## Chloraminated Concentrated Drinking Water for Disinfection Byproduct Mixtures Research: Evaluating Free Chlorine Contact Times

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Complex mixtures of disinfection by-products (DBPs) are formed when the disinfectant oxidizes constituents (e.g., natural organic matter (NOM) and organic pollutants) present in the source water. Since 1974, over 600 DBPs have been identified in drinking water, yet a large portion of the total organic halogens formed remain unidentified. Concerns for public health continue to drive DBP research as increased exposure has been associated with carcinogenic and/or endocrine disrupting properties. Toxicological evaluation of whole DBP mixtures, including the unidentified DBPs, allows a more accurate accounting of the magnitude of health effects. A previous presentation at the 2016 WQTC reported on chloramination by preformed monochloramine; this work evaluates chloramination that is preceded by various free chlorine contact periods and is a continuation required because of the complexity of chemical reactions with respect to chloramines, bromide, iodide, and the resulting DBPs formed. The primary objective of this research was to create DBPs that are representative of chloraminated water systems while producing concentrated whole mixtures of DBPs that scale with total organic carbon (TOC) concentration for future DBP toxicology studies.

Ohio River water was collected post-ultrafiltration (UF1X) and as reverse osmosis concentrate that had been concentrated 142-times the UF1X TOC concentration (CONC142X). A portion of the CONC142X was freeze-dried to produce a solid NOM that was reconstituted at defined TOC concentrations, representing 1-times (RECON1X), 142-times (RECONC142X), and 500-times (RECON500X) the UF1X TOC. The CONC142X was also diluted down to an equivalent 1X TOC (CONC1X). Bromide (1X=115  $\mu$ g/L) and iodide (1X=11.5  $\mu$ g/L) were added to a pH 8 phosphate buffered water and scaled by the TOC concentration. All samples were analyzed for 57 individual DBPs. Chloramination was conducted by dosing 1X waters with 2.5 mg/L free chlorine followed by ammonia (4.75:1 chlorine to ammonia-nitrogen ratio).

For the 1X waters, a 3-minute ("short") and a 20-minute ("long") free chlorine contact time respectively corresponded to 80% and 100% bromide oxidation and 65% and 100% iodide oxidation. Prior to DBP experiments, initial experiments and a free chlorine/chloramine kinetic model were used to establish initial dosing concentrations and reaction times required to scale 1X to 142X and 500X. Results show increases in nearly all DBPs with increasing free chlorine contact time and more brominated THMs, HAAs, and some other DBPs are formed. Initial evaluation indicates concentrated whole mixture DBPs are not scaling well compared to 1X DBPs but further data analysis is ongoing. For DBP formation, comparisons will be presented for the (1) various chloramine dosing scenarios, (2) impact of concentration, (3) and impact of NOM processing (e.g., freeze-drying and reconstitution).