destruct unit. To conduct the tests, each raw sample was carefully mixed and placed in a large beaker. These beakers were placed on magnetic stir plates and stirred vigorously to maintain a uniform suspended solids concentration throughout each test. Untreated sample aliquots were taken from the beakers for each test run and placed in graduated cylinders. For each run, an entire untreated sample aliquot was charged to the reactor, making sure to swirl the graduated cylinder so that solids accumulated at the bottom, if any, were not separated when transferring. Hydrogen peroxide was added to the contents of the reactor before ozone injection.

Each sample aliquot was treated with a different ozone dose so that dose/response curves can be developed for each sample. Hydrogen peroxide was added at the gas/liquid separator prior to the testing and periodically added during the test.

After each test run, APTwater personnel measured and recorded dissolved ozone residual, dissolved hydrogen peroxide residual, pH, alkalinity, turbidity, ultraviolet transmittance, COD, and temperature. Samples of the treated water were then placed in appropriate containers supplied by the laboratories and shipped to Frontier Analytical Laboratory for dioxin and furan analysis and to Alpha Analytical for total suspended solids analysis. The water that had been spiked with PCBs prior to treatment was also analyzed by Frontier Analytical Laboratory for PCBs.

Results and Discussion:
The chemical analysis results are pending as of the date of preparation of this abstract. We will evaluate the effectiveness of the advanced oxidation treatment using both the total TEQ of the treated samples and the concentrations of individual dioxin and furan congeners in the treated samples. We will also estimate the ozone dose needed to achieve the treatment goal for each sample and the influence of potentially recalcitrant congeners on the effectiveness of advanced oxidation. Finally, we will evaluate whether dioxins and/or furans are created from PCBs during advanced oxidation treatment of samples containing PCBs.

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References:
1. U.S. Environmental Protection Agency (2000); Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule, 40 CFR Part 131, May 18.