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REPORT ON THE CONTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) TO THE MARINE ENVIRONMENT FROM DIFFERENT INDUSTRIES

By

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INTRODUCTION

The polycyclic or polynuclear aromatic hydrocarbons, also called PAH, have been the focus of considerable interest for many years because of their possible carcinogenic effects. Considerable research has also been devoted to the presence of PAH, especially benzo(a)-pyrene, in sediments and marine organisms. The uptake of PAH in marine organisms from oil polluted areas has been described in several reports. CAHNMANN and KURATSUNE (1957) found benzo-(a)pyrene and other PAH components to be present at a level of approx. 0.2 mg/kg in oysters. LEE et al. (1972 a, b), working on the uptake of petroleum hydrocarbons by marine invertebrates, reported that neither straight chain nor aromatic hydrocarbons were metabolized by the invertebrate system examined. In a later paper (LEE et al. 1972 c), they reported that three fish species rapidly (within minutes) took up ^{14}C-naphthalene and ^{3}H-3,4-benzo(a)pyrene through the gills and were able to metabolize the compounds.

They further reported that the marine copepod Calanus helgolandicus was killed by benzo(a)pyrene at a concentration of 4µg/1.

The majority of investigations of PAH in the marine environment have been performed by MALLET and his co-workers (SUESS 1970). They made systematic studies of benzo(a)pyrene in the Atlantic ocean, the English Channel and along the Mediterranean coast of France. ANDELMAN and SUESS (1970) have reviewed reports on concentrations of benzo(a)pyrene in marine flora, fauna and sediments.

The main sources of PAH have been referred to as being petroleum refineries, petrochemical industries, the burning of fossile fuels (coal and oil) and other urban activities.

The contribution of PAH described in this report refers to industries using Søderberg electrodes, i.e. aluminium smelters, ferro-silicium- and iron works, etc.. Søderberg electrodes are made of anthracite, coke tar, pitch and anthracene oil. During the production of aluminium, ferro-silicium, calciumcarbide, etc., the Søderberg electrode is burned continuously and the high boiling polycyclic aromatic hydrocarbons escape with the fumes. (The production of one ton of aluminium, for example, consumes half a ton of electrode material).

There are two ways for environmental contamination of PAH to occur from this type of industry. The first is the distribution to the environment with the fumes; this is especially the case with open ferro-silicium furnaces. The second is the contribution from the gas scrubber systems used. Some factories use sea water in their wet scrubbers and release the effluent directly to the sea. Others use closed systems, neutralisation with calcium hydroxide and release of the sludge to the sea.

The purpose of this preliminary investigation has been to identify the polycyclic aromatic hydrocarbons from industries using Søderberg electrodes and to map the gradients of PAH in the respective fjord systems.

MATERIALS

In May 1972 sludge was collected from the gas scrubber system in an aluminium smelter situated in Sognefjord. Sediments and sea water were collected from the harbour area and 24 different benthic organisms were collected by a frogman. Reference organisms were collected at the public aquarium in Bergen and reference sea water from another fjord. Later, core samples from 9 fjords have been collected (Figure 1, Table I). Raw material and by-products from the production of Søderberg electrodes have also been analysed for PAH components.

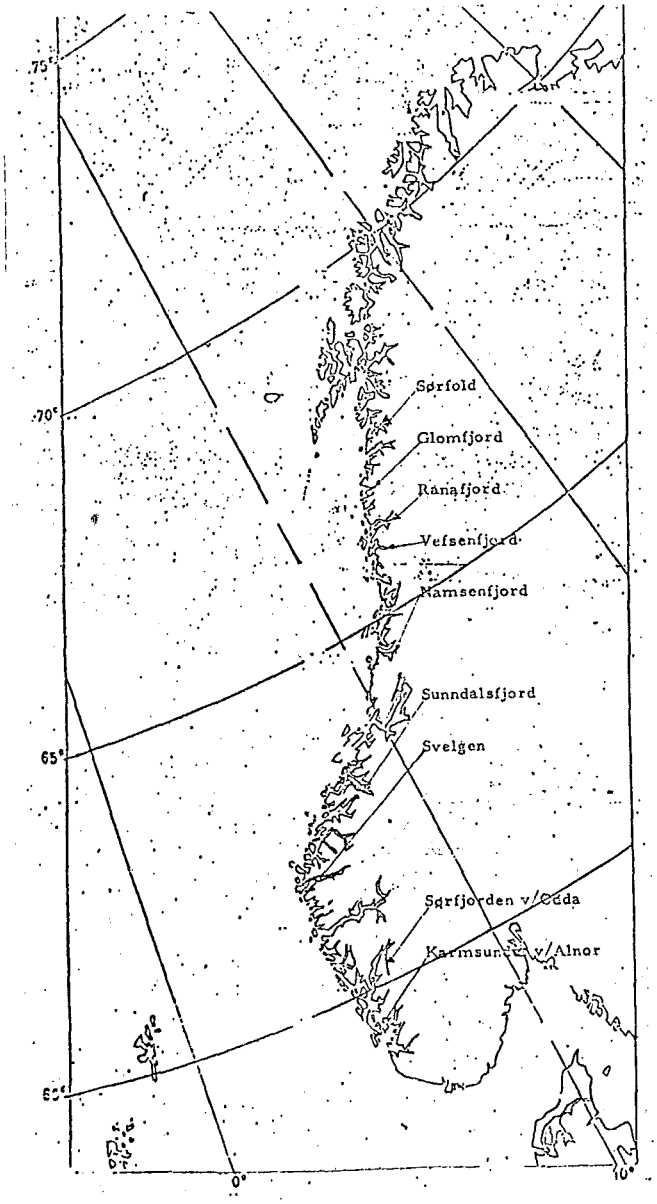


Figure 1

Geographic distribution of core sampling localities.

Table I

Summary of sample areas, station numbers and positions.

Area	Station no. / Position													
Sørfold May 1973	347	348	349	350	351	352	353							
	North	67°33'	67°36,5'	67°35,3'	67°31,8'	67°29,7'	67°26'	67°23,5'						
	East	14°46,5'	15°01'	15°09,2'	15°16'	15°30'	15°32,2'	15°34,8						
	Depth in meters	540	510	356	563	420	133	64						
Area	Station no. / Position	356	357	358	359	360	361							
Glomfjord May 1973	North	66°43,6'	66°46,5'	66°48,2'	66°49'	66°48,5'	66°45,1'							
	East	13°11'	13°15,2'	13°24'	13°37'	13°48'	13°59,2'							
	Depth in meters	223	103	139	370	274	179							
Area	Station no. / Position	362	363	364	365	366	367	368	369	370x	371	372	373	374
Ranafjord May 1973	North	66°15'	66°08'	66°09,2'	66°12'	66°13,8'	66°12,8'	66°14,2'	66°15,1'	66°15,9'	66°18'	66°20'	66°19'	66°18'
	East	12°37'	12°41'	12°57'	13°13,5'	13°23,2'	13°36,3'	13°36,4'	13°44,6'	13°55'	14°02'	14°07'	14°04,5'	14°05,5'
	Depth in meters	400	306	438	380	307	76	317	530	474	331	430	220	270
Area	Station no. / Position	395	396	397	398	399	400	401	402	403				
Velsenfjord May 1973	North	65°49,8'	65°55'	65°57,4'	65°58,7'	65°55,5'	65°54,2	65°51,5'	65°51,1'	65°51,2'				
	East	12°31,7'	12°38,3'	12°44,8'	12°51,8'	12°58,5'	13°8,4'	13°10,5'	13°10,7'	13°10,9'				
	Depth in meters	326	269	233	484	480	410	171	106	192				
Area	Station no. / Position	340	341	342	343	344	345	346						
Namsenfjord May 1973	North	64°42'	64°38'	64°34'	64°30'	64°28,5'	64°27,4	64°27,3'						
	East	10°42'	10°58'	11°06'	11°11,7'	11°19,8'	11°25'	11°30'						
	Depth in meters	201	532	448	345	328	280	122						
Area	Station no. / Position	49	50	51	52	53								
Sørfjord April 1972	North	60°04,8'	60°07,4'	60°10,6'	60°18'	60°24,8'								
	East	6°32,6'	6°33'	6°34'	6°37,4'	6°55'								
	Depth in meters	(45)	(190)	(360)	(370)	(700)								
Area	Station no. / Position	1x	2	3x	4	5								
Karmøy-sund Oct. 1972	North	59°21,7'	59°19,7'	59°18,8'	59°17,6'	59°15,8'								
	East	05°18,2'	05°19,6'	05°19,7'	05°19,7'	05°20,5'								
	Depth in meters	35	82	26	78	180								
Area	Station no. / Position	1	2	3	4	5								
Sunndals-fjord Nov. 1972	North	62°41,2'	62°41,5'	62°44'	62°48,6'	62°59,2'								
	East	08°32'	08°31,5'	08°30'	08°13'	07°59'								
	Depth in meters	87	102	190	320	290								
Area	Station no. / Position	1	2	3	4									
Svelgen, Bremanger Oct. 1972	North	61°46,3'	61°46,3'	61°45,9'	61°45,2'									
	East	05°16,2'	05°14,9'	05°11,4	05°07,5'									
	Depth in meters	95	135	135	170									

x = No core sample.

( ) = No ecco depth.

The following marine organisms collected by a frogman have been identified.

Modiolus modiolus

Hiatella arctica

Eupagurus pubescens

Monia patelliformis

Asterias rubens

Littorina sp.

Echinus esculentus

Strongylocentrotus droebachiensis

Fucus serratus

Lithodes maja

Hyas coarctatus

Balanus balanoides

Ichnochiton albus

Cibrillina punctata

Callopora linéata

Cribrilina annulata

Stomatopora diastoporides

Escharella ventricosa

Tubulipora sp.

Electra catenularia

Spirorbis sp.

Hydroides norvegicus

Pomatoceros triqueter

Corella parallellogramma

ANALYTICAL METHODS

The dry samples, powdered material from electrodes and used cathodes were extracted for approx. 4 hours in Soxhlet apparatus with chloroform.

Water samples were extracted with 3 x 20 ml chloroform. Sludge samples were dried at 90 °C overnight before extraction.

The biological samples were cut into small pieces and dried at 90 °C overnight before extraction.

The chloroform extract were dried over anhydrous sodium sulphate, evaporated under redused pressure and taken up in a measured volume of chloroform

Gas chromatography

Separation was carried out with a Perkin Elmer 900 gas chromatograph using a 100 ft x 0.5 mm i.d. SCOT column packed with polyphenyl-ether OS-138.

Conditions:

Inj. temp.:	240 °C
Column temp.:	150 - 240 °C, prog. at 2 °C/min.
Carrier gas:	approx. 1.5 ml He/min.

Thin layer chromatography

The polycyclic aromatic hydrocarbons were separated on precoated Silicagel G thin layer plates run in two systems.

System I:	Hexane
System II:	Benzene - pentane - acetic acid (50:30:2), used for examination of heavier components.

Examination of the thin layer chromatograms was carried out under UV-light (254 nm).

Combined gas chromatography-mass spectrometry

Identification of the different polycyclic aromatic hydrocarbons was made using a Varian Series 1400 gas chromatograph coupled directly to a Finnigan Model 3000-003 mass spectrometer. Recorder Perkin Elmer 165. The columns employed and operating temperatures were identical to those described above.

Core sampling

The core sampler used measured 18 mm i.d. x 660 mm and was based upon the design of MOORE and NEIL (1930).

RESULTS

Figures 2, 3 and 4 show that the gas chromatographic patterns of chloroform extracts of sediments, Hyas coarctatus and anthracene oil are similar. The thin layer chromatograms of extracts of Modiolus modiolus, Asterias rubens and Hyas coarctatus (fig. 5) collected near an aluminium smelter indicate the presence of polycyclic aromatic hydrocarbons whereas the same organisms from the public aquarium in Bergen do not contain detectable amounts of these compounds. Thin layer chromatograms of waste water and sea water from the area near an aluminium smelter also exhibit PAH-components (fig. 6)

Identification of the main polycyclic aromatic hydrocarbons in anthracene oil, used in the production of electrodes for aluminium smelters, has been achieved using the combination of gas chromatography-mass spectrometry. The components are in the boiling range of 182°C, for indene, to 393°C, for pyrene (Table II).

Table III summarizes the identified PAH components from anthracene oil and those components found in the wet gas scrubber systems. Furthermore, the table gives a summary of the components found in "lurgi tar" (a byproduct) and used cathodes and anodes, together with the raw materials (anthracite and coke).

At the end of the table are shown the components identified in fjord sediments and the marine organism, Hyas coarctatus.

Petrol coke and pitch were also analysed, but none of the identified PAH components were found.

The quantitative analysis of the sediment cores is based on the measurement of anthracene + phenanthrene, fluoranthene and pyrene. Table IV shows the content of these components in sludge from the gas scrubber system in an aluminium smelter and in fjord sediment in the area where the sludge is released.

Tables V to X show the results from Sørfjord with an aluminium smelter and calcium carbide works, Karmsund with an aluminium smelter, Svelgen with a ferro silicium works, Sunndalsfjord with an aluminium smelter at Sunndalsøra, Vefsenfjord with an aluminium smelter at Mosjøen, and Ranafjord with iron and coke works at Mo. The figures 7 to 11 show the gradient of PAH in the respective fjords.

PAH components in sediment cores from the Sørfold- and Glomfjord-areas, representing ferro-silicium and fertilizer industries respectively, were not detectable in the amount of material (the upper 1 cm of the core) chosen for the gradient studies.

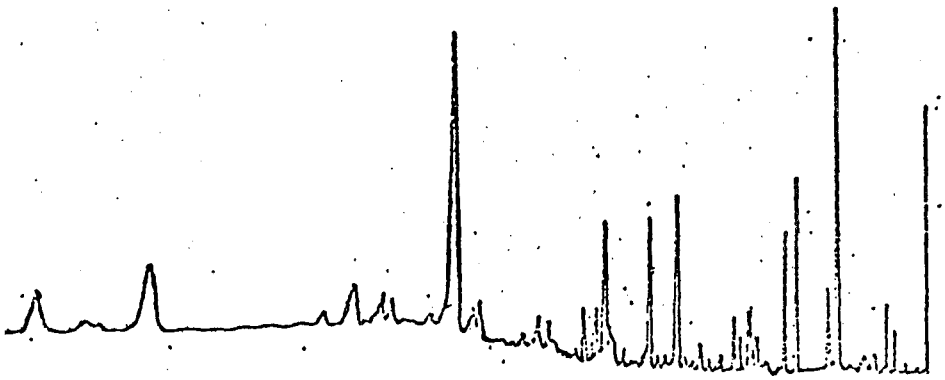


Figure 2.

Gas chromatogram of anthracene oil.

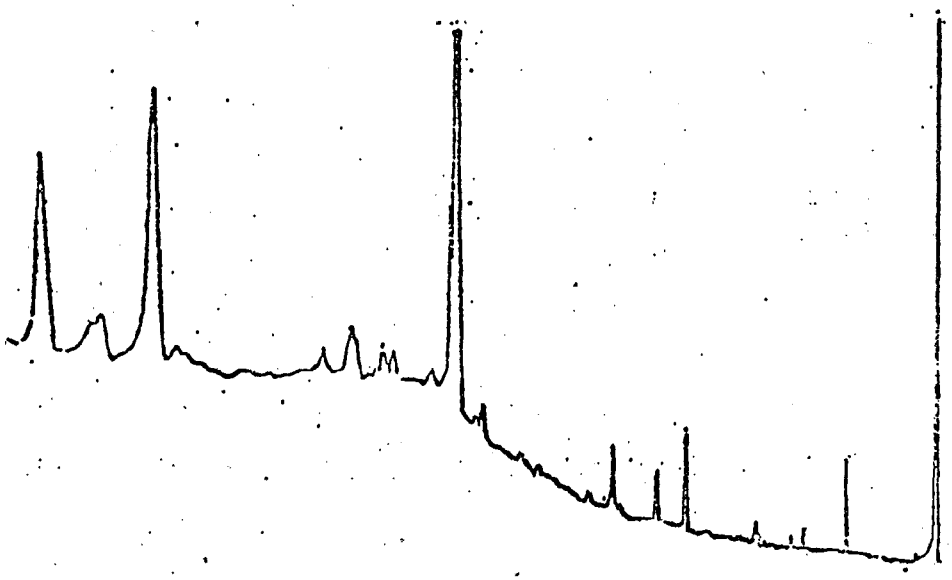


Figure 3.

Gas chromatogram of a chloroform extract of bottom sediment in the vicinity of an aluminium smelter.

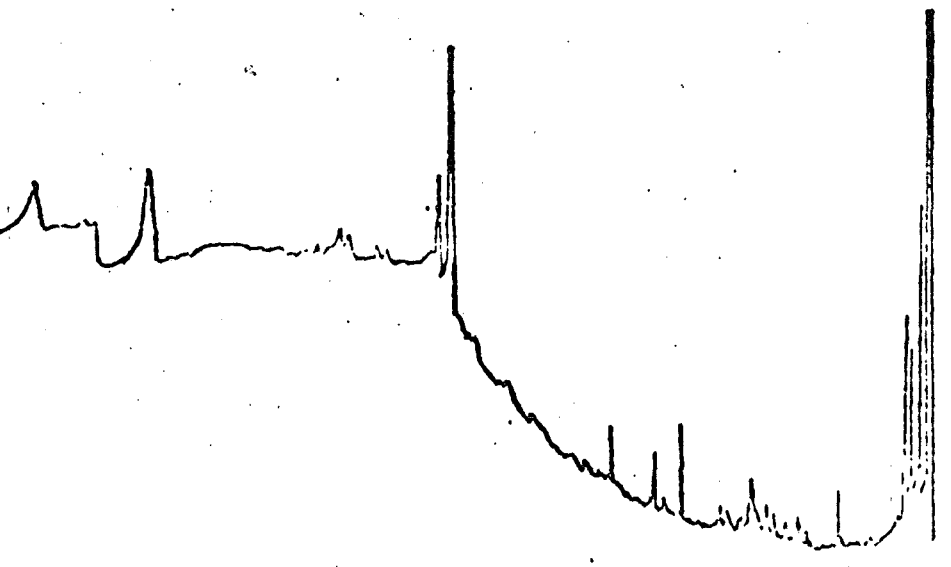


Figure 4.

Gas chromatogram of a chloroform extract of Hyas coarctatus collected in the vicinity of an aluminium smelter.

Figure 5.

Thin layer chromatogram of chloroform extracts from marine organisms.

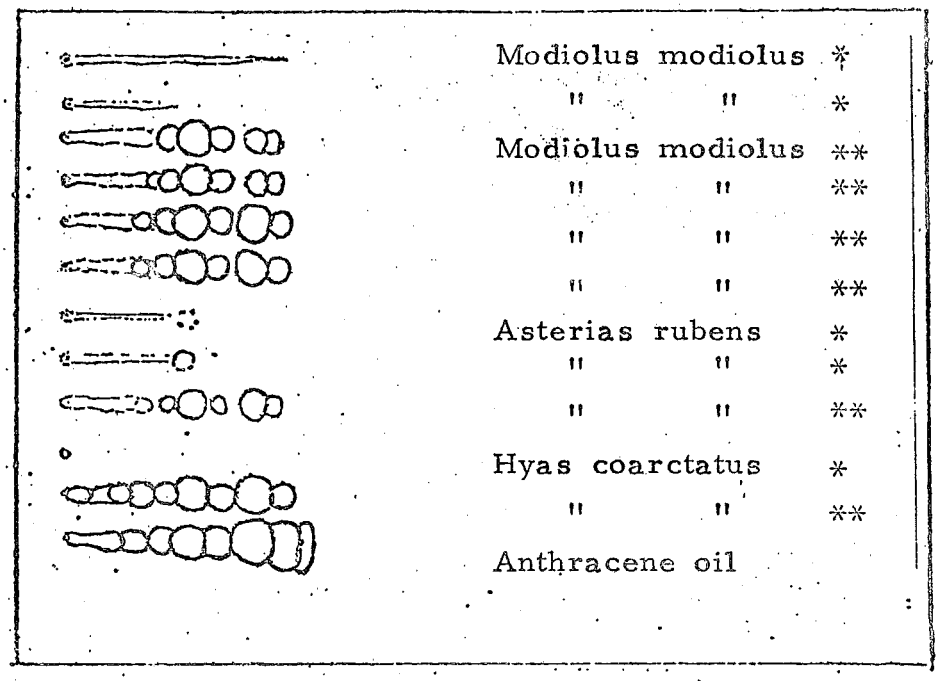
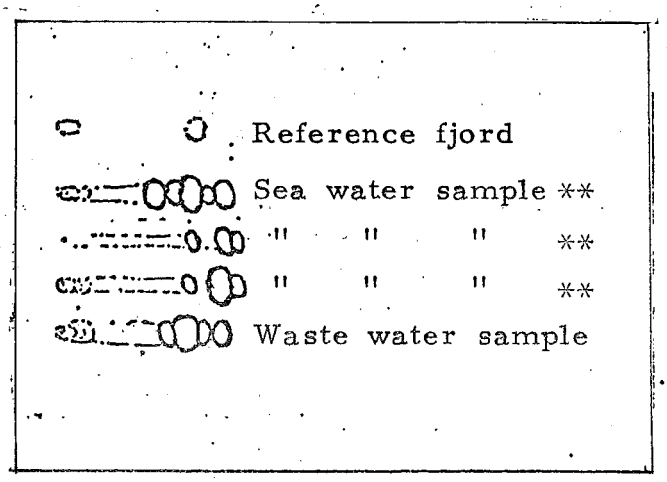


Figure 6.

Thin layer chromatogram of chloroform extracts from samples of sea water and aluminium smelter waste water.



* Sample from the public aquarium Bergen

** Samples from the vicinity of an aluminium smelter.

Table II.

Summary of identified polycyclic aromatic hydrocarbons in anthracene oil

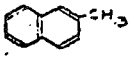
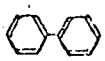
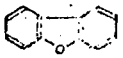
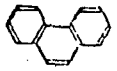
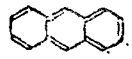
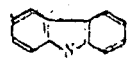
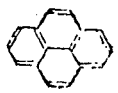
Polycyclic aromatic hydrocarbons	Boiling point °C	Mol. weight	Formula	Structure
Indene	182	116	C_9H_8	
Naphthalene	218	128	$C_{10}H_8$	
β-methylnaphthalene	241	142	$C_{11}H_{10}$	
Isoquinoline	243	129	C_9H_7N	
α-methylnaphthalene	245	142	$C_{11}H_{10}$	
Biphenyl	256	154	$C_{12}H_{12}$	
Dimethylnaphthalene	268	156	$C_{12}H_{12}$	
"		"	"	isomers
"		"	"	
Acenaphthene	279	154	$C_{12}H_{10}$	
Dibenzofuran	287	154	$C_{12}H_8O$	
Fluorene	293	166	$C_{13}H_{10}$	
Phenanthrene	340	178	$C_{14}H_{10}$	
Anthracene	340	178	$C_{14}H_{10}$	
Methylphenanthrene	150[6]	192	$C_{15}H_{12}$	
"		"	"	isomers
"		"	"	
Carbazole	355	167	$C_{12}H_9N$	
Fluoranthene	375	167	$C_{16}H_{10}$	
Pyrene	393	202	$C_{16}H_{10}$	

Table III. Summary of identified polycyclic aromatic hydrocarbons in the material analysed.

Polycyclic aromatic hydrocarbons	Anthracene oil	Sludge	Used cathodes	Anthra-cite	Used anodes	Coke	Lurgi-tar	Fjord sediment	Hyas coarctatus
Indene	+								
Naphthalene	+		+	+	+	+		+	+
β -methylnaphthalene	+		+	+	+	+		+	+
Isoquinoline	+								
α -methylnaphthalene	+		+	+	+	+		+	+
Biphenyl	+		+	+	+	+		+	+
Dimethylnaphthalene	+					+			
"	+					+			
"	+					+			
Acenaphthene	+		+	+	+	+		+	+
Dibenzofuran	+		+	+	+	+	+	+	+
Fluorene	+	+	+	+	+	+	+	+	+
Phenanthrene	+	+	+	+	+	+	+	+	+
Anthracene	+	+	+	+		+	+	+	+
Methylphenanthrene	+	+				+	+	+	+
"	+	+				+	+	+	+
"	+	+				+	+	+	+
Carbazole	+	+					+	+	+
Fluoranthene	+	+	+	+	+	+	+	+	+
Pyrene	+	+	+	+	+	+	+	+	+
Extractable organic material in %	-	1.0	0.01	0.03	0.02	0.15	-	4.0	-

Table IV.

Concentration of some polycyclic aromatic hydrocarbons in mg/kg dry weight of scrubber sludge and fjord sediment.

Analysed components	mg/kg dry weight	
	Scrubber sludge	Fjord sediment
Anthracene + Phenanthrene	240	560
Fluoranthene	250	680
Pyrene	220	520

Table V.

Concentration of some polycyclic aromatic hydrocarbons in mg/kg wet weight of sediment cores from Sørfjorden.

Analysed components	mg/kg wet weight				
	St. 49	St. 50	St. 51	St. 52	St. 53
Anthracene + Phenanthrene	1.4	0.79	0.63	0.76	0.66
Fluoranthene	0.4	0.64	0.08	0.11	0.06
Pyrene	0.5	0.50	0.50	0.06	0.06
Σ	2.3	1.9	0.8	0.9	0.8

Table VI.

Concentration of some polycyclic aromatic hydrocarbons in mg/kg dry weight of sediment cores from Karmsundet near Alnor.

Analysed components	mg/kg dry weight				
	St. 1	St. 2	St. 3	St. 4	St. 5
Anthracene + Phenanthrene	-	0.5	-	0.81	0.2
Fluoranthene	-	1.0	-	1.3	0.4
Pyrene	-	0.9	-	1.4	0.4
Σ	-	2.4	-	3.51	1.0

Table VII.

Concentration of some polycyclic aromatic hydrocarbons in mg/kg dry weight of sediment cores from Svelgen.

Analysed components	mg/kg dry weight			
	St. 1	St. 2	St. 3	St. 4
Anthracene + Phenanthrene	0.2	n.d.*	n.d.	n.d.
Fluoranthene	0.4	n.d.	n.d.	n.d.
Pyrene	0.4	n.d.	n.d.	n.d.
Σ	1.0			

* n.d. = not detectable.

Table VIII

Concentration of some polycyclic aromatic hydrocarbons in mg/kg dry weight of sediment cores from Sunndalsfjord.

Analysed components	mg/kg dry weight				
	St. 1	St. 2	St. 3	St. 4	St. 5
Anthracene + Phenanthrene	1,3	0,83	0,06	0.1	n.d.*
Fluoranthene	1.9	1,3	0,2	0.2	n.d.
Pyrene	1,7	1,4	0,2	0.2	n.d.
Σ	4.9	3,53	0,46	0,5	n.d.

* n.d. = not detectable

Figure 7.

Map showing positions of core samples and gradient of polycyclic aromatic hydrocarbons in Sørfjorden. (Aluminium smelter and calcium carbide works at Odda).

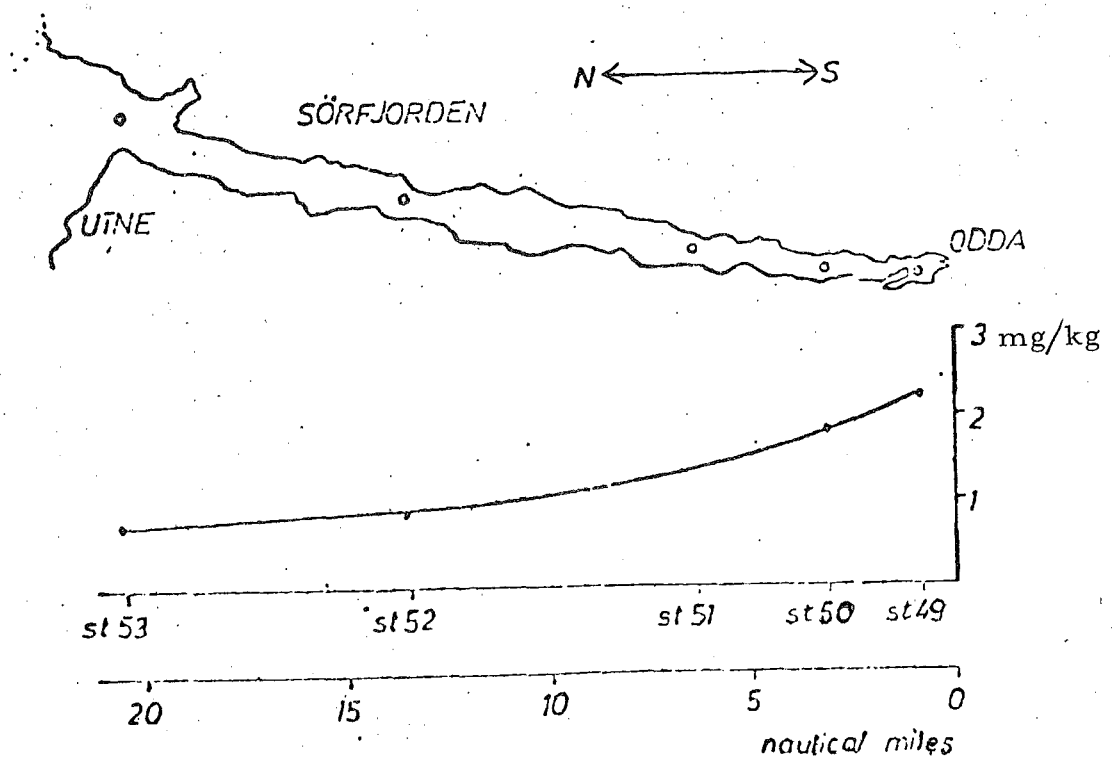


Table IX.

Concentration of some polycyclic aromatic hydrocarbons in mg/kg dry weight of sediment cores from Vefsenfjord.

Analysed components	mg/kg dry weight								
	St. 395	St. 396	St. 397	St. 398	St. 399	St. 400	St. 401	St. 402	St. 103
Anthracene + Phenanthrene	n.d.*	trace	0.05	0.24	0.2	0.79	1.57	1.82	0.5
Fluoranthene	n.d.	"	0.12	0.29	0.34	1.05	2.04	3.54	0.75
Pyrene	n.d.	"	0.12	0.24	0.28	0.83	1.96	2.97	0.7
Σ			0.29	0.77	0.82	2.67	5.57	8.33	2

* n.d. = not detectable

Table X

Concentration of some polycyclic aromatic hydrocarbons in mg/kg dry weight of sediment cores from Ranafjord.

Analysed components	mg/kg dry weight												
	St. 362	St. 363	St. 364	St. 365	St. 366	St. 367	St. 368	St. 369	St. 370	St. 371	St. 372	St. 373	St. 374
Anthracene + Phenanthrene	trace	trace	0.24	0.17	0.12	0.15	0.17	0.07	-	0.33	trace	0.77	0.27
Fluoranthene	"	"	0.09	0.20	0.30	0.10	0.37	0.17	-	0.50	"	0.85	0.30
Pyrene	"	"	0.09	0.20	0.20	0.098	0.25	0.15	-	0.42	"	0.74	0.27
Σ			0.4	0.6	0.62	0.35	0.80	0.40		1.25		2.36	0.84

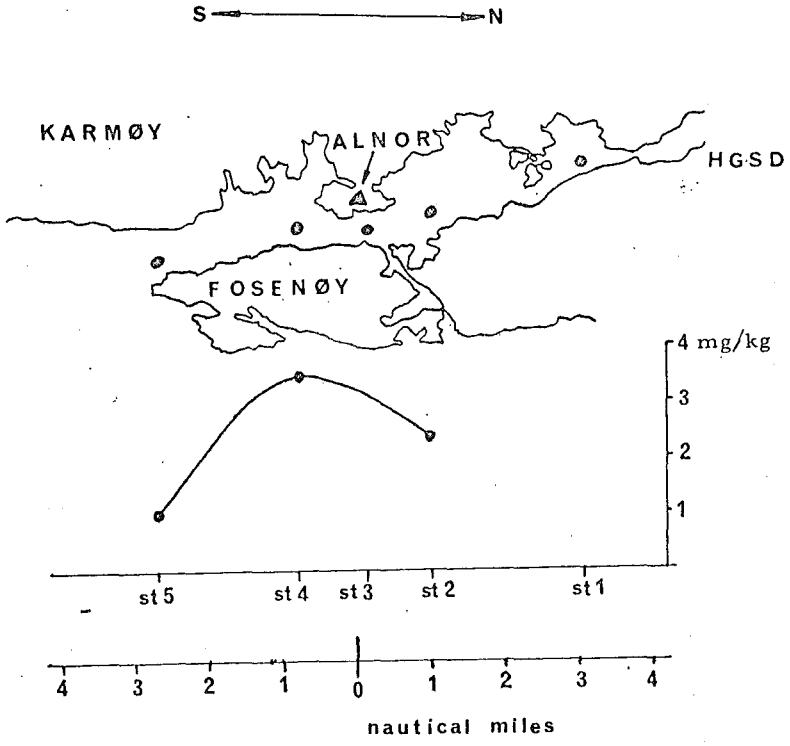


Figure 8

Map showing positions of core samples and the gradient of polycyclic aromatic hydrocarbons in Karmsund. (Alnor aluminium smelter).

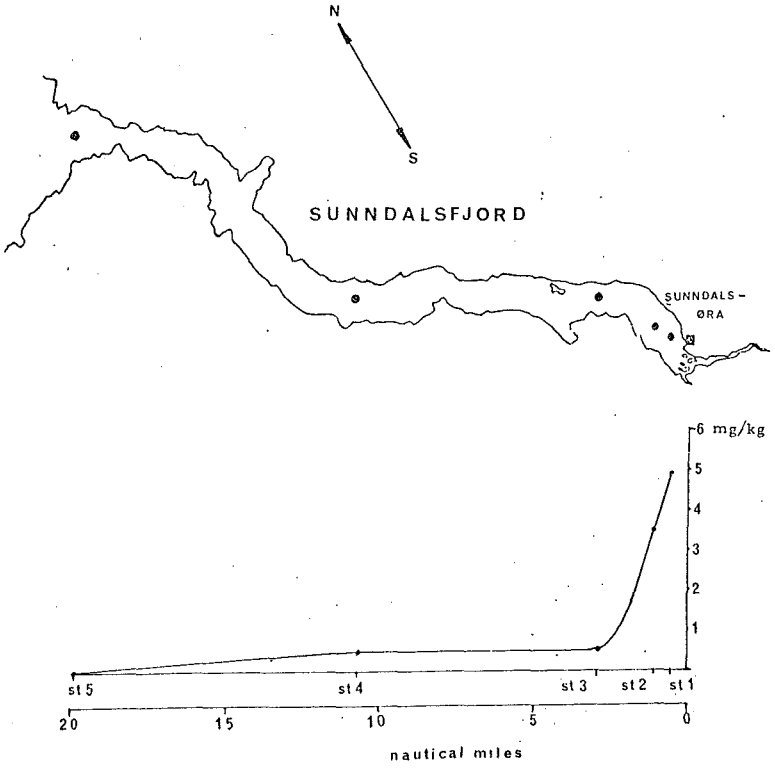


Figure 9

Map showing positions of core samples and the gradient of polycyclic aromatic hydrocarbons in Sunndalsfjord. (Aluminium smelter at Sunndalsøra).

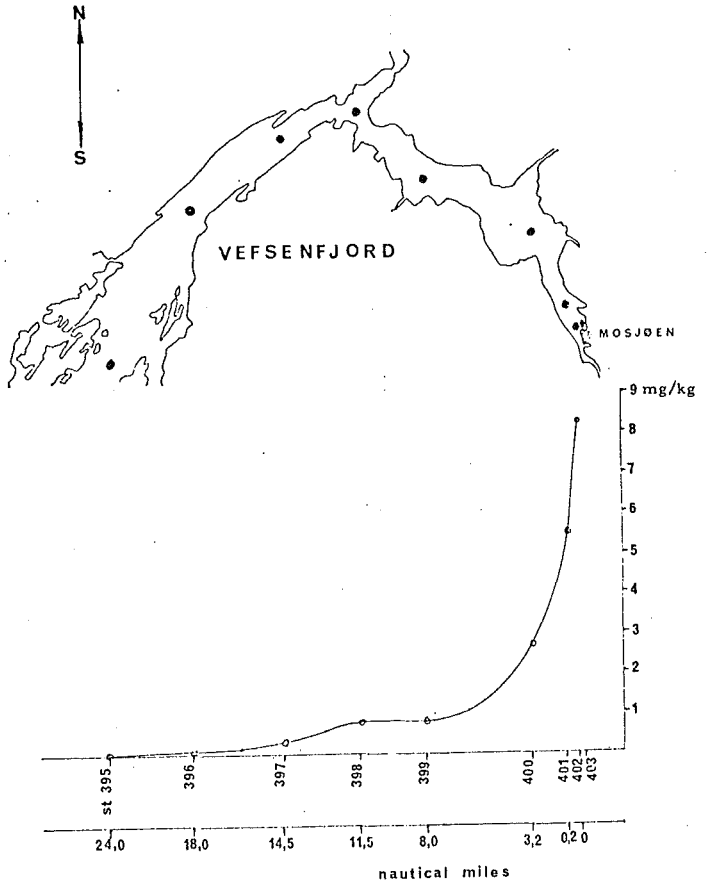


Figure 10.

Map showing positions of core samples and the gradient of polycyclic aromatic hydrocarbons in Vefsenfjord. (Aluminium smelter at Mosjøen).

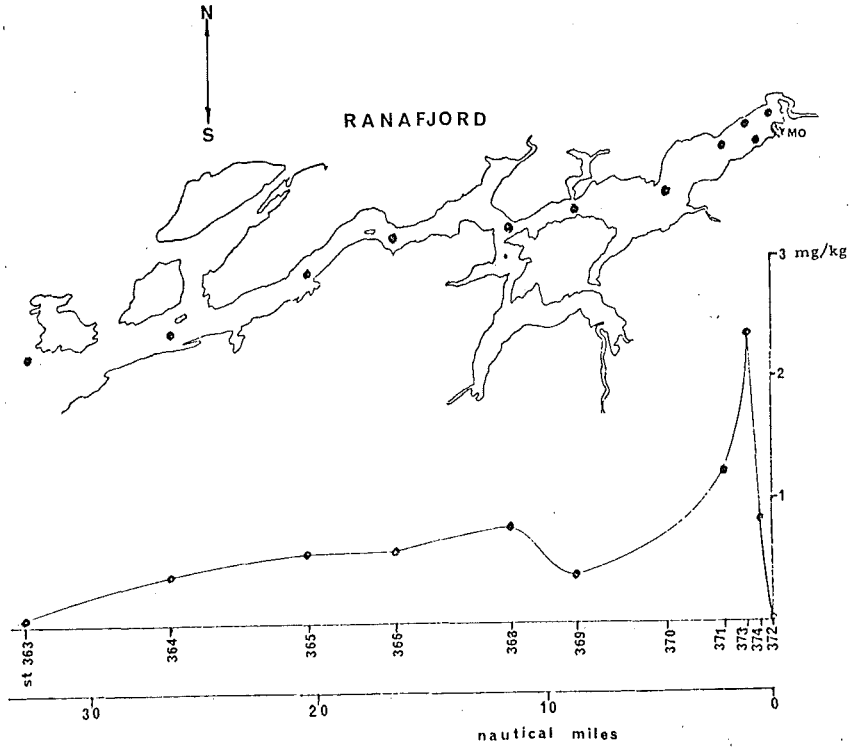


Figure 11.

Map showing positions of core samples and the gradient of polycyclic aromatic hydrocarbons in Ranafjord. (Iron and coke works at Mo).

DISCUSSION

The solubility of polycyclic aromatic hydrocarbons in pure water is extremely low as should be expected from their high molecular weights and lack of polar substituents. An illustrating example is given by BORNEFF and KNERR (1960) who equilibrated distilled water with crystals of 1,2,5,6-dibenzanthracene for two years and could not detect the compound in the water using an analytical technique sensitive to 0.01µg/l. Several mechanisms exist, however, for increasing the concentration of such components. McBAIN and HUTCHINSON (1955) have described a solubilization phenomenon in which otherwise insoluble matter is brought into solution by colloidal matter, specifically by micelles. Micelles containing PAH are for example formed in water containing synthetic detergents.

Another phenomenon, mentioned by ANDELMAN and SUESS (1970), is hydrotrophy, which is described as the increase in solubility of PAH in water caused by other organic compounds which is not associated with the formation of colloids. Butyric- and lactic-acid (EKWALL and SJØBLOM 1952) are given as examples of such compounds and it is therefore reasonable to believe that an increased solubility of PAH may occur due to a wide range of organic compounds occuring naturally in sea water.

A third important factor in the distribution of PAH in the marine environment is the sorbtion to surfaces such as activated charcoal, silicia, calcareous material, etc.. It is therefore reasonable that the distribution of PAH, as seen from the gradient studies in this report, depends on suspended material like sludge from wet gas scrubbers, river- and glacier material and also the amount and kind of urban sewage.

The contribution of PAH to the sea from an aluminium smelter can be calculated, based on information from one company, as follows: 1.) the production of 160,000 tons of aluminium consumes 80,000 tons of electrode material, 2.) the formation of 12,000 tons of scrubber sludge containing 20% dry matter resulting from the washing of fumes.

Based upon the values shown in table III, this is equivalent to 24 tons of extractable organic material. The approximate amounts of pyrene, fluoranthene and anthracene + phenanthrene will then be 500, 600 and 600 kg, respectively.

Western Europe has a yearly production of nearly 3 million tons of aluminium, which indicates that the contribution from pyrene alone amounts to 150 tons.

The possible effects of PAH on the marine eco-system are unclear. The marine organisms collected from the vicinity of an aluminium smelter seemed to be in good condition. Modiolus modiolus found to be over 20 years old, did not show any obvious morphological differences compared with specimens collected at the public aquarium in Bergen. We have not, however, examined the different organs or tissues.

The possibility that the PAH content in the examined areas has resulted in an alteration of the biotope during the period of operation of this type of industry (25 years in the present case of an aluminium smelter) is a question which requires further studies on the part of biologists and botanists.

This report shows that PAH is introduced into the marine environment by aluminium smelters, ferrosilicium-, iron- and coke-works in addition to the amounts coming from crude oil, refineries, petro-chemical industries and urban activities.

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