Analysis of volatile organic compounds in estuarine sediments using dynamic headspace and gas chromatography–mass spectrometry

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(First received June 28th, 1990; revised manuscript received December 4th, 1990)

ABSTRACT

In our previous paper (*J. Chromatogr.*, Vol. 467, p. 111) we reported a modified variant of the purge-and-trap gas chromatographic analysis of volatile organic carbon compounds in water. In this paper we report the application of the modified open-loop dynamic headspace technique for the stripping and trapping of volatile organic compounds (VOCs) from estuarine sediments. Sediment samples (*ca.* 300–400 g wet weight) are transferred into all-glass 1-l bottles and purged at 60°C for 70 min in an ultrapure helium gas stream. Volatile eluates are quantitatively trapped onto three different sorbent beds arranged in series. Analysis is then performed using thermal desorption with capillary column chromatography and simultaneous flame ionisation with ion-trap detection. As with water samples, stripping temperature had the greatest effect upon compound recovery, with smaller variances in recovery observed when comparing different sediment types.

The method is capable of quantifying many individual volatile organic compounds down to a detection limit between 10 and 100 ng kg^{-1} (dry weight). The linear dynamic range for a broad range of compounds fell between the lower limit of detection to approximately 500–700 μg kg^{-1} (dry weight). The results of a case study on sediments taken from the Southampton Water estuary are presented as an example of the method application. A list of component concentration ranges are also presented.

INTRODUCTION

Within the past ten years much attention has been focused on the detection and quantification of volatile organic compounds (VOCs) in sludges, muds and sediments. Many types of VOC, originating from diverse sources ranging from oil spills [1,2] and industrial wastewaters [3], to natural, biogenic compounds [4] have been identified in estuarine sediments. Some of these compounds are mutagens, teratogens or carcinogens [5,6] and resistant to microbial or photochemical degradation [2]. Studies concerning their occurrence, behaviour and fate in estuarine sediments are comparatively limited, a fact which reflects the necessity for research and vigilance in this area.

There has been extensive reporting of analytical methods for measuring low level concentrations of VOCs in surface waters. These are based mainly on static (equilibrium) and purge-and-trap (non-equilibrium) headspace analysis [7–12]. However, the direct application of these methods for analysing VOCs in sediments is not straightforward and must take account of complicating factors such as sediment composition, the physico-chemical properties of the sediments and the organic compound classes involved. These properties may also necessitate an appreciation of factors such as particle-size distribution, organic carbon content and the geographical variability of different sediment types [13].

Previous research on the composition of sediments as media for sorbing organic compounds has provided clues regarding the key factors which determine sorbability. Examples of such research included studies of the relationship between the partition coefficients (K_p) of hydrophobic organic compounds and the sediment matrix [14]. An important conclusion arising from this work stated that sorptive action by shallow estuarine sediments was directly involved in the removal of individual VOCs from overlying waters, regardless of the sediment type. Accordingly, much research has been aimed at studying the affinity of different sediment types for various classes of organic compounds [15].

Unfortunately, there are no universally recognised and approved methods for the analysis of VOCs in sediments, especially marine sediments. Rigorous analytical approaches have been used to evaluate the efficiency of static (equilibrium) headspace methods for determining VOCs in coastal sediments [16] and in estuarine sediments [17]. Similarly, purge-and-trap stripping methods have been applied with a degree of success to the laboratory analysis of sediments [18,19] and in field studies of sediment and fish tissues [20]. Purge-and-trap methods utilise purging of the sample matrix by purified inert gases, followed by trapping of the volatile compounds onto adsorbent beds, typically Tenax or carbon-based sorbents. Another interesting analytical variant used vacuum-extraction techniques to partition VOCs from solid materials, followed by transfer of the extracted organic vapour to a conventional purge-and-trap device. Analysis was then conducted according to standard gas chromatographic (GC) protocols [21].

One of the most commonly used purge-and-trap methods used for stripping VOCs from sediment matrices is the United States Environmental Protection Agency Method 5030. This method is used for volatile organics, defined as those organic compounds with boiling points below 200°C and which are insoluble or only slightly soluble in water. Method 5030 includes a low-level variant intended for samples containing less than 1 mg kg^{-1} of individual VOCs, although it is limited to sediment samples that are of a similar (granular and porous) consistency. Volatile water-soluble (*i.e.* alcohols and ketones) compounds can be included in this method. However, as a general observation, quantitation limits [by GC or gas chromatography–mass spectroscopy (MS)] were stated to be approximately ten times higher than non-polar hydrophobic organic compounds, because of their poor purging efficiencies.

In this sediment purge-and-trap method, VOC were purged from sediment samples at elevated temperatures onto a similar three-stage sorbent trap. After the purging step, the trapping tube arrangement was disconnected, and the individual tubes thermally desorbed using a Perkin-Elmer automated thermal desorber (ATD-50; Perkin-Elmer, Beaconsfield, U.K.). The ATD-50 is a multi-functional instrument

developed initially for the United Kingdom Health & Safety Executive environmental laboratories [22]. The principal role of the ATD-50 is for the analysis of organic vapours at low concentrations (sub-ppm). An integral two-stage desorption facility is available whereby organic compounds desorbed from adsorption tubes, within an oven held at 150°C, are then re-trapped inside an electronically cooled cold-trap packed with a secondary adsorbent bed, at a temperature down to -30°C. The cold-trap is then electronically heated at a rate exceeding 1000°C min^{-1} to an upper limit of 300°C, sending a discrete band of concentrated sample through the fused-silica transfer line to the GC capillary column where the transferred components are chromatographed.

The sediment purging method, which uses the ATD-50, has separated over 100 volatile organic compounds found mainly as trace contaminants or naturally occurring compounds in estuarine sediments within approximately 70 min. The method utilises flame ionisation detection (FID) with the added facility of ion-trap detection to provide confirmation of peak identity. This work conducted on VOCs in British estuarine sediment [23] and water samples [24] has revealed a wide range of volatile compounds to be present.

EXPERIMENTAL

The experimental details have been described previously [24]. However, this section shall include details pertinent to the analysis of sediment, as opposed to water samples.

Reagents

Standards were prepared using re-distilled analytical grade materials (Aldrich, Wimborne, U.K.). Stock standard mixtures were prepared gravimetrically in all-glass containers according to both EPA [25] and CONCAWE [26] methods. Replicate standards containing organic compounds covering materials varying in boiling point range from *n*-pentane to *n*-octadecane were prepared in 1-litre flasks, inverted, and spiked through aluminium-coated teflon septa using plunger-in-needle hypodermic syringes (SGE, Milton Keynes, U.K.). Sodium azide, recommended as a poison to prevent further biological reaction after sampling [27], was added to all samples. Internal standards, *i.e.* 1-chloroalkanes, were obtained from Aldrich.

Organic-free water was prepared by purging pure AnalaR grade water (BDH, Poole, U.K.) overnight in a stream of purified nitrogen. Aliquots (500 ml) were then heated at 95°C for 30 min to remove any remaining volatile components, cooled under a purified nitrogen blanket, and stored under zero-headspace immediately prior to use.

Standard sediment

The optimum standard matrix to use has been stated to be that of the sample matrix itself [28]. Sediment particle size distribution and organic matter content tend to vary between and within estuarial sites, and may affect the sorption and subsequent desorption of volatile organic compounds on sediments [14]. According to Bartlett [29], the majority of sediments within the 10-km length of Southampton Water exhibit seasonally constant physical characteristics which show little variation from year to year. Individual grain size properties of Southampton Water sediments were

determined using standard techniques developed and reported by Little *et al.* [30] and McLaren [31]. The organic matter content of the sediments was determined using the simple combustion method reported by Froelich [32].

Sediment grain size data for representative sediment samples taken from the head (sediment 1), mid-point (sediment 2) and mouth (sediment 3) of the estuary are presented in Table I. All three sites are composed of a mixture of good to moderately sorted fine silts (*e.g.* 70–80% silt), although some poorly sorted silts are found at the fringes of the estuarine mouth where the estuary opens into the Solent waterway. Clay contents increase from the head towards the mouth of the estuary, whereas silt contents follow the opposite trend. The organic matter content of the sediments follows the same pattern as silts, *i.e.* decreasing steadily from the head towards the mouth of the estuary.

TABLE I

SEDIMENT GRAIN SIZE DATA FOR SAMPLES TAKEN FROM THE HEAD (SEDIMENT 1), MID-POINT (SEDIMENT 2), AND MOUTH (SEDIMENT 3) OF THE ESTUARY

Sediment	Depth (cm)	Mud (%)	Gravel (%)	Organic matter (%)	Sorting index	Wentworth grade
1	0–10	94.56	0	20.79	Good	Fine silt
2	0–10	97.45	0	15.14	Good	Fine silt
3	0–10	94.70	0	13.21	Moderate	Fine silt

Grain size distribution[a]

Grain size	Sediment 1	Sediment 2	Sediment 3
Sand	1.35	2.18	5.31
Silt	80.29	72.78	70.35
Clay	18.36	20.04	24.34

[a] Grain size key: sand = $7.07 \cdot 10^{-1}$ to $6.25 \cdot 10^{-2}$ mm; silt = $6.25 \cdot 10^{-2}$ to $3.91 \cdot 10^{-3}$ mm; clay = $3.91 \cdot 10^{-2}$ to $1.38 \cdot 10^{-3}$ mm (Reference: *British Standards Institution*, (1975) BS 1377).

Sediments from the head, mid-point and mouth of the estuary were taken in order to prepare "blank" organic-free sediment suitable for spiking experiments. These were prepared according to protocols already described by Bianchi and Varney [17], and Lee *et al.* [33]. Procedures intended to remove volatile organics from sediments may modify adsorptive sites within the particle matrix. However, a suitable compromise was sought between the practical necessity to prepare "blank" sediment material and the retention of the basic physico-chemical integrity of the original, unaltered estuarine sediment.

Preparation of spiked blank sediment

Sub-samples of dried sediment (300 g) were gravimetrically added to a 1-litre glass vessel with a metal spoon. The vessels were prepared in a glass-blowing workshop from 1-litre "Dreschel" jars. These were fitted with 19/26 mm ground-glass necks and ground-glass stoppers. Aliquots (100 ml) of spiked standard water were added to the sample vessels, shaken vigorously for 10 min and let to stand under purified nitrogen

for 15 min at 4°C. Pure gaseous standards, *e.g.* chloromethane, (obtained from BDH) were added by injecting known aliquots of diluted gas from Tedlar gas bags (SKC, Shaftesbury, U.K.) directly into inverted vessels containing blank sediment slurry. These were injected through 1-litre glass vessels fitted with PTFE-coated silicone septa lined caps using 10-μl gas syringes (SGE) and shaken gently for 5 min. Samples were then purged according to the protocol described in the following section.

Sorbents and tubes

Tenax-TA, Chromosorb-106 and Spherocarb sorbents (all 60–80 mesh), obtained from Perkin-Elmer, were conditioned overnight according to manufacturers instructions in $\frac{1}{4}$ in. diameter stainless-steel tubes in a flow of purified nitrogen. After conditioning, sorbents were packed into desorption tubes (90 mm × 5 mm I.D.). Each tube set, containing sequentially, Tenax-TA, Chromosorb-106 and Spherocarb were inter-connected using standard $\frac{1}{4}$ in.–$\frac{1}{4}$ in. PTFE ferrules and $\frac{1}{4}$ in. stainless-steel Swagelok unions.

Sampling apparatus

The purge-and-trap stripping apparatus consists of an all-glass 1-litre bottle (nominal capacity, 1150 ml). A modified dreschel head assembly incorporating a ground-glass collar (19/24 mm) was inserted into the ground-glass neck of the sample bottle (19/24 mm) and locked using a PTFE cage. Ultrapure helium was metered via a metal-glass joint into a 7-mm O.D., 7-cm length of glass tubing fabricated onto the inlet of the purge head assembly. The internal glass tubing of the inlet purge head was fitted with a coarse porosity frit (Grade 2) suitable for producing sufficient agitation within the sediment slurry mixture. A schematic of this arrangement is shown in Fig. 1. The heated "jaws" unit consists of a thermostatically controlled, spring-loaded, heated metal block which clamps over the exit tubing. By heating the glass tubing the unit minimises the collection of water vapour droplets which condense out on the inner walls. The strip gas then passes directly through the three trapping tubes which are connected in series. The apparatus was immersed in a heated water bath (Grant Instruments, Cambridge, U.K.), and agitated at regular intervals allowing 30 min for thermostatic equilibrium to be attained.

Instrumentation and capillary column

The automated thermal desorber (ATD-50) was connected to a Perkin-Elmer 8700 gas chromatograph via a 1-m length of deactivated fused-silica transfer line, 0.22 mm I.D., held at 150°C [24].

The gas chromatograph was fitted with a cradle-mounted, 50 m × 0.22 mm I.D. OV-1701 wall coated open-tubular fused-silica capillary column, 0.5-μm film thickness (SGE). This column was found to offer satisfactory performance for the analysis of volatile compound in sediments and was used as the basis for many of the following experiments. The exit point of the column was connected to a twin-hole split ferrule permitting 50% of the column eluant to be routed to a flame ionisation detector. The remaining 50% is swept via a second 1-m length of transfer line at 250°C into an ion-trap detector (Finnigan MAT).

Carbon dioxide gas for cooling the chromatograph oven below ambient temperature was piped into the rear of the oven via a 4-m length of 3.0 mm O.D. copper
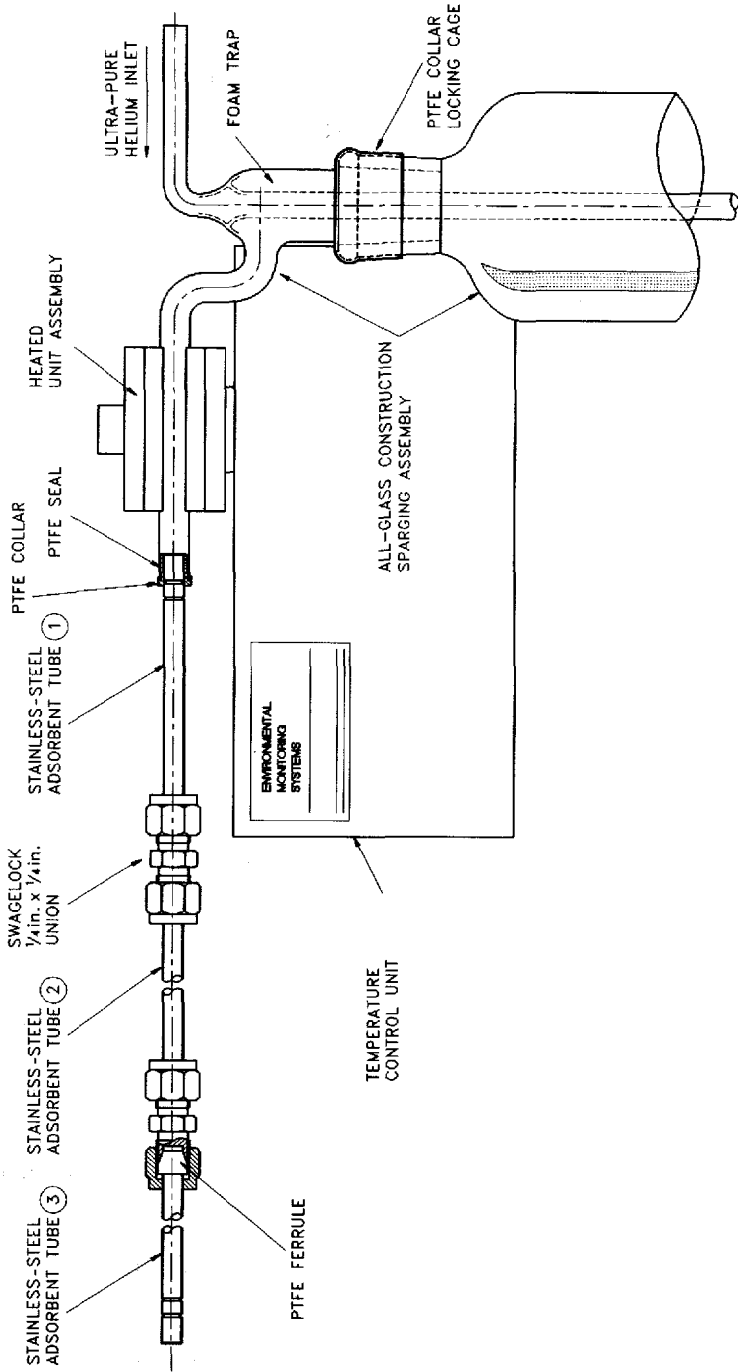
Fig. 1. Schematic of the modified open-loop stripping apparatus for analysing VOCs in sediments.

tubing. The feed rate for carbon dioxide gas is gauged by a microprocessor-controlled valve in the gas chromatograph.

Analytical operating conditions

Carrier gas. Ultrapure helium 5.5 grade (Air Products, Basingstoke, U.K.); carbon dioxide (Air Products, Southampton, U.K.).

ATD-50. Cold-trap packing, 10 mg Tenax-TA + 10 mg Chromosorb-106; cold-trap low temperature, $-30°C$; cold-trap high temperature, 250°C; split ratio (combined), 100:1; desorption oven temperature, 250°C; adsorbent tube desorption time, 10 min; desorption gas flow-rate, 10 ml min^{-1}, carrier gas pressure, 25 p.s.i. (*i.e.* 174 kPa).

Gas chromatograph. Detector temperature, 300°C; carrier gas flow-rate, 1 ml min^{-1} (20 cm s^{-1} at 10°C). Temperature conditions: oven temperature, 10°C; isothermal time 1, 10 min; ramp rate 1, 6°C min^{-1}; oven temperature 2, 300°C; final hold time 2, 10 min.

Ion trap detector. Ionisation voltage, 70 eV; s/scan, 1.0; mass range, 25–250 mass units; transfer temperature, 250°C; ion source temperature, 250°C; multiplier delay, 200 s; mass defect, 100 m.m.u./100 a.m.u.; acquire time, 70 min.

Collection of sediment samples

Since it is very difficult to assess the losses of volatile compounds from sediments after sampling, care and speed is necessary to transfer sediments into sealed glass containers as quickly as possible after sampling. Sediment samples [*ca.* 300–400 g (wet weight)] were immediately transferred after sampling into clean 1-litre glass purging vessels. Mid-estuarine samples were collected using a shipborne Wan-Ween sediment grab, cored with an all-glass cylinder, and inserted into the glass vessel. Solid materials such as stones or shells were quickly removed by hand before placing into the glass vessels. Intertidal mud samples were sampled using steel corers and inserted into the glass vessel. Sodium azide (*ca.* 0.5 g) was promptly added to sediment samples, and sample vessels immediately chilled on dry-ice inside sealed polystyrene lined "cool-boxes". As the sample storage vessels are then directly used for the purge analysis, volatilisation losses are kept to a practical minimum.

Analysis of sediment samples

After preliminary addition of (i) standard spiked water (100 ml) to standard blank sediment, or (ii) organic-free water (100 ml) to estuarine sediment samples, all samples were shaken gently for 10 min. Following this, standard samples were stood for 15 min under nitrogen at 4°C to allow mixing then settling of the spiked organic material into the sediment and the supernatant liquid. In order to determine longer term changes in composition arising from storage, duplicate standards were spiked with sodium azide, chilled in a refrigerator at $-4°C$ and subsequently analysed after 24 and 48 h respectively.

After assembly of the apparatus, standard and estuarine sediment samples were immersed in the heated water bath. After 30 min equilibration, samples were purged in a flow of ultrapure helium (5.5 grade) for 70 min at 100 ml min^{-1}. All connections between the purge-gas line, purge-head and adsorbent "tube-train" were checked for leakage of purging gas using a soap solution. The effluent gas leaving the final tube of

the trapping arrangement was also connected to an on-line flowmeter (Chrompack U.K., London, U.K.). The initial purge rate through the purging apparatus was set at 100 ml min^{-1} and monitored throughout the purging cycle for loss of flow due to a leakage in the system.

The purging experiments were performed initially at 30°C, then at 60°C. Following the purge and trap cycle, the purge gas was switched off and disconnected. The trap tubes were removed from the sample vessel, disconnected and independently analysed on the thermal desorber–gas chromatographic system. This involves placing analytical end-caps on each tube, locating the tube in the desorber carousel and activating the desorption mechanism on the ATD. The tubes are analysed on the ATD-50 thermal desorber by placing stainless-steel pressure caps (or "analytical" end-caps) on the ends of the tubes [22]. These caps contain a small valve which opens when a discrete gas pressure is applied by the desorption unit on the ATD-50. The tubes are placed sequentially in a carousel arrangement which is pre-programmed to interface the tubes to the desorption mechanism according to a user-specified method. Before analysis, each tube is individually pressurised by the ATD-50 to check for leakage in the end-cap seals (if the leak check cycle identifies loss of pressure, the tube is rejected for analysis). If the leak-test is successful, the desorption cycle is automatically implemented. Basically, the tube is heated within the oven unit of the desorption unit whilst a flow of pure helium carrier gas is passed through each tube. Organic vapours are desorbed off the tube to be passed onto the cold-trap. Here, the organic vapours are cooled and re-trapped. Following a desorption time of 10 min, the cold trap is "fired", which sends the organic vapours to the GC column via the fused-silica transfer line.

The results of recoveries of VOCs from water, at these stripping temperatures, have already been reported [24], and were used as a basis for investigating similar effects on sediments. Following stripping, attention was paid to the identification of any apparent losses or thermal degradation effects on organic compounds with increasing stripping temperature. Internal standards, 1-chlorohexane and 1-chloro-octane were initially used as a means of monitoring recoveries. For routine analyses, an external standard calibration technique was used. The concentration of individual components were determined by multiplying component peak area by the external standard response factor. Response factors were calculated directly from calibration standard data. Hence, it was necessary to determine the linear dynamic range of the method before starting sample analyses.

Calculation of absolute dry weights (*i.e.* of sediments) and recovery data on actual samples were made by decanting off separated supernatant liquid several hours after the purging. The remaining slurry was then collected in a pre-weighed, wide-mouth pyrex glass dish (500 ml), cooled further and then evaporated to dryness in an oven held at 105°C for 8–12 h. The dried residue was then placed in a dessicator for 2 h, and re-weighed to obtain the absolute dry weight. The mean recovery for reweighed sediments was 99.41 $\pm$ 0.19%, based on 44 consecutive sediment samples.

RESULTS AND DISCUSSION

Detection limits

The lower detection limit in GC analysis is generally considered to be that amount of analyte which gives a peak area response three times as great as the standard

deviation of the response obtained from the blank. In equilibrium headspace experiments developed to detect trace organochlorine compounds in effluent water, Pizzie [28] defined the lower detection limit (*D.L.*) mathematically as:

$$D.L. = 3.o_b/m$$

where o_b is the standard deviation of the blank response, and *m* is the slope (or sensitivity) of the calibration curve for the analyte in question. Using this definition, the lower limits of detectability for a range of VOCs using the purge-and-trap stripping method were determined. These data are presented in Table II.

Linear dynamic range

The linear dynamic range of the method was investigated by preparing and analysing serial dilutions of master standard mixtures. The bottom of the range is set by the limits of detection for each component. However, at higher concentrations, diminishing recoveries and/or overloading of the sample tube with analyte occurs, leading to loss of linear response at the flame ionisation detector. To test for linearity, the response factor for each component was compared with the actual peak area and the known concentration in the calibration blends. The response factor should yield the correct concentration for the component (allowing for the accuracy and precison of the method) within the linear range of the component. Linear dynamic range data for a series of volatile organic compounds are also presented in Table II.

Repeatability

The short term precision (*i.e.* repeatability) of the purging method is expressed as the relative standard deviation (R.S.D.) over three concentration levels. This data is presented in Table III. The data illustrate that the R.S.D. decreases with increasing concentration for all the model VOC classes tested during these experiments. However, not all compound classes yielded similar values. For example, volatile alcohols and ketones exhibited R.S.D. values up to 12.2% for alcohols (*i.e. n-* and 2-butanol), and up to 24.2% for ketones (*i.e.* 2-decanone). Conversely, alkanes, aromatics and halogenated compounds exhibited R.S.D. values between 1.1 and 4.3% at the 100 μg kg^{-1} concentration level.

Accuracy

Accuracy is expressed as the bias. Bias is a directional value which shows how much the sample results differ from the reference value. This can be summarised as (bias = average value − reference value). The bias value can therefore be positive or negative. The bias values for the model VOC at three concentration levels are presented in Table IV. Accuracies were generally within ± 20% at the 100 ng kg^{-1} level, ± 3.8% at the 1000 ng kg^{-1} level, and ± 6% at the 100 μg kg^{-1} concentration level. This indicates that the method accuracy is highest mid-way between the dynamic linear range of the method, diminishing slightly towards the lower and upper limits respectively.

TABLE II

LIMITS OF DETECTION AND LINEAR DYNAMIC RANGE FOR SELECTED VOLATILE
ORGANIC COMPOUNDS RECOVERED FROM SEDIMENTS AT 60°C

Compound Name	Limits of detection (ng kg^{-1}, dry weight)	Linear dynamic range (dry weight)	
		Lower limit (ng kg^{-1})	Upper limit (μg kg^{-1})
n-Pentane	10	10	550
n-Hexane	30	40	510
n-Heptane	30	60	510
n-Octane	40	75	500
n-Nonane	50	80	500
n-Decane	80	100	490
n-Undecane	100	115	490
n-Dodecane	100	120	480
n-Tridecane	100	120	480
n-Tetradecane	100	150	460
Isopentane	30	10	550
3-Methyl-1,3-butadiene	30	40	600
2,2-Dimethylbutane	40	50	520
2,3-Dimethylbutane	40	50	520
2-Methylpentane	45	60	520
3-Methylpentane	45	60	520
Cyclopentane	50	70	500
2,2,4-Trimethylpentane	70	90	450
2,4,4-Trimethylpentene-2	90	110	440
Benzene	10	10	650
Methylbenzene	10	10	660
1,3-Dimethylbenzene	20	25	600
1,2-Dimethylbenzene	20	25	600
Ethylbenzene	20	25	600
Isopropylbenzene	30	45	590
n-Propylbenzene	30	50	550
1,2,3-Trimethylbenzene	40	70	490
1,2,4-Trimethylbenzene	40	70	480
1,3,5-Trimethylbenzene	40	70	480
1,2,3,4-Tetramethylbenzene	70	110	460
1,2,3,5-Tetramethylbenzene	70	110	460
1,2-Dichlorobenzene	60	90	380
Dichloromethane	10	20	370
Trichloromethane	10	30	360
1,1,1-Trichloroethane	10	70	340
Trichloroethylene	15	130	340
Chloroethane	30	250	130
1,1,2-Trichlorotrifluoroethane	40	170	50
Dimethylsulphide	10	10	700
Dimethyldisulphide	10	10	700
Dimethyltrisulphide	20	40	670
2-Methylthiophene	60	90	580
Ethanol	200	280	200
Propanol	270	300	300
$tert.$-Butanol	270	330	380
n-Butanol	300	330	380
2-Butanol	300	370	370

TABLE II *(continued)*

Compound Name	Limits of detection (ng kg^{-1}, dry weight)	Linear dynamic range (dry weight)	
		Lower limit (ng kg^{-1})	Upper limit (μg kg^{-1})
Propanal	50	70	480
Pentanal	50	70	480
Hexanal	70	80	470
Heptanal	70	80	470
Benzaldehyde	70	90	450
2-Butanone	300	390	390
2-Pentanone	300	300	390
2-Heptanone	300	300	370
2-Decanone	320	350	290
Naphthalene	100	120	430
Indene	100	120	430
1,3-Dimethylnaphthalene	170	190	400
1,2-Dimethylnaphthalene	165	190	400
2-Methylfuran	40	70	450
2,5-Dimethylfuran	40	70	450
1-Chloroheptane	40	180	400
1-Chlorooctane	50	190	400

The effect of sediment type

The effect of different grain size distribution and organic matter content on the efficiency of the stripping method was examined. Analysis was performed on samples from the head (sediment 1), mid-point (sediment 2) and mouth of the estuary (sediment 3). The physical data was presented in Table I. Briefly, sediment 1 contains the lowest clay (18.36%) and sand (1.35%) content and highest organic carbon (20.79%) and silt (80.29%) content. Sediment 2 contains the highest proportion of mud (97.45%). Sediment 3 contains the highest proportion of sand (5.31%) and clay (24.34%) and the smallest proportion of organic matter (13.21%) and silt (70.35%).

The recoveries of volatile organic compounds from each of the three sediment types were measured. These experiments were conducted at 30°C and 60°C to determine the relative effect of sediment type and stripping temperature upon recovery. The results are presented in Table V.

Inspection of the data show that, in general, high clay and sand contents correspond with lowest recoveries, *i.e.* sediment 3 recoveries were up to 2–4% lower than sediment 1, which contains the highest proportion of silt. A similar observation was made by Karickhoff *et al.* [15] who stated that the linear partition coefficients (K_p) were directly related to organic carbon content for different particle size isolates in different sediments. In particular, the sand fraction (> 50 μm particle size) acts as a less effective sorbent. Less conclusive funtional relationships were found when comparing relative recoveries with the percentage of organic carbon and clays within the sediments. However, the general observation was made that the higher the silt contents, the better the recoveries. This observation was also reflected in data reported

TABLE III

THE REPEATABILITY OF MODEL VOLATILE ORGANIC COMPOUNDS PURGED FROM SEDIMENTS AT 60°C

Short term precision is expressed as % relative standard deviation (R.S.D.) at three concentration levels.

Compound name	Concentrations (dry weight)		
	100 ng kg^{-1}	1000 ng kg^{-1}	100 μg kg^{-1}
n-Pentane	5.5	4.6	1.9
n-Hexane	5.7	4.6	2.0
n-Heptane	5.7	4.7	2.0
n-Octane	5.9	4.8	2.2
n-Nonane	6.2	4.9	2.2
n-Decane	6.7	5.1	2.3
n-Undecane	—	5.0	2.5
n-Dodecane	—	5.2	2.6
n-Tridecane	—	5.2	2.9
n-Tetradecane	—	5.9	3.0
Isopentane	4.4	4.7	2.2
3-Methyl-1,3-butadiene	4.3	4.3	2.1
2,2-Dimethylbutane	4.4	4.1	2.1
2,3-Dimethylbutane	4.4	4.1	2.1
2-Methylpentane	4.3	4.1	2.0
3-Methylpentane	4.3	4.1	2.0
Cyclopentane	5.0	4.3	2.1
2,2,4-Trimethylpentane	5.6	4.5	2.2
2,4,4-Trimethylpentene-2	—	4.6	2.3
Benzene	3.3	2.6	1.1
Methylbenzene	3.3	2.7	1.2
1,3-Dimethylbenzene	3.4	2.9	1.3
1,2-Dimethylbenzene	3.4	2.9	1.4
Ethylbenzene	3.5	2.8	1.3
Isopropylbenzene	3.7	3.0	1.5
n-Propylbenzene	3.7	3.0	1.7
1,2,3-Trimethylbenzene	3.8	3.1	1.9
1,2,4-Trimethylbenzene	3.9	3.4	2.1
1,3,5-Trimethylbenzene	4.1	3.6	2.2
1,2,3,4-Tetramethylbenzene	—	3.6	2.5
1,2,3,5-Tetramethylbenzene	—	3.7	2.5
1,2-Dichlorobenzene	4.4	4.1	2.4
Dichloromethane	3.2	3.9	1.8
Trichloromethane	3.7	3.0	2.1
1,1,1-Trichloroethane	3.1	2.9	2.1
Trichloroethylene	—	2.9	2.2
Chloromethane	—	3.4	2.7
1,1,2-Trichlorotrifluoroethane	—	5.4	4.3
Dimethylsulphide	3.2	2.2	1.2
Dimethyldisulphide	3.3	2.3	1.4
Dimethyltrisulphide	3.4	2.5	1.6
2-Methylthiophene	3.7	2.3	1.9

TABLE III *(continued)*

Compound name	Concentrations (dry weight)		
	100 ng kg^{-1}	1000 ng kg^{-1}	100 μg kg^{-1}
Ethanol	—	9.9	8.4
Propanol	—	10.1	8.8
tert.-Butanol	—	11.2	9.0
n-Butanol	—	12.2	10.3
2-Butanol	—	12.2	10.3
Propanal	4.8	4.0	3.4
Pentanal	4.8	4.2	3.7
Hexanal	4.9	4.8	3.9
Heptanal	4.9	4.7	3.9
Benzaldehyde	4.0	3.4	2.2
2-Butanone	—	16.2	13.4
2-Pentanone	—	17.2	14.7
2-Heptanone	—	24.6	18.3
2-Decanone	—	30.1	24.2
Naphthalene	—	5.1	4.2
Indene	—	5.1	4.3
1,3-Dimethylnaphthalene	—	5.2	4.5
1,2-Dimethylnaphthalene	—	5.2	4.7
2-Methylfuran	5.4	4.6	3.9
2,5-Dimethylfuran	5.5	4.9	3.9
1-Chloroheptane	—	3.1	2.5
1-Chlorooctane	—	3.3	2.8

by Charles and Simmons [13]. In their report, which investigated the stripping of chlorinated solvents from sediments at ambient temperatures, the authors concluded that neither sediment weight, sediment type, nor the conductivity of the desorbing solution had noticeable effects on the recovery performance of a simple purge-and-trap method. Using their method, recoveries were quoted of 38% for trichloromethane, 48% for trichloroethylene and 54% for chlorobenzene. However, concern over the wide variance in reproducibility (*i.e.* between 4% and 55%) was expressed [13]. Our experiments using the modified open-loop stripping method [24], revealed an improvement in the recovery of the same compounds (*i.e.* trichloromethane, 84%; trichloroethene, 87%; and chlorobenzene, 84%, respectively), with a standard deviation ($n = 15$) for all compounds of less than 10%. These improvements reflect the comparative influence of method parameters on overall recoveries, relative to differences in sediment type.

The efficiency of multi-sorbent trapping

The use of a multi-sorbent trapping system for trace VOC analyses have been previously discussed by the authors [24]. The combination of sorbents, with individual affinities and retentive capacities for different compounds, traps those compounds

TABLE IV

THE ACCURACY OF MODEL VOLATILE ORGANIC COMPOUNDS PURGED FROM SEDIMENTS AT 60°C

The accuracy is expressed as the bias of the method for individual VOCs at three concentration levels.

Compound name	Concentrations (dry weight)		
	100 ng kg^{-1}	1000 ng kg^{-1}	100 μg kg^{-1}
n-Pentane	9	-15	6
n-Hexane	7	16	2
n-Heptane	7	19	2
n-Octane	-9	19	2
n-Nonane	12	19	2
n-Decane	17	-11	-3
n-Undecane	—	20	5
n-Dodecane	—	22	6
n-Tridecane	—	-32	-9
n-Tetradecane	—	29	7
Isopentane	4	17	2
3-Methyl-1,3-butadiene	3	13	1
2,2-Dimethylbutane	-9	-11	2
2,3-Dimethylbutane	12	-23	4
2-Methylpentane	9	28	5
3-Methylpentane	10	19	3
Cyclopentane	12	-23	4
2,2,4-Trimethylpentane	5	11	3
2,4,4-Trimethylpentene-2	10	23	-1
Benzene	8	4	-1
Methylbenzene	9	4	-1
1,3-Dimethylbenzene	11	-5	2
1,2-Dimethylbenzene	12	-4	1
Ethylbenzene	13	3	2
Isopropylbenzene	-16	7	-1
n-Propylbenzene	17	7	-1
1,2,3-Trimethylbenzene	-11	2	3
1,2,4-Trimethylbenzene	-12	7	3
1,3,5-Trimethylbenzene	18	23	3
1,2,3,4-Tetramethylbenzene	—	24	-2
1,2,3,5-Tetramethylbenzene	—	-30	2
1,2-Dichlorobenzene	10	19	1
Dichloromethane	16	19	-2
Trichloromethane	9	10	2
1,1,1-Trichloroethane	9	11	2
Trichloroethylene	—	16	-1
Chloromethane	—	-33	-5
1,1,2-Trichlorotrifluoroethane	—	-28	-3
Dimethylsulphide	2	5	1
Dimethyldisulphide	3	8	1
Dimethyltrisulphide	4	5	2
2-Methylthiophene	7	3	1

TABLE IV *(continued)*

Compound name	Concentrations (dry weight)		
	100 ng kg^{-1}	1000 ng kg^{-1}	100 μg kg^{-1}
Ethanol	–	– 9	–4
Propanol	–	– 1	–5
tert.-Butanol	–	– 3	–3
n-Butanol	–	– 2	–3
2-Butanol	–	– 2	–3
Propanal	5	4	1
Pentanal	8	– 2	1
Hexanal	11	– 3	2
Heptanal	–23	– 3	1
Benzaldehyde	21	5	2
2-Butanone	–	– 23	–2
2-Pentanone	–	– 24	–2
2-Heptanone	–	– 35	–2
2-Decanone	–	– 38	–3
Naphthalene	–	28	2
Indene	–	24	2
1,3-Dimethylnaphthalene	–	30	– 1
1,2-Dimethylnaphthalene	–	28	–2
2-Methylfuran	7	10	–2
2,5-Dimethylfuran	– 5	– 10	1
1-Chloroheptane	–	11	1
1-Chlorooctane	–	13	– 1

which would otherwise be unretained by single adsorbent traps. Multi-sorbent trapping has therefore been an increasingly popular approach in purge-and-trap analysis in recent years. In general, Tenax-TA quantitatively retains most volatile compounds in a boiling-point range extending roughly from benzene and *n*-heptane upwards, although it will retain more volatile compounds at very low concentrations. Tenax has a limited retention volume capacity for low boiling organics and more efficient sorbents must be substituted [34] to achieve quantitative trapping. Although this method uses Chromosorb-106 and Spherocarb as the second and third traps respectively, newer sorbents such as Carbopack B, a graphitised carbon black, offer realistic alternatives. Multi-sorbent trapping also minimises overloading which is encountered when employing single tubes, with organics, and interferences which may occur between the sorbates. The practical value of employing this three-stage trapping arrangement was also discussed in more detail in the previous paper [24].

The effect of stripping temperature
        The results of these experiments show that the stripping temperature of the sediments has a significant effect on compound recovery. When compared to the recoveries of VOCs from water samples [24], Table V shows that, in general, recoveries at both 30°C and 60°C are lower from sediments.

TABLE V

RECOVERIES OF VOLATILE ORGANIC COMPOUNDS FROM DIFFERENT SEDIMENT TYPES AT 30°C AND 60°C

Conditions: helium flow-rate, 100 ml min⁻¹; sampling time, 70 min.

Compound name	Sediment type	Molecular mass	Boiling point (°C)	Recovery	
				30°C	60°C
n-Pentane	1	72.1	35	84	97
	2			82	95
	3			81	93
n-Hexane	1	86.2	69	84	88
	2			83	87
	3			82	86
n-Heptane	1	100.2	98	76	85
	2			75	83
	3			75	82
n-Octane	1	114.2	126	73	79
	2			72	78
	3			71	77
n-Nonane	1	128.2	151	73	77
	2			72	76
	3			71	75
n-Decane	1	142.3	174	70	74
	2			69	73
	3			67	71
n-Undecane	1	156.3	196	65	71
	2			63	70
	3			61	69
n-Dodecane	1	170.3	216	59	67
	2			56	66
	3			55	64
n-Tridecane	1	198.4	234	53	65
	2			50	63
	3			47	61
n-Tetradecane	1	198.4	254	46	65
	2			65	62
	3			64	60
Isopentane	1	72.1	28	87	95
	2			86	94
	3			85	93
3-Methyl-1,3-butadiene	1	68.1	34	85	92
	2			84	91
	3			81	90
2,2-Dimethylbutane	1	86.2	50	79	84
	2			78	84
	3			78	83
2,3-Dimethylbutane	1	86.2	58	77	83
	2			76	82
	3			75	81
2-Methylpentane	1	86.2	62	76	85
	2			75	84
	3			73	83

TABLE V *(continued)*

Compound name	Sediment type	Molecular mass	Boiling point (°C)	Recovery	
				30°C	60°C
3-Methylpentane	1	86.2	64	75	84
	2			75	84
	3			74	83
Cyclopentane	1	70.1	50	77	85
	2			76	84
	3			74	82
2,2,4-Trimethylpentane	1	114.2	98	75	86
	2			73	85
	3			74	82
2,4,4-Trimethylpentene-2	1	112.2	102	73	84
	2			70	83
	3			69	82
Benzene	1	78	79	80	92
	2			80	90
	3			80	90
Methylbenzene	1	92.1	83	78	84
	2			77	83
	3			76	82
1,3-Dimethylbenzene	1	106.2	139	68	78
	2			67	77
	3			66	76
1,2-Dimethylbenzene	1	106.2	144	66	77
	2			65	76
	3			64	75
Ethylbenzene	1	116.2	135	59	78
	2			58	77
	3			57	76
Isopropylbenzene	1	120.2	153	57	76
	2			56	75
	3			55	74
n-Propylbenzene	1	120.2	159	55	74
	2			54	73
	3			50	71
1,2,3-Trimethylbenzene	1	120.2	176	57	74
	2			55	73
	3			53	71
1,2,4-Trimethylbenzene	1	120.2	168	54	73
	2			52	72
	3			49	70
1,3,5-Trimethylbenzene	1	120.2	163	54	75
	2			54	74
	3			52	71
1,2,3,4-Tetramethylbenzene	1	134.2	205	47	68
	2			45	68
	3			44	65
1,2,3,5-Tetramethylbenzene	1	134.2	199	48	69
	2			45	68
	3			44	65

TABLE V *(continued)*

Compound name	Sediment type	Molecular mass	Boiling point (°C)	Recovery	
				30°C	60°C
1,2-Dichlorobenzene	1	147	179	56	73
	2			55	72
	3			53	71
Dichloromethane	1	86.9	40	85	92
	2			83	91
	3			80	89
Trichloromethane	1	120.4	61	69	85
	2			68	85
	3			68	84
1,1,1-Trichloroethane	1	133.4	75	73	87
	2			71	86
	3			69	85
Trichloroethylene	1	131.4	86.9	71	86
	2			69	85
	3			69	84
Chloromethane	1	51	−24	83	94
	2			80	92
	3			75	89
1,1,2-Trichlorotrifluoroethane	1	187.4	47	71	87
	2			68	87
	3			66	85
Dimethylsulphide	1	62	38	71	91
	2			70	90
	3			70	87
Dimethyldisulphide	1	94.2	109	69	79
	2			69	77
	3			67	77
2-Methylthiophene	1	98.2	113	68	84
	2			67	83
	3			65	82
Ethanol	1	46	78	45	70
	2			45	70
	3			42	67
2-Propanol	1	60	82	44	69
	2			45	69
	3			44	67
tert.-Butanol	1	75	118	38	61
	2			38	60
	3			35	58
n-Butanol	1	75	118	37	61
	2			37	60
	3			35	57
2-Butanol	1	74	98	37	69
	2			34	63
	3			34	60
Propanal	1	58	48	80	88
	2			77	86
	3			74	84

TABLE V *(continued)*

Compound name	Sediment type	Molecular mass	Boiling point (°C)	Recovery	
				30°C	60°C
Pentanal	1	86	103	70	84
	2			68	84
	3			66	80
Heptanal	1	114	153	65	76
	2			64	76
	3			60	74
Benzaldehyde	1	106	179	55	73
	2			55	72
	3			54	70
2-Butanone	1	72.1	80	38	73
	2			35	71
	3			33	67
2-Pentanone	1	86.1	101	37	70
	2			35	67
	3			31	65
2-Heptanone	1	114.2	150	29	59
	2			29	58
	3			27	55
2-Decanone	1	156	211	25	47
	2			25	46
	3			24	42
Naphthalene	1	128	217	46	62
	2			44	59
	3			40	57
Indene	1	116	182	49	64
	2			48	63
	3			47	60
1,3-Dimethylnaphthalene	1	156	263	38	54
	2			38	54
	3			36	50
1,2-Dimethylnaphthalene	1	156	267	35	53
	2			35	52
	3			34	50
Internal standards					
1-Chloroheptane	1	134.7	159–161	69	79
	2			67	78
	3			65	73
1-Chlorooctane	1	148.7	223	58	70
	2			57	69
	3			54	67

Total recoveries in excess of 50% were obtained for a broad range of organic compounds stripped at 30°C. Strip recoveries were increased by amounts ranging from 10–40% for most compounds when strip temperatures were raised to 60°C, regardless of differences in the physical composition of the sediments. This effect may be

important when very low concentrations (ng kg^{-1}) need to be purged from the sediment matrix or when poor recoveries are achieved when using ambient strip temperatures, as experienced by Charles and Simmons [13].

However, at temperatures above 60°C, recoveries of some volatile compounds such as chloromethane and 3-methyl-1,3-butadiene began to fall off with increasing temperature, regardless of their physical composition. This may have occurred as
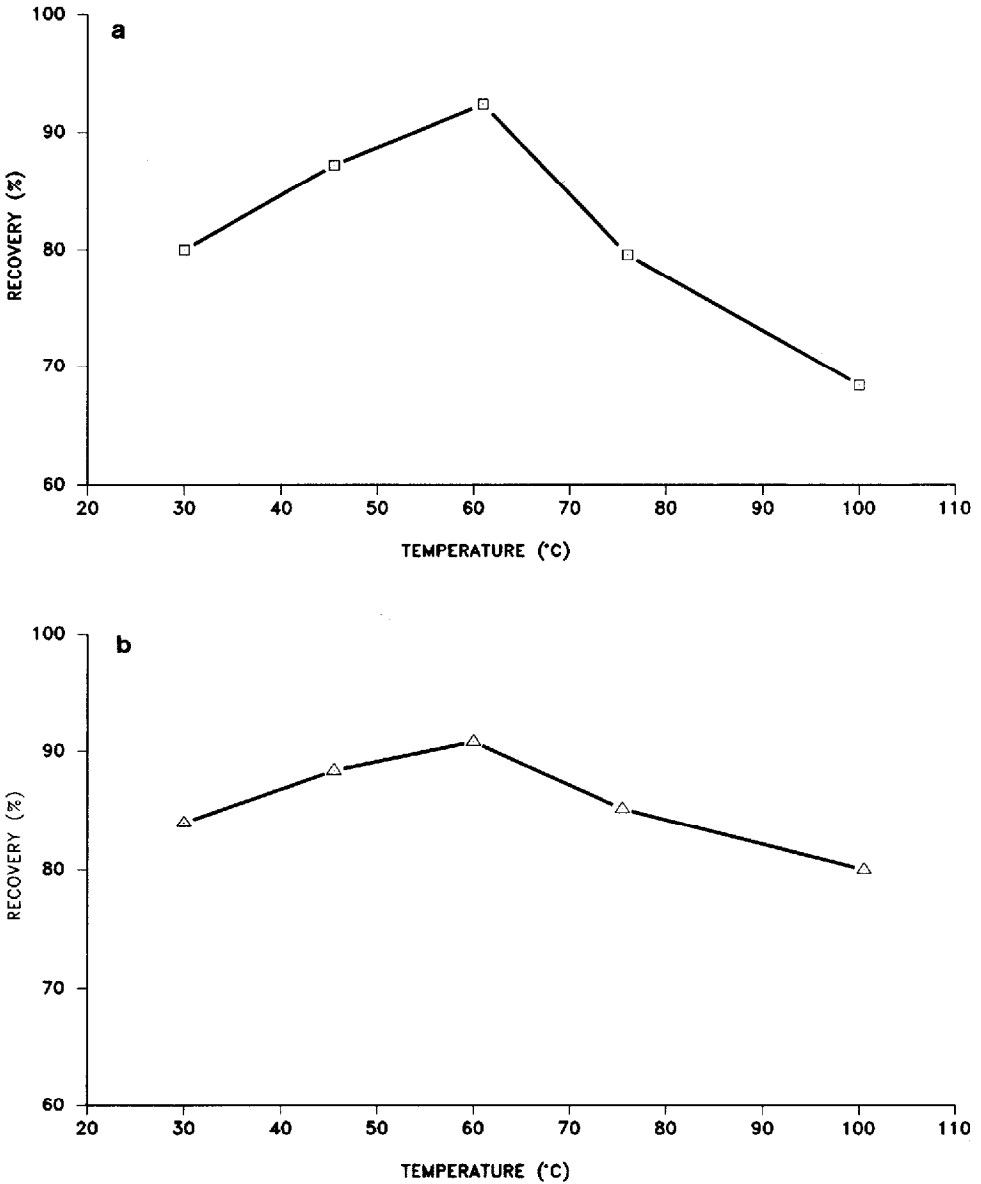

Fig. 2. The variation in recovery of (a) chloromethane and (b) 2-methyl-1,3-butadiene with increasing stripping temperature.

a result of thermal degradation or following reaction with other analytes. This effect is illustrated in Fig. 2 which shows the loss in recovery of both analytes as the stripping temperature is stepped above 60°C. There was no evidence of leakage from the stripping apparatus, and the selective removal of these compounds suggests a degradative pathway specific to these compounds.

The effect of boiling point on recovery

According to Charles and Simmons [13], the performance of sediment purge-and-trap methods are primarily dependent on the physico-chemical properties of the analytes, rather than intrinsic properties of the sediments. Three of the most common physico-chemical properties of VOCs are their boiling points, vapour pressures and aqueous solubilities. Table V included corresponding boiling points of the model VOCs used in this study listed alongside the recoveries of the same VOCs from the three different sediment matrices. When the recoveries of all 60 tabulated compounds (at 60°C) are plotted against their respective boiling points, the correlation coefficient ($R = -0.806$) suggests that a reasonably good correlation exists between both parameters. This is illustrated in Fig. 3a. However, most of the individual plotted data points which fall below the line in Fig. 3a correspond to the values for volatile alcohols and ketones. When the recovery values for the alcohols and ketones are excluded from the correlation data table, the modified correlation coefficient value ($R = -0.955$) shows a much higher correlation between boiling point and recovery for the remaining compounds. See Fig. 3b. This indicates that the relationship between recovery and boiling point depends significantly upon the functional organic compound class. Hence, comparatively non-polar, hydrophobic compounds such as the volatile alkanes, aromatics and organohalogens, for example, exhibit a more consistent and linear relationship between boiling point and recovery (*i.e.* at 60°C) than the polar, hydrophilic alcohols and ketones, especially when purging is carried out at above ambient temperatures.

The effect of vapour pressure on recovery

There are less data in the literature on the vapour pressures of organic compounds than corresponding boiling point data. However, when recovery was plotted against vapour pressure (mmHg at 20°C) for a representative group of the model VOCs (*i.e.* for which vapour pressure values are available, listed in Table VI), a moderate correlation coefficient ($R = 0.715$) was obtained. As a general observation, organic compounds with recoveries below 80% and/or vapour pressures below 30 mmHg at 20°C correlated only marginally (*i.e.* $R = <0.5$). As Table V and VI show, these compounds correspond mainly with the volatile alcohols, ketones or with those *n*-alkanes with boiling points above 100°C. However, by excluding compounds with recoveries below 80% and vapour pressures less than 30 mmHg at 20°C from the original data set, the correlation coefficient ($R = 0.733$) improves only slightly. Hence, the experimental data obtained from this study suggest that, in general, the higher the vapour pressure of the selected VOC, the better the recovery. The relationship between vapour pressure and recovery is, however, less well established than the relationship between boiling point and recovery.
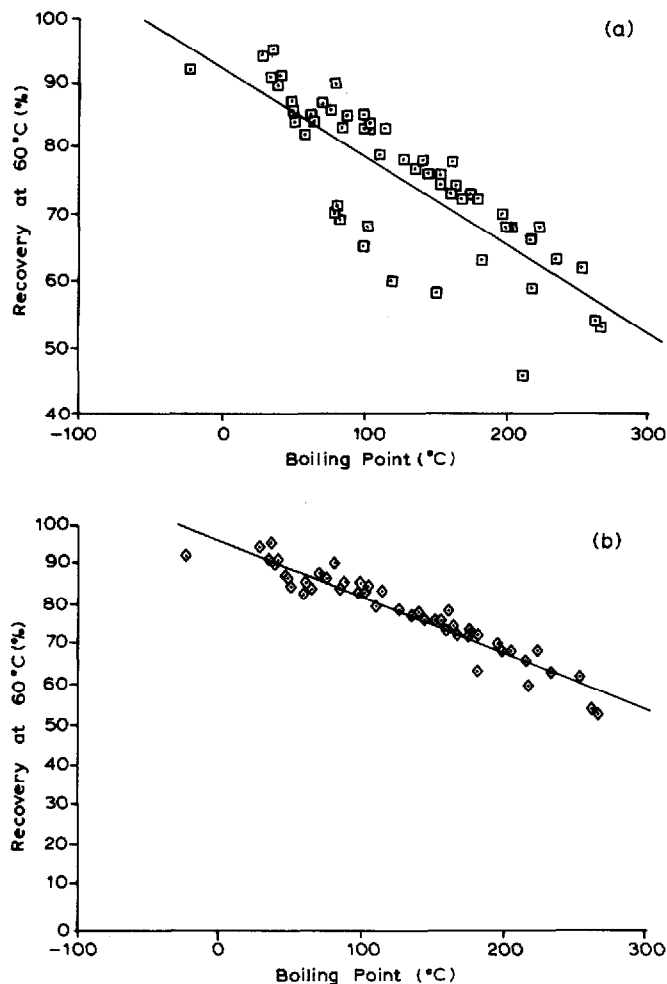
Fig. 3. (a) Correlation line obtained by plotting recovery (at 60°C) from sediment against the boiling points (°C) of 60 model VOCs listed in Table V; $y = 92.31 - (-0.1338)x$, $r = -0.806$. (b) Correlation line obtained by replotting the data in (a) excluding all the data points for the volatile alcohol and ketone compounds; $y = 95.10 - (-0.1364)x$, $r = -0.955$.

The effect of solubility on recovery

When recoveries were plotted against the corresponding aqueous solubility data (also presented in Table VI), a very low correlation coefficient ($R = -0.414$) was obtained. However, as Table VI shows, the solubilities of the model VOCs vary widely from, for example, 0.009 mg l^{-1} for n-decane to 353 000 mg l^{-1} for 2-butanone. According to McAuliffe [35], it is the nature of the chemical bonding and size of individual organic compounds which largely determines their solubility in water. Research by McAuliffe concluded that for each homologous series of hydrocarbons, the logarithm of the solubility in water is a linear function of the hydrocarbon molar

TABLE VI

SOLUBILITIES (AT 25°C) AND VAPOUR PRESSURES (AT 20°C) OF SELECTED VOLATILE ORGANIC COMPOUNDS

Data from refs. 35 and 40.

| Compound	Vapour pressure (mmHg at 20°C)	Solubility (mg l^{-1} at 25°C)
n-Pentane	430	38.5
n-Hexane	120	9.5
n-Heptane	35	293
n-Octane	11	0.66
n-Nonane	3.22	0.07
n-Decane	2.70	0.009
n-Undecane	0.90	—
3-Methyl-1,3-butadiene	493	642.0
2,2-Dimethylbutane	—	18.4
2,3-Dimethylbutane	200	—
2-Methylpentane	190 (approximate)	13.8
3-Methylpentane	—	12.8
Cyclopentane	300 (approximate)	156.0
Isopentane	—	47.8
2,2,4-Trimethylpentane	—	2.44
Benzene	76	1780
Methylbenzene	22	515
1,3-Dimethylbenzene	6	—
1,2-Dimethylbenzene	5	175
Ethylbenzene	7	152
1,2,4-Trimethylbenzene	—	57
Isopropylbenzene	—	50
1,2-Dichlorobenzene	1	100
Dichloromethane	349	20000
Trichloromethane	160	8000
1,1,1-Trichloroethane	100	4400
Trichloroethylene	60	1100
1,1,2-Trichlorotrifluoroethane	270	—
Dimethylsulphide	420	6300
Ethanol	43.9	—
Propanol	14.5	—
tert.-Butanol	31	—
n-Butanol	4.4	—
2-Butanol	12	125000
Propanal	235	—
Pentanal	48	—
Heptanal	2	—
Benzaldehyde	0.8	—
2-Butanone	77.5	353000
2-Pentanone	12	—
2-Heptanone	2.6	—
Naphthalene	0.4 (approximate)	—
2-Methylfuran	142	—
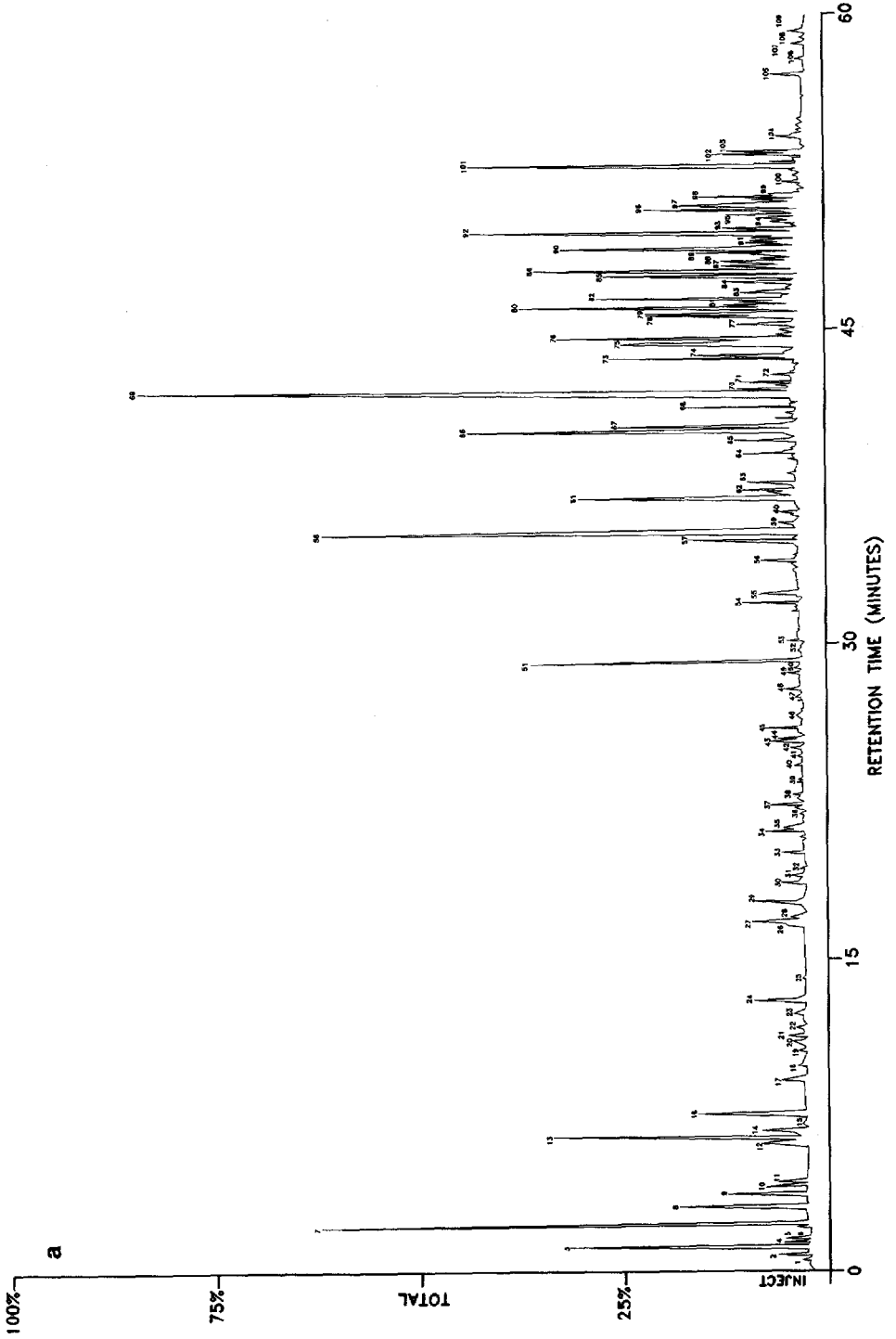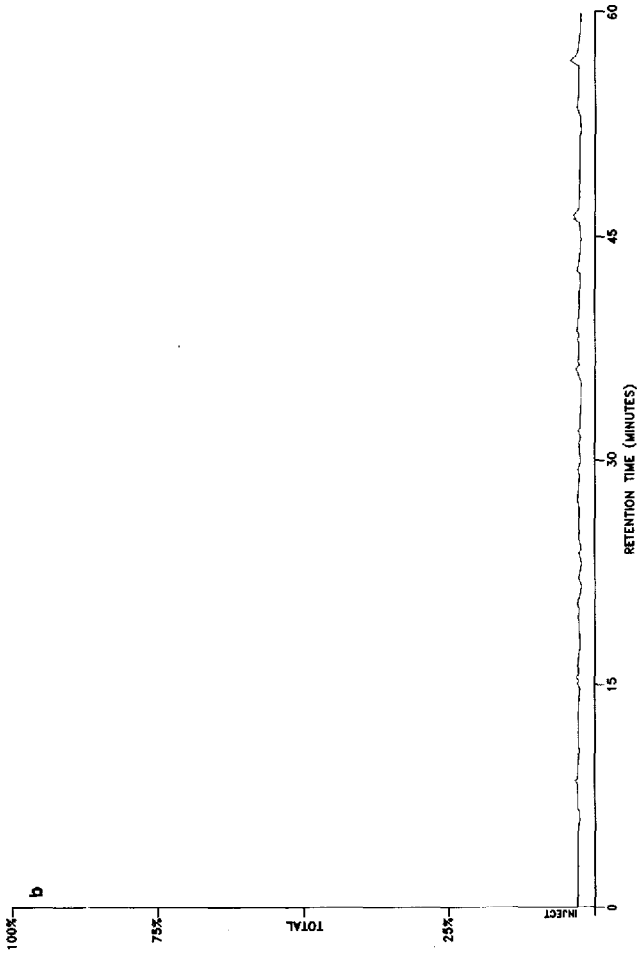
Fig. 4.
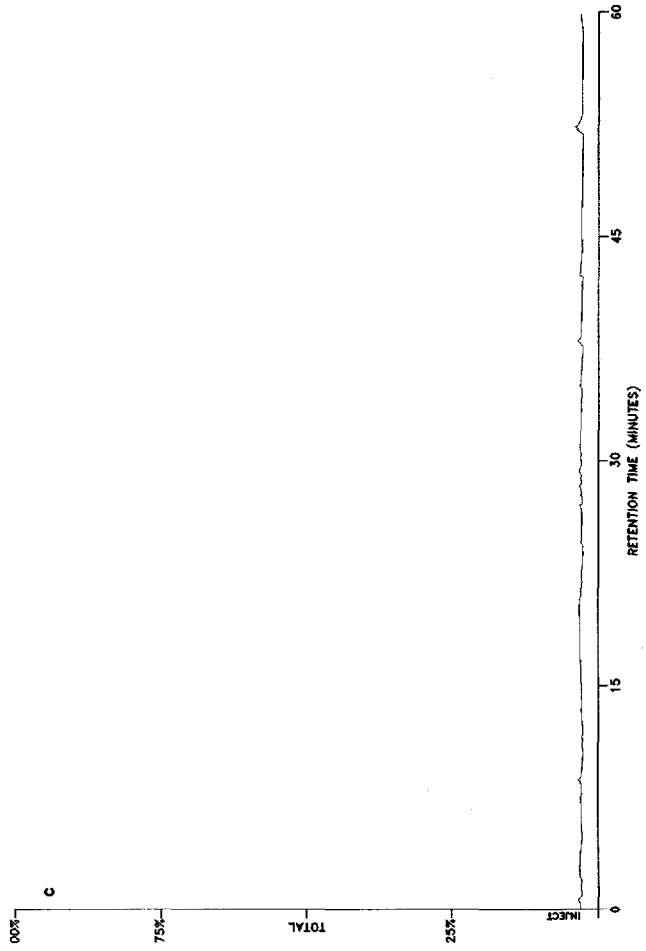
Fig. 4. (a) Reconstructed ion-chromatogram (RIC) of a gasoline contaminated sediment sample taken from the Itchen river in the Southampton Water estuary. This trace was obtained by desorbing the organic analytes trapped on the Tenax-TA tube. (b) Reconstructed ion-chromatogram (RIC) of "blank" water and sediment mixture purged onto the Tenax-TA tube prior to the sample analysis. (c) Reconstructed ion-chromatogram (RIC) of "blank" water and sediment mixture purged onto the Tenax-TA tube after the sample analysis. Peaks: 1 = Propane; 2 = iso-butane; 3 = n-butane; 4 = $trans$-butene-2; 5 = cis-butene-2; 6 = 3-methyl-butene-1; 7 = isopentane; 8 = n-pentane; 9 = 2-methylbutene-1; 10 = $trans$-pentene-2; 11 = cis-pentene-2 + 2,2-dimethylbutane; 12 = 2,3-dimethylbutane; 13 = 2-methylpentane; 14 = cyclopentane; 15 = 4-methylpentene-2; 16 = 3-methylpentane; 17 = n-hexane; 18 = 2-methylpentene-1; 19 = $trans,cis$-hexene-2; 20 = $trans$-hexene-2; 21 = 2-methylpentene-2; 22 = cis-3-methylpentene-2; 23 = 4-methylcyclopentane; 24 = $trans$-3-methylpentene-2 + cis-hexene-2 + 2,4-dimethyl-pentane; 25 = methyl cyclopentane; 26 = 4-methylcyclopentene; 27 = 2-methylhexane + cyclohexane; 28 = 2,3-dimethylpentane; 29 = 3-methylhexane; 30 = 2,2,4-trimethylpentane; 31 = cis-2,3-dimethylcyclopentane; 32 = $trans$-1,2-dimethylcyclopentane; 33 = cyclohexene; 34 = 2,3-dimethylpentene-2; 35 = n-heptane; 36 = 3-methylhexene-1; 37 = benzene; 38 = $trans$-1,2-dimethylcyclopentane; 39 = hexene-2; 40 = 3-methylhexene-2; 41 = C$_4$ olefin; 42 = methylcyclohexane; 43 = 2,5-dimethylhexane; 44 = 1,4-dimethylhexane; 45 = n-octane; 46 = octene; 47 = 2,3,4-trimethylpentane; 48 = 2,3,3-trimethylpentane; 49 = 2,3-dimethylhexane; 50 = 2,2-dimethylheptane; 51 = methylbenzene; 52 = 2,6-dimethylheptane; 53 = 3,5-dimethylheptane; 54 = 2- + 4-methyloctane; 55 = 3-methyloctane; 56 = n-nonane; 57 = ethylbenzene; 58 = 1,2- + 1,4-dimethylbenzene; 59 = dimethyloctane; 60 = C$_{10}$ alkene + cyclodiene; 61 = 1,3-dimethylbenzene; 62 = 4-methylnonane; 63 = isopropylbenzene; 64 = n-decane; 65 = n-propylbenzene; 66 = 1-methyl-3-ethylbenzene + 1-methyl-4-ethylbenzene; 67 = 1,3,5-trimethyl-benzene; 68 = 1-methyl-2-ethylbenzene; 69 = 1,2,4-trimethylbenzene + C$_{11}$ alkene; 70 = secondary butylbenzene; 71 = C$_{11}$ alkane; 72 = aromatic?; 73 = 1,2,3-trimethylbenzene; 74 = n-undecane; 75 = nonene-1; 76 = 1-methyl-3-propylbenzene; 77 = 1-methyl-2-propylbenzene; 78 = 1,4-dimethyl-3-ethylbenzene; 79 = 1,3-dimethyl-4-ethylbenzene; 80 = 2-dimethyl-4-ethylbenzene; 81 = C$_{10}$ aromatic; 82 = substituted indene aromatic?; 83 = C$_{12}$ alkane; 84 = 1,3-dimethyl-2-ethylbenzene; 85 = 1,2,4,5-tetramethylbenzene; 86 = 1,2,3,5-tetramethylbenzene; 87 = n-dodecane; 88 = C$_{11}$ alkane + C$_{11}$ alkene; 89 = C$_{11}$ aromatic; 90 = C$_{11}$ aromatic; 91 = C$_{11}$ aromatic; 92 = 2,3-dihydro, 4-methyl-indene; 93 = dimethylpropylbenzene; 94 = C$_{11}$ aromatic; 95 = 2,3-dihydro-1,3-dimethylindene; 96 = n-tridecane; 97 = 2,3-dihydro-1,6-dimethylindene; 98 = C$_{12}$ aromatic; 99 = C$_{12}$ aromatic; 100 = C$_{12}$ aromatic; 101 = naphthalene; 102 = 2,3-dihydro-4,7-dimethylindene; 103 = C$_{13}$ aromatic; 104 = dihydrodimethylindene; 105 = 1-methylnaphthalene; 106 = 2-methylnaphthalene; 107 = 1,3-di-methylnaphthalene; 108 = C$_{13}$ alkene; 109 = 1,2-dimethylnaphthalene.

volume. Solubility decreases in the order alkynes > alkenes > alkanes. McAuliffe also stated that branching of the molecule increases the water solubility for alkane, alkene and alkyne hydrocarbons but not for cycloalkane, cycloalkene or aromatic hydrocarbons. However, for a given carbon number, ring formation increases water solubility. Double bond addition to a molecule, ring or chain also increases water solubility. The increased solubilities due to branching are not due to structural features of the molecules, but to the higher vapour pressure of the branched chain hydrocarbons relative to the corresponding alkane or alkene hydrocarbon.

Hence, it is more useful to compare the experimental recoveries of VOCs from sediments with the solubilities of VOCs from within their own particular functional class, rather than across compounds with, for example, similar boiling ranges. When this is done, the increased correlation coefficients obtained (n-alkanes, $R = 0.864$; aromatics, $R = 0.916$; organohalogens, $R = 0.721$) show that improved correlations between the recovery and solubilities of groups of compounds are obtained. Solubility is therefore a reasonable guide to recovery of VOCs from the sediments found in Southampton Water, second to the boiling points.

Once again, it is the nature of the individual functional class which determines the reliability and predictability of these relationships. This suggests that by developing sound, experimentally based performance models for groups of compounds within individual organic classes, purge-and-trap analysis of sediment matrices can be reliably performed to obtain good quality analytical data.

Losses of VOCs following storage of sediments

Analysis of standard samples stored for 48 h in the refrigerator at $-4°C$ were found to be within the repeatability (*i.e.* short term precision, R.S.D.) of the method for all 60 model volatile compounds at three concentration levels (as quoted in Table III). The retention of chilled sediment samples under zero headspace in all-glass vessels is therefore an effective short-term storage option should it not be possible to immediately analyse samples. We did not determine the lifetime of chilled samples beyond a 48-h storage period.

Since most samples were analysed within 24 h of sampling, losses due to microbial attack, respiration and chemical alteration were minimised. However, for sediment samples kept in the laboratory at ambient temperature which *were not spiked* with sodium azide, it was observed that volatile organosulphide concentrations began to increase with time. For example, after 48 h storage at 24°C, dimethylsulphide, dimethyldisulphide and dimethyltrisulphide were recovered at higher concentrations (*i.e.* typically by 5–10%) relative to spiked samples analysed shortly after sampling. This phenomenon was previously noticed by Schwarzenbach *et al.* [36] who considered the *in-situ* synthesis of volatile organosulphides to be due to ongoing anaerobic microbial activity taking place after the samples were taken.

The Solent estuary —a case study

The Solent estuary forms a body of water separating the Isle of Wight from the submerged channel of Southampton Water on the coastline of central southern England. Southampton Water is a semi-industrialised estuary accommodating a broad range of activities including oil-refining, petrochemical processing, electricity generation and intense recreational and merchant-marine activities. In addition, the

estuary receives input from six sewage treatment plants, agricultural run-off and flush-water from enclosed marinas. The latter developments present a growing pollution problem for estuarine ecosystems. For example, Bianchi *et al.* [37] found high levels of volatile aromatic compounds (*i.e.* $> 500 \, \mu g \, l^{-1}$ per compound) in anoxic sediments adjacent to a new marina site in Southampton Water. Spillages of fuels occur from time to time and lead to localised contamination of water and underlying sediments. For example, Fig. 4a shows a reconstructed ion-chromatogram (RIC) obtained from the upper 5-cm of sediment in the River Itchen following the spillage of gasoline from a barge moored alongside fuel storage tanks. Fig. 4b and c show the respective ion-chromatograms obtained following purging of the Tenax-TA tube with a mixture of "blank" water and "blank" sediment before and after the Itchen sediment sample was analysed. The total mass of organic material (*i.e.* total area under the summed peaks) due to the petroleum spill was calculated to be 395 $\mu g \, kg^{-1}$. An interesting observation from this analysis is that some of the more volatile compounds (*e.g.* C_4 and C_5 compounds) have been recovered from the sediment and trapped/desorbed from the Tenax-TA tube. It was also noted that the comparatively high mass of gasoline components sorbed onto the surface sediments effectively "blanks-out" any natural, biogenic VOC present in the sediments at much lower concentrations from the analysis.

With so many potential sources of organic compounds it has become a major analytical challenge to identify, categorise and quantitate every single volatile compound found during purge-and-trap analysis of large numbers of water and sediment samples. Tables of concentration ranges of key compounds are a valuable aid in understanding how sediments act as repositories for VOCs. Sediments have the potential to accumulate and concentrate much higher levels of VOCs than might normally be found in the water column, especially within estuaries where large volumes of anthropogenic substances are channelled in the path from rivers to the open sea. Table VII shows the broad range of VOCs found in the estuarine sediments as well as the typical variation in concentrations which were observed between water and sediment samples over an 18-month period. The majority of the compounds listed in Table VII were found in all three sediments, *i.e.* head, mid-point and mouth of the estuary. This suggests that the many of the mechanisms responsible for their production and/or deposition in sediments behave similarly across the length of Southampton Water. Apart from random pollution related events (*i.e.* oil spills), the most significant variations in VOC concentrations occurred as a result of seasonal changes. For example, total VOC concentrations in sediments reach their minimum during July–August and their maximum from October–January. Higher summer temperatures accelerate evaporation from surface water relative to sorption and deposition processes. During autumn and winter, cooler sea-surface temperatures combined with significant increases in organic load to the estuary from its source rivers contribute to the build-up of VOCs in sediments from both synthetic and natural sources, *e.g.*, autumn leaf-fall. Increases in the anthropogenic input to the estuary during autumn (*i.e.* from increased rainfall run-off, increased use of fossil fuels and urban pollution) also contribute additional VOCs to the sediments. A gas chromatogram (*i.e.* Fig. 5a, obtained by desorption of a Chromosorb-106 trap tube) of surface sediment taken from the Test river during October illustrates the diversity of VOCs which can be recovered during the autumn cycle. Fig. 5b shows the respective "blank" analysis performed on the same tube prior to analysis of the sample.

TABLE VII

COMMON VOLATILE ORGANIC COMPOUNDS RECOVERED FROM WATER AND SEDIMENT SAMPLES IN SOUTHAMPTON WATER OVER AN 18-MONTH PERIOD

Compound	Concentration ranges	
	Water (ng l⁻¹)	Sediment (ng kg⁻¹)
Methanethiol	10–73	103–1950
n-Butane	28–60199[a]	55–86353[a]
2-Methylpropane	50–60100	70–80000
2-Methyl-1,3-butadiene	5–1233	28–97951
n-Pentane	25–327	50–35292[a]
Isopentane	25–250	70–10100
2-Methylbutene-1	50–700	100–1110
Propanone	<10–300	150–380
Dichloromethane	15–1004	20–2742
Dimethylsulphide	10–814[b]	10105–350900[c]
Carbon disulphide	10–100	10–747
Propanal	30–300	120–350
Propanol-1	60–430	350–980
Propanol-2	70–300	350–700
Freon-113	25–70	170–21550
Propanethiol	<10–70	200–3200
2,2-Dimethylbutane	33–94	68–12019
2,3-Dimethylbutane	38–109	60–13786
Methyl tert.-butyl ether	15–81	15–20645
Butanone-2	25–240	390–570
Butanone-1	25–200	400–450
n-Hexane	47–496	70–1335
Pentanone-2	35–230	100–380
2-Methylpentene-1	130–700	489–1590
Trichloromethane	10–7502	97–22940
2-Methylfuran	10–17	75–496
1,2-Dichloroethane	15–955	70–11045
1,1,1-Trichloroethane	< 5–2788	70–31031
Benzene	100–55380	298–96735
2,2,3-Trimethylbutane	85–290	200–580
Carbon tetrachloride	<10–311	75–1856
n-Butanol	<10–440	335–607
2-Butanol	<10–400	350–380
Thiophene	<10–190	95–174
4-Methyl-2,3-dihydrofuran	<10–200	90–550
3-Methyl-2-butenal	<10–180	100–390
1,2-Dibromoethane	<10–176	65–6442
Cyclohexane	30–801	100–1440
Trichloroethylene	<10–603	70–4005
Pentanal	<10–170	75–208
2,2,4-Trimethylpentane	<10–400	100–15150
2,4,4-Trimethylpentene-2	<10–490	170–3000
2,5-Dimethylfuran	<10–50	100–312
n-Heptane	50–260	80–19400
Methyl isobutylketone	<10–347	300–420
Dimethyldisulphide	<10–5250[b]	55–72000
Methylcyclohexane	<10–100	100–300
1,1,2,2-Tetrachloroethylene	<10–343	85–20177
Methylbenzene	10–48850	548–120200
3-Ethylhexane	50–110	200–400
Chlorodibromomethane	10–2200	150–27350
3-Methylthiophene	<10–50	120–410

TABLE VII *(continued)*

Compound	Concentration ranges	
	Water (ng l^{-1})	Sediment (ng kg^{-1})
Hexanal	<10–100	80–260
n-Octane	90–290	154–25700
Octene-1	25–75	10–130
1,3-Dimethylbenzene	10–402070	875–480200
1,2-Dimethylbenzene	10–400020	870–480560
Chlorobenzene	<10–120	95–550
Ethylbenzene	10–312008	505–201100
Tribromomethane	10–2597	75–62609
Styrene	30–296	50–2930
Dimethyltrisulphide	25–411	125–795
n-Nonane	95–357	100–41627
Nonene-1	90–300	130–150
Isopropylbenzene	10–47307	250–43370
1,5-Cyclooctadiene	<10–400	170–1000
Cyclooctene	<10–380	230–980
α-Pinene	25–412	150–506
Camphene	25–99	170–303
2,4-Dimethyl-4-vinylcyclohexane	45–31	155–290
n-Propylbenzene	15–2391	60–20004
Benzaldehyde	15–569	95–11937
p-Cymene	35–45	200–350
1,3,5-Trimethylbenzene	20–1500	80–7397
1,2,4-Trimethylbenzene	20–8000	100–1570
1,2,3-Trimethylbenzene	50–6200	90–11775
2,3-Dihydroindene	30–400	200–950
Limonene	25–633	105–807
Indene	55–277	125–1702
1,2-Dichlorobenzene	35–107	95–1055
n-Undecane	87–619	115–1056
1-Methyl-3-propylbenzene	25–550	120–3020
1-Methyl-2-propylbenzene	25–590	120–3010
1,4-Dimethyl-3-ethylbenzene	25–200	90–1000
1,3-Dimethyl-3-ethylbenzene	25–210	90–1120
2-Dimethyl-4-ethylbenzene	30–100	110–980
1,3-Dimethyl-4-ethylbenzene	35–120	135–1200
1,2,3,5-Tetramethylbenzene	25–1430	130–4205
1,2,3,4-Tetramethylbenzene	25–1247	150–8767
Naphthalene	45–894	125–25766
n-Dodecane	95–707	190–1966
Biphenyl	15–42	29–6052
2-Methylnaphthalene	15–490	87–11020
1-Methylnaphthalene	55–450	80–10202
1,3-Dimethylnaphthalene	55–403	200–20300
1,2-Dimethylnaphthalene	25–356	220–20530
n-Hexadecane	30–238	160–23040
n-Heptadecane	15–209	170–25035
n-Octadecane	35–300	200–18030
Pristane	30–155	170–1010
n-Nonadecane	35–250	200–14300
Phytane	30 200	180–1120
n-Eicosane	55–73	180–300

[a] High concentrations mainly from sewage outfalls.
[b] High concentrations associated with plankton blooms.
[c] High concentrations associated with anaerobic marsh sediments.

The functional organic distribution of the major VOCs in water and sediments fall into five major groups. These are (i) the volatile aromatics, (ii) alkanes and alkenes, (iii) oxygen-containing compounds such as alcohols, ketones, ethers and aldehydes, (iv) organosulphur compounds and (v) organohalogens. Although many of these compounds are of anthropogenic origin, many individual compounds such as the terpenes, aldehydes, organosulphides and some of the substituted alkanes (*e.g.* 2,2-dimethylbutane) are contributed to sediments by biological processes.

Volatile aromatics are ubiquitous in the estuary, accounting for between 48–74% of all VOCs found in water samples and 32–78% of all VOCs found in sediments, taking into account variability due to time and place of sampling. This explains why there are such broad concentration ranges for aromatic compounds listed in Table VII. Their sources are numerous and equally as diverse, ranging from exhaust gases from fossil fuel powered engines and ballast water from marine craft to inputs from raw sewage, road run-off and industrial effluents. Methylbenzene is the only volatile aromatic in Southampton Water which has a natural as well as anthropogenic source. The stepwise generation of biogenic methylbenzene has been determined previously in sediments at the bottom of anoxic lakes, showing that methylbenzene also has several discrete biological formation pathways via microbiological mechanisms [38]. Recent studies by the authors suggest that methylbenzene is generated by identical processes *in situ* within surface sediments in Southampton Water, especially in the weeks following the autumn leaf fall. Methylbenzene was also synthesised in river bed sediments 15 miles upstream of the Test river. This was monitored in an unpolluted rural area, in the complete absence of any other aromatic compounds.

Volatile alkane and alkene compounds comprise up to 40% of VOCs in both water and sediments throughout the estuary. They are therefore numerically the second major class of VOCs found in the estuary. Although many of these compounds originate from industrial effluents, they are also produced as a by-product following intense planktonic activity occurring in the estuary. During the midsummer "red-tide bloom" of the photosynthetic ciliate "*Mesodinium rubrum*", concentrations of substituted alkenes, including terpenes such as 2-methyl-1,3-butadiene (isoprene), α-pinene and limonene increase significantly to very high relative concentrations (*i.e.* 90 000, 500 and 800 ng kg^{-1} respectively, in sediments). During autumn, concentrations of isoprene show a second sharp seasonal increase, suggesting that this simple terpene compound is a major participant or intermediary in biologically related processes in Southampton Water.

Volatile organosulphides, notably dimethylsulphide, are consistently found at high concentrations (*i.e.* up to 360 000 ng kg^{-1}) in Southampton Water sediments. Dimethylsulphide is the single most abundant non-aromatic volatile compound occurring in sediments, rarely found in concentrations less than 1000 ng kg^{-1}. It is produced *in-situ* within the anoxic muds and sediments in Southampton Water by biological fermentation processes. However, it is also found in surface water samples (a) near sewage outfalls, and (b) during the mid-summer plankton "blooms". During the *Mesodinium rubrum* bloom, concentrations of the disulphide homologue, dimethyldisulphide, reach an annual maximum both in water and sediments, exceeding even the concentrations of dimethylsulphide in the water column. This annual peak in dimethyldisulphide concentration is uniquely due to the June–July proliferation of the plankton in the estuary. Dimethyldisulphide is formed by the oxidative coupling of
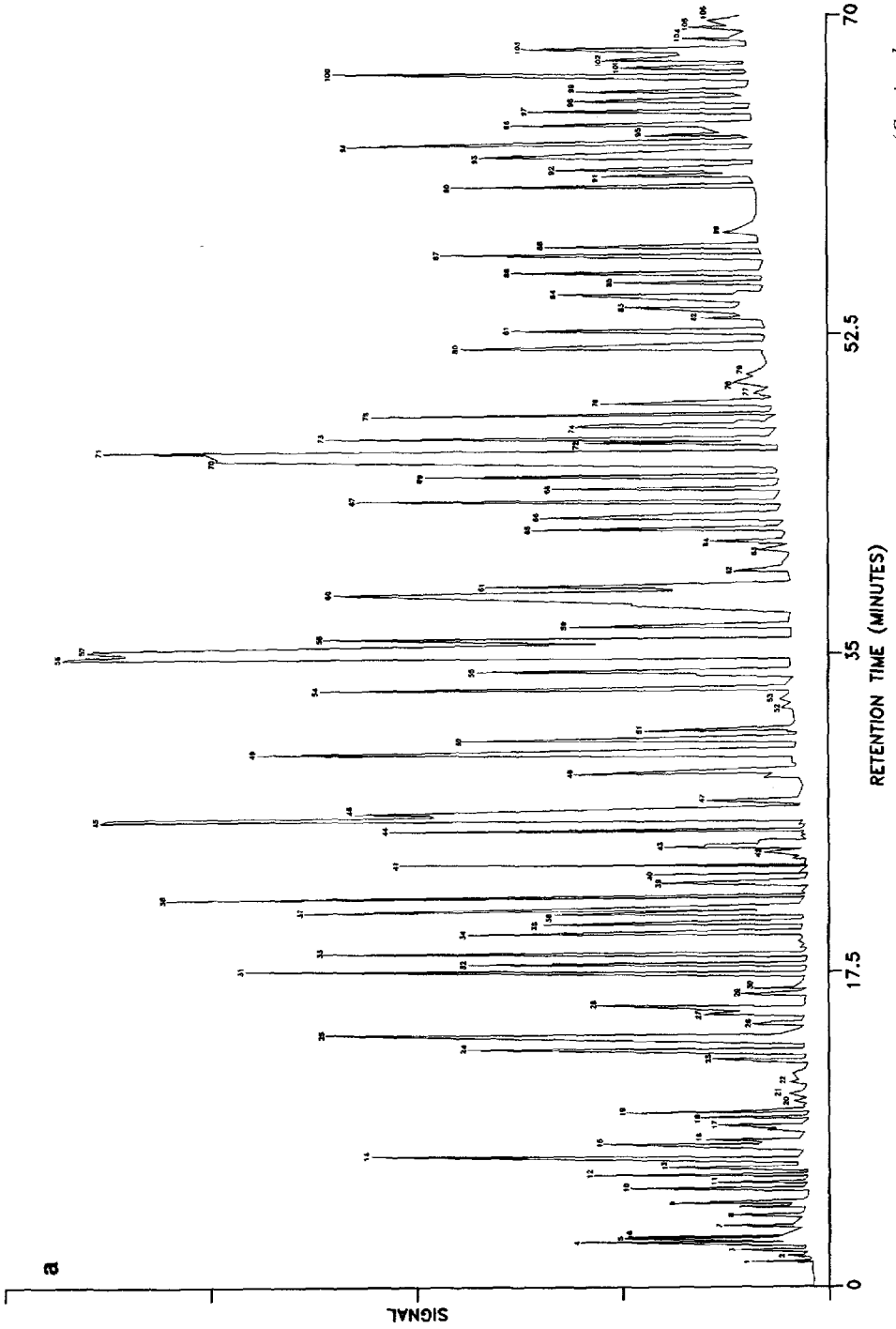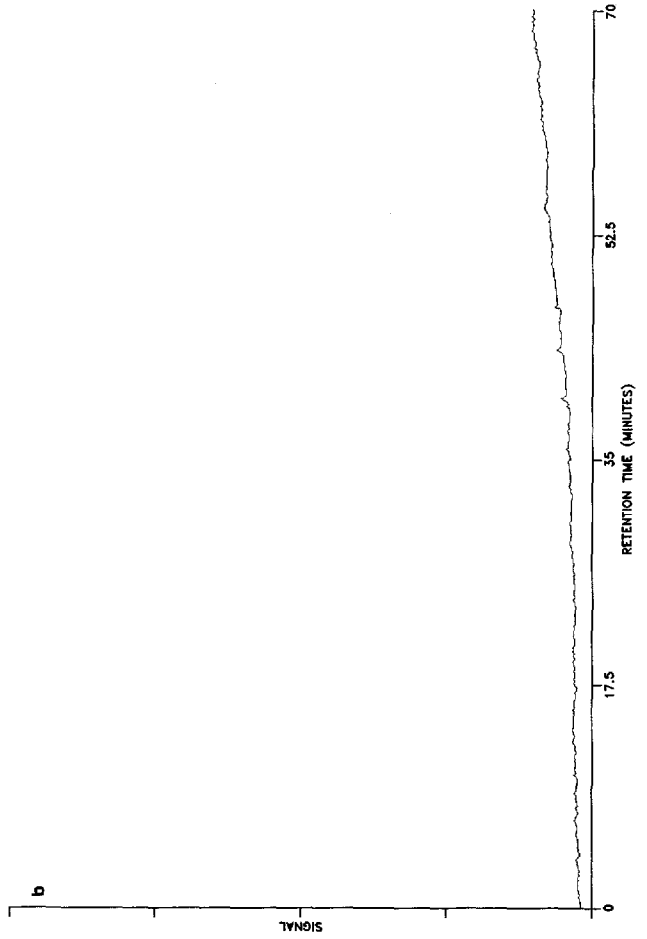
Fig. 5.

Fig. 5. (a) Gas chromatogram of a sediment sample taken from the River Test. This chromatogram was obtained following thermal desorption of a Chromosorb-106 sorbent "trap" tube. Peak numbers: 1 = Propane; 2 = isobutane; 3 = n-butane + 2-methylpropane; 4 = $trans$- + cis-butene; 5 = isopentane + methanethiol; 6 = n-pentane; 7 = fluorotrichloromethane; 8 = 2-methyl-1,3-butadiene; 9 = 2,2-dimethylbutane; 10 = $trans$-1,2-dichloroethylene + 2,3-dimethylbutane; 11 = 2-methylbutene-2 + 2-methylpentane; 12 = 3-methylpentane; 13 = cyclopentane + 4,4-dimethylbutane; 14 = dimethylsulphide; 15 = $tert.$-butanol; 16 = carbon disulphide; 17 = 2-butanone; 18 = n-butanal; 19 = n-hexane; 20 = trichloromethane; 21 = methyl $tert.$-butyl ether; 22 = 2-methylfuran; 23 = $trans$- + cis-hexene-3; 24 = 2-methylpentene-2; 25 = cis-3-methylpentene-2; 26 = 3-methylcyclopentene; 27 = 4,4-dimethylpentene-1; 28 = cis-2-hexene; 29 = 2,3-dimethyl-1,3-butadiene; 30 = 3-methyl $trans$-2-heptene; 31 = ethylcyclobutane; 32 = 1,2-dichloroethane; 33 = 2,2-dimethylpentane; 34 = n-heptane; 35 = 3-methyl hexene-1; 36 = 1,1,1-trichloroethane; 37 = 3-methylbutanal; 38 = benzene; 39 = 2-methylhexene-2; 40 = 2,2,3-trimethylbutane; 41 = carbon tetrachloride; 42 = n-butanal; 43 = dimethyldisulphide; 44 = ethylcyclopentane; 45 = methylcyclohexane; 46 = 2,2,3-trimethylpentane; 47 = n-octane; 48 = 3,3-dimethylhexane; 49 = methylbenzene; 50 = 2,6-dimethylheptane; 51 = 3,5-dimethylheptane; 52 = 2- + 4-methyloctane; 53 = 3-methyloctane; 54 = n-nonane; 55 = chlorobenzene; 56 = ethylbenzene; 57 = 1,3- + 1,4-dimethylbenzene; 58 = styrene; 59 = C_9 alkene; 60 = 1,2-dimethylbenzene; 61 = C_9 alkene; 62 = dimethyltrisulphide; 63 = isopropylbenzene; 64 = α-pinene; 65 = n-decane; 66 = n-propylbenzene; 67 = 1-methyl-3-ethylbenzene; 68 = 1,3,5-trimethylbenzene; 69 = C_{11} alkane; 70 = 1-methyl-2-ethylbenzene; 71 = 1,2,4-trimethylbenzene; 72 = octanal; 73 = terpene (?); 74 = terpene (?); 75 = 1,2,3-trimethylbenzene; 76 = dimethyltetrasulphide; 77 = 1-methyl-2-propylbenzene; 78 = 2-dimethyl-4-ethylbenzene; 79 = n-undecane; 80 = 1,3-dimethyl-2-ethylbenzene; 81 = indene; 82 = C_{12} alkene; 83 = 1,2,4,5-tetramethylbenzene; 84 = 1,2,3,5-tetramethylbenzene; 85 = n-dodecane; 86 = C_{11} aromatic; 87 = dimethylpropylbenzene; 88 = n-tridecane; 89 = naphthalene; 90 = 2,2-dihydro-4,7-dimethyl indene; 91 = a substituted naphthalene (?); 92 = C_{13} aldehyde; 93 = n-tetradecane; 94 = 1-methylnaphthalene; 95 = 2-methylnaphthalene; 96 = C_{12} aldehyde; 97 = n-pentadecane; 98 = 1,3-dimethylnaphthalene; 99 = n-hexadecane; 100 = 1,2-dimethylnaphthalene; 101 = C_{14} aldehyde; 102 = n-heptadecane; 103 = pristane; 104 = pentadecanal; 105 = C_{14} alkene; 106 = phytane. (b) Gas chromatogram of a "blank" sediment sample analysed using the same purge-and-trap/thermal-desorption analytical method as used for samples. This chromatogram was obtained following thermal desorption of a Chromosorb-106 sorbent "trap" tube.

methyl mercaptan, a simple organosulphide which is bio-synthesised *in situ* by the organisms [39]. By early autumn, dimethyldisulphide concentrations dwindle rapidly to background concentration levels determined by constant low-level inputs supplied by sewage effluents and microbial fermentation processes in muds.

In contrast, volatile organohalogens in Southampton Water originate almost exclusively from the activities of man and are commonly found around both raw and treated-sewage outfalls. Highest concentrations are found in effluent discharge zones around the city of Southampton. Compounds such as carbon tetrachloride, 1,1,1-trichloroethane and 1,2-dichlorobenzene are consistently found at concentrations up to ten times higher in sediments than in water. Unlike many of the other volatile organic compound classes, these compounds are also found in deeper sediments (*i.e.* down to 50-cm in depth), suggesting that they can migrate readily through sediments and are comparatively resistant to biodegradation. As such, they are probably the most stable volatile compounds found in sediments.

Oxygen-containing volatiles, such as aldehydes, ketones and alcohols were found generally at lower concentrations than the VOCs mentioned in the foregoing discussion. Aldehydes, especially pentanal, hexanal and benzaldehyde were found all year round in water and sediments. Their concentrations varied mainly with planktonic activity, reaching their annual maxima in conjunction with the midsummer peak in *Mesodinium rubrum* and chlorophyll *a*.

This brief discussion of the VOCs found in Southampton Water shows that volatile organics are contributed from both man-made and natural sources. This field study also demonstrates how the application of the stripping method has revealed much detailed information about the occurrence and behaviour of VOCs in estuarine environments. Hence, it offers additional insight into geochemical and environmental processes.

CONCLUSIONS

This study shows that the modified purge-and-trap method, developed initially for the analysis of water samples, can be usefully applied to detect VOCs in estuarine sediments. The adoption of a simple purging apparatus with multi-sorbent trapping facilitates quantitative trapping of VOCs at very low concentrations. The sorbent traps are adapted for use from well established analytical methodologies. Thermal desorption analysis and gas chromatography can be automated, making it possible for laboratories to analyse significant numbers of samples with more efficient use of manpower.

Results of basic studies on the recovery of VOCs from different sediment matrices illustrate that desorption was marginally affected by differences in the physical composition of different sediment types representative of the Southampton Water estuary. This may not be the case when stripping different sediment matrices, *e.g.* those containing an exceptionally high clay or sand content. Major factors affecting the stripping of sediments include the efficiency of the method, the concentration of the VOCs and physico-chemical properties (*e.g.* boiling point, vapour pressures and aqueous solubilities) of the functional classes of organic compounds present. Consequently, it is the ability of the analytical method to quantitatively strip VOCs from the sediments that determines the efficiency and usefulness of the

technique to the environmental chemist. Knowing the composition of VOCs in sediments is potentially very useful for determining the pollution status of an estuary and for providing an improved understanding of the nature of both biogenic and anthropogenic inputs.

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