

# Ambient Air Quality Research Project (1996–2001)

Internal working paper no. 2

Ambient concentrations of  
toxic organic compounds  
in NSW



Department of  
**Environment and  
Conservation (NSW)**

This report was prepared by staff of the Atmospheric Science Section of the Department of Environment and Conservation (NSW)

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This is an internal working paper and has not been reviewed by experts in the field who are independent of the study or of the Department of Environment and Conservation.

The original research contained herein is being submitted to a peer-reviewed scientific journal for publication.

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## Acronyms and glossary

AVOCS	ambient volatile organic canister sampler
CARB	California Air Resources Board
CBD	central business district
ESL	effects screening levels
GC/MS	gas chromatography / mass spectrometry
IARC	International Agency for Research on Cancer
<i>m-</i>	<i>meta</i>
NSW EPA	New South Wales Environment Protection Authority
<i>o-</i>	<i>ortho</i>
<i>p-</i>	<i>para</i>
ppb	parts per billion ( $10^{-9}$ )
ppbV	parts per billion by volume
ppt	parts per trillion ( $10^{-12}$ )
pptV	parts per trillion by volume
stratosphere	layer of the atmosphere that extends from 20 kilometres up to approximately 50 kilometres
TO-14	Toxic Organic Method 14
troposphere	layer of the atmosphere that extends from the surface to about 20 kilometres
US EPA	United States Environmental Protection Agency
VOC	volatile organic compound



## Executive Summary

**In September 2003, the EPA became part of the Department of Environment and Conservation (NSW). Since all research in this report was conducted before September 2003, the organisation is referred to as the EPA throughout.**

Many organic compounds are found naturally but others have industrial or domestic sources. Some have the potential to adversely affect the health of humans or the environment after exposure to airborne concentrations over extended periods. These include some known human carcinogens, such as benzene.

The purpose of this study was to measure the ambient concentrations of 41 volatile organic compounds. This study was one of four studies on groups of air pollutants that together form the Ambient Air Quality Research Project (1996–2001) (NSW EPA 2002).

The sampling and analysis method used in the study was US EPA TO-14. The forty TO-14 compounds plus 1,3-butadiene represent a wide range of recognised ‘hazardous air pollutants’, as the US EPA refers to them, plus several significant ozone-depleting substances. This latter group is known to damage the ozone layer, which shields the Earth from the Sun’s ultraviolet radiation. These ozone-depleting substances are of interest as global pollutants; they have been banned or are being phased out under the internationally agreed treaty, the Montreal Protocol.

Measurement sites in this study included the Sydney central business district (CBD), Rozelle (inner urban), St Marys (outer urban), Wollongong (Illawarra regional urban centre) and Newcastle (lower Hunter regional urban centre). A 24-hour sample was taken every six days at these five primary sites for five years (1996 to mid 2001) in the Sydney CBD, Rozelle and St Marys, and for four years (mid 1997 to mid 2001) in Newcastle and Wollongong.

A supplementary although less intensive sampling program was also undertaken in the lower Hunter (Beresfield and Wallsend) and Illawarra (Albion Park, Kembla Grange and Warrawong) regions, which confirmed that concentrations measured at the Newcastle and Wollongong sites were the highest in each region. The data from these five supplementary subregional sites showed a range of concentrations comparable with those at the primary sites. It should be noted that the supplementary site data could not be directly compared with international annual average benchmarks, because of the shorter sampling period of three to four months at a time, rather than continuously throughout the year.

Over 1000 samples were collected at the five primary sites. Analysis of the samples collected found that:

- 12 of the 41 targeted compounds were not detected in any sample
- 10 compounds were detected in fewer than 1% of samples
- 19 compounds were detected in more than 1% of samples; most of these were present at very low concentrations.

Motor vehicles are a significant source of many of these compounds (see Table ES1). Although ozone-depleting substances are the next largest group, they are no longer in production or use. Concentrations of these substances were not significantly higher than those at remote sites in Tasmania and Alaska. Concentrations of chloromethane were also only slightly higher than the global background concentrations measured at other international remote sites. The three compounds primarily emitted by industry (Table ES1) were measured at low concentrations.

**Table ES1: Compounds detected at the five primary sites classified by likely source**

	Organic compound
Motor vehicles	toluene benzene ( <i>p+m</i> )-xylene <i>o</i> -xylene 1,2,4-trimethylbenzene ethylbenzene 1,3-butadiene 4-ethyltoluene 1,3,5-trimethylbenzene styrene
Past use in equipment (e.g. air conditioning and refrigeration units) <sup>1</sup>	Freon 11 Freon 12 Freon 113 carbon tetrachloride 1,1,1-trichloroethane
Industrial	dichloromethane trichloroethylene tetrachloroethylene
Natural, domestic and industrial	chloromethane

<sup>1</sup> These compounds are ozone-depleting substances with atmospheric lifetimes of five to 150 years

The highest annual average concentrations for many compounds were found in the Sydney CBD. St Marys, Rozelle, Newcastle and Wollongong had better air quality, although Rozelle showed a more pronounced effect from motor vehicle sources. Higher concentrations of some compounds were observed in winter and autumn, which is partly due to poor dispersion.

At all sites, the concentrations of benzene were below the UK (2003) annual average goal of five parts per billion by volume (ppbV) (UK DETR 2000)<sup>1</sup>. Even the more stringent long-term European Commission annual average goal of 1.5 ppbV (to be achieved by 2010; European Commission 1999) was met at all sites, except the Sydney CBD with its proximity to heavy traffic. The concentrations of 1,3-butadiene were below the UK (2003) annual average goal of 1 ppbV at all sites. The results for benzene and 1,3-butadiene in this study are broadly consistent with the concentrations found in comparable overseas locations.

The annual average concentrations of organic air toxics were very low. The sampling sites were generally representative of urban parts of Sydney, Newcastle and Wollongong. Many of the commonly recognised organic air toxics were not detected in any samples. While the results of this study are reassuring about the presence of organic air toxics in major NSW regional areas, the data do not allow for complacency on benzene or 1,3-butadiene. Health-based recommendations from international agencies suggest that current goals may need to be reduced further to control the risks posed by these two substances.

<sup>1</sup> Since the publication of the summary report (NSW EPA 2002), the UK Government (DEFRA 2003) has reviewed its benzene standard and adopted the following new objectives to be achieved by the end of 2010:

- an annual average of 1.5 ppbV for England and Wales
- a running annual average of 1 ppbV for Scotland and Northern Ireland.

## 1. Introduction

Many organic compounds are found naturally, but others have industrial or domestic sources. Some have the potential to adversely affect the health of humans or the environment exposed to elevated airborne concentrations over extended periods. These organic compounds include some known human carcinogens, such as benzene.

The Commonwealth Government's Living Cities Air Toxics Program defines air toxics as follows:

*gaseous, aerosol or particulate pollutants (other than the six criteria pollutants) which are present in the air in low concentrations with characteristics such as toxicity or persistence so as to be a hazard to human, plant or animal life. The term 'air toxics' and 'hazardous air pollutants' (HAPs) are used interchangeably* (Environment Australia 2001).

The New South Wales Environment Protection Authority (NSW EPA) measured the ambient concentrations of a subset of 40 organic air toxics as part of a pilot study beginning in 1995. This subset of air toxic compounds are those specified in the United States Environmental Protection Agency's (US EPA's) Toxic Organic Method TO-14 (US EPA 1988). Measurement in this pilot study consisted of a screening survey of 18 sites in the Sydney region. A summary of the findings of this study has been published (NSW EPA 1998).

The work in this Ambient Air Quality Research Project (1996–2001) extended work conducted in the pilot study, with continued measurement of TO-14 compounds in the Sydney region and the commencement of measurement in the Illawarra and lower Hunter regions. Annual summaries of these data have been published (NSW EPA 2001a, b). The purpose of this study was to measure concentrations of 41 organic air toxic compounds in ambient air at five representative sites over several years. This report presents the measurement results and a statistical analysis of these data.

### 1.1 Target compounds

The TO-14 methodology provides the means of sampling and analysing the air samples for 40 volatile organic compounds (Table 1) which represent a wide range of recognised 'hazardous air pollutants', as the US EPA refers to them, plus several significant ozone-depleting substances. This latter group is known to damage to the ozone layer, which shields the Earth from the Sun's ultraviolet radiation. These ozone-depleting substances are of interest as global pollutants; they have been banned or are being phased out under the internationally agreed treaty, the Montreal Protocol.

In addition to the 40 TO-14 compounds, and because of current international attention, 1,3-butadiene was also included in the analysis. As 1,3-butadiene is not a target analyte specified in TO-14, the NSW EPA validated the TO-14 methodology for this compound (Linfoot and Chau 2000). 1,3-Butadiene has been included in the analysis since June 1998.

A list of International Union of Pure and Applied Chemistry (IUPAC) names and common names for these 41 compounds is presented in Appendix 1.

**Table 1: Target compounds**

		<b>Halogenated alkanes</b>
	vinyl chloride	bromomethane
	1,1-dichloroethene	chloromethane
	<i>cis</i> -1,2-dichloroethene	dichloromethane
	trichloroethylene	chloroform
	tetrachloroethylene	carbon tetrachloride
	3-chloropropene	chloroethane
	<i>cis</i> -1,3-dichloropropene	1,1-dichloroethane
	<i>trans</i> -1,3-dichloropropene	1,2-dichloroethane
	1,3-butadiene	1,2-dibromoethane
<b>Halogenated aromatics</b>	hexachloro-1,3-butadiene	1,1,1-trichloroethane
chlorobenzene	<b>Chlorofluorocarbons</b>	1,1,2-trichloroethane
	Freon 11	1,1,2,2-tetrachloroethane
	Freon 12	1,2-dichloropropane
	Freon 114	

## 1.2 Sources

Some of the compounds occur naturally in the environment, others have industrial or domestic sources, and some are emitted from a combination of both. Some compounds occur as a natural constituent of crude oil and plant volatiles, and others can be released during bush fires. Other sources include motor vehicle exhaust, wood and coal burning, lawn mowers, solvent and chemical usage, industrial emissions, and leaking refrigeration or air conditioning units. Further details of sources of each compound are presented in Appendix 2.

## 1.3 Atmospheric persistence

The atmospheric persistence and primary removal mechanism for each compound are different. Some compounds are highly reactive and are broken down quickly, while other compounds are extremely stable and can persist in the atmosphere for many years.

The dominant removal mechanism for most of the compounds is by reaction with the hydroxyl (OH·) radical. For example, the atmospheric lifetime of benzene is 12 days and of toluene is two to four days, owing primarily to the reaction with the hydroxyl radical (CARB 1997). Some of the compounds, however, do not react with the hydroxyl radical. For example, the only loss process from the troposphere for Freon 11 and Freon 12 is by transport to the stratosphere. The atmospheric lifetimes of the Freon compounds range from 50 to 150 years (CARB 1997). Atmospheric lifetimes for other compounds are presented in Appendix 3.

Data interpretation and analysis requires an understanding of these potential sources, the length of time each compound persists in the atmosphere, and any spatial and seasonal variations. An example is the potential impact of wood heater usage in winter.

## **2. Materials and methods**

### **2.1 Project design**

The purpose of this study was to measure ambient concentrations of 41 volatile organic compounds at five representative sites. This report presents the measurement results and a statistical analysis of these data. The five primary regional sites were:

- Sydney CBD (peak), Sydney region
- Rozelle (inner urban), Sydney region
- St Marys (outer urban), Sydney region
- Wollongong (regional urban centre), Illawarra region
- Newcastle (regional urban centre), lower Hunter region

Samples were collected over 24-hour periods at these five primary sites for over five years (January 1996 to August 2001) in the Sydney CBD, Rozelle and St Marys, and for four years (July 1997 to August 2001) in Newcastle and Wollongong. Samples were collected during the entire year and over several years, allowing for comparison with international annual average goals and for the establishment of a baseline, which takes inter-annual variability into account.

The Sydney CBD site was selected as being representative of the expected peak ambient concentrations due to motor vehicle emissions of organic air toxics. The other sites were generally representative of urban ambient concentrations.

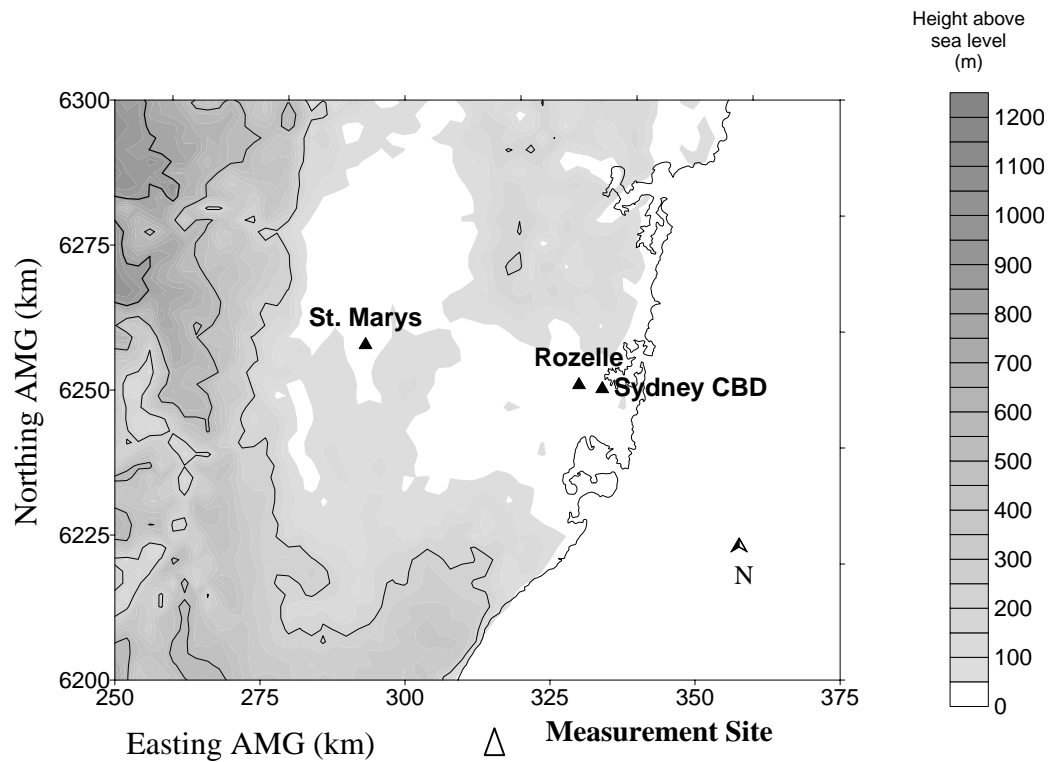
A supplementary, although less intensive, sampling program was also undertaken in the lower Hunter and Illawarra regions to confirm that the Newcastle and Wollongong sites were representative of each region. The sites were:

- Beresfield and Wallsend (lower Hunter)
- Albion Park, Kembla Grange and Warrawong (Illawarra)

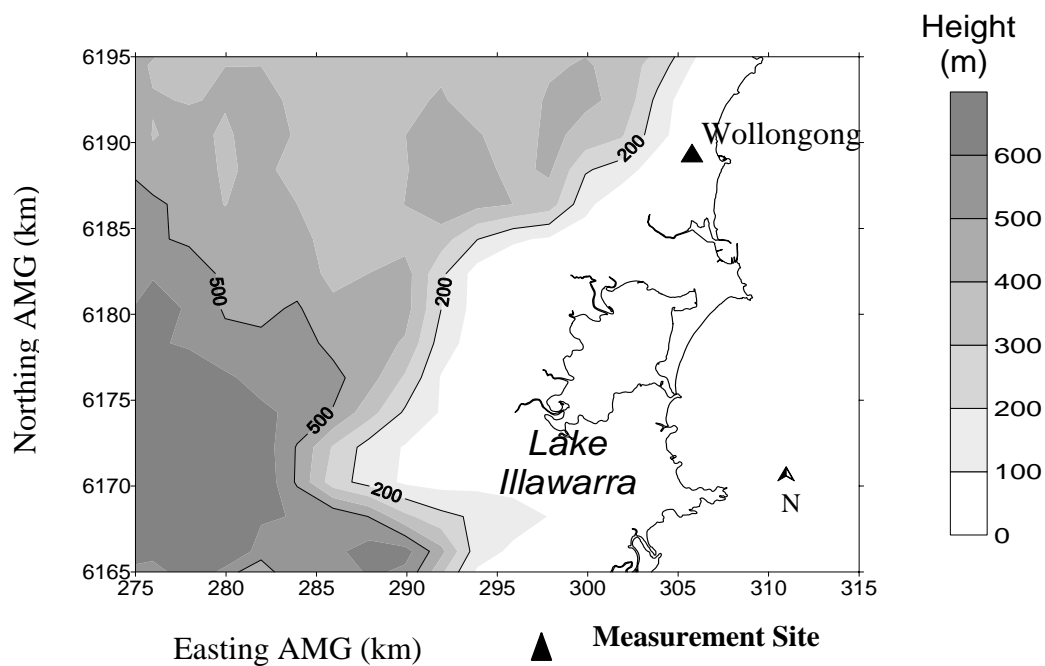
The data from this supplementary sampling program allow comparison of the range of concentrations measured at these sites with those measured at the Wollongong and Newcastle sites. These supplementary data could not be directly compared with international annual average benchmarks, because of the shorter sampling period of three to four months at a time, rather than continuously throughout the year. Results of the supplementary sampling confirmed that concentrations measured at the primary sites, Newcastle and Wollongong, were the highest in each region. The data from the supplementary study sites showed a range of concentrations comparable with those at the primary sites. Further results of this work are presented in Appendix 4.

### **2.2 Site locations and characteristics**

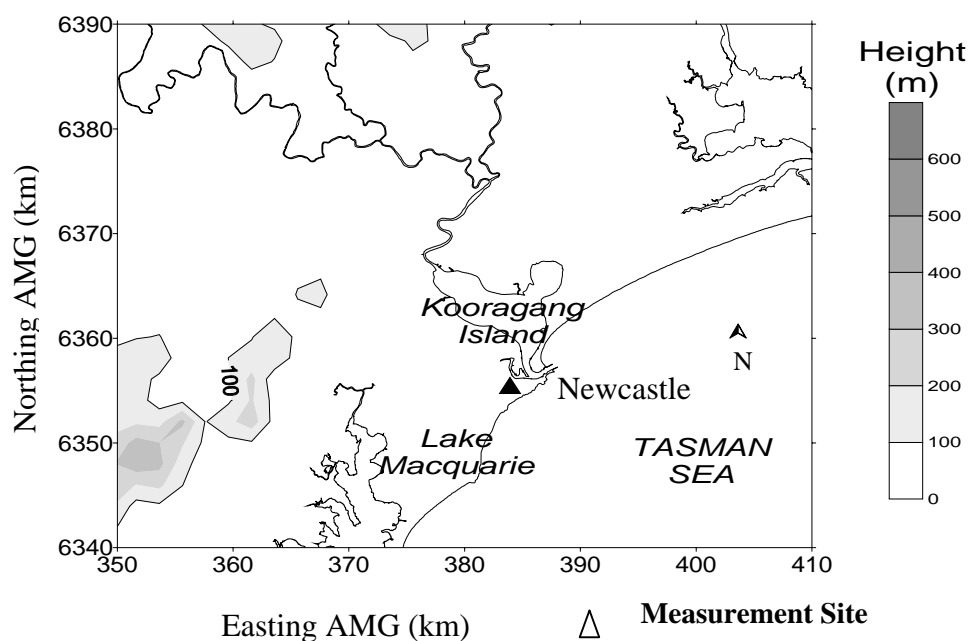
Figures 1 to 3 show the locations of the five primary measurement sites. Table 2 provides descriptions of these sites.



**Figure 1: Measurement sites in the Sydney region**



**Figure 2: Measurement site in the Illawarra region**



**Figure 3: Measurement site in the lower Hunter region**

**Table 2: Measurement site descriptions**

		Description
Sydney CBD	Sydney	On the corner of George and Market Streets, either on the awning of the Gowings building (until January 1999) or the awning of the Grace Brothers (Myer) building (opposite side of the intersection, after May 2000), above a very high-traffic area intersection.
Rozelle	Sydney	In the grounds of Rozelle Hospital on Balmain Road. Monitoring is at the north-western end of the hospital grounds, with Victoria Road and Balmain Rd/Darling St some 300 m distant. Traffic on Victoria Road becomes congested in both the morning and afternoon peak hours, as this road carries city workers.
St Marys	Sydney	In a privately owned, open, grass-covered paddock, approximately 1 km from the heavily trafficked M4 motorway and 200 m from Mamre Rd.
Wollongong	Illawarra	In the Australian Army Depot on Gipps St. This site is in a residential area, approximately 1 km north-west of the Wollongong city centre.
Newcastle	Lower Hunter	In the grounds of the athletics field on Dumaresq St, Hamilton South. This is a residential area approximately 2 km from the Newcastle city centre.

## 2.3 Sampling schedule

The sampling period for all measurements was 24 hours. Before July 1997, it was necessary to have various sample start times owing to the nature of sampling schedules. Beginning in July 1997, all samples were collected from midnight to midnight (Australian Eastern Standard Time) on a one-in-six-day cycle where possible. The six-day cycle is used so that each day of the week is equally represented when calculating long-term averages.

## 2.4 Sampling and analytical procedure

The US EPA's TO-14 methodology was used for sample collection and analysis. The NSW EPA has gained National Association of Testing Authorities (NATA) accreditation for both the measurement and analytical techniques. Samples were collected using ambient volatile organic canister samplers (AVOCS). The AVOCS collects air samples into a canister for subsequent laboratory analysis and quantification by gas chromatography / mass spectrometry. Further details are presented in Appendix 5.

## 2.5 Measurement units and detection limits

Concentrations are reported in parts per billion by volume (ppbV). In some cases the concentration of a particular compound in a sample was less than the detection limit. Established US practice was adopted for reporting concentrations below the detection limit; if a compound is detected in some samples and not others, samples in which the compound is not detected are assumed to contain the compound at half the detection limit (BAAQMD 1995). For some compounds this resulted in the overall average concentrations being less than the limit of detection.

Until the end of 1999, the detection limit was 0.2 ppbV for each compound, as specified in Method TO-14. In 2000, the NSW EPA's Analytical and Environmental Chemistry Section demonstrated that the limit of detection could be reduced from 0.2 to 0.1 ppbV for 27 of the 41 compounds (Table 3). The limit of detection for the remaining 14 compounds was unchanged. The new detection limits have been applied to the reporting of data from all samples collected from 2000 onwards.

A discussion on uncertainty is presented in Appendix 6.

**Table 3: Compounds with detection limits of 0.1 ppbV from 2000 onwards**

1,1,2,2-tetrachloroethane	chlorobenzene	1,1,1-trichloroethane
1,1,2-trichloroethane	chloroform	<i>o</i> -xylene
1,2,4-trimethylbenzene	dichloromethane	1,4-dichlorobenzene
1,2-dibromoethane	ethylbenzene	styrene
1,2-dichloroethane	Freon 11	<i>trans</i> -1,3-dichloropropene
1,3-butadiene	Freon 113	tetrachloroethylene
benzene	Freon 114	trichloroethylene
<i>cis</i> -1,3-dichloropropene	Freon 12	vinyl chloride
carbon tetrachloride	hexachloro-1,3-butadiene	1,1-dichloroethene



### 3. Results and discussion

#### 3.1 Number of samples

Over 1000 samples were collected at the five primary measurement sites. Sampling was conducted at the three Sydney sites from January 1996 to August 2001, and samples were collected at the Newcastle and Wollongong sites from July 1997 to August 2001. The number of samples collected at each site is presented in Table 4. The entire data set for each site was used for the calculation of overall averages unless stated otherwise.

**Table 4: Number of samples collected**

	Number of 24-hour samples
Sydney CBD	200
Rozelle	276
St Marys	237
Wollongong	177
Newcastle	184

#### 3.2 Frequency of detection

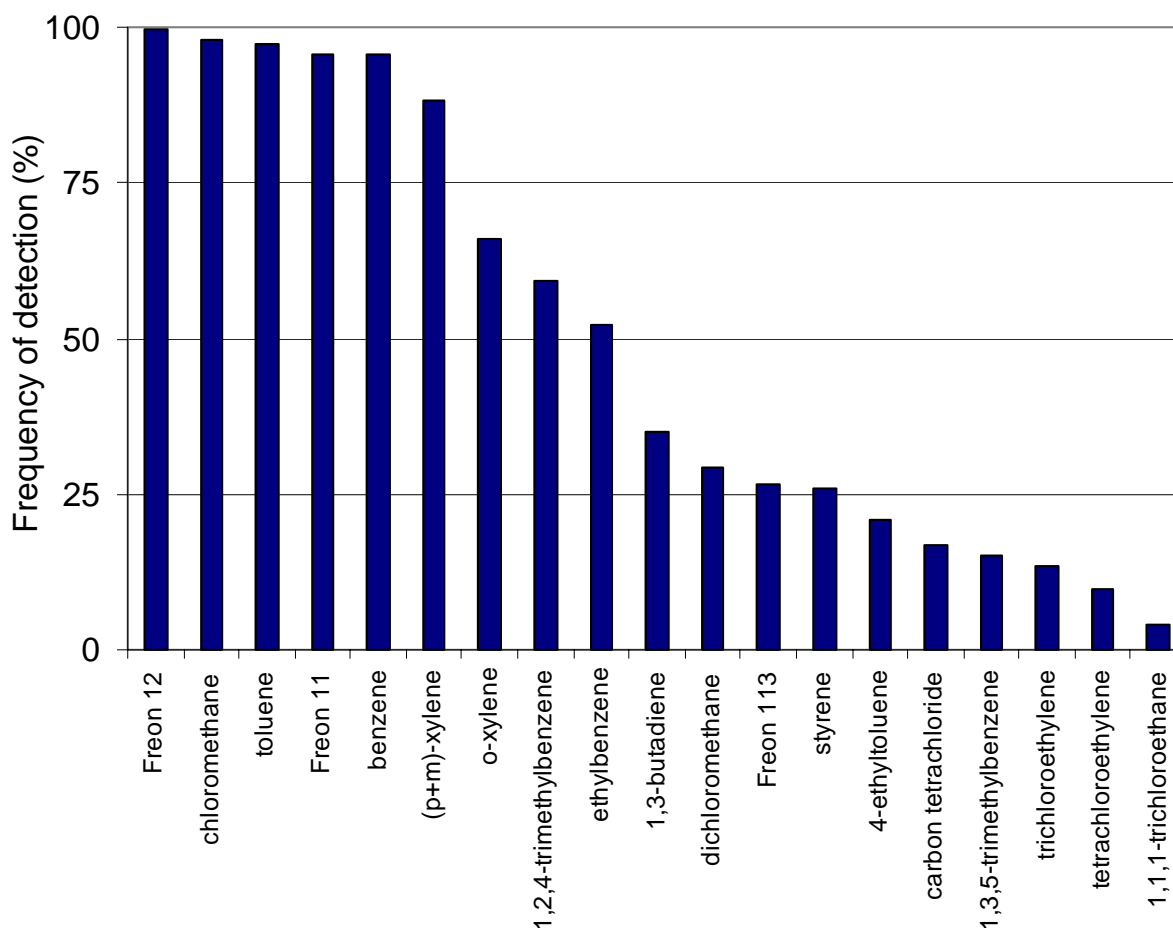
Twelve of the compounds were not detected in any of the samples collected at any of the primary measurement sites (Table 5). Although these twelve compounds had a lower detection limit from 2000 onwards, their concentrations were still below the detection limit.

Ten compounds were rarely encountered, being found in fewer than 1% of the samples collected (Table 5).

**Table 5: Compounds never or rarely detected**

	Detected in <1% of samples
1,1,2,2-tetrachloroethane	1,2-dichloroethane
1,1,2-trichloroethane	1,3-dichlorobenzene
1,1-dichloroethene	chloroform
1,2-dibromoethane	3-chloropropene
1,2-dichlorobenzene	hexachloro-1,3-butadiene
1,2-dichloropropane	vinyl chloride
1,4-dichlorobenzene	1,2,4-trichlorobenzene
<i>cis</i> -1,3-dichloropropene	1,1-dichloroethane
chlorobenzene	bromomethane
chloroethane	<i>cis</i> -1,2-dichloroethene
Freon 114	
<i>trans</i> -1,3-dichloropropene	

Figure 4 presents the cumulative frequency of detection for all samples at the five primary sites for the remaining nineteen compounds. The frequency of detection of each compound at each site both before and after the change in detection limit is presented in Appendix 7.



**Figure 4: Frequency of detection for all samples at the five primary sites**

### 3.3 Detected compounds

Of the nineteen compounds detected, thirteen are classified as hazardous air pollutants by the US EPA (Table 6) and eight are classified as priority air toxics by the Commonwealth Government (Appendix 8).

The scientific community's understanding of these compounds is evolving, and because of these knowledge limitations, lists of 'priority' compounds vary between countries and states. Examples of priority air toxics lists prepared by various organisations are presented in Appendix 8.

The International Agency for Research on Cancer (IARC) has classified some of these compounds as known or suspected carcinogens. The IARC classifications for the detected compounds are also presented in Table 6. The US EPA's carcinogen classifications are presented in Appendix 8.

**Table 6: Compounds detected in more than 1% of samples and corresponding classifications**

		<b>IARC cancer classification</b>
toluene	yes	not classifiable
benzene	yes	carcinogenic
( <i>p+m</i> )-xylene	yes	not classifiable
chloromethane	yes	not classifiable
<i>o</i> -xylene	yes	not classifiable
ethylbenzene	yes	possibly carcinogenic
1,3-butadiene	yes	probably carcinogenic
dichloromethane	yes	possibly carcinogenic
styrene	yes	possibly carcinogenic
trichloroethylene	yes	probably carcinogenic
tetrachloroethylene	yes	probably carcinogenic
carbon tetrachloride	yes	possibly carcinogenic
1,1,1-trichloroethane	yes	not classifiable
Freon 12	no	no IARC listing
1,2,4-trimethylbenzene	no	no IARC listing
Freon 11	no	no IARC listing
4-ethyltoluene	no	no IARC listing
1,3,5-trimethylbenzene	no	no IARC listing
Freon 113	no	no IARC listing

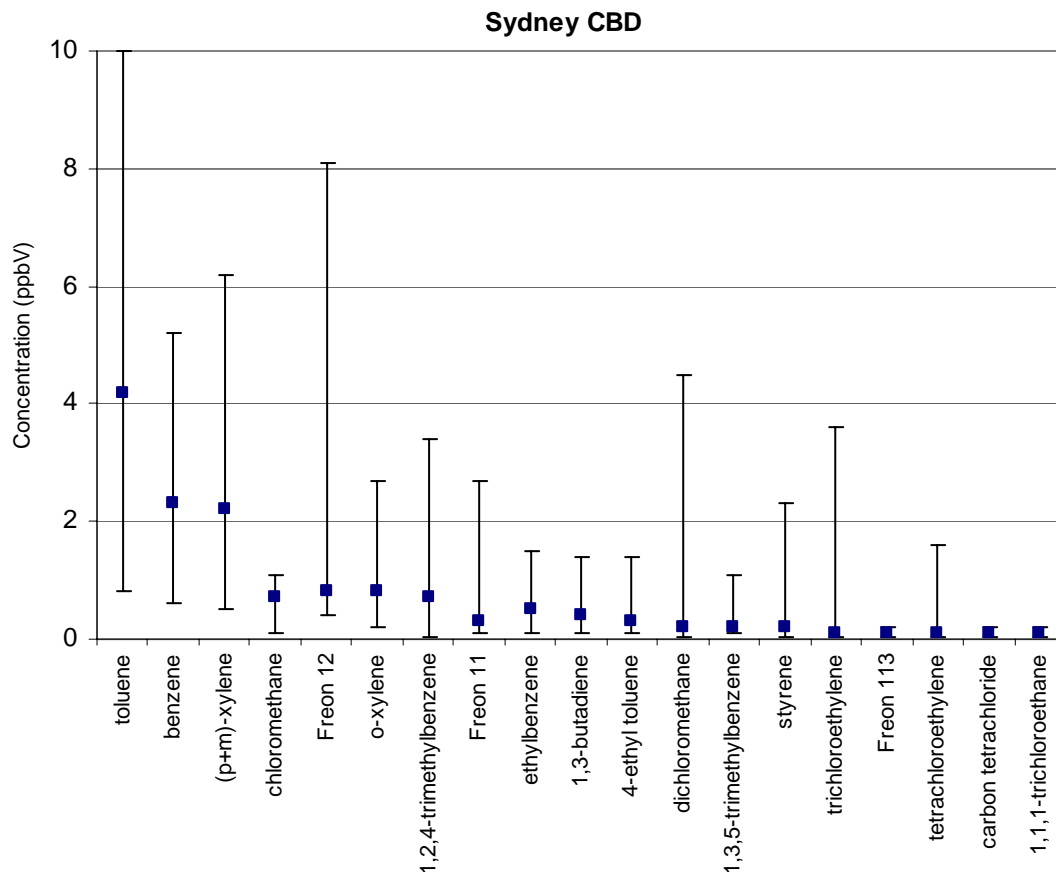
**Note:** Some compounds are ‘not classifiable’ owing to insufficient evidence or no available data

### 3.4 Average concentrations

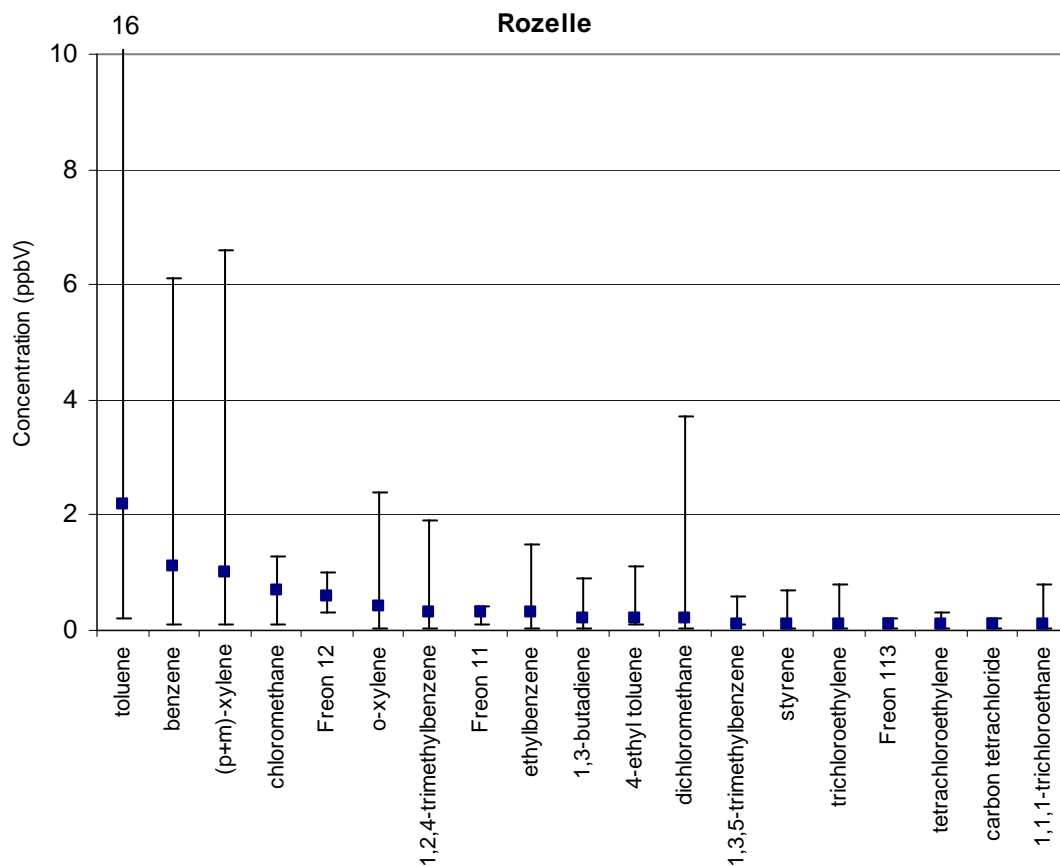
Figures 5a to 5e present the overall average, minimum 24-hour and maximum 24-hour average concentrations (in ppbV) of the detected compounds measured at each of the five primary measurement sites. Overall averages were calculated by using the total number of individual 24-hour samples from each site (Table 4). Most compounds were measured at very low concentrations, often close to the detection limit of 0.2 ppbV (or 0.1 ppbV after 2000 for some compounds). See Appendix 9 for further details.

Although overall average concentrations for many compounds are low (close to 0.2 ppbV), the maximum 24-hour average concentrations of some compounds were an order of magnitude higher. For example, the overall average concentration of dichloromethane was 0.2 ppbV at both Sydney CBD and Rozelle, whereas the maximum 24-hour average concentrations were 4.5 and 3.7 ppbV respectively. Compounds such as Freon 113 had a limited range of concentrations, and maximum 24-hour average concentrations of 0.2 ppbV.

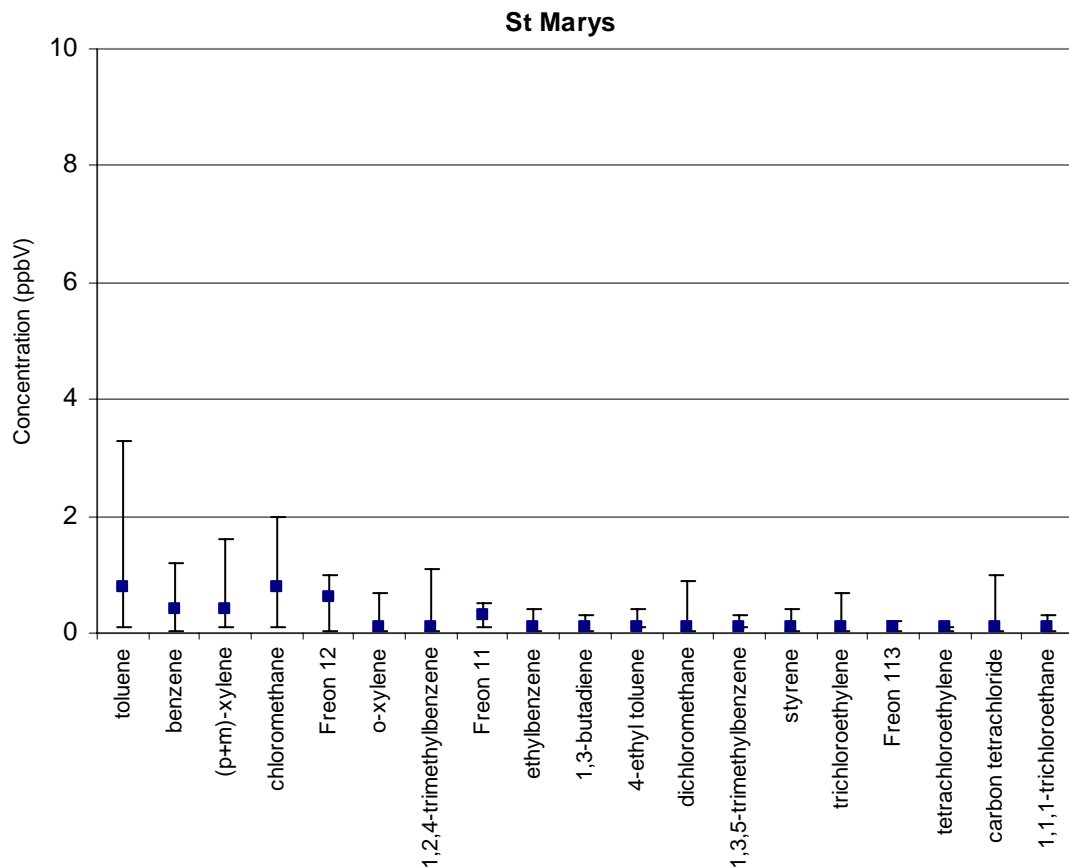
The highest overall average concentrations of many of the detected compounds were found in the Sydney CBD (see Figure 5a). Rozelle, St Marys, Newcastle and Wollongong had better air quality (see Figures 5b to 5e), although Rozelle showed a more pronounced effect from motor vehicle emissions (listed in Table 7).



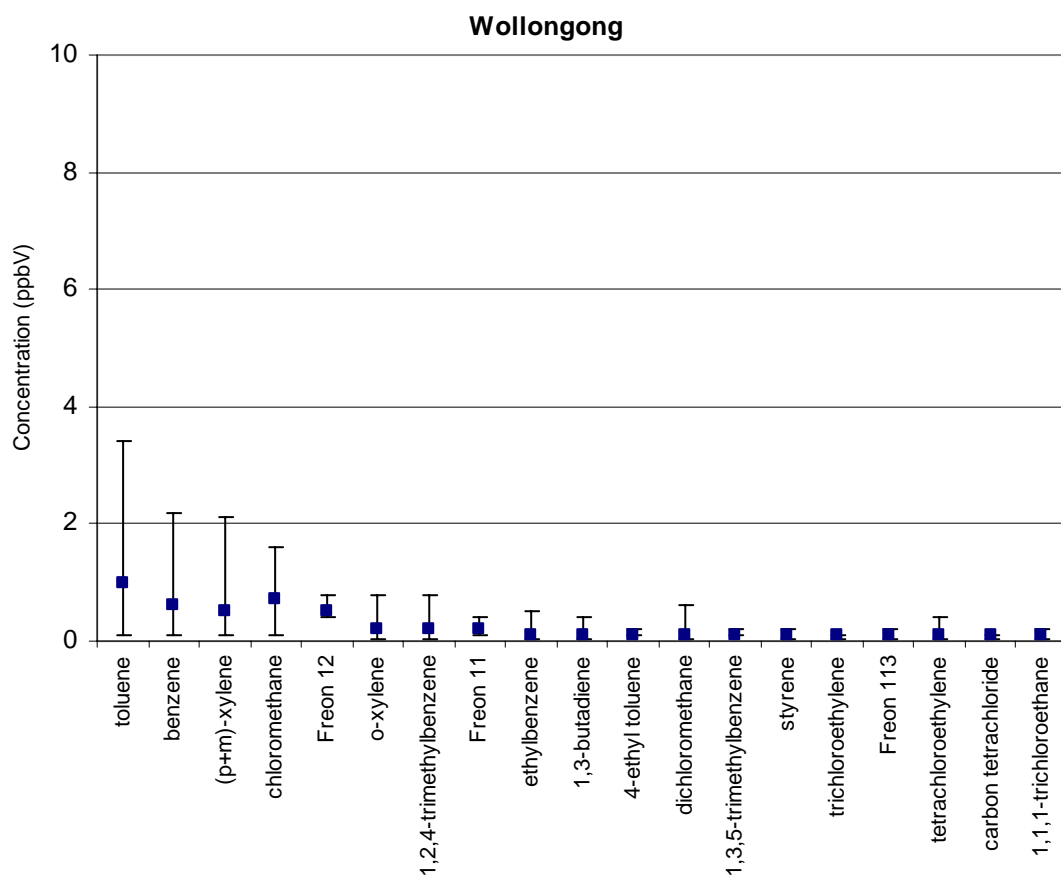
**Figure 5a: Overall average, minimum 24-hour average and maximum 24-hour average concentrations in Sydney CBD (January 1996 to August 2001)**



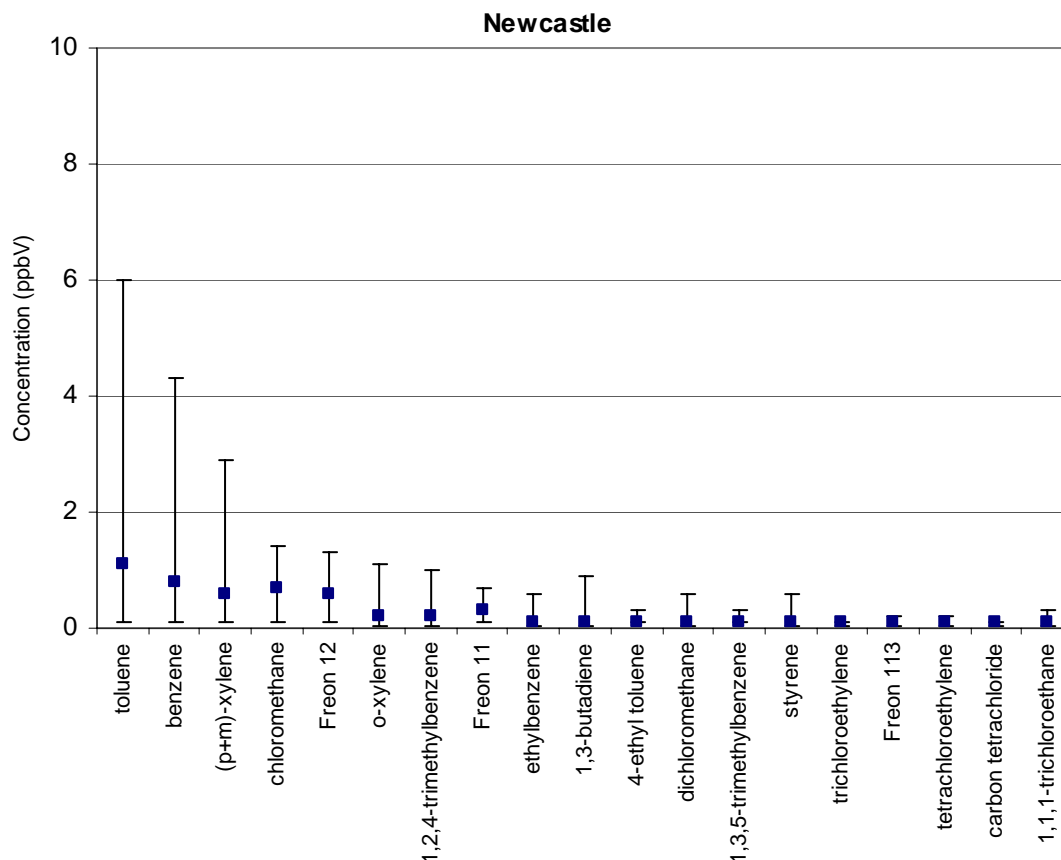
**Figure 5b: Overall average, minimum 24-hour average and maximum 24-hour average concentrations at Rozelle (January 1996 to August 2001)**



**Figure 5c: Overall average, minimum 24-hour average and maximum 24-hour average concentrations at St Marys (January 1996 to August 2001)**



**Figure 5d: Overall average, minimum 24-hour average and maximum 24-hour average concentrations in Wollongong (July 1997 to August 2001)**



**Figure 5e: Overall average, minimum 24-hour average and maximum 24-hour average concentrations in Newcastle (July 1997 to August 2001)**

### 3.5 Likely sources of detected compounds

Some of the compounds occur naturally in the environment, others are emitted entirely from industrial and domestic sources, and some come from a combination of these sources. Table 7 presents the likely source of each of the 19 compounds detected.

**Table 7: Compounds detected at the five primary sites classified by likely source**

	Organic compound
Motor vehicles	toluene benzene ( <i>p+m</i> )-xylene <i>o</i> -xylene 1,2,4-trimethylbenzene ethylbenzene 1,3-butadiene 4-ethyltoluene 1,3,5-trimethylbenzene styrene
Past use in equipment (e.g. air conditioning and refrigeration units) <sup>1</sup>	Freon 11 Freon 12 Freon 113 carbon tetrachloride 1,1,1-trichloroethane
Industrial	dichloromethane trichloroethylene tetrachloroethylene
Natural, domestic and industrial	chloromethane

<sup>1</sup> These compounds are ozone-depleting substances with atmospheric lifetimes of five to 150 years.

**Source:** NSW EPA 1997; CARB 1997; EPA Victoria 2001

### 3.5.1 Motor vehicles

Motor vehicles (Table 7) are the most significant source of 10 of the 19 compounds, although many compounds also have natural, industrial or domestic sources. These compounds all have relatively short atmospheric lifetimes (hours to days), and are therefore likely to be confined to the local airshed where they are emitted (CARB 1997).

Where it is known that two compounds can be emitted from the same source, the correlation between them may indicate whether they are being emitted from the same source. The correlation between benzene and toluene for each site ranged between 0.87 and 0.90 (Appendix 10). This high correlation indicates that it is likely that these two compounds are being emitted from the same source.

The ratio of the concentration of two compounds is one indicator that can also be used to differentiate between sources of pollutants in ambient air. For example, toluene-to-benzene ratios at locations where vehicle emissions are the dominant source will be different from those at locations where industries are the major source. Note that the ratio of two compounds can, however, vary according to many different factors. For example, the toluene-to-benzene ratio can vary in vehicle exhaust with the speed of the vehicle (Bailey *et al.* 1990; Field *et al.* 1994), the type and age of vehicles in the fleet and the fuel composition. Table 8 presents ratios of several compounds (associated primarily with motor vehicle emissions) based on concentrations measured at each of the five primary sites. Ratios of the estimated exhaust emissions from motor vehicles fuelled with petrol and diesel and evaporative emissions from petrol-fuelled vehicles are also presented (EPA Victoria 2001). The ratios at each of the sites are similar to each other and similar to the estimated ratios for motor vehicle emissions (Table 8). The ratios are closer to the estimated motor vehicle exhaust emissions than to the estimated evaporative emissions. Both the correlation between benzene and toluene at the primary sites and the ratios of several compounds suggest that motor vehicle emissions are the primary source of several organic compounds.

**Table 8: Ratios at the primary measurement sites compared with inventory results**

					benzene/ 1,3-butadiene
Sydney CBD	1.8	1.3	1.4	4.7	5.7
Rozelle	2.1	1.4	1.6	4.7	8.1
St Marys	2.0	1.4	1.5	3.7	5.2
Newcastle	1.6	1.1	1.5	5.3	8.2
Wollongong	1.7	1.2	1.5	5.1	6.3
					9.4

1 EPA Victoria 2001

### 3.5.2 Ozone-depleting substances

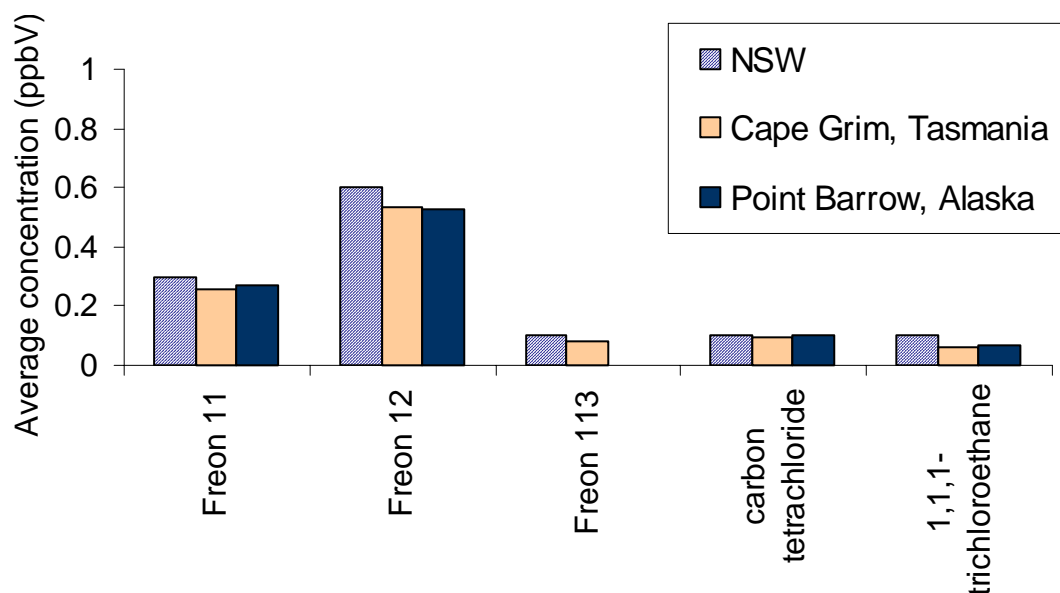
Five of the nineteen detected compounds are known to be ozone-depleting substances and are no longer in production or use. These compounds were banned from production, export and import in Australia in January 1996 under the internationally agreed treaty, the Montreal Protocol (NSW EPA 1997), as they are known to damage the ozone layer, which shields the Earth from the Sun's ultraviolet radiation.

Concentrations of these compounds measured in NSW have been compared with concentrations measured at remote background sites located at Cape Grim in north-western Tasmania and Point Barrow Observatory in Alaska (World Meteorological Organization 2001). There are no local industrial sources at Cape Grim, and mainland Australia is approximately 300 km to the north (Fraser 2001). Figure 6 shows that the concentrations of these compounds in the urban environment were not significantly higher than those at remote sites at Cape Grim (Tasmania) and Point Barrow (Alaska) over the same time period. Note that different instrumentation was used at those remote sites, resulting in much lower detection limits (parts per trillion by volume).

Other studies have confirmed that carbon tetrachloride is present in the atmosphere at a global background concentration estimated to be between 0.11 and 0.15 ppbV (CARB 1997).

Although these compounds have been banned from production in NSW since 1996, they are very stable in the atmosphere, having atmospheric lifetimes ranging from five to 150 years. It is therefore likely that current concentrations are primarily due to past emissions; however, these compounds may also be emitted from equipment that is still in operation, such as older air conditioners and refrigeration units.





**Note:** No Freon 113 data were available for Point Barrow, Alaska

**Figure 6: Comparison between concentrations in NSW and remote background sites (1997–2000) (World Meteorological Organization 2001)**

### 3.5.3 Industry

Industrial, commercial or domestic sources are the major sources of only three of the compounds detected (i.e. they are not emitted by motor vehicles and do not occur naturally in the environment). The specific sources of each compound are:

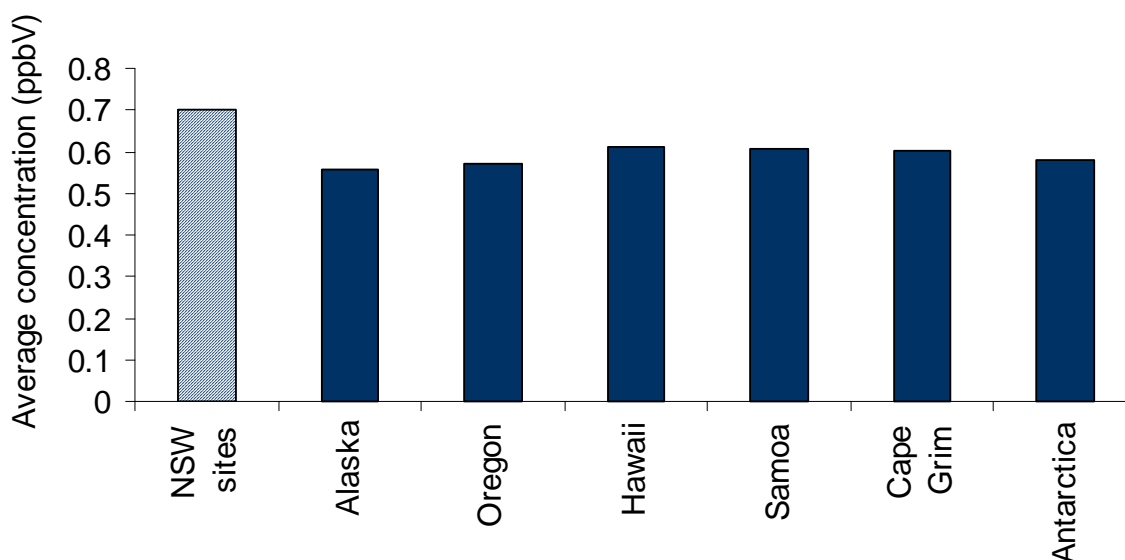
- dichloromethane (surface coating and solvent use)—found in 29% of samples, with an overall average of 0.1–0.2 ppbV at all primary sites
- tetrachloroethylene (dry cleaning and solvent use)—found in 10% of samples, with an overall average of 0.1 ppbV at all primary sites
- trichloroethylene (solvent use and waste burning)—found in 13% of samples, with an overall average of 0.1 ppbV at all primary sites (EPA Victoria 2001).

The prevalence of these three compounds was low, and when they were detected, concentrations were often close to or below the detection limit.

### 3.5.4 Natural, domestic and industrial

Chloromethane is generated from industrial and domestic sources as well natural sources such as oceans and biomass. Chloromethane is used in manufacturing and as a solvent. It has been detected in emissions from solid fuel heaters and is formed as a by-product of chlorination of water (CARB 1997). Chloromethane has an atmospheric lifetime ranging from months to years.

Concentrations of chloromethane in NSW (1996–2001) were compared with concentrations measured at remote background sites around the world (Figure 7) and were only slightly higher than those global background concentrations.



**Figure 7: Concentrations of chloromethane in NSW (1996–2001) and several remote sites (1996) (Khalil and Rasmussen 1999)**

### 3.6 Comparison with international benchmarks

There are currently no Australian ambient air quality goals or standards for air toxics. The National Environment Protection Council is currently considering the practicality of developing standards or goals for selected air toxics through an Air Toxics National Environment Protection Measure.

Ambient air quality goals for air toxics are usually based on annual average concentrations to ensure that health effects do not occur as a result of long-term exposure. Short-term goals do, however, exist for some compounds.

Annual average concentrations measured in this study have been compared with the following international annual goals. Further international goals are presented in Appendix 11.

- UK Government standards

The UK government has adopted standards as part of its National Air Quality Strategy. The annual standards for benzene of 5 ppbV and for 1,3-butadiene of 1 ppbV (both measured as rolling annual average concentrations) are to be achieved by 31 December 2003 (UK DETR 2000)<sup>2</sup>. These standards are based on recommendations made by the Expert Panel on Air Quality Standards in 1994 (UK DoE 1994a, b).

- European Commission Limit Value

In December 1999, the European Commission began its formal processes for the adoption of a directive relating to limit values for benzene. The directive provides an annual air quality goal of 5 µg/m<sup>3</sup> (1.5 ppbV) to be met by 1 January 2010 (European Commission 1999).

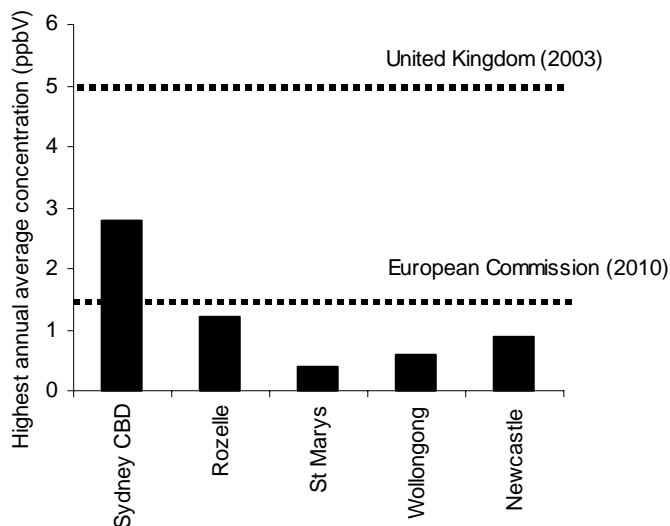
The European Commission goal for benzene is based on fuel control measures that came into effect in Europe in 2000 when a 1% benzene limit in petrol was put in place, allowing a 10-year lead time to achieve the goal. Australia will introduce a 1% benzene limit in 2006.

At all sites annual average concentrations of benzene were below the UK (2003) goal of 5 ppbV. Even the more stringent long-term European Commission annual average goal of 1.5 ppbV, to be achieved by 2010, was met at all sites except the Sydney CBD with its heavy traffic. Figure 8 presents the highest annual average concentration of benzene at each of the primary measurement sites based on samples collected from 1996 to 2000 for the Sydney sites and 1998 to 2000 for Wollongong and Newcastle. Data collected during 2001 at all sites were excluded from this analysis, as the full year's data were not available. Other years excluded from the calculation of annual averages at individual sites owing to the low number of samples collected are annotated later in Table 13.

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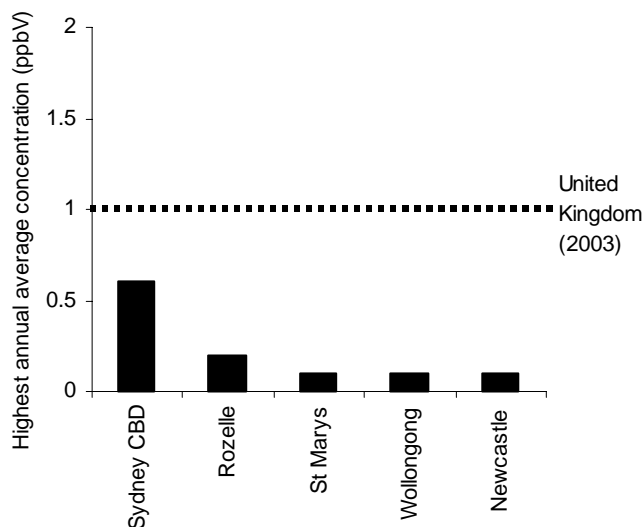
<sup>2</sup> Since the publication of the summary report (NSW EPA 2002), the UK Government (DEFRA 2003) have reviewed their benzene standard and adopted the following new objectives to be achieved by the end of 2010:

- an annual average of 1.5 ppbV for England and Wales
- a running annual average of 1 ppbV for Scotland and Northern Ireland.



**Figure 8: Highest annual average benzene concentrations in NSW compared with EC and UK goals**

The concentrations of 1,3-butadiene were below the UK annual average goal of 1 ppbV at all sites. The highest annual average of 0.6 ppbV was measured at the Sydney CBD site. Figure 9 presents the highest annual average concentration of 1,3-butadiene at the primary sites measured over the period 1998 to 2000 (as analysis for 1,3-butadiene began in 1998). The highest annual average for 1,3-butadiene at the Sydney CBD site is based on 1998 only, as other years were excluded owing to a low number of samples collected.



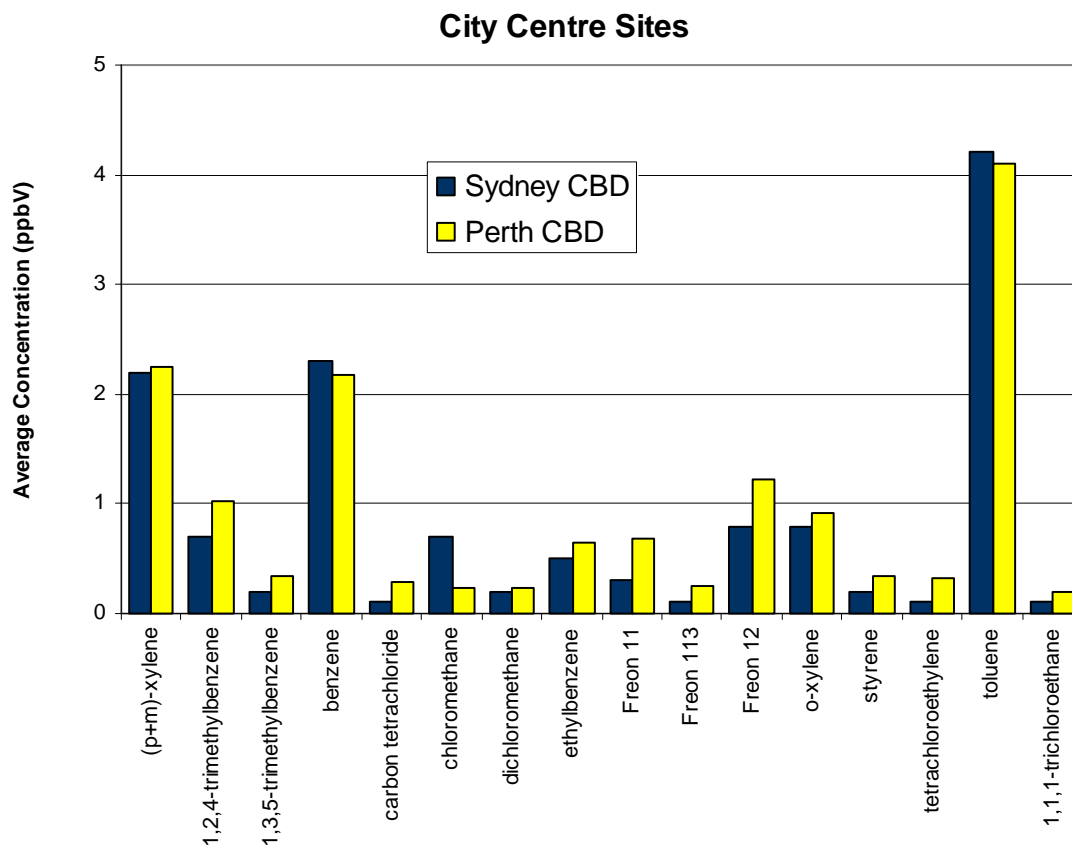
**Figure 9: Highest annual average 1,3-butadiene concentrations in NSW compared with UK goal**

### **3.7 Comparison with concentrations measured in other studies**

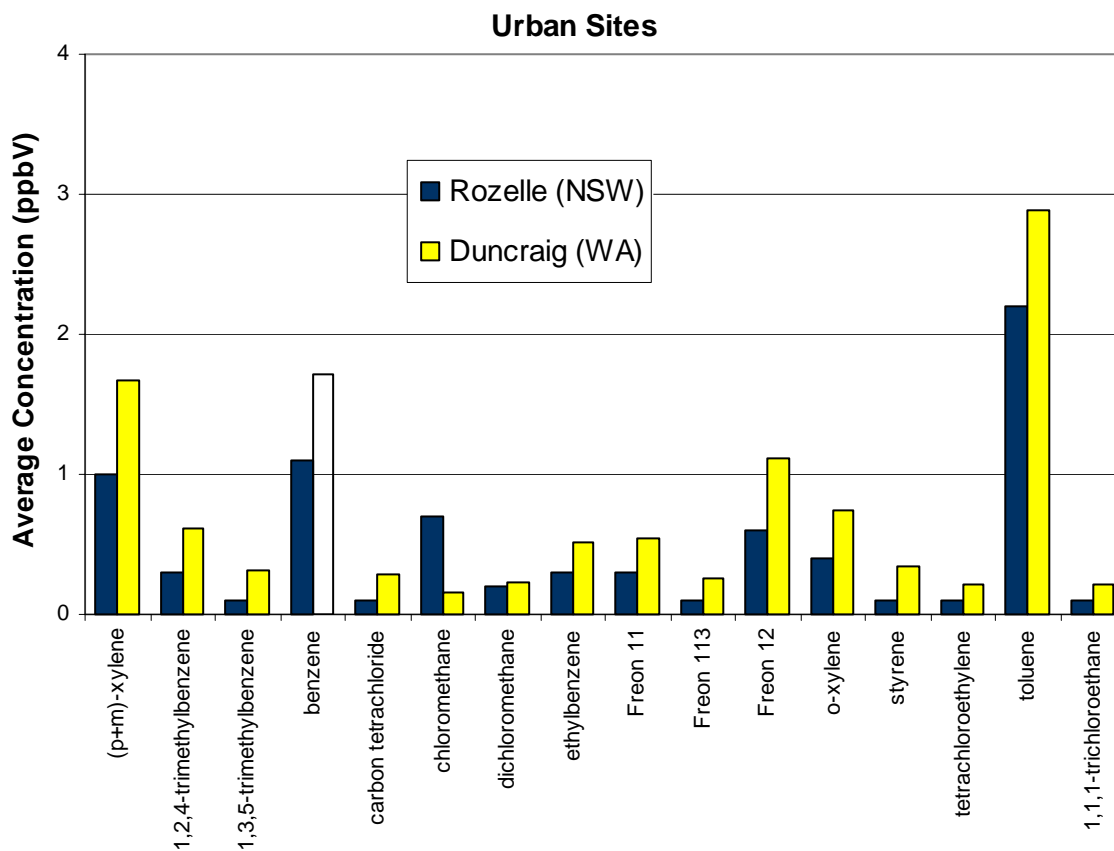
#### **3.7.1 Australian cities**

Concentrations of organic compounds measured in Perth (Western Australia) have been compared with concentrations measured in NSW. The sites have been grouped into city centre sites and urban sites. When comparing data collected in other studies, it is important to consider differences such as site location characteristics and sampling and analysis methods. Further data from other capital cities in Australia were excluded owing to the nature of the study, different sampling and analysis techniques or different sample durations.

Average concentrations of samples collected over 24 hours in the CBD in Perth from March 1997 to November 1998 (DEP WA 2000) were similar to overall average concentrations measured in this study (1996–2001) at the Sydney CBD site (Figure 10). Overall average concentrations at Rozelle were comparable with those concentrations measured at an urban site in Perth (Figure 11).



**Figure 10: Overall average concentrations measured at the Sydney CBD sites compared with Perth CBD (DEP WA 2000)**

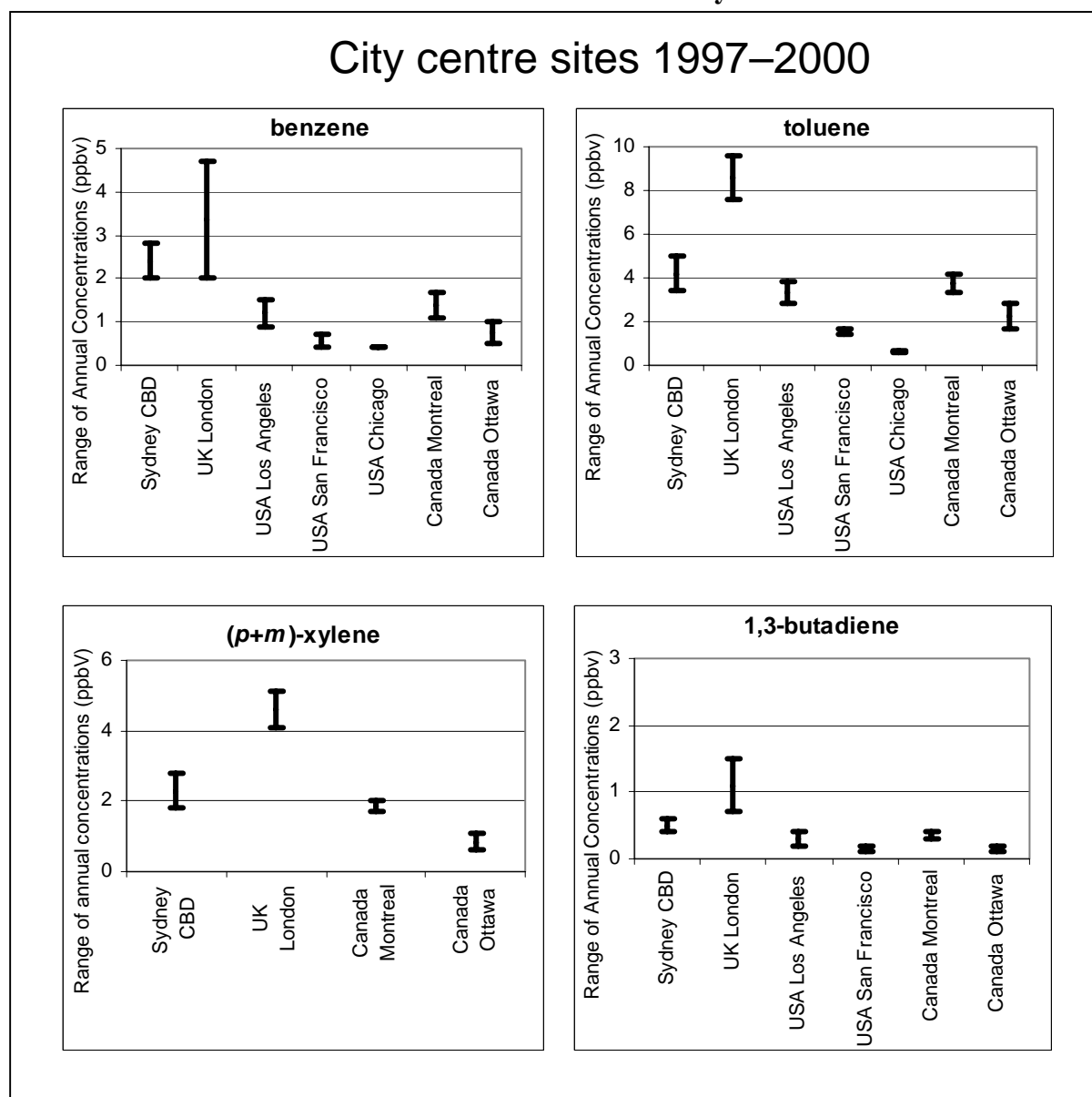


**Figure 11: Overall average concentrations measured at Rozelle (urban site) compared with an urban site in Perth (DEP WA 2000)**

### 3.7.2 International cities

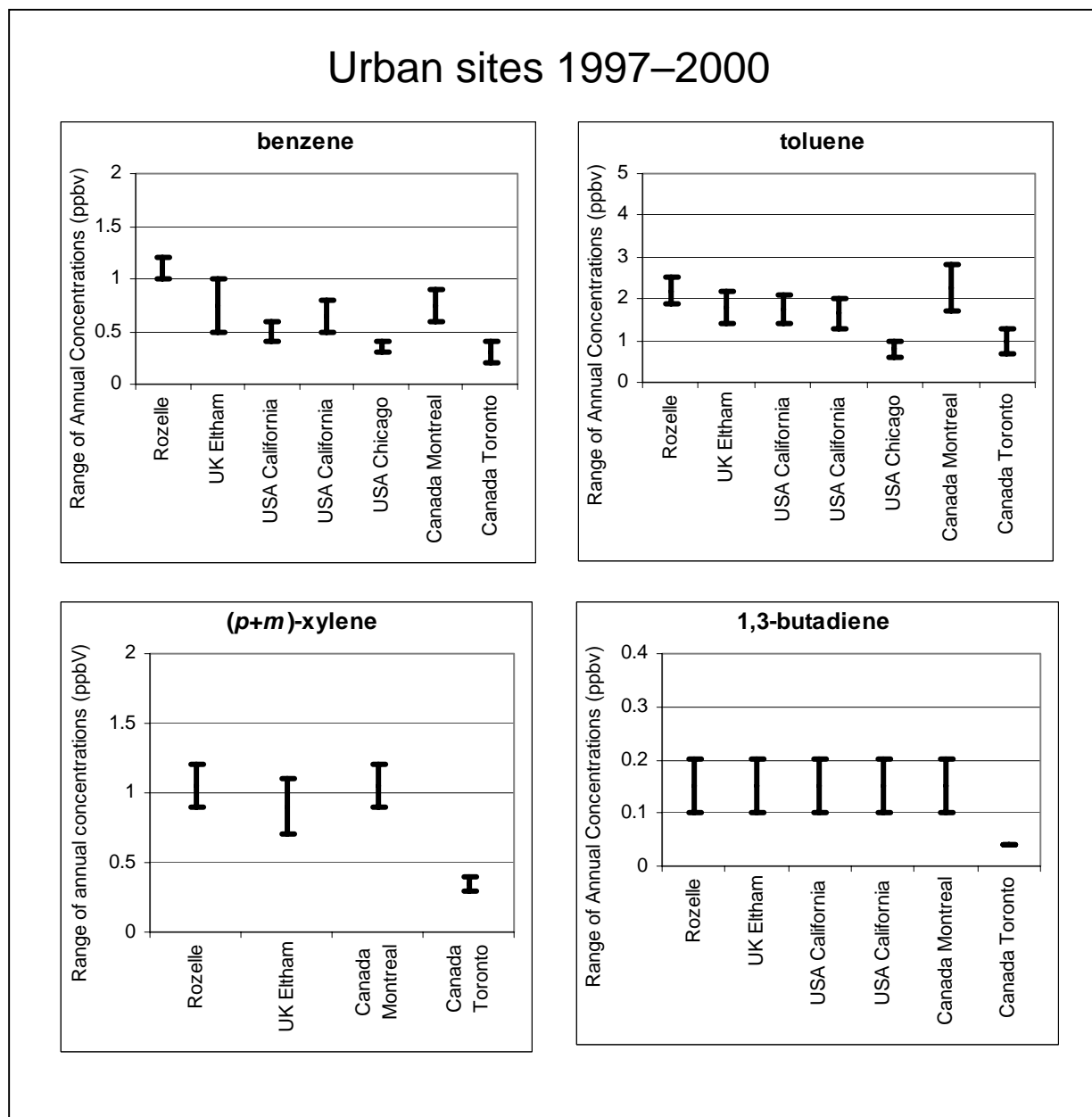
Concentrations at measurement sites in this study have been compared with concentrations measured at comparable international sites (selected on the basis of the descriptions provided in each study). The range of annual average concentrations measured between 1997 and 2000 in this study were compared with those at similar sites in the UK, the USA and Canada for the same time period. The sites have been grouped into city centre sites, urban sites and outer urban/rural sites (Figures 12a to 12c). The ranges presented represent the lowest to the highest annual average concentrations. The concentrations of pollutants associated with motor vehicle emissions in this study, including benzene, 1,3-butadiene, toluene and (*p+m*)-xylene, are broadly consistent with the concentrations found at comparable locations overseas. However, some cities that are further advanced in fuel quality and motor vehicle emission programs have somewhat lower average concentrations.

**Figure 12a: Annual average concentrations at Sydney CBD compared with concentrations measured in international city centre sites**



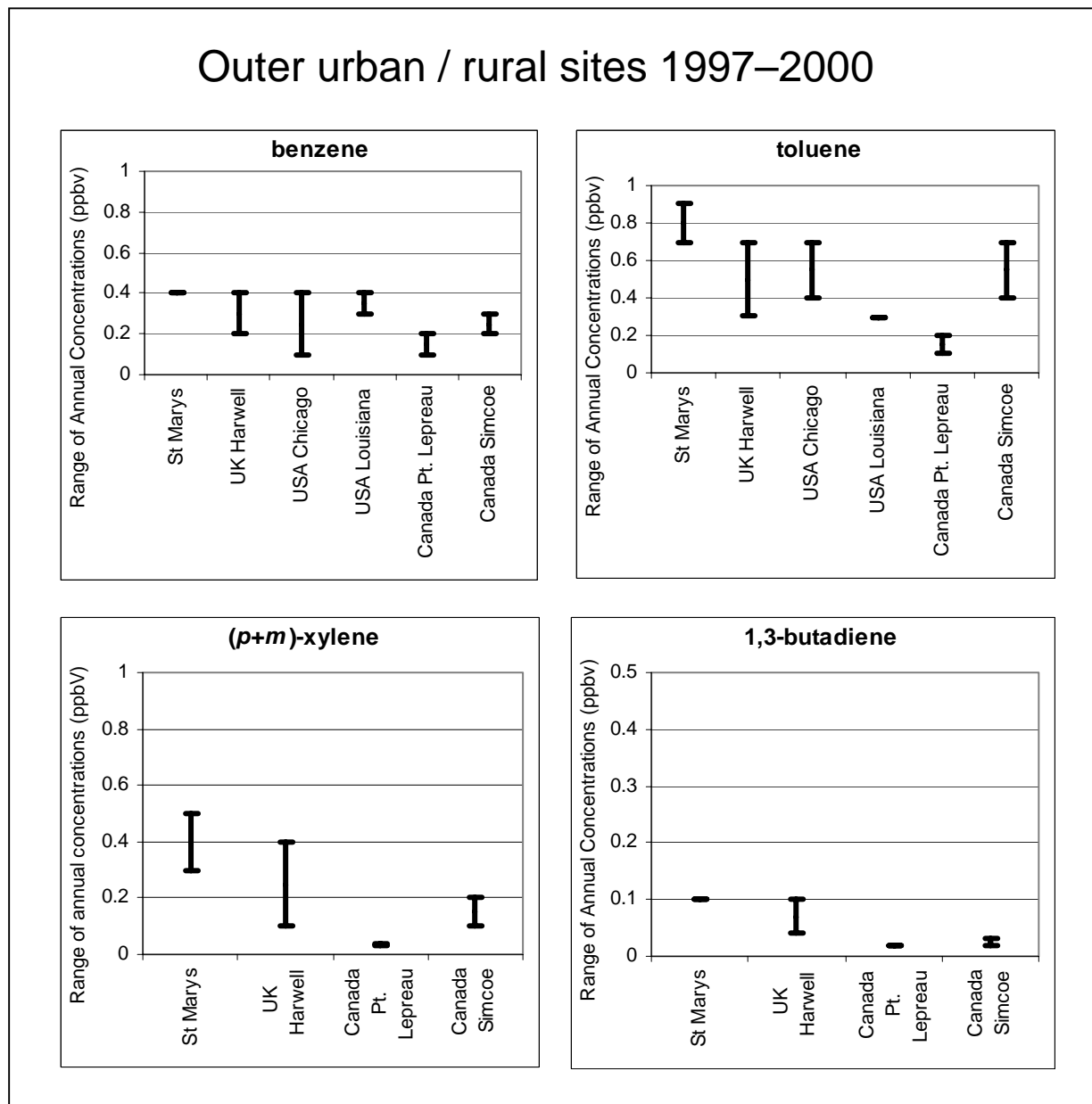
**Note:** The annual average of 1.7 ppbV for 1999 at the Sydney CBD was excluded as only 4 samples were collected owing to site relocation.

**Figure 12b: Annual average concentrations at Rozelle (urban) compared with concentrations measured at international urban sites**





**Figure 12c: Annual average concentrations at St Marys (outer urban site) compared with concentrations measured at international rural sites**



**Note:** There were no data available for (p+m)-xylene in 1997 or benzene in 2000 at Pt Lepreau, Canada. The ranges of 1,3-butadiene concentrations in Canada are based on the overall average from 1996–1998 and annual averages for 1999 and 2000.

**Source:** UK DETR 2002; US EPA 2002; personal communication, Tom Dann, January 2000, Analysis and Air Quality Division, Environment Canada.

### 3.8 Statistical analysis

The data collected at the five primary measurement sites were statistically analysed for the following patterns:

- spatial variability between sites
- seasonal variability between months at each site
- annual variations between years at each site.

#### 3.8.1 Spatial variability

The variability in pollutant concentrations between sampling sites is due to a number of factors, including differences in emissions (e.g. the level of motor vehicle usage, solid fuel heater usage and the type of industrial emission sources) and the influence of local topographical and meteorological factors (Environment Australia 2001).

Average concentrations of the nineteen detected compounds were analysed for statistical differences between sites. The number of samples collected at each site is presented in Table 4. Owing to problems with analytical instrumentation, a slightly lower number of samples were available for 1,3-butadiene, 1,2,4-trichlorobenzene, Freon 11 and Freon 12 (explanation in Appendix 5). To represent differences in concentrations of compounds between measurement sites, Figure 13 presents the average concentrations at each site and the upper and lower bounds of an 80% confidence interval for the average.

Figure 13 shows that average concentrations of several compounds do vary between sites. The Kruskal–Wallis test is a non-parametric method of testing the hypothesis that several samples have been derived from populations having the same continuous distribution versus the alternative that concentrations tend to be higher in one or more of the populations. The independent samples from the various sites were jointly ranked, and the sum of the ranks within each site was used to calculate the Kruskal–Wallis statistic. The larger the value of the calculated statistic, the more unlikely it is that all the samples come from populations with a common distribution. The Kruskal–Wallis test showed statistically significant differences between concentrations at different sites for nine of the 19 compounds. For each of these nine compounds, the highest overall average concentrations were found at the Sydney CBD site, followed by four similar groupings of the remaining sites. The patterns are as follows:

- For toluene, benzene and (*p+m*)-xylene, average concentrations fall into four statistically different groups from highest to lowest:
  - Sydney CBD
  - Rozelle
  - Newcastle and Wollongong
  - St Marys.
- For ethylbenzene, *o*-xylene and 1,2,4-trimethylbenzene, average concentrations fall into three statistically different groups from highest to lowest:
  - Sydney CBD
  - Rozelle
  - St Marys, Wollongong and Newcastle.
- For 1,3-butadiene and 4-ethyltoluene, average concentrations fall into two statistically different groups from higher to lower:
  - Sydney CBD
  - Rozelle, St Marys, Wollongong and Newcastle.

- For Freon 12, average concentrations fall into three statistically different groups from highest to lowest:
  - Sydney CBD
  - Rozelle and Newcastle
  - St Marys and Wollongong.

Differences in average concentrations between sites were **not** found for 1,3,5-trimethylbenzene, styrene, tetrachloroethylene, trichloroethylene, Freon 11, dichloromethane, chloromethane, Freon 113, 1,1,1-trichloroethane or carbon tetrachloride.

Eight of the nine compounds with statistically significant spatial differences are primarily associated with motor vehicles. Note that although these eight compounds fall into three statistical groupings, the groupings are very similar, with concentrations in the Sydney CBD being statistically higher in each group. Several other national and international studies have also reported higher concentrations of benzene, toluene and xylenes in the CBD as opposed to urban and rural sites (ETC 1999; DEP WA 2000; UK DETR 2002).

Table 9 presents the distance of each site from the nearest road and the traffic volume on these roads. The Sydney CBD has less passing traffic than Rozelle, but the site is situated immediately next to the road, possibly explaining the higher concentrations at the Sydney CBD site. The site at St Marys is closer to the road than that at Rozelle, but with less passing traffic and consequently lower concentrations of these motor-vehicle-related compounds. From these data it can be seen that benzene concentrations are not only a function of traffic volume, but also depend on the distance of the measurement site from the road. The degree of traffic congestion can also affect the concentrations of benzene in ambient air, as vehicle emissions increase at lower speeds (US Department of Transportation 2002). Other factors affecting benzene concentrations include the type and age of vehicles and the fuel composition.

**Table 9: Traffic volumes near measurement sites in Sydney**

				Vehicle counts* 1999
Sydney CBD	2.3	George St	(Roadside)	23 225
		Market St	(Roadside)	14 492
Rozelle	1.1	Victoria Rd	(300 m)	85 550
		Balmain Rd	(300 m)	20 347
St Marys (South of M4)	0.4	Mamre Rd	(200 m)	12 153
		M4 freeway	(1 km)	(south of M4) 74 716

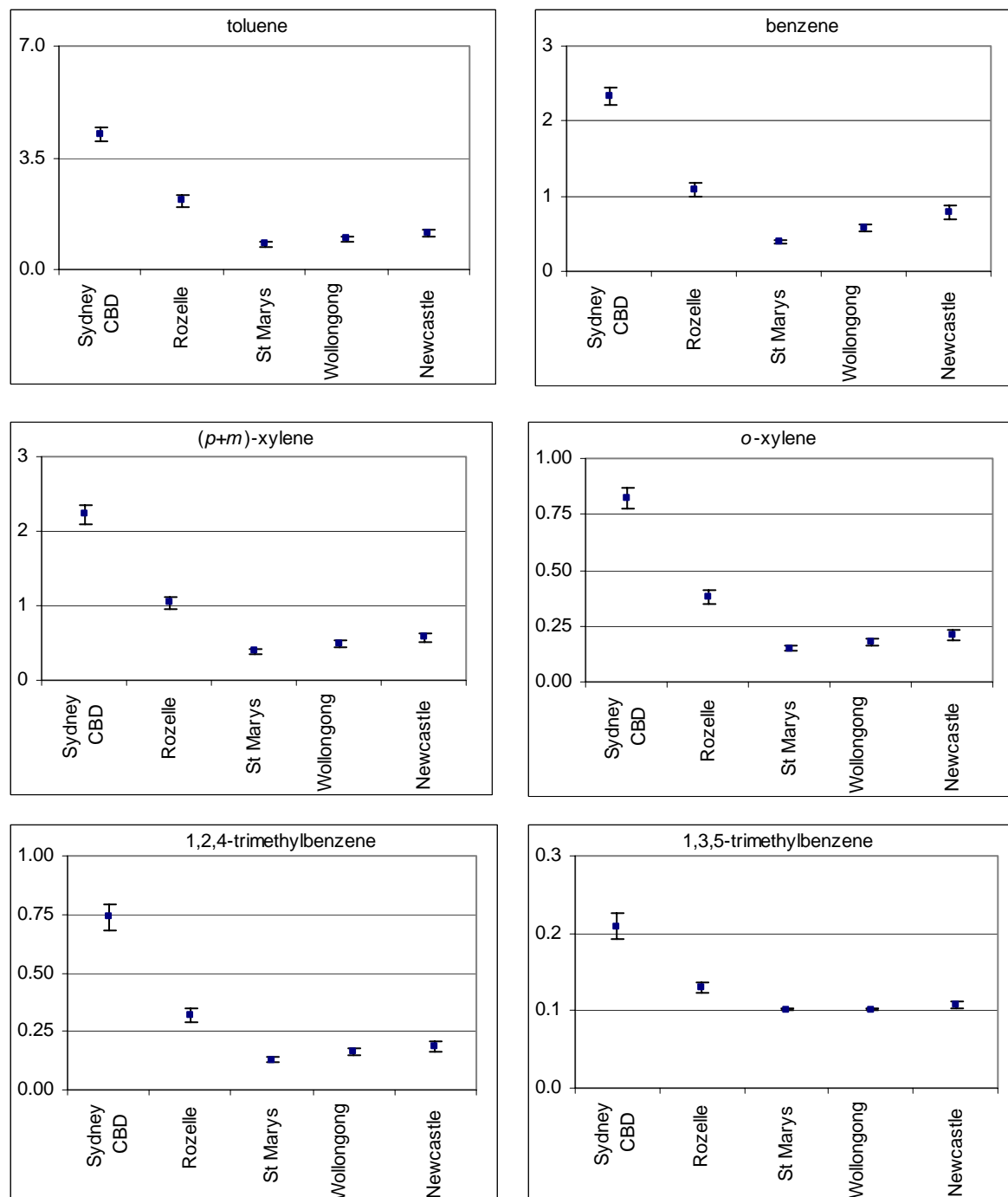
\* Annual average daily traffic

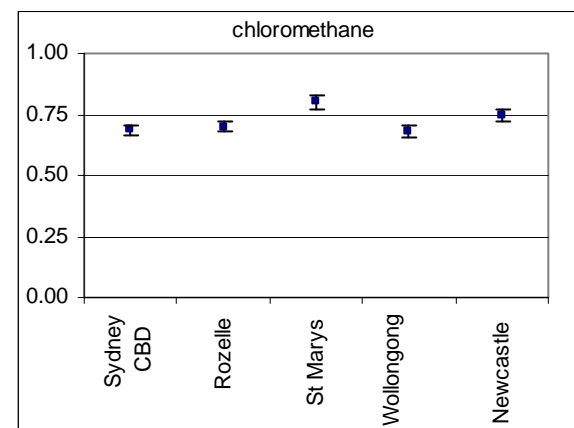
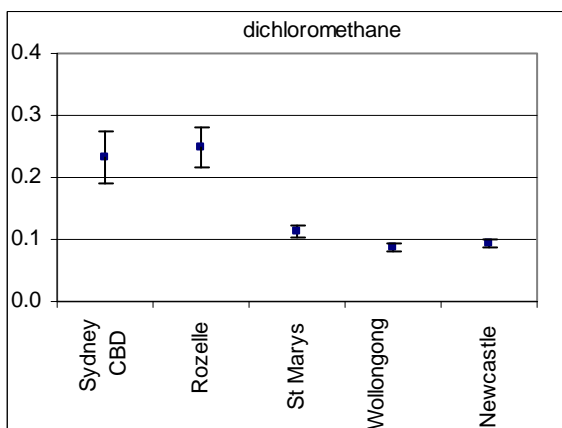
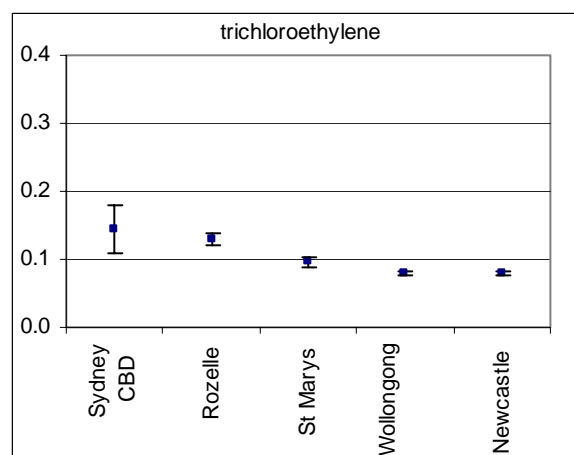
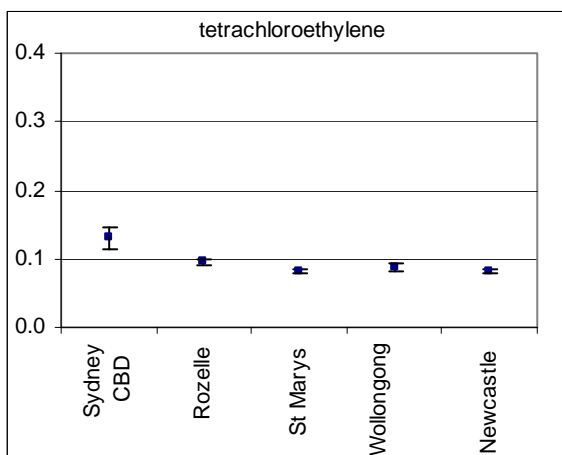
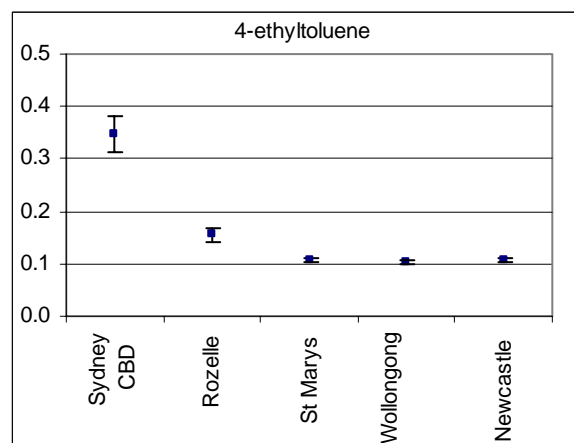
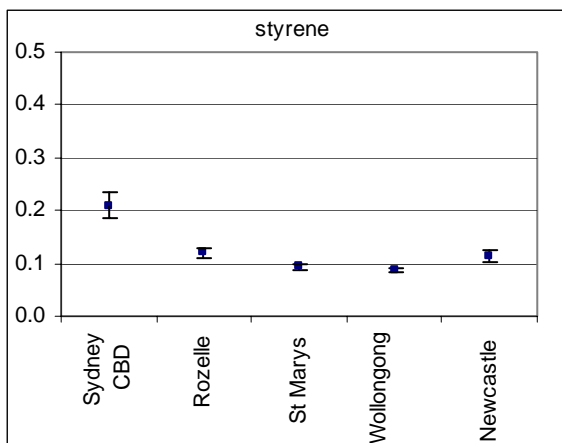
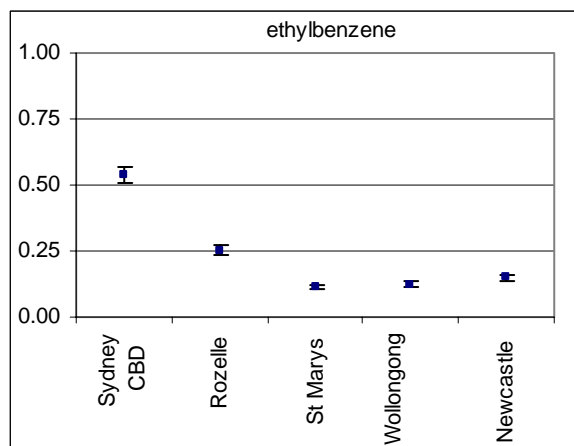
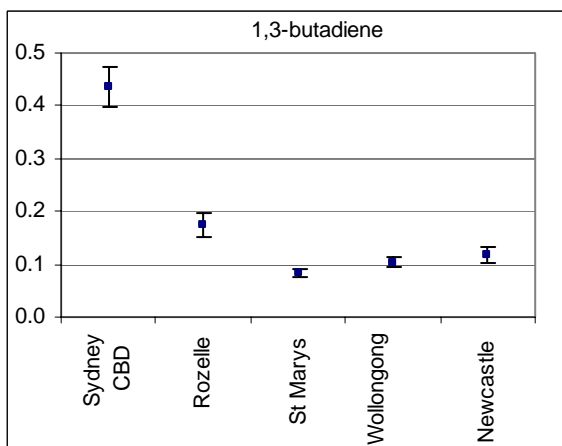
**Note:** Vehicle counts at Rozelle and St Marys are in real vehicle numbers e.g. a car and a semi-trailer are counted as two vehicles. Source: RTA NSW 2000.

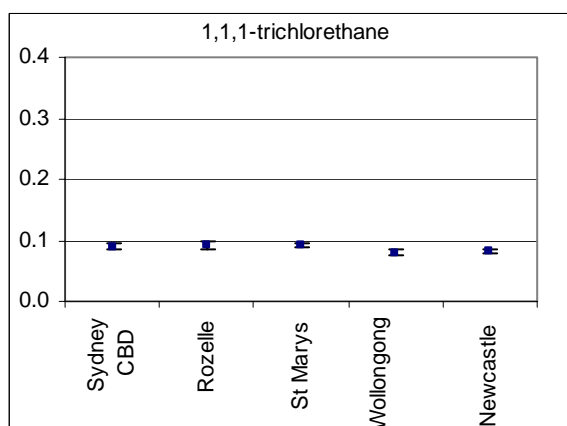
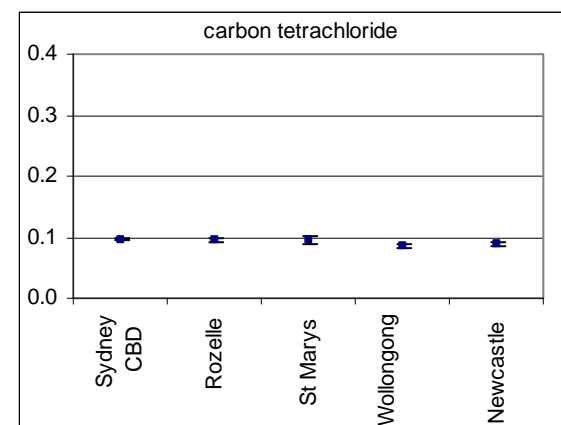
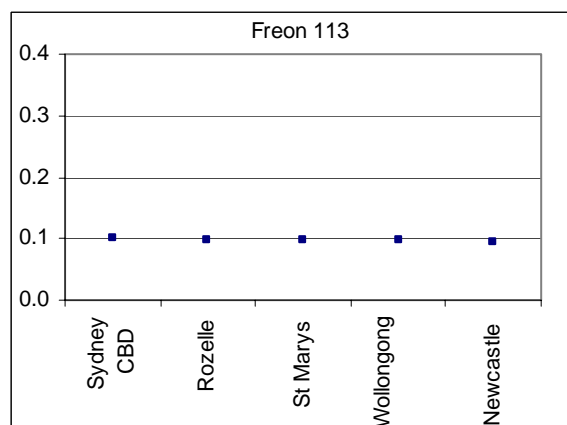
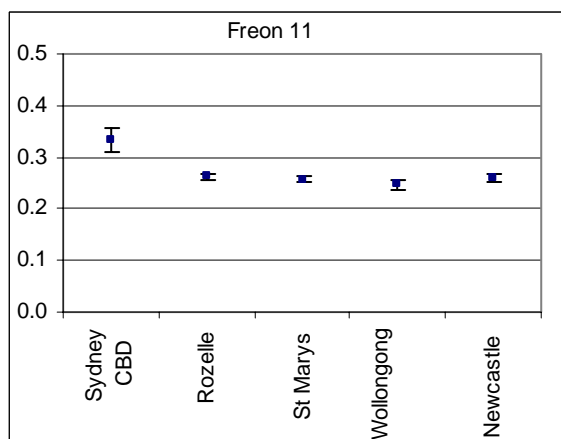
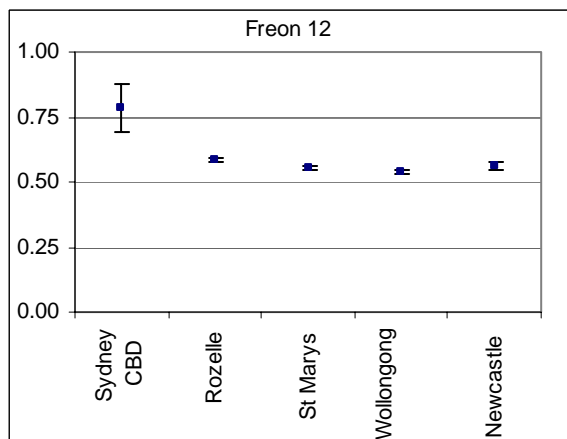
**Note:** Vehicle counts at Sydney CBD are based on 2000 data and are in axle-pairs, e.g. a semi-trailer is regarded to be equivalent to three cars in terms of the number of axle-pairs. Sydney CBD traffic volumes were derived from the RTA's Sydney Coordinated Adaptive Traffic System (SCATS).

The remaining compound (of the nine compounds showing statistically significant spatial differences), Freon 12, was also measured at concentrations statistically higher at the Sydney CBD site. The average concentrations found at this site are only slightly higher than global background concentrations (Figure 6), although a maximum concentration of 8.1 ppbV was measured (Figure 5a). The range of concentrations at the Sydney CBD site was also larger than at the other sites. The cause of the higher concentrations of Freon 12 at the Sydney CBD is not known but could be due to either the number of buildings in the CBD using older air conditioning equipment or older motor vehicles also using Freon 12 in the air conditioning systems. A study conducted in Perth found a similar trend for Freon 12, with higher concentrations at the city site than at other sites (DEP WA 2000).

**Figure 13: Overall averages and the upper and lower bounds of an 80% confidence interval for the average at each site (concentrations are in ppbV)**







### 3.8.2 Seasonal variability

Seasonal variations in concentrations of compounds can occur owing to different meteorological mechanisms and different rates of photochemical reactions. Winter meteorological conditions tend to lead to a reduction in mixing in the atmosphere due to stronger and more frequent temperature inversions. As a result, pollutants can be trapped in a shallow layer at the surface, leading to higher concentrations. This is often compounded by very still conditions, further limiting dispersion of pollutants.

Meteorological conditions in summer may also be conducive to lower concentrations of pollutants, as highly reactive compounds participate in photochemical reactions. Removal rates of benzene from the atmosphere are much lower in winter than in summer owing to the greater abundance of hydroxyl radicals in summer (ETC 1999).

Variations in emissions can also lead to seasonal differences in concentrations. For many compounds that are emitted by motor vehicles, cold starts in winter lead to longer periods of incomplete combustion and longer warm-up times for catalytic converters, leading to higher emissions. Pollutants sourced from domestic solid fuel heaters are clearly more prevalent in winter, owing to higher usage.

Appendix 12 presents the monthly average concentrations over the entire sampling period at each site for each of the detected compounds and the upper and lower bounds of an 80% confidence interval for the average.

Statistical analysis of the data set for each of the 19 detected compounds at each of the five primary sites found nine different seasonal patterns. The most prevalent pattern, found 74 times, is pattern O, with consistent concentrations across all seasons. The next most dominant pattern, found 10 times, is pattern A, with the highest concentrations occurring in winter and autumn and the lowest concentrations in spring and summer. Patterns A to E are similar, with statistically higher concentrations in winter and the lowest concentrations in summer. Patterns F and G are similar, with the highest concentrations in autumn. Pattern H occurred only once (i.e. for one compound at one site) and has the highest concentrations in summer. The statistical groupings of seasons for all patterns are presented in Table 10. The locations where each pattern occurred and the corresponding compounds are presented in Table 11. Higher concentrations during winter and autumn are likely to be attributable to meteorological conditions such as inversions, but may also be associated with an increase in sources such as solid fuel heaters.

**Table 10: Statistical groupings of seasons**

A				10
	winter, autumn	spring, summer		
O	No statistical difference in the seasons			74

**Table 11: Results of seasonal statistical analysis**

					Newcastle
	O	B	A	A	B
	O	A	A	A	B
( <i>p+m</i> )-xylene	E	A	A	D	B

Remaining 11 compounds	O	O
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**Note:** Entries in Table 11 refer to the key in Table 10 and indicate the seasonal pattern for the combination of site and compound.

Benzene, toluene and (*p+m*)-xylene showed the most consistent statistically significant differences between seasons, with higher concentrations measured in winter and autumn at all sites except in the Sydney CBD. A study conducted by the Department of Environmental Protection in Western Australia also found statistically significant seasonal variations in concentrations of benzene, toluene and xylenes measured at a suburban area north of Perth and no statistically significant seasonal differences in the concentrations of benzene at the Perth CBD site. At the Perth CBD site the concentrations of toluene were higher in winter, but not statistically significantly higher than in summer (DEP WA 2000). A study conducted by the South Coast Air Quality Management District in California, USA, also reported higher concentrations in winter than in summer for benzene, 1,3-butadiene, tetrachloroethylene and dichloromethane. This pattern was attributed to seasonal meteorological conditions resulting in light winds and surface temperature inversions trapping the pollutants. An increase in 1,4-dichlorobenzene in summer and autumn was also observed (SCAQMD 2000). Seasonal differences in concentrations of benzene have also been found in a measurement study conducted at various sites in Canada. Lower concentrations of benzene were found in summer, and the highest concentrations in winter were recorded at all sites. These differences were attributed to seasonal differences in emission rates, meteorological conditions and the rate of removal of benzene from the atmosphere.

Statistically higher concentrations of *o*-xylene, 1,2,4-trimethylbenzene and ethylbenzene were also found in winter and autumn at Rozelle. Concentrations of 1,2,4-trimethylbenzene were highest in autumn at the Sydney CBD site. Seasonal differences were also found for 1,2,4-trimethylbenzene, with the lowest concentrations found in summer at both the city and suburban sites in Perth (DEP WA 2000).

Despite the Sydney CBD site having statistically higher concentrations than the other sites, less seasonal variations were found. The Sydney CBD site is located within a street canyon and is therefore within the friction layer associated with the buildings, and mixing is determined by flow in and around them. As a consequence, it is likely that the seasonal variation in mixing height has little influence on pollutant concentrations at this site. Seasonal sources such as solid fuel heaters may also play a less important role in the Sydney CBD.

Pattern G, with the highest concentrations in autumn then summer and the lowest concentrations in winter, was found for chloromethane at St Marys. The reason for this observed pattern is not known. Figure 13 shows that the concentrations of chloromethane



were also slightly higher at St Marys than at the other sites (although not statistically significantly higher).

Pattern H is characterised by higher concentrations in summer. This is opposite to the general trend of higher concentrations in winter and autumn. This pattern was found only once with concentrations of Freon 11 being highest in summer at the Sydney CBD site. The cause of this is not known but could be due to a higher proportion of older buildings with air conditioning equipment that still contain Freons or from motor vehicles with Freons in the air conditioning system. Figure 13 shows that there are slightly higher concentrations of Freon 11 at the Sydney CBD site in comparison with other sites (although not statistically significantly higher). Note that Freon 12 was found to be statistically significantly higher at the Sydney CBD site (section 3.8.1), but was not higher in summer.

Pattern O, with no statistical difference in concentrations between seasons, was the most predominant pattern found in this study. While a statistical difference was not found between seasons, some compounds, such as 1,3-butadiene at Rozelle, were found at slightly higher concentrations in winter (see Appendix 12).

Peaks of 1,2,4-trichlorobenzene and 1,1,1-trichloroethane were found in spring in the Perth study (DEP WA 2000). These two compounds were detected in samples collected at the Perth CBD site and at an urban site in Perth in more than 25% and 50% of samples respectively, but were detected in fewer than 5% of samples in NSW. No seasonal differences for these two compounds were found in NSW.

### 3.8.3 Winter-to-summer ratios

Winter-to-summer ratios can be used to demonstrate seasonal differences in concentrations of individual organic pollutants. A ratio greater than one indicates that concentrations are higher in winter, and a ratio less than one represents higher concentrations in summer. Winter-to-summer ratios at each of the measurement sites for compounds with an overall frequency of detection of more than 50% are presented in Table 12.

**Table 12: Winter-to-summer ratios for compounds with an overall frequency of detection of >50%**

					Newcastle
benzene	1.1	2.9	1.7	1.8	2.8
toluene	1.2	2.6	1.8	1.8	2.6
( <i>p+m</i> )-xylene	1.2	2.7	2.1	2.0	2.9
<i>o</i> -xylene	1.2	2.5	1.9	1.9	2.5
ethylbenzene	1.2	2.6	1.5	1.6	2.2
1,2,4-trimethylbenzene	1.1	2.4	1.5	1.8	2.6
4-ethyltoluene	1.1	1.7	1.1	1.0	1.2
Freon 11	0.7	1.1	1.0	1.1	1.1
Freon 12	1.5	1.1	1.0	1.0	1.1
chloromethane	1.0	1.1	0.8	0.9	1.1

Table 12 shows that winter-to-summer ratios at Rozelle and Newcastle are greater than two for many compounds, representing higher concentrations in winter. The Sydney CBD ratios are closer to one for all compounds, indicating that there is little variation between concentrations in winter and summer. For example, the ratio for benzene in the Sydney CBD was 1.1, while ratios at Rozelle and St Marys were 2.9 and 1.7 respectively. Data collected during 1998 in the UK also showed that the winter-to-summer ratios for benzene were closer to one for the roadside site (Marylebone Rd, London), with a ratio of 1.3, while the ratio at the suburban site (Eltham) was 1.7 and at the rural site (Harwell) was 1.9 (UK DETR 2002).

In a Canadian study conducted during 1990–1997, winter-to-summer ratios for benzene were approximately three at all rural, suburban and urban sites (ETC 1999). Both the UK and Canada have climate features that are similar to those of NSW, with winter being the coldest and most stable time of year, and summer being the warmest and most convective. Both studies found similar winter-to-summer ratios to those found in NSW.

### 3.8.4 Annual variations

Data collected over several years are required for analysis of trends over time. Trends over time can occur owing to changes in emissions from sources, changes in reduction strategies or changes in meteorological patterns.

Statistical analysis for annual variations was conducted on the data set collected at the five primary sites. Data collected during 2001 were excluded from the annual variation analysis only, as the full year of data was not yet available. Other years excluded from analysis owing to the low number of samples collected are annotated in Table 13. For example, the data collected at the Sydney CBD site during 1999 and 2000 were excluded on account of the low number of samples collected owing to site relocation. Note that analysis for 1,3-butadiene began in 1998.

Annual average concentrations and the upper and lower bounds of an 80% confidence interval for the average for each site and each compound are presented in Appendix 13. Only those compounds detected in greater than 1% of samples have been plotted. Table 13 presents the number of samples collected each year at each site.

**Table 13: Number of samples collected each year**

					Newcastle
1996	33	38	17*	NA	NA
1997	56	53	51	18*	20*
1998	48	56	52	45	50
1999	4*	50	34	37	39
2000	28*	51	53	47	43

\* Excluded from the annual variation analysis owing to low sample numbers.

Table 14 presents the results of the statistical analysis of trends over time. The locations and the corresponding compounds for which statistically significant differences in concentrations between years were found are presented along with the statistical groupings of years (based on concentration).

Table 14 shows that there were only eight occurrences (out of a possible 95) where there were statistical differences in concentrations between years. Therefore, most compounds at each site were present at consistent concentrations between years. For example, no statistically significant differences in concentrations between years were found at Rozelle or Wollongong for any compound. Only one compound at Newcastle (*o*-xylene) and St Marys (*p+m*-xylene) showed a downward trend.

Statistical differences in concentrations across the years were found for six compounds at the Sydney CBD site. For example, there was a significant difference between concentrations of xylenes and ethylbenzene between 1996–97 and 1998, suggesting a possible downward trend. The exclusion of 1999 and 2000 data for this site prevents analysis of a continuing downward trend. This downward trend could be attributed to a change in the motor vehicle fleet, traffic volumes or meteorology.

Many international studies have found trends over time, but the conclusions in these studies are based on a greater number of years. For example, in Canada there has been a reduction in benzene concentrations since 1989 (ETC 1999). The California Air Resources Board (CARB) has also reported that concentrations of 1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene and trichloroethylene in California have been reduced significantly since 1990 (SCAQMD 2000).

**Table 14: Results of statistical analysis of trends over time**

		Lowest
Sydney CBD 1,2,4-trimethylbenzene	1997	1996, 1998
Sydney CBD 1,3,5-trimethylbenzene	1997	1996, 1998
Sydney CBD ethylbenzene	1996, 1997	1998
Sydney CBD <i>o</i> -xylene	1996, 1997	1998
Sydney CBD ( <i>p+m</i> )-xylene	1996, 1997	1998
Sydney CBD 4-ethyltoluene	1997	1996, 1998
St Marys ( <i>p+m</i> )-xylene	1997, 1998	1996, 1999, 2000
Newcastle <i>o</i> -xylene	1998	1999, 2000

## 4. Conclusions

The NSW EPA has taken measurements of 41 organic compounds in the Sydney CBD (peak site), Rozelle (inner urban), St Marys (outer urban), Wollongong (Illawarra regional centre) and Newcastle (lower Hunter regional centre). A supplementary study undertaken in the lower Hunter and Illawarra regions confirmed the selection of Newcastle and Wollongong as being representative of the highest concentrations in each region.

The annual average concentrations of organic air toxics measured in this study, which were generally representative of urban parts of the Sydney–Newcastle–Wollongong area, were very low. Many of the commonly recognised organic air toxics were not detected in any samples.

Most of the detected compounds are primarily generated by motor vehicles. Concentrations of benzene and 1,3-butadiene were below the UK (2003) goal for these compounds at all sites<sup>3</sup>. Only one site, the Sydney CBD, exceeded the longer-term (2010) European Commission goal for benzene. The measured results for benzene and 1,3-butadiene in this study are broadly consistent with concentrations measured in comparable locations within Australia and overseas.

Ozone-depleting substances no longer in production or use were found at concentrations that were not significantly higher than those at remote sites in Tasmania and Alaska. Concentrations of chloromethane from natural, domestic and industrial sources were also only slightly higher than the global background concentrations measured at remote sites internationally.

The three compounds emitted mainly by industry—tetrachloroethylene, trichloroethylene and dichloromethane—were measured at low concentrations.

Statistical analysis of the data from the five primary sites found the following, particularly for those compounds associated with motor vehicle emissions:

- Spatial patterns: Higher average concentrations were found in the Sydney CBD followed by Rozelle. Concentrations at Newcastle and Wollongong were similar to those at St Marys.
- Seasonal patterns: Most of the detected organic compounds were at a consistent concentration over the seasons, but for some pollutants outside the CBD, higher average concentrations were measured in winter and autumn.
- Annual variations: Most of the detected organic compounds were at a consistent concentration over the years. A slight downward trend over time was found for some compounds at the Sydney CBD site.

While the results of this study are reassuring about the presence of organic air toxics in Sydney and the Illawarra and lower Hunter regions, the data do not allow for complacency on benzene and 1,3-butadiene. International agencies recognise benzene as a human carcinogen, and 1,3-butadiene is categorised as a probable human carcinogen. Health-based recommendations from these agencies suggest that current goals may need to be reduced further to control the risks posed by these two substances. Air quality programs aimed at reducing the contribution of these substances from all sources will remain a priority, to maintain compliance with the longer-term international standards for these substances.

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<sup>3</sup> Since the publication of the summary report (NSW EPA 2002), the UK Government (DEFRA 2003) have reviewed their benzene standard and adopted the following new objectives to be achieved by the end of 2010:

- an annual average of 1.5 ppbV for England and Wales
- a running annual average of 1 ppbV for Scotland and Northern Ireland.

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## Appendix 1 Compound names

	Common name
1,1,1-trichloroethane	methyl chloroform
1,1,2,2-tetrachloroethane	tetrachloroethane
1,1,2-trichloro-1,2,2-trifluoroethane	Freon 113
1,1,2-trichloroethane	trichloroethane
1,1-dichloroethane	ethylidene dichloride
1,1-dichloroethene	vinylidene chloride
1,2,4-trichlorobenzene	1,2,4-trichlorobenzene
1,2,4-trimethylbenzene	pseudocumene
1,2-dibromoethane	1,2-dibromoethane
1,2-dichloro-1,1,2,2-tetrafluoroethane	Freon 114
1,2-dichlorobenzene	<i>o</i> -dichlorobenzene
1,2-dichloroethane	ethylene dichloride
1,2-dichloropropane	1,2-dichloropropane
1,3,5-trimethylbenzene	mesitylene
1,3-butadiene	1,3-butadiene
1,3-dichlorobenzene	<i>m</i> -dichlorobenzene
1,4-dichlorobenzene	<i>p</i> -dichlorobenzene
3-chloropropene	
4-ethylmethylbenzene	4-ethyltoluene
benzene	benzene
bromomethane	methyl bromide
chlorobenzene	chlorobenzene
chloroethane	ethyl chloride
chloroethene	vinyl chloride
chloromethane	methyl chloride
<i>cis</i> -1,2-dichloroethene	<i>cis</i> -dichloroethylene
<i>cis</i> -1,3-dichloropropene	<i>cis</i> -1,3-dichloropropylene
dichlorodifluoromethane	Freon 12
dichloromethane	methylene chloride
ethylbenzene	ethylbenzene
hexachloro-1,3-butadiene	hexachlorobutadiene
<i>m</i> -xylene	1,3-xylene
<i>o</i> -xylene	1,2-xylene
<i>p</i> -xylene	1,4-xylene
styrene	styrene
tetrachloroethene	tetrachloroethylene
tetrachloromethane	carbon tetrachloride
toluene	toluene
<i>trans</i> -1,3-dichloropropene	<i>trans</i> -1,3-dichloropropylene
trichloroethene	trichloroethylene
trichlorofluoromethane	Freon 11
trichloromethane	chloroform

\* International Union of Pure and Applied Chemistry

**Source:** Lide 1992; Ash & Ash 1994; Merck Index 1996; CARB 1997; NIST 2000



## Appendix 2 Sources and uses

	Sources and uses
1,1,1-trichloroethane	<b>No longer sold or manufactured in Australia, but may still exist in old equipment etc.</b> Used in cold-type metal cleaning and in cleaning plastic moulds. Solvent for natural and synthetic resins, oils, waxes, tars, alkaloids, adhesives and coatings. Dry cleaning agent; coolant and lubricant in metal cutting oils; extraction solvent; component of inks and drain cleaners; in aerosols. Cleaning of electrical equipment, motors and photographic film. An intermediate for 1,1-dichloroethene.
1,1,2,2-tetrachloroethane	A non-flammable solvent for fats, waxes, oils and rubber. Used in the manufacture of paint, bleach, varnish, rust removers, artificial silk and artificial pearls. A component of some weed killers and insecticides. Used for cleansing and degreasing metals. In paint removers, cement, lacquers and photographic film. A moth-proofing agent for textiles; a solvent in the preparation of adhesives. Recently, it has been used in the estimation of water content in tobacco and many drugs. An intermediate for trichloroethene and tetrachloroethene.
1,1,2-trichloroethane	Used in rubber and heavy equipment manufacturing, the timber products industry, the chemicals industry, the plastics and synthetics industries, the electronics industry and laundries. Used by manufacturers of fabricated metal parts. A solvent for fats, waxes, natural resins and alkaloids. In adhesives, lacquer and coating formulations, and used in the production of Teflon tubing. An intermediate in the production of 1,1-dichloroethene.
1,1-dichloroethane	A solvent for plastics, oils and fats. A cleaning agent, degreaser, fumigant and insecticide spray. Used in fabric spreading, fire extinguishing, medication, paint, varnish, paint removers and rubber cementing. An intermediate in the production of chloroethene and 1,1,1-trichloroethane.
1,1-dichloroethene	Used in the plastics industry and in adhesives. A component of synthetic fibre. An intermediate in the production of chloracetyl chloride.
1,2,4-trichlorobenzene	Solvent in chemical manufacturing, dyes, synthetic transformer oils, lubricants and insecticides. In degreasing agents, septic tank and drain cleaners, wood preservatives and abrasive formulations. A heat-transfer medium.
1,2,4-trimethylbenzene	Occurs naturally in coal tar and in many petroleum-based products. Used in the manufacture of dyes, perfumes, resins and pharmaceuticals. Used for sterilising catgut; a solvent and paint thinner.
1,2-dibromoethane	Used in anti-knock gasoline and waterproofing preparations. A solvent for resins, gums, and waxes. A chemical intermediate in the synthesis of dyes and pharmaceuticals. A fumigant and a scavenger for lead in gasoline.

	Sources and uses
1,2-dichlorobenzene	A solvent for waxes, resins, tars, rubbers and oils. A herbicide, insecticide, soil fumigant, solvent in motor-oil additive formulations and a degreasing agent for metals, leather and wool. In paints, paint removers, firearm cleaners and repellents. Used for industrial odour control and for removing lead and carbonaceous deposits from engine parts. A component of rust-proofing mixtures and metal polishes. An intermediate in the manufacture of dyes and for organic synthesis of pesticides.
1,2-dichloroethane	A solvent for fats, resins, asphalt, bitumen, oils, waxes and rubber and for processing pharmaceutical products. In paint, varnish and finish removers, soaps and scouring compounds, degreaser compounds, rubber cement, acrylic adhesives and medication. Used in photography and water softening; a fumigant; dry cleaning agent; a lead scavenger in anti-knock gasoline. Used in the leather cleaning and metal cleaning industries. Used in the production of chloroethene, trichloroethene, nylon, viscose rayon, 1,1-dichloroethene, 1,1,2-trichloroethane and styrene-butadiene rubber and cosmetics. In motor vehicle emissions. Emitted by plastic, chemical, paint and varnish manufacturing facilities and by refineries making leaded petrol.
1,2-dichloropropane	A solvent for fats, oil and waxes. In dry cleaning fluids and insecticidal fumigant mixtures. Used for degreasing. A solvent in plastics and resins; a lead scavenger for anti-knock fluids; spotting agent. An intermediate for tetrachloroethene and tetrachloromethane and used in rubber processing.
1,3,5-trimethylbenzene	Occurs naturally in coal tar and in petroleum crudes. A solvent and paint thinner. An important stabiliser (antioxidant) for plastics, adhesives, rubber and waxes. Emitted in motor vehicle exhaust.
1,3-butadiene	Used as a component in the manufacture of polymers such as synthetic rubbers, plastics and resins. Emitted in motor vehicle exhaust. A chemical intermediate in the production of many industrial materials. Emitted from petroleum refining and oil and gas extraction. Smoking tobacco, agricultural burning and bush or forest fires also result in emissions to air.
1,3-dichlorobenzene	Fumigant and insecticide
1,4-dichlorobenzene	Domestic use against clothes moths. Used in dyes. A deodorant for garbage and restrooms and an insecticidal fumigant. Used in the pharmaceutical industry. An intermediate in the production of plastics for electronic components and an intermediate in organic synthesis.
3-chloropropene	Synthesis of intermediates for manufacture of polymers, resins and plastics. Synthesis of pharmaceuticals and insecticides. An intermediate for diuretics.
4-ethyltoluene	A natural component of coal tar and of oil-derived products.

	Sources and uses
benzene	Obtained in the coking of coal and in the production of illuminating gas from coal. Produced during petroleum refining. A gasoline additive. A natural component of coal tar and of oil-derived products. Emitted in motor vehicle exhaust. Evaporation of fuels during petrol refilling and from vehicle fuel tanks. Releases to air from service stations, the rubber industry, chemical plants, footwear manufacturing. Used in the manufacture of detergents, pesticides, varnishes, lacquers, pharmaceuticals, dyes, plastics and resins. Used for printing and lithography, paint, rubber, dry cleaning, adhesives and coatings, detergents, preparation and use of inks. A thinner for paints and a degreasing agent. A solvent for waxes, resins, oils and natural rubber. In glues, household cleaning products and paint strippers. Used primarily as a raw material in the synthesis of styrene, phenol, cyclohexane, aniline, chlorobenzenes and other products. Present in crude oil, petrol and cigarette smoke. Occurs naturally in forest fires.
bromomethane	Used for degreasing wool and extracting oils from nuts, seeds and flowers. Used in food sterilisation for pest control in fruit, vegetables, dairy products, nuts, and grain. A solvent in aniline dyes and an insect fumigant. In leaded petrol and some treated logs and wood. Emitted by motor vehicles, refineries making leaded petrol, timber treatment facilities and plastics manufacturing facilities.
carbon tetrachloride	<b>No longer sold or manufactured in Australia, but may still exist in old equipment etc.</b> A solvent for fats, oils, varnishes, rubber, waxes and lacquers. A grain fumigant and pharmaceutical aid (solvent).
chlorobenzene	Used in manufacture of insecticides and phenol. An intermediate in the manufacture of dyestuffs. A solvent in the manufacture of adhesives, paints, polishes, waxes, pharmaceuticals and natural rubber. A dye carrier in textile processing; a tar and grease remover; a solvent in surface coatings and in surface coating removers.
chloroethane	A refrigerant; propellant in aerosols; solvent for phosphorus, sulfur, fats, oils, resins and waxes. In medication and insecticides. Used in the manufacture of dyes, drugs and perfumes. Evaporation from some landfills. Released in fumes from the burning of plastics and other materials.
chloroform	A solvent for fats, oils, rubber, waxes, resins; a cleansing agent; in fire extinguishers; in the rubber industry.
chloromethane	Used in the manufacture of fumigants, synthetic rubber, silicone resins, medication and timber products. A refrigerant; methylating agent, herbicide; an extractant for oils, fats and resins and a blowing agent for some polystyrene foams. Used in the plastics and stainless steel industries. A chemical intermediate for dichloromethane and trichloromethane.

	Sources and uses
<i>cis</i> -1,2-dichloroethene	A solvent for perfumes, dyes, lacquers, waxes, resins, fats, phenols, camphor and natural rubber. Used in the extraction of rubber and in the extraction of oils and fats from fish and meat. A refrigerant and an agent in retarding fermentation. Used in the manufacture of pharmaceuticals and artificial pearls. An intermediate for chlorinated compounds.
<i>cis</i> -1,3-dichloropropene	Used primarily in soil fumigants or as component of soil fumigant mixtures and an insecticide and fumigant.
dichloromethane	Used for paint stripping, degreening citrus fruits and degreasing. In adhesive and aerosol products. A fumigant. Solvent for plastic film, resins, adhesives and protective coatings. Used in the pharmaceutical industry and in furniture and chemical processing. A blowing and cleaning agent in the urethane foam industry. Emitted by plastic product manufacturers, manufacturers of synthetics, the electronics industry (electroplating, circuit board manufacturing and metal degreasing) and the paint industry. Used in commercial and household paint removal and electronics cleaners. A chemical intermediate for bromochloromethane and other chemicals. Does not occur naturally in the environment.
ethylbenzene	A solvent and a natural component of coal tar and of oil-derived products. Emitted from coal tar and petroleum processing facilities. A component of automotive and aviation fuels. Released from fuel filling and from vapours from motor vehicle fuel tanks. Used in the production of synthetic rubber. Present in tobacco smoke.
Freon 11	<b>No longer sold or manufactured in Australia, but may still exist in old equipment etc.</b> Used in aerosol propellants, air conditioning, solvents for the electronics industry, bedding and packaging. Used in the manufacture of cleaning compounds and in fire extinguishers. A refrigerant, a degreasing agent and a blowing agent in the production of polyurethane foams. Used in electrical insulation.
Freon 113	<b>No longer sold or manufactured in Australia, but may still exist in old equipment etc.</b> In aerosol propellants, fire extinguishers, air conditioning, cleaning fluids, bedding and packaging. Used for solvent drying. Dry cleaning solvent for all fabrics. Selective solvent in degreasing electrical equipment, photographic films, magnetic tapes, precision instruments, plastics, glass or metal components.
Freon 114	<b>No longer sold or manufactured in Australia, but may still exist in old equipment etc.</b> In air conditioning, solvents for the electronics industry, bedding and packaging. Used for cleaning and degreasing printed circuit boards and for extraction of volatile substances. A foaming agent in fire extinguishing and aerosols and a refrigerant in industrial cooling. Used in inhibiting metal erosion in hydraulic fluids, strengthening glass bottles, magnesium refining, medications (vet) and the preparation of explosives.

	Sources and uses
Freon 12	<b>No longer sold or manufactured in Australia, but may still exist in old equipment etc.</b> In aerosol propellants, air conditioning, refrigeration, solvents for the electronics industry, bedding and packaging. A leak-detecting agent and for freezing of foods by direct contact. Used in the manufacture of aerosols for cosmetics, pharmaceuticals, insecticides, paints and adhesives.
hexachloro-1,3-butadiene	A heat-transfer liquid, transformer fluid and hydraulic fluid. An intermediate for fluorinated lubricants.
<i>m</i> -xylene	A natural component of coal tar and of oil-derived products. Occurs in vehicle exhaust. Used in the manufacture of dyes, polyester and alkyl resins. A solvent for paints, coatings, adhesives and rubbers. In insecticides and aviation fuel.
<i>o</i> -xylene	A natural component of coal tar and of oil-derived products. Occurs in vehicle exhaust. Used in the manufacture of dyes. A solvent for paints, coatings, adhesives and rubbers.
<i>p</i> -xylene	A natural component of coal tar and of oil-derived products. Occurs in vehicle exhaust. Used in the manufacture of dyes. A solvent for paints, coatings, adhesives and rubbers. Used in the printing trade and in insecticides.
styrene	Emitted to air from industrial processes that use or manufacture styrene or where it is formed as a by-product. Used in the manufacture of plastics, synthetic rubber and resins. An insulator. Styrene polymerises with many other monomers and polymers to produce wide variety of plastics, paints and lacquers. Present in car exhaust and in combustion products such as cigarette smoke.
tetrachloroethylene	Used in dry cleaning, textile processing, degreasing metals. A component of aerosol laundry-treatment products, typewriter correction fluids and medications (vet). An insulating fluid and cooling gas in electrical transformers. A solvent and a chemical intermediate in the production of fluorocarbons.
toluene	A natural component of coal tar, crude oil and oil-derived products. A gasoline additive. Produced in the refining of petrol. Occurs in vehicle exhaust. Emissions from vapours and spillage of petrol, commercial and household painting and paint, tobacco smoke, and consumer products containing toluene. Emitted by the chemical industry, rubber manufacturers, the pharmaceutical industry, printing, manufacturers of paints, varnishes and lacquers. Naturally emitted from forest fires. In medication, explosives, insecticides and dyes. Used for metal degreasing and metal recovery. A solvent for paints, resins, oils, fats, lacquers, varnishes, rubber cement and perfumes and a thinner for inks. A cleaning agent for machinery and electrical equipment and a grain fumigant. Used in refrigerants. An intermediate for fluorocarbons and pesticides. Used in organic synthesis for chlorination of organic compounds.
<i>trans</i> -1,3-dichloropropene	Used primarily in soil fumigants. Used as a chemical intermediate and a corrosion inhibition agent.

Sources and uses	
trichloroethylene	A solvent for fats, waxes, resins, oils, rubber, paints and varnishes. Used for solvent extraction and in dry cleaning and metal degreasing. A diluent in paints and adhesives, a household cleaner and a carrier solvent for the active ingredients of insecticides and fungicides. Used in the manufacture of chemicals and pharmaceuticals, in the preparation of insecticidal fumigants and in textile processing. In medications. An intermediate in the production of pentachloroethane.
vinyl chloride	An adhesive for plastics and a refrigerant. Used in the manufacture of numerous products in building and construction, the chemical industry, the automotive industry, electrical wire insulation and cables, piping, industrial and household equipment, and medical supplies. Depended on heavily by the rubber, paper and glass industries. Used also in the plastics industry. A chemical intermediate for 1,1,1-trichloroethane.

(Merck Index 1996; CARB 1997; Vic EPA 1997)

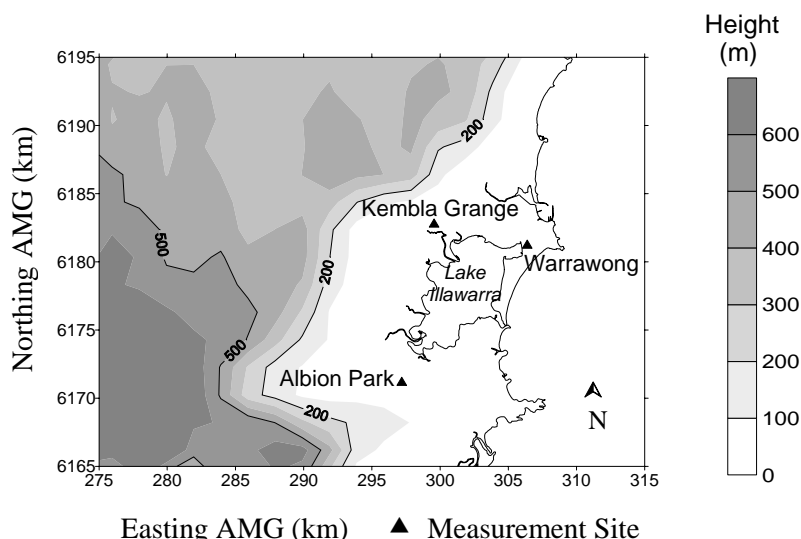
## Appendix 3 Atmospheric lifetimes

	Atmospheric lifetime
( <i>p+m</i> )-xylene	<i>m</i> - 14–15 hours <i>p</i> - 24–25 hours
1,1,1-trichloroethane	5.4 years
1,2,4-trimethylbenzene	11 hours
1,3,5-trimethylbenzene	5 hours (half-life)
1,3-butadiene	1–9 hours (half-life)
benzene	12 days
carbon tetrachloride	50 years
chloromethane	months to years
dichloromethane	100–500 days
ethylbenzene	2 days
Freon 11	50–150 years
Freon 113	50–150 years
Freon 12	50–150 years
<i>o</i> -xylene	25–26 hours
styrene	6 hours
tetrachloroethylene	3 months
toluene	2–4 days
trichloroethylene	6 days

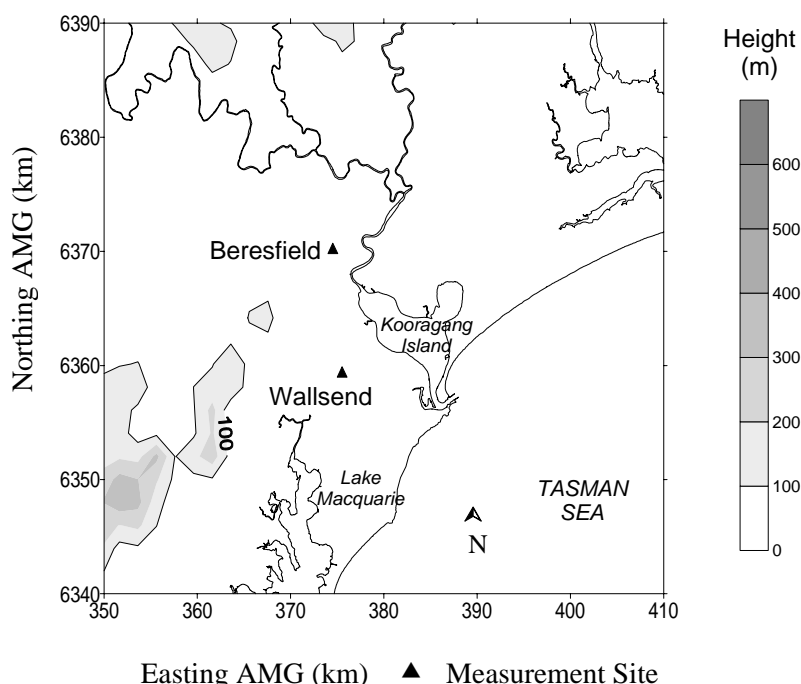
**Source:** CARB 1997; US EPA 2001

## Appendix 4 Supplementary study

A supplementary (although less intensive) sampling program was undertaken in the lower Hunter (Beresfield and Wallsend) and Illawarra regions (Albion Park, Kembla Grange and Warrawong), to confirm that the concentrations measured at the Newcastle and Wollongong sites were representative of the highest concentrations in each region. The supplementary site data could not be directly compared with the international annual average goals because of the shorter sampling period of three to four months at a time, rather than continuously throughout the year. One instrument was assigned to each region for this purpose and these were operated on a rotational basis. Although results at these sites do not represent annual averages, they do give an indication of the range of concentrations of air toxics in these regions. Figures A4.1 and A4.2 show the locations of the supplementary measurement sites and Table A4.1 provides descriptions of these sites.



**Figure A4.1: Supplementary measurement sites in the Illawarra region**



**Figure A4.2: Supplementary measurement sites in the lower Hunter region**



**Table A4.1: Supplementary measurement site descriptions**

		Description
Albion Park	Illawarra	Within the grounds of the Croom Sporting Complex (Croom Rd), surrounded by residential and rural areas.
Kembla Grange	Illawarra	Within the grounds of Kembla Grange Racecourse, surrounded by residential and rural areas and located approximately 500 m from the Princes Hwy and the Southern Freeway.
Warrawong	Illawarra	In the grounds of Darcy Wentworth Park (Carlotta Cres), within a residential area approximately 2 km south of the Port Kembla industrial area.
Beresfield	Lower Hunter	In the grounds of Francis Greenway High School, Lawson Ave, Woodberry, in a rural/residential area with no major roads nearby.
Wallsend	Lower Hunter	Within the grounds of the swimming pool located on the corner of Frances St and John St, in a residential/open area.

**A4.1 Number of samples**

Samples have been collected on a rotational basis at five sites (two in the Lower Hunter and three in the Illawarra region) as part of a screening survey of concentrations in each region from mid 1997 to mid 2001. A total of 317 samples were collected at these sites. The numbers of samples collected at each site are presented in Table A4.2.

**Table A4.2: Number of samples collected at the supplementary sites**

	Number of samples
Albion Park (Illawarra)	39
Kembla Grange (Illawarra)	61
Warrawong (Illawarra)	68
Wallsend (lower Hunter)	68
Beresfield (lower Hunter)	81

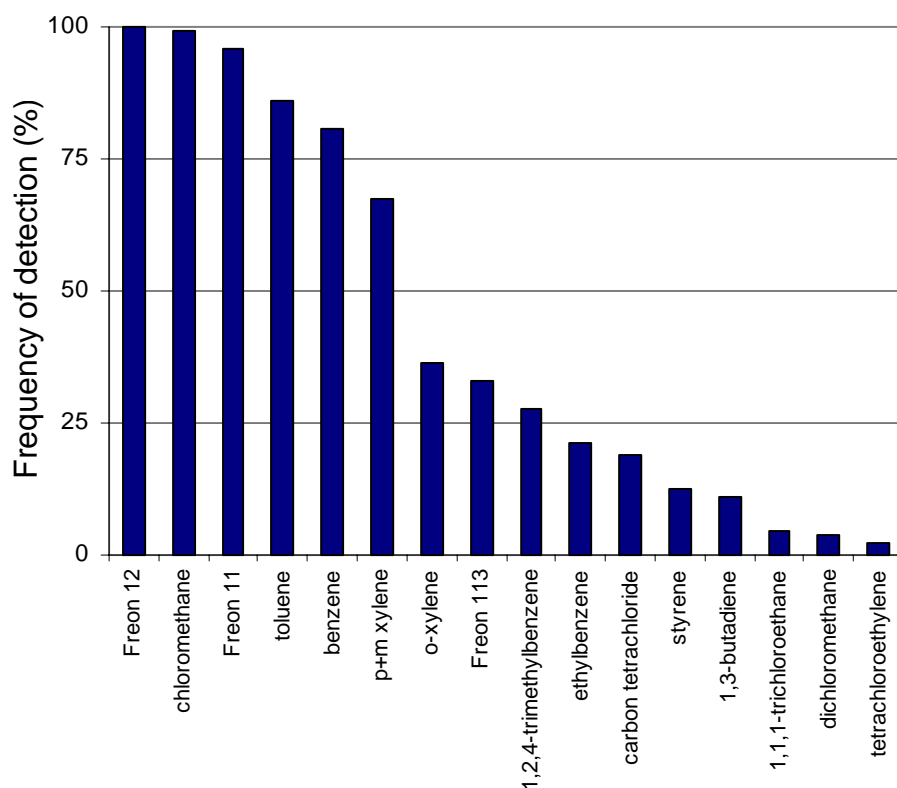
**A4.2 Frequency of detection**

Nineteen of the 41 targeted compounds were not detected in any of the samples collected at the supplementary sites, and a further six compounds were rarely encountered, being found in fewer than 1% of samples collected (Table A4.3).

**Table A4.3: Compounds never or rarely detected at the supplementary sites**

		Detected in <1% of samples
1,2-dichloroethane	1,2-dibromoethane	4-ethyltoluene
1,3-dichlorobenzene	1,2-dichlorobenzene	1,3,5-trimethylbenzene
vinyl chloride	1,2-dichloropropane	trichloroethylene
1,2,4-trichlorobenzene	1,4-dichlorobenzene	chloroform
1,1-dichloroethane	<i>cis</i> -1,3-dichloropropene	3-chloropropene
bromomethane	chlorobenzene	hexachloro-1,3-butadiene
<i>cis</i> -1,2-dichloroethene	chloroethane	
1,1,2,2-tetrachloroethane	Freon 114	
1,1,2-trichloroethane	<i>trans</i> -1,3-dichloropropene	
1,1-dichloroethene		

Figure A4.3 presents the cumulative frequency of detection for the remaining 16 compounds in all samples at the supplementary sites. The frequency of detection of each compound at each site both before and after the change in detection limits is presented in Appendix 7. Of the 16 compounds detected in more than 1% of samples, 12 are classified as US EPA hazardous air pollutants and eight are classified by the Commonwealth Government as priority air toxics.



**Figure A4.3: Frequency of detection at the supplementary sites in the Illawarra and lower Hunter**

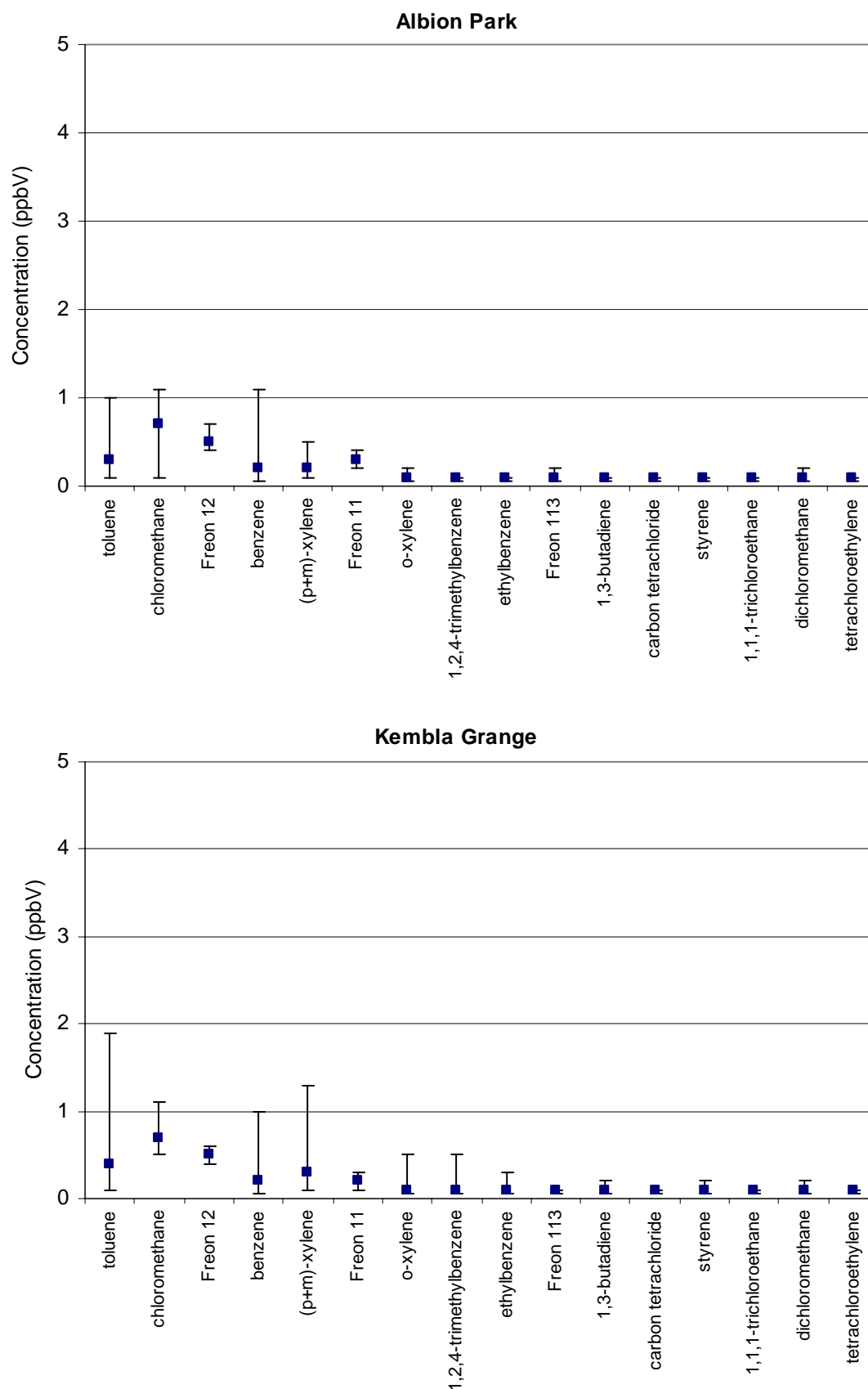
#### A4.3 Average concentrations

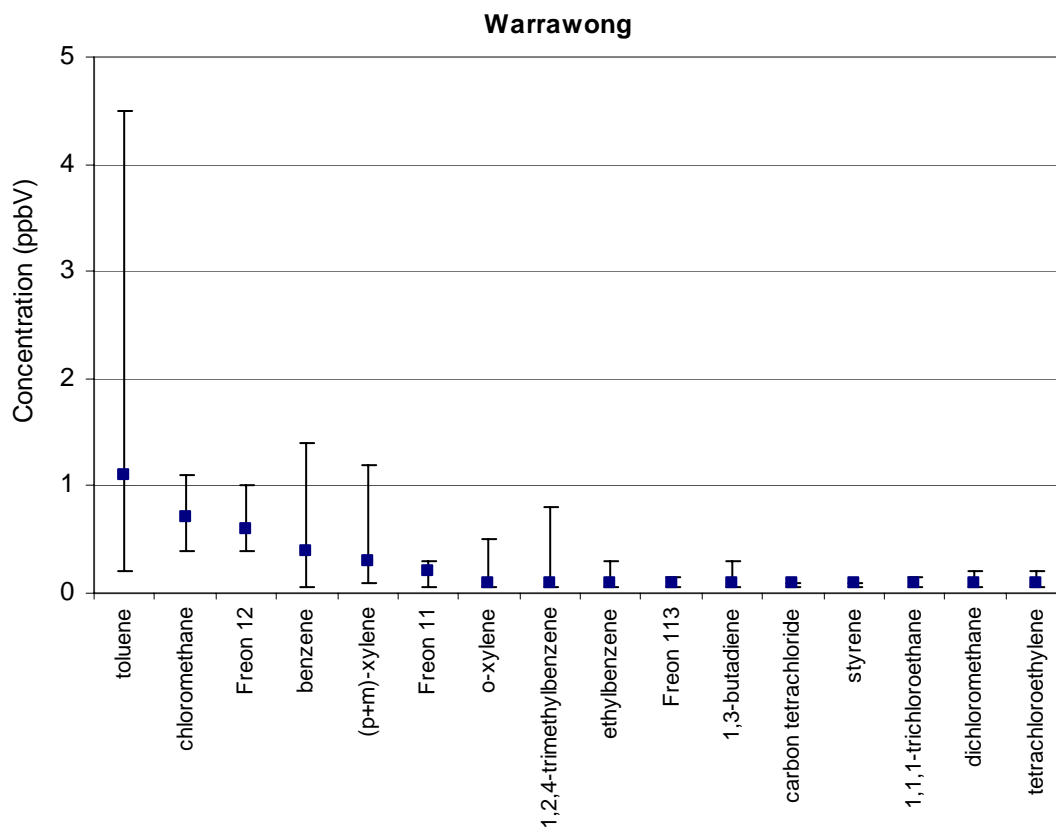
Figure A4.4 presents the overall average, minimum 24-hour and maximum 24-hour average concentrations (in ppbV) of the detected compounds measured at each of the five supplementary sites in the lower Hunter and the Illawarra. Many of the compounds were measured at very low concentrations often close to the detection limit of 0.2 ppbV (or 0.1 ppbV after 2000 for selected compounds). See Appendix 9 for further details.

The results of this work confirmed that the concentrations at the Newcastle and Wollongong sites were the highest in each region. The data from these five supplementary sites showed a range of concentrations comparable with those at the five primary sites.

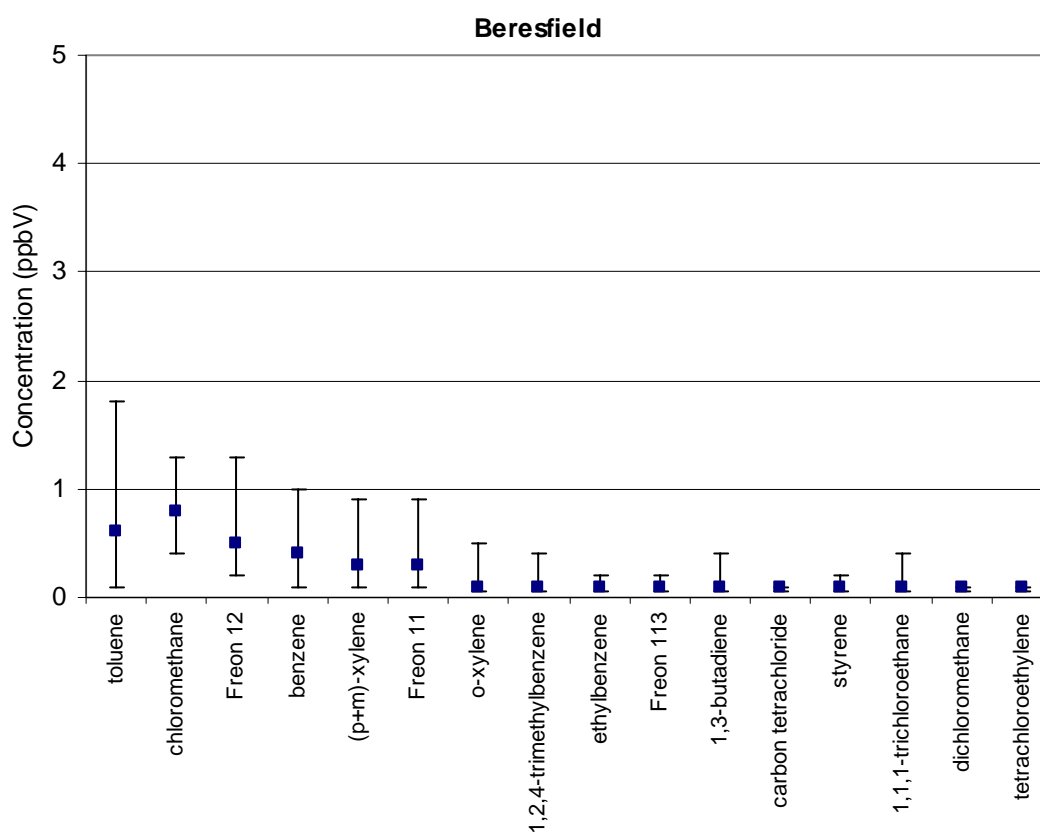
**Figure A4.4: Overall average, minimum 24-hour average and maximum 24-hour average concentrations measured at the supplementary study sites**

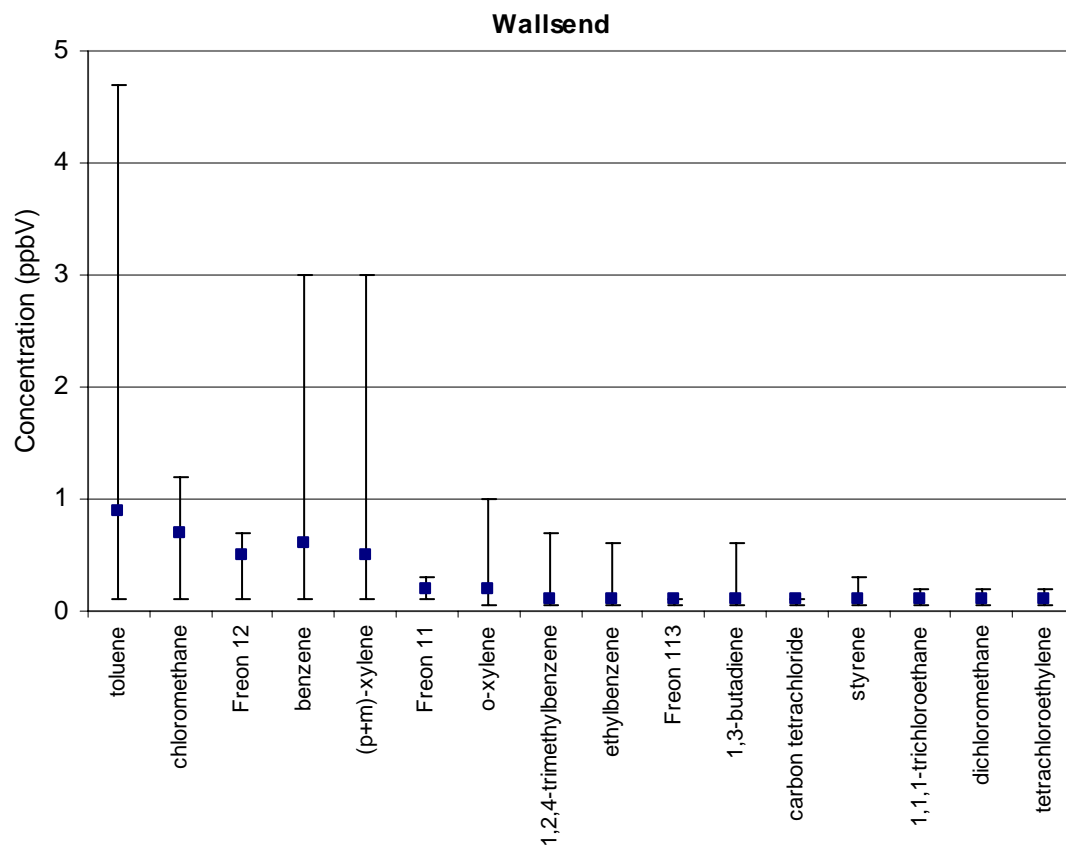
### Illawarra Region





## Lower Hunter Region





## Appendix 5 Sampling and analytical methods

The US EPA's TO-14 method was used for sampling and analysis. The NSW EPA gained accreditation from the National Association of Testing Authorities (NATA) for the analytical technique in 1996 and for sample collection in 1999.

Samples were collected using ambient volatile organic canister samplers (AVOCS).

The method is based on collection of air samples at a constant flow rate for a selected sampling time into a canister for subsequent laboratory analysis. A fan draws a stream of air into the system via a sampling wand. The air passes through a filter to reduce the amount of dust entering the system. A pump then draws the sample from this air stream at a constant flow rate of approximately 8 millilitres per minute, maintained by a flow controller. The sample flows to the output ports, where an evacuated Summa (Anderson Instruments Inc., Ohio, USA) or SilcoCan (Restek Corporation, Pennsylvania, USA) canister is attached so that the sample can be stored. At the end of the sampling period, the canister is sealed and transported to a laboratory for analysis. This is carried out as soon as possible after the samples are collected.

For each sample, the initial and final canister pressures and the initial and final flow rates were measured and recorded. To ensure quality control, final canister pressures were assessed against calculated pressures before analysis.

Stands were used to support the AVOCS units to place the air inlets approximately 1.5 m above ground level. At Wallsend, Kembla Grange, Wollongong, Warrawong and the Sydney CBD sites the units were placed on the roof of existing sheds or shop awnings. In these cases the samples were collected approximately 4 m from the ground.

Samples were analysed for the 41 organic compounds. In addition to the forty TO-14 compounds, and because of its possible health effects, 1,3-butadiene was included as a target compound for routine measurement. As 1,3-butadiene is not a target analyte specified in TO-14, the NSW EPA validated the TO-14 methodology for this compound (Linfoot and Chau 2000). 1,3-Butadiene has been included in the analysis since June 1998.

All samples were analysed by the NSW EPA. Field samples were analysed and quantified by gas chromatography / mass spectrometry (GC/MS) using a Varian (California, USA) GC (model 3400GC) with an ion trap, against certified standard gas mixtures in humid air. The standards used were traceable to the US National Institute of Standards and Technology. The standard gas mixture of forty target analytes, excluding 1,3-butadiene, was manufactured by Air Liquide (France) and had a concentration of 2 ppmV (parts per million by volume) for each analyte. 1,3-Butadiene was manufactured at 10 ppmV by Scott Specialty Gases (USA) and was added to all routine calibration standards. The instrument was calibrated monthly with four volatile organic compound (VOC) standard mixtures (0.5, 1.0, 5.0 and 10.0 ppbV).

Canisters were cleaned by repetitive evacuation and flushed with humid zero air or nitrogen, free of VOCs, as per TO-14, using an Entech canister cleaning system. The canisters were batch-certified free of VOC contamination if they contained less than 0.2 ppbV of each analyte. Canisters were also evacuated and checked for leaks. All AVOCS sampler units were similarly certified free of VOC contamination before release for field sampling.

In accordance with the TO-14 working procedure, the following quality assurance measures are practised:

- 20% of the samples are analysed in duplicate.
- Duplicate results must agree to within 20% or the samples are reanalysed.
- A 1 ppbV check-standard is run each day of sample analysis to demonstrate system calibration, and results must be within  $\pm 20\%$ .
- The GC/MS is tuned before calibration to verify that acceptable performance criteria are achieved. To meet this requirement, a 4-bromofluorobenzene tune standard was run on each day of analysis.

#### **A5.1 Variations to the limits of detection**

Until the end of 1999, the detection limit was 0.2 ppbV for each compound, as specified in Method TO-14. In 2000, the NSW EPA demonstrated that the limit of detection could be reduced from 0.2 ppbV to 0.1 ppbV for 27 of the 41 compounds (Table 3). The limit of detection for the remaining 14 compounds was unchanged.

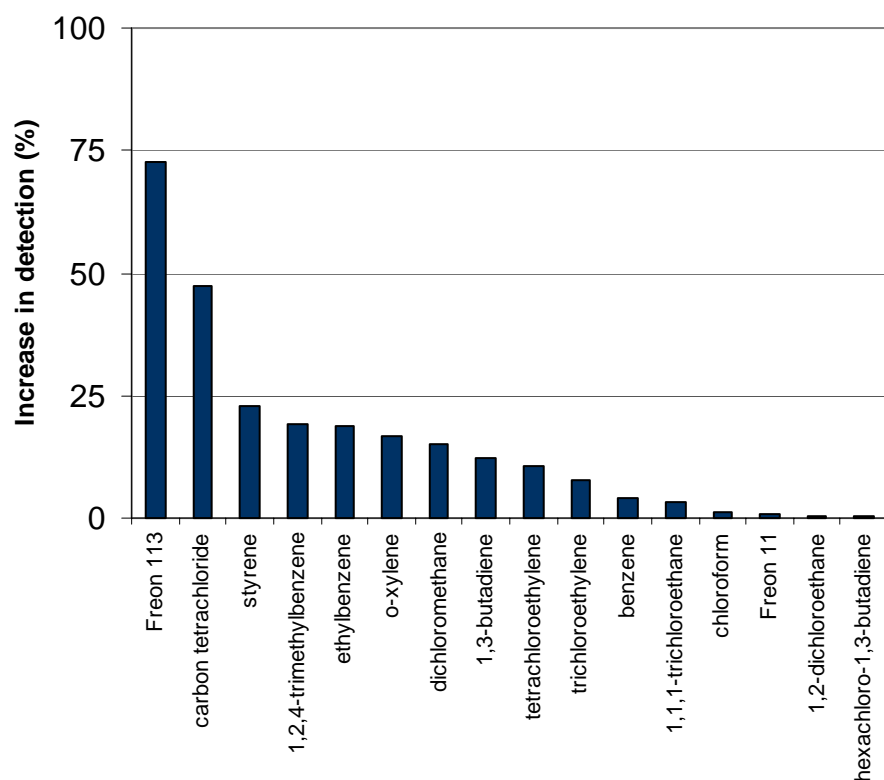
Owing to a minor and temporary instrumentation fault in 1999, the limit of detection was raised slightly above 0.2 ppbV for all compounds in three samples. These three samples were collected at Rozelle. The limit of detection was raised to 0.6 ppbV for two samples and 0.3 ppbV for the third sample. Owing to a similar fault in 2000, the limit of detection was raised slightly (to a maximum of 0.3 ppbV) for all compounds in one sample collected at St Marys. The calculation technique for non-detects (described in section 2.5) was applied to these data. In 2001 two samples collected at Beresfield had a slightly higher detection limit of 0.3 ppbV for some compounds.

In August 1999 the laboratory instrumentation used for analysis of samples (GC/MS ion trap) lost sensitivity to 1,2,4-trichlorobenzene, and so thereafter the limit of detection for this compound was raised to concentrations between 0.5 and 5 ppbV. This problem continued through to the end of 2000. 1,2,4-Trichlorobenzene was not detected above the raised limit of detection during this period. 1,2,4-Trichlorobenzene data from this period were excluded from average calculations.

The GC/MS system was contaminated with trace concentrations of Freon 12 from January to May 2000 and of Freon 11 from January to March 2000. Therefore, analysis for these compounds could not occur.

From January to July 2000, Freon 114 and 1,1,1-trichloroethane had a limit of detection of 0.05 ppbV. This limit of detection was subsequently raised to 0.1 ppbV. For consistency it was assumed that the detection limit was 0.1 for the whole year and concentrations were adjusted accordingly.

As outlined in section 2.5, the detection limit for several compounds was improved (lowered) at the beginning of 2000. Figure A5.1 shows the percentage increase in detection as a result of the improvement in the method (excludes data points over the original detection limit). This improvement in detection has had the largest advantage for Freon 113 and carbon tetrachloride, for which the benefit was seen in 73% and 48% of samples respectively.



**Figure A5.1: Percentage increase in detection as a result of improvement in method**



## Appendix 6 Uncertainty

When reporting scientific measurements, it is important to demonstrate the quality of the results by providing a measure of the confidence that can be placed on them. Reporting uncertainty is one method of providing this information. Uncertainty is defined as:

*a parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand*  
(EURACHEM/CITAC 2000)

Uncertainty refers to the normal variability that occurs when one is making repeated measurements of the same or similar properties. In the case of air toxics as measured in this report, uncertainty arises from two major areas:

- The processes associated with collecting the sample, called sampling uncertainty.
- The processes associated with the analytical measurements made in the laboratory, called analytical uncertainty.

To estimate the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source.

### A6.1 Sampling Uncertainty

In the measurements reported here, sampling uncertainty arises because:

- The air flow rate of the sampler can vary with temperature, so there is a tendency for a slightly greater proportion of the sample to be taken at night.
- The performance of the pressure sensors and flow controllers in the samplers can vary with time, so there may not be precisely the same mass of sample collected each time.
- Samples are collected every sixth day. The concentrations on other days are not known and so there is the issue of how well each sample represents the time period surrounding the sampling date.
- The concentrations of contaminants in the atmosphere vary from place to place. Sampling sites are selected so that the air mass that is sampled is generally representative of the air in the local area. However, it is not possible to guarantee that samples will be representative under all meteorological conditions.

Many of the above sources of uncertainty interact, and so it is not possible to provide reliable, deconvoluted estimates of each source of uncertainty. Rather, estimates may be made of the cumulative uncertainty from several sources combined. The US EPA thus reports sampling uncertainty to be in the range of 10%–20% (US EPA 1988).

Data collected during 1997 and 1998 have been examined to determine whether sampling uncertainty could be estimated. Using a ‘select, examine and replace’ technique (commonly known as ‘bootstrapping’), it was possible to calculate an estimate of the sampling uncertainty at each site. The results of this analysis for two compounds, benzene and toluene, are presented in Tables A6.1 and A6.2.

**Table A6.1: Annual mean concentrations with 95% confidence intervals of benzene derived from 24-hour samples (6-day cycle), in parts per billion ( $10^{-9}$ ) by volume (ppbV)**

				<i>n</i> *
Sydney CBD	2.7 (2.4, 3.0)	56	2.3 (2.1, 2.6)	48
Newcastle	0.6 (0.4, 0.8)	20	0.8 (0.7, 1.0)	50
Rozelle	1.2 (0.9, 1.4)	53	1.0 (0.9, 1.2)	56
St Marys	0.4 (0.4, 0.5)	51	0.4 (0.3, 0.5)	52
Wollongong	0.6 (0.5, 0.7)	18	0.6 (0.5, 0.7)	45

\* n = The number of individual 24-hour samples collected over the time period used to calculate the annual average concentration.

**Table A6.2: Annual mean concentrations with 95% confidence intervals of toluene derived from 24-hour samples (6-day cycle), in parts per billion ( $10^{-9}$ ) by volume (ppbV)**

				<i>n</i> *
Sydney CBD	4.9 (4.3, 5.4)	56	4.3 (3.9, 4.9)	48
Newcastle	0.9 (0.7, 1.2)	20	1.3 (1.0, 1.6)	50
Rozelle	2.4 (1.9, 3.0)	53	1.9 (1.6, 2.3)	56
St Marys	0.9 (0.8, 1.1)	51	0.8 (0.6, 0.9)	52
Wollongong	1.0 (0.8, 1.2)	18	0.9 (0.7, 1.2)	45

\* n = The number of individual 24-hour samples collected over the time period used to calculate the annual average concentration.

## A6.2 Analytical uncertainty

The NSW EPA has calculated analytical uncertainty according to a published process (EURACHEM 2000). The first step in this process is to identify the sources contributing to uncertainty. These sources have been identified as:

- the certified reference standard
- calibration of the GC
- uncertainty in syringe volume
- uncertainty in the pressure gauge readings
- variations in replicate analysis
- uncertainty in canister volume
- uncertainty in GC flow.

The uncertainty arising from these sources was quantified and expressed as standard deviations. The combined standard uncertainty and the expanded uncertainty were calculated according to published guidelines (EURACHEM 2000). At 1.0 ppbV, the expanded uncertainty was calculated to be  $\pm 0.14$  ppbV; it is not expected to show much change from this value as compound concentrations change.

### **A6.3 Cumulative sampling and analytical uncertainties**

Many of the compounds reported here are present at concentrations very close to the limit of detection. At these concentrations, the sampling and analytical variations become more significant in comparison with the value being measured. At higher concentrations, the variations are a much smaller proportion of the value being measured. Thus, at low concentrations, relative uncertainty is higher than when higher concentrations are being measured.

In general, where the concentration of a compound is close to the detection limit (0.2 ppbV), the overall uncertainty (i.e. sampling plus analytical uncertainty) is approximately 35%–40%; whereas when a compound is present at higher concentrations ( $>\sim 1.2$  ppbV), the overall uncertainty reduces to about 10%–15%.

## Appendix 7 Frequency of detection

The frequencies of detection of the target compounds, both before and after the 2000 change in the detection limits, at each of the primary and supplementary sites are presented in Tables A7.1 and A7.2 respectively. Compounds that were never detected at the primary and supplementary sites are presented in Table 5 and Appendix 4 respectively.

**Table A7.1: Primary sites—frequency of detection (% samples detected in)**

												post 2000
1,1,1-trichloroethane *	6	2	1	–	3	1	7	12	1	4	4	4
1,1-dichloroethane	1	–	–	–	–	–	–	–	–	–	–	–
1,2,4-trichlorobenzene	–	–	–	–	1	–	–	–	–	–	–	–
1,2,4-trimethylbenzene *	100	98	35	65	67	86	22	40	33	65	54	69
1,2-dichloroethane *	4	2	–	–	2	–	–	–	–	–	1	–
1,3,5-trimethylbenzene	65	27	6	4	18	9	1	–	2	1	20	7
1,3-butadiene *	97	100	15	25	29	51	8	12	11	25	30	39
1,3-dichlorobenzene	4	–	–	–	1	–	–	–	–	–	1	–
3-chloropropene	–	–	–	3	–	1	–	1	–	–	–	1
4-ethyltoluene	82	20	9	4	31	6	7	–	6	–	29	5
benzene *	100	100	94	100	99	100	81	98	93	100	94	99
bromomethane	1	–	–	–	–	–	–	–	–	–	–	–
cis-1,2-dichloroethene	–	–	–	–	–	–	–	–	–	1	–	–
carbon tetrachloride *	1	68	–	43	1	51	–	46	–	36	–	48
chloroform *	1	–	–	–	–	5	–	1	–	–	–	1
chloromethane	98	98	99	99	97	100	97	100	95	100	97	99
dichloromethane *	44	71	5	17	39	77	11	30	2	16	23	41
ethylbenzene *	99	100	27	48	59	81	19	37	20	49	48	61
Freon 11 *	98	100	94	100	94	100	92	100	89	100	94	100
Freon 113 *	1	85	1	71	–	75	–	78	–	71	–	76
Freon 12 *	100	100	99	100	99	100	100	99	100	100	100	100
hexachloro-1,3-butadiene *	–	–	–	1	–	1	–	–	–	–	–	1
o-xylene *	100	100	43	68	76	94	34	53	39	68	61	75
(p+m)-xylene	100	100	86	76	98	97	82	60	89	79	92	82
styrene *	61	80	17	33	15	37	7	13	1	26	21	35
tetrachloroethylene *	28	46	–	4	6	19	–	–	4	9	8	14
toluene	100	100	100	92	100	100	94	87	99	100	98	95
trichloroethylene *	23	34	–	–	22	38	3	16	–	–	12	17
vinyl chloride *	1	–	–	–	–	–	–	–	–	–	–	–

\* Detection limit lowered in 2000.

**Table A7.2: Supplementary sites—frequency of detection (% samples detected in)**

												post 2000
1,1,1-trichloroethane *	–	–	–	–	–	2	11	24	3	–	4	6
1,2,4-trimethylbenzene *	–	25	7	28	15	50	13	41	13	68	10	48
1,3,5-trimethylbenzene	–	–	2	–	5	–	–	–	–	–	1	–
1,3-butadiene *	–	–	–	11	38	13	6	15	5	26	5	15
3-chloropropene	–	–	–	–	–	2	–	–	–	–	–	1
4-ethyltoluene	–	–	–	–	5	–	–	–	–	3	1	1
benzene *	30	83	47	89	75	98	85	100	93	100	66	97
carbon tetrachloride *	–	58	–	28	–	40	–	53	–	29	–	40
chloroform *	–	–	–	–	–	–	–	3	–	3	–	1
chloromethane	93	100	100	100	100	100	100	100	100	97	99	99
dichloromethane *	7	–	–	11	–	8	–	–	–	11	1	7
ethylbenzene *	–	25	12	28	5	38	4	26	17	50	8	36
Freon 11 *	100	100	79	100	100	97	98	100	93	100	93	99
Freon 113 *	–	67	–	50	–	75	2	74	–	66	1	69
Freon 12 *	100	100	100	100	100	100	100	100	100	100	100	100
hexachloro-1,3-butadiene*	–	–	–	–	–	–	–	–	–	3	–	1
<i>o</i> -xylene *	7	25	23	39	20	63	21	41	23	74	20	55
( <i>p+m</i> )-xylene	33	25	65	50	80	73	70	68	83	87	66	69
styrene *	–	33	–	33	–	2	–	59	–	24	–	27
tetrachloroethylene *	–	–	–	–	–	13	–	–	–	3	–	5
toluene	56	42	79	67	100	100	89	94	93	95	83	89
trichloroethylene *	–	–	–	–	5	2	–	–	–	–	1	1

\* Detection limit lowered in 2000.

## **Appendix 8 Carcinogenic classifications and priority lists**

A large number of pollutants can be classified as air toxics. Organisations nationally and internationally have identified groups of air toxics that should be given priority attention. Scientific understanding of the identity and risk posed by these pollutants is evolving. As a result of this still limited knowledge, the compounds viewed with the greatest concern vary between countries and states. The status of the 19 organic compounds detected in this study in respect to various priority lists is presented in Table A8.1.

### **Environment Australia**

Environment Australia has identified a list of 28 priority air toxics. This list will be open to review over time and will be used as a starting point for focusing attention on the development of national strategies for the management of air toxics (Environment Australia 2001). The list was developed by making use of existing work in prioritisation by the US EPA, EPA Victoria and the National Pollutant Inventory (NPI) Australia. For the NPI, ninety pollutants were selected from a list of 400 substances on the basis of human health effects, environmental effects and exposure (Environment Australia 2002).

### **US EPA**

The US EPA has classified 188 compounds as hazardous air pollutants. During 1999, the US EPA identified 33 air toxics that present ‘the greatest threat to public health in the largest number of urban areas’ (US EPA 1999).

### **California Air Resources Board (CARB)**

A report by CARB has identified ten key toxic compounds that result in the highest contribution to cancer risk in California on the basis of ambient concentrations and cancer unit risk factors (SCAQMD 2000).

### **IARC and US EPA Carcinogenic Classifications**

The IARC (2004) and the US EPA (2003) have classified several compounds as to their carcinogenicity (Table A8.1).

**Table A8.1: Priority lists and carcinogenic classifications**

( <i>p+m</i> )-xylene	✓						3
1,1,1-trichloroethane							3
1,2,4-trimethylbenzene							
1,3,5-trimethylbenzene							
1,3-butadiene	✓						2A
4-ethyltoluene							
benzene	✓						1
carbon tetrachloride							2B
chloromethane							3
dichloromethane	✓						2B
ethylbenzene							2B
Freon 11							
Freon 113							
Freon 12							
<i>o</i> -xylene	✓						3
styrene	✓						2B
tetrachloroethylene	✓						2A
toluene							3
trichloroethylene	✓						2A

\* The US EPA is in the process of revising its cancer risk assessment guidelines and is currently reassessing this pollutant.

**Source:** (IARC 2004; US EPA 2003)

#### IARC

- Group 1      carcinogenic to humans
- Group 2A     probably carcinogenic to humans
- Group 2B     possibly carcinogenic to humans
- Group 3      not classifiable as to its carcinogenicity to humans
- Group 4      probably not carcinogenic to humans

#### US EPA

- Group A      human carcinogen
- Group B1     probable human carcinogen, limited human data are available
- Group B2     probable human carcinogen, sufficient evidence in animals and inadequate or no evidence in humans
- Group C      possible human carcinogen
- Group D      not classifiable as to human carcinogenicity (insufficient evidence, or no data available, in animals and humans)
- Group E      evidence of non-carcinogenicity for humans

## Appendix 9 Average and maximum concentrations

The overall averages and the maximum 24-hour average concentrations for each compound at each of the primary and supplementary sites are presented in Tables A9.1 and A9.2 respectively. Compounds that were never detected at the primary and supplementary sites are presented in Table 5 and Appendix 4 respectively.

**Table A9.1: Primary sites—overall average and maximum (24-hour) average concentrations (ppbV)**

concentrations (ppb v/v)										
	1,1,1-trichloroethane		1,1-dichloroethane		1,2,4-trichlorobenzene		1,2,4-trimethylbenzene		1,2-dichloroethane	
	1,3,5-trimethylbenzene		1,3-butadiene		1,3-dichlorobenzene		3-chloropropene		4-ethyltoluene	
	benzene		bromomethane		cis-1,2-dichloroethene		carbon tetrachloride		chloroform	
	chloromethane		dichloromethane		ethylbenzene		Freon 11		Freon 113	
	Freon 12		hexachloro-1,3-butadiene		o-xylene		(p+m)-xylene		styrene	
	tetrachloroethylene		toluene		trichloroethylene		vinyl chloride		Maximum 24 hour average	
1,1,1-trichloroethane	0.1	0.2	0.1	0.8	0.1	0.3	0.1	0.2	0.1	0.3
1,1-dichloroethane	0.1	0.9	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
1,2,4-trichlorobenzene	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
1,2,4-trimethylbenzene	0.7	3.4	0.3	1.9	0.1	1.1	0.2	0.8	0.2	1
1,2-dichloroethane	0.1	0.5	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
1,3,5-trimethylbenzene	0.2	1.1	0.1	0.6	0.1	0.3	0.1	0.2	0.1	0.3
1,3-butadiene	0.4	1.4	0.2	0.9	0.1	0.3	0.1	0.4	0.1	0.9
1,3-dichlorobenzene	0.1	0.2	0.1	0.5	0.1	0.1	0.1	0.1	0.1	0.1
3-chloropropene	0.1	0.1	0.1	0.6	0.1	0.2	0.1	0.1	0.1	1.1
4-ethyltoluene	0.3	1.4	0.2	1.1	0.1	0.4	0.1	0.2	0.1	0.3
benzene	2.3	5.2	1.1	6.1	0.4	1.2	0.6	2.2	0.8	4.3
bromomethane	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
cis-1,2-dichloroethene	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.8	0.1	0.1
carbon tetrachloride	0.1	0.2	0.1	0.2	0.1	1	0.1	0.1	0.1	0.1
chloroform	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
chloromethane	0.7	1.1	0.7	1.3	0.8	2	0.7	1.6	0.7	1.4
dichloromethane	0.2	4.5	0.2	3.7	0.1	0.9	0.1	0.6	0.1	0.6
ethylbenzene	0.5	1.5	0.3	1.5	0.1	0.4	0.1	0.5	0.1	0.6
Freon 11	0.3	2.7	0.3	0.4	0.3	0.5	0.2	0.4	0.3	0.7
Freon 113	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2
Freon 12	0.8	8.1	0.6	1	0.6	1.0	0.5	0.8	0.6	1.3
hexachloro-1,3-butadiene	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
o-xylene	0.8	2.7	0.4	2.4	0.1	0.7	0.2	0.8	0.2	1.1
(p+m)-xylene	2.2	6.2	1.0	6.6	0.4	1.6	0.5	2.1	0.6	2.9
styrene	0.2	2.3	0.1	0.7	0.1	0.4	0.1	0.2	0.1	0.6
tetrachloroethylene	0.1	1.6	0.1	0.3	0.1	0.1	0.1	0.4	0.1	0.2
toluene	4.2	10	2.2	16	0.8	3.3	1.0	3.4	1.1	6
trichloroethylene	0.1	3.6	0.1	0.8	0.1	0.7	0.1	0.1	0.1	0.1
vinyl chloride	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1



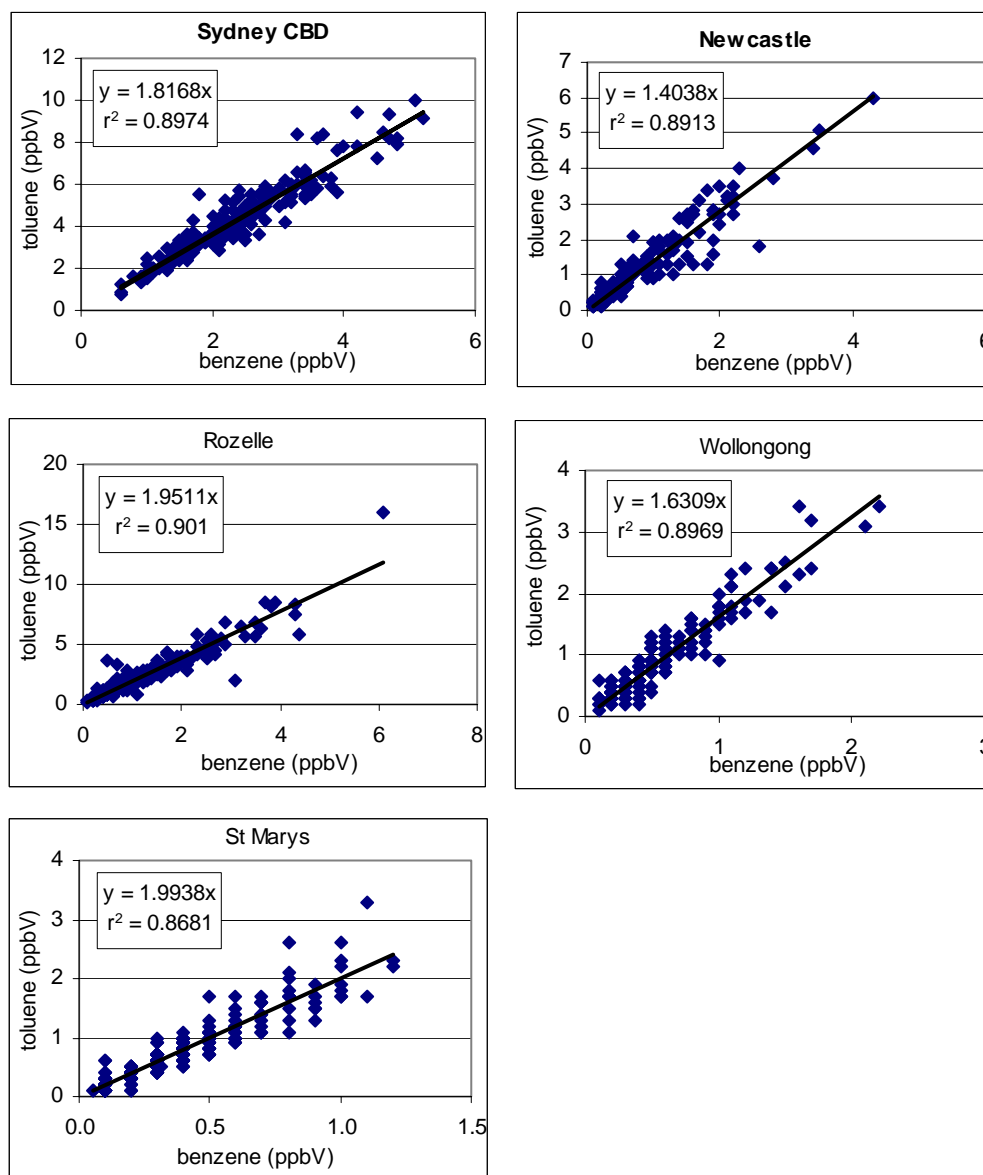
**Table A9.2: Supplementary sites—overall average and maximum (24-hour) average concentrations (ppbV)**

	Various sampling periods from July 1997 to August 2001									
	Overall average									Maximum 24 hour average
1,1,1-trichloroethane	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.4	0.1	0.2
1,2,4-trimethylbenzene	0.1	0.1	0.1	0.5	0.1	0.8	0.1	0.4	0.1	0.7
1,3,5-trimethylbenzene	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1
1,3-butadiene	0.1	0.1	0.1	0.2	0.1	0.3	0.1	0.4	0.1	0.6
3-chloropropene	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1
4-ethyltoluene	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2
benzene	0.2	1.1	0.2	1.0	0.4	1.4	0.4	1.0	0.6	3.0
carbon tetrachloride	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
chloroform	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
chloromethane	0.7	1.1	0.7	1.1	0.7	1.1	0.8	1.3	0.7	1.2
dichloromethane	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.2
ethylbenzene	0.1	0.1	0.1	0.3	0.1	0.3	0.1	0.2	0.1	0.6
Freon 11	0.3	0.4	0.2	0.3	0.2	0.3	0.3	0.9	0.2	0.3
Freon 113	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1
Freon 12	0.5	0.7	0.5	0.6	0.6	1.0	0.5	1.3	0.5	0.7
hexachloro-1,3-butadiene	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
<i>o</i> -xylene	0.1	0.2	0.1	0.5	0.1	0.5	0.1	0.5	0.2	1.0
( <i>p+m</i> )-xylene	0.2	0.5	0.3	1.3	0.3	1.2	0.3	0.9	0.5	3.0
styrene	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.3
tetrachloroethylene	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2
toluene	0.3	1.0	0.4	1.9	1.1	4.5	0.6	1.8	0.9	4.7
trichloroethylene	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1

## Appendix 10 Correlation between benzene and toluene

The correlation between benzene and toluene for each site ranged between 0.87 and 0.90 (Figure A10.1). This high correlation, together with other supporting reasons such as both compounds being emitted in vehicle exhaust, indicate that it is likely that these two compounds are being emitted from the same source at each of these sites.

**Figure A10.1: Correlation between benzene and toluene at each of the primary sites**



## Appendix 11 Further international goals

Annual average goals for a number of compounds have been developed for a variety of purposes by different international organisations. Table A11.1 presents these goals along with the range of annual concentrations measured in this study for comparison purposes. A comparison of ambient concentrations of benzene and 1,3-butadiene, in relation to the UK and European Commission goals, is discussed in detail in section 3.6.

The Texas Natural Resource Conservation Commission (TNRCC) has developed Effects Screening Levels (ESLs) for ambient air. ESLs are used to evaluate the potential for effects to occur as a result of exposure to concentrations in the air. ESLs are based on data concerning health effects, odour nuisance potential, effects with respect to vegetation, and corrosion effects. The TNRCC (2004) states:

*ESLs are not ambient air standards. If measured airborne levels do not exceed the screening level, adverse health or welfare effects would not be expected to result. If ambient levels in air exceed the screening levels, it does not necessarily indicate a problem, but rather, triggers a more in-depth review.*

Note that the detection limit in this study was higher than the following goals:

- hexachloro-1,3-butadiene > Texas ESL
- 1,2-dibromoethane > Texas ESL and Louisiana goal
- 1,3-butadiene > Swedish goal.

Many of these goals are substantially higher than the concentrations measured in NSW. Benzene and 1,3-butadiene are the only compounds with concentrations above these goals (see Table A11.1).

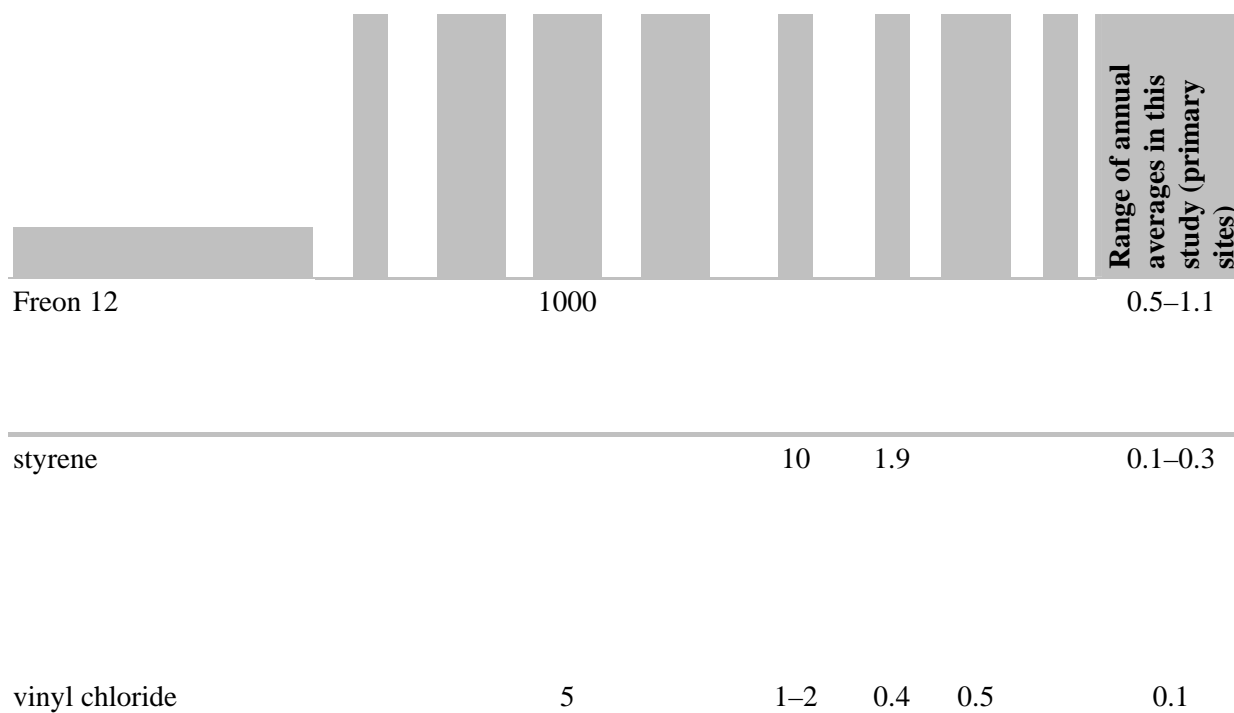
Although the highest annual concentrations of benzene at each site were below the benzene goals for Louisiana and New Zealand, they were above several other goals. For example, the highest annual average concentrations of benzene measured at the Sydney CBD (2.8 ppbV) and Rozelle (1.2 ppbV) sites were above both the Japanese goal of 0.9 ppbV and the long-term Texas ESL of 1 ppbV. The highest annual average concentrations of benzene at all primary sites were above the Dutch benzene goal of 0.3 ppbV (St Marys 0.4, Newcastle 0.9 and Wollongong 0.6 ppbV).

The annual average concentration of 1,3-butadiene in 1998 at the Sydney CBD site was above the Louisiana goal. Annual average concentrations at the remaining primary sites were below international 1,3-butadiene goals. Note that the Swedish goal is lower than the detection limit in this study, making comparison impossible.

Parameter	Range of annual averages (primary sites)
Temperature	0.5 to 1.5
Salinity	0.5 to 1.5
Dissolved oxygen	0.5 to 1.5
Turbidity	0.5 to 1.5
Chlorophyll a	0.5 to 1.5
Nitrate	0.5 to 1.5
Ammonia	0.5 to 1.5
Nitrite	0.5 to 1.5
Phosphate	0.5 to 1.5
Silicate	0.5 to 1.5
Sulfate	0.5 to 1.5

<sup>4</sup> Since the publication of the summary report (NSW EPA 2002), the UK Government (DEFRA 2003) have reviewed their benzene standard and adopted the following new objectives to be achieved by the end of 2010:

- an annual average of 1.5 ppbV for England and Wales
- a running annual average of 1 ppbV for Scotland and Northern Ireland.



Goals originally in  $\mu\text{g}/\text{m}^3$  have been converted to ppbV at 25 °C.

A year in parentheses indicates the date by which the goal is to be achieved.

ND—not detected; NRL—negligible risk levels

**Sources:** UK DETR 2000; European Commission 1999; MOE Japan 2001; EPA Victoria 1999; Ministry for the Environment (New Zealand) 2002; TNRCC 2004; Louisiana DEQ 2003

## Appendix 12 Seasonal variability

Seasonal variations in concentrations of compounds can occur owing to different meteorological mechanisms and different rates of photochemical reactions. Variations in emissions can also lead to seasonal differences in concentrations.

Winter meteorological conditions tend to lead to a reduction in mixing in the atmosphere owing to stronger and more frequent temperature inversions. As a result, pollutants can be trapped in a shallow layer at the surface, leading to higher concentrations. This is often compounded by very still conditions, further limiting dispersion of pollutants. Meteorological conditions in the summer months may also be conducive to lower concentrations of pollutants as highly reactive compounds participate in photochemical reactions. Rates of removal of benzene from the atmosphere are much lower in winter than in summer owing to the greater abundance of hydroxyl radicals in summer (ETC 1999).

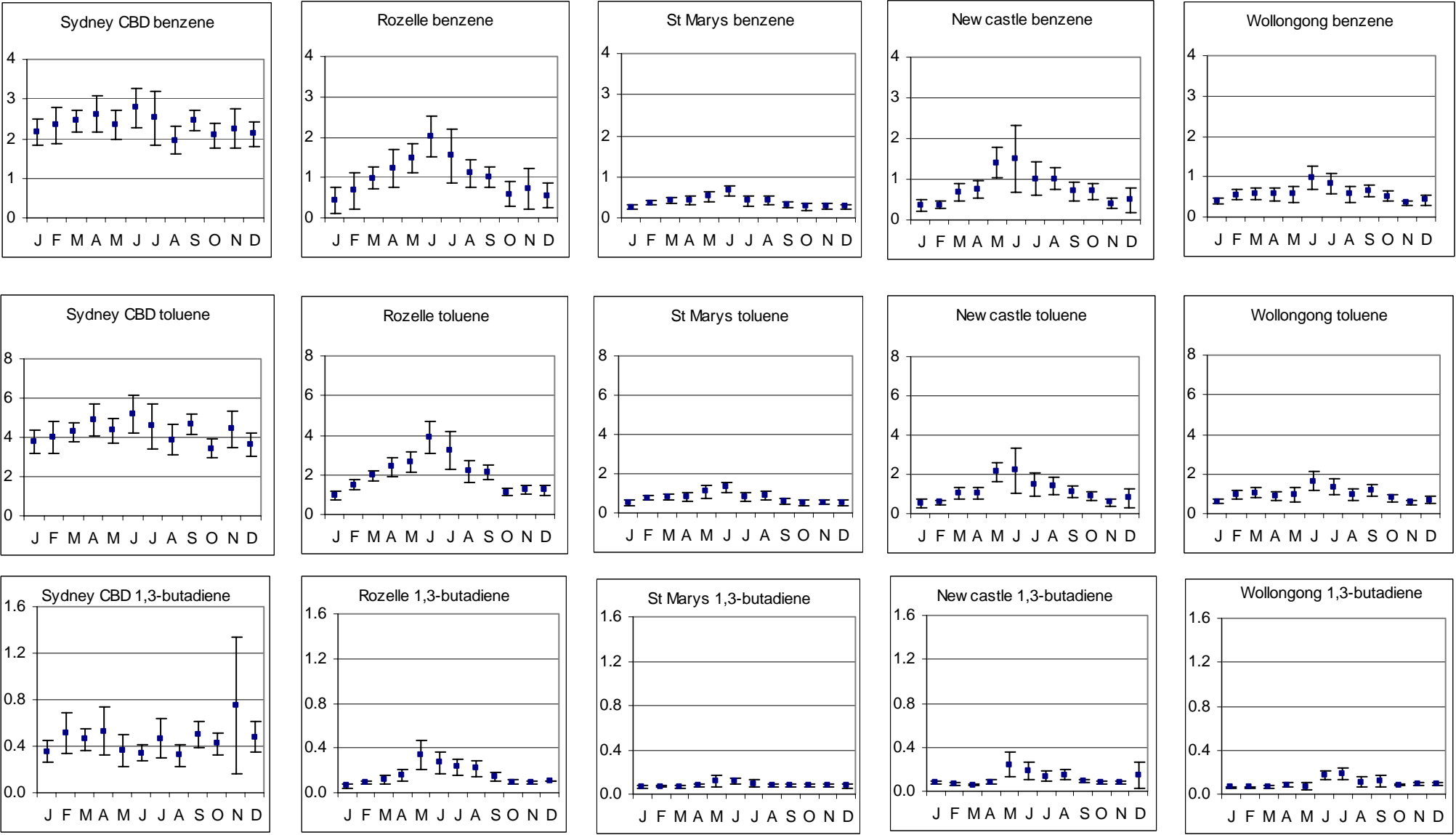
Table A12.1 presents the number of samples collected at each site in each month. Owing to problems with analytical instrumentation slightly lower numbers of samples were available for Freon 11, Freon 12, 1,3-butadiene and 1,2,4-trichlorobenzene (see Appendix 5 for explanation).

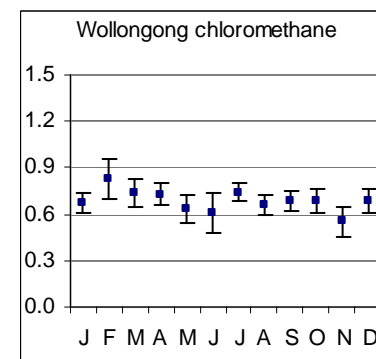
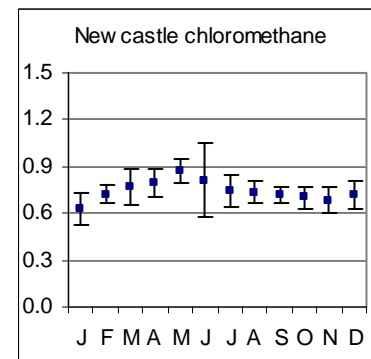
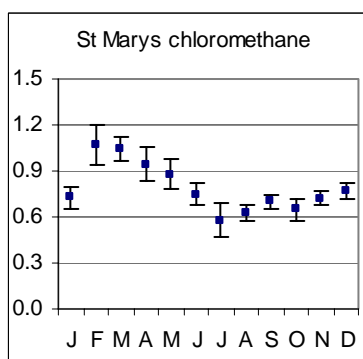
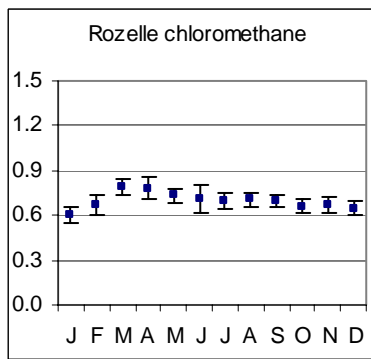
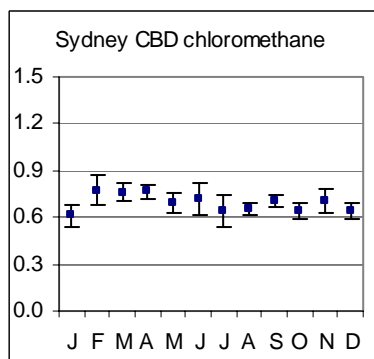
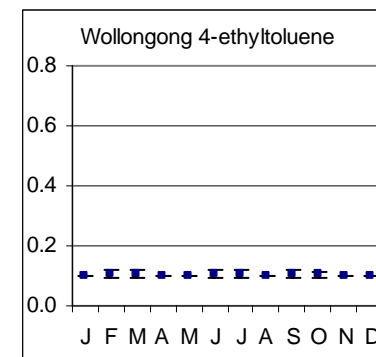
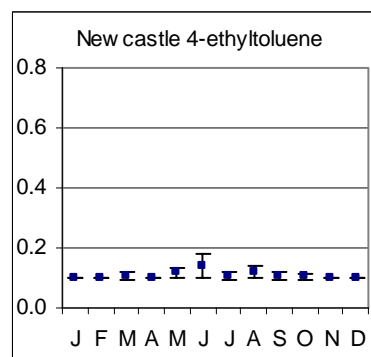
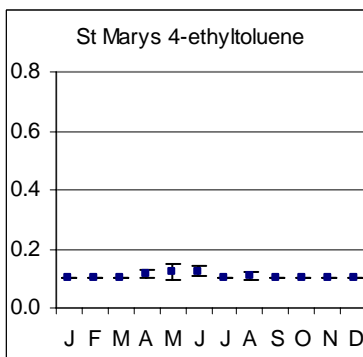
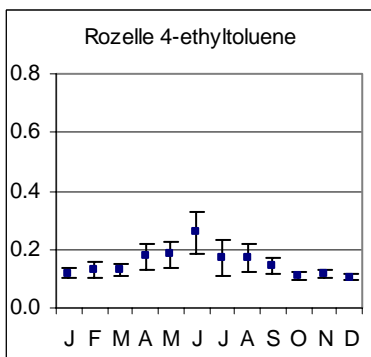
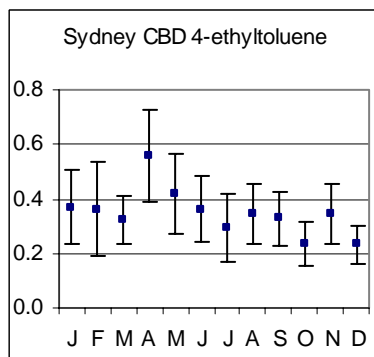
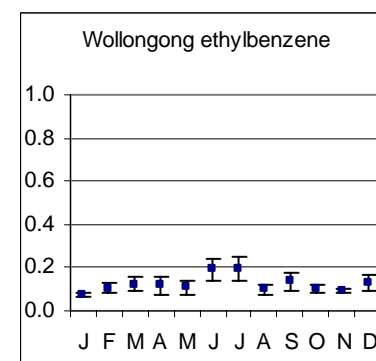
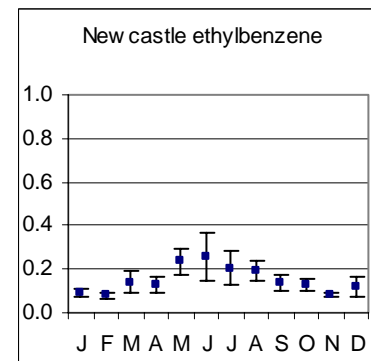
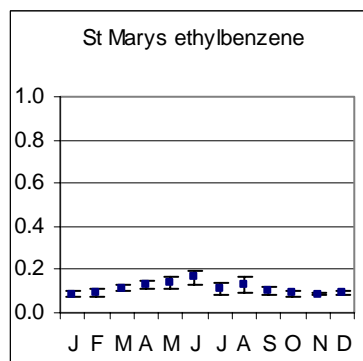
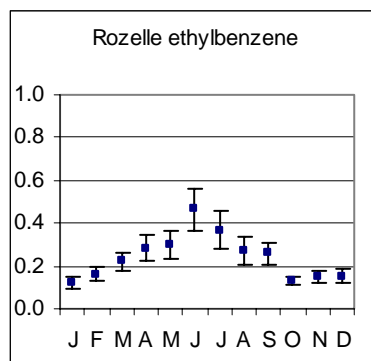
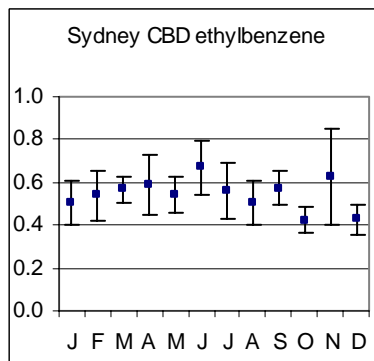
**Table A12.1: Number of samples collected each month**

					Wollongong
January	20	17	22	13	16
February	8	19	20	17	13
March	18	24	25	15	14
April	19	24	21	19	15
May	16	25	20	18	11
June	19	30	24	10	16
July	13	29	18	13	15
August	23	23	18	19	13
September	15	17	16	16	13
October	17	26	13	18	19
November	11	25	20	14	16
December	21	17	20	12	16

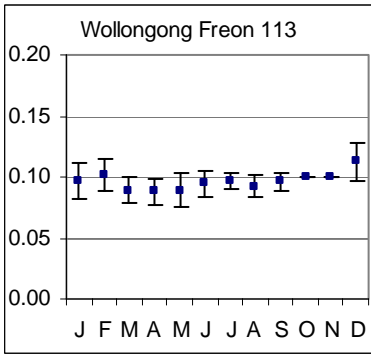
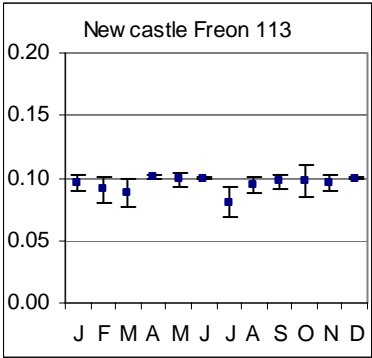
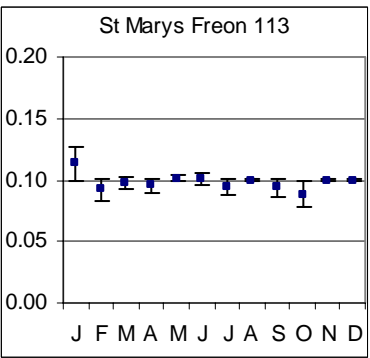
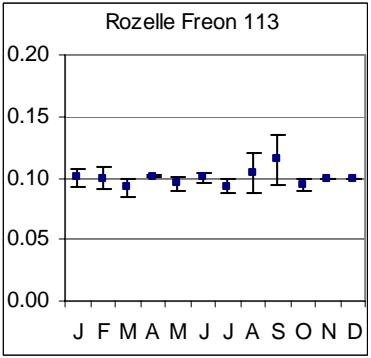
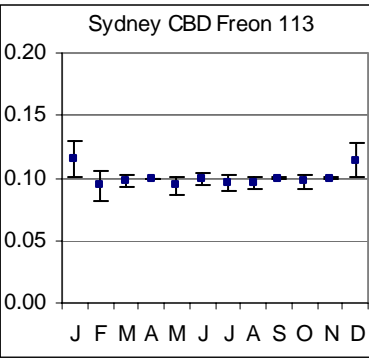
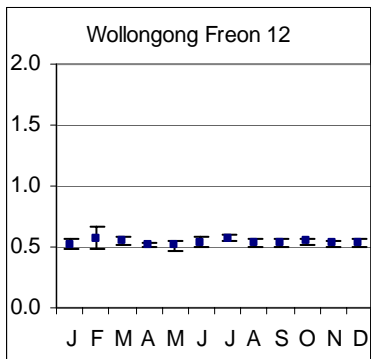
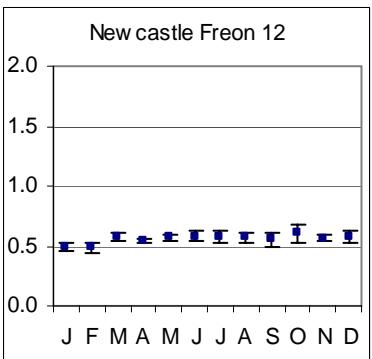
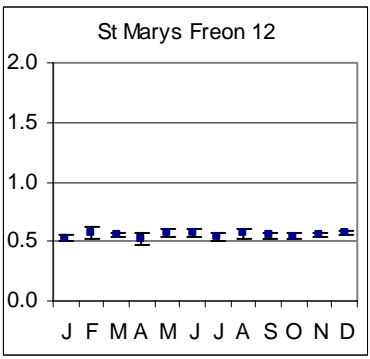
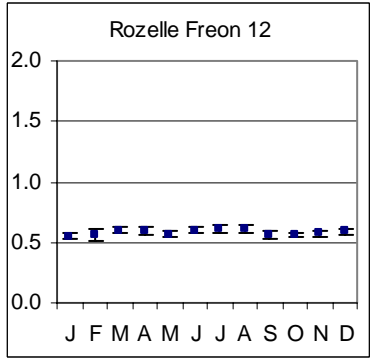
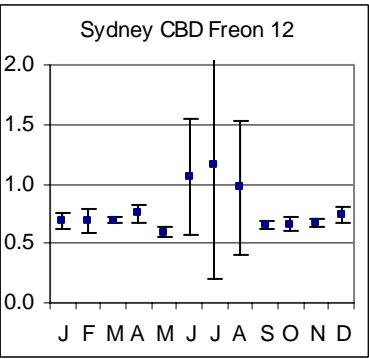
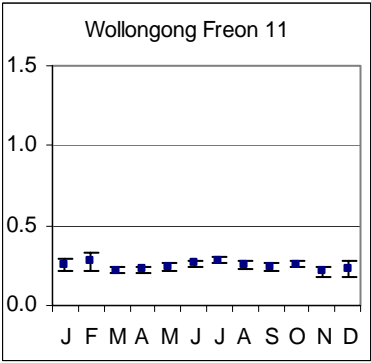
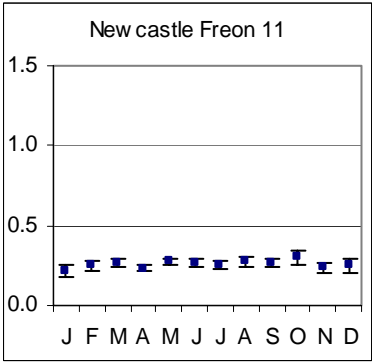
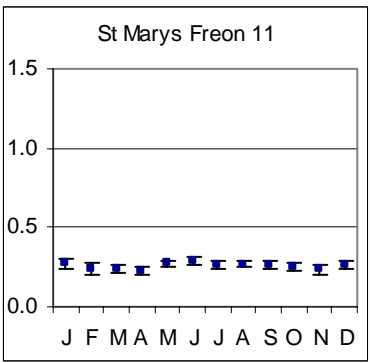
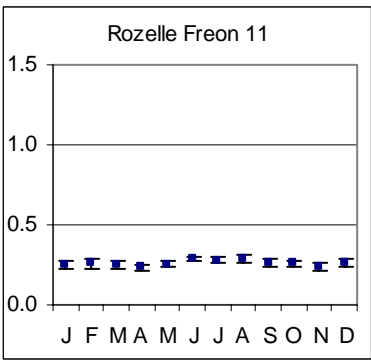
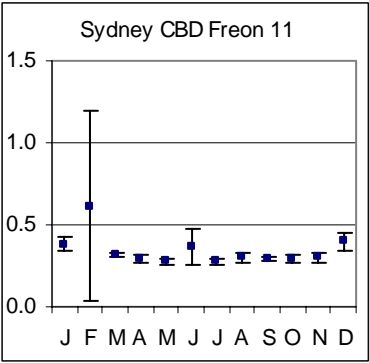
Figure A12.1 presents the monthly average concentrations over the entire sampling period and the upper and lower bounds of an 80% confidence interval for the average at each site for each of the detected compounds. Wider confidence intervals may be due to a lower number of samples (e.g. in June in Newcastle) or to one unusually higher or lower concentration (e.g. trichloroethylene in November in the Sydney CBD). The Sydney CBD site has the widest confidence intervals for several compounds and St Marys has the narrowest.

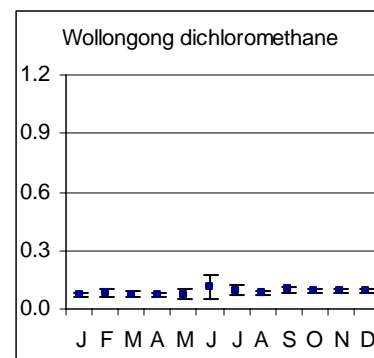
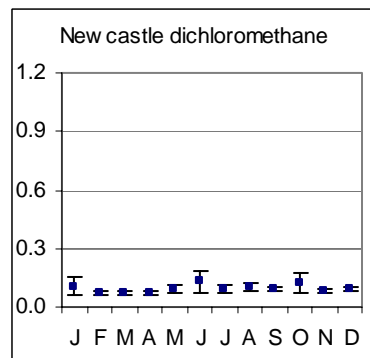
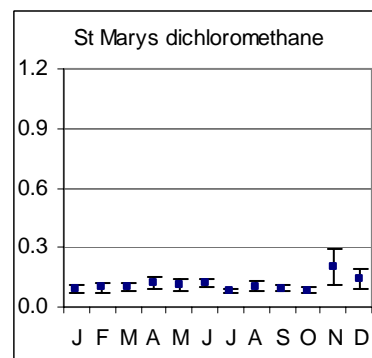
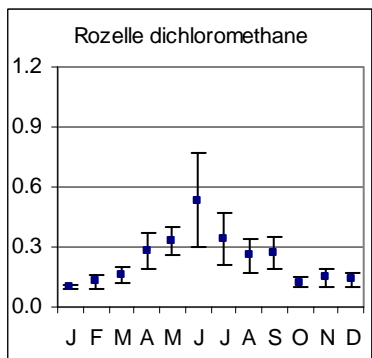
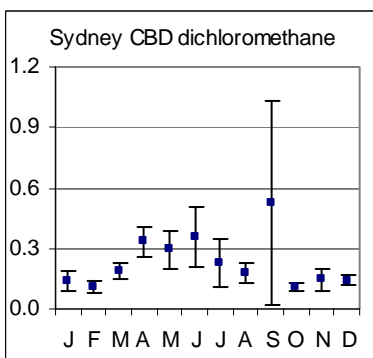
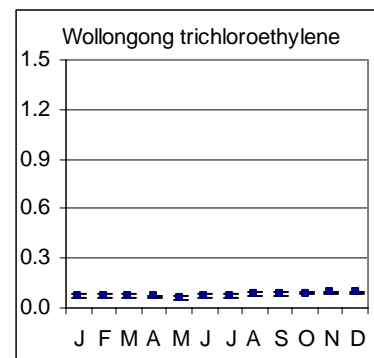
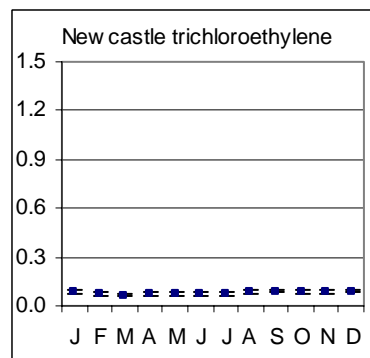
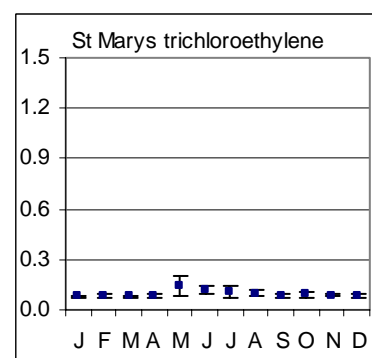
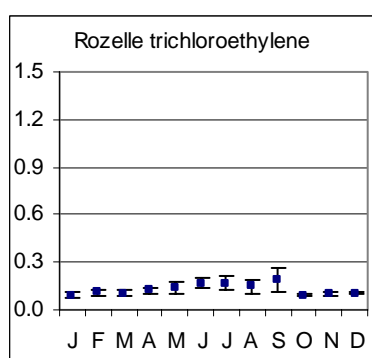
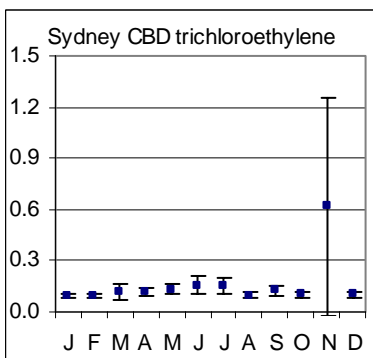
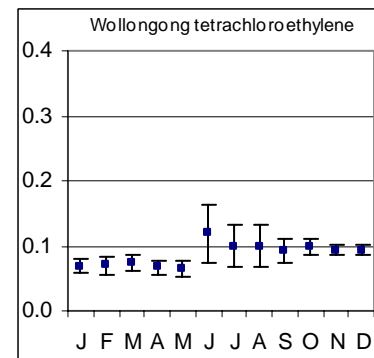
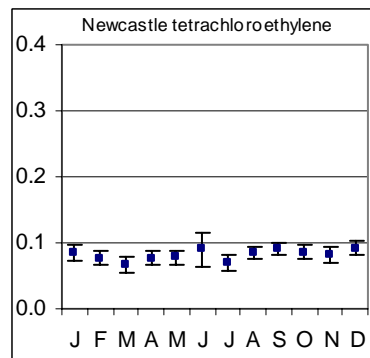
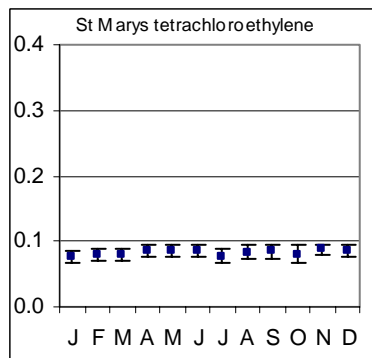
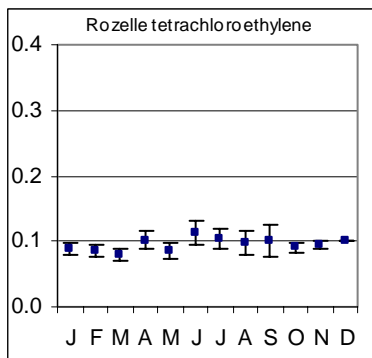
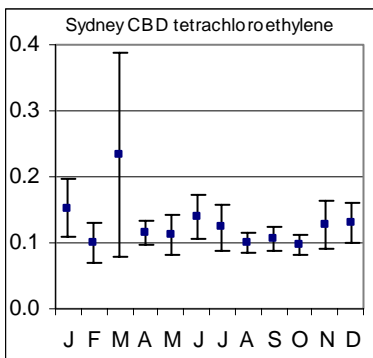
**Figure A12.1: Monthly averages and the upper and lower bounds of an 80% confidence interval for the average at each site (concentrations are in ppbV)**

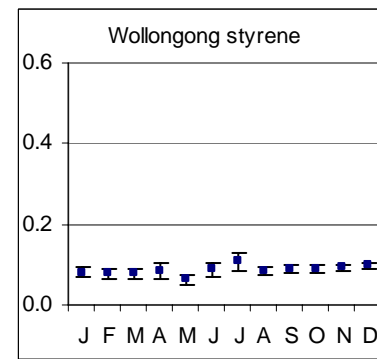
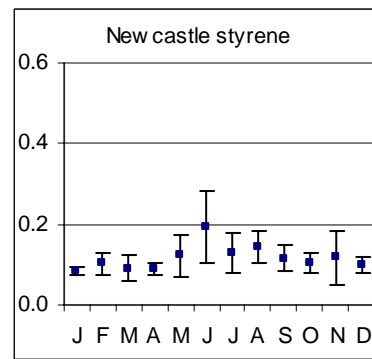
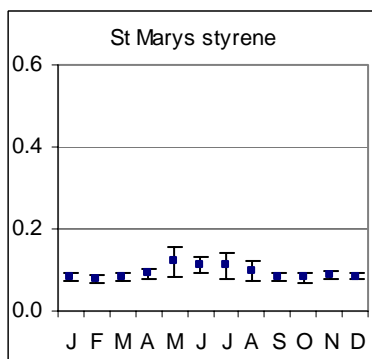
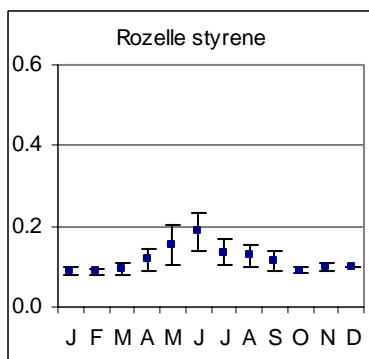
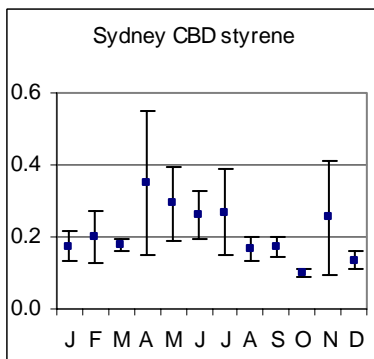
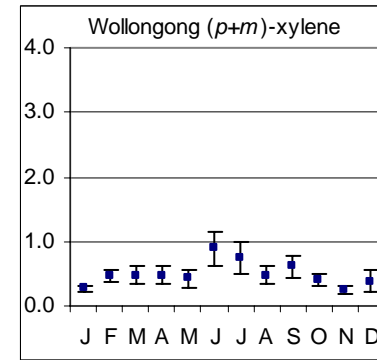
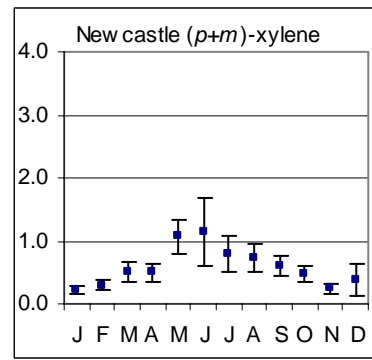
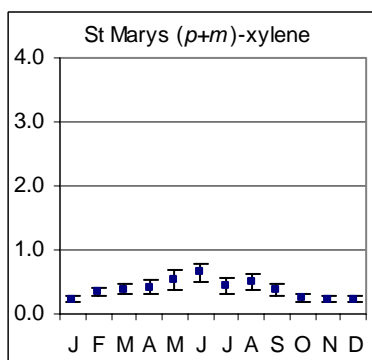
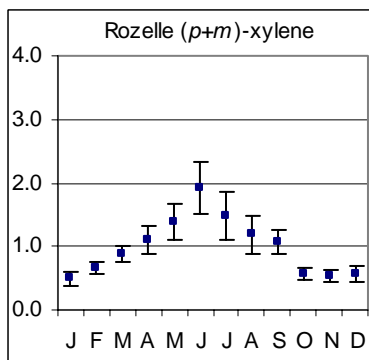
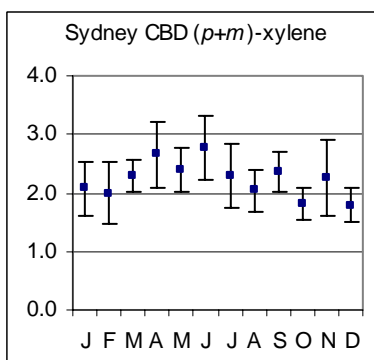
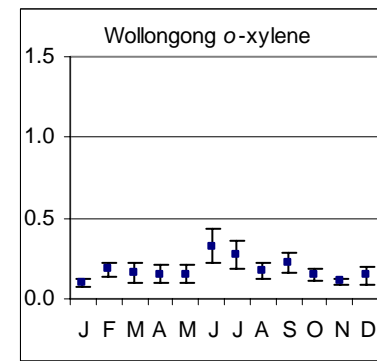
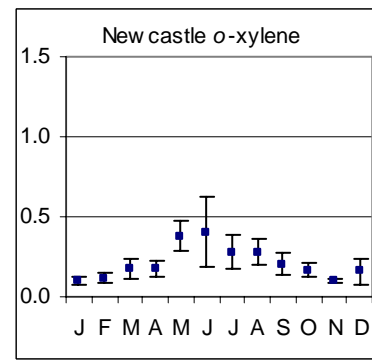
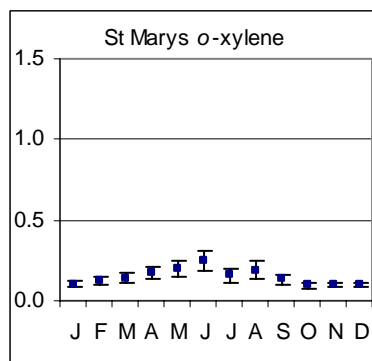
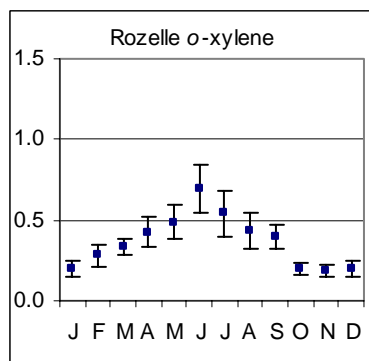
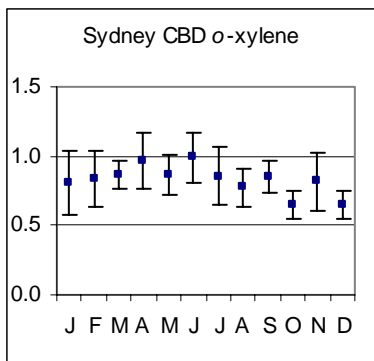


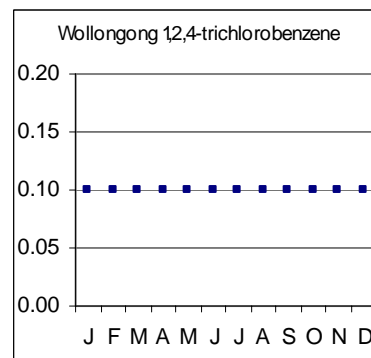
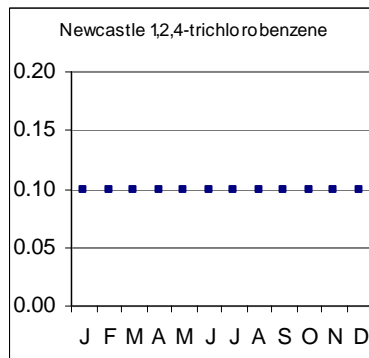
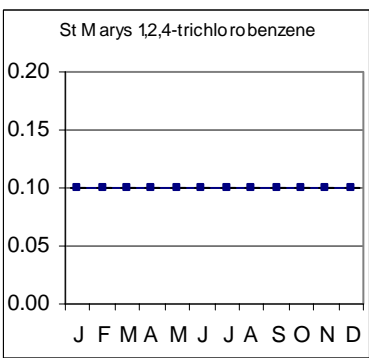
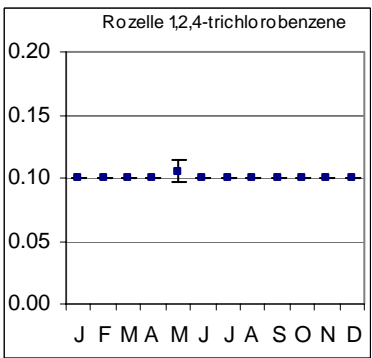
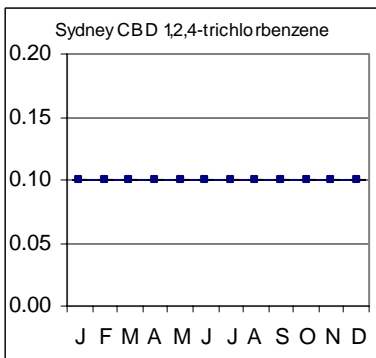
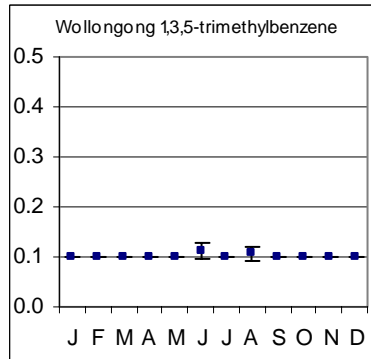
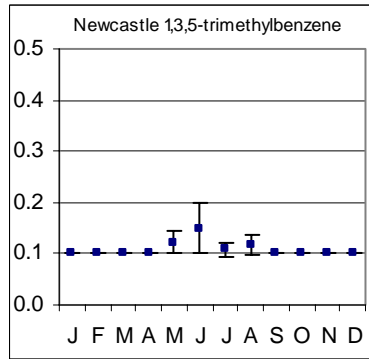
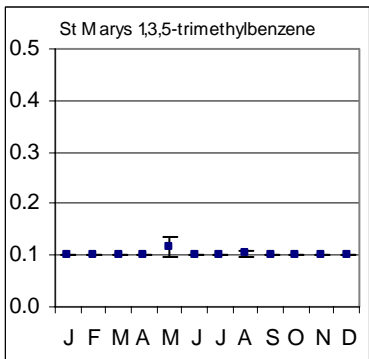
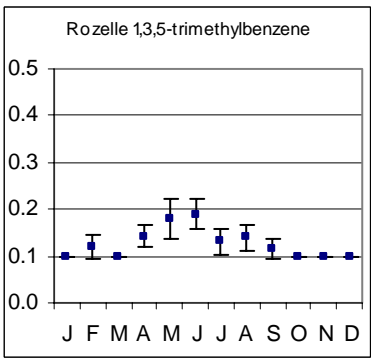
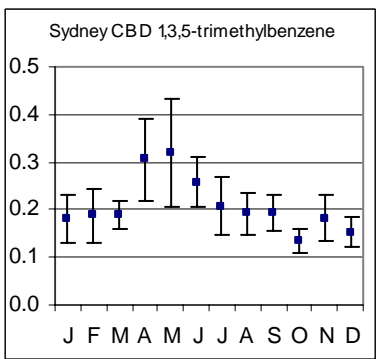
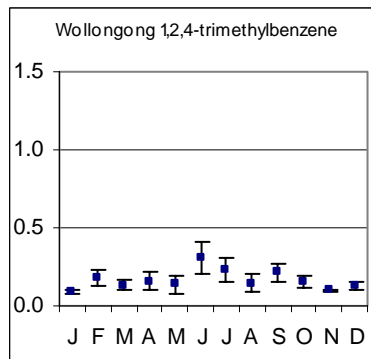
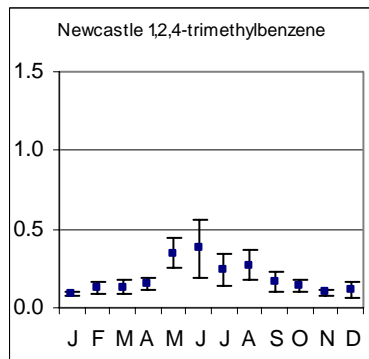
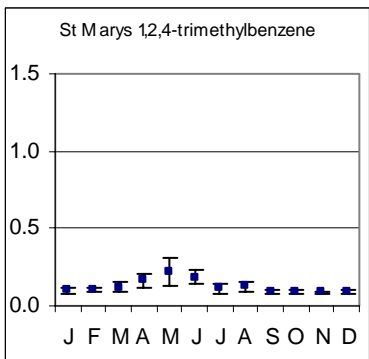
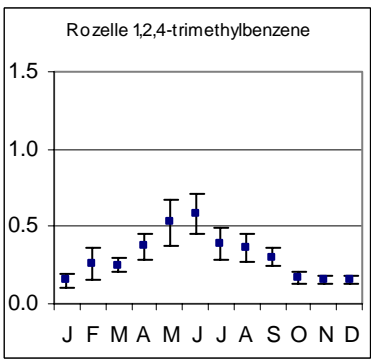
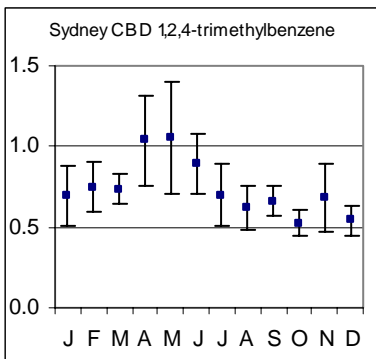


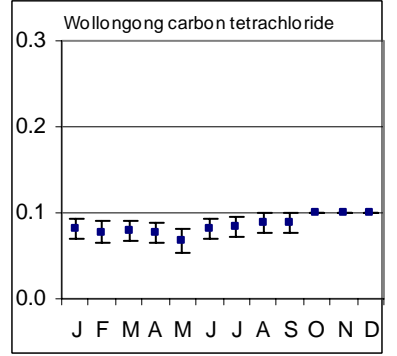
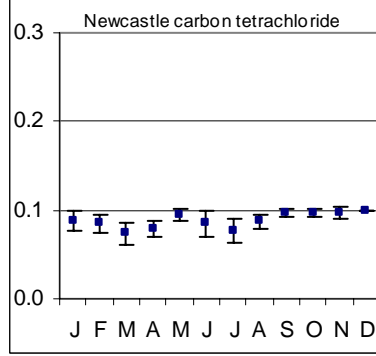
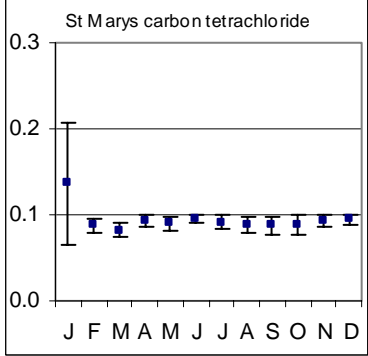
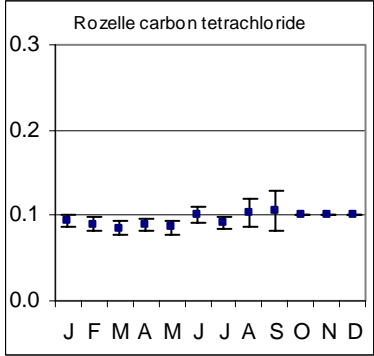
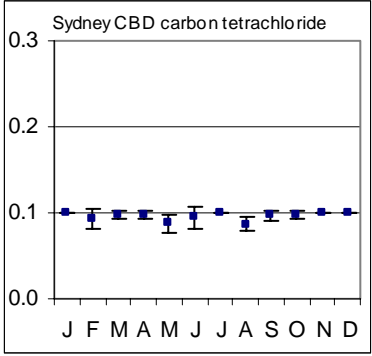












## **Appendix 13 Annual variability**

Data collected over several years are required for analysis of trends over time. Trends over time can occur owing to changes in emissions from sources, in reduction strategies or in meteorological patterns.

Statistical analysis for annual variations was conducted on the data set collected at the five primary sites. Data collected during 2001 were excluded from the annual variation analysis only, as the full year of data was not yet available. Other years excluded from analysis owing to the low number of samples collected are annotated in Table 13. For example, the data collected in the Sydney CBD during 1999 and 2000 were excluded on account of the low number of samples collected owing to site relocation. Note that analysis for 1,3-butadiene began in 1998.

Annual average concentrations and the upper and lower bounds of an 80% confidence interval for the average for each site and each compound are presented in Figure A13.1. Only those 19 compounds detected in more than 1% of samples have been plotted.

Figure A13.1: Annual averages and the upper and lower bounds of an 80% confidence interval for the average at each site (concentrations are in ppbV)

