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# Benzene, 1, 3 Butadiene and Other Volatile Organic Compounds in Auckland

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# Benzene, 1, 3 Butadiene and Other Volatile Organic Compounds in Auckland

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**Prepared for**  
Auckland Regional Council

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# 1 Executive Summary

This report summarises hydrocarbon measurements that have been undertaken in Auckland over the past ten years. Understanding hydrocarbons in air is important because some of them are carcinogenic or cause other health effects and/or lead to reactions in air during summer which cause new pollutants (e.g. ozone) to form.

Hydrocarbon monitoring has been funded over the years by a number of organisations including the Auckland Regional Council (ARC), the National Institute of Water and Atmospheric Research (NIWA), Ministry for the Environment (MfE) and the Ministry of Health (MoH). Most of the studies focussed on the health effects of particular hydrocarbons such as benzene, but some of the earlier work also investigated whether hydrocarbons could contribute to the formation of other pollutants.

Following a number of short-term investigations of volatile organic compounds (VOCs) in Auckland in the 1990's, long-term passive VOC sampling was undertaken at several Auckland locations between June 2000 and 2006. Continuous monitoring of benzene and 1,3 butadiene commenced at Khyber Pass Road in late 2005. The purpose of this report is to summarise air monitoring of hydrocarbons carried out in Auckland to the end of the 2007 calendar year, with a focus principally on benzene and 1,3 butadiene.

This report:

- Summarises results of benzene, toluene, ethylbenzene and xylenes from passive sampling undertaken in the Auckland region.
- Summarises results from benzene and 1,3 butadiene continuous monitoring at Khyber Pass Road, Auckland.
- Compares results with relevant ambient guideline values, along with data from previous investigations in Auckland and other urban areas in New Zealand.
- Shows the trends spatially and temporally.
- Provides recommendations for future monitoring.

Benzene, toluene, ethylbenzene and xylenes (BTEX) were sampled using passive techniques between 2001 and 2006 at four Auckland sites, while benzene and 1,3 butadiene were monitored continuously using a GC-PID<sup>1</sup> at Khyber Pass Road from 2005. Concentrations of toluene, ethylbenzene and xylenes were orders of magnitude lower than international screening levels and there is no immediate need for more detailed investigation of these contaminants.

Concentrations of all contaminants were three to four times greater at Khyber Pass Road than at Henderson, Mount Eden, Penrose, Takapuna and Kingsland. There has been a 30%-40% reduction of annual mean concentrations of benzene at Khyber Pass Road since 2003. Changes in fuel quality, vehicle technology, traffic density, fleet composition or meteorology will affect ambient benzene concentrations at these sites. Therefore, while there is no immediate demand for more detailed investigation of

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<sup>1</sup> Gas Chromatograph – Photo Ionisation Detector (see section 4.3)

benzene concentrations at the latter sites, the continuation of the passive sampling campaign would be useful as a relatively low cost means of monitoring trends. This would provide data for future assessments of spatial variability or inter-annual trends of hydrocarbons including benzene.

Prior to fuel specifications that implemented the reduction of benzene in petrol to 1% in 2006, monthly (GC-equivalent<sup>2</sup>) concentrations of ambient benzene were consistently above the current annual guideline of  $10 \mu\text{g m}^{-3}$  at Khyber Pass Road. Ambient benzene concentrations have been declining since progressive reductions of benzene in petrol were initiated in 2002, but monthly mean benzene concentrations at Khyber Pass Road have generally remained above the guideline of  $3.6 \mu\text{g m}^{-3}$  that will apply from 2010.

The highest recorded annual average 1,3 butadiene concentration of  $1.8 \mu\text{g m}^{-3}$  occurred in 2007 and is 75% of the MfE guideline value of  $2.4 \mu\text{g m}^{-3}$ . This falls within the alert category in the MfE list of environmental performance indicators.

Patterns of diurnal and seasonal variation of benzene, 1,3 butadiene, carbon monoxide (CO) and nitrogen dioxide (NO<sub>2</sub>) were all similar. However, the temporal variability of particulate matter (PM<sub>10</sub>) did not follow the same diurnal and seasonal trends. This is likely to be a consequence of PM<sub>10</sub> source variability, as substantial contributions of PM<sub>10</sub> from sea salt, domestic heating and other sources have been reported for Khyber Pass Road (Davy et al. 2007) and temporal variation of emissions from these sources differs from that of motor vehicles.

Annual average benzene results from Mount Eden and Penrose are consistent with MfE Global Environmental Monitoring System (GEMS) results from the same sites (which are taken as three month samples). Moreover, benzene concentrations in Auckland are consistent with results from other urban areas in New Zealand.

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<sup>2</sup> Monthly average benzene concentrations measured by passive sampling at Khyber Pass Road were consistently lower than data from continuous monitoring with the GC. Passive sampling results were therefore scaled up to GC-equivalency using a linear regression model ( $r^2=0.74$ ). See section 6.3.



## Key Results

- Benzene concentrations have reduced in recent years due to changes in fuel quality standards.
- Benzene concentrations in Auckland meet current annual ambient air quality guidelines, but may not meet the 2010 guidelines at major transport corridors in future (e.g. Khyber Pass Road).
- 1,3 butadiene concentrations meet the current annual ambient air quality guideline, but could increase with increasing traffic levels.
- BTEX passive samplers were shown to underestimate ambient concentrations by about 20%, but are useful for monitoring trends and spatial variability.
- Three monthly passive BTEX sampling is adequate to measure annual trends at non-peak sites, although this does not provide information on monthly variation. This non-regulatory method also only provides information on spatial and temporal relativity rather than absolute values.
- The two different methods of BTEX passive sampling showed similar results, although there was greater variability between the samplers in the CSIRO passive sampler pairs<sup>3</sup>.

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<sup>3</sup> Note: The reasons for this variability are not known.

## 2 Introduction

Volatile organic compounds (VOCs) are organic chemical compounds that vaporise under normal ambient conditions to enter the atmosphere as gases. Many VOCs, such as benzene and 1,3 butadiene (the main focus of this report) are hazardous to human health, causing cancer and other adverse health effects.

Initial surveys of some VOCs in New Zealand during the 1990's were commissioned by the Ministry of Health (MoH) and included measurements of benzene and 1,3 butadiene using passive samplers in Auckland (Stevenson and Narsey 1998). Following the prohibition of lead in petrol in 1996, controversy arose over the revelation that the new lead-free petrol had elevated levels of aromatic hydrocarbons including benzene (MfE 1997). Further VOC monitoring was consequently initiated in Auckland, commencing with open path investigations of selected hydrocarbon concentrations and conventional point measurements of total non-methane hydrocarbons (e.g. Kuschel et al. 1998, Kuschel et al. 2001).

One conclusion drawn from these short-term investigations was that long-term monitoring was required to confirm estimates of annual average concentrations (Kuschel et al. 1998). In a scientific review of the Auckland Regional Council (ARC) air monitoring network, Rolfe & Graham (1999) recommended monitoring of priority hazardous air pollutants including benzene, toluene, xylene and 1,3 butadiene. To evaluate photochemical smog formation, Rolfe & Graham (1999) recommended that monitoring of non-methane hydrocarbons (NMHC) be undertaken along with oxides of nitrogen (NO<sub>x</sub>).

Long-term passive VOC sampling was consequently initiated in June 2000 at several Auckland locations and continued at these sites until June 2006. The introduction of continuous monitoring of benzene and 1,3 butadiene at Khyber Pass Road commenced late 2005.

The purpose of this report is to summarise the monitoring of VOCs in Auckland to the end of the 2007 calendar year. With a focus principally on benzene and 1,3 butadiene, a description of monitoring methods is followed by data summaries, analysis and interpretation of results.

The objectives are:

- Overview VOC monitoring undertaken in the Auckland region.
- Summarise results of benzene, toluene, ethylbenzene and xylenes from passive sampling undertaken in Auckland.
- Summarise results from benzene and 1,3 butadiene continuous monitoring at Khyber Pass Road, Auckland.
- Compare results with relevant ambient guideline values, along with data from previous investigations in Auckland and other urban areas in New Zealand.
- Present spatial and temporal trends.
- Make recommendations for future monitoring.

## 3 Background

### 3.1 Characteristics and sources of VOCs

#### 3.1.1 Benzene

Benzene ( $C_6H_6$ ) has a very stable ring-shaped structure that forms the base of the aromatic hydrocarbon family. It is a colourless liquid with a sweet odour that occurs naturally in crude oil and boosts octane levels in petrol. Following the removal of lead based antiknock additives from petrol during the 1990s, aromatics such as benzene were increasingly blended into petrol due to their antiknock properties (MfE 1997).

Atmospheric, or ambient, benzene is usually produced by both evaporative and combustion processes associated with the storage and burning of fuels for activities such as transportation and heating. Traffic emissions are widely understood to be the most significant source of benzene in urban areas (Karakitsios et al. 2007), with detrimental human health effects including increased risk of cancer. Combustion emissions from traffic are recognised as the most significant benzene source, but evaporative benzene losses are also important when considering health effects, particularly in the immediate vicinity of large petrol stations or storage facilities (Jones 2000, Karakitsios et al. 2007).

Home heating emissions are also known to be a significant source of benzene during winter months in New Zealand, although research by Stevenson and Narsey (1998) suggested that motor vehicles were the most significant source of ambient benzene concentrations in Auckland. This premise was supported by the most recent air emissions inventory for Auckland (Metcalf et al. 2006), which estimated a 52% contribution from transport sources to the total annual VOC emissions of 64,200 t in the Auckland region. The remainder of VOCs in Auckland were from industrial (26%), biogenic (13%) and domestic sources (9%).

Other potential benzene sources include evaporative losses and petrol stations are widely documented as the most significant evaporative source of benzene (Karakitsios et al. 2007). Unlike petrol, diesel does not contain added benzene and USEPA (2004) reports that diesel contains only a very small amount of benzene: between a range of 0.003% and 0.1% by weight.

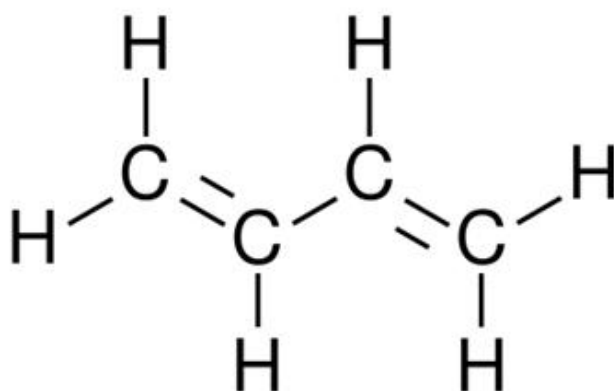
#### 3.1.2 1,3 butadiene

1,3 butadiene ( $C_4H_6$ ) is a colourless gas that has a slight odour and a boiling point of  $-4.41^\circ\text{C}$ . The chemical structure of 1,3 butadiene is illustrated in Figure 3.1. Unlike benzene, evaporative emissions are not a significant source of 1,3 butadiene because it is produced via combustion processes and is not a component of petrol or diesel

(Dollard et al. 2001). While some industrial processes contribute to ambient concentrations of 1,3 butadiene (e.g. manufacture of tyres and of 1,3 butadiene), the main source in the United Kingdom (UK) is exhaust emissions from motor vehicles (Dollard et al. 2001). In New Zealand the main source of ambient 1,3 butadiene is also road transport emissions (Stevenson and Narsey 1998, 1999). While diesel powered vehicles produce some 1,3 butadiene emissions, in the UK 60% of total 1,3 butadiene emissions are from petrol vehicles whereas the contribution from diesel engine road vehicles (8.5%) is much smaller (Dollard et al. 2001).

**Figure 3.1**

Chemical structure of 1,3 butadiene.



### 3.1.3 Other VOCs

Along with benzene and 1,3 butadiene, priority VOCs identified by Rolfe & Graham (1999) include toluene, ethylbenzene and xylenes. Together with benzene, these VOCs are commonly referred to as BTEX. Toluene ( $C_7H_8$ ) is also known as methylbenzene and, like benzene, is a colourless liquid with a sweet odour and is used as a solvent or as an octane booster in petrol. Ethylbenzene is present in small amounts in crude oil, although its main use is for production of polystyrene. Xylene is the term used to describe the group of three isomers of dimethylbenzene: *o*-xylene, *m*-xylene and *p*-xylene. The most common use of xylene is as a solvent and small amounts are naturally present in petrol.

Sometimes a more comprehensive suite of VOCs (as in Appendix B) may be included in laboratory analyses of filters, however benzene and 1,3 butadiene have been the VOCs of most concern in New Zealand.

## 3.2 Health effects and ambient guidelines

Commonly, the VOC monitoring in New Zealand has been for the BTEX compounds: benzene, toluene, ethylbenzene and xylenes (Iremonger 2002; McCauley 2005; Smith 2006). Of the BTEX suite, benzene is the contaminant of most concern when considering health effects from exposure to ambient air.

Ambient concentrations of toluene, ethylbenzene and xylenes, observed in New Zealand by Stevenson and Narsey (1999), were not considered to have any toxicological significance due to their low ambient concentrations. However, adverse health effects are associated with benzene and 1,3 butadiene and, consequently, the health based Ministry for the Environment (MfE) ambient air quality guidelines (MfE 2002) include limits for these two compounds. Health effects of benzene and 1,3 butadiene are discussed further in the following sections.

### 3.2.1 Benzene

Benzene is accepted as being a human carcinogen (Kahn 2007) and acute exposure is also known to cause non-cancer effects including dizziness, headache, vertigo, drowsiness, delirium and loss of consciousness (USEPA 2002). Benzene metabolites (products of metabolism) are produced mainly in the liver and manifest human health effects including bone marrow and blood disorders (USEPA 2002). Metabolites are also held responsible for carcinogenic, genotoxic and mutagenic effects (i.e. deleterious alteration of genetic material), although it is not known whether these are linked to the same processes that cause non-cancer health effects (Kahn 2007).

One of the most recognized adverse health effects from benzene exposure is leukaemia. The World Health Organisation (WHO) established a benzene exposure risk range such that, for every  $0.17 \mu\text{g m}^{-3}$  increase in ambient benzene concentrations, one leukaemia case could be expected in every one million people (WHO 2000). Expressed in another way, at ambient concentrations of  $1 \mu\text{g m}^{-3}$ , the geometric mean excess lifetime risk of leukaemia was estimated to be  $6 \times 10^{-6}$  (WHO 2000). Other risk estimates for benzene exposure include the USEPA unit risk estimate of  $8.3 \times 10^{-6}$ , and the California Air Resources Board value of  $29 \times 10^{-6}$  (MfE 2002).

Combustion emissions from traffic are recognised as the most significant benzene source, but Karakitsios et al. (2007) calculated that residents living in the immediate vicinity of urban petrol stations may be exposed to an additional 3% to 21% increased leukaemia risk from the evaporative benzene losses. Jones (2000) monitored benzene concentrations at residential properties 10 m from petrol station boundaries in London, Birmingham and Bristol. It was identified that benzene concentrations in the vicinity of petrol stations were affected most by distance from the petrol pumps and the petrol throughput of the station (Jones 2000).

Only at very large petrol stations (throughput of petrol in excess of  $1000 \text{ m}^3/\text{annum}$ ), and at residences in the immediate vicinity, was there predicted to be a potential for difficulty meeting the 2010 UK limit of  $5 \mu\text{g m}^{-3}$  annual average benzene concentration (Jones 2000). It was predicted that the installation of vapour recovery would

sufficiently mitigate losses of benzene vapour from refuelling vehicles, so that the 2010 limit would be met at these locations. At smaller petrol stations, it was calculated that reductions of benzene levels in petrol (to 1% in January 2000) would be sufficient to ensure the 2010 UK limit was achieved.

As a consequence of these established adverse health effects, the European Commission (EC) adopted an annual benzene limit value<sup>4</sup> of  $10.0 \mu\text{g m}^{-3}$  for the European Union (EU) from December 2000 (Directive 2000/69/EC). Moreover, the EU Directive also requires a continuous reduction in Member States of  $1.0 \mu\text{g m}^{-3}$  each year from 2006 until 2010, following which a benzene limit of  $5.0 \mu\text{g m}^{-3}$  (annual average) will apply.

Following this approach, the UK adopted an Air Quality Objective for annual average benzene of  $16.25 \mu\text{g m}^{-3}$  and a 2010 target of  $5 \mu\text{g m}^{-3}$  for England and Wales (DEFRA 2007). The 2010 target for Scotland and Northern Ireland is  $3.25 \mu\text{g m}^{-3}$ .

The MfE's current air quality guideline for benzene is  $10 \mu\text{g m}^{-3}$  when averaged over a year. However, because of the known carcinogenic effects and the desire for a precautionary approach, the lower annual guideline value of  $3.6 \mu\text{g m}^{-3}$  will come into force in 2010. The New Zealand benzene guideline development was based on the WHO (2000) recommendations, with the 2010 guideline established using an acceptable implied risk (based on the WHO risk factors) of 16 per million (MfE 2000b). The current guideline of  $10 \mu\text{g m}^{-3}$  was adopted to be consistent with the EC proposal at the time of guideline development (European Commission 1998), while the 2010 guideline was chosen to be consistent with the UK long-term goal (MfE 2000a).

### 3.2.2 1,3 butadiene

Metabolites of 1,3 butadiene are carcinogenic and there is evidence of mutagenicity caused by 1,3 butadiene exposure in mice and rats (WHO 2000). Acute inhalation exposure has also been shown to cause irritation of eyes, throat, lungs and nasal passages, along with neurological human health effects including blurred vision, fatigue, headache and vertigo (MfE 2002). Chronic exposure to 1,3 butadiene also causes non-cancerous human health effects, including cardiovascular and blood disorders (MfE 2002).

Epidemiological and toxicological studies indicate that 1,3 butadiene is carcinogenic and possibly genotoxic in humans. Therefore, the International Agency of Research on Cancer (IARC) classified it as a group 2A (probable) carcinogen (IARC 1999). However, due to uncertainty of the application of genotoxic carcinogenicity observed in rats and mice to estimating human health effects, the WHO (2002) has not specified a guideline value for 1,3 butadiene.

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<sup>4</sup> At reference temperature 20°C. Note that, unless stated otherwise as in this footnote, ambient concentrations cited in this report are at reference temperature 0°C, as commonly used in New Zealand and recommended by MfE.

Nevertheless, the UK Expert Panel on Air Quality Standards has accepted that carcinogenic and genotoxic human health effects occur from 1,3 butadiene exposure (UK EPAQS 1998). Accordingly, the Air Quality Strategy for England, Scotland, Wales and Northern Ireland (DEFRA 2007) specifies a National Air Quality Objective<sup>5</sup> of  $2.25 \mu\text{g m}^{-3}$  for annual average 1,3 butadiene concentrations in ambient air. DEFRA (2007) acknowledge that there is no absolutely safe limit for 1,3 butadiene in ambient air, but has set a target value based on a risk level that is considered sufficiently low to be undetectable.

Despite the ambivalence of evidence relating to the genotoxic carcinogenicity of 1,3 butadiene, the New Zealand Ministry for the Environment (MfE 2002) adopted a precautionary approach and chose an annual guideline of  **$2.4 \mu\text{g m}^{-3}$**  (at standard temperature 0°C) to be consistent with the UK (MfE 2000b).

### 3.2.3 Guidelines for toluene, ethylbenzene and xylenes

In a review of the previous 1994 New Zealand Ambient Air Quality Guidelines, MfE (2000b) recommended annual average guidelines of  $190 \mu\text{g m}^{-3}$  and  $950 \mu\text{g m}^{-3}$  for toluene and total xylenes respectively. However, these recommended limits were not included in the final published guidelines (MfE 2002) and the MfE has subsequently suggested that Australian National Environment Protection Council (NEPC) criteria (NEPC 2004) should be used for assessments of toluene and xylene (MfE 2006). The Australian National Environment Protection Measures (NEPM)<sup>6</sup> monitoring investigation levels for toluene and xylenes are  $410 \mu\text{g m}^{-3}$  and  $950 \mu\text{g m}^{-3}$  respectively<sup>7</sup> (Australian NEPC 2004). If these levels are exceeded, further investigation is deemed necessary.

There is also no New Zealand guidance on appropriate limits for ethylbenzene. However, in the absence of a guideline, MfE (2006) suggests using Texas screening levels for assessment of annual average concentrations. Although based on odour, the Texas effects screening level for annual average ethylbenzene concentrations is  $200 \mu\text{g m}^{-3}$  (TCEQ 2008) and concentrations above this would warrant a more detailed investigation.

## 3.3 Fuel specifications

Following the prohibition of lead in petrol, controversy arose when it was revealed that that the new fuel had elevated levels of aromatic hydrocarbons, including benzene, to boost the octane rating of unleaded fuel (MfE 1997). To address the harmful effects of benzene emissions from traffic sources in New Zealand, fuel specifications were introduced in 1998 that mandated a maximum percentage of benzene in petrol of 4.2% and 4.3% for Regular91 and Premium95 octanes respectively (MfE 2006). Fuel

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<sup>5</sup> At reference temperature 20°C.

<sup>6</sup> NEPM has similarities to New Zealand's National Environmental Standards but may consist of any combination of goals, standards, protocols, and guidelines.

<sup>7</sup> Conversion of NEPM limits from ppm to  $\mu\text{g m}^{-3}$  was made using reference temperature 0°C and molecular weight of 92.13 g/mol and 106.16 g/mol for toluene and mixed xylenes respectively.

specifications have continued to be updated, with benzene in both grades of petrol set to a maximum of 4% in 2002 and 3% in 2004.

Ultimately, in January 2006, the Ministry for Economic Development (MED) implemented a fuel specification to match the UK, with a maximum of 1% benzene in petrol. Recent history regarding benzene in fuel specifications is summarised in Table 3.1. The percentage of total aromatics in petrol has also been reduced from 48% in 1998 to 42% in 2006 (MfE 2006).

**Table 3.1**

Summary of recent New Zealand fuel specifications relating to VOCs in petrol.  
Source: MED 2002b. Pool average refers to the average from all fuel batches produced or imported in each calendar month.

Fuel type	Percentage (%) by volume of fuel			
	Pre-2002	September 2002	January 2004	January 2006
	<b>Benzene</b>			
Regular grade	< 5%	< 4%	< 3 % (if 20% max. olefins, or 1 max. if 25% max. olefins)	< 1 %
Premium grade	< 5%	< 4%	< 3 % (if < 20% olefins, or < 1% if < 25% olefins)	< 1 %
	<b>Total aromatic compounds including benzene</b>			
Regular grade	< 48%	< 42% pool average and 45% maximum cap	< 42% pool average and 45% maximum cap	< 42% pool average and 45% maximum cap
Premium grade	< 48%	< 48%	< 48%	< 42% pool average and 45% maximum cap
	<b>Olefins</b>			
Regular grade	N/A	N/A	< 25 % (if <1% benzene, or < 20% if < 3% benzene)	< 18 %
Premium grade	N/A	N/A	< 25 % (if < 1% benzene, or < 20% if < 3% benzene)	< 18 %



### 3.4 Previous investigations and research

The first major investigation of VOC concentrations in New Zealand was commissioned by the MoH in 1996 and involved passive sampling at Auckland, Hamilton, Christchurch and Dunedin (Stevenson and Narsey 1999). Annual average benzene concentrations from this investigation ranged from  $1 \mu\text{g m}^{-3}$  for the outer suburbs of Dunedin and Hamilton, to  $17 \mu\text{g m}^{-3}$  at Khyber Pass Road in Auckland. These results indicated that the current MfE guideline of  $10 \mu\text{g m}^{-3}$  would be exceeded at Khyber Pass Road and two roadside sites in Christchurch. The 2010 guideline of  $3.6 \mu\text{g m}^{-3}$  was exceeded at one site in Dunedin and several in Christchurch and Auckland.

Stevenson and Narsey (1999) also reported that kerbside sites on busy urban roads were expected to exceed the British air quality objective for 1,3-butadiene of 1 ppb ( $2.25^8 \mu\text{g m}^{-3}$ ), although urban background sites were not expected to exceed more than 50% of this objective.

Further passive sampling of the BTEX compounds was undertaken in Christchurch during 2001 (Gunatilaka 2003) and 2004-05 (McCauley 2005). Results from these investigations indicated that annual average benzene concentrations were decreasing, however the 2010 guideline value of  $3.6 \mu\text{g m}^{-3}$  was still exceeded in 2004-2005 at three roadside sites in Christchurch (McCauley 2005).

BTEX sampling also continues in Hamilton, with Environment Waikato reporting annual average benzene concentrations that exceeded the 2010 MfE guideline of  $3.6 \mu\text{g m}^{-3}$  at two Hamilton locations in 2006 (Smith 2006). Benzene concentrations were observed to be trending downward, however, and in 2007 no exceedances of the 2010 guideline were observed at any of the six sampling sites in Hamilton (Wilton and Baynes 2008). Passive sampling was also conducted in Tokoroa during 2003, but has not continued because results in 2003 indicated that benzene concentrations at Tokoroa were lower than both the current and 2010 guidelines (Smith 2006b).

Passive BTEX sampling was also undertaken in 2000-2001 by Environment Bay of Plenty at urban sites in Mount Maunganui, Tauranga, Whakatane, Rotorua and at a rural background site at Pongakawa. Annual average benzene concentrations between  $1.3 \mu\text{g m}^{-3}$  and  $5.4 \mu\text{g m}^{-3}$  were reported at the urban locations (Iremonger 2002). Passive sampling undertaken on the West Coast of the South Island from June to August in 2001 and 2002 showed that the highest observed winter average benzene concentration of  $3.5 \mu\text{g m}^{-3}$  (measured in Reefton) was lower than both the current and 2010 annual guideline values. A comparison of results from passive BTEX sampling is included in Section 7.3 of this report.

Open path VOC monitoring conducted in Nelson city between 1 April and 31 August 2001 was accompanied by some passive BTEX sampling. The average benzene concentration during the five month monitoring period was  $6.8 \mu\text{g m}^{-3}$  (NCC 2001). Home heating was estimated to be the greatest contributor to benzene emissions in Nelson during 2001 (NCC 2001). Due to lower home heating emissions and augmented dispersion of contaminants during spring and summer, Nelson City Council (NCC) considered that the annual average benzene concentration would be lower than

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<sup>8</sup> At reference temperature 20°C

6.8  $\mu\text{g m}^{-3}$  (NCC 2001). However it is not possible to extrapolate the autumn-winter data to an annual average benzene concentration for a robust comparison to the MfE guideline.

In Auckland, monitoring of non-methane hydrocarbons has been undertaken since 1996 and was accompanied by open path monitoring of VOCs, initiated in 1997 using differential optical absorption spectrometer (DOAS) (e.g. Kuschel et al. 1998, Kuschel et al. 2001). Observations from the DOAS included a range of hourly benzene concentrations between 35  $\mu\text{g m}^{-3}$  and 171  $\mu\text{g m}^{-3}$  at Khyber Pass Road over 17 days in May/June 1997, although it was difficult to draw robust conclusions about long-term average concentrations from the limited data series (Kuschel et al. 1998).

Monthly passive BTEX sampling has been undertaken at several Auckland sites by ARC since June 2000. This has been accompanied by three-monthly passive BTEX sampling by MfE at Penrose and Mount Eden since April 2001 and (more recently) at Kingsland in Auckland. The MfE sampling is undertaken as part of the WHO's environmental quality reporting under the Global Environmental Monitoring System (GEMS).

Aside from some open path VOC monitoring, passive BTEX sampling has been the most common means of measuring ambient benzene concentrations in New Zealand. In 2005 ARC installed an analyser for continuous monitoring of benzene and 1,3 butadiene. This is currently the only instrument that is known to be used for long-term, continuous VOC monitoring in New Zealand.

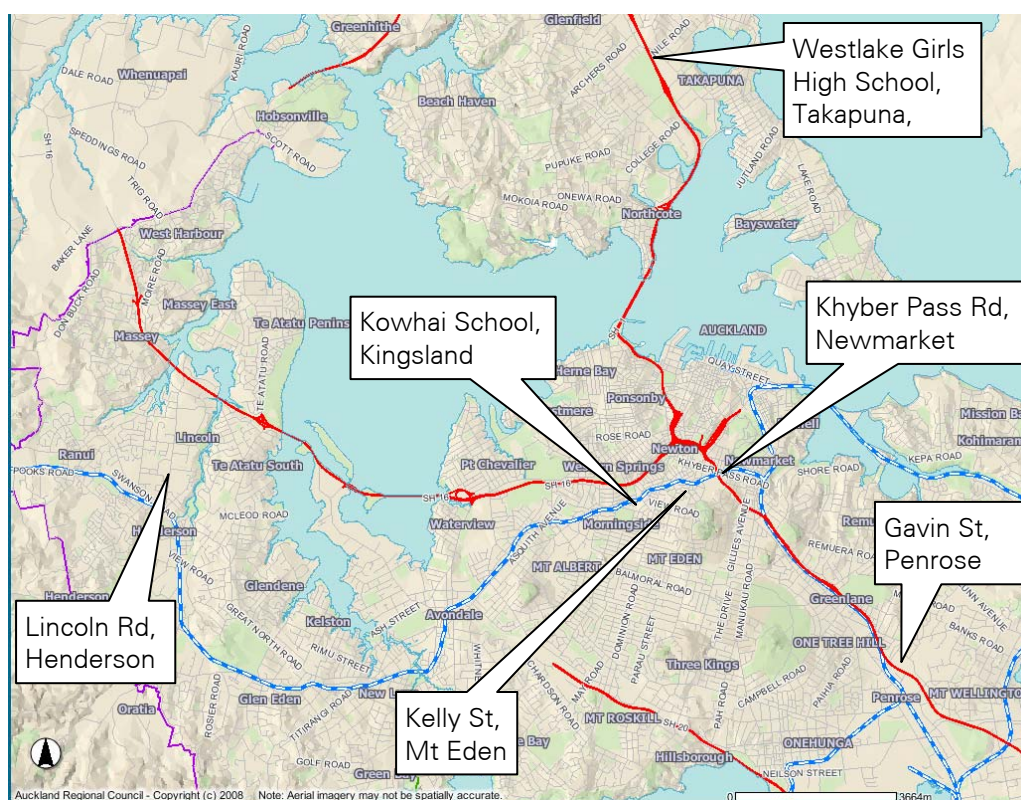
## 4 Methodology and site descriptions

### 4.1 Recent Auckland VOC monitoring sites

Passive sampling of benzene, toluene, ethylbenzene and xylenes (BTEX) has been conducted between 2001 and 2008 by ARC at the sites indicated in Figure 4.1. Continuous sampling of benzene and 1,3 butadiene has been undertaken at Khyber Pass Road (one of the passive sampling sites) since late 2005.

**Figure 4.1**

Approximate locations of Auckland Regional Council BTEX passive sampling sites in Auckland between 2001 and 2008. North Shore City Council's Takapuna site is also shown, along with MfE site at Kingsland.



BTEX sampling was also undertaken during 2006 at Westlake Girls High School (WGHS) Takapuna by North Shore City Council (NSCC) and at Kowhai, Kingsland by MfE as part of their obligations to WHO GEMS reporting (Figure 4.1).

The locations and monitoring periods of the most recent VOC monitoring in Auckland city are summarised in Table 4.1. More information about site descriptions can be found in Appendix A.

**Table 4.1**

Summary of recent VOC monitoring sites in the Auckland region

	<b>Monitoring period:</b>	<b>NZTM coordinates</b>
<b>Site</b>	<b>(start– finish date)</b>	<b>(Easting and Northing)</b>
Khyber Pass (BTEX)	Jun 2001 – Feb 2008	E1757826 N5918507
Khyber Pass (GC*)	Sep 2005 – continuing	E1757826 N5918507
Lincoln Road, Henderson	Jul 2001 – Jun 2006	E1745140 N5918533
Kelly Street, Mt Eden	Jul 2001 – Jun 2006	E1756895 N5918020
Gavin Street, Penrose	Jul 2001 – Jun 2006	E1761751 N5914176
WGHS, Takapuna	Jan 2006 – Dec 2006	E1756059 N5928077
Kowhai School, Kingsland	Jul 2004 – Dec 2007	E1755691 N5197772

\* Gas chromatograph

## 4.2 Passive sampling

At all sites indicated in Figure 4.1, 3M organic vapour monitor badges were used to sample BTEX compounds. These badges were initially developed for monitoring of personal exposure to organic compounds over time periods related to occupational guidelines (e.g. eight hours). However, they have since been used successfully as a survey method for sampling BTEX compounds over time periods of up to three months (Stephenson and Narsey 1998).

At each site, the BTEX badges were installed at around 3 m height and were protected by a rain hood. Badges were collected after exposure for one month, during which time air diffuses at a known rate across a membrane under which BTEX are adsorbed onto an activated carbon wafer. After sampling, the badges are retrieved for laboratory processing and analysis, including de-sorption and analysis using a gas chromatograph mass spectrometer (GC-MS). Laboratory analysis of the BTEX filters is undertaken byASUREQuality (a division of AgriQuality, New Zealand) using an IANZ<sup>9</sup> accredited method derived from the NIOSH<sup>10</sup> Method 1500 (NIOSH 1994). Earlier passive sampling has also been undertaken at these sites using CSIRO<sup>11</sup> tubes (see section 4.4.3).

Following the manufacturer's instructions (3M Technical Bulletin 1028), results are converted to mixing ratios (ppbv<sup>12</sup>) and then concentrations ( $\mu\text{g m}^{-3}$ ) at standard temperature 0°C and pressure 101.3kPa. Watercare Services Limited were contracted by ARC for this service and to provide quality assured BTEX data.

Stevenson and Narsey (1998) compared BTEX data, obtained using 3M badges, with results from pumping air through activated charcoal tubes. In addition, spike recovery

<sup>9</sup> International Accreditation New Zealand

<sup>10</sup> National Institute for Occupational Safety and Health (United States)

<sup>11</sup> Commonwealth Scientific and Industrial Research Organisation (Australia)

<sup>12</sup> Part per billion by volume

tests were undertaken, with excellent recovery rates not more than 12% different from the expected amount. These validations, along with a check of the additivity of passive sampler data, demonstrated that the 3M badges were reliable for sampling up to three months at least.

It should be noted that passive sampling is regarded as a screening method and does not always provide accurate estimates of absolute concentrations (MfE 2000c). Passive sampling is however a relatively low cost means of survey monitoring to evaluate long-term averages and high pollution areas (MfE 2000c). For screening purposes, the passive sampling data may be used to establish if concentrations are close to, or exceed, guideline values. If this is the case, further investigation using a more accurate technique is warranted. Otherwise, if concentrations are much lower than guidelines, there is no requirement for more detailed monitoring in that particular area (MfE 2000c).

Between July 2001 and February 2002, passive samplers were analysed for a suite of VOCs other than BTEX. Raw data covering the suite of contaminants for the period July 2001 to February 2002 were supplied by Watercare Services Limited and are included in Appendix B.

#### 4.3 Continuous monitoring of benzene and 1,3 butadiene

In September 2005, continuous monitoring instrumentation was installed at the Khyber Pass Road site (see Figure 4.1) to provide a record of hourly benzene and 1,3 butadiene concentrations.

A Synspec GC955 gas chromatograph photoionisation detector (GC-PID) collects air samples over a 30 minute period by using a sample piston to pump air into a pre-concentration tube. A volume of 35 ml of sample gas is collected in the pre concentration tube. A 10 port switching valve then allows the sample to be desorbed by heating the pre-concentration tube and flushing it with nitrogen carrier gas. The sample then passes into the gas chromatograph separation column. The separation column has two parts: a stripper column and an analysis column, with both columns being heated during the stripping phase.

The switching valve then allows the air sample to be separated out using the different boiling points of the hydrocarbons and the separated compounds are then measured in the instrument's photoionisation detector. The output is a chromatograph of hydrocarbons in the sample and, following calibration with standard gases, the concentration of benzene and 1,3 butadiene peaks are determined.

## 4.4 Other VOC monitoring in the Auckland region

### 4.4.1 Non-methane hydrocarbons

Total non-methane hydrocarbons (NMHC) were monitored continuously using the DANI TNMHC 451 monitor. This instrument uses a flame ionisation detector (FID) to measure hydrocarbons in air. Data were recorded as 10 minute averages. This instrument was installed at Khyber Pass Road in 1997 and was moved around various locations in the Auckland region.

NMHC data are expressed as the mixing ratio parts per million carbon (ppmC). Because the mix of hydrocarbon species is unknown and is likely to vary over time, it is impossible to identify the molecular weight for conversion to concentration units (e.g.  $\mu\text{g m}^{-3}$ ).

NMHC was initially monitored because of concerns about photochemical smog formation in Auckland (Rolfe & Graham 1999). Monitoring commenced at Gavin Street (Penrose) in 1994 and Khyber Pass Road (Newmarket) in 1998, although Rolfe & Graham (1999) considered it would be more useful to monitor NMHC: NO<sub>x</sub> ratios in a mobile facility at a variety of sites.

### 4.4.2 VOC canisters

In a collaborative study between NIWA<sup>13</sup> and York University, 14 VOC canister air samples were taken by NIWA staff from three sites in Auckland (Khyber Pass Road, Takapuna and Musick Point) between March and August 1999. These samples were taken by filling an evacuated canister with ambient air. The canisters were then shipped to the Atmospheric Science Department, York University (Canada) to be analysed for a variety of VOCs, including BTEX and 1,3 butadiene, using sample enrichment and GC-FID (Gas Chromatography – Flame Ionisation Detection). The samples were also analysed for C<sup>13</sup> isotopes, but the data is not discussed in this report.

### 4.4.3 CSIRO BTEX sampler tubes

Between June 2000 and February 2002, passive samplers developed by the CSIRO were installed at the Khyber Pass Road, Henderson, Mount Eden and Penrose sites (Figure 4.1). These samplers were constructed with stainless steel tube, of 6.35 mm diameter and 90 mm length, and packed with an adsorbent material. The CSIRO tubes were deployed by removing end caps to expose the adsorbent to gases.

At the end of every one month sampling period, end caps were replaced and the tubes retrieved for laboratory analysis. Following desorption in the laboratory, desorbed gases were analysed with a gas chromatograph to determine the concentrations of BTEX compounds.

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<sup>13</sup> Under the FRST program – Urban Air Quality Processes – Objective 2 – Pollution Sources and Trends, 1999

#### 4.4.4 USEPA TO-17 trial

In 2004 at the Gavin Street (Penrose) site, a trial was undertaken using a technique based on USEPA Method TO-17 'Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes' (TO-17). This method requires air to be drawn through a sorbent tube to collect benzene and other VOCs. Thermal desorption and analysis using gas chromatography is undertaken after the sampling period, to quantify the concentrations of ambient VOCs.

Two identical instruments were employed for this trial between May and July 2004, and benzene concentrations were elucidated from sampling at daily, weekly, fortnightly, three weekly and four weekly periods (Hannaby 2004). While the results suggested that benzene concentrations could be measured by the method for periods up to one week, benzene losses by breakthrough were observed at 4.2% for weekly periods and at least 37% for sampling greater than one week. Therefore, it was decided not to proceed with this method.

## 5 BTEX passive sampling results

Running annual means of monthly 3M passive BTEX data are plotted in Figure 5.1. Following ARC policy and recommendations by MfE (2002), averages were not calculated when less than 75% of monthly data were available. Running means were therefore calculated for 12 month periods when nine or more valid monthly data were available; otherwise a gap was entered in the running mean data.

In Figure 5.1, the maximum running annual mean concentrations of toluene and total xylenes, at all sites, are orders of magnitude lower than NEPM monitoring investigation levels of  $410 \mu\text{g m}^{-3}$  and  $950 \mu\text{g m}^{-3}$  respectively. Likewise, running annual mean concentrations of ethylbenzene are orders of magnitude lower than the Texas effects screening level of  $200 \mu\text{g m}^{-3}$ . There is no indication that more detailed monitoring of toluene, ethylbenzene or xylenes is required at the Auckland sites.

There is evidence of interannual variation of toluene, ethylbenzene and xylenes in Figure 5.1, with around 30% - 40% reduction of annual mean concentrations of these contaminants since 2003. Continuation of the passive sampling campaign may be useful as a relatively low cost means of monitoring trends, to provide data for future assessments of spatial and interannual temporal variability.

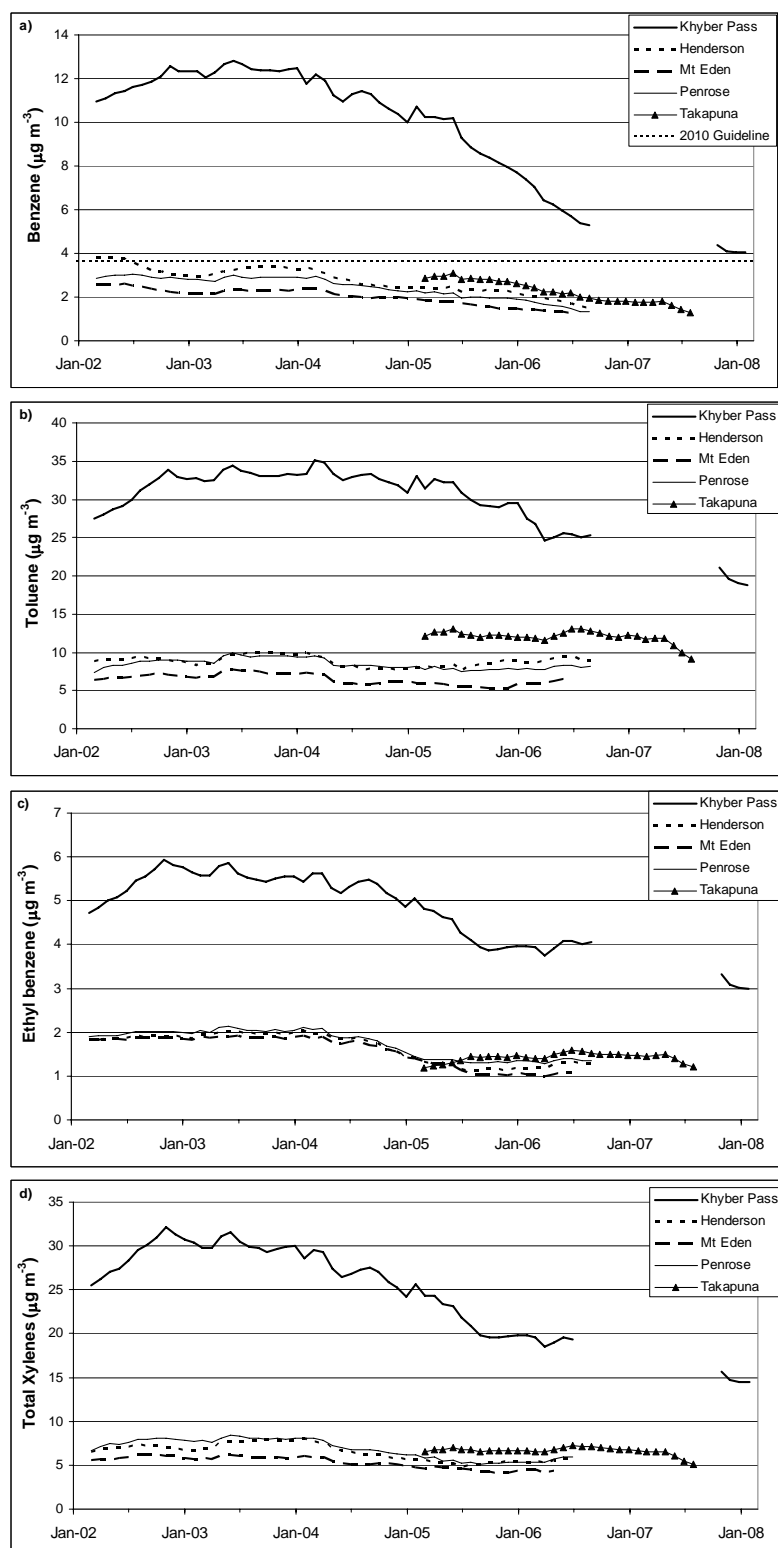
Invariably, concentrations of all contaminants were three to four times greater at Khyber Pass Road than at Henderson, Mount Eden and Penrose (Figure 5.1). The Takapuna running means are based on monthly sampling conducted by North Shore City Council at Westlake Girls High School (WGHS) during 2006. Running means for Takapuna are included in Figure 5.1, apart from ethylbenzene which had less than 75% of data available for the year. While the Takapuna data are restricted to 2006 only, concentrations of benzene, toluene and xylenes at WGHS were less than those recorded at the Khyber Pass Road monitoring site, but slightly greater than concentrations observed at other Auckland locations.

With the exception of data from Khyber Pass Road, all measured benzene concentrations have been less than the current MfE guideline value of  $10 \mu\text{g m}^{-3}$ . Moreover, apart from at Khyber Pass Road, running annual mean benzene concentrations were around  $2 \mu\text{g m}^{-3}$  at the passive sampling sites when monitoring was discontinued in 2006. The most recently available annual mean data from the Henderson, Mount Eden, Penrose and Takapuna sites are thus lower than the guideline of  $3.6 \mu\text{g m}^{-3}$  that will apply from 2010.



**Figure 5.1**

Running annual mean concentrations of a) benzene; b) toluene; c) ethylbenzene; and d) total xylenes from monthly passive sampling, July 2001 to December 2007. Takapuna data were provided by North Shore City Council.



The passive sampling survey assessment therefore indicates that there is no immediate demand for a more detailed investigation of benzene concentrations at the Henderson, Mount Eden, Penrose and Takapuna sites. However, because changes in fuel quality, vehicle technology, traffic density, fleet composition or meteorology may affect ambient benzene concentrations at these sites in future years, continued passive sampling would be worthwhile to monitor inter-annual trends.

At Khyber Pass Road, running annual mean benzene concentrations have been observed at levels above  $10 \mu\text{g m}^{-3}$  (Figure 5.1), although concentrations have been declining since 2004. The mean benzene concentrations in air at Khyber Pass have declined by around 75% from a peak of  $12 \mu\text{g m}^{-3}$  in 2003, to  $4 \mu\text{g m}^{-3}$  in 2007. This is coincidental with fuel specifications that mandated a reduction of benzene in petrol from 4% to 3% in 2004 and subsequently, in January 2006, down to a maximum of 1%. This represents a 75% reduction in allowable benzene content since 2004, although in reality average benzene concentrations in fuel prior to 2004 have typically been less than specified in the earlier regulations (MED 2000, 2001, 2002a, 2003). Annual running mean benzene concentrations at the other sites also decreased over the same sampling period.

Other factors that may affect the annual VOC concentrations include vehicle technology, traffic density, fleet composition or meteorology. If the only influence on ambient benzene concentrations since 2003 was the reduction of benzene in petrol, it may be expected that the reduction of ambient concentrations might be observed for benzene only. However, ambient concentrations of other BTEX compounds have also declined at Khyber Pass Road (albeit not as profoundly as the 75% reduction of ambient benzene), yet there were no major reductions of toluene, ethylbenzene or xylenes mandated by Government. It is possible that other influences such as vehicle technology, traffic density, fleet composition or meteorology may have also had some impact on ambient benzene concentrations at Khyber Pass Road, along with the improvements in fuel quality.

While declining, the most recent annual mean benzene data from passive sampling at the Khyber Pass Road site are around  $4 \mu\text{g m}^{-3}$ . This is above the guideline of  $3.6 \mu\text{g m}^{-3}$  that will apply from 2010. The nature of passive sampling is that it is a survey method only and, because of the higher benzene concentrations observed at Khyber Pass Road that currently exceed the 2010 guideline value, a more detailed investigation of benzene is warranted at this site. Section 6 includes results from continuous monitoring of benzene and an evaluation of compliance with the MfE guideline is more appropriate using data from that more robust analysis (in that section).

## 6 Continuous monitoring of benzene and 1,3 butadiene

### 6.1 Daily variation of benzene and 1,3 butadiene concentrations

Average hourly concentrations of benzene and 1,3 butadiene in Figure 6.1 show the diurnal variability of all data. Two distinct peaks are evident for both benzene and 1,3 butadiene: with high points at 8–9 am and 5–6 pm. The timing of these peaks suggests that the dominant source of the contaminants is traffic emissions during peak hour commuter traffic. While the absolute magnitude of concentrations throughout the day differs between the plots of benzene and 1,3 butadiene, the diurnal patterns are remarkably similar. This is evidence that the sources of each contaminant are the same and supports the hypothesis that (predominantly petrol powered) motor vehicles are the dominant source of maximum hourly benzene and 1,3 butadiene concentrations.

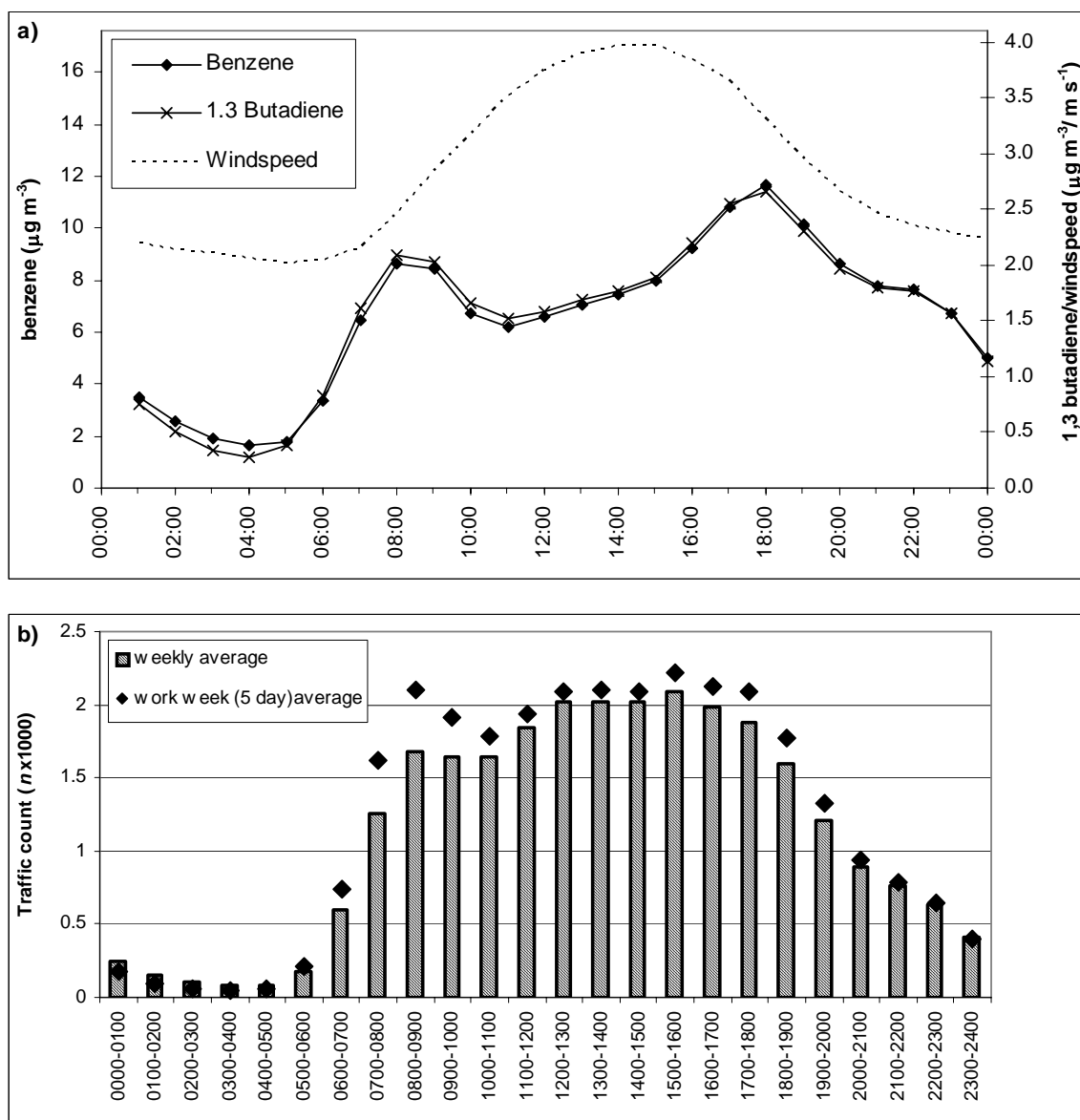
Meteorological effects are also likely to be influencing the diurnal variation of VOC concentrations. Kuschel et al. (1998) observed a considerable impact of windspeed on the diurnal variation of VOC concentrations, especially during the middle of the day when traffic levels were high but pollutant concentrations were mitigated by higher windspeeds.

Figure 6.1a shows that benzene and 1,3 butadiene concentrations at Khyber Pass Road generally increase during the early morning hours. This is likely to be a consequence of increasing vehicle emissions, because traffic counts also increase at the same time (Figure 6.1b). After 0900hr the association of VOC concentrations and traffic counts is confounded by meteorological influence.

Figure 6.1a also shows a reduction of benzene and 1,3 butadiene concentrations between 0900hr and 1400hr, which is coincidental with relatively high average windspeed at this time (Figure 6.1b). This is consistent with the mitigating effect of windspeed on VOC concentrations observed by Kuschel et al. (1998).

**Figure 6.1**

Diurnal variation of: **a)** benzene concentrations on primary axis, with 1,3, butadiene concentrations and windspeed on secondary axis; and **b)** traffic counts. All data are ensemble averages from hourly observations at Khyber Pass Road between 2005-2007.

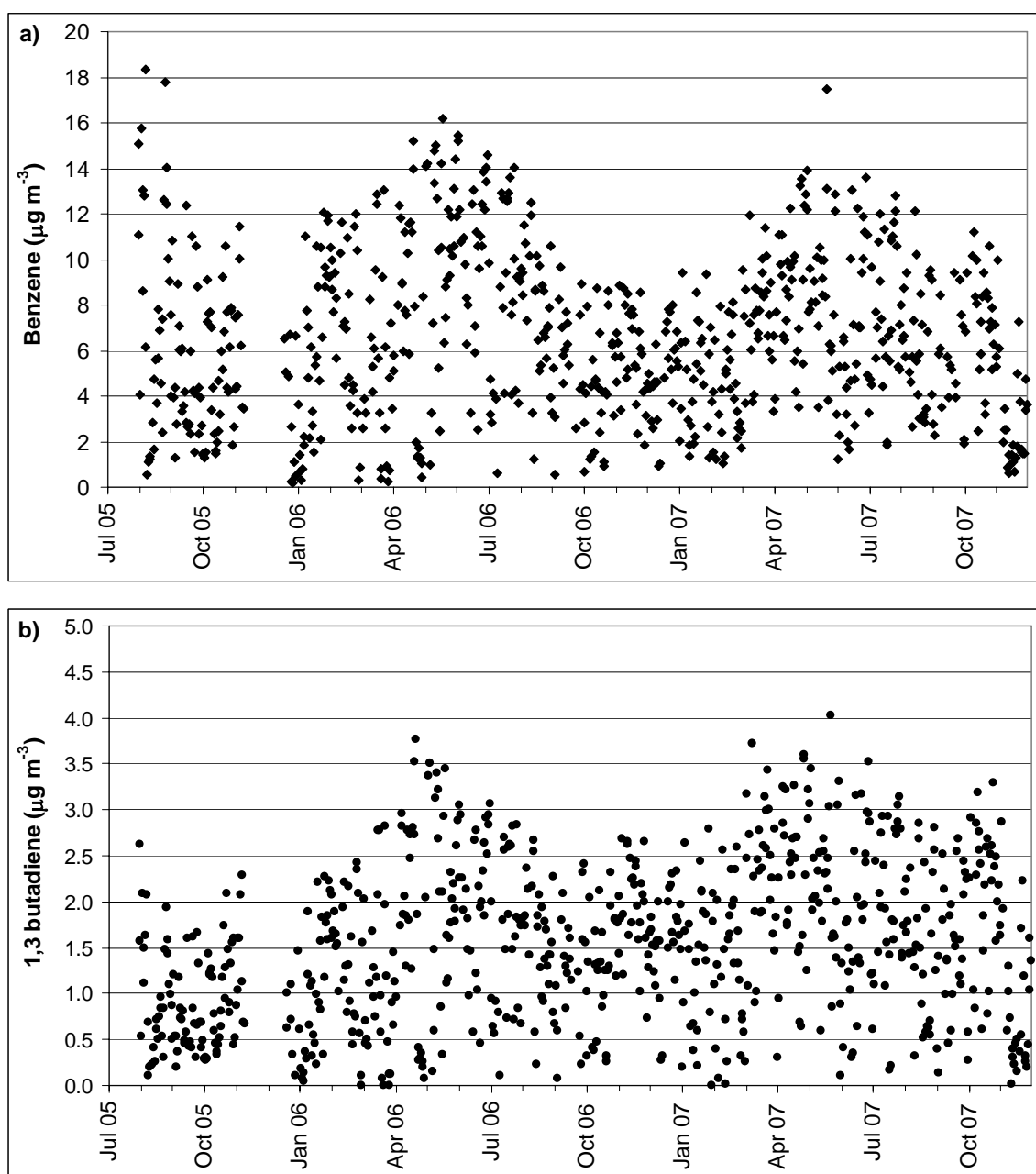


## 6.2 Seasonal variation of benzene and 1,3 butadiene concentrations

Daily average concentrations of benzene and 1,3 butadiene are plotted in Figure 6.2a and Figure 6.2b respectively. The maximum observed 24 hour average concentrations of each contaminant are  $18.3 \mu\text{g m}^{-3}$  (Sept 2005) and  $4.0 \mu\text{g m}^{-3}$  (June 2007) for benzene and 1,3 butadiene respectively.

**Figure 6.2**

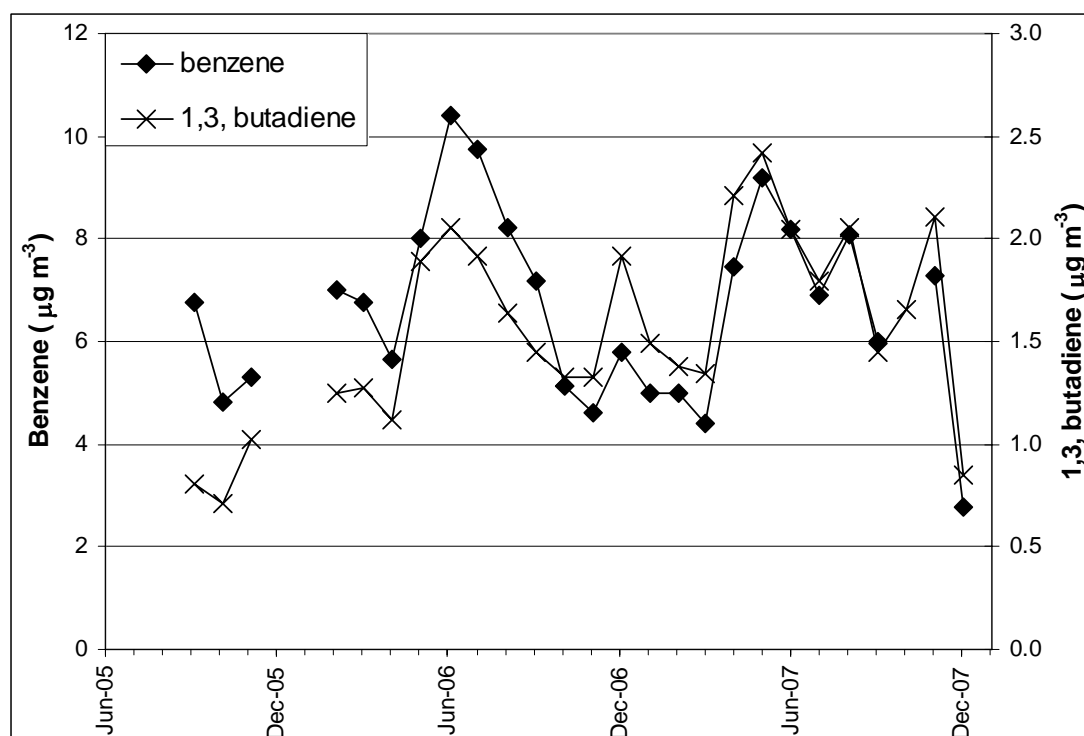
Daily average concentrations of a) benzene and b) 1,3, butadiene obtained by GC continuous monitoring at Khyber Pass Road, August 2005 – December 2007. Note different scales on y-axes.



Seasonal variation of both contaminants is evident in Figure 6.2 and this is also appears to be the case in plots of monthly averages in Figure 6.3. As with the diurnal plot in Figure 6.1a, the variability of monthly concentrations of benzene and 1,3 butadiene is similar for the two contaminants (Figure 6.3). Peak concentrations occur in winter for both contaminants and this may be a consequence of meteorological variation, as Kuschel et al. (1998) note that wind speeds tend to be lowest during winter and autumn.

**Figure 6.3**

Monthly average concentrations of benzene and 1,3, butadiene obtained by GC continuous monitoring at Khyber Pass Road, August 2005 – December 2007.



### 6.3 Benzene, 1,3 Butadiene Ratios

Due to the similarity of diurnal and monthly plots in Figure 6.1 and Figure 6.3 respectively, it is worth exploring the ratio of 1,3 butadiene to benzene concentrations. There is potential to use this ratio to estimate ambient concentrations of 1,3 butadiene based on benzene data obtained by passive sampling. Stevenson and Narsey (1999) adopted this approach and reported a range of 1,3 butadiene/benzene ratios between 10% and 20%, from various research in Australia, USA and UK during 1997-1998. Stevenson and Narsey (1999) chose a 1,3 butadiene/benzene ratio of 15% to facilitate assessment of 1,3 butadiene exposure in their research.

The mean (with 95% confidence limits in brackets) of hourly 1,3 butadiene/benzene ratios from Khyber Pass Road during 2005-2007 is 24.3% (±0.4%), which is greater

than the ratios reported by Stevenson and Narsey (1999). The reason for a higher ratio in more recent years is most likely to be a consequence of benzene in petrol being reduced by 75% since 2004. Emissions from 1,3 butadiene are mainly a product of olefin combustion and the contaminant is not present in petrol itself. Changes to fuel specifications for olefins in petrol (from 25% maximum in 2004 to 18% in 2006) have not been as substantial as the regulations for benzene. Therefore, emissions of 1,3 butadiene are unlikely to have varied by as much as benzene emissions.

The ratio of 1,3 butadiene/benzene will have been greatly affected by the progressive 75% reduction of benzene in petrol since 2003. Therefore, while the ratio of 1,3 butadiene/benzene may be used to infer ambient concentrations of 1,3 butadiene based upon benzene data from BTEX sampling, it is not appropriate to undertake a wholesale analysis of 1,3 butadiene using the historic BTEX data from Khyber Pass Road and other Auckland sites. However, provided that sources of 1,3 butadiene and benzene are similar and if fuel specifications do not change in the meantime, the ratio of 24% could be used to infer 1,3 butadiene concentrations from passive BTEX sampling undertaken at other Auckland sites in the future. For validation of this investigation, it would be useful to continue passive BTEX sampling at Khyber Pass Road, along with the continuous GC measurements, to monitor any variation of the ratio over time.

## 6.4 Comparison of passive and continuous benzene data

As a first step in assessing the validity of the passive BTEX data, Figure 6.4 is a time series plot of monthly benzene concentrations obtained using the passive 3M records, along with monthly averages from the continuous GC data. Despite some gaps in the BTEX record (due to samplers not being deployed July-December 2006 and August-September 2007), seasonal variation from the time series' of both techniques is similar. Winter peak concentrations and reductions during summer are evident from both plots in Figure 6.4, however the passive data are invariably lower than monthly averages obtained from the GC records.

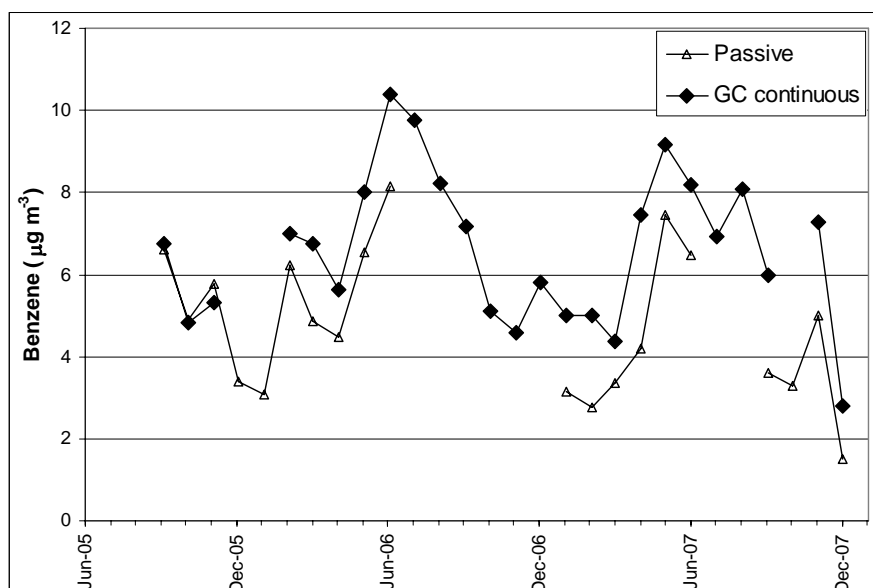
To statistically evaluate the equivalency of the passive BTEX data, a Reduced Major Axis (RMA) linear regression was fit to the one-to-one plot of passive and GC data in Figure 6.5. RMA regression is more appropriate than ordinary least squares (OLS) regression when the independent variable values are not known precisely. When comparing air quality data obtained using two different techniques, as is the case in Figure 6.5, deviations between the observations and one-to-one line occur in both  $x$  and  $y$  directions, which necessitates the application of RMA regression rather than OLS (Ayers 2001).

The RMA regression model is described by Equation 1 and, with a correlation coefficient of 0.74, this provides a model for adjusting benzene data obtained by passive sampling in Auckland to GC equivalency.

Equation 1       $y=1.05x+1.2$        $r^2=0.74$

**Figure 6.4**

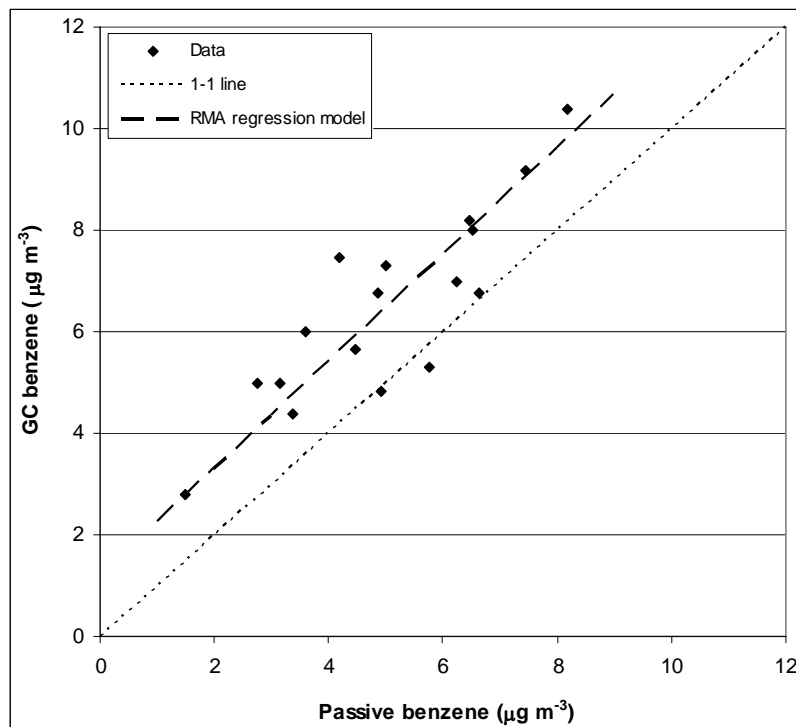
Time series of monthly average benzene concentrations obtained by passive sampling and GC continuous monitoring at Khyber Pass Road, August 2005 – December 2007.





**Figure 6.5**

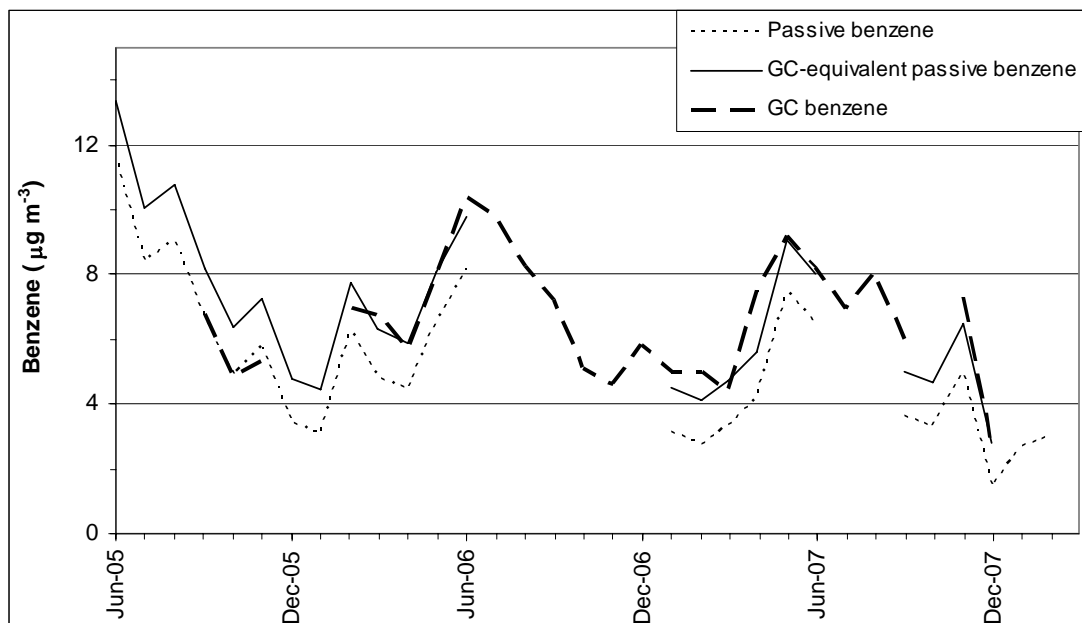
Monthly average benzene data by passive sampling versus GC continuous monitoring. RMA regression model (Equation 1) has correlation coefficient  $r^2=0.744$ . Dotted line is one-to-one line.



When the passive benzene data are scaled up for GC-equivalency, using Equation 1, the monthly passive benzene data provide an approximation to monthly averages of the GC data (Figure 6.6). This allows the BTEX data to be used for a long-term analysis of interannual variation and comparison against annual guidelines since 2001 (see section 7).

**Figure 6.6**

Monthly average benzene concentrations at Khyber Pass Road, 2005–2008. Data were obtained by passive sampling, GC continuous monitoring and GC-equivalent data obtained by scaling up passive data, using Equation 1.



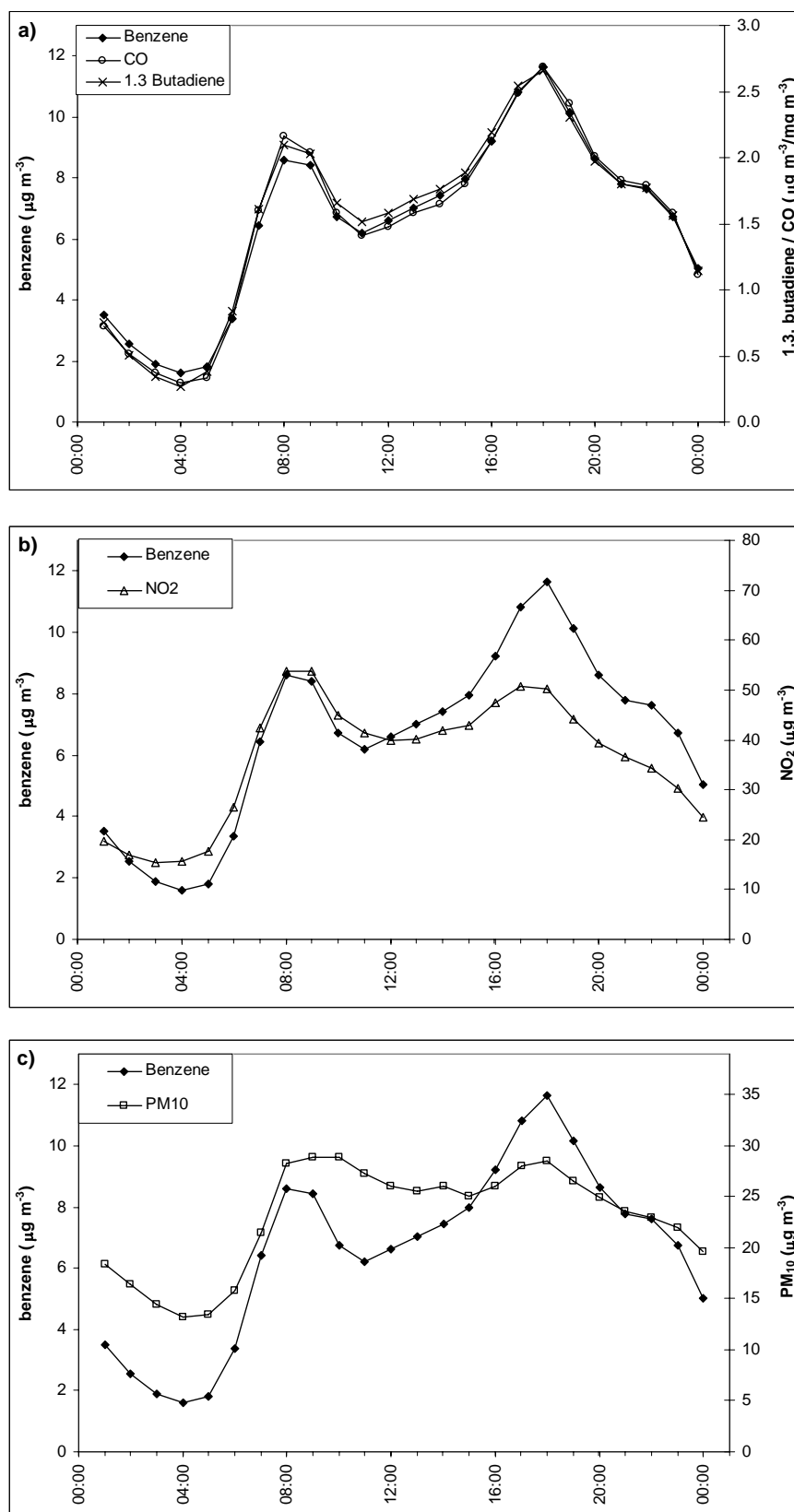
## 6.5 Comparison with carbon monoxide, nitrogen dioxide and particulate matter

### 6.5.1 Diurnal variation of other contaminants

Ensemble hourly average benzene concentrations are used in Figure 6.7 as a benchmark for comparing the diurnal variability of other air contaminants. The diurnal variations of hourly average benzene, 1,3 butadiene and carbon monoxide (CO) concentrations are entirely consistent with each other (Figure 6.7a). This indicates that the source of all three contaminants is the same (i.e. motor vehicles) and there are no other confounding influences associated with ambient concentrations of these air pollutants. The diurnal variability of hourly nitrogen dioxide (NO<sub>2</sub>) concentrations is similar to benzene, however an attenuation of NO<sub>2</sub> appears to occur during late afternoon and evening.

**Figure 6.7**

Diurnal variation of benzene and: **a)** 1,3, butadiene and CO; **b)** NO<sub>2</sub>; and **c)** PM<sub>10</sub> concentrations shown by ensemble average hourly concentrations from data collected at Khyber Pass Road, 2005 –2007.



The diurnal variation of particulate matter ( $PM_{10}$ ) appears to be even more inconsistent (than  $NO_2$ ) with that of benzene. This is most likely a consequence of variable sources of  $PM_{10}$ , compared with benzene which is predominantly from motor vehicles. Using receptor modeling, Davy et al. (2007) reported that motor vehicles contribute 46% of  $PM_{10}$  concentrations at Khyber Pass Road on an annual basis, while marine aerosols contribute 29%, biomass burning (including domestic home heating) contributes 12% and soil 10% of annual  $PM_{10}$ . The timing of  $PM_{10}$  contributions from sources other than motor vehicles are likely to vary from the diurnal variation of benzene, which is dominated by motor vehicle contributions. For example, sea salt is most likely to be dominant during periods with high windspeed, while contributions from domestic (biomass burning) sources are likely to be greatest in evenings and night time when solid fuel heating appliances are used most often.

## 6.5.2 Seasonal variation of other contaminants

Figure 6.8 displays three month running mean plots, to show seasonal variation of the same contaminants included in Figure 6.7. Whereas the seasonal plots of benzene, 1,3 butadiene, CO (Figure 6.8a) and  $NO_2$  (Figure 6.8b) show similar variability, the seasonal variation of  $PM_{10}$  is relatively unique (Figure 6.8c).

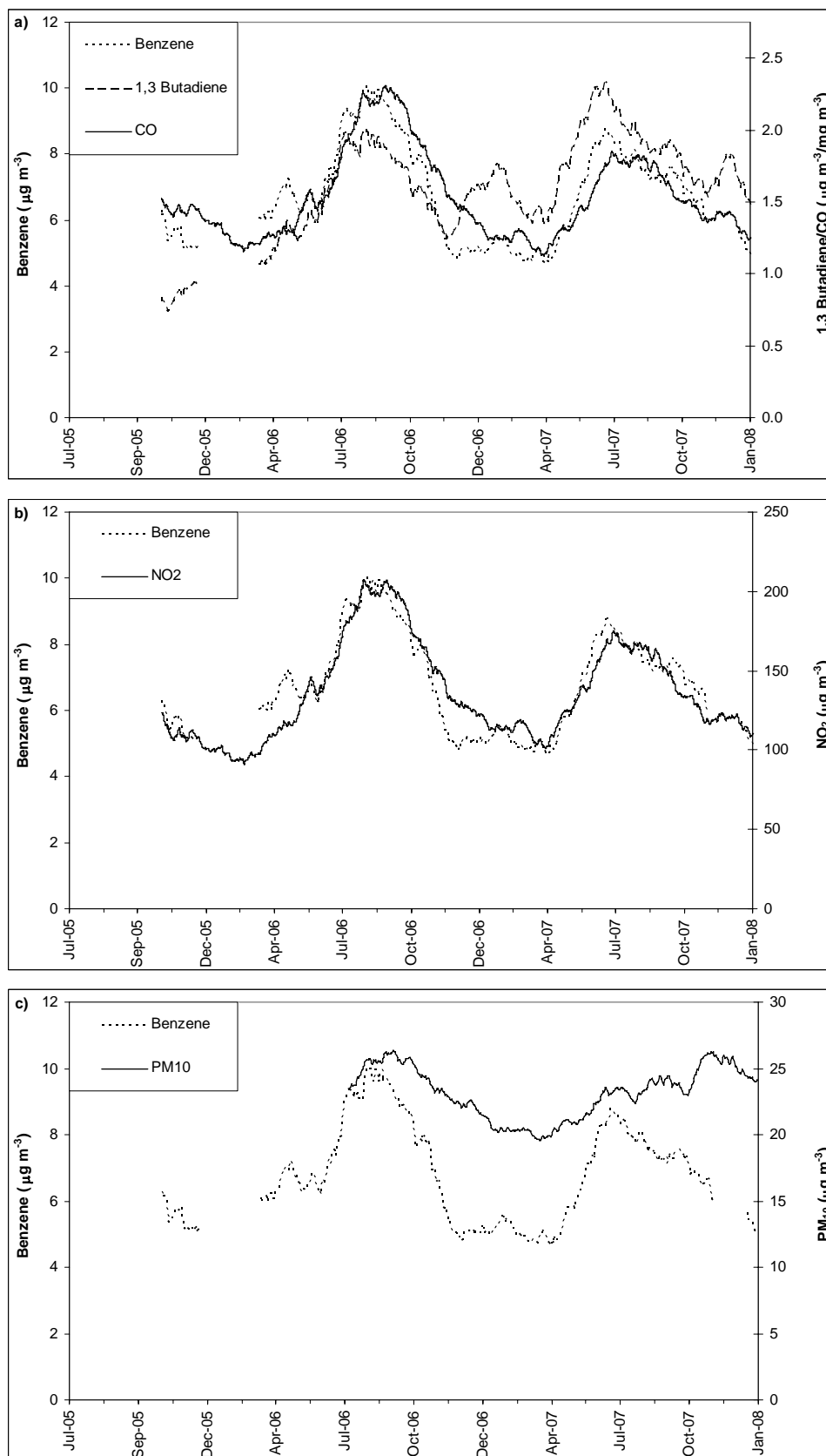
CO, benzene and 1,3 butadiene concentrations are greatest in winter and there is a distinct decline during summer and autumn (Figure 6.8a). This may be a consequence of lower average windspeed during winter, which would retard dispersion of the contaminants.

The seasonal variation of  $NO_2$  in Figure 6.8b closely resembles the plots of other contaminants in Figure 6.8a. However, the seasonal variation of  $NO_2$  is likely to be influenced by meteorological conditions and also the availability of ozone. Following an airshed modeling investigation, Gimson (2005) considered that  $NO_2$  concentrations in Auckland were limited by ozone availability, rather than being a consequence of changes in traffic congestion. Xie et al. (2007) considered that higher winter  $NO_2$  concentrations across the Auckland region were a consequence of "higher background ozone levels and poor dispersion conditions in winter, rather than an increase in  $NO_x$  emissions during that period".

In Figure 6.8c, the pattern of seasonal variation of  $PM_{10}$  does not resemble that of the other contaminants in Figure 6.8a and Figure 6.8b. Unlike the other contaminants, it is likely that seasonal variability of  $PM_{10}$  is influenced by both source variability and meteorological phenomena. Compared with the plots in Figure 6.8a and Figure 6.8b, there is much less attenuation of  $PM_{10}$  concentrations (Figure 6.8c) during summer at Khyber Pass Road. This is likely to be a consequence of considerable sea salt contributions to  $PM_{10}$  during summer. Davy et al. (2007) estimated that marine aerosol sources contribute 17% of overall  $PM_{10}$  during winter at Khyber Pass Road, but contributed 64% of  $PM_{10}$  on a peak day in summer when the 24 hour average  $PM_{10}$  concentration was  $32 \mu g m^{-3}$ . Source variability is therefore a likely explanation of the different pattern of seasonal  $PM_{10}$  concentrations, when compared to the other contaminants in Figure 6.8.

**Figure 6.8**

Seasonal variation of benzene and **a)** 1,3, butadiene and CO; **b)** NO<sub>2</sub>; and **c)** PM<sub>10</sub>, concentrations, shown by 3 month running means of concentrations recorded at Khyber Pass Road, 2005 –2007.



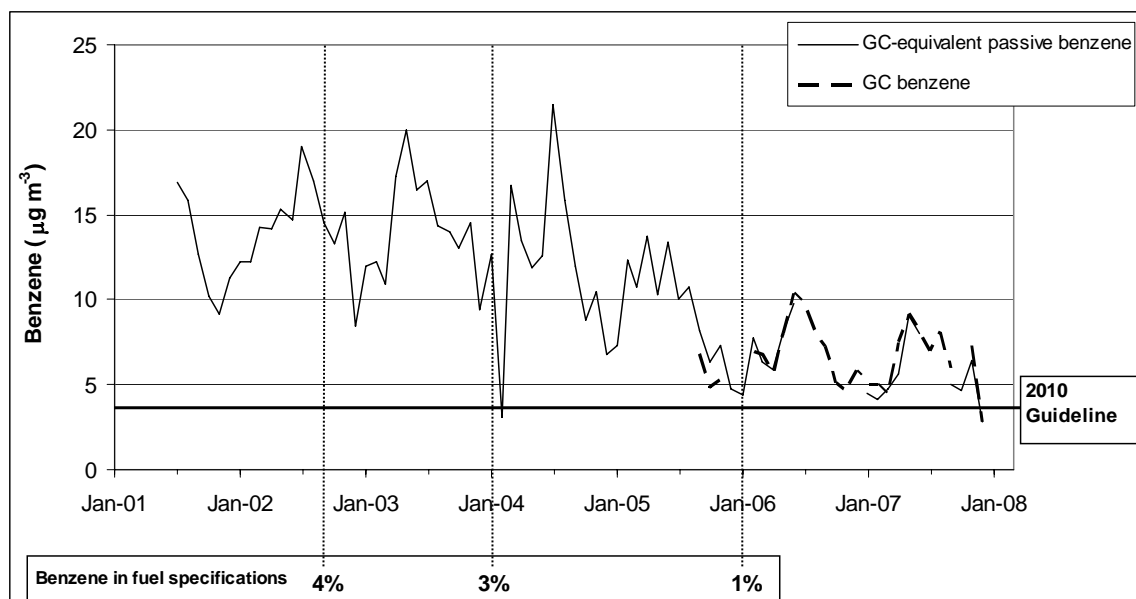
## 7 Interannual variation and comparison with ambient air quality guidelines

### 7.1 Interannual variation of benzene concentrations at Khyber Pass Road

The GC dataset provides only limited analysis of interannual variation because it only commenced in 2005. The longer term passive sampling benzene data are more suited for evaluating long-term trends. After adjusting the 3M benzene concentrations for GC equivalency (Equation 1), the time series of monthly data from passive sampling at Khyber Pass Road are plotted in Figure 7.1.

**Figure 7.1**

Monthly benzene concentrations at Khyber Pass Road, obtained by monthly passive sampling data, scaled up for GC equivalency using Equation 1. Data from the GC are also included for gap filling. Changes to specifications for benzene in petrol are indicated by vertical dotted lines.



While the MfE 2010 guideline of 3.6  $\mu\text{g m}^{-3}$  that will apply from 2010 is shown in Figure 7.1 as a benchmark, caution is required because the data in Figure 7.1 are monthly averages, yet the MfE guideline is for comparison with annual averages. Therefore, the data in Figure 7.1 are not intended for evaluation of guideline compliance per se, however the trends may be compared against the current annual air quality guideline of 10  $\mu\text{g m}^{-3}$  and the 2010 guideline of 3.6  $\mu\text{g m}^{-3}$ .

Monthly benzene concentrations generally remained above  $10 \mu\text{g m}^{-3}$  until the latter half of 2005. The petroleum industry was faced with fuel specifications that required a maximum benzene content in petrol of 1% from January 2006 and the reduction of ambient benzene concentrations in late 2005 is possibly a reflection of reductions starting to be implemented ahead of time. Despite the reduction in January 2006 to 1% benzene in petrol, monthly benzene concentrations at Khyber Pass Road since this time have remained above the 2010 guideline of  $3.6 \mu\text{g m}^{-3}$ , apart from a value of  $2.8 \mu\text{g m}^{-3}$  in December 2007.

## 7.2 Comparison with benzene and 1,3 butadiene guidelines

When evaluating ambient benzene and 1,3 butadiene concentrations against annual guideline values in the UK, running means of daily averages are used (Stedman and Dore 1998). Following this approach, the maximum running annual means from ARC GC and 3M passive sampling of benzene are reported here for comparison with ambient guidelines.

As noted by Stedman and Dore (1998), the magnitude of reported annual average VOC concentrations is influenced by the averaging method. A fixed annual mean is the average across a calendar year, whereas the maximum annual running mean will include data from up to two calendar years. The maximum annual running mean is usually slightly larger than the fixed annual mean (Stedman and Dore 1998).

Therefore, fixed annual means for data collected across the calendar years 2006 and 2007 are also included in Table 7.1, for comparison with other reports that may present fixed annual averages.

**Table 7.1**

Summary of annual statistics for concentrations of benzene and 1,3 butadiene obtained using continuous GC at Khyber Pass Road, 2005-2007.

	Benzene ( $\mu\text{g m}^{-3}$ )			1,3 butadiene ( $\mu\text{g m}^{-3}$ )		
	2005	2006	2007	2005	2006	2007
<b>% valid data<sup>14</sup></b>	28%	84%	88%	28%	85%	92%
<b>Maximum daily concentration</b>	18.3	16.2	17.5	2.6	3.8	4.0
<b>Fixed annual mean</b>	N/A	7.0	6.3	N/A	1.5	1.7
<b>Maximum running annual mean</b>	N/A	7.2	7.1	N/A	1.5	1.8

<sup>14</sup> Note that due to the duration of calibrations and annual servicing (and as ARC does not have a spare GC-PID) and problems with the spectra due to moisture, the percent valid data is less than what can usually be achieved with the standard gas analysers.

The maximum running annual mean for benzene has remained around  $7 \mu\text{g m}^{-3}$  for both 2006 and 2007. This is below the current MfE guideline value of  $10 \mu\text{g m}^{-3}$ , but is nearly twice the guideline of  $3.6 \mu\text{g m}^{-3}$  that will apply in 2010.

The maximum annual running mean for 1,3 butadiene was  $1.5 \mu\text{g m}^{-3}$  in 2006 and  $1.8 \mu\text{g m}^{-3}$  in 2007. This is less than the MfE guideline value of  $2.4 \mu\text{g m}^{-3}$ . The 2007 annual average of  $1.8 \mu\text{g m}^{-3}$  is 75% of the MfE guideline and falls within the alert category in the MfE list of environmental performance indicators. The alert category is regarded as a warning that levels of a pollutant may lead to exceedances if trends are not curbed (MfE 2002).

### 7.3 Comparison with results from other benzene monitoring in New Zealand

Annual average benzene concentrations in New Zealand are commonly reported as fixed annual averages. The results from this study are presented in Table 7.2 as both running annual means and fixed annual averages. To be consistent with other reports, the fixed annual averages from this study should be used when comparing results from other New Zealand urban areas.

The benzene results from this study are consistent with those from other urban areas in New Zealand. The fixed annual mean benzene concentrations from Khyber Pass Road, obtained using 3M passive filters ( $4.1 \mu\text{g m}^{-3}$ ) and GC ( $6.3 \mu\text{g m}^{-3}$ ), are consistent with results from Nelson, Mt Maunganui and roadside sampling in Christchurch (Table 7.2). The fixed annual mean benzene concentrations from other Auckland sites ( $1.3$  to  $2.2 \mu\text{g m}^{-3}$ ) are consistent with results from Hamilton, Tauranga, Whakatane and Christchurch residential sites.



**Table 7.2**

Summary of recently reported annual average concentrations of ambient benzene. Khyber Pass Road GC concentrations are reported as both fixed annual and maximum running annual means. All other concentrations are fixed annual means

Location	Sampling duration	Concentration ( $\mu\text{g m}^{-3}$ )	Monitoring method
Khyber Pass – this study	Continuous, 2007 Calendar year	7.1 (running mean)	GC
Khyber Pass – this study	Continuous, 2007 Calendar year	6.3 (fixed mean)	GC
Khyber Pass – this study	Monthly, 2007 Calendar year	4.1	3M passive badges (not corrected for GC equivalency)
Other Auckland locations – this study <sup>15</sup>	Monthly, Jul 2005 to Jun 2006	1.3 to 2.2	3M passive badges (not corrected for GC equivalency)
Christchurch – 3 roadside sites <sup>16</sup>	Monthly, Feb 2004 to Feb 2005	5.5 to 9.1	3M passive badges
Christchurch – 7 residential sites <sup>7</sup>	Monthly, Feb 2004 to Feb 2005	0.7 to 2.7	3M passive badges
Nelson City <sup>17</sup>	2003-2004	4.2	Passive diffusion tubes
Hamilton City – 6 sites <sup>18</sup>	3 monthly, Dec 2006 to Dec 2007	1.1 to 3.5	3M passive badges
Tauranga <sup>19</sup>	3 monthly, Aug 2000 to Jul 2001	1.3	3M passive badges
Mt Maunganui <sup>10</sup>	3 monthly, Aug 2000 to Jul 2001	5.4	3M passive badges
Whakatane <sup>10</sup>	3 monthly, Aug 2000 to Jul 2001	2.0	3M passive badges
Rotorua <sup>10</sup>	3 monthly, Aug 2000 to Jul 2001	1.7	3M passive badges

<sup>15</sup> Other Auckland locations include Mt Eden, Penrose, Henderson, NSCC Takapuna and MfE Kowhai sites.

<sup>16</sup> McCauley (2005)

<sup>17</sup> Cited by McCauley (2005)

<sup>18</sup> Wilton and Baynes (2008)

<sup>19</sup> Iremonger (2002)

Annual average benzene results from MfE GEMS monitoring sites in Auckland are shown in Table 7.3. The trend of GEMS data is consistent with the interannual variation of ARC results that showed benzene concentrations have been declining in recent years.

GEMS results are generally consistent with the ARC results, except that the concentration for Mount Eden in 2004 is overestimated for the GEMS result ( $3.0 \mu\text{g m}^{-3}$ ) compared with the ARC data ( $2.0 \mu\text{g m}^{-3}$ ). This anomaly is possibly a consequence of GEMS data not being available for the 3<sup>rd</sup> quarter of 2004 at Mount Eden. While 74% of the data were available, this data gap would have biased the 2004 GEMS data at this site, so that the winter period was over-represented. This is very likely to have been responsible for at least some of the disparity with ARC data for 2004.

**Table 7.3**

Annual average benzene concentrations obtained from 3M passive sampling at ARC and MfE GEMS monitoring sites. ARC results are averaged from monthly samples, while MfE results are averages of three-monthly samples. All concentrations are fixed annual means over full calendar years unless specified.

	Annual average benzene concentration ( $\mu\text{g m}^{-3}$ )					
	Mt Eden		Penrose		Kowhai	
Sampling period	ARC	MfE	ARC	MfE		MfE
2007				1.1		1.3
2006				1.1		1.3
2005	1.5	1.4	1.9	1.9		2.2
Mt Eden Jan-Oct; Penrose all 2004	2.0	3.0	2.3	2.2		
2003	2.3	2.0	2.9	2.6		
2002	2.2	2.1	2.9	2.8		
April 2001 to December 2001		2.5		2.9		

## 8 Other VOC monitoring in Auckland

The purpose of this section is, for completeness, to briefly describe results from other monitoring of VOCs in Auckland.

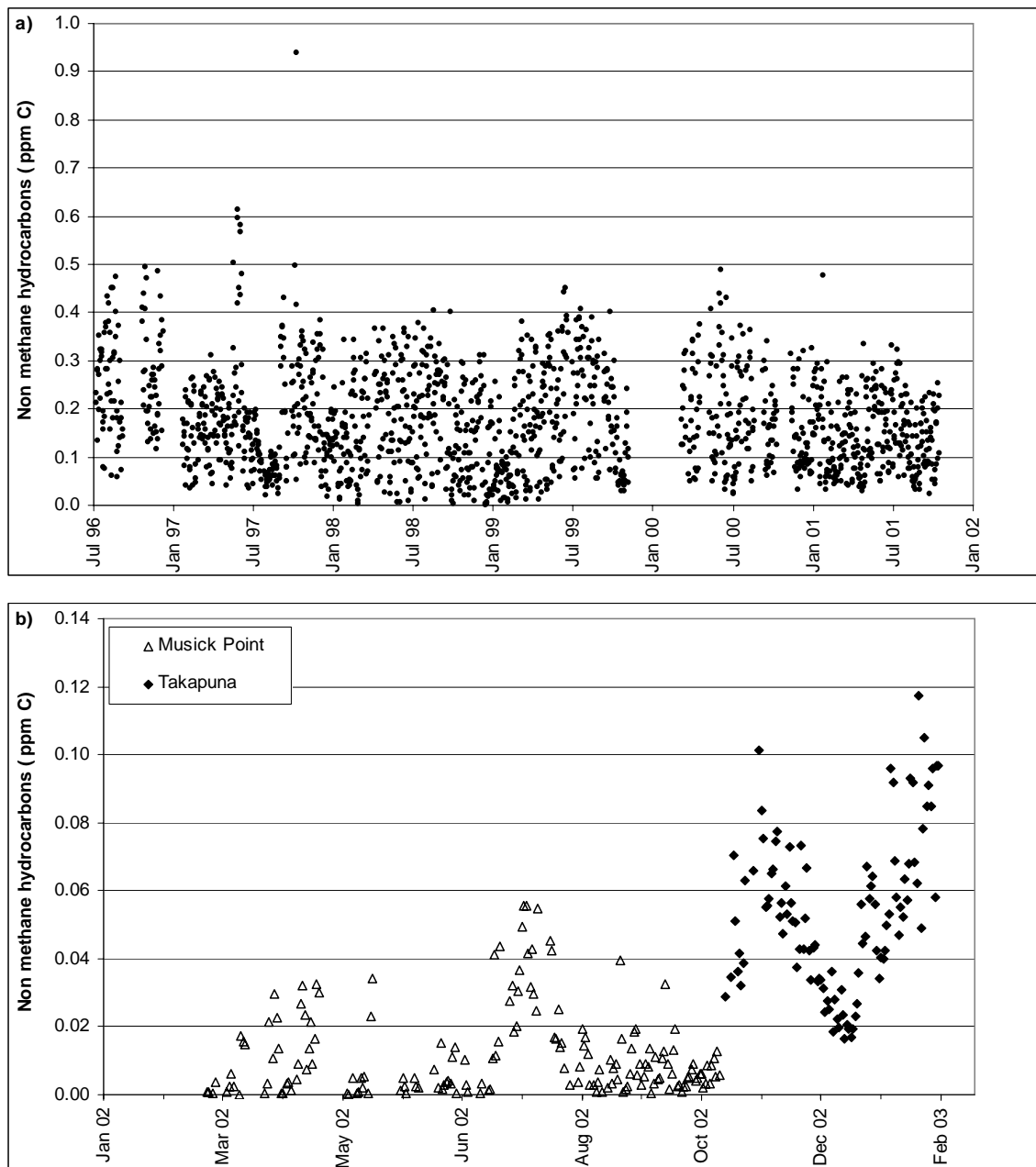
### 8.1 Non-methane hydrocarbons

Daily (24 hour) averages of hourly non-methane hydrocarbon (NMHC) concentrations are plotted as parts per million carbon in Figure 8.1 for Khyber Pass Road (Figure 8.1a), along with Musick Point and Westlake Girls High School (Takapuna) (Figure 8.1b). The seasonal variation of NMHC concentrations is similar to that of benzene (Figure 6.2), with highest concentrations occurring during winter. Following ARC and MfE requirements for at least 75% data availability for averaging, there are insufficient data for calculating NMHC annual averages for Musick Point and Takapuna.

There are sufficient data for determining annual averages at Khyber Pass Road during 1997, 1998, 1999 and 2001 (Figure 8.2), although gaps in the 2000 data are such that annual averages were unable to be determined for that year. Annual average NMHC concentrations at Khyber Pass Road varied from 0.145 to 0.175 between 1997 and 2001 (Figure 8.2).

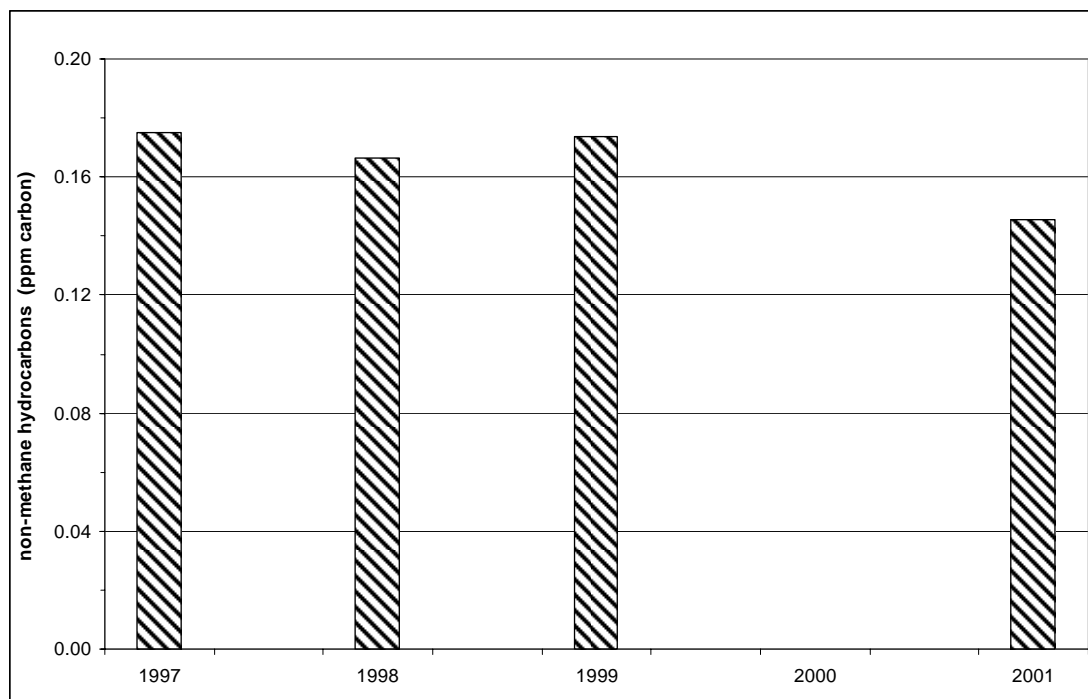
**Figure 8.1**

24 hour averages of non-methane hydrocarbons at: **a)** Khyber Pass Road; and **b)** Musick Point and Takapuna. Separate plots are used for clarity (note different y-axis scales).



**Figure 8.2**

Annual averages of non-methane hydrocarbons at Khyber Pass Road, calculated using hourly average data for years when greater than 75% of data were available.



## 8.2 VOC canisters

Table 8.1 below summarises the maximum and minimum BTEX concentrations that were measured by using the VOC canisters in 1999. Note that these results are effectively instantaneous readings and are therefore higher than what you would expect to measure with monthly average passive sampling (or average hourly readings from the GC-PID at Khyber Pass Road). In addition, there are a small number of samples so results can only be regarded as indicative.

**Table 8.1**

Summary of data from VOC canisters (Thompson, 2003).

Location  (number of samples)	Concentration ( $\mu\text{g m}^{-3}$ )									
	Benzene		Toluene		Ethyl-benzene		Xylene		1,3 butadiene	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Khyber Pass Rd (4)	5.6	31.5	12.6	76.2	2.3	13.8	11.8	69.2	0.3	3.1
Takapuna (3)	3.2	25.2	7.8	69.0	1.0	9.4	5.4	54.0	0.4	2.2
Musick Pt (4)	0.32	2.3	1.3	4.1	0.1	0.2	0.2	1.0	0.01	0.05

### 8.3 CSIRO BTEX tubes

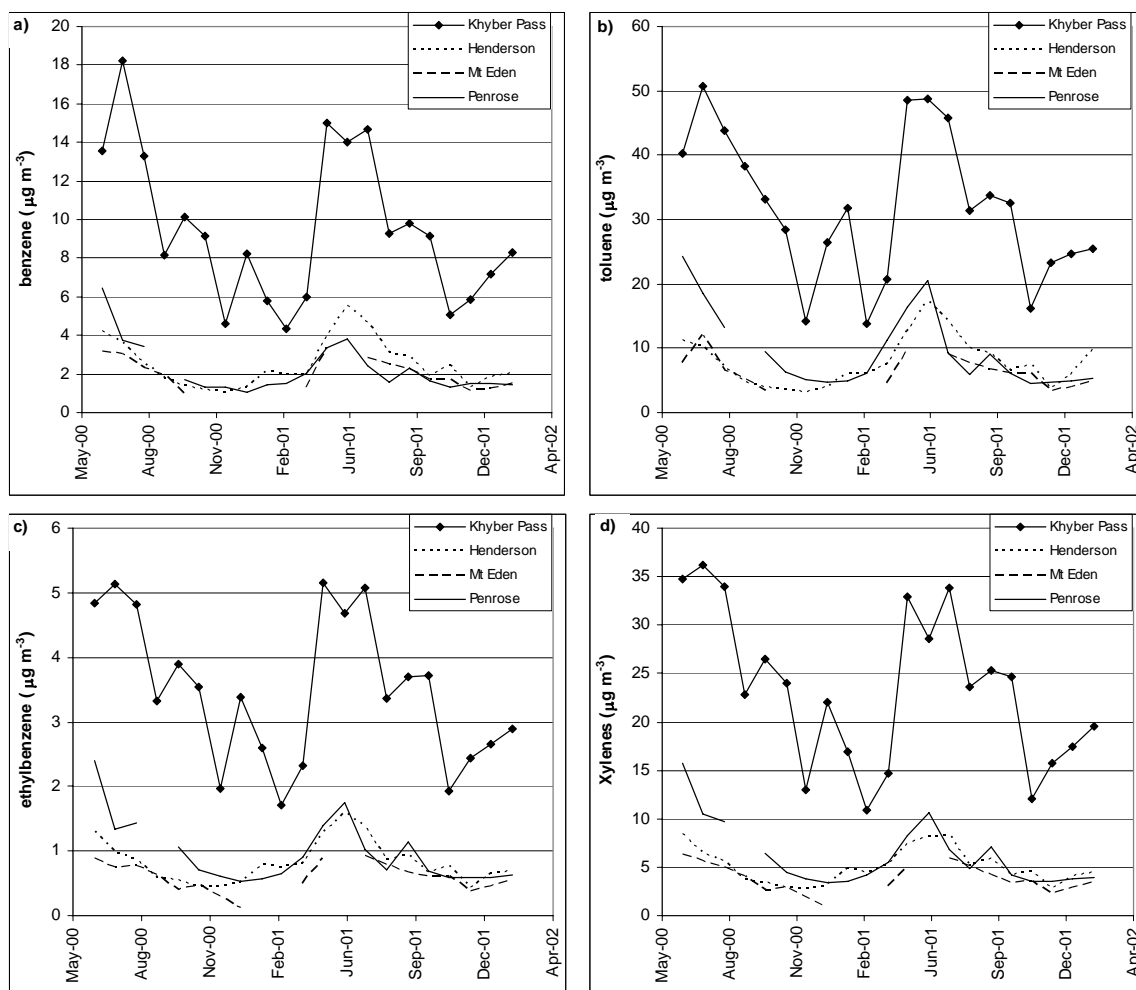
Figure 8.3 shows the results of monthly BTEX monitoring using CSIRO tubes at Khyber Pass Road, Mount Eden, Penrose and Henderson. As with the 3M passive sampling, the CSIRO data show that the greatest concentrations of all BTEX contaminants was observed at Khyber Pass Road. There is a similar temporal variation for all contaminants, with lowest concentrations observed during spring and summer. The running annual average mean benzene concentrations at Khyber Pass Road measured using the CSIRO BTEX tubes ranged between 9 – 10  $\mu\text{g m}^{-3}$ .

It was considered whether the CSIRO data could be used to extend the 3M passive sampling dataset back to May 2000. Therefore the CSIRO data were compared with the 3M data to check the relationship between the two sets of results and to investigate the variability within the sample pairs. Data are available for both CSIRO and 3M passive sampling between July 2001 and February 2002 and plotted against each other, along with RMA regression results (Figure 8.4). The RMA regression models show a good relationship between CSIRO and 3M measurements of benzene, toluene, ethylbenzene and total xylenes. However, the difference of the samples between the sampler pair means was better than 10% for 90% of the 3M samplers for all of the pollutants, whereas it was better than 10% for only 60% of the CSIRO samplers<sup>20</sup>. Based on this result and given that the dataset from the 3M samplers is sufficient to show the recent trends in benzene data, it was decided not to proceed with extending the dataset further back using the CSIRO data.

<sup>20</sup> Note: It is not known whether the large variability arose from the field procedures or the laboratory analysis.

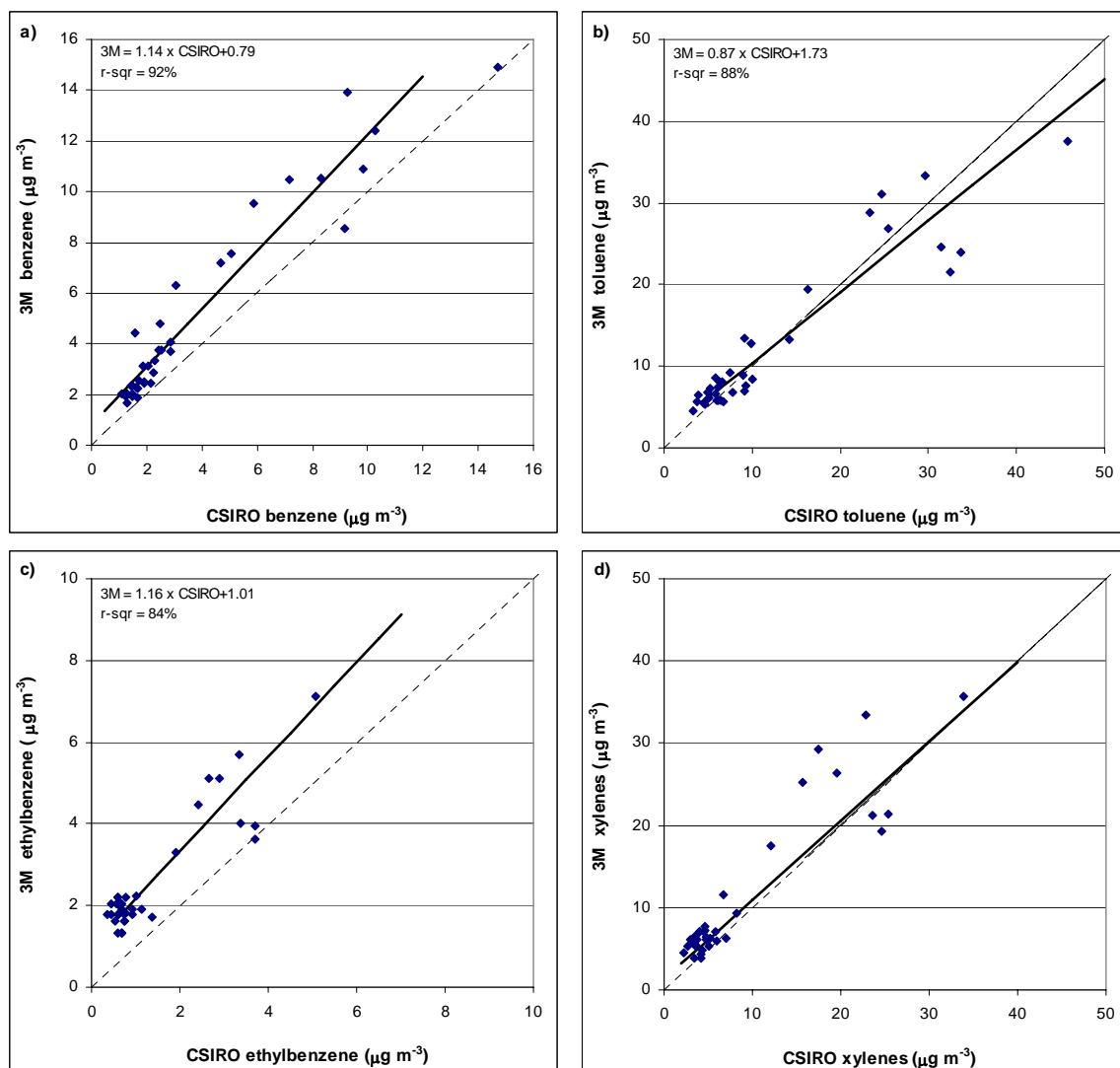
**Figure 8.3**

Monthly data by passive sampling with CSIRO tubes for VOCs: a) benzene; b) toluene; c) ethylbenzene; and d) xylenes at Khyber Pass Road, Henderson, Mt Eden and Penrose.



**Figure 8.4**

Monthly data by passive sampling with 3M badges versus CSIRO tubes for VOCs: a) benzene; b) toluene; c) ethylbenzene; and d) xylenes. RMA regression models are shown as solid lines along with equations with correlation coefficients in each plot. Dotted lines are one-to-one lines.





## 9 Conclusions

Survey results from passive BTEX sampling between 2001 and 2006 at four Auckland sites indicated that concentrations of toluene, ethylbenzene and xylenes are orders of magnitude lower than relevant investigation and screening levels used overseas. There is no indication that a more detailed investigation of toluene, ethylbenzene or xylenes is required at the Auckland sites.

Concentrations of all contaminants were three to four times greater at Khyber Pass Road than at Henderson, Mount Eden, Penrose, Takapuna and at MfE's Kowhai site. The passive sampling survey assessment also indicated that there is no immediate demand for more detailed investigation of benzene concentrations at the Henderson, Mount Eden, Penrose and Takapuna sites. While there has been a 30-40% reduction of annual mean concentrations of benzene since 2003, continuation of the passive sampling campaign may be useful as a relatively low cost means of monitoring trends, to provide data for future assessments of spatial and interannual temporal variability. Changes in fuel quality, vehicle technology, traffic density, fleet composition or meteorology may affect ambient VOC concentrations at these sites in future years and therefore continued sampling would be worthwhile to monitor trends.

Along with passive BTEX sampling since 2001, continuous monitoring of benzene and 1,3 butadiene has been undertaken at Khyber Pass Road since September 2005. Benzene concentrations measured by passive sampling were consistently lower than concentrations recorded by continuous monitoring with a GC-PID. To provide a longer record of benzene concentrations than the GC-PID dataset, monthly benzene results from passive sampling were scaled up to GC equivalency using a linear regression model ( $r^2=0.74$ ). Prior to fuel specifications that implemented the reduction of benzene in petrol to 1% in 2006, monthly GC-equivalent concentrations of ambient benzene were consistently above the current guideline of  $10 \mu\text{g m}^{-3}$  at Khyber Pass Road. While ambient benzene concentrations have been declining since progressive reductions of benzene in petrol were initiated in 2002, monthly mean benzene concentrations at Khyber Pass Road have generally remained above the guideline of  $3.6 \mu\text{g m}^{-3}$  that will apply from 2010.

The highest recorded annual average 1,3 butadiene concentration of  $1.8 \mu\text{g m}^{-3}$  occurred in 2007 and is 75% of the MfE guideline value of  $2.4 \mu\text{g m}^{-3}$ . This falls within the alert category in the MfE list of environmental performance indicators.

Patterns of diurnal and seasonal variation of benzene, 1,3 butadiene, CO and NO<sub>2</sub> were all similar, although the temporal variability of PM<sub>10</sub> did not follow the same diurnal and seasonal trends. This is likely to be a consequence of PM<sub>10</sub> source variability. Whereas motor vehicles alone are the main source of benzene, 1,3 butadiene, CO and NO<sub>2</sub>, non-trivial contributions of PM<sub>10</sub> from sea salt and domestic heating have been reported for Khyber Pass Road. Diurnal and seasonal variation of emissions from domestic heating and marine sources differ from that of motor vehicles.

Annual average benzene results from Mount Eden and Penrose are consistent with MfE GEMS results from the same sites. Moreover, benzene concentrations in

Auckland are consistent with recently published results for other urban areas in New Zealand including Christchurch, Bay of Plenty, and Hamilton.

## Key Results

- Benzene concentrations have reduced in recent years due to changes in fuel quality standards.
- Benzene concentrations in Auckland meet current annual ambient air quality guidelines, but are unlikely to meet the 2010 guidelines at major transport corridors (e.g. Khyber Pass Road) in future.
- 1,3 butadiene concentrations just meet the current annual ambient air quality guideline, but could increase with increasing traffic levels.
- BTEX passive samplers were shown to underestimate ambient concentrations, but are useful for monitoring trends and spatial variability.
- Three-monthly passive BTEX sampling is adequate to measure annual trends at non-peak sites, although this does not provide information on monthly variation.
- The two different methods of BTEX passive sampling showed similar results, although there was greater variability between the individual samplers in the CSIRO passive sampler pairs<sup>21</sup>.

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<sup>21</sup> Note: The reasons for this variability are not known.

## 10 Recommendations

### *1) Continue to monitor benzene and 1,3 butadiene at Khyber Pass Road.*

Continue operation of the continuous GC analyser at Khyber Pass Road, to monitor the trend of annual average concentrations.

### *2) Continue passive sampling with 3M badges at Khyber Pass Road.*

This will provide a more robust validation of the passive sampling technique. Continued operation of the GC and passive sampling at Khyber Pass would also be useful to monitor variation of 1,3 butadiene at other sites where only benzene is measured using passive sampling (by using the 1,3 butadiene:benzene ratio to estimate 1,3 butadiene).

### *3) Encourage continuation of three-monthly sampling at the MfE GEMS sites.*

The GEMS data will be valuable for continued monitoring of spatial variation of benzene and for estimating the concentrations of 1,3 butadiene at these locations by applying the 1,3 butadiene:benzene ratio.

### *4) Investigate the spatial variation of VOCs in the Auckland region.*

Spatial variation of VOCs may be investigated by using the relatively low cost BTEX passive samplers at other Auckland locations.

### *5) Evaluate exposure to benzene.*

A short-term spatial network of passive samplers around the Khyber Pass Road site may be used to evaluate exposure to benzene. The Khyber Pass Road monitoring site is located very close to a busy intersection where people are generally unlikely to be exposed for long periods of time, except at residential units that are located close to the road. It would be valuable to undertake passive sampling at nearby locations, where people are usually exposed for longer periods and the annual guideline for ambient benzene concentrations may be more applicable.

### *6) Investigate concentrations of other hazardous air pollutants in Auckland.*

There are a number of other hazardous air pollutants outlined in the ambient air quality guidelines that have not yet been fully investigated for Auckland. For example, the maximum hourly formaldehyde concentration measured by DOAS in 1997 was  $29 \mu\text{g m}^{-3}$ , which is much lower than the MfE (30 minute) guideline of  $100 \mu\text{g m}^{-3}$ . However, this monitoring was conducted over a short period of 17 days in winter and has not been repeated since then. A more robust assessment of compliance with the formaldehyde guideline would be achieved from survey monitoring for at least one year.

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Lou Reddish was involved in the NIWA continuous monitoring of benzene and 1,3 butadiene at Khyber Pass Road, along with NMHC campaigns.

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MfE provided passive BTEX sampling data from GEMS monitoring sites

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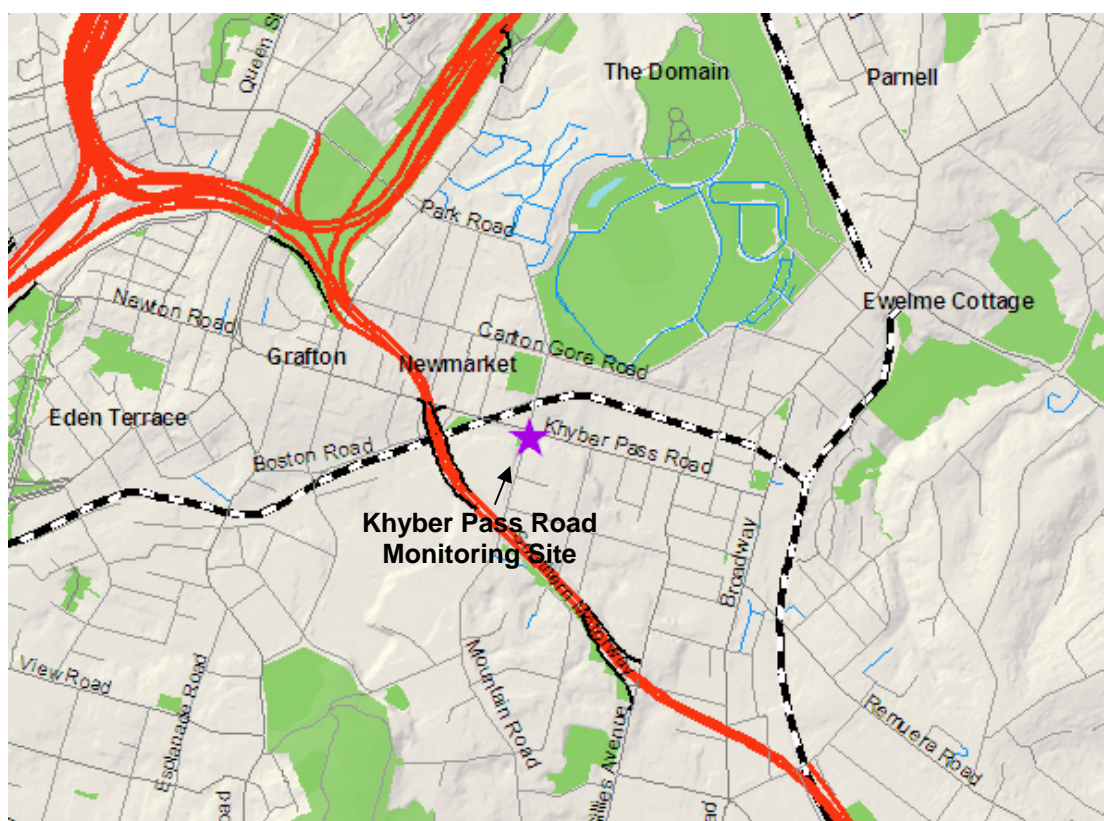
# Appendix A: Descriptions of monitoring sites

## Khyber Pass Road, Newmarket site

The Khyber Pass Road monitoring site is located in Newmarket (NZTM E1757826 N5918507), on the Khyber Pass Road arterial, around 10 m from the busy intersection with Mountain Road and approximately 250 m from the State Highway 1 Southern Motorway (Figure A1). Motor vehicles are the main source of air pollution at the site, with a daily volume of around 27,000 vehicles (7 day average) reported for Khyber Pass Road (Petersen and Harper 2006).

**Figure A1**

Location of BTEX passive sampling (indicated with star), Khyber Pass Road.

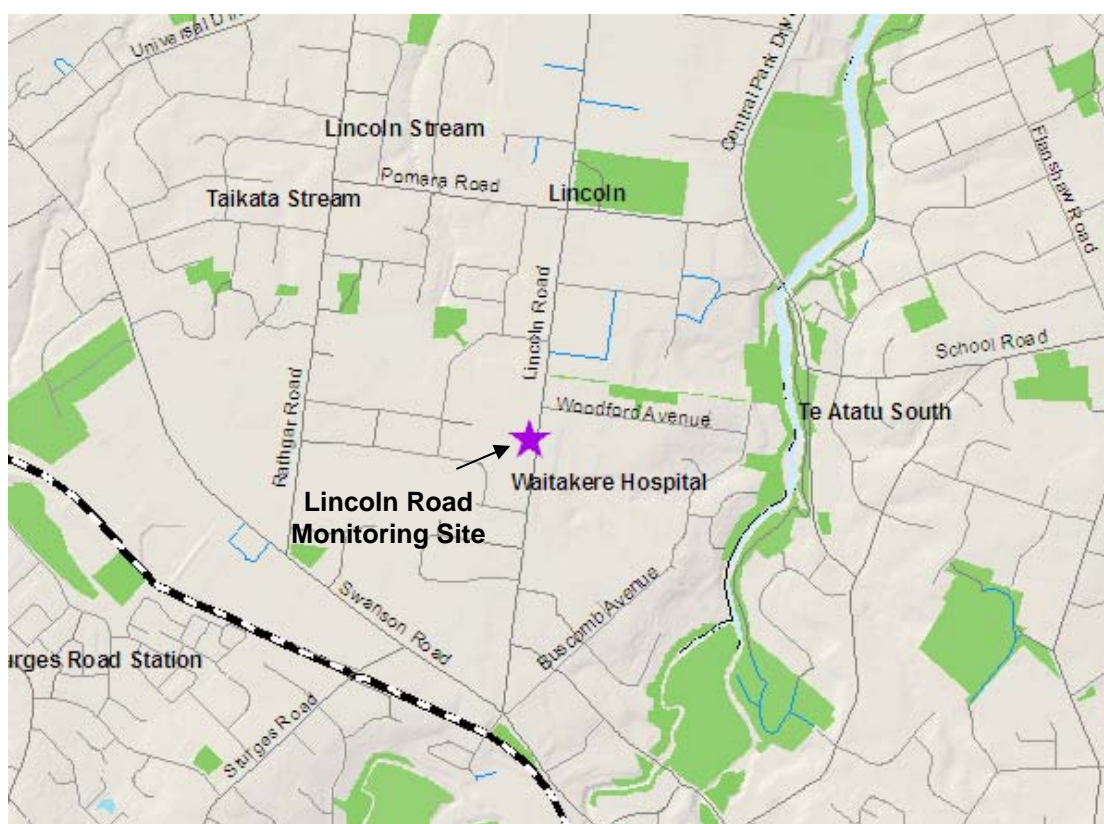


## Lincoln Road, Henderson site

The Lincoln Road (Henderson) site is located in West Auckland at NZTM coordinates E1745140 N5918533 (Figure A2). The predominant sources of air pollution at this site are residential during winter and motor vehicles all year. The site is 10 m from the Lincoln Road arterial, where daily vehicle counts of 13,300 (7 day average) were reported in 1999 (Petersen and Harper 2006).

**Figure A2**

Location of BTEX passive sampling (indicated with star), Lincoln Road, Henderson.



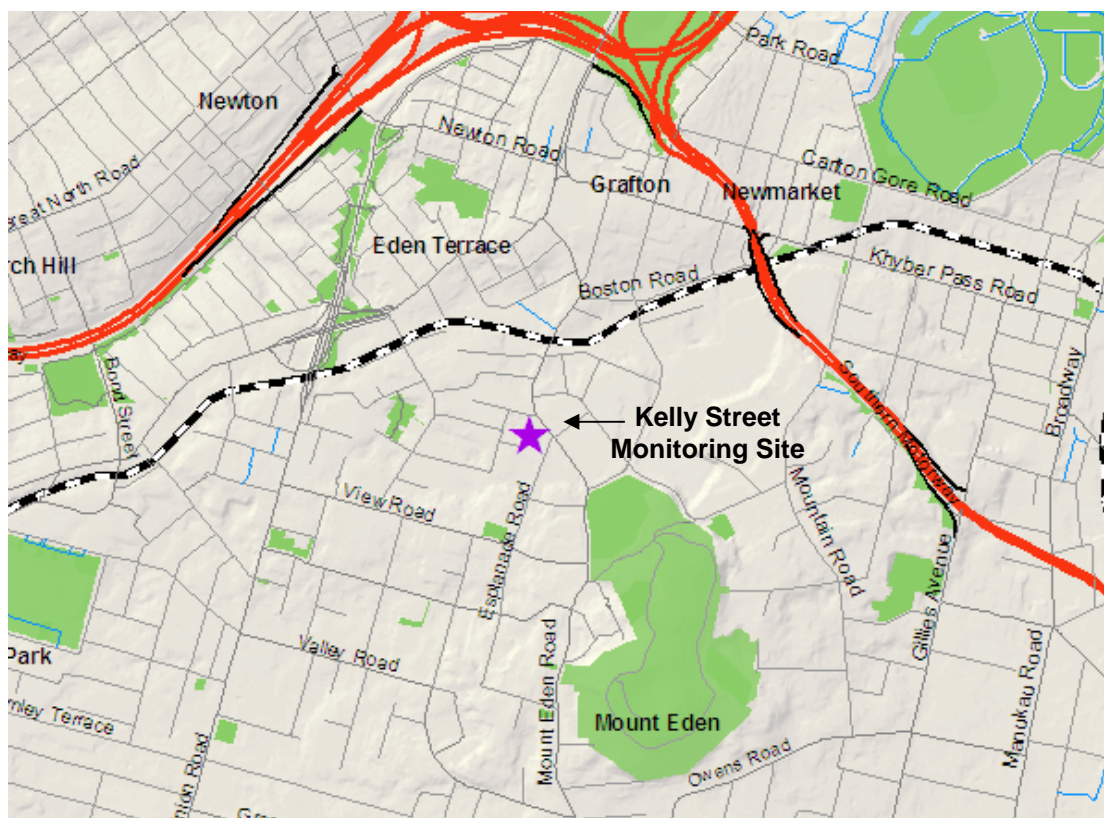
## Kelly Street, Mount Eden site

The Kelly Street monitoring site was located in Mount Eden (NZTM E1756895 N5918020), approximately 1 km southwest from the Khyber Pass Road site (Figure A3). The Kelly Street site was 20 m from the Mount Eden arterial road and approximately 800 m southwest of the State Highway 1 Southern Motorway. Motor vehicles are the main source of air pollution at this location, although the volume (7 day average, 1999) of around 15,000 vehicles per day is nearly half of the traffic flow recorded at Khyber Pass Road (Petersen and Harper 2006).

Along with the ARC passive sampling undertaken Mount Eden, this site was also used by MfE for GEMS monitoring of BTEX. After the Mount Eden ARC site was decommissioned in 2006, the MfE badges were redeployed to a housing attached to a pole on the corner of Kelly Street and Mount Eden Road.

**Figure A3**

Location of BTEX passive sampling (indicated with star), Kelly St, Mt Eden.



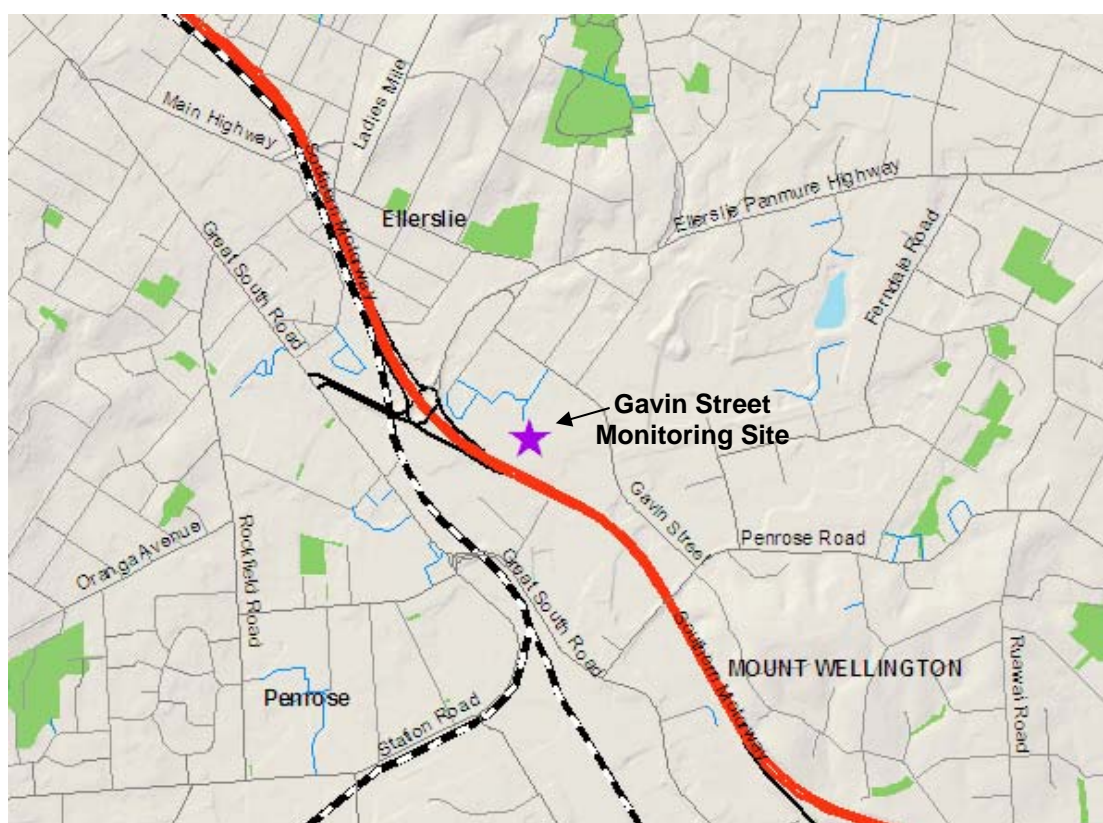


## Gavin Street, Penrose site

The Gavin Street monitoring site is located within a major substation in Penrose (NZTM E1761751 N5914176), approximately 100 m northeast from SH1 Southern Motorway (Figure A4). Motor vehicles and industry are the main sources of air pollution at the site, with a daily traffic volume of around 140,000 vehicles (annual average, 2005) recorded on the motorway (Petersen and Harper 2006). This site continues to be used by MfE for passive sampling of BTEX for GEMs reporting.

**Figure A4**

Location of BTEX passive sampling (indicated with star), Gavin Street, Penrose.

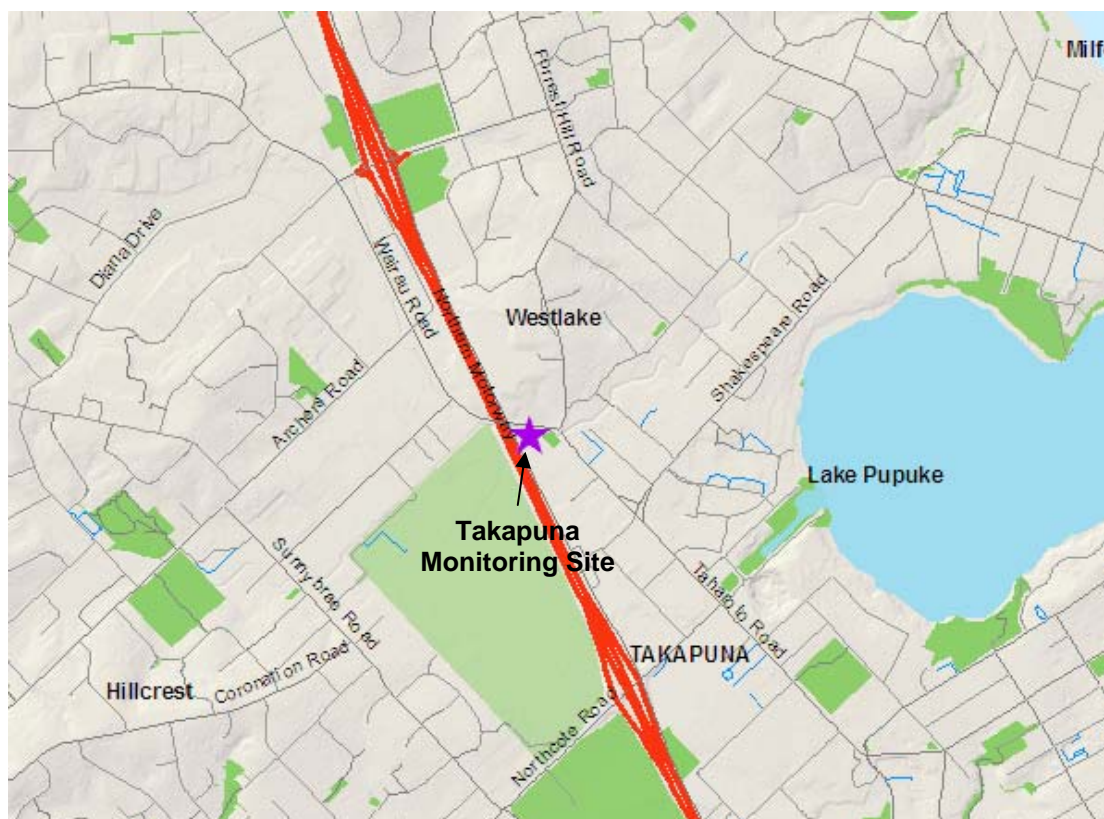


## Takapuna site

Passive BTEX sampling was undertaken during 2006 by North Shore City Council (NSCC) at Westlake Girls High School (NZTM E1756059 N5928077) in Takapuna (Figure A6). The site is approximately 30 m north of the Wairau Road arterial and 60 m west of SH1 Northern Motorway. Motor vehicles are the main sources of air pollution at the site (with some residential), and a daily traffic volume of around 110,000 vehicles (annual average, 2005) has been recorded on the motorway and 24,000 per day (7 day average, 1996) on the Wairau Rd arterial (Petersen and Harper 2006).

**Figure A6**

Location (indicated with star) of BTEX passive sampling undertaken by NSCC at Westlake Girls High School, Takapuna.



## Kowhai School, Kingsland site

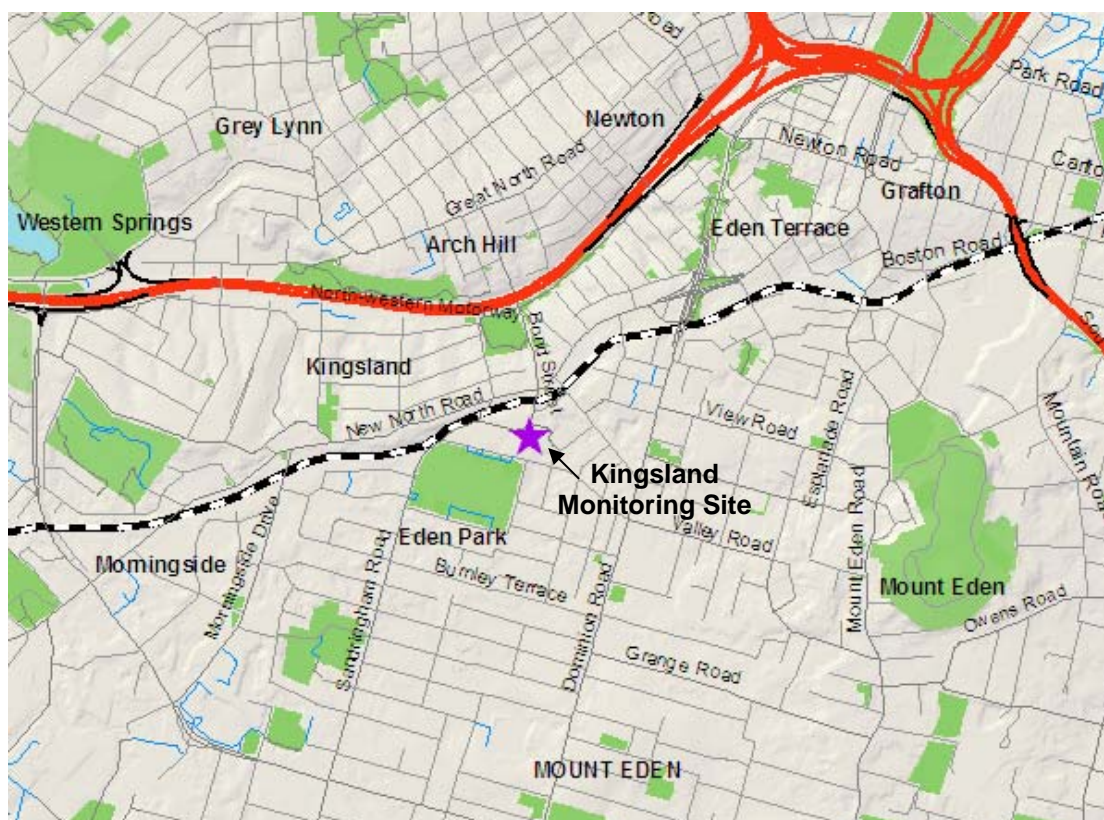
The Kowhai Intermediate School monitoring site (NZTM 1755691 E; 5197772 N) is operated by Watercare Services for the ARC Regional Air Quality Monitoring Network and the MfE as part of the Global Environmental Monitoring System / Air Pollution Programme (GEMS/AIR) conducted in conjunction with the World Health Organisation. The Kowhai site is located in Kingsland, Auckland (Figure A7) and passive BTEX sampling is undertaken with a three-monthly sampling frequency.

The site was established in early 2004 and decommissioned in 2007. It is approximately 3.5 kms southwest from the central business district of Auckland City. The area is mainly residential, with some light commercial and industrial activities, and the north-western motorway is 300 m to the north.

Further details are available at <http://www.mfe.govt.nz/publications/air/gems/>.

**Figure A7**

Location (indicated with a star) of BTEX passive sampling undertaken by MfE for GEMS monitoring at Kowhai School, Kingsland.



# Appendix B: Passive sampling results

The following raw data for contaminants other than BTEX, obtained from 3M passive sampling, were supplied by Watercare Services Limited.

July 2001

Analyte	LOD ( $\mu\text{g}/\text{m}^3$ )	Results ( $\mu\text{g}/\text{m}^3$ )							
		Khyber Pass 1 RH2051	Khyber Pass 2 RH2029	Henderson 1 RB5451	Henderson 2 RH1928	Mt Eden 1 RH1569	Mt Eden 2 RH2104	Penrose 1 RH1924	Penrose 2 RH1901
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	6.3	14	13	10	13	<LOD	<LOD	7	7
dichloromethane									
butan-2-one									
hexane	1.4	6	6	3	<LOD	<LOD	2	<LOD	2
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.2	14	14	9	4	4	4	4	4
2-methylhexane	1.5	3	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,3-dimethylpentane									
3-methylhexane	1.5	3	3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
heptane	1.5	2	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
trichloroethene									
propyl acetate	1.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2	2
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.4	36	36	14	12	8	8	13	13
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.6	7	7	2	2	<LOD	<LOD	2	2
m+p-xylene	1.6	25	25	6	6	5	5	8	8
o-xylene	1.6	8	8	2	2	2	2	2	2
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene	1.7	3	3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
beta pinene									
decane									
1,2,4-trimethylbenzene	1.7	8	8	2	2	2	2	3	3
limonene									
undecane									
dodecane									
tetradecane									



August 2001

Analyte	LOD (µg/m <sup>3</sup> )	Results (µg/m <sup>3</sup> )							
		Khyber Pass 1 RF5745	Khyber Pass 2 RF5560	Henderson 1 RF5469	Henderson 2 RF5708	Mt Eden 1 RF6276	Mt Eden 2 RF6296	Penrose 1 RF5688	Penrose 2 RF5697
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	6.3	10.8	10.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
dichloromethane									
butan-2-one									
hexane	1.4	4.2	4.9	2.2	2.2	<LOD	<LOD	1.4	1.4
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.2	11.4	14.5	5.8	5.8	3.8	3.2	4.4	3.8
2-methylhexane	1.5	1.6	1.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,3-dimethylpentane									
3-methylhexane	1.5	1.6	1.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
heptane	1.5								
trichloroethene									
propyl acetate	1.5								
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.4	23.6	23.6	8.1	8.1	6.5	6.5	6.4	6.4
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.6	4.1	3.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
m+p-xylene	1.6	14.8	14.8	4.2	4.2	3.3	3.3	4.1	4.1
o-xylene	1.6	4.9	4.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene	1.7	<LOD	1.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
beta pinene									
decane									
1,2,4-trimethylbenzene	1.7	4.3	4.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

September 2001

Analyte	LOD (µg/m <sup>3</sup> )	Results (µg/m <sup>3</sup> )							
		Khyber Pass 1 RF6495	Khyber Pass 2 RF6587	Henderson 1 RF6663	Henderson 2 RF6469	Mt Eden 1 RF6489	Mt Eden 2 RF6566	Penrose 1 RF5896	Penrose 2 RF6736
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	6.8	12.9	14.9	9.5	10.2	<LOD	<LOD	<LOD	<LOD
dichloromethane									
butan-2-one									
hexane	1.5	5.0	5.0	2.0	2.0	1.5	1.5	2.2	1.8
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.3	10.1	10.1	3.5	3.4	2.7	2.6	3.3	2.9
2-methylhexane	1.7	1.7	1.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,3-dimethylpentane									
3-methylhexane	1.7	1.8	1.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
heptane									
trichloroethene									
propyl acetate									
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.5	22.9	22.9	7.7	7.0	5.5	5.3	6.8	6.4
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.8	3.7	3.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
m+p-xylene	1.8	14.9	14.9	3.8	3.7	2.8	2.6	4.1	3.9
o-xylene	1.8	5.3	4.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene	1.8	1.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
beta pinene									
decane									
1,2,4-trimethylbenzene	1.8	4.6	4.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

October 2001

Analyte	LOD (µg/m <sup>3</sup> )	Results (µg/m <sup>3</sup> )							
		Khyber Pass 1 RV1440	Khyber Pass 2 RV0949	Henderson 1 RV0891	Henderson 2 RV0931	Mt Eden 1 RV0733	Mt Eden 2 RV0112	Penrose 1 RV0958	Penrose 2 RV0767
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	4.7	14.5	14.1	5.2	5.6	<LOD	<LOD	<LOD	<LOD
dichloromethane									
butan-2-one									
hexane	1.0	4.7	3.6	2.1	1.6	1.6	1.6	1.6	2.1
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	0.9	8.9	7.0	2.8	1.9	1.9	2.3	1.9	2.3
2-methylhexane	1.1	1.7	1.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,3-dimethylpentane									
3-methylhexane	1.1	1.7	1.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
heptane	1.1	1.7	1.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
trichloroethene									
propyl acetate									
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.1	22.1	19.0	6.3	4.7	5.3	5.8	5.3	5.8
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.2	3.6	3.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
m+p-xylene	1.2	13.9	13.3	2.4	2.4	2.4	2.4	3.0	2.4
o-xylene	1.2	4.2	4.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene	1.3	1.3	1.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
beta pinene									
decane									
1,2,4-trimethylbenzene	1.3	4.4	3.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

November 2001

Analyte	LOD ( $\mu\text{g}/\text{m}^3$ )	Results ( $\mu\text{g}/\text{m}^3$ )							
		Khyber Pass 1 RS0988	Khyber Pass 2 RS1088	Henderson 1 RS1140	Henderson 2 RS0973	Mt Eden 1 RS1195	Mt Eden 2 RS2373	Penrose 1 RS0967	Penrose 2 RS1090
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	7.8	12.6	12.6	9.4	8.6	<LOD	<LOD	<LOD	<LOD
dichloromethane									
butan-2-one									
hexane	1.7	3.5	3.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.6	7.0	7.0	3.1	3.9	2.4	2.4	1.6	1.6
2-methylhexane									
2,3-dimethylpentane									
3-methylhexane									
heptane									
trichloroethene									
propyl acetate									
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.8	18.5	18.6	8.8	8.8	7.1	7.1	5.3	5.3
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	2.0	3.0	3.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
m+p-xylene	2.0	12.2	12.2	5.1	5.1	4.1	4.1	3.0	3.0
o-xylene	2.0	4.1	4.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene									
beta pinene									
decane									
1,2,4-trimethylbenzene	2.1	3.2	3.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

December 2001

Analyte	LOD (µg/m <sup>3</sup> )	Results (µg/m <sup>3</sup> )							
		Khyber Pass 1 RS1445	Khyber Pass 2 RS2429	Henderson 1 RS2125	Henderson 2 RS2359	Mt Eden 1 RS2358	Mt Eden 2 RS2264	Penrose 1 RS1673	Penrose 2 RS1945
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	6.4	7.6	7.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
dichloromethane	5.9	<LOD	<LOD	<LOD	<LOD	<LOD	16.6	<LOD	<LOD
butan-2-one									
hexane	1.4	4.2	4.2	<LOD	<LOD	<LOD	6.3	<LOD	<LOD
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.3	8.9	8.9	1.9	1.9	1.9	19.6	1.9	1.9
2-methylhexane	1.6	1.6	1.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,3-dimethylpentane									
3-methylhexane	1.6	2.3	2.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
heptane									
trichloroethene									
propyl acetate									
methylcyclohexane	1.6	<LOD	<LOD	<LOD	<LOD	<LOD	3.1	<LOD	<LOD
4-methylpentan-2-one									
toluene	1.4	27.2	27.9	5.7	5.0	4.3	8.6	5.0	5.0
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.6	4.1	4.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
m+p-xylene	1.6	17.3	18.1	3.3	3.3	2.5	2.5	3.3	3.3
o-xylene	1.6	5.8	5.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene									
beta pinene									
decane									
1,2,4-trimethylbenzene	1.7	5.1	5.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

January 2002

Analyte	LOD (µg/m <sup>3</sup> )	Results (µg/m <sup>3</sup> )							
		Henderson 1 RS8947	Henderson 2 RS8200	Khyber Pass 1 RS8398	Khyber Pass 2 RS8831	Mt Eden 1 RS8779	Mt Eden 2 RS8141	Penrose 1 RS8959	Penrose 2 RS8760
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone									
pentane	7.3	<LOD	<LOD	7.3	7.3	<LOD	<LOD	<LOD	<LOD
dichloromethane									
butan-2-one									
hexane	1.6	<LOD	<LOD	4.0	4.0	<LOD	<LOD	<LOD	<LOD
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.4	2.9	2.9	10.1	9.4	1.4	2.2	2.2	2.2
2-methylhexane									
2,3-dimethylpentane									
3-methylhexane	1.8	<LOD	<LOD	1.8	1.8	<LOD	<LOD	<LOD	<LOD
heptane									
trichloroethene									
propyl acetate									
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.6	8.2	8.2	30.2	29.4	5.7	6.5	6.5	6.5
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.9	<LOD	<LOD	4.7	4.7	<LOD	<LOD	<LOD	<LOD
m+p-xylene	1.9	4.7	4.7	20.7	20.7	3.8	3.8	3.8	3.8
o-xylene	1.9	<LOD	<LOD	6.6	6.6	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene	2.0	<LOD	<LOD	2.0	2.0	<LOD	<LOD	<LOD	<LOD
beta pinene									
decane									
1,2,4-trimethylbenzene	2.0	<LOD	<LOD	4.9	4.9	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

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Feb-02 Analyte	LOD (µg/m <sup>3</sup> )	Results (µg/m <sup>3</sup> )							
		Henderson 1 RS7737	Henderson 2 RS7794	Khyber Pass 1 RU7060	Khyber Pass 2 RU7816	Mt Eden 1 RU7869	Mt Eden 2 RU7923	Penrose 1 RS7449	Penrose 2 RS7496
<b>Target VOCs</b>									
ethanol									
isopropyl alcohol									
acetone	7.3	<LOD	<LOD	8.0	8.7	<LOD	<LOD	<LOD	<LOD
pentane									
dichloromethane									
butan-2-one									
hexane	1.6	<LOD	<LOD	5.6	8.0	<LOD	<LOD	<LOD	<LOD
ethyl acetate									
trichloromethane									
1,1,1-trichloroethane									
benzene	1.4	2.9	2.9	9.4	10.1	2.2	1.4	2.2	2.2
2-methylhexane	1.8	<LOD	<LOD	1.8	1.8	<LOD	<LOD	<LOD	<LOD
2,3-dimethylpentane									
3-methylhexane	1.8	<LOD	<LOD	1.8	2.7	<LOD	<LOD	<LOD	<LOD
heptane									
trichloroethene									
propyl acetate									
methylcyclohexane									
4-methylpentan-2-one									
toluene	1.6	12.3	12.3	25.3	26.2	5.7	5.7	6.5	7.3
octane									
tetrachloroethene									
butyl acetate									
ethylbenzene	1.9	<LOD	<LOD	4.7	4.7	<LOD	<LOD	<LOD	<LOD
m+p-xylene	1.9	2.8	2.8	9.4	9.4	<LOD	<LOD	1.9	1.9
o-xylene	1.9	<LOD	<LOD	5.6	5.6	<LOD	<LOD	<LOD	<LOD
nonane									
alpha pinene									
propylbenzene									
1,3,5-trimethylbenzene	2.0	<LOD	<LOD	2.0	2.0	<LOD	<LOD	<LOD	<LOD
beta pinene									
decane									
1,2,4-trimethylbenzene	2.0	<LOD	<LOD	4.9	4.9	<LOD	<LOD	<LOD	<LOD
limonene									
undecane									
dodecane									
tetradecane									

# Appendix C: VOC canister results

**Table C1**

Average and standard deviations of the concentration of NMHC in Auckland and Hamilton, New Zealand. All concentrations are given in ppt (Thompson, 2003).

	Khyber Pass N=5		Takapuna N=3		Hamilton N=5		Musick Point N=4	
	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
ethene	12659	8635	12343	8924	2518	2171	508	615
ethyne	8432	6186	8495	7281	1705	1747	392	509
ethane	2902	1711	2263	1410	1174	797	397	235
propene	3536	2415	3717	2666	622	499	117	117
propane	1977	881	1605	1160	612	376	237	259
n-butane	7499	3379	4806	3401	1405	1203	631	789
i-butane	3365	1452	2889	2081	804	685	281	364
n- pentane	4143	2263	3823	2810	690	572	458	354
i-pentane	6179	3327	6272	4583	1300	1141	579	490
n-hexane	1776	1136	1500	1165	278	220	185	140
n-heptane	523	335	381	314	80	64	50	37
n-octane	141	97	107	79	24	19	10	4
n-nonane	97	75	105	97	13	9	8	5
benzene	4643	3153	4178	3152	803	632	280	264
toluene	9364	6321	912	7455	1484	251	588	361
o-xylene	1870	1258	1730	1332	218	205	36	18
m+p xylene	5338	3711	4953	3841	584	522	109	53
ethylbenzene	1418	987	1151	886	168	149	35	12

Note conversion rates to  $\mu\text{g}/\text{m}^3$  are as follows:

Benzene in ppt	Multiply by 0.0035
1,3 Butadiene in ppt	Multiply by 0.0024
Toluene in ppt	Multiply by 0.0041
Xylene in ppt	Multiply by 0.0047
Ethyl benzene in ppt	Multiply by 0.0047