Supporting Information

for

Naphthenic Acids in Coastal Sediments after the *Hebei Spirit* Oil Spill: A Potential Indicator for Oil Contamination

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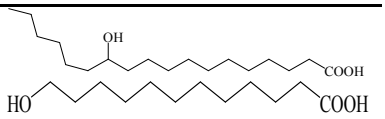
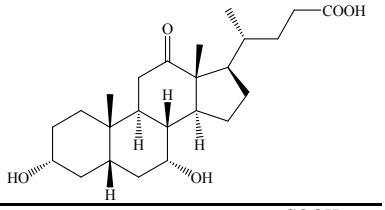
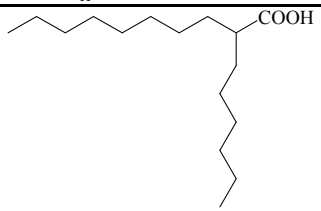
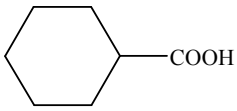
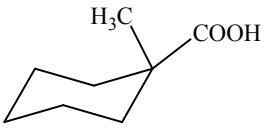
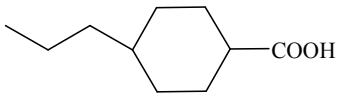
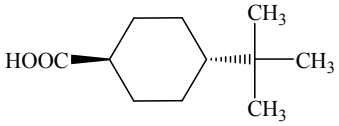
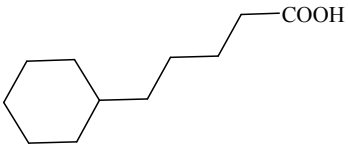
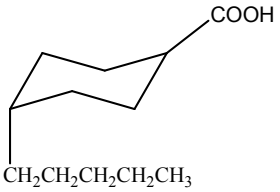
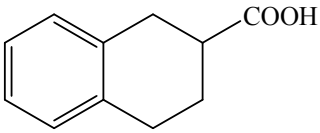
Table S1. Name and structure of model compounds in UPLC-QTOF-MS analysis.

Name	CAS No.	Molecular Weight	Structure
12-hydroxysteric acid	106-14-9	$C_{12}H_{24}O_3$, MW= 300.2664	
12-hydroxydodecanoic acid	505-95-3	$C_{18}H_{36}O_3$, MW= 216.1725	
12-oxochenodeoxycholic acid	2458-08-4	$C_{24}H_{38}O_5$, MW= 406.2719	
2-hexyldecanoic acid	25354-97-6	$C_{16}H_{32}O_2$, MW= 256.2402	
cyclohexanecarboxylic acid	98-89-5	$C_7H_{12}O_2$, MW= 128.0837	
1-Methyl-1-cyclohexane carboxylic acid	1123-25-7	$C_8H_{14}O_2$, MW= 142.0994	
4-n-propylcyclohexanecarboxylic acid (*cis*- and *trans*- mixture)	943-29-3	$C_{10}H_{18}O_2$ (cis- and trans-), MW= 170.1307	
trans-4-tert-butylcyclohexanecarboxylic acid	5962-88-9	$C_{11}H_{20}O_2$-butyl, MW= 184.1463	
cyclohexane pentanoic acid	943-29-3	$C_{11}H_{20}O_2$, MW= 184.1463	
trans-4-pentylcyclohexane carboxylic acid	38289-29-1	$C_{12}H_{22}O_2$, MW= 198.1620	
1,2,3,4-tetrahydro-2-naphthoic acid	53440-12-3	$C_{11}H_{12}O_2$, MW= 176.0837	

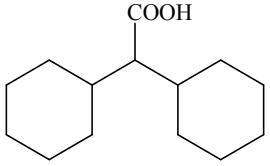
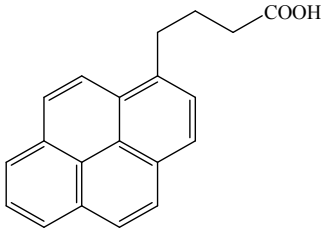
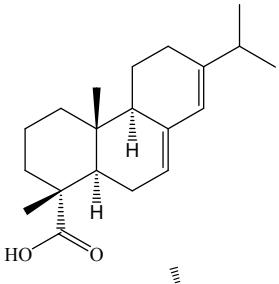
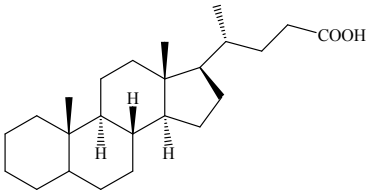
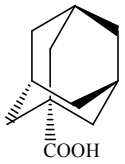
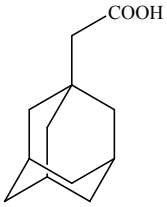
dicyclohexylacetic acid	52034-92-1	$C_{14}H_{24}O_2$, MW= 224.1776	
1-pyrenebutyric acid	3443-45-6	$C_{20}H_{16}O_2$, MW= 288.1150	
abietic acid	514-10-3	$C_{20}H_{30}O_2$, MW= 302.2246	
5-beta-cholanic acid	546-18-9	$C_{24}H_{40}O_2$, MW= 360.3028	
1-adamantane carboxylic acid	828-51-3	$C_{11}H_{16}O_2$, MW= 180.1150	
1-adamantaneacetic acid	4942-47-6	$C_{12}H_{18}O_2$, MW= 194.1307	

Table S2. Description of sampling sites and sediment samples including sediment type, water content, and TOC (total organic carbon), collected in Taean oil spill area, Korea.

Sites	Locations	Latitude (°N)	Longitude (°E)	Sediment types	Water contents (%)	TOC (%)
A1	Sinduri Dune	36° 50′4″	126° 10′45″	Sand	22.4	1.22
A2	Sinduri Dune	36° 50′6″	126° 10′48″	Sand	22.9	3.15
A3	Sinduri Dune	36° 50′5″	126° 10′46″	Sand	21.0	3.64
A4	Sinduri Dune	36° 50′3″	126° 10′44″	Sand	19.0	8.54
B1	Sinduri Mudflat	36° 49′18″	126° 11′12″	Mud	37.8	21.63
B2	Sinduri Mudflat	36° 49′20″	126° 11′13″	Mud+gravel	21.0	3.91
B3	Sinduri Mudflat	36° 49′22″	126° 11′14″	Mud+gravel	27.3	7.64
B4	Sinduri Mudflat	36° 49′24″	126° 11′15″	Mud+gravel	32.6	5.88
C1	Sogenri Mudflat	36° 49′9″	126° 10′17″	Mud	27.9	4.89
C2	Sogenri Mudflat	36° 49′8″	126° 10′15″	Mud	32.9	4.98
C3	Sogenri Mudflat	36° 49′6″	126° 10′14″	Mud	30.8	4.54
C4	Sogenri Mudflat	36° 49′5″	126° 10′13″	Mud	32.8	4.39
R1	Manlipo beach	36° 47′11″	126° 8′4″	Sand	5.4	0.27
R2	Anmyundo beach	36° 31′30″	126° 19′48″	Sand	4.4	0.38

Table S3. Efficiency of different extraction solutions and methods to model compounds of NA and oxy-NA from sediment samples (about 1 g dried sediment spiked with 0.1 μg of standard for each compounds).

Chemicals	Oscillation extraction					Ultrasonic extraction		Soxhlet extraction		
	Hex×3	MTBE×3	DCM×3	EA×3	Hex/MTBE (1:1)×3	Hex/MTBE (1:1)×3	Hex/MTBE (1:1), 2% FA×3	Hex/MTBE (1:1)	Hex/MTBE/ ACN (1:1)	Hex/MTBE/ MeOH (1:1)
$C_{16}H_{32}O_2$	82.5	86.4	81.5	59.9	109.8	106 ± 6.0	104 ± 1.4	106 ± 5.7	100 ± 8.5	113 ± 12
$C_7H_{12}O_2$	16.9	41.5	32.9	10.8	44.3	42 ± 9.7	46 ± 3.6	49 ± 3.3	54 ± 37	84 ± 5.1
$C_8H_{14}O_2$	44.0	50.0	49.4	25.6	66.6	36 ± 12	45 ± 0.4	66 ± 2.2	56 ± 51	88 ± 8.0
$C_{10}H_{18}O_2$[a]	49.0	58.2	41.2	21.6	68.3	71 ± 3.0	87 ± 9.2	79 ± 7.7	78 ± 30	88 ± 1.3
$C_{11}H_{20}O_2$	57.5	68.4	47.8	22.9	79.4	93 ± 9.8	100 ± 8.1	78 ± 10	81 ± 25	91 ± 2.9
$C_{11}H_{20}O_2$-butyl	49.1	63.1	49.3	15.1	63.6	78 ± 4.3	89 ± 2.8	74 ± 8.0	81 ± 19	98 ± 14
$C_{12}H_{22}O_2$	58.0	68.6	44.8	14.0	71.6	86 ± 16	96 ± 7.1	73 ± 4.2	82 ± 15	92 ± 9.5
$C_{11}H_{12}O_2$	9.3	59.5	22.5	8.1	38.1	94 ± 8.6	90 ± 7.1	83 ± 4.3	83 ± 15	102 ± 9.5
$C_{14}H_{24}O_2$	85.0	95.0	84.4	63.9	130.0	105 ± 12	114 ± 0.7	63 ± 8.2	93 ± 30	102 ± 2.7
$C_{20}H_{16}O_2$	2.5	72.1	18.0	5.9	23.6	71 ± 15	75 ± 8.3	95 ± 8.5	84 ± 13	108 ± 8.1
$C_{20}H_{30}O_2$	66.6	84.4	67.9	35.4	93.9	107 ± 1.6	93 ± 5.9	52 ± 9.1	70 ± 1.6	121 ± 30
$C_{24}H_{40}O_2$	70.4	62.0	50.2	25.9	79.9	97 ± 1.7	80 ± 12	79 ± 18	70 ± 3.8	69 ± 1.1
$C_{11}H_{16}O_2$	52.1	69.7	44.5	21.5	71.5	81 ± 1.2	84 ± 2.4	60 ± 1.0	79 ± 26	90 ± 3.1
$C_{12}H_{18}O_2$	55.9	72.7	61.6	31.2	80.9	78 ± 0.2	87 ± 5.7	79 ± 10	77 ± 18	85 ± 3.7
$C_{24}H_{38}O_5$	0.0	0.7	0.5	0.3	0.3	37 ± 9.3	23 ± 0.2	0.5 ± 0.2	28 ± 2.6	88 ± 8.1
$C_{18}H_{36}O_3$	9.0	51.4	34.5	12.9	43.6	99 ± 8.0	101 ± 4.0	67 ± 8.7	82 ± 15	101 ± 3.1
$C_{12}H_{24}O_3$	0.2	39.1	18.0	5.2	18.0	88 ± 1.4	90 ± 0.5	33 ± 2.5	64 ± 11	87 ± 9.3

Table S4. 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 sediment samples from Taean coasts.

Precursor ion	Collision energy (eV)	Retention time (min)	Compound	Z	Mass fragment ions			
					$[M-H]^-$	$[M-H-H_2O]^-$	$[M-H-CO_2]^-$	$[M-H-H_2O-CO_2]^-$
227	15-25	10.5-11.8	$C_{14}H_{28}O_2$	0	227.2015 (1.8 ppm)	-	-	-
		5-8	$C_{13}H_{24}O_3$	-2	227.1637 (-4.4 ppm)	209.1549 (3.3 ppm)	183.1741 (-4.4 ppm)	-
		4-5	$C_{12}H_{20}O_4$	-4	227.1274 (-4.0 ppm)	209.1172 (-2.9 ppm)	183.1401 (8.7 ppm)	165.1284 (3.0 ppm)
323	20-30	13-14.4	$C_{21}H_{40}O_2$	-2	323.2944 (-1.9ppm)	-	-	-
		10-13	$C_{20}H_{36}O_3$	-4	323.2580 (-1.9 ppm)	305.2482 (0.3 ppm)	279.2680 (-2.9 ppm)	-
		6-9	$C_{19}H_{32}O_4$	-6	323.2234 (3.7 ppm)	305.2119 (0.7 ppm)	279.1761 (4.3 ppm)	261.2231 (5.0 ppm)
293	15-25	12-14	$C_{19}H_{34}O_2$	-4	293.2478 (-1.0 ppm)	-	-	-
		8-11.4	$C_{18}H_{30}O_3$	-6	293.2114 (-1.0 ppm)	275.2003 (-2.9 ppm)	249.2215 (-1.2 ppm)	-
		5.8-6.4	$C_{17}H_{26}O_4$	-8	293.1755 (0.7 ppm)	275.1635 (-4.6 ppm)	249.1847 (-3.2 ppm)	231.1750 (0.4 ppm)
291	20-30	12-14	$C_{19}H_{32}O_2$	-6	291.2320 (-1.4 ppm)	-	-	-
		7-11	$C_{18}H_{28}O_3$	-8	291.1963 (1.0 ppm)	273.1844 (-4.0 ppm)	247.2065 1.2 ppm)	-
		2-3	$C_{17}H_{24}O_4$	-10	291.1589 (-2.4 ppm)	273.1511 (7.3 ppm)	247.1682 (-6.5 ppm)	229.1585 (-3.1 ppm)
387	20-30	13.5-15	$C_{26}H_{44}O_2$	-8	387.3256 (-1.8 ppm)	-	-	-

		11-13	$C_{25}H_{40}O_3$	-10	387.2888 (-2.8 ppm)	369.2748 (-12.5 ppm)	343.2984 (-5.0 ppm)	-
		8-9	$C_{24}H_{36}O_4$	-12	387.2550 (3.9 ppm)	369.2422 (-2.2 ppm)	343.2621 (-4.7 ppm)	325.2518 (-4.0 ppm)
455	20-30	14-15.5	$C_{31}H_{52}O_2$	-10	455.3882 (-1.5 ppm)	-	-	-
		12-14	OH-$C_{30}H_{48}O_3$	-12	455.3529 (0.9 ppm)	437.3440 (4.6 ppm)	411.3616 (-2.7 ppm)	-
		10-12	$C_{29}H_{44}O_4$	-14	455.3170 (2.0 ppm)	437.3051 (-1.1 ppm)	411.3263 (0.0 ppm)	393.3147 (-2.5 ppm)

Mass errors of fragmentation ions of 183.1401, 369.2748, 273.1511, 247.1682 were higher than 5 ppm possible due to the low abundance of the compounds.

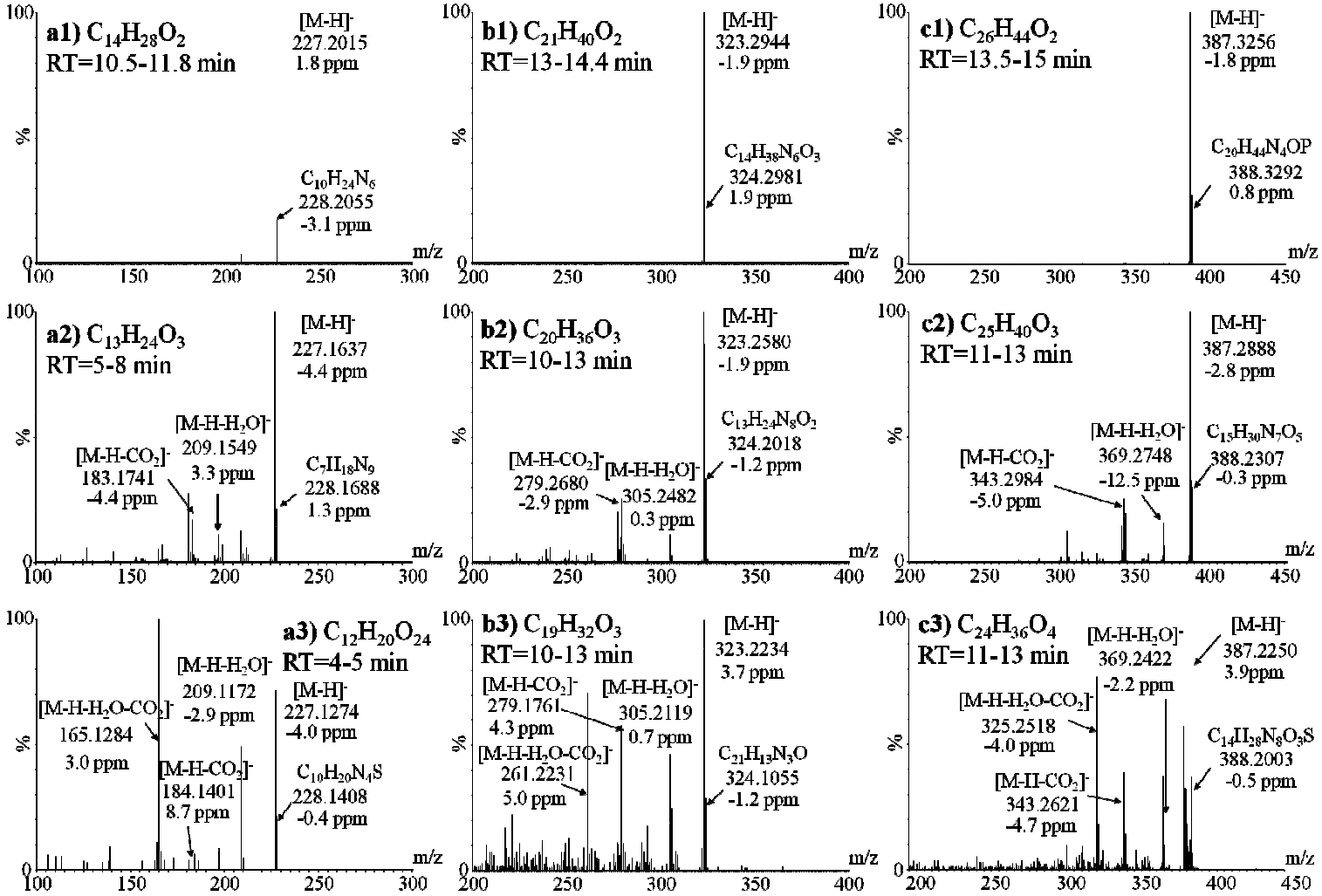


Figure S1. MS/MS spectra of NAs, O_3-NAs and O_4-NAs with precursor ions of 227 (a1-a3), 323 (b1-b3) and 387 (c1-c3) in extracts of sediment.