Dependence of algogenic organic matter derived DBPs on its EEM fluorescent properties

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Eutrophication of algae in reservoirs frequently impedes unit operation in water treatment plants (WTPs) because of its exponential rise in a cell population in the water body (Tomlinson *et al.*, 2016). Importantly, algal eutrophication always accompanies with a remarkable increase in the concentration of algogenic organic matter (AOM), which is well-proven as a major organic precursor to organic halogenated disinfection-by-products (DBPs) upon chlor(am)ination or ozonation (Fang *et al.*, 2010b, Hua *et al.*, 2017, Zhu *et al.*, 2015). Better understanding and control of AOM-derived DBPs, especially when algal eutrophication occurs, thus has become the greatest challenge for the sustainable production of safe drinking water.

In this study, the dependence of AOM-derived DBPs was investigated by characterizing the fluorescent properties, via excitation-emission matrix spectroscopy (EEM), and the chemical structure of AOM. The formations of two major DBPs from AOM water samples, including trihalomethanes (THMs) and haloacetic acids (HAAs), were examined. According to the classification of Chen *et al.*, 2003, four major regional EEM components were identified in AOM water samples, including aromatic protein-(AP), soluble microbial product- (SMP), humic acid- (HA), and fulvic acid- (FA) like substances. The average fluorescent intensities calculated after the subtraction to the DI water intensity and Rayleigh and Raman scattering to remove the background and interference. The results show that the formation of AOM-derived DBPs strongly depended on its EEM fluorescence and chemical properties, as shown in **Fig.1**. Particularly, AOM precursors exhibiting the AP- and SMP-like fluorescence had greater potentials to significantly produce both THMs and HAAs than that of the HA- and FA-like. This is because of the abundance of aliphatic/aromatic carbon sites and amide content in their chemical structures. In contrast, AOM precursors with HA- and FA-like fluorescence likely comprise an abundance of carboxylic group,



which is an unfavorable site for DBP formation. As a result, the regional EEM intensities of AP and/or the ratio (AP & SMP)/ (HA & FA) were mostly correspondent to the formation of THMs and HAAs. The results of this study thus imply that EEM spectroscopy is a sensitive and promising technique for AOM-derided DBP prediction.

Fig.1 Overall EEM spectra of (a) original, (b) large fraction >100 kDa, (c) small fraction <1 kDa of AOM derived from M. aeruginosa and their corresponding THM and HAA formation

References

Chen, W., Westerhoff, P., Leenheer, J.A. and Booksh, K., **2003**. Fluorescence Excitation–Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. *Environ. Sci. Technol.* 37 (24), 5701–5710.

Fang, J., Yang, X., Ma, J., Shang, C. and Zhao, Q., **2010**. Characterization of algal organic matter and formation of DBPs from chlor (am) ination. *Water Res.* 44(20), 5897–5906.

Hua, L.C., Lin, J.L., Chen, P.C. and Huang, C.P., **2017**. Chemical structures of extra- and intra-cellular algogenic organic matters as precursors to the formation of carbonaceous disinfection byproducts. *Chem. Eng. J*. 328, 1022–1030.

Tomlinson, A., Drikas, M. and Brookes, J.D., **2016**. The role of phytoplankton as pre-cursors for disinfection by-product formation upon chlorination. *Water Res.* 102, 229–240.

Zhu, M., Gao, N., Chu, W., Zhou, S., Zhang, Z., Xu, Y. and Dai, Q., **2015**. Impact of pre-ozonation on disinfection by-product formation and speciation from chlor(am)ination of algal organic matter of Microcystis aeruginosa. *Ecotoxicol. Environ. Saf.* 120, 256–262.