Benzene, 1,3 butadiene and other volatile organic compounds in Auckland, 2001-2013

November 2014 Technical Report 2014/037

Auckland Council
Technical report, TR2014/037
ISSN 2230-4525
ISSN 2230-4533

ISBN 978-1-927216-22-4
ISBN 978-1-927216-23-1

This report has been peer reviewed by the Peer Review Panel.

Submitted for review on 25 August 2014

Review completed on 20 November 2014

Reviewed by two reviewers

Approved for Auckland Council publication by:

Name: Grant Barnes

Position: Manager, Research, Investigations and Monitoring Unit

Date: 20 November 2014

Recommended citation:

Reid, N (2014). Benzene, 1,3 butadiene and other volatile organic compounds in Auckland, 2001-2013. Auckland Council technical report, TR2014/037

Benzene, 1,3 butadiene and other volatile organic compounds in Auckland, 2001-2013

Nick Reid
Research, Investigations and Monitoring Unit
Auckland Council

Executive summary

Volatile organic compounds (VOCs) are organic chemical compounds that vaporise under normal ambient conditions to enter the atmosphere as gases. In Auckland, benzene and 1,3 butadiene have been identified as priority VOCs and have been monitored more or less continuously since 2001. Benzene is monitored as a component of the BTEX (benzene, toluene, ethylbenzene and xylenes) passive sampling suite. Benzene and 1,3 butadiene are also monitored using a continuous instrument at Khyber Pass.

Benzene and 1,3 butadiene concentrations in ambient air are primarily from transport emissions, with smaller contributions from industrial processes, domestic heating and evaporative loss from petrol stations. The majority of the transport component is from petrol vehicle emissions.

Many VOCs are hazardous to human health (especially benzene and 1,3 butadiene). Health effects are broad, ranging from dizziness and unconsciousness from short-term exposure to cancer from long-term exposure (group one carcinogen).

Monitoring data between 2001 and 2007 were reported in 2009 (TR2009/048, Smith et al., 2009). Since then, monitoring has continued at three sites (Khyber Pass, Crowhurst Street and Penrose).

This report:

- Summarises results of benzene, toluene, ethylbenzene and xylenes from passive sampling undertaken in the Auckland region from 2001 to the end of 2013
- Summarises continuous benzene and 1,3 butadiene data from Khyber Pass
- Assesses the trends in these pollutants through time
- Compares temporal trends in VOC concentrations to other transport source pollutants
- Assesses performance of the airshed against relevant ambient air quality guidelines and standards.

Between 2001 and 2013, ambient concentrations of all measured VOCs have declined steadily. However, since 2009 the decline has slowed, and ambient concentrations have stabilised. Annual averages since 2009 have significantly reduced compared to pre-2009 ambient concentrations, however annual averages remain variable, to the point of exceeding the Ministry for the Environment (MfE) Ambient Air Quality Guideline (MfE AAQG) and Auckland Ambient Air Quality Standards (AAAQS) in the Proposed Auckland Unitary Plan (PAUP, AC, 2013A).

The significant 2001-2009 reductions can largely be attributed to reductions in VOC (especially benzene) in New Zealand petrol, which came into force with increasing severity in 2002, 2004, 2006 and 2011. The lack of reduction in ambient concentrations since 2011 suggests that the peak effectiveness of these management tools has passed, and that further measures are needed to continue reducing ambient concentrations.

Benzene concentrations recorded at Khyber Pass and Crowhurst Street are elevated, and remain a cause for concern. In 2011, the annual average for benzene exceeded both the MfE guideline, and the AAAQS. It must be noted that the passive sampling method is not a standard method recommended by MfE (MfE, 2009) however due to the ease of deployment and cost effective analysis, these methods have been compared to MfE guidelines as a screening method. The passive sampling method is widely used in New Zealand studies and yields reliable data. The continuous instrument operating at Khyber Pass complies with the MfE recommendations.

The Crowhurst Street site was commissioned in 2009 and since then annual averages from Crowhurst Street remained over the MfE guideline and AAAQS, peaking in 2011, before returning to close to the guidelines in 2013. Ambient concentrations at Crowhurst Street are higher than Khyber Pass. The location of the Crowhurst Street site near a petrol station suggests that evaporative loss also plays a significant role in

elevating ambient concentrations, potentially exacerbated by topography and buildings reducing the effectiveness of dispersion.

Comparison of this data with other transport sourced pollutants (CO and PM_{10}) at the site show significant similarities in temporal patterns between benzene, 1,3 butadiene and these pollutants, suggesting the dominance of traffic emissions in elevating ambient concentrations.

Key results:

- Ambient benzene concentrations appear of most concern, as levels are close to MfE Ambient Air Quality guidelines and the AAAQS.
- Ambient concentrations of 1,3 butadiene are significantly below the MfE Ambient Air Quality guidelines and the AAAQS.
- BTEX (passive) concentrations at Khyber Pass have declined significantly between 2001 and 2013, with the strongest reductions between 2001 and 2008, coinciding with the largest reductions in benzene levels in fuel. Since 2008 reductions have slowed significantly.
- The peak effectiveness of benzene reduction in petrol may have passed given the stabilisation in concentrations at Khyber Pass
- Benzene concentrations at Khyber Pass, while levelling off, remain variable and may still exceed AAAQS and MfE Ambient Air Quality guidelines
- Continuous benzene and 1,3 butadiene data at Khyber Pass reflects the same trend of reduction and stabilisation as the BTEX passive results
- The TEX component of the BTEX suite remains low and does not appear to be of concern
- Benzene concentrations at Crowhurst Street remain significantly elevated compared to Khyber Pass, potentially due to compounding of both traffic and evaporative sources.

Contents

1.0 Introduction 9

2.0 Background 10

2.1 Benzene 10

2.1.1 1,3 butadiene 10

2.1.2 Other volatile organic compounds, VOCs 11

2.2 Health effects and ambient guidelines 11

2.2.1 Benzene – health effects 11

2.2.2 Benzene – ambient air quality guidelines 11

2.2.3 1,3 butadiene – health effects 12

2.2.4 1,3 butadiene – ambient air quality guidelines 12

2.2.5 Guidelines for toluene, ethylbenzene and xylenes 12

2.3 Fuel specifications 12

3.0 Site descriptions and methodology 14

3.1 Recent passive VOC monitoring in Auckland 14

3.2 Passive BTEX and VOC methodology 17

3.3 Continuous monitoring of benzene and 1,3 butadiene 17

3.4 Data analysis methods 18

4.0 BTEX passive sampling results 18

4.1 Benzene 18

4.2 Toluene 23

4.3 Ethylbenzene 27

4.4 Total xylenes 31

4.5 BTEX results summary 35

5.0 Continuous benzene and 1,3 butadiene results (Khyber Pass) 39

5.1 Temporal variation of benzene, 1,3 butadiene and other pollutants 41

6.0 Benzene, 1,3 butadiene and ambient air quality standards and guidelines 44

7.0 Vehicle fleet composition: implications for ambient VOC concentrations 46

8.0 Conclusions 47

9.0 Recommendations 49

10.0 Acknowledgements 49

11.0 References 50

12.0 Appendix A. Monitoring site details (from Petersen and Harper, 2006) 54

13.0 Appendix B. 2008 project results 67

14.0 Appendix C. 2009 project results 68

List of Figures

Figure 1 Locations of VOC sampling sites 15

Figure 2 Monthly passive benzene data, 2001 – 2013........ 19

Figure 3 Annual Average passive benzene, 2001 – 2013........ 20

Figure 4 Deseasonalised Theil-Sen trend analysis for passive benzene at Khyber Pass, 2001 – 2013....... 21

Figure 5 Deseasonalised Theil-Sen trend analysis for passive benzene at Khyber Pass, 2001 – 2007........ 21

Figure 6 Deseasonalised Theil-Sen trend analysis for passive benzene at Khyber Pass,2008-2013............ 22

Figure 7 Theil-Sen trend analysis for passive benzene at Crowhurst St, 2009 – 2013. 22

Figure 8 Monthly passive toluene data, 2001 – 2013........ 23

Figure 9 Annual Average passive toluene, 2001 – 2013........ 24

Figure 10 Deseasonalised Theil-Sen trend analysis for passive toluene at Khyber Pass, 2001 – 2013........ 25

Figure 11 Deseasonalised Theil-Sen trend analysis for passive toluene at Khyber Pass, 2001 – 2007........ 25

Figure 12 Deseasonalised Theil-Sen trend analysis for passive toluene at Khyber Pass, 2008-2013........... 26

Figure 13 Theil-Sen trend analysis for passive toluene at Crowhurst St, 2009 – 2013. 26

Figure 14 Monthly passive ethylbenzene data, 2001 – 2013. 27

Figure 15 Annual Average passive ethylbenzene, 2001 – 2013. 28

Figure 16 Deseasonalised Theil-Sen trend analysis for passive ethylbenzene at Khyber Pass, 2001 – 2013. 29

Figure 17 Deseasonalised Theil-Sen trend analysis for passive ethylbenzene at Khyber Pass, 2001 – 2007. 29

Figure 18 Deseasonalised Theil-Sen trend analysis for passive ethylbenzene at Khyber Pass, 2008-2013. 30

Figure 19 Theil-Sen trend analysis for passive ethylbenzene at Crowhurst St, 2009 – 2013........ 30

Figure 20 Monthly passive total xylenes data, 2001 – 2013 31

Figure 21 Annual Average passive total xylenes, 2001 – 2013. 32

Figure 22 Deseasonalised Theil-Sen trend analysis for passive total xylenes at Khyber Pass, 2001 – 2013.33

Figure 23 Deseasonalised Theil-Sen trend analysis for passive total xylenes at Khyber Pass, 2001 – 2007.33

Figure 24 Deasonalised Theil-Sen trend analysis for passive total xylenes at Khyber Pass 2008-2013. 34

Figure 25 Theil-Sen trend analysis for passive total xylenes at Crowhurst St, 2009 – 2013. 34

Figure 26 Monthly average benzene and 1,3 butadiene results (Khyber Pass), 2005 -2013. 39

Figure 27 Annual average benzene and 1,3 butadiene results (Khyber Pass), 2005 -2013. 40

Figure 28 Deseasonalised Theil-Sen trend analysis for continuous benzene at Khyber Pass, 2005 – 2013. 40
Figure 29 Deseasonalised Theil-Sen trend analysis for continuous 1,3 butadiene at Khyber Pass, 2005 – 2013. 41
Figure 30 Temporal trend for continuous benzene and 1,3 butadiene at Khyber Pass, 2005 – 2013. 42
Figure 31 Temporal trend for continuous benzene, 1,3 butadiene CO and PM_{10} at Khyber Pass, 2005 – 2013. 43
Figure 32 Annual average passive benzene 2001 – 2013. 44
Figure 33 Annual average continuous benzene 2005 – 2013. 45
Figure 34 Annual average continuous 1,3 butadiene 2005 – 2013. 45

List of Tables

Table 1 Summary of recent fuel specifications relevant to VOCs in petrol/diesel in New Zealand. 13
Table 2 Details of recent VOC monitoring in Auckland. 16
Table 3 Benzene trends, 2001 - 2013 35
Table 4 Toluene trends, 2001 - 2013 35
Table 5 Ethylbenzene trends, 2001 - 2013. 35
Table 6 Total xylenes trends, 2001 - 2013 35
Table 7 Annual data capture % for Passive BTEX sites, 2001-2013 36
Table 8 Annual average benzene ($\mu g / m^3$) concentrations at Passive BTEX sites, 2001-2013 36
Table 9 Annual average toluene ($\mu g / m^3$) concentrations at Passive BTEX sites, 2001-2013 37
Table 10 Annual average ethylbenzene ($\mu g / m^3$) concentrations at Passive BTEX sites, 2001-2013. 37
Table 11 Annual average m+p xylene ($\mu g / m^3$) concentrations at Passive BTEX sites, 2001-2013 38
Table 12 Annual average o xylene ($\mu g / m^3$) concentrations at Passive BTEX sites, 2001-2013. 38
Table 13 Data capture and annual averages for continuous benzene and 1,3 butadiene at Khyber Pass. ... 39

1.0 Introduction

Volatile organic compounds (VOCs) are organic chemical compounds that vaporise under normal ambient conditions to enter the atmosphere as gases. Many VOCs are hazardous to human health (especially benzene and 1,3 butadiene). Health effects are broad, ranging from dizziness and unconsciousness from short-term exposure to cancer from long-term exposure (group one carcinogen).

Passive VOC sampling has been carried out in Auckland since 1990, initially by the Ministry of Health (MoH), which included benzene and 1,3 butadiene (Stevenson and Narsey, 1998). With the introduction of lead-free petrol (with elevated levels of hydrocarbons) (MfE, 1997) concerns were raised around ambient levels of VOC. Consequently, a short-term open path and passive hydrocarbon monitoring programme was initiated (Kuschel et al., 1998, Kuschel et al., 2001). Results from these studies showed elevated levels of hydrocarbons, but the period of the studies was too short to confirm estimates of annual average concentrations (Kuschel et al., 1998).

Consequently, when the Auckland Regional Council (ARC) commissioned an external review of the air quality monitoring programme (Rolfe and Graham, 1999) there were recommendations to commission monitoring of important hazardous air pollutants, including benzene, toluene, xylenes (known collectively as BTEX when sampled by passive samplers) and 1,3 butadiene.

Thus, long-term passive VOC sampling was initiated in June 2001, at several Auckland locations and ran to June 2006. Continuous benzene and 1,3 butadiene was also commenced in 2005. The results of this monitoring programme (to end 2007) were reported in an ARC technical report in 2009 (TR2009/048) (Smith et al., 2009).

Since then, the VOC monitoring programme has continued, in the form of BTEX (benzene, toluene, ethylbenzene and xylenes) passive sampling at Khyber Pass and Crowhurst Street, continuous benzene and 1,3 butadiene at Khyber Pass and VOC passive sampling (target VOCs benzene, toluene, ethylbenzene, m+p-xylene and o-xylene) at Penrose (Gavin Street air quality site). The purpose of this report is to summarise and provide trend analysis of this additional data, and assess any changes since TR2009/048 (Smith et al, 2009), to the end of 2013.

The objectives are:

- Overview current VOC monitoring in Auckland
- Summarise the additional benzene, toluene, ethylbenzene and xylenes results collected at Khyber Pass since 2007 (data to 2007 are reported in TR2009/048)
- Summarise the additional benzene and 1,3 butadiene continuous monitoring at Khyber Pass since 2007 (data to 2007 are reported in TR2009/048)
- Perform trend analysis for the entire dataset (i.e. for data reported in TR2009/048 and data collected since, to the end of 2013.
- Summarise performance of the Auckland Airshed relative to the MfE Ambient Air Quality Guidelines and Auckland Ambient Air Quality Standards (AAAQS) as contained in the Proposed Auckland Unitary Plan.

2.0 Background

2.1 Benzene

Benzene (C_6H_6) is a clear, colourless and flammable liquid, with a petrol-like odour that can volatize to vapours in air. Benzene is usually found in ambient air as a result of emissions from burning coal, motor vehicle exhaust, petrol vapours at service stations and wood burning (USEPA, 2002, 2009). Removal of lead from petrol in the 1990s led to additional benzene being added as a substitute for smoother running of vehicle engines (MfE, 1997). Benzene is also present from natural sources, notably volcanoes and forest fires (Beim et al, 1998).

In urban areas, the majority of benzene in ambient air comes from transport emissions (Karakitsios et al., 2007). Evaporative benzene from facilities such as petrol stations is also an important contributor (Jones, 2000, Karakitsios et al., 2007)

Domestic heating emissions also contribute during winter in New Zealand, but both the 2006 and 2011 Auckland emissions inventories (Metcalfe et al., 2006; Xie et al., 2014) and Stevenson and Narsey (1998) confirmed the dominant transport source; accounting for 52% of VOC emissions. Results reported in 2009 by ARC (Smith et al., 2009), confirmed significantly elevated levels of benzene at the two Khyber Pass sites. These sites are known peak traffic and petrol station sites. Furthermore, comparisons to other transport-sourced pollutants (CO, NO_2 and PM_{10}) showed 'rush hour' peaks in all pollutants.

A study carried out in Christchurch (Gunaltilaka, 2003) confirmed the dominance of transport and domestic heating emissions in elevating levels of BTEX in ambient air. Sites with higher traffic volumes recorded the highest BTEX concentrations, and higher concentrations during winter, coinciding with a period of many exceedances of the National Environmental Standards for Air Quality (NES-AQ) for PM_{10} in the Christchurch airshed, showing the importance of the domestic heating contribution. Five sites from the study also exceeded or were very close to exceeding the MfE guideline levels for benzene. Similar results were also found in a study by ECAN conducted in 2009 and 2010 (Salomon, 2013) which found similar sources and patterns, but with reduced concentrations from the dataset reported in 2003. A similar decline in concentrations has also been seen in studies by Environment Waikato (Wilton and Baynes, 2008; EW, 2013).

Evaporative loss from petrol stations and other facilities also contribute to ambient concentrations (Karakitsos et al., 2007; Jones, 2000) who found elevated levels in the vicinity of petrol stations, decreasing with distance from pumps. Given the number of petrol stations in Auckland, and their proximity to residential areas in many cases, evaporative loss potentially forms an important component in exposure to ambient benzene.

2.1.1 1,3 butadiene

1,3 butadiene (C_4H_6) is a colourless gas, with a slight petrol-like odour. Sources of 1,3 butadiene in ambient air differ slightly from benzene. 1,3 butadiene is entirely produced by combustion sources (especially transport) (Dollard et al., 2001, Stevenson and Narsey 1998, 1999) and is not a component of additive in diesel or petrol. Petrol vehicles are the main contributors, accounting for 60% of transport – sourced emissions, with diesel vehicles contributing 8.5%. Evaporative emissions are not a significant contributor (Dollard et al., 2001). Some industrial processes (notably rubber, plastics and acrylic production) also contribute to ambient concentrations (HEI, 2006, USEPA, 2009)

2.1.2 Other volatile organic compounds, VOCs

In addition to benzene and 1,3 butadiene, monitoring is also carried out for additional VOCs. The target VOCs were identified by Rolfe and Graham (1999) in their review of monitoring in Auckland. A full suite of VOCs are analysed from the samples at Penrose. The highest concentrations are of benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene.

Toluene (C_7H_6) (also known as methylbenzene) is a clear, colourless liquid with a sweet odour. Usage includes as a solvent or petrol octane booster. Ethylbenzene is found in crude oil but is mainly used in production of polystyrene. Xylene is the term used to describe the three isomers of dimethyl benzene; m-xylene, p-xylene and o-xylene. Xylene is mainly used as a solvent and is naturally present in petrol. This report reports total xylenes, which is the sum of the three isomers.

Passive VOC samples from Penrose are analysed for a suite of 39 VOCs, however in practise many of these VOCs are below or just above the detection limit of the test.

2.2 Health effects and ambient guidelines

Traditionally, most attention in New Zealand has been focused on the BTEX suite and 1,3 butadiene due to their dominant transport source (Iremonger 2002; Gunaltilaka, 2003; McCauley 2005; Smith 2006; Smith et al., 2009; Salomon; 2013). Of the BTEX suite, benzene is usually considered of most concern, due to its known and significant health effects.

Due to the low concentrations of toluene, ethylbenzenes and xylenes (Stevenson and Narsey, 1999) these VOCs have generally been considered as of little toxicological significance. The significant negative health effects of benzene and 1,3 butadiene are well known domestically and internationally (NEPC, 2004; WHO, 2013A; WHO, 2013B). The concern over health effects of benzene and 1,3 butadiene are reflected in their inclusion in Ministry for the Environment (MfE) air quality guidelines, and the inclusion of standards (Auckland Ambient Air Quality Standards) in the Proposed Auckland Unitary Plan (PAUP) (Auckland Council, 2013A). The next two sections describe these further.

2.2.1 Benzene – health effects

Benzene is long established as a group one carcinogen (IARC, 1987; ICPS, 2004; WHO, 2010). Chronic exposure to benzene is known to cause acute myeloid leukaemia, as well as lymphatic and non-Hodgkin's lymphoma (ICPS, 2004; Kahn, 2007). Benzene can also reduce the body's ability to produce red and white blood cells from bone marrow, which can result in aplastic anaemia (ICPS, 1993). In vitro studies on animal species have also shown significant mutations and fertility affects (USEPA, 2009; WHO, 2010). Less severe health effects include narcosis, headache, dizziness, drowsiness, confusion and loss of consciousness (USEPA, 2002; WHO, 2010).

The World Health Organisation (WHO) has established a benzene exposure risk range, which asserts that for every 0.17 µg m^{-3} increase in ambient benzene concentrations, one leukaemia case per one million people should be expected (WHO, 2000). Thus, with ambient concentrations of 1 µg m^{-3}, 6 cases per million people can be expected. USEPA rates the risk slightly higher at 8.3 cases, and California Air Resources Board (CARB) higher still at 29 cases (MfE, 2002).The WHO has not set a guideline value, instead asserting that there is no safe level of exposure, due to the carcinogenic nature of benzene (WHO, 2010)

2.2.2 Benzene – ambient air quality guidelines

With the initial release of ambient air quality guidelines in 2002 by MfE, the annual average for benzene was set a 10 µg m^{-3}, and revised to 3.6 µg m^{-3} in 2010. This reflected international best practise and including the WHO's 'no safe level' (WHO, 2010; 2013A; 2013B), and the long-term goal set by the UK Department for Environment, Food and Rural Affairs (DEFRA) (MfE 2000a). In Auckland, the Proposed Unitary Plan (PAUP) has set the Auckland Ambient Air Quality Standard (AAAQS) at 3.6 µg m^{-3} (annual average), consistent with the MfE Ambient Air Quality Guidelines.

2.2.3 1,3 butadiene – health effects

After epidemiological studies indicated that 1,3 butadiene was possibly carcinogenic, it was classified as a probable carcinogen (IARC, 1999). 1,3 butadiene was then later classified as a known human carcinogen (WHO, 2000; USEPA, 2009; NTP 2011). Genotoxicity has also been noted in studies on rats, but it is unknown if this transfers to humans (IARC, 1999). Acute inhalation also causes irritation to eyes, throat, lungs and nasal passages. Neurological effects include blurred vision, fatigue, headache and vertigo. Cardiovascular and blood disorders are also possible (MfE, 2002).

2.2.4 1,3 butadiene – ambient air quality guidelines

The 2011 revision of the MfE ambient air quality guidelines saw the annual average for 1,3 butadiene set at 2.4 µg m^{-3}. Similar to the benzene target, this reflected international best practise including the 2.25 µg m^{-3} National Air Quality Objective (annual average) set in the UK by DEFRA (UK EPAQS, 1998; DEFRA, 2007). DEFRA also noted that there was no 'safe' level for 1,3 butadiene concentrations in ambient air. The European Commission has also set similar levels (EC, 1998). In Auckland, the Proposed Unitary Plan (PAUP) has set Auckland Ambient Air Quality Standard (AAAQS) at 2.4 µg m^{-3} (annual average).

2.2.5 Guidelines for toluene, ethylbenzene and xylenes

The 1994 New Zealand Ambient Air Quality Guidelines (MfE, 1994) recommended annual average guidelines of 190 µg m^{-3} (toluene) and 950 µg m^{-3} (xylenes). These guidelines did not however appear in the final guidelines in 2002. MfE however recommends the use of odour based Texas effects screening model (TECQ, 2008) intended to detect levels over 200 µg m^{-3}. Similarly, there are no formal guidelines in New Zealand for toluene, ethylbenzene and xylene concentrations in ambient air. This is potentially due to the greater importance placed on reducing benzene and 1,3 butadiene concentrations.

2.3 Fuel specifications

With the removal of lead in petrol, petrol in New Zealand was expected to have elevated levels of hydrocarbons (i.e. benzene) to elevate octane levels for smoother running (MfE, 1997). To control the emission of excess benzene into ambient air, fuel specifications were introduced in 1998, setting maximum percentages of benzene (see Table 1). These specifications have been further refined, with the most recent update in 2011, which kept benzene levels at < 1%, after they were initially set in 2006. This fuel specification matches the current specification in the UK. Accordingly VOCs in New Zealand fuel have been considerably lower since 2002. The confirmation of VOC levels at their current levels (in 2011) should help reduce ambient concentrations in areas affected by transport emissions, and ease pressure on the environment from point sources such as petrol stations.

Table 1 Summary of recent fuel specifications relevant to VOCs in petrol/diesel in New Zealand. Sources MED 2000; 2002; 2002A; 2002B; 2003, Smith et al., 2009 and Engine Fuel Specifications (2011).

Fuel Type	Percentage (%) by volume of fuel				
	Pre – 2002	September 2002	January 2004	January 2006	October 2011
Benzene					
Regular Grade	< 5 %	< 4 %	< 3 % (if 20% max. olefins, or 1 max. if 25% max. olefins)	< 1 %	< 1 %
Premium Grade	< 5 %	< 4 %	< 3 % (if 20% max. olefins, or 1 max. if 25% max. olefins)	< 1 %	< 1 %
Total aromatic compounds including benzene					
Regular Grade	< 48 %	< 42% pool average and 45% maximum cap	< 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	< 42% pool average and 45% maximum cap
Olefins					
Regular Grade	-	-	< 25 % (if <1% benzene, or < 20% if <3% benzene)	< 18 %	< 18 %
Premium Grade	-	-	< 25 % (if <1% benzene, or < 20% if <3% benzene)	< 18 %	< 18 %

3.0 Site descriptions and methodology

3.1 Recent passive VOC monitoring in Auckland

Passive BTEX monitoring was carried out between January 2001 and June 2006 at four sites (Henderson AQ site, Khyber Pass AQ site, Mt Eden (Kelly Street) AQ site and Penrose (Gavin Street) AQ site. The then North Shore City Council also conducted passive BTEX sampling from January 2005 to June 2007. These data are reported in ARC TR2009/048 (Smith et al., 2009).

In January 2007, passive BTEX sampling was restarted at Khyber Pass AQ site, with an additional site started nearby at Crowhurst Street. Initially this sampling was done in winter only, before becoming continuous in January 2009.

In October 2008, passive BTEX sampling was carried out at a childcare centre in Manukau, in collaboration with the Auckland Regional Public Health Service. This project demonstrated declining concentrations with distance from roads. The results of this project are summarised in Appendix B.

In 2009, 3 months (June, July and August) of BTEX sampling was carried out at 16 sites, as a short-term screening project, to assess peak VOC concentrations in Auckland. The project concluded that Khyber Pass and Crowhurst Street were both sufficiently representative of peak ambient concentrations in Auckland. The results of this project are summarised in Appendix C.

In July 2011, passive VOC sampling (3 monthly) was begun at Penrose (Gavin Street) AQ site. In the same year, passive BTEX sampling was also carried out in collaboration with University of Auckland Public Health Department. The history of VOC monitoring in Auckland is summarised in table 2 and figure 1.

This report uses data collected at Khyber Pass since 2001. Data from January 2001 to June 2006 was reported by Smith et al. (2009). This report adds data to end 2013 to assess changes and trends. This includes the continuous gas chromatograph data.

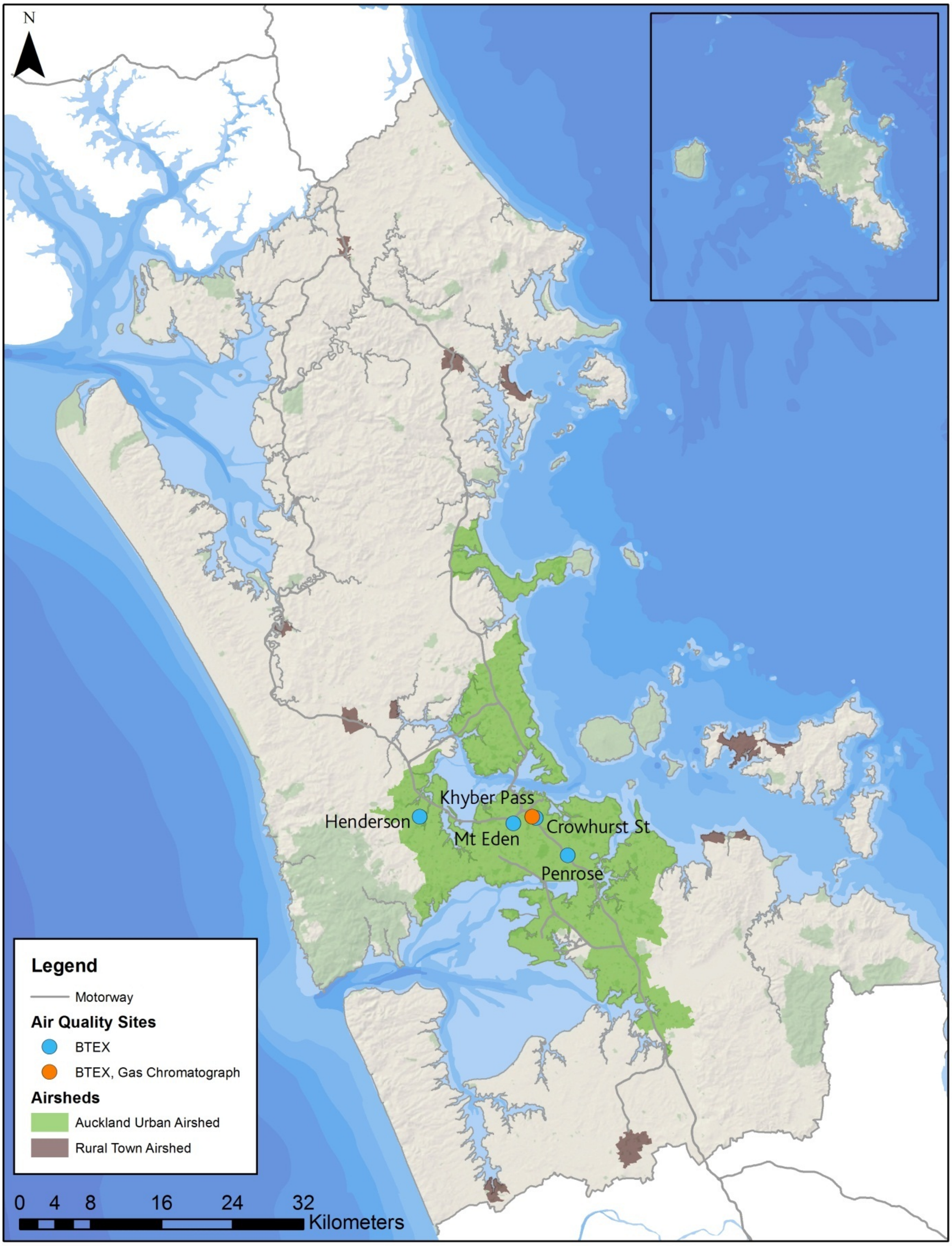


Figure 1 Locations of VOC sampling sites

Table 2 Details of recent VOC monitoring in Auckland.

Site	Period	Location	Easting (NTZM)	Northing (NZTM)	Parameters
Henderson	January 2001- June 2006	Lincoln Rd AQ site[1]	1745140	5918507	BTEX
Mt Eden	January 2001- June 2006	Kelly St AQ site[2]	1755691	5197772	BTEX
Penrose	January 2001- Ongoing[3]	Gavin St AQ site[1]	1761751	5914176	BTEX
Crowhurst St	January 2007- Ongoing	BTEX only	1758244	5918386	BTEX,
Khyber Pass	January 2001- Ongoing[4]	Khyber Pass AQ Site[1]	1757826	5918507	BTEX, GC[5]

Site	Year												
	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Henderson	Full year	Full year	Full year	Full year	Full year	Jan - Jun	-	-	-	-	-	-	-
Mt Eden	Full year	Full year	Full year	Full year	Full year	Jan - Jun	-	-	-	-	-	-	-
Penrose	Full year	Full year	Full year	Full year	Full year	Jan - Jun	-	-	-	-	Jul - Dec	Full year	Full year
Crowhurst St	-	-	-	-	-	-	-	-	Jun-Aug, Nov-Dec	Full year	Full year	Full year	Full year
Khyber Pass	Full year	Full year	Full year	Full year	Full year	Jan - Jun	Jan–Jun, Sept - Dec	Jan, Feb	Jun-Aug, Nov- Dec	Full year	Full year	Full year	Full year

1 – Ongoing air quality site as part of Auckland Council AQ network.

2 – Site now closed.

3 – There is a gap at Penrose between June 2006 and July 2011

4 - There is a gap in passive BTEX data in Khyber Pass from June 2006 to January 2007.

5 - Gas chromatograph instrument (see section 3.3)

3.2 Passive BTEX and VOC methodology

Passive sampling in the Auckland region is carried out using 3M organic vapour monitor badges, which were initially developed for monitoring of occupational exposure to VOCs, where compliance monitoring of occupational guidelines is required. After the demonstration of their reliability over longer exposure times (e.g. months) by Stephenson and Narsey (1998), the technique has become widely used in New Zealand, with both studies and long-term monitoring carried out using the technique (Iremonger 2002; Gunaltilaka, 2003; McCauley 2005; Smith 2006; Smith et al., 2008; Salomon; 2013). It must be noted that the passive sampling method is not a standard method recommended by MfE (MfE, 2009) however due to the ease of deployment and cost effective analysis, these methods have been compared to MfE guidelines as a screening method. The passive sampling method is widely used in New Zealand studies and yields reliable data. The continuous instrument operating at Khyber Pass complies with the MfE Guidelines.

BTEX (or VOC, in the case of Penrose) badges were installed at around 3m height above ground, protected by a rain hood. This technique has generally become the default standard for VOC passive sampling in New Zealand (Gunalatika, 2003; Salomon, 2013). Badges are exposed for one month, during which the air diffuses at a known rate, across a membrane under which BTEX and VOC are absorbed onto an activated carbon wafer. After sampling, the badges are retrieved for laboratory analysis, using a de-sorption process and analysis using gas chromatograph mass spectrometer (GC-MS).

The field component of this work is undertaken by Watercare Services. Laboratory analysis is carried out by AsureQuality using an IANZ[1] accredited method, derived from the NIOSH[2] Method 1500 (NIOSH, 1994).

Results are converted to mixing ratios (ppbv[3]) then concentrations ($\mu g\ m^{-3}$) at a standard temperature (0°C) and pressure (101.3kPa) as per the manufacturer's instructions (3M Technical Bulletin 1028). Watercare Services provide this component of the project.

Despite the proven reliability of the 3M method, it should be noted that passive sampling is regarded as a screening method, and accurate estimates of concentrations may not always be achieved. The method does not carry regulatory approval like many other air quality monitoring methods currently in use by Auckland Council. However the easy of deployment, low cost and proven analytical methods allow relatively dense networks and flexible deployment options which may not be possible with other methods.

3.3 Continuous monitoring of benzene and 1,3 butadiene

In September 2005 continuous monitoring of benzene and 1,3 butadiene was begun at Khyber Pass, in addition to the existing suite of air quality parameters currently monitored there (Passive BTEX, continuous CO, NOx, PM_{10} and $PM_{2.5}$). The instrument (Synspec GC955 gas chromatograph photoionization detector) provides hourly average benzene and 1,3 butadiene concentrations.

The instrument 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

[1] International Accreditation New Zealand
[2] National Institute for Occupational Safety and Health (United States)
[3] Part per billion by volume

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 is determined.

The instrument is operated and the data quality assured by Watercare Services Limited. This instrument complies with MfE (2009) recommended methods for benzene monitoring. The dataset from the instrument is useful for both its precision and resolution, which allows identification of hourly resolution patterns.

3.4 Data analysis methods

BTEX and continuous benzene and 1,3 butadiene are analysed in this report using arithmetic annual means and raw data. Trends in datasets are analysed using the TheilSen tool, in the Openair package for R (Ropkins and Carslaw, 2011; Carslaw, 2013)

The Theil-Sen technique is an extension of the non-parametric Mann-Kendall method, and is commonly used for environmental analysis (Hirsh et al, 1982; Helsel and Hirsh, 2012, USGS, 2012). Its development dates back to the 1950s (Theil, 1950; Sen, 1968), however it did not gain momentum until the development of modern computers (Carslaw, 2013).

Given a set of *n x,y* pairs, the slopes between all sets of pairs are calculated. The Theil-Sen estimate of slope is the median of all these slopes. The Theil-Sen approach has several characteristics which lend themselves to ambient air quality time–series analysis. Firstly, it tends to yield accurate confidence intervals in non-normal data. Secondly, it is generally considered to be resistant to autocorrelation (Yue et al, 2004). Thirdly, the Theil-Sen technique is generally resistant to outliers, which is critical in ambient air quality analysis (Carslaw, 2013).

Forth, The Theil-Sen approach also provides an estimate of *p-value*, allowing assessment of the relative statistical significant of a result. In this context, *p-value* estimates the statistical significance of the trend result. A *p-value* of <0.05 is considered statistically significant, and a *p-values* <0.001 is considered statistically highly significant, representing less than a one in a thousand chance of being incorrect. Finally, the Openair version of Theil-Sen also has the ability to remove the impact of seasonality (crucial in ambient air quality analysis). The approach is based on the seasonal decomposition by loess method provided by Cleveland et al. (1990).

4.0 BTEX passive sampling results

Annual averages of concentrations from the BTEX suite of contaminants were calculated for all data available. Years with less than 75% data coverage (i.e. more than three months missing) were excluded from analysis. Data capture % is shown in Table 7. Tables 8-12 provide annual average results for the BTEX passive suite.

4.1 Benzene

Smith et al. (2009) reported significantly elevated benzene concentrations in the 2001- 2006 results from Khyber Pass, and Crowhurst Street, with concentrations around 3-4 times higher than Mt Eden, Penrose and Henderson. It appears that concentrations at Khyber Pass and Crowhurst Street have declined significantly since, as shown in figures 2 and 3.

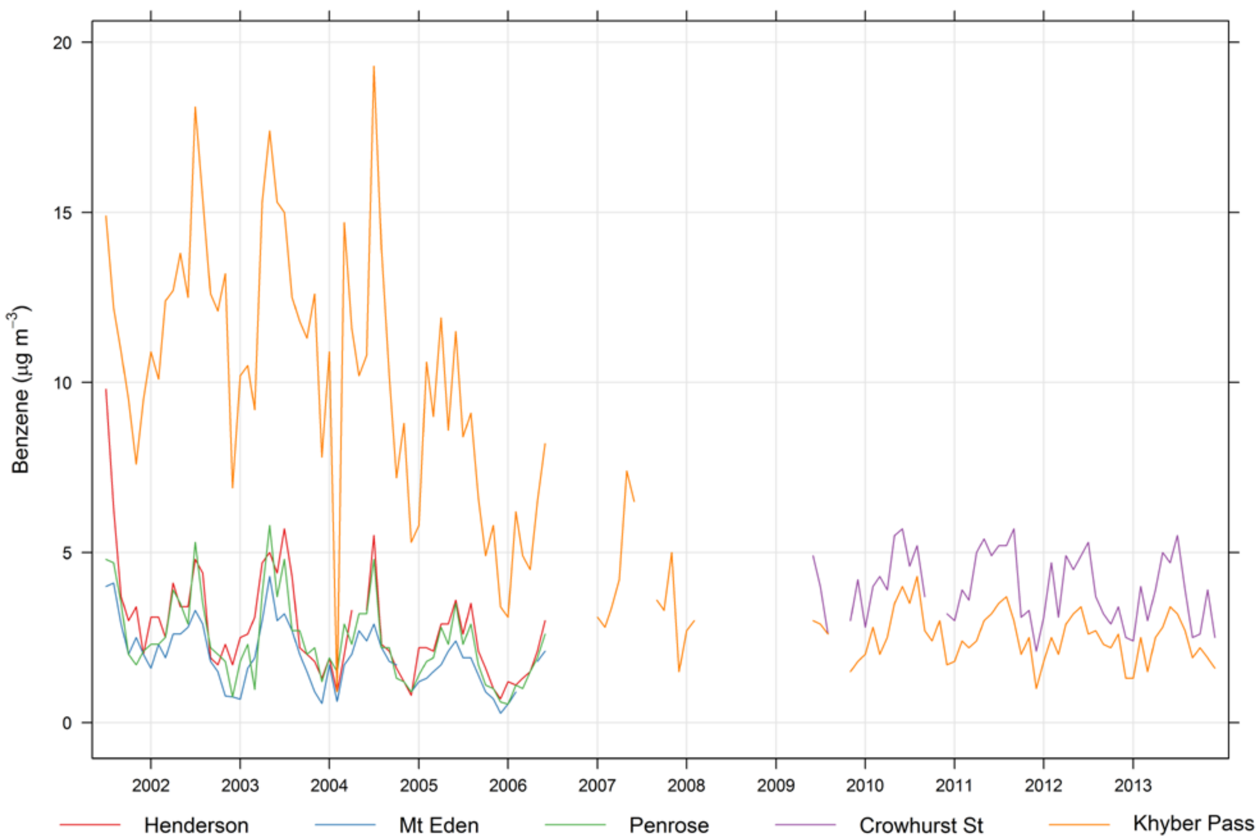


Figure 2 Monthly passive benzene data, 2001 – 2013. Gaps in traces indicate that no sampling was done. Results below Limit of Detection (LOD) are displayed as half the LOD.

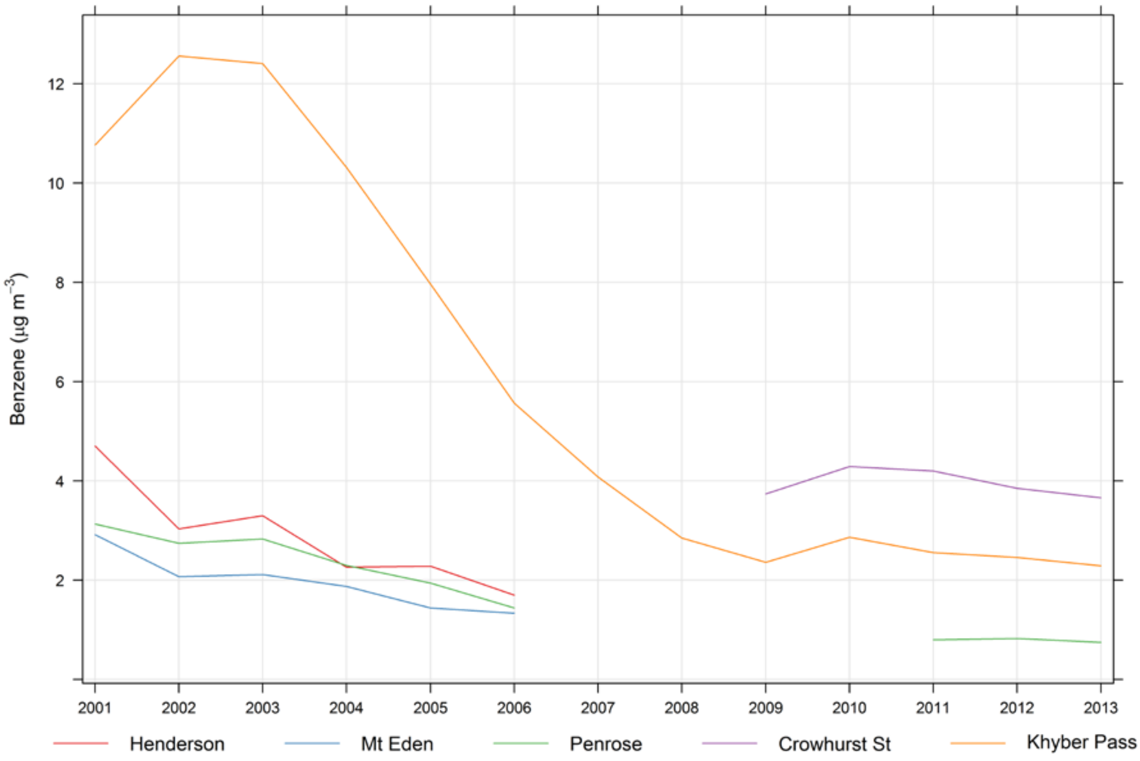


Figure 3 Annual Average passive benzene, 2001 – 2013**.**

Significantly, results since 2009 at Khyber Pass and Crowhurst Street show two important results. Firstly, benzene concentrations at these sites appear to have stabilised, with the degree of concentration reduction beginning to slow. Secondly, benzene concentrations at Khyber Pass and Crowhurst appear to be roughly similar to 2001-2007 benzene concentrations at Mt Eden, Penrose and Henderson. Benzene concentrations at Crowhurst Street are higher than at Khyber Pass, potentially due to additional benzene contributions from evaporative loss at the nearby petrol station, and local difference in topography.

When the Khyber Pass passive benzene data set (eg. 2001 – 2013) is considered as whole, there is a strong reduction in concentrations, but around 2010, the trend in concentrations depart from the overall trend, suggesting that two different periods of trends are present (figure 4). Data between 2001 and 2007 show significant reduction in concentrations - 1.62 µg / m^3 /year (figure 5). However this trend has all but disappeared since 2010 (figure 6).

Figures 5 and 6 show the overall trend for the dataset, with the trends for these two periods separated. Deseasonalised Theil-Sen analysis of benzene concentrations at Khyber Pass, shows that between 2001 and 2008 concentrations were declining by 1.62 µg / m^3 /year (*p*-value <0.001), but between 2008 and 2013, these concentrations only decreased by 0.07 µg / m^3 /year with no statistical significance, suggesting a levelling out in concentrations.

Over the entire period, 2001-2013, concentrations declined by 0.87 µg / m^3 /year (*p*-value <0.001). Crowhurst Street shows a similar trend between 2009 and 2013, with no significant trend up or down (0.07 µg / m^3 /year with no statistical significance). This suggests that ambient benzene concentrations in the area are largely stable. This however, is an issue as concentrations are still elevated in regard to ambient air quality guidelines. This is discussed in section 7.

These reductions in concentrations can largely be attributed to the continual reduction in benzene concentrations in petrol since 2002 (see table 1) (Smith et al., 2009; Engine Fuel Specifications, 2011) However, no further changes to VOCs in petrol have been made since 2016, which may be responsible for the scarce reduction in concentration since 2010.

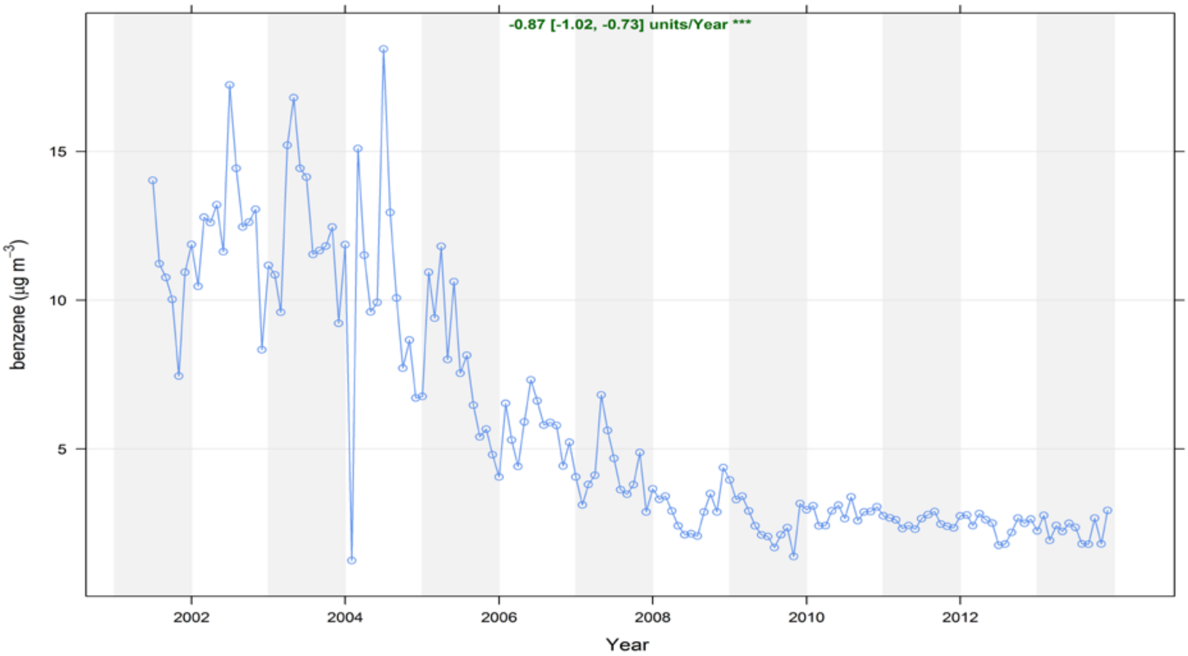


Figure 4 Deseasonalised Theil-Sen trend analysis for monthly passive benzene at Khyber Pass, 2001 – 2013. The overall trend is shown at the top in green, (-0.87 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

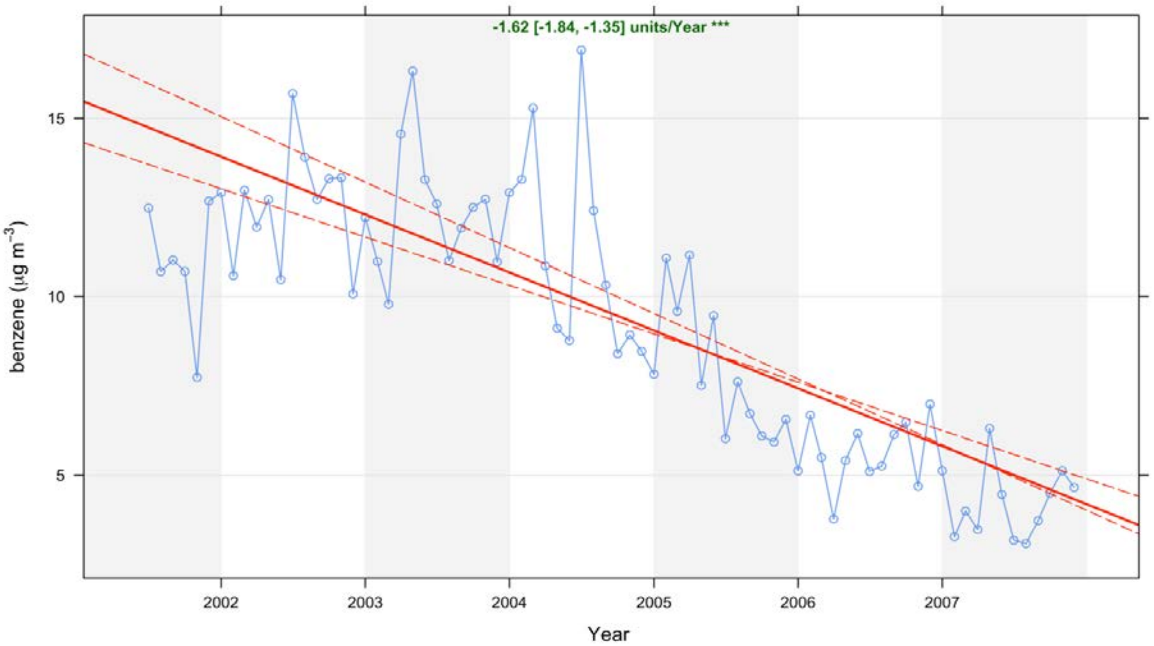


Figure 5 Deseasonalised Theil-Sen trend analysis for monthly passive benzene at Khyber Pass, 2001 – 2007. The overall trend is shown at the top in green, (-1.62 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

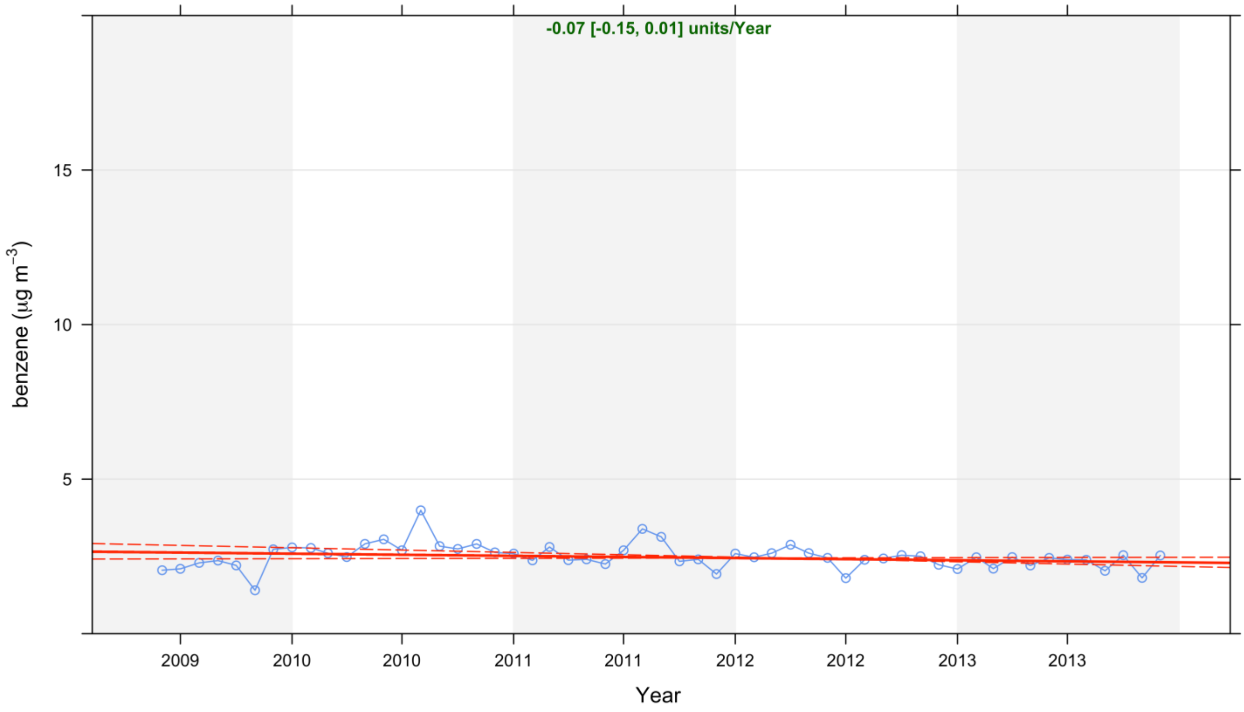


Figure 6 Deseasonalised Theil-Sen trend analysis for monthly passive benzene at Khyber Pass, 2008-2013, the trend is -0.07 µg / m^3 /year, with no statistical significance**.**

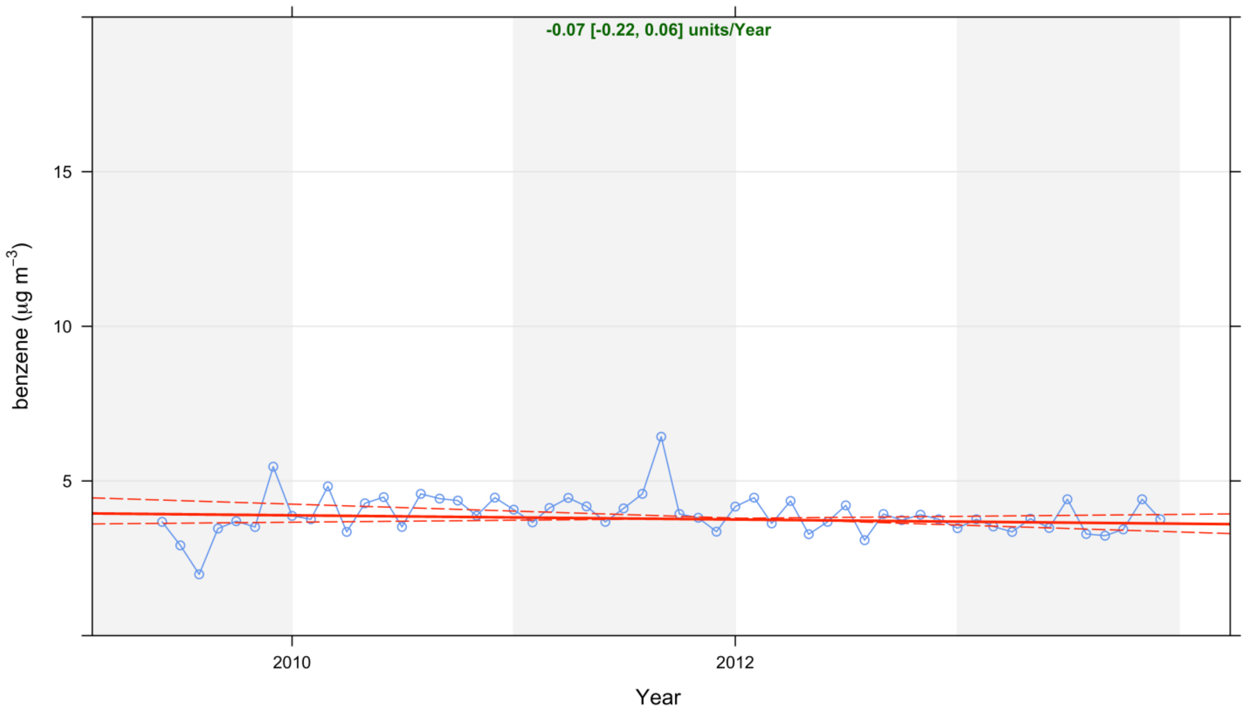


Figure 7 Deseasonalised Theil-Sen trend analysis for monthly passive benzene at Crowhurst Street, 2009 – 2013. The overall trend is shown at the top in green, (-0.07 µg / m^3 /year) but the trend is not statistically significant.

4.2 Toluene

Passive toluene results show similar patterns to the passive benzene results from section 4.1. The raw monthly values (figure 8) and annual averages (figure 9) at Khyber Pass and Crowhurst show declines between 2001 and 2009, with lowest concentrations found in 2009. However, since 2009, ambient toluene appears to have increased again, peaking in winter 2011 at both Khyber Pass and Crowhurst Street.

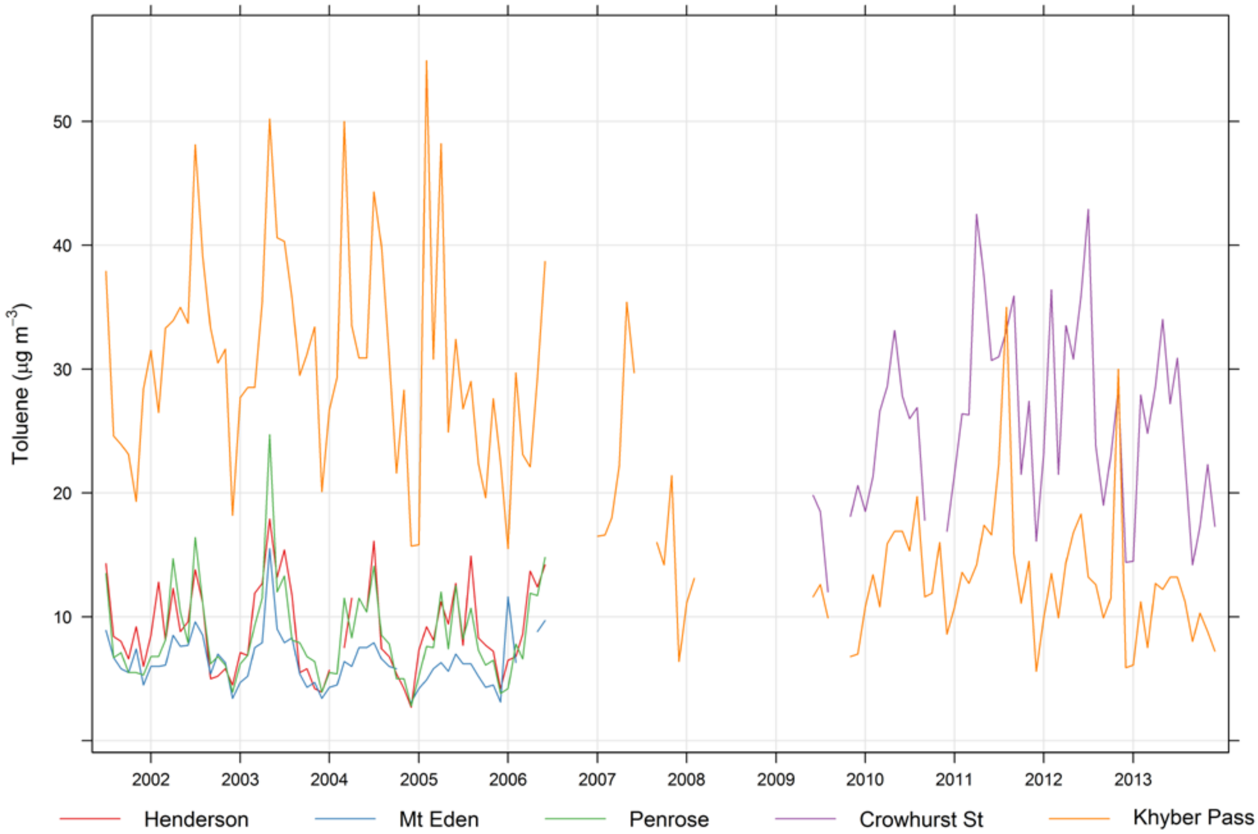


Figure 8 Monthly passive toluene data, 2001 – 2013. Gaps in traces indicate that no sampling was done. Results below Limit of Detection (LOD) are displayed as half the LOD.

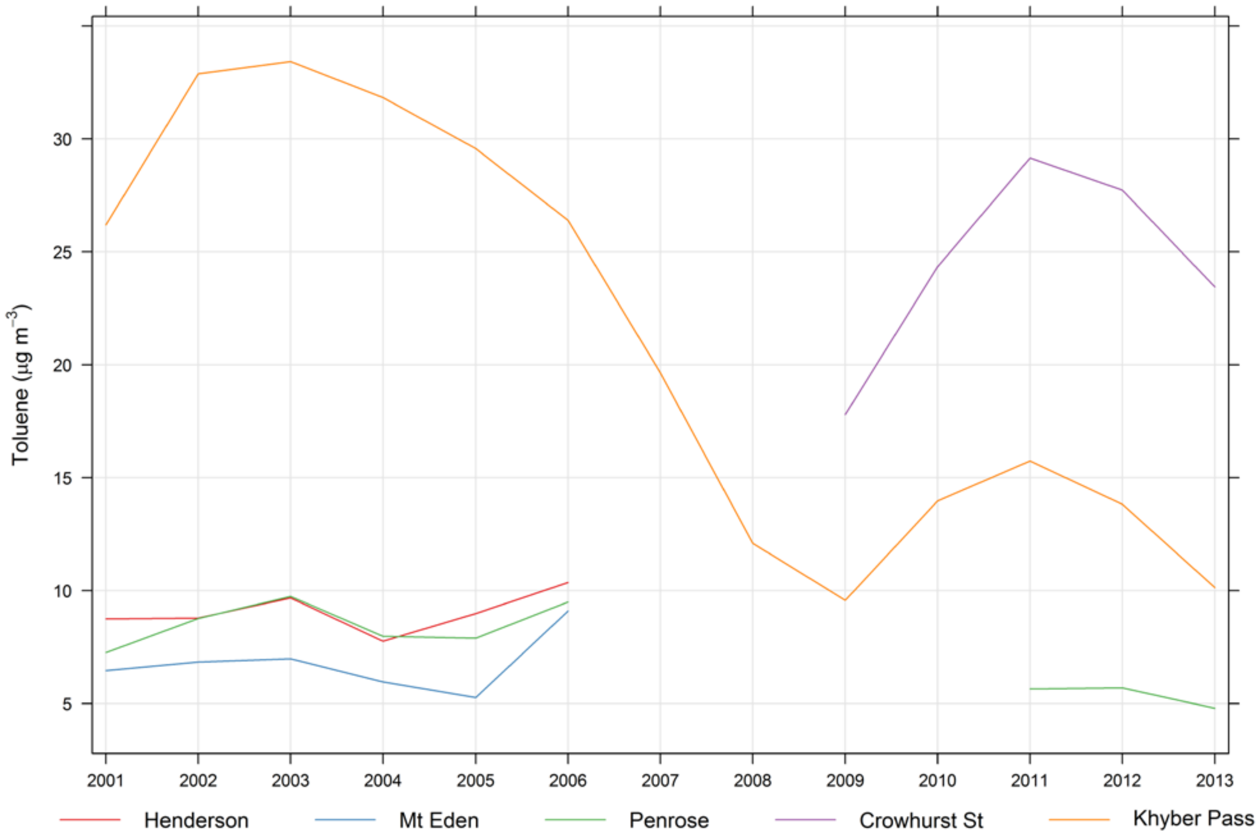


Figure 9 Annual Average passive toluene, 2001 – 2013.

Passive toluene data from Khyber Pass and Crowhurst Street show similar trends to the benzene data. At Khyber Pass the entire dataset (2001-2013) shows a reduction in ambient toluene concentrations of 2.12 µg / m^3 /year (*p*-value <0.001) (figure 10). For the period 2001 – 2008, ambient toluene decreased by 1.88 µg / m^3 /year (*p*-value <0.01) (figure 11). Similar to benzene, between 2008 and 2013 there was a sharp change in ambient toluene trends, with the trend reducing to -0.61 µg / m^3 /year with no statistical significance (figure 11). At Crowhurst Street, the trend between 2008 and 2013 is an increase of 0.41 µg / m^3 /year, with no statistical significance, suggesting stable ambient toluene concentrations. This is a similar result to benzene.

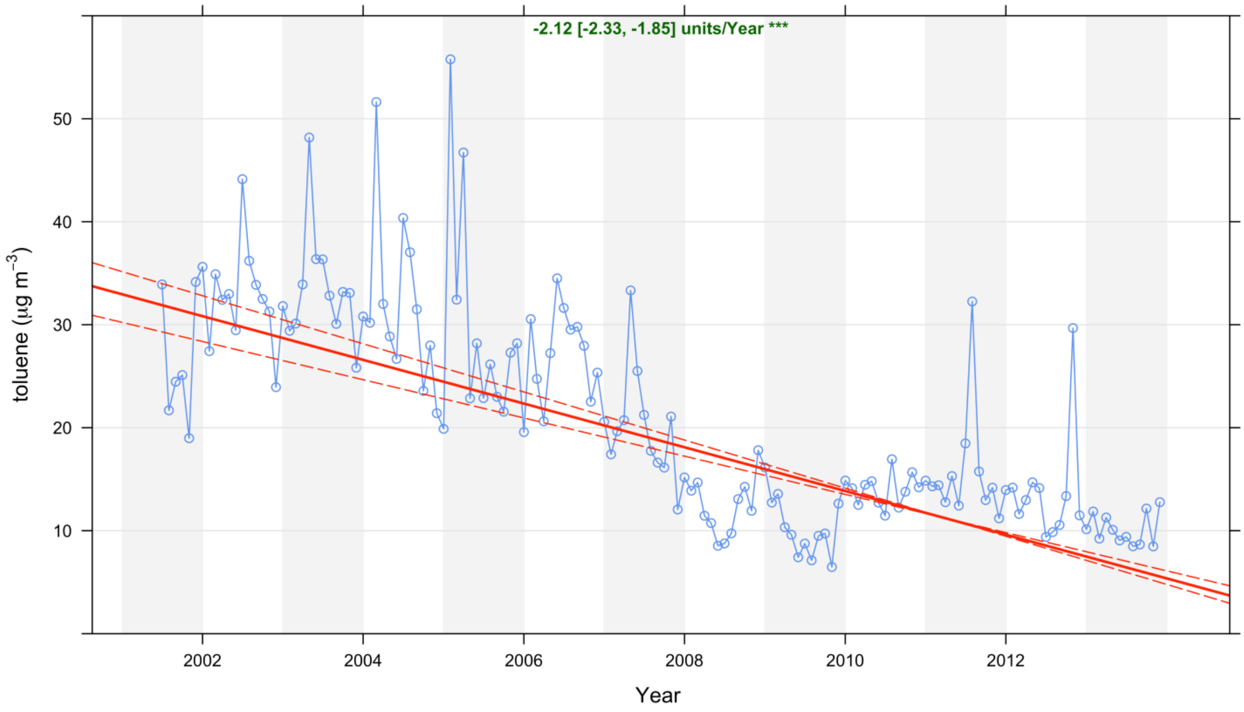


Figure 10 Deseasonalised Theil-Sen trend analysis for passive toluene at Khyber Pass, 2001 – 2013. The overall trend is shown at the top in green, (-2.12 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

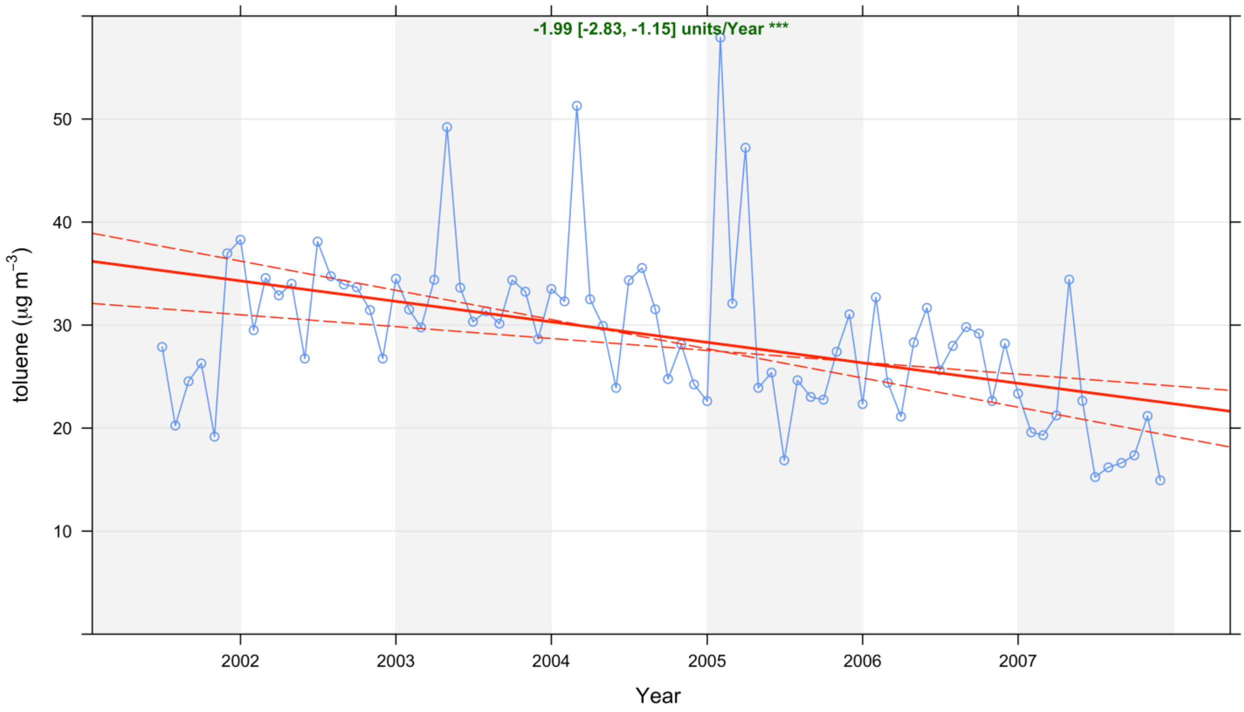


Figure 11 Deseasonalised Theil-Sen trend analysis for passive toluene at Khyber Pass, 2001 – 2008. The overall trend is shown at the top in green, (-1.99 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

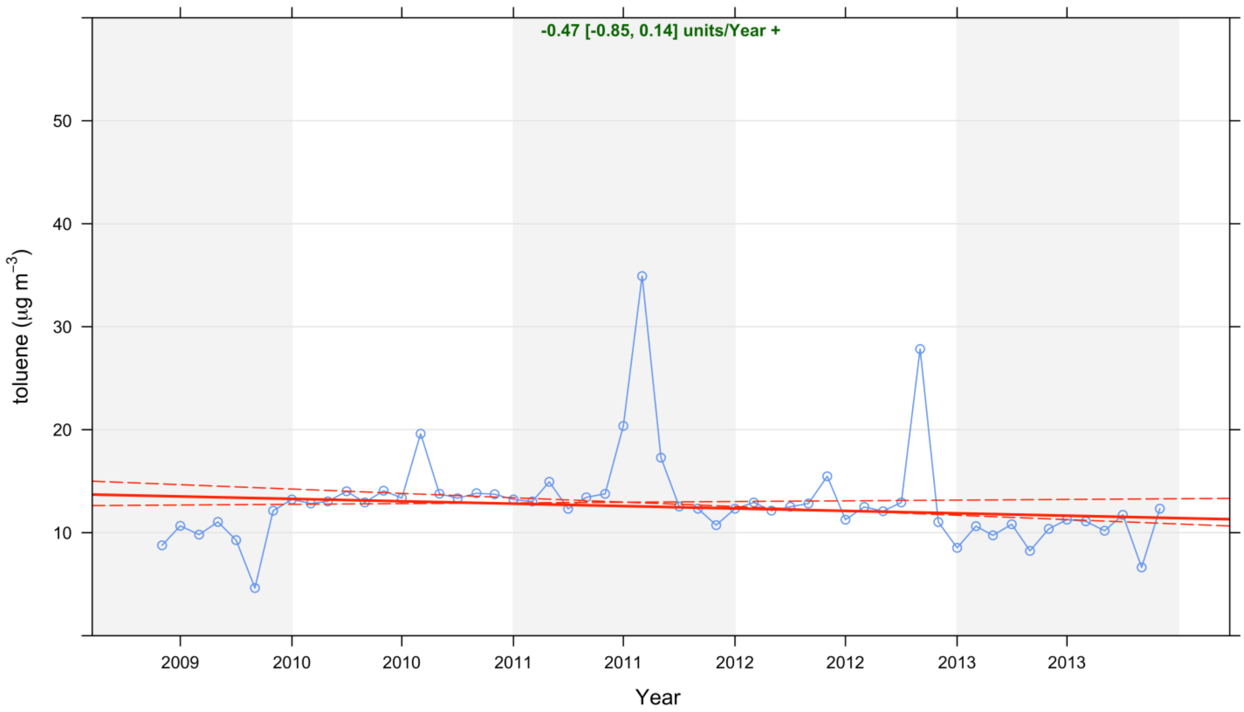


Figure 12 Deseasonalised Theil-Sen trend analysis for passive toluene at Khyber Pass, 2008-2013, The trend is -0.47 µg / m3 /year, statistically significant to the 0.1 level**.**

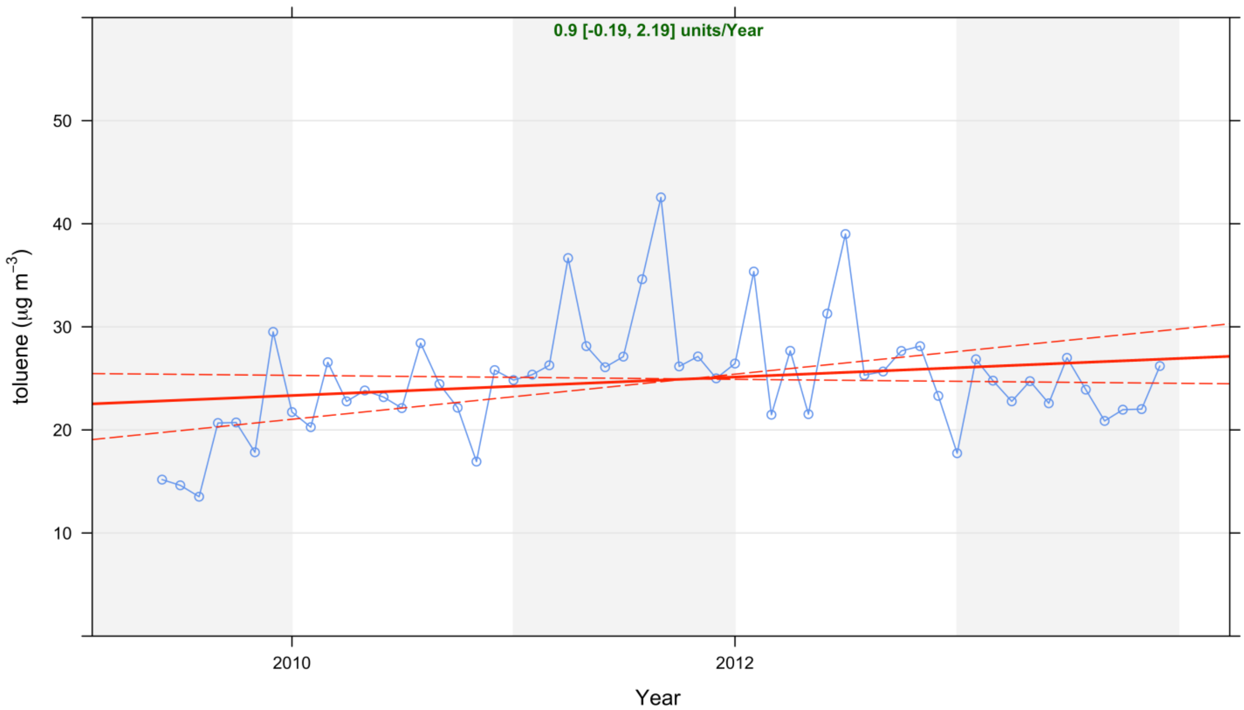


Figure 13 Deseasonalised Theil-Sen trend analysis for passive toluene at Crowhurst Street, 2009 – 2013. The overall trend is shown at the top in green, (0.9 µg / m^3 /year) but the trend is not statistically significant.

4.3 Ethylbenzene

Ethylbenzene shows similar results to benzene and toluene, with a couple of important differences. As with other pollutants, ethylbenzene concentrations are significantly higher at Khyber Pass and Crowhurst Street than Penrose, Henderson and Mt Eden (figure 14 and figure 15). Concentrations are significantly lower at Khyber Pass and Crowhurst Street after 2009, as seen in the benzene and toluene results. Importantly, between 2001 and 2006, concentrations at Penrose, Henderson and Mt Eden are below detection limits for significant periods of time (76%, 56% and 21% respectively). Annual averages for Khyber Pass and Crowhurst Street are also declining.

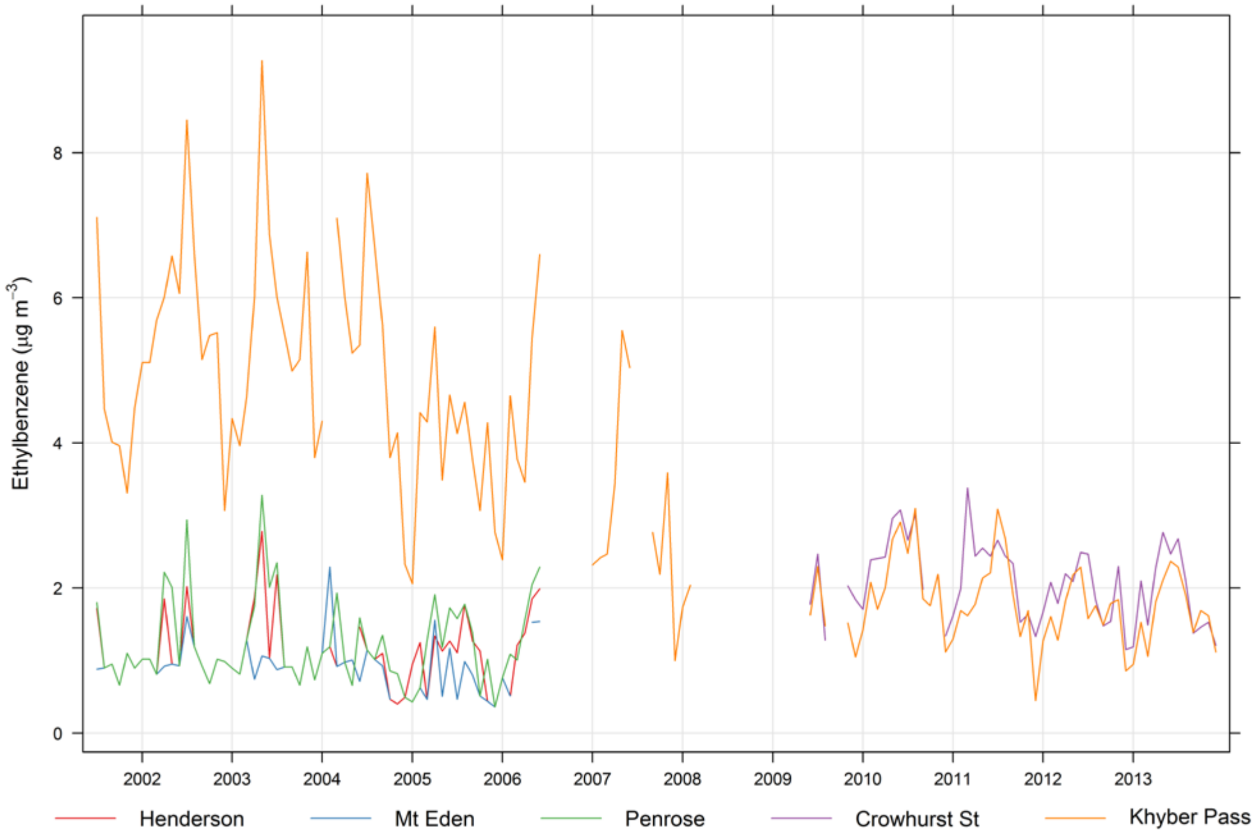


Figure 14 Monthly passive ethylbenzene data, 2001 – 2013. Gaps in traces indicate that no sampling was done. Results below Limit of Detection (LOD) are displayed as half the LOD.

Figure 15 Annual Average passive ethylbenzene, 2001 – 2013.

Ethylbenzene results from Khyber Pass and Crowhurst Street also shows the two trend pattern, as seen in benzene and toluene data. Between 2001 and 2009, there is a clear downward trend in concentrations. However, after 2009, the reduction in concentrations does not continue at the same rate (figure 16. Between 2001 and 2013, the overall trend is a reduction of 0.38 µg / m^3 /year (p-value <0.001). Splitting these trends into the two periods present shows the slowing of reduction after 2009 well. Between 2001 and 2008, concentrations of ethylbenzene at Khyber Pass were reducing by 0.4 µg / m^3 /year (p-value <0.001) (figure 17). After 2008, the trend slows considerably (-0.04 / m^3 /year with no statistical significance), suggesting a stabilisation of concentrations (figure 16)

At Crowhurst Street concentrations have reduced by 0.08 / m^3 /year (p-value <0.01) from 2008.

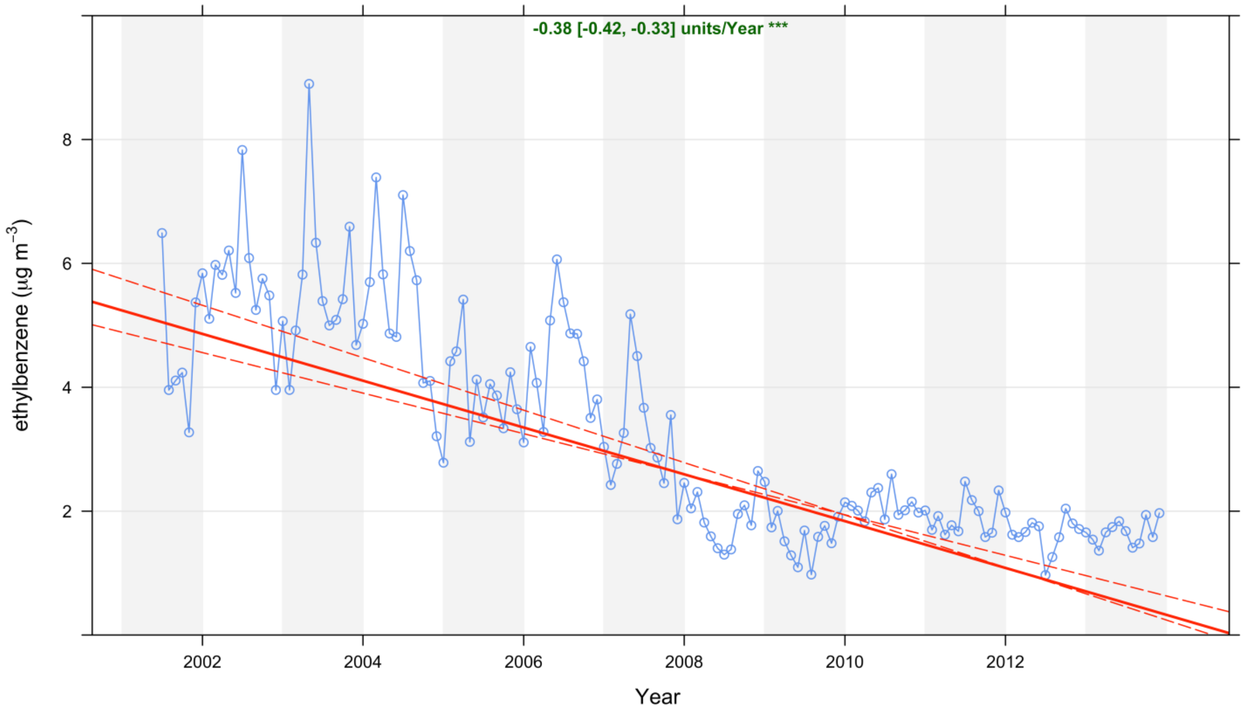


Figure 16 Deseasonalised Theil-Sen trend analysis for passive ethylbenzene at Khyber Pass, 2001 – 2013. The overall trend is shown at the top in green, (-0.38 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

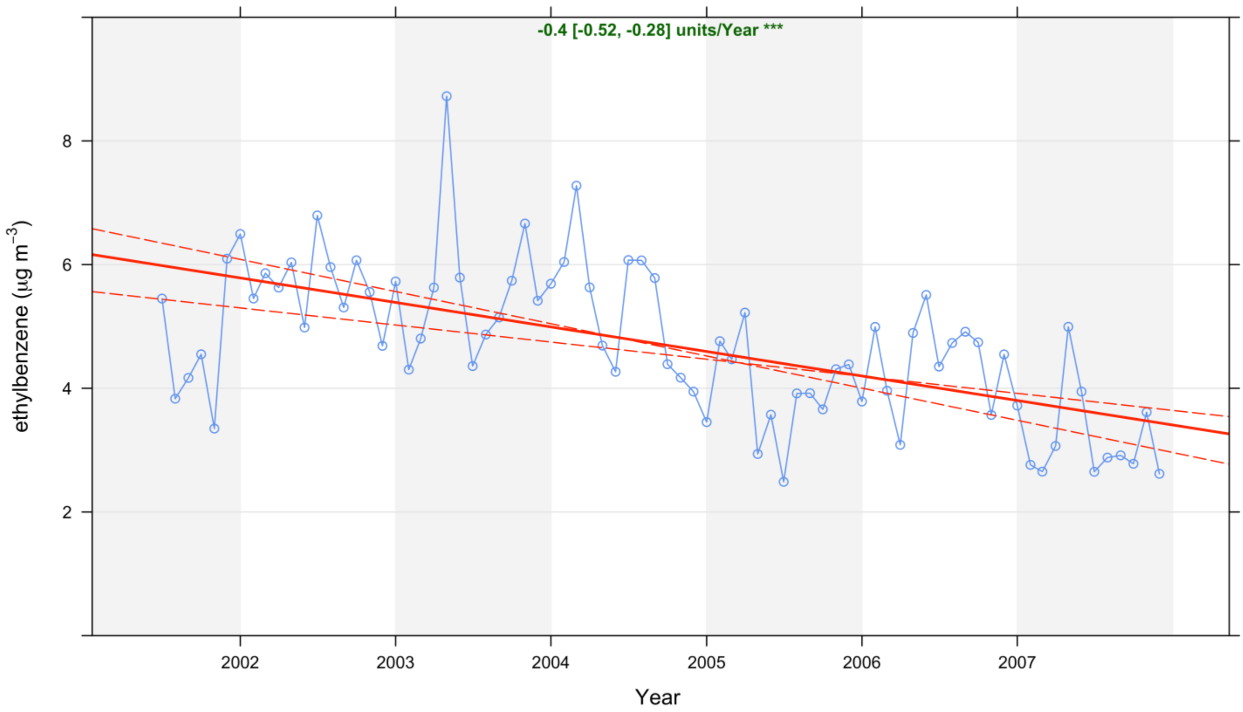


Figure 17 Deasonalised Theil-Sen trend analysis for passive ethylbenzene at Khyber Pass, 2001 – 2008 the overall trend is shown at the top in green, (-0.4 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

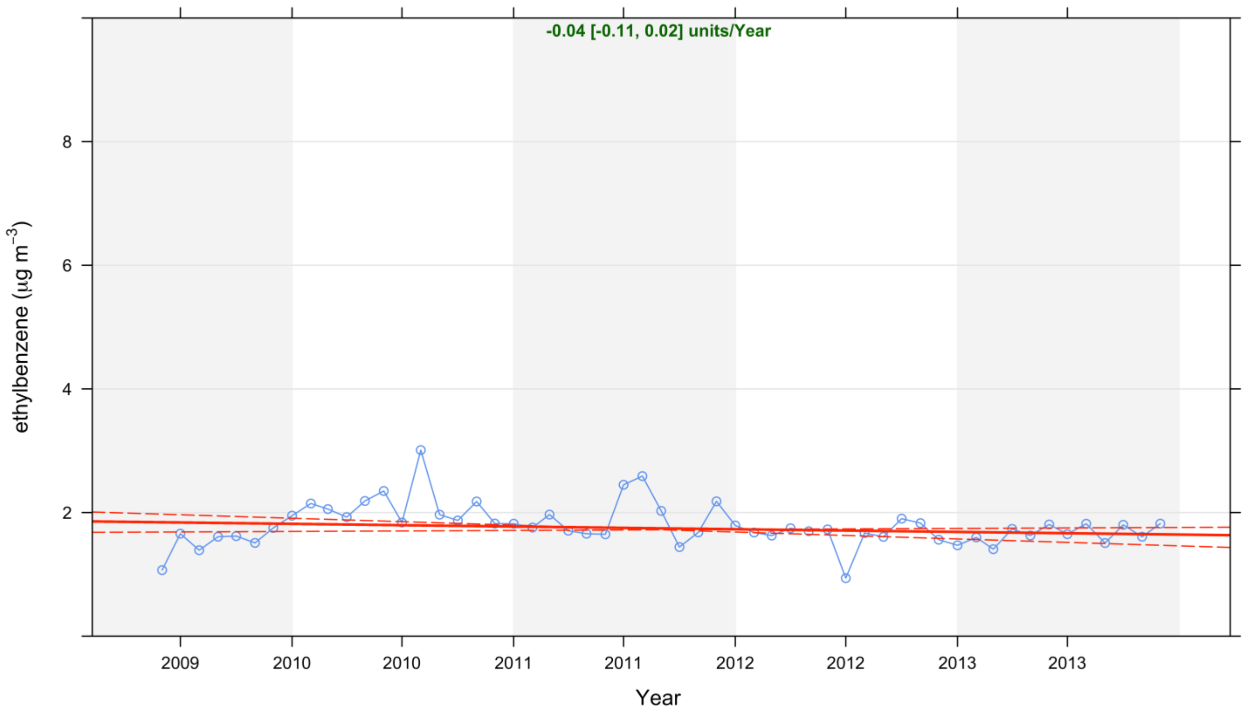


Figure 18 Deseasonalised Theil-Sen trend analysis for passive ethylbenzene at Khyber Pass, 2008-2013 the trend is -0.04 µg / m^3 /year, with no statistical significance.

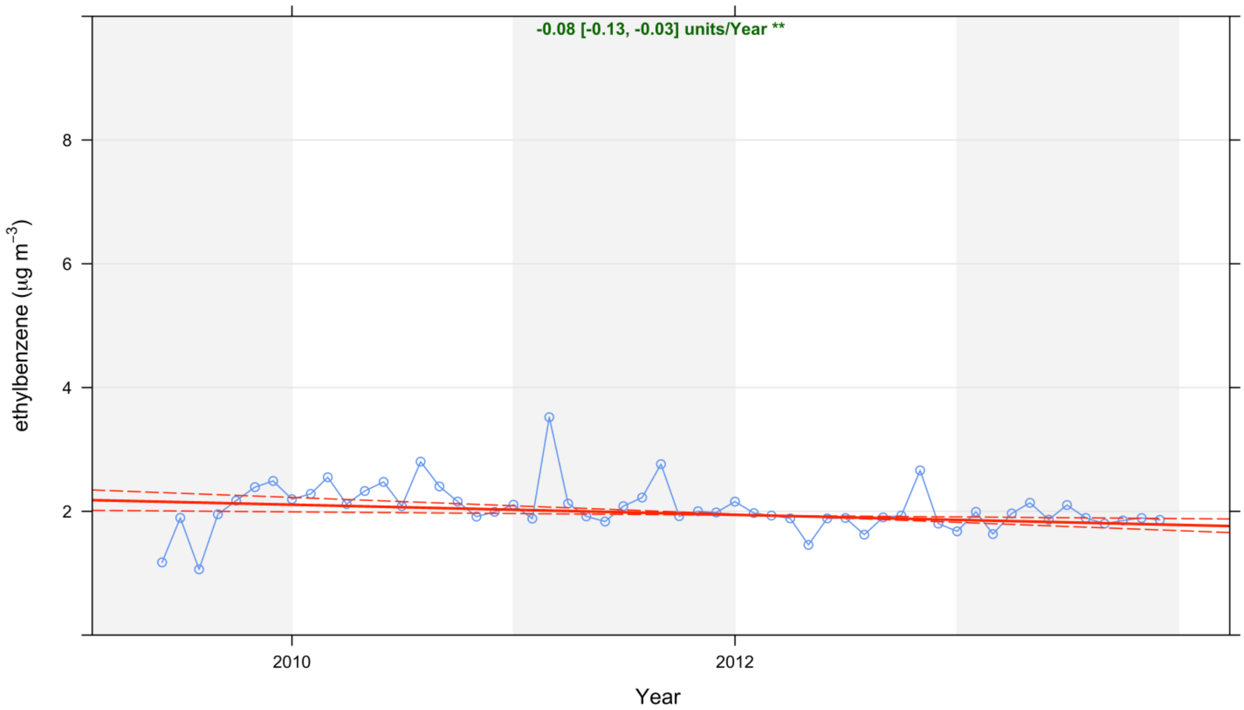


Figure 19 Deseasonalised Theil-Sen trend analysis for passive ethylbenzene at Crowhurst Street, 2008 – 2013. The overall trend is shown at the top in green, (-0.08 µg / m^3 /year) (P-value <0.01).

4.4 Total xylenes

Total xylenes data shows similar results to the remainder of the BTEX suite, with a couple of important differences. As with other pollutants, ethylbenzene concentrations are significantly higher at Khyber Pass and Crowhurst Street than Penrose, Henderson and Mt Eden (figure 20. Concentrations are significantly lower at Khyber Pass and Crowhurst Street after 2009, as seen in the benzene and toluene results. Importantly, between 2001 and 2006, concentrations at Penrose, Henderson and Mt Eden are below detection limits for significant periods of time. Annual averages for Khyber Pass and Crowhurst Street are also declining, despite a brief peak in 2010-2011 (figure 2).

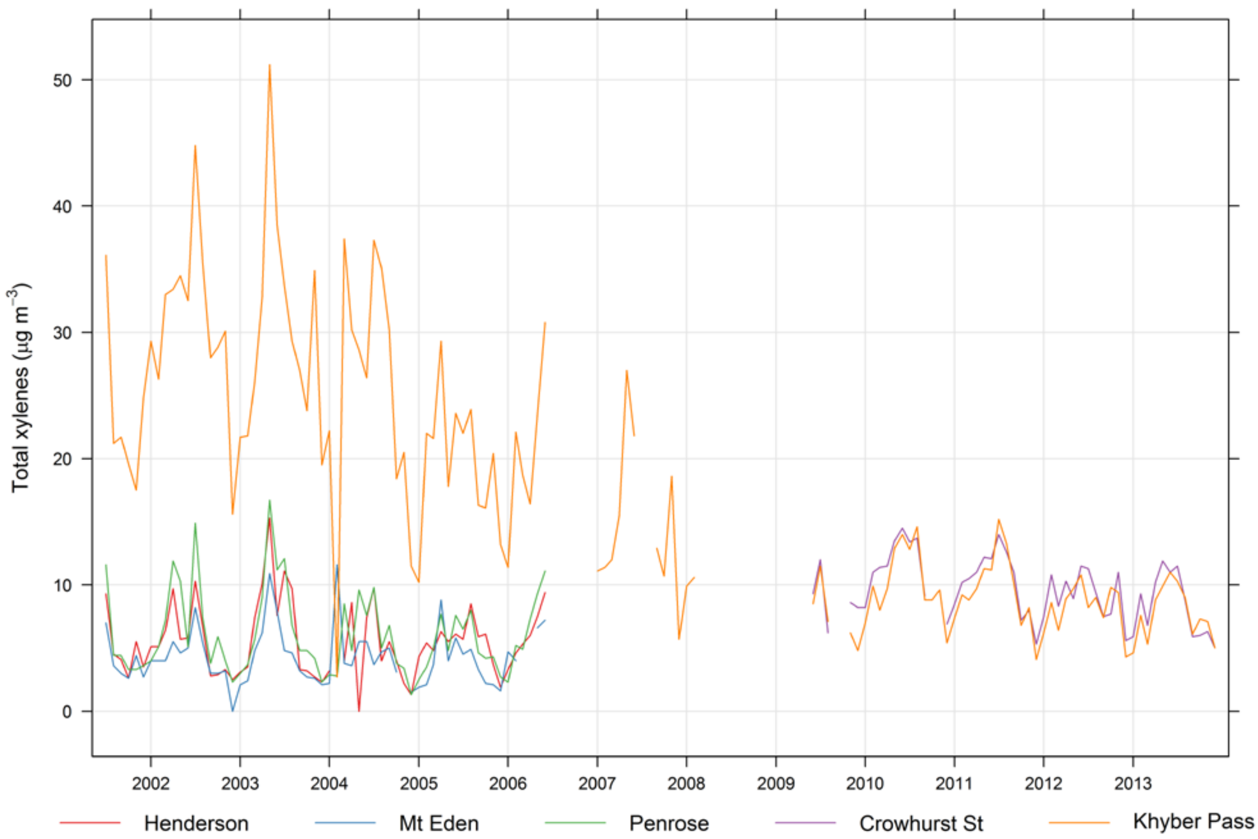


Figure 20 Monthly passive total xylenes data, 2001 – 2013. Gaps in traces indicate that no sampling was done. Results below Limit of Detection (LOD) are displayed as half the LOD.

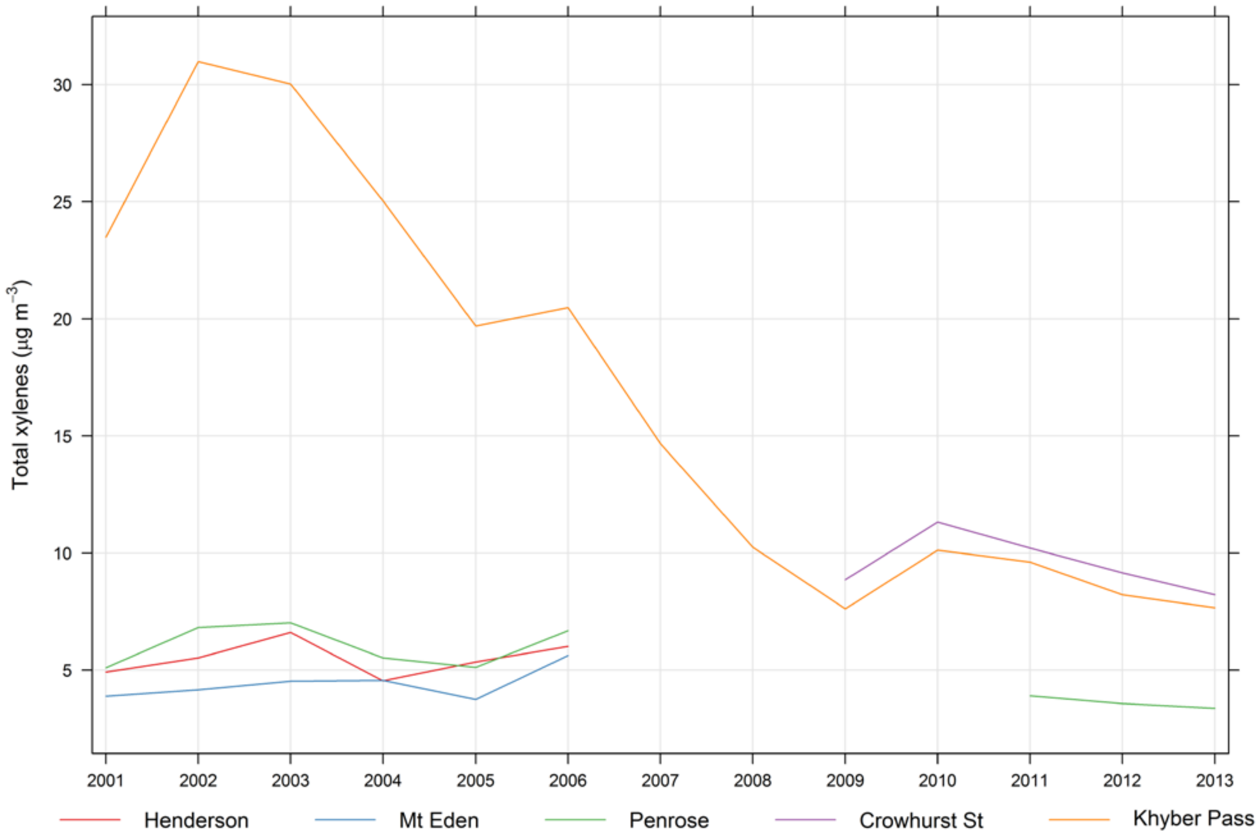


Figure 21 Annual Average passive total xylenes, 2001 – 2013.

Total xylenes results from Khyber Pass and follows the same two trend pattern, as seen in the remainder of BTEX data. Between 2001 and 2009, there is a clear downward trend in concentrations. However, after 2009, the reduction in concentrations does not continue at the same rate (figure 22). Between 2001 and 2013, the overall trend is a reduction of 2.01 µg / m^3 /year (*p*-value <0.001). Splitting these trends into the two periods present shows the slowing of reduction after 2009. Between 2001 and 2008, concentrations of total xylenes at Khyber Pass were reducing by 2.65 µg / m^3 /year (*p*-value <0.001) (figure 23. After 2008, the trend slows considerably (-0.36 µg / m^3 /year). The statistical significance is reduced (*p*-value <0.05) and there is a slow in decline in concentration (figure 24).

At Crowhurst Street total xylenes concentrations have reduced by 0.6 µg / m^3 /year (*p*-value <0.05).

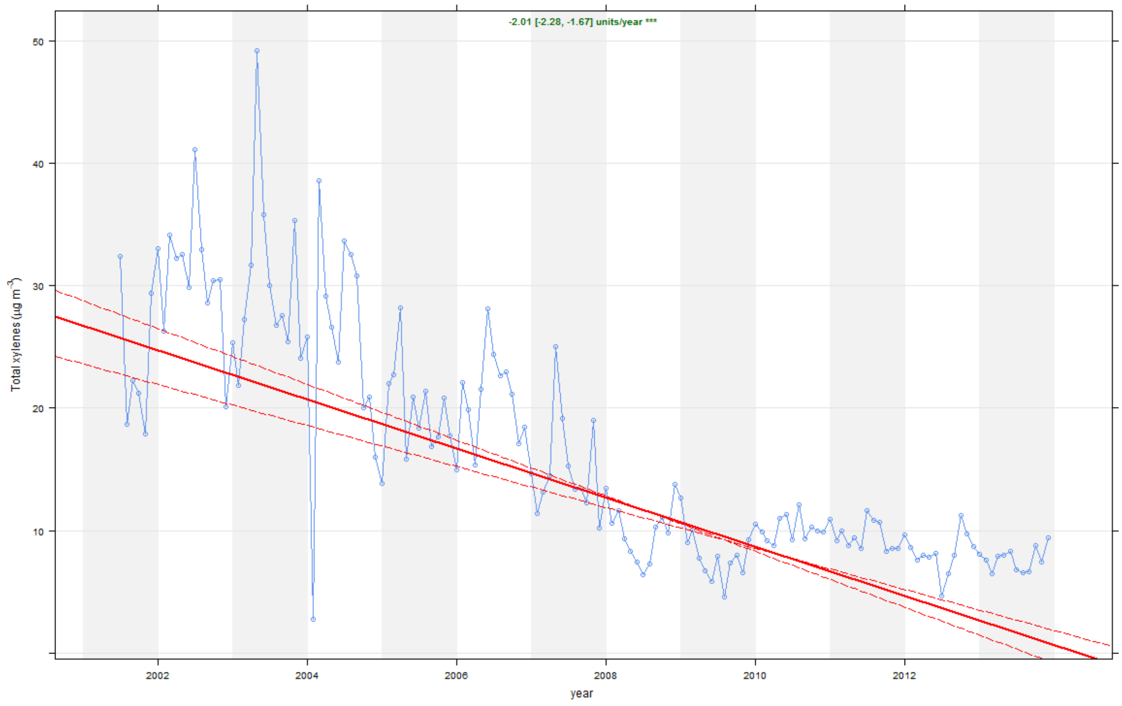


Figure 22 Deseasonalised Theil-Sen trend analysis for passive total xylenes at Khyber Pass, 2001 – 2013. The overall trend is shown at the top in green, (-2.01 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

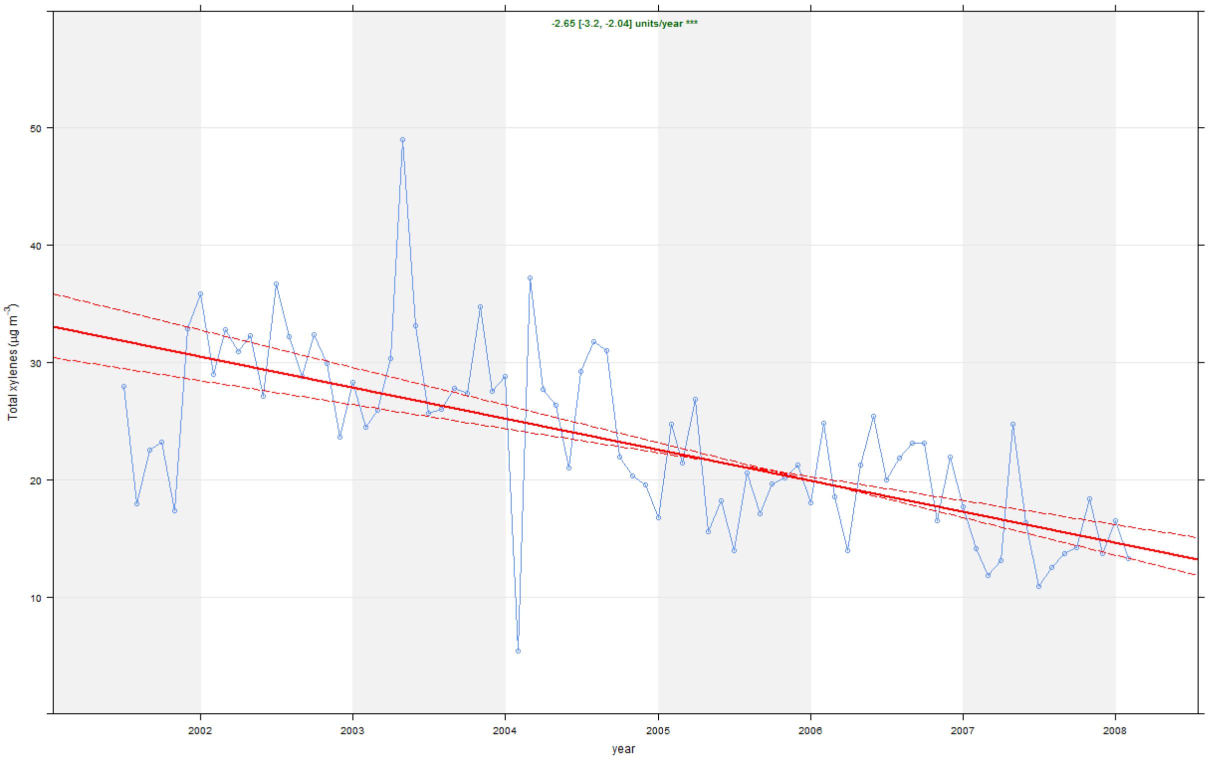


Figure 23 Deasonalised Theil-Sen trend analysis for passive total xylenes at Khyber Pass, 2001 – 2008. The overall trend is shown at the top in green, (-2.65 µg / m^3 /year) with the 95% confidence intervals in the slope in brackets. The *** signifies that the trend is significant to the 0.001 level.

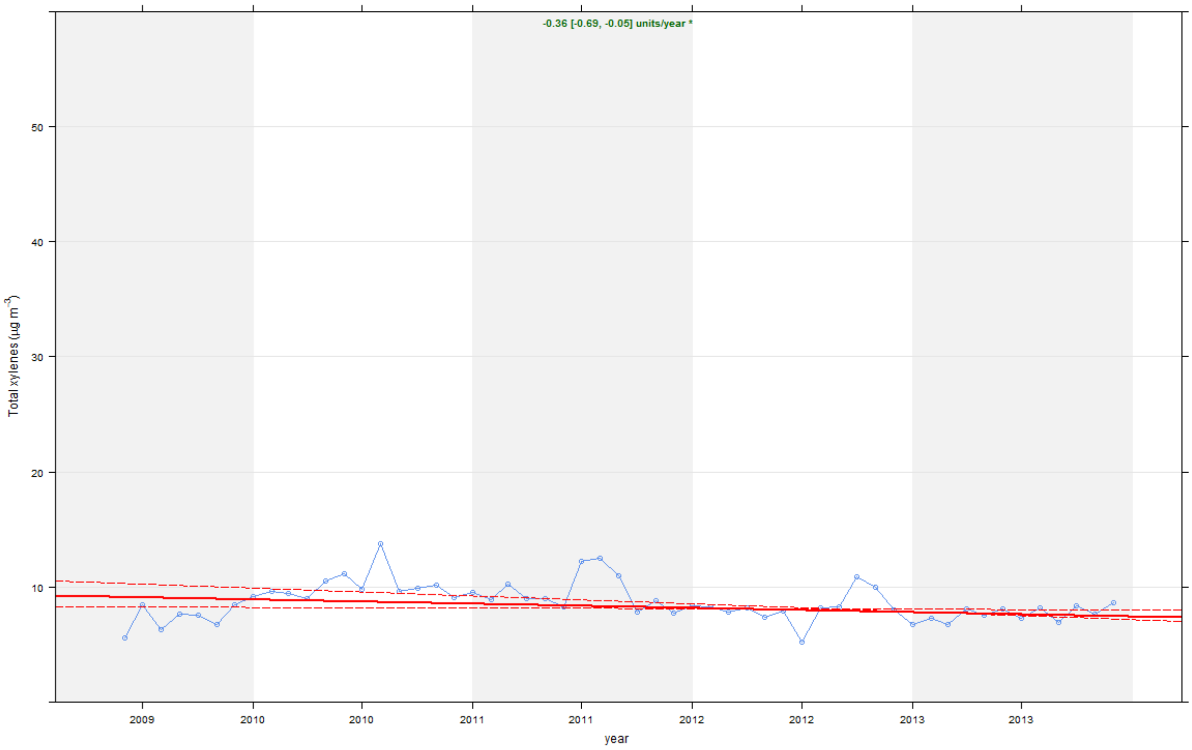


Figure 24 Deseasonalised Theil-Sen trend analysis for passive total xylenes at Khyber Pass 2009-2013 The trend is -0.36µg / m^3 /year, significant to the <0.05 level.

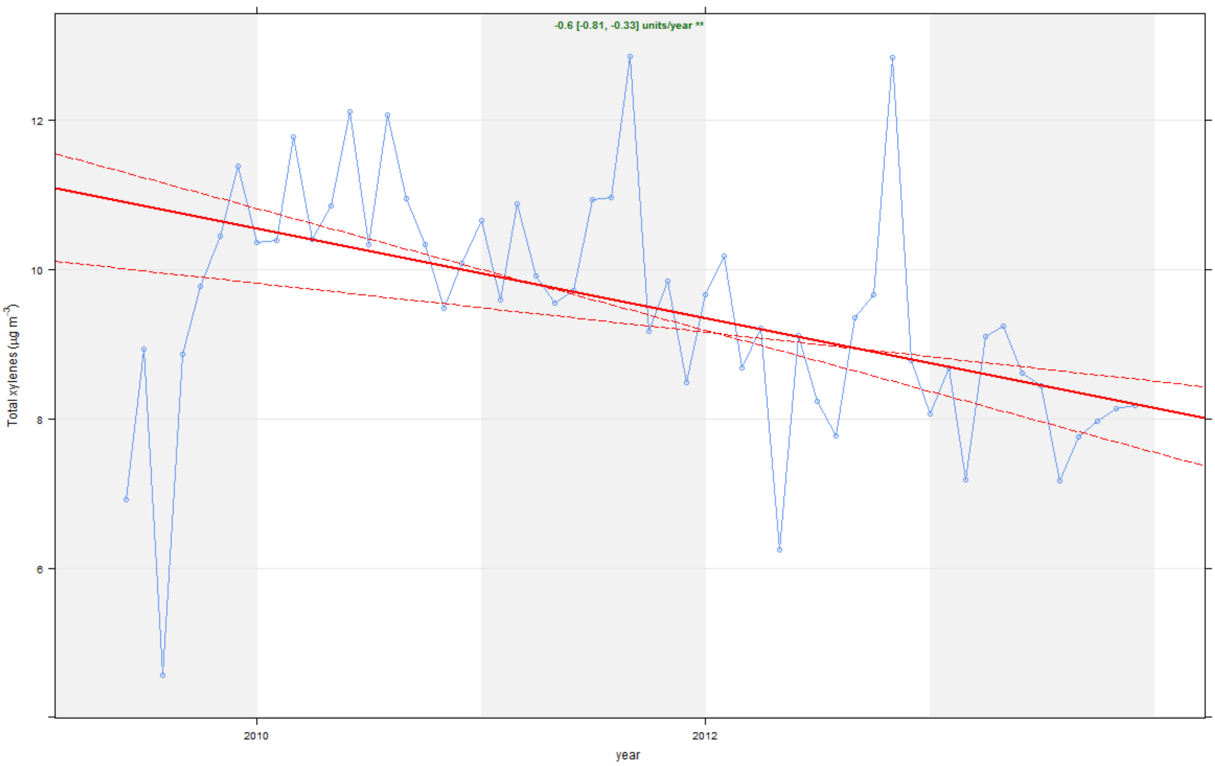


Figure 25 Deseasonalised Theil-Sen trend analysis for passive total xylenes at Crowhurst Street, 2009 – 2013. The overall trend is shown at the top in green, (-0.6 µg / m^3 /year) (P-value <0.05).

4.5 BTEX results summary

This section summarises the results for BTEX at Khyber Pass and Crowhurst Street. All components of the BTEX suite showed reduction between 2001 and 2013, with the strongest (in terms of unit reduction per year, and statistical significance) seen between 2001 and 2009. Trends since then have either been largely stable, or small unit reductions with weak statistical significance (tables 3 - 6)

Annual means and data capture % is also presented in this section (Tables 7 - 12).

Table 3 Benzene trends, 2001 - 2013

Site	2001 – 2013		2001- 2008		2008 - 2013	
	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value
Crowhurst St	-	-	-	-	-0.07	>0.1
Khyber Pass	-0.87	<0.001	-1.62	<0.001	-0.07	>0.1

Table 4 Toluene trends, 2001 - 2013

Site	2001 – 2013		2001- 2008		2008 - 2013	
	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value
Crowhurst St	-	-	-	-	-0.9	>0.1
Khyber Pass	-2.12	<0.001	-1.99	<0.001	-0.47	<0.1

Table 5 Ethylbenzene trends, 2001 - 2013

Site	2001 – 2013		2001- 2008		2008 - 2013	
	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value
Crowhurst St	-	-	-	-	-0.08	<0.01
Khyber Pass	-0.38	<0.001	-0.4	<0.001	-0.04	>0.1

Table 6 Total xylenes trends, 2001 - 2013

Site	2001 – 2013		2001- 2008		2008 - 2013	
	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value	Trend (±µg / m^3 /year)	*p*- Value
Crowhurst St	-	-	-	-	-0.6	<0.05
Khyber Pass	-2.01	<0.001	-2.65	<0.001	-0.36	<0.05

Table 7 Annual data capture % for Passive BTEX sites, 2001-2013

Site	***Annual data capture % for Passive BTEX sites, 2001-2013***												
	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Henderson	50	100	100	83.3	100	50	-	-	-	-	-	-	-
Mt Eden	50	83.3	75	83.3	91.7	25	-	-	-	-	-	-	-
Penrose	50	91.7	91.7	100	100	41.7	-	-	-	-	50	100	100
Crowhurst St	-	-	-	-	-	-	-	-	41.7	83.3	100	100	100
Khyber Pass	50	100	100	91.7	100	50	83.3	16.7	41.7	100	100	100	100

Table 8 Annual average benzene (µg / m^3) concentrations at Passive BTEX sites, 2001-2013

Site	***Annual average benzene (µg / m^3) concentrations at Passive BTEX sites, 2001-2013***												
	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Henderson	4.7	3.0	3.3	2.4	2.3	1.7	-	-	-	-	-	-	-
Mt Eden	2.9	2.3	2.6	2.0	1.6	1.6	-	-	-	-	-	-	-
Penrose	3.1	2.9	3.0	2.3	1.9	1.6	-	-	-	-	0.8	0.825	0.75
Crowhurst St	-	-	-	-	-	-	-	-	3.7	4.3	6.3	3.9	3.7
Khyber Pass	10.8	12.6	12.4	11.2	8.0	5.6	4.1	2.8	2.4	2.9	3.7	2.5	2.3

Table 9 Annual average toluene (µg / m³) concentrations at Passive BTEX sites, 2001-2013

Site	***Annual average toluene (µg / m³) concentrations at Passive BTEX sites, 2001-2013***												
	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Henderson	8.8	8.8	9.7	7.8	9.0	10.4	-	-	-	-	-	-	-
Mt Eden	6.5	6.8	7.0	9.7	5.3	9.1	-	-	-	-	-	-	-
Penrose	7.3	8.8	9.7	8.0	7.9	9.5	-	-	-	-	5.65	5.7	4.8
Crowhurst St	-	-	-	-	-	-	-	-	17.8	24.4	29.1	27.7	23.4
Khyber Pass	26.2	32.9	33.4	31.8	29.6	26.4	19.6	12.1	9.6	14	15.8	13.8	10.1

Table 10 Annual average ethylbenzene (µg / m³) concentrations at Passive BTEX sites, 2001-2013

Site	***Annual average ethylbenzene (µg / m³) concentrations at Passive BTEX sites, 2001-2013***												
	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Henderson	1.7	1.9	2.3	1.3	1.2	1.6	-	-	-	-	-	-	-
Mt Eden	<LOD*	1.6	<LOD*	1.4	1.1	1.5	-	-	-	-	-	-	-
Penrose	1.8	2.4	2.3	1.3	1.5	1.6	-	-	-	-	0.8	0.85	0.85
Crowhurst St	-	-	-	-	-	-	-	-	1.9	2.4	2.2	1.9	1.9
Khyber Pass	4.6	5.7	5.6	5.3	3.9	4.4	3.1	1.9	1.6	2.1	1.9	1.6	1.7

*LOD = Limit Of Detection

Table 11 Annual average m+p xylene (µg / m^3) concentrations at Passive BTEX sites, 2001-2013

Site	Annual average m+p xylene (µg / m^3) concentrations at Passive BTEX sites, 2001-2013												
	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Henderson	4.5	5.0	5.6	4.1	4.0	4.6	-	-	-	-	-	-	-
Mt Eden	3.6	4.4	4.0	4.0	3.0	4.5	-	-	-	-	-	-	-
Penrose	4.6	5.8	5.8	4.5	3.6	5.1	-	-	-	-	2.9	2.8	2.5
Crowhurst St	-	-	-	-	-	-	-	-	6.8	8.4	7.8	6.9	6.1
Khyber Pass	17.7	23.7	22.5	18.6	14.6	15.3	11.0	7.8	5.8	7.5	7.0	6.1	5.7

Table 12 Annual average o xylene (µg / m^3) concentrations at Passive BTEX sites, 2001-2013

Site	Annual average o xylene (µg / m^3) concentrations at Passive BTEX sites, 2001-2013												
	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Henderson	2.5	2.1	2.9	1.9	1.5	1.7	-	-	-	-	-	-	-
Mt Eden	1.8	1.9	2.1	1.7	1.3	1.5	-	-	-	-	-	-	-
Penrose	2.7	2.4	2.5	1.8	1.5	1.9	-	-	-	-	1.0	1.0	0.875
Crowhurst St	-	-	-	-	-	-	-	-	2.1	2.9	2.4	2.3	2.1
Khyber Pass	5.8	7.3	7.5	7	5.1	5.2	3.7	2.5	1.8	2.6	2.6	2.1	2.0

5.0 Continuous benzene and 1,3 butadiene results (Khyber Pass)

Data from the continuous instrument at Khyber Pass shows similar results to the passive data presented in section 4. A summary of annual averages and data capture percentage is presented in table 13. Note that instrument issues and site changes in 2009 and 2012 have meant that the continuous dataset is below the recommended annual 75% valid data recommended by MfE (MfE, 2009). Accordingly the results presented in this section should be considered as guidance only. These data are still reported here as the increase in temporal resolution (1-hour average) is useful for assessing temporal change.

Table 133 Data capture and annual averages for continuous benzene and 1,3 butadiene at Khyber Pass.

Year	Valid data (%)	Annual average	
		Benzene (µg / m^3)	1,3 butadiene (µg / m^3)
2005	75.6	6.07	0.925
2006	88.2	6.85	1.48
2007	90.8	6.37	1.74
2008	66.8	2.98	0.40
2009	27.2	2.75	0.18
2010	28.6	2.10	0.23
2011	91.3	2.49	0.37
2012	59.3	5.13	0.44
2013	84.1	3.09	0.55

Between 2005 and 2008, data shows consistent decline in concentrations, both at monthly time series and annual average periods. Between 2008 and 2010, concentrations were at their lowest, before an increase in concentrations after 2010 and 2011. This increase is most noticeable in benzene results (figures 26 and 27).

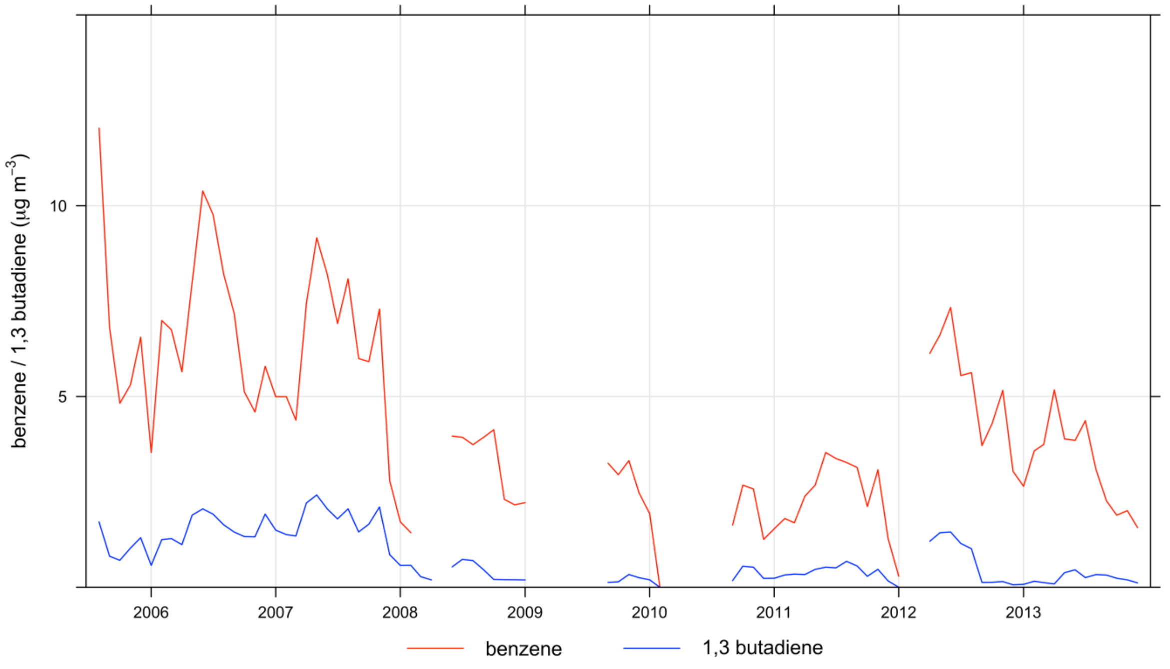


Figure 26 Monthly average benzene and 1,3 butadiene results (Khyber Pass), 2005 -2013.

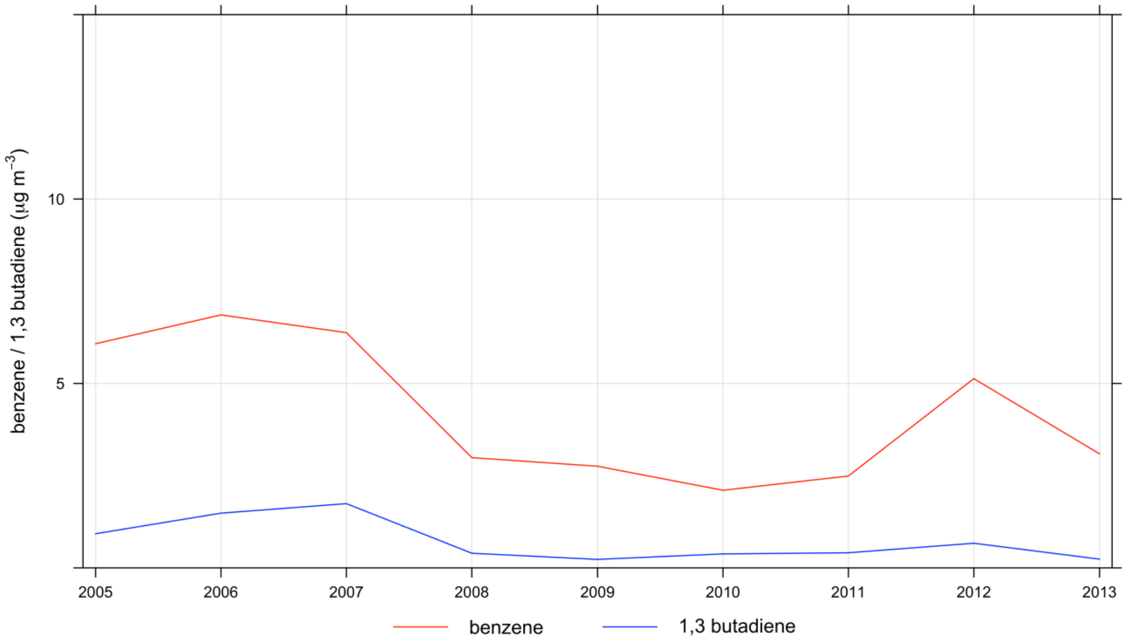


Figure 27 Annual average benzene and 1,3 butadiene results (Khyber Pass), 2005 -2013.

Deseasonalised Theil-Sen analysis for continuous benzene and 1,3 butadiene data from Khyber Pass show strong declines in concentrations between 2005 and 2013 (figures 28 and 29. The two trend pattern observed in passive BTEX data is less obvious, though there is an increase in concentrations from 2011 on. Between 2005 and 2013, benzene concentrations measured by the continuous instrument declined by 0.45 µg / m^3 /year (P-value <0.001) and 1,3 butadiene declined by 0.13 µg / m^3 /year (P-value <0.001).

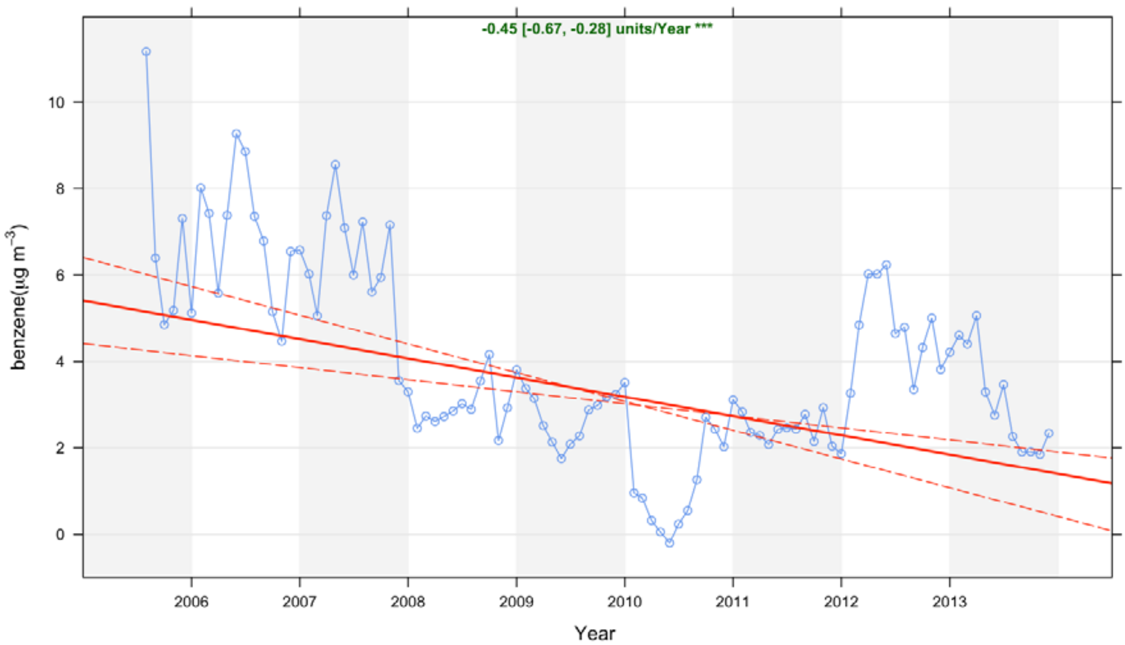


Figure 28 Deseasonalised Theil-Sen trend analysis for continuous benzene at Khyber Pass, 2005 – 2013. The overall trend is shown at the top in green, (-0.45 µg / m^3 /year) (P-value <0.001).

Figure 29 Deseasonalised Theil-Sen trend analysis for continuous 1,3 butadiene at Khyber Pass, 2005 – 2013. The overall trend is shown at the top in green, (-0.13 µg / m^3 /year) (P-value <0.001).

5.1 Temporal variation of benzene, 1,3 butadiene and other pollutants

Continuous benzene and 1,3 butadiene data from Khyber Pass shows significant temporal trends (figure 30). Note that in figures 30 and 31 data is normalised by dividing the traces by their means, allowing comparison of different data ranges on the same axis (Carslaw, 2013). Due to the dominance of vehicle emissions at Khyber Pass, there is a strong pattern following peak traffic times. Concentrations rise steeply during the week from 0600, peaking around 1000, with the morning peak in traffic volumes. Concentrations decline before noon, before climbing steeply again in the afternoon with the traffic peak.

In the weekend, concentrations rise from 0600, peaking at 1800. These peaks are approximately half of the weekday concentrations. Importantly, the concentrations increase through the week, with less recovery in baseline concentrations (i.e., the lowest values increase through the week), even in the weekend. These trends suggest a strong traffic signal in concentrations.

At a monthly average scale, concentrations through winter are over double those seen in summer. These higher concentrations are potentially linked to home heating emissions which are known to peak in winter, or to lower average wind speed slowing pollutant dispersal (Jones et al., 2009).

When continuous benzene and 1,3 butadiene data is compared with CO and PM_{10} data from Khyber Pass, the traffic influence is more obvious. CO and PM_{10} follow the pattern of peaks described above, suggesting a strong link between traffic sources and all pollutants. The peaks are less marked in the PM_{10} trace, but it still follows the same two peak pattern. The same accumulation pattern is also seen through the week, with baseline concentrations increasing as the week progresses. Given the patterns seen here, it is safe to assume that all pollutants have the same source, vehicle/traffic emissions and predominant emissions sources at Khyber Pass (Davy et al., 2011).

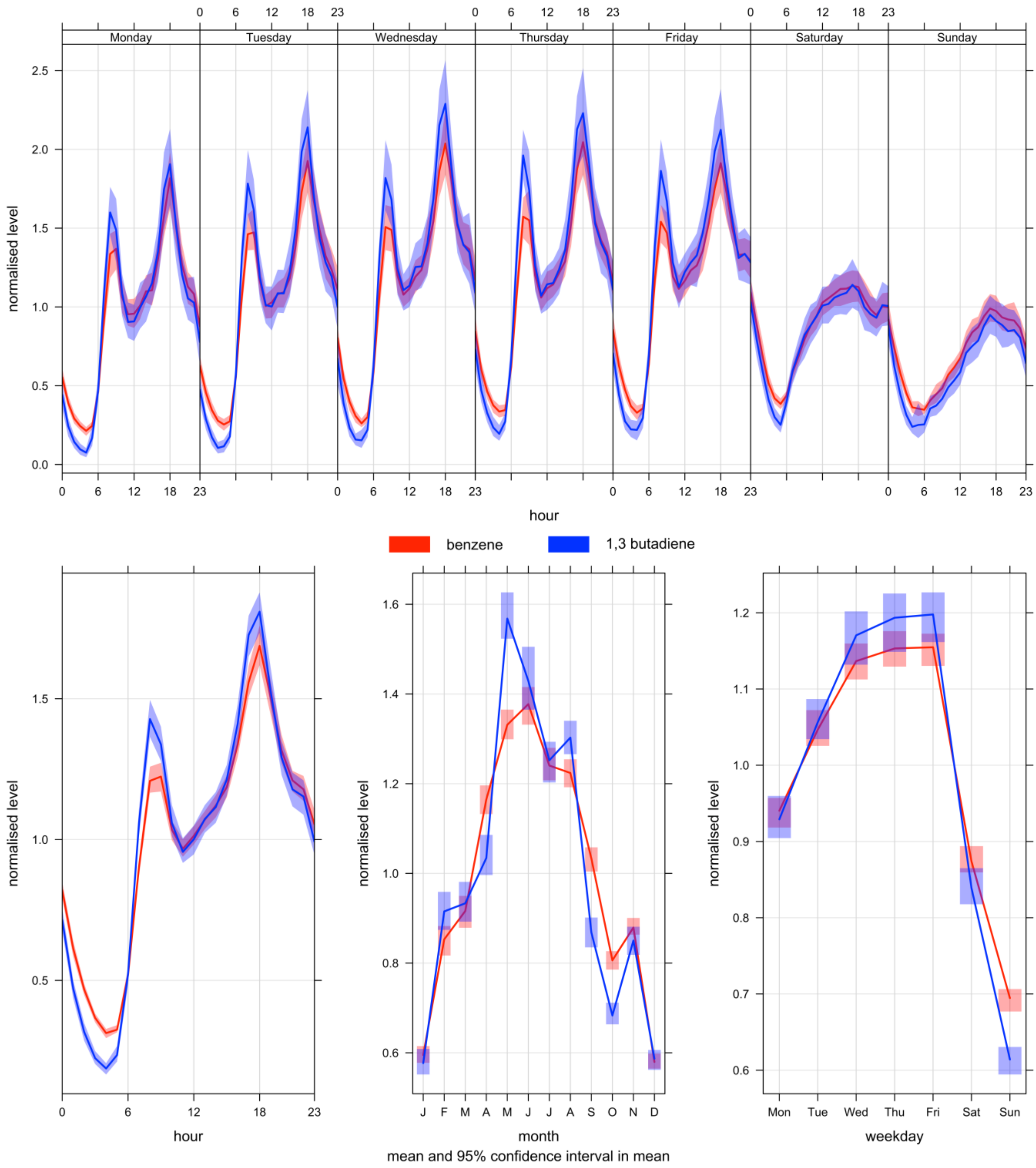


Figure 30 Temporal trend for continuous benzene and 1,3 butadiene at Khyber Pass, 2005 – 2013. Data is normalised by dividing the traces by their means allowing comparison of different data ranges on one plot.

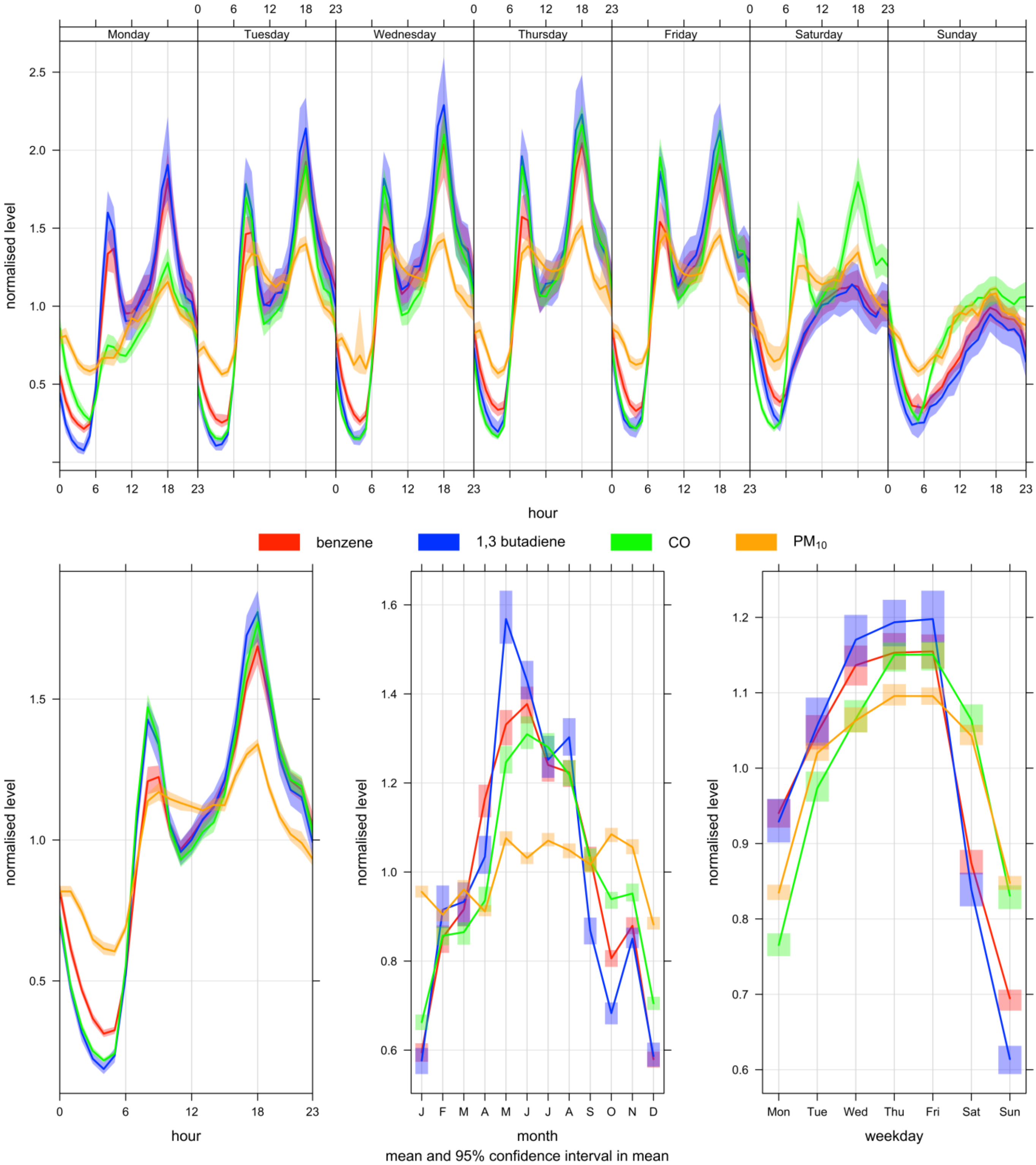


Figure 31 Temporal trend for continuous benzene, 1,3 butadiene, CO and PM_{10} at Khyber Pass, 2005 – 2013. Data is normalised by dividing the traces by their means allowing comparison of different data ranges on one plot

6.0 Benzene, 1,3 butadiene and ambient air quality standards and guidelines

Annual average benzene concentrations must not exceed the MfE guideline value of 3.6 µg / m^3. For 1,3 butadiene the annual average must not exceed 2.4 µg / m^3 (MfE, 2002). These guidelines have also been adopted as Auckland Ambient Air Quality Standards (AAAQS) in the Proposed Auckland Unitary Plan (PAUP) (Auckland Council, 2013A).

It must be noted that the passive sampling method is not a standard method recommended by MfE (MfE, 2009). However due to the ease of deployment and cost effective analysis, these methods have been compared to MfE guidelines as a screening method. The passive sampling method is widely used in New Zealand studies and yields reliable data. The continuous instrument operating at Khyber Pass complies with the MfE recommendations.

Figures 32, 33 and 34 show annual average values and guideline values for passive BTEX benzene, continuous benzene and 1,3 butadiene from Khyber Pass. The passive sampling data (figure 32) shows that Khyber Pass annual averages have been below the guideline level since 2008. In 2011, Khyber Pass exceeded by 0.1 µg / m^3. Concentrations have since declined to well below the annual guideline value. Crowhurst Street reflected the same pattern, with a significant exceedance of the guideline in 2011. The stronger peak at Crowhurst Street may reflect the additional contribution of evaporation from a nearby petrol station, on top of a similar traffic signal to Khyber Pass.

In figures 33 and 34 (Khyber Pass continuous data) a similar pattern is evident, with a strong spike in benzene annual average in 2011. Averages have since declined since then to below the guideline value. 1,3 butadiene on the other hand, has never exceeded the guideline values, suggesting benzene as the more dominant pollutant. Despite concentrations declining to below the guideline (Khyber Pass) and close to the guideline (Crowhurst Street) there is still potential for exceedances to occur (as in 2011).

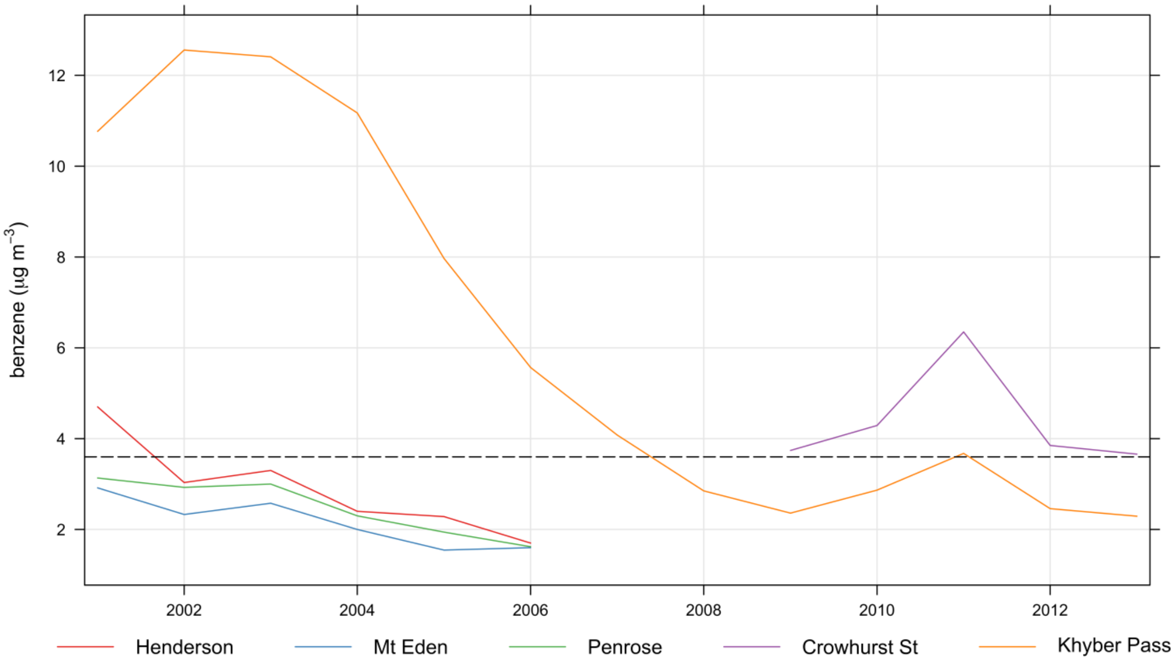


Figure 32 Annual average passive benzene 2001 – 2013. The dashed line is the MfE Guideline and AAAQS for benzene.

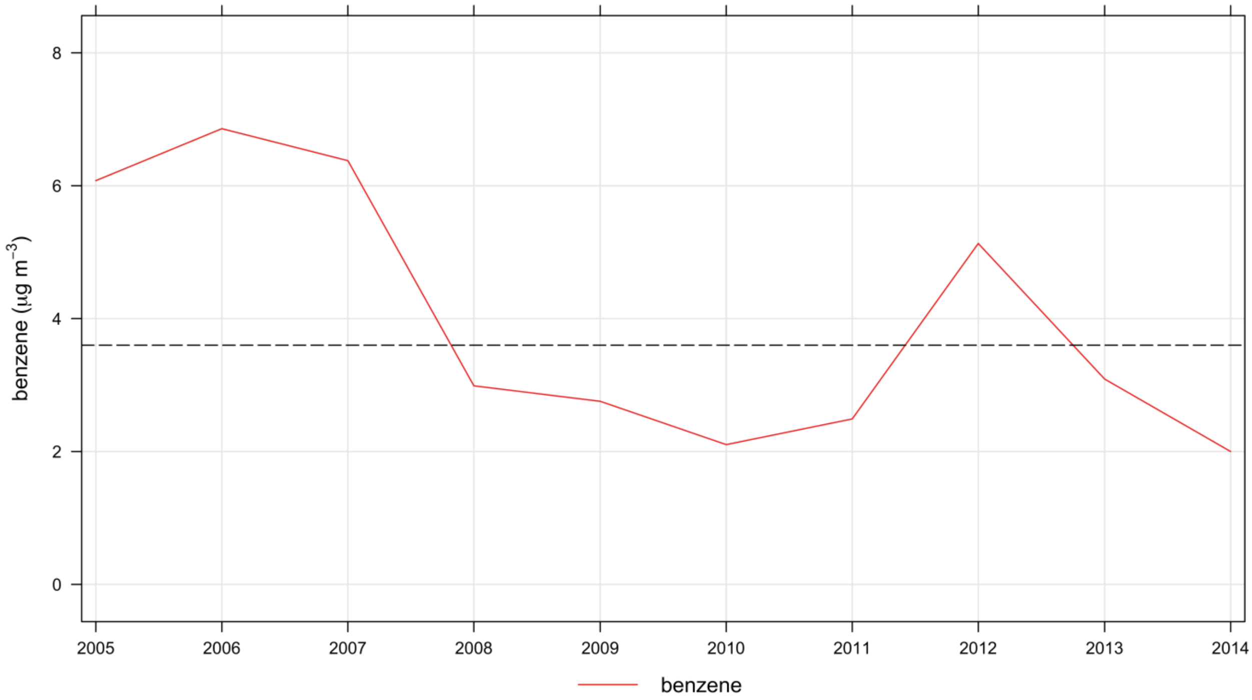


Figure 33 Annual average continuous benzene 2005 – 2013. The dashed line is the MfE Guideline and AAAQS for benzene.

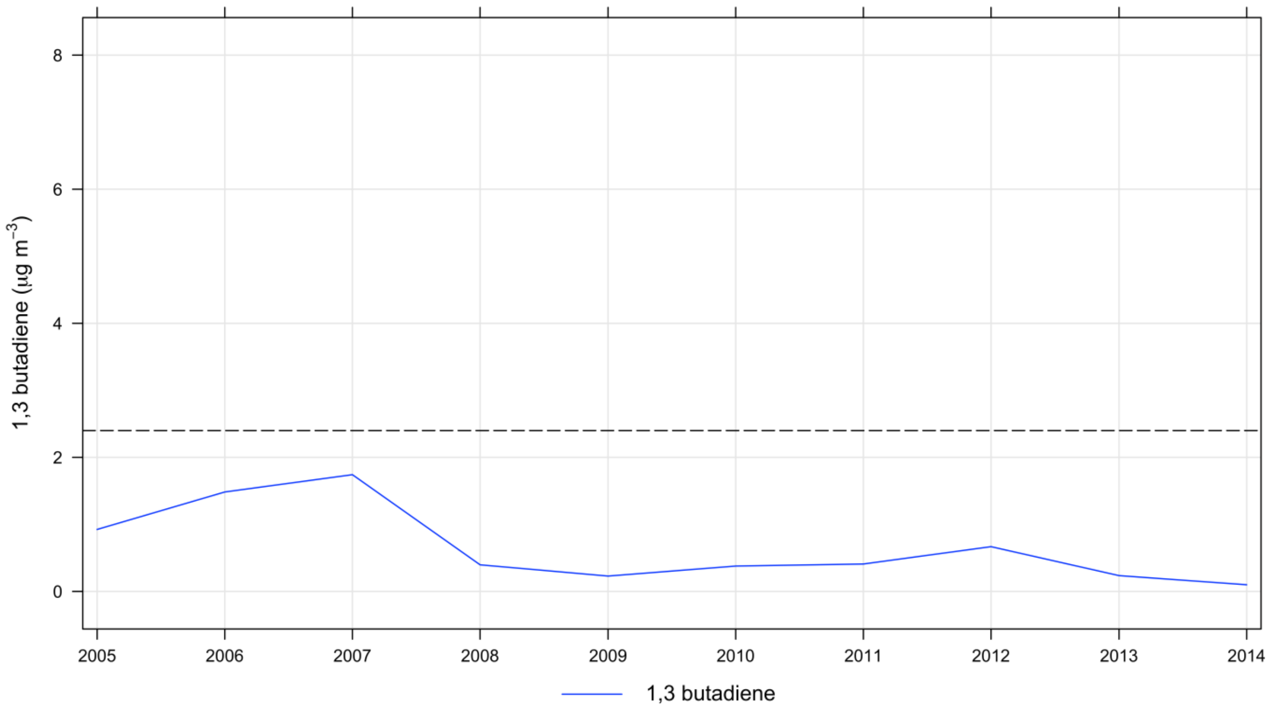


Figure 34 Annual average continuous 1,3 butadiene 2005 – 2013. The dashed line is the MfE Guideline and AAAQS for 1,3 butadiene.

7.0 Vehicle fleet composition: implications for ambient VOC concentrations

As outlined in section 6, ambient VOC concentrations at Khyber Pass and Crowhurst Street have declined significantly since 2001, largely in response to reduction in VOC concentrations in petrol. The last of these reductions occurred in 2011 (see table 1), and ambient VOC concentrations have largely stabilised since then. Reduction of VOC concentrations in petrol has been an effective management tool, as ambient concentrations declined rapidly between 2001 and 2008. The stabilisation in ambient VOC concentrations since 2008 however, suggests that the effectiveness of this management tool has largely passed, and that further options are required to reduce concentrations further.

The composition of the vehicle fleet also plays an important role in driving ambient VOC concentrations. The New Zealand vehicle fleet is generally ageing, meaning that older, and more polluting, vehicles are remaining on the road for longer (MoT, 2011). In 2011, the average vehicle age was around 12.5 years. This age is predicted to increase to between 12.8 and 13.1 years by 2020 (MoT, 2011). The aging fleet means that older, more polluting vehicles are staying on the road for longer, and despite improved fuel quality, emissions of VOC may remain high. Vehicle registrations are also increasing (MoT, 2013), suggesting an increasing vehicle fleet. Higher numbers of vehicles on the road may be translated into higher ambient VOC concentrations. Of these new vehicles entering the fleet, however, increasing numbers are compliant with Euro 4 and Euro 5 emissions standards (MoT, 2013). The effectiveness of these improved emissions standards may however be ‘cancelled out’ by the aging fleet, built to older emissions standards. The penetration of Euro 4 and Euro 5 standards into the vehicle fleet may determine reductions in ambient VOC concentrations.

Accordingly, it may be prudent for additional management tools to be introduced to ensure that the benefits of newer, less polluting (eg Euro 4 and 5) vehicles in the New Zealand vehicle fleet are realised. Given that benzene concentrations in New Zealand petrol are in-line with world standards, benzene VOC levels in petrol are already at low levels, and it may prove impractical to reduce them further. The peak effectiveness of this tool may therefore have passed. Managing Traffic volume and fleet composition may provide more effective tools for reducing ambient VOC concentrations. As demonstrated by the data reported here, VOC concentrations have declined steeply, and stabilised since 2001. This is despite an aging, and growing fleet (MoT, 2011; 2013), and high volumes of traffic through Khyber Pass (13345 vehicles per day in 2008 (Auckland Transport, 2014).

8.0 Conclusions

Passive BTEX results show that between 2001 and 2006 ambient concentrations of benzene, toluene, ethylbenzene and xylenes declined steadily, as reported by Jones et al. (2009).

At Khyber Pass where passive BTEX monitoring has been conducted since 2001, ambient BTEX concentrations have declined steadily. Periods of major decline have generally been associated with reductions of benzene concentrations in petrol, in 2002, 2004, 2006 and 2011. Decline in ambient benzene between 2001 and 2013, was of 0.87 µg / m^3 / year. However, this decline in ambient concentrations was not uniform across the study period. Between 2001 and 2007, ambient concentrations declined by 1.62 µg / m^3 / year, and between 2009 and 2013 the decline was 0.08 µg / m^3 / year. These trends suggest that firstly ambient benzene concentrations have largely stabilised, and that perhaps the peak effectiveness of benzene reductions in petrol has passed.

Importantly, despite the decline and stabilisation of ambient benzene concentrations, annual average concentrations remain very close to the AAAQS and MfE guidelines. Khyber Pass breached this guideline in 2011 (passive benzene), and 2012 (continuous benzene by GC). At Crowhurst Street, annual average benzene concentrations consistently exceed the AAAQS and MfE guidelines. It must be noted that the passive sampling method is not a standard method recommended by MfE (MfE, 2009). However due to the ease of deployment and cost effective analysis, these methods have been compared to MfE guidelines as a screening method. The passive sampling method is widely used in New Zealand studies and yields reliable data. The continuous instrument operating at Khyber Pass complies with the MfE recommendations.

Ambient concentrations of benzene remain elevated at Crowhurst Street and are potentially a function of the combined traffic and evaporative sources near the site. Despite the reduction in concentrations generally reported by these data, there is still significant risk of concentrations exceeding relevant guidelines, due to the fluctuation of concentrations seen in these data.

The remainder of the BTEX suite (toluene, ethylbenzene and xylenes) showed the same pattern non-uniform trends (i.e strong decline in the early 2000s before stabilising since 2008). Ambient concentrations of these pollutants remain low, and are often below detection limits.

Continuous benzene and 1,3 butadiene show similar trends. Between 2005 and 2013, continuous benzene concentrations at Khyber Pass declined by 0.45 µg / m^3 / year. 1,3 butadiene declined by 0.13 µg / m^3 / year. The stabilisation trend since 2008 is also evident here, though less pronounced than in the passive results. As seen in the passive results, ambient benzene concentrations are close to both the AAAQS and NES-AQ guidelines, with an exceedance in 2012. 1,3 butadiene annual averages are considerably below the guidelines.

Temporal patterns of benzene and 1,3 butadiene strongly follow other pollutants monitored at Khyber Pass (CO, and PM_{10}). Strong peaks are observed in all pollutants during peak travel times. Concentrations both build during the day, and over the week. The relationship between PM_{10} and the other pollutants is weaker, possibly driven by the mixed sources of PM_{10} at Khyber Pass (ie. Traffic, natural) whereas benzene and CO can be attributed to transport sources. Concentrations of all pollutants are higher during the winter months, and are probably driven by domestic home heating emissions, traffic emissions and lower wind speeds during the winter period reducing pollutant flushing ability.

Key results:

- BTEX (passive) concentrations at Khyber Pass have declined significantly between 2001 and 2013, with the strongest reductions between 2001 and 2008, coinciding with the largest reductions in benzene levels in fuel. Since 2008 reductions have slowed significantly.
- The peak effectiveness of benzene reduction in petrol may have passed given the stabilisation in concentrations at Khyber Pass
- BTEX concentrations at Khyber Pass, while stabilising, remain volatile and may still exceed AAAQS and MfE guidelines
- Continuous benzene and 1,3 butadiene data at Khyber Pass reflects the same trend of reduction and stabilisation as the BTEX passive results
- The TEX component of the BTEX suite remains low and doesn’t appear to be of concern
- Benzene concentrations at Crowhurst Street remain significantly elevated compared to Khyber Pass, potentially due to both traffic and evaporative sources.

9.0 Recommendations

1. Continue BTEX and continuous benzene and 1,3 butadiene at Khyber Pass and Crowhurst Street
   - Trends and annual averages presented here show that concentrations may still remain volatile
   - As vehicle emissions technologies continue to improve, these data can be used to assess their success
   - Both sites (Khyber Pass and Crowhurst Street) represent ‘peak’ or ‘worst case’ sites for Auckland and are therefore useful for tracking compliance with the AAAQS and MfE guidelines
   - Useful baseline data has been collected, and VOCs are gaining worldwide recognition as important pollutants to manage into the future (WHO, 2013A; 2013B)
   - The continuous GC at Khyber Pass is nationally relevant as the only field deployed instrument of its type
2. Investigate new instrumentation for VOCs which may improve temporal resolution and data quality.
3. Investigate what drives higher concentrations of benzene at Crowhurst Street
   - Investigate relative importance of traffic and evaporative contributions
   - Potential additional sites to separate the evaporative contribution
4. Investigate relationship between sources and benzene and 1,3 butadiene concentrations at Khyber Pass
   - Potential further study to ascertain relative importance of sources through existing source apportionment studies carried out at Khyber Pass

10.0 Acknowledgements

The authors acknowledge comments from reviewers which strengthened this report.

11.0 References

3M Technical Data Bulletin (1028). Organic Vapour Monitor Sampling and Analysis Guide. Retrieved from: http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSufSevTsZxtUo8_U4x2vevUqevTSevTSevTSeSSSSSS--&fn=OVMAnalysisGuide.pdf

Auckland Council, 2013A. The Proposed Auckland Unitary Plan (notified 30th September 2013). Retrieved from http://unitaryplan.aucklandcouncil.govt.nz/Pages/Plan/Book.aspx

Auckland Council, 2013B. The Auckland Plan. Retrieved from: http://theplan.theaucklandplan.govt.nz/.

Auckland Transport, 2014. Traffic count data. Retrieved from: https://at.govt.nz/about-us/reports-publications/traffic-counts/

Australian National Environmental Protection Council (NEPC), 2004. National Environmental Protection Measure (Air Toxics). Australian Government Department of Heritage and Environment.

Beim H J, Spero J, Theodore L. 1998. Rapid guide to hazardous air pollutants. Van Nostrand Reinhold.

Carslaw, D. and Ropkins, K. 2011 openair — an R package for air quality data analysis. *Environmental modelling and Sortware (Preprint)*

Carslaw, D. 2013. The openair manual open-source tools for analysing air pollution data. Kings College London.

Cleveland, R., Cleveland, W., McRae, J. and Terpenning, I. 1990 STL: a seasonal decomposition based on Loess. *Journal of official statistics* 19:1, 3-73.

Davy P., Trompetter B. and Markwitz A., 2011. Source apportionment of airborne particles in the Auckland region. GNS Science Consultancy Report 2010/262 prepared for Auckland Regional Council.

Department for Environment, Food and Rural Affairs (DEFRA), 2007. The Air Quality Strategy for England, Scotland, Wales and Northern Ireland – Volume 1. Department for Environment, Food and Rural Affairs in partnership with the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland.

Dollard G., Dore C. and Jenkin M., 2001. Ambient concentrations of 1,3 butadiene in the UK. Chemico-Biological Interactions, v135-136, pp 177-206. Elsevier.

European Commission (EC), 1998. Commission proposes ambient air quality limit values for benzene and carbon monoxide. Press release, 2 December 1998. IP/98/1049. Cited in MfE (2000a) Health Effects of Eleven Hazardous Air Contaminants and Recommended Evaluation Criteria.

Engine Fuel Specifications (2011). SR2011/352. Retrieved from http://www.legislation.govt.nz/regulation/public/2011/0352/latest/whole.html

Environment Waikato. 2013. Benzene report card. Retried from: http://www.waikatoregion.govt.nz/Environment/Environmental-information/Environmental-indicators/Air/Air-quality/benzene-levels-report-card/

Gimson N., 2005. Modelling the air quality of Auckland – application to changing emissions in the ozone-limited atmosphere. Clean Air and Environmental Quality, v39(1), pp32-38.

Gunatilaka M., 2003. Hazardous Air Pollutants Concentrations of BTEX (Benzene, Toluene, Ethylbenzene and Xylene) in Christchurch (2001/2002). Environment Canterbury Report No. R03/9.

Hannaby R., 2004. Ambient Benzene USEPA TO 17 Method Trial Gavin Street, Penrose, Auckland May to July 2004, Watercare Laboratory Services – Air Quality Group Report AQ5002 prepared for Auckland Regional Council.

Hirsh, R., Slack, J. and Smith, R. (1982). Techniques of trend analysis for monthly water-quality data. *Water Resources Research* 18.1.

Helsel, D. and Hirsh, R. 2002. Statistical methods in water resources. Techniques of Water-Resources Investigations of the United States Geological Survey, Book 4, Hydrologic Analysis and Interpretation, chapter A3.

International Agency for Research on Cancer (IARC) (1987). Summaries & evaluations: Benzene (Group 1). Lyon, International Agency for Research on Cancer, p. 120 (IARC Monographs on the Carcinogenicity of Chemicals to Humans, Supplement 7.

International Agency for Research on Cancer (IARC), 1999. IARC monographs on the valuation of carcinogenic risks to humans. 1,3-Butadiene, Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide (Part one), vol. 71, 1999, pp. 109–225.

IPCS (2004). *Benzene*. Geneva, World Health Organization, International Programme on Chemical Safety (International Chemical Safety Card 0015. Retrieved from: http://www.who.int/ipcs/features/benzene.pdf

Iremonger S., 2002. NERMN Air Monitoring NOx, SOx and VOC's Passive Sampler Project 2000-2001. Environment Bay of Plenty Environmental Report 2002/04.

Jones B.,2000. The Measurement of Benzene Concentrations in the Vicinity of Petrol Stations. Report prepare for The Department of the Environment, Transport and the Regions, the National Assembly for Wales, the Scottish Executive and the Department of Environment in Northern Ireland.

Kahn H., 2007. Benzene's toxicity: a consolidated short review of human and animal studies. Human & Experimental Toxicology, v26(9) pp677-685

Karakitsios S., Delis V., Kassomenos P. and Pilidis G., 2007. Contribution to ambient benzene concentrations in the vicinity of petrol stations: Estimation of the associated health risk. Atmospheric Environment, 41(1889-1902). Elsevier.

Kuschel G., Petersen J., Reddish L. and Gray S., 1998. Study of hydrocarbon emissions from transport. NIWA report AK97130, prepared for the Ministry for the Environment.

Kuschel G., Petersen J. and Reddish L., 2001. Study of background levels of NOx and hydrocarbons at the Whau River in Auckland. NIWA report AK01079, prepared for Auckland Regional Council, 17 October 2001.

McCauley M., 2005. Concentrations of benzene, toluene, ethylbenzene and xylene in ambient air, Christchurch, 2004/2005. Environment Canterbury report No. R05/21.

Metcalfe J., Fisher G., Sherman M. and Kuschel G., 2006. Auckland Air Emissions Inventory: 2004. Prepared for Auckland Regional Council by Endpoint Limited. ARC technical publication, TP292.

Ministry for the Environment (MfE), 1994. Ambient Air Quality Guidelines. Retrieved from: http://www.mfe.govt.nz/publications/air/ambient-air-quality-may02/ambient-guide-may02.pdf

Ministry for the Environment (MfE), 1997. The State of New Zealand's Environment. Retrieved from: http://www.mfe.govt.nz/publications/ser/ser1997/

Ministry for the Environment (MfE), 2000a. Health Effects of Eleven Hazardous Air Contaminants and Recommended Evaluation Criteria. Air Quality Technical Report No 13 prepared by Chiodo et al. for the Ministry for the Environment's (NZ) Review of the Ambient Air Quality Guidelines.

Ministry for the Environment (MfE), 2009. Good-Practice Guide for Air Quality Monitoring and Data Management. Ministry for the Environment report, April 2009.

Ministry for the Environment (MfE), 2002. Ambient Air Quality Guidelines: 2002 Update. Air Quality Report No 32 prepared by the Ministry for the Environment and the Ministry of Health, New Zealand.

Ministry of Economic Development (MED), 2000. Petroleum Fuel Quality in New Zealand 1992-1999, Vallabh Patel, ISBN 0-478-23481-3.

Ministry of Economic Development (MED), 2001. Petroleum Fuel Quality In New Zealand: Update for the year 1999-2000 Paul Stannard, ISBN 0-0-478-24237-9.

Ministry of Economic Development (MED), 2002a. Petroleum Fuel Quality In New Zealand: Update for the year 2001-2002 Paul Stannard, ISBN 0-478-26314-7.

Ministry of Economic Development (MED), 2002b. Petroleum Products Specifications 2002.

Ministry of Economic Development (MED), 2003. Petroleum Fuel Quality In New Zealand: Update for the year 2002-2003 Paul Stannard, ISBN: 0-478-26368-6.

Ministry of Transport (MoT) 2011. Sector report – ageing of the light vehicle fleet, May 2011. Retrieved from: http://www.transport.govt.nz/assets/Import/Documents/Light-vehicle-sector-report-aging-of-the-fleet-June-11.pdf

Ministry of Transport (MoT) 2013. The New Zealand vehicle fleet: Quarterly update December 2013. Retrieved from: http://www.transport.govt.nz/assets/Uploads/Research/Documents/2013-Fleet-report-final.pdf

National Institute of Occupational Safety and Health (NIOSH), 1994. Manual of Analytical Methods, Fourth edition. Method No. 1500, HYDROCARBONS, BP 360-216 1500.

National Toxicology Program (NTP), 2011. 1,3 butadiene CAS -109-99-0. 12th report on carcinogens. Retrieved from: http://ntp.niehs.nih.gov/ntp/roc/content/profiles/butadiene.pdf

Petersen, J. and Harper, B. 2006. The Ambient Air Quality Monitoring Network in Auckland. Auckland Regional Council Technical Report 2006/296.

Rolfe K. and Graham B., 1999. A scientific review of the ARC ambient air quality monitoring network. A report to the Auckland Regional Council by Kevin Rolfe and Associates Limited. December 1999.

Salomon, V. 2013. Concentrations of benzene, toluene, ethylbenzene and xylenes in ambient air in Christchurch, Waimate, Geraldine, Ashburton, Rangiora and Kaiapoi, 2009-2010.Report No. R13/42.

Sen, P. K., 1968. Estimates of regression coefficient based on Kendal's tau. *Journal of the American Statistical Association* 63(324).

Smith J., 2006. Air Quality Monitoring 2006. Environment Waikato Technical Report 2006/52.

Smith, J., Peterson, J. and Gray, S. 2009. Benzene 1,3 butadiene and other volatile organic compounds in Auckland. Auckland Regional Council Technical Report 2009/048.

Stevenson C. and Narsey H., 1998. Survey of benzene and other toxic organic compounds in air: July 1996 - June 1997. Prepared as part of a Ministry of Health contract for scientific services, August 1998.

Stevenson C. and Narsey H., 1999. Survey of benzene and other toxic organic compounds in air: July 1996 – May 1999 summary report. Prepared as part of a Ministry of Health contract for scientific services, September 1999.

Theil, H. (1950) A rank-invariant method of linear and polynomial regression analysis," I, II, and III, Nederl. Akad. Wetensch. Proc., 53 386-92, 521-5 and 1397-412.

UK Expert Panel on Air Quality Standards (UK EPAQS), 1998. Recommendation for a United Kingdom Air Quality Standard for 1,3-Butadiene. Department of the Environment, Transport and Regions, United Kingdom.

USGS, 2012. Water-Quality Characteristics and Trends for Selected Sites at and Near the Idaho National Laboratory, Idaho, 1949–2009. Scientific Investigations Report 2012–5169.

USEPA, 2002. Toxicological Review of Benzene (Noncancer Effects): in support of summary information on the integrated risk information system (IRIS) October 2002. United States Environmental Protection Agency Report EPA/635/R-02/001F, Washington DC.

USEPA, 2009. TEACH Chemical Summary: Benzene. Retrieved from: http://www.epa.gov/teach/chem_summ/BENZ_summary.pdf

Wilton E. and Baynes M., 2008. Air Quality monitoring 2007 for Hamilton, Tokoroa, Taupo, Te Kuiti, Matamata and Putaruru. Environment Waikato technical report 2008/11.

World Health Organisation (WHO), 2000. Air Quality Guidelines for Europe: Second Edition. WHO Regional Publications, European Series, No. 91. World Health Organization Regional Office for Europe, Copenhagen.

World Health Organisation (WHO), 2010. Preventing disease through healthy environments exposure to benzene: a major public health concern.

World Health Organisation (WHO), 2013A. Review of evidence on health aspects of air pollution (REVIHAPP): First Results. *WHO Report.*

World Health Organisation (WHO), 2013B. Health risks or air pollution in Europe – HRAPIE project: New emerging risks to health from air pollution – results from the survey of experts.

Xie, S., Sridhar, S and Metcalfe, J (2014). Auckland air emissions inventory 2006. Auckland Council technical report, TR2014/015.

Yu, K., Y. Cheung, T. Cheung and R. Henry (2004). “Identifying the impact of large urban airports on local air quality by nonparametric regression”. *Atmospheric Environment* 38.27, pp. 4501–4507

12.0 Appendix A. Monitoring site details (from Petersen and Harper, 2006)

Henderson

Site name

Henderson I (A)
(Lincoln Road)

Address

Henderson Intermediate School

70 Lincoln Rd

Henderson, Waitakere

	Easting	Northing	Elevation (m)
NZMG	2655570	6480255	29.9
NZTM	1745140	5918533	

General site characteristics

Urban

Topography

Surrounding area is flat.

Site viewed from the south.

Micro met characteristics

Site is exposed to winds from all directions.

Site description and area characteristics

Air conditioned shed at the front of the Henderson Intermediate School grounds, approximately 10m from the western side of Lincoln Rd. Henderson commercial district <1km N; Houses in area 1960s onward; approximately 50% with chimneys. Note: PM_{10}Minivol (03.01.01 – 29.12.05) located approximately 150m NW of shed, in self-contained housing attached to school building and facing north over playing fields.

Air Quality Management Area

Urban

Predominant sources

Vehicle and residential (during winter)

Distance from road and other major sources

10 m E to Lincoln Rd (arterial road, aligned N-S)

Vehicle counts

Lincoln Rd 13,300 7 day ADT 1999.

Any nearby features that could affect measurements?

There are a number of trees (~8m tall, canopy ~6m diameter) to the west of the shed in the school grounds. There is a school incinerator > 20m W of the site. Parking for 25 cars within 50m of shed, plus parking for 6 cars (school drop off point) on access road adjacent to Lincoln Rd. Lighted pedestrian crossing 10m SE of site on Lincoln Rd.

AS/NZS 3580.1.1:2007 compliant?

No; 12m tree ~5m to SW, 13m tree ~10m to N

Monitoring commenced

15.12.93

Monitoring ceased

On-going

Pollutants monitored (current)

CO: 12.06.98 to date

NOx: 11.04.03 to date

PM_{10} (Beta Gauge): 01.01.03 to date

PM_{10} (Partisol): 18.07.98 to date

Pollutants monitored (past)

TSP (HD Med Vol): 15.12.93 - 24.12.97

Lead: 15.12.93 - 31.12.97

PM_{10} (MiniVol (non regulatory method)):

01.01.03 – 31.12.05

Site viewed from east side of Lincoln Rd.

Aerial view.

Inlet height (m)

3.0 gas

3.5 particulate

Meteorological parameters measured on site

Wind speed, wind direction, ambient temperature,
relative humidity, solar radiation.

Mast height (m)

6

Data owner

Auckland Council

Location map.

Source: Auckland Council GIS Viewer, extracted January 2006.

Mt Eden

Site name

Kingsland

(Kowhai)

Address

Kowhai Intermediate School

26 Onslow Rd

Mt Eden, Auckland

	Easting	*Northing*	*Elevation (m)*
NZMG	2666121	6479473	60
NZTM	1755691	5917772	

General site characteristics

Urban

Topography

Undulating to hilly. Mt Eden (summit 196m) 1.5km to ESE.

Site viewed from south west.

Micro met characteristics

Site is relatively well exposed to winds from all directions with the exception of SW - house and tree belt (5m tall, 30m from shed) may shelter from this direction.

Site description and area characteristics

Within the grounds of Kowhai Intermediate School, at the western end of playing fields, adjacent to outdoor pool enclosure. Residential to W, S and E (mostly larger older houses dating from 1920s with small sections, some later additions); commercial premises to N-NE. Mt Eden rugby stadium 120m to SW.

Air Quality Management Area

Urban

Predominant sources

Vehicle and residential home heating (during winter)

Distance from road and other major sources

100m N to New North Rd (arterial road, aligned NW-SE); approximately 50m W to Sandringham Rd (arterial road, aligned NW-SE)

Vehicle counts

23,958; 5-day average (23/03/2005) Sandringham Rd S of New North Rd

Any nearby features that could affect measurements?

Railway line and Kingsland station 140m to NW.

AS/NZS 3580.1.1:2007 compliant?

Yes

Monitoring commenced

02.04.04

Monitoring ceased

07.09.05

Pollutants monitored

NOx: 02.04.04 to 07.09.05

PM_{10} (Beta Gauge): 08.04.04 to 07.09.05

PM_{10} (Partisol): 23.04.04 to 07.09.05

$PM_{2.5}$ (Partisol): 22.04.04 to 07.09.05

TSP: 12.05.04 to 07.09.05

Lead: 01.06.04 to 07.09.05

Ozone: 20.05.04 to 07.09.05

Inlet height (m)

3

Meteorological parameters measured on site

Wind speed, wind direction, ambient temperature, relative humidity, solar radiation

View west from site to Sandringham Road.

View south from site.

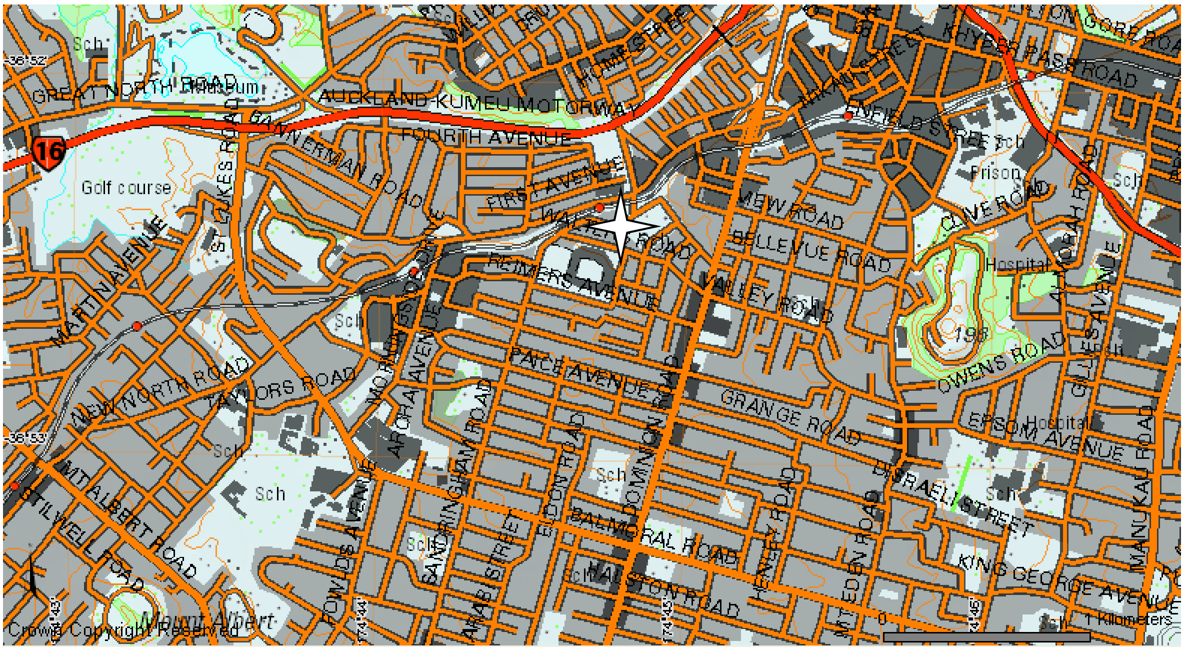
Mast height (m)

6

Data owner

Auckland Council own NOx, particulate and ozone data;

Ministry for the Environment own TSP and lead data



Penrose

Site, viewed from north west.

Site name

Penrose II (B)

(Gavin Street Substation)

Address

19 Gavin Street

Penrose, Auckland

	Easting	Northing	Elevation (m)
NZMG	2672174	6475864	40
NZTM	1761751	5914176	

General site characteristics

Industrial

Topography

Flat

Micro met characteristics

Surrounding structures will both shield the monitor and introduce more turbulence into the flow.

Site description and area characteristics

Air conditioned shed within the Gavin Street substation, approximately 106m NE of the Southern Motorway. The motorway is approximately 2m lower than the ground level at the monitoring site. There is also a mobile trailer here (exact location varies). From NW-S and to the NE are industrial premises; residential to the N and SW. Houses date from 1930s onward; about 50% with chimneys.

Air Quality Management Area

Industrial

Predominant sources

Vehicle and industry

Distance from road and other major sources

106m SW to Southern Motorway (aligned N-S)

Vehicle counts

130,161 AADT (2011) SH1 Ellerslie Panmure Hwy (Source: NZTA Spatial Viewer)

142,110 AADT (2009) SH1 Ellerslie Panmure Hwy to South Eastern Hwy

140,380 AADT (2005) SH1 Ellerslie Panmure Hwy to South Eastern Hwy

Any nearby features that could affect measurements?

Substation structures and buildings near to shed - NE; Three stacks (300m S) at ACI Glass.

AS/NZS 3580.1.1:2007 compliant?

Yes

Monitoring commenced

November 2000

Monitoring ceased

On-going

Pollutants monitored (current)

NOx: November 2000 to date

PM_{10} (Beta Gauge): 22.05.03 to date

PM_{10} (HiVol): 20.05.03 to date

Speciation Sampling: 18.10.05 to date

TSP: 17.05.04 to date

SO_2: 01.04.03 to date

Lead (HD Med Vol): 01.06.04 to date

Site viewed from the south.

Pollutants monitored (past)

PM_{10} (TEOM) 19.04.00 - 02.02.03

Inlet height (m)

2.5 NOx, SO_2 and Beta Gauge

1.8 HiVol and RAAS

Meteorological parameters measured on site

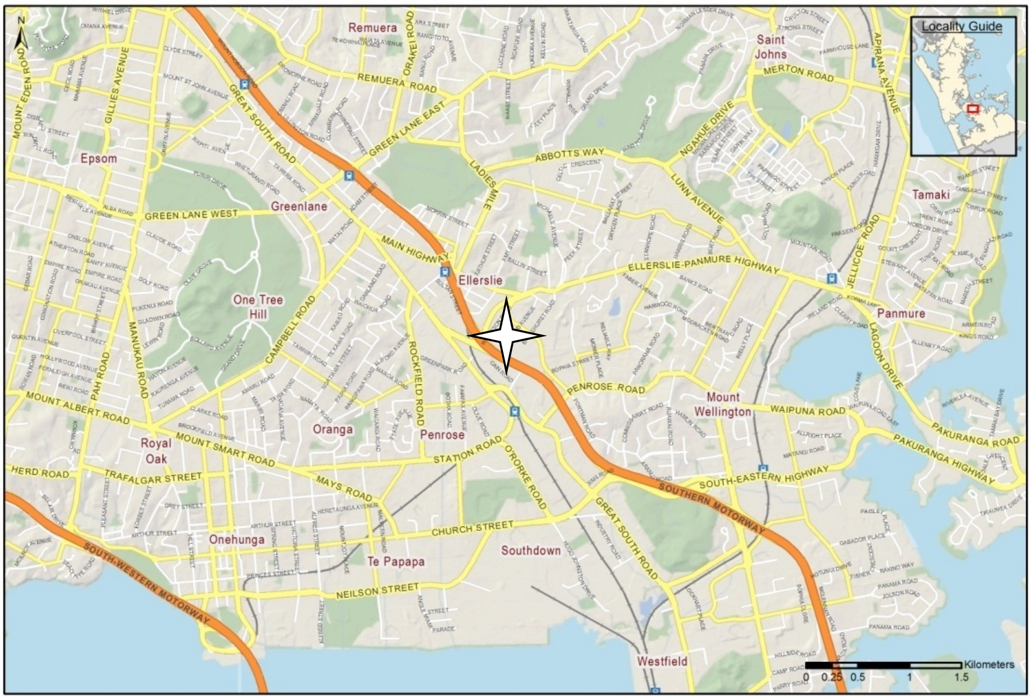
Wind speed, wind direction, ambient temperature, relative humidity, solar radiation.

Mast height (m)

6

Data owner

Auckland Council owns the particulate data. Ministry for the Environment own the NOx and SO_2 data



Khyber Pass

Site name

Khyber Pass I (Gas)

Address

269 Khyber Pass Rd

Newmarket, Auckland

	Easting	*Northing*	*Elevation (m)*
NZMG	266830517	6480185	81
NZTM	57874	5918488	

General site characteristics

Urban

Topography

Khyber Pass slopes down gently W-E; Mountain Rd dips at the junction with Khyber Pass.

Micro met characteristics

Buildings on the southern side of Khyber Pass will shield the intakes from southern flow. The buildings on the southern side and the valley nature of the road may result in some canyon effect.

View east along Khyber Pass Rd towards Newmarket.

Site description and area characteristics

SE corner of Khyber Pass and Mountain Rd intersection. Khyber Pass slopes down to the east and Newmarket shopping centre (700m E). The Southern Motorway is approximately 250m W-SW from the site. Mixed residential to NW, (older houses -approximately 60% with chimneys)/commercial/light industry. Newmarket shopping precinct <1km E; Auckland Domain is 250m to N. Lion Nathan brewery is located across the road to N but is in the process of relocating. The site is to become a retail-residential mixed development that could take up to 10 years to complete. In 2008 the site was moved 20m SE along Khyber Pass Rd, coinciding with the relocation of the NIWA offices. The new site records CO, NOx, Benzene and 1,3 Butadiene only.

Air Quality Management Area

Urban

Predominant sources

Vehicle

Distance from road and other major sources

Gas inlet 3.9m S of Khyber Pass Rd (arterial, aligned WNW-ESE) and 28m from intersection. Traffic frequently queues beyond the position of the inlet. 250m W to Southern Motorway (aligned NW-SE).

Vehicle counts

194,501 AADT (2011) State Highway 1, west of Mountain Rd, 2011 (Source: NZTA Spatial Viewer)

28,547; 7 day average; Khyber Pass Rd, west of Mountain Rd (19/03/2007)

27,027; 7 day average; Khyber Pass Rd, west of Mountain Rd (19/02/2006)

Any nearby features that could affect measurements?

The lighted intersection and sloping topography of Mountain Rd (dipping at the intersection) and Khyber Pass Rd will increase average vehicle emissions. Railway line 70m to NW.

AS/NZS 3580.1.1:2007 compliant?

No: but not deemed necessary as site purpose is to monitor peak pollutant levels.

Monitoring commenced

29.10.96

Monitoring ceased

On-going

Pollutants monitored (current)

CO: 29.10.96 to date

NOx: 15.04.98 to date

Benzene and 1,3 Butadiene:

September 2005 to date

Pollutants monitored (past)

Non-Methane Hydrocarbons:

17.07.96 - 31.10.01

Inlet height (m)

4.05

Meteorological parameters measured on site

Nil

Mast height (m)

N/a

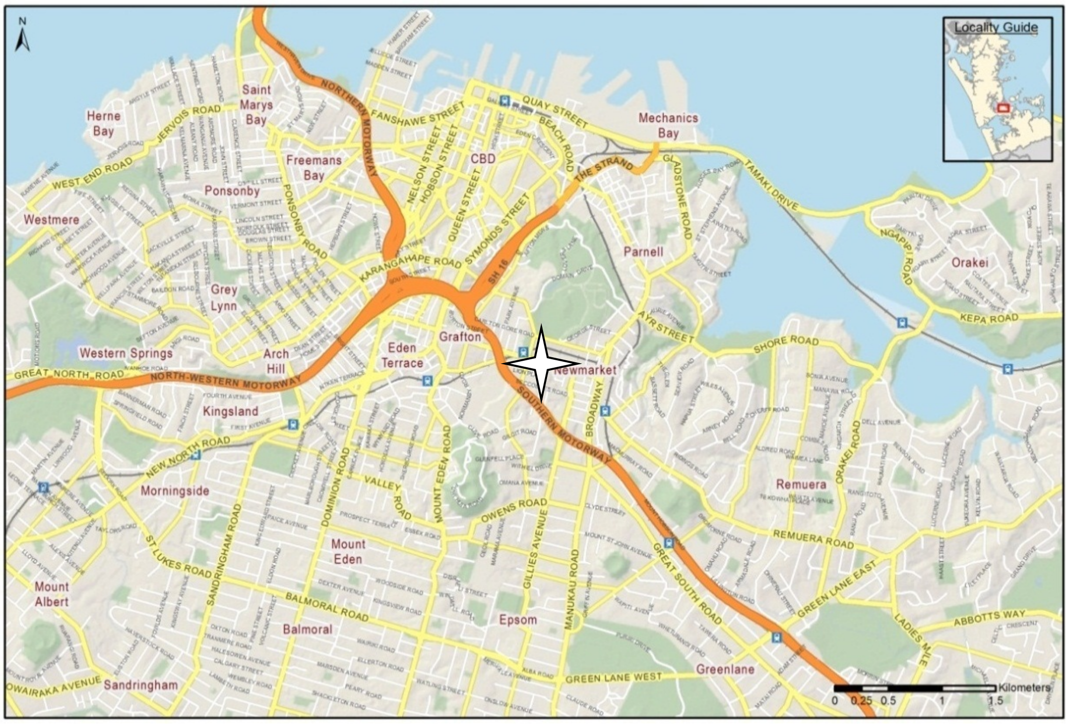
Data owner

Auckland Council (originally Auckland Regional Council)

Site looking W – Khyber Pass Rd and Mountain Rd Intersection at right

Aerial view of site.

Source: Auckland Council GIS Viewer, extracted September 2010.



Locality Guide
Herne Bay
Saint Marys Bay
Freemans Bay
CBD
Mechanics Bay
Westmere
Ponsonby
Parnell
Orakei
Grey Lynn
Western Springs
Arch Hill
Eden Terrace
Grafton
Newmarket
Kingsland
Morningside
Remuera
Mount Eden
Mount Albert
Balmoral
Epsom
Greenlane
Sandringham
NORTHERN MOTORWAY
NORTH-WESTERN MOTORWAY
SOUTHERN MOTORWAY
GREAT NORTH ROAD
NEW NORTH ROAD
GREAT SOUTH ROAD
TAMAKI DRIVE
REMUERA ROAD
GREEN LANE WEST
GREEN LANE EAST
BALMORAL ROAD
DOMINION ROAD
SANDRINGHAM ROAD
MANUKAU ROAD
BROADWAY
KEPA ROAD
SHORE ROAD
Kilometers
0 0.25 0.5 1 1.5

13.0 Appendix B. 2008 project results

Oct-08

Sample Description	Results (µg/m³)	M02S01	M02S02	M02S03	M02S04	M02S05	M02S06	M02S07	M02S08
	LOD								
Target VOCs									
benzene	0.726	1.3	1.0	0.8	<LOD	Missing	Missing	0.9	0.8
toluene	0.797	6.7	5.6	4.5	4.2	Missing	Missing	4.8	4.2
ethylbenzene	0.954	1.0	<LOD	<LOD	<LOD	Missing	Missing	<LOD	<LOD
m+p-xylene	0.944	3.6	2.7	2.4	2.1	Missing	Missing	2.4	2.1
o-xylene	0.944	1.2	1.0	<LOD	<LOD	Missing	Missing	<LOD	<LOD
total xylene	-	4.8	3.8	2.4	2.1	Missing	Missing	2.4	2.1
distance (m)		0.6	8.5	36.0	113.0	0.5	10.0	45.7	122.0

14.0 Appendix C. 2009 project results

ARC BTEX Results June - August 2009

Period	June 2009 - August 2009
Report Type:	Mean
Time Base:	Monthly

Sites	June 2009 Results* (µg/m^3)						July 2009 Results* (µg/m^3)						August 2009 Results* (µg/m^3)					
	benzene	toluene	ethylbenzene	m+p-xylene	o-xylene	total xylene	benzene	toluene	ethylbenzene	m+p-xylene	o-xylene	total xylene	benzene	toluene	ethylbenzene	m+p-xylene	o-xylene	total xylene
Auckland Airport	1.3	4.9	<LOD	2.6	<LOD	2.6	1.2	5.4	1.0	3.8	1.0	4.8	0.9	3.4	<LOD	1.7	<LOD	1.7
Britomart	2.6	12.4	1.6	6.0	2.1	8.1	2.4	10.8	2.1	8.0	2.1	10.1	1.9	9.1	1.4	4.8	1.7	6.6
Crowhurst Street	4.9	19.8	1.8	7.0	2.3	9.3	4.0	18.5	2.5	9.5	2.4	12.0	2.6	12.0	1.3	4.7	1.5	6.2
Gillies Ave	2.6	9.1	1.3	5.2	1.8	7.0	2.3	9.1	1.8	7.0	1.9	8.8	2.1	7.9	1.1	4.1	1.5	5.5
Henderson AQ Shed	1.9	7.0	<LOD	3.3	1.1	4.4	1.4	5.6	0.9	3.7	1.0	4.6	1.1	6.6	<LOD	1.9	<LOD	1.9
Kingsland	1.9	7.5	1.0	3.7	1.3	5.0	2.0	10.5	1.5	5.9	1.5	7.5	1.1	5.0	<LOD	2.2	<LOD	2.2
Mountain Road	3.0	11.6	1.6	6.3	2.2	8.5	2.9	12.6	2.3	9.1	2.4	11.5	2.6	9.9	1.5	5.3	1.8	7.1
Otahuhu (A)	2.0	8.3	1.1	4.1	1.4	5.5	2.1	8.4	1.6	6.4	1.7	8.0	1.2	4.8	<LOD	2.3	<LOD	2.3
Pakuranga AQ Shed	2.7	14.1	1.8	6.9	2.3	9.2	2.3	11.9	1.8	7.2	1.8	9.0	1.3	5.6	<LOD	2.6	<LOD	2.6
Penrose AQ Shed	1.3	7.8	<LOD	3.4	1.2	4.6	1.3	5.9	1.1	4.2	1.1	5.2	<LOD	3.8	<LOD	1.7	<LOD	1.7
Pukekohe Town	1.5	6.4	<LOD	3.0	1.0	4.1	1.3	6.5	1.0	3.8	1.0	4.8	<LOD	3.1	<LOD	1.3	<LOD	1.3
Queen Street	1.8	8.5	1.1	4.3	1.4	5.7	2.2	9.8	1.7	6.8	1.7	8.6	1.4	6.5	<LOD	3.0	1.1	4.1
Red Beach	<LOD	1.6	<LOD	<LOD	<LOD	<LOD	<LOD	1.7	<LOD	1.2	<LOD	1.2	<LOD	0.9	<LOD	<LOD	<LOD	<LOD
Regent Street	2.7	9.9	1.4	5.3	1.9	7.2	2.2	9.1	1.7	6.6	1.7	8.3	1.4	6.3	<LOD	3.3	1.1	4.4
Takapuna AQ Shed	1.7	7.6	<LOD	3.3	1.1	4.5	1.9	10.5	1.5	5.7	1.5	7.2	0.9	5.6	<LOD	2.0	<LOD	2.0
Waiheke AQ Shed	<LOD	2.3	<LOD	<LOD	<LOD	<LOD	<LOD	1.5	<LOD	1.0	<LOD	1.0	<LOD	1.2	<LOD	<LOD	<LOD	<LOD

* For averaging purposes when a sample is <LOD the pollutant limit of detection value is used.