

Sampling and analysis of volatile organic compounds in estuarine air by gas chromatography and mass spectrometry

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ABSTRACT

The spatial and temporal distribution of volatile organic compounds (VOCs) in air samples taken beside a semi-industrialised estuary was intensively studied over a two-year period. Samples were collected by trapping VOCs onto multi-bed traps packed with graphitised carbon black sorbents capable of selectively trapping a wide range of volatile substances. Samples were then analysed using an automated thermal desorption technique followed by capillary column gas chromatography with simultaneous detection of volatile eluates using flame ionisation and ion trap detectors. The lower limit of detection was circa 0.5 ng m^{-3} for most compounds. The major groups of organic compounds collected were C_1 – C_4 alkylbenzenes, alkanes and alkenes, and chlorinated solvents. Terpenes were also found in high concentrations in forested areas which fringe the estuary. Significant seasonal differences in the distribution and concentration of VOCs occur between summer and winter. A case study from the VOCs research in and around the Southampton Water estuary on the central southern coastline of England is presented as an example of the method application.

INTRODUCTION

Airborne volatile organic compounds (VOCs) have been the subject of interest for some years, particularly those associated with emissions from gasoline and diesel powered engines. Although vehicle exhausts have long been recognised as a major source of pollutant VOCs in urban air [1,2] along with petroleum and solvent-based industries [3], forests and woodlands were also recognised as a significant source of biogenic VOCs, particularly those emitted directly from trees and vegetation [4,5]. Of more immediate concern is the harmful effects that toxic airborne VOCs impose on human

health, particularly the known and suspected carcinogenic properties of VOCs (*e.g.* alkylbenzenes). Volatile compounds are highly mobile and are capable of being inhaled by people living and/or working in proximity to vehicle emissions and specific industrial activities [6–8]. As yet, environmental health professionals have insufficient data on the behaviour and long-term concentration trends of airborne VOCs in order to accurately assess their chronic effects on health and air quality. It is therefore not surprising that increasing emphasis should be placed on long-term sampling studies of airborne VOC concentrations.

In this study, another important reason for long-term study of VOCs was to integrate data on airborne concentrations with those previously measured in estuarine and coastal waters, principally in order to examine source and sink relationships be-

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tween air and sea. Methods for the analysis of VOCs in estuarine water and sediments were reported in previous papers [9,10], along with typical concentration data for key volatile compounds in the aforementioned sample matrices.

Within the last few years, technical approaches towards the sampling and analysis of low-level airborne VOCs have taken on new dimensions. Popular alternatives include trapping volatile compounds in glass vessels, followed by cryogenic trapping and thermal desorption [11]. Other methods rely on cryotrapping VOCs directly from air, followed by injection onto the chromatographic column via multi-port gas valves [12]. Increasingly, commercial manufacturers are developing remote sampling and analytical GC systems for semi-continuous analysis of urban air [13].

Historically, conventional methods use low-flow sampling pump to trap airborne VOCs onto adsorbent beds consisting of activated charcoals [14], porous polymers *e.g.* Tenax-TA [15], or combinations of sorbents *e.g.* charcoal and polyurethane foam [16]. However, recent developments in the production of thermally modified carbon blacks and carbon molecular sieve adsorbents for quantitatively trapping VOCs has been reflected in their superior performance over “traditional” sorbents such as activated charcoal and porous polymers which tend to lack uniform adsorbent characteristics necessary for adsorbing and retaining the different physico-chemical properties of VOCs encountered within airborne environments. Deleterious effects include poor retentivity for certain functional groups, susceptibility to water vapour, or poor desorption characteristics for strongly retained compounds [17]. Instead, the use of non-specific, Type I sorbents such as the graphitised carbon blacks and carbon molecular sieves have overcome concerns about which functional group(s) an adsorbate possesses. The application of such adsorbents has minimised problems with contamination and artefact formation [18,19], characteristics which render them attractive alternatives for sampling VOCs in quite different environments, and which were extensively used in this study.

A newer alternative for sampling VOCs is the use of Summa passivated canisters [20]. Although canisters represent an excellent option, until quite recently, they have not been readily available outside

of the USA. In a recent paper on Summa canisters the authors quoted a lower limit of detection of 1–2 ppb (10^{-9} v/v) per component (or lower in full-scan MS mode) and possible problems with excess moisture [20]. Despite the advantages Summa canisters offer over adsorbent-type sampling, current questions over their use for prolonged sampling periods, the inability of the method to attain the desired limit of detection (*i.e.* 5 ng m^{-3} minimum), and concerns over moisture-initiated contamination with salt-laden sea air only add further potential complexities.

In this study we report the use of triple-packed adsorbent tubes using a combination of carbon black and molecular sieve sorbents, followed by thermal desorption of the volatile eluates from the adsorbent tubes using a Perkin-Elmer automated thermal desorber (ATD-50) (Perkin-Elmer, Beaconsfield, UK). The method was successfully used to analyse over 300 samples collected from ground-level sites around the estuary over a 2-year period.

EXPERIMENTAL

Reagents and materials

Standards were prepared using both analytical and high-purity spectrophotometric-grade materials (Aldrich, Wimborne, UK). Stock standard (liquid) mixtures were prepared gravimetrically in all-glass flasks according to both EPA [21] and CONCAWE [22] methods and spiked onto standard sorbent tubes. Certified calibration gas standards (*i.e.* for substances which are gaseous at room temperature) were purchased externally on a custom order specification (Air Products, Bracknell, UK; and Electrochem Specialty Gases, Stoke-on-Trent, UK) and quantitatively spiked onto adsorbent tubes via all-glass cylinders fitted with motorised hypodermic syringes.

Adsorbent tubes (stainless-steel, 90 mm × 5 mm I.D.) obtained from Supelco (Supelco, Bellefonte, PA, USA) were packed with Carbotrap 300 specification sorbents [*i.e.* Carbotrap C (250 mg) 20/40 mesh; Carbotrap B (175 mg) 20/40 mesh; Carbo-sieve S-III (105 mg) 60/80 mesh]. Carbotrap B and C are graphitised carbon black sorbents and Carbo-sieve S-III is a carbon molecular sieve. The principle behind the packing (and sampling) regime is that the most volatile components (*i.e.* C_2 – C_5) will slow-

ly migrate through the carbon black sorbents and are eventually trapped on the carbon molecular sieve. Compounds of progressively higher molecular weight are successively trapped on the carbo-trap adsorbents, an arrangement which theoretically serves to quantitatively adsorb a range of VOC from the highest to the lowest volatility across the entire length of the sampling tube. The theoretical (and experimental) details which underpin this multi-sorbent trapping arrangement have been presented in detail by Betz and Gisch [17]. A second sorbent tube was attached *via* 1/4-in. (0.64 cm) Swagelok unions “in-series” to each sampling tube to check that breakthrough had not occurred during sampling. The use of a back-up tube also offers the analyst the opportunity to carry out a semi-quantitative analysis should breakthrough of organic compounds occur due to breakdown of the first sorbent bed, or due to massive overload in the event of an extreme pollution event. Small silanised and head-treated glass-wool plugs were then inserted into the front end of each sampling tube as a pre-filter for coarse airborne particles (*i.e.* dusts, grits, pollen). The adsorbent tubes were prepared freshly by being conditioned overnight (*i.e.* by passing a stream of ultra-pure helium at 100 ml min⁻¹ through each tube for 8 h at 280°C). The tubes were then analysed in the normal way to guarantee the absence of artefacts or contamination. The tubes were then capped with Swagelok end-caps and stored in sealed glass jars immediately prior to use, normally within 12 h of preconditioning.

Sampling

Sample pumps [low-flow (Accuhaler 808 Model): MDA, Lincolnshire, IL, USA] and low/medium-flow [(Flo-Lite): MSA, Pittsburg, PA, USA] pumps were attached to individual sorbent tubes using 30 cm lengths of clear, inert polythene tubing suitable for low-level organics sampling (BDH-Merck, Eastleigh, UK). Each pump/tube assembly was then calibrated using a bubble flow meter (SKC UK, Blandford Forum, UK) in order to attain precise flow-rates. The pumps were adjusted to sample at 50 ml min⁻¹ (*i.e.* MDA pumps) and 500 ml min⁻¹ (*i.e.* MSA pumps), respectively. Pairs of pump/tube assemblies were then mounted onto heavy duty tripods (12 off, 1.5 m height) using locating brackets. Each tripod was capped with a curved aluminium

sheet “umbrella” (40 cm radius × 2 mm thick) for weather protection. The tripods were then placed in fixed sampling locations for 1.0 (MDA) and 4.0 (MSA) h time periods, respectively, and successively replaced by fresh pump/tube assemblies on an ongoing basis (*i.e.* 4, 8, 12, 16 and 24 h) depending on the sampling schedule. Individual flow-rates were rechecked at the end of the sampling period in order to obtain assurance about the integrity of the pump flow-rate and the total sampling volume. Tubes were then sealed with Swagelok end-caps, sealed in all-glass jars with ground-glass stoppers, cooled to approximately -10°C and analysed within 24 h of sampling. Measurements of air temperature (dry bulb), barometric pressure, relative humidity (%) and wind direction were made at regular intervals (*i.e.* hourly and four-hourly). In some cases, a platform-mounted thermohygrograph (Casella, London, UK) was used to continuously monitor and record temperature and relative humidity in the sampling zone.

Instrumentation and capillary column

The Perkin-Elmer 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. The ATD-50 is a multi-functional instrument designed 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 gas chromatographic (GC) capillary column where the transferred components are chromatographed. The eluted components were then passed through an effluent splitter for simultaneous flame ionisation and ion trap detection.

The gas chromatograph was fitted with a cradle-mounted, 50 m × 0.22 mm I.D. aluminium-clad BP-1 wall coated open-tubular capillary fused-silica capillary column, 0.25 µm film thickness (SGE, Milton Keynes, UK). The exit point of the column was

connected to a twin-hole split ferrule permitting 50% of the column eluent 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). The repeatability, reproducibility and linearity of response of this system was checked *via* intercalibration exercises and the use of multi-range standards.

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

Analytical operating conditions

The analytical operating conditions were similar to those already described by Bianchi and Cook [23].

Carrier gas: ultrapure helium 5.5 grade (Air Products, Basingstoke, UK); carbon dioxide (Air Products, Hythe Depot, Southampton, UK). ATD-50: cold-trap packing, 20 mg Chromosorb-106; cold-trap low temperature, -30°C ; cold-trap high temperature, 250°C ; split ratio (combined), 50:1; desorption oven temperature, 250°C ; adsorbent tube desorption time, 10 min; desorption gas-flow through tube, 10 ml min^{-1} , carrier gas pressure, 170 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, -35°C ; isothermal time 1, 7.0 min; ramp rate 1, $20^{\circ}\text{C min}^{-1}$; oven temperature 2, 60°C , isothermal time, 0.1 min; ramp rate 2, $5^{\circ}\text{C min}^{-1}$, oven temperature 2, 300°C ; final hold time 2, 1.0 min.

Ion trap detector. Ionisation voltage, 70 eV; *s*/scan, 1.0; mass range, 45–300 mass units; transfer temperature, 250°C ; ion source temperature, 250°C ; multiplier delay, 120 s; mass defect, 100 molecular mass units (m.m.u.)/100 u; acquire time, 60 min.

Compound quantitation and method performance

The qualitative and quantitative identification of compounds was carried out by direct comparison of the specific GC retention data (*i.e.* from the flame ionisation detector) in tandem with the confirmatory mass spectral data. Identifications were also carried out by co-injection of authentic standards and

subsequent comparison with an “in-house” retention index library containing over 1000 separate compounds (*i.e.* for non-polar, chemically bonded methylsilicone capillary columns). Absolute concentrations of individual compounds were calculated in terms of the mass (μg) per unit volume (1.0 m^3) per component. Whereas ratio expressions (*i.e.* ppb) are independent of pressure and temperature, weight/volume (w/v) expressions vary according to the gas laws (*i.e.* according to temperature and pressure). Using the calibration and standard spiking protocols previously discussed, individual response factors for each component were determined at the ng l^{-1} level (*i.e.* external standard method). These values, expressed in ng, were then divided by the total pumped air volume through the adsorbent tube, and corrected for ambient temperature (K) and pressure (mmHg) to yield the corrected $\mu\text{g m}^{-3}$ concentration per component. Further details of the procedure and calculations are provided in the CONCAWE guidance document 8/86 [22].

Specific data on the sorbent characteristics and the field performance of the graphitised carbon blacks and the carbon molecular sieves has been previously reported [17–19]. Our results were generally consistent with those reported by Betz and co-workers [18,19]. The short term precision (*i.e.* repeatability) of our air sampling method is expressed as the relative standard deviation (R.S.D.), and is presented in Table I. The data show that R.S.D. is generally in the order of $\pm 10\%$ except for the most highly volatile compounds (*e.g.* ethene, 14%) and the least volatile compounds (*e.g.* *n*-heptadecane, 15%). In contrast, the R.S.D. for aromatics (*i.e.* among the most toxic of the airborne VOCs, and those with a high potential for producing ground-level ozone) is excellent *e.g.* benzene, 3.3%; 1,2,3-trimethylbenzene, 3.9%). The overall accuracy of the method (*i.e.* recovery + precision) was within $\pm 25\%$ for all components. The absolute detection limit was between 0.1 and 0.4 ng m^{-3} for the volatile aromatic and organohalogen compounds, and between 0.3 and 1.0 ng m^{-3} for the remaining compounds listed in Table I, comparable with the absolute detection limits reported by Rosell *et al.* [16] in their analysis of Barcelona air. In our study, these detection limits were found to be at least a factor of 1000 times more sensitive than typical minimum VOC concentrations observed in real samples, ren-

TABLE I

THE REPEATABILITY OF MODEL VOLATILE ORGANIC COMPOUNDS SAMPLED FROM AMBIENT AIR IN THE SOUTHAMPTON WATER ESTUARY

Short term precision is expressed as % relative standard deviation (R.S.D.) ($n = 10$). (Note that the compound list is presented according to their general elution order from the capillary column.)

| Compound Name | % R.S.D. | Compound Name | % R.S.D. |
|---|----------|--|----------|
| Ethene | 14.1 | <i>n</i> -Hexane | 5.4 |
| Ethane | 10.3 | Trichloromethane | 4.7 |
| Propene | 10.5 | 1,2-Dichloroethane | 4.7 |
| Propane | 9.6 | 1,1,1-Trichloroethane | 4.6 |
| Chloromethane | 10.1 | Benzene | 3.3 |
| Cyclopropane | 9.2 | Carbon tetrachloride | 4.3 |
| iso-Butane | 9.3 | <i>n</i> -Butanol | 9.7 |
| <i>n</i> - and iso-Butene | 8.2 | Cyclohexane | 5.4 |
| 1,3-Butadiene | 9.3 | Trichloroethylene | 4.9 |
| Methanethiol | 7.6 | 2-Methylhexane | 7.7 |
| <i>n</i> -Butane | 8.9 | Pentanal | 8.7 |
| <i>trans</i> -Butene-2 | 7.2 | Cyclohexene | 7.9 |
| 2,2-Dimethylpropane (neopentane) | 7.6 | Trichloroethylene | 5.0 |
| Chloroethane | 8.3 | Heptene-1 | 6.8 |
| <i>cis</i> -Butene-2 | 7.7 | 2,2,4-Trimethylpentane (iso-octane) | 5.3 |
| Cyclobutene | 8.3 | 3-Pentanone (diethyl ketone) | 9.0 |
| 3-Methylbutene-1 | 8.4 | <i>n</i> -Heptane | 6.4 |
| Cyclobutane | 9.8 | Dimethyldisulphide | 6.6 |
| iso-Pentane | 6.2 | Methylcyclohexene | 6.7 |
| Pentene-1 | 6.3 | Toluene | 3.6 |
| 2-Methylbutene-1 | 8.5 | <i>n</i> -Octane | 5.5 |
| 2-Methyl-1,3-Butadiene (isoprene) | 6.7 | Chlorobenzene | 4.3 |
| <i>n</i> -Pentane | 5.7 | Ethylbenzene | 3.4 |
| Fluorotrichloromethane | 6.7 | 1,1,3-Trimethylcyclohexane | 5.6 |
| <i>trans</i> -1,2-Dichloroethylene | 6.8 | 1,3-Dimethylbenzene (<i>p</i> -xylene) | 4.0 |
| 2-Methylbutene-2 | 7.3 | 1,4-Dimethylbenzene (<i>m</i> -xylene) | 4.2 |
| Dichloromethane | 4.6 | Styrene | 5.0 |
| Dimethylsulphide | 4.9 | 1,2-Dimethylbenzene (<i>o</i> -xylene) | 4.3 |
| <i>tert</i> -Butanol (2-methylpropan-2-ol) | 6.5 | <i>n</i> -Nonane | 6.7 |
| Carbon disulphide | 6.2 | Isopropylbenzene (cumene) | 3.9 |
| Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) | 4.3 | α -Pinene/dipentene terpinene | 7.8 |
| Cyclopentadiene | 5.6 | β -pinene | 7.8 |
| 2,2-Dimethylbutane | 7.3 | <i>n</i> -Propylbenzene | 3.9 |
| Cyclopentene | 8.3 | Benzaldehyde | 8.5 |
| 4-Methylpentene-1 | 7.9 | 1,3,5-Trimethylbenzene (<i>mesitylene</i>) | 3.9 |
| 3-Methylpentene-1 | 7.6 | <i>n</i> -Decane | 7.9 |
| 2,3-Dimethylbutene-1 | 8.3 | <i>n</i> -Undecane | 9.2 |
| Cyclopentane | 8.9 | 1,2,3,5-Tetramethylbenzene | 4.4 |
| 2,3-Dimethylbutane | 9.0 | Naphthalene | 6.9 |
| Methyl- <i>tert</i> -butyl ether [m-TBE] | 7.8 | <i>n</i> -Tridecane | 9.3 |
| 2-Methylpentane | 5.8 | <i>n</i> -Tetradecane | 9.4 |
| 3-Methylpentane | 5.8 | <i>n</i> -Pentadecane | 9.9 |
| Methyl ethyl ketone (2-butanone) | 9.3 | Tridecanal | 8.9 |
| <i>n</i> -Butanal | 9.0 | <i>n</i> -Hexadecane | 10.0 |
| 2-Butanol | 7.9 | Pristane | 9.4 |

dering the pursuance of greater analytical sensitivity and uneconomic and unnecessary exercise.

RESULTS AND DISCUSSION

The Southampton Water case study

Southampton Water is a semi-industrialised estuary on the coastline of southern central England. It accomodates a wide range of industries and activities including a large petrochemical complex and an electric power generating plant on its southwestern shore, plus three large marinas on its west-

ern, northern and eastern shores, respectively. An assemblage of boat-building industries are dotted along its coastline. In summer, it plays host to intense watersports which are often in conflict with free access of merchant ships en-route to this busy port. Both city and housing development have mushroomed in size over the last 20 years, with doubling of traffic density and sewage flows to the estuary. Taken together, such development has placed the estuary under intense environmental pressure. Across the United Kingdom, deteriorating air quality is a formidable manifestation of simi-

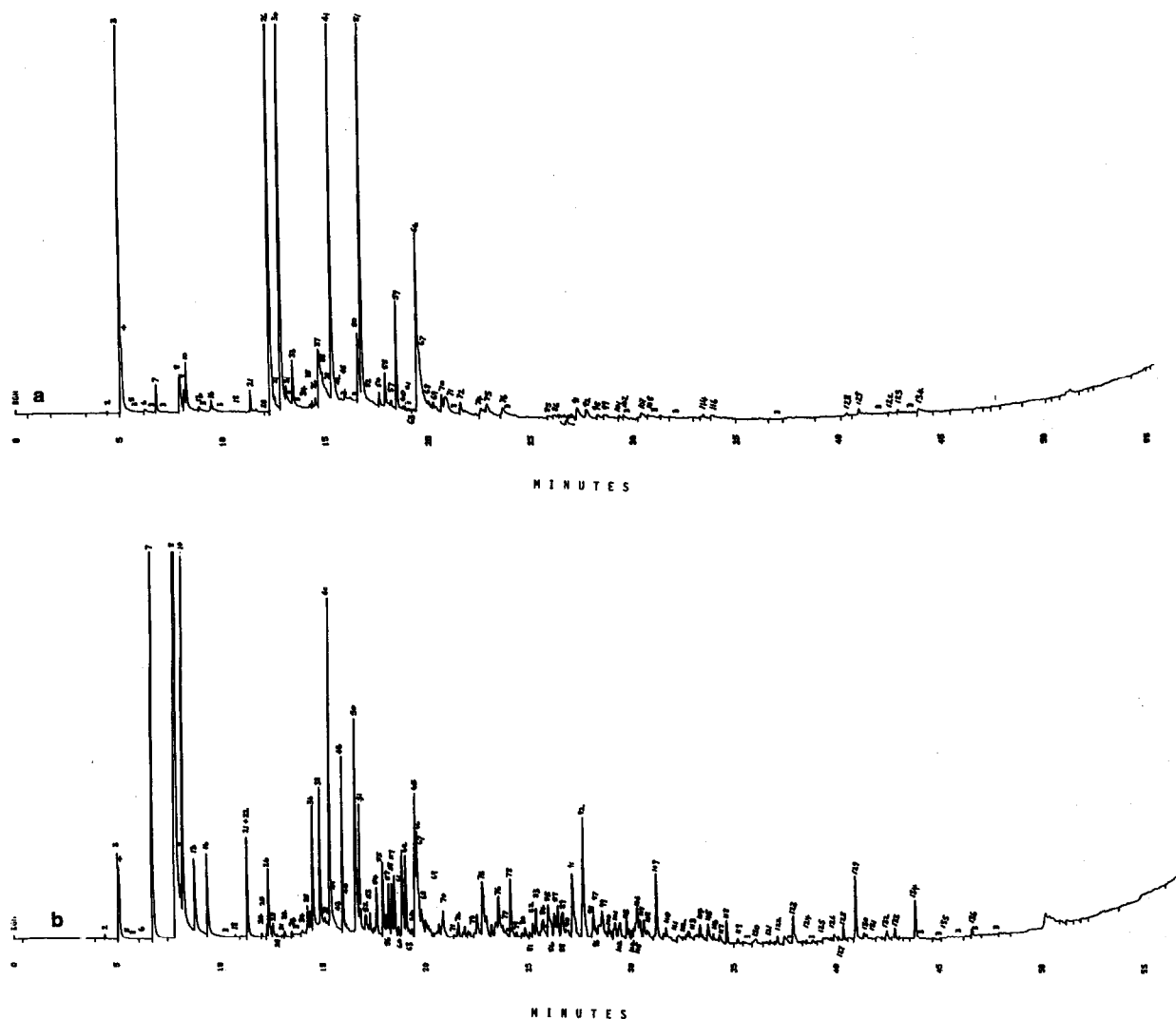


Fig. 1.

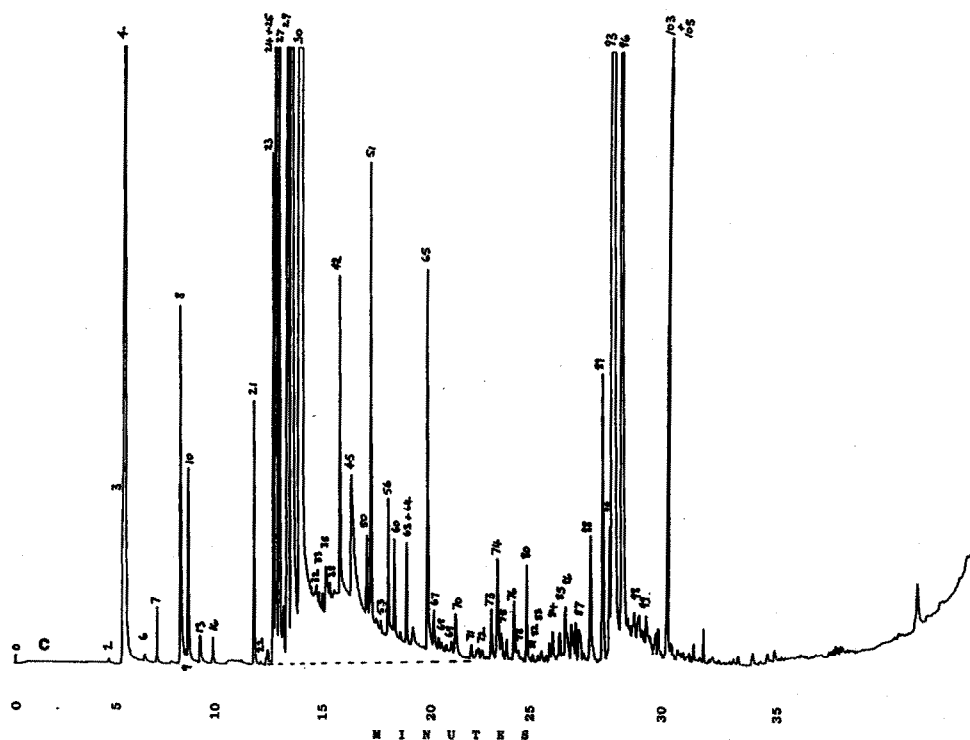


Fig. 1. (a) A representative gas chromatogram obtained from analysis of ambient air taken from a sampling station 2 km downwind from the Southampton Water petrochemical complex (July 1991). Range: $\times 1$; attn.: $\times 32$. (b) A representative gas chromatogram obtained from analysis of ambient air taken near the rural village of Beaulieu in the New Forest, Hampshire, UK (August 1991). See component key for compound assignments. Range: $\times 1$, attn.: $\times 8$. (c) A gas chromatogram obtained from analysis of ambient air taken 0.5 km downwind of a ship-repairers yard. The chromatogram reveals a large number of solvent hydrocarbons associated with glass-fibre moulding and construction activity at the yards. Range: $\times 1$; attn.: $\times 64$. See Table II for compound assignments.

lar pressures, and levels of ozone, nitrogen oxides and sulphur dioxide have reached all-time maxima within the past two years, and are attributed as major causative factors in the steady increase of respiratory disorders such as asthma within the local populace [24–26].

Total VOC concentrations in Southampton Water airborne environments are quite high, ranging from $100 \mu\text{g m}^{-3}$ to $5000 \mu\text{g m}^{-3}$ in over 250 air samples taken in and around the Southampton Water estuary over a two year period. In a 2-km zone downwind of the petrochemical complex itself, C_1 – C_4 alkylbenzenes, *n*-alkanes and *n*-alkenes were the major constituents of the VOCs. Conversely, in forested locations which lie about 18 km west of the estuary (e.g. Beaulieu village), less than 10% of the typical urban levels of VOCs were found. Although some VOCs attributable to air pollution were found

within forest air, many more compounds were of biogenic origin (e.g. volatile terpenes and aldehydes such as isoprene, limonene and *n*-pentanal). In locations such as the Southampton City Centre and its industrial fringes (i.e. which lie about 20 km north west of the petrochemical complex), high levels of airborne contamination were found. Typical (summertime) chromatograms from the aforementioned locations are shown as Fig. 1a, b and c, respectively. Fig. 1c reveals particularly high concentrations of solvent hydrocarbons in ambient air sampled about 0.5 km downwind of ship-repairers yards specialising in fibre-glass work.

Concentrations of volatile organohalogenes, particularly common chlorinated solvents (i.e. 1,1,1-trichloroethane, tetrachloroethylene and carbon tetrachloride) were consistently high near shipbuilding and repairing factories regardless of season i.e. up

TABLE II
COMPONENT KEY FOR FIGS. 1 AND 2

| Peak no. | Compound | Peak no. | Compound |
|----------|---|----------|---------------------------------------|
| 1 | Ethene | 54 | 3-Methylhexane |
| 2 | Ethane | 55 | Pentanal |
| 3 | Propene | 56 | Trichloroethylene |
| 4 | Propane | 57 | 3-Ethylpentane |
| 5 | Chloromethane | 58 | 2,2,4-Trimethylpentane |
| 6 | Cyclopropane | 59 | <i>trans</i> -Heptene-2 |
| 7 | iso-Butane | 60 | <i>n</i> -Heptane |
| 8 | <i>n</i> -Butene | 61 | Methylcyclohexane |
| 9 | iso-Butene | 62 | Ethylcyclopentane |
| 10 | 1,3-Butadiene | 63 | 2,5- + 2,4-Dimethylhexane |
| 11 | Methanethiol | 64 | 2,3,4-Trimethylpentane |
| 12 | <i>n</i> -Butane | 65 | Methylbenzene (toluene) |
| 13 | <i>trans</i> -Butene-2 | 66 | 4-Methylcyclohexanone |
| 14 | 2,2-Dimethylpropane (neopentane) | 67 | 4-Methylheptane |
| 15 | Chloroethane | 68 | Hexanal |
| 16 | <i>cis</i> -Butene-2 | 69 | Tetrachloroethylene |
| 17 | 2-Methylbutane | 70 | <i>n</i> -Octane |
| 18 | Cyclobutene | 71 | 3-Methyl-2-heptene |
| 19 | Pentene-1 | 72 | Ethylcyclohexane |
| 20 | 2-Methylbutene-1 | 73 | Ethylbenzene |
| 21 | <i>n</i> -Pentane | 74 | 1,2- + 1,4-Dimethylbenzene |
| 22 | 2-Methyl-1,3-butadiene (isoprene) | 75 | Heptanal |
| 23 | Fluorotrichloromethane | 76 | 1,3-Dimethylbenzene |
| 24 | <i>trans</i> -Pentene-2 | 77 | 3,3,4-Trimethylhexane |
| 25 | <i>cis</i> -Pentene-2 | 78 | Styrene |
| 26 | 2-Methylbutene-2 | 79 | <i>n</i> -Nonane |
| 27 | Dichloromethane | 80 | Isopropylbenzene |
| 28 | Dimethylsulphide | 81 | Benzaldehyde |
| 29 | <i>tert.</i> -Butanol (2-Methylpropan-2-ol) | 82 | α -Pinene |
| 30 | Freon-113 (1,1,2-Trichloro-1,2,2-trifluoroethane) | 83 | a dipentene (terpene?) |
| 31 | 2,2-Dimethylbutane | 84 | Cyclooctene |
| 32 | Cyclopentene | 85 | <i>n</i> -Propylbenzene |
| 33 | Ethylcyclopropane + cyclopentane | 86 | Camphene |
| 34 | 2,3-Dimethylbutane | 87 | Carene |
| 35 | Methyl- <i>tert.</i> -butyl ether [mTBE] | 88 | 1-Methyl-3- + 1-methyl-4-ethylbenzene |
| 36 | 2-Methylpentane | 89 | 1,3,5-Trimethylbenzene |
| 37 | 2-Butanone | 90 | Methyl-2-ethylbenzene |
| 38 | 3-Methylpentane | 91 | β -Pinene |
| 39 | <i>n</i> -Butanal + 1-Hexene | 92 | Octanal |
| 40 | <i>sec</i> -Butanol | 93 | 1,2,4-Trimethylbenzene |
| 41 | <i>n</i> -Hexane | 94 | <i>sec</i> -Butylbenzene |
| 42 | Trichloromethane | 95 | <i>n</i> -Decane |
| 43 | <i>trans</i> -2-Hexene | 96 | 1,2,3-Trimethylbenzene |
| 44 | <i>cis</i> -2-Hexene | 97 | <i>p</i> -Cymene |
| 45 | 2- + 3-Methylpentene-2 | 98 | Indane |
| 46 | Methylcyclopentane | 99 | Linonene |
| 47 | 2,4-Dimethylpentane | 100 | 1H-Indene |
| 48 | 1,1,1-Trichloroethane | 101 | β -Phellandrene |
| 49 | 3-Methyl butanal | 102 | <i>n</i> -Butylbenzene |
| 50 | Benzene | 103 | 1,4-Dimethyl-2-ethylbenzene |
| 51 | Cyclohexane | 104 | 2-Nonenol-1 |
| 52 | 2-Methylhexane | 105 | 1-Methyl-2-propylbenzene |
| 53 | 2,3-Dimethylpentane | 106 | γ -Terpinene |

TABLE II (continued)

| Peak no. | Compound | Peak no. | Compound |
|----------|---|----------|---|
| 107 | 1,3-Dimethyl-2- + 1,2-Dimethyl-4-ethylbenzene | 123 | <i>n</i> -Tridecane |
| 108 | Dimethylethylbenzene | 124 | a biphenyl ether |
| 109 | Nonanal | 125 | Dodecanal |
| 110 | <i>n</i> -Undecane | 126 | <i>n</i> -Tetradecane |
| 111 | 1,2,4,5-Tetramethylbenzene | 127 | 2-Ethyl-naphthalene |
| 112 | 1,2,3,5-Tetramethylbenzene | 128 | Acenaphthalene |
| 113 | 2,3-Dihydro-5-methyl-1H-indene | 129 | C ₁₄ alkene (?) |
| 114 | 4-Terpineol | 130 | 1,3- + 1,4-Dimethylnaphthalene |
| 115 | Naphthalene | 131 | <i>n</i> -Pentadecane |
| 116 | α -Terpineol | 132 | Tridecanal |
| 117 | Decanal | 133 | Tetradecanal (?) (a C ₁₄ aldehyde) |
| 118 | <i>n</i> -Dodecane | 134 | <i>n</i> -Hexadecane |
| 119 | 2-Methylnaphthalene | 134 | <i>n</i> -Pentadecane |
| 120 | a C ₁₁ aldehyde | 135 | Pristane |
| 121 | 3-Methylnaphthalene | 136 | a C ₁₅ alkene (?) |
| 122 | Geraniol | | |

to a maximum of $50.0 \mu\text{g m}^{-3}$ per component. Volatile freons such as 1,1,2-trichloro-1,2,2-trifluoroethane (*i.e.* Freon-113) were also commonly found in air samples. Rigorous preparation and checking of blank sample tubes (*i.e.* including those taken to and from sampling sites) confirmed that the freons were neither contaminants nor artifacts but regular constituents of the airborne environment.

Volatile aromatics are also ubiquitous in ambient air, particularly those sampled in and around Southampton City where traffic volume is highest. On both sides of the estuary aromatics such as benzene, methylbenzene, di- and tri-methylbenzenes prevail. Benzene concentrations vary from about $1\text{--}50 \mu\text{g m}^{-3}$ in summer to about $5\text{--}500 \mu\text{g m}^{-3}$ in winter. Methylbenzene and dimethylbenzene concentrations tended to be between 1.3 and 2.0 times higher than benzene concentrations. These levels may be considered to be of prime environmental interest, particularly the higher wintertime concentrations. For example, as a result of the perception of a potential health risk to the public, ambient air quality standards for benzene have recently been proposed in Germany and in the Netherlands of $2.5 \mu\text{g m}^{-3}$ and $10 \mu\text{g m}^{-3}$, respectively. Our data suggest that ambient air from the South Hampshire area would not fall well below these proposed limits, particularly during the winter.

Interestingly, no major differences in VOC concentrations were found when comparing air quality near the petrochemical complex with air from the city centre and some of its suburbs, and total VOCs in both locations appeared to co-vary with season rather than any other clearly identifiable factor. This is highlighted in Table III which lists typical summer and winter concentration ranges for a spectrum of VOCs regularly found in estuarine air samples. On an annual basis, 75–80% of the prevailing winds are from the south-west (*i.e.* which tracks directly from the petrochemical complex towards the eastern suburbs of the city some 20 km away). However, even when the prevailing wind direction is from the opposite direction, the ambient air VOC concentrations in the city do not differ widely, and wintertime concentrations are frequently higher than levels downwind of the complex. The dominance of season over concentration is illustrated more clearly in Fig. 2a and b, which shows the total VOC concentrations at (a) a fixed sampling point adjacent to a yacht marina, (about 10 km southwest of Southampton City), and (b) a sampling point beside a busy (4-lane) road-bridge, 4 km west of Southampton City. Fig. 2 reveals the co-variance of total volatile aromatics (*i.e.* shown as the crossed points) with total VOCs (*i.e.* shown as the filled circles) from October 1990 through October 1991. In both diagrams, February was the worst month (typical air temperature, 2°C) whereas lowest VOC con-

TABLE III

TYPICAL AIRBORNE CONCENTRATION RANGES OF SELECTED VOCs IN AMBIENT AIR FROM THE SOUTHAMPTON WATER ESTUARY DURING SUMMER AND WINTER

All results are expressed as $\mu\text{g m}^{-3}$.

| Atmospheric conditions | Summer | Winter |
|---------------------------------------|--------------|--------------|
| Temperature | 19–32°C | –12–10°C |
| Relative humidity | 38–98% | 55–100% |
| Barometric pressure | 749–790 mmHg | 721–782 mmHg |
| VOCs | Min–Max | Min–Max |
| Ethane | 1.6–18.4 | 2.9–155.6 |
| Ethene | 2.0–20.5 | 2.6–169.6 |
| Propane | 0.9–23.2 | 3.2–289.4 |
| Propene | 3.2–27.3 | 4.7–398.2 |
| iso-Butane + <i>n</i> -Butane | 3.7–34.5 | 5.3–605.3 |
| <i>n</i> + iso-Butene | 5.8–44.3 | 5.3–497.3 |
| <i>trans</i> - + <i>cis</i> -Butene-2 | 2.2–24.3 | 4.3–338.5 |
| <i>n</i> -Pentane | 0.4–50.3 | 3.3–570.1 |
| <i>n</i> -Hexane | 0.3–44.5 | 3.0–449.3 |
| <i>n</i> -Heptane | 0.3–39.6 | 2.7–250.7 |
| <i>n</i> -Nonane | 0.6–34.4 | 2.3–147.2 |
| <i>n</i> -Decane | 0.3–37.7 | 4.3–153.5 |
| <i>n</i> -Undecane | 0.3–24.3 | 0.9–138.6 |
| <i>n</i> -Dodecane | 0.6–24.5 | 0.5–132.1 |
| 2,2-Dimethylbutane | 3.4–22.4 | 4.5–198.9 |
| 2,3-Dimethylbutane | 3.1–26.4 | 4.0–230.3 |
| 2-Methylpentane | 4.6–58.4 | 8.5–296.9 |
| 3-Methylpentane | 6.4–67.4 | 5.8–355.7 |
| 2,4,4-Trimethylpentane | 2.3–55.3 | 4.3–389.4 |
| Benzene | 1.1–53.2 | 5.3–498.4 |
| Methylbenzene (toluene) | 4.6–76.6 | 10.3–944.3 |
| 1,3-Dimethylbenzene | 4.5–84.4 | 7.8–895.7 |
| 1,2-Dimethylbenzene | 2.3–77.8 | 5.6–800.4 |
| Ethylbenzene | 1.2–67.9 | 5.3–797.5 |
| 1,3,5-Trimethylbenzene | 1.4–55.4 | 4.5–532.8 |
| 1,2,3-Trimethylbenzene | 1.2–53.8 | 3.4–433.6 |
| 1,2,4-Trimethylbenzene | 0.9–47.9 | 4.0–450.2 |
| Isopropylbenzene | 0.6–40.3 | 3.4–410.1 |
| <i>n</i> -Propylbenzene | 0.4–38.3 | 3.2–390.3 |
| 1,2,3,5-Tetramethylbenzene | 0.4–23.2 | 2.2–260.2 |
| Naphthalene | 0.2–19.2 | 4.6–155.3 |
| Dichloromethane | 0.1–76.6 | 1.2–96.5 |
| 1,1,1-Trichloroethane | 0.2–85.5 | 1.0–90.4 |
| Tetrachloroethene | 0.1–24.5 | 0.4–33.6 |
| Freon-113 | 3.2–66.8 | 5.5–438.7 |
| 2-Butanone | 0.5–57.7 | 0.9–110.2 |
| 2-Pentanone | 0.4–45.4 | 0.4–54.7 |
| 4-Methylcyclohexanone | 0.5–66.8 | 0.8–87.8 |
| Methylisobutylketone | 0.3–37.7 | 0.6–68.6 |
| <i>n</i> -Butanol | <0.1–6.4 | 0.4–10.2 |
| 2-Butanol | <0.1–5.4 | 0.5–9.6 |
| Hexanal | <0.1–9.7 | 0.7–43.4 |
| Octanol | | |

centrations were typically found from June to September (*i.e.* in two successive years, 1990–91) when typical air temperatures are much higher (*i.e.* 19°C–32°C). Despite higher volumes of traffic which occur during the peak summer tourist season, faster volatilisation rates combined with rapid photodegradation of volatile products partly explains why VOC levels are lower in summer. During winter-time, cooler air temperatures and slower photodegradation rates (*i.e.* high cloud cover, fog etc.) combined with greater inputs of combusted fossil-fuel products (*i.e.* aromatics) are major contributory factors to high VOC concentrations in winter months. Similar observations were made by Brodinin *et al.* [27] in urban environments. Airborne hydrocarbons in aerosol fractions have also been identified further afield in North Sea atmospheres. Preston and Merrett [28] have shown that saturated hydrocarbons and PAH reach their highest levels in

air which has been transported from terrestrial sources, particularly during winter.

Another important medium where the significant seasonal differences manifest themselves is in the estuarine waters of Southampton Water. As Table IV shows, higher levels of VOCs occur in the sea water during winter than in summer, and the estuary itself has a complex source-sink relationship with the atmosphere. Sauer [29] determined that reservoir and material fluxes of VOCs to and from sea water could be appropriately estimated using a stagnant film model developed by Broecker and Peng [30]. The model predicts that the flux, F , of gas (VOCs) from sea water to the atmosphere is dependent on the molecular diffusivity of the gas and the thickness of the stagnant diffusion-controlled boundary layer, z :

$$F = D_i (dc/dz) \text{ (i.e. } F = K_i \Delta C_i)$$

where $K_i = D_i/z$, D_i = coefficient of molecular diffusion (cm^2s^{-1}), z = film thickness (cm), and ΔC_i = concentration difference across the film layer, $C_{ii} - C_{ig}$ (mol l^{-1}). C_{ig} is the gas concentration at equilibrium with the overlying air, $C_{ig} = \alpha p$, where α is the solubility of gas and p is the partial pressure of gas in the atmosphere (*i.e.* in these flux estimates, C_{ig} is assumed to be negligible). C_{ii} is the concentration of gas in the aqueous mixed layer. Fluxes are determined on the assumption that there is no con-

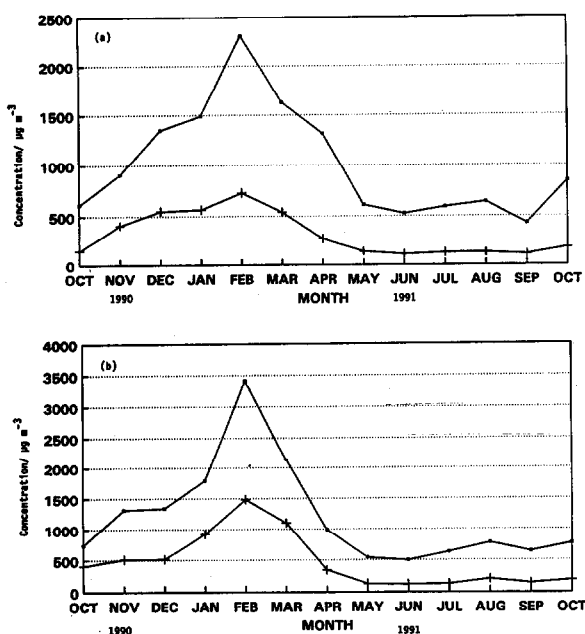


Fig. 2. (a) The monthly variation of total VOCs (●) and total aromatics (+) in ambient air at Hythe Marina in Southampton Water. This sampling station accommodates approximately 100 yachts and motor cruisers and is located approximately 10 km south-west of Southampton City. (b) The monthly variation of total VOCs (●) and total aromatics (+) in ambient air at the Redbridge 4-lane roadbridge 4 km west of Southampton City. This roadbridge typically accommodates over 50 000 vehicle movements in a single 24-h period.

TABLE IV

TYPICAL CONCENTRATION RANGES OF SELECTED VOCs IN THE WATER COLUMN OF SOUTHAMPTON WATER DURING SUMMER AND WINTER

Note that these concentrations refer to estuarine water from the head of the estuary. All results are expressed as $\mu\text{g l}^{-1}$.

| VOCs | Summer | Winter |
|-------------------------|-----------|-----------|
| <i>n</i> -Hexane | 0.08–0.91 | 0.55–1.03 |
| <i>n</i> -Decane | 0.04–0.20 | 0.19–1.10 |
| Methylcyclohexane | 0.01–0.29 | 0.36–0.92 |
| Benzene | 0.05–0.51 | 0.44–1.57 |
| Methylbenzene (Toluene) | 0.43–1.33 | 1.24–4.23 |
| 1,2-Dimethylbenzene | 0.07–1.01 | 1.23–2.92 |
| Ethylbenzene | 0.09–0.92 | 0.81–1.77 |
| 1,2,4-Trimethylbenzene | 0.02–0.18 | 0.14–0.83 |
| Naphthalene | 0.05–0.44 | 0.17–4.33 |

TABLE V

EQUILIBRIUM CONCENTRATIONS (ng l^{-1}) IN SEA WATER EQUILIBRATED WITH AIRBORNE CONCENTRATIONS OF 1 AND 50 ppb (v/v)Numbers in parentheses beside each component represent the 1 and 50 ppb (v/v) concentrations expressed respectively in $\mu\text{g m}^{-3}$ units. e.g. 1 ppb (v/v) of benzene = $3.2 \mu\text{g m}^{-3}$ in air. See text for details.

| VOCs | M.W. | H_{iR}^a | C_i (ng l^{-1}) ^b | |
|------------------------|------|---------------------|---|--------------|
| | | | 1 ppb (v/v) | 50 ppb (v/v) |
| <i>n</i> -Hexane | 86 | 47 | 0.063 (3.5) | 3.8 (176) |
| <i>n</i> -Decane | 142 | 252 | 0.024 (5.4) | 1.2 (270) |
| Methylcyclohexane | 98 | 11.4 | 0.36 (4.03) | 18.0 (201.5) |
| Benzene | 78 | 0.12 | 27.0 (3.2) | 1370.0 (160) |
| Methylbenzene | 92 | 0.18 | 21.0 (3.8) | 1070.0 (189) |
| 1,2-Dimethylbenzene | 106 | 0.24 | 19.0 (4.3) | 930.0 (217) |
| Ethylbenzene | 106 | 0.25 | 18.0 (4.3) | 890.0 (217) |
| 1,2,4-Trimethylbenzene | 130 | 0.20 | 27.0 (4.9) | 1370.0 (246) |
| Naphthalene | 128 | $8.4 \cdot 10^{-3}$ | 640.0 (5.2) | 3200.0 (260) |

^a Effective Henry's Law constant derived from vapour pressure and solubility data [35].^b $(P_i/H_{iR}RT) \cdot (\text{M.W.}_i) \cdot 10^9$; C_i = concentration in sea water (ng l^{-1}), P_i = concentration in the atmosphere (atm), $R = 82.05 \cdot 10^{-3}$ (atm l g mol⁻¹ K⁻¹), and $T = 290\text{K}$.

tribution from the atmosphere. However, if VOCs are appreciable in the atmosphere, $C_{ig} \neq 0$ and the flux from marine waters will be reduced due to the decrease in the concentration difference, $C_{il} - C_{ig}$. Near urban areas atmospheric concentrations are appreciable enough to retard the flux from the water column and, if high enough, will contribute VOCs to the water column. Using Sauer's model, equilibrium concentrations of key VOCs in Southampton air and in its estuary were calculated and the results are presented in Table V for atmospheric concentrations varying from 1 to 50 ppb (v/v). The equivalent mass per unit volume concentration for each component is presented in parentheses for direct comparison with its v/v concentration. By applying Southampton sea water concentration data published previously by Bianchi and co-workers [9, 10, 31–34] to the equilibrium model developed by Sauer [35], and calculating the equilibrium concentrations (presented in Table V), it is possible to see that atmospheric concentrations of VOCs in Southampton Water will contribute VOCs to surface sea water, especially during colder winter months. For example, a 50 ppb (v/v) ($160 \mu\text{g m}^{-3}$) concentration of benzene in estuarine air could conceivably yield a single component equilibrium concentration of $1.37 \mu\text{g l}^{-1}$ in surface water.

CONCLUSION

The sampling and analytical method has proved to be very reliable in routine use. Despite new developments in sampling methodology, low-flow sampling pumps used in tandem with the Carbotrap and Carbosieve adsorbents have proved to be a sustainable and cost-effective option for taking over 300 individual samples. The use of thermal desorption ensures that all volatile compounds are quantifiable, minimising the disadvantages incurred with solvent-based desorption *i.e.* elution of components under the solvent peak, contamination from impurities in the solvent. Unlike a similar study of volatile hydrocarbons in ambient air within the city of Rome by Ciccioli *et al.* [36], no problems with water build-up on the Carbosieve S-III were found in this study, even when relative humidities were high (*i.e.* > 90%), permitting efficient sampling, thermal desorption and GC-MS analysis of every sample taken over the 2-year period.

This brief discussion about airborne VOCs in the ambient air of the Southampton Water region reveals a complex picture. Furthermore, the long-range aspect of this study has shown a clear and repeatable seasonal variability in the total VOC concentration profile. VOC concentrations are gen-

erally high, and when compared to similar studies carried out in cities such as Barcelona [16] and Rome [36], the concentrations of toxic compounds such as benzene appear to be slightly higher. However, since no seasonally varying data from the aforementioned surveys has been published, it is impossible to compare these studies directly. At minimum we believe that Southampton City would find it difficult to comply with the airborne standards for benzene concentrations proposed by the German and Dutch governments. We suspect that this conclusion would also apply to many other major British cities. The seasonal variation in VOC concentrations is also important because equilibrium models predict that many VOCs will partition into and out of surface sea water (depending on the concentration gradient across the air–sea interface for example). Previous long-term studies carried out on the Southampton Water estuary by the author(s) have already revealed marked increases in marine volatile aromatic concentrations during winter months which parallel increases in local ambient air concentrations, an observation which can be substantiated by Sauer's predictive model. This sampling and analytical exercise also reinforces the concept of a dynamic balance in VOC concentrations taking place at the air–sea interface and suggests that marine VOCs are unlikely to be in equilibrium with VOCs in the local atmosphere on a year-round basis. New air–sea exchange models are continuously being developed, particularly those based on dual tracer techniques [37], which will undoubtedly enhance our understanding of these complex processes now and in the future.

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