Clustering chlorine reactivity of haloacetic acid precursors in inland lakes of central North America

TENG ZENG[1,2]* AND WILLIAM A. ARNOLD[1]

[1]Department of Civil Engineering, University of Minnesota, Minneapolis, MN 55455, USA (*correspondence: zengx067@umn.edu)

[2]Present addresss: Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305, USA

Over the past decades, rising levels of dissolved organic matter (DOM) in inland lakes and streams have been widely observed in North America and Europe. Increasing DOM levels in source waters presents a challenge to downstream drinking water treatment utilities in that the chemical disinfectants (e.g., chlorine) applied to inactivate waterborne pathogens promote the formation of toxic disinfection byproducts (DBPs), such as haloacetic acids (HAAs), via reactions with DOM moieties. A defined picture of the chlorine reactivity of HAA precursors is essential for planning of pretreatment options specific to short-term meteorologic and hydrologic events as well as long-term trends driven by climate and land-use change.

In this study, the formation kinetics of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), the two predominant HAA species, were delineated upon chlorination of seventeen model DOM precursors and sixty-eight inland lake water samples collected from the Upper Midwest, USA. A comparative method built upon the hierarchical cluster analysis of combined DCAA and TCAA kinetic datasets was established to enable a direct profiling of the chlorine reactivity of HAA precursors in inland lakes.

Of particular interest was the finding that the DCAA and TCAA formation rate constants could be grouped into four statistically distinct clusters reflecting the core structural features of model DOM precursors, including non-β-diketone aliphatics, β-diketone aliphatics, non-β-diketone phenolics, and β-diketone phenolics. Over 70% of lake water samples investigated were classified as the “phenolics” groups based on the notion of proximity measure, suggesting that the reactivity of the inland lake DOM with respect to DCAA and TCAA formation resembled that of phenolic moieties. Furthermore, the clustering patterns of selected lake water samples shifted after photobleaching treatment and long-term dark incubation. Results from this work highlight the potential for implementing an integrated kinetic-statistical approach to constrain the chlorine reactivity of DOM in inland source waters.