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Title:

Effects of visible and UV light on the characteristics and properties of crude oil-in-water emulsions

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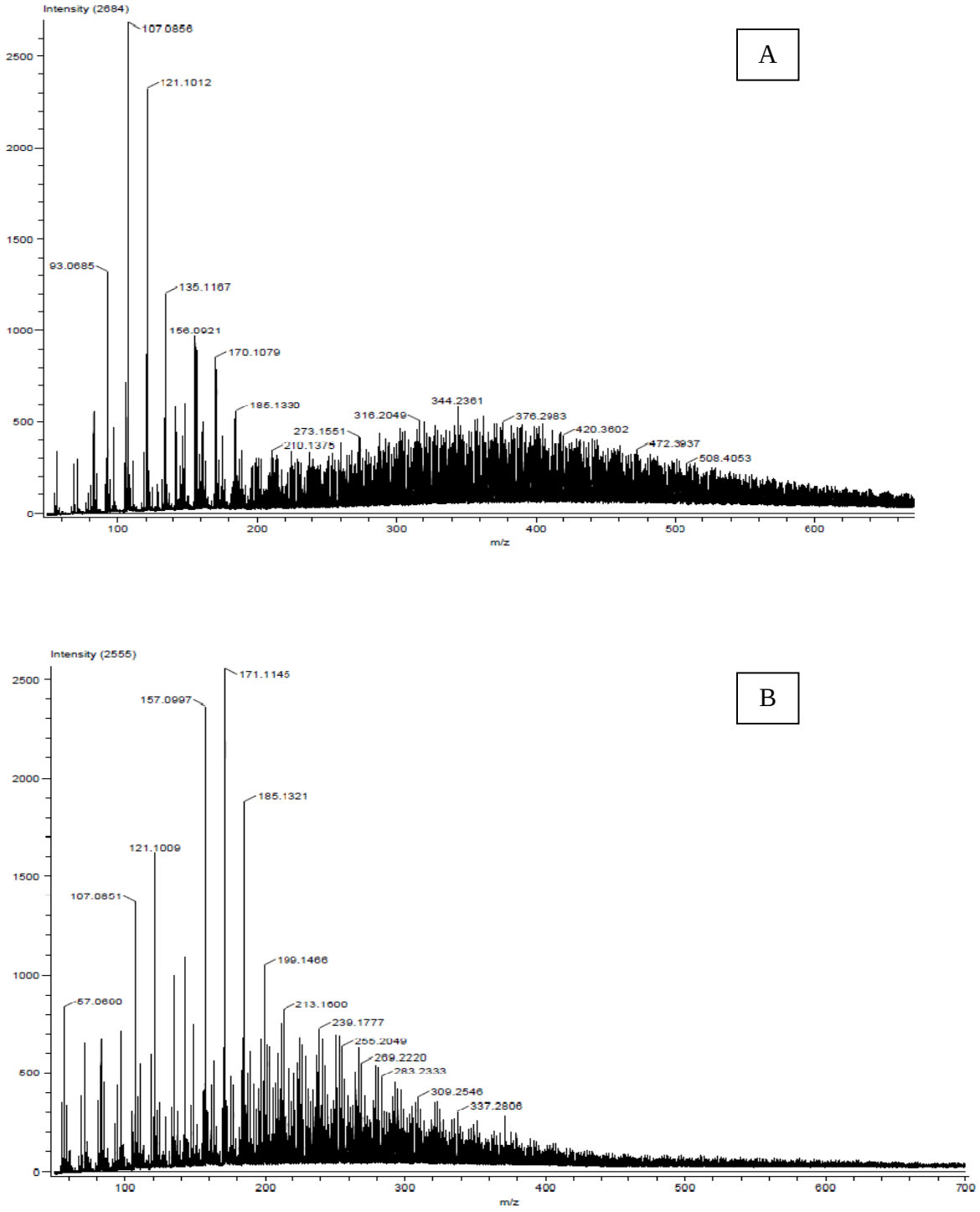

Fig. S1 DART/MS signatures of the (A) Prudhoe Bay and the (B) South Louisiana crude oils obtained by introducing the samples directly into the DART gas stream.

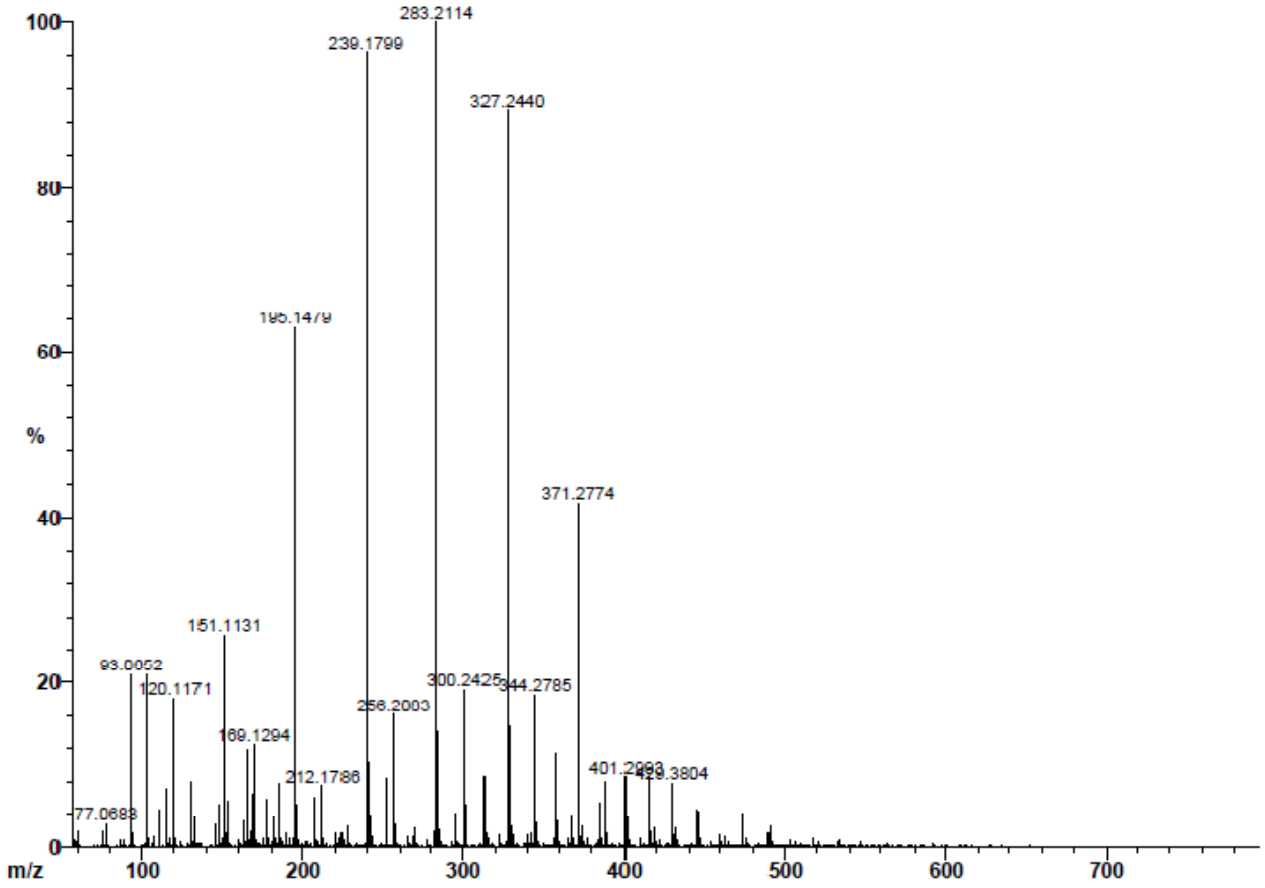

Fig. S2 DART mass spectrum of the non-irradiated VeruSOL®-Marine-200 surfactant obtained by introducing the sample directly into the DART gas stream.

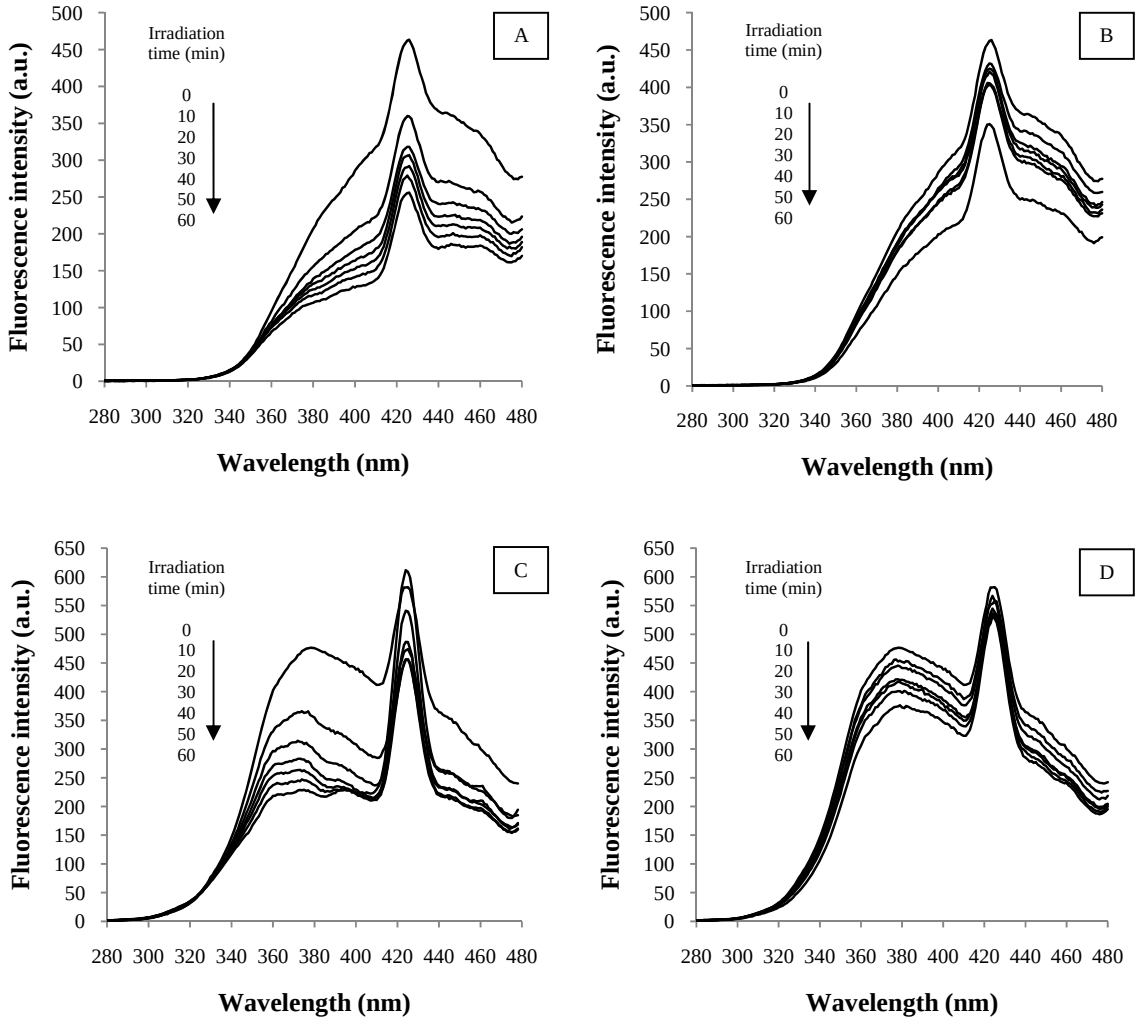

Fig. S3 Fluorescence emission spectra of the Prudhoe Bay emulsions [(A) visible and (B) UV light irradiated] and of the South Louisiana emulsions [(C) visible and (D) UV light irradiated] with 1% H_2O_2 as a function of irradiation time. Excitation wavelengths were set at 250 nm. Excitation and emission slit widths were set at 5 nm. Data reported are the average of three replicate measurements.

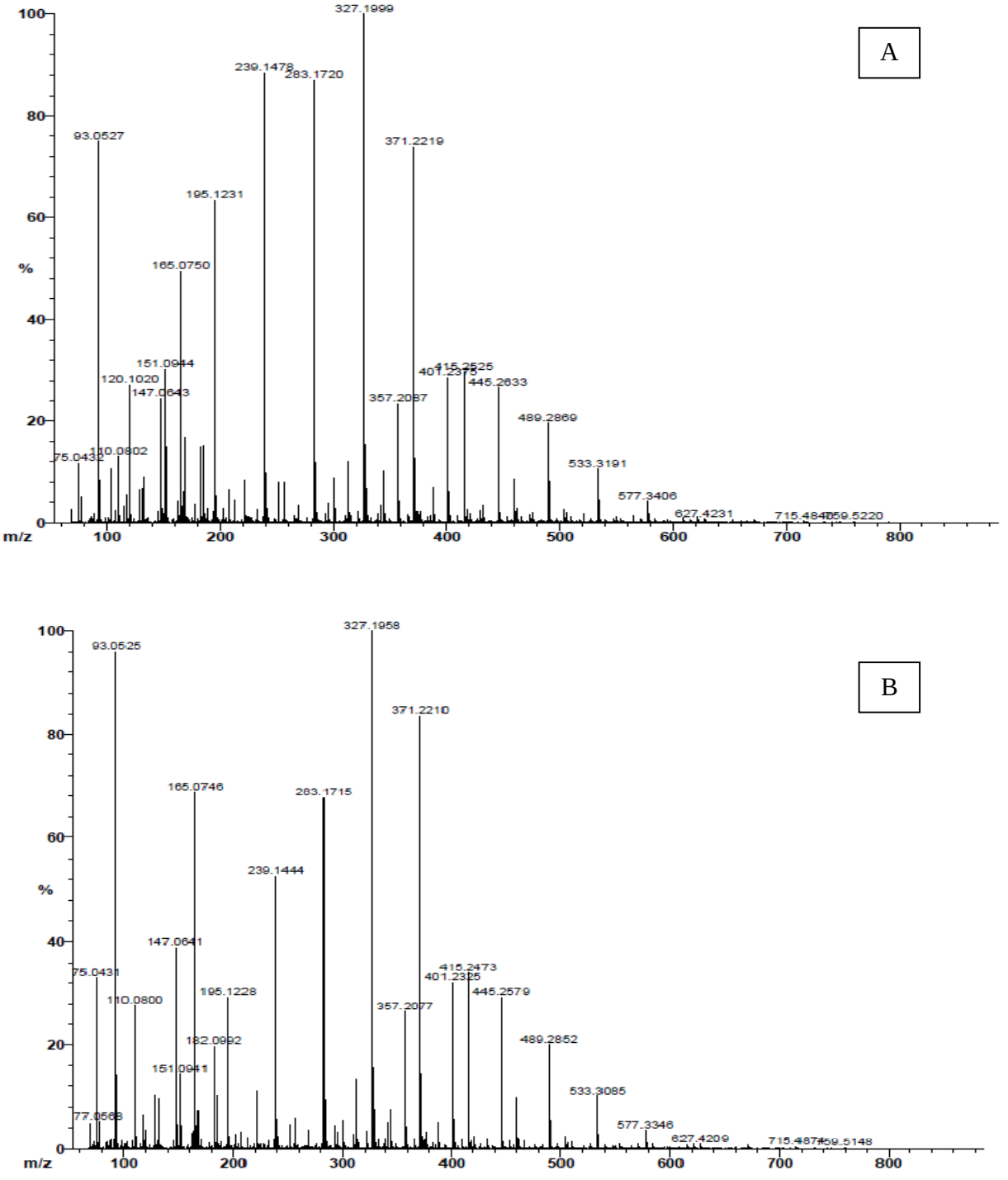

Fig. S4 DART mass spectra of the VeruSOL®-Marine-200 surfactant after 120 min (A) visible and (B) UV light irradiation, obtained by introducing the sample directly into the DART gas stream.

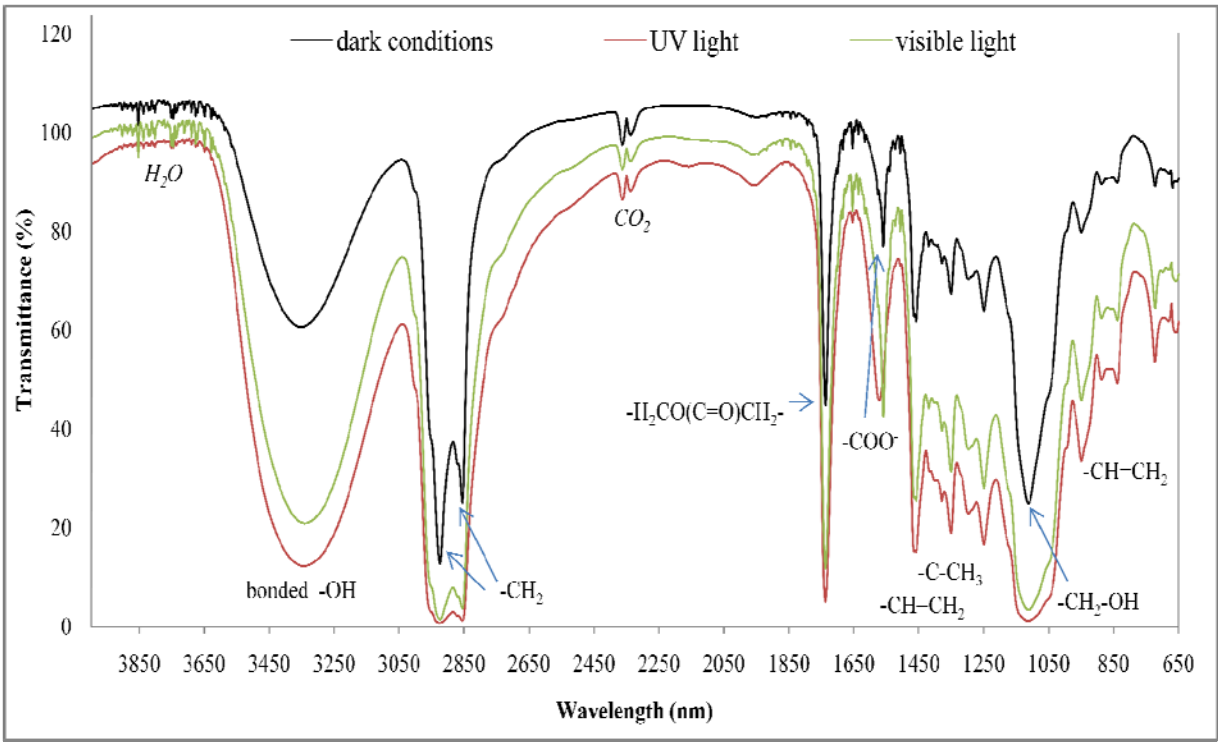

Fig. S5 FT-IR spectra of the VeruSOL®-Marine-200 surfactant before and after visible and UV light irradiation (120 min).

Table S1 Some important physical properties of Prudhoe Bay (PB) and South Louisiana (SL) reference crude oils[a]

	PB crude oil	SL crude oil
API gravity at 60 ^{o}F, degree	26.6	37.0
Specific gravity at 60/60 ^{o}F	0.8950	0.840
Sulfur, wt. %	1.06	0.23
Nitrogen, wt. %	0.25	0.031
Nickel, mg/L	11.8	1.1
Vanadium, mg/L	31.4	0.95
Pour point, ^{o}C	-11	-17.8
Viscosity, cSt at 40 ^{o}C	18.0	3.582
Viscosity, cSt at 100 ^{o}C	5.5	1.568
Viscosity index	282	(not calculable)

[a] Source: US EPA dispersant tests using ASTM standard methods. Concentration of Iron not reported.

Table S2 ^{1}H and ^{13}C NMR assignment for the major components of the VeruSOL®-Marine-200 surfactant.

^{1}H (ppm)	^{13}C (HSQC)	^{13}C (HMBC)
5.34 (m, 0.78 H)	130.4	27.6
4.24 (m, 2 H)	63.7	174.4, 69.8
3.72 (m, 2H)	69.8, 61.2	
3.67 (bs, 16H)	70.6	
3.58 (m, 2H)	72.7	
2.35 (t,1.24H, *J*=7.6 H)	34.7	174.4, 25.4
2.21 (t, 0.47H, *J*=7.6 H)	37.5	180.1
2.01 (m, 1.27H)	27.6	130.4
1.63 (m, 2H)	25.4	
1.27 (m, 16H)	32.5, 30.0, 23.2	
1.15 (d, 0.61H, *J*= 6.7H)	19.7	67.3 (propan-2-ol)
0.89 (t, 3H, *J*=6.9 H)	14.4	

Assignment of peaks:

^{1}H: 3.72 3.58 3.67 3.69 4.24 2.35 1.63 1.27 0.89
^{13}C: 61.2 72.7 69.8 63.7 174.4 34.7 25.4 14.4
$HOCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2O(C=O)CH_2CH_2(CH_2)_8CH_3$

^{1}H: 3.72 3.58 3.67 3.69 4.24 2.21 2.01 5.34 1.27 0.89
^{13}C: 61.2 72.7 69.8 63.7 180.1 37.5 27.6 130.4 14.4
$HOCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2O(C=O)CH_2CH_2CH=CH(CH_2)_8CH_3$

Table S3 Concentrations in µg/L of the Semi-Volatile Organic Compounds (SVOCs) present in the Prudhoe Bay emulsion before and after irradiation.

SVOCs	Dark conditions	UV light (30 min)	Visible light (30 min)
Nitrobenzene	2800	1200	350
Naphthalene	840	520	720
2-Methylnaphthalene	1700	1200	1600
Fluorene	130	ND[a]	140
Phenanthrene	350	340	410
1,4,7,10,13,16-Hexaoxanonadecane, 18-(2-	8100	20000	ND
1,4,7,10,13,16-Hexaoxanonadecane, 18-pro (11.76260)	27000	ND	ND
12-Crown-4	7900	ND	ND
2,2-Dichloro-1,1-bis(4-methoxyphenyl)eth	9300	ND	ND
2,6-Octadiene,4-methyl-	11000	ND	ND
2-Fluoro-4-methyl-10H-acridin-9-one	8400	ND	ND
9,17-Octadecadienal, (Z)-	7800	ND	ND
Hexadecane	18000	ND	ND
Hexadecenoic acid, Z-11-	21000	ND	ND
Hexagol (10.11155)	9900	ND	ND
Hexagol (11.39243)	7900	ND	ND
n-Hexadecanoic acid	18000	22000	50000
Octaethylene glycol (11.11628)	8800	ND	ND
Octaethylene glycol (9.31835)	8100	ND	ND
Oleic acid	180000	99000	210000
Oleic acid, 3-hydroxypropyl ester	16000	ND	ND
Pentaethylene glycol (10.55810)	22000	ND	ND
Pentaethylene glycol (9.69440)	14000	ND	ND
Tetradecanoic acid	26000	20000	27000

[a] ND means not detectable

Table S4 Concentrations in µg/L of the Semi-Volatile Organic Compounds (SVOCs) present in the South Louisiana emulsion before and after irradiation.

SVOCs	Dark conditions	UV light (30 min)	Visible light (30 min)
Nitrobenzene	240	ND[a]	180
Naphthalene	790	420	630
2-Methylnaphthalene	1200	880	1300
Phenanthrene	130	120	170
1,4,7,10,13,16-Hexaoxacyclooctadecane (10.23497)	11000	ND	ND
1,4,7,10,13,16-Hexaoxacyclooctadecane (12.96710)	46000	ND	ND
1,4,7,10,13,16-Hexaoxanonadecane, 18-pro (11.32195)	14000	ND	ND
1,4,7,10,13,16-Hexaoxanonadecane, 18-pro (9.35363)	11000	ND	ND
1,6-octadiene,3,5-Dimethyl-, trans	18000	ND	ND
15-Crown-5	23000	ND	ND
1H-Indole, 5-methyl-2,3-diphenyl-	12000	ND	ND
2-Methyl-9-chloro-acridine	16000	ND	ND
9-Hexadecenoic acid	ND	3900	ND
Dodecanoic acid	ND	3700	ND
9-Octadecenoic acid, (Z)-, 2-hydroxy-	ND	ND	30000
9-Octadecenoic acid, (E)	180000	ND	ND
Hexagol	35000	ND	ND
n-Hexadecanoic acid	11000	5500	ND
Octaethylene glycol	9300	ND	ND
Oleic acid	ND	ND	79000
Oleic acid, 3-Hydroxypropyl ester	44000	8300	ND
Pentaethylene glycol	33000	ND	ND
Tetradecanoic acid	15000	6100	8500
Eicosane, 10-methyl	7500	ND	ND
Tetraethylene glycol monododecyl ether	21000	2800	12000
Undecane	16000	ND	ND

[a] ND means not detectable

Table S5 Average concentrations in mg/L of the Total Petroleum Hydrocarbon (TPH)-Diesel Range Organic (DRO) and Gasoline Range Organic (GRO) in the Prudhoe Bay (PB) and the South Louisiana (SL) emulsions with 1% H_2O_2 as a function of irradiation time.[a]

Irradiation time (min)	TPH-DRO		TPH-GRO	
	PB emulsion		SL emulsion	
	Visible light	UV light	Visible light	UV light
0	231.7	231.7	122.4	122.4
10	201.7	153.0	117.7	82.3
20	148.0	177.1	137.2	103.9
30	148.5	177.1	122.7	95.1
40	172.2	155.9	113.3	85.7
50	176.1	142.0	109.5	75.8
60	162.4	160.5	108.0	67.5

[a] Data reported are the average of three trials.

Table S6 Concentrations in µg/L of the Volatile Organic Compounds (VOCs) in the Prudhoe Bay emulsion before and after irradiation.

VOCs	Dark conditions	UV light (30 min)	Visible light (30 min)
Chloroethane	17	ND[a]	ND
1,2 Dichloroethane	30	ND	ND
Toluene	270	6.3	300
Ethylbenzene	110	9.9	150
m, p-Xylene	370	56	540
o-Xylene	170	22	230
Xylene (total)	540	78	770
Isopropylbenzene	22	9.7	55
n-Propylbenzene	36	27	140
1,3,5-Trimethylbenzene	51	38	160
1,2,4-Trimethylbenzene	140	100	430
sec-Butylbenzene	11	16	72
n-Butylbenzene	21	34	140
1,2,4-Trichlorobenzene	2.3	ND	ND
Hexachlorobutadiene	3.2	ND	ND
1,2,3-Trichlorobenzene	3.3	ND	ND
Naphthalene	180	120	18
1,2,3-Trimethylbenzene	75	ND	200
1-Ethyl-2-methylbenzene	110	ND	ND
Cyclooctane	130	ND	ND
Decanal	150	ND	ND
Heptanal	87	ND	ND
Hexadecane	68	ND	ND
1-Methylnaphthalene	82	ND	ND
2-Methylnaphthalene	66	ND	ND
Octanal	130	ND	ND
Tetradecane	82	150	ND
Undecane	92	550	ND

[a] ND means not detectable

Table S7 Concentrations in µg/L of the Volatile Organic Compounds (VOCs) in the South Louisiana emulsions before and after irradiation.

VOCs	Dark conditions	UV light (30 min)	Visible light (30 min)
Acetone	57	62	23
Benzene	54	0.61	ND[a]
Toluene	420	5.8	ND
1,2-Dichloropropane	3.4	0.53	ND
Ethylbenzene	200	7.2	ND
m, p-Xylene	730	43	ND
o-Xylene	450	17	ND
Xylene (total)	1200	60	ND
Isopropylbenzene	67	3.6	ND
n-Propylbenzene	130	5.9	ND
1,3,5-Trimethylbenzene	260	14	2.0
1,2,4-Trimethylbenzene	720	41	9.4
sec-Butylbenzene	50	3.0	ND
n-Butylbenzene	95	ND	ND
Naphthalene	230	12	13
Pentylcyclohexane	170	ND	ND
1-Ethyl-2-methylbenzene	190	ND	ND
1-Methylethylcyclohexane	950	ND	ND
Butylcyclohexane	180	ND	ND
Pentylcyclohexane	170	ND	ND
Dodecane	330	51	ND
1-Chlorohexadecane	210	ND	ND
Octane (8.01312)	700	ND	ND
Octane (9.13925)	790	ND	ND
2-Methyldecane	170	69	ND
4-Methyldecane	190	ND	ND
Undecane	350	ND	33
2-Methylnonane	950	ND	ND

[a] ND means not detectable