UV Photolysis of Free Chlorine: The Good and the Bad

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When UV light is applied to prechlorinated water, the photolysis of chlorine occurs. This degradation of chlorine is governed by the type of UV light applied (monochromatic low pressure [LP] or polychromatic medium pressure [MP] UV), the speciation of the chlorine, and the background water quality. The decay of chlorine may be unwanted in the case of water treatment or desirable in the production of ultrapure water for industry. The fundamentals of chlorine decay under UV disinfection conditions and situations of ultrapure water production were studied and the effects on the reaction from background water quality such as nitrate were evaluated.

Both field and synthetic waters were used for this study. The synthetic water was prepared by buffering laboratory grade water with 50 mM potassium phosphate buffer and adjusting to pH 5 or 10. A free chlorine concentration of 2 mg-Cl_2/L and nitrate concentrations of 1 and 3 mg-N/L were assessed. When nitrate is photolyzed with MPUV, nitrite and hydroxyl radicals form. The nitrite can react with chlorine directly or the radicals may interact with free chlorine increasing the rate of decay. To evaluate the hydroxyl radical promoted decay of free chlorine during photolysis of nitrate a radical scavenger (10 μM t-butanol) was used. The amount of nitrite produced during these reactions was also measured.

During direct photolysis, hypochlorite (OCl^-) decayed faster than hypochlorous acid (HOCl), (2.21×10^{-3} and 6.60×10^{-4} cm^2/mJ, respectively). The presence of nitrate enhanced the degradation of chlorine, especially HOCl, during MP irradiation. Radical production at pH 10 was minimized and nitrite did not significantly interact with OCl^-. During the photolysis of chlorine, the nitrate concentration remained constant at pH 5, likely due to the oxidation of the photolysis-formed nitrite back to nitrate by the chlorine, and decreased at pH 10 when OCl^- dominated. A model of chlorine decay in the presence of nitrate is being developed, incorporating the pH, chlorine speciation, and UV wavelength effects. Improved knowledge of the photochemistry behind chlorine decay mechanisms will help this process be avoided (in the case of disinfection) or enhanced (in the case of ultrapure water production) depending on the application.