ISSN-1680-9955

Pak. J. Anal. Chem. Vol. 5, No. 2, (2004) 77-87

Volatile Organic Compounds (VOCs) and Polycyclic Aromatic Hydrocarbons (PAHs) in the Water-Soluble Fraction (WSF) of Kerosene and Aviation Fuel in Seawater

TALAT SAEED[*] AND MAHA AL-MUTAIRI

[*]Environmental Sciences Department, Earth and Environmental Sciences Division,
Kuwait Institute for Scientific Research, P.O. Box 24885, Safat-13109, Kuwait.

Abstract

Detailed compositions of the water-soluble fraction (WSF) of kerosene and of aviation turbine kerosene (aviation fuel) were investigated. WSF was prepared by stirring kerosene and aviation fuel for 24 hrs with seawater. Three different temperatures (15°, 25° and 35°C) were used during the preparation. Volatile organic compounds in the WSFs were analyzed by purge & trap/GC and PAHs were determined in the concentrated extract by GC/MS in single ion monitoring mode. The results showed that WSF of kerosene contained 30 volatile organic compounds the total of which amounted to about 7 mg/l. Aromatics and naphthenes were the dominant groups. The concentration of VOCs in the WSF of aviation fuel was slightly less than kerosene (about 5 mg/l) but contained more compounds (39 compounds). VOCs consisted, almost entirely, of aromatic compounds. There were, however, significant differences, in the distribution and quantity of PAHs in the WSFs. The levels were relatively low (0.132 mg/l) in the WSF of kerosene. The WSF of aviation fuel, on the contrary, contained relatively large amounts of PAHs (about 4 mg/l). Naphthalene and its methylated homologs were the dominant PAHs in the WSF of both refined products.

Keywords: Aviation fuel; kerosene; polycyclic aromatic hydrocarbons; volatile compounds; water-soluble fraction.

Introduction

Petroleum hydrocarbons enter the marine environment from many diverse sources. The major sources include: natural sources (seepage), offshore oil production, marine transportation (operational discharges, dry docking, marine terminals, bunker operations, bilge and fuel oil transfer, and accidental spillage); atmospheric fallout; coastal, municipal and industrial wastes and runoff; and ocean dumping. Transport-related inputs remain the major focus of the marine environment because the world's petroleum continues to be produced and transported from countries different from those in which the petroleum is refined and consumed. It has been estimated that the discharge of petroleum hydrocarbons into the oceans as a result of maritime transportation activities ranges from 1.0 to 2.6 million metric tons per year [1]. The Arabian Gulf countries supply about 40% of the world's supply of crude oil. These countries export about 60% of all the oil transported by ships around the world [2]. In addition, there is a growing trend in the region to increase the refining capacity and export value-added refined petroleum products to the world market.

Petroleum oils (crude oil and refined petroleum products) on entering the marine environment undergo many diverse processes. These include evaporation, dissolution, photolysis, oxidation, adsorption on to particles, sedimentation, biodegradation and uptake by biota. These processes collectively determine the fate of the oil and its impact on the environment. Among these processes, dissolution is of special importance and significance especially from toxicity point of view. The amount of oil that dissolves in water is generally small (less than 1%). It is this fraction that contacts and impacts the marine organisms and is therefore an important determinant of the oil toxicity.

Dissolution of crude oils has been extensively studied [3 - 9]. The water-soluble fraction of refined petroleum products has also been reported by many authors [10 – 19]. These studies indicated that the water-soluble fraction (WSF) of crude oils and most of the petroleum products is a complex mixture ranging from pentane to polycyclic aromatic hydrocarbons (PAHs), phenols, and nitrogen- and sulfur-containing heterocyclic compounds. PAHs are known to be neurotoxic, cytotoxic and carcinogens.

In the literature, the composition of WSF of kerosene has been rarely mentioned. One of the reasons of this lack of interest was the fact that very few high profile-accidents involved kerosene spillage into the marine environment. Boylan and Tripp [4] reported the aromatics present in the WSF of kerosene in seawater. Many isomers of C_3-benzene, C_4-benzene, naphthalene and methylated naphthalene were detected. The total concentration of these compounds amounted to 610 μg / L^{-1}. Coleman [16] described the major components in the WSF of kerosene prepared in tap water. Anderson [3] pointed out that all oils bearing the same name do not necessarily have identical chemical composition. The actual composition of the pure petroleum product is dependent upon the raw source, the degree of chemical modification (for example, cracking) and the physical separation method employed [16]. It can, therefore, be reasonably expected that refined petroleum products produced from diverse crude oils may produce different composition of the petroleum product especially in minor components (mostly quantitative) and hence variable composition of the water-soluble fraction.

Petroleum pollution of the Arabian Gulf has been the subject of many studies [20, 21]. Most of pollution has been attributed to crude oil spills. However, little attention has been given to the soluble hydrocarbons in the seawater [22, 23]. The main objective of the present study was to determine the volatile organic compounds and PAHs in the water-soluble fraction of locally produced kerosene and aviation fuel prepared in the local seawater and at temperatures encountered locally.

Materials and Methods

Authentic samples of kerosene and aviation fuel (also known as aviation turbine kerosene: ATK) were obtained from Kuwait National Petroleum Company (KNPC). The samples were kept in an airtight container and stored in a freezer at -20^{o}C. The seawater used in the preparation, was from an offshore intake well. The water was filtered through a series of filter to remove any biota and particulate matter and tested for the presence of any organic compounds by running it as a blank.

Preparation of water-soluble fraction

The setup used for the preparation of WSF was described previously [24]. It consisted of a 2 l bottle that was kept in a water bath. The temperature of the bath was controlled by employing a water-chiller/heater circulator. The circulator controlled the set temperature to $\pm$0.1^{o}C. The water level in the bath was adjusted so that water and oil layers in the bottle were below the water level of the bath. The bath was placed on a magnetic stirrer. A Teflon-coated stirring bar (2 cm long) was placed in the bottle. The stirring speed was adjusted so as not to form a large vortex. The oil sample was introduced slowly on top of the water layer through a glass tube with the help of a syringe. The headspace was purged with nitrogen through another tube to expel air. WSF sample was collected by applying a slight nitrogen pressure that caused the WSF to rise in a glass delivery tube. The stirring was continued for 24 hr after which the WSF was removed immediately for analysis or extraction.

Preparation of concentrated extract for GC/MS analysis

About 1.5 liter of the water-soluble fraction was taken in a separatory funnel and extracted three times with 10 ml portions of 3:7 mixture of hexane: dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and concentrated on a rotary evaporator to about 5 ml and then under a stream of nitrogen to near dryness. The final volume was adjusted to 100 μl with dichloromethane.

Purge and trap-gas chromatographic analysis

The volatile compounds in the WSF were analyzed by purge & trap/GC using a flame ionization detector. Varian-3600 GC was linked to a Tekmar-3000 purge and trap concentrator. A Tekmar cryofocusing module was employed to refocus the volatile desorbed from the trap. Data was acquired and reprocessed by Varian Star Chromatography Software. A sample of the WSF (3 ml) was introduced into the purging vessel with a Luer-lock syringe. A preset method (equivalent to EPA Method-502) was used for purging and trapping the volatiles. Briefly, the sample was purged for 11 min with helium. The purged volatile compounds were trapped on a Tenax trap. The trap was heated to 225^{o}C to desorb and kept at the same temperature for 2 min during desorption. The desorbed compounds were refocused at the head of analytical column at -150^{o}C after which the cryofocusing interface was heated to 180^{o}C and the compounds introduced into the GC.

The conditions for gas chromatographic analysis were as follows: Fused silica capillary column, coated with SPB-624 (Supleco), 1.4 μm film thickness, 30 m long and 0.25 mm internal diameter. Helium was used as carrier gas at 2-ml/min. Initial column temperature was 40^{o}C, maintained for 5 min and then programmed to 220^{o}C at 4^{o}/min. The final temperature was held for 10 min. Flame ionization detector used for detection. An external standard method was employed for quantitation.

P&T/GC/MS Analysis

The identity of the peaks was ascertained by linking the P&T/GC with a mass spectrometer. The Tekmar-3000 purge and trap concentrator was linked to Shimadzu GC-14A through a Tekmar cryofocusing module. GC was coupled with a Shimadzu QP-2000 quadruple mass spectrometer. The conditions used for GC analysis were same as given for P&T/GC. The mass spectra of unknown peaks were compared with those standards as well as with the EPA/NIH mass spectral database.

GC/MS Analysis of PAHs

Polycyclic aromatic hydrocarbons (PAHs) in the WSF were identified and quantified by analysis of the concentrated extract of WSF on GC/MS operated in single ion monitoring (SIM) mode. A Shimadzu GC-14A/QP-2000 with a split/splitless injector in splitless mode was used for analysis. The GC conditions for the analysis were: fused silica capillary column, coated with SPB-5, 25 m long and 0.25 internal diameter. Initial temperature was set at 100^{o}C, held for 5 min and then programmed to 280^{o}C at 6^{o}/min. The final temperature was held for 20 min. An external standard method was used for quantitation of PAHs. A commercially available mixture of PAHs (M-610, Supelco) was diluted after the addition of standard solutions of methylated-PAHs. The response factors of the available methylated PAHs were used for the isomers for which the standards were not available. The response factor of 1-methyl naphthalene, for example, was used for the calculation of quantities of all of methyl naphthalene isomers.

Results and Discussions

Kerosene is one of the commonly used petroleum products. It contains large number of compounds, mostly in the range of C_8 to C_{14}. Mononuclear aromatic compounds (e.g. benzene, toluene, xylenes etc.) are present in only small amounts. Aliphatic compounds form the bulk of this product. Aviation fuel (also known as jet fuel or ATK i.e. aviation turbine kerosene) is specially formulated kerosene and has a similar range.

Volatile compounds in the WSF of kerosene

After gasolines, kerosenes are the next most important refined petroleum products. Kerosenes contain compounds that are higher in molecular weight than those found in gasolines. The range of carbon atoms found in kerosene is from C_8 to C_{15}. Kerosene is predominately aliphatic in nature; however, small amounts of aromatic compounds (benzene and its derivatives) are also present. The composition of the WSF of kerosene at different temperatures and after different stirring times is presented in Table 1. The composition of the WSF of kerosene is a good reflection of the parent product. As it is a higher cut of the refining process, lower molecular weight compounds that were present in the WSF of the Kuwait crude oil [24] and gasolines [25] are either absent or present in very low concentrations in kerosene. On the other hand, the WSF of kerosene contained many higher molecular weight compounds and in higher concentrations; however, the total concentration of volatile organic compounds dissolved in seawater was much lower than gasolines. The total was comparable with that of the WSF of Kuwait crude oil [24]. The total of the WSF after the first 2 h of stirring ranged from 1336 to 2061 μg / L^{-1} (1.33 to 2.06 ppm), which increased to a range of 6438 to 7426 μg / L^{-1} (6.4 to 7.4 ppm). A total of 30 volatile organic compounds were detected in the WSF. Most of these compounds were aromatics (C_2- to C_4-benzenes). A rich variety of C_4-benzene isomers were especially noteworthy compared with crude oil and gasolines. Benzene and toluene, which were dominant in the more volatile products, constituted only a small part of the total. Another interesting feature of the WSF was that no aliphatic compounds were detected. Heteroatom containing-compounds were also almost completely absent. Only one naphthenic compound was present (cyclohexane). The concentration of cyclohexane was unexpectedly high; it was the single most abundant compound in the WSF.

Table 2 presents the group summary of the WSF of kerosene. Naphthenes comprised about 40% of the total and aromatics the rest. Cyclohexane was the only naphthenic compound present and was the single largest component (about 40%) of the WSF. Aliphatics and heteroatom containing compounds were not detected. Among the aromatics, the relative composition was very different from gasolines. Benzene and toluene, at maximum, constituted only 17% of the total aromatics. C_2- and C_3-aromatics formed the bulk (about 80%) of the total aromatics in the WSF. Significant amounts of C_4-benzenes were also present.

Effect of stirring time on the composition of WSF of kerosene

The total concentration of WSF after 2 h of stirring ranged from 1335 μg / L^{-1} to 2061 μg / L^{-1}. After another 2 h (4 h stirring), the concentration increased from 2193 to 3437 μg / L^{-1}. After 24 h, the increase in concentration was 482% at 15^oC, whereas at 25^oC, the increase was 441% and, at 35^oC, the increase was 360%. Individually, all of the compounds detected increased with time; however, the effect of stirring time on the different groups and subgroups was not uniform. After 2 h of stirring at 15^oC, naphthenes formed about 43% of the total soluble compounds. This percentage remained the same in the sample collected after 24 h of stirring. A significant decrease in the contribution of naphthenes was recorded over time when the WSF was prepared at 25^o and 35^oC. Correspondingly, aromatics as a group, increased over time at 25^oC and 35^oC. Among the subgroups of aromatics, the share of volatile aromatics (benzene and toluene) decreased or remained constant over 24 h stirring time. The higher aromatics (C_2-benzenes, C_3-benzenes and C_4-benzenes) increased at 15^oC and at 25^oC and 35^oC increased slightly or remained constant over the 24 h period.

Effect of temperature on the WSF of kerosene

The increase in the temperature of the seawater resulted in the expected increase in the solubilities of the compounds in the WSF of kerosene. The effect on the overall composition was pronounced in the first 4 h. A 17% increase was observed in the overall levels when the temperature was increased from 15^oC to 25^oC. Increase of another 10^oC resulted in an increase of 54% in the first 2 h of stirring. In the 4 h sample, increasing the temperature from 15^o to 25^oC caused an increase of 25%, and to 35^oC, raised the levels by 56%.

Volatile compounds in the WSF of aviation fuel (ATK)

Aviation turbine kerosene (aviation fuel) is kerosene especially blended for use as fuel for jet engines in the aviation industry. Its qualitative chemical composition is very similar to kerosene. It was therefore expected that the WSF of this product would be similar to that of kerosene. The detailed chemical composition of the WSF prepared at three different temperatures and at different stirring times is presented in Table 3**.** A total of 39 volatile organic compounds were detected and quantified. The concentration of the WSF, on the whole, was 40% less than that of kerosene after 24 h of stirring. The bulk of the WSF consisted of higher molecular weight aromatic compounds. Only a few of the lower molecular weight components were present in small amounts. It is also clear from Table 4 that the WSF of aviation fuel was quite similar to that of the kerosene; however, the WSF of aviation fuel did not contain as much cyclohexane as the WSF of kerosene. On the other hand, the WSF of aviation fuel contained considerably more benzene and toluene than kerosene's WSF.

Table 4 presents the summary of the composition of the WSF of aviation fuel. Aliphatics, naphthenes and hetero-atom-containing compounds were present only in trace amounts, especially in the sample collected after 24 h of stirring. The WSF consisted almost entirely of the aromatic compounds. Among the different subgroups of aromatics, C_2-benzene and C_3-benzenes made up about 70% of the aromatics. Toluene and C_4-benzene were also present in appreciable concentrations.

Effect of stirring time on the composition of the WSF of aviation fuel

The composition of the WSF of aviation fuel was affected in the same way as the samples discussed previously by the different stirring times. Increasing stirring time caused increase in the concentration of the organic compounds. This increase was reflected in the overall levels of these compounds in the WSF. The total concentration of the WSF after 2 h of stirring was 762 μg/l (0.76 ppm) at 15°C, which increased to 1445 μg/l (1.44 ppm) after another 2 h. The final concentration determined after 24 h of stirring was 4853 μg/l (4.85 ppm). The individual components, in general, followed the same trend. The effect of stirring time on aliphatics, naphthenes and hetero-atom-containing compounds was that, with stirring time, their share in the total decreased slightly. Since the contribution of these groups towards the total was relatively low, the change was not very significant. Different aromatic subgroups were affected differently by increasing the stirring time. In general, volatile aromatics (benzene and toluene) decreased and C_2- and C_3-benzenes increased with time.

Effect of temperature on the composition of WSF of aviation fuel

The effect of different temperatures on the composition of the WSF of aviation fuel is presented in Tables 4 and 5. In brief, the total concentration of organic compounds in seawater increased by about 40% when the temperature was increased from 15°C to 25°C in the samples collected after 2 and 4 h. A further increase of 10°C (from 25° to 35°C) caused an increase of about 20% in the same period. In the sample collected after 24 h stirring, the effect of temperature was relatively very small. The effect on aromatics, by far the largest group, was that, at higher temperatures, their percent contribution to the total increased slightly. The subgroups of aromatics were differently affected by the increase in the temperature. Lighter compounds, generally, decreased with increasing temperature. C_4-benzenes, the heavier compounds, increased appreciably in the WSF at higher temperatures.

Comparison of VOCs in WSF of kerosene and aviation fuel

Aromatics constitute the bulk of the volatiles in the WSF of petroleum oils including the kerosene and aviation fuel. The volatiles present in the WSFs of these oils presented a rather similar profile. Fig. 1 shows the comparison of volatile aromatic compounds in the WSFs of these oils.

PAHs in the WSF of kerosene

Table 5 presents the composition of the PAHs in the WSF of kerosene prepared at three different temperatures. The results showed that seven PAHs were present in the WSF. Naphthalene, methyl naphthalene and dimethyl

Table 1. Composition of the VOCs in the WSF of Kerosene in seawater (µg / L^{-1})

		15°C			**25°C**			**35°C**		
Peak	**Name**	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**
1	Cyclohexane	583	1036	2809	768	1287	2772	888	1417	2710
2	Benzene	26	2	5	1	5	6	1	4	6
3	Toluene	105	77	205	46	87	223	60	106	244
4	Ethylbenzene	47	79	253	54	99	277	74	128	231
5	*p*- & *m*-Xylenes	135	205	656	142	167	729	195	335	847
6	*o*-Xylene	102	180	574	126	229	653	173	299	764
7	Cumene	8	14	47	10	18	53	14	25	42
8	*n*-Propylbenzene	9	17	56	12	23	77	18	31	33
9	C_3-Benzene isomer	58	107	342	71	138	359	107	182	359
10	Mesitylene	15	27	86	17	36	104	28	48	124
11	C_3-Benzene isomer	51	96	301	65	126	362	98	168	431
12	C_3-Benzene isomer	83	151	473	104	201	574	158	268	681
13	2-Methyl,propylbenzene	3	5	16	3	7	21	5	11	18
14	*p*-Cymene	5	10	29	7	14	37	11	18	44
15	*m*-Cymene	3	5	15	4	7	17	6	10	20
16	C_3-Benzene isomer	39	73	217	51	99	274	77	132	327
17	Indane	13	23	72	17	32	90	25	43	109
18	C_4-Benzene isomer	2	5	17	3	8	21	6	11	20
19	3-Methyl, propylbenzene	4	9	26	6	13	34	10	18	39
20	C_4-Benzene isomer	3	5	17	4	8	13	6	11	11
21	*o*-Cymene	5	9	26	6	14	34	11	19	36
22	1,2 Diethylbenzene	3	5	15	4	8	21	7	11	25
23	1,4-Diethylbenzene	7	12	36	8	20	53	16	28	62
24	C_4-Benzene isomer	4	9	29	6	16	42	12	22	50
25	Ethyldimethylbenzene	8	15	37	9	23	53	18	30	61
26	C_4-Benzene isomer	6	11	33	8	19	46	15	25	53
27	1-Methyl indane	5	8	19	5	11	26	9	15	31
28	C_4-Benzene isomer	2	4	13	3	8	22	6	12	24
29	2-Methyl indane	0	1	4	1	2	7	1	3	8
30	4-Methyl indane	1	3	9	2	5	17	4	8	16
	Total	**1335**	**2193**	**6438**	**1561**	**2731**	**6885**	**2061**	**3437**	**7425**

Table 2. Group Summary of the WSF of Kerosene

	15^oC			25^oC			35^oC		
Group Name	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**
Total Aliphatics (μg/l)	0	0	0	0	0	0	0	0	0
Total Naphthenes (μg/l)	583	1036	2809	768	1287	2772	888	1417	2710
Total Aromatics (μg/l)	752	1157	3627	793	1444	4223	1173	2020	4714
Total Others (μg/l)	0	0	2	0	0	0	0	0	0
Aliphatics %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Naphthenes %	43.7	47.2	43.6	49.2	47.1	38.7	43.1	41.2	36.5
Aromatics %	56.3	52.8	56.3	50.8	52.9	61.3	56.9	58.8	63.5
Others %	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Benzene %	3.4	0.2	0.2	0.2	0.3	0.2	0.1	0.2	0.1
Toluene %	14.0	5.7	5.7	5.8	6.1	5.3	5.1	5.3	5.2
C_2-Benzenes %	37.8	40.0	40.9	40.6	34.3	39.0	37.7	37.7	39.1
C_3-Benzenes %	35.0	42.0	42.0	41.5	44.4	42.4	42.7	42.3	42.3
C_4-Benzenes %	7.4	9.0	8.5	8.8	11.4	9.8	11.0	11.2	9.8

naphthalene were the only major components, with other PAHs being present in much smaller amounts. The total levels were also much lower (132 μg / L^{-1} at 35^oC) than the gasolines. The increasing temperature caused the concentration to increase appreciably. Total PAHs in the WSF prepared at 15^oC were about 47 μg/l which increased to 69 μg / L^{-1} at 25^oC and to 132 μg / L^{-1} at 35^oC.

PAHs in the WSF of aviation fuel

This refined product closely resembled kerosene in its composition, as it is special kerosene. The PAHs in the WSF were also expected to closely resemble the PAHs in the WSF of kerosene; however, the PAHs in the WSF of aviation fuel were quantitatively much higher than kerosene. Table 6 presents the levels of PAHs observed in the WSF of aviation fuel. The overall levels of PAHs in the WSF of this sample were in the range of 2000 - 4000 μg / L^{-1} while, in kerosene, these levels ranged from 47 to 132 μg / L^{-1}. The total PAHs in this sample were surprisingly high, especially in view of the fact that the levels of volatile organic compounds in the WSF of this sample (Table 4) were quite comparable with those of kerosene (Table 2). As in other samples, the PAHs in the WSF of aviation fuel were mostly due to the presence of naphthalene, methyl naphthalene and dimethyl naphthalene, which accounted for about 97% of the total PAHs. The other PAHs were present in relatively small amounts. The effect of different temperatures on the composition of PAHs in the WSF can also be seen from Table 6. The total PAHs were about 2000 μg / L^{-1} at 15^oC and 25^oC but increased dramatically in the sample prepared at 35^oC to about 3900 μg / L^{-1}.

Comparison of PAHs

Fig. 2 shows comparative composition of the PAHs in the WSF of kerosene and aviation fuel. While the profile for the volatile aromatics in the WSF was not dissimilar, the PAH profile was dramatically different. The extent to which these differences exist in the PAHs in the WSF of these oils can be readily assessed from this figure.

Conclusions

Chemical analysis of WSFs of kerosene and aviation fuel in seawater showed that these were complex mixtures of wide range of organic compounds. These included volatile organic compounds and polycyclic aromatic hydrocarbons. WSF of kerosene contained 30 VOCs while that of aviation fuel contained 39 volatile compounds. Quantitatively, WSF of kerosene contained about 7 mg / L^{-1} of VOCs while WSF of aviation contained about 5 mg / L^{-1}. The VOCs consisted of almost entirely of aromatic compounds which are known to be more toxic than the aliphatic compounds. There were significant qualitative and quantitative differences in the composition of the polycyclic aromatic hydrocarbons. WSF of kerosene contained relatively low amounts of PAHs (about 0.13 mg / L^{-1}) as compared to the WSF of aviation fuel (about 4 mg / L^{-1}).

Table 3. Composition of VOCs in the WSF of Aviation Fuel in seawater (μg/l)

		15^{o}C			25^{o}C			35^{o}C		
Peak	**Name**	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**
1	Methylcyclopentane	8	4	15	2	6	16	2	4	13
2	Cyclohexane	5	4	16	2	6	12	5	4	13
3	Benzene	44	77	169	42	78	169	44	81	167
4	Methylcyclohexane	3	4	8	2	5	0	2	3	1
5	Octane isomer	7	3	31	0	5	3	6	3	9
6	Toluene	123	234	726	154	285	752	170	338	764
7	*n*-Octane	1	2	2	0	4	0	1	1	0
8	Ethylmethylcyclohexane	0	0	2	0	0	0	6	2	0
9	Methylphenol	0	0	7	0	0	0	0	0	0
10	Methylthiophane	2	0	0	0	0	0	0	0	0
11	Ethylbenzene	39	79	268	55	108	272	60	121	285
12	*p*- & *m*-Xylenes	105	207	701	147	282	729	160	322	756
13	Dimethylthiophane	0	0	0	0	7	0	0	0	0
14	*o*-Xylene	73	144	493	103	199	525	115	232	542
15	Cumene	5	10	37	8	15	38	8	17	41
16	*n*-Propylbenzene	9	17	63	14	26	63	14	29	68
17	C$_3$-Benzene isomer	37	76	283	89	108	285	60	127	318
18	C$_3$-Benzene isomer	18	35	113	0	50	103	31	56	107
19	Mesitylene	16	34	123	28	51	127	29	58	136
20	C$_3$-Benzene isomer	47	92	323	74	132	341	79	157	358
21	C$_3$-Benzene isomer	95	189	772	157	278	695	177	328	739
22	2-Methyl, propylbenzene	2	5	18	5	9	19	5	10	21
23	*p*-Cymene	5	9	31	8	14	32	2	16	34
24	*m*-Cymene	4	6	20	6	11	21	6	11	22
25	C$_3$-Benzene isomer	47	93	308	77	136	338	86	165	354
26	Indane	10	20	64	16	29	75	18	35	78
27	C$_4$-Benzene isomer	3	7	25	6	12	25	7	13	30
28	3-Methyl, propylbenzene	5	10	34	10	17	36	11	20	43
29	C$_4$-Benzene isomer	4	7	25	7	13	21	7	14	25
30	*o*-Cymene	6	12	37	12	21	39	12	23	35
31	1,2 Diethylbenzene	3	6	19	6	10	21	6	12	36
32	1,4-Diethylbenzene	7	14	47	14	26	53	17	32	69
33	C$_4$-Benzene isomer	4	10	36	10	22	41	13	24	52
34	Ethyldimethylbenzene	9	17	50	17	30	57	20	36	71
35	C$_4$-Benzene isomer	6	13	43	13	25	49	16	29	60
36	1-Methyl indane	3	7	19	7	11	22	8	13	27
37	C$_4$-Benzene isomer	2	5	19	5	13	24	8	15	29
38	2-Methyl indane	0	1	6	1	4	7	2	4	9
39	4-Methyl indane	2	3	11	3	9	14	5	9	18
	Total	**762**	**1445**	**4853**	**1101**	**2060**	**5023**	**1207**	**2377**	**5330**

Table 4. Group Summary of WSF of Aviation Fuel

	15°C			25°C			35°C		
Group Name	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**	**2 h**	**4 h**	**24 h**
Total Aliphatics (μg/l)	5	6	10	2	9	0	3	5	1
Total Naphthenes (μg/l)	20	11	64	4	17	32	18	13	36
Total Aromatics (μg/l)	734	1429	4773	1094	2026	4991	1186	2348	5293
Total Others (μg/l)	2	0	7	0	7	0	0	0	0
Aliphatics %	0.6	0.4	0.2	0.2	0.5	0.0	0.2	0.2	0.0
Naphthenes %	2.7	0.8	1.3	0.4	0.8	0.6	1.5	0.6	0.7
Aromatics %	96.4	98.9	98.4	99.4	98.4	99.4	98.3	99.3	99.3
Others %	0.3	0.0	0.1	0.0	0.4	0.0	0.0	0.0	0.0
Benzene %	6.0	4.6	3.5	3.9	3.8	3.4	3.7	3.4	3.2
Toluene %	16.8	16.4	15.2	14.0	14.1	15.1	14.4	14.4	14.4
C_2-Benzenes %	29.6	30.1	30.6	27.9	29.1	30.6	28.2	28.8	29.9
C_3-Benzenes %	37.4	38.3	40.1	40.8	39.4	39.9	40.0	39.9	40.1
C_4-Benzenes %	8.2	8.4	8.5	10.9	11.0	8.8	11.0	10.8	10.0

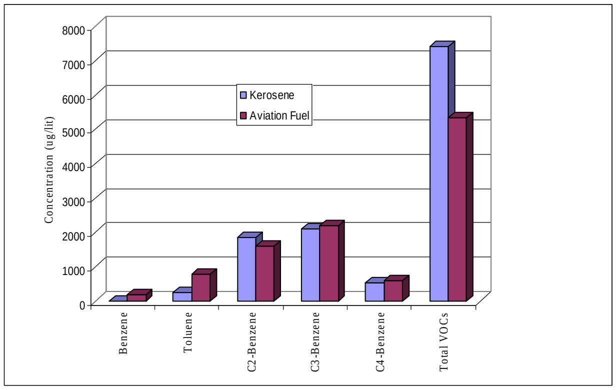

Fig. 1. Comparison of volatile aromatics in the WSF of kerosene and aviation fuel oils

Table 5. Levels of PAHs (μg/l) in the WSF of Kerosene by GC/MS.

No.	PAH	15°C	25°C	35°C
1	Naphthalene	11.5	15.7	31.0
2	Methyl naphthalene	26.9	38.6	80.3
3	Dimethyl naphthalene	3.8	8.2	15.8
4	Trimethyl naphthalene	0.0	0.8	1.2
5	Fluorene	0.2	0.3	0.5
6	Methyl Fluorene	1.1	2.5	0.6
7	Dimethyl phenanthrene	3.9	2.9	2.8
	Total PAHs	47.3	69.0	132.4

Table 6. Levels of PAHs (μg/l) in the WSF of Aviation Fuel by GC/MS.

No.	PAH	15°C	25°C	35°C
1	Naphthalene	497.7	445.2	819.8
2	Methyl naphthalene	1505.7	1404.4	2693.7
3	Dimethyl naphthalene	224.5	201.5	364.3
4	Acenaphthene	0.6	0.6	0.5
5	Trimethyl naphthalene	23.9	20.0	15.2
6	Fluorene	0.4	0.5	0.3
7	Methyl Fluorene	1.7	5.5	2.4
8	Phenanthrene	0.9	1.4	0.4
9	Methyl phenanthrene	6.7	5.7	2.0
10	Dimethyl phenanthrene	9.8	5.5	5.3
11	Fluoranthene	0.1	0.1	0.0
12	Pyrene	0.0	0.1	0.0
	Total PAHs	2272.0	2090.4	3903.9

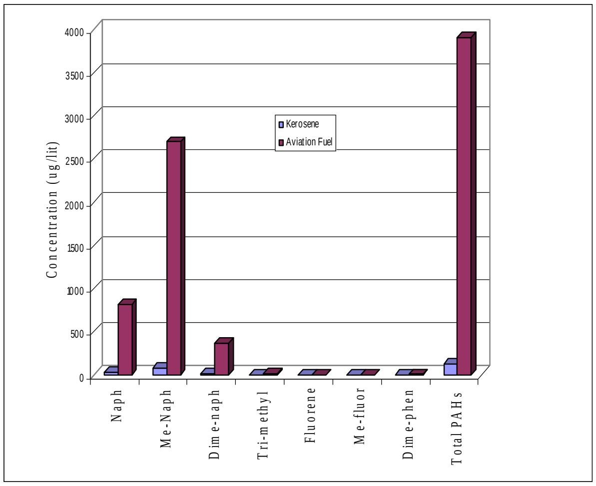

Fig. 2. Comparison of PAHs in the WSF of kerosene and aviation fuel oils.

Acknowledgements

The authors wish to gratefully acknowledge the partial funding of this study by Kuwait Fund for the Advancement of Sciences (KFAS).

References

1. National Academy of Sciences**.** *Oil in the Sea - III: Input, Fate and Effects.* (2003) Washington, D.C. National Academy Press.

2. R. Golob and E. Brus. IMCO/UNEP *International workshop on combating marine pollution from oil exploration, exploitation, and transport in the Kuwait Action Plan Region.* Manama, Bahrain, 6-10 December. Cambridge, Massachusetts (1980) World of Information Systems.

3. J.W. Anderson, J.M. Neff, B.A. Cox, H.E. Tatem and G. M. Hightower. *Mar. Biol*., 27 (1974) 75.

4. C.C. Boylan and B.W. Tripp. *Nature*. 230 (1971) 44.

5. C.C. Lee, W.K. Craig and P.J. Smith. *Bull. Environ. Contam. Toxicol*. 12 (1974) 212.

6. D. Mackay and W. Y. Shiu. *Bull. Environ. Contam. Toxicol*. 15 (1976) 101.

7. W.Y. Shui, M. Bobra, A.M. Bobra, A. Maijanen, L. Sunito and D. Mackay. *Oil & Chem. Poll.* 7 (1990) 57.

8. K. Winters and P. L. Parker. *Water soluble components of crude oils, fuel oils and used crank-case oils.* Proceedings of 1977 Oil Spill Conference. New Orleans, Louisiana, March 8-10 (1977) 679.

9. T. Saeed and M. Al-Mutairi. *Wat. Air, Soil Poll*. 120 (2000) 107.

10. T. Saeed and M. Al-Mutairi. *Adv. Environ. Res*. 4 (2000) 141.

11. F. Zucher and M. Thuer. *Environ. Sci. Tech*. 12 (1978) 838.

12. R.B. Laughlin, O. Linden and J.M. Neff**.** *Chemosphere*, 10 (1979) 741.

13. W.E. Montz, R.L. Puyear and J.D. Brammer. *Arch. Environ. Contam. Toxicol.* 11 (1982) 561.

14. J.H. Smith and J.C. Harper. *Behavior of hydrocarbons in aquatic systems. Air Force Aerospace Medicine Research Lab.* (Tech. Report), AFAMRL-TR-81-149. Proceedings of Conference on Environmental Toxicology, (1982) 336.

15. R.H. Brieri, A.L. Walker, B.W. Lewis, G. Losse and R. J. Haggert. *Identification of hydrocarbons in extract from estuarine water accommodated with No. 2 fuel oil.* NBS Spec. Publ. 499. Marine Pollution Monitoring (Petroleum), Proceedings of Symposium Workshop. Gaithersburg, Maryland, (1984) 13-17.

16. W.E. Coleman, J.W. Munch, R.O. Stricher, H.P. Ringhand and F.C. Kopfler**.** *Arch. Environ. Contam. Toxicol.* 13 (1984) 171.

17. D.A.J. Murray, W.L. Lockhar and G.R.B. Webster**.** *Oil Petrol. Poll*. 2 (1984) 39.

18. M.S. Dale, B. Koch, R.F. Losee, E.W. Crofts and M.K. Davis. *J. Amer. Wat. Works. Assoc*. 92 (2000) 42.

19. M.F. Fingas and B. Hollebone. *The fate and behavior of oil in freezing environments*. In: Marine Oil Spills in Ice and Cold Conditions. National Board of Waters and Environment, Helsinki, Finland (2001) 14.

20. M.S. Massoud, F. Al-Abdali and A.N. Al-Ghadban. *Environ. Int*. 24 (1998) 11.

21. S. Sato, A. Matsumura, Y. Urushigawa, M. Metwally and S. Al-Muzaini. *Environ. Int*. 24 (1998) 67.

22. M.I. El-Samra, H. I. Emara and F. Shunbo**.** *Mar. Poll. Bull*. 17 (1986) 65.

23. T. Saeed, H. Khordagui and A. Al-Bloushi. *Wat. Sci. Tech*. 40(1999)99.

24. T. Saeed, M. Al-Mutairi, L.N. Ali, T. Al-Obaid and M.U. Beg. *Int. J. Environ. Anal. Chem*. 72 (1998) 275.

25. T. Saeed and M. Al-Mutairi. *Environ. Int*. 25 (1999) 117-129.