

## Memorandum

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## Air monitoring survey of hydrocarbon compounds (BTEX) in the Taranaki Region

### Introduction

In April 2012 a survey of ambient air quality sampling was carried out by the Taranaki Regional Council at four regional monitoring sites located in New Plymouth- CBD, New Plymouth- busy traffic intersection, Tariki- pristine farmland and in Stratford Township.

The main objective was to measure the concentrations of the volatile organic compounds (VOC) benzene, toluene, ethylbenzene and xylenes (BTEX) using a passive sampling method.

Monitoring for BTEX has been undertaken by the Council as part of the Council's SEM programme. The location of the BTEX passive samplers are presented in Figure 1.

The findings of this study are presented in this report. The Council has previously undertaken BTEX monitoring in March 2003 around a BP Petrol station in New Plymouth and in March 2005 around two large gas production stations. This current study allows comparison of relative levels to be made between differing activities.

### Benzene

Benzene occurs naturally in fossil fuels and is produced in the course of natural processes and human activities that involve the combustion of organic matter such as wood, coal and petroleum products. Natural sources of benzene emissions to the atmosphere are estimated in order of 3-5% while more than 90% are estimated to come from anthropogenic sources (gasoline vapours, vehicle exhaust, and chemical production).

### Toluene

Toluene occurs naturally as a component of crude oil and is a major aromatic constituent of petrol which contains about 5-7% toluene by weight. It is produced in the process of making gasoline and other fuels from crude oil, in making coke from coal, and as by-product in the manufacture of styrene. It is used as an intermediate in the manufacture of many end products. Toluene is also used in a mixture added to gasoline to improve octane ratings. Toluene is released into the atmosphere principally from the volatilization of petroleum fuels, from motor vehicle exhaust and from toluene-based solvents and thinners with the largest sources of release the production, transport, and use of gasoline.

## Ethylbenzene

Ethylbenzene is naturally present in crude petroleum. It is also a by-product of biomass combustion. Ethylbenzene is almost exclusively (>99%) used as an intermediate for the manufacture of styrene monomer. Ethylbenzene will enter the atmosphere primarily from fugitive emissions during the use of fuel and solvents (which account for the bulk of emissions) and exhaust connected with its use in gasoline.

## Xylenes

Xylenes exist in ambient air as a mixture of ortho (o-), meta (m-) and para (p-) isomers (the term "xylenes" refers to all three isomers). Xylenes are primarily synthetic chemicals produced from petroleum but also occur naturally in petroleum and coal tar. In this study concentrations of o-, p-, and m-xylene were summed and reported as xylene total. Xylenes are released to the atmosphere primarily as fugitive emissions from industrial sources (e.g., petrochemical and chemical plants), in automobile exhaust, and through volatilization from their use as solvents.

The term BTEX reflects that benzene, toluene, ethylbenzene and xylenes are often found together.

## Health effects

Exposure to BTEX can occur by ingestion (consuming water contaminated with BTEX), inhalation (exposure to BTEX present in the air) or absorption through the skin. Inhalation of BTEX can occur while pumping gasoline. Absorption of these chemicals can occur by spilling gasoline onto one's skin. Acute exposures to high levels of gasoline and its BTEX components have been associated with skin and sensory irritation, central nervous system depression, and effects on the respiratory system. These levels are not likely to be achievable from drinking contaminated water, but are more likely from occupational exposures. Prolonged exposure to these compounds has effects on the kidney, liver and blood systems. According to the United States Environmental Protection Agency (USEPA), there is sufficient evidence from both human and animal studies to believe that benzene is a human carcinogen. Workers exposed to high levels of benzene in occupational settings were found to have an increased incidence in leukaemia.

## Summary of method

Passive absorption samplers that absorb the target gas into activated carbon and are subsequently analysed using gas chromatography, are employed to determine the average concentration of the gas in the air during the time of exposure. BTEX concentration is reported as  $\mu\text{g}/\text{m}^3$  (mass of BTEX per volume of air).

## Guidelines

In New Zealand, benzene is the only member of the BTEX group subject to a national guideline value. The Ministry for the Environment guideline, based on benzene's known mutagenic and carcinogenic properties, was  $10\mu\text{g}/\text{m}^3$  as an annual average, reducing to  $3.6\mu\text{g}/\text{m}^3$  in 2010. There are no national ambient air quality guidelines for toluene, ethylbenzene or xylene. The Ministry for the Environment had prepared an internal technical document "Health Effects of Eleven Hazardous Air Contaminants and Recommended Evaluation Criteria" (October 2000) that suggested a 1 hour average value of

22  $\mu\text{g}/\text{m}^3$  for Benzene, 500  $\mu\text{g}/\text{m}^3$  for Toluene and 1000  $\mu\text{g}/\text{m}^3$  for Xylene as recommended guidelines values. However, these recommendations were not carried through to the final Ministry for the Environment guidelines published in 2002.

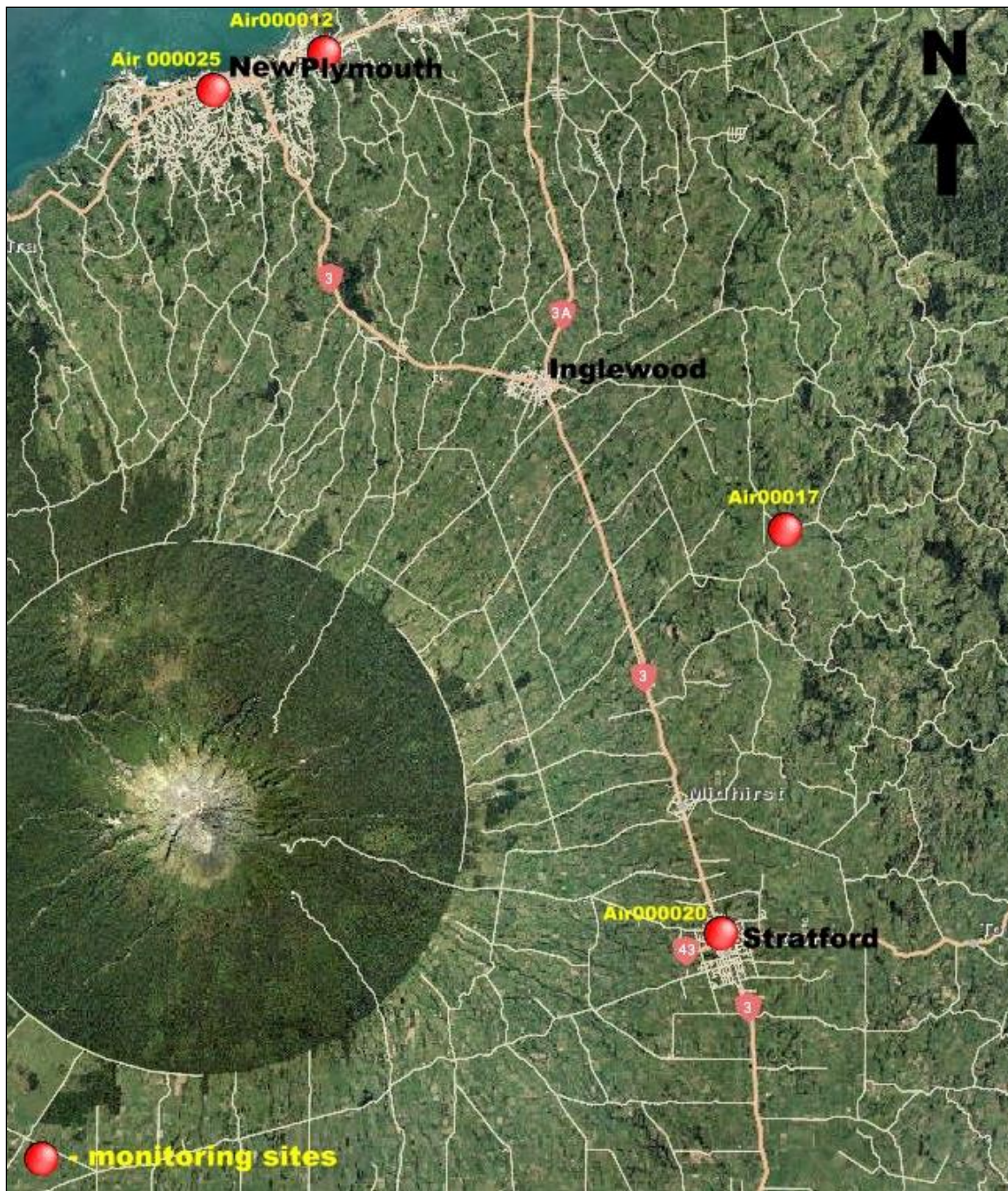


Figure 1 Regional BTEX monitoring sites

## Results

The duration of sampling for VOCs varied between 375 minutes (6 hours 15 minutes) and 510 minutes (8 hours 30 minutes). The absorption activated carbon badge method provides an average concentration over the period of exposure. It does not provide a range (eg maximum or minimum concentrations).

The issue is therefore that of estimating an indicative equivalent exposure concentration over alternative time periods of interest (eg as referenced in guidelines or other criteria). For comparison with the Ministry for the Environment guideline for BTEX, from the average concentration measured, it is desirable to calculate an indicative theoretical one hour concentration. There are mathematical equations used by air quality scientists to predict equivalent concentrations over varying time periods. These are somewhat empirical, in that they take little account of local topography, micro-climates, variations in activity processes, diurnal variation, etc. Nevertheless, they are conservative (they tend to over-estimate) and have some recognition of validity as a screening tool. One formula in general use is of the form:

$$C(t_2) = C(t_1) \times \left(\frac{t_1}{t_2}\right)^p$$

where  $C(t)$  = the average concentration during the time interval  $t$ , and  $p$  = a factor lying between 0.17 and 0.20. When converting from longer time periods to shorter time periods, using  $p = 0.20$  gives the most conservative estimate (i.e. the highest calculated result for time period  $t_2$  given a measured concentration for time period  $t_1$ ).

Using the 'worst case' factor of  $p = 0.20$ , the monitoring data reported herein have also been converted to equivalent 'maximum' one hour exposure levels (Table 1).

**Table 1** Actual and recalculated (p0.2) BTEX results around Taranaki region

Site	Site ID / Where	Time: start stop	Time total Min.	Benzene		Toluene		Ethyl Benzene	o,m,p – Xylene Total	
				Lab. Results	1 hr. Calc.	Lab. Results	1 hr. Calc.	Lab. Results	Lab. Results	1 hr. Calc.
1	AIR000025 New Plymouth CBD	07:45 16:15	510	<4.6	<7.06	24	36.8	<3.0	<12.6	<19.3
2	AIR000012 NPGHS busy traffic intersection	08:00 16:00	480	9.7	14.5	20	30.4	<2.4	<7.1	<10.8
3	AIR000017 Tariki, pristine farmland	08:45 16:35	410	<5.7	<8.37	<7.8	11.4	<2.8	<8.3	<12.2
4	AIR000020 Stratford, rural town, roundabout	09:00 15:15	375	<6.2	<8.93	<11	15.8	<3.1	<9.1	<13.1
Blank				<5.3	<7.9	<2.6	<3.8	<2.6	<7.7	<11.5
MfE recommended <b>guidelines</b> (2000), one -hour average.					<b>22</b>		<b>500</b>			<b>1000</b>

\* All results in  $\mu\text{g}/\text{m}^3$

< = less than  
Corrected data

## Discussion

The calculated 1-hour theoretical maximum concentrations of benzene (using a power law exponent of 0.2) ranged from less than 7.06  $\mu\text{g}/\text{m}^3$  to 14.5  $\mu\text{g}/\text{m}^3$ . The only actual concentration present at a detectable level was obtained from the site located in New Plymouth's urban area near a busy traffic intersection. It should be noted that 3 of the 4 results are 'less than' results, and further, that in all 3 cases the results show no difference to the result for the field blank. That is, no benzene was actually detected at these 3 sites. Further, while the concentration of benzene detected at the NPGHS site was analysed by the laboratory as equivalent to 9.7  $\mu\text{g}/\text{m}^3$ , this is in the context of the blank result lying somewhere between 0 and 7.9  $\mu\text{g}/\text{m}^3$ , that is, the 'real' one-hour average concentration of benzene at this site actually lies somewhere between 14.5 and  $(14.5 - 7.9 = )$  6.6  $\mu\text{g}/\text{m}^3$ .

The results from monitoring of toluene, ethylbenzene and xylene have all been extremely low. As with the results for benzene, all the results for ethyl benzene and xylene measurements, and two of the results for measurements of toluene, indicate that these gases were actually not detectable at the limits of detection of the analytical method used. While the numbers given for each '<' (less than) result in the above table represent the maximum concentration that could have been present, the fact that these numbers are not significantly different from the analytical results of the blank (unexposed) sample suggests that any concentration of these gases is in fact very close to zero.

All values were within the Ministry for the Environment recommended guidelines (2000). This continues the pattern found in previous years.

## Environmental Performance Indicator

Ministry for the Environment uses an environmental performance indicator to categorise air quality. These categories are set out in Table 2 and further details of the BTEX results are set out in Table 3. It should be noted that for the purpose of this comparison, 'less than' results have been deemed equivalent to their maximum possible value rather than considered as more or less equivalent to 'not present'.

**Table 2** Environmental Performance Indicator air quality categories

Measured value	Less than 10% of guideline	10-33% of guideline	33-66% of guideline	66-100% of guideline	More than 100% of guideline
Category	<i>excellent</i>	<i>good</i>	<i>acceptable</i>	<i>alert</i>	<i>action</i>

**Table 3** Categorisation of results - Benzene (2012)

MfE guideline (2000) Benzene = 22 $\mu\text{g}/\text{m}^3$ - 1 hour average.		
Category	Measured values	
Excellent	<10% of the guideline, (0-2.2 $\mu\text{g}/\text{m}^3$ )	0 (0%)
Good	10-33% of the guideline, (2.2-7.3 $\mu\text{g}/\text{m}^3$ )	1 (25%)
Acceptable	33-66% of the guideline, (7.3-14.5 $\mu\text{g}/\text{m}^3$ )	3 (75%)
Alert	66-100% of the guideline, (14.5-22 $\mu\text{g}/\text{m}^3$ )	0 (0%)

Total number of samples	4 (100%)
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The levels of toluene and xylene obtained in the current work are far below ambient guideline values, and all results fall into 'excellent' Ministry's air quality category. Three of the four benzene results were (at worst) within 'acceptable' MfE's category and one result fell within the 'good' category.

## Comparison with other monitored sites in the region

The Council has previously undertaken BTEX monitoring in March 2003 around a BP Petrol station in New Plymouth and in March 2005 around two large gas production stations. This current study allows comparison of relative levels to be made between differing activities. The results from two previous BTEX surveys are presented in Table 4.

**Table 4** Actual and recalculated (p0.2) BTEX results found in previous surveys. (2003 and 2005)

Site	Site ID / Where	From	To	Benzene		Toluene		Ethyl Benzene	o,m,p – Xylene Total	
				Lab. Results	1 hr. Calc.	Lab. Results	1 hr. Calc.	Lab. Results	Lab. Results	1 hr. Calc.
1	AIR000038 (W) BP Petrol Station	05/03/2003 14:45	13/03/2003 06:25	6.61	18.2	16.8	46.3	1.83	10.5	29.1
2	AIR000039 (E) BP Petrol Station	05/03/2003 15:00	13/03/2003 06:15	11.1	<b>30.6</b>	27.4	75.5	2.77	16.6	45.8
3	AIR003410 (NW) STOS Kapuni	03/03/2005 08:30	11/03/2005 11:30	0.06	0.17	0.13	0.37	0.04	0.18	0.52
		11/03/2005 11:30	18/03/2005 12:00	1.20	3.34	2.02	5.63	0.28	2.43	6.77
4	AIR003411 (NE) STOS Kapuni	03/03/2005 09:00	11/03/2005 11:50	6.62	1.78	0.81	2.32	0.10	0.68	1.95
		11/03/2005 11:50	18/03/2005 12:30	0.30	0.84	0.46	1.28	0.04	0.16	0.45
5	AIR003412 (SE) STOS Kapuni	03/03/2005 09:30	11/03/2005 12:00	4.12	11.82	5.13	14.72	0.24	2.25	6.46
		11/03/2005 12:00	18/03/2005 12:40	0.83	2.31	1.14	3.18	0.06	0.73	2.03
6	AIR007906 (E) McKee PS	03/03/2005 11:30	11/03/2005 09:30	8.88	<b>25.3</b>	16.32	46.6	0.60	4.49	12.82
7	AIR007902 (SE) McKee PS	03/03/2005 11:35	11/03/2005 09:15	22.3	<b>63.7</b>	26.2	74.8	1.40	9.78	27.92
MfE recommended <b>guidelines</b> (2000), one -hour average. ( All results in $\mu\text{g}/\text{m}^3$ )					<b>22</b>		<b>500</b>	<b>N/A</b>		<b>1000</b>

## Discussion (BTEX surveys in years 2003 and 2005)

The calculated theoretical concentrations of Benzene (highlighted in bold in Table 4) exceeded the Ministry for the Environment recommended ambient guideline for continuous exposure of  $22\mu\text{g}/\text{m}^3$  when measured at any one monitoring site for 60 minutes. The guideline was exceeded at three sites, two located around McKee gas production station and one at BP Petrol Station in New Plymouth.

The results for McKee Production Station are significantly higher than those measured at the Kapuni industrial area. On first analysis these results are unusual as there is significantly more petrochemical industry at Kapuni. However, the McKee Production Station is located in the low point of a depression surrounded on all sides by hills. The local topography and meteorological conditions mean that there is less dispersal of BTEX compounds discharged from the site.

BP service station would represent worst case conditions for exposure to motor vehicle-related emissions in New Plymouth, presenting a combination of fumes arising from the dispensing of fuels and vehicle emissions discharged under conditions of poor engine efficiency (stop/start and idling).

However, given the short-term nature of exposure within the environment of the BP service station and in the vicinity of the McKee production station, and the significant distance from dwellings, any effects are likely to be insignificant.