

## 7. GLOSSARY

**Active sampling** - Pollutants samples are collected by drawing air into the collector such as a filter or chemical solution for a known period of time.

**BTEX gases** - benzene, toluene, ethylbenzene and xylene

**Cabin Monitoring** – air sampling within the vehicle

**CSIRO** – Commonwealth Scientific and Industrial Research Organisation

**EPA** – NSW Environment Protection Authority

**Exposure** – The dose of pollutant which a person could receive during time spent in a given environment

**External Monitoring** – air sampling outside the vehicle

**Gravimetric** – denoting a method of analysing compound bodies by finding the weight of their elements

**IARC** – International Agency for Research on Cancer

**µg/m<sup>3</sup>** - micrograms per cubic metre – a measure of concentration

**Mean** – The sum of all the measurements in a data set divided by the number of measurements in the data set

**NEPC** – National Environment Protection Council, Australia

**Passive sampling** - A sample integrated over a defined exposure time (typically a week to a month) is collected by molecular diffusion to a pollutant-specific absorbent material.

**Pearson Correlation Co-efficient** –A measure of linear association between two variables. Values of the correlation coefficient range from -1 to 1. The sign of the coefficient indicates the direction of the relationship, and its absolute value indicates the strength, with larger absolute values indicating stronger relationships.

**ppbv** – parts per billion – a measure of concentration

**ppm** – parts per million – a measure of concentration

**Standard Deviation (SD)** –A measure of dispersion around the mean. In a normal distribution, 68% of cases fall within one SD of the mean and 95% of cases fall within 2 SD.

**RTA** – New South Wales Roads and Traffic Authority

**US EPA** – United States Environment Protection Agency

**WHO** – World Health Organization

## APPENDIX A: SUMMARY OF AIR QUALITY STANDARDS

Pollutant	Standard	Time Average	Country	Institution
NO <sub>2</sub>	120ppbv	1 hr	Australia	NEPC [4]
	98ppbv	1 hr	International	WHO [3]
	250ppbv	1 hr	US (California)	SCAQMD [37]
	150 ppb	1 hr	UK	UK [38]
CO	9 ppm	8 hr	Australia	NEPC [4]
	87 ppm	15 min	International guidelines	WHO [3]
	50 ppm	30 min		
	25 ppm	1 hr		
	10 ppm	8 hr		
	35 ppm	1 hr	US	USEPA [39]
	9 ppm	8 hr	US (California)	SCAQMD [37]
20 ppm	1 hr			
	10 ppm	8 hr	UK	UK [38]
PM <sub>10</sub>	50 µg/m <sup>3</sup>	24 hr	Australia	NEPC [4]
	150 µg/m <sup>3</sup>	24 hr	US	USEPA [39]
	50 µg/m <sup>3</sup>	24 hr	US (California)	SCAQMD [37]
	50 µg/m <sup>3</sup>	24 hr	UK	UK [38]
PM <sub>2.5</sub>	25 µg/m <sup>3</sup>	24 hour	Australia	NEPC [6] Advisory reporting standard for non-peak sites
	65 µg/m <sup>3</sup>	24 hr	US	USEPA [40]
	30 µg/m <sup>3</sup>	24 hr	Canada	NEPC [6]
	25 µg/m <sup>3</sup>	24 hr	New Zealand	proposed interim guideline [6]
Benzene	10ppm (3.2 mg/m <sup>3</sup> )	15 min limit	US	NIOSH STEL--National Institute of Occupational Safety and Health's short term exposure limit [41]
	5 ppbv (16.25 µg/m <sup>3</sup> )	long term - annual	UK	UK [38]

## APPENDIX B: DAILY RECORD MONITORING SHEET

### Daily Record Sheet

Date: _____
Ventilation Type:      Windows up & air con off with external air intake
Windows up & air con on & recirculating
Windows down air con off
<b><i>Passive Sampling ID Numbers</i></b>
CABIN
Nitrogen Dioxide _____ BTEX _____
PM2.5 _____
EXTERNAL
Nitrogen Dioxide _____

### TRIP DIRECTION: MORNING EAST

Research Officers:    TC            SC            SH            Other \_\_\_\_\_

Criteria	Number of trips	Total Duration
CO (in)		
PM 2.5		
CO (out)		

Incidents:

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### TRIP DIRECTION: AFTERNOON WEST

Research Officers: TC DS SH Other \_\_\_\_\_

	Number of trips	Total Duration
CO (cabin)		
PM 2.5		
CO (external)		

Incidents:

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### TRIP DIRECTION: AFTERNOON EAST

Research Officers: TC DS SH Other \_\_\_\_\_

Criteria	Total Number of trips	Total Duration
CO (cabin)		
PM 2.5		
CO (external)		
BTEX, PM2.5, NO <sub>2</sub>		

Incidents:

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## APPENDIX C: CSIRO ANALYTICAL METHODS

According to Ferm (1991) the ambient concentration of the gas of interest,  $C_x$ , may be calculated from a knowledge of the amount trapped on the sorbant filter located at the end of the sampler tube,  $X$ , the mean absolute temperature,  $T$ , during sampling, the diffusion coefficient of the gas of interest,  $D_x$ , and a number of geometric factors:

$$C_x = \frac{X}{TD_x} \left( \frac{L_R}{A_R} + \frac{L_F}{A_F} + \frac{L_N}{A_N} + \frac{L_{LBL}}{A_R} \right), \quad (1)$$

where:

$L_R$  is the length of the stagnant tube,

$A_R$  is the cross-sectional area of the tube,

$L_F$  the thickness of the membrane filter,

$A_F$  the total area of pores in the membrane (calculated from the exposed area,  $A_R$  and the filter porosity),

$L_N$  is the thickness of the stainless steel screen,

$A_N$  open area of the stainless steel screen,

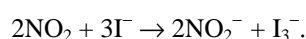
$L_{LBL}$  is the thickness of the laminar boundary layer that exists in contact with the external face of the sampler.

Ferm (1991) measured the laminar boundary layer thickness under a range of ambient atmospheric conditions and suggested a mean value of order  $1.5 \pm 0.6$  mm for  $L_{LBL}$ .

The first three terms in parenthesis represent the resistances due to diffusion along the stagnant sampler tube, diffusion through the membrane, and diffusion through the stainless steel screen. All three are geometrically fixed. The final term represents diffusion through the laminar boundary layer, the thickness of which will vary with atmospheric turbulence.

The membrane filters employed on the samplers were 25 mm MFS, PTFE Cat. No. J100A025A, while the paper filters employed as the trapping medium were 24 mm Whatman paper filters, Cat. No. 1440024. Blanks on the paper filters were virtually eliminated by a clean-up procedure in which the filters were washed in high purity (HPLC-grade) water, twice in AR grade methanol, and dried in a stream of high purity nitrogen. The coating solution for the  $\text{NO}_2$  sampler was 0.44g NaOH plus 3.95g NaI made up to 50 ml with AR grade methanol. In both cases 50  $\mu\text{l}$  of coating solution was added by pipette to a paper filter that was then placed directly into a sampler body under clean laboratory conditions. Samplers were sent to and from the field in sealed plastic bottles as recommended by Ferm (1991).

The reaction to trap  $\text{NO}_2(\text{g})$  on the filter can be expressed as follows :



After exposure the sample filters were extracted in 5 ml HPLC-grade water in sealed plastic bags. The  $\text{NO}_2$  filter extracts were analysed colorimetrically at 540 nm for nitrite, after mixing with a diazotizing reagent (Ferm, 1991).

### More Detailed Experimental Section

Upon receipt of the sealed sampler, the paper filter is removed and sealed in a small clean polythene bag and stored at 4°C for later analysis. It is extracted in 5  $\text{cm}^3$  of Milli-Q water.

A NaI solution of 0.79 g NaI  $\text{l}^{-1}$  of Milli-Q water is made up and used for dilution of standards so that sample and standards have the same NaI concentration :

Table 1. Standard nitrite concentrations.

100 $\mu\text{M}$	100 $\mu\text{l}$ of 0.1 M $\text{NaNO}_2$ diluted with NaI solution to 100 $\text{cm}^3$ .	(=100 $\text{cm}^3$ )
75 $\mu\text{M}$	1.5 $\text{cm}^3$ of 100 $\mu\text{M}$ std + 0.5 $\text{cm}^3$ of NaI solution.	(= 2 $\text{cm}^3$ )
50 $\mu\text{M}$	1.0 $\text{cm}^3$ of 100 $\mu\text{M}$ std + 1.0 $\text{cm}^3$ of NaI solution.	(= 2 $\text{cm}^3$ )
20 $\mu\text{M}$	400 $\mu\text{l}$ of 100 $\mu\text{M}$ std + 1.6 $\text{cm}^3$ of NaI solution.	(= 2 $\text{cm}^3$ )
10 $\mu\text{M}$	200 $\mu\text{l}$ of 100 $\mu\text{M}$ std + 1.8 $\text{cm}^3$ of NaI solution.	(= 2 $\text{cm}^3$ )
5 $\mu\text{M}$	100 $\mu\text{l}$ of 100 $\mu\text{M}$ std + 1.9 $\text{cm}^3$ of NaI solution.	(= 2 $\text{cm}^3$ )
2 $\mu\text{M}$	40 $\mu\text{l}$ of 100 $\mu\text{M}$ std + 1.96 $\text{cm}^3$ of NaI solution.	(= 2 $\text{cm}^3$ )

### Reagent solution

The following three chemicals should be weighed into a 100  $\text{cm}^3$  volumetric flask. The chemicals are dissolved by the addition of Milli-Q water to make a solution of 100  $\text{cm}^3$ . The solution must be freshly made for each analysis period.

0.8 g sulfanilamide

0.02 g N-1-Naphthylethylenediamine dihydrochloride (NEDA)

0.8 ml  $\text{H}_3\text{PO}_4$

### Measurement

A 2  $\text{cm}^3$  aliquot of each standard and of each sample are placed into separate 30  $\text{cm}^3$  Nalgene plastic bottles to which an equal amount (2  $\text{cm}^3$ ) of the reagent is added. The solution turns pink. The spectrophotometer is adjusted to a wavelength of  $\lambda = 540 \text{ nm}$  with the visible lamp turned on and in absorption mode. The samples are left for a 15 minute period so they can fully react, then the absorbances of the samples and standards are measured with the spectrophotometer.

### Calculation of ambient $\text{NO}_2$ concentration

A straight line is fitted to the standards using a least squares regression program. The line is then used to calculate the  $\text{NO}_2^-$  concentration in the sample solutions. The concentration of  $\text{NO}_2(\text{g})$  can be calculated in nanomoles  $\text{m}^{-3}$  in the same way as for the acid gases, using  $\text{EV} = 5 \text{ cm}^3$  and the appropriate diffusion coefficient:

$$\text{NO}_2(\text{g}) = \frac{L \times \text{EV} \times [\text{SO}_4^{2-}]}{T \times \text{DC}}$$

Where :

L = total air resistance = 41.2  $\text{m}^{-1}$

EV = extraction volume ( $\text{cm}^3$ )

$[\text{SO}_4^{2-}]$  = sulfate concentration ( $\mu\text{moles l}^{-1}$ )

T = sampling time (seconds)

DC = diffusion coefficient ( $1.54 \times 10^{-5} \text{ m}^2 \text{ sec}^{-1}$  for  $\text{NO}_2$ )

This figure for  $\text{NO}_2(\text{g})$  can then be converted to ppbv using :

$$p = \frac{n \times R \times T}{V}$$

Where :

n = number of moles (in a  $\text{m}^3$ )

R = gas constant = 0.08206 l atm  $\text{mol}^{-1} \text{ K}^{-1}$

T = temperature during sampling ( $^{\circ}\text{K}$ )

V = air volume (=1000 l)

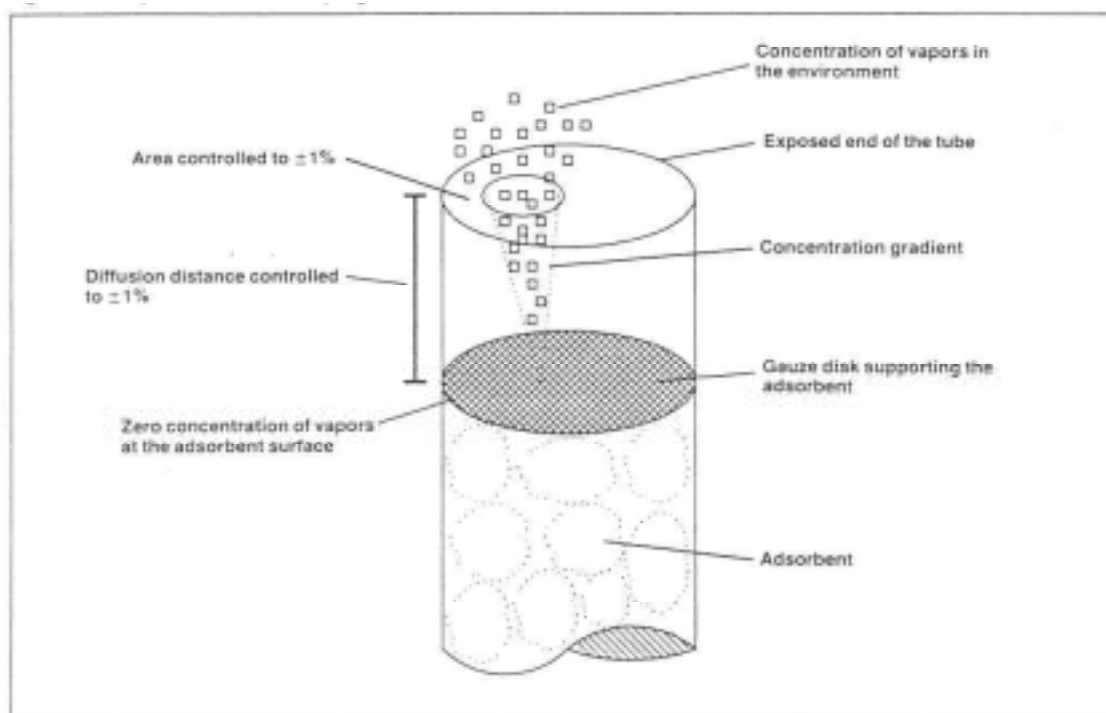
## BTEX Sampling

### Principles of passive gas sampling

Diffusive monitoring is a technique that uses the physical process of gas diffusion to collect gases of interest on a solid adsorbent. Such a technique has several important advantages. Some of these are that the sampler is very small, light, uses no power and generates no noise. This makes them eminently suitable for use in personal sampling where high frequency sampling is not required.

To be effective, diffusive monitors must be capable of maintaining the following conditions during the sampling process:

- ambient concentration of the components of interest at the surface of the monitor
- zero concentration of the components at the surface of the adsorbent material
- a linear concentration gradient between the two (see Figure 1 below).



**Figure 1.** Principles of diffusive sampling

Under these conditions, Fick's 1<sup>st</sup> law of Diffusion applies and components will migrate to the adsorbent at a rate, which is dependent on:

- The path-length between the top surface of the monitor and the adsorbent bed
- The cross-sectional area of the sampler
- The time of exposure
- The diffusion coefficient of the analyte through air

- The ambient concentration of the components

This can be expressed by the formula:

$$U_m = \frac{60 \times D_1 \times A}{Z} \quad (1)$$

Where:

$U_m$  = sampling rate ( $\text{cm}^3 \text{min}^{-1}$ )

$D_1$  = diffusion coefficient through air of the vapour under study ( $\text{cm}^2 \text{s}^{-1}$ ).

$A$  = cross-sectional area of the sampling tube ( $\text{cm}^2$ ).

$Z$  = path-length of the air gap (cm).

In this case, for the ATD 400 Perkin-Elmer tube,  $A = 0.2 \text{ cm}^2$  and  $Z = 1.5 \text{ cm}$ .

If the gas mixing ratio is required in ppmv a published uptake rate can be used or else it can be calculated from the following expression:

$$U_p = \frac{60 \times D_1 \times A \times MW_{gas}}{V_m \times Z} \quad (2)$$

where :

$U_p$  = Uptake rate ( $\text{ng ppm}^{-1} \cdot \text{min}^{-1}$ ).

$MW_{gas}$  = molecular weight of gas of interest (g).

$V_m$  = molar volume (L).

The mixing ratio (C) of a compound in ppbv can then be calculated from:

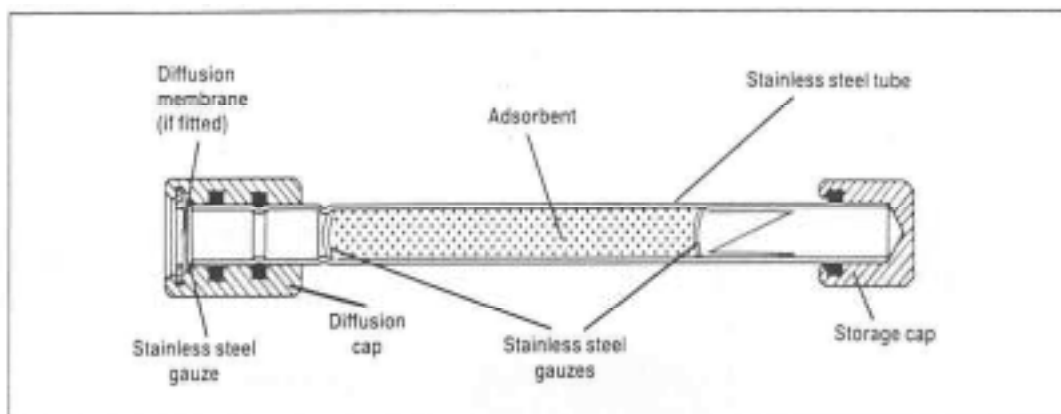
$$C = \frac{W_t \times 1000}{U_p \times T} \quad (3)$$

where :

$W_t$  is the mass of sample adsorbed on the Chromosorb 106 in the tube (ng)

### BTEX sampler design

The aim of the sampling procedure is to adsorb BTEX (benzene, toluene, ethyl benzene, o-xylene, m-xylene and p-xylene) gases onto the absorbent bed during the period of exposure. The adsorbent is packed into a stainless steel tube 6.35 mm diameter and 90 mm in length. For this study the BTEX samplers will be packed with Chromosorb 106. Figure 2 shows a diagram of a BTEX sampler fitted with a diffusion cap. The BTEX samplers will be pre-cleaned before each sampling period by heating under a stream of ultra high purity helium and then sealed with Swagelok caps using PTFE ferrules. The cap should be tightened to ensure that the BTEX sampler is sealed to at least 3 psi; this is sufficient to allow for the lower pressure the BTEX samplers will experience during transportation by air. The BTEX samplers will be transported by airfreight, tightly sealed in a metal container. Charcoal bags will be added to absorb any BTEX gases in the unlikely event they penetrate the metal container.



**Figure 2.** Diagram of a BTEX sampler

BTEX Analysis

Adsorbed BTEX species are desorbed by heating the tubes under a stream of ultra high purity helium gas in a Perkin Elmer ATD 400 thermal desorber (automated thermal desorber). The desorbed species are transferred through a heated line to a Perkin Elmer AutoSystem XL gas chromatograph where they are separated by an SGE BP 20 column and detected with a flame ionization detector. Table 1 gives details of the column and temperature program used for the analysis.

**Table 1.** Gas Chromatography conditions

Item	Description
Column	25 m x 0.32mm I.D. fused silica capillary column with 1.0 $\mu\text{m}$ BP20 bonded phase
Injector	ATD 400 (mode 2)
Carrier gas	Helium 50psig
Oven Temperature	60°C for 6 minutes programmed at 20°C $\text{min}^{-1}$ to 220°C
Detector	Flame Ionization Detector

A test calibration has been carried out using the Perkin Elmer system. Peak areas were determined by integration using a Turbochrom workstation and converted to mass after injection of standards. The standard is a mixture of benzene, toluene, ethyl benzene, m-xylene and o-xylene with mixing ratios of 10.1 ppm, 10.1 ppm, 10.1 ppm, 10.1 ppm and 10.0 ppm respectively and an accuracy of  $\pm 2\%$  (Scott Specialty Gases, San Bernadino, CA, USA). Since the chemical properties of p-xylene are similar to m-xylene the m-xylene calibration was applied to p-xylene.

The calibration was carried out by loop injection onto the ATD during each analytical run. For all calibrations the loop was flushed for 1 minute with the BTEX standard at a flow rate of between 50 and 60 cm<sup>3</sup> min<sup>-1</sup>. The loop volume was 812 µl and it was heated to 80°C (353K). The mass of each species injected during each calibration is given in Table 2 and was calculated as follows:

$$mass = \frac{V_{loop} \times C_{gas} \times MW_{gas}}{R \times T} \quad (4)$$

Where :

R = gas constant (0.082054 l atm mol<sup>-1</sup> K<sup>-1</sup>)

T = temperature (353K)

V<sub>loop</sub> = loop volume (0.000812 l)

MW<sub>gas</sub> = molecular weight of gas of interest (g).

C<sub>gas</sub> = gas concentration (ppmv)

**Table 2.** Mass of gases for one ATD loop injection

Gas	Mass injected (ng)
Benzene	22.15
Toluene	26.12
Ethyl-benzene	30.12
m-xylene and p-xylene	30.12
o-xylene	29.82

Therefore, dividing this mass by the peak area, gives the mass per unit area ratio and multiplication of this ratio by the peak area of each species gives the mass of each species collected by the passive sampler.

The ATD 400 enables the analysis of up to 50 samples and entire procedure can be automated from desorption of the sample tube to the final printed report. The system utilizes a unique electrically-cooled, packed cold trap minimizing the risk of blockages by ice-plug formation and allowing compatibility with samples containing significant amounts of water.

There are two modes of operation to be used in the pilot trial:

- Mode 1 is tube conditioning which is employed to purge the tubes before they are used.

- Mode 2 is a two stage desorption that allows the tubes to be analysed; Table 3 shows the ATD 400 settings employed during the mode 2 desorption stage.

**Table 3.** ATD 400 Conditions for mode 2.

Procedure	Setting
Mode	2
Primary desorption	220°C
Primary desorption time	1 min
Transfer line temperature	200°C
Cold trap low temp	-30°C
Cold trap high temp	200°C
Inlet split flow	No
Primary desorption Time	Depends on experiment
Transfer line temperature	Depends on experiment
Valve temperature	175°C
Cold trap hold	1 min
Trap fast	Yes

**Analysis of the BTEX samplers was performed at CSIRO Atmospheric Research, Aspendale, Victoria.**

## APPENDIX D: CALCULATIONS OF EXPOSURE INCREMENT FOR NON-THRESHOLD POLLUTANTS

### PM<sub>2.5</sub>

Assuming:

Ambient concentration:	17µg/m <sup>3</sup>
Usual commuting cabin concentration:	25µg/m <sup>3</sup>
Cabin concentration in M5 tunnel:	89µg/m <sup>3</sup>
Commute duration <sup>#</sup> :	79mins/day
Tunnel duration:	13mins/day
Cigarettes/day	0
Exposure to ETS:	0
Home heating:	electric

Then:

Daily PM<sub>2.5</sub> exposure

$$= (\text{time}_{\text{ambient}} * \text{ambient} + \text{time}_{(\text{commuting-tunnel})} * \text{commute} + \text{time}_{\text{tunnel}} * \text{tunnel}) / 24$$

$$= (1361\text{mins} * 17\mu\text{g}/\text{m}^3 + 66\text{mins} * 25\mu\text{g}/\text{m}^3 + 13\text{mins} * 89\mu\text{g}/\text{m}^3) / 24$$

$$= 18\mu\text{g}/\text{m}^3$$

By contrast, for a similar commuter not using the tunnel, daily PM<sub>2.5</sub> exposure is estimated to be 17.4µg/m<sup>3</sup>.

### Benzene

Assuming:

Ambient concentration <sup>2</sup> :	1.4ppbv
Usual commuting cabin concentration:	12.1ppbv
Cabin concentration in M5 tunnel (windows down):	19ppbv
Commute duration:	79mins/day
Tunnel duration:	13mins/day
Cigarettes/day	0
Exposure to ETS:	0
Home heating:	electric

Then:

Daily benzene exposure

$$= (\text{time}_{\text{ambient}} * \text{ambient} + \text{time}_{(\text{commuting-tunnel})} * \text{commute} + \text{time}_{\text{tunnel}} * \text{tunnel}) / 24$$

$$= (1361\text{mins} * 1.4\text{ppbv} + 66\text{mins} * 12.1\text{ppbv} + 13\text{mins} * 19\text{ppbv}) / 24$$

= 2.05ppbv

The exposure for a similar commuter not using the tunnel, is not substantially different at 1.98ppbv.

Following the methodology of Wadge and Salisbury (National Environmental Health Forum Monograph, Benzene, 1997), the impact on lifetime benzene exposure can be calculated as follows:

Assuming a respiration rate of  $0.83\text{m}^3/\text{hour}$ , and a conversion of 1ppbv benzene to  $3.24\mu\text{g}/\text{m}^3$ , and using a scenario of living in a suburb and commuting daily by car to Sydney CBD for 79 minutes round trip:

Intake during commuting:

Using tunnel:

$(13\text{min} * 61.6\mu\text{g}/\text{m}^3 + 66\text{min} * 39.2\mu\text{g}/\text{m}^3) * 79\text{min} * 0.83\text{m}^3/60\text{min} = 46.9\mu\text{g}$

Alternate commute

$(39.2\mu\text{g}/\text{m}^3 * 79\text{min}) * 79\text{min} * 0.83\text{m}^3/60\text{min} = 42.8\mu\text{g}$

Intake from 8.5hr to  $9.7\mu\text{g}/\text{m}^3$  (3ppbv) ambient city benzene:

$(9.7\mu\text{g}/\text{m}^3 * 8.5\text{hr}) * 0.83\text{m}^3/\text{hour} = 68.6\mu\text{g}$

Intake from 14.2hr to  $1.3\mu\text{g}/\text{m}^3$  (0.4ppbv) ambient suburban benzene:

$(1.3\mu\text{g}/\text{m}^3 * 14.2) * 0.83\text{m}^3/\text{hour} = 15.3\mu\text{g}$

On a lifetime basis, assuming a working life of 40years, with commuting 5 days/week and 48 weeks/year:

Intake during commuting using tunnel:

$5\text{ days/week} * 48\text{ weeks/year} * 40\text{years} * 46.9\mu\text{g} = 450\ 240\mu\text{g}$  benzene

Intake during commuting alt route:

$5\text{ days/week} * 48\text{ weeks/year} * 40\text{years} * 42.8\mu\text{g} = 410\ 880\mu\text{g}$  benzene

Intake over 40years, excluding commuting:

$(5\text{ days/week} * 48\text{ weeks/year} * 40\text{years} * 68.6\mu\text{g}) + (5\text{ days/week} * 48\text{ weeks/year} * 40\text{years} * 15.3\mu\text{g}) + (124\text{days/year} * 1.3\mu\text{g}/\text{m}^3 * 24\text{hours} * 0.83\text{m}^3/\text{hour}) = 808\ 651\mu\text{g}$  benzene

Total working life benzene exposure (including tunnel):

= 1 258 891  $\mu\text{g}$  benzene

Thus commuting contributes approximately 36% of benzene exposure. The working life benzene exposure can be reduced by about 3% by avoiding the tunnel, or closing the vehicle windows. By contrast, Wadge and Salisbury estimated that additional intake of benzene for a 20 cigarette/day smoker would be 8 760 000  $\mu\text{g}$  (approx 700% increase).

<sup>2</sup>from NSW EPA "Ambient Air Quality Research Project (1996 – 2001) Dioxins, Organics, Polycyclic Aromatic Hydrocarbons and Heavy Metals"

sourced at <http://www.epa.nsw.gov.au/publications/dioxinsorganicsetc.pdf>, June 2003. Assuming a commuter spends 9 hours a day at CBD levels (3ppbv) and the remainder of the day at suburban levels (0.4ppbv)

<sup>#</sup> from NSW Transport Data Centre – typical commute duration in Sydney.

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