



Field fluorometers as dispersed oil-in-water monitors

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Abstract

A laboratory study of the Turner Instrument flow-through models 10AU and 10 fluorometers was conducted to review their ability to measure real-time oil-in-water concentrations, to compare the results to other total petroleum hydrocarbon (TPH) procedures and to improve the understanding of the relationship of the fluorescence to the chemical composition of the oils. Comparison of the fluorometer results to standard infrared and gas chromatography laboratory procedures showed all methods capable of detecting and differentiating between small changes in oil concentration. The infrared and gas chromatography generated similar values while the fluorometer values were of the same order of magnitude but typically 20–80% higher. The chemical composition of the oils was determined by gas chromatographic techniques and compared to the signal outputs of the fluorometers. It was found that the fluorometer data could not be directly linked to the concentration of any specific aromatic hydrocarbon such as naphthalene or to the sum of the polycyclic aromatic hydrocarbon (PAH) compounds. Evidence suggests that the fluorescence signal is generated by a combination of PAH compounds. Also, the response of the fluorometers may also be influenced by the presence of volatile aromatic compounds such as benzene, toluene, ethyl benzene and xylene (BTEX) and C3-benzenes (BTEX + C3B) in combination with the PAH compounds.
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1. Objectives

This paper reports on the findings from a laboratory study examining the ability of the Turner Instruments flow-through-type fluorometer to measure the concentration of oil-in-water.

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2. Introduction

The use of chemical dispersants as an oil spill countermeasure is controversial. Much of the negative bias stems from the lack of certainty regarding the effectiveness of the dispersant in transferring the oil from the surface of the water into the water column. Determining the amount of oil dispersed or dissolved in water is always a concern at major oil spills. Many different methodologies exist for measuring oil-in-water concentration. Fluorescence spectroscopy and more specifically, Turner Instruments flow-through-type fluorometers, have been employed extensively worldwide as a means of measuring levels of oil contamination in the field. The unique advantages of flow-through-type fluorometers include: instrumentation constructed specifically for field use, ease of operation, low detection limits, and no sample preparation is required. Nevertheless, total petroleum hydrocarbon (TPH) concentrations obtained with flow-through fluorometers have not been well accepted in the scientific community in comparison to conventional laboratory analysis. One major drawback has been in relating the signals generated by the instrument to the “true” concentration of the oil in the water. Oil is a mixture of hundreds of different chemical compounds yet only a portion of these, specifically some of the aromatic compounds, fluoresce. As well, the relative proportion of aromatic compounds differs between oils and changes as an oil weathers. Calibration of the fluorometer is generally carried out using a specific oil, thus, the concentration results obtained in the field are relative to the specific oil and the procedure used to calibrate the instrument. Developing a suitable calibration procedure is a challenge and has a definite impact on results. A comparison of the total petroleum hydrocarbon concentration in water using various analytical procedures will provide an insight into the correlation of these methods and gives an opportunity to compare field and laboratory data. In addition, through the examination of the individual compounds in the stock oil and the oil dispersed in the water column, a better understanding of the nature of the chemical processes occurring when oil is dispersed into the water column can be achieved.

3. Procedures

A closed-loop experimental system was set up in which a pump and tubing was used to draw water from a 20 l vessel, containing 3.3% salt water, through the sample chamber of two successive fluorometers and then return the water to the original vessel. At noted time intervals, a known amount of an oil and dispersant mixture, or premix, was added to the vessel. The oil concentration was allowed to equilibrate throughout the system at which time the fluorometer value was recorded and a sample of the oily water was collected. The oils and dispersant used in the program were Alberta Sweet Mixed Blend (ASMB) crude oil (0 and 26% weathered samples), Prudhoe Bay (PB) crude oil (0 and 27% weathered samples), Bunker C (BC) fuel oil (0 and 8.4% weathered samples), Diesel (DF) fuel (0 and 37% weathered samples) and Corexit 9500, respectively. The analysis consisted of measuring the oil-in-water concentration, determining dispersed oil droplet size and studies into the chemical composition of the stock oil versus dispersed oil. Instrumentation included two Turner fluorometer units (Sunnyvale, CA). One was the model 10AU and the other a model 10. The model 10AU instrument was equipped with the manufacturer’s long wavelength

optical kit while the model 10 was outfitted with their short wavelength optical kit. The short wavelength kit for fuels has an excitation at 254 nm and emission at 350 nm while the long wavelength kit for crude oils employs excitation at 350 nm and emission at 410–550 nm. The procedure is discussed in detail in the references by Lambert et al. [1]. Particle size analysis was determined using a Coulter Counter Multisizer instrument (Coulter Electronics Ltd., Luton Beds, England). Solvent extraction and analysis methods used to measure TPH via infrared (IR) instrumentation are described in Lambert et al. [2]. The only variation was the substitution of Freon solvent with perchloroethylene. The stock oils and oily water samples collected from the fluorometer's discharge line underwent a detailed chemical analysis to determine the TPH as well as identify and quantify the alkanes and polycyclic aromatic hydrocarbons using gas chromatography (GC)/FID and GC/MS techniques. The gas chromatographic analysis procedures are described elsewhere in Wang and co-workers [3–5].

A summary of the gas chromatography procedure is given as it pertains to points addressed in the paper's discussion. Aliquots of the oils were weighed, directly dissolved in hexane and made up to the final volume of 5.0 ml. The final oil concentrations were around 80 mg/ml. Next, 200 μ l of the oil solution (containing \sim 16 mg of oil) was quantitatively transferred to a silica gel column for the oil fractionation. Hexane (12 ml) was used to elute aliphatic hydrocarbons, and 15 ml of 50% benzene in hexane (v/v) was used to elute aromatic hydrocarbons. Half of the hexane fraction (F1) was used for analysis of saturates and biomarker compounds; half of 50% benzene fraction (F2) was used for analysis of alkylated PAH homologues and other target PAHs. The remaining half of F1 and F2 were combined (F3) and used for determination of total GC-detectable TPHs, GC-resolved peaks, and the GC-unresolved complex mixture (UCM) of hydrocarbons. These three fractions were concentrated to appropriate volumes, spiked with appropriate internal standards and then adjusted to an accurate preinjection volume for GC/FID and GC/MS analyses. Quantization of alkanes and isoprenoid compounds, target PAHs, and biomarkers was achieved using 5- α -androstane, terphenyl- d_{14} , and C_{30} - $\beta\beta$ -hopane as internal standards, respectively. The GC/MS was operated in the selected ion monitoring (SIM) mode for quantitation of target PAH compounds. The only variation with the oily water samples was that the "oil" was actually a mixture of oil and the dispersant Corexit 9500 at a ratio of 4 parts oil to 1 part dispersant. Dichloromethane solvent was used to extract the 1 l water samples and this solvent extract was used in the subsequent sample preparation and GC analysis as described above.

4. Results

Table 1 presents selected total petroleum hydrocarbon values for the oily water samples collected. Listed is the predicted concentration based on the volume of premix added to the vessel, the concentration from solvent extraction and infrared analysis, from solvent extraction and gas chromatography analysis and from the two fluorometers. The fluorometer TPH concentration was derived using the prepared fluorescence versus concentration calibration curve and the fluorescent value recorded when the sample was collected. The calibration procedure for the fluorometer was carried out in the same manner as the test program using

Table 1
A comparison of the TPH values

Oil type	Predicted oil-in-water value ($\mu\text{g/l}$)	IR oil-in-water value ($\mu\text{g/l}$)	Model 10AU oil-in-water value ($\mu\text{g/l}$)	Model 10 oil-in-water value ($\mu\text{g/l}$)	GC oil-in-water value ($\mu\text{g/l}$)
ASMB (0% weath.)	0	12.1	0	0	658 (contaminated?)
ASMB (0% weath.)	364	189	218	504	522
ASMB (0% weath.)	728	407	655	936	366
ASMB (0% weath.)	1456	464	1383	1512	1374
ASMB (0% weath.)	3640	1752	3422	2448	2172
ASMB (0% weath.)	9100	3116	10410	7344	4488
PB (0% weath.)	0	8	0	0	53
PB (0% weath.)	364	122	291	576	569
PB (0% weath.)	728	376	728	1008	680
PB (0% weath.)	1456	888	1529	1656	1027
PB (0% weath.)	3640	2248	4295	3168	1873
PB (0% weath.)	9100	5825	11794	6408	4179
PB (0% weath.)	9100	6683	7529	4326	Not available
PB (0% weath.)	9100	7137	11349	5599	Not available
PB (0% weath.)	9100	6702	10957	5542	Not available
PB (0% weath.)	9100	3147	9145	8540	Not available
PB (27% weath.)	9100	10623	9301	9053	Not available
ASMB (0% weath.)	9100	6535	9534	5580	Not available
ASMB (27% weath.)	9100	11018	9363	8952	Not available
Diesel fuel (0% weath.)	9100	8701	9842	8771	Not available
Diesel fuel (37% weath.)	9100	6792	10448	10619	Not available
BC (0% weath.)	9100	4822	9378	9167	Not available
BC (8% weath.)	9100	6896	7735	7436	Not available

successive additions of a known volume of premix to the 20l vessel of salt water. Note the concentration values were converted from $\mu\text{l/l}$ to $\mu\text{g/l}$ using the premix density and then adjusted by 80% to take into account that portion of the premix which was dispersant.

Tables 2 and 3 contain selected concentration data and the fluorometer value (unitless) as displayed on the instrument. The tables are separated based on the data obtained from the

Table 2
Fluorometer values for the model 10AU fluorometer

Premix-in-water conc. ($\mu\text{l/l}$)	ASMB		Diesel fuel		Bunker C		Prudhoe Bay	
	0% weath.	27% weath.	0% weath.	37% weath.	0% weath.	8.3% weath.	0% weath.	27% weath.
0	0	0	0	0	0	0	0	0
0.5	6.3	5.6	0.1	0.1	2.4	0.7	4.1	3.5
1	12.4	11.3	0.2	0.2	5.5	1.7	10.8	7.3
2	24.1	23	0.3	0.3	11.1	3.5	24.3	14.6
4	46.9	46.3	0.6	0.6	21.2	6.1	53.7	29.2
7.5	87.0	87.3	1.0	1.2	39.1	10.0	105.3	54.7
12.5	142.6	149.8	1.5	2.1	63.9	16.6	184.3	91

Table 3
Fluorometer values for the model 10 fluorometer

Premix-in-water conc. (μl/l)	ASMB		Diesel fuel		Bunker C		Prudhoe Bay	
	0%	27%	0%	37%	0%	8.3%	0%	27%
	weath.	weath.	weath.	weath.	weath.	weath.	weath.	weath.
0	0	0	0	0	0	0	0	0
0.5	5.5	6.3	6.5	6.8	5.0	1.5	5.3	4.5
1	13.3	14.0	14.0	15.3	13.3	3.8	13.3	10.0
2	26.3	27.3	26.0	30.5	25.0	8.5	27.3	20.3
4	45.8	54.3	51.0	61.3	46.0	15.5	53.0	38.8
7.5	95.0	108.3	108.5	129.8	88.8	25.0	103.3	73.0
12.5	135.0	163.3	176.0	224.3	134.8	45.3	155.3	122.5

model 10AU and 10 instruments. The data has been corrected for the baseline fluorometer value produced by the salt water and the initial fluorometer value resulting from the addition of the 1 ml of dispersant used to coat the tubing. Two runs were carried out for each oil type. The average value of the fluorescence value is shown in the tables.

The stock oils, both fresh and weathered, as well as samples of the oily water taken from the discharge hose of the fluorometer were subjected to detailed chemical analysis to identify and quantify their respective chemical compositions. During the sample preparation stage, the total solvent extractable hydrocarbon material is transferred to a column containing silica gel. Various solvents were used to elute out portions of the oil. The GC-total petroleum hydrocarbon is the sum of the petroleum compounds eluted from the silica gel column during sample preparation. Table 4 presents the GC-TPH analysis results determined by GC/FID. To calculate the concentrations of total petroleum hydrocarbons in the oil samples by GC, the area response attributed to the petroleum hydrocarbons must be determined. This area includes all of the resolved peaks and the unresolved “envelope” of petroleum hydrocarbons. The total GC-TPH is calculated as follows:

$$\text{TPH } (\mu\text{g/g}) = \frac{A_{\text{TPH}} \times W_{\text{IS}} \times D}{A_{\text{IS}} \times \text{RRF}_{\text{TPH}} \times W_{\text{S}}}$$

Table 4
GC-TPH analysis of the eight stock oils

Description	GC-TPH (mg/g of oil)
ASMB (0% weath.)	625
ASMB (26% weath.)	641
Diesel fuel (0% weath.)	838
Diesel fuel (37% weath.)	865
Prudhoe Bay (0% weath.)	624
Prudhoe Bay (27% weath.)	634
Bunker C fuel (0% weath.)	477
Bunker C fuel (8% weath.)	418

where A_{TPH} is the corrected total area of the sample chromatogram, unit is area counts; RRF_{TPH} is average relative response factor of all target Balkanes plus pristane and phytane, obtained from calibration standards; A_{IS} is response for the internal standard 5- α -androstane in the sample, units same as A_{TPH} ; W_{IS} is amount (μg) of internal standard added to the sample and D is the dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, $D = 1$, dimensionless. W_{S} is the weight of sample extracted, g . Either a dry or wet weight may be used, depending upon the specific application of the data.

Table 5 summarizes the quantitative-alkane results for the eight stock oils. An equation similar to the one used to calculate the GC-TPH was used to quantify the n -alkanes.

Figs. 1 and 2 present the GC/MS total ion chromatograms (in SIM mode) highlighting the aromatic volatile organic compounds (VOCs) and the targeted alkylated PAH homologues analysis for the eight stock oils. An abbreviated name for each oil is used to describe the Alberta Sweet Mixed Blend crude oil, Diesel fuel (Diesel), Prudhoe Bay crude oil (Prudhoe Bay) and Bunker C. The percentage in brackets is the mass lost due to evaporation. The approximate location of the benzene, toluene, ethyl benzene and xylene (BTEX) and C3-benzene compounds (BTEX + C3B) and naphthalenes is shown on the plot for each fresh oil.

Table 6 summarizes the quantitative results of the alkylated PAH homologues and the other EPA priority unsubstituted PAHs for the stock oils.

Figs. 3 and 4 presents the GC/MS total ion chromatograms (in SIM mode) displaying the VOCs and target alkylated PAH homologues analysis for a selected oil-in-water samples.

Table 7 summarizes the results of the PAH analysis of the alkylated PAH homologues and other EPA priority unsubstituted PAHs for selected oily waters samples.

5. Discussion

The first paragraph of this discussion review the TPH results of the fluorometer and compare the fluorometer's data to traditional laboratory extraction techniques in conjunction with either IR or GC analysis. From a review of the data in Table 1, it can be seen that in terms of absolute numerical values none of the analysis techniques produce equivalent results. However, is that standard too high? TPH is a generic non-specific term. Quantifying the amount of TPH in a sample is a challenge due in part to the varied and complex chemical composition of oils. TPH analysis using different analytical procedures will inevitably give numerically different results as most often, for each individual procedure, the sample preparation and detection method isolate a different segment of the TPH. Followed by some manipulation to obtain the total concentration. Nevertheless, all the methods shown in Table 1 show the same capability to differentiate between the concentrations and display similar trends. There is a high degree of consistency in the readings of the fluorometer. The exception is the Diesel fuel values with the model 10AU fluorometer. Again, the influence of the optical kit is responsible. The infrared and gas chromatography values are numerically quite similar. The fluorometers gave concentrations higher than either of the laboratory extraction methods. Predicted and fluorometer concentrations are similar. This brings us back to a point made in the introduction. That being, methods developed to calibrate the fluorometers have varied and can significantly impact the final results. In this program, the

Table 5
n-Alkane results for the eight stock oils

Sample type alkanes	ASMB (mg/g oil)		Diesel (mg/g oil)		PB		BC	
	0%	26%	0%	37%	0%	27%	0%	8%
	weath.	weath.	weath.	weath.	weath.	weath.	weath.	weath.
<i>n</i> -C8	3.78		1.56		2.89			
<i>n</i> -C9	5.28	1.19	9.9		4.32		0.20	
<i>n</i> -C10	5.52	3.24	11.72	0.20	4.55		0.73	
<i>n</i> -C11	5.47	5.31	14.28	4.99	4.94		1.76	0.05
<i>n</i> -C12	5.06	5.47	12.98	11.79	4.11	1.48	2.10	0.42
<i>n</i> -C13	4.94	5.74	11.38	13.97	3.93	3.00	2.39	1.36
<i>n</i> -C14	4.88	5.58	10.99	15.66	3.91	3.98	2.03	1.56
<i>n</i> -C15	4.52	5.57	10.69	16.58	3.61	4.51	1.24	1.18
<i>n</i> -C16	4.33	5.46	11.03	16.76	3.40	4.68	1.02	1.04
<i>n</i> -C17	4.28	5.34	11.82	18.77	3.66	4.85	0.78	0.79
Pristane	2.54	3.12	5.66	7.95	1.99	2.63	0.47	0.50
<i>n</i> -C18	3.44	4.11	6.73	11.18	2.70	3.51	0.51	0.50
Phytane	2.11	2.53	3.21	5.23	1.29	1.73	0.23	0.24
<i>n</i> -C19	3.19	3.85	4.10	6.28	2.50	3.28	0.73	0.83
<i>n</i> -C20	2.80	3.45	1.55	2.42	2.28	3.13	0.49	0.54
<i>n</i> -C21	2.59	3.20	0.48	0.73	2.13	2.88	0.69	0.65
<i>n</i> -C22	2.35	2.87	0.18	0.26	2.12	2.90	0.71	0.75
<i>n</i> -C23	2.05	2.50	0.08	0.14	1.92	2.68	0.78	0.83
<i>n</i> -C24	2.02	2.35	0.06	0.09	1.68	2.34	0.86	0.91
<i>n</i> -C25	1.88	1.98	0.04	0.06	1.63	2.01	0.88	0.94
<i>n</i> -C26	1.69	1.79	0.03	0.03	1.33	1.83	0.76	0.76
<i>n</i> -C27	1.35	1.72			1.08	1.51	0.71	0.71
<i>n</i> -C28	1.13	1.52			0.81	1.14	0.63	0.63
<i>n</i> -C29	0.90	1.20			0.62	0.92	0.46	0.46
<i>n</i> -C30	0.81	0.96			0.53	0.74	0.38	0.40
<i>n</i> -C31	0.67	0.88			0.45	0.65	0.32	0.32
<i>n</i> -C32	0.51	0.64			0.35	0.53	0.23	0.24
<i>n</i> -C33	0.40	0.56			0.28	0.48	0.19	0.21
<i>n</i> -C34	0.35	0.43			0.27	0.41	0.15	0.17
<i>n</i> -C35	0.22	0.29			0.21	0.33	0.11	0.10
<i>n</i> -C36	0.18	0.15			0.13	0.22	0.06	0.06
<i>n</i> -C37	0.12	0.12			0.13	0.20	0.04	0.05
<i>n</i> -C38	0.11	0.10			0.12	0.19		
<i>n</i> -C39	0.08	0.09			0.10	0.15		
<i>n</i> -C40								
<i>n</i> -C41								
Total	81.53	83.31	128.46	133.09	65.97	58.91	22.61	17.21
C17/pristane	1.68	1.71	2.09	2.36	1.84	1.84	1.67	1.60
C18/phytane	1.64	1.63	2.10	2.14	2.09	2.02	2.25	2.11
Pristane/phytane	1.21	1.23	1.76	1.52	1.54	1.52	2.05	2.10
CPI	0.97	1.04	1.10	1.05	1.01	1.01	1.06	1.06

CPI: carbon preference index defined as the sum of the odd Balkane over the sum of the even Balkanes.

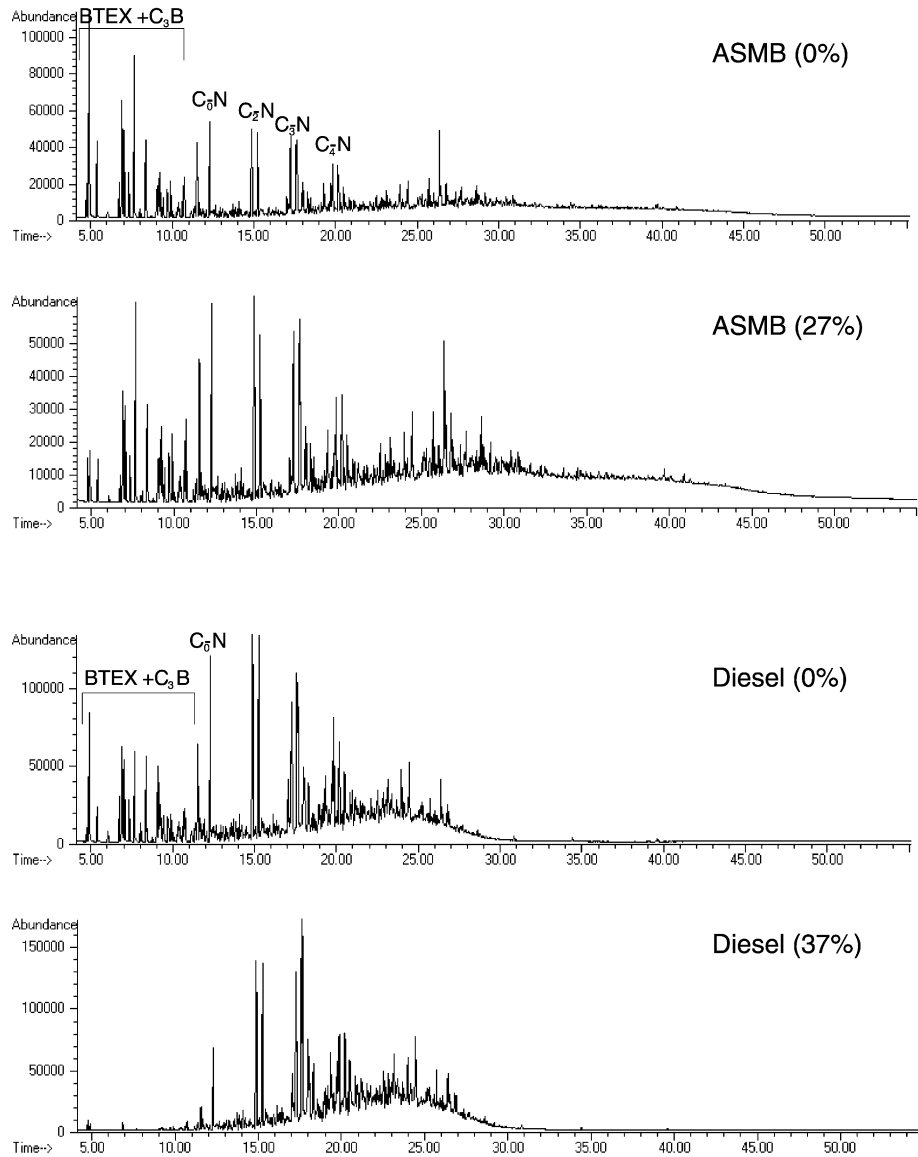


Fig. 1. Chromatograph for VOCs and PAHs in ASMB crude and Diesel fuel.

fluorometer value versus oil concentration calibration curves were obtained by successively adding a known volume of the premix to the water. One can correct the observed fluorescence value for the background water and dispersant reading to give an initial “zero” fluorescence TPH. However, even when the IR and GC data is corrected for background data, as it was in Table 1, it can be seen that the values were not zero. Immediately it is possible to see that the

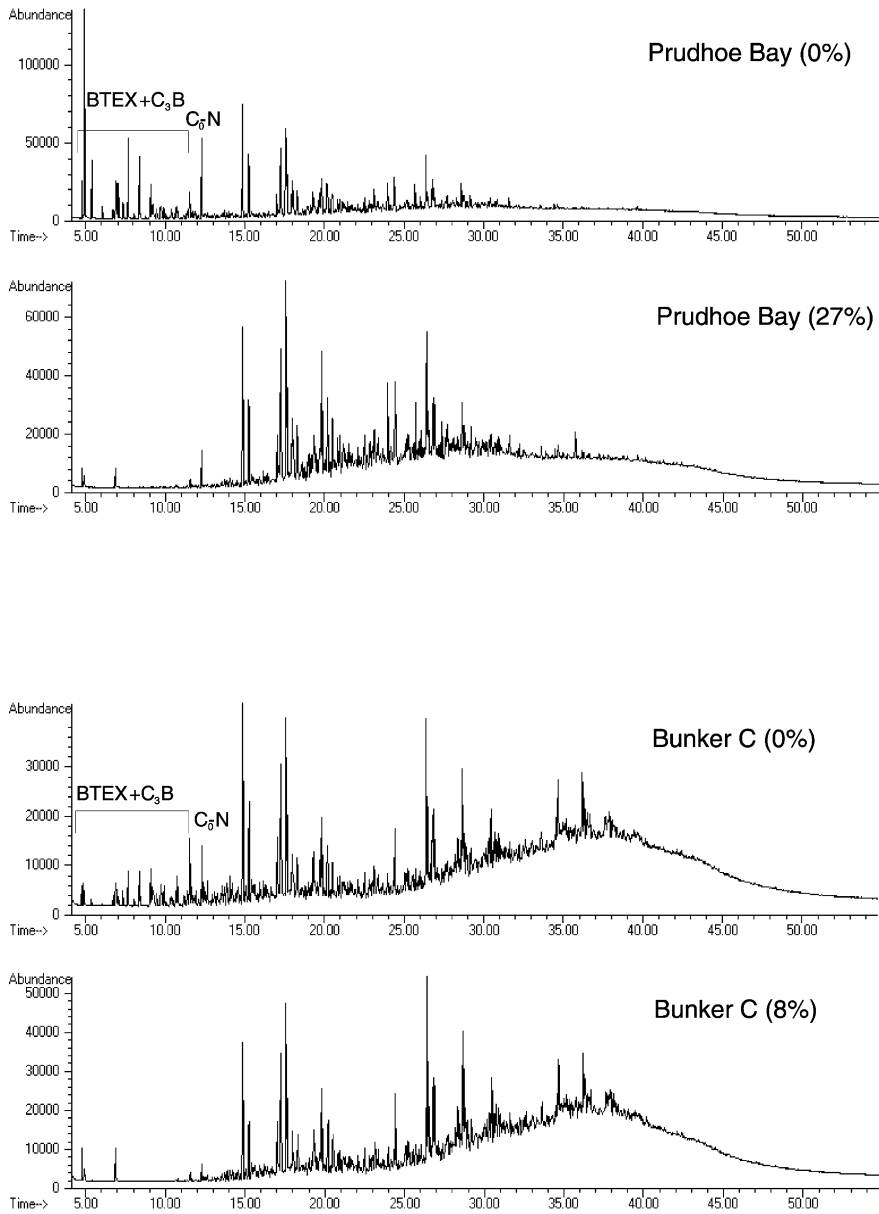


Fig. 2. Chromatograph for VOCs and PAHs in Prudhoe Bay crude and Bunker C fuel.

TPH are not identical for the different methods. The predicted concentration assumes the oil has been uniformly dispersed throughout the system. Numerous measures were taken to ensure the uniform oil distribution and included ensuring the premix was recently blended and the fixed location of the intake and outflow tubes. Yet, there are limitations as to how

Table 6
PAH results for the eight stock oils

Sample type formula PAH	ASMB ($\mu\text{g/g}$ oil)		Diesel ($\mu\text{g/g}$ oil)		PB ($\mu\text{g/g}$ oil)		BC	
	0%	26%	0%	37%	0%	27%	0%	8%
	weath.	weath.	weath.	weath.	weath.	weath.	weath.	weath.
Naphthalene								
C0–N	614.2	614.7	809.5	859.7	678.3	161.1	233.5	67.4
C1–N	2092.0	2159.6	5821.3	5938.8	2285.5	1678.5	1333.7	971.5
C2–N	2934.0	3187.0	7751.6	10272.9	3174.3	3297.0	1842.0	1737.0
C3–N	2529.3	2790.2	6003.6	8487.4	2501.6	3118.3	1792.8	1808.5
C4–N	1087.9	1226.5	3222.0	4637.0	1236.7	1565.0	824.0	836.6
Sum	9257	9978	24608	30196	9876	9820	6026	5421
Phenanthrene								
C0–P	161.4	187.8	457.3	632.3	251.5	333.1	258.7	270.8
C1–P	572.9	656.9	637.3	942.7	735.8	978.4	1269.7	1359.4
C2–P	537.8	609.6	167.8	252.5	588.0	772.7	1490.6	1585.2
C3–P	380.8	430.5	29.7	42.7	388.1	517.5	1209.3	1268.6
C4–P	194.9	235.1	8.7	11.9	215.4	274.6	707.9	828.0
Sum	1848	2120	1301	1882	2179	2876	4936	5312
Dibenzothiophene								
C0–D	164.6	187.8	353.6	530.5	207.9	276.3	64.9	68.6
C1–D	271.6	319.5	332.1	489.1	284.2	377.8	130.4	141.8
C2–D	349.3	399.4	174.3	259.0	319.9	441.0	217.0	229.7
C3–D	219.2	257.3	40.2	56.6	214.9	300.5	204.5	210.4
Sum	1005	1164	900	1335	1027	1395	617	651
Fluorene								
C0–F	90.0	97.4	226.4	299.7	106.1	133.8	68.8	68.7
C1–F	213.2	241.8	523.0	737.6	237.3	297.6	194.0	196.3
C2–F	334.9	386.1	575.1	835.6	186.1	390.6	341.8	328.4
C3–F	310.2	361.2	262.5	370.5	235.2	289.5	313.4	309.3
Sum	948	1087	1587	2243	765	1111	918	903
Chrysene								
C0–C	36.4	39.6	0.7	1.1	48.7	67.3	300.4	319.0
C1–C	58.2	62.1	1.3	1.5	68.2	92.9	755.7	788.8
C2–C	97.1	108.4	2.3	1.7	95.0	119.9	1095.1	1107.4
C3–C	74.6	86.9	1.6	1.5	71.7	91.0	763.5	716.4
Sum	266	297	6	6	284	371	2915	2932
Total	13324	14646	28402	35662	14131	15574	15412	15218
Other PAHs								
Biphenyl	85.1	93.4	551.0	687.7	224.7	249.2	49.2	40.3
Acenaphthalene	17.2	20.3	61.6	85.5	35.9	36.4	17.4	15.8
Acenaphthene	27.3	31.5	102.0	112.6	53.6	59.9	48.5	54.7
Anthracene	3.3	4.5	24.0	24.1	5.0	3.1	35.7	31.5
Fluoranthene	1.7	1.9	0.5	0.7	6.4	10.8	14.1	17.5
Pyrene	13.8	15.9	0.9	1.1	9.8	7.8	105.0	106.6
Benz(a)anthracene	2.4	2.7	0.1	0.1	3.2	8.3	127.7	126.3

Table 6 (Continued)

Sample type formula PAH	ASMB ($\mu\text{g/g}$ oil)		Diesel ($\mu\text{g/g}$ oil)		PB ($\mu\text{g/g}$ oil)		BC	
	0% weath.	26% weath.	0% weath.	37% weath.	0% weath.	27% weath.	0% weath.	8% weath.
Benzo(b)fluoranthene	3.5	4.4	0.1	0.1	4.9	5.5	7.6	7.5
Benzo(k)fluoranthene	0.3	0.2	0.1	0.1	0.2	0.2	41.9	43.0
Benzo(e)pyrene	9.8	10.9	0.1	0.1	11.0	12.9	4.8	6.9
Benzo(a)pyrene	2.3	2.7	0.1	0.1	0.3	0.3	94.9	94.2
Perylene	0.4	0.4	0.1	0.1	1.0	0.7	42.5	44.4
Indeno(1,2,3cd)pyrene	0.1	0.1	0.1	0.1	0.1	0.1	1.0	2.0
Dibenz(a,h)anthracene	1.3	1.2	0.1	0.1	0.5	0.6	1.6	1.4
Benzo(g,h,i)perylene	4.0	4.0	0.1	0.1	3.0	3.2	30.0	32.5
Total	172	194	741	912	360	399	622	625

Table 7
PAH results for the oil-in-water samples

Sample type formula PAH	ASMB ($\mu\text{g/g}$ oil)		Diesel ($\mu\text{g/g}$ oil)		PB ($\mu\text{g/g}$ oil)		BC ($\mu\text{g/g}$ oil)	
	0% weath.	26% weath.	0% weath.	37% weath.	0% weath.	27% weath.	0% weath.	8% weath.
Naphthalene								
C0–N	357	444	1325	706	341	106	202	99
C1–N	794	1787	4170	4290	1171	929	854	552
C2–N	1045	2991	5668	7510	1540	2172	1620	1210
C3–N	839	2681	4786	6827	1189	1880	1373	1070
C4–N	362	1282	2386	3784	546	1201	656	524
Sum	3397	9185	18335	23117	4787	6288	4706	3455
Phenanthrene								
C0–P	65	182	372	478	147	260	242	212
C1–P	211	679	554	842	399	780	1164	995
C2–P	225	760	175	282	369	775	1556	1342
C3–P	151	486	33	60	228	454	1187	939
C4–P	82	271	9	19	116	243	707	586
Sum	734	2378	1143	1681	1259	2513	4855	4074
Dibenzothiophene								
C0–D	61	173	269	379	99	200	57	43
C1–D	99	319	246	414	156	318	138	105
C2–D	119	435	119	228	161	372	227	163
C3–D	81	254	31	57	107	229	188	130
Sum	360	1181	665	1077	523	1119	610	441
Fluorene								
C0–F	36	90	176	223	56	91	54	44
C1–F	105	233	453	592	146	232	194	129
C2–F	112	371	392	641	152	313	309	240
C3–F	99	352	166	292	115	245	292	212
Sum	351	1046	1187	1748	468	881	848	624

Table 7 (Continued)

Sample type formula PAH	ASMB ($\mu\text{g/g}$ oil)		Diesel ($\mu\text{g/g}$ oil)		PB ($\mu\text{g/g}$ oil)		BC ($\mu\text{g/g}$ oil)	
	0% weath.	26% weath.	0% weath.	37% weath.	0% weath.	27% weath.	0% weath.	8% weath.
Chrysene								
C0–C	11	30	1	3	23	42	201	162
C1–C	18	56	1	6	32	65	564	432
C2–C	29	91	1	8	38	82	807	641
C3–C	22	71	1	6	23	55	537	417
Sum	80	248	5	23	117	245	2109	1653
Total	4922	14038	21335	27647	7154	11046	13128	10246
Other PAHs								
Biphenyl	171	351	1689	1962	517	467	129	150
Acenaphthalene	19	57	149	209	47	60	31	36
Acenaphthene	46	126	231	319	70	93	163	194
Anthracene	38	14	33	32	22	5	100	91
Fluoranthene	6	11	7	6	13	16	62	56
Pyrene	24	68	6	11	28	52	373	327
Benz(a)anthracene	4	18	0	4	7	21	422	336
Benzo(b)fluoranthene	6	18	1	2	15	26	158	112
Benzo(k)fluoranthene	1	2	0	0	0	1	17	16
Benzo(e)pyrene	14	42	1	4	27	54	309	218
Benzo(a)pyrene	4	10	0	2	3	7	221	150
Perylene	1	4	0	1	0	2	166	95
Indeno(1,2,3cd)pyrene	0	1	0	0	0	1	20	15
Dibenz(a,h)anthracene	1	3	0	0	0	4	78	49
Benzo(g,h,i)perylene	4	13	0	1	3	14	135	92
Total	339	739	2118	2553	752	823	2384	1937

successful this can be. Thus, the distribution of the oil during the calibration may differ from other runs with a corresponding impact on results.

In summary, the fluorometer results were not numerically similar to the laboratory extraction and analysis procedure with fluorometer results tending to be higher. The assumption regarding the uniformity of the dispersed oil when calibrating the fluorometer is a prime cause the higher fluorometer results.

The remaining discussion addresses the performance of the fluorometer as it relates to the different oil types and weathered states of the oils. This in turn leads to a review of the influence an oil's chemical composition has on the instrument and detection technique. In order to be accurate one must acknowledge that several factors in addition to an oil's chemical composition can effect the response of the fluorometer. The manufacturer's technical notes [6] describes the effect of temperature, dissolved oxygen, concentration quenching, absorption quenching, suspended solids, solvents and solvent impurities on the fluorometer's performance. Even if one focuses on the items which cause a fluorescent signal, potential interferences include; the background water, the dispersant, target oil compounds in the oil and dissolved in the water, scattered signal from turbidity and secondary fluorescence caused by the other compounds in the oil.

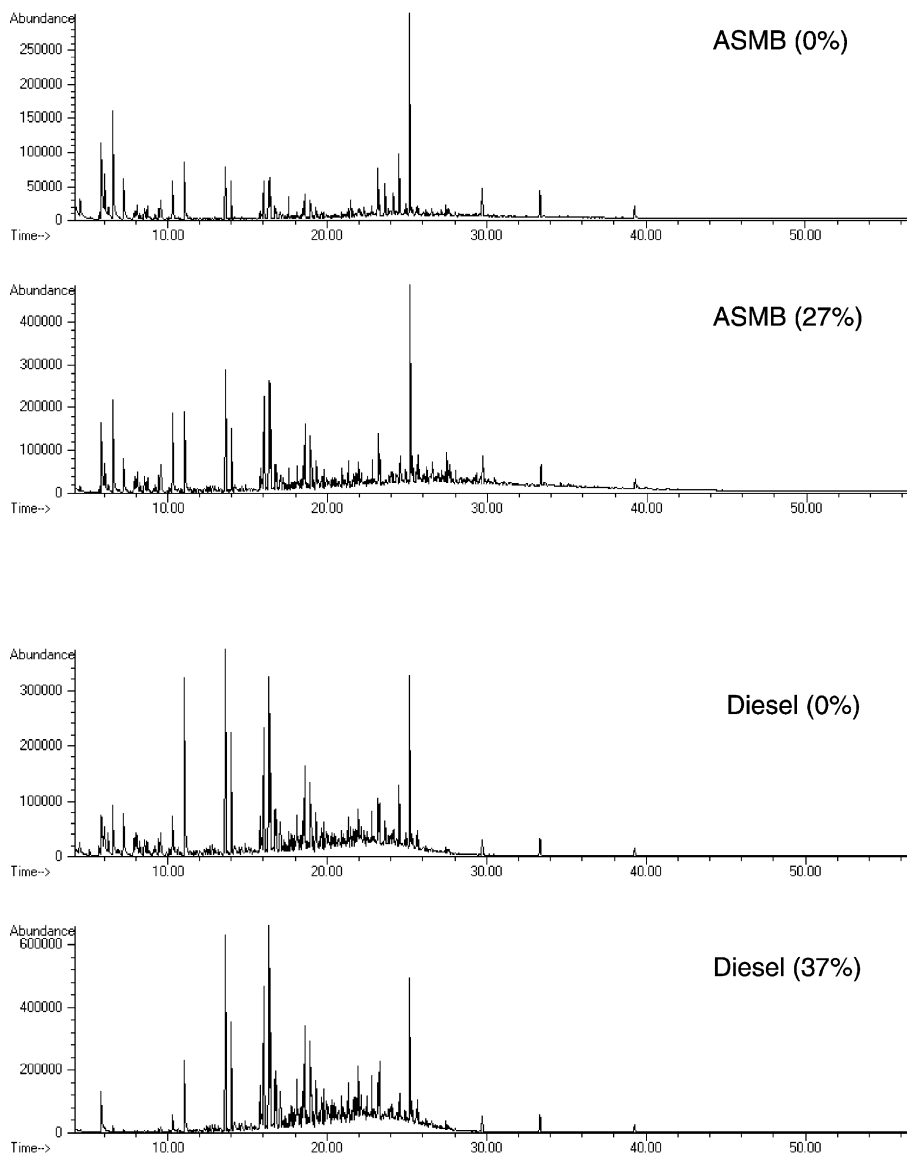


Fig. 3. Chromatograph for VOCs and PAHs in ASMB crude and Diesel fuel.

The fluorescence values and concentration data provided in [Tables 2 and 3](#) are used in the ensuing discussion. [Table 2](#) displays the fluorescence intensity and concentration data for each oil type, both the fresh and weathered fractions, measured on the model 10AU instrument. [Table 3](#) is the fluorescence intensity and concentration data for each oil type, both fresh and weathered fractions, measured on the model 10 instrument. There are large differences in the absolute fluorescence values from the two instruments although they are

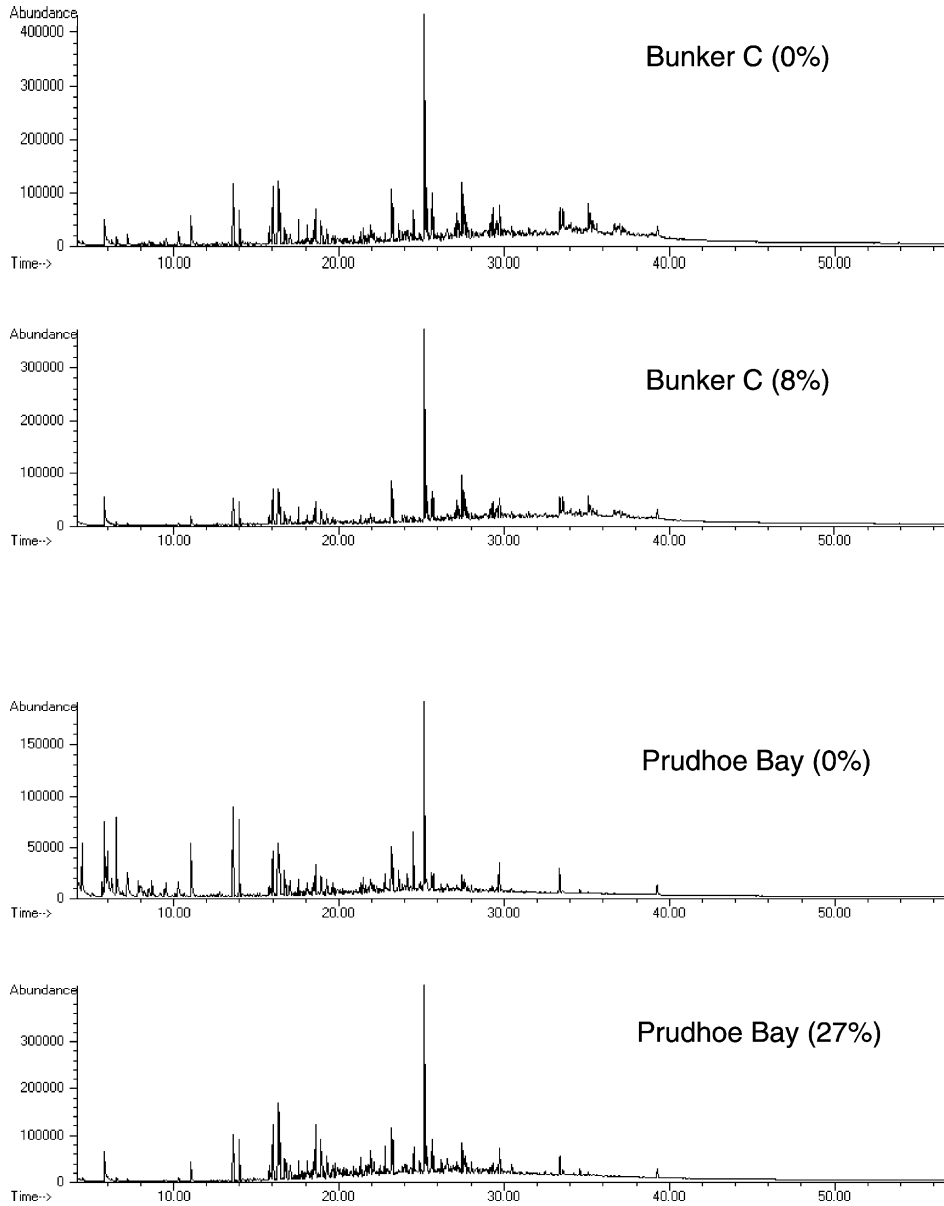


Fig. 4. Chromatograph for VOCs and PAHs in Bunker C fuel and Prudhoe Bay crude.

generally within the same order of magnitude. When comparing the two instruments, the ASMB values are most similar while Prudhoe Bay, Bunker C and Diesel fuel show ever large variations. A plausible explanation is reported by Wakeham [7]. It is reported that the location of the peak fluorescence emission is related to the number of aromatic rings on the

compound. Generally, there is a shift to longer wavelengths as the complexity of the cyclic compounds increases. Noting that Wakeham's work was carried out using a scanning fluorometer, benzenes emit at 280–290 nm, naphthalenes at 310–320 nm, three and four ringed compounds at 340–380 nm and compounds with five or more rings at 390–480 nm. The different wavelength kits installed in each fluorometer offer an explanation for the observed differences in the Diesel fuel intensity values and to a lesser extent, the other oils. The selected wavelength of each kit focus on a particular group of compounds. The manufacturer's technical literature describes the model 10 short wavelength kit with excitation at 254 nm and emission at 350 nm as predominantly focussing on naphthalene compounds. The dominance of naphthalene when using the short wavelength kit is confirmed in the results from Wakeham. One should note that the Turner fluorometers are fixed wavelength instruments as opposed to the variable wavelength instrument used by Wakeham. Care must be exercised when comparing data from the two types of fluorometers because the scanning fluorometer varies both the excitation and emission wavelength while the conventional fluorometer employs fixed wavelengths. Meanwhile, the model 10AU's long wavelength kit for crude oils employs excitation at 350 nm and emission at 410–550 nm. Turner Instruments literature indicates the model 10AU detects three and four ringed aromatic compounds which are abundant in crude oils. As described by Wakeham [7], the broad range of 410–550 nm was an attempt to capture the emission of a number of the larger PAH compounds contained in the oil. Thus, even though the different wavelength kits are the prime reason that specific oil types show a difference in the fluorescence intensity between the two instruments, there is a direct link between the wavelength kit and chemical composition.

A subsequent observation is that for each oil type, ASMB, Diesel fuel, Bunker C and Prudhoe Bay, there is a notable difference in the fluorescence intensity values between the fresh oil and its weathered counterpart. In percent, the changes were as follow:

- ASMB fluorescence intensity values increase by 5% on the model 10AU and 21% on the model 10 from the fresh to weathered oils;
- Diesel fuel fluorescence intensity values increase by 40% on the model 10AU and 27% on the model 10 from the fresh to weathered oils;
- Bunker C fluorescence intensity values decrease by 74% on the model 10AU and 66% on the model 10 from the fresh to weathered oil; and,
- Prudhoe Bay fluorescence intensity values decrease by 51% on the model 10AU and 21% on the model 10 from the fresh to weathered oils.

The previous points regarding the link between the wavelength employed in each kit and chemical composition are useful in explaining the difference between the two instruments in terms of the percent change of the fluorescence intensity values for each oil. The tendency of each oil towards increased or decreased intensity is consistent between the two instruments indicating that this phenomena is dictated by the oil's chemical makeup and not the instrumentation. Interesting to note is that ASMB and Diesel fuel had increasing fluorescence intensity values from fresh to weathered oil while Prudhoe Bay and Bunker C had a decreasing relationship. This phenomena was seen but not discussed in the paper by Frank [8]. The paper discusses the use of fluorescence spectroscopy as a means of identifying crude oils. Figures provided in the paper show fluorescence profiles of the maximum emission intensity at excitation wavelength from 220 to 500 nm for fresh and weathered

#2, and 6 fuel, Louisiana crude and Bachaquero crude. As was seen in the results presented in [8], there was no consistent relationship between weathered state and intensity of the fluorescent signal. The author, citing previous reports by Mackay and Latham [9,10] stated that the PAHs were the primary contributor to fluorescence but no effort was made to relate the fluorescence signal to the chemical composition of the oil.

First, prior to further examination the relationship between composition and fluorescence values, the following points are made to eliminate other potential sources of experimental error. It was reported in [1] that the volume mean diameter of the dispersed oil droplet was consistent at 2–4 μm irrespective of oil type and degree of weathering. This fact would indicate there is a low probability of any droplet size interference on fluorometer values. In Table 4 of this report the GC-TPH results for the stock oils are as expected. These numbers tell us that for each gram of oil undergoing gas chromatography analysis the technique can resolve the indicated amount in milligrams of the initial gram of oil. The TPH values were determined to be 838 and 865 mg/g oil and 418 and 477 mg/g oil for the fresh and weather fractions of Diesel and Bunker C, respectively. The ASMB (625 and 641 $\mu\text{g/g}$) and Prudhoe Bay oil (624 and 634 $\mu\text{g/g}$) have similar GC-TPH values. The GC-TPH values for the fresh and weathered oils are similar for each respective oil which shows that the weathered state of an oil did not effect the recovery and resolution of the GC technique. It is understandable that Bunker C shows the lowest GC-TPH values because it contains large amounts of asphaltenes and polar compounds which were retained on the silica gel cleanup column. With the exception of Bunker C, the GC-TPH values are slightly higher for the weathered fraction of each oil than the fresh oils. This is a different trend than was seen with the fluorescence intensity values indicating the gas chromatography procedure was not the source of the experimental differences in fluorescence intensity noted earlier.

To proceed with this discussion it is necessary to review the chemical properties of the oils. Most of the oil properties data has been obtained from the reference *Properties of Crude Oil and Oil Products* [11]. Oils are composed of hundreds of individual chemical compounds. A way of categorizing the compounds is by hydrocarbon group analysis. Table 8 provides the hydrocarbon group analysis of these oils taken from the aforementioned reference.

Aromatic compounds are the most likely to fluoresce when excited by ultraviolet light. Each aromatic compound has a unique fluorescence intensity however, the potential for

Table 8
Hydrocarbon group analysis of the eight stock oils

Oil type	Saturates weight (%)	Aromatics weight (%)	Resins weight (%)	Asphaltenes weight (%)	Waxes weight (%)
ASMB (0% weath.)	65	27	5	3	6
ASMB (26% weath.)	57	32	6	3	7
Diesel (0% weath.)	74	24	1	0	Not available
Diesel (37% weath.)	75	23	1	0	Not available
Prudhoe Bay (0% weath.)	53	34	10	4	4
Prudhoe Bay (27% weath.)	43	38	15	5	5
Bunker C (0% weath.)	25	47	17	11	2
Bunker C (8% weath.)	23	42	20	15	2

fluorescence increases as the number of rings on a compound increases. Substitution on an aromatic ring causes a shift in the wavelength of maximum absorption and corresponding changes in the peak fluorescence wavelength [12]. As categorized by hydrocarbon groups, the aromatic compounds would play the dominant role in emitting fluorescence. Some of the more common aromatic compounds are benzene, toluene, ethyl benzene and xylene, C3-benzene and polycyclic aromatic hydrocarbons. A report by Wang et al. [13] provides detailed information of the analysis of BTEX and C3-benzene.

No simple relationship can be found from an examination of the concentration for the aromatic hydrocarbon groups or the relationship between the aromatic value and the entire makeup of the oil which would explain the change in the fluorescence intensity as an oil weathers. What is notable are the similarities between ASMB and Prudhoe Bay crude oils. A further review of their properties as listed in the catalogue indicates that of the four oils used in this program ASMB and Prudhoe Bay are the most similar. Yet, in Tables 2 and 3 they exhibit opposing trends in their relationship between the oil's weathered state and fluorescence intensity.

Further discussion on the relationship between oil composition and fluorescence intensity can not be made without a detailed review of the chemical composition of the oil. Table 5 displays the *n*-alkane data for the stock oils. These compounds do not play a role in producing a fluorescence signal but the results provide information on the change in the chemical composition of an oil as it weathers. For each of the oils, the small alkane compounds are removed in the weathering process. This can be clearly seen with the Prudhoe Bay, 27% weathered oil where compounds less than C12 are no longer present. The overall total of the *n*-alkanes does not differ significantly between the fresh and weathered oil because the effect on mass of the loss of the low molecular weight alkanes is opposed by an increase in the proportion of higher molecular weight components caused by the reduction in the oil volume [14]. Nevertheless, the loss of the low molecular weight alkanes accounts for only a small portion of the total loss in mass of the weathered oils. Other aromatic compounds must have evaporated as well to make up the total percentage of mass lost. The chromatograph in Figs. 1 and 2 provides additional relevant information. They show that fresh ASMB, Prudhoe Bay and Diesel fuel contain significant amounts of BTEX and alkylated (largely C3 and C4-benzene) benzene compounds. The fresh Bunker C oil contains smaller amount of BTEX and C3-benzene compounds. These single-ring aromatic compounds can absorb ultraviolet light and emit fluorescence. For the weathered oil counterparts, ASMB (26% weathered) oil still contains large amounts of BTEX and alkylated benzene compounds but nearly all the targeted BTEX and C3-benzene compounds were lost in the 27% weathered Prudhoe Bay, 8% weathered Bunker C and 37% weathered Diesel fuel.

Table 6 lists the alkylated PAH homologues and the other EPA priority unsubstituted PAH results from the compositional analysis of the stock oils. Figs. 1 and 2 display the chromatographs for the targeted alkylated PAH homologues analysis. It can be seen from the data in Table 6 that Diesel fuel shows the highest concentrations of the five targeted alkylated PAH compounds with the alkylated naphthalenes being dominant. Bunker C oil shows a distribution of the alkylated PAHs somewhat different from other oils in that, in addition to the alkylated naphthalenes there is an abundance of the alkylated phenanthrenes and chrysenes. A trend for most of the PAH compounds is that weathered oil has a higher concentration of the particular PAH compound than the equivalent fresh oil. Naphthalene

compounds in Prudhoe Bay along with naphthalene and fluorene compounds in Bunker C are the exception. Of note is the similarity between the values for each PAH compound for the fresh and weathered fraction of the oils. For example, the total naphthalene mass for the fresh ASMB oil was 9257 $\mu\text{g/g}$ and the 27% weathered sample was 9978 $\mu\text{g/g}$. In the work in [14] a thorough discussion of the changes in an oil's composition during weathering is presented. To summarize, like the *n*-alkanes, the evaporation rate of the larger, high molecular weight, aromatic compounds is less than that of the low molecular weight single-ring aromatic compounds. As the oil evaporates the low molecular weight compounds make up the largest portion of the lost mass. Conversely, the high molecular weight cyclic compounds make up a larger portion of the remaining oil. However, in terms of absolute numerical values, evaporation results in the loss of mass for all the compounds. An equation is given in the paper [14] to determine the mass loss of an individual compound on an equivalent basis with the total mass of the fresh oil. As an example using the same ASMB numbers as above, the converted concentration for the naphthalenes derived from the GC result (9978 $\mu\text{g/g}$) multiplied by (1% weathered) or $(1-26/100)$ resulting in a value of 7384 $\mu\text{g/g}$. On a mass equivalent basis the fresh oil would have 9257 $\mu\text{g/g}$ of naphthalene while the 26% weathered ASMB would have 7384 $\mu\text{g/g}$ of naphthalenes. It is not probable that the reduction in the absolute amount of the PAH compounds relative to the fresh oil impacted the fluorometer results. There are two reasons for this conclusion. First, the 26% weathered oil was used in the experiment and its naphthalene concentration was 9978 $\mu\text{g/g}$. It was not a case of using fresh oil which weathered over the duration of the testing indirectly influencing the relative proportion of naphthalene. The experimental oils used were fresh ASMB oil having 9257 $\mu\text{g/g}$ of naphthalene and the 26% weathered ASMB had 9978 $\mu\text{g/g}$ of naphthalene. Secondly, all the oils were treated consistently when making the premix and carrying out the experimental portion of the experiment. Therefore, the actual mass of oil placed in the test vessel is as listed in Tables 2 and 3.

The preceding paragraphs have discussed the chemical composition of the fresh and weathered stock oils. The premix employed in the experiments was made using aliquots of the stock oils combined with the dispersant Corexit 9500 at a 4 to 1 oil to dispersant ratio. Potentially, the interaction of the oil and dispersant and the exposure of the oil to the salt water environment in the test vessel may have affected the composition of the oil in a manner not detected in the chemical analysis of the stock oils. A calibration run was carried out for each oil and dispersant mixture by adding known volumes of the premix into a known amount of water. At the end of calibration run a sample of the oily water for each oil type was collected and analyzed for PAHs. Figs. 3 and 4 presents the chromatograph for the target alkylated PAH homologues analysis while Table 7 summarizes the quantitative results of the alkylated PAH homologues and the other EPA priority unsubstituted PAHs. These samples had a concentration of 12.5 μl of the premix per litre of water. Using the density of each oil, taken from [11], the values in Table 7 have been converted to the more traditional units of $\mu\text{g/g}$. From the chromatogram, it can be seen that oil extracted from the water and the stock oils showed a similar pattern with respect to the loss of compounds by evaporation. That is, the extracts of the fresh oil-in-water samples for all oil types along with the 26% weathered ASMB oil-in-water sample contain significant amounts of BTEX and alkylated (largely C3 and C4-benzenes) benzene compounds. Again consistent with the stock oils, oily water samples of the 27% weathered Prudhoe Bay, 8% weathered Bunker C, and 37% weathered

Diesel fuel contain only trace amounts of the target BTEX and C3-benzene compounds. The diesel-in-water samples show the highest concentrations of the five targeted alkylated PAH compounds with the alkylated naphthalenes being dominant. Similar to the starting oil, the Bunker C oil-in-water extract sample also shows the distribution of the alkylated PAHs with the alkylated phenanthrenes and chrysenes being abundant in addition to the high abundance of alkylated naphthalenes. In a manner similar to the stock oils, the trend with the oily water extracts shows that for most of the PAH compounds the weathered oil has a higher concentration of the particular PAH compound than the equivalent fresh oil. This time, for the oily water samples the naphthalene compounds in Prudhoe Bay are consistent with this trend, however all of the PAH compounds in the weathered Bunker C have lower results than their fresh oil counterpart. Of note is the overall lower amount of PAHs in each oil and the significant difference in the numerical values of the fresh oil's PAH compounds versus the weathered oil's PAH compounds for each type of oil when compared to the stock oil results in Table 6. There is no evidence to suggest that this would impact the results of this study however it is hypothesized that the difference is caused by the influence of the dispersant. Dispersants favour interacting with the lighter molecular compounds present in the fresh oil but absent in the weathered oils thereby creating a situation with the fresh oils for increased loss through dissolution into the water column. These losses would not be accounted for using dichloromethane as the extraction solvent. A second potential source for loss of the PAH compounds in both the weathered and fresh oils is some compounds may have bonded with the dispersant and remained on the silica gel column during sample preparations.

In the discussion on the relationship between an oil's composition and the fluorometer response, the focus has been on the PAH compounds as the primary source of fluorescing aromatic compounds. Since the PAH values in Table 6 and especially Table 7 show that the weathered samples have a higher proportion of PAH compounds than the fresh oil counterpart, one would expect that the fluorescence intensity value of the weathered oil in Tables 2 and 3 should be proportionately higher. As discussed earlier this is not consistent with the results in Tables 2 and 3. Prudhoe Bay and Bunker C have lower fluorescence intensity values for the weathered oils. Recall that the technical literature in [6] stated that the short wavelength kit uses the fluorescence of naphthalene as the principle method of detection. Considering the results in Table 7, it can be seen that naphthalene is by far the most prominent PAH in Diesel fuel. The Diesel fuel results found in Table 3, for the fluorometer equipped with a short wavelength kit, lend support the naphthalene theory by Turner Instruments. The fluorescence value increases by 27% from the fresh to weathered oil and the increase in the total naphthalene content for the fresh to weathered Diesel fuel is 26%. Unfortunately, this relationship does not hold for the other oils. The ASMB naphthalene content increases by 170% while the fluorescence value increases by 21%. Bunker C has a decrease in naphthalene content of 26% and a decrease in fluorescence value of 66%. Finally, the worst case is Prudhoe Bay with an increase in naphthalene content of 31% and a decrease in fluorescence value of 21%. If one was to continue with this type of comparison and extended it to the different oils, the relationships become even more random. For example, the difference between the naphthalene content of weathered Diesel fuel and weathered Bunker C is a decrease of 85% and the corresponding change in fluorescence value of 80%. There is a 150% increase in naphthalene content for weathered Diesel

fuel over weathered ASMB while the fluorescence intensity only shows a 37% increase. Thus, it is difficult to say that the short wavelength kit is influenced exclusively by naphthalene content. The role of naphthalene and the importance of the other PAH compounds is not clear and it would appear that some compounds other than naphthalene are playing a role. The long wavelength kit is designed for the larger three and four ring compounds such as phenanthrene, anthracene and pyrene. A similar analysis of the fluorometer data for the long wavelength kit taken from Table 2 and compared to chemical composition results in Table 7 was no more conclusive. Recall the discussion earlier on the data from Wakeham [7]. The author reported that the location or wavelength of the peak emission intensity was related to the number of cyclic rings in an aromatic compound. Single-ring compounds such as benzene had maximum emission at approximately 280 nm while five ring and larger compounds emitted strongly at 400 nm and higher. However, there is not a clean break at a specific wavelength where one compound stops emitting energy and the next size compound begins. The emission band for each of the specific compounds are broad and bands overlap. Excitation at a specific wavelength may result in two or more aromatic compounds emitting energy at approximately the same wavelength. In addition, they would likely have different emission intensities. Finally, stating that the peak emission intensity for a particular compound occurs at a certain wavelength does not preclude that compound from emitting fluorescence energy if exposed to excitation energy outside that range. Wakeham displays plots of data from a conventional fluorometer illustrating emission intensity versus wavelength for four oils, a #2 fuel, Kuwait crude, South Louisiana crude and Bunker C. Unlike the excitation wavelengths of 254 and 350 nm and emission wavelength of 350 and 410–550 nm used in this research, the excitation wavelength was 310 nm and fluorescence was detected between 350 and 380 nm. The four oils have the same complex chemical composition as the oils tested in this project. Therefore, regardless of using the long or short wavelength kit, a fixed excitation wavelength can not exclusively target a group of chemical compounds in the oil resulting in only those compounds emitting fluorescence. Instead it is likely that many of the PAH compounds in the oil are simultaneously effected by the excitation energy however the relative amount of the effect differs for each group of PAHs. This is reflected in the emission spectrum and resulting fluorescence signal.

The focus of the discussion to this stage has been on the multi-ringed PAH compounds, yet this has not offered a solution to the question of why there is an inconsistent pattern with the fluorescence signal for fresh and weathered oils. The decrease in the fluorescence intensity value for the fresh and weathered Prudhoe Bay may be a key to the connection with composition. Why, when Prudhoe Bay and ASMB oil are similar in many ways, do they differ in their respective fluorescence intensity for the weathered oils? Are there some fluorescent compounds that Prudhoe Bay loses on evaporation and ASMB does not? In Figs. 1–4, it was noted that the fresh ASMB, Prudhoe Bay and Diesel fuel show ample amounts of the BTEX and C3-benzene compounds. Even the Bunker C fuel oil contained a limited amount of these compounds. However, after evaporation, only the weathered ASMB still contained a significant amount of these compounds. The BTEX and C3-benzene levels in the other three weathered oils were minimal. The quantification of the volatile organic compounds, BTEX and C3-benzene, was not undertaken for this report. Nevertheless, information provided in [11] under the heading volatile organic compounds provides evidence

of the almost complete loss of total VOCs for all but ASMB oil as they weather. These aromatic compounds do fluoresce.

Previous reports such as [7] and those discussed earlier [8–10] form the foundation of much of the subsequent fluorescence work especially in regard to the choice of excitation and emission wavelengths. All of the above references have almost consistently stated that it was the PAH compounds that had the strongest impact on an oil's fluorescence emission. However, a review of these reports shows the work was carried out on oil extracted with solvent, usually cyclohexane, which would not necessarily "see" the VOCs and that the role of the lower molecular weight VOCs was not examined. The paper [7] contains some relevant information but the objective of the paper was still to compare scanning wavelength fluorescence spectroscopy to fixed wavelength spectroscopy. In [7], Kuwait crude oil was divided up into aromatic fractions based on polarity of the particular fraction. Pentane was used to extract the aliphatic hydrocarbons. A benzene-dominated fraction was eluted using a solvent of 10% benzene in pentane. A naphthalene-dominated fraction was eluted using a solvent of 20% benzene in pentane. Finally, 100% benzene was used to elute the remainder of the three or more ringed compounds. When excited at 310 nm the emission scan (approximately 300–480 nm) for benzene- and the naphthalene-dominated fractions was almost identical. The intensity increased rapidly from 300 nm to the peak at 350 nm then dropped off quickly so that by 400 nm the intensity was less than the value at 300 nm. Throughout the scan the intensity of the benzene fraction was actually greater than the naphthalene fraction. The emission scan of the three ring and greater PAH fraction increased even more rapidly with a secondary peak at 350 nm, rose further to a primary peak at 370 nm then decreased slowly such that at 450 nm it had returned to its baseline. This clearly displays the importance of the benzene or aromatic VOC fluorescence.

It is possible to see the importance of the VOCs in an oil when one considers their potential contribution. For example, in the hydrocarbon group analysis for ASMB fresh oil the breakdown was saturates (65%), aromatics (27%), resins (5%), asphaltenes (3%) and waxes (6%). The total VOC mass as reported in [11] was 29,020 $\mu\text{g/g}$ and the total PAH mass taken from Table 7 was 5261 $\mu\text{g/g}$. The mass of the aromatic VOCs is significantly higher than the PAHs. Even combined these two numbers account for 3.4% of the mass of the whole oil which is far less than the 27% aromatic hydrocarbon group value. Also, VOCs have distinctive properties within an oil which effect analysis techniques. They possess a type of solvent-like property within an oil and often when lost due to weathering the oil takes on a tar-like texture resulting in a change in the oil's physical properties. Volatile organic compounds are far more soluble in water relative to the three and four ring PAHs. Therefore, even if they are transferred into the water column during the weathering process, their impact on fluorescence may remain.

From the information in the previous paragraphs it would appear that, in addition to the PAH compounds, the BTEX and C3-benzenes play an important role in the fluorescence of an oil. A discussion was presented earlier on the overlap of the excitation and emission spectrums for the PAH compounds. The same holds true for the VOCs whose spectrum overlaps with the two ringed PAHs. The near complete loss of VOCs and the resulting impacts would explain why the fluorescence intensity for the weathered Prudhoe Bay was less than the fresh oil counterpart. Bunker C decreased in VOCs and PAHs which is reflected in a dramatic loss in fluorescence signal with a weathered oil. ASMB shows predictable

trends as a result of the continued presence of VOCs and PAHs in the weathered oil. Diesel fuel is not explained as easily. The fresh Diesel fuel possess significant VOCs yet the response is low for the instrument equipped with the long wavelengths kit (model 10AU, Table 2). It should be noted however that the concentration of benzene in the Diesel fuel used in this experiment is very low compared to the other VOC compounds. In [7], it was seen that the benzene emission peak was almost identical to the naphthalene emission peak. In Diesel fuel, naphthalene is the predominant PAH and there is a minimal amount of the high molecular weight PAHs. Assuming that the combination of the VOCs and PAHs is responsible for the fluorescent signal then without the benzene and the higher molecular weight PAHs in the Diesel fuel, the fuel may not be detected by the long wavelength kit.

An effort was undertaken to isolate the group of compounds or combinations thereof having the most significant role with each wavelength kit. The statistical software package TableCurve was employed. Individual plots of fluorescence intensity value versus chemical compounds were generated by the software. The fluorescence intensity used were the numbers at for the 4 $\mu\text{l/l}$ concentration listed in Tables 2 and 3. The concentration values were taken from Table 7 except for the BTEX concentrations which were obtained from literature [11]. Thus, as an example, for each instrument, or wavelength kit, there was a series of plots of fluorescence intensity value versus BTEX concentration, versus naphthalene concentration, etc. A trendline was determined for each plot. None of the equations were linear but ranged from polynomial to exponential to logarithmic. Each plot had a unique correlation co-efficient, however the correlations were weak. A comparison was made between the correlation co-efficient and the chemical composition. It showed that indeed, BTEX and naphthalene were the dominate groups with the model 10 short wavelength kit, the influence decreasing with phenanthrene and dibenzothiophene but increased again with fluorenes and chrysene compounds. The long wavelength kit in the model 10AU had its strongest correlation with naphthalene and fluorene compounds.

What can be taken from this work is that there is a complex relationship between chemical composition an oil and its fluorescent signal. Further work would include the analysis of the stock oil and the oily water extracts for BTEX and C3-benzenes and the experimentation with a full spectrum fluorescence spectrometer to determine the response to the volatile organic compounds.

6. Conclusion

This paper has presented information on a laboratory test program to evaluate the performance of the Turner Instruments flow-through model 10AU and model 10 fluorometer. In a study of the chemical composition of the selected oils used in the experiment, it was found that the results of the fluorometer could not be directly linked to the concentration of any specific aromatic hydrocarbon such as naphthalene or to the sum of the PAH compounds. Evidence suggests that the fluorescence signal is generated by a combination of PAH compounds. The relative contribution of each PAH compound is not equal. Finally, the response of the fluorometers may also be influenced by the presence of volatile organic compounds such as BTEX and C3-benzenes in combination with the PAH compounds

References

- [1] P. Lambert, B. Fieldhouse, Z. Wang, M. Fingas, M. Goldthorp, L. Pearson, E. Collazzi, Preliminary results from the laboratory study of a flow-through fluorometer for measuring oil-in-water levels, in: Proceedings of the 23rd Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 2000, pp. 69–98.
- [2] P. Lambert, M. Fingas, M. Goldthorp, An evaluation of field total petroleum hydrocarbon (TPH) systems, *J. Hazard. Mater.* 83 (2001) 65–81.
- [3] Z. Wang, M. Fingas, Analytical Method for the Determination of Individual and Total petroleum Hydrocarbons, Polycyclic Aromatic Hydrocarbons and Biomarker Triterpanes and Steranes in Crude Oil, Weathered Oil and Oil-Spill-related Environmental Samples, Internal Report, Emergencies Science Division, Environment Canada, Ottawa, Ont., 1994, 23 pp.
- [4] Z. Wang, M. Fingas, K. Li, Fractionation of a light crude oil and identification and quantification of aliphatic, aromatic, and biomarker compounds by GCFID and GCMS. Part I and II, *J. Chromatogr. Sci.* 32 (September 1994) 361–382.
- [5] Z. Wang, M. Fingas, Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil spill related environmental samples by gas chromatography, *J. Chromatogr.* 774 (1997) 51–78.
- [6] Turner Instruments, *Oil in the Environment*, Turner Designs Inc., Sunnyvale, CA, 1989, 16 pp.
- [7] S. Wakeham, Synchronous fluorescence spectroscopy and its application to indigenous and petroleum-derived hydrocarbons in Lacustrine sediments, *Environ. Sci. Technol.* 11 (3) (1977) 272–276.
- [8] U. Frank, Identification of petroleum oils by fluorescence spectroscopy, in: Proceedings of the 1975 Conference on Prevention and Control of Oils Pollution, American Petroleum Institute, Washington, DC, 1975, pp. 87–91.
- [9] J.F. McKay, D.R. Lantham, Fluorescence Spectrometry in the characterization of high-boiling petroleum distillates, *Anal. Chem.* 44 (13) (1972) 2132–2137.
- [10] J.F. McKay, D.R. Lantham, Polyaromatic hydrocarbons in high-boiling petroleum distillates, *Anal. Chem.* 45 (7) (1973) 1050–1055.
- [11] P. Jokuty, S. Whitar, Z. Wang, M. Fingas, P. Lambert, B. Fieldhouse, J. Mullin, in: *A Catalogue of Crude Oil and Oil Product Properties*, 1999 ed., Environment Canada Manuscript Report Number EE-165, Ottawa, Ont., 1999, 956 pp.
- [12] D. Skoog, D. West, in: *Fundamentals of Analytical Chemistry*, CBS College Publishing, New York, NY, 1982, 859 pp.
- [13] Z. Wang, M. Fingas, M. Landriault, L. Sigouin, N. Xu, Identification of alkylbenzenes and direct determination of BTEX and (BTEX + C3-benzenes) in oils by GC/MS, *Anal. Chem.* 67 (19) (1995) 3491–3500.
- [14] Z. Wang, M. Fingas, Study of the effects of weathering on the chemical composition of a light crude oil using GC/MSGC/FID, *J. Microemul. Sep.* 7 (6) (1995) 617–639.