



Determination of disinfection byproduct precursors in lake water by fluorescence EEM- PARAFAC technique

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Disinfection by-products

- Disinfection byproducts
 - Trihalomethanes (THMs).
 - Haloacetic acids (HAAs).
 - Bromate
 - Chlorite
 - Many others.

- D/DBP rule
 - MCL for TTHM: 80 $\mu\text{g}/\text{l}$

Considering the formation mechanism of DBPs, one of the basic approaches for DBP control is to identify DBP precursors and remove the precursors prior to the addition of disinfectants.



DPB precursors: dissolved organic matter

- Heterogeneous mixture from breakdown of bacterial, algal, and high plant organic materials.
 - Distinctive chemical characteristics associated with origins.
 - Seasonally dependent.
 - Hydrological and biogeochemical processes.
- It has been found that THM precursors are likely those substances containing “activated” aromatic structures, i.e., aromatic sites substituted with oxygen- and nitrogen-containing functional groups.

A knowledge of the abundance and structure of DOM components, and how they relate to DBP formation, is central to understanding how to control DBPs in water treatment processes.

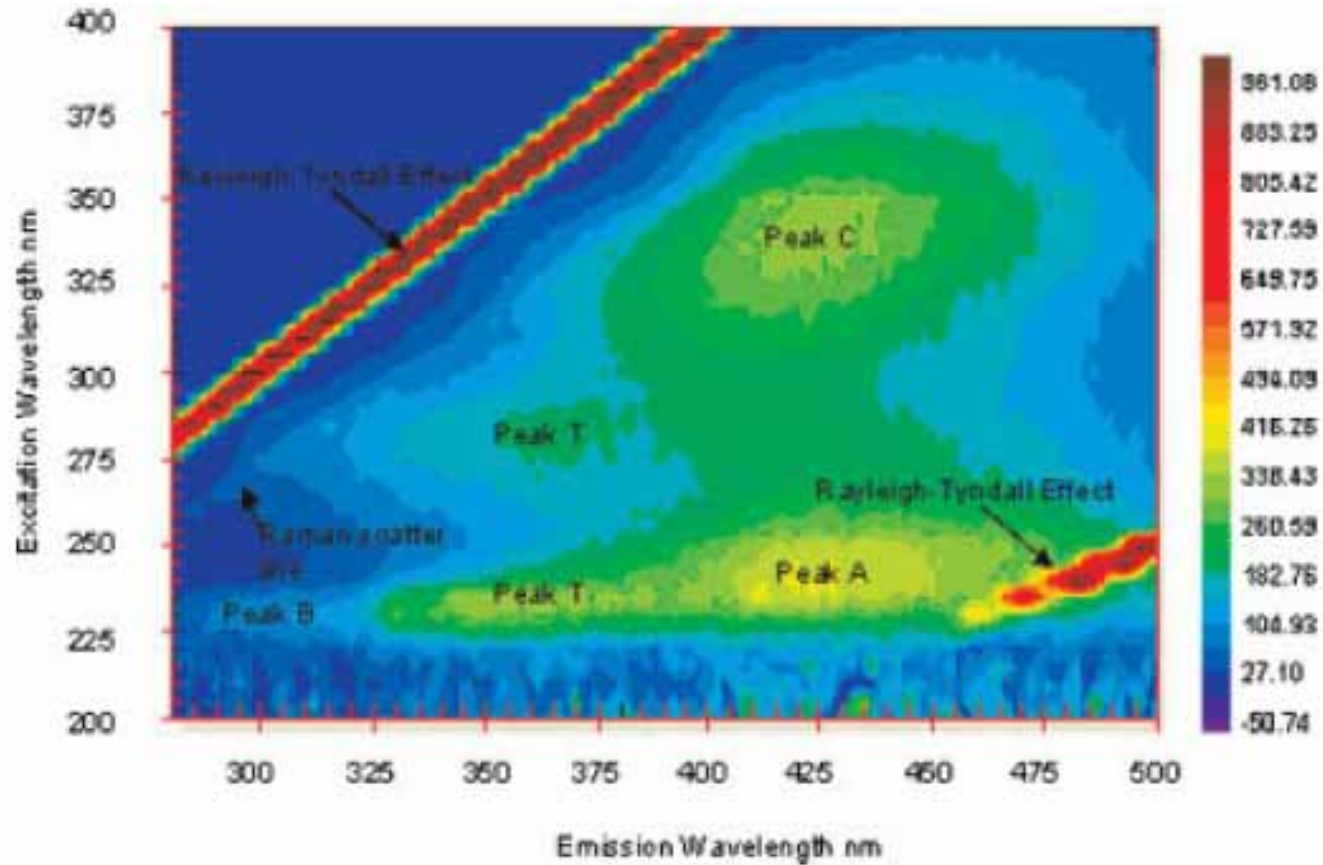


Characterization of DOM

- Fractionation of DOM with XAD (nonionic macroporous sorbents).
- Ultrafiltration and size exclusion chromatography.
- UV and fluorescence spectroscopic techniques.
 - CDOM: compounds containing aromatic rings, aliphatic and alicyclic carbonyl compounds with highly conjugated double-bond structures
 - Non-destructive
 - Require only a short measurement time



Fluorophores in natural water

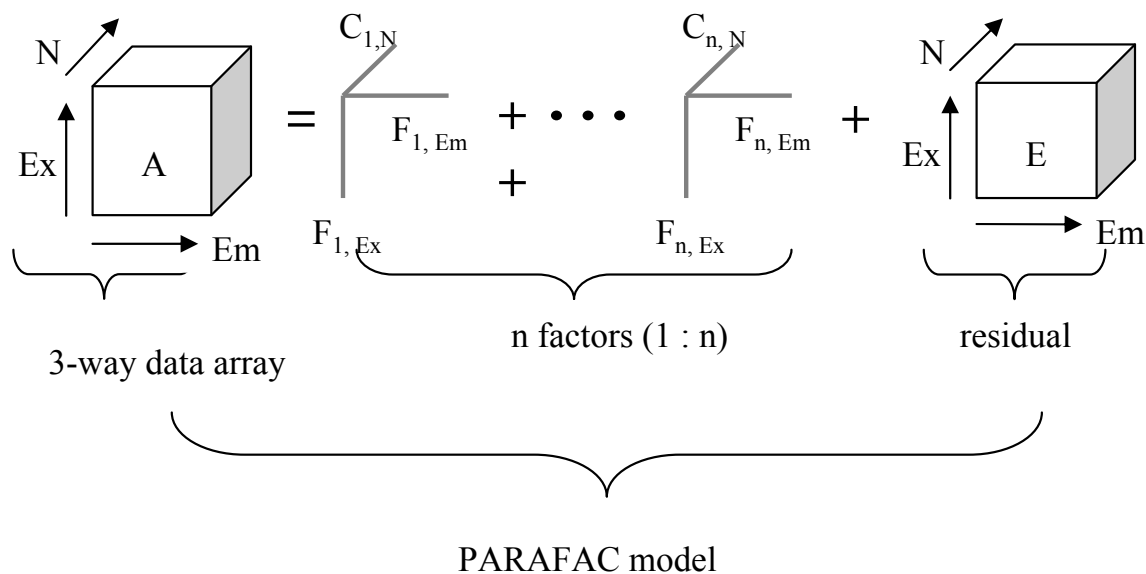


EEM displays common fluorescent peaks in natural water system.

Source: *Hudson et al. River Res. Applic. 2007, 23, 631-649*



EEM decomposition: PARAFAC model



$$A = C(\text{Em}| \otimes |\text{Ex})' + E.$$



Hypothesis, objective and methodology

- Hypothesis
 - CDOM and DBP precursors should have some intrinsic correlation.
- Objective
 - To develop a sensitive fluorescence EEM technology applicable to the online water quality monitoring of DBP formation potential for water treatment utilities.
- Methodology
 - Fraction DOM in lake waters by fluorescence EEM using PARAFAC analysis, and correlate the factors generated by PARAFAC analysis with the TTHM formation potentials to identify THM precursors.

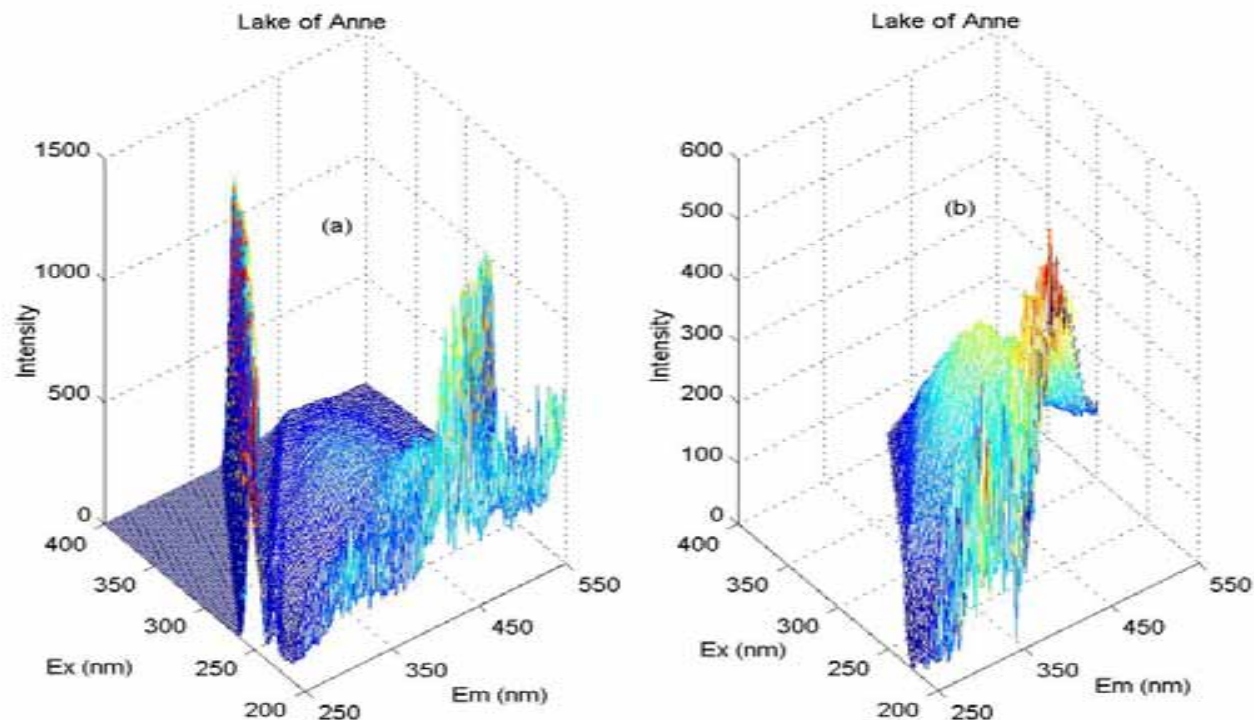


Methods

- **Sample collection**
 - Epilimnetic surface water samples were collected from 55 lakes in the state of Missouri, USA
- **TTHM analysis**
 - Fujiwara method was adapted for TTHM analysis
- **Fluorescence EEM**
 - Emission spectra were collected from 250 nm to 550 nm in 3 nm steps, whereas the excitation wavelengths were stepped in 2 nm from 200 nm to 400 nm (Hitachi F-4500 Spectrograph).



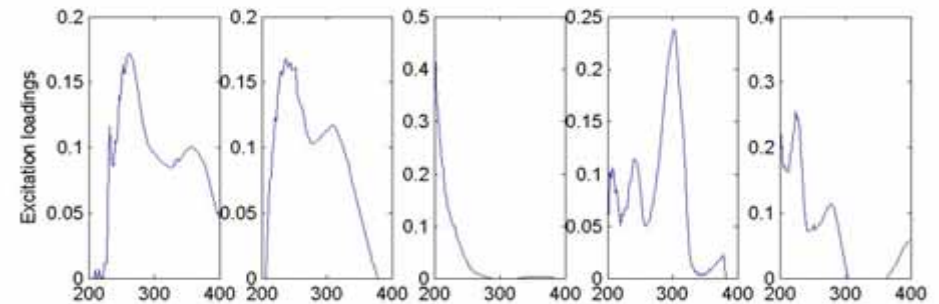
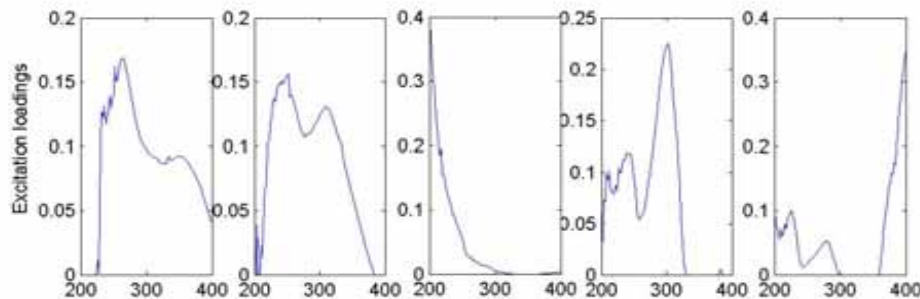
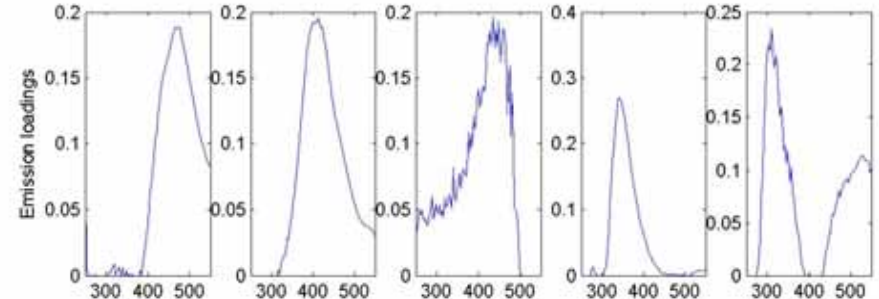
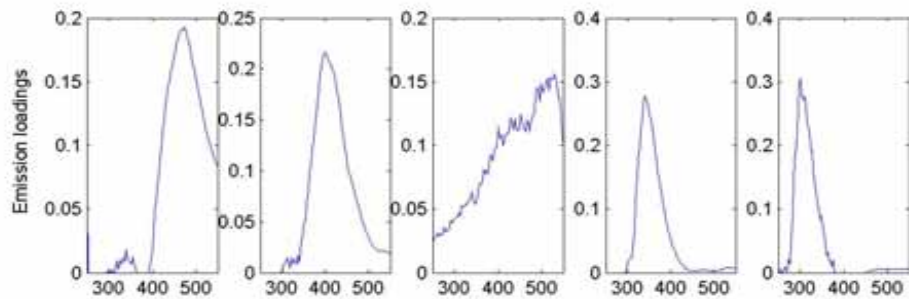
Spectrum correction: Rayleigh and Raman scatters



Fluorescence spectra of Lake of Anne in the state of Missouri, USA. (a) Original spectrum. The first and second order Rayleigh scatters dominate the spectrum; (b) the spectrum after the reduction of a blank EEM from the scan of deionized water and the removal of the first and second order Rayleigh scatters.



Method validation for PARAFAC: split-half



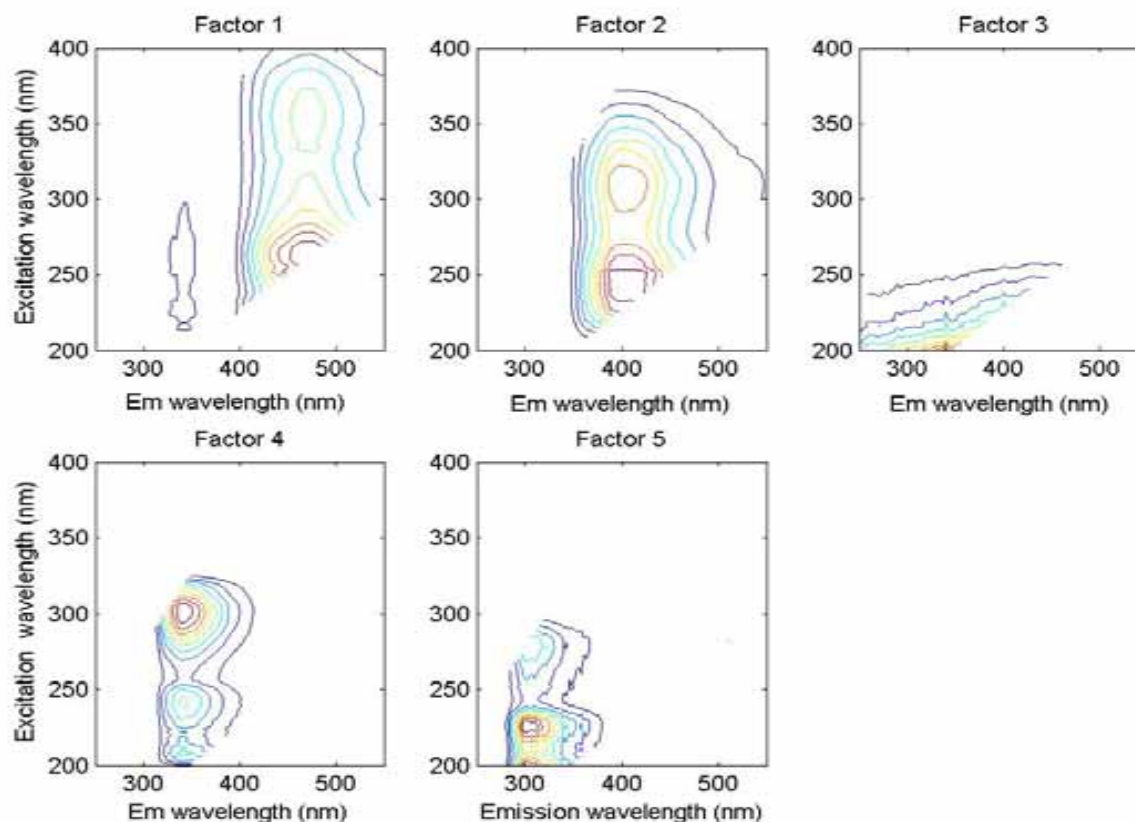
(a)

(b)

Excitation and emission loadings of five factors obtained from two randomly half-split data sets. (a) A data set includes 27 lakes; (b) the other data set includes 28 lakes left. The validity of PARAFAC analysis can be justified by the similarity of the corresponding spectra of each of the five factors in (a) and (b).



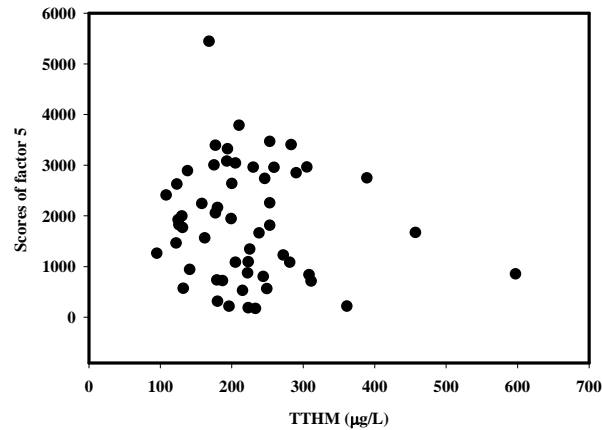
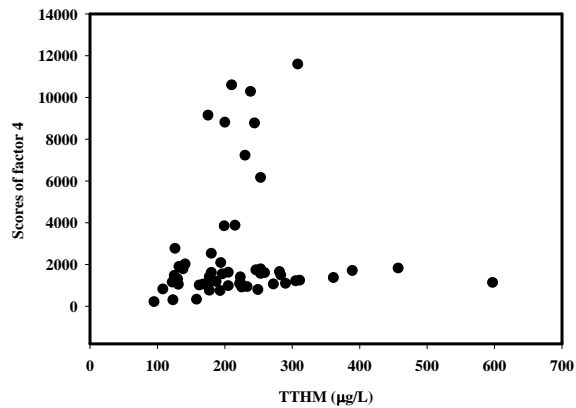
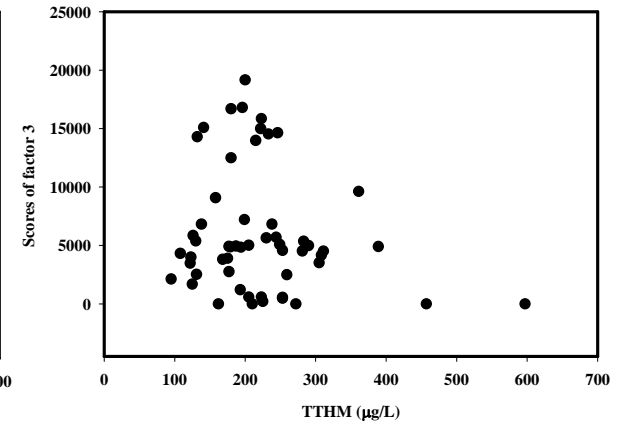
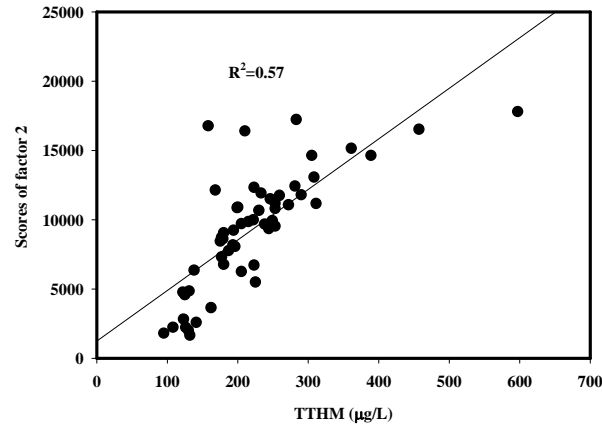
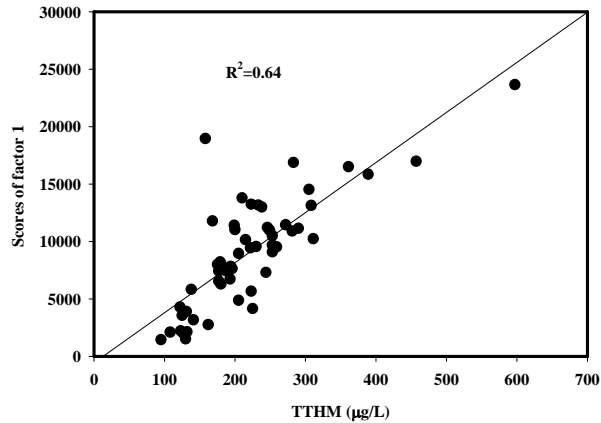
Results: the origins of the components



The decomposed spectra of five factors obtained from PARFAC analysis of the whole data set. Factors 1 and 2 are from humic matter, factor 3 from xenobiotic organic matter, and factor 5 from protein-like fluorophores. Factor 4 is not similar to any previously identified peaks.



Results: identification of THM precursors



The correlation between component scores of each of the five factors with the TTHM formation potentials. The linear relationships between component scores of factors 1 and 2 and TTHM formation potentials suggests that factors 1 and 2 are responsible for the formation of TTHM.



Summary

- Decomposition of EEMs from 55 lakes by PARAFAC analysis suggests 5 major factors of different origins.
- Factors 1 and 2, originated from terrestrial humic materials, are positively related to the formation of TTHM.
- The established method could be potentially used by water treatment utilities for online water quality monitoring.



Acknowledgements

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