Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Monitoring of polycyclic aromatic hydrocarbon contamination at four oil spill sites using fluorescence spectroscopy coupled with parallel factor-principal component analysis

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Supplementary Information

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Reagents and materials

HPLC grade cyclohexane, dichloromethane, and acetone were purchased from Fisher Scientific (Markham, ON, Canada). Customized mixed PAHs and 610 EPA-priority PAH standards were purchased from Restek (Bellefonte, PA, USA). Dissolved organic matter standards were purchase from Sigma Aldrich (St. Louis, MO, USA).

Quality control

Multiple validation, calibration, and correction steps were applied weekly/daily to ensure the stability of the instrument and the accuracy and reliability of the measurement. The instrument was validated on a weekly basis including checks for wavelength accuracy and reproducibility (Ex. and Em.), spectral band accuracy (Ex and Em), stray light, and water Raman sensitivity (Ex at 350 and 500 nm). Daily quality controls were also preformed systematically to evaluate any changes in the instrumental response or any potential contamination in the sample or system: 1) A blank sample of dichloromethane was scanned at the beginning, middle, and end of each day. The intensity of blank background signal and Rayleigh peaks spectra were logged for each run to track changes in the instrument and check for any contamination of the solvent. 2) A mixture of 16 EPA-priority PAH standard (12.5–25 ppb concentration range) was analyzed daily for monitoring instrumental stability, sensitivity and accuracy. 3) Raman scatter peak of water (Ex.: 350 nm, Em.: 380-420 nm) was scanned at beginning, middle, and end of each day. The area of the Raman peak was tracked to monitor the sensitivity, repeatability and accuracy of the instrument performance over time.

All the petroleum and environmental samples were run as duplicates to ensure the repeatability of the analysis. The duplicates having more than 7% deviation in total fluorescence intensity were rejected and re-analyzed.

Supporting Tables:

Table S1. Environmental samples collected from the North Saskatchewan River (NSR), Husky Energy pipeline spill, Lloydminster, SK.

ESTS Sample #	Collection date	Days after spill	~Months after spill	Latitude	Longitude	Distance from point of entry (POE) (km)*	Sample type	Sample description	Note on sampling location	Note on sampling depth
3479	2016/09/01	42	1.5	53.37988	-109.40370	11 MC	Oil/Veg/ Sed*	Oily debris	Flat on downriver side	-
3480	2016/08/31	42	1.5	52.58364	-108.38396	90 RB	Oil/Veg/ Sed	A small amount of oil containing trapped sediment	-	-
3484	2016/09/01	42	1.5	52.98644	-108.73174	83 RB	Oil/Veg/ Sed	Oil/Sed		Top sediment
3485	2016/09/01	42	1.5	53.39241	-109.34600	7 RB	Oil/Veg/ Sed	Oily debris	-	-
3487	2016/09/01	42	1.5	53.39241	-109.34600	7 RB	Oil/Veg/ Sed	Large oil mat and woody debris	-	-
3537	2016/09/26	68	2.2	53.39411	-109.32066	16 RB	Oil/Sed	Fresh oil on sediment	-	-
3556	2016/10/13	85	3	53.39443	-109.29857	18.25 RB	Sed	Patty	-	-
3564	2016/10/14	86	3	53.52074	-109.61769	Upstream (Deer Creek) RB	Water			
3567	2016/10/14	86	3	53.02276	-108.82613	78 LB	Oil/Sed	Patty	Shoreline Sed	Top (on top of fine sand)
3570	2016/10/14	86	3	53.02280	-108.82639	78 LB	Oil/Sed	Tar ball/patty	Shoreline Sed	Top
3660	2017/05/09	293	10	53.39443	109.30793	18 RB	Oil/Veg	Patty	-	Surface level
3665	2017/05/10	294	10	53.13116	-108.94692	60 MC	Oil/Sed	Oil sheen or film on debris		Surface level
3676	2017/05/10	294	10	53.39361	-109.33102	15.8 RB	Water/oil sheen	Sheen of oil on water	Floating water	Surface of water column
3695	2017/05/12	296	10	52.75740	-108.26772	8.1 RB	Oil/Sed	Vegetated Oil/Sed	Shoreline Sed	Top (5 cm)
3902	2017/10/18	455	15	53.39437	-109.29773	18.25	Oil/Sed	Patty	Shoreline Sed	Surface level
3903	2017/10/18	455	15	53.39437	-109.29773	18.25	Oil/Sed	Patty	Shoreline Sed	Surface level
3905	2017/10/18	454	15	53.39363	-109.33086	15.5RB	Sed	Globules	Shoreline Sed	0-15 cm from surface level
3912	2017/10/18	454	15	53.37181	-109.41980	10 RB	Water/oil sheen	Sheen of oil on water	Floating water	Surface of water column
3914	2017/10/19	455	15	53.25082	-110.00819	POE RB	Sed	Patties	Shoreline Sed	Top (0–5 cm)

* MC: mid-channel; RB: right bank; LB: left bank; Sed: Sediment; Veg: Vegetation

Table S2. The list of environmental samples collected from the Gogama Canadian National (CN) derailment site, Gogama, ON.

Sample #	Collection date	Sample type	Sample description	Note on sampling location
3584	2016/11/01	Water	Surface upstream water sample-1	Makami River - upstream
3585	2016/11/01	Sed*	River bottom sediment collected by Ponar sampler- significant sheen was produced when sediment was disturbed	Under bridge - Makami River
3587	2016/11/01	Water/Oil sheen	Oil sheen and water collated from the water surface caused by disturbing the river bottom	Under bridge - Makami River
3589	2016/11/01	Water	Surface upstream water sample-2	Makami River - upstream
3590	2016/11/01	Water	Visible rainbow sheen and water collected from surface of the pool	East side of the rail pool
3593	2016/11/01	Sed	River bottom sediment sample collected by Ponar sampler	Makami River - downstream-shoreline beside the rail
3604.1	2016/11/02	Oil sheen	Surface water and oil sheen - the water and oil sheen separated for individual analysis	West side train rail pool
3604.2	2016/11/02	Water	Surface water and oil sheen - the water and oil sheen separated for individual analysis	West side train rail pool
3608	2016/11/02	Sed	Dark colored sediment sampled from the shore of the pool	West side of rail shore
3612	2016/11/02	Sed	Surface shoreline out of water	North end of guard rail on the east side of the river

*Sed:Sediment

Table S3. The list of oils and environmental samples collected from the SS Arrow and Irving Whale spills.

Sample #	**Collection date**	**Sample type**	**Sample description**
Oil source Arrow oil-Weathered	Unknown–older than 1992	Oil	From ESTS archived samples (Wang et al, 1994)
3048	2015/09/23	Oil	Sample from Tank #7 of the SS Arrow (received as oil at water surface)
3281	2015/11/01	Oil	Sampled from the Tank #9 of the SS Arrow, provided by the Canadian Coast Guard
3282	2016/06/22	Oil	Environmental weathered oil, collected from Black Duck cove shoreline - Chedabucto Bay, NS
Irving Whale oil	1996/07/30	Oil	Sampled from Tank # 1P, 4P, & 4S of the Irving Whale

Supplementary Figures:

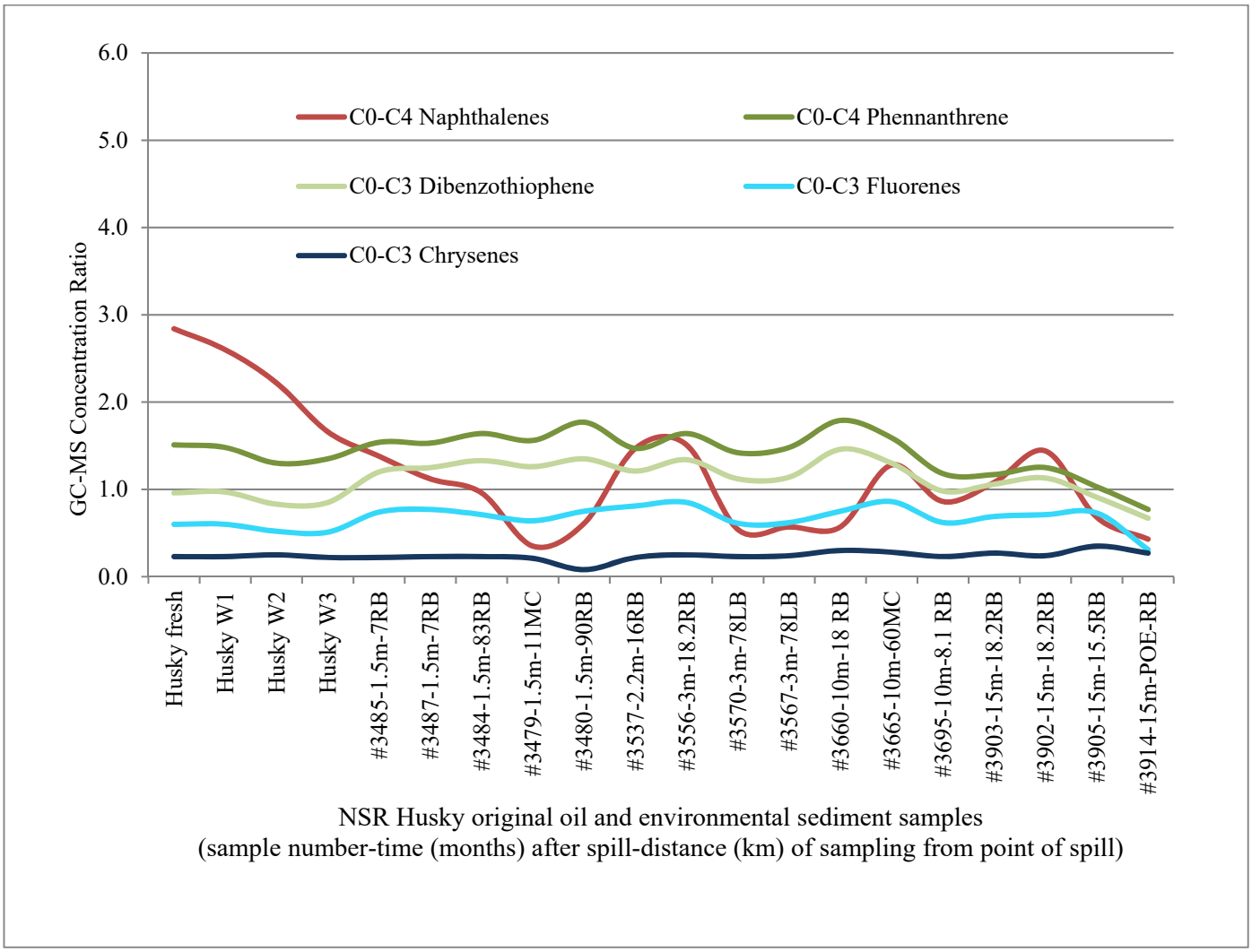
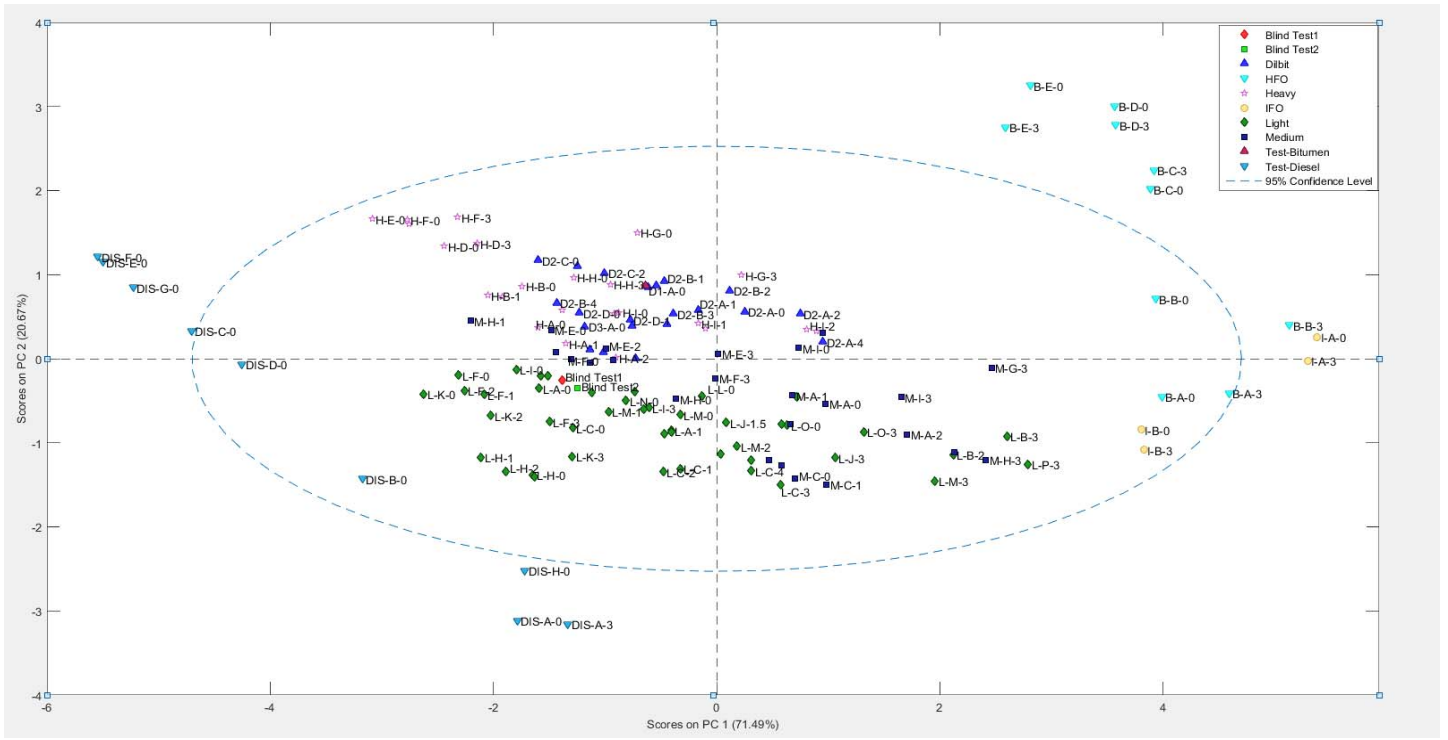
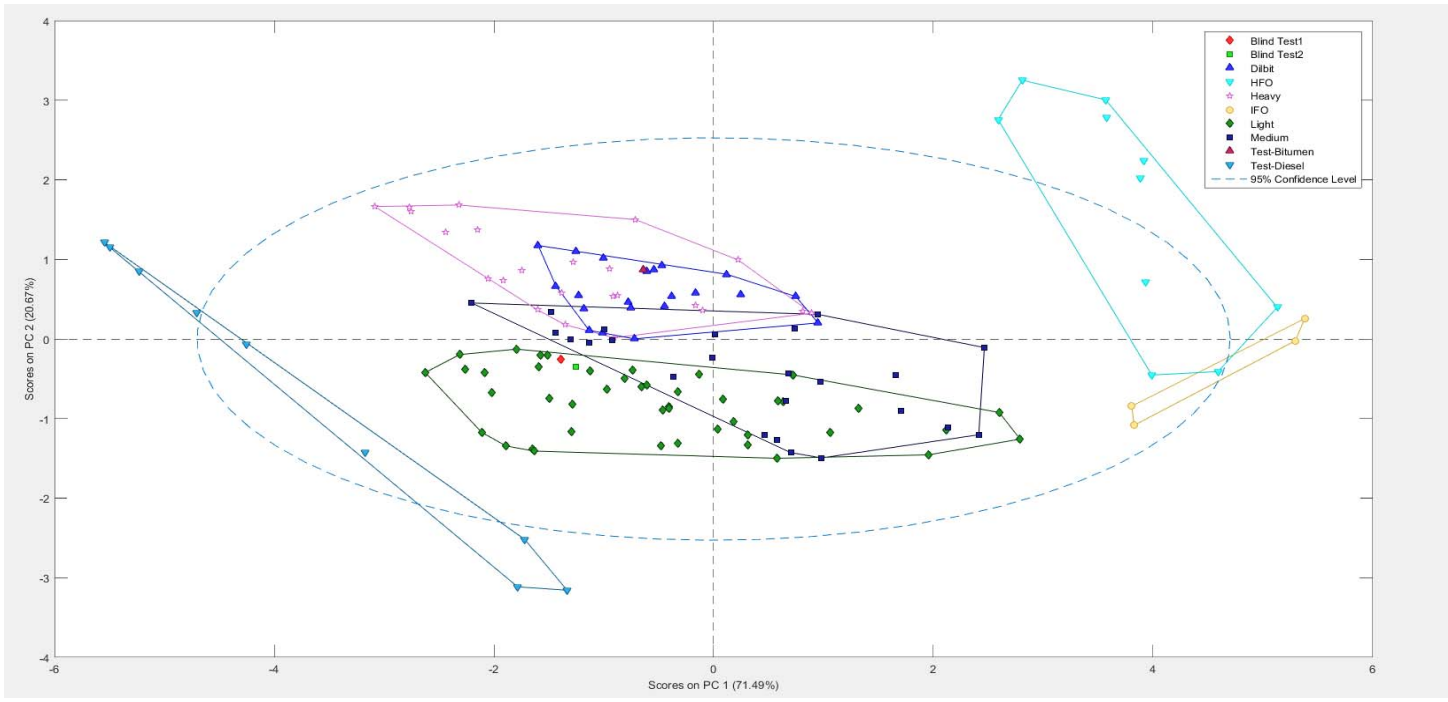


Fig. S1 Ratio of GC-MS concentration of alkylated PAH groups to sum concentration of selected biomarkers (C29+C30 hopane + C27-29 steranes) for the North Saskatchewan River (NSR) Husky Energy pipeline spill source oils and environmental samples.



a



b

Fig. S2: The original fingerprinting EEM-PARAFAC-PCA classification based on 130 petroleum products, a) with sample code labels and b) with score boundaries. Sample name (letter-letter-number): are derived from first letter indicating the category of oil (L: light crude oil, M: medium crude oil, H: heavy crude oil, B: heavy fuel oil (HFO/Bunkers), I: intermediate fuel oil (IFO), D1: bitumen, D2: dilbit, D3: synbit; DIS: diesel, the second letter indicating the oil within the group; and the number indicating the weathering state of the oil (0: fresh, 1: lightly weathered, 2: moderately weathered, 3: heavily weathered, 4: very heavily weathered). Reprinted with permission from Mirnaghi et. al.[1] The sample name can be decoded using Table S1 in Mirnaghi et. al.

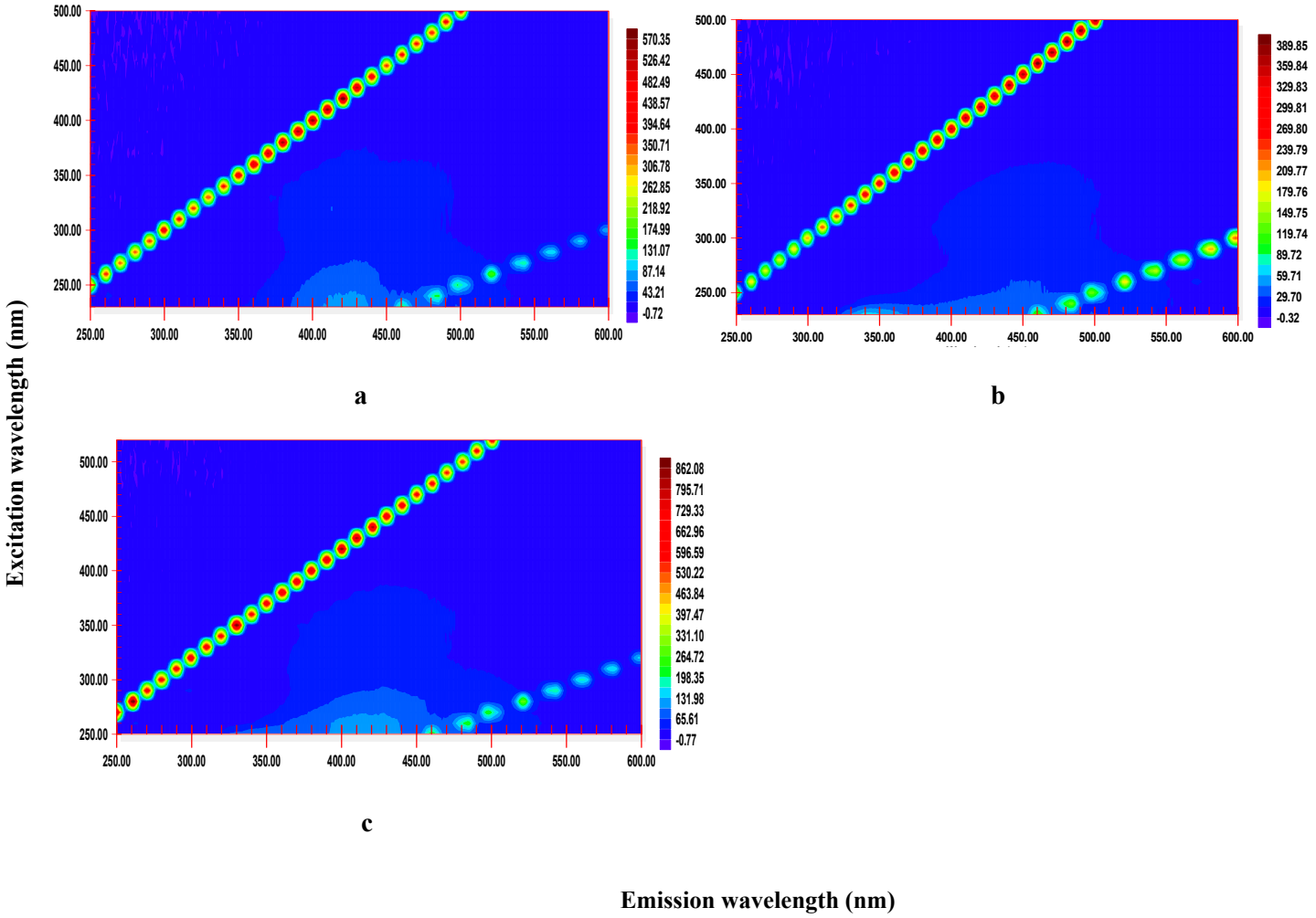


Fig. S3. Fluorescence spectroscopy counterplots of the North Saskatchewan River (NSR) Husky Energy environmental water samples a) Sample# 3564 (water collected 3 months post-spill), b) Sample# 3676 (water and oil sheen collected 10 months post-spill), c) Sample #3912 (water and oil sheen collected 15 months post-spill).

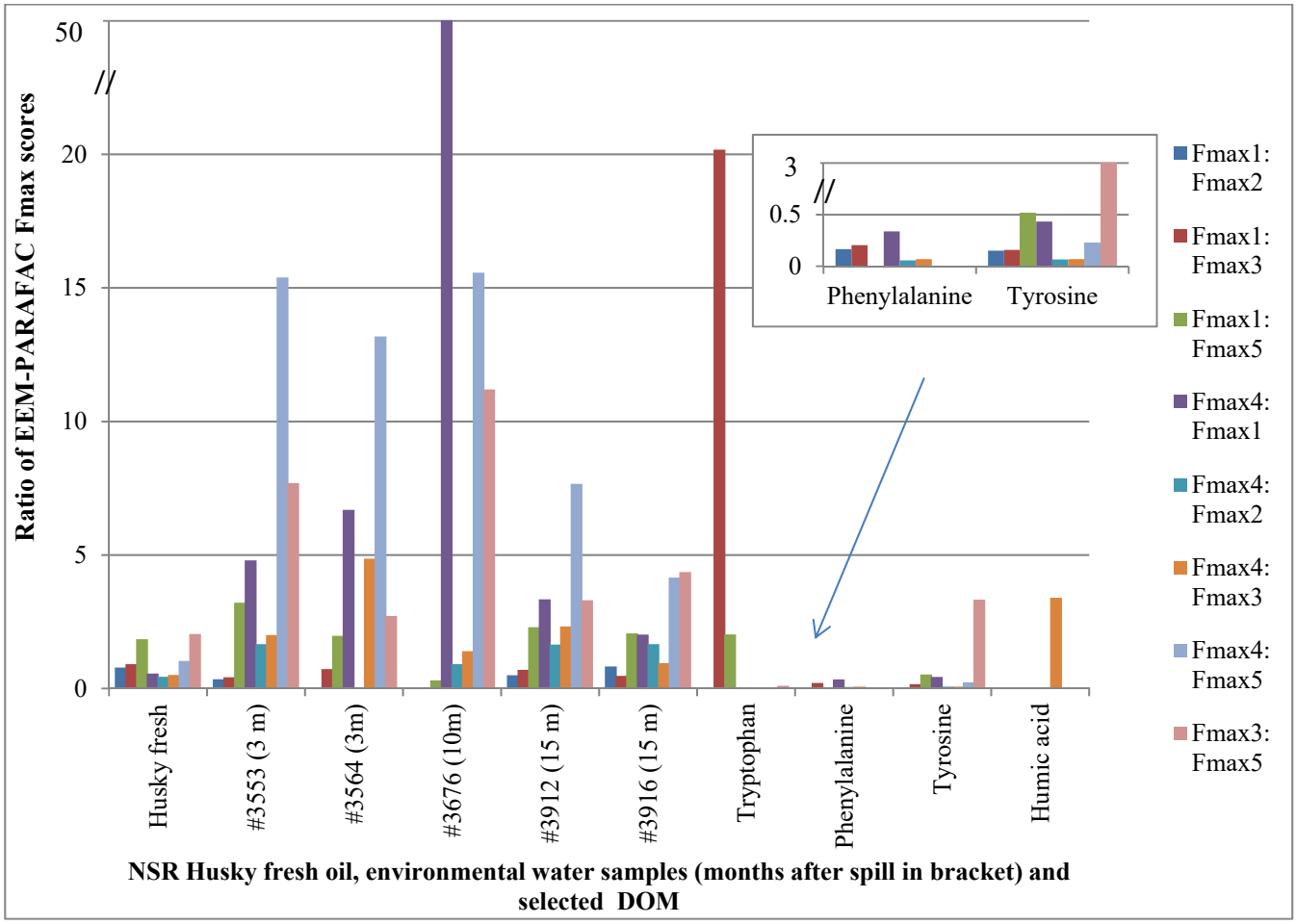


Fig. S4. Comparison of ratios of EEM-PARAFAC F_{max} scores for the North Saskatchewan River (NSR) Husky Energy environmental water samples (collected after 3, 10, and 15 months after spill) with that of fresh oil as well as selected background dissolved organic matters. Fmax1 to Fmax5 correspond to 4-ring PAHs, 2-ring PAHs, 3-ring PAHs, ≥5 ring PAHs and lighter 3-ring PAHs, respectively.

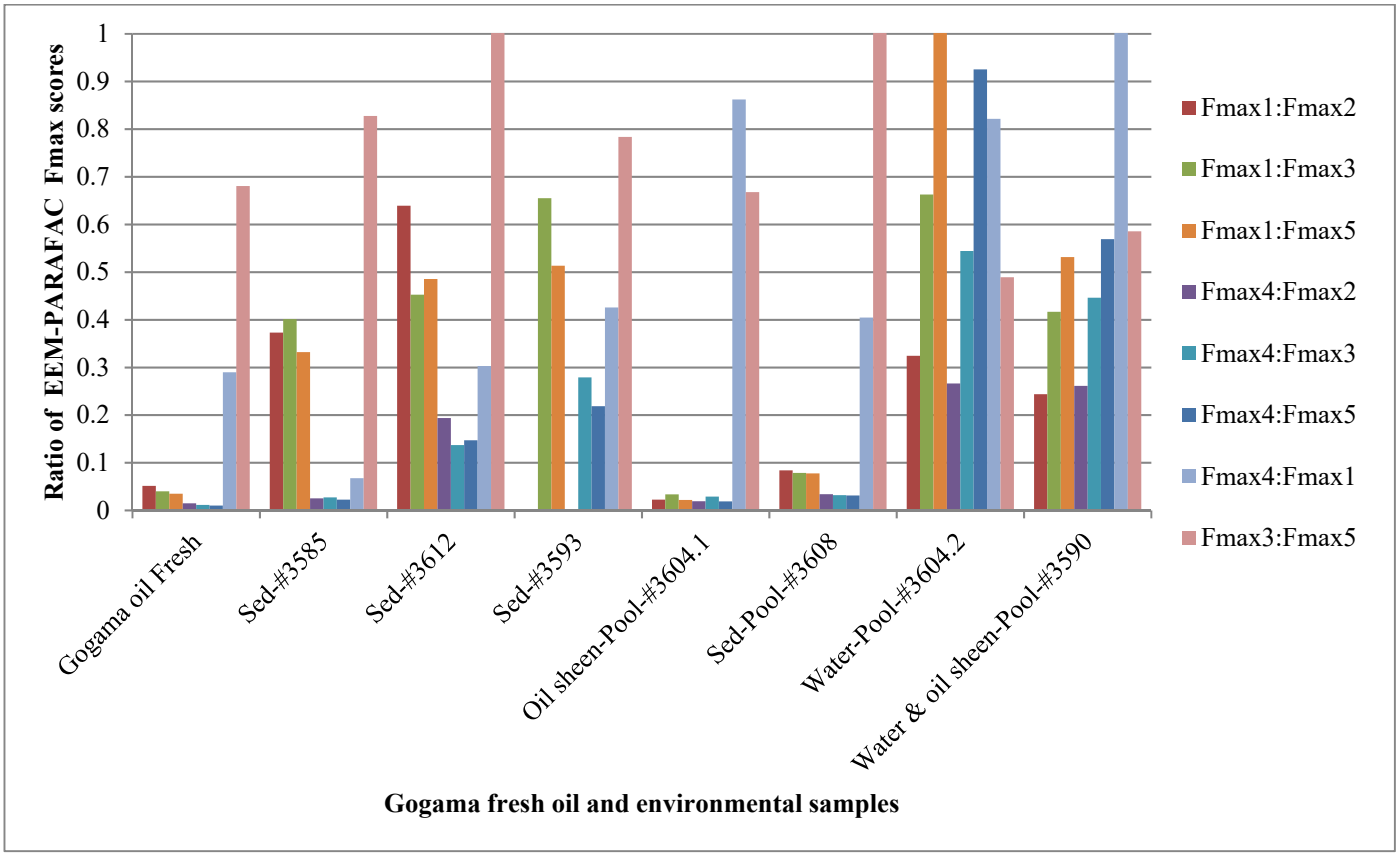


Fig. S5: Comparison of EEM-PARAFAC F_{max} score ratios for the Gogama CN derailment spill source oil and environmental samples. Fmax1 to Fmax5 correspond to 4-ring PAHs, 2-ring PAHs, 3-ring PAHs, ≥5 ring PAHs and lighter 3-ring PAHs, respectively.

a

b

c

d

e

Fig. S6. Water fountains (shown in the red ellipses in photos b and c) have been installed alongside of the rail line to constantly spray water over the areas alongside the track. The residual oils washed out with this excess water are collected in four pools: two on each side of the rail line. a) passing train and rail line at the Gogama spill site; b) collection pool on the eastern side of the rail; c) collection pool on the western side of the rail; d) sheen of oil on the water surface of the western pool; e) darkened sediment along the shore of the western collection pool.

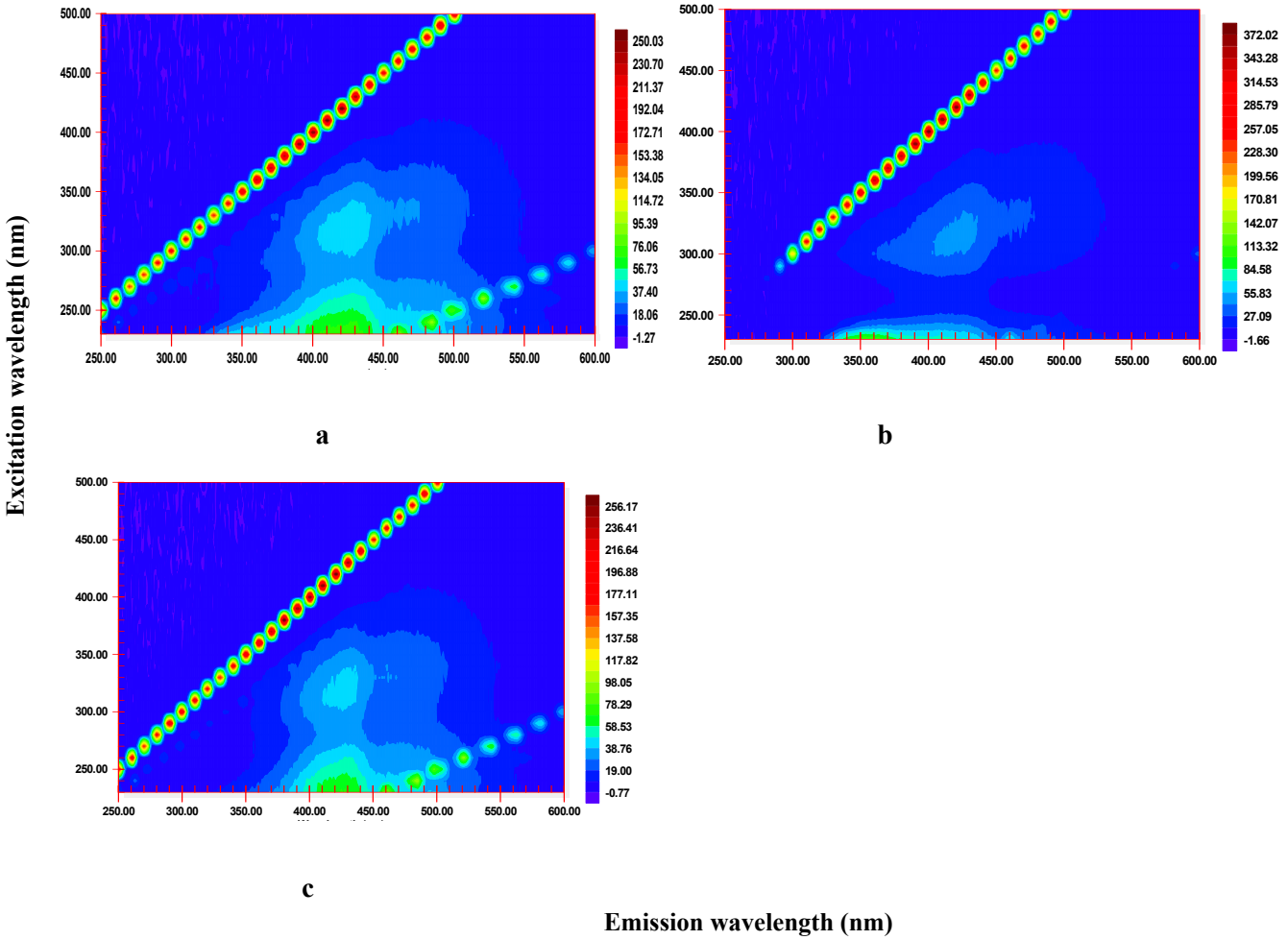


Fig. S7. Fluorescence spectroscopy contour plots of water samples collected November 1–2, 2016 (20 months post-spill), from the Gogama derailment spill site. The samples are presented as collected (at different concentrations). a) Sample # 3587 (collected sheen and water from the water surface caused by disturbing the bottom sediment of the Makami River), b) Sample # 3584 (upstream water sample-1 collected from the Makami River), and c) Sample #3589 (upstream water sample-2 collected from the Makami River).

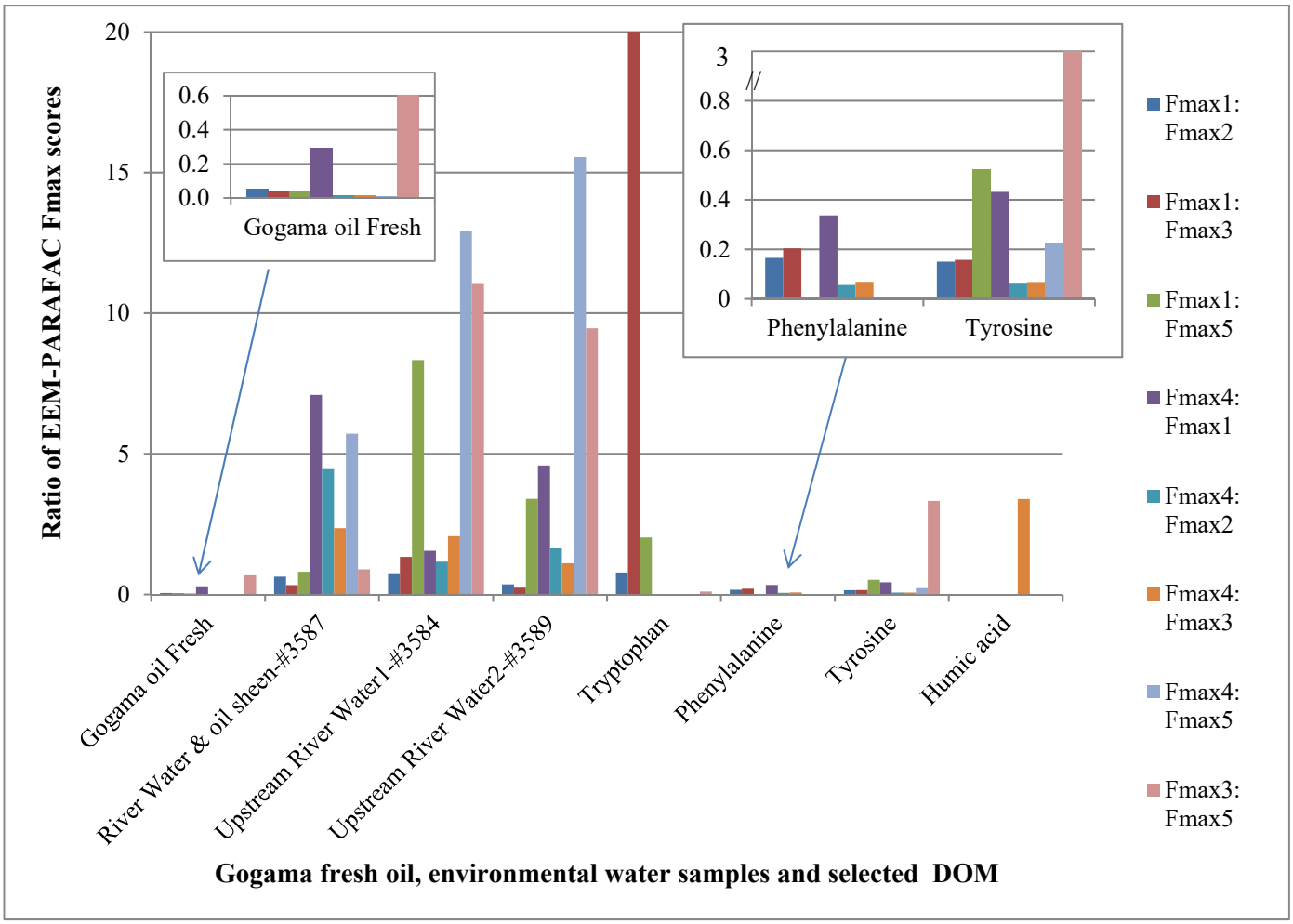
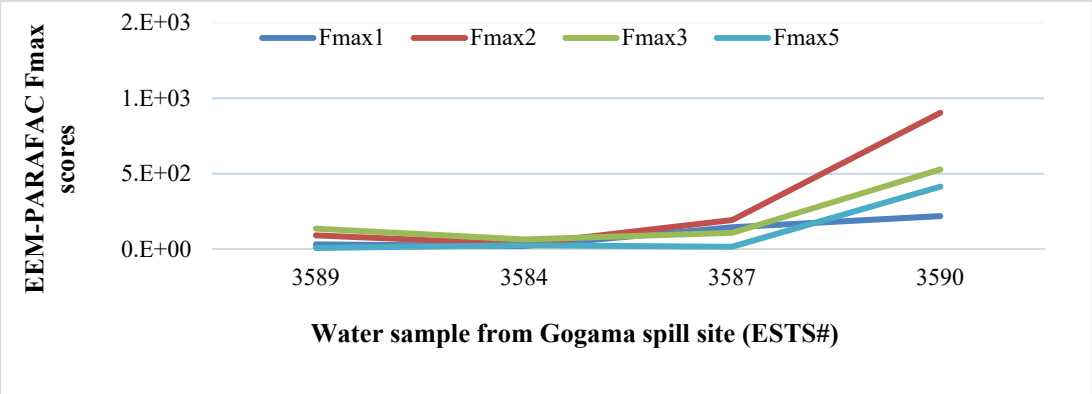


Fig. S8. Comparison of the ratios of EEM-PARAFAC F_{max} scores for environmental water samples collected from the Gogama CN derailment site with that of fresh oil. The description of the samples is provided in Table S2. F1 to F5 correspond to $F_{max}1$ to $F_{max}5$ (i.e., 4-ring PAHs, 2-ring PAHs, heavier 3-ring PAHs, ≥5 ring PAHs and lighter 3-ring PAHs, respectively).



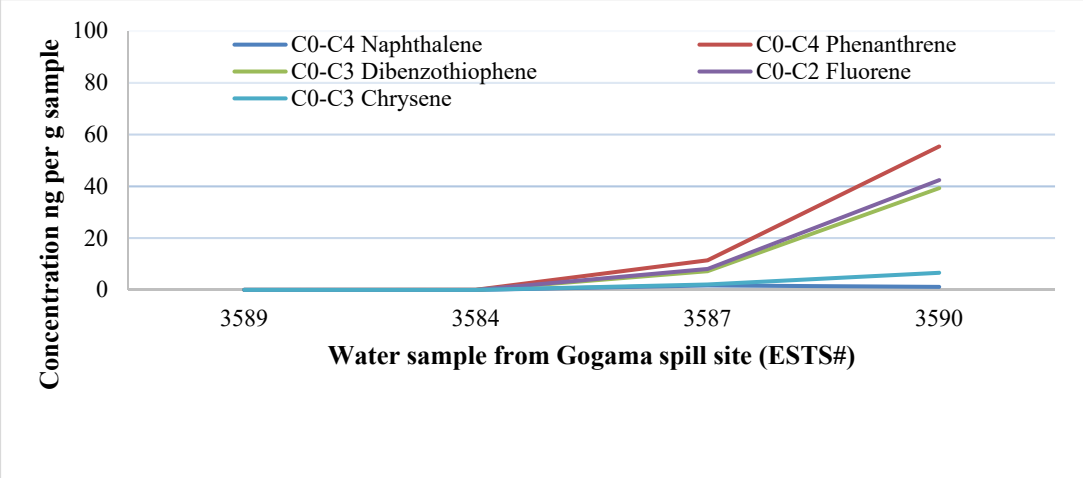


Fig. S9. Comparison of the trend of EEM-PARAFAC Fmax scores of Gogama water samples with their GC-MS PAH concentration

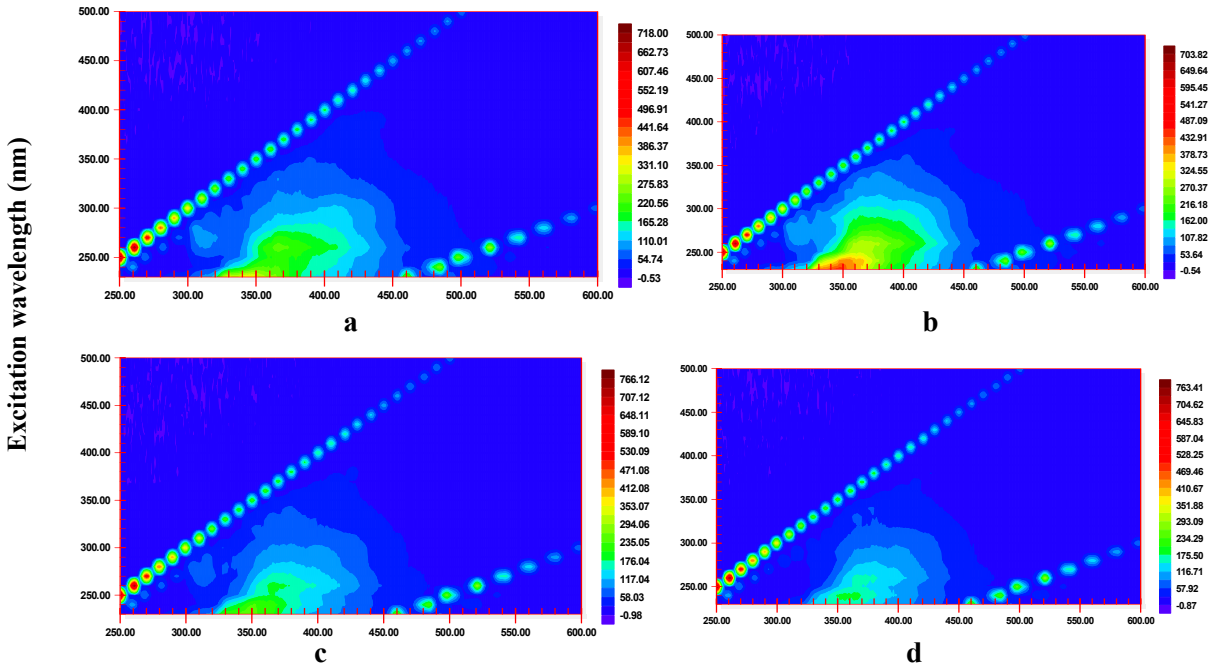


Fig. S10. Fluorescence spectroscopy counterplots of the SS Arrow and Irving Whale spill samples. a) 1 ppm Irving Whale oil, sample collected in 1996 from Tank 4S (the results for the 1P and 4S tanks were very similar, therefore were not shown); b) 2 ppm weathered old source SS Arrow oil; c) 1 ppm sample# 3048, sample collected in 2015 from the SS Arrow; d) 1 ppm sample# 3282, environmentally weathered sample collected in 2016 from Duck cove shoreline - Chedabucto Bay, NS.

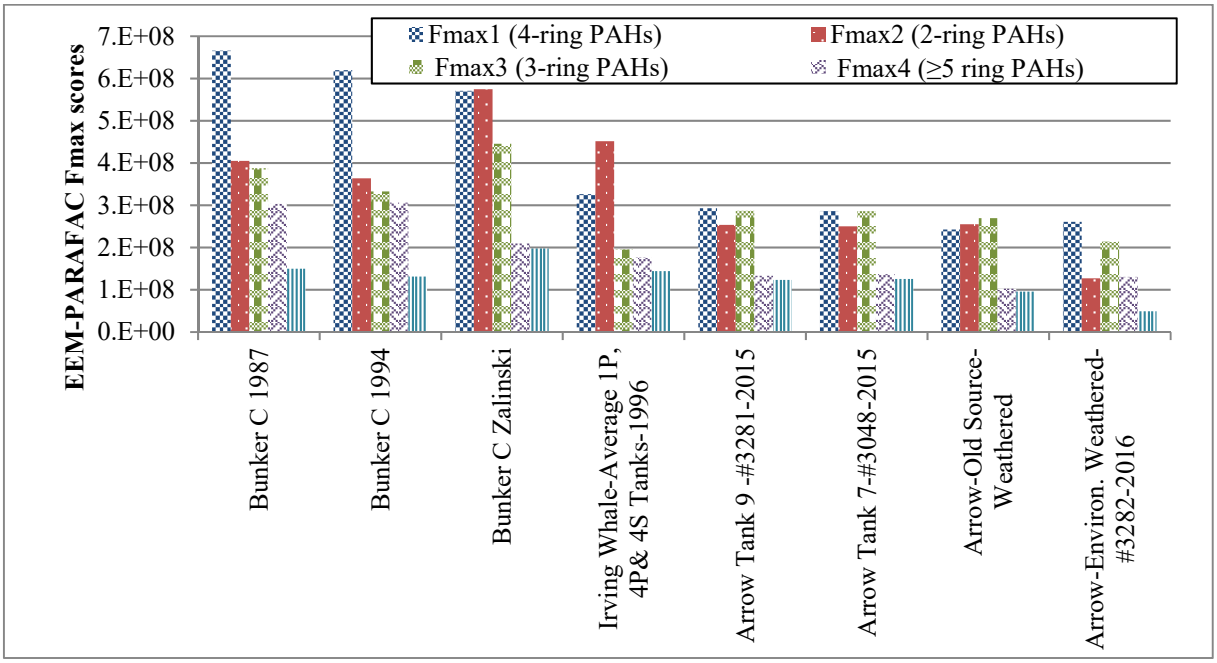


Fig. S11. EEM-PARAFAC F_{max} scores of the SS Arrow and Irving Whale spill samples as well as the F_{max} scores of Bunker C products used in the fingerprinting model.[1]

Reference:

1 F. S. Mirnaghi, N. Soucy, B. P. Hollebone, C. E. Brown, Rapid fingerprinting of spilled petroleum products using fluorescence spectroscopy coupled with parallel factor and principal component analysis, *Chemosphere*, 2018, 208,185–195.