Characterization of Oil Sands Naphthenic Acids in Oil Sands Process-Affected Waters Using Fluorescence Technology

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Presentation Outline

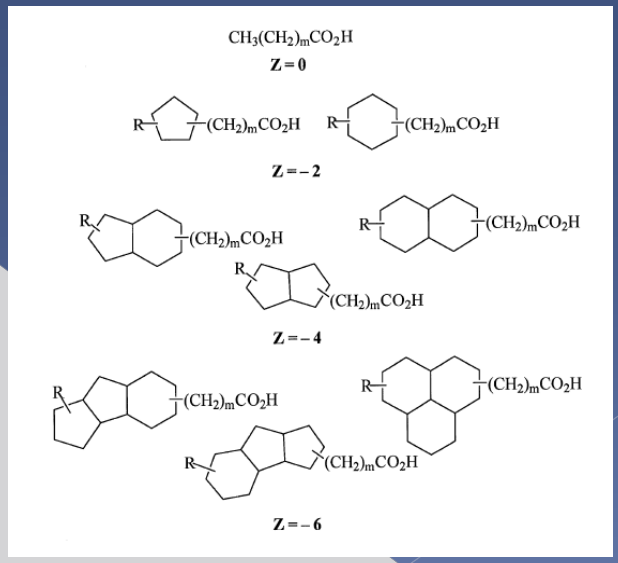
- Introduction – Oil Sands
- Background – Naphthenic Acids
- Background – Fluorescence
- Method and Materials
- Results
- Discussion
- Concluding Remarks
- Acknowledgements

Athabasca Oil Sands

- Oil sands largest deposit outside the Middle East
  - 1.7 trillion barrels recoverable with current technologies
- Tailings generated during Hot Water Extraction
  - 1.25 m^3 of tailings per barrel of oil
  - Policy of zero discharge results in large wastewater storage ponds
  - Ponds cover over 70 km^2

Naphthenic Acids

- Extraction process releases naphthenic acids to oil sands process-affected water
  - Concentrate in tailings ponds: average 110 mg/L
- Identified as cause of process water toxicity
  - Toxic effects observed at < 5 mg/L
- No quantitative analytical technique
- Polar organic carboxylic acids found in crude oil
  - Alkyl-substituted acyclic and cycloaliphatic
  - General formula $C_nH_{2n+Z}O_2$
    - n = carbon number
    - Z = degree of cyclization



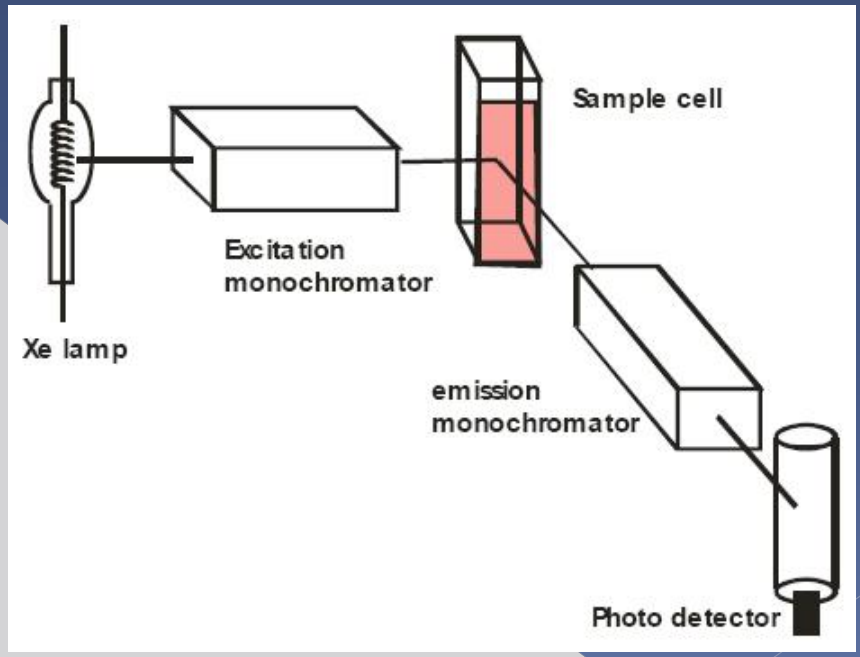
Holowenko et al. 2001

Fluorescence

- Fluorescence spectrophotometry used as a routine analytical technique in medical and environmental applications.
  - Highly sensitive, simple, quick, cost effective.
  - Samples not affected or destroyed.
  - No hazardous by-products generated.
- Primarily used to analyze aromatic or highly unsaturated organic molecules. Fluorescence detects the presence of double bonds.

Fluorescence Theory

- Ultra-violet light provides energy to promote electrons to an excited state.
  - Electrons decay back to ground state, releasing light photons at a characteristic wavelength, resulting in a fluorescent signal.



wikipedia.org/wiki/Fluorescence_spectroscopy

Research Objectives

- Develop fluorescence spectrophotometry as a method to characterize and measure oil sands naphthenic acids.
- Generate fingerprint signatures for oil sands process-affected water and groundwater samples.
  - Determine if contrast between process and ground water samples significant.

Method and Materials

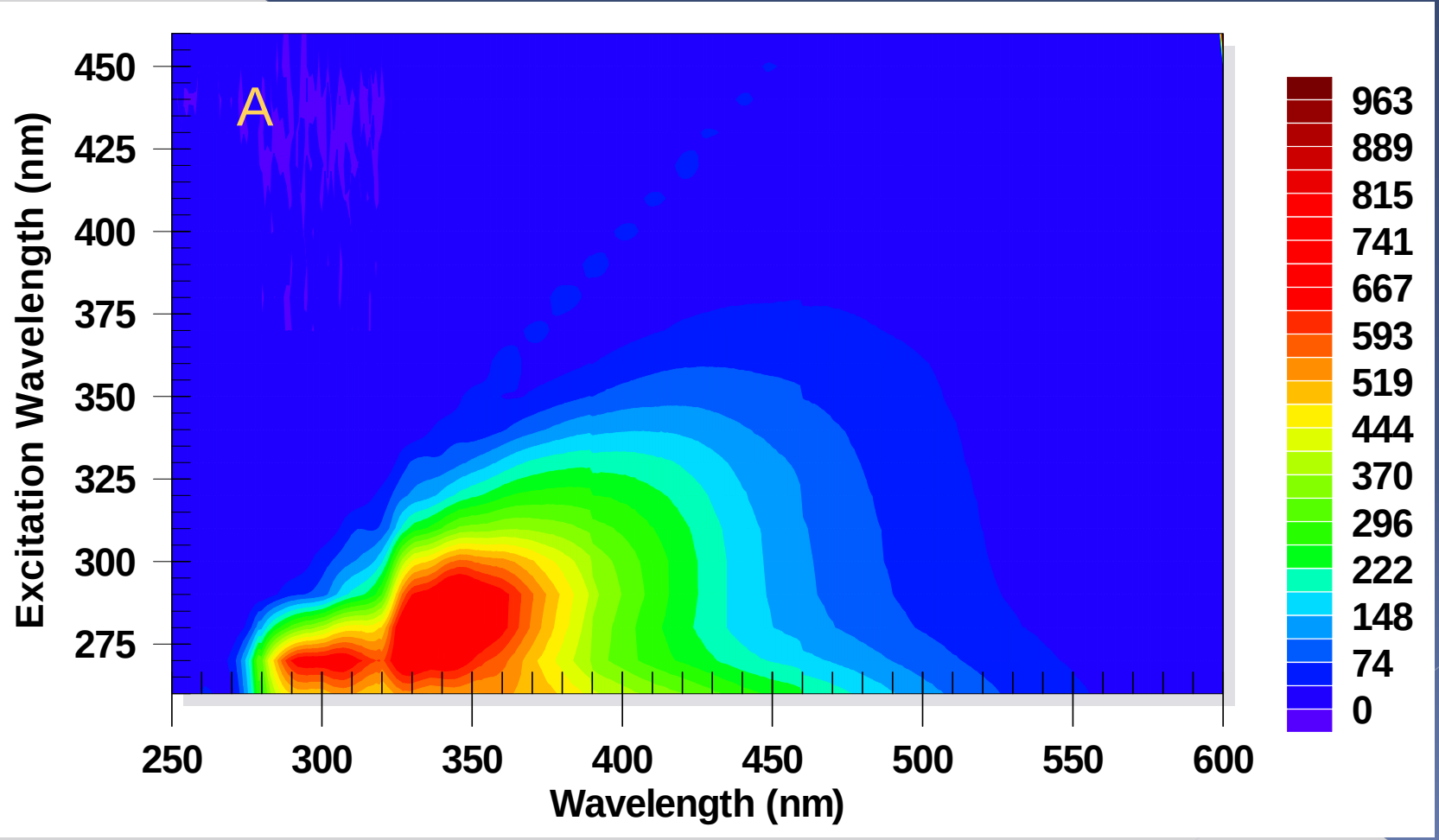
- Five samples analyzed
  - Oil sands process-affected water from three oil sands operators
  - Groundwater collected on site of one oil sands operator
    - GW1 in clay till, GW2 in sand aquifer
- Emission scans prepared for each sample
  - Excitation wavelengths 260 to 450 nm, 10 nm increments
  - Emission wavelengths 250 to 600 nm, 1 nm increments

Results

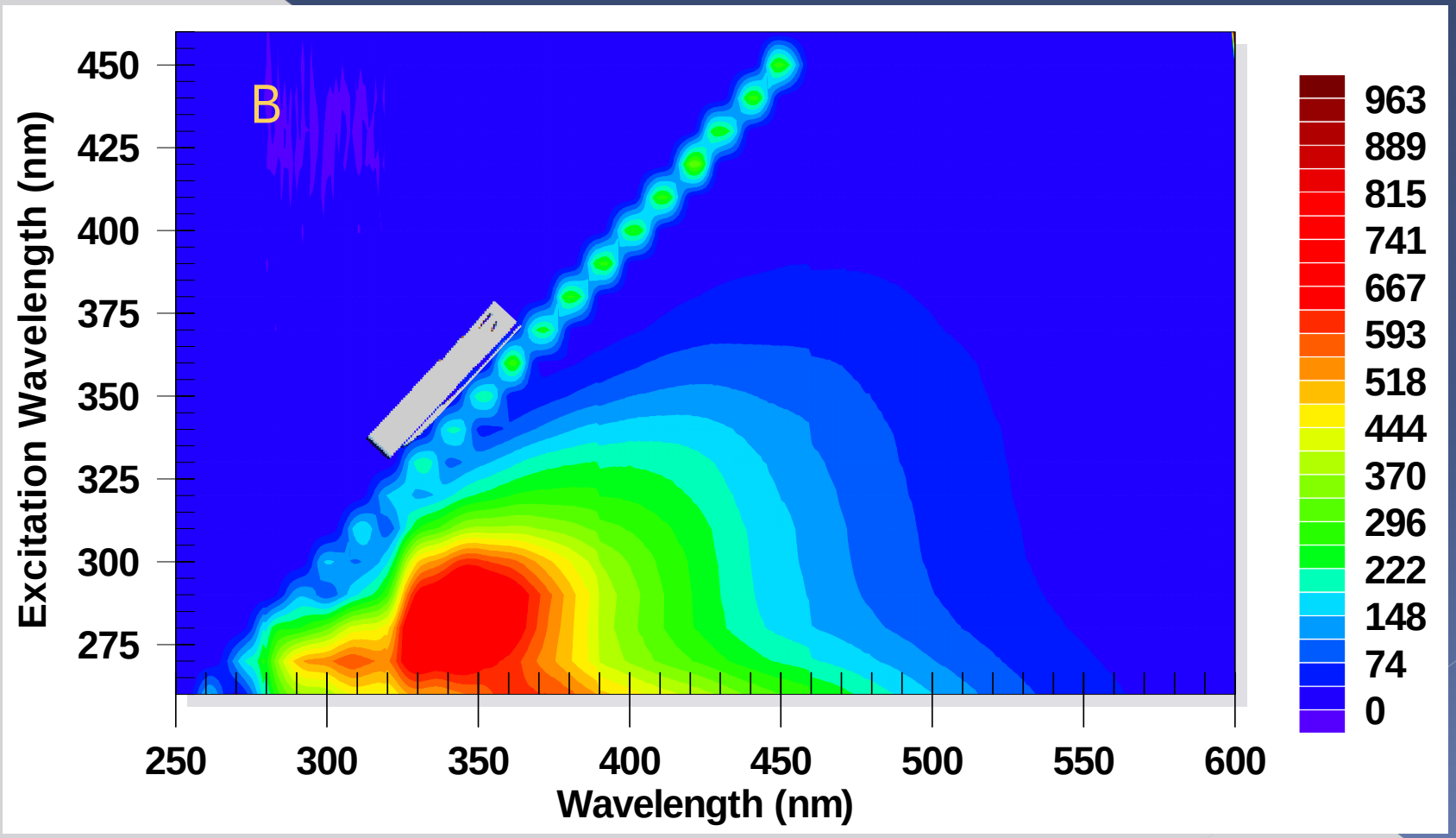
- Qualitative analysis conducted to determine if unique signals, or “fingerprints”, would be detected in samples
- Excitation-Emission Matrices and emission spectra prepared for each sample.

- Unique features detected in each sample.
  - Indicates that fluorescence has promising potential to discriminate and characterize oil sands naphthenic acids.

Process-Affected Water



Process-Affected Water



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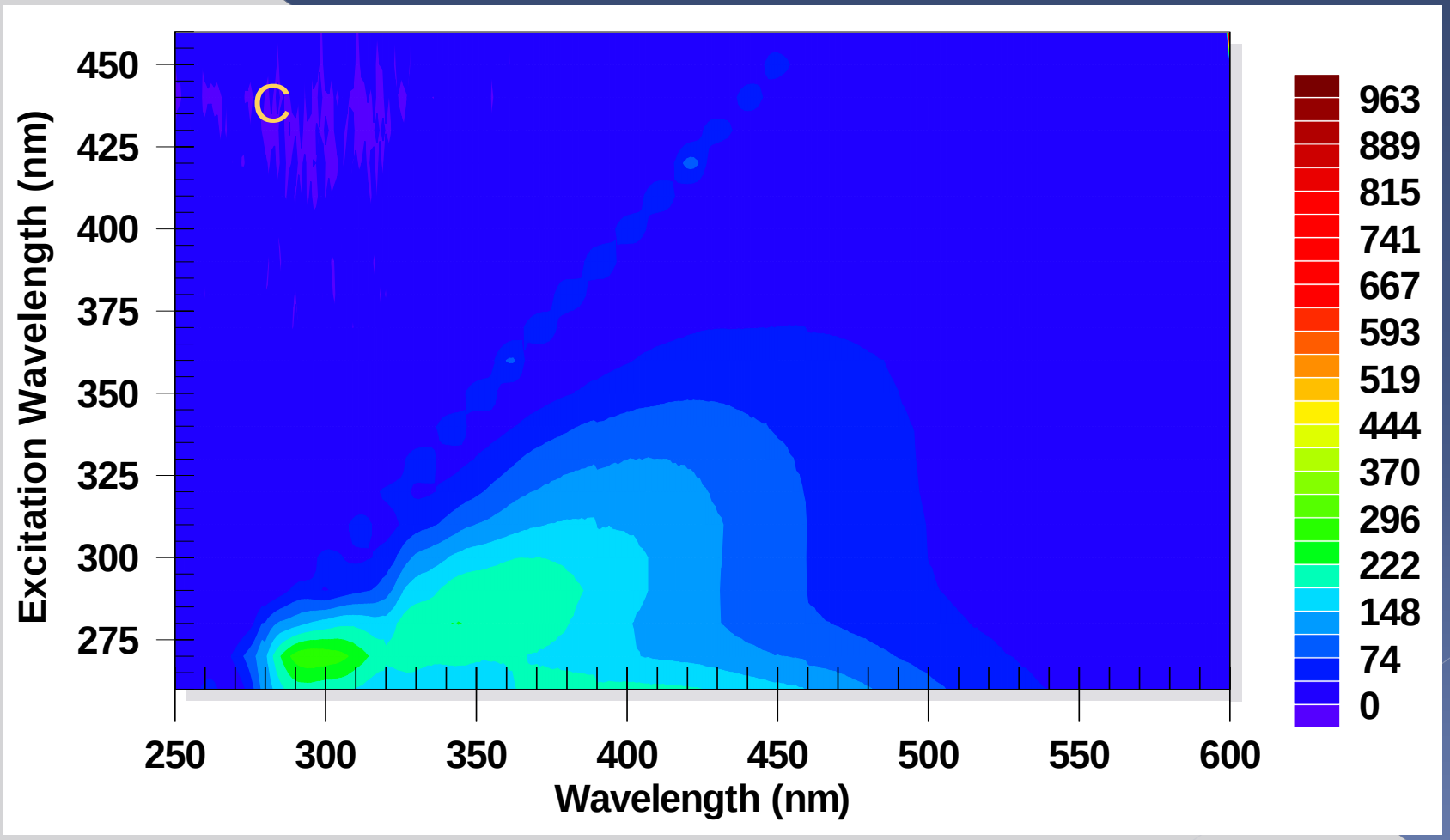
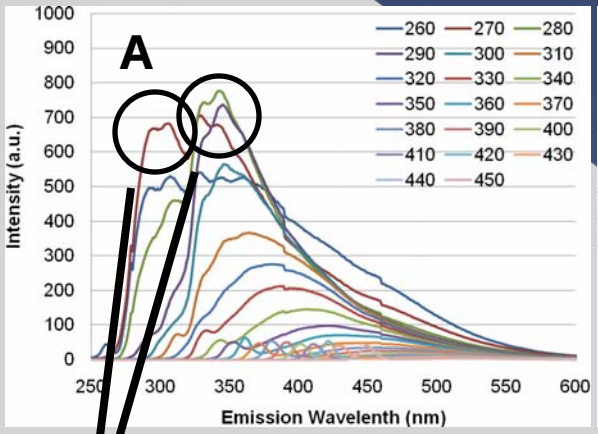
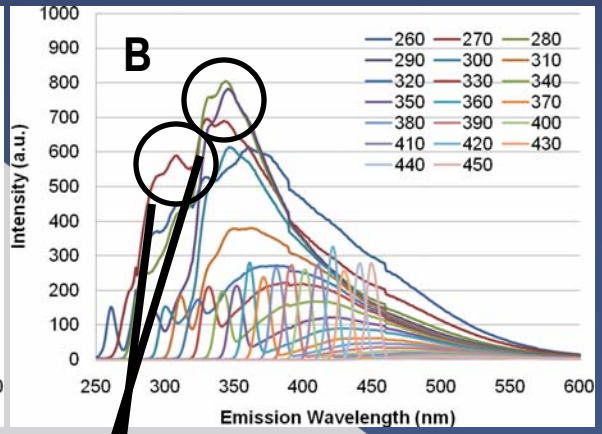


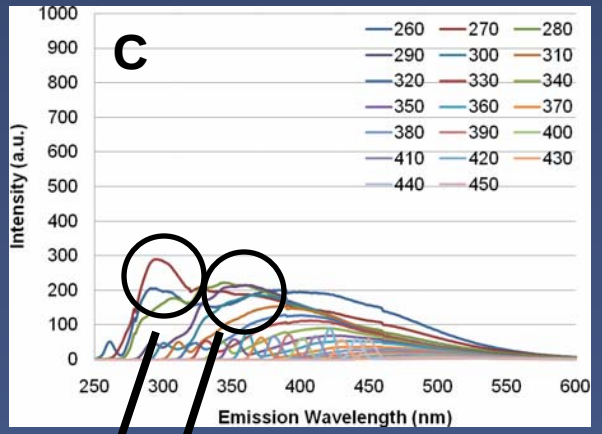
Process-Affected Water



- Peak 1 @ Ex 280 nm, Em 340 nm, Int 765
- Peak 2 @ Ex 270 nm, Em 305 nm, Int 680

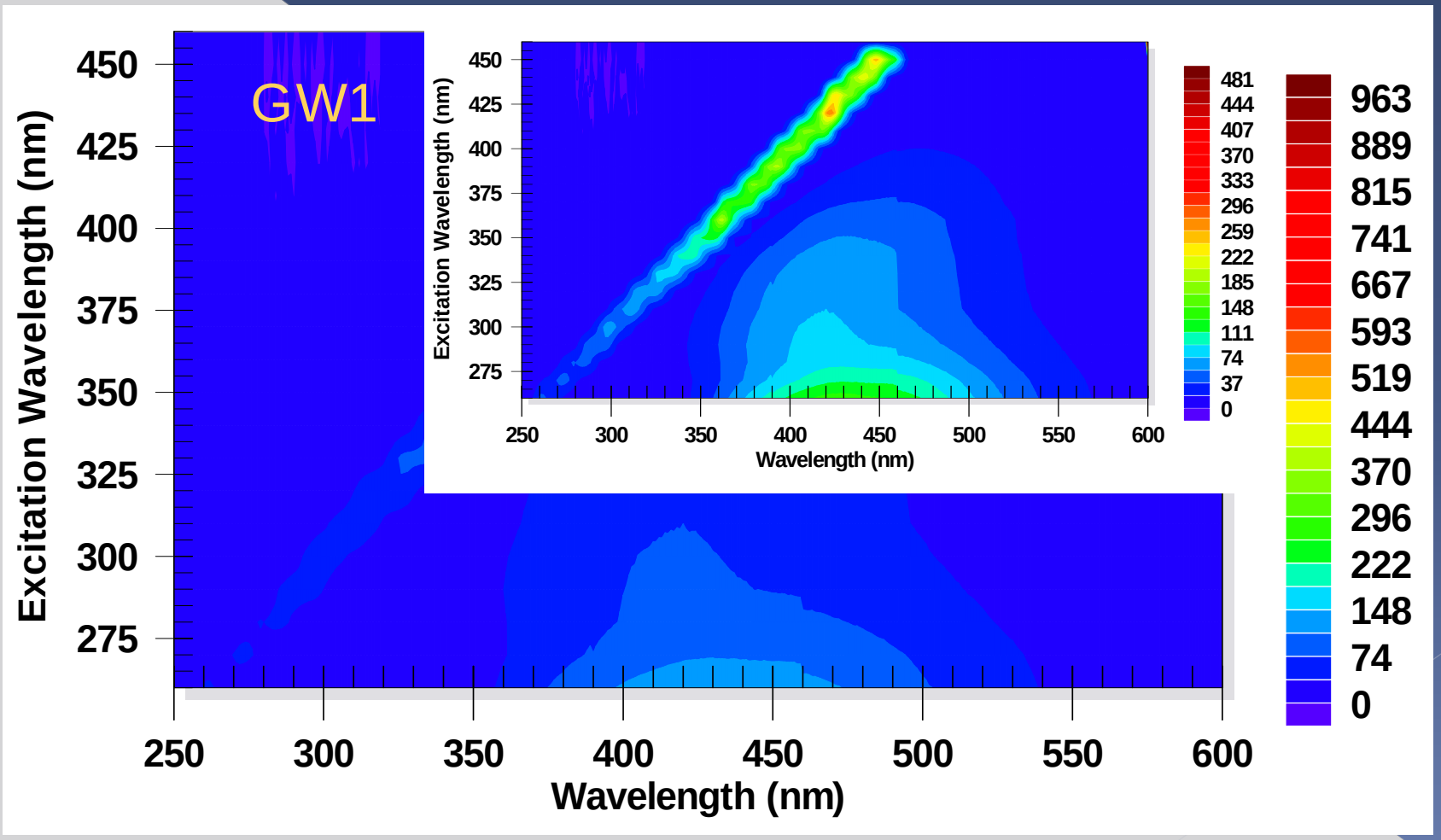


- Peak 1 @ Ex 280 nm, Em 340 nm, Int 799
- Peak 2 @ Ex 270 nm, Em 305 nm, Int 580

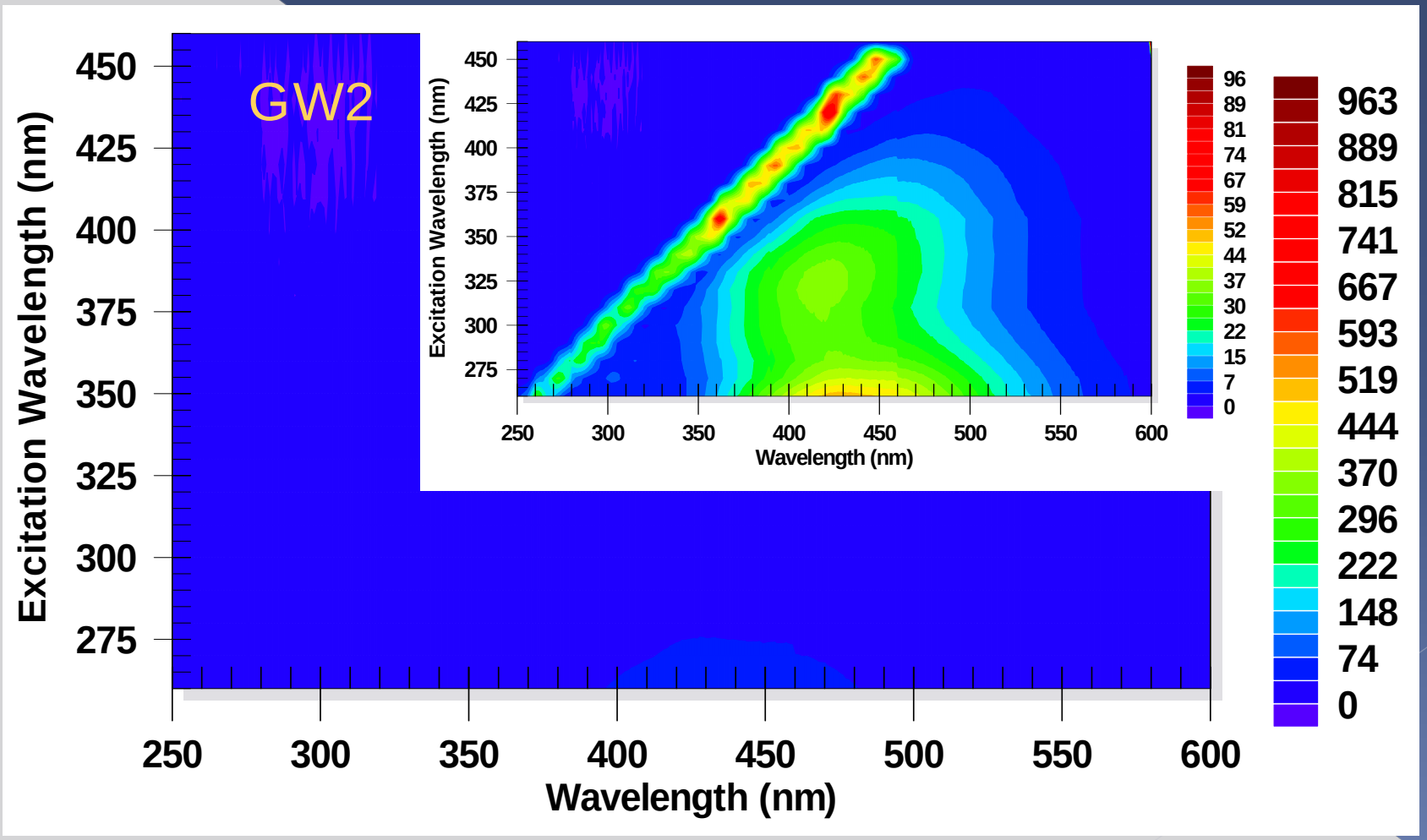


- Peak 1 @ Ex 270 nm, Em 290 nm, Int 287
- Peak 2 @ Ex 290 nm, Em 360 nm, Int 213

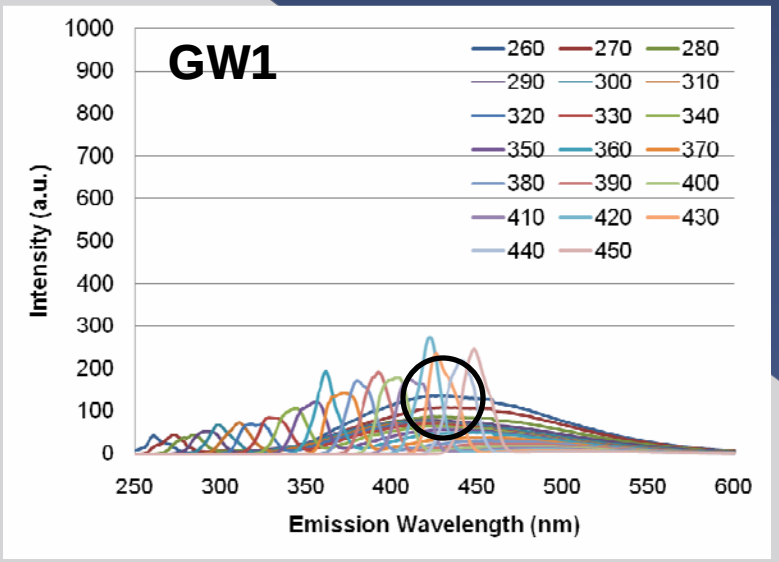
Groundwater – clay till

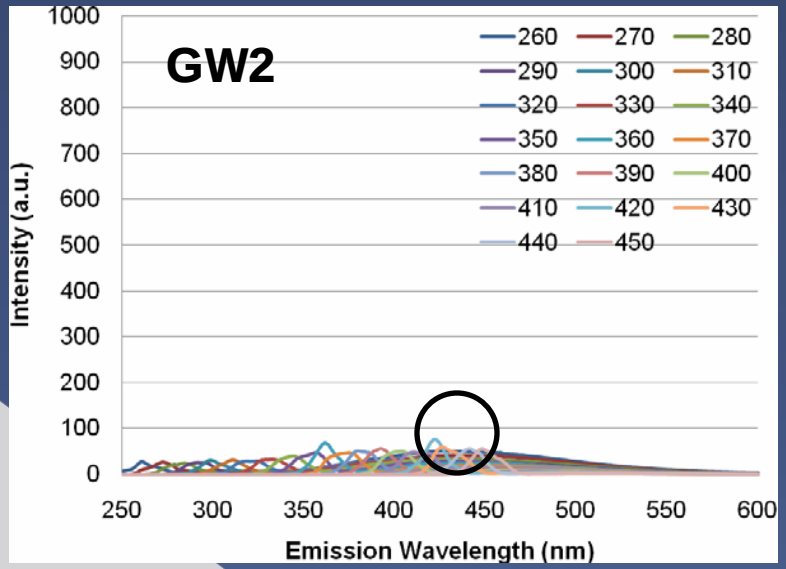


Groundwater – sand aquifer



Groundwater

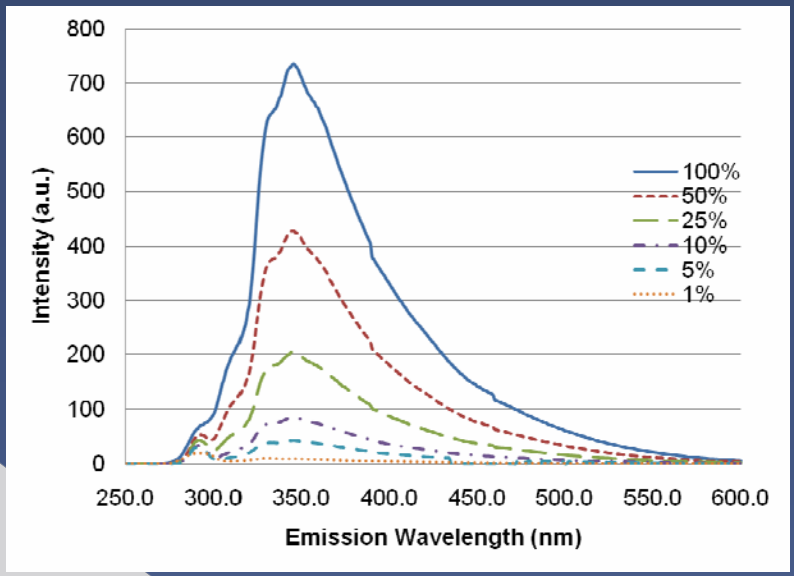


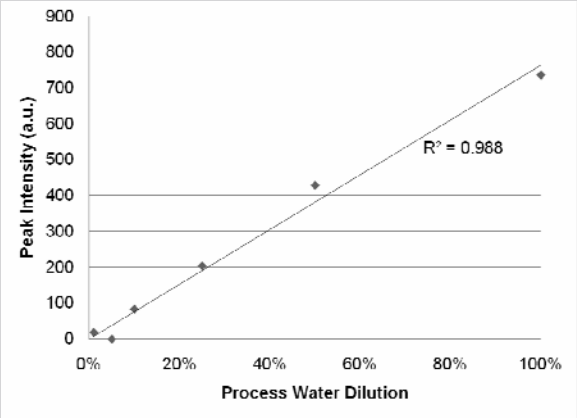


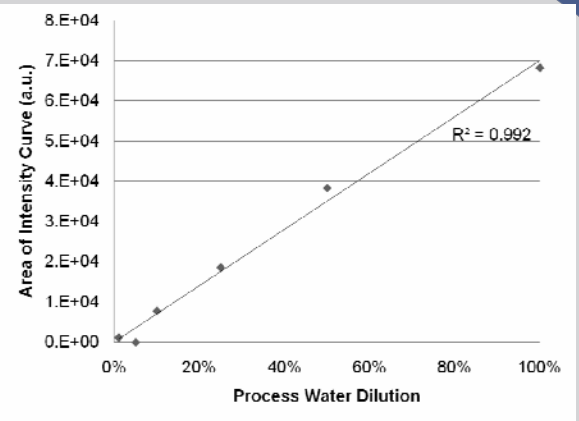
- Peak @ Ex 260 nm, Em 430 nm
  - GW1 Int 135, GW2 Int 50
  - Soil organics (humic substances) may be source of fluorescence signal

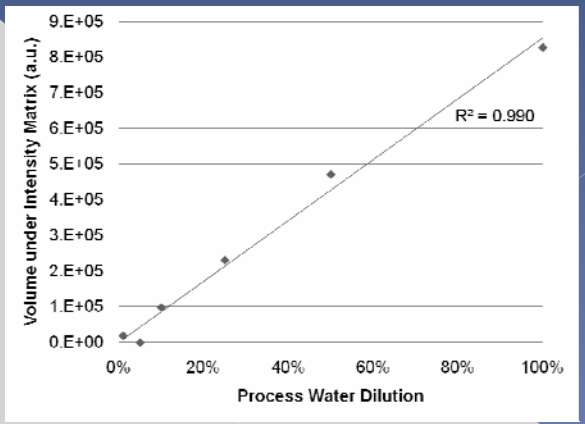
Quantitative Analysis

- Dilution series completed with process-affected water
- Emission spectra at excitation wavelength 290 nm used









Conclusions

- Oil sands naphthenic acids generate fluorescence signals.
  - Signals appear to be unique to sample.
  - Fingerprinting of samples may be possible.
- A linear response curve prepared from dilution series demonstrates potential for quantitative analysis.
- Fluorescence will enable analysis of aqueous samples, as is.
  - Potential for field analysis.

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Questions?

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- Thank you!