INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

CHEMISTRY AND THE ENVIRONMENT DIVISION
COMMISSION ON ATMOSPHERIC CHEMISTRY

THE USE OF DIFFUSIVE SAMPLING FOR MONITORING OF BENZENE, TOLUENE AND XYLENE IN AMBIENT AIR

(Technical Report)

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Abstract: A diffusive sampler, originally developed for workplace monitoring of organic vapours has been evaluated for its potential for monitoring ambient air quality, particularly for benzene, toluene and xylene.

The diffusive sampling rate, which is different for workplace and ambient air applications because of the wide differences in concentration levels and times of exposure, has been determined accurately, and been shown to be similar to other independent estimates determined from field studies or by exposing samplers to standard test atmospheres. In each case, the actual mass concentration of the aromatic hydrocarbons in ambient air or test atmosphere has been established by an independent calibrated method, usually using pumped sampling and the diffusive sampling rates of parallel diffusive samplers determined from these concentrations.

The potential for using such samplers for monitoring ambient air has been demonstrated in two local studies, at car parks and in a street canyon, and in three area studies, at urban (Sheffield), regional (UK) and global (world) levels. In addition, the diffusive sampler has been evaluated alongside the UK VOCair measuring instruments in the UK fixed monitoring stations, where in view of the uncertainties involved, similar results were obtained.

These studies also gave useful insight into the practicability of employing these devices, their use by untrained personnel and their ruggedness in transportation and use.

INTRODUCTION

Diffusive sampling is particularly relevant to Articles 5 and 6 of the EC Directive on Ambient Air Quality Assessment and Management (96/62/EC), which will, via daughter Directives, extend the list of atmospheric pollutants to be regulated in current Directives against new pollution indicators. The framework and daughter Directives will also allow for the use of noncontinuous measurement techniques for the monitoring of air quality, provided they meet the relevant data quality objectives. Of these techniques, diffusive sampling is ideally suited, because of its low cost and ease of deployment at multiple locations, to serve the indicative and possibly also the mandatory measurement requirements in a number of specific areas of the Directive: tool for the siting of network stations (Art. 4.3); preliminary assessment of ambient air quality (Art. 5); air quality monitoring in areas not exceeding limit values (Art. 6.3); and, classification of zones (Art. 8 and 9).

A particularly attractive candidate for ambient air monitoring by diffusive sampling is benzene. This can be sampled readily by using sorption tubes, thermal desorption and gas chromatography; a method which has been fully validated for workplace air monitoring [1]. Other aromatic hydrocarbons, such as toluene and xylene can be monitored similarly, although such monitoring is not currently required by the Directive(s).

However, as noted in the previous review [2], much longer sampling times are required for ambient air monitoring than for workplace air monitoring, and it is necessary as part of the validation process to establish reliable diffusive uptake rates for periods of up to four weeks.

A second feature of a full validation of the environmental diffusive sampler is a comparison with other longer-established techniques, such as the fixed monitoring instruments employing semicontinuous VOCair analysers as used in the UK monitoring stations.

A third activity, more relevant to the practical application of the sampling method specifically in support of the Directive, is to undertake pilot surveys at local, urban, regional and world levels, both to demonstrate potential for area mapping and to identify any potential problems in practical use, such as transportation and storage.

OBJECTIVE

The objective or the reported research is to provide technology at low cost, enabling air quality surveys to be routinely executed at multiple locations within urban and rural areas, industrial sites and forests. This requires the examination of the performance characteristics of the diffusive sampler over long sampling periods, in comparison with established methods, and in practical applications of urban monitoring as described at the end of the 'Introduction'.

The project is strongly aligned with EU programmes and Directives, and supports the (IUPAC) Division's focus on solving environmental problems by developing appropriate analytical methodologies.

EXPERIMENTAL METHOD

Pumped sampling

A measured volume of air was drawn through a sorbent tube containing either Chromosorb 106 or Carbograph TD-1, which retains the benzene, toluene and xylene [3] (BTX). Where the measured volume exceeds the safe sampling volume for benzene ($87 \, dm^3/g$ sorbent at $20 \, °C$), toluene ($270 \, dm^3/g$) and xylene ($2600 \, dm^3/g$) [4], breakthrough may occur. The total volume of air pumped was set at either approximately $28 \, dm^3$ (14 h/tube) or approximately $20 \, dm^3$ (4, 6 and 12 h/tube) as this volume range has been shown to fall within the safe sampling range (Table 1). Samples were taken from outside the second floor of the Health and Safety Laboratory (HSL) Robens Building using a calibrated SKC Personal Air Sampling pump model 222-3 at a rate of either $0.7 \, dm^3/h$ (12 and 14 h/tube) or $3–3.5 \, dm^3/h$ (4 and 6 h/tube). This was linked to a Perkin-Elmer SDS-25 Sequential Tube Sampler, which allowed sequential exposure of sorbent tubes for preselected time periods without interruption by use of a carousel system. During the sampling period, passive diffusion of air occurs in all tubes not being actively pumped. This is minimised by a restrictive diffusion cap through which air can be pumped actively but diffuse in a limited manner only (Fig. 1). In such a system (Perkin-Elmer L428 9005C) the rate of passive diffusion onto the sorbent is $0.63 \, cm^3/h$, i.e. between 0.3 and 0.7% of the volume sampled actively in these experiments. The contribution of passive diffusion may therefore be ignored. A control sorbent tube was included in the carousel and also capped with an identical restrictive diffusion cap plus other permanently closed control tubes.

Table 1 Pumped sampling survey Location: HSL Laboratories Floor 2

Period	Pump time (h)	Total volume (dm^3)	Mass concentration ($\mu g/m^3$)			
			Toluene	*m/p*-Xylene	*o*-Xylene	Benzene
1.8.95–2.8.95	17.0	15.12	2.3	5.3	6.2	2.2
2.8.95–3.8.95	24.0	20.2	2.2	7.0	6.0	1.4
3.8.95–4.8.95	23.0	22.60	1.4	4.1	4.6	0.7
4.8.95–5.8.95	23.0	21.22	1.2	3.1	3.6	0.7
7.8.95–9.8.95	40.5	44.64	2.0	5.8	6.4	1.3
9.8.95–10.8.95	23.7	26.75	3.4	9.9	11.1	2.6
10.8.95–12.8.95	44.5	51.20	3.0*	10.3	8.3	2.1
13.8.95–16.8.95	66.5	87.81	1.9†	8.9	7.1	1.7

* Breakthrough just noticeable at 44.5 h.
† Breakthrough occurred for benzene at a ratio of approximately 3 : 1 (sample/back-up tube).
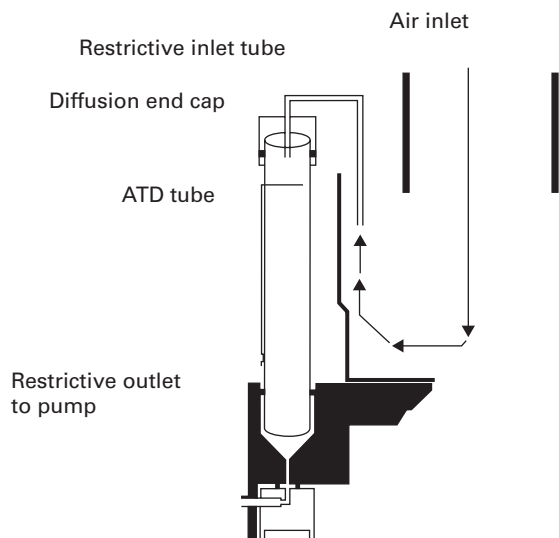
Fig. 1 Sequential pumped sampling ATD tube mounting.

All sorbent tubes were conditioned prior to use (Chromosorb 106, 3×30 min at $250\,°C$; Carbograph 3×30 min at $300\,°C$) to ensure no contaminants were present.

Diffusive sampling

Preconditioned sorbent tubes of Chromosorb 106 and Carbograph TD-1 were located as appropriate for the study (see below). In studies 1–3, the tubes were protected from adverse weather conditions with plastic sheeting, whilst maintaining ambient air movement past the diffusion cap. In later studies, a more standardised approach was used, employing plastic funnels (Fig. 2). Individual tubes were exposed by removal of protective end caps and replacement with a diffusion cap. Sampling was carried out using replicate tubes plus replicate capped control tubes for each type of sorbent and after sampling periods of 1, 2 and 4 weeks these sets of tubes were sealed prior to analysis, and returned to the laboratory for analysis.
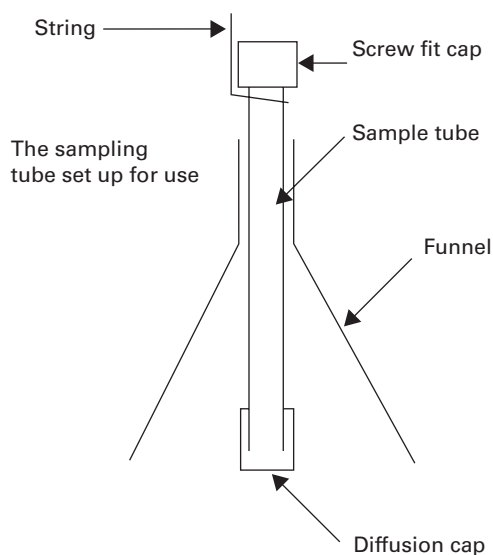
Fig. 2 Sampling tube with protective weather hood.

   In nearly all cases, diffusion caps without membranes were used, and the diffusive uptake rates quoted reflect this. Where membranes were used for one sampling period in study 1, the practical uptake rate was corrected using a ratio determined experimentally for each analyte from comparative tests.

Study 1: Establishment of diffusive sampling rates

Diffusive samplers were exposed simultaneously with the SDS-25 sequential sampler containing pumped sample tubes outside the HSL building on the second floor, such that the sampling area of the diffusive samplers was close to the pumped air sampling system inlet.

Study 2: Sheffield underground car parks

Diffusive samplers were placed on the ground floor and first floor of an underground car park in the city centre by Sheffield Environmental Protection Unit (EPU) staff along with unexposed control tubes for a period of 2 weeks in January 1996. The car park is situated at or below ground and is covered on all sides. Samples were also placed in an above ground multistorey car park (open at the sides) for comparison.

Study 3: Canyon study

EPU staff also set up diffusive samplers in a canyon study across Charter Row, a busy city-centre dual carriageway in Sheffield, with the low level tubes positioned on a foot bridge crossing over it, and the high-level sampling position on roof tops on either side. The study was conducted in February 1996.

Study 4: Pilot survey of Sheffield

Diffusive tubes were distributed to 17 in-house HSL staff who had volunteered to take part in the pilot survey. Volunteers were also supplied with 'instructions for use' for the samplers. Tubes were set up in the front or back gardens, mostly in residential areas at the approximate height of 1.5–2.0 m and from between 50 and 100 m from the nearest major roadway. Paired sampling tubes of both Chromosorb 106 and Carbograph TD-1 were exposed by removal of protective end caps and replacement with diffusion caps. Sampling (with both tube types) was carried out alongside a capped control (blank) tube and a capped tube preloaded with known quantities of analyte. Weather conditions were mostly mild, although there were some periods of strong winds. Sampling occurred for approximately 4 weeks within the period May to June 1996, after which the sets of tubes were sealed and returned for analysis.

Study 5: Pilot survey of the United Kingdom

Diffusive tubes were sent out using standard postal services to in-house HSE staff, who had volunteered to take part in the pilot survey. Tubes were set up in urban, suburban or rural areas at the approximate height of 1.5–2.0 m and from between 50 and 100 m from the nearest major roadway. Exceptions to this were Ellesmere Port where the site was on the top of a Council building at 11 m elevation and was within 3 miles of an oil refinery, power station, chemical works and waste incinerator; Birmingham where there were rubber, vehicle and petroleum facilities/manufacturing within two miles and Cwmbran where there was a chemical plant nearby. In addition to this the site at Northwich was close to a construction site and the location at Longridge, Preston was some 500 m from the road in a rural environment. The prevailing weather conditions at each site were noted and all sites were exposed to more or less the same weather patterns. All sites experienced some snow, fog, strong winds and rain. However, the data requested and supplied was of a limited nature and no conclusions were made from the weather information available. Sampling conditions were otherwise as for the Sheffield survey, except that the sampling period was within the period mid-November to mid-December 1996.

Study 6: Comparison with the VOCair UK network

Diffusive tubes were sent out using standard postal services to each location of the VOCair monitoring stations that was taking part in the study. Tubes were set up in urban areas at the approximate height of 1.5–2.0 m and from between 50 and 100 m from the nearest major roadway. Exceptions to this are

Edinburgh Site 2 which was on the roof of a mobile monitoring unit situated in Haymarket Terrace (Edinburgh Site 1 was adjacent to the VOCair monitoring system) and Cardiff where the VOC inlet for the analyser was around the corner of the site building in a different street (approximate distance between locations of 20 m). The Harwell system was on top of a Portakabin roof in a field. The prevailing weather conditions at each site were noted although the data requested and supplied was of a limited nature and no conclusions were made from the weather information available. However, two sample tubes were lost due to severe winds in Leeds. Sampling conditions were otherwise as for the UK survey, except that the sampling period was four weeks within the period end-February to mid-May 1997.

Study 7: Pilot world survey

Sampling conditions were as for the UK survey, except that locations were world-wide. Siting information is included in Table 13.

Spiked control tubes

Preconditioned sorbent tubes of Chromosorb 106 and Carbograph TD-1 were spiked with known amounts of benzene, toluene and *m*-xylene and the caps tightly closed. In study 5, the spiked amounts of each hydrocarbon were approximately 80 ng; in studies 6 and 7, the amounts were approximately 200 ng. The spiked tubes were hung outside next to the sampling tubes without being opened and were analysed at the end of the sampling period.

Chrompack VOCair Analysis System (study 6)

Benzene, toluene and xylene (together with other hydrocarbons) are monitored in automated thermal desorption/gas chromatograph systems situated at each of the sampling sites. These systems collect and download data to a central data logging system. A sample of air (300 mL in 30 min) is drawn through a cooled 3-bed adsorbent trap (–20 °C) followed by backflushing in helium onto a cryofocusing trap at –100 °C. This is then flash heated to 120 °C and the volatiles are injected on an Al_2O_3 (PLOT) capillary column at 50 °C by a flow of helium carrier gas and detected by a flame ionisation detector. One analysis is performed per hour and quantification of the peaks is by using a certified gas cylinder as a reference. Various quality checks are carried out automatically on the raw peak data in order to detect anomalies.

Thermal desorption and GC analysis

Analysis was carried out using a Perkin-Elmer ATD-400 AutoGC system for all samples. In all cases a two-stage desorption of the sorbent tube was carried out with a transfer of desorbed vapours to the gas chromatograph flame ionisation detector by a regulated flow of helium. The gas chromatograph was fitted with BP1 and BP10 capillary columns in a dual-column arrangement running on a temperature ramp of 5 °C/min from 50 °C to 130 °C. Primary desorption was for 10 min at 230 °C (Chromosorb 106) or 280 °C (Carbograph) followed by secondary desorption from the cold trap at 300 °C for 5 min. The amount of sample vapour entering the GC is controlled by split flow regulators and this split ratio (50 : 1) and subsequent calibration was set specifically for each different analysis. In all cases noncontrol blank tubes were run between calibration tubes and sample tubes to ensure no residues remained on the cold trap from previous analyses. In-house calibration standards were prepared by temperature corrected gravimetric method on a calibrated Mettler AT21 digital balance. Standards on conditioned Tenax sorbent tubes (30 min at 350 °C) were desorbed at 300 °C and analysed as for the samples.

RESULTS AND DISCUSSION

All 2–4 week diffusive sampler results are subject to an estimated overall uncertainty of $\pm$ 20% which includes both bias and random error. The overall uncertainty for 1 week results is $\pm$ 30–40%.

Blank levels of analyte on sample tubes

A summary of the blank levels observed from field blanks exposed in studies 5–7 is given in Table 2. Blank levels on both sorbents are similar for benzene (5–10 ng Chromosorb: 3–7 ng Carbograph); toluene

Table 2 Blank levels for benzene, toluene and xylene for Chromosorb 106 and Carbograph TD-1

		Chromosorb 106						Carbograph TD-1					
		Benzene		Toluene		Xylene		Benzene		Toluene		Xylene	
Study		(μg/m^3)	(ng)	(μg/m^3)	(ng)	(μg/m^3)	(ng)	(μg/m^3)	(ng)	(μg/m^3)	(ng)	(μg/m^3)	(ng)
5: UK	Mean	0.39	7.69	0.06	1.39	0.16	3.23	0.27	7.22	0.08	2.04	0.26	5.59
survey	$\pm$ SD	0.12	1.96	0.03	0.55	0.09	1.64	0.11	2.75	0.03	0.78	0.12	2.28
	n	20		20		20		18		19		19	
6: VOCair	Mean	0.58	10.38	0.15	3.26	0.08	1.46	0.28	6.88	0.15	3.34	0.12	2.35
comparison	$\pm$ SD	0.13	2.28	0.11	2.55	0.08	1.44	0.13	2.70	0.07	1.3	0.08	1.39
	n	14		14		14		14		14		14	
7: World	Mean	0.25	5.63	0.09	2.09	0.04	0.96	0.12	2.61	0.2	4.39	0.07	1.63
survey	$\pm$ SD	0.14	3.04	0.11	2.36	0.02	0.51	0.05	1.13	0.28	6.19	0.05	1.17
	n	16		16		16		16		16		16	

Values in the ng columns are the blank values and the values in the μg/m^3 columns are the mass concentration equivalents of the blank value for a 4-week diffusive sample.

(2–4 ng Chromosorb; 3–6 ng Carbograph) and xylene (0.5–3.0 ng Chromosorb; 1–5 ng Carbograph). It was not possible to reduce the blank levels below these values by repetitive conditioning/desorptions.

For the diffusive sampling surveys the uncorrected level of analyte is very low, approximately 80 ng benzene, 180 ng toluene and 140 ng xylene for a 4-week diffusion period, and therefore blank levels become significant. Whilst for toluene and xylene the blanks are less than 5% of the actual tube loading for both sorbents, for benzene it is up to 10%. The blank becomes more significant for 1 or 2-week exposures. Similar considerations apply to the pumped tubes (study 1).

Table 3 Recovery (%) of benzene, toluene and xylene from spiked tubes

		% Recovery					
		Chromosorb 106			Carbograph TD-1		
Study		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
5: UK	Mean recovery %	82.7	87.5	95.9	95.1	100.1	100.6
survey	$\pm$ SD	8.3	6.7	10.4	12.1	4.4	10.0
	n	20	19	19	19	20	20
6: VOCair	Mean recovery %	93.1	99.1	100.5	98.7	100.3	98.5
comparison	$\pm$ SD	11.9	7.9	5.0	3.0	2.7	2.0
	n	13	13	13	13	13	13
7: World	Mean recovery %	104.8	105.9	98.7	103.7	100.7	100.1
survey	$\pm$ SD	11.3	10.1	7.8	4.6	3.2	2.3
	n	16	16	16	16	16	16
5. to 7.	Mean of means %	93.5	97.5	98.3	99.2	100.4	99.7
	$\pm$ SD	11.1	9.3	2.3	4.3	0.3	1.1
	n	3	3	3	3	3	3

In study 5, the spiked amounts of each hydrocarbon were approximately 80 ng; in studies 6 and 7, the amounts were approximately 200 ng.
Recoveries above 100% are within the range 100 $\pm$ the quoted uncertainty (95% confidence interval) in every case.

Recoveries from spiked control tubes

Recoveries are reported in Table 3. In study 5, the toluene and xylene values for Chromosorb 106/ Inverness and the benzene value for Carbograph/London were anomalous (150–300%). In study 6, the benzene value for Chromosorb 106/Cardiff and the benzene and toluene values for Chromosorb 106/ Harwell were anomalous (about 75% or about 125%). In study 7, the benzene value for Chromosorb 106/ China and the benzene and xylene values for Chromosorb 106/Brazil were low (about 80%). All these values were treated as outliers and excluded from the means. The overall mean recoveries are also given in Table 3, assuming that the recovery is not loading-dependent in the range 80–200 ng. All recoveries were 100% within the stated errors, but the standard deviations were largest for benzene and toluene on Chromosorb, which sorbent also seemed to give the greater number of outliers.

Studies

Study 1: Establishment of diffusive sampling rates

The effective uptake rate can be recalculated from the simultaneous pumped and diffusive sampling data using Eqn 1. In this method the mass concentration of each analyte found by means of pumped sampling (Table 4) is assumed to be the true value. This value is applied to the equation along with the absolute amount of analyte detected on each tube for the specified exposure time period. Recalculated values for the individual sampling series for Tenax TA, Carbograph TD-1 and Chromosorb 106 are summarised in Table 5. The reliability of these values is dependent on the accuracy of the initial measurements including the determination of absolute mass

Table 4 Mean pumped sampling results for mass concentration of analyte over the simultaneous diffusive sampling period. Pumped sampling time is shown as % total simultaneous diffusive sampling period. Blank corrected BP1 results for n x 6 h sequential tube exposures (series 2,3 and 3), 4 h (series 1),14 h (series 6 and 7) and 12 h (series 8)

				Mean mass concentration ($\mu g/m^3$)		
Measurement period				Benzene	Toluene	Xylene
1 week						
Series 2	$n = 24$	8640 min (78%)	23.10.95–31.10.95	2.6	7.6	6.4
Series 3	$n = 29$	10 440 min (103%)	22.11.95–29.11.95	2.0	5.5	4.5
Series 4	$n = 29$	10 440 min (103%)	12.12.95–19.12.95	2.5	5.8	4.2
Series 8	$n = 14$	10 080 min (100%)	15.3.96–22.3.96	3.6	8.9	4.6
2 weeks						
Series 1	$n = 24$	5760 min (24%)	6.10.95–23.10.95	2.2	5.5	3.9
Series 2	$n = 48$	17 280 min (87%)	23.10.95–6.11.95	2.8	7.5	6.0
Series 3	$n = 57$	20 520 min (102%)	22.11.95–6.12.95	2.2	6.4	5.1
Series 6	$n = 24$	20 160 min (100%)	12.1.96–26.1.96	3.8	8.4	6.9
4 weeks						
Series 2	$n = 95$	34 200 min (86%)	23.10.95–20.11.95	2.5	6.8	5.4
Series 3	$n = 110$	39 600 min (98%)	22.11.95–19.12.95	3.1	8.2	6.3
Series 7	$n = 48$	40 320 min (100%)	9.2.96–8.3.96	1.9	4.5	3.4

Table 4A Mean pumped sampling results for mass concentration of analyte over the simultaneous diffusive sampling period (1999 results)

	Blank corrected ambient air mass concentration ($\mu g/m^3$)		
	Benzene	Toluene	Xylene
1 week ($n = 28$)	1.75	3.48	2.28
2 weeks ($n = 56$)	1.73	3.81	2.47
4 weeks ($n = 112$)	2.13	4.84	3.15

Table 5 Summary of recalculated effective uptake rates

| | Uptake rate (ng/ppm/min) | | | | | | | | | | | |
| | Benzene | | | | Toluene | | | | Xylene | | | |
Time	HSL1[1]	SD[2]	HSL 2[3]	SD	HSL 1	SD	HSL 2	SD	HSL 1	SD	HSL 2	SD
Tenax TA												
1 week	–	–	1.36	0.04	–	–	1.66	0.05	–	–	1.97	0.12
2 week	–	–	1.15	0.07	–	–	1.51	0.03	–	–	1.89	0.04
4 week	–	–	0.93	0.02	–	–	1.41	0.01	–	–	1.86	0.04
Carbograph TD–1												
1 week	1.99	0.19	2.21	0.13	1.75	0.03	2.02	0.08	2.16	0.04	2.16	0.14
2 week	2.00	0.16	1.90	0.08	2.11	0.04	1.90	0.04	2.19	0.09	2.01	0.04
4 week	2.00	0.11	1.75	0.05	2.39	0.05	1.93	0.04	2.18	0.07	2.02	0.04
Chromosorb 106												
1 week	1.46	0.11	1.46	0.19	1.64	0.07	1.92	0.10	2.20	0.28	1.93	0.08
2 week	1.45	0.17	1.40	0.17	1.89	0.09	1.74	0.05	2.08	0.07	1.93	0.02
4 week	1.47	0.14	1.22	0.04	2.10	0.09	1.72	0.05	2.07	0.06	1.84	0.07

[1]HSL data from 1995–96 tests.
[2]Standard deviation.
[3]HSL data from 1999 tests.

values, the errors introduced by significant blank levels and the extent to which the two measurement periods were simultaneous. This last is shown in Table 4, where pumped sampling time is shown as a percentage of the total diffusive sampling period. No reliability can be attached to any series that is not covered by at least 85% or exceeding 115% of the simultaneous pumped sampling data, and such data have been excluded from the calculation.

$$U = (m - m_b)/C \times t \tag{1}$$

where: U = uptake rate (ng/(mg/m^3)/min); m = mass uptake (ng); m_b = blank value (ng); C = mass concentration [5] (mg/m^3); t = time (min).

Data obtained by other laboratories is reproduced in ref. [6]. All values in Table 5 are within the ± 2 standard deviation ranges of the consensus means in [6] and most are within the ± 1 standard deviation ranges. Ref. [6] data includes HSL 1 not HSL 2.

Study 2: Sheffield underground car parks

The results of the underground car park survey are shown in Table 6. There is reasonable agreement between the two types of sorbent tube and there is no distinct difference due to location. The mass concentration level is approximately 10 times higher than typical environmental levels but the relative concentration is maintained in the general ratio of $3:6:4$. The higher values are most likely due to the confined nature of the sampling site and perhaps the slow moving stop-start traffic conditions. As expected, the levels in the overground car park (Table 7) are lower.

Study 3: Canyon study

The results of the canyon survey are shown in Table 8. Although there is no large mass concentration gradient, there would appear to be a greater concentration of analyte along the footbridge above the roadway compared to on the roof tops. This would be in keeping with the expectation that a region of high traffic flow would cause greater amounts of pollution. Also it may well be that on a roof top there is greater dispersal due to wind as well as the remote situation in relation to the pollution source.

Study 4: Pilot survey of Sheffield

The results of the pilot survey of Sheffield are given in Table 9. Benzene levels were typically 0.5–1.5 μg/m^3, with the front of properties giving values up to double that of the back.

Table 6 Sheffield car parks survey: Town Hall car park. Mean ambient air mass concentration of benzene, toluene and xylene by diffusive sampling for each sorbent

Sampling location	Sorbent	Mass concentration ($\mu g/m^3$)		
		Benzene	Toluene	Xylene
Upper basement	Chromosorb 106	26.3	90.1	49.7
		21.9	82.0	49.2
	Carbograph	24.8	94.6	48.5
		24.4	91.3	48.2
Lower basement	Chromosorb 106	26.2	99.7	55.6
		25.6	99.9	59.1
	Carbograph	25.8	105.7	56.3
		25.6	108.0	55.4
Lower basement kiosk	Chromosorb 106	11.3	44.1	26.6
	Carbograph	16.0	45.3	24.9
Blank				
(Upper basement)	Chromosorb 106	1.2	<0.5	<0.5
	Carbograph	<0.5	<0.5	<0.5

Table 7 Sheffield car parks survey: Charter Row car park—stepped levels. Mean ambient air mass concentration of benzene, toluene and xylene by diffusive sampling for each sorbent

Sampling location	Sorbent	Mass concentration ($\mu g/m^3$)		
		Benzene	Toluene	Xylene
Levels 9/10	Chromosorb 106	10.7	40.0	25.4
	Carbograph	10.3	40.0	21.6
Levels 6/7	Chromosorb 106	43.8	155.6	85.2
	Carbograph	40.6	167.6	88.9
Levels 4/5	Chromosorb 106	46.6	175.0	101.4
	Carbograph	29.3	179.3	100.0
Blank				
(Levels 6/7)	Chromosorb 106	1.3	<0.5	<0.5
	Carbograph	<0.5	<0.5	<0.5

Table 8 Canyon study: Sheffield, Charter Row. Mean ambient air mass concentration of benzene, toluene and xylene by diffusive sampling for each sorbent

Location	Sorbent	Mass concentration ($\mu g/m^3$)		
		Benzene	Toluene	Xylene
Chesham House roof	Chromosorb 106	3.4	6.6	5.2
"	Carbograph	No tube supplied		
Chesham House footbridge	Chromosorb 106	4.6	9.2	7.2
"	Carbograph	2.8	4.0	3.6
Milton House roof	Chromosorb 106	2.9	5.3	3.9
"	Carbograph	2.7	5.4	3.5
"	Carbograph	2.5	4.6	4.1
Milton House footbridge	Chromosorb 106	3.4	8.5	6.9
"	Carbograph	3.0	5.7	6.2

Table 9 Pilot Survey of Sheffield. Mean ambient air mass concentration of benzene, toluene and xylene by diffusive sampling for each sorbent

Location	Sampling position	Exposure time (min)	Sorbent	Mass concentration ($\mu g/m^3$)		
				Benzene	Toluene	Xylene
Walkley	#NA	40 305	Chromosorb 106	0.7	2.1	1.4
		40 305	Chromosorb 106	1.0	3.1	1.5
		40 305	Carbograph	0.9	3.0	1.6
Wybourne	#NA	42 615	Chromosorb 106	1.1	2.4	(2.6)
		42 615	Chromosorb 106	1.1	2.4	1.2
		42 615	Carbograph	0.9	2.7	1.5
Malin Bridge	Back	40 320	Chromosorb 106	1.0	2.8	1.2
	Front	40 320	Chromosorb 106	1.3	3.6	2.5
	Back	40 320	Carbograph	0.9	2.3	1.2
Penistone	#NA	30 360	Chromosorb 106	1.0	2.1	1.0
		30 360	Chromosorb 106	0.9	1.6	1.5
		30 360	Carbograph	0.7	2.1	0.9
Sothall	Back	41 090	Chromosorb 106	1.5	3.1	2.5
	Front	41 090	Chromosorb 106	1.9	4.4	3.0
	Back	41 090	Carbograph	#	3.3	2.1
Deepcar	Back	40 375	Chromosorb 106	0.5	1.1	1.6
	Front	40 375	Chromosorb 106	0.6	1.4	0.8
	Side	40 375	Carbograph	0.8	1.3	(0.2)
Crookes	Front	40 175	Chromosorb 106	#	3.5	1.8
	Back	40 175	Chromosorb 106	0.8	2.3	0.9
	Front	40 175	Carbograph	#	3.2	1.9
Millhouses S11	Front	40 335	Chromosorb 106	1.1	2.0	0.8
	Back	40 335	Chromosorb 106	1.0	1.6	0.6
	Side	40 335	Carbograph	#	1.9	0.8
Bents Green S11	Front	40 275	Chromosorb 106	1.1	2.8	1.4
	Back	40 275	Chromosorb 106	0.7	1.2	0.6
Tickhill	#NA	45 465	Chromosorb 106	0.9	2.0	0.9
Doncaster		45 465	Chromosorb 106	1.0	2.6	1.3
		45 465	Carbograph	0.8	3.4	1.0
Heeley	Front	47 605	Chromosorb 106	1.3	3.8	2.5
	Back	47 605	Chromosorb 106	1.0	2.6	1.7
	Back	47 605	Carbograph	1.0	3.0	1.9
Ecclesall S11	Front	40 755	Chromosorb 106	1.8	5.1	3.3
	Back	40 755	Chromosorb 106	1.1	2.2	1.2
	Side?	40 755	Carbograph	1.5	4.6	2.9
Hayfield	#NA	44 340	Chromosorb 106	0.7	1.5	0.5
Stockport		44 340	Chromosorb 106	0.8	1.8	0.6
		44 340	Carbograph	1.2	1.8	0.6
Pitsmoor	Back	40 290	Chromosorb 106	1.0	2.2	1.1
	Back	40 290	Chromosorb 106	1.0	1.9	0.9
	Back	40 290	Chromosorb 106	0.9	2.1	1.2
	Front	40 290	Chromosorb 106	2.8	9.2	7.3
	Front	40 290	Chromosorb 106	2.7	9.2	7.1
	Back	40 290	Carbograph	0.9	2.4	1.3
High Wincobank	Front	40 265	Chromosorb 106	1.6	4.0	2.8
	Back	40 265	Chromosorb 106	0.9	2.2	1.3
	Back	40 265	Chromosorb 106	0.7	2.2	1.3
	Back	40 265	Carbograph	1.0	2.6	1.5
	Front	40 265	Carbograph	1.4	4.1	2.8
	Back	40 265	Carbograph	0.9	2.5	1.5

Table 9 *Continued*

Location	Sampling position	Exposure time (min)	Sorbent	Mass concentration (μg/m^3)		
				Benzene	Toluene	Xylene
Low Wincobank	#NA	41 220	Chromosorb 106	1.3	3.2	2.7
		41 220	Chromosorb 106	1.4	3.1	2.2
		41 220	Chromosorb 106	1.4	3.1	2.1
		41 220	Carbograph	1.1	3.4	2.4
		41 220	Carbograph	1.3	3.6	2.6
		41 220	Carbograph	1.1	3.1	2.1
Lowfields	Front	33 195	Chromosorb 106	3.1	10.0	8.9
	Back	33 195	Chromosorb 106	1.7	5.9	4.5
	Not put out	33 195	Carbograph	Blank levels only		
HSL Balcony	#NA	40 215	Chromosorb 106	1.2	3.1	2.3
Floor 2		40 215	Chromosorb 106	0.4	2.5	2
		40 215	Carbograph	1.4	3.6	2.6
		40 215	Carbograph	1.1	3.5	2.5

Figures in parentheses are suspect data (outliers).
temporary contamination problem with benzene peak

Study 5: Pilot survey of the United Kingdom

Results for the UK pilot survey are shown in Table 10. Of the industrial locations, Birmingham and Cwmbran have mean values higher than the overall mean as might be expected. The construction site at Northwich appears to have had no obvious influence and the values for Longridge, Preston are in keeping with the other non-urban regions of Inch, Aberdeenshire and of Inverness. The results for Ellesmere Port were lower than the overall mean despite the presence of heavy industrial plants nearby. This site was elevated but this should only mean that the recorded level of BTX associated with petrol engines is lower; exposure to diffused pollution from industrial sources should be the same at ground level as at 11 m elevation when at reasonable distances from the pollution source. Either there were no relevant pollutants being discharged or the prevailing wind conditions meant that the sampling site was not exposed. Consequently the observed reduction in recorded levels of BTX strongly indicates that traffic rather than industry is the predominant pollution source.

Both London sites (Garston and Bermondsey) gave similar high results as did Wakefield with most other sites ranged around the mean. The levels recorded for Blackpool were surprisingly high since there was a constant wind from out to sea. The location was displaced from the active centre of this resort and measurements were in the 'off-season'.

The overall ratio was 2 : 4 : 3 (benzene : toluene : xylene), agreement between sites was close and the ratio compares reasonably well with the other surveys.

Study 6: Comparison with the VOCair UK network

A comparison of the data obtained from the diffusive samplers and from the VOCair network is presented in Table 11. In a few cases, where there was an obvious anomaly in a replicate tube judged from the BTX ratio, diffusive sampler results were excluded from the mean values. Shaded areas in the Table indicate where data capture efficiency of the VOCair systems was too low for a meaningful comparison to be made with the diffusive sampler results.

In general the results for the VOCair system are about 20–40% greater than those for the diffusive sampling tubes. Correlation plots of the data for benzene. toluene and xylene, excluding suspect data as above have the characteristics shown in Table 12. These suggest that the diffusive data for BTX are on average 36, 24 and 2% low, respectively, relative to the VOCair analysers. This may indicate the

Table 10 Pilot survey of the United Kingdom. Mean ambient air mass of benzene, toluene and xylene by diffusive sampling for both sorbents combined. Ratio is of concentration relative to benzene

| Location | Mass concentration) $\pm$ SD (μg/m^3) | | | Ratio of means | n |
	Benzene	Toluene	Xylene		
Cambridge	3.44 ± 0.44	6.73 ± 1.48	5.46 ± 1.26	1 : 1.9 : 1.6	4
Garston	5.18 ± 0.17	10.79 ± 0.45	6.99 ± 0.28	1 : 2.1 : 1.3	4
Birmingham	3.9 ± 0.25	8.37 ± 0.37	7.67 ± 0.24	1 : 2.1 : 2	4
Sheffield HSL	3.17 ± 0.05	6.64 ± 0.1	5.37 ± 0.16	1 : 2.1 : 1.7	4
Cwmbran	4.32 ± 0.15	7.89 ± 0.14	6.48 ± 0.08	1 : 1.8 : 1.5	4
Aberdeen	1.44 ± 0.21	1.49 ± 0.36	1.48 ± 0.39	1 : 1 : 1	4
London S.E.	5.02 ± 0.07	12.20 ± 3.17	7.64 ± 0.53	1 : 2.4 : 1.5	4
Newcastle-upon-Tyne(1)	1.62 ± 0.25	3.05 ± 0.46	1.94 ± 0.21	1 : 1.9 : 1.2	4
Sutton Coldfield	3.61 ± 0.19	5.99 ± 0.34	5.08 ± 0.43	1 : 1.7 : 1.4	4
Manchester	3.53 ± 1.21	5.88 ± 0.98	4.28 ± 0.94	1 : 1.7 : 1.2	4
Inverness	0.81 ± 0.44	0.86 ± 0.17	0.88 ± 0.08	1 : 1 : 1.1	4
Northwich	2.8 ± 0.21	5.37 ± 2.47	3.16 ± 0.13	1 : 1.9 : 1.1	4†
Poole	3.0 ± 0.98	5.24 ± 1.11	4.08 ± 0.26	1 : 1.7 : 1.4	4
Preston	1.91 ± 0.18	3.55 ± 0.2	4.01 ± 2.92	1 : 1.8 : 2.1	4*
Newcastle(2)	3.74 ± 0.45	8.73 ± 0.05	7.49 ± 1.51	1 : 2.3 : 2	4*
Norwich	3.81 ± 0.53	6.85 ± 1.63	5.75 ± 2.19	1 : 1.8 : 1.5	4*
Wakefield	4.37 ± 0.12	9.19 ± 1.06	5.3 ± 0.85	1 : 2.1 : 1.2	4
Stoke-on-Trent	2.61 ± 0.36	4.25 ± 0.43	3.28 ± 0.53	1 : 1.6 : 1.3	4
Bristol	3.41 ± 0.31	5.27 ± 0.19	3.62 ± 0.16	1 : 1.5 : 1.1	4
Blackpool	2.49 ± 0.2	6.43 ± 0.17	4.66 ± 0.17	1 : 2.6 : 1.9	4
Ellesmere Port	2.72 ± 0.12	4.76 ± 0.27	3.71 ± 0.42	1 : 1.7 : 1.4	4
Northampton	2.41 ± 0.35	3.58 ± 0.21	2.96 ± 0.38	1 : 1.5 : 1.2	4
Overall mean	3.15 ± 0.33	6.05 ± 0.72	4.6 ± 0.64	2 : 4 : 3	22

*Values for $n = 3$ for toluene at Preston, Newcastle(2) and Norwich.
†Values for $n = 3$ for xylene at Northwich.

Table 11 Comparison with the UK VOCair network. Diffusive sampling results are expressed as mean $\pm$ standard deviation and Chrompack VOCair data expressed as the overall mean for all available data

| Location | Mass concentration (μg/m^3) | | | | | |
| | Benzene | | Toluene | | Xylene | |
	Diffusive	VOCair	Diffusive	VOCair	Diffusive	VOCair
Leeds	2.27 ± 0.07	3.33	5.30 ± 0.01	6.75	3.44 ± 0.07	3.99
Belfast	2.10 ± 0.36	2.94	4.44 ± 0.15	6.82	3.34 ± 0.14	3.55
Bristol	2.90 ± 0.33	2.25	6.45 ± 0.86	6.11	4.70 ± 0.26	2.70
Cardiff	3.70 ± 0.46	(9.5)	7.90 ± 0.12	8.38	5.67 ± 0.10	5.15
Eltham	2.55 ± 0.35	4.65	5.92 ± 0.69	10.36	3.55 ± 0.30	3.10
Liverpool	2.12 ± 0.16	(1.23)	4.55 ± 0.19	(0.93)	3.86 ± 0.19	(0.84)
Middlesborough	2.35 ± 0.27	2.93	4.23 ± 0.22	4.59	2.66 ± 0.14	(No Data)
Southampton	3.87 ± 0.73	1.90	8.12 ± 0.68	11.14	5.50 ± 0.20	5.49
UCL (London)	4.06 ± 0.14	6.05	9.67 ± 0.16	10.87	6.79 ± 0.27	7.79
Edinburgh	1.29 ± 0.20	1.81	3.29 ± 0.42	3.78	2.00 ± 0.27	1.89
Harwell	0.66 ± 0.03	(0.90)	1.46 ± 0.31	(0.98)	0.60 ± 0.04	(No Data)
Birmingham	1.87 ± 0.27	2.54	4.76 ± 0.31	6.75	4.46 ± 0.27	5.59

Values in parentheses are excluded from correlations in Table 12, due to low coverage during the corresponding diffusive sampling period.

Table 12 Correlation between Chrompack VOCair and diffusive sampling of benzene at each site

Compound	Line of best fit	Correlation coefficient, r^2
Benzene	$y = 1.37\,x$	0.65
Toluene	$y = 1.24\,x$	0.66
Xylene	$y = 1.02\,x$	0.56

(y = VOCair; x = diffusive)

application of incorrect diffusion uptake rates (but see study 1, where HSL values were similar to those of independent laboratories) or may indicate instrument calibration errors in one or other method.

However, it must be emphasised that the low data capture efficiency of some of the VOCair data makes comparisons less than rigorous. Data obtained by ERLAP [6] indicates closer agreement between diffusive samplers and the VOCair system. [Note that the ERLAP study, although also at Eltham, was not conducted at the same time as study 6.]

Study 7: Pilot world survey

Results for the diffusive sampling tubes are shown in Table 13. The results for the sample tubes exposed in China show significant increases in the levels of benzene, toluene and xylene. The benzene levels are increased in proportion to toluene and xylene and the BTX ratio (1 : 1.9 : 0.9) is consistent with the approximate average of 2 : 4 : 3 (Table 10). However, the results for the sample tubes exposed in Mexico City show significant increases in the levels of toluene and xylene but not for benzene.

During this survey, some of the participants also exposed diffusive samplers of their choice, and results

Table 13 Pilot world survey. Mean ambient air mass concentration of benzene, toluene and xylene by diffusive sampling for both sorbents combined. Ratio is concentration, B:T:X relative to benzene = 1

Location	Elevation (m)	Distance (m)	Mass concentration ± SD (μg/m^3) Benzene	Toluene	Xylene	Ratio of means	n
Sweden	6	1.5	1.95 ± 0.08	5.63 ± 0.77	3.49 ± 0.29	1 : 2.9 : 1.8	4
Denmark	2.5	20	0.99 ± 0.04	1.44 ± 0.03	0.80 ± 0.07	1 : 1.5 : 0.8	4*
USA	2	40	0.43 ± 0.07	0.76 ± 0.09	0.47 ± 0.09	1 : 1.8 : 1.1	4
Australia	1.75	55	1.94 ± 0.2	5.23 ± 0.69	3.87 ± 0.28	1 : 2.7 : 2	4
Hungary	1.7	250	2.65 ± 0.09	4.7 ± 0.19	3.27 ± 0.18	1 : 1.8 : 1.2	4
Germany	2.5	50	1.75 ± 0.15	5.85 ± 0.56	3.74 ± 0.33	1 : 3.3 : 2.1	4
China	#	#	12.3 ± 1.08	23.04 ± 2.32	11.64 ± 0.51	1 : 1.9 : 0.9	4
Finland	16.5	25	0.84 ± 0.16	2.16 ± 0.6	1.58 ± 0.03	1 : 2.6 : 1.9	4
Netherlands	1.5	10	1.55 ± 0.14	3.51 ± 0.27	2.28 ± 0.14	1 : 2.3 : 1.5	4
Israel	1.6	50	1.42 ± 0.17	3.24 ± 0.1	2.79 ± 0.08	1 : 2.3 : 2	4
Mexico	2	15	3.05 ± 0.51	23.43 ± 1.28	8.79 ± 0.25	1 : 7.7 : 2.9	4
Italy	2	15	1.59 ± 0.15	5.39 ± 0.11	3.36 ± 0.41	1 : 3.4 : 2.1	4
Brazil	2	6	0.42 ± 0.33	2.00 ± 0.59	1.81 ± 0.15	1 : 4.8 : 4.3	4†
France	1.5	25	1.81 ± 0.25	7.32 ± 0.31	3.87 ± 0.13	1 : 4 : 2.1	4
Ulster	3	7	2.10 ± 0.36	4.44 ± 0.15	3.34 ± 0.14	1 : 2.1 : 1.6	4
England	15	50	1.37 ± 0.25	4.24 ± 0.09	3.36 ± 0.11	1 : 3.1 : 2.5	4

*Denmark n = 3 for toluene and xylene.
†Brazil n = 3 for toluene.

Table 14 Comparison of diffusion tube data with other sampling systems operated by the participants

Location	Mean diffusive sampling mass concentration $\pm$ SD (μg/m^3)			Alternative sampling method mass concentration $\pm$ SD (μg/m^3)		
	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
Sweden	Survey data ($n = 4$)			By diffusive sampling on Tenax ($n = 8$)		
	1.95 ± 0.08	5.63 ± 0.77	3.49 ± 0.29	2.6 ± 0.87	7.2 ± 3.15	3.35 ± 1.52
Germany	Survey data ($n = 4$)			By diffusive sampling on ORSA 5 ($n = 4$)		
	1.75 ± 0.15	5.85 ± 0.56	3.74 ± 0.33	2.4 ± 0.04	6.6 ± 0.15	3.2 ± 0.04

for diffusive sampling on Tenax thermal desorption tubes (Sweden) and by Draeger ORSA-5 solvent desorption tubes (Germany) are given in Table 14. The results agreed with the world survey data within the quoted errors, except for the benzene/Germany value.

Efficiency of operational procedures

The written experimental procedure was generally found to be straightforward for the untrained volunteer to perform and there were no losses due to vandalism or theft, although one site lost tubes due to severe weather.

There are a few outliers, but these can be readily identified by checking the BTX ratios. Greater care may be needed in conditioning and securing the end caps to avoid potential contamination of the tube sorbent. However, problems with conditioning are unlikely, since no outliers are observed in the blanks.

The protective rain hoods (funnels) appeared to have performed in a satisfactory way and there were only a few minor questions concerning the instruction sheets provided. The most frequently mentioned problem concerned the difficulty of removing the closed end caps to replace them with the diffusion caps. Once fitted within the funnel access is restricted and if tightly fitted are hard to remove by hand. On assembly these were firmly tightened by hand as it was not felt that most people would necessarily have the correct sized spanners to remove very tight nuts. It is hard to see how this problem could be easily overcome as the caps must seal the tubes.

CONCLUSIONS FROM THE THREE PILOT SURVEYS

The primary intention of the pilot surveys was to demonstrate, at urban, regional and global level, the practicality of using diffusive samplers. It has been shown that such samplers are readily amenable to widespread distribution, operation by relatively unskilled personnel, and with minimal losses of equipment or data. Such data can be used for a variety of purposes, as outlined above.

ACKNOWLEDGEMENTS

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3 In this text, xylene refers to the sum of *m*-xylene and *p*-xylene unless indicated otherwise

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5   If the contraction is in volume fraction (ppm) instead of mass concentration, then the units of U become ng/ppm/min: in this text, ppm refers to a volume fraction (ϕ) of 10^{-6}.

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