Fluorescence Emission Excitation Matrices (EEMs): Identifying Signatures for Constituents of Concern

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Outline

• What is spectrofluorescence and why use it?
  – Desire to find reliable, inexpensive methods to measure constituents
  – Brief Introduction to Spectrofluorescence
  – Application to measuring drinking water Constituents of Concern

• Spectrofluorometer Special Study
  – Goals, Study Design
  – Example Data
  – Progress & Next Steps
Spectrofluorescence Intro

• Fluorescence: When an electron is excited to a higher energy level (electron orbit) by absorption of light energy, and then releases energy as light as it drops to a lower energy level.
Intro, continued: Instruments

- **A fluorometer**: one pair of light wavelengths to measure, e.g., chlorophyll in algal cells.
  - Turner 10AU,
  - in-situ FDOM probe

- **A spectrofluorometer**: Performs multiple measurements across bands of light wavelengths.
  - Horiba/Jobin-Yvon Fluoromax-4 purchased by QAQC Program.
Each *excitation-emission matrix (EEM)* consists of hundreds of measurement combinations of a single water sample, with excitation wavelength is on one axis, emission wavelength is the second, and fluorescence intensity forms a third axis.
Spectrofluorescence Special Study

• To investigate the usefulness of spectrofluorescence as a way of quickly and easily quantify constituents of concern (CoCs) in source waters.
  – Organic carbon: Demonstrated
  – Nitrosamines: Possible?
    • Hua et al., 2007, Fluorescence fingerprints to monitor total trihalomethanes and N-nitrosodimethylamine formation potentials in water. Environ Chem. Lett. 5:73–77.

• Source water “fingerprinting”
  – Find distinctive fluorescence features in sources
Study Design

• Two-year study, approved in the Work Plan
  – 11 stations sampled monthly (piggy-backed on MWQI routine sampling program), plus several other sites sampled at other frequencies.
  – Sample analysis for DOC, THMFP, HAAFP, Nitrogen chemical species, Spectrofluorescence EEM, Nitrosamine formation (~quarterly sampling).
  – Numerical analysis to identify features in the EEMs that correlate highly with Constituents of Concern.
Monthly Sampling Stations

Represents:
- Major tributaries
- Seasonal variation
- Spatial variation
- Diff. Source waters
  - AMR “Pristine”
  - Colusa Ag runoff
  - NEMDC Urban
  - Waste Water
Example EEM Data: Spatial Variation

San Joaquin R, Downstream of Stockton WWTP 12 Sept 2011

Stockton WWTP 05 Oct 2011

Natomas East Main Drain (NEMDC) 07 Mar 2011
Example EEM Data: Spatial Variation

Pure Water Blank, 16 July 2012

West Sac Intake, 09 July 12

Colusa Basin Drain, 09 July 2012

Old River at Bacon Island, 09 July 2012
Example EEM Data: Time variation
Example EEM Data: Correlation

![Graph showing correlation between DOC and fluorescence]

- **DOC, mg/L**
- Fluorescence "A" Peak
- Fluorescence "C" Peak
Chloroform and EEM features
Bromoform and EEM features

- Mostly a function of source waters
- EEMs not very predictive of Bromoform FP
Halogens vs DOC
Chloroform variation
THMs & HAAs vs T1 Fluorescence
Likely FDOM sensor response

Linear fit
DOC = (0.4282 ± 0.299) + (13.85 ± 1.14) * FDOM_peak
values ± 95% Conf. Interval

Barker Slough

NEMDC

Am.R.
Progress

• Successfully analyzing monthly water samples from 11 monthly + 8 other sites for Spectrofluorescence EEM, DOC, THMFP, HAAFP, Nitrogen chemical species likely to be nitrosamine precursors.
  – Nitrosamine correlation pending.

• Products: Final study report, feasibility for future monitoring, peer-reviewed article
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Questions & Comments?
Selected References

