**Supporting Information**

**for**

# Determination and Characterization of Oxy-Naphthenic Acids in Oilfield Wastewater

Beili Wang[1], Yi Wan[1]*, Yingxin Gao[2], Min Yang[2], Jianying Hu[1]

[1]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

[2]Chinese Acad. Sci., State Key Lab Environ Aquat Chem, Ecoenviron Sci Res Ctr, Beijing 100085, Peoples R China

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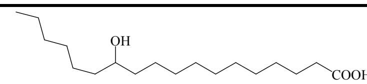
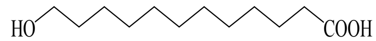
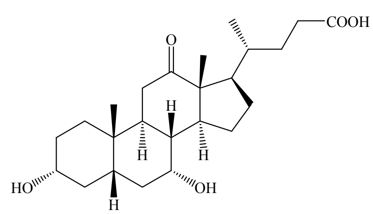
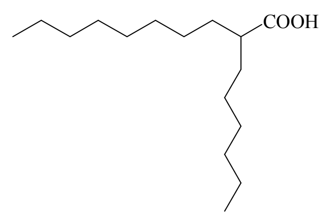
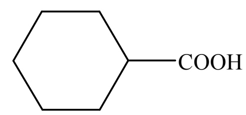
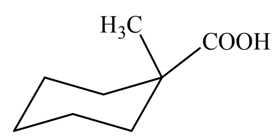
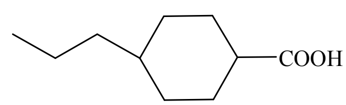
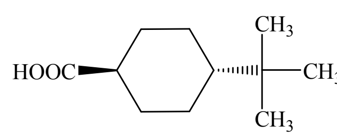
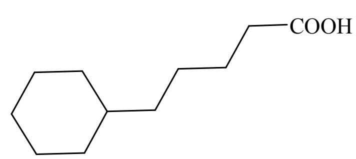
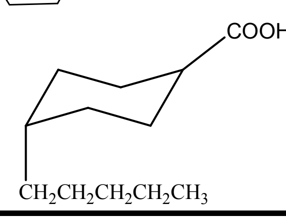
This file includes: (1) Table S1, name, structure and retention time of model compounds, (2) Table S2, IDLs of model compounds, (3) Table S3, MS/MS fragment ions and retention of NAs, $O_3$-NAs and $O_4$-NAs in oilfield wastewater, (4) Table S4, MS/MS fragment ions and retention of NAs, OH-NAs and $(OH)_2$-NAs derivatized with dansyl chloride in oilfield wastewater, (5) Figure S1, chromatography of model compounds in standard mixtures, (6) Figure S2, chromatography of NAs in commercial mixtures and oilfield wastewater, (7) Figure S3, recovery of model compounds with different eluent solvent, (8) Figures S4, comparisons of recoveries of model compounds in different SPE cartridges, (9) Figures S5 and S6, MS/MS spectra of model oxy-NAs before or after derivatization with dansyl chloride, (10) Figures S7, MS/MS spectra of extracts in oilfield wastewater before derivatization with dansyl chloride, and (11) Figures S8, calibration curves for one ion from three commercial mixtures.

Table S1. Name, structure and retention time of model compounds in UPLC-QTOF-MS analysis.

| Name | CAS No. | Molecular Weight | RT (min) | Structure |
|---|---|---|---|---|
| 12-hydroxysteric acid | 106-14-9 | $C_{12}H_{24}O_3$, MW= 300.2664 | 9.32 |  |
| 12-hydroxydodecanoic acid | 505-95-3 | $C_{18}H_{36}O_3$, MW= 216.1725 | 4.87 |  |
| 12-oxochenodeoxycholic acid | 2458-08-4 | $C_{24}H_{38}O_5$, MW= 406.2719 | 4.44 |  |
| 2-hexyldecanoic acid | 25354-97-6 | $C_{16}H_{32}O_2$, MW= 256.2402 | 11.05 |  |
| cyclohexanecarboxylic acid | 98-89-5 | $C_7H_{12}O_2$, MW= 128.0837 | 3.31 |  |
| 1-Methyl-1-cyclohexane carboxylic acid | 1123-25-7 | $C_8H_{14}O_2$, MW= 142.0994 | 4.18 |  |
| 4-propylcyclohexanecarboxylic acid (*cis*- and *trans*- mixture) | 943-29-3 | $C_{10}H_{18}O_2$ (cis- and trans-), MW= 170.1307 | 5.05; 5.23 |  |
| *trans*-4-tert-butylcyclohexanecarboxylic acid | 5962-88-9 | $C_{11}H_{20}O_2$-butyl, MW= 184.1463 | 5.34 |  |
| cyclohexane pentanoic acid | 943-29-3 | $C_{11}H_{20}O_2$, MW= 184.1463 | 5.84 |  |
| *trans*-4-pentylcyclohexane carboxylic acid | 38289-29-1 | $C_{12}H_{22}O_2$, MW= 198.1620 | 7.00 |  |

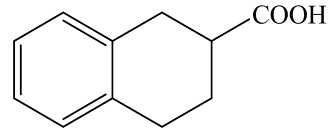
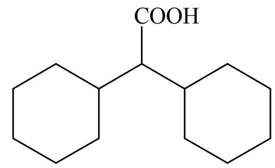
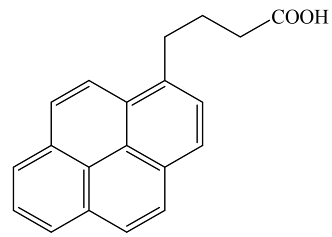
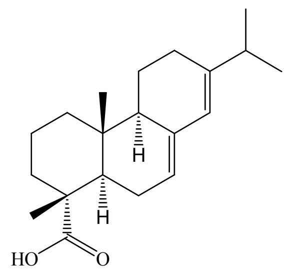
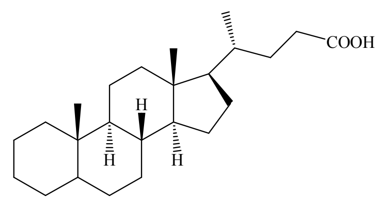
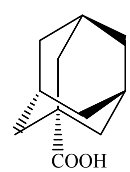
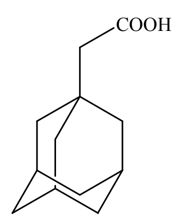
| | | | | |
|---|---|---|---|---|
| 1,2,3,4-tetrahydro-2-naphthoic acid | 53440-12-3 | $C_{11}H_{12}O_2$, MW= 176.0837 | 3.97 |  |
| dicyclohexylacetic acid | 52034-92-1 | $C_{14}H_{24}O_2$, MW= 224.1776 | 7.88 |  |
| 1-pyrenebutyric acid | 3443-45-6 | $C_{20}H_{16}O_2$, MW= 288.1150 | 6.25 |  |
| abietic acid | 514-10-3 | $C_{20}H_{30}O_2$, MW= 302.2246 | 10.98 |  |
| 5-beta-cholanic acid | 546-18-9 | $C_{24}H_{40}O_2$, MW= 360.3028 | 12.95 |  |
| 1-adamantane carboxylic acid | 828-51-3 | $C_{11}H_{16}O_2$, MW= 180.1150 | 4.70 |  |
| 1-adamantaneacetic acid | 4942-47-6 | $C_{12}H_{18}O_2$, MW= 194.1307 | 4.98 |  |

Table S2. Instrumental detection limits (IDLs), intra-batch precision and inter-batch precision of UPLC-QTOF-MS analysis of the model compounds with the concentration ranges of 1-1000 μg/L.

| Model compound | | | IDL (μg/L) | Intra-day RSDs[a] | Inter-day RSDs[b] | Calibration $r^2$ |
|---|---|---|---|---|---|---|
| oxy-NAs | $C_{18}H_{36}O_3$ | Z=0 | 0.4 | 4.4 | 1.5 | 0.999 |
| | $C_{12}H_{24}O_3$ | Z=0 | 0.3 | 5.9 | 3.5 | 0.997 |
| | $C_{24}H_{38}O_5$ | Z=-10 | 1.0 | 2.8 | 3.0 | 0.999 |
| NAs | $C_{16}H_{32}O_2$ | Z=0 | 15 | 1.8 | 3.8 | 0.998 |
| | $C_7H_{12}O_2$ | Z=-2 | 4.9 | 2.0 | 8.1 | 0.981 |
| | $C_8H_{14}O_2$ | Z=-2 | 1.1 | 3.1 | 3.3 | 0.994 |
| | $C_{10}H_{18}O_2$ | Z=-2 | 11 | 3.7 | 2.8 | 0.996 |
| | $C_{11}H_{20}O_2$ | Z=-2 | 5.0 | 3.5 | 5.2 | 0.997 |
| | $C_{11}H_{20}O_{2\text{-butyl}}$ | Z=-2 | 0.6 | 3.2 | 5.9 | 0.998 |
| | $C_{12}H_{22}O_2$ | Z=-2 | 0.4 | 4.8 | 5.4 | 0.999 |
| | $C_{11}H_{12}O_2$ | Z=-10 | 0.9 | 3.8 | 8.3 | 0.999 |
| | $C_{14}H_{24}O_2$ | Z=-4 | 0.3 | 2.8 | 6.9 | 0.999 |
| | $C_{20}H_{16}O_2$ | Z=-14 | 1.0 | 6.9 | 8.3 | 0.995 |
| | $C_{20}H_{30}O_2$ | Z=-10 | 0.9 | 8.6 | 6.0 | 0.998 |
| | $C_{24}H_{40}O_2$ | Z=-8 | 0.6 | 8.3 | 9.8 | 0.98 |
| | $C_{11}H_{16}O_2$ | Z=-6 | 0.4 | 3.8 | 4.0 | 0.994 |
| | $C_{12}H_{18}O_2$ | Z=-6 | 0.3 | 2.3 | 4.8 | 0.998 |

Table S3. Precursors, MS/MS fragment ions and retention time of NAs, $O_3$-NAs and $O_4$-NAs generated in MS/MS mode of QTOF-MS in oilfield wastewater, and the MS/MS spectra with precursor ions of 225, 249 and 287 were showed in Figure 2.

| Precursor ion | Collision energy (eV) | Retention time (min) | Compound | Z | Mass fragment ions | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $[M-H]^-$ | $[M-H-H_2O]^-$ | $[M-H-CO_2]^-$ | $[M-H-H_2O-CO_2]^-$ |
| 283 | 20-30 | 12.2-13.2 | $C_{18}H_{36}O_2$ | 0 | 283.2647 (3.5 ppm) | - | - | - |
| | | 6-8 | $C_{17}H_{32}O_3$ | -2 | 283.2259 (-4.9 ppm) | 265.2129 (15.1 ppm) | 239.2397 (9.2 ppm) | - |
| | | 5-6 | $C_{16}H_{26}O_4$ | -4 | 283.1904 (-1.8 ppm) | 265.1793 (-4.1 ppm) | 239.2017 (2.5 ppm) | 221.1914 (4.1 ppm) |
| 225 | 20-30 | 8.5-10.5 | $C_{14}H_{26}O_2$ | -2 | 225.1850 (-2.2 ppm) | - | - | - |
| | | 4.5-5 | $C_{13}H_{22}O_3$ | -4 | 225.1485 (-2.7 ppm) | 207.1382 (-1.4 ppm) | 181.1586 (-3.3 ppm) | - |
| | | 2-3.5 | $C_{12}H_{18}O_4$ | -6 | 225.1135 (3.6 ppm) | 207.1026 (2.4 ppm) | 181.1228 (-0.6 ppm) | 163.1117 (-3.7 ppm) |
| 265 | 15-25 | 9-11 | $C_{17}H_{30}O_2$ | -4 | 265.2158 (-3.8 ppm) | - | - | - |
| | | 6-7.5 | $C_{16}H_{26}O_3$ | -6 | 265.1797 (-2.6 ppm) | 247.1695 (-1.2 ppm) | 221.1905 (0 ppm) | - |
| | | 3-5 | $C_{15}H_{24}O_4$ | -8 | 265.1440 (0 ppm) | 247.1335 (0.4 ppm) | 221.1535 (-3.2 ppm) | 203.1443 (3.4 ppm) |
| 249 | 20-30 | 8-11 | $C_{16}H_{26}O_2$ | -6 | 249.1853 (-0.8 ppm) | - | - | - |
| | | 4-6 | $C_{15}H_{22}O_3$ | -8 | 249.1490 (-0.4 ppm) | 231.1375 (-4.3 ppm) | 205.1591 (-0.5 ppm) | - |
| | | 2-3 | $C_{14}H_{18}O_4$ | -10 | 249.1130 (1.2 ppm) | 231.1024 (1.3 ppm) | 205.1227 (-1 ppm) | 187.1126 (1.6 ppm) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 9-11.5 | $C_{18}H_{28}O_2$ | -8 | 275.2016 (1.8 ppm) | - | - | - |
| 275 | 20-30 | 4-7 | $C_{17}H_{24}O_3$ | -10 | 275.1650 (1.1 ppm) | 257.1548 (2.3 ppm) | 231.175 (0.4 ppm) | - |
| | | 3-4 | $C_{16}H_{20}O_4$ | -12 | 275.1289 (2.2 ppm) | 257.1175 (-1.2 ppm) | 231.1385 (0 ppm) | 213.1279 (0 ppm) |
| | | 9.5-11.5 | $C_{19}H_{28}O_2$ | -10 | 287.2008 (-1 ppm) | - | - | - |
| 287 | 20-30 | 4-7 | $C_{18}H_{24}O_3$ | -12 | 287.1649 (0.7 ppm) | 269.1538 (-1.5 ppm) | 243.1751 (0.8 ppm) | - |
| | | 3-4.5 | $C_{17}H_{20}O_4$ | -14 | 287.1289 (2.1 ppm) | 269.1185 (2.6 ppm) | 243.1395 (4.1 ppm) | 225.1290 (4.9 ppm) |

Mass errors of fragmentation ions of 283.2259 were higher than 5 ppm possible due to the low abundance of the compounds.

Table S4. Precursors and MS/MS fragment ions of OH-NAs and $(OH)_2$-NAs derivatized with dansyl chloride in oilfield wastewater, and the MS/MS spectra with precursor ions of 460, 484 and 522 were showed in Figure 3.

| Precursor ion | Collision energy (eV) | Compound | Z | Mass fragment ions | | |
|---|---|---|---|---|---|---|
| | | | | $[M+H]^+$ | $[DNS]^+$ | $[DNS-SO_3]^+$ |
| 518 | 20-30 | OH-$C_{17}H_{31}O_2$+DNS ($C_{29}H_{43}NO_5S$) | -2 | 518.2930 (-1.9 ppm) | - | 171.1046 (-1.2 ppm) |
| | | $(OH)_2$-$C_{16}H_{26}O_2$+DNS ($C_{28}H_{39}NO_6S$) | -4 | 518.2576 (0 ppm) | - | 171.1045 (-1.8 ppm) |
| 460 | 20-30 | OH-$C_{13}H_{21}O_2$+DNS ($C_{25}H_{34}NO_5S$) | -4 | 460.2157 (-0.2 ppm) | - | 171.1050 (1.2 ppm) |
| | | $(OH)_2$-$C_{12}H_{16}O_2$+DNS ($C_{24}H_{30}NO_6S$) | -6 | 460.1787 (-1.5 ppm) | - | 171.1050 (1.2 ppm) |
| 500 | 20-30 | OH-$C_{16}H_{25}O_2$+DNS ($C_{28}H_{38}NO_5S$) | -6 | 500.2478 (1.4 ppm) | - | 171.1043 (-2.9 ppm) |
| | | $(OH)_2$-$C_{15}H_{22}O_2$+DNS ($C_{27}H_{34}NO_6S$) | -8 | 500.2107 (0 ppm) | - | 171.1044 (0.8 ppm) |
| 484 | 20-30 | OH-$C_{15}H_{21}O_2$+DNS ($C_{27}H_{34}NO_5S$) | -8 | 484.2160 (0.4 ppm) | 252.0697 (1.2 ppm) | 171.1045 (-1.8 ppm) |
| | | $(OH)_2$-$C_{14}H_{16}O_2$+DNS ($C_{26}H_{30}NO_6S$) | -10 | 484.1790 (-0.8 ppm) | 252.0686 (-3.2 ppm) | 171.1040 (-4.7 ppm) |
| 510 | 20-30 | OH-$C_{17}H_{23}O_2$+DNS ($C_{29}H_{36}NO_5S$) | -10 | 510.2323 (1.8 ppm) | - | 171.1040 (-4.7 ppm) |
| | | $(OH)_2$-$C_{16}H_{18}O_2$+DNS ($C_{28}H_{32}NO_6S$) | -12 | 510.1948 (-0.4 ppm) | - | 171.1040 (-4.7 ppm) |
| 522 | 20-30 | OH-$C_{18}H_{23}O_2$+DNS ($C_{30}H_{36}NO_5S$) | -12 | 522.2327 (2.5 ppm) | 252.0693 (-0.4 ppm) | 171.1048 (-1.2 ppm) |
| | | $(OH)_2$-$C_{17}H_{18}O_2$+DNS ($C_{29}H_{32}NO_6S$) | -14 | 522.1956 (1.1 ppm) | 252.0700 (2.4 ppm) | 171.1042 (-3.5 ppm) |

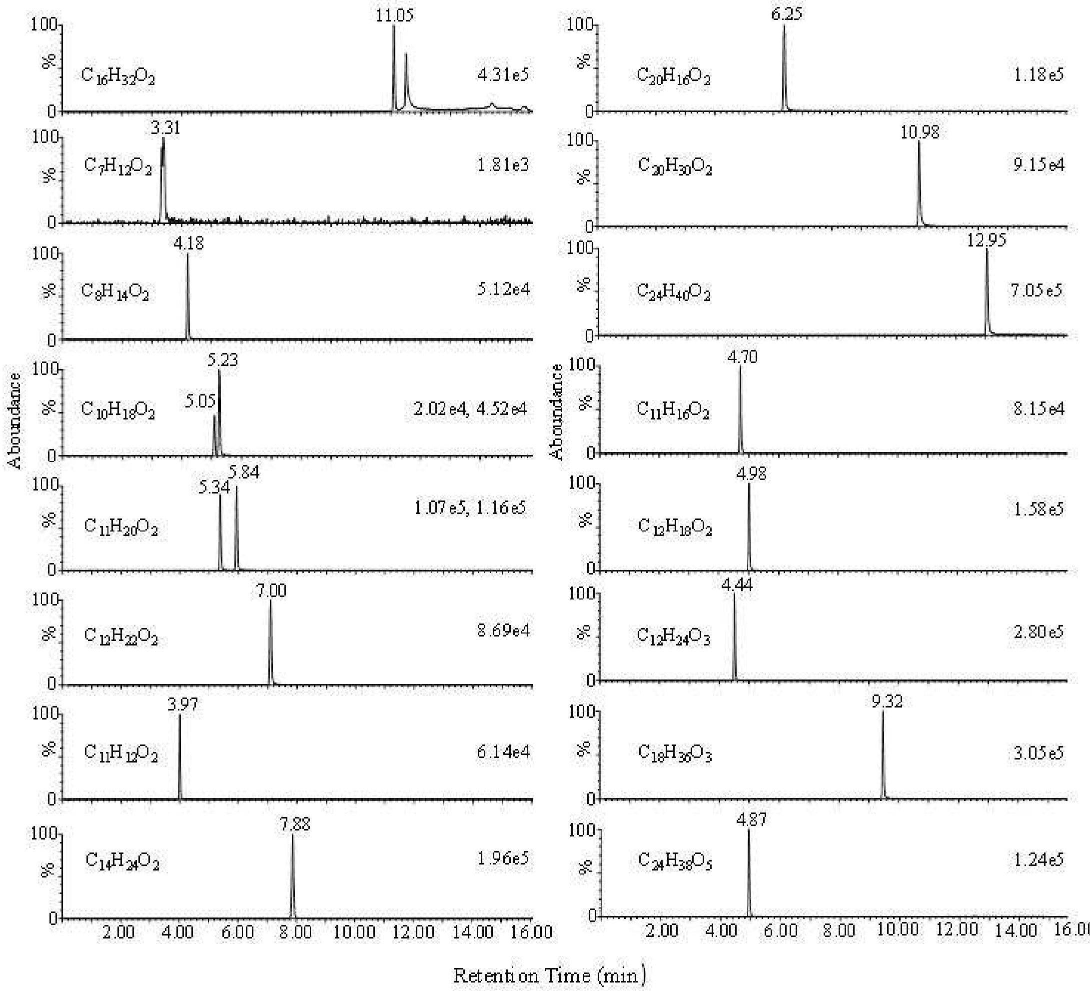



Figure S1. Extracted ion chromatograms of model compounds in a standard mixture of 1 μg/mL analyzed on a C18 column (1.7 μm, 2.1×50 mm, Waters BEH). $C_{10}H_{18}O_2$ (4-propylcyclohexanecarboxylic acid) was a mixture of *cis*- and *trans*- compounds, and $C_{11}H_{20}O_2$ showed a mixture of trans-4-tert-butylcyclohexanecarboxylic acid and cyclohexane pentanoic acid.

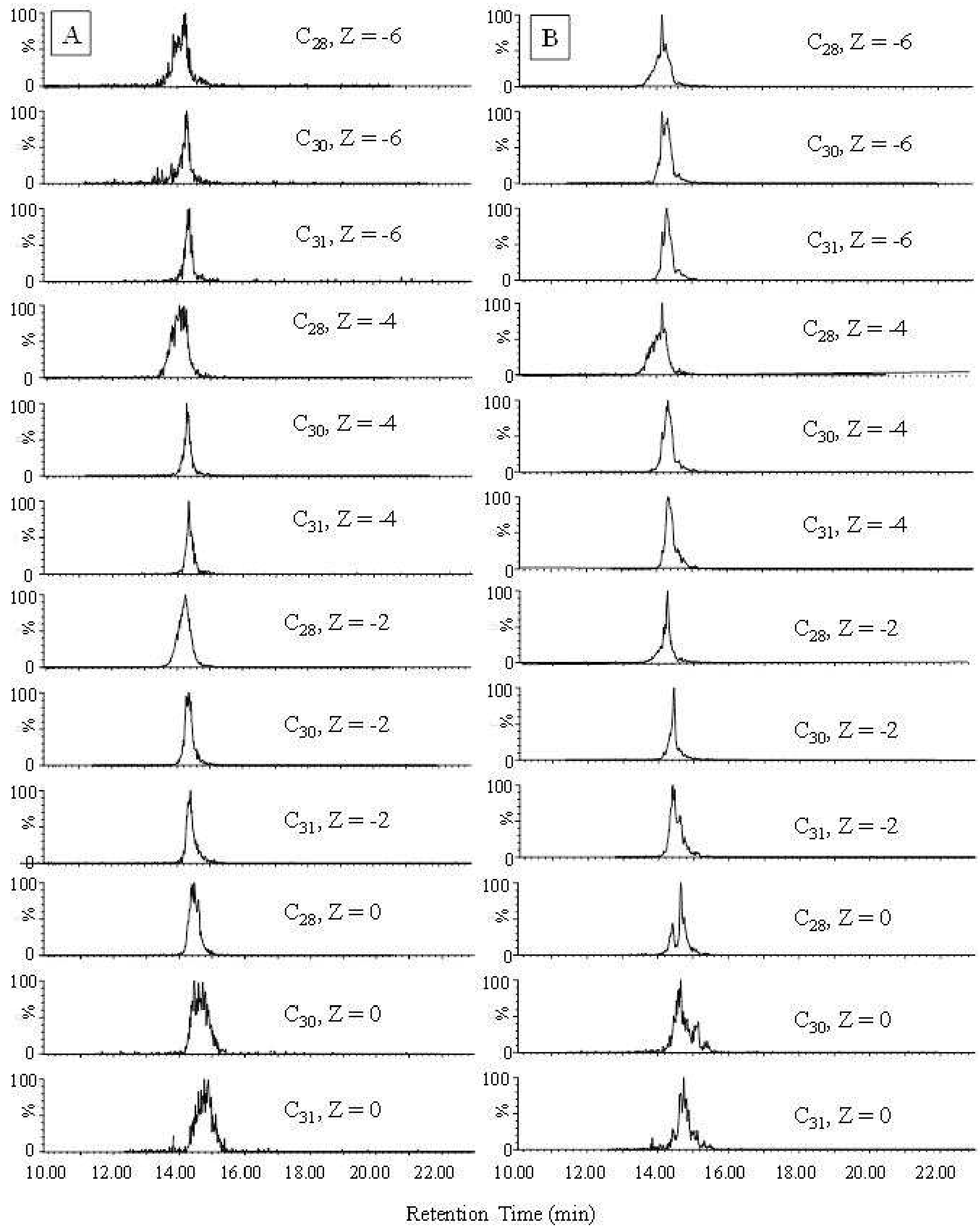



Figure S2. UPLC-QTOF-MS chromatograms of naphthenic acid mixtures in commercial mixtures (A) and oilfield wastewater (B).

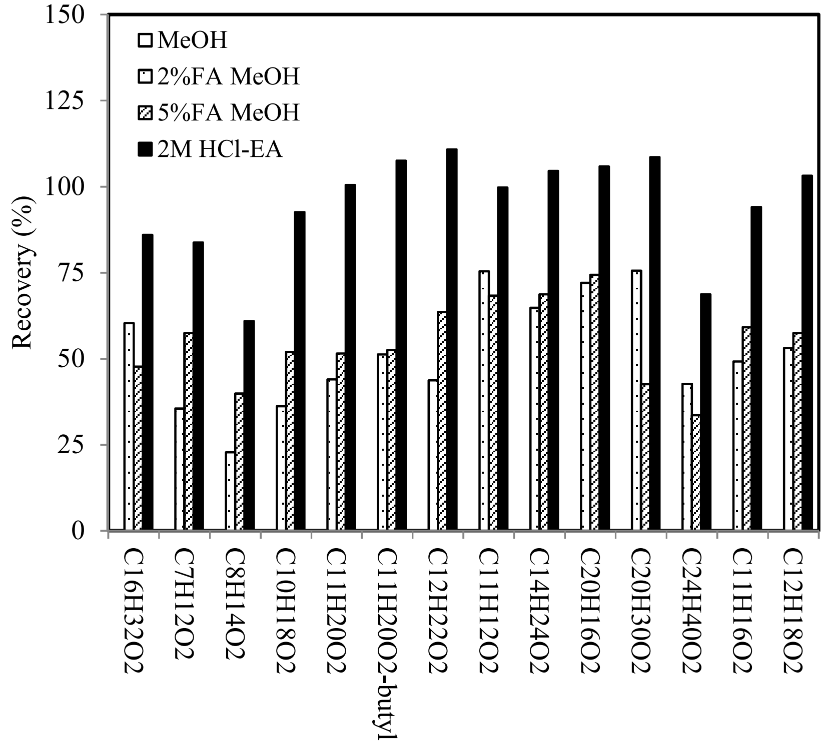



Figure S3 Effect of elute solvent on the recoveries of model compounds through WAX cartridge.

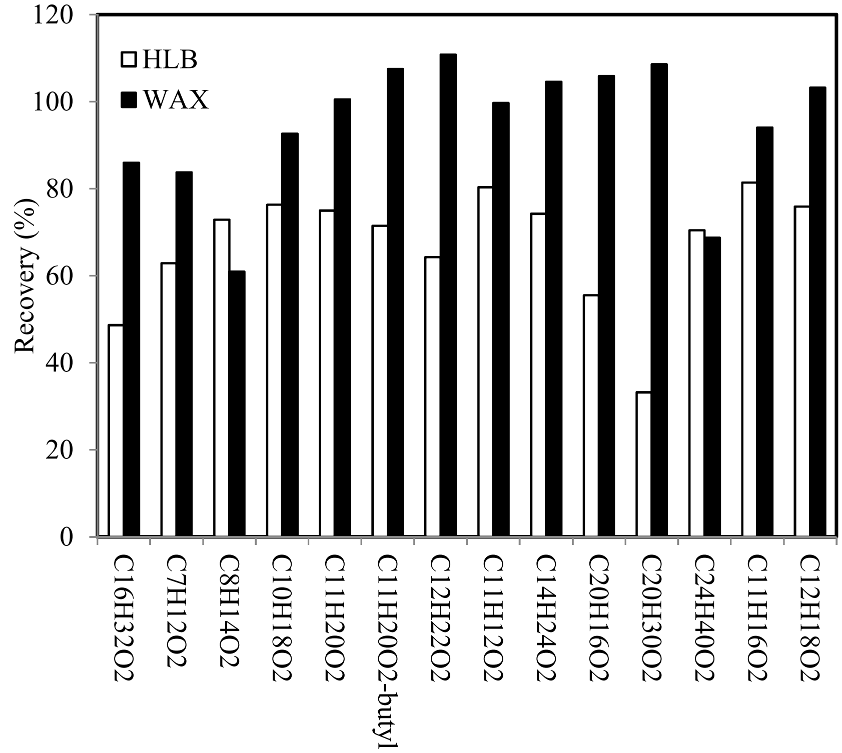



Figure S4. Comparisons of recoveries (%) of model compounds in HLB and WAX cartridges.

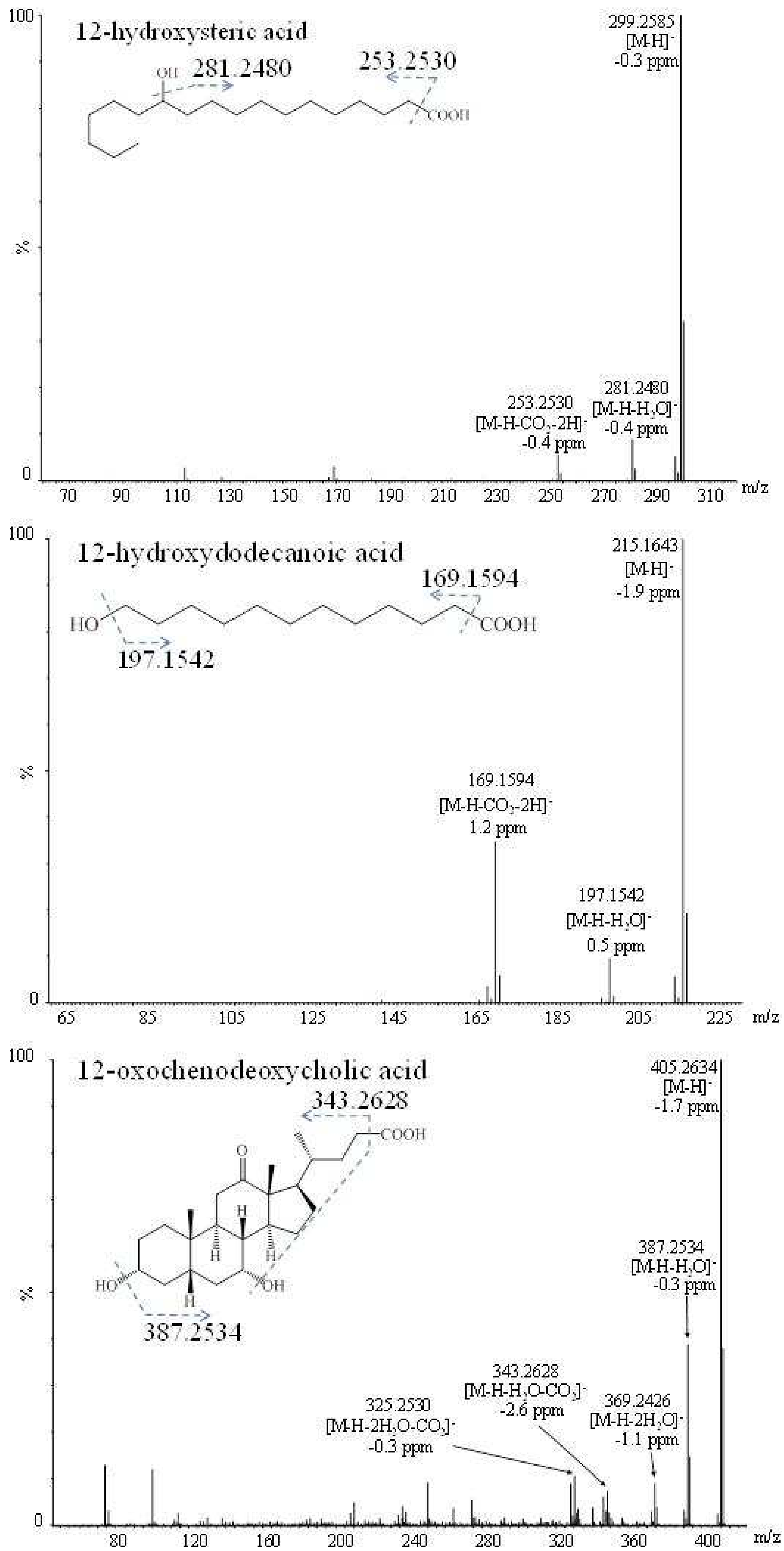



Figure S5. MS/MS spectra of model compounds of oxy-NAs.

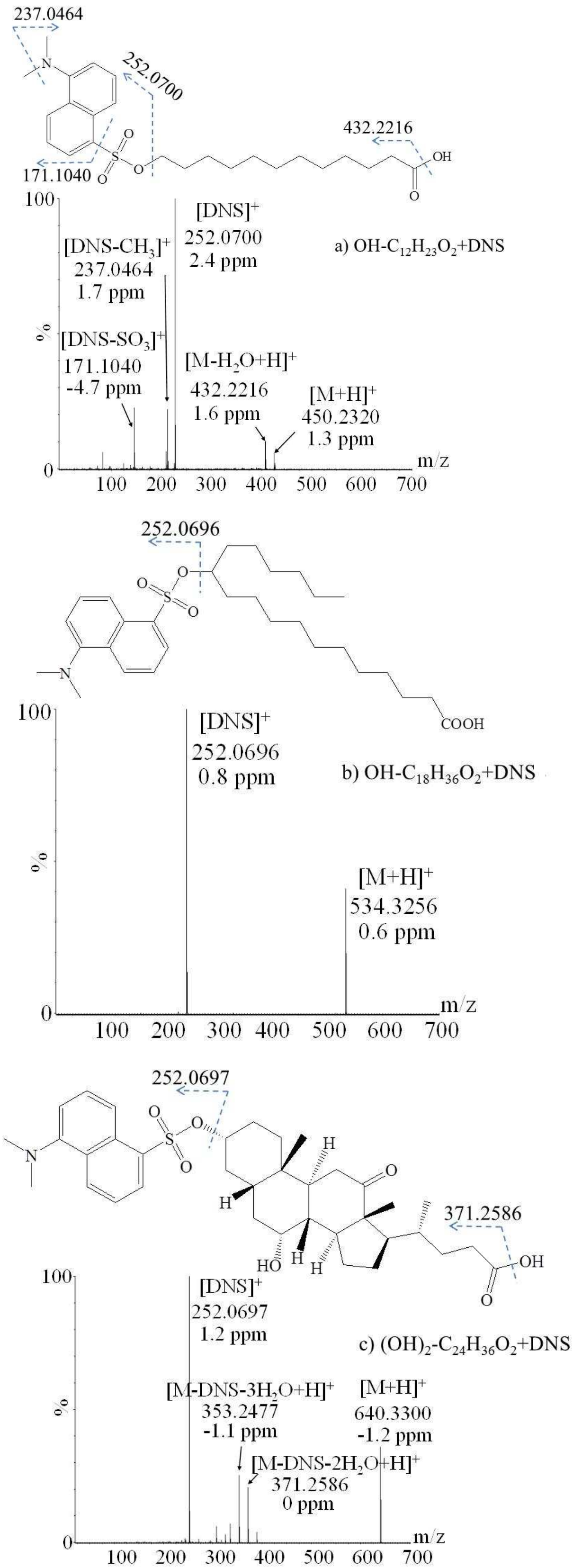



Figure S6. MS/MS spectra of model oxy-NAs derivatized with DNS.

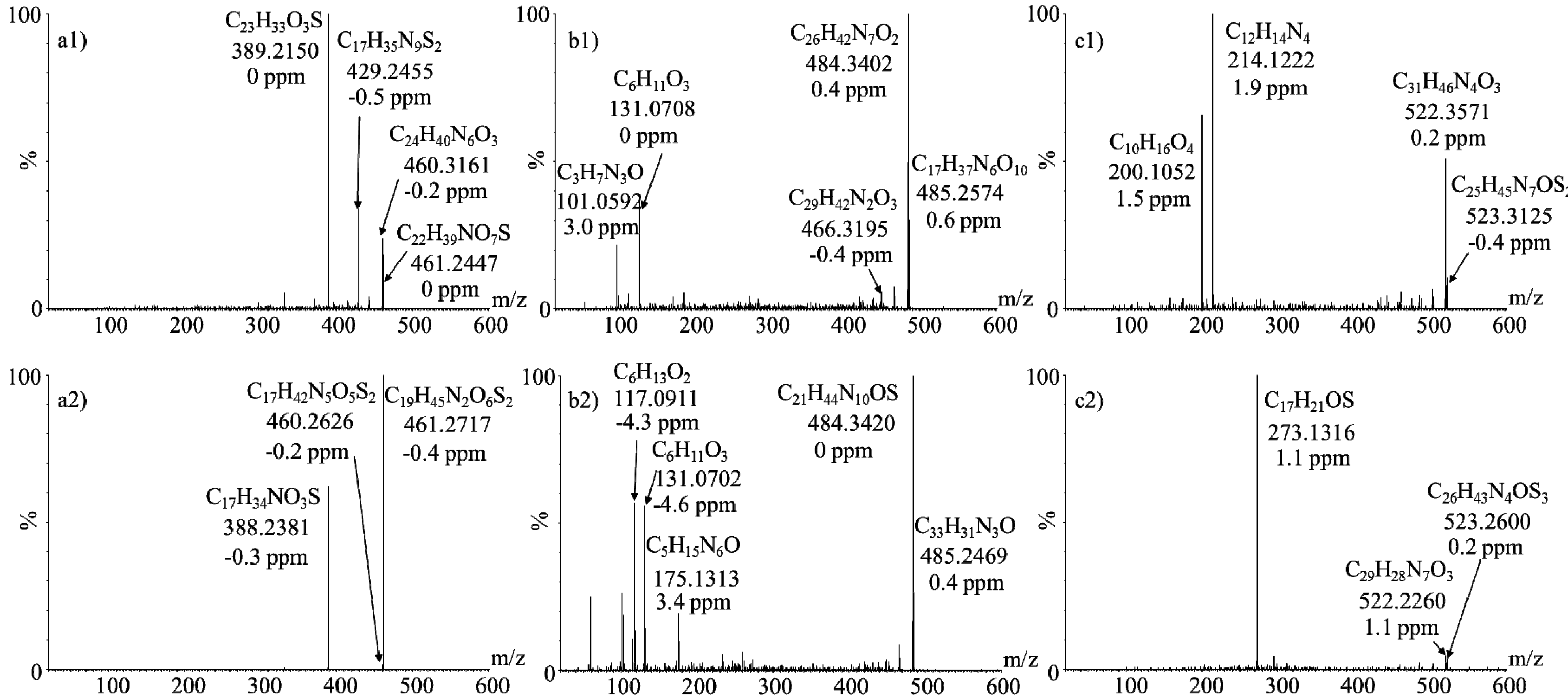



Figure S7. MS/MS spectra of molecluars with precursor ions of 460 (a1-a2), 484 (b1-b2) and 523 (c1-c2) in extracts of oilfield wastewater without derivatization with DNS.

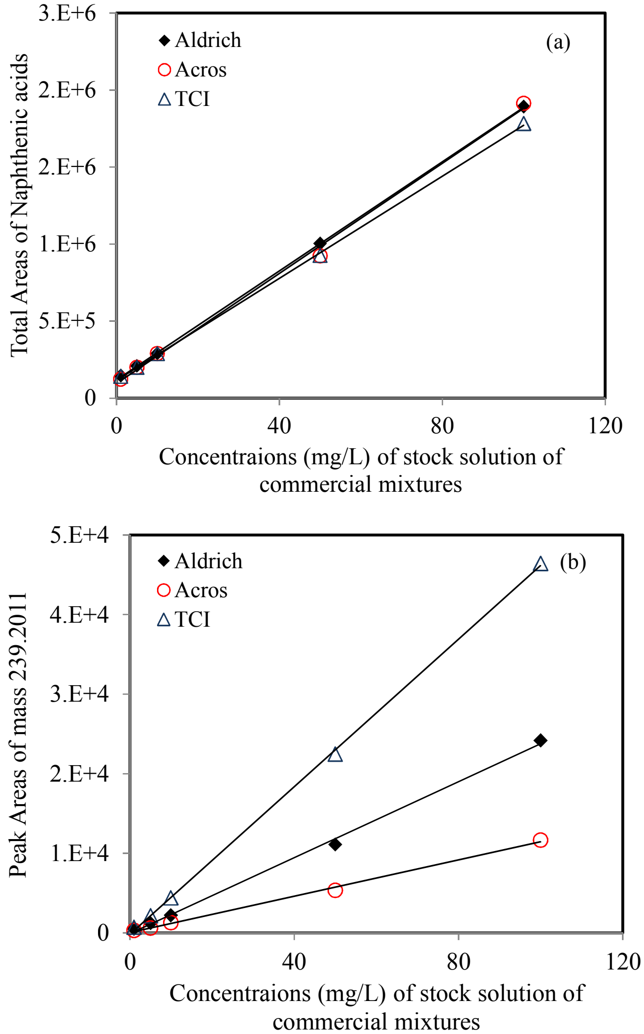



Figure S8. Calibration curves for three commercial mixtures of NAs by UPLC-QTOF-MS, the x-axis is based on total concentration of the NA mixtures. (a) total areas of NAs, (b) area of extracted ion 239.2011.