

# REMOVAL OF DIOXINS FROM SURFACE WATER AND GROUNDWATER GENERATED DURING WETLAND SEDIMENT REMOVAL 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 removal of dioxins and furans from water using the HiPOx<sup>®</sup> advanced oxidation process, developed by APTwater, Inc.

The occurrence of dioxins and furans in water is primarily the result of adsorption onto particles, especially organic particles, entrained in the water. Although some particles are readily removed by filtration, the effectiveness of filtration depends on the size distribution of the particles with adsorbed dioxins and furans and the type of filtration. The water used in this study was generated during excavation of a wetland impacted by dioxins and furans. Elevated concentrations of dioxins and furans were found in sediment in a wetland adjacent to a former sawmill and plywood mill in Northern California. The selected remedy for impacted soil and sediment was excavation and disposal at a landfill, followed by restoration of the wetland. Due to the presence of surface water and shallow groundwater, a significant quantity of water was generated during excavation activities. The water was treated at the site using a complex, costly, and labor-intensive multi-stage filtration system to achieve the discharge limit of none-detected imposed by the local publicly owned treatment works. This study was performed to evaluate advanced oxidation as an alternative or complementary means of treating the water generated during excavation and as a possible alternative for treating groundwater and surface water containing dioxins and furans. 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.<sup>1</sup>

## Materials and Methods

Groundwater and surface water that accumulated in the excavation was pumped into 20,000-gallon storage tanks and treated at the site prior to discharge to the sanitary sewer. The on-site water treatment system included a series of pumps, tanks, sand and gravel filters, bag and cartridge filters, organic clay filters, and granular activated carbon vessels. The system was expanded as needed during project implementation in order to achieve the none-detected discharge limit. The specific final system components, listed in their order in the treatment train, were as follows: two 20,000-gallon weir tanks in series; one 9,000-gallon clarifier tank; three 36-inch-diameter sand and gravel filters in series; two 5-micron (nominal) bag filters in parallel; one 1-micron (nominal) cartridge filter; two 1,000-pound organic clay filters in parallel; two 2,000-pound granular activated carbon vessels in parallel; one 20,000-gallon intermediate holding tank; two 1-micron (nominal) bag filters in parallel; one 0.5-micron (nominal) cartridge filter; two 2,000-pound granular activated carbon vessels in parallel; and one 0.3-micron (absolute) cartridge filter. In addition, a chitosan flocculant was added to the influent entering the first 20,000-gallon weir tank and additional flocculant was added to the 20,000-gallon intermediate holding tank.

We conducted this study using three water samples collected from the treatment system. AMEC personnel collected two water samples in November 2009 and one water sample in December 2009 from two locations within the treatment system, representing two different levels of filtration. In November, the first sample was collected after flocculation, passing through the weir tanks, the sand and gravel filters, a 5-micron bag filter, and the 1-micron

cartridge filter (sample “SPA-1 micron”). The second November sample was collected from the intermediate holding tank after flocculation, passing through the sand and gravel filters, a 5-micron bag filter, the 1-micron cartridge filter, a clay filter, and a 2,000-pound granular activated carbon vessel (sample “SPB-carbon”). In December 2009, one water sample (sample “SPC-1 micron”) was collected from the same location as the first (November 2009) sample in an effort to replicate the data generated from the first sample.

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 three samples in this study.

All three pre-test samples were analyzed by third party laboratories for dioxins and furans, total organic carbon, chemical oxygen demand (COD), total dissolved solids, total suspended solids, total settleable solids, chlorinated phenols, and total petroleum hydrocarbons. Samples SPA-1 micron and SPB-carbon were also analyzed for oil and grease, total zinc, polycyclic aromatic hydrocarbons, dissolved organic carbon, and general chemistry. Dioxin and furan analyses were performed by Frontier Analytical Laboratory, Inc. in El Dorado Hills, California, using U.S. EPA Method 8290. All other analyses were performed by Alpha Analytical, Inc. in Sparks, Nevada. In addition, prior to treatment, APTwater personnel measured and recorded the alkalinity, pH, turbidity, ultraviolet transmittance (UVT), temperature, and COD of the untreated water.

APTwater’s semicontinuous 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 poured into large beakers. These beakers were placed on magnetic stir plates and stirred vigorously to maintain a uniform suspended solid concentration throughout each test run. For each run, a graduated cylinder was filled to 1.8–2.1 liters with untreated sample. The entire contents of the graduated cylinder were charged to the reactor, making sure to swirl the cylinder so that any solids accumulated at the bottom were not separated when transferring. Hydrogen peroxide was added to the contents of the reactor before ozone injection.

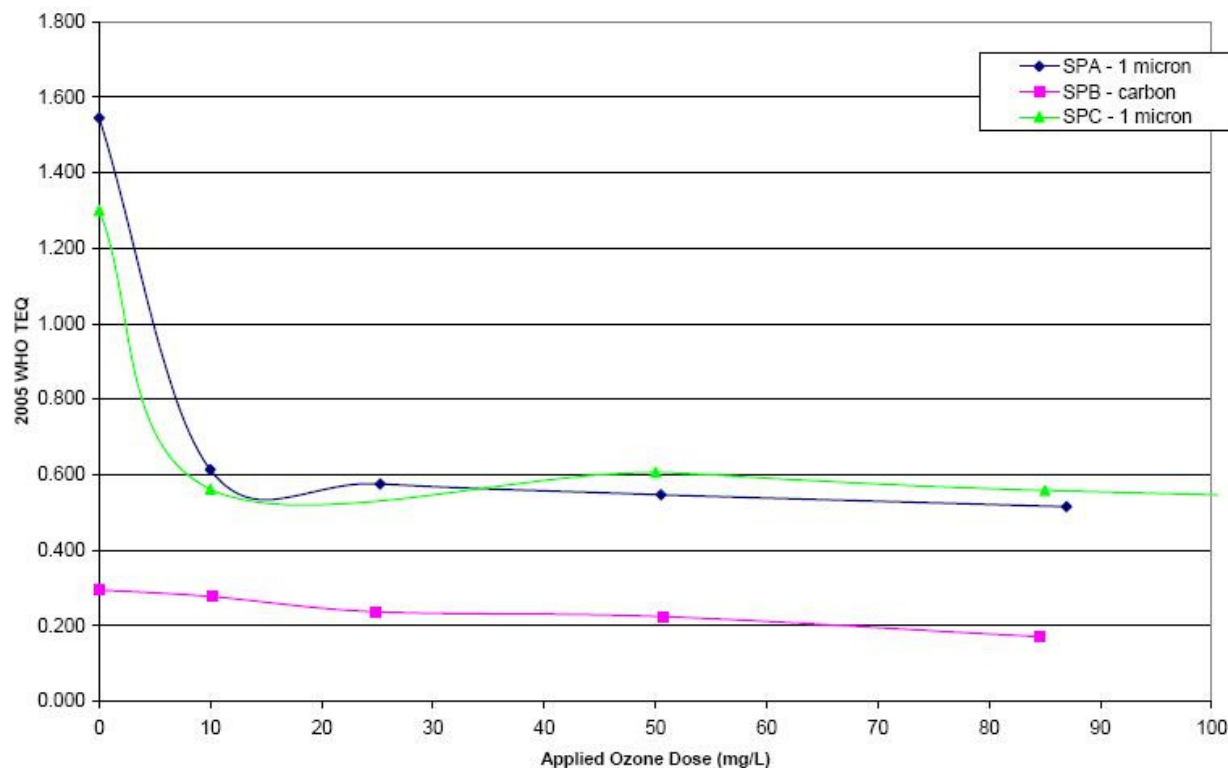
The 1-micron and carbon-treated samples (SPA-1 micron and SPB-carbon, respectively) were tested with ozone doses of 10, 25, 50, and 85 milligrams per liter (mg/L). The replicate 1-micron sample (SPC-1 micron) was tested with ozone doses of 10, 50, 85, 500, and 1000 mg/L. Hydrogen peroxide was added at the gas/liquid separator prior to the testing and periodically added during the test. A hydrogen peroxide mole ratio of 0.7 was used for all tests.

After each test run, APTwater personnel immediately measured and recorded dissolved ozone residual, dissolved hydrogen peroxide residual, pH, alkalinity, turbidity, UVT, 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 using U.S. EPA Method 8290, and to Alpha Analytical for total suspended solids and total settleable solids analyses using Standard Method 2540D.

## Results and Discussion

We evaluated the effectiveness of the tests using both the total TEQ of the treated samples and the concentrations of individual dioxin and furan congeners in the treated samples. A graphical summary of the reduction in total TEQ relative to ozone dose is shown on Figure 1.

Figure 1: 2005 WHO TEQ Ozone Dose Response



Of the nine detected congeners, four dioxin congeners (1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,6,7,8-HxCDF; and 2,3,4,6,7,8-HxCDF) demonstrated immediate destruction to below the detection limit at < 10 mg/L of applied ozone and one additional congeners (1,2,3,4,7,8,9-HpCDF) demonstrated destruction to below the detection limit at < 25 mg/L of applied ozone. The remaining four congeners were still detected after advanced oxidation treatment. One congener, OCDF, did not demonstrate significant reduction in concentration with high doses of advanced oxidation treatment in the SPC 1-micron test sample.

The 1-micron filtered water collected in December 2009 (sample SPC-1 micron) was a repeat test of the initial 1-micron filtered water collected in November 2009 (sample SPA-1 micron). The total TEQs of the raw, untreated water differed by approximately 16%. However, the treatment trends match relatively closely with the exception of the OCDF ozone dose response trend.

Based on the ozone dose response curves, the carbon filtered water (SPB-carbon) would need a moderate ozone dose to reach the conservative treatment goal of 0.013 pg/L total TEQ established for this study. The 1-micron filtered waters (SPA-1 micron and SPC-1 micron) would likely need much higher ozone doses to achieve the same goal. The following congeners appear more difficult to destroy than the other congeners and are the leading factors contributing to the high ozone doses required: 1,2,3,4,6,7,8-HpCDD; OCDD; 1,2,3,4,6,7,8-HpCDF; and OCDF.

The OCDF congener in the 1-micron filtered water collected in December (SPC 1-micron) showed no sign of degradation with increased ozone dose. Considering the OCDF toxicity equivalency factor of 0.0003, this sample has a minimum OCDF TEQ value of approximately 0.01 pg/L. Thus 0.01 pg/L OCDF TEQ is the lowest concentration achievable with advanced oxidation in this water sample, effectively requiring complete destruction of all other congeners that contribute to the total TEQ calculation in order to meet the treatment goal. Based on a curve

fit with the total TEQ data, we predict that approximately 2,581 mg/L of applied ozone would be needed to achieve the treatment goal of 0.013 pg/L total TEQ established for this study. However, using an aggressive curve fit, which evaluates the performance at the bottom end of the dose response curve, we predict doses upwards of 5,423 mg/L. The carbon filtered water sample (SPB-carbon) had a lower initial total TEQ and a significantly lower OCDF concentration. We predict that 507 mg/L of ozone would be needed to reach the goal of 0.013 pg/L total TEQ.

For the 1-micron filtered water sample SPA-1 micron, we predict an ozone dose of 1,756 mg/L to achieve the goal of 0.013 pg/L total TEQ. This sample had a higher initial total TEQ but a lower OCDF concentration compared to sample SPC-1 micron. The lower initial OCDF concentration resulted in the lower predicted ozone dose.

The results of this study indicate that significant reduction in the total TEQ values for dioxins and furans in groundwater or surface water may be achieved using the HiPOx advanced oxidation system, and advanced oxidation can be used in conjunction with filtering to reduce the total TEQ concentration of water prior to discharge. The pre-treatment concentrations of certain congeners, especially OCDF, have a significant influence on the ozone dose needed to achieve the treatment goal, and hence on the efficiency and cost-effectiveness of advanced oxidation. The conservative treatment goal established for this study is also a major factor in predicting the ozone dose needed. Site-specific dioxin and furan chemistry and treatment goals must be considered when evaluating advanced oxidation as an alternative for water treatment. The findings reported herein indicate that, given appropriate site-specific conditions, advanced oxidation may be a viable alternative for treatment of groundwater or surface water containing dioxins and furans.

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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.