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

NWQMC

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CleanWater Services

CMOP Center for Coastal Margin Observation & Prediction

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Oregon Health & Science University

NSF

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.

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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

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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






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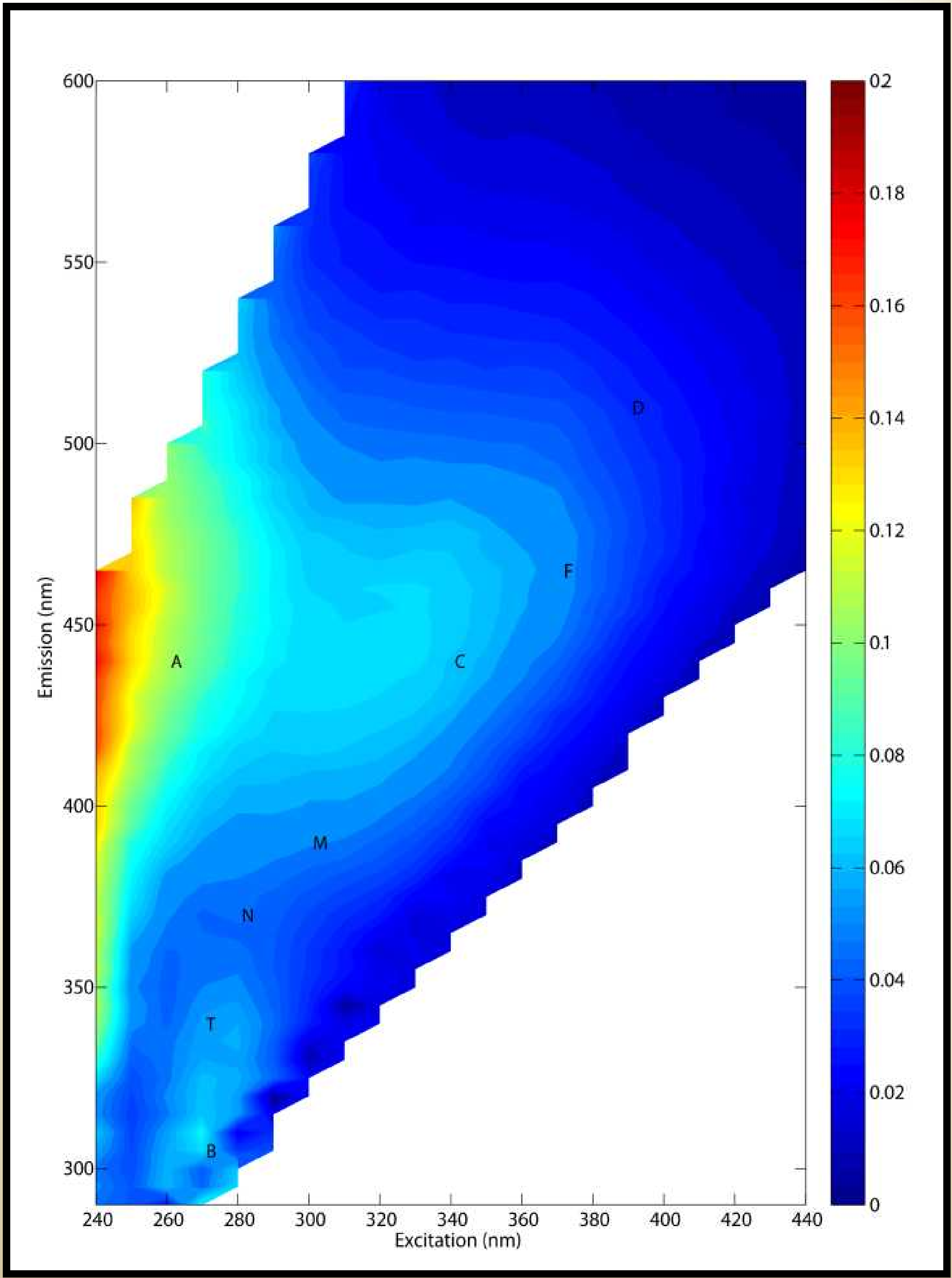
Technology:

- 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

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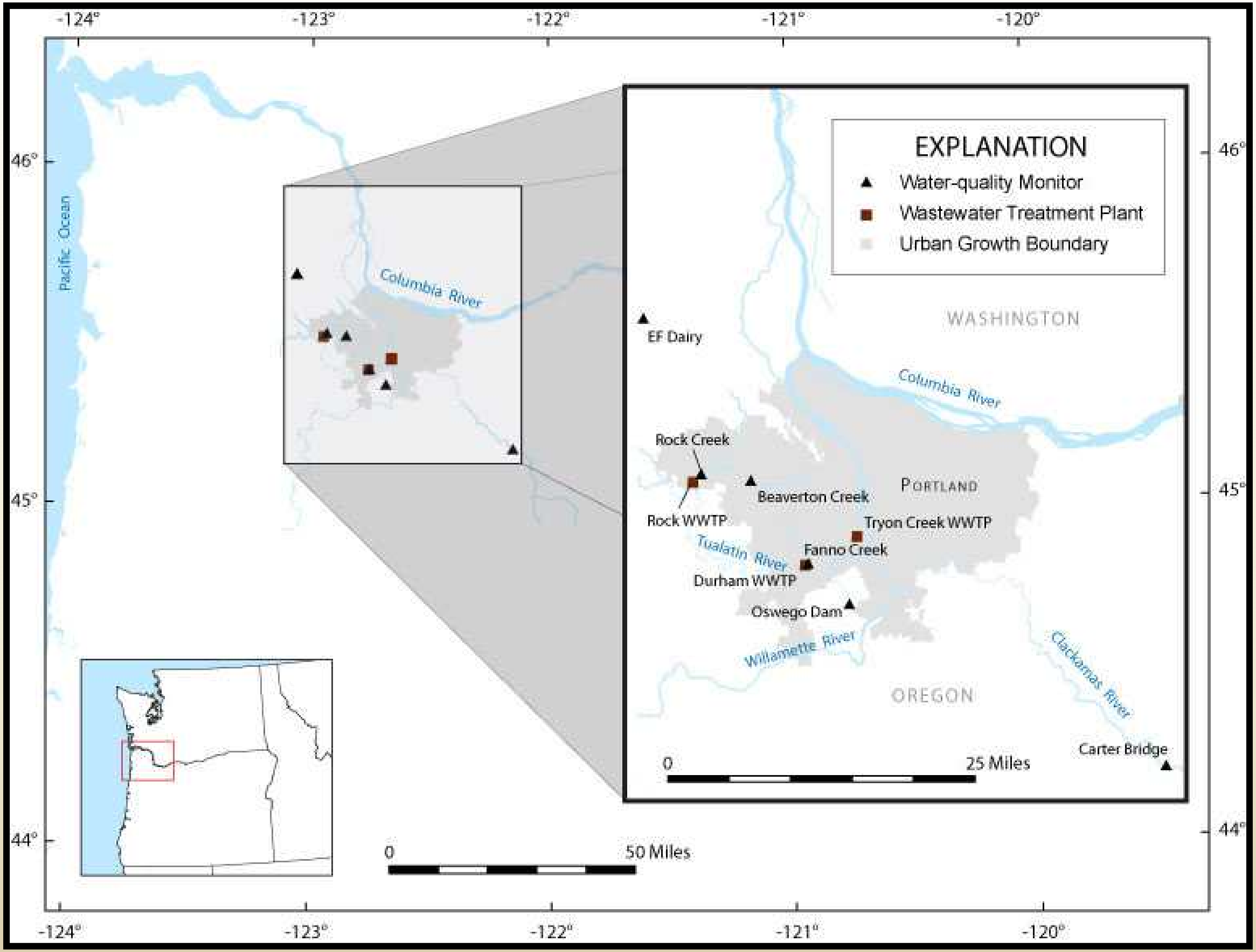
Site Map



(Map designed by Steve Sobieszczyk)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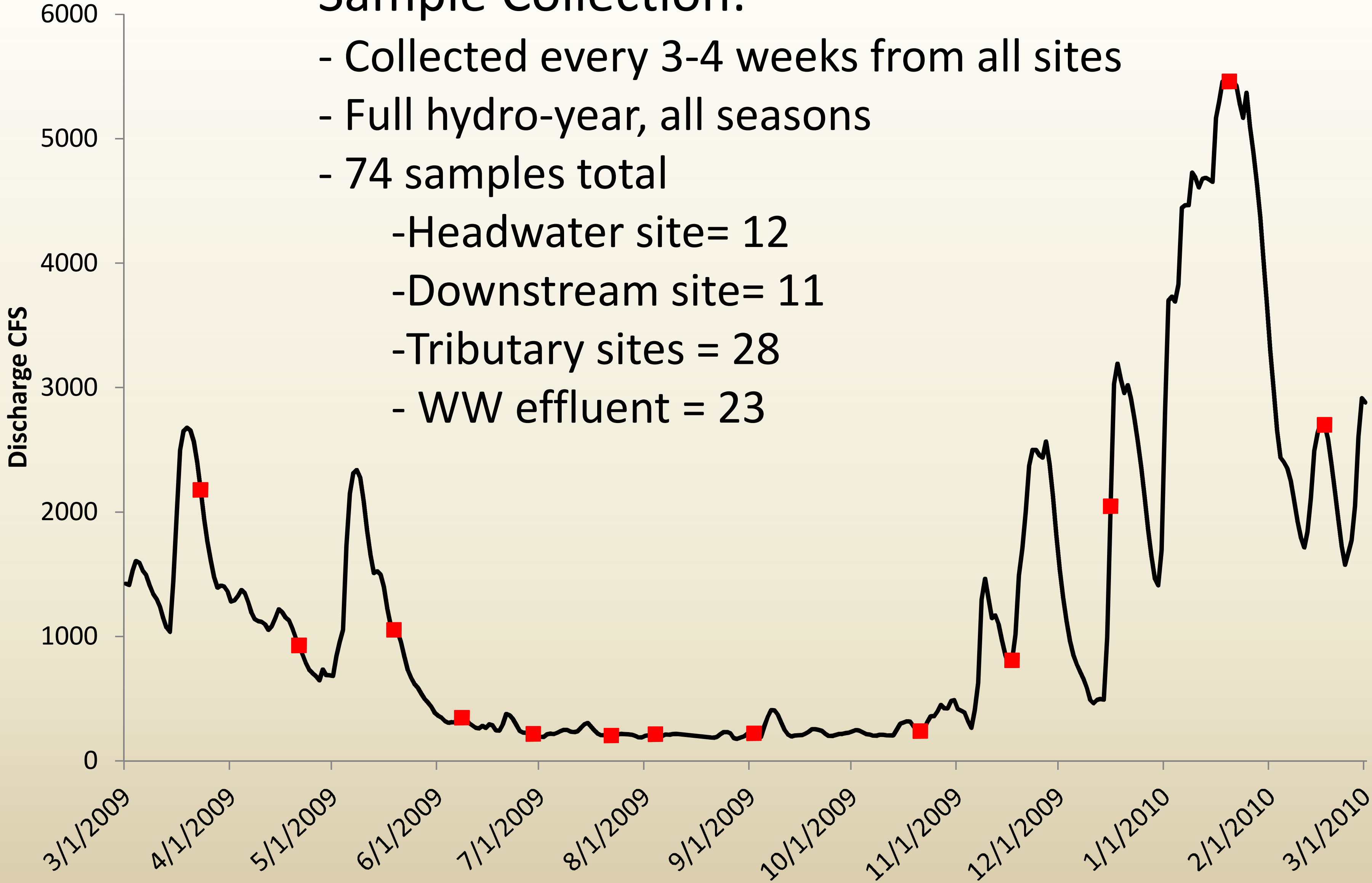
Sample Collection:

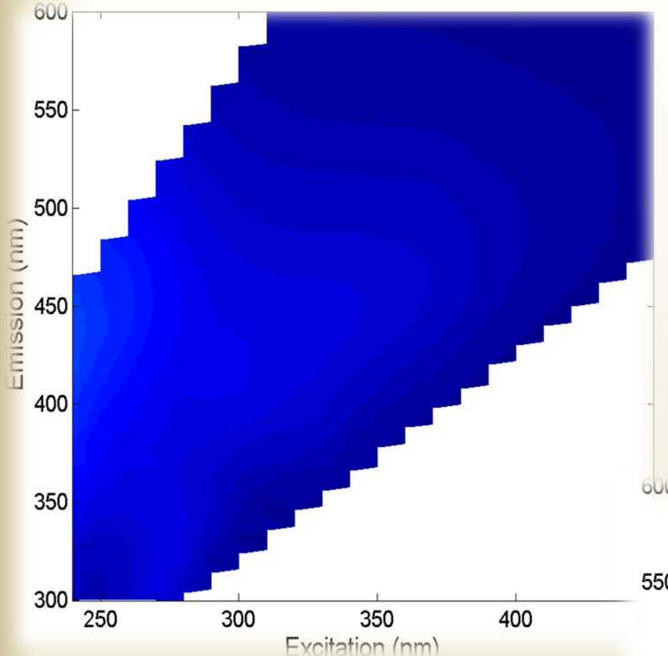
- Collected every 3-4 weeks from all sites
- Full hydro-year, all seasons
- 74 samples total
    - -Headwater site= 12
    - -Downstream site= 11
    - -Tributary sites = 28
    - - WW effluent = 23



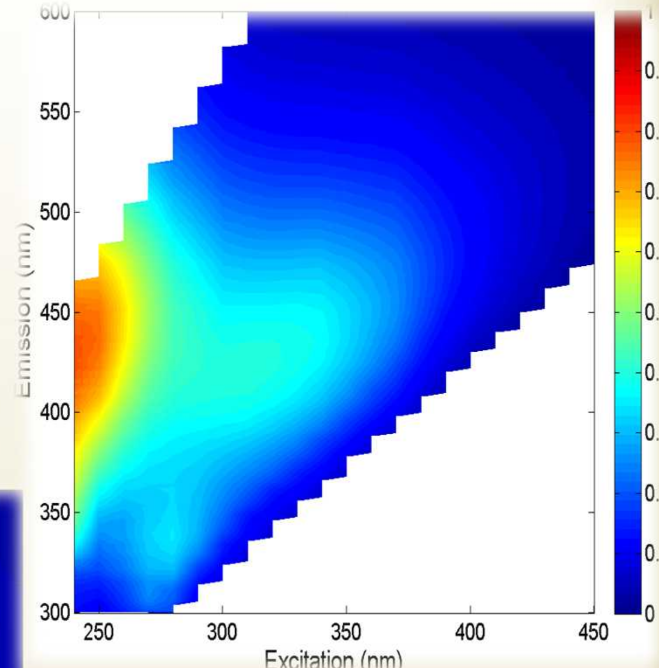
Downstream river site – Tualatin River @ Oswego Dam

Methods:

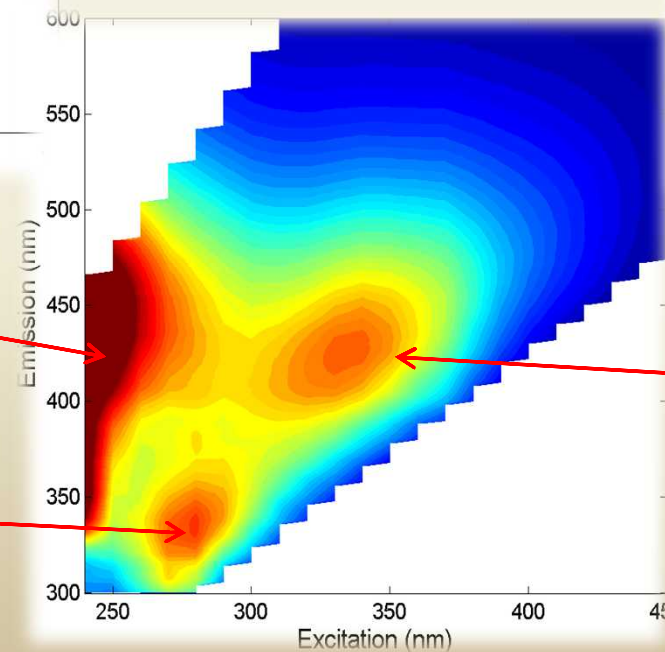
Headwater site



Downstream river site



WWTP site



Peak A

Peak C

Peak T

Parameters of Interest for this study

Fluorescence Peak/Parameter	**Excitation/Emission (nm)**	**Description**
T	270/340	Tryptophan-like, protein like
A	260/450	Humic-like
C	340/440	Humic-like
Fluorescence Index (FI)	Ex370→Em470/Em520	Higher values indicate algal(microbial) vs. terrestrially derived DOC
$SUVA_{254}$	Absorbance at 254nm normalized to DOC	Correlated to aromatic content

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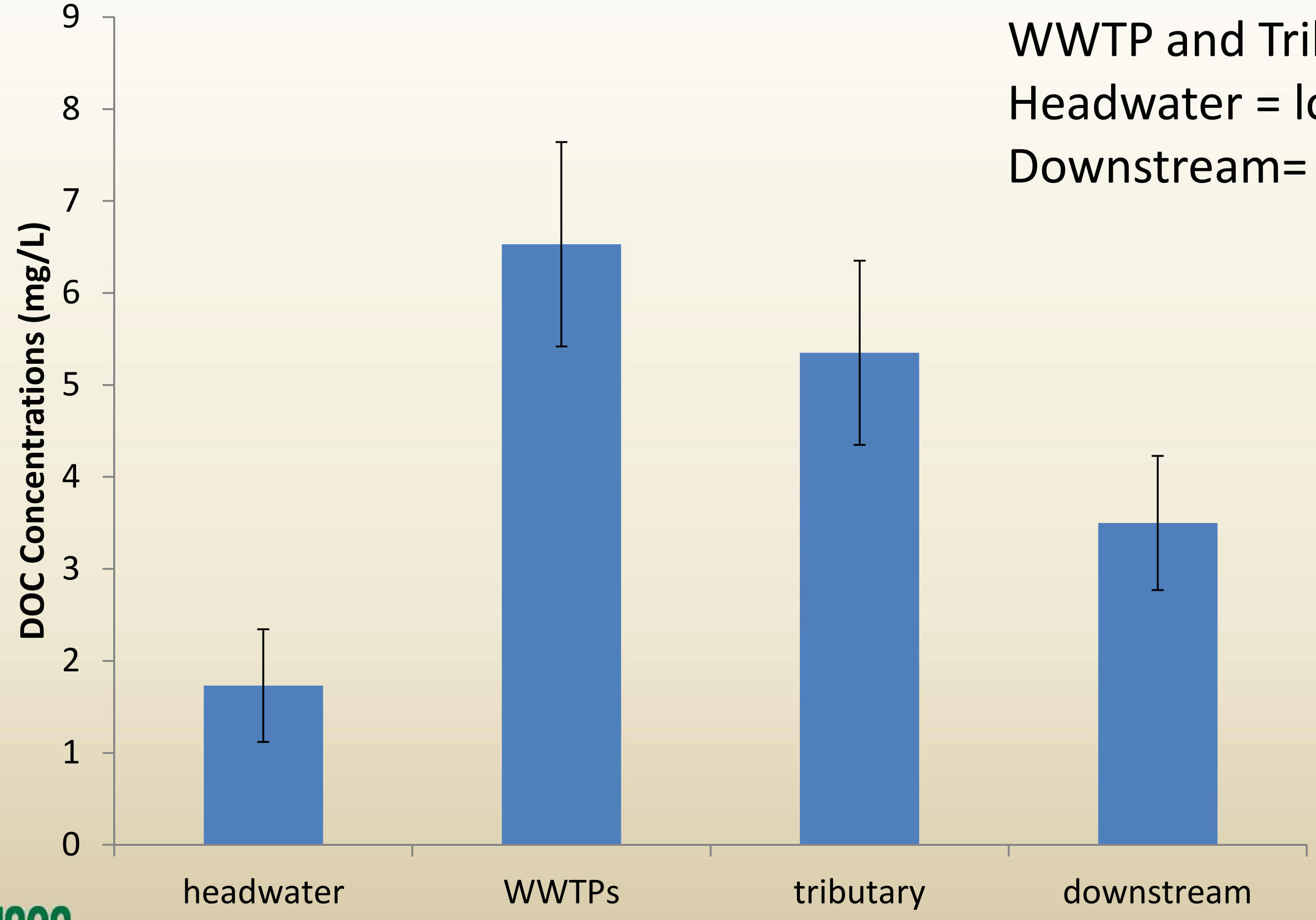
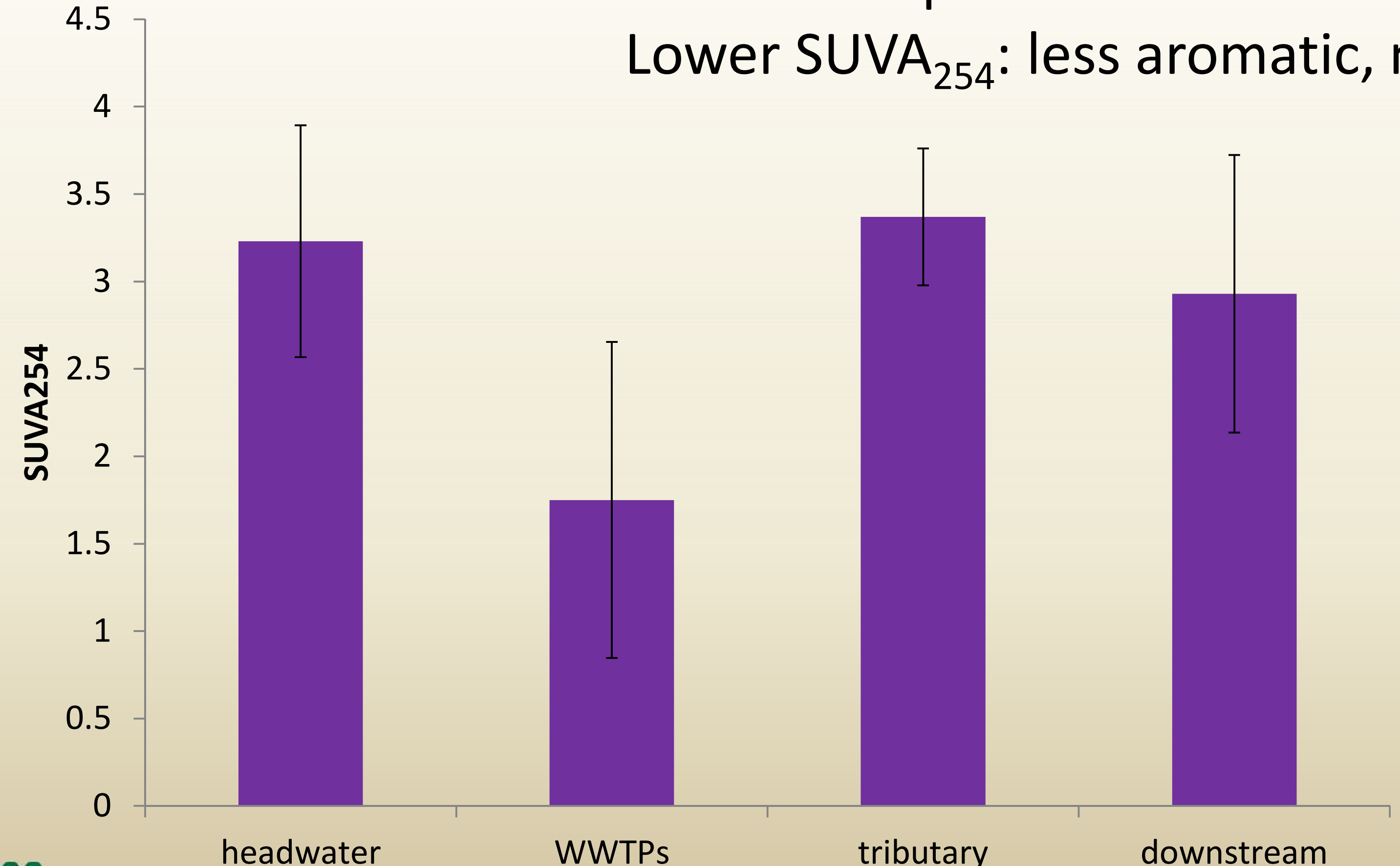
DOC Annual Average Concentrations:



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



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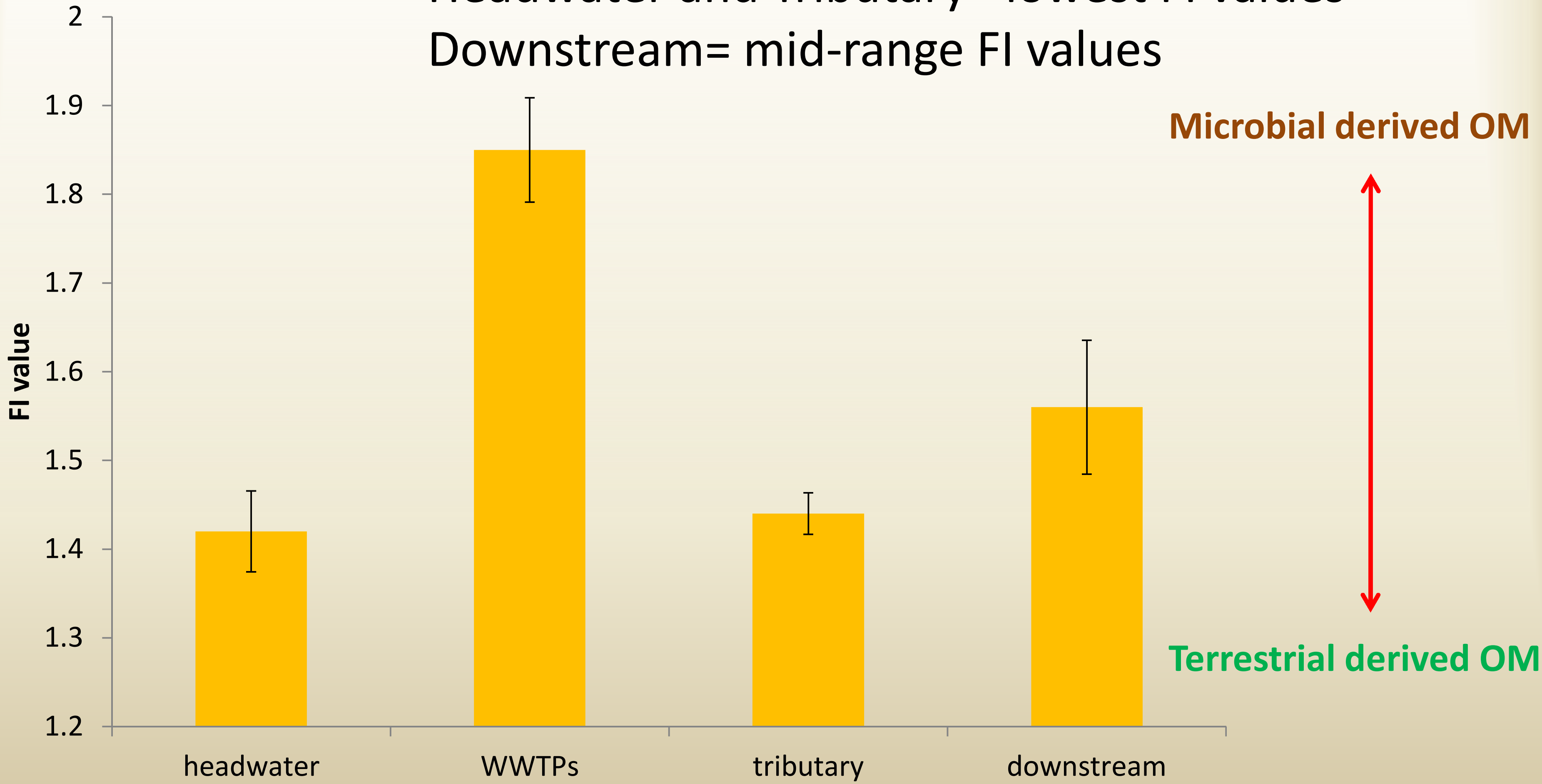
FI Annual Average Values:

WWTP = highest FI values

Headwater and Tributary= lowest FI values

Downstream= mid-range FI values



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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

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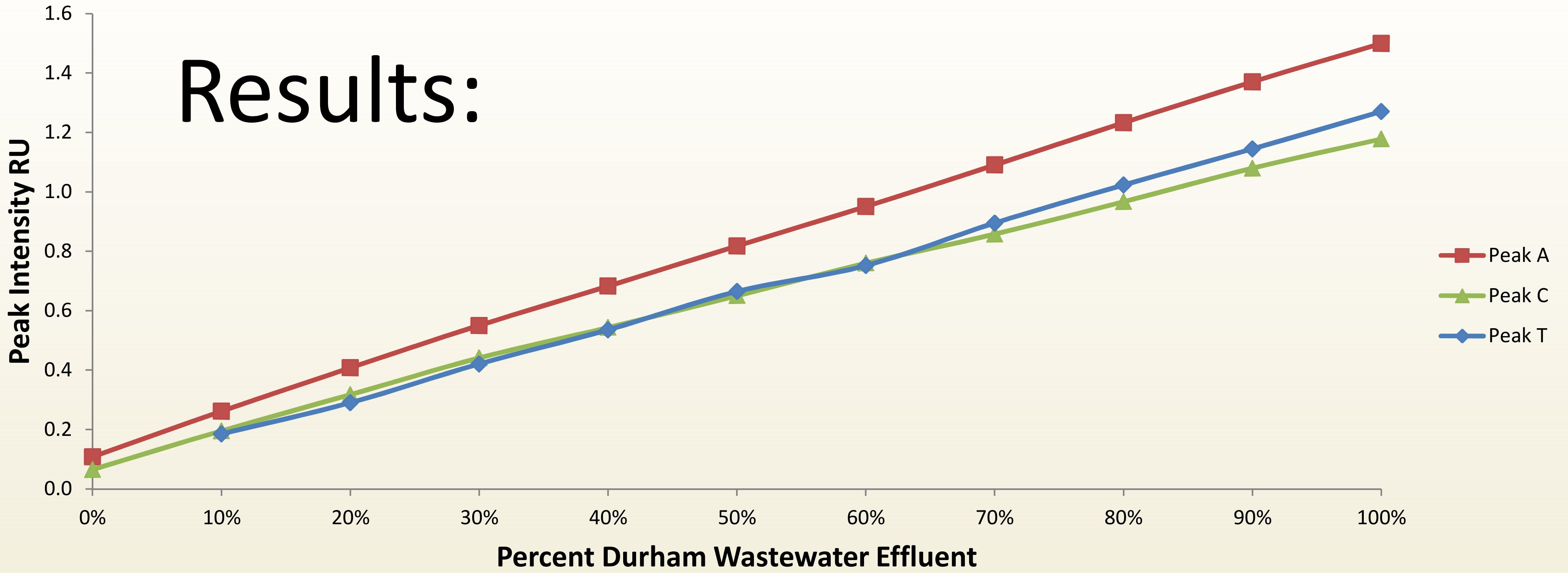
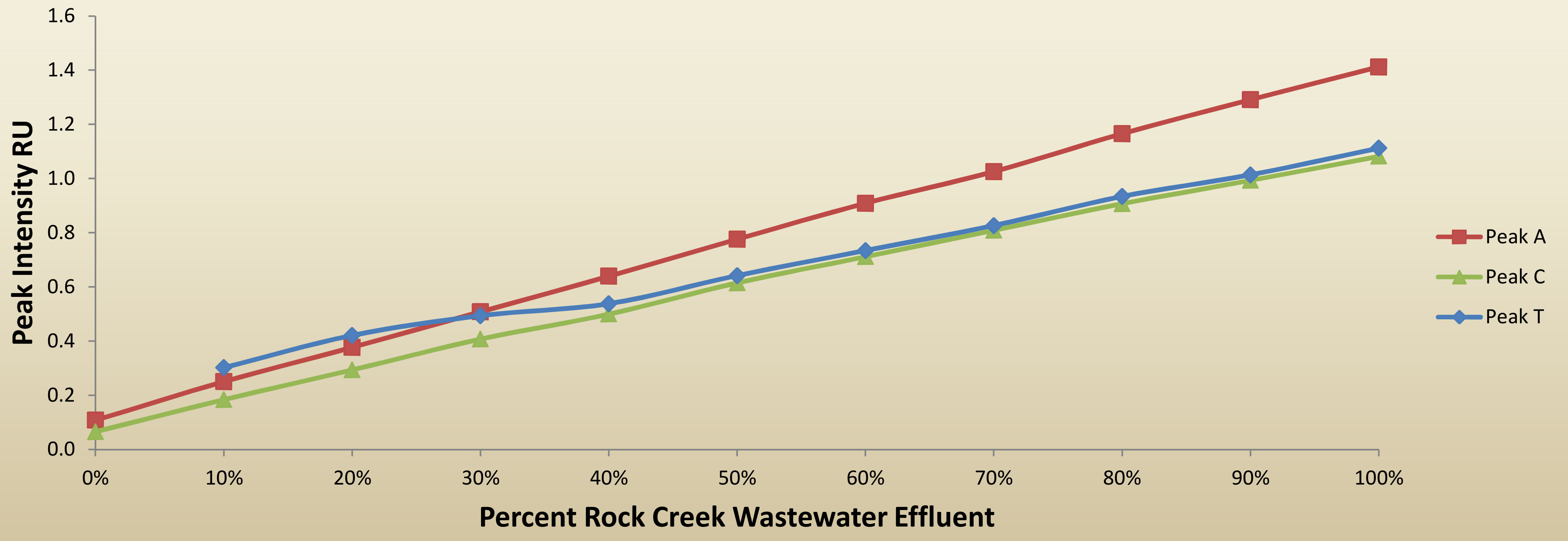
Results:



1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Peak Intensity RU
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Percent Durham Wastewater Effluent
Peak A
Peak C
Peak T



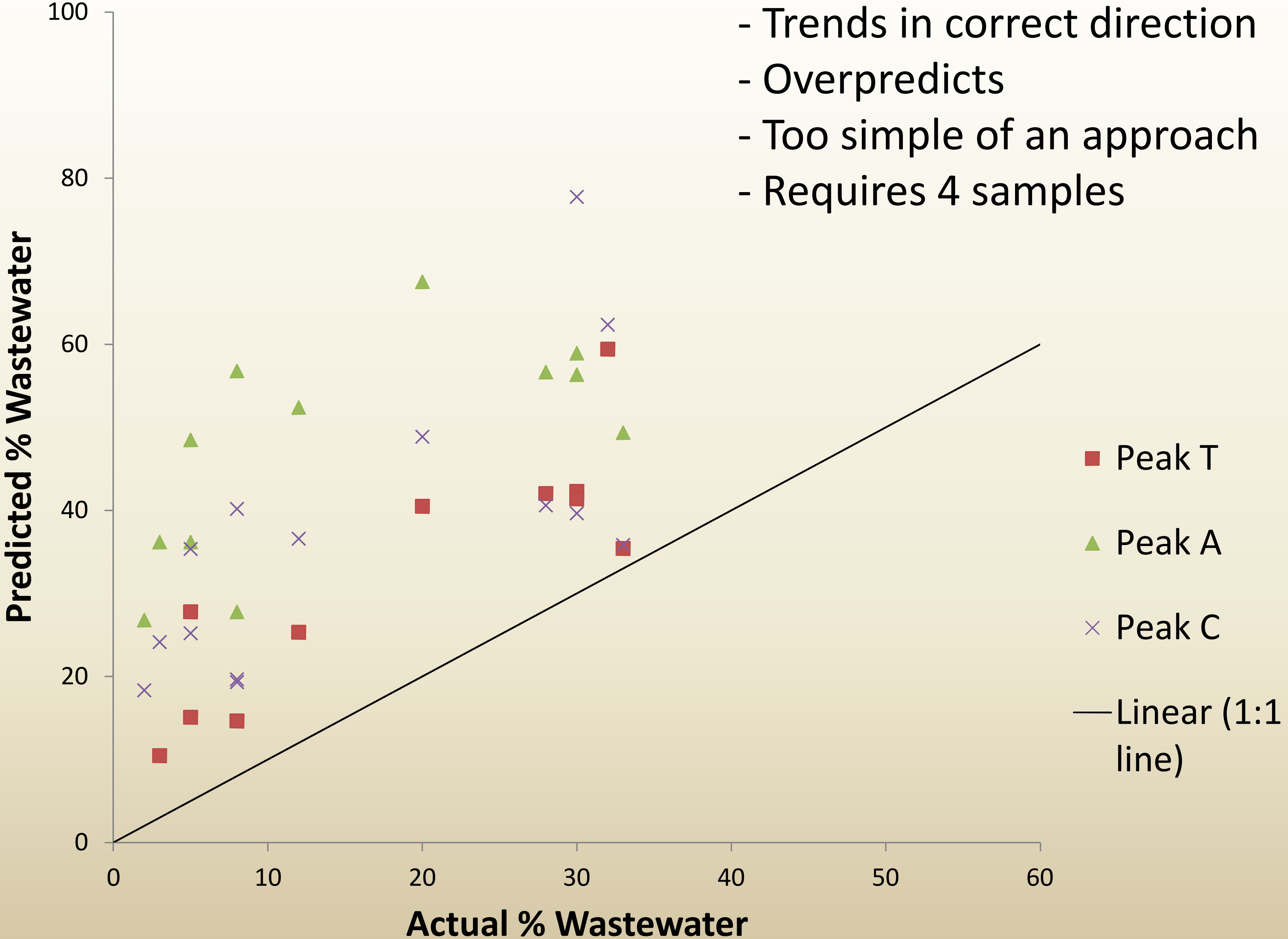
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Peak Intensity RU
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Percent Rock Creek Wastewater Effluent
Peak A
Peak C
Peak T

End-Member Mixing Model

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

$$\text{Percent Wastewater} = \frac{\text{Headwater} - \text{Downstream}}{(\text{Headwater} - (\frac{WW_1 + WW_2}{2}))} * 100$$

- 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

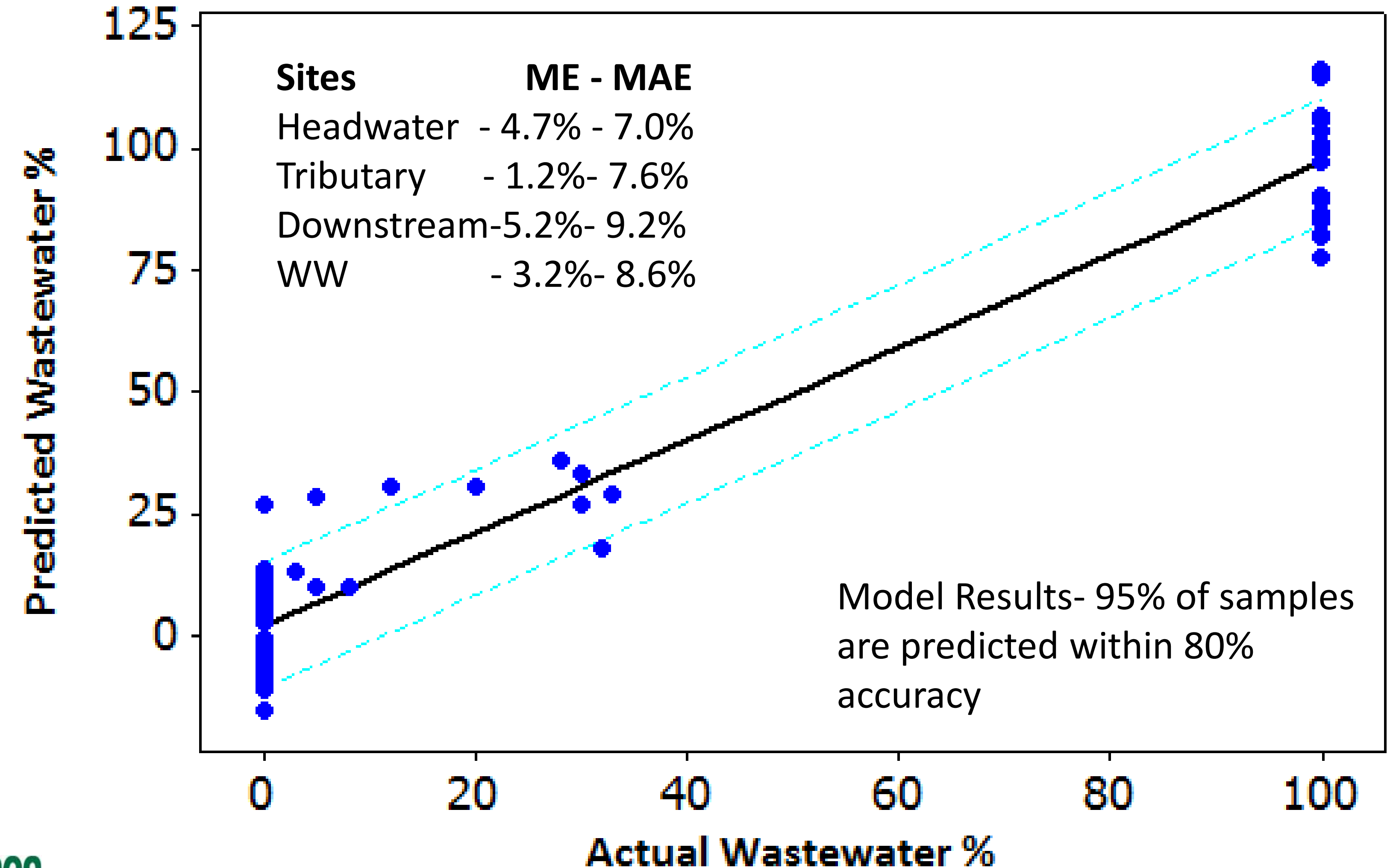
- Goal: Construct a model using multiple fluorescence peaks to quantify percent WW at downstream river site
  - Model Inputs: 74 total samples (12 headwater, 28 tributary, 11 downstream, 23 WWTP)
    - Headwater and tribs set at 0% WW
    - WWTP set at 100% WW
    - Downstream %WW calculated from Tualatin 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%)

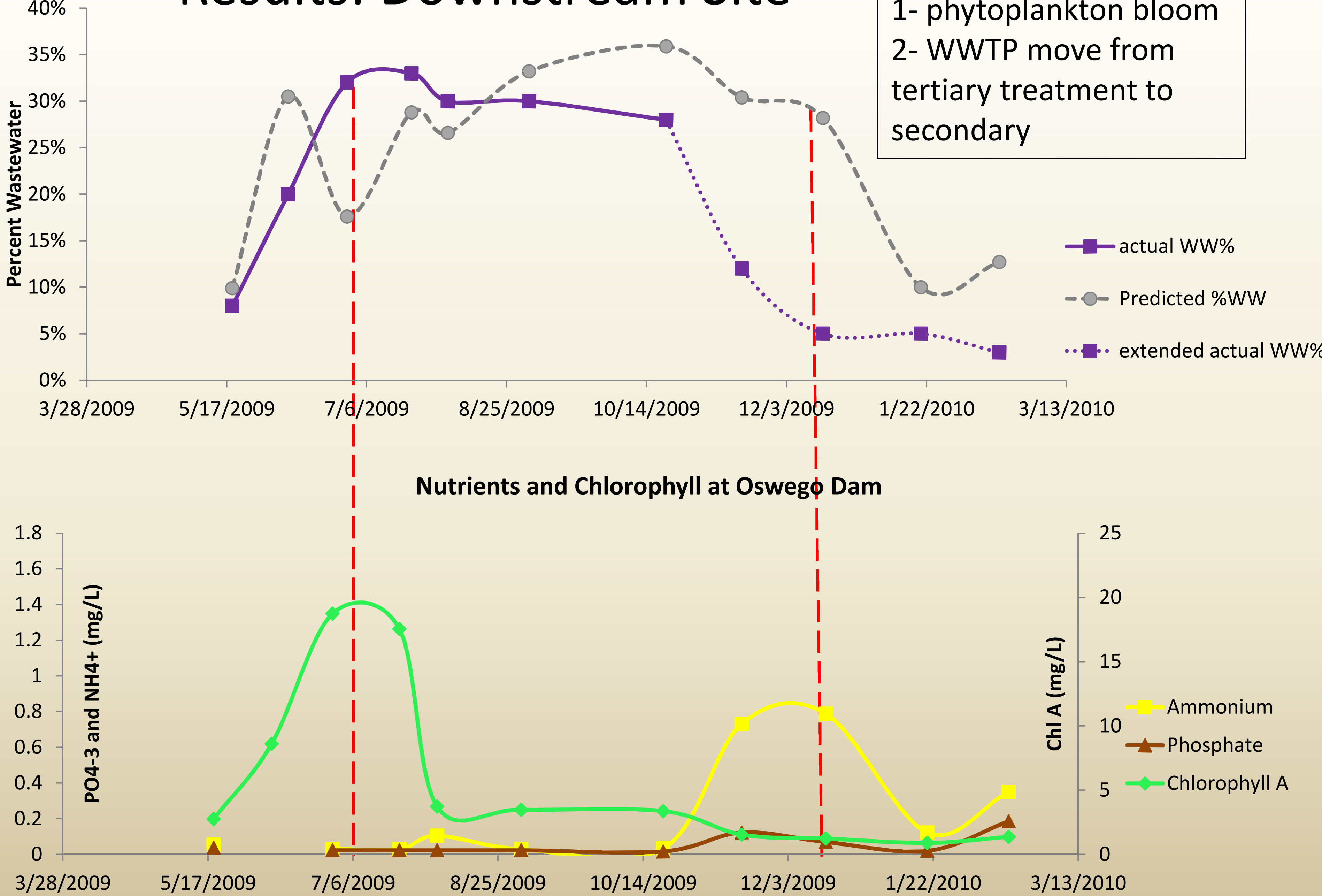
Results:

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



Results: Downstream Site

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



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

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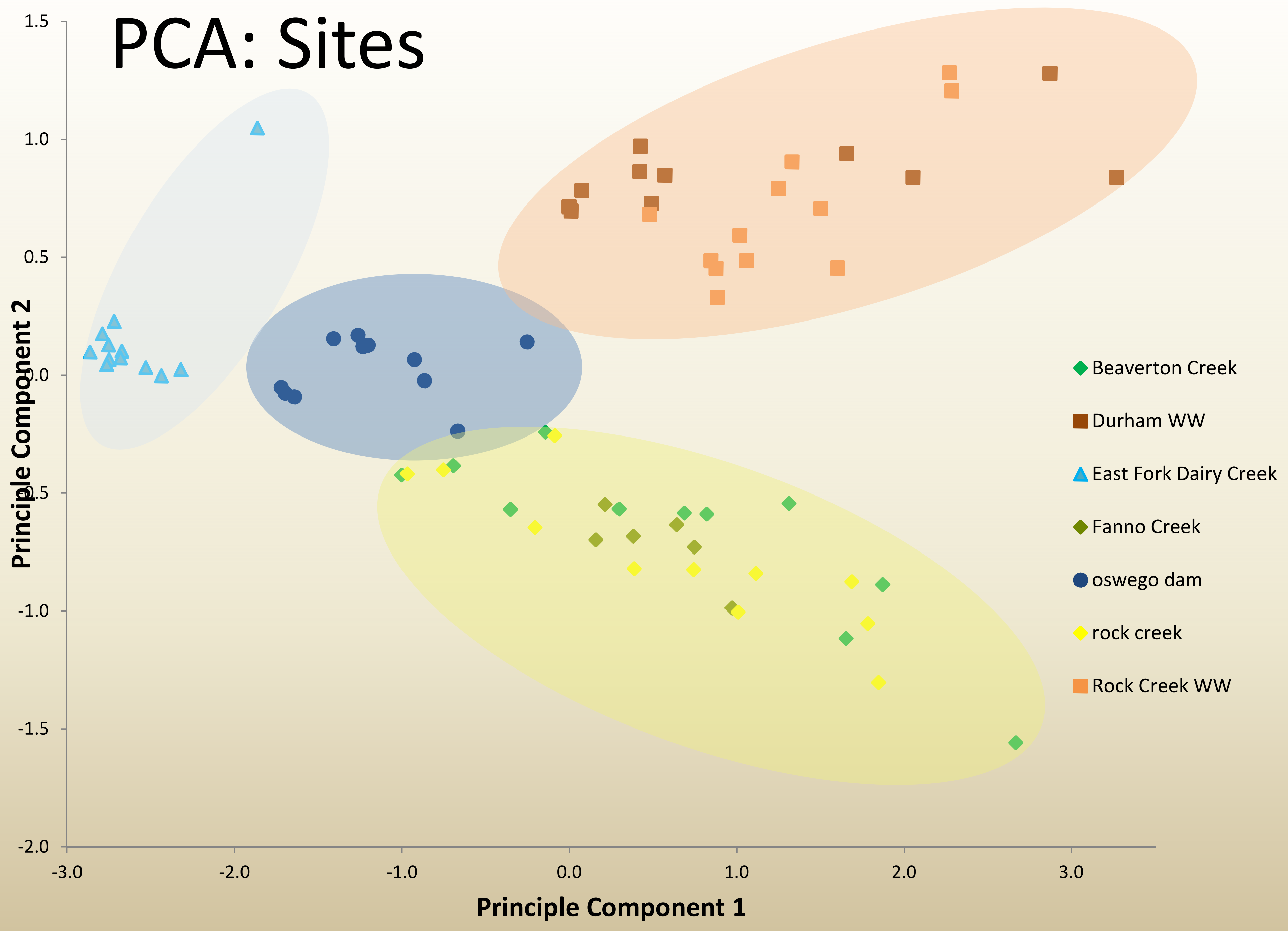
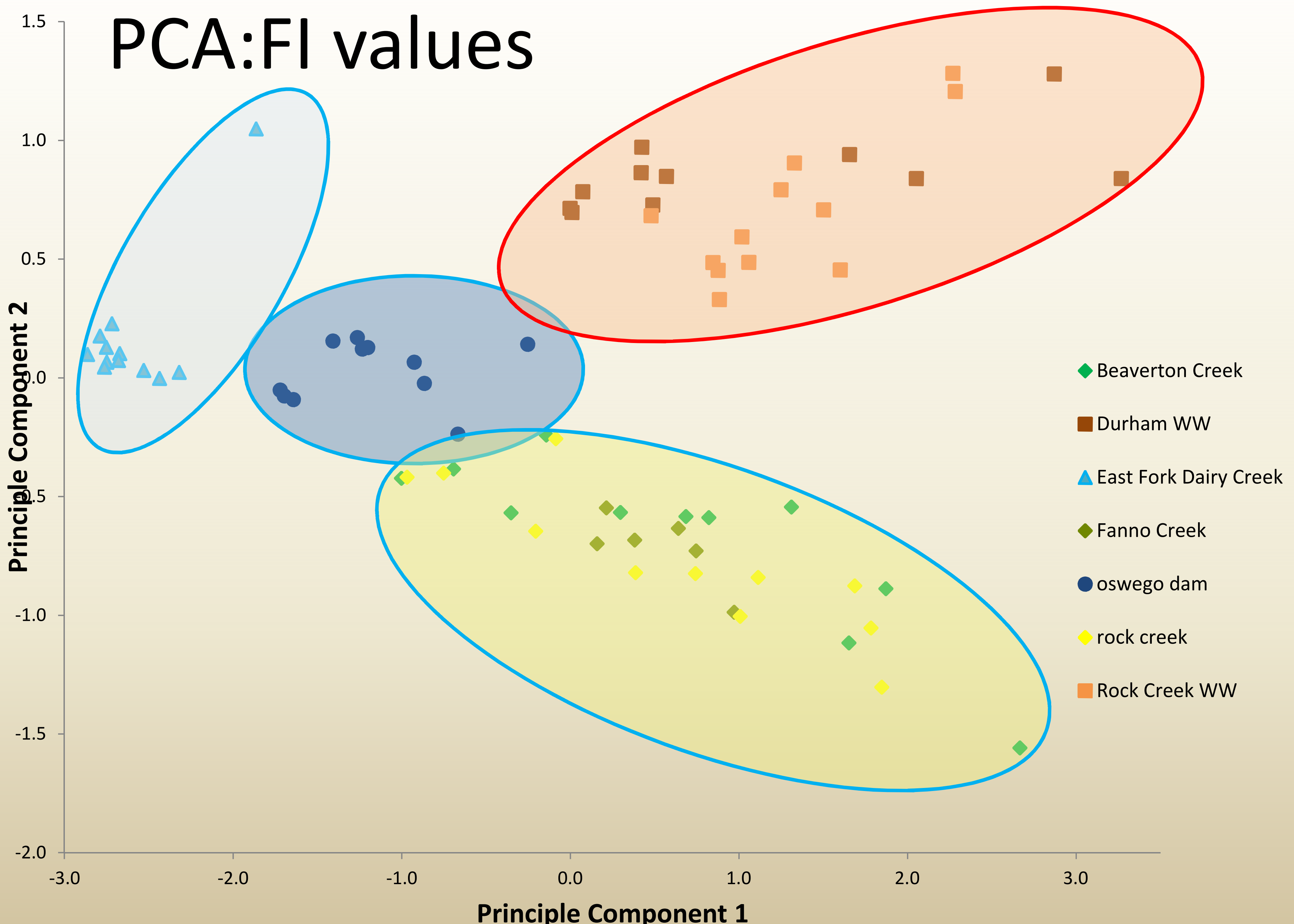
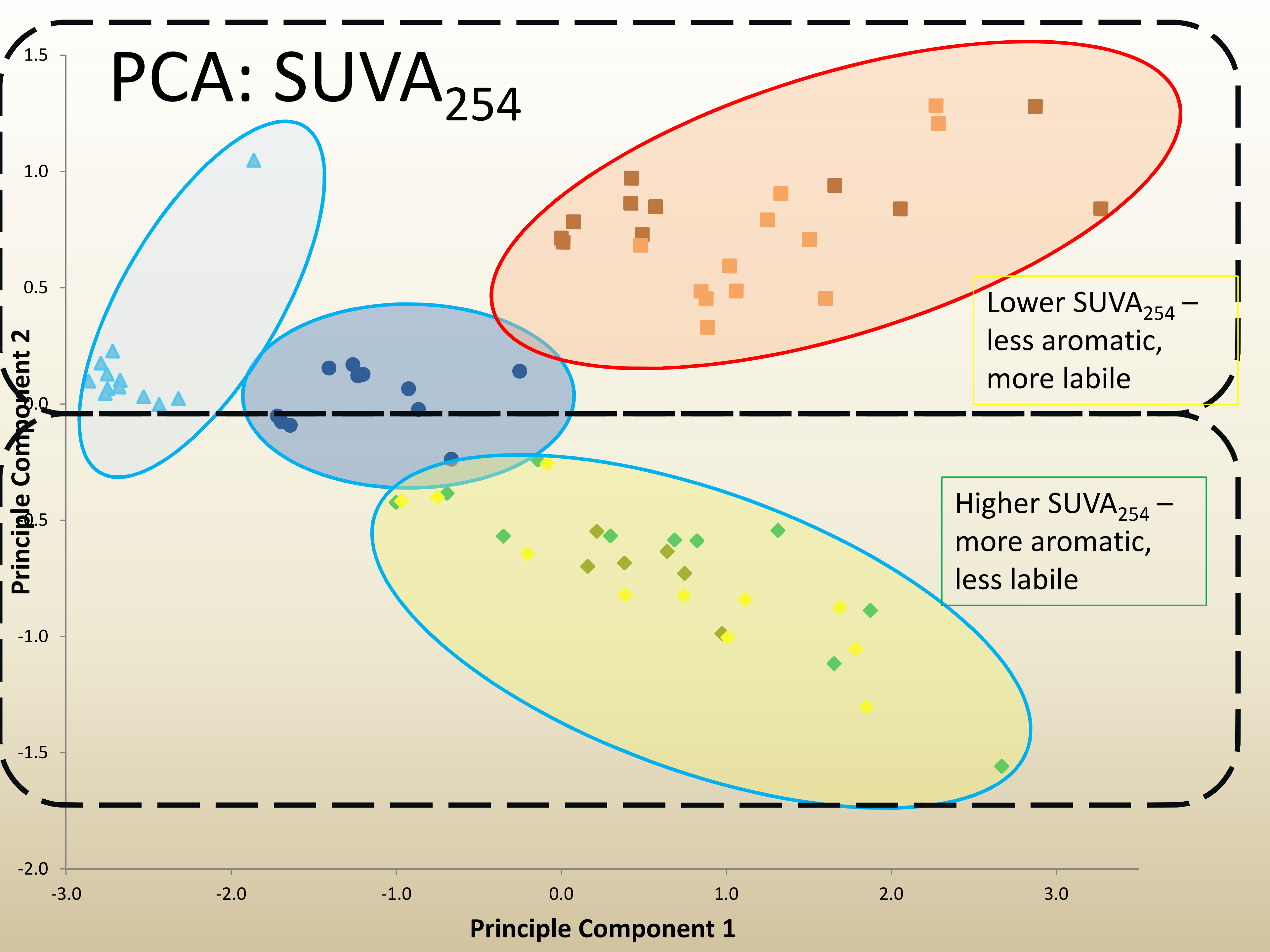
PCA: Sites



1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
Principle Component 1
Principle Component 2
Beaverton Creek
Durham WW
East Fork Dairy Creek
Fanno Creek
oswego dam
rock creek
Rock Creek WW

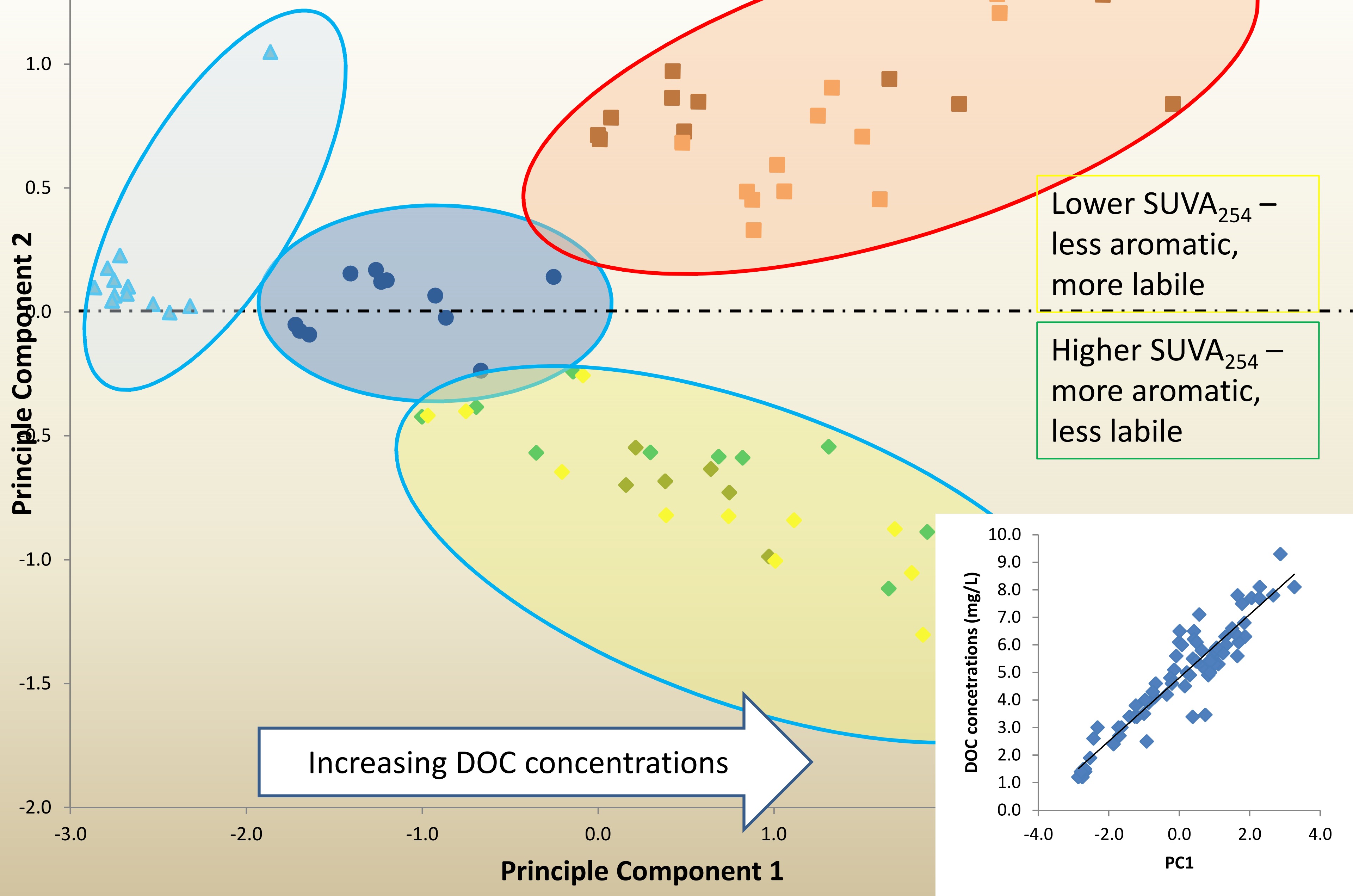
PCA:FI values





PCA: $SUVA_{254}$
Lower $SUVA_{254}$ – less aromatic, more labile
Higher $SUVA_{254}$ – more aromatic, less labile
Principle Component 2
Principle Component 1
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0

PCA: DOC



1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-3.0
-2.0
-1.0
0.0
1.0
Principle Component 2
Principle Component 1
Lower $SUVA_{254}$ – less aromatic, more labile
Higher $SUVA_{254}$ – more aromatic, less labile
Increasing DOC concentrations
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-4.0
-2.0
0.0
2.0
4.0
DOC concetrations (mg/L)
PC1

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 $SUVA_{254}$

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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)

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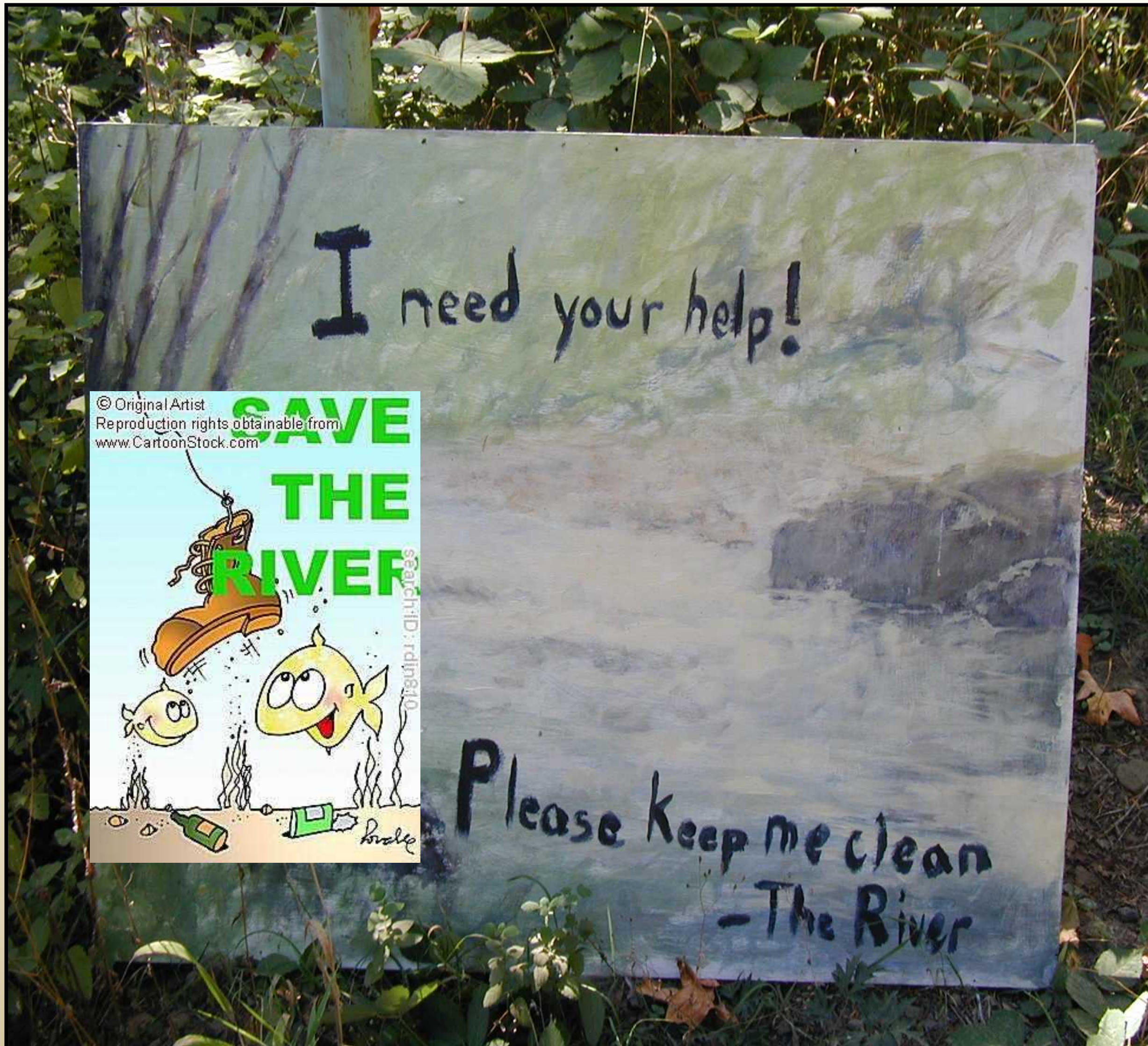

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