

Supporting Information for

**Ionization selectivity of electrospray and atmospheric pressure photoionization FT-ICR MS
for petroleum refinery wastewater dissolved organic matter**

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Table S1. Operating parameters of the FT-ICR MS for various ionization sources

Parameters	Negative-ion ESI		Positive-ion ESI		Positive-ion APPI	
	RWDOM	SRNOM	RWDOM	SRNOM	RWDOM	SRNOM
Spray shield voltage (kV)	4.0	3.3	-4.5	-4.0	-1.5	-1.5
capillary column front end voltage (kV)	4.5	3.8	-5.0	-4.5	-2.1	-2.1
capillary column end voltage (V)	-320	-300	320	320	320	320
ion accumulation time in the hexapole (s)	0.001	0.001	0.001	0.001	0.001	0.001
accumulation time in the collision cell (s)	0.3	0.2	0.5	0.4	1.0	0.5
Ion flight time into the ICR cell (ms)	1.0	1.2	0.9	1.0	0.9	1.2
collision voltage in the collision cell (V)	3.0	1.5	-1.5	-1.5	-1.5	-1.5

Table S2. Number of total assigned formulae and CHO-formulae, and relative percentages, depending on ionization mode and samples.

Ionization mode	RWDOM				SRNOM			
	all formulae	percent	CHO	percent	all formulae	percent	CHO	percent
Total	6226	100	1398	100	7196	100	4117	100
(-) ESI	3909	62.8	1094	78.3	3785	52.6	2331	56.6
(+) ESI	3096	49.7	388	27.8	1914	26.6	1643	39.9
(+) APPI	3001	48.2	662	47.4	4818	67.0	2710	65.8
(-) ESI only	1708	27.4	633	45.3	1353	18.8	583	14.2
(+) ESI only	813	13.1	20	1.4	146	2	95	2.3
(+) APPI only	1107	17.8	245	17.5	3159	43.9	1596	38.8
(-) ESI & (+) ESI	1886	30.3	329	23.5	1662	23.1	1370	33.3
(-) ESI & (+) APPI	1497	24.1	378	27.0	1553	21.6	1018	24.7
(+) ESI & (+) APPI	1579	25.4	285	20.4	889	12.5	735	17.9
(-) ESI & (+) ESI & (+) APPI	1182	19	246	17.6	783	10.9	640	15.5

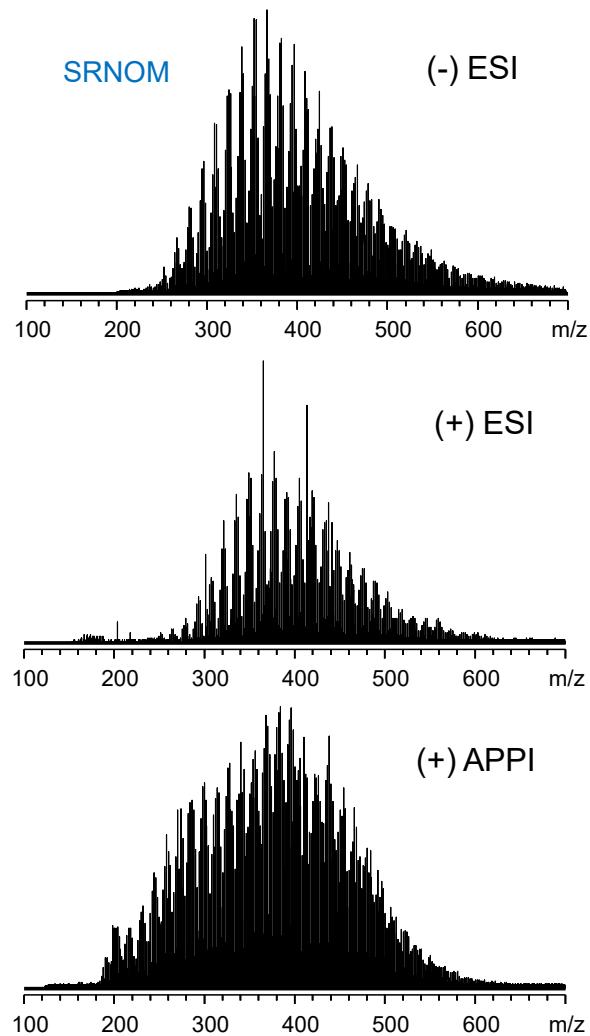


Figure S1. Broadband FT-ICR mass spectra of SRNOM with negative-ion ESI (top), positive-ion ESI (middle) and positive-ion APPI (bottom).

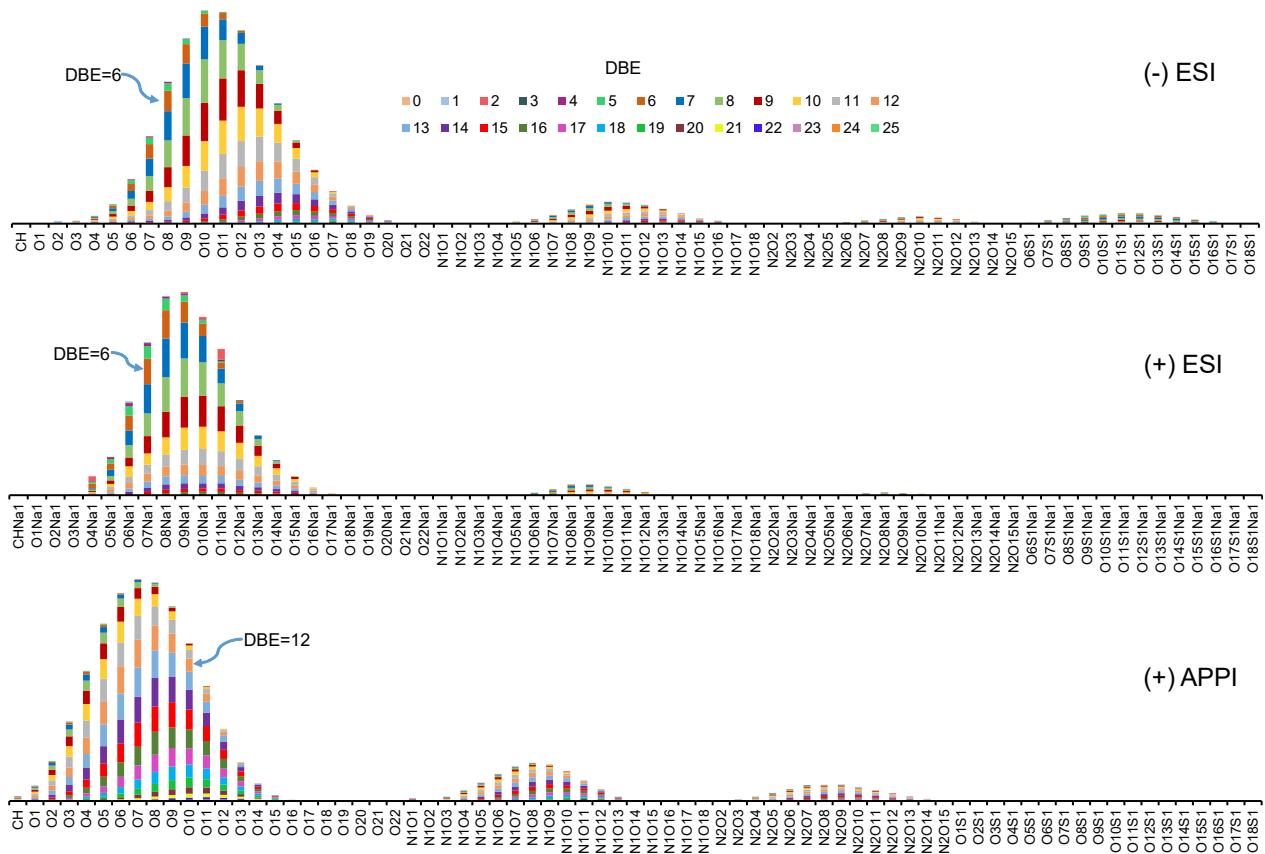


Figure S2. Relative abundance of heteroatom class species in SRNOM obtained by negative-ion ESI (top), positive-ion ESI (middle) and positive-ion APPI (bottom) FT-ICR MS as well as the double bond equivalent (DBE) distribution.