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

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ABSTRACT
Naphthenic acids represent the toxic component of oil sands process-affected water. A current challenge is the development of a rapid analytical technique to characterize naphthenic acids in process water. Fluorescence spectrophotometry is developed as a potential solution for generating sample signatures and quantitative analysis. Samples of process waters produced fluorescence signals that differed from groundwater collected in the Athabasca region. A dilution series prepared with process water produced a linear response curve, following correction for inner filtering effects. Fluorescence spectrophotometry is a potentially powerful tool for characterizing and quantifying naphthenic acids in waters.

RÉSUMÉ
Les acides naphténiques représentent la composante toxique des eaux de procédé produites lors de l'extraction des sables bitumineux. Un défi actuel est de développer une méthode d'analyse rapide qui pourrait identifier et caractériser les acides naphténiques. La spectrométrie de fluorescence est une telle méthode d'analyse qui pourrait produire une « signature » des acides naphténiques et quantifier les acides naphténiques. Indiquent que les échantillons d'eaux de procédé donnent un signal de fluorescence qui est différent du signal d'un échantillon d'eau souterraine de la région Athabasca. De plus, la méthode produit une réponse linéaire lorsqu'un échantillon d'eau de procédé est dilué et analysé.

1 INTRODUCTION

The Athabasca oil sands deposit represents a portion of one of the largest global reserves, with over 1.7 trillion barrels of proven recoverable oil available (Alberta Government 2008). To protect surface waters in the region, oil sands operations cannot discharge process-affected water to the surrounding environment (Allen 2008). The Clark Hot Water Process utilized for bitumen extraction generates approximately 1.25 m^3 of tailings for every barrel of oil produced (Alberta Chamber of Resources 2004). The extraction process enhances the release of naphthenic acids in oil sands process-affected water that is stored in tailings impoundments that occupy over 70 km^2 of land (Allen 2008).

The term "naphthenic acids" is used to collectively describe the polar organic carboxylic acids that are present in crude oil (Brient et al. 1995). Naphthenic acids are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids with the general chemical formula $C_nH_{2n+Z}O_2$, where *n* indicates the carbon number and *Z* specifies a homologous series, or the degree of cyclization (Brient et al. 1995). The *Z* variable is an even negative integer between 0 and -12, which indicates the loss of covalently bonded hydrogen due to the presence of ring structures (Marsh 2006). The saturated ring structures predominantly contain five or six carbon atoms, and each multiple of -2 indicates the presence of another ring.

MacKinnon and Boerger (1986) identified naphthenic acids as the primary source of acute toxicity when aquatic life is exposed to oil sands process-affected water. Studies have also shown that toxicity is greatly attributed to naphthenic acids with less than 22 carbon atoms (Holowenko et al. 2002, Lo et al. 2006, Frank et al. 2008). Although naphthenic acids are found in many crude oil deposits (Tissot and Welte 1984), development in the Athabasca oil sands presents unique challenges due to the concentration of naphthenic acids in large wastewater storage ponds where the potential for significant impacts on the surrounding environment is immense. Reported naphthenic acid concentrations in tailings ponds have averaged 110 mg/L (Headley and McMartin 2004). Past research has focused on environmental fate and improved measurement techniques of naphthenic acids to facilitate the development of appropriate treatment technologies (Clemente and Fedorak 2005). There is a need for quick and robust naphthenic acid measurement in both research and industrial applications.

Fluorescence spectrophotometry has been established as a routine analytical technique in medical and environmental applications due to high sensitivity, reproducibility, simplicity, and cost effectiveness. Samples are not affected or destroyed in measurement, nor are hazardous by-products generated. Ultraviolet-visible light provides energy to promote electrons to an excited state. When electrons decay back to the ground state, light photons are released at a characteristic wavelength, resulting in a fluorescent signal. Fluorescence predominantly occurs from aromatic molecules (Lakowicz 2006).

Mohamed et al. (2008) demonstrated the use of fluorescence technology for naphthenic acid

measurement and observed a linear response for concentrations ranging from 1 to 100 mg/L of oil sands process-affected water-derived naphthenic acids. Mohamed et al. (2008) suggest that various levels of unsaturation and aromaticity in oil sands acids enable the absorption of ultraviolet-visible light and subsequent fluorescence emission. Kavanagh et al. (2009) utilized synchronous fluorescence spectroscopy to analyze oil sands process-affected waters from two companies and suggest that aromatic acids that are closely associated with naphthenic acids may be fluorescing.

Objectives of this research include developing, verifying and optimizing fluorescence spectrophotometry as a quick, accurate, and cost-effective analytical technique to characterize naphthenic acids in a variety of samples collected from the Athabasca oil sands region, including process-affected water and groundwater by generating fingerprint signatures.

2 MATERIALS AND METHODS

2.1 Sources and preparation of samples

For this study, process-affected water samples were collected from three oil sands operations. Company A supplied water from a recycle line located in the extraction plant. Process-affected waters from companies B and C were collected directly from tailings ponds. Groundwater samples were supplied by Company B, collected from a nested monitoring well near a tailings pond outfitted with five foot slotted screens, at depths of 4.5 m (GW 1) and 26.5 m (GW 2), located in clay till and sand aquifer, respectively.

All water samples were obtained in winter 2009, refrigerated at 4°C and stored in the dark in glass bottles at the Applied Environmental Geochemistry Research Facility at the University of Alberta, with the exception of water from Company C, which had been stored in plastic (versus glass) since the summer of 2008.

Naphthenic acid concentrations in the oil sands process-affected waters were on the order of 10 mg/L, as measured by a commercial laboratory using Fourier transform infrared spectroscopy, and 0.3 mg/L in groundwaters, as meausured by University of Alberta personnel using capillary HPLC/QTOF-MS (Bataineh et al. 2006).

Prior to analysis, samples were filtered using plastic syringes and 0.45 μm Teflon filters to remove suspended particles in the samples that cause light scatter during measurement. Sample preparation was conducted in triplicate.

Unless stated otherwise, all supplies were obtained from Fisher-Scientific (Edmonton, AB). All laboratory glassware was rinsed with methanol and air-dried prior to use.

2.2 Fluorescence and absorbance measurements

A Varian Cary Eclipse fluorescence spectrophotometer was utilized with right angle detection. A collection of emission scans from 250 to 600 nm with 1 nm increments were obtained at excitation wavelengths ranging from 260 to 450 nm with 10 nm increments. The bandwidth (slit width) was 10 nm for excitation and 5 nm for emission for scans of process-affected water and 20 nm for excitation and 5 nm for emission when scanning groundwater samples. A correction factor of 1.8 was applied to measurements taken with the 20 nm excitation slit width to facilitate comparison. The scan rate was 600 nm/min, allowing for a scan time of approximately 20 minutes per sample. Both excitation and emission filters were set to automatic and the PMT voltage was 600 V for all scans.

Absorbance measurements were conducted using a Shimadzu UV2401-PC UV-VIS Recording Spectrophotometer, coupled with Shimadzu UVProbe software. Absorbance readings were obtained for wavelengths from 250 to 600 nm with 1 nm increments.

Samples were processed in clear quartz 1.24x1.24x4.5 cm cuvettes supplied by Varian.

2.3 Data preparation

Absorbance measurements were obtained to correct for both primary and secondary inner filtering effects, using the method described by Tucker et al. (1992). The average, corrected intensity values were then used to develop Excitation-Emission Matrices and emission spectra. Excitation-Emission Matrices were generated using the Scan function of the Varian Cary Eclipse software and emission spectra.

Light scatter, an artifact of fluorescence spectroscopy due to reflection of excitation light by impurities in the analyzed samples, was not removed from the data, but is seen as a 45° line across the Excitation-Emission Matrix and is also observed in the emission spectra.

3 RESULTS

3.1 Qualitative Analysis

Qualitative analysis was conducted in this study to determine if unique signals, or “fingerprints”, would be detected in environmental samples from the Athabasca oil sands region using fluorescence spectrophotometry. Both oil sands process-affected and ground water samples were analyzed to determine if signals differed between samples.

Excitation-Emission Matrices and emission spectra at different excitation wavelengths were prepared for all five water samples and are provided. Figures 1 through 6 are of oil sands process-affected waters and figures 7 through 10 are groundwater samples. All matrices are shown with the same contour intervals to facilitate comparison between samples.

Chemical analysis conducted by a commercial laboratory indicated that aromatic hydrocarbons were non-detectable using GC-MS and that concentration of total phenols was insufficient to generate significant fluorescence signals (data not shown). It is suspected

that the fluorescence signals generated are mainly related to substituted naphthenic acids.

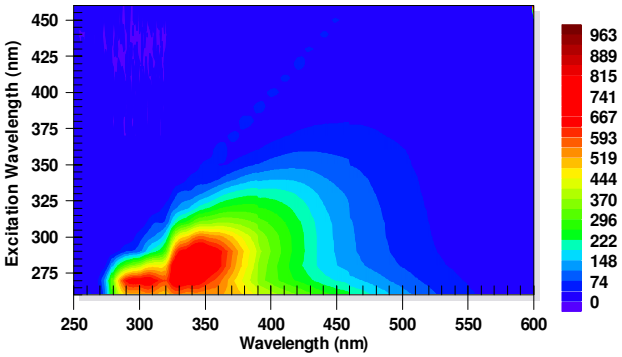

Figure 1. Excitation-Emission Matrix for process-affected water from Company A

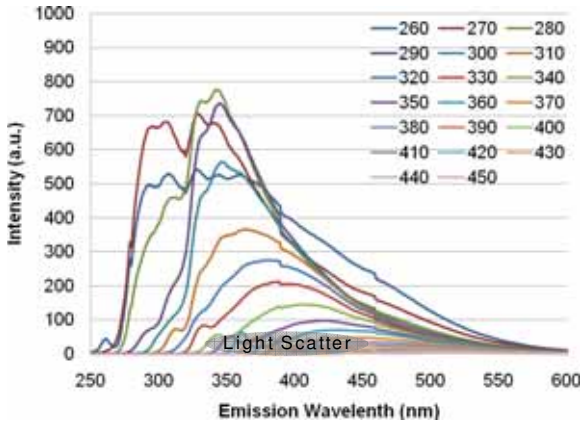

Figure 2. Emission spectra for process-affected water from Company A at different excitation wavelengths in nm

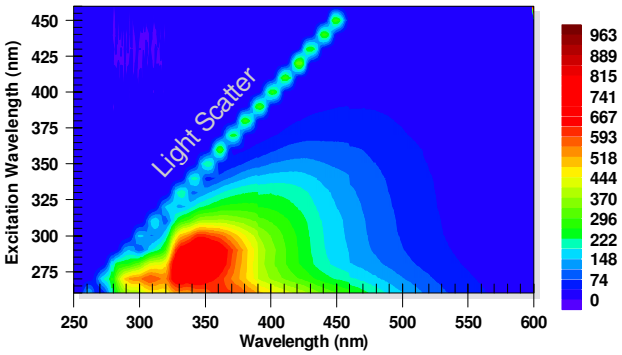

Figure 3: Excitation-Emission Matrix for process-affected water from Company B

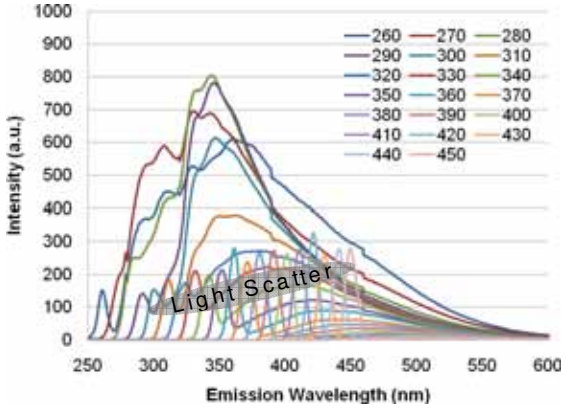

Figure 4. Emission spectra for process-affected water from Company B at different excitation wavelengths in nm

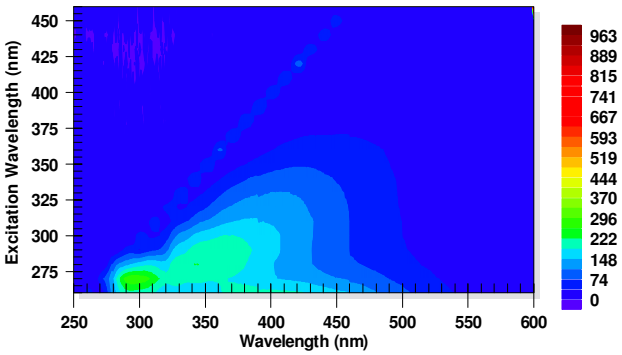

Figure 5: Excitation-Emission Matrix for process-affected water from Company C

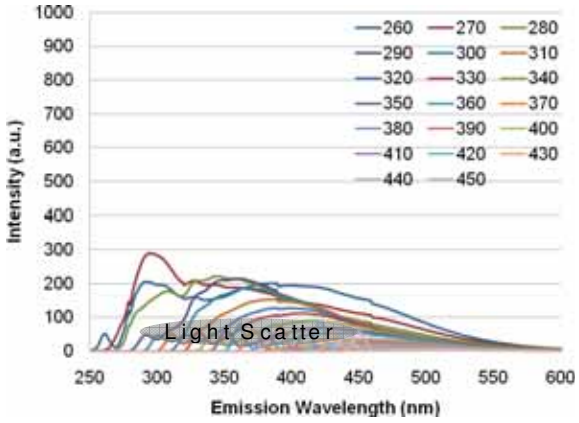

Figure 6. Emission spectra for process-affected water from Company C at different excitation wavelengths in nm

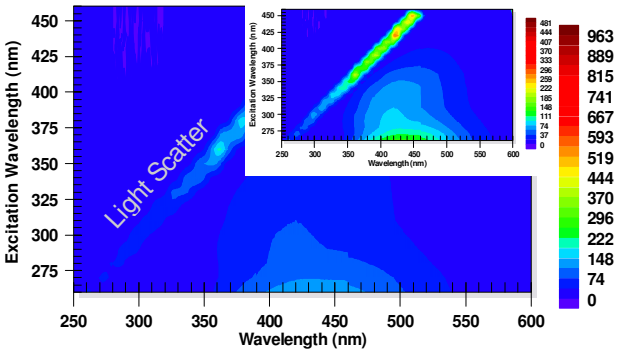

Figure 7. Excitation-Emission Matrix for GW 1 from Company B

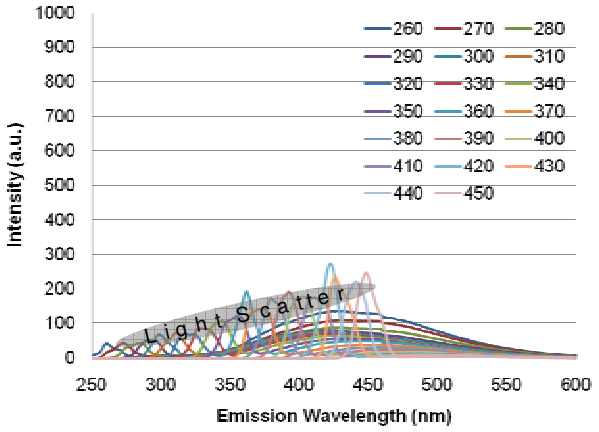

Figure 8. Emission spectra for GW 1 from Company B at different excitation wavelengths in nm

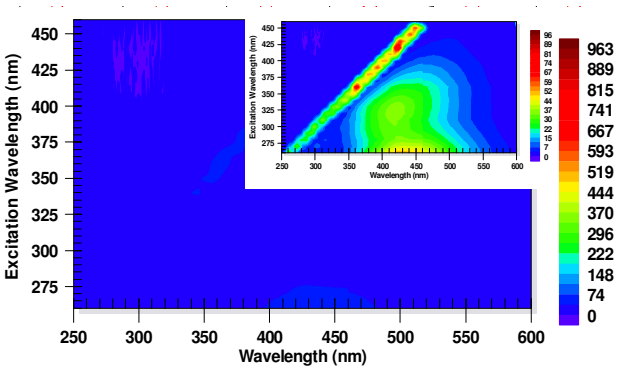

Figure 9. Excitation-Emission Matrix for GW 2 from Company B

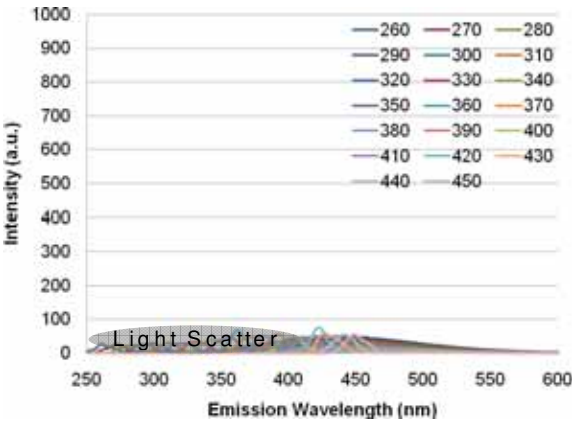

Figure 10. Emission spectra for GW 2 from Company B at different excitation wavelengths in nm

3.2 Quantitative Analysis

To determine if fluorescence technology can be utilized to quantitatively analyse naphthenic acid concentrations, a dilution series of oil sands process-affected water from Company A was prepared. Emission spectra are shown at an excitation wavelength of 290 nm at various dilutions of process water in Figure 11.

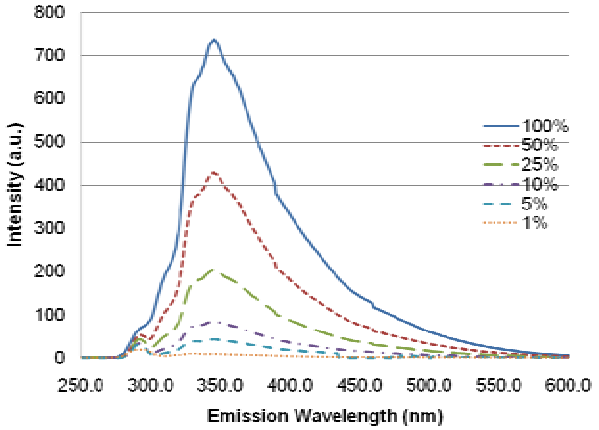

Figure 11. Emission spectra of oil sands process-affected water dilution series at excitation 290 nm

Three calibration curves were generated to determine the parameter that resulted in the best linear response: peak intensity at 290 nm excitation wavelength (Figure 12), integration of the intensity curve at 290 nm excitation wavelength (Figure 13), and integration of the entire Excitation-Emission Matrix (Figure 14). An excitation wavelength of 290 nm was chosen for calibration due to the prominent signal and singular peak response observed both in this study and by Mohamed et al. (2008).

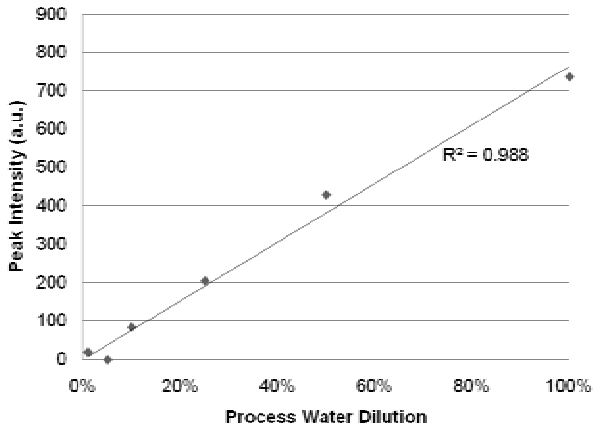

Figure 12. Linear calibration curve of peak intensity of oil sands process-affected water fluorescence signal at excitation 290 nm

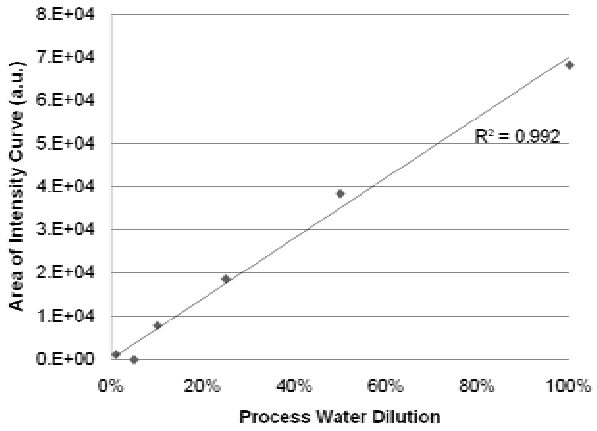

Figure 13. Linear calibration curve of intensity curve integration of oil sands process-affected water fluorescence signal at excitation 290 nm

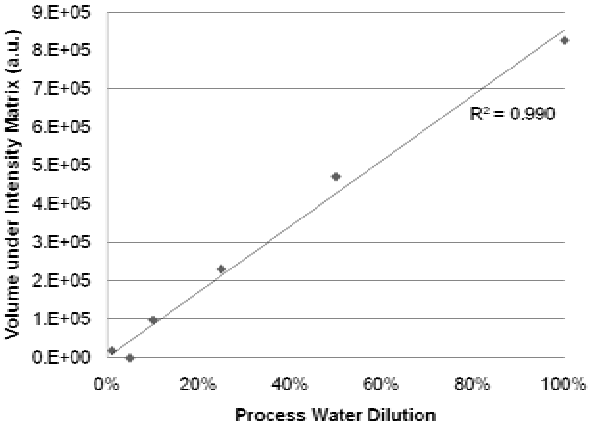

Figure 14. Linear calibration curve of intensity surface integration of oil sands process-affected water fluorescence signal at excitation wavelengths 240 to 450 nm.

4 DISCUSSION

4.1 Qualitative Analysis

Fluorescent signals were detected from both oil sands process-affected and ground water samples. The signals from oil sands process-affected water samples differed significantly from the groundwater samples.

As seen in Figures 1 through 6, all oil sands process-affected water samples exhibited pronounced fluorescence peaks that reflect the composition of naphthenic acids they contain. Of the three, samples from companies A and B are most similar. Two emission peaks are observed, as seen in Figures 2 and 4, both at excitation wavelengths ranging from 260 to 300 nm: one at an emission wavelength of 305 nm and the more prominent one at an emission wavelength of 340 nm. The 305 nm emission peak is more prominent in the sample from Company A than Company B, which indicates that oil sands process-affected water from Company A may contain more lower molecular weight naphthenic acid compounds that yield fluorescence at shorter wavelengths. The intensities of the 340 nm peak are similar for both companies A and B.

In contrast, the lower emission peak is most prominent in the sample from Company C and occurs at emission wavelength of 290 nm. The peak at 340 nm is still present, albeit muted. The lower intensity seen in the Company C sample may be attributed to the age and storage of the sample.

For both groundwater samples, the peak is located at the emission wavelength of 430 nm and is most intense at the excitation wavelength of 260 nm. GW 1, which was collected from the clay till, produced a more intense signal than GW 2, collected from the sand aquifer beneath the clay till.

Mohamed et al. (2008) observed similar peaks in emission spectra of samples of oil sands process-

affected water-derived naphthenic acids generated using fluorescence spectrophotometry. One peak was observed at an emission wavelength of 340 nm and excitation wavelengths ranging from 270 to 300 nm. A second, more intense peak was observed at excitation and emission wavelengths of 250 and 380 nm, respectively, similar to a peak observed in our study (data not shown).

The unique features of the generated fluorescence signals of the analyzed samples indicate that fingerprinting has promising potential to be an important tool to discriminate and characterize naphthenic acids, especially in environmental samples collected from the Athabasca oil sands region. Fingerprints could be used as a forensic tool to identify the source of ground or surface water contamination if different signals are detected between operators, based on treatment (extraction) process, bitumen source, or specific tailings pond. In addition, determining the total naphthenic acid concentration has been found to be insufficient in describing toxic effects because molecular structure and composition of the naphthenic acid mixture need to be understood and identified (Clemente and Fedorak 2005). Fingerprints of naphthenic acid samples generated using fluorescence spectrophotometry could be correlated to toxicity, thus resulting in a quick and effective method for toxicity monitoring in environmental samples. Fingerprinting also will improve understanding of the changes naphthenic acid mixtures undergo; fluorescence spectrophotometry could be utilized for online monitoring in oil sands production plants or process water treatment processes.

4.2 Quantitative Analysis

A quick, accurate, and cost effective method to measure naphthenic acid concentrations is needed to facilitate increased access to analysis for research groups, analytical laboratories, and operators.

Figure 11 shows the preservation of the peak response through the dilution series performed with oil sands process-affected water. High R^2 values (>0.99) of all three linear calibration curves, in Figures 12 through 14 demonstrate that, after correction, all wavelengths respond equally to change in concentration of the fluorescing compounds found in oil sands process-affected water. Thus, no wavelength is preferred for quantitative analysis with respect to generating a linear response. Without correction, the data fits a second order polynomial (data not shown), demonstrating that correction for inner filtering effects when utilizing emission spectra is essential, especially as concentrations of fluorescent compounds in samples increase. As concentrations in the sample increase, there is a greater chance of intensity reduction due to adsorption.

Mohamed et al. (2008) utilized both the maximum intensity at the excitation wavelength of 290 nm and the emission wavelength of 346 nm and peak area integration to develop linear calibration curves with R^2 values of 0.985 and 0.983, respectively. For this study, emission scans of oil sands process-affected water samples from companies A and B generated a peak at excitation and emission wavelengths of 290 and 346 nm, respectively, but this peak shifted slightly after correction for adsorption.

Currently, quantitative analysis methods utilize commercially available naphthenic acid mixtures for calibration, which renders these methods semi-quantitative (Martin et al. 2008). Since naphthenic acid mixtures differ (Headley and McMartin 2004), relevant naphthenic acid mixture is needed for calibration of all quantitative analytical techniques.

5 CONCLUSIONS

Fluorescence spectrophotometry was used to generate fluorescence signals of oil sands process-affected water from three oil sands operators that differed from the signals of groundwater samples collected near a tailings pond. In addition, a dilution series with oil sands process-affected water produced a linear response curve, following correction for inner filtering effects, thus demonstrating the potential for quantitative analysis. Fluorescence spectrophotometry is a powerful tool for developing signatures of oil sands process-affected waters that will enable sample “fingerprinting”.

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