Advances in analytical detection methods have made it possible to quantify 1,4-dioxane contamination in groundwater, even at well-characterized sites where it had not been previously detected. Although 1,4-dioxane is difficult to treat because of its chemical and physical properties, recent bench- and pilot-scale testing has shown better-than-expected effectiveness using ozone with and without hydrogen peroxide; the reaction rate of ozone with 1,4-dioxane is too slow to account for the observed decreases in 1,4-dioxane concentration during in-situ treatment. It was hypothesized that constituents of the groundwater, such as iron and olefins, acted as catalysts to produce hydroxyl radicals (•OH) in situ during treatment with ozone. The goal of this work was to perform laboratory-scale testing to determine whether •OH chemistry is responsible for the observed decay in 1,4-dioxane from treatment with ozone alone and with potential catalysts, including hydrogen peroxide, iron(II), and olefin [trichloroethylene, (TCE)].

An indirect chemical probe method, similar to those used previously to detect •OH in various matrices, was chosen. The chemical probe, salicylic acid (SA), was selected because it reacts readily with •OH at a known rate and can easily be measured. The decays of 1,4-dioxane and salicylic acid were monitored during ozonation and in the presence of several potential catalysts. The observed ratios of the 1,4-dioxane and SA decay rates were compared to their known relative reaction rates to determine whether ozone or •OH was more effective in removal of the analytes for each variable. Ozone was delivered to the 1,4-dioxane/SA mixture over a period of approximately three hours, during which samples for 1,4-dioxane and possible by-products were removed from the reactor every 20 to 45 minutes and analyzed immediately by solid phase microextraction (SPME) gas chromatography (GC) with mass spectrometric (MS) detection. Samples for SA were removed every 5 to 15 minutes and analyzed immediately by liquid chromatography tandem mass spectrometry (LC-MS/MS). All experiments were conducted in a deionized water matrix, with treatment of ozone at approximately 4 mg/hour. For each experiment, the ratio of the SA decay rate to the 1,4-dioxane decay rate was calculated and compared to the ratio of the known rate constants for reaction with ozone (>9,000) and •OH (~2.1 -- 4.5). The observed decay rate ratios ranges from 8 to 52, indicating that •OH chemistry was likely responsible for much of the observed decays but that ozone also contributed. In general, the highest decay rate ratios, with an average decay rate ratio of 23, and therefore the greatest impact from ozone versus •OH were observed for ozone as the sole treatment. The average decay rate ratios for ozone with hydrogen peroxide, iron(II), and TCE were comparable, all around 10. This result suggests that •OH chemistry was more responsible for the observed decay in the presence of the potential catalysts. However, treatment with hydrogen peroxide and ozone resulted in absolute decay rates for 1,4-dioxane and SA that were a factor of 2 and 8, respectively, slower than treatment ozone alone. These results suggest that •OH chemistry plays a significant role in the destruction of 1,4-dioxane by treatment with ozone, even in deionized water and in the absence of potential catalysts.