

Comparison of the Effects of Extraction Techniques on Mass Spectrometry Profiles of Dissolved Organic Compounds in Oil Sand Process-Affected Water

Hattan A. Alharbi,[†] Garrett D. Morandi,[‡] Paul D. Jones,^{‡,§} Steve B. Wiseman,^{||} and John P. Giesy^{*,‡,⊥,#,¶}

[†]Department of Plant Protection, College of Food and Agriculture Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

[‡]Toxicology Centre, [§]School of Environment and Sustainability, and [⊥]Department of Veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5B3, Canada

^{||}Department of Biological Sciences and Water Institute for Sustainable Environments (WISE), University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada

[#]Zoology Department, Center for Integrative Toxicology, Michigan State University, East Lansing, Michigan 48824, United States

[¶]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, People's Republic of China

ABSTRACT: Recent advances in mass spectrometry have facilitated chemical characterization and profiling of complex environmental mixtures such as oil sand process-affected water (OSPW) and identification of previously unresolved chemicals. However, because OSPW is a complex mixture of salts, metals, suspended particulate matter, and dissolved organics, extraction techniques are required to reduce the effects of signal suppression/enhancement. In this work, Orbitrap, ultrahigh resolution mass spectrometry was used to perform a comprehensive comparison of solid phase extraction (SPE) and liquid–liquid extraction (LLE) techniques on profiling of dissolved organic chemicals in OSPW. When operated in negative ion mode, extraction of naphthenic acid (NAs–O₂) was dependent on acidification of OSPW samples for C₁₈ and LLE techniques. However, when applying a hydrophilic lipophilic balance (HLB) sorbent (ABN) SPE technique, the extractability of NAs was independent of pH. When operated in positive ion mode, for all extraction methods, nitrogen- and sulfur-containing species were more abundant and diverse in basic extracts than in acidic extracts and ABN extracted the greatest number of chemical species including nitrogen-, sulfur-, and oxygen-containing species. Overall, this study supports the utility of HLB SPE techniques for profiling of species of dissolved organic chemicals in OSPW at environmentally relevant pH.

INTRODUCTION

The surface mining oil sand industry in Alberta, Canada, uses large volumes of water in the extraction of bitumen. This process results in production of significant quantities of process water, commonly referred to as oil sand process-affected water (OSPW) that contain solids such as sand, clays, and inorganic and organic compounds.^{1,2} Organic compounds in OSPW can be classified as dissolved organic compounds or water-soluble polar organic acid fraction containing a group of organic acids generally known as naphthenic acids (NAs) as well as other nitrogen- and sulfur-containing compounds, which are of ecotoxicological concern.³ Currently, to limit the use of freshwater, OSPW is recycled during extraction; however, this process concentrates organic and inorganic components in OSPW. Over time, the quality of OSPW deteriorates to a point where it is no longer effective in bitumen extraction and as a result is stored in large tailing ponds (or on-site active settling basins) to be remediated and eventually returned to the receiving environment.⁴

Polar chemicals in petroleum mixtures are water-soluble compounds, which can be classified as acidic, basic, and neutral compounds.⁵ Recent advances in high-resolution mass spectrometry such as Orbitrap or Fourier transform ion

cyclotron resonance mass spectrometry have greatly improved chemical profiling of water-soluble or dissolved organic compounds in OSPW and provide selective detection supported by accurate mass measurements.^{6–11} An additional advantage of ultrahigh-resolution techniques such as Orbitrap instruments is the ability to obtain full scan and MS/MS data with high accuracy to support elucidation of chemical structures.⁷ However, an inherent issue in analysis of organic chemicals in petroleum mixtures, including OSPW, is the complexity of the mixture requiring extraction/fractionation and clean-up steps. Therefore, sample preparation is critical to analysis of such complex mixtures. Selective isolation of analytes of interest is important to facilitate their detection and identification. Solid-phase extraction (SPE) is one of the most powerful and efficient sample preparation techniques for isolation, clean-up, preconcentration, and de-salting of analytes from their matrices.¹² There are many types of SPE materials (i.e., sorbents), which are commercially available and

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extraction methods can be adjusted depending on mechanisms of interaction between sorbents and analytes. The most commonly used sorbents are polymeric sorbents without ion-exchange moieties such as hydrophilic–lipophilic-balance (HLB), silica-based materials modified with C_{18} chains and phenyl groups, and hyper-crosslinked polymeric sorbent modified with hydroxyl groups. These types of sorbents can isolate acidic, basic, and neutral compounds when present in their neutral form, whether polar or nonpolar.¹³

Isolation and identification of components in OSPW has focused primarily on characterizing acutely toxic chemicals that are referred to as “acid-extractable organics”, “organic acids”, or “NA fraction”.^{1,14–22} However, other sulfur- and nitrogen-containing compounds have been demonstrated to exert effects on some aquatic species.^{9,23} Most extraction techniques developed for characterizing dissolved organic fraction of OSPW aim to isolate a broad range of chemicals with differing physicochemical properties.⁷ However, a systematic approach for assessing extraction efficiencies of various methods, such as recovery, has not been undertaken with OSPW, because of the lack of individual authentic standards. Liquid–liquid extraction (LLE) is the most commonly used method for isolation of acid-extractable chemicals,^{7,23,24} but other methodologies including SPE such as ISOLUTE ENV+,¹¹ HLB,^{25–27} C_{18} ,²⁸ or anion exchange⁹ have been employed to separate acid-extractable fractions of OSPW. These methods can achieve large recoveries for NAs and require acidification ($\sim$ pH 2) before extraction, but this approach does not support simultaneous extraction of chemicals in OSPW with different physicochemical properties, solubility, molecular mass, and hydrophobicity that can affect extraction efficiencies.

Sample preparation techniques are required for analysis of oil sand-related environmental samples, which can lead to robust characterization of a diverse range of chemicals present in OSPW. There is a lack of information about a detailed comparison among extraction methods of NAs and other dissolved organic compounds in OSPW. Therefore, it is necessary to evaluate sample preparation, which is a critical requirement for development of a standard analytical method to be used for environmental analysis of NAs and other dissolved organic compounds in OSPW. The objective of the current study was to compare efficiencies of various extraction methods for characterization of acidic, and basic extractable fractions of OSPW using liquid chromatography coupled to full-scan high-resolution mass spectrometry to identify a robust method capable of isolating the broad range of dissolved organic compounds present in OSPW.

■ EXPERIMENTAL SECTION

Samples of OSPW were collected in September 2015 from Base Mine Lake (previously the West-In-Pit settling basin) from a permanent sampling barge (Syncrude Canada Ltd.). The dissolved organic compounds in OSPW were extracted using SPE or LLE. First, samples of OSPW were passed through a glass microfiber filter (GF/D 0.47 mm, Whatman) to remove any particulate matter. Cartridges for SPE methods used in this study included EVOLUTE ABN Cartridge at 500 mg/6 mL (HLB; Biotage, Charlotte, NC, USA); Strata-X-A Cartridge at 500 mg/6 mL (anion-exchange and reversed-phase; Phenomenex, Torrance, CA, USA); Strata-X-C Cartridge at 500 mg/6 mL (cation-exchange and reversed-phase; Phenomenex, Torrance, CA, USA); HyperSep C_{18} Cartridge at 500 mg/6 mL (hydrophobic reversed-phase; Rockwood, TN, USA); and Supelclean ENVI-Carb Cartridge at 500 mg/6 mL (reversed-phase; Sigma-Aldrich, Oakville, ON, Canada). For SPE and LLE, OSPW was extracted under acidic

($\sim$ pH 2–2.5 using hydrochloric acid, Sigma-Aldrich) and basic conditions (pH 9 using ammonium hydroxide solution, Sigma-Aldrich). Dichloromethane (DCM) and methanol were of high-performance liquid chromatography grade and purchased from Fisher Scientific (Ottawa, ON, Canada). Ultrapure Milli-Q water was obtained from Millipore (Mississauga, ON, Canada).

For extraction of acidic compounds, SPE cartridges that were used included ABN and C_{18} . For each extraction method, the same procedure was used and included the following steps: (1) adjustment of pH to around 2.5 for 500 mL samples of OSPW by use of concentrated hydrochloric acid. (2) Conditioning of the SPE cartridge with 6 mL of methanol followed by 6 mL of water containing 0.1% (v/v) hydrochloric acid. (3) Samples were passed through each cartridge at a rate of approximately 1 mL/min using a vacuum SPE manifold. (4) Cartridges were washed with 6 mL of ultrapure Milli-Q water. (5) SPE cartridges were dried under vacuum for 15 min. (6) Total organic fraction was eluted with methanol for ABN and C_{18} . For isolation of acidic compounds using Strata-X-A, the pH of OSPW in the first step was adjusted to around 9, addition of 1% ammonium hydroxide (v/v) in methanol was used for conditioning (step 2), and the loaded organic fraction (step 6) was eluted with 0.1% hydrochloric acid (v/v) in methanol.

The procedure for extraction of basic compounds was similar to the abovementioned procedure, with some exceptions. The pH of OSPW was adjusted to around 9 for ABN and C_{18} , and ENVI-Carb, pure water, and methanol were used without addition of organic acid. For Strata-X-C (to isolate basic compounds), the steps included acidification of OSPW, use of 0.1% hydrochloric acid in water (v/v) for conditioning (step 2), and use of 1% ammonium hydroxide in methanol for elution (i.e., step 6). For LLEs, 500 mL of filtered OSPW was extracted twice at either pH 2 or 9 with 250 mL of DCM (a total of 500 mL) in a separatory funnel to yield the acid-extractable fraction and basic-extractable fraction, respectively.

Extracts from SPE and LLE were evaporated under a gentle stream of N_2 gas to obtain a concentrated extract of 500 $\times$ in methanol. For quality control, method blanks were prepared by use of ultrapure Milli-Q water (Millipore, Mississauga, Canada) in place of OSPW for all the procedures outlined above. To evaluate the effects on signal response in the sample extracts, myristic acid^{24-1-¹³C} and palmitic acid- d_{31} (Sigma-Aldrich, Oakville, ON, Canada) were used for analysis when operated in negative ion mode (ESI^-) and 1-Benzylimidazole when operated in positive ion mode (ESI^+). Briefly, sample extracts were spiked with each internal standard at 100 ng/L and their signal responses were compared to the same concentration in pure methanol.

The heteroatom classes distribution in each extract was determined by use of a Q-Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a Dionex UltiMate 3000 UHPLC system (Thermo Fisher Scientific). Separation of organic compounds was achieved on a Betasil C_{18} column (5 μ m; 2.1 mm $\times$ 100 mm; Thermo Fisher Scientific) with an injection volume of 5 μ L. The mobile phase consisted of ultrapure water (A) and methanol (B). Initially, 20% B was increased to 80% in 3 min, then increased to 100% at 8 min and held static for 19.5 min, followed by a decrease to initial conditions of 20% B and held for 2 min to allow for equilibration of the column. The flow rate was 0.25 mL/min. The temperature of the column and sample chamber were maintained at 30 and 10 $^{\circ}$ C, respectively. Data were acquired using full scan mode in both positive (ESI^+) and negative (ESI^-) ion modes. Briefly, MS scans (100–1000 m/z) were recorded at resolution $R = 70\,000$ (at m/z 200) with a maximum of 3×10^6 ions collected within 200 ms, based on predictive automated gain control. General mass spectrometry settings applied for ESI^- and ESI^+ were as follows: spray voltage, 2.8 kV; capillary temperature, 400 $^{\circ}$ C; sheath gas, 35 L/h; auxiliary gas, 8 L/h; probe heater temperature, 350 $^{\circ}$ C. Chemical species were grouped according to heteroatom empirical formula classes in ESI^- or ESI^+ electrospray: $O_x^{+/-}$ (where $x = 1-5$), $N^{+/-}$, $NO_x^{+/-}$ (where $x = 1-4$), $S^{+/-}$, $SO_x^{+/-}$ (where $x = 1-5$), or $NO_xS^{+/-}$ (where $x = 1-4$).

RESULTS

Chemical profiles of organic compounds in OSPW were investigated by comparing traditional LLE with other SPEs conducted under acidic and basic conditions using both ESI^{+/−}. In OSPW, NAs have been the focus of most investigations and can be efficiently isolated under acidic conditions (i.e., pH 2, the acid-extractable fraction).^{11,29} In ESI[−], the *m/z* distribution was similarly distributed for all sample extracts spanning *m/z* 150–500 (Figure 1A,B). For all

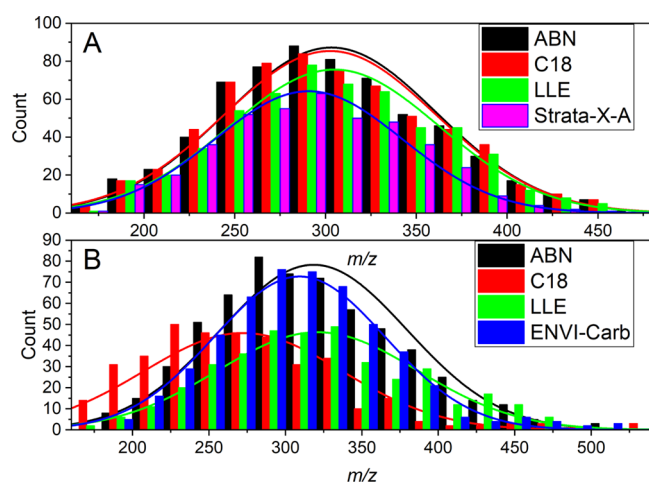


Figure 1. Comparison of *m/z* distribution of samples of OSPW extracted under (A) acidic and (B) basic conditions by use of ESI[−]-Orbitrap MS (Strata-X-A and ENVI-Carb were used for acidic and basic compounds, respectively).

extracts (regardless of the extraction methods and pH), most detected ions eluted between 8 and 23 min and generally spanned *m/z* 200–450. However, the number of ions with *m/z* 200–350 detected in samples extracted under acidic conditions was greater in samples extracted by ABN > C₁₈ > LLE > Strata-X-A (Figure 1A). The trend was somewhat different when samples were extracted at pH 9; the range of masses (*m/z* 150–250) that had the greatest number of ions were observed in C₁₈ but at *m/z* 250–450, the greater number of ions were extracted by ABN > ENVI-Carb > LLE (Figure 1B). This indicates that HLB (ABN) sorbents might be most efficient in extracting a greater number of ions at both pH of 2 and 9.

The contribution of oxygen-containing compounds (i.e., O_{1–6}[−]) to total intensity was greatest in both acidic and basic extracts when detected using ESI[−]. In acidic extracts, total intensity of O_x[−] species was lesser in extracts from C₁₈ (72%) than ABN (74%), and LLE (84%), and greatest in extracts produced by use of Strata-X-A (86%) (the total intensity of individual classes presented in Figure 2A). Conversely, in samples extracted under basic conditions, the total intensity of O_x[−] was lesser in extracts from ABN (70%) and ENVI-Carb (70%) than LLE (82%) and greatest in extracts produced by use of C₁₈ (88%) (Figure 2B). Among all the extraction methods used, the distributions of oxygen-containing compounds were similar, and had greater intensity when compared to other heteroatom classes, which is consistent with previously reported results.²⁹ Total intensity of O₄[−] species was greater in samples extracted at pH 2 when compared to those extracted at pH 9 (Figure 3), with greatest intensity detected in LLE > Strata-X-A > ABN > C₁₈ for acidic extracts.

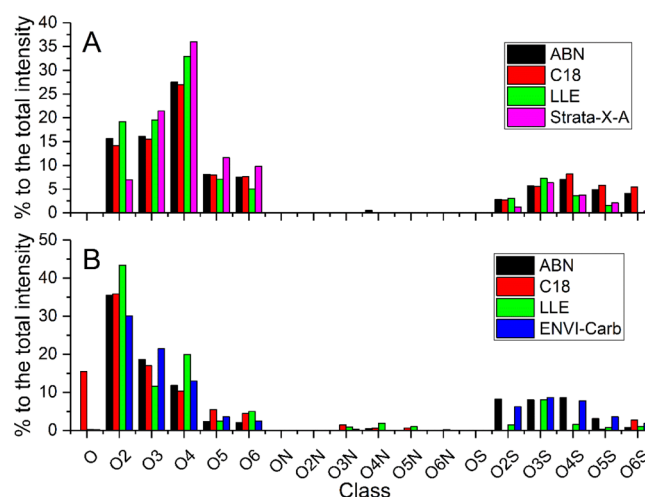


Figure 2. Comparison of heteroatom class distribution for extracts of OSPW produced by use of (A) LLE, C₁₈, and ABN under acidic conditions, and (B) LLE, C₁₈, ABN, and ENVI-Carb under basic conditions by use of ESI[−]-Orbitrap MS (Strata-X-A was used for acidic compounds).

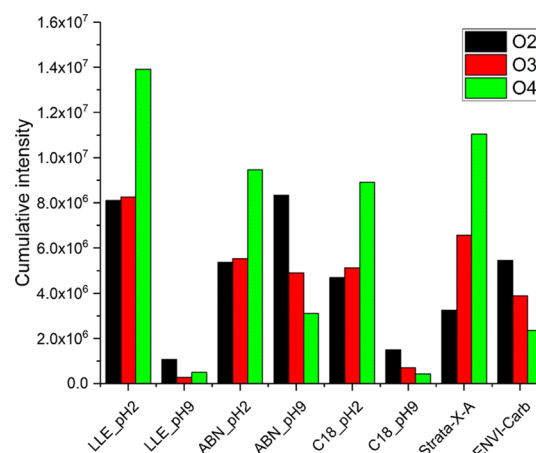


Figure 3. Cumulative ion intensity for O₂[−], O₃[−], and O₄[−]-containing species extracted by use of various extraction methods at acidic and basic conditions by use of ESI[−]-Orbitrap MS (Strata-X-A and ENVI-Carb were used for acidic and basic compounds, respectively).

However, profiles of O₄[−] were different when samples were extracted at pH 9 as the greatest intensity of O₄[−] was observed in ABN > ENVI-Carb > LLE = C₁₈. For O₃[−], the rank order of intensity was LLE > Strata X-A > ABN = C₁₈ at acidic conditions with a similar intensity observed at basic conditions of ENVI-Carb and ABN (Figure 3).

When extracted under basic conditions, classical NAs (O₂[−]) exhibited greater cumulative intensity (ranging from 30 to 44%) when compared to other heteroatom classes for all extraction methods tested (Figure 2B). Extraction of organic acids was pH-dependent where NAs are extracted efficiently under acidic conditions,^{11,24,30,31} when NAs are predominantly present in their neutral form (97 to 99% in molar percentage) at pH 2. In electrospray ionization, the efficiency of ionization is affected by several molecular properties such as pK_a, hydrophobicity, and surface activity.³² The pK_a of O₃[−] and O₄[−]-containing species is greater than that of O₂[−], and it has been suggested that O₃[−] and O₄[−] are addition of extra oxygen atoms to O₂[−]-NAs species, and present as hydroxyl groups

[i.e., O_4^- -NAs exist as $(\text{OH})_2\text{-NAs}$]^{24,33,34} compared to the other assumption that O_4^- are dicarboxylic acids.¹⁶ Lesser intensity of O_2^- species observed under acidic conditions (i.e., pH 2) in ABN, LLE, and C_{18} compared to basic conditions might be due to the greater concentration of O_4^- observed under acidic conditions (Figure 3). It has been suggested that ion-suppression and matrix effects might affect the signal responses of all chemical species in samples of OSPW,³⁵ which might affect quantification. The signal responses of both myristic acid- $1\text{-}^{13}\text{C}$ and palmitic acid- d_{31} in spiked samples of each extraction method are presented (Table 1). Some

Table 1. Signal Response (%) of Myristic Acid- $1\text{-}^{13}\text{C}$ and Palmitic Acid- d_{31} in Spiked Samples of Each Extraction Method Detected by Use of ESI[−]-Orbitrap MS, and 1-Benzylimidazole in Spiked Samples of Each Extraction Method Detected by Use of ESI⁺, Orbitrap MS

	extraction method	signal response (%)		
		palmitic acid- d_{31}	myristic acid- $1\text{-}^{13}\text{C}$	1-benzylimidazole
acidic	C_{18}	85.9	56.6	88.2
	LLE	121.7	107.9	95.3
	ABN	114.6	124.3	84.8
	Strata-X-A	73.4	75.5	NA
basic	C_{18}	97.9	132.2	94.3
	LLE	127.0	155.5	93.2
	ABN	125.9	92.1	96.4
	Strata-X-C	NA	NA	95.8
	ENVI-Carb	79.3	68.4	86.3

suppression and/or enhancement of analyte signal responses were observed. This indicates that detection and trace quantification of organic acids in OSPW might be affected, but detailed evaluation of matrix effects is challenging in a complex matrix such as OSPW. Overall, effects on analyte responses observed (Table 1) were small and support utility of LLE and SPE approaches for generating extracts, which limit the effects of ion suppression/enhancement on signal response.

It has been suggested that O_3^- to O_6^- species are degradation products of classical O_2^- species (i.e., weathered NAs).³⁵ In addition, it has been suggested that measurement of ratios of $\text{O}_2^-/\text{O}_4^-$ ion classes (based on the intensity) can be used for identification of sources of chemical mixtures in OSPW that might migrate to groundwater in oil sands area.³⁵ A comparison of cumulative intensity of O_2^- , O_3^- , and O_4^- species between LLE, ABN, C_{18} , Strata-X-A, and ENVI-Carb at different pH is presented in Figure 3. Effect of extraction pH on chemical profiles was observed in both LLE, and C_{18} , as the cumulative intensity substantially increased when the extraction pH was decreased, but ABN sorbent showed quite similar intensity distribution as O_2^- , O_3^- , and O_4^- regardless of the pH used for extraction (Figure 3). On the basis of profiles of O_2^- , O_3^- , and O_4^- species, extracts of OSPW generated at pH 2 had greater prevalence of O_4^- species than O_2^- species compared to extracts generated at pH 9 (Figure 3), which demonstrates the importance of acidification of samples of OSPW before extraction when diagnostic measurements for source identification are required. The ratio of $\text{O}_2^-/\text{O}_4^-$ was >1.0 for extracts from ABN, LLE, C_{18} , and ENVI-Carb at pH 9, whereas samples extracted at pH 2 had ratios of $\text{O}_2^-/\text{O}_4^-$ that were <1.0 . In addition, the ratio of $\text{O}_2^-/\text{O}_4^-$ decreased with increasing numbers of carbons (Figure 4). Use of $\text{O}_2^-/$

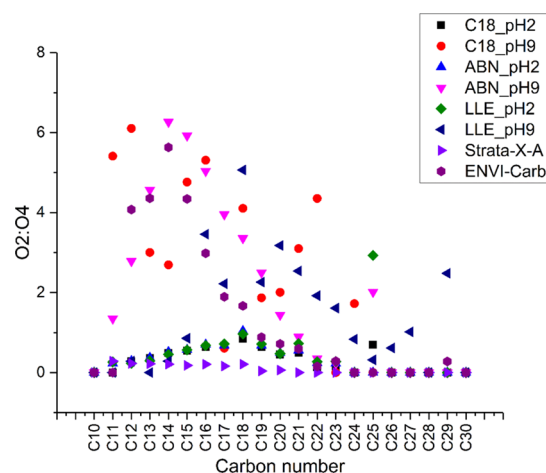


Figure 4. Profile of ratio of $\text{O}_2^-/\text{O}_4^-$ -containing species in extracts generated by use of various SPE and LLE extraction techniques under acidic and basic conditions detected by use of ESI[−]-Orbitrap MS (Strata-X-A and ENVI-Carb were used for acidic and basic compounds, respectively).

O_4^- ion classes ratios to differentiate natural sources of bitumen influences water from OSPW sources and weathering is more useful for molecules of lesser carbon number.³⁵

The pH of extraction did not clearly affect the distribution of sulfur-containing compounds (S_x^-) detected in ESI[−] and resulted in comparable cumulative intensity of 15 and 13% in LLE extracts, and of 24 and 28% in ABN extracts, for pH 2 and 9, respectively (Figure 2A,B). However, the sample extract from C_{18} had enriched signal intensity of sulfur-containing species with 28% under acidic conditions, but small intensities of 3% under basic conditions. The sample extract from Strata-X-A (acidic compounds) had comparable intensity as LLE but slightly lower (except for SO_3^-) than ABN (Figure 2A), which indicates that HLB sorbents and LLE can extract ionizable and nonionizable sulfur-containing organic compounds regardless of extraction pH.

Contributions of nitrogen-containing species (N_x^-) detected in ESI[−] were small for all extraction methods tested at pH 2; however, extraction of OSPW at pH 9 resulted in a slightly greater intensity of nitrogen-containing species (Figure 2A,B, respectively). The lesser intensity of nitrogen-containing compounds in ESI[−] has been previously observed in extracted organic fraction of OSPW,^{9,11,23} when compared to that of ESI⁺. Moreover, the absence of nitrogen-containing compounds and the small contribution of sulfur-containing compounds might be due to the intensity threshold of $\geq 2\%$ relative intensity that was applied for the identified peaks. Because the majority of nitrogen-containing compounds in OSPW are either neutral or basic,⁹ it is possible that basic nitrogen-containing compounds are detected efficiently in ESI⁺, whereas neutral nitrogen ions were detected by use of both ESI[−] and ESI⁺.^{36,37} It should be noted that nitrogen-containing compounds have been efficiently detected by use of atmospheric pressure photoionization when compared to ESI.^{11,38} Moreover, acidic nitrogen-containing compounds have been detected in OSPW⁷ and it is possible that concentration of carboxylic acid-containing compounds might compete with other classes of ions present during ionization.³⁹ As a result, nitrogenous compounds were not detected in ESI[−], but this does not necessarily indicate absence of acidic nitrogen compounds in OSPW. The same principle

might be applied to oxygen-containing species (i.e., O_2^- and O_4^-), whereas O_2^- was observed to be more abundant when extracted under basic conditions compared to acidic conditions. Charge competition between ions affects the ESI process in the presence of a mixture having a greater number, different physicochemical properties, and larger concentrations of analytes. Greater concentrations of O_4^- species observed in acidic extracts might lead to charge competition and decrease the capacity of ionization for O_2^- species.

When extracts of OSPW were characterized using ESI^+ , the heteroatom compound classes detected were broader compared to those detected by use of ESI^- , which is consistent with results of several previous studies.^{11,29,40,41} When comparing distributions of ions detected in samples extracted at pH 2, both ABN and LLE exhibited near identical ion numbers detected in the range of m/z 150–450 (Figure 5A),

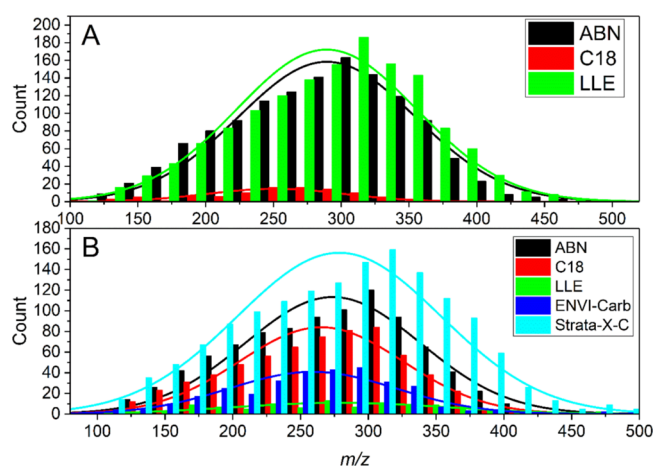


Figure 5. Comparison of m/z distributions for samples of OSPW extracted under (A) acidic and (B) basic conditions when detected by use of ESI^+ -Orbitrap MS (Strata-X-C and ENVI-Carb were used for basic compounds).

and fewer ions (but with higher intensity) were detected in samples extracted by C_{18} . When extracted at pH 9 (Figure 5B), the cation exchange sorbent (i.e., Strata-X-C) extracted the greatest number of ions over the entire range (m/z 150–450) followed by ABN and C_{18} , whereas ENVI-Carb and LLE had a lesser number of ions detected. LLE can extract all compounds in OSPW based upon manipulation of aqueous pH. In the ABN cartridge, the balanced combination of polar (hydrophilic) and nonpolar (hydrophobic) interactions enables extraction of polar and nonpolar compounds, whereas C_{18} sorbent can extract nonpolar compounds more efficiently than polar compounds. However, the lesser number of ions detected in LLE at pH 9 might indicate lower efficiency of LLE to extract basic compounds from OSPW. In addition, these results demonstrated the utility of cation exchange sorbents for improving extraction of basic and neutral compounds in OSPW. The signal response of 1-benzylimidazole used to investigate the ion response in ESI^+ indicated no clear differences between the extraction methods (Table 1). This indicates that chemicals detected in ESI^+ encounter less ion suppression compared to organic acids and other sulfur and nitrogen compounds detected in ESI^- .

In ESI^+ , elemental compositions of dissolved organic compounds and percentage contributions of each class for samples extracted under acidic conditions are presented

(Figure 6). Nitrogen- (NO^+ , NO_2^+ , NO_3^+ , and NO_4^+), and sulphur- (SO^+ , SO_2^+ , and SO_3^+) containing compounds were

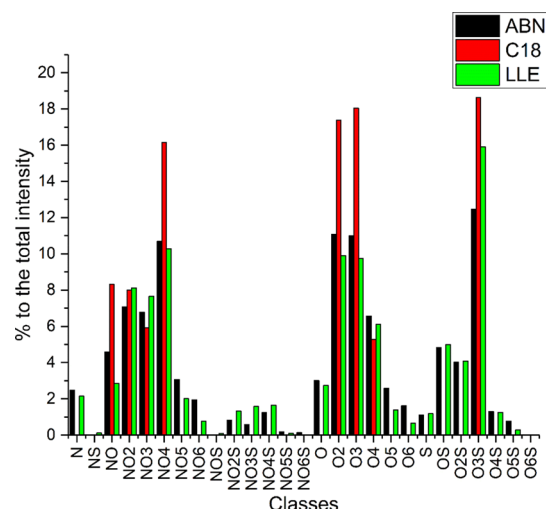


Figure 6. Comparison of heteroatom class distribution for extracts of OSPW produced by use of by ABN, C_{18} , and LLE under acidic conditions as detected by use of ESI^+ -Orbitrap MS.

enriched in extracts of ABN, LLE, and C_{18} analyzed by ESI^+ , when compared to the same fractions analyzed in ESI^- (Figure 2). Although the C_{18} sample extracts exhibited greater intensity for some species (NO^+ , NO_4^+ , O_2^+ , O_3^+ , and SO_3^+), heteroatomic species extracted by use of LLE and ABN were more diverse (Figure 6). OSPW extracted under basic conditions (Figure 7) exhibited enriched signal intensity and chemical classes' diversity for all extraction methods when compared to the same extracts detected in ESI^- (Figure 2B). The total intensity of O_x^+ classes in samples extracted under acidic conditions (the total intensity for individual classes is presented in Figure 6) were 40, 36, and 31% for C_{18} , ABN, and LLE, respectively. For basic conditions, O_x^+ accounted for 32, 31, 29, 28, and 27% for Strata-X-C, ENVI-Carb, C_{18} , ABN, and LLE, respectively (the total intensity for individual classes is presented in Figure 7A). Greater intensity of nitrogen- and sulphur-containing compounds were observed in ESI^+ (Figures 6, and 7) when compared to ESI^- (Figure 2) in both acidic and basic extracts. For SO_x^+ species, the total intensity in acidic extracts (Figure 6) of LLE, ABN, and C_{18} were 27, 24, and 18%, respectively; however, the same species had an almost similar cumulative intensity under basic conditions (Figure 7B) with 28, 27, 27, 25, and 20% for C_{18} , ABN, LLE, Strata-X-C, and, ENVI-Carb, respectively. Profiles of nitrogen- and nitrogen-sulphur-containing species (NO_xS^+) were unique in ESI^+ in acidic extracts when compared to ESI^- . Species containing nitrogen and nitrogen-sulphur accounted for approximately 40, 39, and 38% for ABN, LLE, and C_{18} , respectively under acidic conditions (Figure 6), and a similar trend of cumulative intensity was observed for the same species in basic conditions with 48, 43, 40, 40, and 39% for LLE, ABN, ENVI-Carb, Strata-X-C, and C_{18} , respectively (Figure 7C).

CONCLUSIONS

This study compared several SPE sorbents with traditional LLE using DCM for their effectiveness to profile heteroatom classes in organic fractions of OSPW extracted under acidic or basic conditions. The present investigation demonstrated that

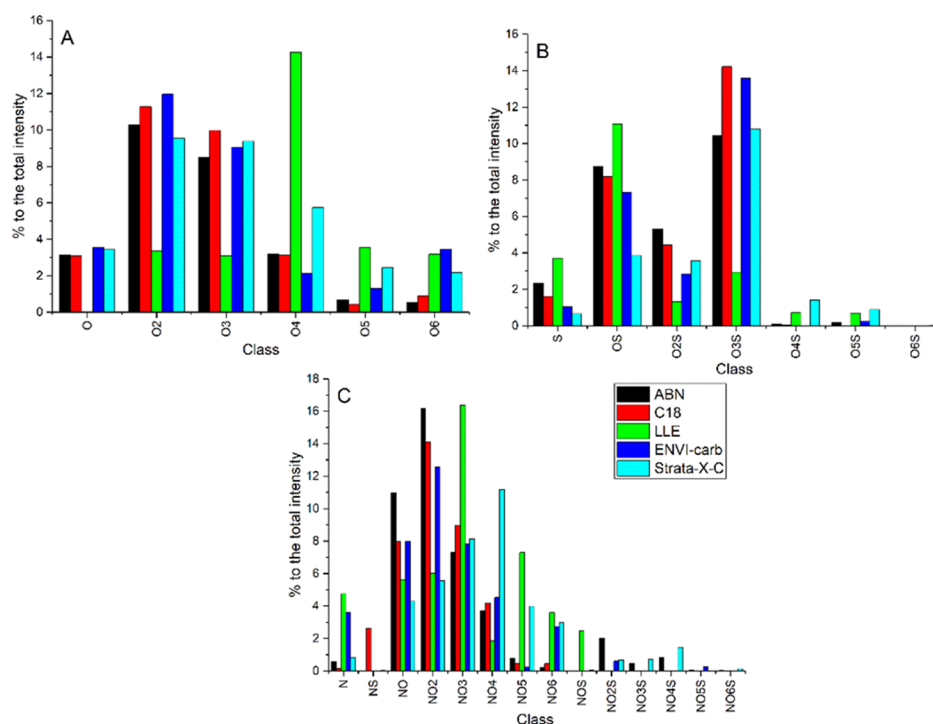


Figure 7. Comparison of heteroatom class distribution of (A) O_x^+ , (B) O_xS^+ , and (C) NO_xS^+ for extracts of OSPW generated by use of various SPE and LLE extraction techniques under basic conditions as detected by use of ESI⁺-Orbitrap MS.

extraction methods could affect the characterization of not only NAs species but also other OSPW constituents such as nitrogen- and sulphur-containing compounds. Acidification of OSPW samples is a critical step in LLE and C₁₈ for isolating O₂–NA species. However, acidification had less influence when using HLB (i.e., ABN-SPE) on profile of O₂[−]–NAs species when detected in ESI[−]. When operated in ESI⁺, the chemical profile of extracts was more diverse for ONS species. The results from this study show that ABN (or HLB) is suitable to extract a diverse group of compounds (that include NAs) in OSPW and outperforms the traditional extraction method (i.e., LLE), and other SPE sorbents. Results of this study emphasize the importance of characterizing the effect of sample preparation techniques on profiling, identification, and source attribution in regards to dissolved organic compounds of OSPW.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jgiesy@aol.com.

ORCID

Hattan A. Alharbi: [0000-0003-3297-729X](https://orcid.org/0000-0003-3297-729X)

Notes

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