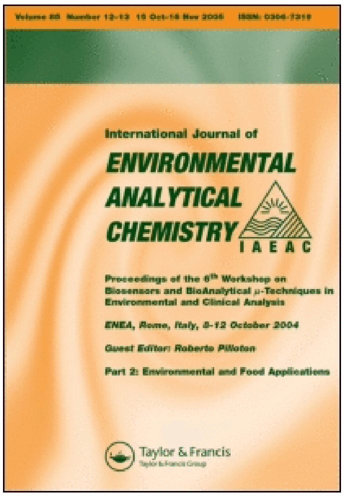

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Measurement of Volatile Aromatic Hydrocarbons in an Industrial Estuary†

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Levels of volatile aromatic hydrocarbons (benzene, toluene, xylenes and ethyl benzene) have been determined in water and sediment samples taken from the River Tees estuary in October 1981. The samples were analysed by a procedure based on the dynamic headspace technique and gas chromatography-mass spectrometry.

During the investigation, the most abundant volatile aromatic hydrocarbon found in the estuarine water was toluene. Concentrations at 1.5 m depth, expressed as averages over approximately one tidal cycle, were 6 μg/l and 60 μg/l at the two sampling stations used. Benzene was the next most abundant aromatic compound, and corresponding mean values of 0.3 μg/l and 1.3 μg/l were determined for this compound.

Some limited work on samples from depths other than 1.5 m indicated that higher aromatic concentrations were found nearer the surface.

The most abundant aromatics in the sediment samples taken were *m*- and *p*-xylene, which were found at 250 μg/kg in one sediment sample. The other volatile aromatic compounds were present at much lower levels.

KEY WORDS: Volatile aromatic hydrocarbons, benzene, toluene, xylenes, ethyl benzene, water sampling, sediments, River Tees estuary.

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INTRODUCTION

Volatile aromatic hydrocarbons are important feedstocks in the chemical industry for the production of synthetic organic chemicals. Annual world production figures for these compounds have been estimated by Merian and Zander (1982) as 15 million t benzene, 5 million t toluene and 20 million t C8 aromatics, for feedstocks, with additional amounts of 15 million t benzene, 30 million t toluene and 40 million t C8 aromatics in motor fuel.[1] Of these amounts Merian estimated that 4 million t benzene, 6 million t toluene and 3 million t xylenes annually enter the environment.[2] Most of these losses are believed to be introduced to the atmosphere, but some will enter the aquatic sphere, either through spillage, industrial discharge or continuous cycling between the atmosphere and water bodies.

Surprisingly there is little information in the literature on the concentrations of these compounds in natural waters. The available data have been summarised by Otter[3] and by Merian and Zander, and are given in Table I.

TABLE I
Concentration of volatile aromatics in natural waters.

	Concentration (μg/l)	
	River waters (after Otter)	Surface, tap and drinking waters (after Merian and Zander)
Benzene	0.1–200	0.1–100
Toluene	0.7–200	0.8– 12
Xylene	0.2–100	2– 8

As part of an exercise to gather further information on the levels of these compounds in natural waters, the Brixham Laboratory, ICI PLC, was commissioned by the U.K. Department of the Environment to carry out measurements in the estuary of the River Tees in north-east England. This estuary was considered a suitable site for such an investigation because several oil refining and petrochemical sites are situated on its banks, as are many other industrial activities.

In October 1981 water samples were taken at 1.5 m depth from two selected points in the estuary on separate days. In addition a small number of sediment samples were also taken. The samples were analysed for benzene, toluene, xylenes and ethyl benzene by a procedure based on the dynamic headspace technique followed by gas chromatography-mass spectrometry.

EXPERIMENTAL

Sample collection

Water and sediment samples were collected from the River Tees estuary at Transporter Bridge (Station A) on 6 October, 1981 and at Tees Dock (Station B) on 8 October, 1981. Both sampling points are situated in the most heavily industrialised segment of the estuary and their exact locations are shown in Figure 1.

Water samples were collected hourly over a nominal 12-hour period approximating to a tidal cycle, although at Station B the sampling period had to be restricted to just over 10 hours. The samples were taken at 1.5 m depth from a rubber dinghy anchored in mid-channel. In addition at each station below the surface, near slack water-high tide, a single set of samples were taken at surface, and then at 0.5 m depth intervals down to 2 m.

At each sampling station, one sediment sample was taken by dredge from the centre of the main channel, and one from the south bank of the estuary just below low water mark.

Sampling procedures

The sampler used for collection of the water samples was specially constructed and is shown in Figure 2. It was made mainly of stainless steel and aluminium with small amounts of brass and polypropylene.

In the sampling procedure an empty glass bottle (100 ml capacity), closed with a polypropylene cap which housed a PTFE faced silicone rubber septum, was securely clamped to the baseplate of the sampler. The cap of the bottle was held by a friction-grip of polypropylene attached to the operating rod of the sampler, which ran upwards through the 3 m long aluminium box section to the

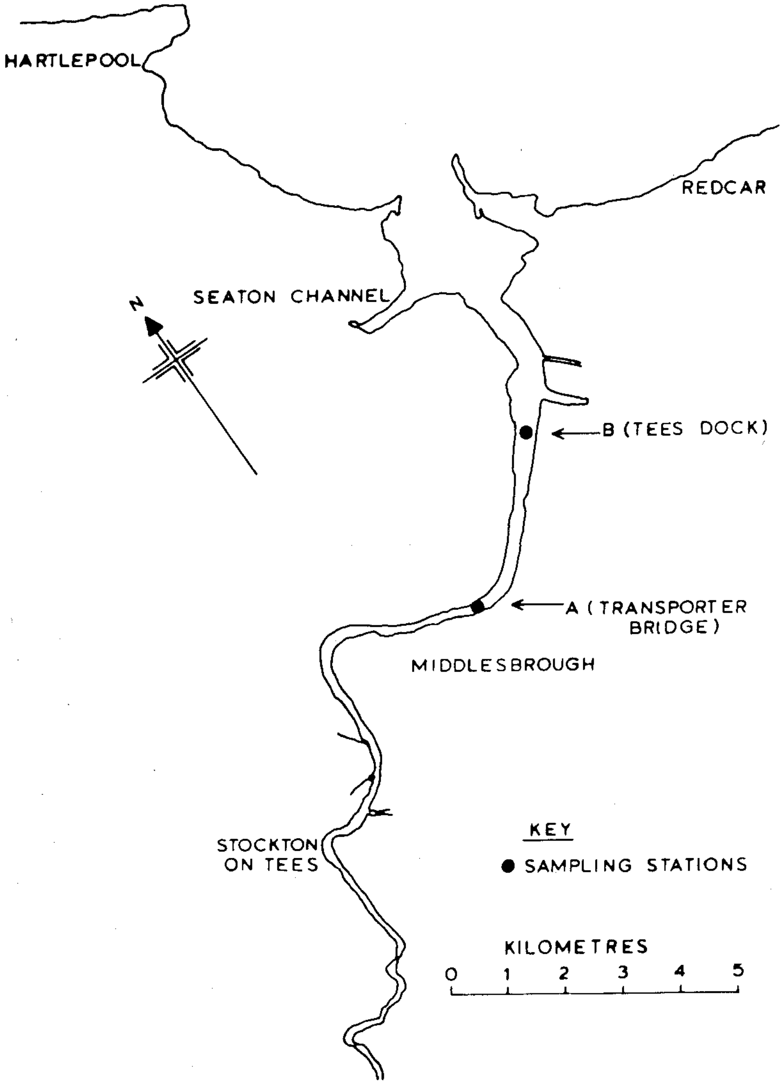

FIGURE 1 The Tees River estuary.

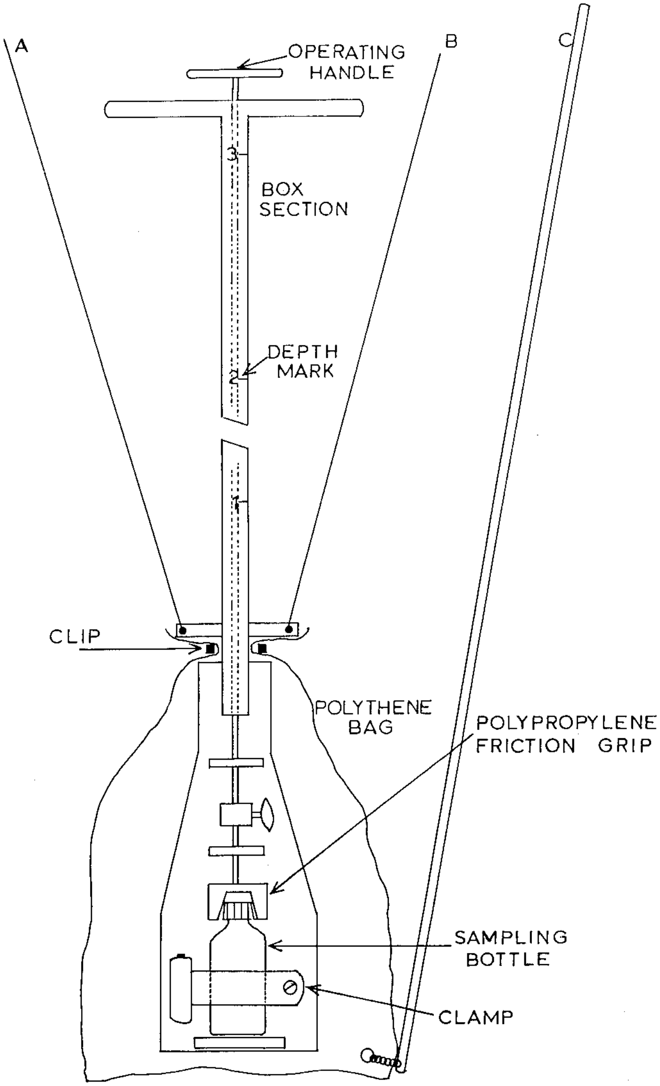

FIGURE 2 Sampler.

support handles and operating handle. The baseplate of the sampler and the bottle were then enclosed by a thick polythene bag to prevent contamination of the bottle by surface layer hydrocarbons. The bag was gathered round the box section (as shown in Figure 2) and secured with a spring clip attached to a line held by the operator.

The sampler was carefully lowered over the side of the dinghy to the desired depth, and was held in place with the aid of strops A and B. The polythene bag was released by pulling off the spring clip, and removed from the area of the sampler by depressing rod C which was attached to it by an eyelet. The bottle cap was unscrewed using the operating rod, and the bottle was allowed to fill completely before being recapped. The sampler was carefully brought to the surface and the bottle removed. Samples were packed in ice until they could be returned to the laboratory for analysis.

Sediment samples were collected using a small stainless steel conical dredge and were placed at once into glass bottles which were securely closed with polyethylene screw caps. The samples, each of approximately 250 ml volume, were held in ice until returned to the laboratory where they were stored in a cold room until analysed (normally within 72 hours of collection).

Dynamic headspace procedures

Water samples were analysed for volatile aromatic hydrocarbons using a dynamic headspace technique which was based on a method for the volatile aromatic compounds in water developed by O'Brien and McTaggart,[4] their method being essentially similar to that of Bellar and Lichtenburg.[5] The dynamic headspace technique involves the removal of the volatile compounds from the aqueous sample by a stream of inert gas, the volatile solutes being trapped on adsorbent tubes. After purging is completed, the trapped volatile solutes are thermally desorbed from the tube onto the head of a gas chromatographic column for separation and analysis. Identities are confirmed by use of a mass spectrometer coupled to the gas chromatograph.

In the procedure used in this work, a 50-ml water sample was transferred from the sample bottle to a clean glass purge vessel (shown in Figure 3) through a funnel in the top inlet port. This inlet was then sealed with a cap and septum (PTFE faced), and a pre-

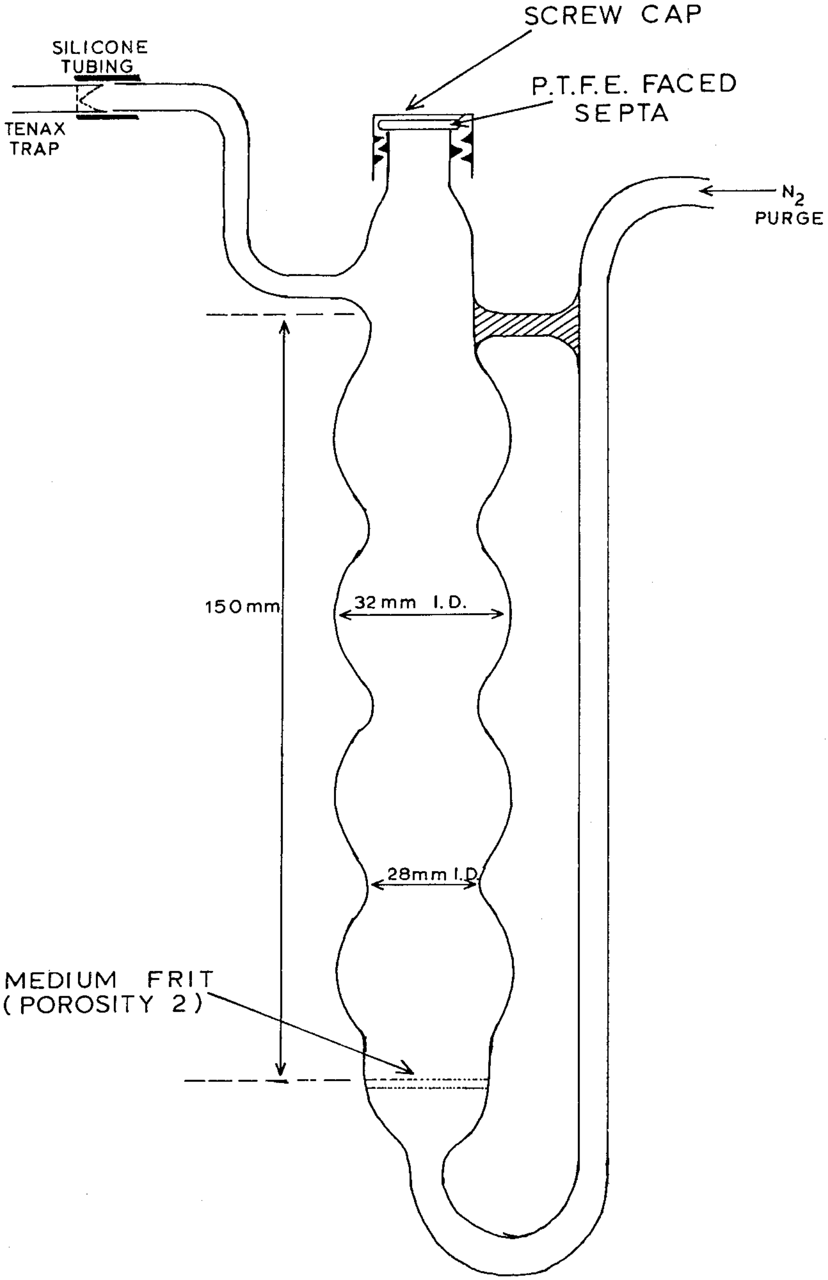

FIGURE 3 Purge apparatus.

cleaned Tenax adsorbent tube was butt-jointed to the exit arm of the purge vessel by use of a short length of silicone rubber tubing. Nitrogen, oxygen-free and purified by passage through molecular sieve, was then passed through the purge vessel at a flow rate of 60 ml/min for 15+/−1 minutes. (At the commencement of purging, both inlet and outlet flows were monitored to ensure there was no leakage in the system.) After purging the Tenax adsorbent tube was removed and placed in a clean glass bottle, closed with a polypropylene screw cap, until required for GC-MS analysis.

The Tenax adsorbent tube (Figure 4) was constructed from 6 mm (od) stainless steel tubing of 9 cm length. The middle 5 cm of the tube was packed with Tenax GC (60–80 mesh) and this was held in place by glasswool plugs followed by stainless steel frits. Traps were conditioned by heating to approximately 250°C for at least 10 minutes with a helium flow of approximately 50 ml/min. Precleaned Tenax stripping tubes were held in nitrogen purged glass bottles, closed with a polypropylene screw cap, until required.

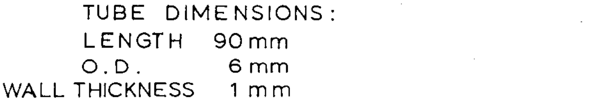

FIGURE 4 Tenax GC trap tube.

Sediment samples were extremely difficult to handle, and the standard purge vessel was replaced by a 75-ml round-bottomed flask which contained a small magnetic stirrer bar. A 5–10 g aliquot of the well-mixed sediment was weighed into this flask, and 50 ml of purged distilled water added and a Tenax tube attached to the gas outlet from the flask. Nitrogen was bubbled at 60 ml/min through the flask from a narrow bore inlet tube submerged in the liquid while the magnetic stirrer was activated. Purging was continued for 15 minutes and the contents of the Tenax trap then analysed as usual.

Gas chromatography-mass spectrometry procedure

The aromatic hydrocarbons trapped in the Tenax packing were thermally desorbed using a fast heat desorber (Environmental Monitoring Systems Ltd.) onto the head of the GC column of the GC-MS system (Finnigan 4000). The heated zone of the desorber was maintained at a temperature of 230°C, and the full carrier gas flow (40 ml/min) was switched through the tube as soon as it was inserted into this zone, this flow system being maintained for several minutes afterwards. The gas chromatograph was equipped with a 2 m × 2 mm (id) glass column packed with 15% Dexsil 300 on Universal Support (60–80 mesh). The injection temperature was 250°C and the column was programmed from 50°C, held for one minute, to 125°C at 12°C/min. Under these conditions, all the compounds for determination, with the exception of *m*- and *p*-xylene which co-eluted, were completely separated from each other.

The gas chromatograph was linked to the mass spectrometer by a glass jet separator (maintained at 250°C). Mass spectra were taken in the electron impact mode, the machine being repetitively scanned at 1 second intervals over the range m/z 60–150.

Quantification

The mass spectral data were processed by an Incos data system, which was used to derive background subtracted specific ion areas for the individual components at their respective retention times. The following specific ions were used for quantification m/z 78 (benzene), m/z 91 (toluene, ethyl benzene), m/z 106 (*o*-xylene, *m*- and *p*-xylene).

Calibration of the system was carried out by the frequent running of external standards. These were prepared by placing 50 ml of purged distilled water into the purge vessel using a funnel placed in the top inlet port. An appropriate aliquot of a standard solution of mixed aromatic hydrocarbons in methanol was then added directly into the water by microlite syringe (and the septum cap replaced) to give aqueous solutions containing 5–400 μg/l of each hydrocarbon. (For this purpose, methanol solutions were prepared containing either 100 mg/l or 1000 mg/l each of the following hydrocarbons in admixture: benzene, toluene, ethyl benzene, *p*-xylene and *o*-xylene.) These aqueous standards were then treated as if they were water samples and the specific ion areas for the various components were obtained and used to construct calibration graphs.

Method recoveries

The recovery of the method for the volatile aromatic hydrocarbons from water samples generally lay in the range 85–125% for all the hydrocarbons. The recoveries from sediment samples were appreciably lower, and for a 5 g sample ranged from 64% for benzene to 40% for *o*-xylene. None of the results quoted has been corrected for recovery.

Blank values

During the course of the analysis of water samples "blank" values were determined by measurements on purged distilled water, processed by the same analytical procedure as the samples. The results of the analyses are shown in Table II and although probably erring on the high side, these figures must effectively represent the detection limit of the method as employed. None of the results quoted has been corrected for these blank values.

TABLE II

Aromatic hydrocarbons found in pre-purged distilled water. All results in ppb (μg/l).

Brixham ref.	Benzene	Toluene	Ethyl benzene	$m+p$ xylene	o xylene
39	0.04	0.29	N.D.	N.D.	N.D.
46	0.13	0.38	0.07	0.04	N.D.
114	0.21	0.29	0.07	0.11	0.9
Mean	0.13	0.32	0.05	0.05	0.03

N.D. = Not detected.

Effect of storage on samples

Storage trials on water samples fortified with the volatile aromatics indicated that water samples held for more than three days at 2–4°C were likely to give low analytical results. A preferable storage procedure was to purge the samples onto Tenax tubes, where storage of these for as long as six days was perfectly acceptable.

Investigation of trapping capacity of the Tenax tubes

The trapping capacity of the Tenax tubes was also investigated, and up to concentrations of 500 μg/l in the 50 ml aqueous sample, no breakthrough of the hydrocarbons was found. At the 1,000 μg/l level, the equivalent of 10 μg/l benzene passed through the trap, all the other hydrocarbons being totally trapped. At the 5,000 μg/l level, the equivalent of 240 μg/l benzene, 2.5 μg/l toluene and 1 μg/l of ethyl benzene broke through the trap.

Precision of the analytical method

Information on the precision of the analytical method is provided in Table III by repeat analysis (reference Bx 43) of one water sample (Bx 34), and by analysis of a duplicate sample (Bx 30) of another (Bx 29). Comparison of the values obtained on these repeat/duplicate samples with those of their corresponding sample shows extremely good agreement for all compounds.

RESULTS AND DISCUSSION

Water samples

Within the central reaches of the estuary, the fresh water from the River Tees flows seaward mostly on the surface, mixing only slowly with the waters below. Near the bed of the estuary the incoming water is almost fully saline and mixes relatively slowly upwards. The intermediate region between the freshwater on the surface and the saline water at depth, is water which has been in the estuary for several days and which should therefore contain contaminants which have accumulated in the estuary. Under the freshwater flow conditions obtaining at the time of the survey, a sampling depth of 1.5 m was used for the majority of samples, which allowed sampling of this intermediate water.

Tables III and IV show the concentrations of the volatile aromatic hydrocarbons determined in the water samples taken at the two sampling stations. The results show that at both stations toluene was the major volatile aromatic hydrocarbon observed. Its mean value (over the sampling period) was found to be 5.6 μg/l at Station A, and was an order of magnitude higher (at 65 μg/l) at Station B. In contrast the mean concentrations of the other compounds were all significantly less than that of toluene. Their mean values were below 1 μg/l with the exception of that for benzene at Station B which was 1.3 μg/l. Each compound was also present at higher mean concentration at Station B than at Station A, the difference for toluene, as observed earlier, being of an order of magnitude. The sampling at these stations was however carried out on different days, so that direct comparison of the distribution of the aromatic hydrocarbons with tidal cycle between the two stations cannot be made.

The fluctuation in concentration of the measured components with time of sampling has been plotted graphically in Figures 5 and 6 for Stations A and B respectively. Both figures show extremely complex patterns and their full interpretation is not possible for a number of reasons. Firstly, effluent discharge rates for each component at their sources on the estuary are not known for the time of this investigation. Secondly, there are no data on current movements at the 1.5 m sampling depth for each station. Whilst lastly, the Tees estuary is an extremely complex hydrographical system.

During the investigation, additional water samples were taken on a single occasion at each station at 0.5 m intervals from the surface to a depth of 2 m. Profiles for these samples for salinity and the concentration of the two more abundant aromatic hydrocarbons: benzene and toluene are shown in Figures 7 and 8. The former indicates that at Station A the maximum concentrations of the two aromatic hydrocarbons were observed between 0.5 and 1.5 m depth, and that both suffered a sharp decline in concentration from 1.5 to 2 m depth, possibly reflecting the sharp increase in the salinity of the water between 1 and 2 m depth. (Unfortunately salinity was not measured at 1.5 m depth.)

At Station B (Figure 8) the maximum concentrations for both compounds were observed at the surface, with generally decreasing concentrations being experienced with increasing depth and salinity.

TABLE III

Station A: Estuary sample composition, 6 October, 1981. 1.5 m samples. All concentrations in ppb (μg/l).

Time	Depth (m)	Brixham ref	Benzene	Toluene	Ethyl benzene	$m+p$ xylene	o xylene
0700	1.5	20	N.D.	1.3	N.D.	N.D.	N.D.
0800	1.5	101	0.04	0.34	0.04	0.08	0.06
0900	1.5	27	0.28	1.4	0.10	0.13	0.04
1000	1.5	102	0.06	0.72	0.13	0.25	0.25
1100	1.5	28	0.40	5.9	0.19	0.33	0.09
1200	1.5	104	0.21	3.9	0.16	0.48	0.24
1300	1.5	29	0.31	3.4	0.13	0.15	0.03
1400	1.5	105	0.09	1.2	0.13	0.49	0.26
1500	1.5	31	0.48	3.3	0.25	0.54	0.24
1600	1.5	107	0.34	4.1	0.18	0.49	0.29
1700	1.5	32	0.54	10	0.15	0.23	0.05
1800	1.5	33	0.66	20	0.20	0.34	0.05
1900	1.5	36	0.74	17	0.18	0.34	0.08
Depth profile							
1800	surface	37	0.50	48	0.07	0.15	N.D.
1800	0.5	38	0.66	92	0.09	0.15	N.D.
1800	1.0	35	0.64	59	0.09	0.27	0.09
1800	1.5	33	0.66	20	0.20	0.34	0.05
1800	2.0	34	0.09	0.42	0.02	N.D.	N.D.
Duplicates/repeat samples							
1300	1.5	(30) duplicate 100 ml sample of 29	0.39	3.8	0.11	0.12	0.03
1800	2.0	(43) repeat measurement on 34	0.04	0.40	0.07	0.10	0.15

ND = Not detected.

TABLE IV

Station B: Estuary sample composition, 8 October, 1981. 1.5 m samples. All concentrations in ppb (μg/l).

Time	Depth (m)	Brixham ref	Benzene	Toluene	Ethyl benzene	*m*+*p* xylene	*o* xylene
0740	1.5	86	0.67	19	0.15	0.37	0.23
0845	1.5	94	2.0	22	0.23	0.44	0.25
0945	1.5	85	1.1	110	0.48	1.1	1.1
1045	1.5	95	1.5	98	0.14	0.58	0.36
1145	1.5	89	5.0	110	1.8	1.5	0.67
1245	1.5	97	1.8	78	0.98	1.1	0.24
1345	1.5	84	0.92	70	0.44	0.76	0.46
1445	1.5	99	0.90	83	0.27	0.60	0.31
1545	1.5	87	0.41	41	0.28	0.45	0.49
1645	1.5	98	0.57	52	0.34	0.65	0.39
1745	1.5	88	0.71	27	0.40	0.58	0.49
1845	1.5	100	0.42	34	0.18	0.41	0.39
Depth profile							
1145	surface	90	12	210	5.9	3.9	0.15
1145	0.5	91	4.6	140	2.2	2.4	0.36
1145	1.0	92	5.6	130	3.4	2.6	0.44
1145	1.5	89	5.0	110	1.8	1.5	0.67
1145	2.0	93	2.5	58	1.1	1.3	0.40

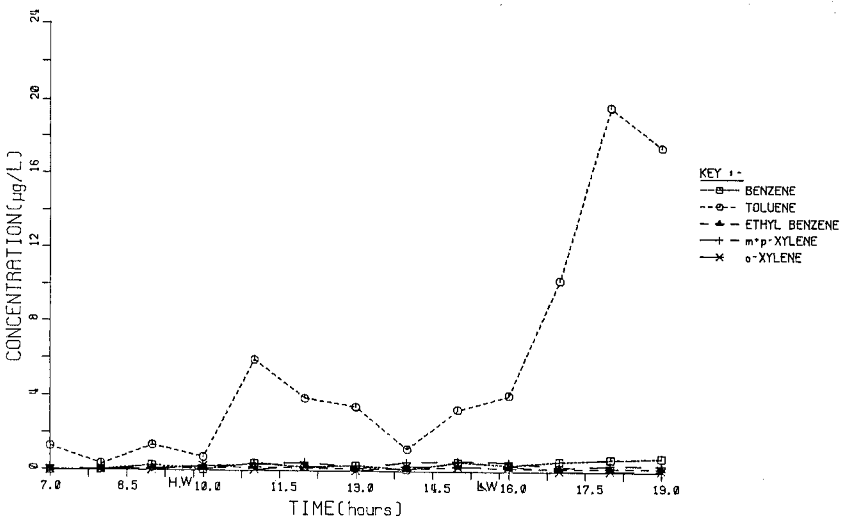

FIGURE 5 Station A—Water samples (1.5 m). Variation of volatile aromatic hydrocarbon concentrations with time of sampling (6 October, 1981).

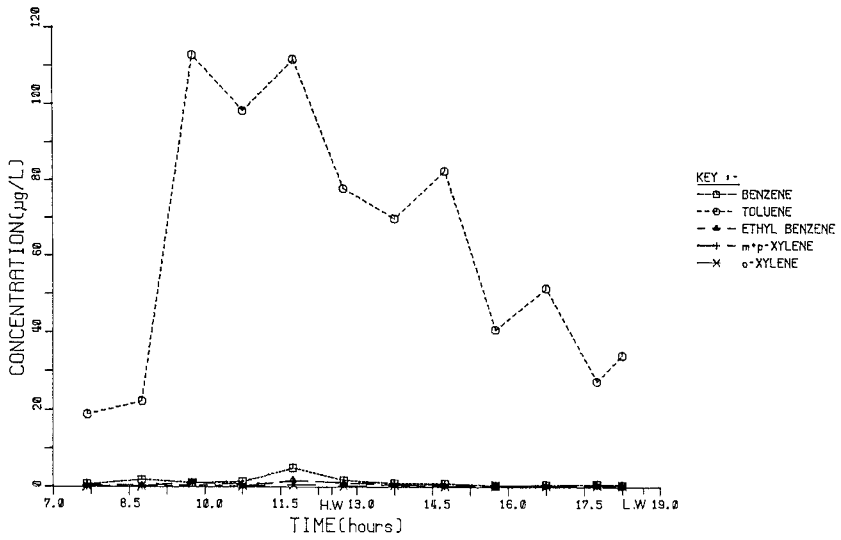

FIGURE 6 Station B—Water samples (1.5 m). Variation of volatile aromatic hydrocarbon concentrations with time of sampling (8 October, 1981).

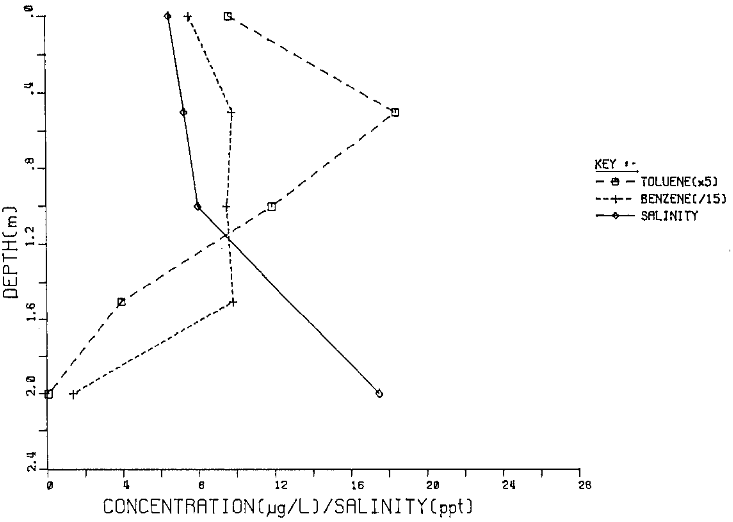

FIGURE 7 Station A—Depth profile. Variation of salinity and benzene and toluene concentrations with depth of sampling (6 October, 1981).

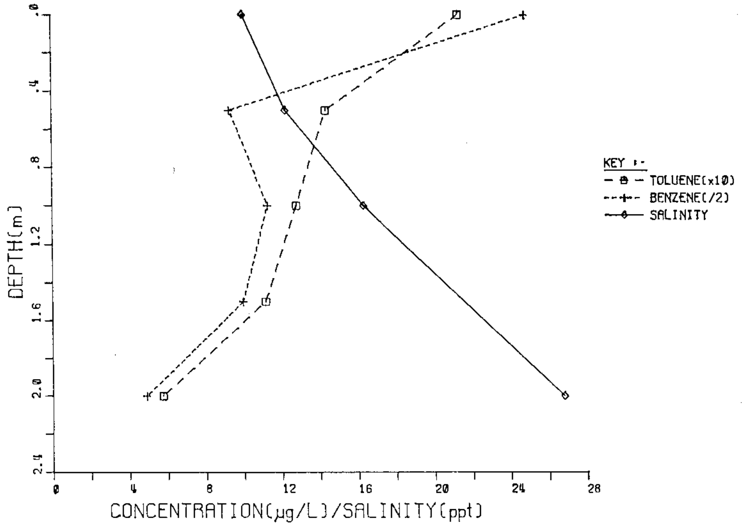

FIGURE 8 Station B—Depth profile. Variation of salinity and benzene and toluene concentrations with depth of sampling (8 October, 1981).

Sediment samples

Two sediments (one from the mid-channel and the other from the south bank of the estuary) were collected from each sampling station. The relatively low concentrations determined on these samples are given in Table V. All values were less than 10 μg/kg, except for *m*- and *p*-xylene at Station B which reached 14 μg/kg in the south bank sample and 250 μg/kg in the mid-channel sample.

CONCLUSIONS

This investigation has provided some preliminary information on the levels of volatile aromatic hydrocarbons existing in a heavily industrialised estuary, that of the River Tees, in October 1981. At the time of this work, toluene was found to be the major volatile aromatic hydrocarbon at both sampling stations, the levels of the other determined aromatic hydrocarbons being significantly less. In

TABLE V

Aromatic hydrocarbon content of Tees sediments. All results given as ppb (μg/kg) and related to sediment (wet weight).

Source	Brixham ref	Benzene	Toluene	Ethyl benzene	*m*+*p* xylene	*o* xylene
STATION A						
Mid-channel	106	1.5	2.2	1.4	3.4	0.6
South bank	103	2.2	3.7	2.9	5.1	1.9
STATION B						
Mid-channel	113	3.9	6.4	N.D.	250	3.9
South bank	133	1.3	1.2	N.D.	14	2.6

Note: These results have not been corrected for the recovery efficiency of the sediment method and are therefore low by a factor not exceeding ×3.

N.D. = Not detected.

addition there was an indication that the higher concentrations of the volatile aromatic hydrocarbons may be associated with the freshwater rather than the more saline water. Analysis of a small number of sediment samples showed *m*- and *p*-xylene (combined) to be the major volatile aromatic hydrocarbons present in the sediments. Further work on this estuary is required before the distribution of the volatile aromatic hydrocarbons, found in the water and sediment samples in this investigation, can be fully understood.

Acknowledgments

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