The determination of polycyclic aromatic hydrocarbons in seawater from the *Fluxmanche* transect (Dover Strait)

Polycyclic aromatic hydrocarbons
Seawater
Fluxmanche
GC/MS
Dover Strait

Hydrocarbures polycycliques aromatiques
Eau de mer
Fluxmanche
CG/SM
Pas-de-Calais

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ABSTRACT

Concentrations of a range of polycyclic aromatic hydrocarbons (PAH) were determined by means of coupled gas chromatography-mass spectrometry (GC-MS). Water samples were collected, using a contamination-free sampling device, at two depths (1 m subsurface and 3 m above the seabed) at each of the six stations established in the Dover Strait. The stations were occupied during June and October 1990, and July 1991. Concentrations of PAH were often close to or below the limits of detection for samples of 10.8 l volume, although a number of samples exhibited high concentrations (of naphthalenes in particular) which were apparently derived from shipping inputs in the Dover Strait. Future work will require the development of methods with lower limits of detection, and which can integrate concentrations over different timescales in order to obtain time-averaged concentrations of PAH.

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RÉSUMÉ

Détermination des niveaux d'hydrocarbures polycycliques aromatiques dans l'eau de mer à partir du transect *Fluxmanche* (Pas-de-Calais)

Les concentrations d'un éventail d'hydrocarbures polycycliques aromatiques (HPA) ont été déterminées en utilisant un couplage de chromatographie en phase gazeuse et spectrométrie de masse (CG-SM). Des échantillons d'eau ont été prélevés, en utilisant un dispositif non contaminant, à deux profondeurs (1 m sous la surface et 3 m au-dessus du fond marin) à chacune des six stations situées dans le Pas de Calais, dans le cadre du programme *Fluxmanche* financé par la CEE. Les stations ont été occupées en juin et octobre 1990, et en juillet 1991. Les concentrations de HPA étaient souvent proches des limites de détection dans les échantillons de 10,8 l de volume, ou inférieures à ces limites; plusieurs échantillons présentaient cependant des concentrations élevées (en naphtalènes en particulier), provenant apparemment des déchets de navigation dans le Pas-de-Calais. Pour les travaux futurs, il faudra mettre au point des méthodes dont les limites de détection seront inférieures, et qui pourront intégrer les concentrations à différentes échelles de temps, pour fournir les moyennes temporelles des concentrations de HPA.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental contaminants, and arise from both natural and anthropogenic sources. The latter are, however, the major contributors (Bartle *et al.*, 1981). PAH enter the marine environment from rivers, from the atmosphere (*via* atmospheric aerosols, precipitation and particulates), and as a result of oil discharges from tankers and other ships. The majority of studies of PAH undertaken in the marine environment (*e.g.*, Klamer *et al.*, 1990) have concentrated on their determination in sediments rather than in water, as PAH (particularly those of higher molecular weight) are hydrophobic, and concentrations are therefore considerably higher in sediments. There is also some evidence that PAH adsorbed to sediments are no longer available for geochemical and biological processes, and that re-equilibration with water therefore no longer occurs (Readman *et al.*, 1987).

This paper reports the results of analyses of water samples taken at two depths (1 m subsurface and 3 m above the seabed) at each of six stations established in the Dover Strait. Full details of the physical characteristics, hydrography, *etc.*, of this area are given in other contributions to this volume. The stations were occupied during June and October 1990, and July 1991. To the best of our knowledge, no data comparable to our own exist for offshore waters of the North Sea or English Channel (Compaan and Laane, 1992). Measurements of the Total Hydrocarbon Concentrations in subsurface seawater at the South Varne station (*Fluxmanche 4*) in 1990 and 1992 using ultra-violet fluorescence spectrometry yielded values of 0.4 and 0.2 µg l-1 Ekofisk crude oil equivalents respectively typical of offshore seawater with a low particulate loading, and close to the limits of detection of the technique (MAFF, 1992 and unpublished data).

Compaan and Laane (1992) have roughly estimated the order of magnitude of the transport of PAH into the North Sea in North Atlantic water as 1000 t per annum. The aim of this study was to estimate the concentrations of a range of PAH in subsurface and near-bottom seawater at the six stations forming the *Fluxmanche* transect, to assess whether the techniques currently in use are adequate for flux measurements to be made. The number and frequency of samples taken in this study would obviously be inadequate to fully describe a system as complex as the Dover Strait. Low-level analyses of trace metals in seawater are more fully developed than those for organic compounds, however, and flux measurements for a range of metals are reported elsewhere in this volume (Statham *et al.*, 1993).

METHODS

Seawater samples were collected in 2.7 l glass Winchester bottles, mounted in a stainless-steel frame and fitted with a removable, spring-loaded PTFE stopper (Law *et al.*, 1988). For subsurface samples the sampler was deployed by means of a hand-held nylon rope, for sampling at depth it was attached to a Kevlar hydrowire which was also used for studies of trace metals in seawater. In this way samples may be taken at depths up to 50-60 m. An aliquot of a dichloromethane solution containing known quantities of three deuterated internal standards (naphthalene-d8, anthracene-d10 and pyrene-d10; Aldrich Chemical Company, Gillingham, Dorset, England) was added prior to extraction of the unfiltered samples with dichloromethane (2 x 50 ml per bottle; glass distilled grade; Rathburn Chemicals, Walkerburn, Scotland), and each sample was a composite of the extracts from four bottles (total seawater volume 10.8 l). Sample extracts were stored in glass hypo-vials (Pierce and Warriner, Chester, England) at - 20°C prior to analysis. GC-MS was conducted in the multiple-ion detection, electron impact mode, utilising a Finnigan-MAT Incos-50 quadrupole instrument (Finnigan-MAT, Hemel Hempstead, Hertfordshire, England). The GC column [25 m x 0.32 mm ID with a 0.5 µm film of 5 % phenyl methyl silicone (HP5-

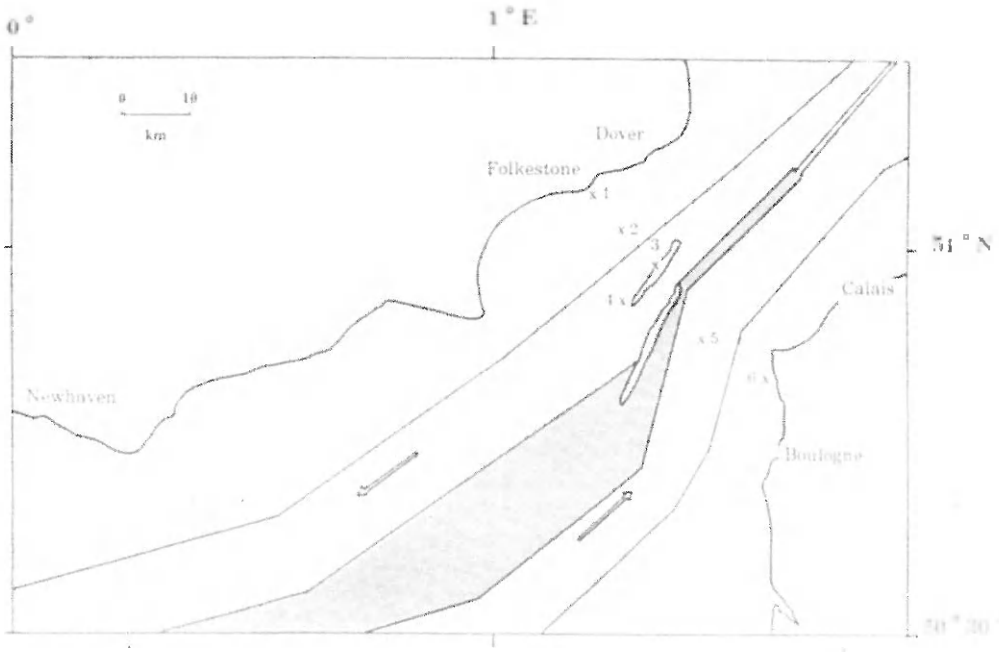

Figure 1

The Dover Strait; stations of the Fluxmanche *transect are indicated by numbers 1 to 6, and the principal shipping traffic separation zones are also shown. Traffic proceeding through the Dover Strait must follow the lanes indicated by arrows and avoid the shaded separation area in the centre of the Strait. Smaller vessels may travel in the inshore areas close to land, and crossing traffic (such as ferries) must cross the lanes at right angles.*

Sample	Salinity (‰)	Chlorinity (‰)	Cruise (1991)
Station 1	35.153	34.994	35.078
Station 2	35.093	35.332	35.090
Station 3	34.990	35.365	35.104
Station 4	35.177	35.319	35.145
Station 5	35.199	35.318	35.153
Station 6	34.676	34.996	34.620

Hewlett-Packard, Winnersh, Berkshire, England) was housed in an HP-5890 gas chromatograph and was directly coupled to the GC ion source *via* a heated transfer line maintained at 300 °C. Sample extracts were reduced to *ca.* 200 µl by means of a stream of nitrogen, care being taken not to allow the concentration to proceed to dryness. GC injections (1 µl; cold on-column) were made *via* an HP7673a autosampler into a 0.5 m x 0.53 mm ID retention gap connected to the analytical column by means of a press-fit zero dead volume connector. The injection temperature of 60 °C was held for 1 minute, then programmed to rise to 300 °C at 5 °C min^{-1}, the final temperature being held for eleven minutes. The MS cycle time was 1 second, and the ions utilised were the parent ions for each of the PAH studied (128 for naphthalene, 136 for naphthalene-d8; 142 for C1-naphthalenes, *etc.*). The limits of detection for each of the compounds and classes can be found in Table 2. A similar analytical scheme has previously been successfully employed in the analysis of industrial chemicals in seawater over a wide volatility range (Law *et al.*, 1991).

RESULTS AND DISCUSSION

The locations of the sampling sites in the Dover Strait (between Folkestone and Cap Gris-Nez) are shown in Figure 1. Table 1 lists the surface salinity values determined for each sampling occasion: all show similar salinity (in the range 35.0 to 35.3) at stations 1 to 5, with a value approximately 0.4 lower at station 6. This presumably reflects the larger freshwater inputs on the French side of the Channel; in this area primarily from the River Seine.

The determined concentrations of PAH are given in Table 2. Naphthalene and phenanthrene were detected in all samples analysed, at concentrations between 0.7 and 18; and 0.9 and 9.3 ng l^{-1} respectively. The higher molecular weight PAH analysed (compounds with molecular weights of 228, 252 and 276) were found in only four samples (three of them from near the sea-bed) and probably reflect a somewhat higher load of suspended particulates, as these compounds are readily adsorbed onto particles. The use of dichloromethane as a solvent yields an efficient extraction of PAH from particulates as well as from the dissolved

Compound	Station 1						Station 2						Station 3					
	S			B			S			B			S			B		
	15	28	48	15	28	48	15	28	48	15	28	48	15	28	48	15	28	48
Naphthalene	4.5	4.3	4.6	11	7.1	6.4	6.1	7.2	7.9	18	9.2	9.1	4.3	4.2	4.4	11	6.3	6.6
C1-Naphthalenes	4.7	4.4	4.7	29	17	9.1	2.5	16	12	66	25	16	4.2	4.1	4.3	33	16	9.8
C2-Naphthalenes	8.0	3.8	3.6	48	21	11	4.1	21	21	110	41	21	3.7	3.6	3.7	43	20	10
C3-Naphthalenes	< 0.2	0.1	< 0.2	15	2.1	1.3	< 0.2	5.1	5.9	150	< 0.2	5.1	< 0.2	< 0.2	< 0.2	42	4.0	2.2
Phenanthrene	4.8	2.1	3.9	9.8	2.3	1.4	2.4	8.9	9.2	8.7	4.1	3.9	2.1	1.9	2.1	9.3	3.3	2.3
Anthracene	< 0.2	0.6	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	1.0	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
C1-Phenanthrenes	< 0.2	< 0.2	< 0.2	2.9	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	2.3	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.4	< 0.2	< 0.2
C2-Phenanthrenes	< 0.2	< 0.2	< 0.2	4.1	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.6	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	4.8	< 0.2	< 0.2
C3-Phenanthrenes	< 0.2	< 0.2	< 0.2	3.1	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.9	< 0.2	< 0.2
Fluoranthene	1.2	1.9	1.9	1.2	1.9	1.9	< 0.5	4.1	9.2	1.2	1.9	1.9	< 0.5	3.9	9.2	1.2	1.9	1.9
Pyrene	2.1	0.9	2.0	1.9	1.2	< 0.1	< 0.1	1.5	6.3	3.3	1.8	< 0.1	< 0.1	1.4	6.4	3.3	1.8	< 0.1
Benzo[a]anthracene	< 1	2.4	< 1	< 1	< 1	< 1	< 1	1.6	3.6	< 1	< 1	< 1	< 1	3.2	3.6	< 1	< 1	< 1
Chrysene/Triphenylene	< 1	3.4	< 1	< 1	< 1	< 1	< 1	2.8	6.8	< 1	< 1	< 1	< 1	1.6	6.9	< 1	< 1	< 1
C1-Benzanthracene	< 1	2.3	< 1	< 1	< 1	< 1	< 1	1.8	6.4	< 1	< 1	< 1	< 1	1.8	6.4	< 1	< 1	< 1
Benzo[b]fluoranthene	< 1	2.5	< 1	< 1	< 1	< 1	< 1	< 1	1.3	< 1	< 1	< 1	< 1	< 1	1.3	< 1	< 1	< 1
Benzo[k]fluoranthene	< 1	1.2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Benzo[e]pyrene	< 1	2.3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Perylene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Indeno[123-cd]pyrene	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Benzo[ghi]perylene	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2

Compound	Station 4						Station 5						Station 6					
	S			B			S			B			S			B		
	15	28	48	15	28	48	15	28	48	15	28	48	15	28	48	15	28	48
Naphthalene	4.3	4.2	4.4	11	6.3	6.6	4.3	4.2	4.4	11	6.3	6.6	4.3	4.2	4.4	11	6.3	6.6
C1-Naphthalenes	4.2	4.1	4.3	33	16	9.8	4.2	4.1	4.3	33	16	9.8	4.2	4.1	4.3	33	16	9.8
C2-Naphthalenes	3.7	3.6	3.7	43	20	10	3.7	3.6	3.7	43	20	10	3.7	3.6	3.7	43	20	10
C3-Naphthalenes	< 0.2	< 0.2	< 0.2	42	4.0	2.2	< 0.2	< 0.2	< 0.2	42	4.0	2.2	< 0.2	< 0.2	< 0.2	42	4.0	2.2
Phenanthrene	2.1	1.9	2.1	9.3	3.3	2.3	2.1	1.9	2.1	9.3	3.3	2.3	2.1	1.9	2.1	9.3	3.3	2.3
Anthracene	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
C1-Phenanthrenes	< 0.2	< 0.2	< 0.2	3.4	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.4	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.4	< 0.2	< 0.2
C2-Phenanthrenes	< 0.2	< 0.2	< 0.2	4.8	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	4.8	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	4.8	< 0.2	< 0.2
C3-Phenanthrenes	< 0.2	< 0.2	< 0.2	3.9	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.9	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.9	< 0.2	< 0.2
Fluoranthene	1.2	1.9	1.9	1.2	1.9	1.9	< 0.5	3.9	9.2	1.2	1.9	1.9	< 0.5	3.9	9.2	1.2	1.9	1.9
Pyrene	3.3	1.8	< 0.1	3.3	1.8	< 0.1	< 0.1	1.4	6.4	3.3	1.8	< 0.1	< 0.1	1.4	6.4	3.3	1.8	< 0.1
Benzo[a]anthracene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	3.2	3.6	< 1	< 1	< 1	< 1	3.2	3.6	< 1	< 1	< 1
Chrysene/Triphenylene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1.6	6.9	< 1	< 1	< 1	< 1	1.6	6.9	< 1	< 1	< 1
C1-Benzanthracene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1.8	6.4	< 1	< 1	< 1	< 1	1.8	6.4	< 1	< 1	< 1
Benzo[b]fluoranthene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1.3	< 1	< 1	< 1	< 1	< 1	1.3	< 1	< 1	< 1
Benzo[k]fluoranthene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Benzo[e]pyrene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Perylene	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Indeno[123-cd]pyrene	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Benzo[ghi]perylene	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2

S = No sample or sample lost. TABLE 3 (PAH stations 1 to 6; S = subsurface B = near-bottom

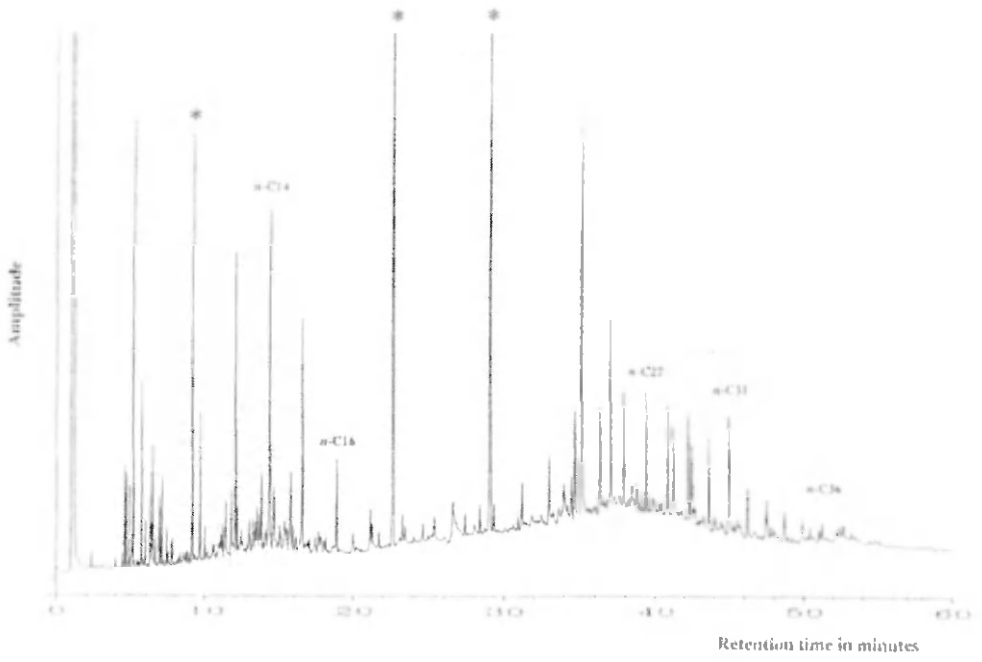

Figure 2

Capillary GC/FID chromatogram of the sample from station 4, July 1991. Asterisks indicate the peaks due to the internal standards, and the peaks due to n-alkanes of chain lengths with 14, 16, 27, 31 and 36 carbon atoms are also indicated.

phase, at least when the concentration of suspended particulate material is relatively low, as is usually the case in the Eastern Channel where fine sediments are uncommon. Concentrations of individual PAH and groups of alkylated PAH ranged from not detected (limits of detection in the range 0.2 to 2 ng l^{-1}) to 410 ng l^{-1}; with alkylated naphthalenes predominating in the majority of samples.

Total hydrocarbon concentrations were not determined in these samples; however during sampling surface oil sheens and small slicks were often apparent, and capillary GC with flame-ionisation detection (GC-FID) of the samples after GC-MS analysis yielded chromatograms which were generally similar to that given as Figure 2. This shows a chromatogram of the subsurface sample from station 4 (July 1991) and clearly indicates the presence of petroleum-derived hydrocarbons, in the boiling ranges *n*-C_{11} to *n*-C_{18}, and *n*-C_{21} to *n*-C_{36}. The latter group (*n*-C_{21} to *n*-C_{36}) probably arise from medium or heavy fuel oils as are used in ships; the former, lighter, group lie within the range of kerosenes and light diesels, and may derive from the smaller ferries operating across the Channel (such as hovercraft and jetfoils). Although, unresolved hydrocarbons within the range C_{17} to C_{23} and *n*-alkanes in the range C_{13} to C_{23} have been found in atmospheric particulates and ascribed to degradation products of algal lipids (Mazurek and Simoneit, 1984; Simoneit *et al.*, 1977), it is unlikely that some contribution may derive from this source. These results mainly suggest that significant local inputs of oil from passing shipping occur in the Straits of Dover. The Dover Strait is one of the world's busiest shipping areas, with major traffic lanes running between the southwest and the northeast connecting the North Atlantic with the main European harbours such as Europoort, and a thriving ferry traffic across the English Channel between ports such as Dover, Ramsgate, Calais and Boulogne. It is estimated that, on average, 500 ships pass through this stretch of water each day; 300 through and 200 across the Strait (Captain WIM Hargreaves, Department of Transport; personal communication). The concentrations of PAH determined in this study therefore presumably reflect those present in English Channel water, with an additional component derived from inputs of oil from ships operating in the Dover Strait. These latter inputs may be highly variable both spatially and temporally, and it would therefore be necessary to sample regularly across the transect in order to make good estimates of average concentrations of PAH and petroleum-derived hydrocarbons, and so to estimate fluxes into the North Sea.

CONCLUSIONS

This study has shown the feasibility of determining PAH concentrations in water from the English Channel with current techniques, although the method utilised here is not sufficiently sensitive to yield positive values for all samples and determinants. In order to improve the sensitivity and repeatability of current methods it will probably be necessary to utilise integrating samplers processing larger volumes of water (*see* Ehrhardt *et al.*, 1991). These could be deployed on varying timescales from hours to weeks to gain information on temporal as well as spatial variability. As a large proportion of the PAH (especially those of high molecular weight) is probably associated with particulate material, it is also desirable to determine dissolved and particulate PAH concentrations separately. This study has also demonstrated that oil inputs from passing shipping in the Straits of Dover, one of the busiest sea-lanes in the world, cannot be neglected in an assessment of the flux of PAH from the English Channel to the North Sea.

Acknowledgement

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