Supporting Information for: Concentrations and Distribution of Naphthenic Acids in the Produced Water From Offshore Norwegian North Sea Oilfields

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S1 Instrumental Conditions

The liquid chromatography (LC) gradient used for the separation of each sample, including the blanks, started with 100% solvent A (i.e. 0.1% ammonium formate in water) and kept the same conditions for 1 min (i.e. desalting/loading). In the second step the gradient was switched to 100% solvent B (i.e. methanol) in the next 6 minutes. The 100% solvent B was maintained for the following 3 minutes. Finally, the gradient was brought back to the initial conditions during the last 2 minutes of the program, thus a total of 12 minutes. We used this method for separating 5 μL of each sample using a 400 μL/min flow rate. This method was a modified version of our previously developed method used for analysis of naphthenic acids in produced water.[1]

S2 LC Method Optimization and Validation

For the optimization and validation of the LC-MS method, we used a 10 fold diluted technical mixture of naphthenic acids (NAs) in isopropanol solution. This solution was infused into the mass spectrometer using a flow rate of 100 μL/min. This exercise was repeated 3 times and during each round we acquired in total 30 scans. These data were referred to as the validation datasets. The validation datasets were used for defining the chemical space (i.e. all the NA isomer groups present in the mixture) of the NAs in the technical mixture. We followed a previously optimized approach for the detection of NAs in the technical mixture.[1–3]

Once the NA chemical space was defined, we dissolved 100 μL of NA mixture into 1 L of sea water in order to simulate produced water by shaking the mixture for 73 hr. Three separate 1 mL samples were taken from this mixture and were used for the optimization of the LC gradient, particularly for the desalting/loading. We decreased the length of the desalting/loading from 4 min in steps of 0.5 min until we were able to clearly detect the smallest NA isomer group in the technical mixture (i.e. $C_8H_16O_2$). This procedure enabled

us to remove the salt residues in the samples without loosing any of our analytes of interest, Fig S1.

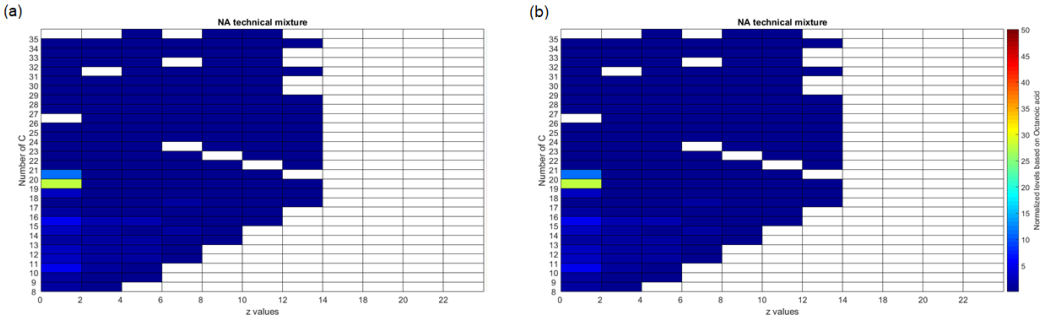

Figure S1: Figure depicting the distribution (i.e. the chemical space) of (a) NA technical mixture directly infused into the mass spectrometer and (b) of NA technical mixture dissolved in seawater and analyzed via the optimized LC-MS method.

S3 NA Quantification Validation

In order to validate our NA quantification procedure, we created three different simulated produced water samples (i.e. NA technical mixture dissolved in sea water) at 150, 250, and 500 μgL^{-1} in triplicates. These samples, then, were analyzed with the optimized LC-MS method and individual NA isomer group as well as the total NAs were quantified using the five level calibration curve ranging from 0.1 to 100 mgL^{-1}. The quantification of these simulated samples showed a standard error of quantification of $\leq 63\%$ for the individual NA isomer groups and of $\leq 34\%$ for the total NA concentration in those samples. Our results were in agreement with the previous studies in terms of linearity of external standard calibration curves.[3–5] Consequently, we considered our approach adequate for the quantification of both individual NA isomer groups and the total NA concentration in the produced water samples.

We also defined the limit of quantification (LOQ) of ≈ 10 μgL^{-1} for each individual acid using the standard deviation of the calibration curves for each acid. The defined LOQ values

for NAs were similar to those reported previously, using similar analytical instrumentation.[2–4]

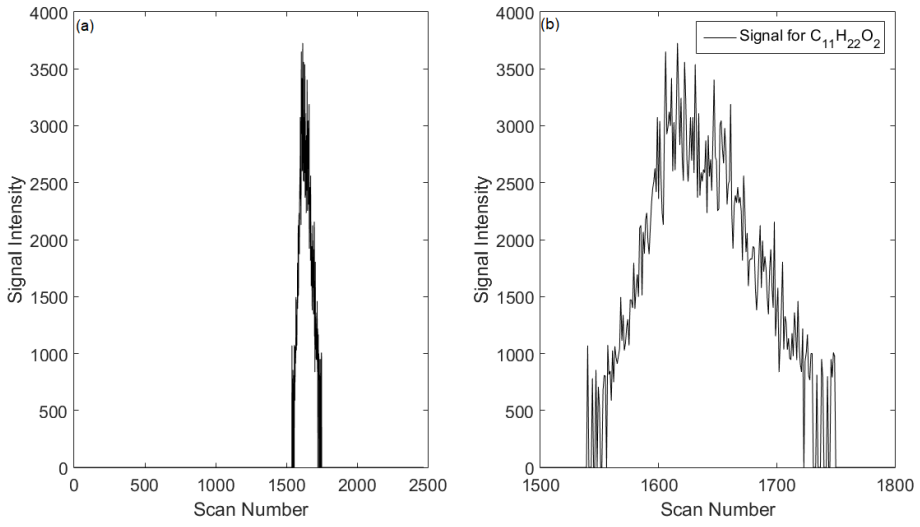

Figure S2: (a) The extracted ion chromatogram (XIC) of $C_{11}H_{22}O_2$ and (b) the zoomed in region for that NA isomer group in a produced water sample.

S4 NA Distribution

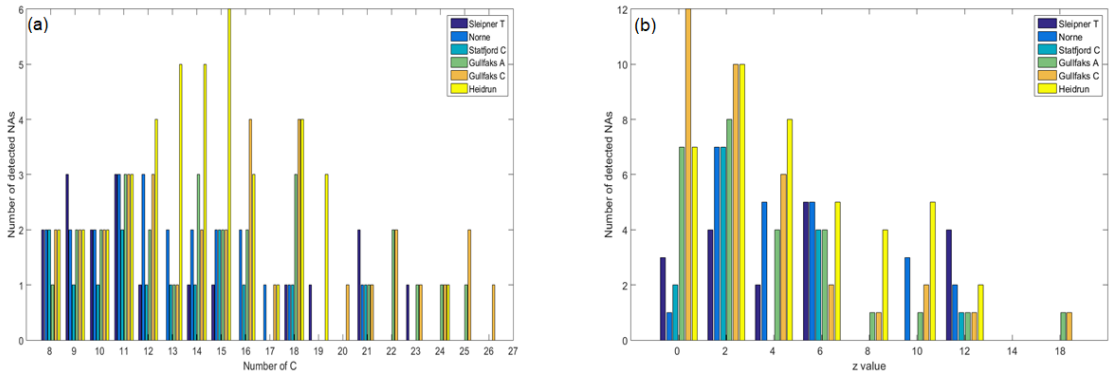

Figure S3: The detection frequency of NAs (a) based on the number of carbons (i.e. n value) and (b) based on the degree of unsaturation (i.e. the -z value) across all six platforms.

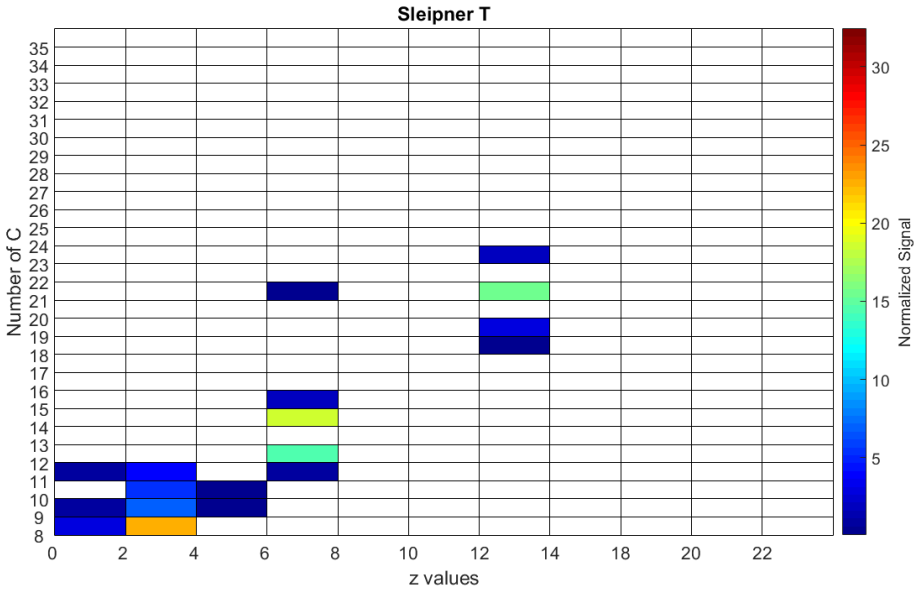

Figure S4: The normalized signal of the detected NAs in the samples from Sleipner T platform. The signal for each NA is scaled by the total signal of all the detected NAs in the sample.

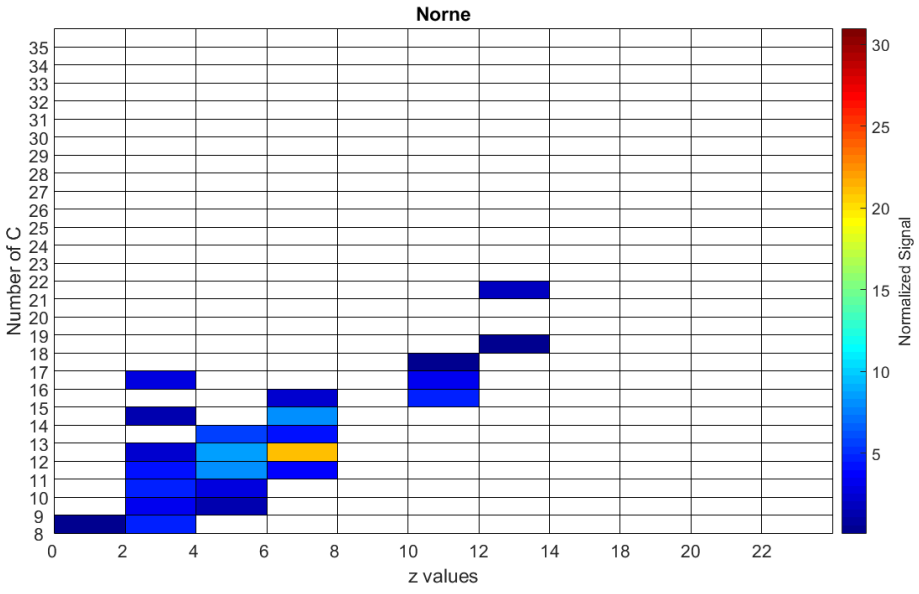

Figure S5: The normalized signal of the detected NAs in the samples from Norne platform. The signal for each NA is scaled by the total signal of all the detected NAs in the sample.

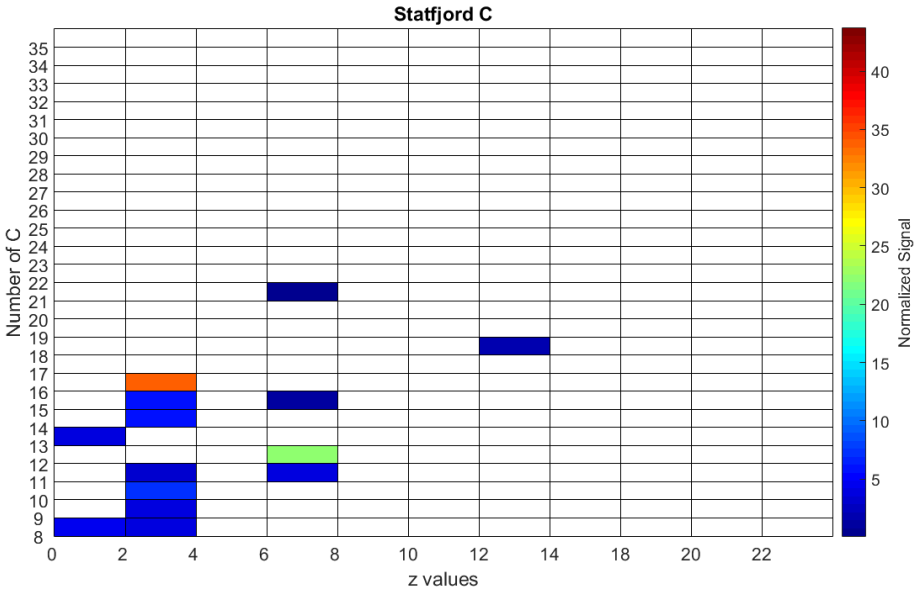

Figure S6: The normalized signal of the detected NAs in the samples from Statfjord C platform. The signal for each NA is scaled by the total signal of all the detected NAs in the sample.

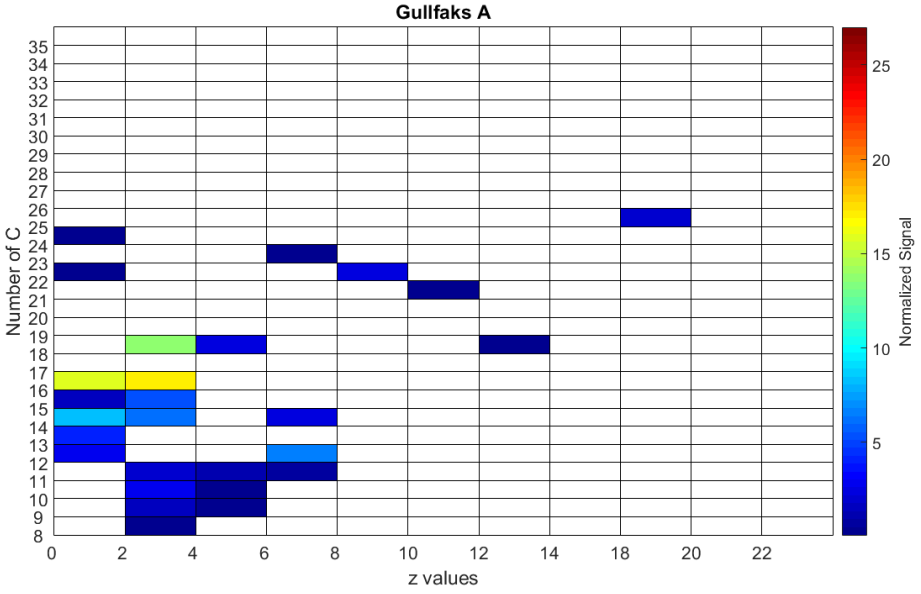

Figure S7: The normalized signal of the detected NAs in the samples from Gullfaks A platform. The signal for each NA is scaled by the total signal of all the detected NAs in the sample.

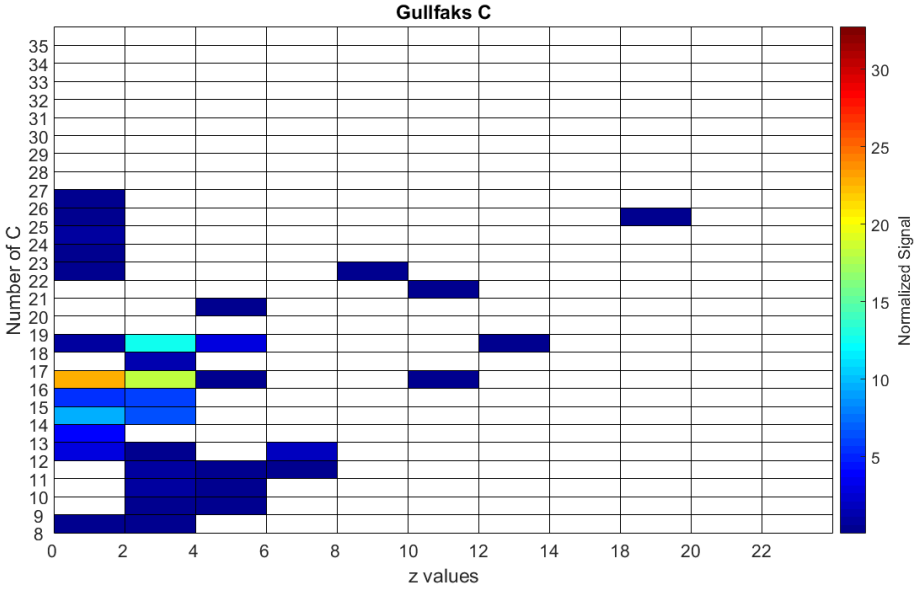

Figure S8: The normalized signal of the detected NAs in the samples from Gullfaks C platform. The signal for each NA is scaled by the total signal of all the detected NAs in the sample.

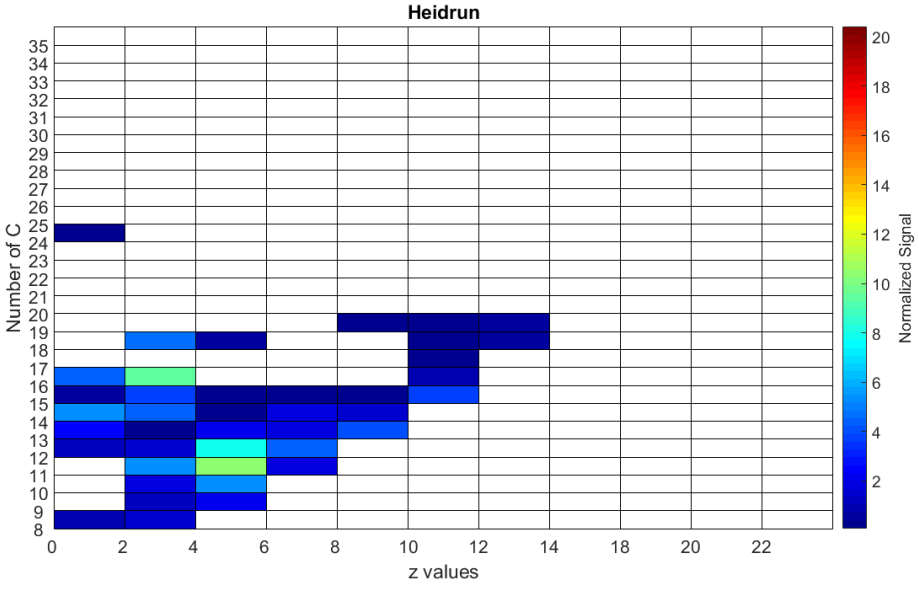

Figure S9: The normalized signal of the detected NAs in the samples from Heidrun platform. The signal for each NA is scaled by the total signal of all the detected NAs in the sample.

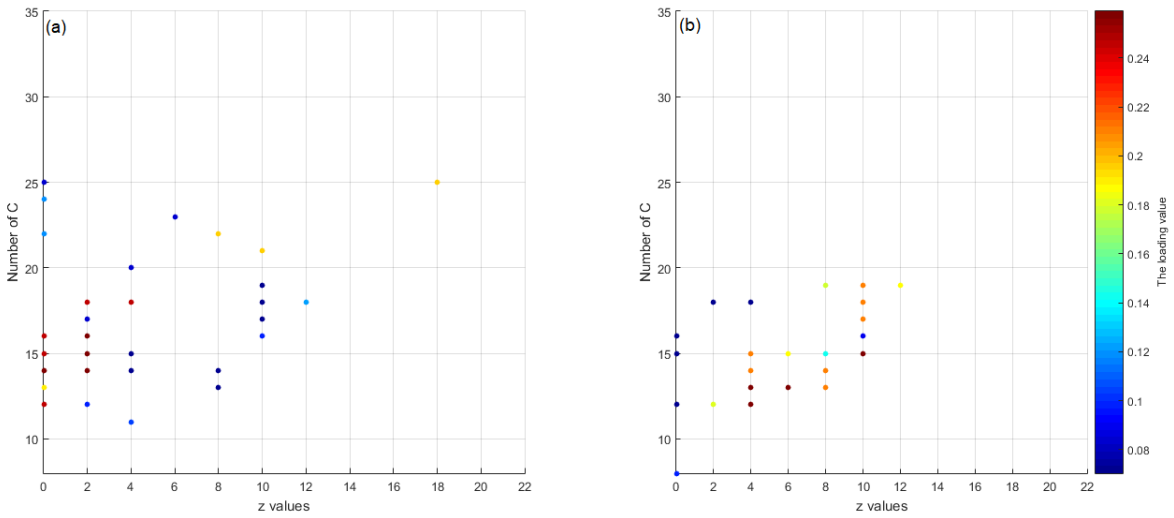

Figure S10: The principal component analysis loading plots for (a) the first PC and (b) the second PC. The color of the dots represent the loading values. Only the variables (i.e. NAs) that their contribution was larger than 20%.

S5 NA Quantification

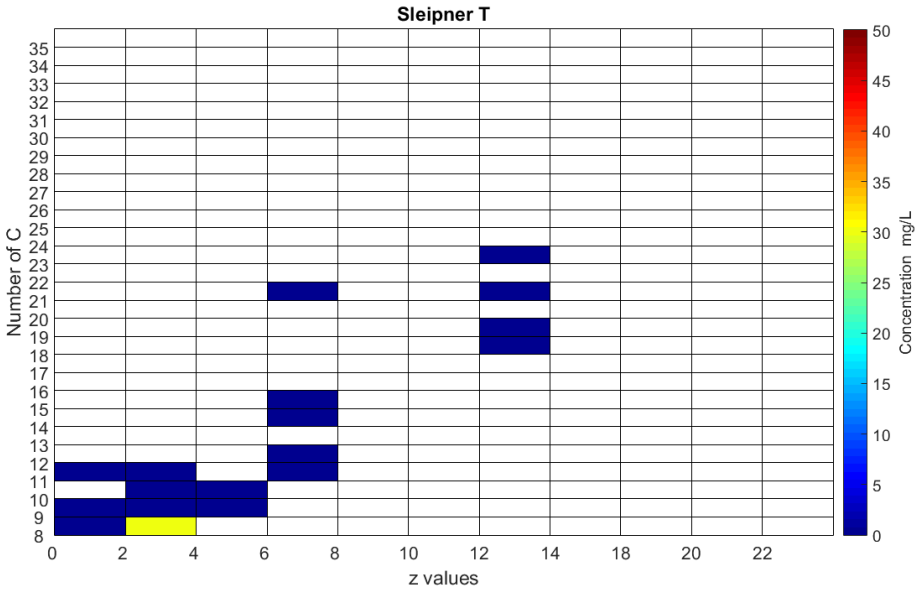

Figure S11: The concentration of individual NA isomer groups measured in PW samples from Sleipner T platform.

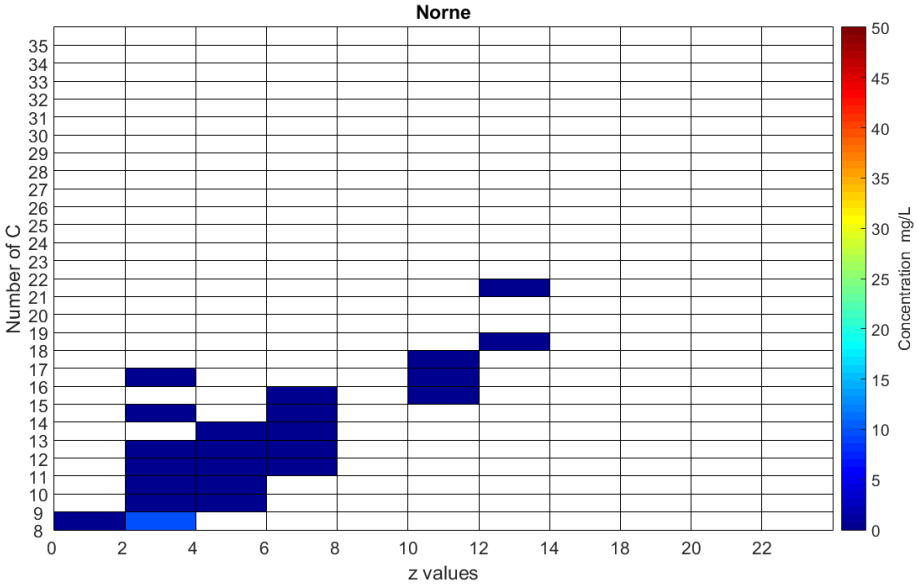

Figure S12: The concentration of individual NA isomer groups measured in PW samples from Norne platform.

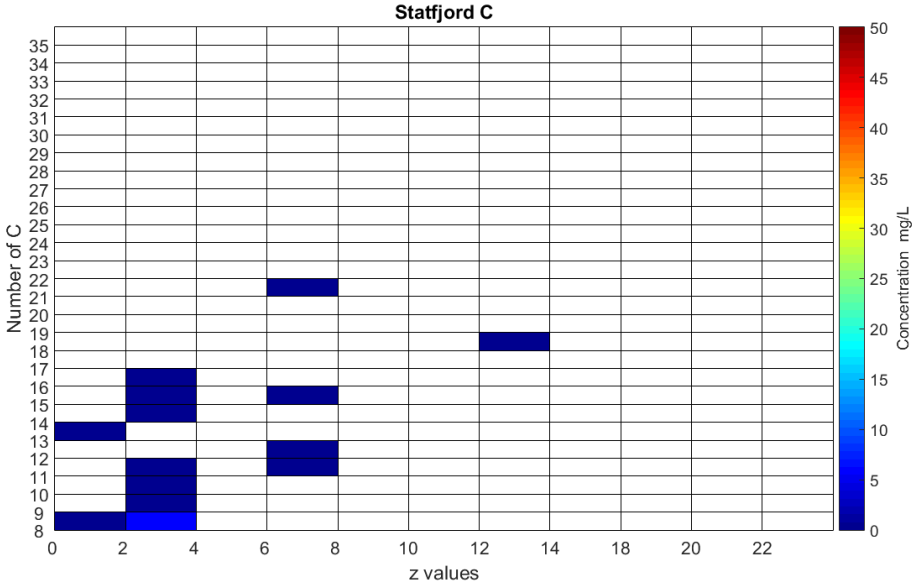

Figure S13: The concentration of individual NA isomer groups measured in PW samples from Statfjord C platform. The sum of all the points equals 100.

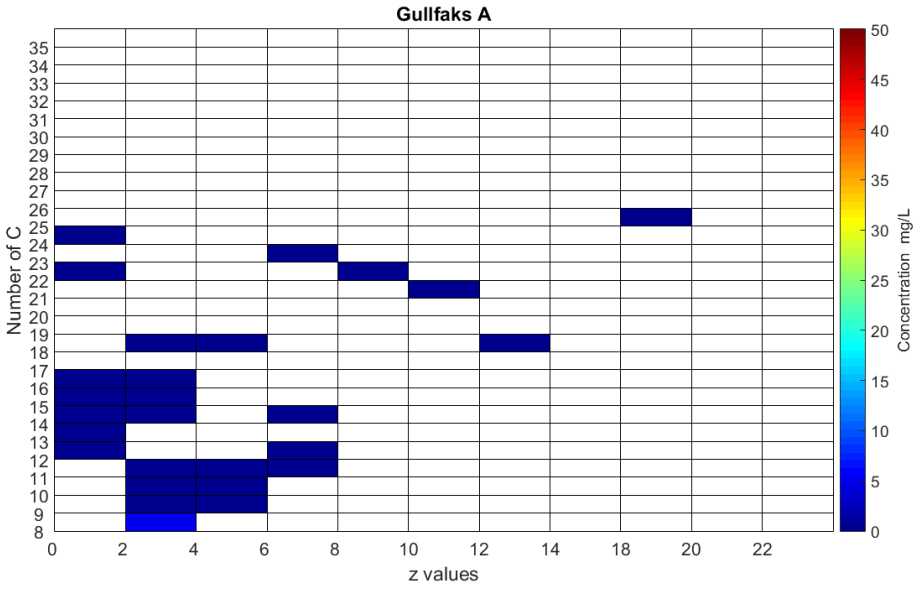

Figure S14: The concentration of individual NA isomer groups measured in PW samples from Gullfaks A platform. The sum of all the points equals 100.

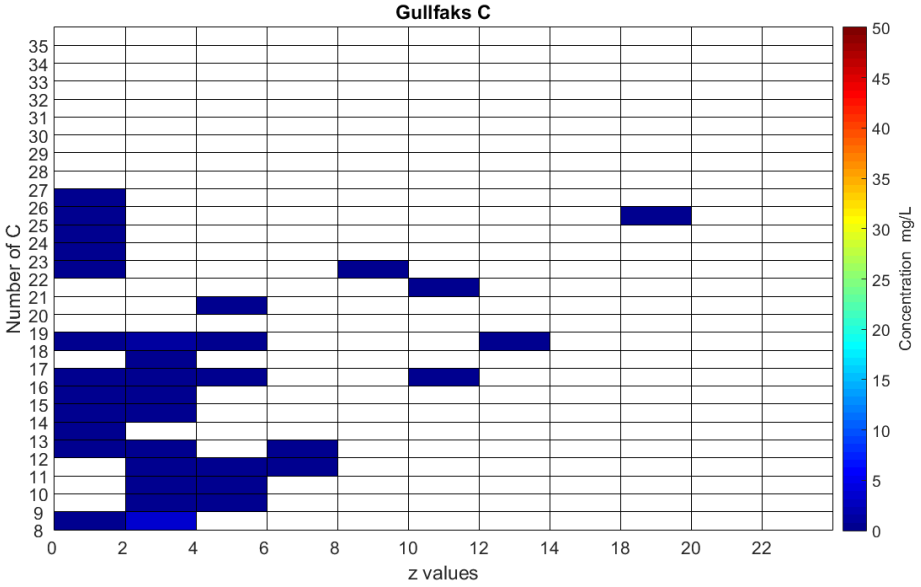

Figure S15: The concentration of individual NA isomer groups measured in PW samples from Gullfaks C platform. The sum of all the points equals 100.

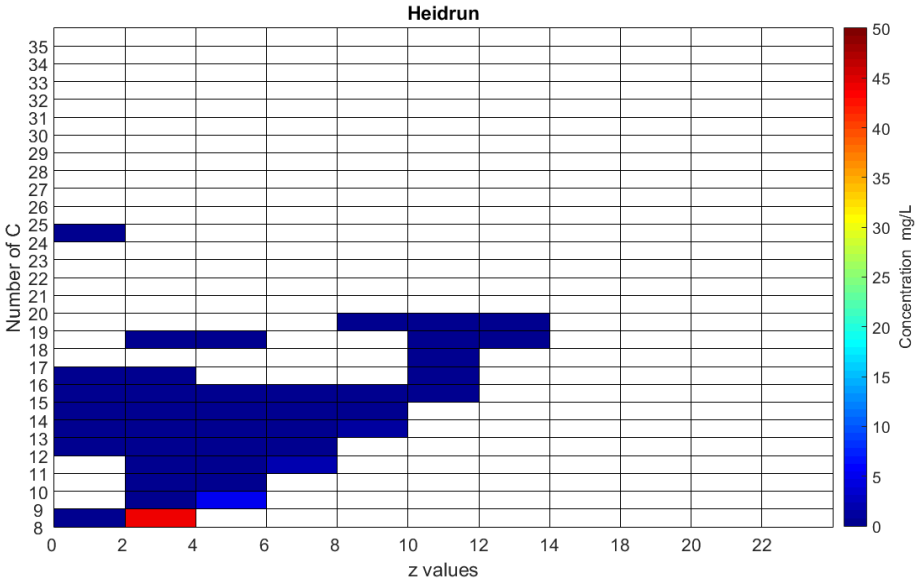

Figure S16: The concentration of individual NA isomer groups measured in PW samples from Heidrun platform. The sum of all the points equals 100.

References

(1) Samanipour, S.; Hooshyari, M.; Baz-Lomba, J. A.; Reid, M. J.; Casale, M.; Thomas, K. V. The effect of extraction methodology on the recovery and distribution of naphthenic acids of oilfield produced water. *Sci. Tot. Environ.* **2019**, *652*, 1416–1423.

(2) Ross, M. S.; Pereira, A. d. S.; Fennell, J.; Davies, M.; Johnson, J.; Sliva, L.; Martin, J. W. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the Canadian oil sands industry. *Environ. Sci Technol.* **2012**, *46*, 12796–12805.

(3) Kovalchik, K. A.; MacLennan, M. S.; Peru, K. M.; Headley, J. V.; Chen, D. D. Standard method design considerations for semi-quantification of total naphthenic acids in oil sands process affected water by mass spectrometry: A review. *Frontiers of Chemical Science and Engineering* **2017**, *11*, 497–507.

(4) Martin, J. W.; Han, X.; Peru, K. M.; Headley, J. V. Comparison of high-and low-resolution electrospray ionization mass spectrometry for the analysis of naphthenic acid mixtures in oil sands process water. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 1919–1924.

(5) Yen, T.-W.; Marsh, W. P.; MacKinnon, M. D.; Fedorak, P. M. Measuring naphthenic acids concentrations in aqueous environmental samples by liquid chromatography. *J. Chromatogr. A* **2004**, *1033*, 83–90.