

# Determination of Diffusive Uptake Rates for a Range of VOCs Using Tube Type Samplers

*Measuring Air Pollutants by Diffusive Sampling and Other Low Cost Monitoring Techniques, Krakow, Poland, September 2009*

## **Determination of Diffusive Uptake Rates for a range of VOCs using Tube Type Samplers**

**Veronica Brown, BRE Associate**

**Co-authors:**

**Derrick Crump, IEH, Cranfield**

**John Rowley and Richard Squire, BRE**

## **Introduction 1**

- Application of diffusive samplers for VOCs still limited by lack of data on diffusive uptake rates. Most rates determined for 8 hours and for single compounds
- Uptake rates using PE type tubes containing Tenax previously investigated at BRE for 6 VOCs for 4 weeks and for 9 VOCs for 2 weeks.
- Samplers applied to several surveys of indoor air quality

## **Introduction 2**

- (1) ALSPAC – 174 homes in Avon area
- (2) IAQ survey of England, >800 homes
- (3) Benzene in 54 homes in Scotland
- (4) IAQ and ventilation in 37 new homes



## **Aims of present work**

Present work aimed to provide some more data applicable to indoor air monitoring

- 6 compounds
- 3 sorbents
- 3 exposure periods
- With and without diffusive end caps

## **Experiment 1**

- 1m<sup>3</sup> environmental chamber, 23±0.5°C, 50±3% RH, 1 ac h<sup>-1</sup>, 0.1 m s<sup>-1</sup>
- Toluene source, 16 mg m<sup>-3</sup> (4.3 ppm)
- Diffusive samplers containing Tenax, in duplicate at 8 locations, no diffusive caps, 24 hours
- Pumped sampling in duplicate at chamber outlet for 5-10 min, 10 occasions

**1m<sup>3</sup> environmental chamber being used for emissions from a material**



# Determination of Diffusive Uptake Rates for a Range of VOCs Using Tube Type Samplers

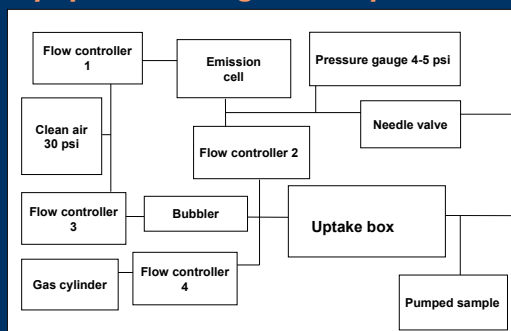
## Experiment 2

- Same equipment and conditions as Experiment 1
- Toluene source, same concentration
- 5 Tenax tubes with caps and 5 without at 1 location
- Duplicate tubes with caps at variety of locations
- Pumped sampling in duplicate at chamber outlet for 30 mins on 10 occasions over 24 hours

## Equipment for Experiment 3



## Equipment Design for Experiment 3



## Experiment 3

- Cylinders of benzene, toluene, butyl acetate,  $\alpha$ -pinene, n-decane and 2-ethylhexan-1-ol in N<sub>2</sub>
- 50-150  $\mu\text{g m}^{-3}$ , 20 $\pm$ 0.2°C, 50 $\pm$ 3%RH
- Diffusive tubes: 14 Tenax, 14 Carbograph 1TD, 14 Unicarb + diffusive end caps
- Periodic pumped sampling at 50 ml min<sup>-1</sup> for 100 min
- Exposure periods: 24 hours, 7 days and 14 days, 7 days no caps

## Analysis of VOC tubes

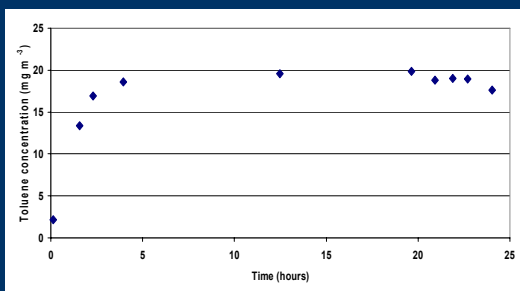


## Analysis details

- Pumped and diffusive tubes analysed using ATD400/ Autosystem GC, FID quantification
- Tenax 280°C for 5 min (Carbograph 300°C, Unicarb 330°C)
- He pressure 20 psi, desorb flow 25 ml min<sup>-1</sup>, inlet split 90 ml min<sup>-1</sup> (Experiments 1 and 2 only), outlet split 10 ml min<sup>-1</sup>, cold trap low -30°C, cold trap high 300°C for 1 min, valve and line temp 200°C
- 50m x 0.22mm id BP10 column, 0.25 $\mu\text{m}$ , 40°C for 1 min, 2°C min<sup>-1</sup> to 75°C then 5°C min<sup>-1</sup> to 250°C
- Calibration by liquid spiking of methanol solutions into conditioned tubes followed by purging.

# Determination of Diffusive Uptake Rates for a Range of VOCs Using Tube Type Samplers

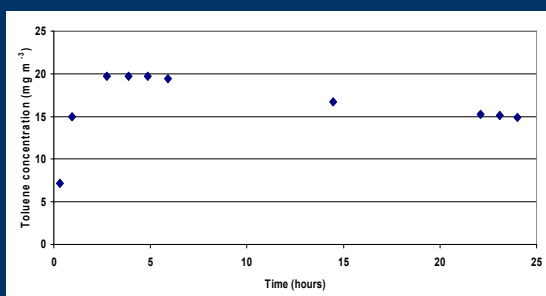
## Experiment 1 – Toluene concentration in chamber



## Experiment 1 – Results for toluene

| Position in chamber     | Diffusive uptake rate |  |
|-------------------------|-----------------------|--|
|                         | ml min <sup>-1</sup>  | ng ppm <sup>-1</sup> min <sup>-1</sup> |
| RLL (mean of 2)         | 0.64                  | 2.44                                   |
| RLH (mean of 2)         | 0.63                  | 2.42                                   |
| RRL (mean of 2)         | 0.63                  | 2.43                                   |
| FLL (mean of 2)         | 0.58                  | 2.23                                   |
| FLH (mean of 2)         | 0.63                  | 2.42                                   |
| FRL (mean of 2)         | 0.56                  | 2.16                                   |
| FRH (mean of 2)         | 0.63                  | 2.40                                   |
| All (mean of 14) (RSD%) | 0.62 (9.6%)           | 2.3 (9.6%)                             |

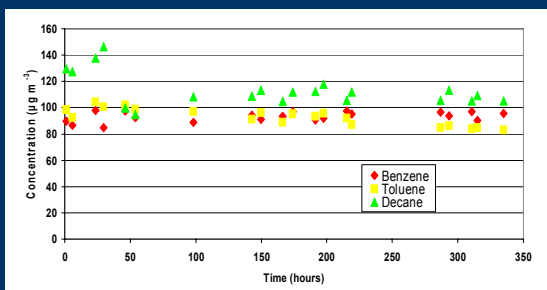
## Experiment 2 – Toluene concentration in chamber



## Experiment 2 – Results for toluene

| Position in chamber                 | Diffusive uptake rate (%RSD) |  |
|-------------------------------------|------------------------------|--|
|                                     | ml min <sup>-1</sup>         | ng ppm <sup>-1</sup> min <sup>-1</sup> |
| RLL (no diffusive cap) (Mean of 5)  | 0.58 (7.4%)                  | 2.21 (7.4%)                            |
| RLL (Mean of 5)                     | 0.47 (3.9%)                  | 1.80 (3.9%)                            |
| RLH (Mean of 2)                     | 0.48                         | 1.83                                   |
| RRL (Mean of 2)                     | 0.48                         | 1.85                                   |
| RRH (Mean of 2)                     | 0.45                         | 1.71                                   |
| FLL (Mean of 2)                     | 0.48                         | 1.83                                   |
| FLH (Mean of 2)                     | 0.48                         | 1.83                                   |
| FRL (Mean of 2)                     | 0.45                         | 1.72                                   |
| FRH (Mean of 2)                     | 0.49                         | 1.89                                   |
| All (Mean of 19 with diffusive cap) | 0.47 (5.3%)                  | 1.81 (5.3%)                            |

## Experiment 3 – Benzene, toluene and n-decane concentrations

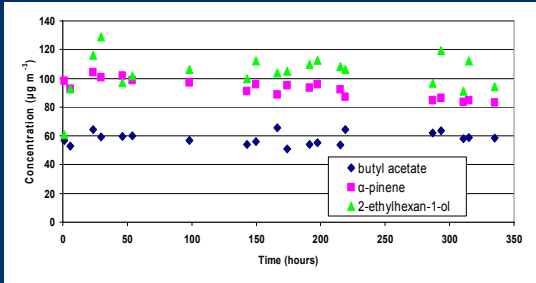


## Experiment 3 - Concentrations

| Period     | Statistic | Mean Concentration (µg m <sup>-3</sup> ) |         |          |
|------------|-----------|--|---------|----------|
|            |           | Benzene                                  | Toluene | n-Decane |
| 24 hours   | Mean      | 90.0                                     | 96.9    | 130.6    |
|            | %RSD      | 6.2                                      | 6.2     | 4.6      |
|            | n         | 4  | 4       | 4        |
| 1st 7 days | Mean      | 90.9                                     | 96.5    | 117.2    |
|            | %RSD      | 5.2                                      | 5.0     | 13.9     |
|            | n         | 12                                       | 12      | 12       |
| 2nd 7 days | Mean      | 94.8                                     | 89.2    | 110.1    |
|            | %RSD      | 2.9                                      | 5.7     | 4.4      |
|            | n         | 11                                       | 11      | 11       |
| 14 days    | Mean      | 92.8                                     | 93.0    | 113.8    |
|            | %RSD      | 4.7                                      | 6.6     | 11.0     |
|            | n         | 23                                       | 23      | 23       |

# Determination of Diffusive Uptake Rates for a Range of VOCs Using Tube Type Samplers

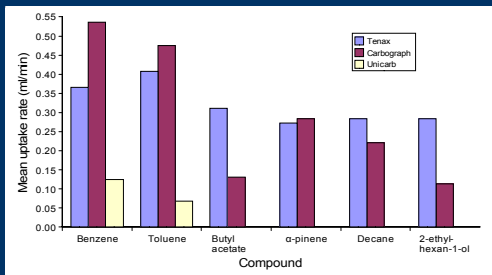
## Experiment 3 – Butyl acetate, $\alpha$ -pinene and 2-ethylhexan-1-ol concentrations



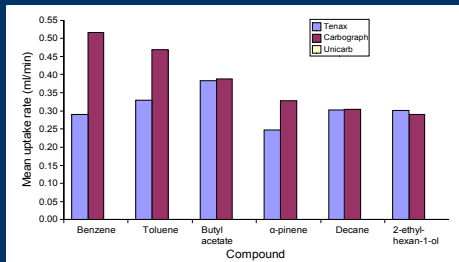
## Experiment 3 - Concentrations

| Period                 | Statistic | Mean Concentration ( $\mu\text{g m}^{-3}$ ) |                  |                   |
|------------------------|-----------|---|------------------|-------------------|
|                        |           | Butyl acetate                               | $\alpha$ -pinene | 2-ethylhexan-1-ol |
| 24 hours               | Mean      | 56.7  | 141.5            | 90.5              |
|                        | %RSD      | 10.3  | 6.1              | 26.6              |
|                        | n         | 4   | 4                | 4                 |
| 1 <sup>st</sup> 7 days | Mean      | 57.9  | 131.1            | 101.5             |
|                        | %RSD      | 7.4   | 7.8              | 16.7              |
|                        | n         | 12  | 12               | 12                |
| 2 <sup>nd</sup> 7 days | Mean      | 57.4  | 126.7            | 105.5             |
|                        | %RSD      | 9.3   | 5.3              | 9.5               |
|                        | n         | 11  | 11               | 11                |
| 14 days                | Mean      | 57.6  | 129.0            | 103.4             |
|                        | %RSD      | 8.2   | 6.8              | 13.5              |
|                        | n         | 23  | 23               | 23                |

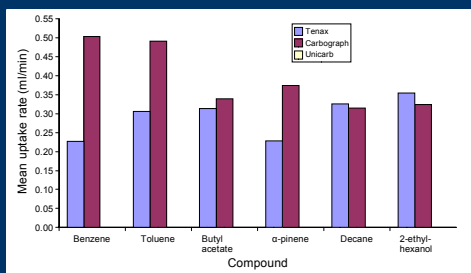
## Experiment 3 – 24 hour uptake rates



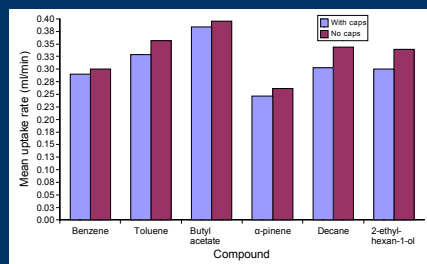
## Experiment 3 – 7 day uptake rates



## Experiment 3 – 14 day uptake rates



## Experiment 3 – Tenax 7 days, cap vs no cap



## Determination of Diffusive Uptake Rates for a Range of VOCs Using Tube Type Samplers

### Summary of benzene, toluene and n-decane uptake rate measurements

| Sorbent    | Time     | Diffusive uptake rate  |             |             |
|------------|----------|--|-------------|-------------|
|            |          | ml min <sup>-1</sup> (ng ppm <sup>-1</sup> min <sup>-1</sup> ) |             |             |
|            |          | Benzene  | Toluene     | n-Decane    |
| Tenax      | 24 hours | 0.37 (1.19)  | 0.41 (1.56) | 0.28 (1.68) |
|            | 7 days   | 0.29 (0.94)  | 0.33 (1.26) | 0.30 (1.79) |
|            | 14 days  | 0.23 (0.74)  | 0.31 (1.17) | 0.33 (1.93) |
| Carbograph | 24 hours | 0.54 (1.74)  | 0.48 (1.82) | 0.22 (1.31) |
|            | 7 days   | 0.52 (1.68)  | 0.47 (1.79) | 0.30 (1.80) |
|            | 14 days  | 0.50 (1.63)  | 0.49 (1.88) | 0.32 (1.86) |

### Summary of butyl acetate, α-pinene and 2-ethylhexan-1-ol uptake rate measurements

| Sorbent    | Time     | Diffusive uptake rate  |             |                   |
|------------|----------|--|-------------|-------------------|
|            |          | ml min <sup>-1</sup> (ng ppm <sup>-1</sup> min <sup>-1</sup> ) |             |                   |
|            |          | Butyl acetate  | α-pinene    | 2-ethylhexan-1-ol |
| Tenax      | 24 hours | 0.31 (1.50)  | 0.27 (1.54) | 0.28 (1.54)       |
|            | 7 days   | 0.38 (1.85)  | 0.25 (1.40) | 0.30 (1.63)       |
|            | 14 days  | 0.33 (1.51)  | 0.23 (1.29) | 0.35 (1.92)       |
| Carbograph | 24 hours | 0.13 (0.63)  | 0.28 (1.61) | 0.11 (0.61)       |
|            | 7 days   | 0.39 (1.87)  | 0.33 (1.86) | 0.29 (1.57)       |
|            | 14 days  | 0.34 (1.64)  | 0.37 (2.12) | 0.32 (1.75)       |

### Summary of toluene uptake rate measurements on Tenax

| Study                   | Time     | Concentration<br>(µg m <sup>-3</sup> ) | Diffusive uptake rate<br>ml min <sup>-1</sup> (ng ppm <sup>-1</sup> min <sup>-1</sup> ) |             |
|-------------------------|----------|--|---|-------------|
|                         |          |  | With diffusive cap  | Without cap |
| Reported in ISO 16017-2 | 8 hours  | Workplace                              | 0.44 (1.67)   |             |
|                         | 2 weeks  | Environmental                          | 0.32 (1.22)   |             |
|                         | 4 weeks  |  | 0.27 (1.03)   |             |
| Previous BRE work       | 14 days  | 390                                    |   | 0.38 (1.43) |
|                         | 29 days  | 515                                    |   | 0.32 (1.13) |
| Experiment 1            | 24 hours | 16,400                                 |   | 0.62 (2.36) |
| Experiment 2            | 24 hours | 16,300                                 | 0.47 (1.81)   | 0.58 (2.21) |
| Experiment 3            | 24 hours | 97                                     | 0.41 (1.56)   |             |
|                         | 7 days   | 97                                     | 0.33 (1.26)   |             |
|                         | 7 days   | 89                                     |   | 0.36 (1.36) |
|                         | 14 days  | 93                                     | 0.31 (1.17)   |             |

### Summary of benzene uptake rate measurements on Tenax

| Study                   | Time     | Concentration<br>(µg m <sup>-3</sup> ) | Diffusive uptake rate<br>ml min <sup>-1</sup> (ng ppm <sup>-1</sup> min <sup>-1</sup> ) |             |
|-------------------------|----------|--|---|-------------|
|                         |          |  | With diffusive cap  | Without cap |
| Reported in ISO 16017-2 | 8 hours  | Workplace                              | 0.41 (1.30)   |             |
|                         | 1 week   | Ambient/<br>indoor                     | 0.46 (1.45)   |             |
|                         | 2 weeks  |  | 0.32 (1.03)   |             |
|                         | 4 weeks  |  | 0.22 (0.70)   |             |
| Previous BRE work       | 14 days  | 740                                    |   | 0.27 (0.88) |
|                         | 29 days  | 841                                    |   | 0.20 (0.65) |
| Experiment 3            | 24 hours | 90                                     | 0.37 (1.19)   |             |
|                         | 7 days   | 91                                     | 0.29 (0.94)   |             |
|                         | 7 days   | 95                                     |   | 0.30 (0.97) |
|                         | 14 days  | 93                                     | 0.23 (0.74)   |             |

### Summary of uptake rate measurements for benzene and toluene on Carbograph

| Study                   | Time     | Diffusive uptake rate  |             |
|-------------------------|----------|--|-------------|
|                         |          | ml min <sup>-1</sup> (ng ppm <sup>-1</sup> min <sup>-1</sup> ) |             |
|                         |          | Benzene  | Toluene     |
| Reported in ISO 16017-2 | 24 hours | 0.67 (2.14)  | 0.57 (2.16) |
|                         | 7 days   | 0.63 (2.02)  | 0.56 (2.13) |
|                         | 14 days  | 0.58 (1.85)  | 0.55 (2.07) |
| Present work            | 24 hours | 0.54 (1.74)  | 0.48 (1.82) |
|                         | 7 days   | 0.52 (1.68)  | 0.47 (1.79) |
|                         | 14 days  | 0.50 (1.63)  | 0.49 (1.88) |

### Conclusions

- Comparison of chambers – equilibration time
- Effect of diffusive caps
- Comparison of sorbents
- Comparison with other published rates
- Future work:  
different concentrations, compound mixtures, humidities, back diffusion, sampler types.