ABSTRACT

Weng, Shih-Chi. Ph.D., Purdue University, May 2013. The dynamics of volatile disinfection byproducts in indoor, chlorinated swimming pools. Major Professor: Ernest R. Blatchley III.

Swimming and aquatic activities are popular among all age group in the United State, but these activities are also associated with health risks for the participants by exposure to microbial pathogens and disinfection byproducts (DPBs). Microbial pathogens can be controlled through water-treatment methods, including Filtration and chlorination. However, less is known about the effects of these processes on DBP dynamic. Many studies have indicated, in general terms, that DPBs in pools are formed form reactions between free chlorine and precursor chemicals that are introduced to pools by swimmers via human fluids (sweat and urine). However, relatively little information is available in the literature to characterize the behavior of volatile DBPs in the gas and liquid phases under this condition.

Ultraviolet (UV) irradiation has emerged as a secondary disinfectant, as well as a process that can alter water and air chemistry in pools. UV-based treatment is commonly used in treatment of swimming pool water, almost always in conjunction with chlorination. The motivations for inclusion of UV in these settings include the ability to inactivate some chlorine-resistant microbes and the ability to reduce the concentration of inorganic chloramines by photolysis. However, conflicting results have been reported in

the literature regarding the effects of UV-based treatment on DBPs formation. This appears to be particularly true when organic-N compounds are present as DBP precursors. However, the mechanisms behind these UV effects are not well defined.

Therefore, this study includes two major goals: 1) to define the behavior of volatile DBPs and their precursors in an indoor, chlorinated swimming pool under a heavy use condition, and 2) to define the effects of the combined use of UV/chlorine on DBP formation from organic-N precursors. For field experiments, liquid- and gas-phase quality monitoring was conducted in several indoor, chlorinated swimming pool facilities to evaluate the dynamic behavior of volatile DBPs in swimming pool area under a heavy use condition. To examine UV-induced effects, UV irradiation and chlorination experiments were conducted with a series of organic-N compounds that are representative of those introduced to swimming pool via human sweat and urine.

In field experiments, swimmer activity was identified to adversely affect air and water quality by promotion of the liquid→gas phase transfer and introduction of DBP precursors. Air quality had a strong correlation with the bather number; gas-phase NCl_3 concentration increased with swimmer activity. Liquid-phase concentrations of several volatile DBPs showed a diurnal pattern where near-surface concentration deceased during periods of pool use (day time) and recovered during period of inactivity. This behavior was believed to be associated with the promotion of liquid→gas phase transfer by swimmer activity (decreasing in daytime) and the recirculation pattern of the pool (overnight). Additionally, a dynamic pattern of behavior of volatile DBPs was observed in near-surface water during a 3-hour swimming practice section. Vertical stratification of the water column was also observed.

In laboratory experiments, volatile DBP formation from nitrous DBP precursors was enhanced with co-exposure of UV irradiation and chlorination (CH_3NCl_2 from creatinine, CNCl for *L*-arginine, *L*-histidine and glycine); free chlorine consumption increased when UV irradiation was involved. In addition, inorganic chloramine re-formation was observed in post-chlorination of UV-irradiated samples. Dichloromethylamine (CH_3NCl_2) was indentified to be UV sensitive, and the photolysis of CH_3NCl_2 resulted in cyanogen chloride (CNCl) formation. Similarly, CNCl formation was also detected from photolysis of chlorinated guanidine or imidazole compounds. Collectively, UV-irradiation appears to promote N-Cl bond cleavage among chlorinated precursor moieties and resulting in formation of DBPs or intermediates that are more susceptible to chlorination.

The results of this work have allowed for understanding the influences of swimmer behavior on water or air quality, and for definition of a mechanism of DBP formation from the combined application of chlorine and UV. The results of field experiments suggest that changes in pool operations and swimmer hygiene habits could improve air and water qualities in swimming pool facilities. The laboratory results of this work have implications with respect to the application of chlorine and UV for water treatment in swimming pool facilities, and in other settings where these two forms of treatment may be used together, including reuse applications and UV/chlorine-based advanced oxidation processes.