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Abstract

Naphthenic acids (NAs) constitute one of the toxic components of the produced water (PW) from offshore oil platforms discharged into the marine environment. We employed liquid chromatography coupled to high resolution mass spectrometry with electron spray ionization in negative mode for the comprehensive chemical characterization and quantification of NAs in PW samples from six different Norwegian offshore oil platforms. In total we detected 55 unique NA isomer groups, out of the 181 screened homologous groups, across all tested samples. The frequency of detected NAs in the samples varied between 14 and 44 isomer groups. Principal component analysis indicated a clear distinction of the PW from the tested platforms based on the distribution

of NAs in those samples. The averaged total concentration of NAs varied between 6 and 56 mgL^{-1}, among the tested platforms whereas the concentration of the individual NA isomer groups ranged between 0.2 and 44 mgL^{-1}. Both based on the distribution and the concentration of NAs in the samples $C_8H_{14}O_2$ isomer group appeared to be a reasonable indicator of the presence and the total concentration of NAs in the samples with a Pearson correlation coefficient of 0.89.

Introduction

Produced water (PW) from the offshore oil-industry discharged into the marine environment represents a significant source of organic and inorganic contaminants.[1–4] The Norwegian oil sector alone discharges approximately 140 million m^3 per year of produced water into the North Sea.[1,5] PW is considered an unresolved complex mixture containing a wide range of chemical substances with diverse chemical and physical properties from metals to naphthenic acids.[2–4,6,7]

Conventional naphthenic acids (NAs) are considered one of the highly toxic components of the PW with potential adverse effects once, discharged into the marine environment.[3,7–12] These are naturally occurring compounds in the oil having the known chemical formula of $C_nH_{2n+z}O_2$, where n represents the number of carbons and z/2 defines the number of rings/unsaturation.[13] However, recent studies have indicated the presence of more complex structures such as aromatic acids and di-acids in the acidic fraction of petroleum and/or PW.[14–16] However, these chemicals appear to be much more abandonment in the petroleum rather than the PW. Therefore, throughout this manuscript the NA refers to the conventional naphthenic acids, unless it is stated otherwise. The NAs, in addition to being toxic to a variety of marine organisms, they also constitute an unresolved mixture of thousands of structural isomers. This complexity is translated into challenges related to their identification and quantification in samples such as PW.[2,17–19] In fact, most of commonly used

quantification approaches for NAs are gravimetric methods and are only able to produce the total concentration of acidic extract of PW or PW like samples (e.g. oil sand affected process water).[18] These methods are coarse and highly dependent on the steps taken during the sample preparation (e.g. extraction procedure),[2,20] which results in different compositions of the final extracts and consequently causes different observed fate and toxicity profiles.

Advanced analytical technologies such as comprehensive two dimensional chromatography (GC×GC) have shown great potential in dealing with complex environmental samples, including PW.[2,4,6,19,21–23] The GC×GC instruments are typically coupled to low resolution mass spectrometers and when used for analysis of NAs they may require the samples to go through some treatments (e.g. esterification and/or reduction to alkanes) before their introduction into the instrument.[16,24,25] These approaches, even though effective for the structural elucidation, are not used for the quantification of NAs in PW. This is due to sample alteration (e.g. esterification and/or reduction to alkanes), which introduces a high level of variability into the data and as such the quantification of NAs in PW becomes unreliable using such methods (i.e. GC×GC).

Another commonly used method for the analysis of NAs in PW is based on the application of ultra high resolution mass spectrometry provided via Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS).[6,18,19] The FTICR-MS instruments are rarely coupled to a chromatographic instrument (e.g. LC and/or GC), due to extremly large and complex datasets produced for the analysis of complex mixtures such as PW.[26] Additionally, this method, even though highly selective, is very expensive and has a low throughput, which reduces its applicability for routine analysis of NAs in PW samples.

Liquid chromatography coupled with high resolution mass spectrometry (LC-HRMS), on the other hand, has shown to be a very powerful analytical tool for the analysis of NAs

in PW, including their quantification.[6,18,19,27,28] Additionally, LC-HRMS based methods can handle the direct injection and/or introduction of the samples into the instrument without any sample pre-treatment.[27] These approaches take advantage of the separation power of the LC and the high selectivity of HRMS to resolve the complex mixtures, such as PW samples. In case of the NAs in the PW the well-established chemical formula of NAs enables the use of suspect screening strategies (i.e. the application of chemical databases) for their identification in those samples.[29–31] Consequently, the detailed classification and quantification of these NAs in PW has become possible utilizing LC-HRMS.

All these advanced analytical technologies produce large amounts of complex data, that must be processed using commercial or open-source tools (i.e. vendor or public software for LC-HRMS data processing) in order for NAs to be identified and quantified in the complex mixture of PW.[6,19,21,29,32] This is an extremely challenging task owing to the fact that the combined resolution provided by liquid and/or gas chromatography and HRMS is still not enough to completely separate the individual NAs (i.e. structural isomers) from each other. Therefore, most of the commercially available software (i.e. vendor packages) are not developed/optimized to handle the complexity of such datasets. As a consequence, the studies that performed the quantification of NAs in different matrices including PW have only provided the total concentration of NAs rather than the concentration of individual isomer groups.

In this study we report on a comprehensive chemical characterization and quantification of NAs in PW samples from six Norwegian North Sea/continental shelf oil platforms. This is the first study producing the detailed characterization and quantification of NAs in offshore oil platform PW samples. In this study we developed and validated an analytical approach based on LC-HRMS and signal processing to identify and quantify individual NA isomer groups. The validated method was used for the identification and quantification of 181 NA

isomer groups across all tested samples. Both the distribution and the concentrations of NAs compared across all the samples. We also investigated the possibility of using a specific NA isomer group as a proxy/marker for both the presence and concentration of NAs in the Norwegian oilfield PW samples, which can be used as tool for future monitoring of NAs in the PW.[15]

Methods

Chemicals

Liquid chromatography grade solvents methanol and 0.1% ammonium formate in water were purchased from Waters (Waters Milford, MA, USA). Technical glass fiber filters were obtained from VWR, Norway. Finally, octanoic acid-d15 analytical standard, ACS grade isopropanol and a technical mixture of naphthenic acids were purchased from Sigma-Aldrich Norway (purchase date 02-2016).

Produced Water Samples

Six different oil platforms from Norwegian offshore sector were sampled. These samples represent around 18% of the Norwegian sector in the North Sea with total of 19 oil fields and 34 platforms.[33] The sampling procedure followed the guidelines provided by Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) and the Norwegian Oil and Gas.[1] In short 500 mL of each PW sample was collected in triplicates and adjacent to the discharge point (i.e. treated PW). The samples were acidified to a pH of 2 with the addition of a 2N HCl solution. The acidified samples were kept in cold (i.e. 4°C) and dark during the transportation and storage until the analysis. The platforms were selected based on their previously observed levels of NAs in the discharged PW.

Sample Preparation and Analysis

The samples were filtered with technical grade glass fiber filters before being transferred to 1.5 mL amber vials with a final volume of 1 mL. Each vial then was spiked with 50 ng of octanoic acid-d15 as internal standard (IS). The spiked vials then were placed in a freezer until the analysis. We did not include any other sample pre-processing/preparation in order to minimize the effects of the used method on the outcome of our analysis.[2,20] Details of the chemical standards, solvents, and equipment used for this study and their suppliers are provided in the Supporting Information, Section .

All the samples were separated on an Acqity BEH C8 (Waters Milford, MA, USA) of 13 nm, 1.7 μm, 2.1 mm $\times$ 100 mm using a Waters Acquity ultra pressure liquid chromatography (UPLC) system (Waters Milford, MA, USA). The samples were analyzed using a 12 min gradient with the first 1.5 min used as sample loading and desalting step. Details of the chromatographic method are provided in the Supporting Information, Section S1. This separation procedure was optimized using a solution of 150 μgL^{-1} of a technical mixture of NAs in sea water. We monitored the peak of the smallest and the most soluble NS present in that mixture (i.e. $C_8H_{16}O_2$) to optimize the desalting time without losing any of NAs, (details of the method validation are provided in Section S2 of the Supporting Information).

The UPLC system was connected to a time of flight high resolution mass spectrometer Xevo G2-S Q-TOF-MS (Waters Milford, MA, US). The HRMS employed an electron spray ionization source (ESI) operated in negative mode with a nominal resolution of 35,000 and a sampling rate of 2 Hz. We set the ionization source to use a 6 eV collision energy. The HRMS instrument was operated in full scan between 50 and 600 Da for our analysis. These instrumental conditions have shown to be effective in the analysis of NAs in PW samples.[2]

The same instrumental conditions, including the chromatography and HRMS, were uti-

lized for the analysis of all the samples consisting of calibration curve injections, validation injections, samples, and the blanks.

Three milliQ water samples were used as procedural blanks and went through all the sample preparation steps and analysis. Additionally, after each triplicates, a solvent injection was carried out to mitigate potential carry over effects. Finally, all the glassware used for the sample preparation and analysis were oven baked overnight at 450°C.

NA isomer group Detection

For the detection and identification of NA isomer groups in the samples we followed a previously optimized procedure.[2,18,34] In short we integrated the signal of each NA isomer group over the whole chromatogram using a mass window of 3 mDa. The NA isomer groups that had their integrated signal larger than the instrumental noise threshold (i.e. 500 counts) were considered present in that sample, Fig. S2. In total we screened our samples for 181 NA isomer groups.[2] This list of NA isomer groups included both the conventional (i.e. NAs following the $C_nH_{2n+z}O_2$ formula) and sulfur containing ones with the number of carbons (i.e. n) ranging between 8 and 35 whereas the degree of unsaturation varied from zero to eleven (i.e. z= $0:-2:-22$). This implied that we only looked for the O2 species in our samples.

In order to assure that the detected NA isomer groups' signals belonged to the analytes rather than noise or background signal, we considered an NA isomer group detected in the sample only if it was present in all triplicates as well as its integrated signal was at least five times the blank levels. The NA isomer groups that did not meet these criteria were removed from the list of the detected NA isomer groups.

NA isomer group Quantification

For the detailed quantification of NA isomer groups in PW, we employed a five level calibration curve with three replicates for each NA isomer group at each level using a commercially available technical mixture of NAs. These external standard calibration curves assume similar response factors for different components of each NA isomer group. We integrated the IS (i.e. octanoic acid d15) scaled signal of each NA isomer group in the technical mixture over the whole chromatogram. These scaled integrated signals were used to generate external calibration curves for each NA isomer groups present in the technical mixture. We fitted a first order polynomial with the intercept term into the data using the least square method.[35] The NA isomer group calibration curves with the regression coefficients (R^2) $\geq$0.85 were considered adequate for our quantification. We utilized these calibration curves for the quantification of NA isomer groups in the PW samples, Fig. S2 in the SI. For the NA isomer groups in PW that were not present in the technical mixture we used the calibration curve of the closest structurally measured NA isomer group, based on the n and z values, in the technical mixture for our quantification. For the total concentration of NAs, on the other hand, we summed up the concentrations of all the already quantified NA isomer groups in the samples. Therefore, this method requires a high level of overlap in terms of the distribution of NA isomer groups in both the technical mixture and the sample. Due to the lack of representative analytical standards when performing the quantification of both the isomer groups and the total NA, a high level of overlap, in terms of the distribution of NAs, between the used technical mixture and the samples is necessary. Therefore, the analysts must assure that the distribution of NAs present in the technical mixture is relevant to the analyzed samples. This is particularly relevant if the technical mixture is used for the measurement of the total concentration of NAs in samples. With a high level of similarity between the samples and the technical mixtures, the applicability of such approach for the analysis of NAs has been previously demonstrated.[18,19,34,36] Additionally, we further validated this method using nine artificial samples (i.e. dissolved NA technical mixture in sea water), Section S3 of the SI.

The concentrations reported in this study, even though providing much more detailed concentration distribution of NA isomer groups, are considered semi-quantitative measures given that the isomer groups in the technical mixture may not be exactly the same as the one in the samples.

Data Analysis Workflow

All the chromatograms were acquired via MassLynx (Waters Milford, MA, US) and converted into netCDF format files via DBridge package provided by MassLynx. Each chromatogram was converted to three files including the MS^1 channel, MS^e channel, and the lock mass channel, which was used for the mass calibration. We did not use the MS^e channel during our data analysis, considering low fragmentation levels of NAs. All the chromatograms were mass calibrated using a second order polynomial function between the observed mass error in the lock mass channel and the scan number before being processed for the identification and quantification of NAs (details provided elsewhere[2,30,37]). The mass calibrated chromatograms appeared to have mass errors $\leq \pm 3$ mDa across the measured mass window. Finally, to minimize the effects of ion suppression we scaled all the chromatograms by the signal of IS (i.e. octanoic acid-d15) before our analysis.

The multivariate statistical method principal component analysis (PCA) was performed on the detection matrix of NA isomer groups in the PW samples. In order to perform these analysis, the NA isomer groups detection matrix was converted to a binary one, where a detected NA isomer group was set to one and a non-detect one was set to zero. This approach enabled us to evaluate whether there was a correlation between the distribution of NA isomer groups and the tested platforms. We did not use the signal intensities or concentrations due to the limited number of replicates, which did not provide us with enough statistical power.[38] For the PCA, we utilized the singular value decomposition to overcome the larger number

of independent variables (i.e. the detected NA isomer groups) compared to the number of measurements.[35] The PCA was performed via Matlab 2015[39] limiting the total number of components to 3. The maximum number of components was selected based on the cumulative variance explained in the data. We initially built our model with n-1 degrees of freedom (i.e. total number of measurements - 1, thus 17). The removal of 14 components did not affect our model. Therefore, we used three components to model our data. Finally, our model was validated using a cross-validation approach, where six randomly selected measurements were removed from the data and the model was rebuilt. This process was repeated 1000 times and the recorded model coefficients were used to define the model boundaries and thus its validity.

All the scripts for the NA isomer group signal extraction and for the data wrangling were developed in julia 1.0.4 language environment.[40] The statistical analysis, on the other hand, were performed via matlab. All the calculations were done on a Windows 7, 64 bit workstation with 128 GB of RAM and 12 CPUs.

Results and Discussion

The Distribution of NA isomer groups in PW Samples

Eighteen (i.e. six platforms in triplicate) produced water samples were screened for 181 commonly detected NA isomer groups including some sulfur containing ones using LC-HRMS. The detected NA isomer groups went through a quality control step in order to remove the noise and background signal from the list of finally detected NA isomer groups in each sample.

Across all six samples on average we detected $\approx$ 22 NA isomer groups in each sample with the Heidrun platform resulting in the highest detection frequency of 42 NA isomer groups while the lowest detection frequency was associated to the samples from Statfjord C platform with 14 detected NA isomer groups, Fig. 1. The detection frequency in this study

refers to the number of detected NA isomer groups in each sample. We did not detect any of the sulfur containing NA isomer groups in the tested samples. This implies either their absence or concentrations smaller than our method limit of detection (LOD) of $\approx 2\ \mu gL^{-1}$ calculated based on the standard deviation of the calibration curves. When looking at the detected NA isomer groups in all the samples based on their number of carbons, on average 2 NA isomer groups were detected. On the other hand the signal of detected NA isomer groups based on the degree of unsaturation showed on average 3 NA isomer groups detected in all the analyzed samples, Fig. S3. The samples from the Heidrun platform showed a peak in the detection frequency for NA isomer group with number of carbons ranging between 12 and 18 while they showed the highest frequency of detected NAs for z values ranging from 0 to 4, Fig. S3. On the other hand the samples from the Gullfaks C platform showed a higher detection frequency for NA isomer group with carbon numbers of 16 and 18 while having the highest frequency of detection for the aliphatic NA isomer groups (i.e. $z = 0$), Fig. S3. For the other samples, we observed an average detection frequency for smaller n and z values. Overall, the heavy NA isomer groups with largerdegree of unsaturation (i.e. $n \geq 19$ and $z \geq 8$) showed lower frequency of detection across all analyzed samples. Finally, all the samples independently from the platform appeared to have a high level of overlap in terms of the presence of one ring NA isomer groups. Our findings related to the distribution of NA isomer groups in different samples were consistent with the previous studies.[2,4,19,23,34,41,42]

When looking at the percentage signal associated with different NA isomer groups across all six platforms, the medium size NA isomer groups with n values of 12, 14, 16, and 18 and z values of 0, 2, and 6 , showed to have the highest cumulative signal abundance, Fig. 2. The averaged cumulative signal of NA isomer groups, across all the samples and based on the number of carbons was $\approx 4\%$ while being $\approx 9\%$ based on thedegree of unsaturation, Fig. 2. The normalized signal of individual NA isomer groups ranged between 3 to 35%, Figs. S4, S5, S6, S7, S8, S9. The largest cumulative signal of 40% based on the carbon number

belonged to NA isomer group with n value of 16 and platform Gullfaks C, Figs. 2 and S8. On the other hand, the one ring NAs isomer group from platform Statfjord C covered 60% of the measured signal for those samples, Figs. 2 and S6.

We observed three distinct groups of PW samples based on their distribution of NA isomer groups in the analyzed samples via PCA, Fig. 1. Our model was able to explain $\approx 80\%$ of the observed variability in data with three principal components. The aliphatic NA isomer groups with n values ranging from 12 to 16; and one ring NA isomer groups (i.e. z=2) with 14, 15,16, and 18 in samples Gullfaks C, Gullfaks A, and Heidrun appeared to be the main distinguishing factor for the first PC, Figs. S10, S4, S5, S6, S7, S8, S9. Moreover, the NA isomer groups with carbon number of 21, 22, and 26 having z values of 8, 10, and 18 caused the separation of the Gullfaks samples from all the other, Figs. S10, S7, S8. The separation of the clusters alongside PC2 was associated to four NA isomer groups with n values of 12, 13, and 15 and z values of 4, 6, and 10, Fig. S10. These NA isomer groups were present in samples from Heidrun and Norne and were absent in PW from the other platform. The clear clustering of the PW samples from different platforms indicates the unique chemical composition of the PW samples from different platforms, particularly in terms of NAs. Furthermore, with a larger sample set (i.e. larger number of samples and from more locations) a model could be built to directly associate the distribution of NA isomer groups in a sample to the discharging platform, which will be the subject of our future study.

Overall, our results show a high level of chemical diversity in the PW samples taken from different platforms both in terms of presence and absence of certain NA isomer groups as well as the cumulative signal associated with different NA isomer groups in those samples. Additionally, our data indicate the possibility of source tracking (i.e. association to the discharging platform) based on the distribution of NA isomer groups in a PW sample. However, the observed diversity and distribution of NA isomer groups in the samples may come from

different sources such as temporal diversity in the composition of the discharge, the oil characteristics, and/or the type of treatment processes used on the platform. Therefore, to fully explain/understand the observed compositions and validate the source tracking capacity of this method more frequent and spatially diverse characterization of NAs in the PWs from the offshore oil platforms is necessary.

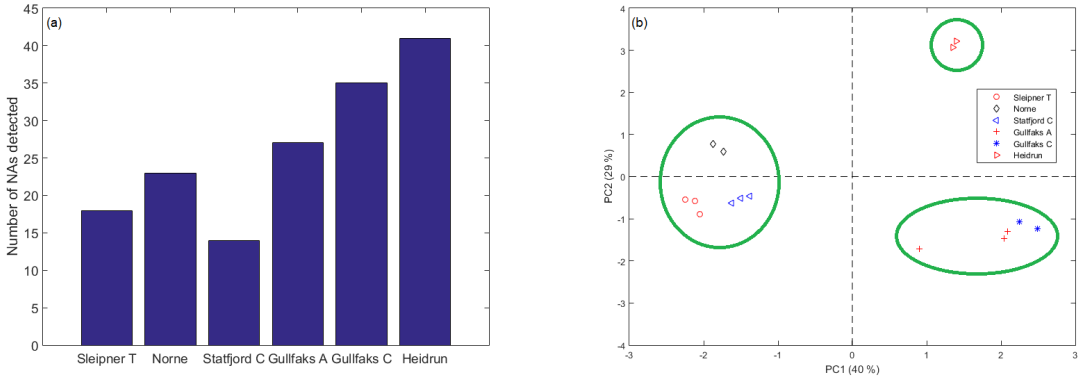

Figure 1: Plot showing (a) the number of detected NA isomer groups in each sampling site and (b) the PCA score plot for the first and second principal components.

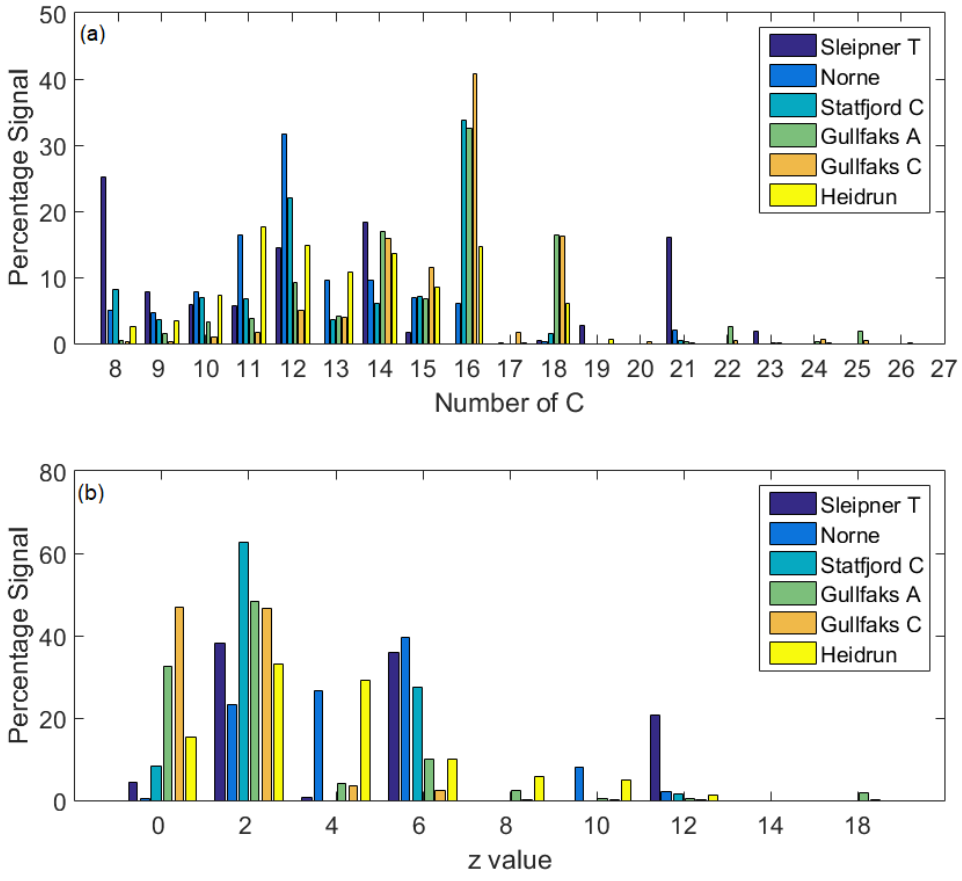

Figure 2: The distribution of the normalized signal of NA isomer groups (a) based on the number of carbons (i.e. n value) and (b) based on the -z value. The signal for each sample is scaled by the total signal of all the detected NA isomer groups in that sample.

Concentration Distribution of NA isomer groups

We also measured the concentration of each NA isomer group as well as the total concentration of NAs in each sample, employing a five level calibration curve based on a technical mixture of NAs. We observed a high level of overlap between the distribution of NA isomer groups in the technical mixture and the real samples, Figs. S1 and 3, which enabled us to quantify the NA isomer groups in our samples. For the NA with 26 carbons and the z value of 18, which was not present in the technical mixture, we used the closest NA present (i.e. $C_{26}H_{38}O_2$) in the mixture.

The total concentration of NA isomer groups in the samples varied between 6 mgL^{-1} from the Statfjord C platform and 56 mgL^{-1} from the Heidrun platform, Fig. 4. For the measured individual NA isomer groups, the concentrations raged between 0.2 mgL^{-1} for $C_{15}H_{24}O_2$ from the Statfjord C platform and 44 mgL^{-1} for $C_8H_{14}O_2$ isomer group measured in the Heidrun platform samples. The NA isomer group $C_8H_{14}O_2$ was present in all the samples and appeared to have a higher concentration compared to the other NA isomer groups in all the samples, Figs. S11, S12, S13, S14, S15, S16. The concentration of this NA isomer group ranged between 4 mgL^{-1} in samples from Gullfaks C platform and 44 mgL^{-1} in Heidrun samples, which appeared to be the main driver of the total concentration of NAs in the tested samples (Pearson correlation coefficient of 0.89). The NA isomer group $C_8H_{14}O_2$ was the only one detected in all the samples and resulting in a Pearson correlation coefficient ≥ 0.5. This may suggest that this NA isomer group could potentially be used as a marker for the presence/total concentration of NAs in PW samples from North Sea oilfields. However, larger sample set both in terms of spatial and temporal diversity is needed in order to confirm that hypothesis. For 20 out of 55 unique isomer group detected and quantified in the samples, their concentrations were above the previously reported effects levels (based on reported LC50 values for NAs) for different endpoints,[3,8–10,43] which further indicates the need for more comprehensive analysis of PW samples for NAs. Additionally,

the potential interactions between different chemical constituents of PW, including different NA isomers, may results in different environmental fate, behavior, and toxicity of the NAs, once discharged into the environment. Finally, it should be noted that the applicability of this quantification approach is relative to the level of overlap between the chemical space of the technical mixture and the samples. In other words, the technical mixture of NAs used in this study may not be adequate for the quantification of NAs in oil sand affected produced water.[44]

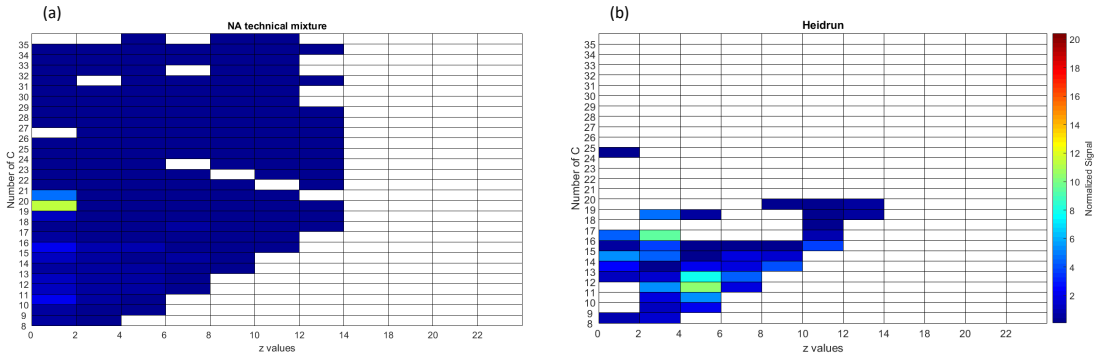

Figure 3: The distribution of the normalized signal of NA isomer groups (a) based on the number of carbons (i.e. n value) in the technical mixture and (b) based on the -z value in the PW sample from Heidrun platform.

Environmental Implications

This is the first study performing the detailed quantification of NA isomer groups in the PW samples from the North Sea offshore oil platforms. As of today, this is the most comprehensive study providing detailed chemical characterization and concentrations of NA isomer groups in the complex unresolved mixture of produced water. Our results showed a high level of diversity in the samples both in terms of detection and concentrations. The observed diversity warrants further and more comprehensive characterization of NAs in the produced water. The observed diversity also indicates the need for more investigations in order to identify a few isomer groups as markers of presence of NAs in the PW samples.

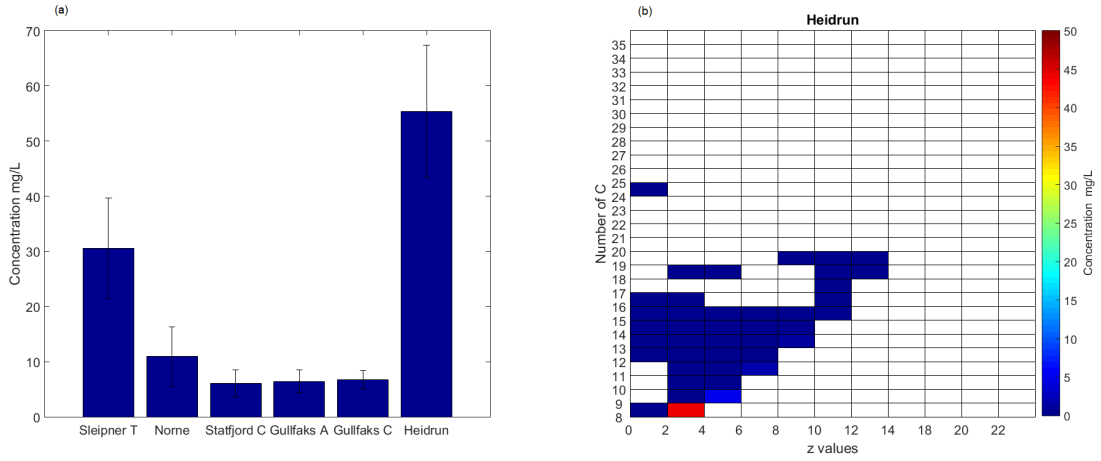

Figure 4: Depicts (a) the total NA concentration with their observed standard deviation for each platform and (b) the detailed averaged concentration distribution of each NA isomer group for the samples taken from Heidrun platform.

This study also showed the potential for utilizing a marker in order to perform detection and semi-quantification of total NAs in PW. This is highly relevant to both the industrial and the regulatory sectors in order to be able to monitor the levels of discharge rapidly. Additionally, the possibility of using the distribution of NAs as a tool for source tracking would be highly relevant to assess the environmental impact of a specific platform, given the difficulties associated with tracking the discharge. However, it should be noted that these results are preliminary and further studies are necessary to generate the fully validated models.

It should be also noted that these concentrations are the most accurate measures possible for these chemicals given the complexity of the mixtures. A more accurate quantification and characterization of individual acids may only be possible by employing the comprehensive two dimensional liquid chromatography coupled to high resolution mass spectrometery (LC×LC-HRMS) due to the complexity of these mixtures. This combination could potentially provide enough resolving power for detailed characterization and quantification of NAs in the unresolved complex mixture PW. However, such system would be extremely difficult to handle both in terms of hardware and the generated data. At the current state of these

technologies they should be considered as complementary tools to currently existing one (e.g. solid phase extraction) due to their limitations.

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Supporting Information Available

The Supporting Information providing details related to the chemicals used; instrumental conditions; quantification validation procedure; and figures related to the detailed chemical characterization and quantification of NAs is available free of charge on the publication website.

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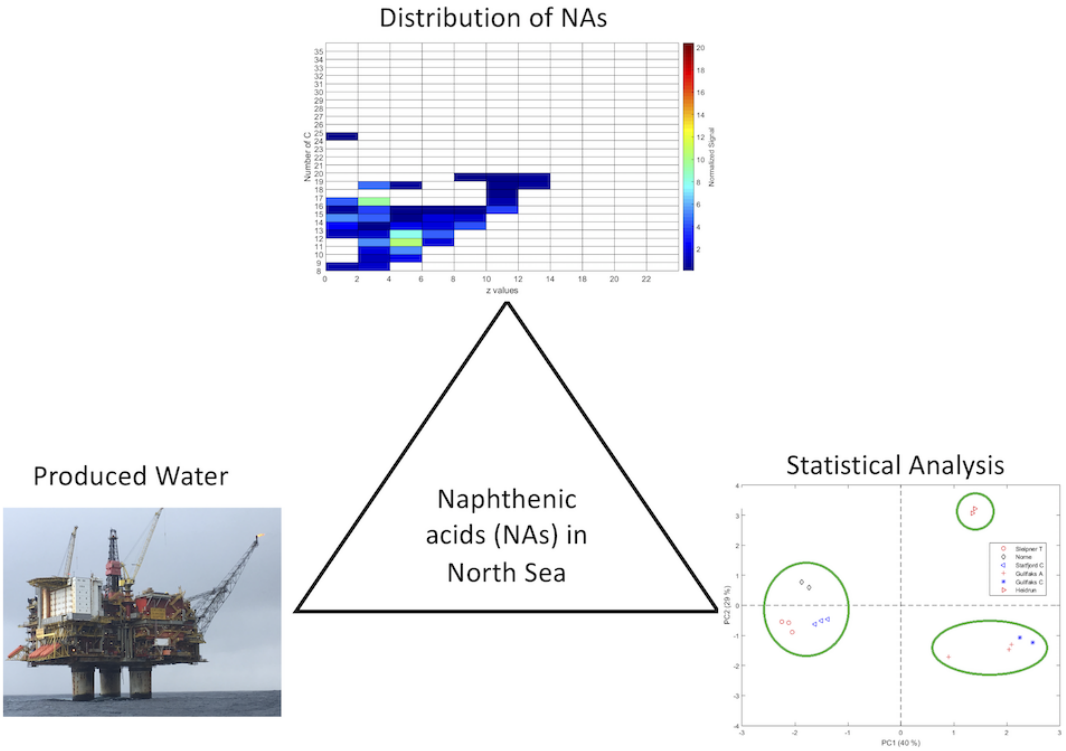

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