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SURVEY OF SOME PERSISTENT POLYAROMATIC HYDROCARBONS IN SAUDIAN RED SEA COASTAL WATERS.

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ABSTRACT

During 6-years monitoring program, 5 of persistent polyaromatic hydrocarbons (PAH), phenanthrene, chrysene, pyrene, benzo-3,4-pyrene and benzo-8,9-perylene, were surveyed in the coastal waters of Saudi Arabia in the Red Sea. 118 surface water samples were collected from 47 fixed stations during the period 1982-1987 and analyzed spectrofluorometrically. The results showed that pyrene is the dominant constituent representing in the majority of samples more than 50% of the total PAH fraction. Concentrations of more than 3000 ng l^{-1} were detected in some areas. Constancy of concentration ratios for some PAH compounds indicates the source of oil pollution in the areas. It was found that the frequent illegal discharge of ships and tankers bilges could be the main source of oil pollution in the studied areas.

INTRODUCTION

In many of oil pollution monitoring and studies in the marine environment, the measurement of total hydrocarbon contents (THC) in different elements of the marine ecosystem has been taken as an indicator of the level of oil contamination. In fact, among the measured total hydrocarbons, biogenic fraction is usually existing in a respective proportion. Sometimes, this fraction exceeds quantitatively that of the anthropogenic one which is the real contaminant looking for (Awad, 1982; Love, 1970 and ACKMAN, 1968). However, the designation of oil pollution level in the marine environment by total hydrocarbon concentration is relative and to some extent misleading. From the other side, while much of the weathering petroleum hydrocarbons is usually lost during in the marine environment, the polyaromatic (PAH) fraction resists degradation and is retained in sediments and fatty tissues and hence will accumulate as it passes up the food chain eventually to man (Dacker, 1981).

Following many major oil spills, the fate of oil in the marine environment has been monitored for long durations and the results show a consistent trend, that is : the major portion of the oil is eliminated rather rapidly, but some of the PAH constituents appear to persist for longer periods (BOEHM et al, 1981; NEFF et al, 1976 and BLUMER et al, 1970). Consequently, when it was decided to evaluate the oil

Analytical methods

Collection and analysis of 1_m depth water samples for measuring the total concentration of dissolved/dispersed hydrocarbons were carried out precisely following the recommended proced e of MAPMOPP (IOCWMO, 1976). Heavy Arabian crude oil which is one of the most possible types of oil to be found all over the investigated area, was considered as reference for expressing oil residue in waters. this is carried out by measuring fluorescence emission intensities of the produced pure water CCl4 - extracts at 382 nm wave length when an excitation wave length of 310 nm is used.

Concentrations of the five selected polyaromatic compounds were measured spectrofluorometrically using the conditions mentioned in SAWICKI al, 1960. The used excitation wave lengths are 252, 264, 330, 381 and 380 nm for phenanthrene, chrysene, pyrene, benzo-3, 4-pyrene and benzo-8,9-perylene respectively. In the same order, the concentrations of these compounds are measured at fluorescence wave lengths : 364, 381, 382, 403 and 419 nm. The used instrument is BAIRD Fluoripoint spectrofluorometer, Ratiometric RC 200.

RESULTS AND DISCUSSION

The goal of the present work is a step in our trials to evaluate the level of oil pollution in seawater taking PAH constituents as reference instead of the traditional THC which could be to some extent leading to unconvencing statements. previously, a squalene index calculation was proposed (AWAD, 1982) and PAH constituents were measured (AWAD, 1987) in fish for the same aim.

BY the examination of results grouped in table 1 for both THC and total PAH contents in waters, it seems that there is a sort of linear correlation between the mean values of the two measurements. Except in area A, the mean total PAH fraction concentration represents almost the same percentage in the corresponding measured THC for areas B, C and D (0.84%; 0.90% and 1.05% respectively). However, the correlation might be in relation with the nature and composition of the dominant source of oil pollution in the areas. In fact, while ballast waters is the main source in the waters of the area A, illegal frequent spillage of ship machine bilges is well known in the other three areas. On the other side, the steady slight gradient in the magnitude of PAH fraction concentration from area D to area B might be in accordance with corresponding mean temperature gradient in the same direction , from higher to lower latitude. ence, the removal of light spilled oil constituents from aters is faster in southern areas than in the northern ies.

Zonal concentrations distributions for the five considered PAH compounds are represented in Fig. 1 for area A and Fig. 2 for area C according to results included in Table 2. From the obtained results, it is obvious that pyrene is the main constituent in the PAH fraction and its magnitude of concentration is proportional to the corresponding total PAH fraction concentrations. Taking into consideration that pyrene concentration is about 15 times more in areas B and D than in area C, it represents almost the same ratio of the total detected PAH concentrations in three areas. Moreover, the ratio of measured mean concentrations of phenanthrene, chrysene and pyrene in the waters of these areas are nearly similar (1 : 4.4 : 12.5; 1 : 5.1 : 6.7 and 1 : 6.3 : 8.5, for areas B, C and D respectively). In the waters of area A, neither the ratio of pyrene concentration in total PAH fraction nor the ratio of the above three PAH constituents concentration (1 : 2.4 : 3,5) are similar to these found for the other three areas. This observation confirms the difference in nature of the main oil pollution source existing in areas B, C and D in one group and that dominating in area A. Since pyrene is not abundant in crude oil but is produced during the high temperature pyrolysis of oil in internal combustion engines, its presence in high concentrations reaching more than 3000 ng l^{-1} in the waters of area B and D is a sufficient indication for the nature of oil pollution source in these areas.

The potential of the magnitude of various PAH constituents concentration along the studied coastal waters could be shown in Fig. 3. From this figure, the waters in areas B and D are the most polluted waters by petroleum hydrocarbons coming essentially from ship bilges spill. In fact, the presence of the main navigation routes in areas B and D could elucidate the nature of oil pollution situation in their waters.

CONCLUSION

Survey of oil pollution along the coastal Red Sea waters of Saudi Arabia taking 5 persistent polyaromatic hydrocarbons as reference indicates that pyrene is the dominant PAH constituent all over the areas of study; it represents more than half of the total PAH fraction in all areas especially where the main navigation routes are existing. The presence of pyrene and to lower extent chrysene in high concentrations ranging from 200 to up t 3000 ng l^{-1} for the first and from 40 to more than 700 n l^{-1} for the second compound, is a sufficient indicator fo the nature of oil pollution source in the areas, which i the discharge of ships and tankers bilges. Comparing tl concentration ratios of some compounds in the correspondi

detected total PAH fraction in the 4 studied areas, it was able to prove the homogeneity of oil pollution source in three of them. NO relationship could be found between the measured concentrations of total hydrocarbon contents in waters and PAH fraction.

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Table 1 - Distribution of total (THC) and aromatic hydrocarbon (PAH) contents in Red Sea waters along Saudi Arabia coast.

Area and period	Zone	Coordinates		No. stations	No. samples	THC as heavy arabian crude oil $\mu g\ l^{-1}$			Total PAH $ng\ l^{-1}$			% of total PAH in THC
		Long.E	Lat.N			range	mean	S.D.	range	mean	S.D.	
A 1982 1983	A_1	37°24' 37°43'	24°03'	3	3	28-51	42.7	12.7	68-613	251.7	312.9	0.59
	A_2	38°09' 38°40'	23°05' 23°25'	4	5	97-224	143	51.9	41-418	205.2	167.3	0.14
	A_3	38°26' 38°58'	22°41' 23°05'	4	9	18.8-412	147.2	126.8	149-1637	706.2	600.4	0.48
	A_4	38°50' 39°02'	21°36' 22°39	4	8	19-129.3	80.5	36.7	19-338	120.6	137.9	0.15
	A_5	38°22' 39°04'	21°35' 21°36'	4	7	18-172	69.3	60.7	119-1137	490.6	375.2	0.71
	TOTAL/AVERAGE			19	32	18-412	103	84.1	19-1637	391.8	438	0.38
B 1987		38°53' 40°01'	18°43' 21°33'	6	6	218-819	479	245	745-7685	4034	2699	0.84
C 1985 1986	C_1	41°55' 42°20'	16°58' 17°15'	4	12	0-228	49	67.3	0-1396	271.2	384.7	0.55
	C_2	41°52' 42°16'	17°10' 17°16'	3	11	4-387	49.8	113.1	0-809	175.8	230.9	0.35
	C_3	42°01' 42°23'	16°57' 17°03'	4	25	0-1382	75	263.9	0-1676	342.8	492.9	0.46
	C_4	42°18' 42°34'	16°43' 16°50'	3	14	0-20	8	6.7	0-834	146.1	257.8	1.83
	C_5	42°20' 42°38'	16°37' 16°40'	2	12	0-299	32	84.3	0-3183	386.2	893.2	1.21
	TOTAL/AVERAGE			16	74	0-1382	30.7	64.5	0-3183	276.2	501.7	0.90
D 1987		41°00' 41°35'	16°30' 17°00'	6	6	0-912	422	424	337-9268	4426	4320	1.05

Table 2 - Relative predominance of the five considered polyaromatic hydrocarbon compounds (% is the percentage of concentration in the total PAH).

zone	Concentration of individual PAH compounds in ng l^{-1}																			
	phenanthrene				chrysene				pyrene				benzo-3,4-pyrene				benzo-8,9-perylene			
	range	mean	S.D.	%	range	mean	S.D.	%	range	mean	S.D.	%	range	mean	S.D.	%	range	mean	S.D.	%
A_1	68-185	109	65.9	43.3	0	0	0	0	0-428	142.7	247.1	56.7	0	0	0	0	0	0	0	0
A_2	0-56	19.4	23.7	9.5	41-201	108.8	59.9	53.0	0-267	77	102.4	37.5	0	0	0	0	0	0	0	0
A_3	0-504	155.9	193.5	22.1	87-304	135.4	70.3	19.2	0-1107	414.9	407*	58.7	0	0	0	0	0	0	0	0
A_4	0-83	23.4	36.2	19.4	19-201	46.3	62.6	38.4	o.233	51	89.5	42.2	0	0	0	0	0	0	0	0
A_5	0-38	15.4	15.7	3.1	17-433	139.6	159.3	28.5	102-666	335.6	210.2	68.4	0	0	0	0	0	0	0	0
Total / average	0-504	66.3	119.5	16.1	0.433	97.2	99.9	24.8	0-1107	228.3	283.7	58.3	0	0	0	0	0	0	0	0
B	67-433	245	167	6.1	167-1500	707	625	17.5	470-5750	3083	2106	76.4	0	0	0	0	0	0	0	0
C_1	0-233	34	70.5	12.5	0-218	39	60.6	14.4	0-1062	190	312.3	70.1	0-52	7	14.9	2.6	0-5	1.2	1.8	0.4
C_2	0-270	41.9	79.7	23.8	0-140	36.4	42.9	20.7	0-513	84	151.1	47.8	0-58	9.2	16.7	5.2	0-15	4.3	5.6	2.5
C_3	0-573	13.5	25.6	3.9	0-1424	29.5	43.3	8.6	0-1541	293.7	466	85.7	0-150	4.6	9.4	1.3	0-10	1.6	3.1	0.5
C_4	0-132	22.7	40.7	15.5	0.204	34.6	65.5	23.7	0-493	80.4	146.8	55	0-42	5.7	11.4	3.9	0-13	2.7	4.2	1.9
C_5	0-340	53.2	94.8	13.8	0-467	66.5	130.8	17.3	0-2376	262.4	672.8	67.9	0-10	2.3	3.6	0.6	0-9.5	1.7	3.3	0.4
Total / average	0-573	29.3	60.8	10.8	0-1424	41.3	72.7	14.2	0-2376	200.2	411.3	72	0-150	5.6	11.4	2.2	0-15	2.2	3.7	0.8
D	43-1118	407	393	9.2	124-1234	550	448	12.4	0-7704	3470	3389	78.4	0	0	0	0	0	0	0	0

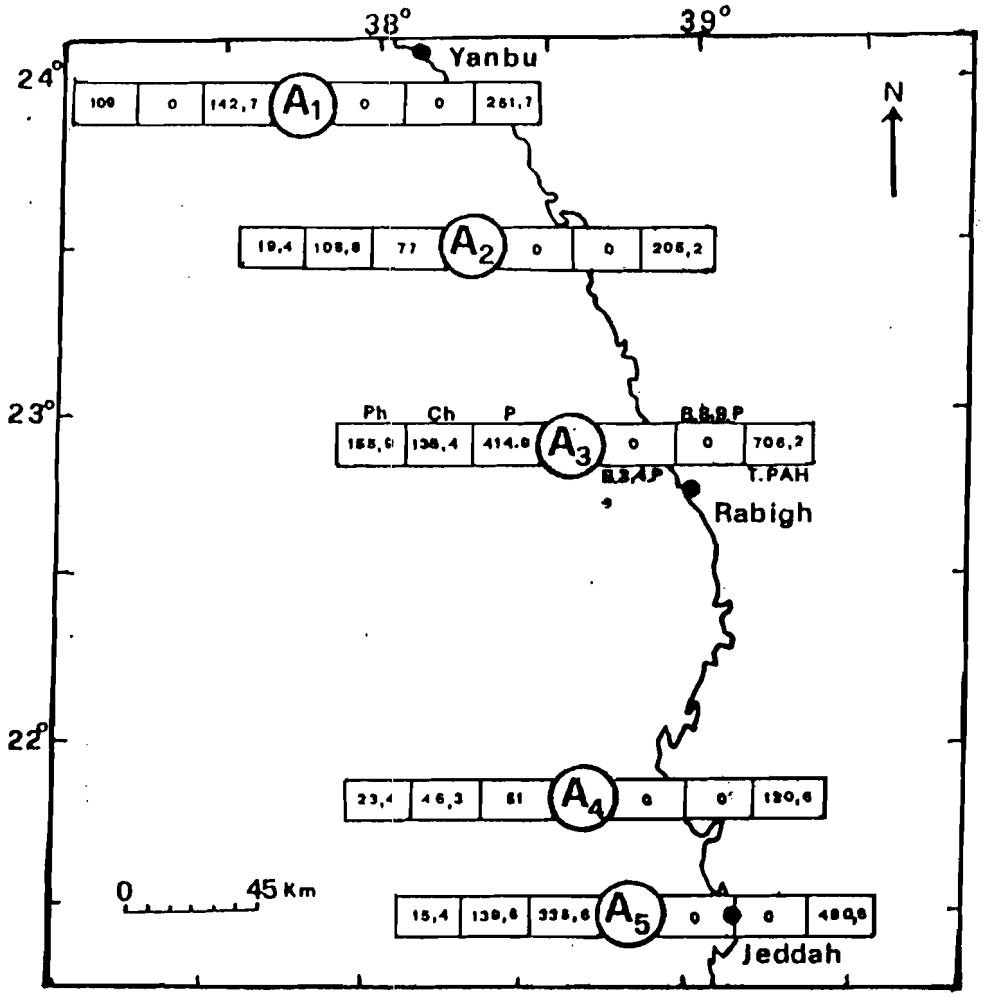

Fig.1 - Zonal distribution of individual PAH concentration in area A
(Ph : phenanthrene; Ch : chrysene; P : pyrene
B3,4P : benzo-3,4-pyrene; B8,9P : benzo-8,9-perylene;
T.PAH : total polyaromatic hydrocarbon, all in ng l^{-1}).

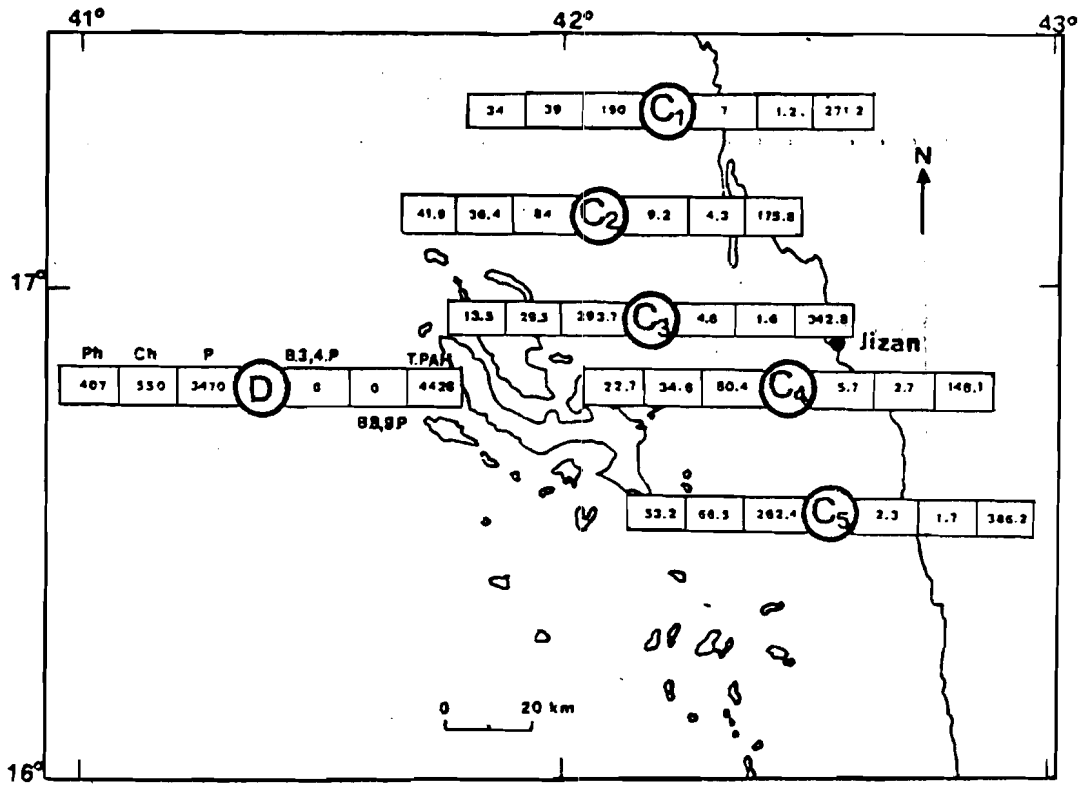

Fig.2 - Zonal distribution of individual PAH concentration in areas C and D (Ph : phenanthrene; Ch : chrysene; P : pyrene; B3,4P : benzo-3,4-pyrene; B8,9P : benzo-8,9-perylene; T.PAH : total polyaromatic hydrocarbon, all in ng l^{-1}).

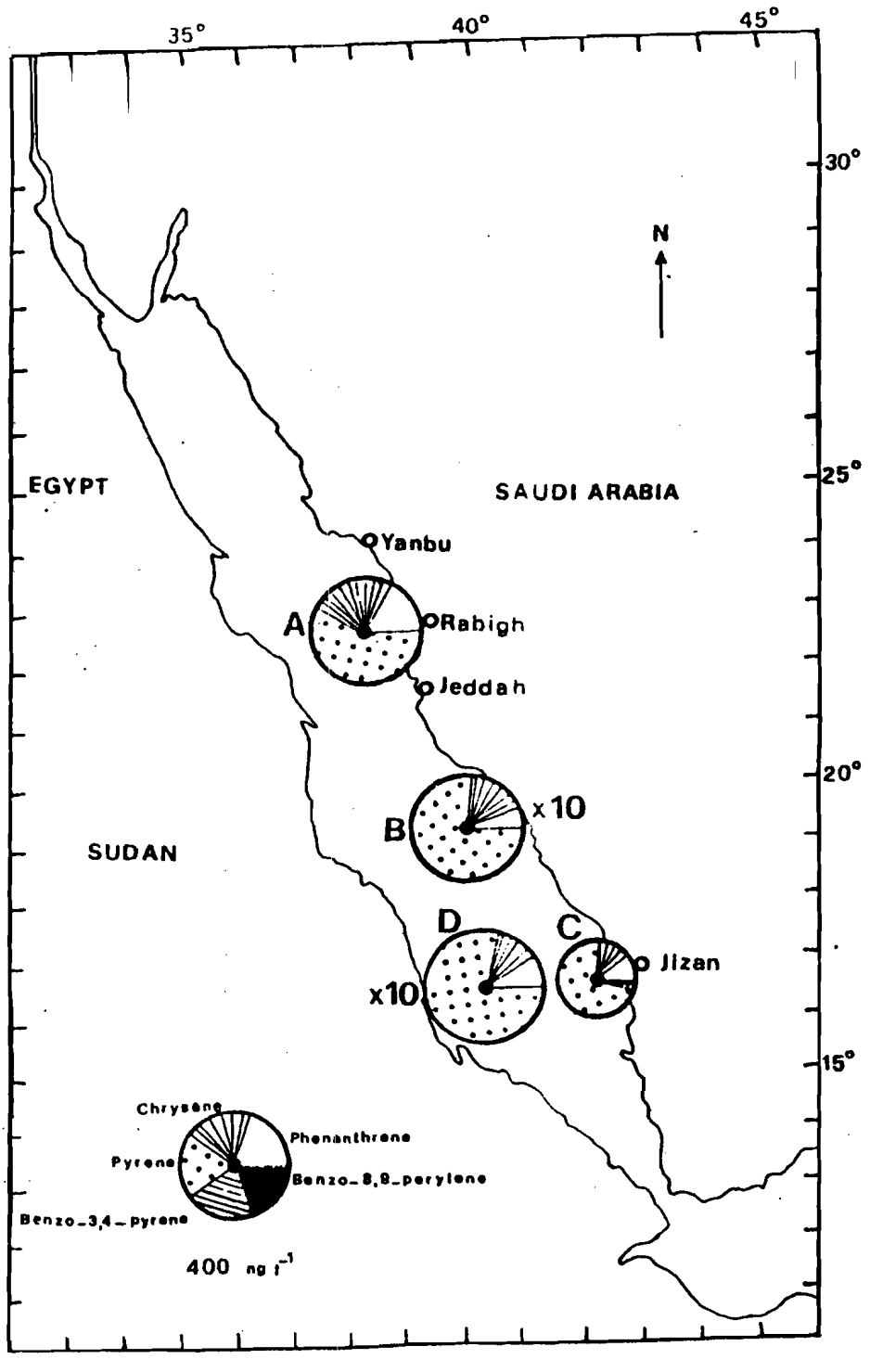

Fig.3 - Relative composition of PAH along the studied areas.