Applications of Fluorescence Spectroscopy for Monitoring Water Quality in an Urban Watershed

NWQMC
Jami Goldman, Stewart Rounds, Joseph Needoba
May 2nd, 2012
Approach:

(1) Develop a robust model using fluorescence spectroscopy for identifying CDOM composition with predictive capabilities for wastewater (WW) effluent detection.

(2) Demonstrate fluorescence linear responsiveness with an end-member mixing experiment and apply to the aquatic system.

(3) Use a multivariate linear regression approach to quantify wastewater found in a sample.

(4) Distinguish sources and qualitative characteristics of organic matter with principle component analysis.
Background

- **Dissolved Organic Matter (DOM) pool** is poorly characterized but integral to ecosystem
  - controls microbial food webs
  - biogeochemical cycles
  - highly variable in natural systems
- Optically active fraction of DOM (CDOM) effective tracer of organic matter
- Spectral fluorescence measurements can distinguish different fractions of the DOM pool

Tualatin River, 2009

Clackamas River, 2009
Organic Matter: Sources

• Natural
  – Leached from soil and terrestrial plants
  – Algae and other in-stream plants
  – Microbial activity

• Anthropogenic
  – Discharge of septic/WW effluents
  – Storm water runoff
Technology:
- Scanning fluorometer creates excitation-emission matrices (EEMs).
- Combines fluorescence (emission) spectra measured from a series of different excitation wavelengths
- Letters represent excitation/emission pairings → specific characteristics of organic matter in the water
- EEMs provide information about presence, concentration, composition and source.
Site Description

• Tualatin River Basin
  – Slow moving urban river
  – Lower reach ~500,000 people
  – Clean Water Services
    • Wastewater and stormwater management utility
    • 60 million gallons per day of wastewater
    • Advanced tertiary treatment
    • Highly controlled system (reservoir releases/WW regulations)
  – Low flow period ~ 40% treated WW
Sample Collection:
- Collected every 3-4 weeks from all sites
- Full hydro-year, all seasons
- 74 samples total
  - Headwater site = 12
  - Downstream site = 11
  - Tributary sites = 28
  - WW effluent = 23

Downstream river site – Tualatin River @ Oswego Dam
Methods:

Headwater site

WWTP site

Downstream river site

Peak A

Peak T

Peak C
### Parameters of Interest for this study

<table>
<thead>
<tr>
<th>Fluorescence Peak/Parameter</th>
<th>Excitation/Emission (nm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>270/340</td>
<td>Tryptophan-like, protein like</td>
</tr>
<tr>
<td>A</td>
<td>260/450</td>
<td>Humic-like</td>
</tr>
<tr>
<td>C</td>
<td>340/440</td>
<td>Humic-like</td>
</tr>
<tr>
<td>Fluorescence Index (FI)</td>
<td>Ex370→Em470/Em520</td>
<td>Higher values indicate algal(microbial) vs. terrestrially derived DOC</td>
</tr>
<tr>
<td>SUVA$_{254}$</td>
<td>Absorbance at 254nm normalized to DOC</td>
<td>Correlated to aromatic content</td>
</tr>
</tbody>
</table>
DOC Annual Average Concentrations:

- WWTP and Tributary = highest DOC
- Headwater = lowest DOC
- Downstream = mid-range DOC
SUVA$_{254}$ Annual Averages:

River Samples =
Higher SUVA$_{254}$: more aromatic, less labile

WWTP Samples=
Lower SUVA$_{254}$: less aromatic, more labile
FI Annual Average Values:

- WWTP = highest FI values
- Headwater and Tributary = lowest FI values
- Downstream = mid-range FI values

Microbial derived OM
Terrestrial derived OM
End-Member Mixing Experiment

- Goal: Determine fluorescence response and degree of linearity (headwater and WW effluents)
  - Headwater sample mixed with both types of WW effluent (2 experiments)
  - 10 samples per experiment
    - 10% incremental increases of WW added to each
  - Mixed and shaken for 2 hours
  - Fluorescence and Absorbance measurements
Results:

- Peak A
- Peak C
- Peak T

Percent Durham Wastewater Effluent

Percent Rock Creek Wastewater Effluent
End-Member Mixing Model

- Goal: Determine if a simple mass balance equation using individual peaks can predict WW effluent for the downstream river site

\[
\text{PercentWastewater} = \frac{\text{Headwater} - \text{Downstream}}{(\text{Headwater} - \left(\frac{\text{WW}_1 + \text{WW}_2}{2}\right))} \times 100
\]

- Samples needed from all 4 sites
- Fluorescence signals for peaks A, T, and C
- Trends in correct direction
- Overpredicts
- Too simple of an approach
- Requires 4 samples
Multivariate Linear Regression Model

- **Goal:** Construct a model using multiple fluorescence peaks to quantify percent WW at downstream river site
  - **Model Inputs:** 74 total samples (12 headwater, 28 tributary, 11 downstream, 23 WWTP)
    - Headwater and tribs set at 0% WW
    - WWTP set at 100% WW
    - Downstream %WW calculated from Tualatin Annual Flow Report
  - **Model Validated:** 30 total samples
    - 17 headwater Clackamas samples set at 0%
    - 13 from secondary WWTP samples set at 100%
  - **Key Model Stats**
    - Mean Error- indicates model bias (ideal close to 0)
    - Mean Absolute Error- typical error with model prediction (ideal <10%)
Results:

**Overall Model Statistics:**
Mean Error (ME) = 0.1%
Mean Absolute Error (MAE) = 8.1%

Sites | ME - MAE
--- | ---
Headwater | -4.7% - 7.0%
Tributary | -1.2% - 7.6%
Downstream | -5.2% - 9.2%
WW | -3.2% - 8.6%

Model Results - 95% of samples are predicted within 80% accuracy
Results: Downstream Site

Model Diverges:
1- phytoplankton bloom
2- WWTP move from tertiary treatment to secondary

Nutrients and Chlorophyll at Oswego Dam

Chl A (mg/L)
PO4-3 and NH4+ (mg/L)

Ammonium
Phosphate
Chlorophyll A
Principle Component Analysis

- Goal: Distinguish among sources and characteristics of organic matter across all samples
  - Input: All 74 samples
  - 3 variables: Peaks A, T, and C
  - PC1 captured 83% of the variability
  - PC2 captured 16% of variability
  - 99% variability in fluorescence data explained with PC1 and PC2
  - Trends were explained for sample location, FI values, SUVA$_{254}$, and DOC concentrations
PCA: Sites

Principle Component 2

Principle Component 1

- Beaverton Creek
- Durham WW
- East Fork Dairy Creek
- Fanno Creek
- oswego dam
- Rock Creek
- Rock Creek WW
PCA: SUVA$_{254}$

- Higher SUVA$_{254}$ – more aromatic, less labile
- Lower SUVA$_{254}$ – less aromatic, more labile
PCA: DOC

- Lower SUVA$_{254}$ — less aromatic, more labile
- Higher SUVA$_{254}$ — more aromatic, less labile

Increasing DOC concentrations
Conclusions:

1. A simple two-component mixing experiment showed a fluorescence linear response.

2. An end-member mixing model using individual peaks is too simplified a method and does not accurately represent the complex downstream mixture.

3. A multivariate regression model using all three peaks can accurately predict %WW effluent within 80% accuracy.

4. PCA distinguished qualitative variability in sample set including DOC, FI values, and SUVA\textsubscript{254}. 
Implications:

- Fluorescence models can be used as predictive tools
- In-situ instrumentation can provide real-time WW monitoring
- Identify point and non-point sources of pollution
- Direct opportune times for expensive discrete analysis (OWC, PCPs, and other emerging contaminants)
Article Info:

http://dx.doi.org/10.1021/es2041114

Contact Info:

Jami Goldman
jgoldman@usgs.gov
503-251-3205