Dissolved Organic Matter in Steam Assisted Gravity Drainage Boiler Blow-Down Water

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S *Supporting Information*

ABSTRACT: Steam assisted gravity drainage (SAGD) boiler blow-down (BBD) water contains high concentrations of dissolved organic matter (DOM) and total dissolved solids (TDS). A detailed understanding of the BBD chemistry, particularly the DOM composition, is important for better management and recycle of this water. In this study, we fractionated the dissolved organic matter in the BBD using DAX-8, Dowex, and Duolite resins into hydrophobic and hydrophilic fractions of acid, base, and neutral compounds. Additionally, the DOM was fractionated on the basis of size by filtering the BBD through a series of membranes with progressively tighter molecular weight cutoffs of 10, 3, and 0.5 kDa. Fluorescence excitation–emission matrix spectroscopy (EEMs), specific UV absorbance (SUVA), and FTIR were used to characterize the water samples and the different fractions. The ion exchange fractionation revealed that the DOM contained a high percentage of hydrophobic acids (39%) and hydrophilic neutrals (28.5%). The different ion exchange fractions had distinct fluorescence excitation–emission signatures. The permeate samples from the membrane fractionation, on the other hand, did not reveal any significant difference in the fluorescence EEM spectra, indicating that the hydrophilic and hydrophobic constituents of the DOM could not be separated on the basis of pore size by these membranes. The SAGD boiler blow-down water was found to be significantly concentrated in DOM compared to oil sands mining process affected water.

INTRODUCTION

Steam assisted gravity drainage (SAGD) is an *in situ* thermally enhanced oil recovery (tEOR) process for bitumen extraction from oil sands in Alberta, Canada. In this process, a medium pressure wet steam is injected into the production wells to thermally reduce the viscosity of the bitumen and facilitate its extraction. The steam condensate and the bitumen flow down along the periphery of the subterranean steam chamber under gravity and are extracted as a mixture of bitumen, clay, and water.[1]

Generally, about 90% of the produced water (PW) is recycled and converted into steam. The produced fluids are first separated using a series of gravity and flotation vessels, namely, the free water knock out vessel to remove the bitumen, followed by gravity skim tanks and induced static flotation to separate residual oil from the produced water, and walnut shell filters to bring the free oil content in the produced water below 20 mg/L. The produced water is then treated in a warm lime softener (WLS) to remove silica and hardness, following which the suspended solids are removed in after-filters and the water is polished in a weak-acid cation exchanger (WAC), where calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions are removed. The treated water is then used as feed in the steam generators. The boilers used in the SAGD operation are known as once through steam generators (OTSGs). The OTSGs are capable of handling a feed with high total dissolved solids (TDS) content. The use of a high TDS feed results in higher blow-down volumes (about 20%) in the OTSGs in comparison to the standard recirculation drum boilers. In the current industrial practice, a portion of the boiler blow-down (BBD) water is recycled back to the WLS and the rest is earmarked for disposal.

The BBD water has extremely high levels of dissolved organic matter (DOM), ranging between 500 and 2500 mg/L, and total dissolved solids (TDS), ranging from 10000 to 17000 mg/L.[2] The high levels of DOM in SAGD produced water and OTSG blow-down have been implicated in numerous problems in the produced water treatment and disposal operation, such as fouling on downstream equipment surfaces, economizers, pipelines, and clogging of injection wells.[3] Knowledge of the nature and effects of high DOM concentrations in SAGD applications is limited. This is in contrast to the extensive literature available on the chemical characteristics of Athabasca oil sands process affected waters (OSPW) associated with the surface mining and extraction of bitumen. Many of these studies conclude that the DOM in mining OSPW consists mainly of naphthenic acid-like compounds,[4,5] although this conclusion is not universal.[6,7] The nature of the SAGD DOM may be different from the mining OSPW DOM due to the difference in the mining and SAGD extraction techniques. SAGD extraction employs higher temperatures (200–250 °C) and pressures (ca. 3.5 MPa), compared to moderate temperatures (70–90 °C) and atmospheric pressure used in the mining process. This fundamentally different temperature and pressure history of the SAGD process under which oil and water are mixed, use of diluents during oil–water separation, and subsequent increase of pH during water treatment may

lead to solubilization of a broader range of organic matter into the water phase.

Jennings et al.[3] examined the chemical characteristics of SAGD heat exchanger deposits and determined that the deposits were predominantly organic matter, with significant concentrations of organic acids and organic acid salts. Further analysis of the organic acids using high-resolution mass spectrometry identified several thousands of organic acids with broad distributions of molecular weight, heteroatom content, aromaticity, and carbon number.[8] Stanford et al.[9] studied the water-soluble nonvolatile components from crude oil by negative-ion ESI and continuous flow FD FT-ICR MS techniques. They concluded that acidic oxygen-containing classes were the predominant water-soluble components compared to acidic nitrogen-containing species. Petersen and Grade[10] used two-dimensional gas chromatography with time-of-flight mass spectrometry to analyze the organic components in SAGD produced water. Again, a wide variety of organic constituents was found, including significant amounts of polar compounds with carboxylic and phenolic functional groups. These studies have provided considerable insight into the organic matter composition of SAGD produced waters. Our recent studies using liquid chromatography followed by ESI Orbitrap MS on SAGD BBD water revealed over 3000 elemental compositions corresponding to a range of heteroatom-containing homologue classes (O_x: $x = 1-6$, NO_x: $x = 1-4$, SO_x: $x = 1-4$, NO_2S, N, and S).[11] Furthermore, it was found that the O_2 species detected in the ESI negative mode were chemically distinct from the corresponding species in the ESI positive mode.

Although the above-mentioned studies collectively provide excellent resolution of the organic compounds present in the produced water, a simple laboratory classification scheme that identifies the solubility of these compounds in water, and quantifies the hydrophobic and hydrophilic constituent fractions of the DOM in SAGD produced water is not reported. Such a technique may enable rapid assessment of the hydrophobic and hydrophilic fractions present in a water sample, and provide guidance regarding selectively removing the class of organic matter that could be associated with operational problems in the plant. The goal of the present study is to explore the applicability of ion exchange and size-based fractionation in conjunction with fluorescence and UV absorbance-based assays to quantitatively assess the hydrophobic and hydrophilic fractions of the organic matter present in a SAGD water sample.

Natural organic matter (NOM) is a complex mixture of organic compounds found in natural waters with a wide distribution of molecular weights, structures, and chemical behaviors. NOM has been the subject of intense research over the last 40 years in relationship to drinking water treatment. This intensive research has led to many techniques for characterizing NOM and understanding its influence on water treatment processes.[12] The NOM from any aquatic system can be fractionated into hydrophobic and hydrophilic acid/base/neutral fractions using a resin-based fractionation procedure as proposed by Leenheer[13] and Thurman et al.[14] This fractionation technique has been used to study the treatability of NOM fractions by various water treatment processes, such as coagulation[15] and membrane filtration.[16]

In this study, we first classified the DOM present in SAGD BBD based on their hydrophobicity and hydrophilicity. The resin-based fractionation technique using DAX-8, Duolite, and Dowex resins commonly used for NOM fractionation was adopted to separate different DOM fractions from the BBD. Following this, size-based fractionation of the BBD was performed by passing it through a series of membranes of progressively lower molecular weight cutoffs (MWCO) to assess the size distribution of the DOM. For the various water samples and fractions, we performed Specific UV absorbance ($SUVA_{254}$), fluorescence excitation emission matrix (EEM) spectroscopy, Fourier transform infrared spectroscopy (FTIR), and total organic carbon (TOC) analysis. The ion exchange and size-based fractionation followed by the spectroscopic analysis provide estimates of the relative abundance of the hydrophobic and hydrophilic classes of water-soluble organic compounds present in SAGD BBD water. These methods could provide insight regarding the deployment of suitable treatment procedures for selective DOM removal during produced water treatment.[17−19] This should have relevance to management, treatment, and disposal of produced water during the thermal recovery of petroleum.

■ MATERIALS AND METHODS

Samples. The water samples used for this study are the SAGD boiler blow-down (BBD), SAGD produced water (SAGDPW), and oil sands process affected water (OSPW) samples received from a large Athabasca oil sands operation. The BBD samples were collected hot and kept under a nitrogen blanket until they were opened for sample analysis to minimize compositional changes during storage.[20] The raw BBD was passed through a 0.22 μm membrane (Cellulose Acetate, Millipore, USA) to remove the suspended solids. This enabled us to use the total organic carbon (TOC) content in the water samples interchangeably with the dissolved organic carbon (DOC) content.[21] The storage temperature of samples was maintained at 25 °C, and all experiments were performed at the storage temperature. The commercial naphthenic acids (Sigma Aldrich, USA) were dissolved in deionized (DI) water to prepare a 500 mg/L solution. The pH of this solution was set to ~11 (a value approximately equal to the pH of BBD) using 0.1 N NaOH (Fisher Scientific, USA) solution.

Resin-Based and Membrane-Based Fractionation. All samples were filtered through a 0.22 μm filter (Whatman, Millipore, USA) to remove suspended particulate matter before the resin-based fractionation. The filtered BBD was fractionated into hydrophobic and hydrophilic fractions of acids, bases, and neutrals using a modified version of Leenheer's method of NOM fractionation.[13] The resins used for our study are DAX-8 (Supelco, Bellefonte, PA, USA), Duolite (Sigma Aldrich, USA), and Dowex 50W X8 (Sigma Aldrich, USA). The amount of DAX-8 resin required was based on a curve-fit equation from the chart provided by Malcolm et al.,[14] whereas a conductivity-based correlation was used for Dowex and Duolite resins.[13] Details of the sample preparation, column treatment, and fractionation procedure are provided in the Supporting Information.

For the membrane-based fractionation of the DOM, the particulate matter free BBD was diluted to a TOC value of ~150 mg/L and sequentially filtered through three different types of membranes of molecular weight cutoffs (MWCO) 10 kDa, 3 kDa, and 0.5 kDa. The 10 kDa (PLGC, Millipore, USA) and 3 kDa (PLBC, Millipore, USA) membranes were made of regenerated cellulose, whereas the 0.5 kDa (YC05, Millipore, USA) membrane was made of cellulose acetate. The pH of the diluted BBD was adjusted to ~11 by adding NaOH solution to minimize any precipitation or aggregation of the organic matter. Prefiltered diluted BBD sample (200 mL) was placed in a stirred batch cell (Millipore, USA). The transmembrane pressure and stirring rate in the cell were set to 207 kPa (30 psi) and 300 rpm, respectively. Permeate (120 mL) was collected through the 10 kDa MWCO membrane. The permeate flux was measured after every 5 mL was collected, and the flux versus time plot showed no significant flux decline till a volume of 120 mL was collected. Then, the 120 mL permeate obtained from the 10 kDa membrane was passed through

the 3 kDa MWCO membrane. 50 mL of the permeate was collected, and the collection was stopped before any observable decline of flux. Finally, 50 mL of the permeate from the 3 kDa membrane was filtered through the 0.5 kDa MWCO membrane. Since a low volume (4 mL) was passed through the 0.5 kDa membrane, flux decline was not observable.

Analytical Methods. The dissolved organic carbon (DOC) was measured using a TOC analyzer (Shimadzu, model TOC-V; detection range 3−25,000 mg/L) after filtering through a 0.22 μm membrane filter (Cellulose acetate, Millipore, USA). There was no significant difference in the TOC values between filtered and unfiltered BBD. Thus, organics in the BBD are mainly water-soluble. Fluorescence excitation emission matrix contour maps for the samples were obtained using a fluorescence spectrophotometer (Varian, model Cary Eclipse, USA). The excitation−emission matrix (EEM) was acquired over a wavelength range of 200−500 nm with 5 nm intervals for excitation wavelength scan and 10 nm intervals for emission wavelengths. The EEM of deionized (DI) water was subtracted from the EEM of the samples to remove most of the Raman peaks. The samples were diluted using DI water to a TOC level of 25 ± 3 mg/L to avoid inner filtration (quenching) effects on fluorescence analysis.[22] The pH values of the samples were adjusted to the pH of the raw BBD (pH = ∼11) to remove the pH induced effects on fluorescence. UV absorbance of the samples was measured at 254 nm using a UV−visible spectrophotometer (Varian, model Cary 50, USA) employing DI water as the blank. The samples were diluted to obtain absorbance in the range 0−1.0. The specific UV absorbance ($SUVA_{254}$) of the samples was calculated using the corresponding DOC value employing the relation $SUVA_{254} = (Abs)_{254} \times 100/(DOC)$ The surface deposits on the membranes (10 kDa, 3 kDa, and 0.5 kDa) due to organic and silica fouling were analyzed using diffused reflectance FTIR (Thermo Nicolet, Nexus 670 FTIR, USA). The spectra of the fouled membrane were recorded after correcting the background spectra using fresh membranes. Twenty scans at 4 cm^{-1} resolution were taken for each sample.

■ RESULTS AND DISCUSSION

Chemical Characteristics of the SAGD Boiler Blow-Down Water. The characteristics of SAGD boiler blow-down (BBD) are compared with different types of produced water obtained from conventional and nonconventional oil extraction in Table 1. The characteristic parameters of the BBD are quite different from the corresponding water quality parameters of other produced waters. Of note, SAGD BBD has a distinctly higher pH, high DOM content (as indicated by chemical oxygen demand and TOC values), high silica, and high TDS

compared to other produced waters. In the current SAGD water treatment practice, no process exists to specifically remove the DOM from the produced water during treatment. Furthermore, during steam generation, the DOM in the BBD is further concentrated by a factor of 5 to 10 compared to the boiler feedwater. It is important to note that the pH of the BBD is higher compared to other produced water types. This is because high pH is maintained during the SAGD produced water treatment process to avoid silica and organic scaling on the equipment surfaces.[2]

Fractionation of DOM Based on Hydrophobic and Hydrophilic Nature. The different hydrophobic and hydrophilic organic matter fractions in the BBD as a percentage of total organic carbon (TOC) are depicted in Figure 1. These
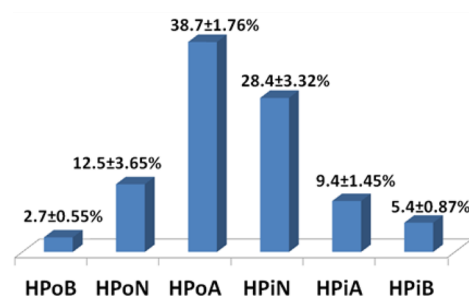

Figure 1. Percentage distribution of different organic fractions in BBD obtained from the resin-based fractionation method.

fractions were obtained using the resin-based fractionation procedure described under Materials and Methods. The hydrophobic acids (HPoA) are found to be the major components in the BBD DOM, constituting 38.7% (±1.76%). The hydrophilic neutral (HPiN) fraction is about 28.4% (±3.22%). Together, these fractions constitute about 65% of the DOM. The hydrophobic neutral (HPoN) and hydrophilic acid (HPiA) fractions constitute 12.5% (±3.65%) and 9.4% (±1.45%) of the organic matter, respectively. The hydrophilic base (HPiB) and hydrophobic base (HPoB) fractions contribute about 5% or less each to the total DOM content.

Fluorescence EEMs of SAGDPW, BBD, OSPW, and Commercial Naphthenic Acids. The fluorescence EEM signatures of DOM in SAGD produced water (SAGDPW, the water obtained after deoiling), SAGD BBD, oil sands process affected water (OSPW, obtained from oil sands mining tailings ponds), and commercial naphthenic acids (NAs) are compared in Figure 2. The fluorescence response for BBD and SAGDPW occur over a wide range of wavelengths, with two dominant peaks at excitation/emission (Ex/Em) wavelength ranges of 225−250/375−425 and 300−340/400−425. The commercial naphthenic acid (NAs) fluorescence peaks were obtained in the Ex/Em wavelength range of 215−230/350−375 nm (Figure 2d). The EEMs of commercial NAs and OSPW appear to have similarities (Figure 2c and d), which corroborate the general notion that the DOM in mining OSPW has similarities with commercial NAs.[4,5,31−37] However, commercial NAs have a much sharper peak compared to the mining OSPW, indicating that the latter has a broader range of fluorophores. It is worth noting that all the EEMs were obtained after diluting the different water samples to an identical TOC of 25 ± 3 mg/L and pH (∼11). Hence, the fluorescence intensity in BBD compared to SAGDPW is not a simple concentration effect.
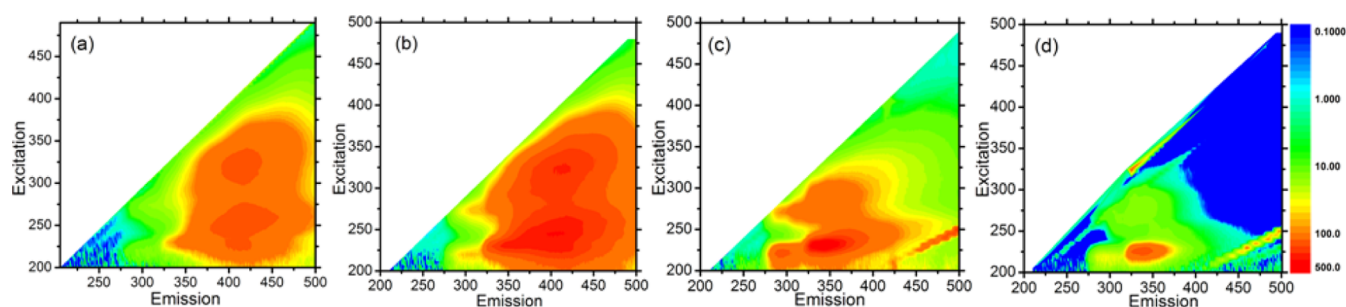
Table 1. Comparison of the Characteristics of Oil-Field Produced Water (OFPW),[23−28] Oil Sands Mining Process-Affected Water (OSPW),[4,5,29−31] SAGD Produced Water (SAGDPW), and SAGD BBD, Which Was Characterized in This Study and Some Data Taken from Maiti et al.[2a]

characteristics	OFPW	OSPW	SAGDPW	BBD
pH	7.4−8.5	8.6−9.12	7.11	10.6
conductivity	1400−5000	2370−3459	1540	18000
TDS	700−2000	2477	1005	17000
TSS	90−180			65
COD	274−431	250		4000
TOC	68−140	48.3−83	232	2400
alkalinity	300−380	490−690	120	2700
Ca^{2+}	2−11	7.3−47.5	2.5	4.2
Mg^{2+}	0.01−1.3	4.2−24	0.05−0.15	0.68
iron (total)	0.1−0.5		0.05	3.3
SiO_2 (soluble)	7−14		102	90

^{a}All units in mg/L except conductivity (μS/cm) and pH.

Figure 2. Comparison of fluorescence excitation–emission matrix spectra (EEMs) of (a) SAGD produced water, (b) SAGD boiler blow-down water, (c) oil sands process affected water (from mining), and (d) commercial naphthenic acids. Excitation at 5 nm intervals from 200 to 500 nm, and emission data collected at an interval of 10 nm. All samples were diluted to have the effective TOC of 25 ± 3 mg/L. The color scale representing the fluorescence intensity is logarithmic in all parts of the figure with the range varying from 0.1 (blue) to 500 (red).

There is a considerable difference in the Ex/Em signatures of SAGDPW and SAGD BBD from those of mining OSPW. Thus, the fluorescence EEMs of the unfractionated water samples provide evidence that the DOM in BBD and SAGDPW have other classes of organic compounds which are quite dissimilar from the DOM components of mining OSPW and commercial naphthenic acids.

Fluorescence EEMs of DOM Fractions in BBD. Figure 3 depicts the EEMs of the six DOM fractions obtained from the resin-based fractionation of BBD. The Ex/Em wavelength ranges for peaks associated with each fraction are presented in Table 2. The fluorophores in individual organic fractions were compared to fluorescence data reported in the literature for various classes of natural organic matter (NOM). Of particular relevance is the data of Marhaba et al.,[38] who used resin-based fractionation and EEMs similar to this work to examine the EEMs of NOM fractions from a surface water. Other researchers have used EEMs in conjunction with various classification schemes to examine NOM.[39–41] The data from these studies are also shown in Table 2 for comparison. The NOM of natural water generally shows three major fluorescence peaks, viz. humic-like, fulvic-like, and amino acid (tryptophan and tyrosine)-like.[42–44] The fluorescence emission intensity peaks of DOM are generally observed due to the presence of high aromaticity, hydroxyl, and amine groups in the organic fluorophores.[12,42–44] The fluorescence intensity of any fluorophore can also be reduced by the interfering effects of other molecules present in a system containing a mixture of fluorophores.[45]

The hydrophobic (HPoA) and hydrophilic acids (HPiA) in SAGD BBD both exhibit Ex/Em peaks in the range 300–400/ 375–475 nm (Figure 3a and b). This Ex/Em range for the BBD water-soluble organic acids is vastly different from the EEMs signatures of DOM present in OSPW or commercial NAs (Figure 2c and d). Literature attributes the signatures of these organic acid fractions to type C/α or type M/β humic acids or marine humics for the hydrophobes and to type T/δ (tryptophan-like fluorophores) for the hydrophilic moieties. SAGD DOM should not be identical to humic substances in natural waters, but the EEMs for the fractions appear to indicate the presence of similar types of fluorophores in these samples.

The HPoB fraction (Figure 3c) has a fluorescence peak intensity in the Ex/Em wavelength range of 260–290/280–320 nm, which is different from the data reported in the literature for NOM (225–237/340–381 nm and 275/340 nm). This difference may be due to differences in the nature of the DOM
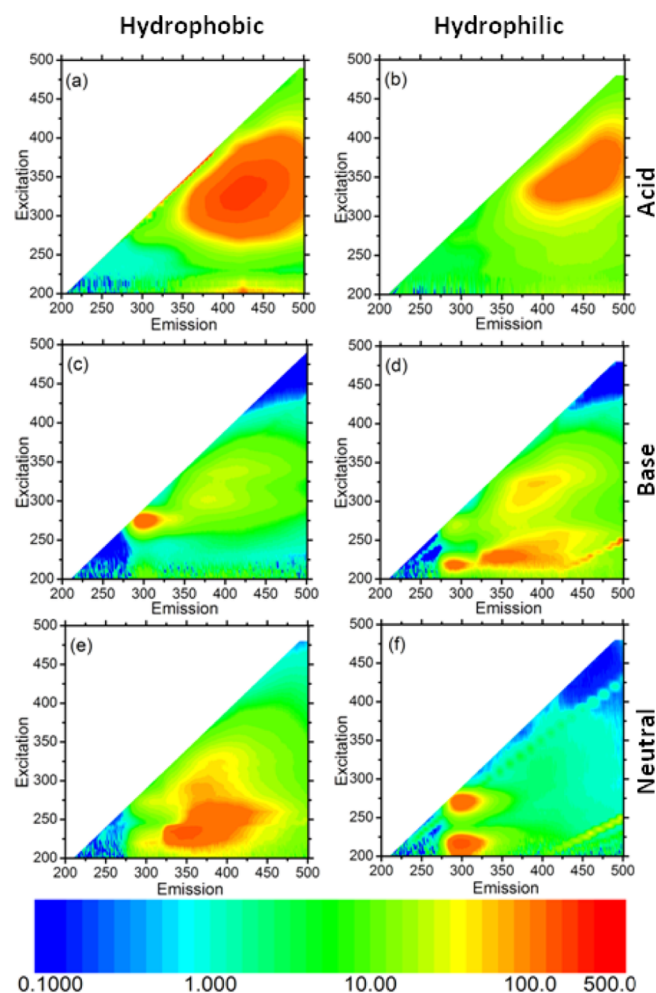

Figure 3. Fluorescence EEMs contours for (a) hydrophobic acid, (b) hydrophilic acid, (c) hydrophobic base, (d) hydrophilic base, (e) hydrophobic neutral, and (f) hydrophilic neutral fractions obtained from BBD. Excitation at 5 nm intervals from 200 to 500 nm, and emission data collected at an interval of 10 nm. All samples were diluted to have the effective TOC of 25 ± 3 mg/L. The color scale representing the fluorescence intensity is logarithmic in all parts of the figure with the range varying from 0.1 (blue) to 500 (red).

present in SAGD BBD and the NOM sources, and it may be attributed to a low Stokes shift[46,47] in the absence of a π-configuration framework (low aromaticity) in the fluorophores of the HPoB fraction.[48]

Table 2. Fluorescence Peak Intensities of Fluorophores in SAGD BBD and Its Comparison with NOM Fluorophores

SAGD DOM fractions	Ex/Em range (in this study)	Ex/Em range (other studies)	chem nature
BBD (unfractionated)	250/375−425 and 300−340/375−480		
hydrophobic acid	310−340/400−500	A/α′: 237−260/400−500[39,40,43]	humic-like
		C/α: 300−370/400−500[39,40,43]	humic-like
		M/β: 312/380−420[39,40,43]	marine humic-like
hydrophobic neutral	225−250/325−380	B/γ: 225−237/309−321 and 275/310	tyrosine-like
hydrophobic base	260−290/280−320	T/δ: 225−237/340−381 and 275/340[39,40,43]	tryptophan-like
hydrophilic acid	320−375/375−500		
hydrophilic neutral	210−225 and 250−275/280−320		
hydrophilic base	210−225/275−310 and 325−400	225−237/357−369[38]	

The hydrophilic base (HPiB) fraction has two peak intensity regions at the Ex/Em wavelength ranges of 210−225/275−310 nm and 210−225/325−400 nm (Figure 3d). Marhaba and Lippincott[38] assigned the peak intensity region for the HPiB fractions in NOM in the Ex/Em range of 225−237/357−369 nm. The EEMs of the HPiB fraction in the SAGD DOM appear similar to the HPiB fractions obtained from river water NOM. Furthermore, this fraction appears to have the most similarity to the DOMs present in mining OSPW (Figure 2c).

The fluorescence EEMs contours of the HPoN fraction shown in Figure 3e exhibit signatures of type B (tyrosine like molecules) as well as type T fluorophores. This fraction also shows similarities in the fluorescence EEMs signatures with mining OSPW (Figure 2c). The fluorescence intensity peaks for the HPiN fraction (Figure 3f) are obtained in the Ex/Em wavelength range of 210−225 and 250−275/280−320. Thus, the fluorophores can be classified as type T[39] or type δ[40] fluorophores.

The various ion exchange fractions of the DOM in SAGD BBD produce distinctly resolved peaks in the fluorescence EEMs. Noting that the dominant fractions of the DOM are the hydrophobic acids and hydrophilic neutrals (Figure 1), it is imperative that the majority of the DOM in SAGD BBD do not contain the same types of fluorophores that are present in mining OSPW or in commercial naphthenic acids.

Specific UV Absorbance. Another widely used metric for NOMs, the specific UV absorbance at 254 nm (SUVA$_{254}$),[49] was evaluated for all the BBD DOM fractions to assess their aromatic nature. For SUVA$_{254}$ of 4 or greater, NOM composition is dominated by humic substances displaying high hydrophobic and aromatic character. For SUVA$_{254}$ of 2 to 4, the water contains a mixture of humic and nonhumic substances, which can be represented as a mixture of aromatic and aliphatic substances. SUVA$_{254}$ < 2 corresponds to high fractions of nonhumic substances with high aliphatic and low hydrophobic character.[50] SUVA$_{254}$ has been shown to be strongly correlated with percent aromaticity for NOM.[49]

The SUVA$_{254}$ results for different DOM fractions in the BBD are presented in Table 3. The SUVA$_{254}$ values for HPoB and

Table 3. SUVA$_{254}$ of Different DOM Fractions and BBD

sample name	SUVA$_{254}$
raw BBD	4.245
hydrophobic acid	4.954
hydrophobic base	0.607
hydrophobic neutral	3.951
hydrophilic acid	2.024
hydrophilic base	1.113
hydrophilic neutral	0.178

HPiN are 0.607 and 0.178 L mg^{-1} m^{-1}, respectively. The lower SUVA$_{254}$ values for both these fractions show that very little aromatic organic matter is present in these two fractions. This also explains the small Stokes shift observed in these two fractions during the EEMs. Hence, we can conclude that the molecules in these DOM fractions are different from the NOM fractions in natural aquatic systems. The HPiA has a SUVA$_{254}$ value of 2.02 L mg^{-1} m^{-1}. The HPoA and HPoN have SUVA$_{254}$ values greater than 3.5, indicating the presence of high aromatic content in these organic fractions. From the SUVA$_{254}$ values in Table 3, it can be observed that, among all the DOM fractions, only the hydrophobic acid and neutral fractions are rich in aromatic content.

DOM Fractions from Membrane Filtration. Hua et al.[51] performed fractionation of NOMs in natural water using ultrafiltration (UF)/nanofiltration (NF) membranes, and they observed that the higher molecular weight NOMs constitute the major fractions in natural water. The DOM in SAGD BBD is also a mixture of organic compounds with different molar masses.[42] In this study, we performed a membrane-based fractionation of the BBD DOM to elucidate whether there is a correlation between the organic matter size fractions and their hydrophilicity or hydrophobicity. The procedure of size-based fractionation is schematically shown in Figure 4.

The diluted BBD sample at pH 11 was filtered through 10 kDa, 3 kDa, and 0.5 kDa membranes in series to determine the molecular weight distribution of the organic fractions. The diluted BBD used as feed solution for a 10 kDa membrane had a DOC value of 153 mg/L. The permeate obtained from the 10 kDa membrane had a DOC of 140.8 mg/L, showing a reduction of only 8% of the organic matter. Following this, the permeate was filtered through a 3 kDa membrane. The DOC of the permeate from the 3 kDa membrane (114 mg/L) indicates that almost 75% of the organic matter passes through this membrane. Finally, the DOC value of the permeate from the 0.5 kDa membrane was 61.3 mg/L, indicating that about 40% of the organic fraction in the BBD passes through this membrane. The SUVA$_{254}$ values of the permeates from 10 kDa, 3 kDa, and 0.5 kDa were 2.178, 1.711, and 1.064 L mg^{-1} m^{-1}, respectively, indicating the progressive reduction of aromatics as molecular weight decreases. Although the high pH (11) maintained during the filtration should keep the organic matter well-dispersed, we cannot rule out the possibility that some of the organic matter aggregated during filtration with the 10 kDa and 3 kDa membranes.

The EEMs contour maps of different molecular weight fractions obtained as permeate through the 10 kDa, 3 kDa, and 0.5 kDa membranes are shown in Figure 4. The contour maps of the permeates all have similar EEMs signatures. This can be interpreted in two ways. First, if there is no aggregation, then
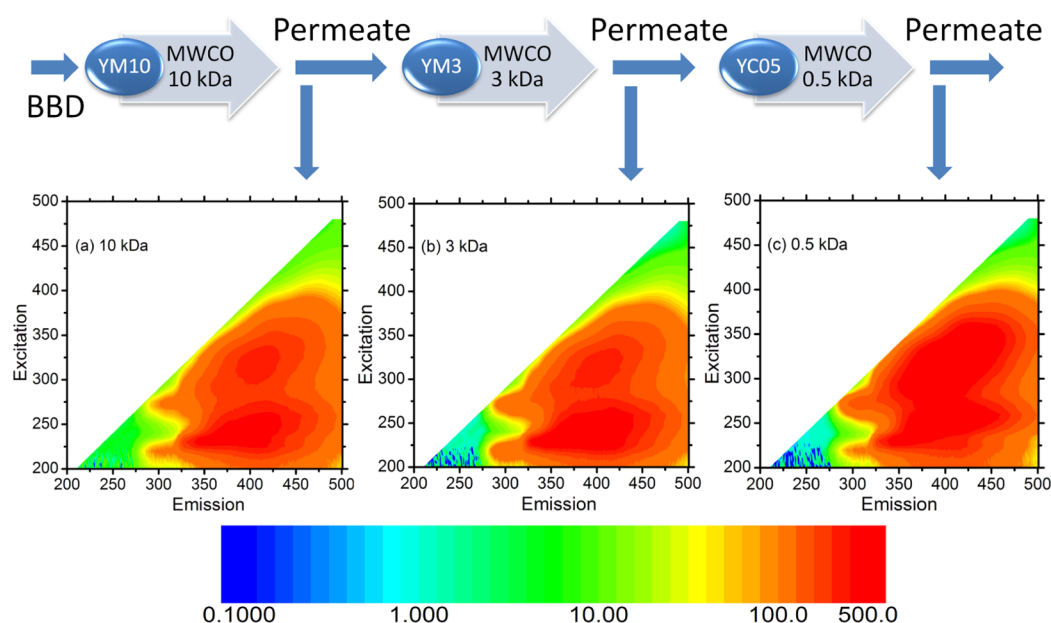
Figure 4. Comparison of the EEMs of permeates obtained from (a) 10 kDa, (b) 3 kDa, and (c) 0.5 kDa membranes. Excitation at 5 nm intervals from 200 to 500 nm and emission data collected at an interval of 10 nm. All samples were diluted to have the effective TOC of 25 ± 3 mg/L. The color scale representing the fluorescence intensity is logarithmic in all parts of the figure with the range varying from 0.1 (blue) to 500 (red).

each molecular weight fraction in the permeates from these membranes retains the entire set of fluorophores present in the unfractionated BBD. In other words, the hydrophobicity or hydrophilicity of these compounds does not correlate with their molecular weights. Second, if we consider the possibility of aggregation, then a majority of the molecules in the original SAGD DOM would be of low molecular weight (<0.5 kDa), and some of them aggregated to yield the DOC rejection by the 10 kDa and 3 kDa membranes. Hence, the permeates from all three membranes contained all types of fluorophores that were originally present in the BBD. This second interpretation of the EEMs would imply that the six classes of hydrophobic and hydrophilic DOM obtained using resin fractionation all have low molecular weights. High resolution ESI Orbitrap mass spectrometric results also lend support to this second conclusion.[11] In either case, we note that SAGD DOM consists of molecules that are considerably smaller than those in aquatic NOM.

The organic matter and silica from BBD deposited on the membranes were characterized using diffused reflectance FTIR scans. These results are presented in Figure 5. The peak intensities are highest for the 0.5 kDa membranes, followed by those for the 3 kDa and 10 kDa membranes. This correlates with the physical observation during the membrane fractionation tests that the tightest membrane (0.5 kDa) retained the largest fraction of solids. The silica peaks observed in the band of 1030−1040 cm^{-1} are most prominent in the material deposited on the 10 kDa membrane. On the other hand, the peaks of the material deposited on the 0.5 kDa membrane are observed in the bands of 1094, 1163, 1272, 1386, 1761, and 2870 cm^{-1}, of which, the band of 2870 cm^{-1} is attributable to C−H bond stretching,[52] and the rest are for different types of aliphatic and aromatic C=O and C−O bond stretching.[52] The diffuse reflectance FTIR scan of the 3 kDa membrane does not show prominent peaks representing either silica or the organic functionalities. This is owing to the fact that most of the silica in its feed was removed after filtration through the preceding 10
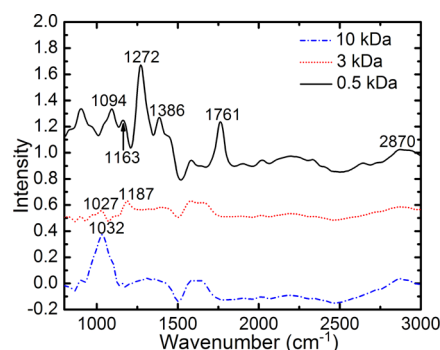

Figure 5. Diffused reflectance FTIR spectra of the material deposited on the 10 kDa, 3 kDa, and 0.5 kDa membranes. The offset for the spectra of permeates from 3 kDa and 0.5 kDa membranes are 0.6 and 1.2, respectively.

kDa membrane, and most of the organic matter passed through it, resulting in the least amount of fouling of the 3 kDa membrane.

■ DISCUSSION

The boiler blow-down water obtained in SAGD operations has a high dissolved organic matter content, which is significantly higher than that found in conventional or low-temperature petroleum extraction produced waters. We speculate that the thermal history of the produced fluid in SAGD during steam generation and the high pH water treatment operations cause this enhanced solubilization. The DOM in the SAGD BBD water can be classified into six discernible classes based on their hydrophobicity and hydrophilicity using resin-based fractionation. The hydrophobic acids and hydrophilic neutrals are the principal fractions, collectively constituting about 65% of the total DOM. The fluorophores in these DOM fractions have different fluorescence excitation−emission signatures. The fluorescence excitation−emission mapping of the hydrophobic acid fraction shows that the fluorophores in these molecules are

more representative of humic acids than naphthenic acids, which is a distinguishing feature of this water stream in SAGD operations from the mining OSPW obtained in oil sands tailings ponds. Since the solubility of NAs in mining OSPW water is at best of the order of 100 mg/L, the extremely high amounts of DOM (typically >2000 mg/L) in BBD also corroborate that a large fraction of the DOM in SAGD BBD are not naphthenic acids. The fluorescence excitation–emission contours for permeate samples from membranes of different MWCO show that size-based fractionation of the DOM fails to separate the different classes of fluorophores from the BBD. Broadly, our study indicates the presence of a significant amount of additional water-soluble class of petroleum organic matter, which needs to be accounted for when dealing with produced waters during thermal EOR.

The characterization of DOM based on its chemical (hydrophobic/hydrophilic) nature may be used to select the appropriate DOM removal technique for boiler blow-down water. For example, since the BBD has a high amount of hydrophobic acids with humic-like signatures, microbial treatment of this type of water may not be suitable for DOM removal,[53,54] as humic substances are generally resistant to microbial degradation under anaerobic conditions.[53] Membrane filtration processes such as microfiltration, ultrafiltration, and nanofiltration have been used for removing dissolved organic components from various aqueous systems.[55–58] A fouling resistant ultrafiltration membrane was reported to remove 45% of the organics from a conventional oil field produced water.[59] In this study, it is observed that only 8% and 25% of the DOM are removed by the 10 kDa and 3 kDa membranes, respectively, indicating the majority of the organic molecules in the DOM have very low molecular weight. Hence, micro- and ultra-filtration cannot be used effectively for DOM removal from BBD unless the DOM is first converted to a solid phase through aggregation, precipitation, or coprecipitation with a coagulant. The 0.5 kDa MWCO membrane was able to remove 60% of the DOM.

It is interesting to note here that $SUVA_{254}$ and fluorescence EEMs are relatively straightforward characterization techniques, but they still could be used effectively to differentiate between different classes of the DOM in our study. Numerous studies are available to characterize NOM/DOM using techniques such as FT ICR mass spectrometry,[6,8] pyrolysis GC-MS,[10,33,36] HPLC-MS/MS,[37] ^{13}C NMR spectroscopy,[60] cyclic voltamme-try,[61] capillary electrophoresis,[62] etc. One can certainly apply such analytical methods in conjunction with ion exchange or size exclusion chromatography to obtain a detailed fingerprint of the organic compounds present in SAGD water. However, spectrofluorescence and UV absorption based analysis of DOM fractions in BBD seem to provide adequate resolution of the different classes of hydrophobic and hydrophilic compounds from a process development standpoint.

CONCLUSIONS

SAGD boiler blow-down water (BBD) has a marked difference in water quality parameters (higher pH, high DOM content, high silica, and high TDS) compared to other produced waters, such as oil-field produced water and mining based oil sands process-affected water (mining OSPW). The fluorescence excitation–emission matrix spectra (EEMs) of BBD, SAGD produced water, mining OSPW, and commercial naphthenic acids show that the dissolved organic matter (DOM) in BBD differ considerably from mining OSPW and commercial

naphthenic acids. The resin-based fractionation of the DOM yields hydrophobic acids and hydrophilic neutrals as the predominant fractions. In contrast, molecular weight based filtration failed to fractionate the DOM into various hydrophobic and hydrophilic classes. This study could assist in understanding DOM characteristics during SAGD produced water treatment operation and to develop efficient technologies for proper management and recycle of SAGD BBD water.

ASSOCIATED CONTENT

Supporting Information
Experimental details of resin-based fractionation of DOM from BBD. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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