

# Methyl Bromide Monitoring Picton, April 2011

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Report Prepared by:  
**Fleur Tiernan**  
Environmental Scientist (water and air quality)  
Environmental Science & Monitoring Group

Marlborough District Council  
Seymour Square  
PO Box 443  
Blenheim 7240  
Phone: 520 7400  
Website: [www.marlborough.govt.nz](http://www.marlborough.govt.nz)



## Executive Summary

This report presents the results of the third round of methyl bromide monitoring carried out by the Council to help determine ambient methyl bromide concentrations in Picton during a fumigation event at Port Marlborough on the 30<sup>th</sup> March. Methyl bromide concentrations were detected at very low levels at both monitoring sites; 1.4 ppbv at Waitohi Wharf and 1.2 ppbv at Picton Jetty. If it is assumed that the gas collected was collected in 1 hour then the estimated 1-hour average at each of the sites is 4.998 ppbv and 4.416 ppbv respectively. The 1-hour average standard is 1000ppbv (1ppmv). The concentrations detected are dependent on wind speed and direction. Gas canisters were used to collect the gas following USEPA method TO-15. This is a simple, cost effective and accurate way to measure low level concentrations of volatile organic compounds (VOC's).



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# 1. Introduction

Methyl bromide is used as a fumigant to treat logs destined for export from Port Marlborough NZ Ltd. Fumigation takes place at Waimahara Wharf in Shakespeare Bay in Picton. Shakespeare Bay lies approximately 1km north-west of Picton and approximately 500m north-west of the ferry terminal in Picton (figure 1). Concern about elevated concentrations of methyl bromide reaching the Picton community due to operations at the Port led Council to establish two monitoring sites in Picton (figure 1) to measure the ambient air concentrations of methyl bromide during fumigation events. To date monitoring has taken place on two occasions, once in December 2010 and once in January 2011. Source Testing New Zealand Limited (STNZ Ltd) was commissioned by Marlborough District Council (MDC) to undertake the methyl bromide monitoring in December 2010 and January 2011. The methodology used to measure ambient methyl bromide concentrations at the two sites has developed as more information on the concentrations and on the limitations of various methods has emerged. The methodology for the past two fumigation events are detailed in reports by STNZ Ltd (Newby 2010, 2011).



**Figure 1: Location of Shakespeare Bay relative to Picton, the Ferry Terminal and the two monitoring locations established by MDC.**

Port Marlborough NZ Ltd commission Sinclair Knight Merz Ltd (SKM) to assess methyl bromide concentrations at the site boundary during each fumigation event of whole logs for export. Their methodology and results are compiled in a report to the Port after each fumigation event. On average there are between 3-6 fumigation events at the Port per year. Fumigation events do not occur during the winter months (June - August inclusive) as the fumigant (methyl bromide) is not as effective in low temperatures. During these months logs are taken further north (e.g. Tauranga and Auckland) where temperatures are warmer (Patrick Burdon, Port Marlborough pers comm.) The objective of the Ports monitoring is to ensure that methyl bromide levels do not exceed the standard\* of 1 ppmv at the site boundary (figure 2).

\* Californian Acute Relative Exposure Limit =  $3.9 \times 10^3 \mu\text{g m}^{-3}$  (1ppmv) 1-hour average. This limit was adopted by ERMA in 2010



Figure 2: Port Marlborough property and security boundaries

## 1.1. Fumigant use at Shakespeare Bay

Fumigation using methyl bromide is generally carried out as follows:

- In shipping containers: fumigation of a variety of merchandise within closed shipping containers;
- Under tarpaulin enclosures: fumigation of logs and timber enclosed within gas tight tarpaulins or covers, sealed to the hard ground surface; and
- In ships holds: fumigation of products of any type including logs and timber within closed holds of ships.

These three types of fumigation differ from one another in size, in terms of mass of product and fumigant used. Total fumigant quantity per container is generally less than 10 kg, while within a tarpaulin enclosure it may exceed 100 kg, and a ship's hold may require a tonne. These quantities vary not only with the volume of the enclosure, but also with bio-security standards of the importing country, and the nature of the product being treated.

At the end of the fumigation period (generally around 24-hours after fumigation commences), the release of methyl bromide is staggered to reduce the likely hood of exceedances at the site boundary.

## 1.2. Objectives of the methyl bromide monitoring in Picton

The objectives of the air monitoring in Picton are:

- i. To determine the ambient concentrations of methyl bromide at the two sites
- ii. To assess the likelihood of elevated (above national standards) levels of methyl bromide reaching the Picton community
- iii. To provide information and data which can be used in the development and calibration of air dispersion models specific to methyl bromide and its uses in New Zealand.

The methods to achieve the objectives are:

- i. Use an established and internationally recognised methodology to measure methyl bromide concentrations as accurately as possible and at concentrations as low as possible.
- ii. To record environmental conditions during the time of sampling i.e. wind speed, wind direction, temperature etc.
- iii. Compile data from each fumigation event for the possible use in air dispersion modelling to help establish the risk of elevated levels of methyl bromide reaching Picton. To date air dispersion modelling using traditional models is not considered accurate enough for the Picton situation and thus no modelling has been carried out to date. Research is being done at a national level to evaluate dispersion models and to identify those thought most appropriate to methyl bromide use in the New Zealand context. The outcome of this research will help establish if air dispersion modelling can be carried out for Picton.

## 2. New Zealand Health Standards for Methyl Bromide

The Environmental Risk Management Authority (ERMA) agreed to the review of the use of methyl bromide in July 2008, the review application was notified in November 2009. Their decision was made final in October 2010 (ERMA, 2010). The decision approved the continued use of methyl bromide but imposed a new management regime for its use. This management regime includes:

- strengthening of the tolerable exposure limits (TELs)
- requiring air quality monitoring and reporting
- establishing minimum buffer zones
- requiring all methyl bromide fumigations to be subject to recapture within a 10-year period.

### 2.1. Tolerable Exposure Limits for Methyl Bromide

The ERMA decision sets out tolerable exposure limits in air or TELs for methyl bromide. Section 16.5.5 of the decision states:

16.5.5 *Accordingly, in accordance with section 77B, the Committee has set the following TELs:*

*TEL<sub>air</sub> (chronic, annual average): 0.0013 ppm (0.005 mg/m<sup>3</sup>)*

*TEL<sub>air</sub> (24 hour): 0.333 ppm (1.3 mg/m<sup>3</sup>)*

*TEL<sub>air</sub> (1 hour): 1 ppm (3.9 mg/m<sup>3</sup>).*

The ERMA decision further states:

16.6.20 *As the TELs must not be exceeded at the boundary of the buffer zone, the control relating to exceeding TELs is varied under section 77A to read:*

*A person in charge of a site and a person who uses methyl bromide must ensure that methyl bromide is used in a manner that does not result in a concentration of methyl bromide, in air at the boundary of the buffer zone, that exceeds the TEL<sub>air</sub> values.*

The chronic (annual average) TEL for methyl bromide of 0.0013 ppm is adopted from the chronic lifetime concentration established by the USEPA (2008). Chronic exposures are generally based on a lifetime of exposure but ERMA imposed the chronic TEL as an annual average to provide a more 'meaningful' exposure timeframe. The chronic TEL is set on the basis that a member of the public exposed to concentrations at or below the chronic TEL for methyl bromide over a one year period would not suffer adverse health effects.

The 24-hour TEL for methyl bromide of 0.333 ppm is also adopted from the standard set by the USEPA (2008). The 24-hour TEL is set on the basis that a member of the public exposed to concentrations at or below the chronic TEL for methyl bromide over a continuous 24 hour period would not suffer adverse health effects.

The acute TEL (1-hour average) for methyl bromide has been set using a low observable adverse effect level (LOAEL) rather than a no observed adverse effect level (NOAEL); an additional uncertainty factor of 6 was applied to the acute TEL due to it being based on a LOAEL rather than on an NOAEL. Low observable adverse effects include mild anorexia, nausea and headache.

### 3. Monitoring Sites

Two sites were chosen on the outskirts of Picton for the measurement of methyl bromide concentrations. Factors which were considered in the choice and number of sites were:

- Proximity to Picton and proximity to Shakespeare Bay.
- Downwind from Shakespeare Bay during the prevailing north-west wind direction.
- Security of the sites.
- Ease of access during the fumigation events.
- Cost of running the sites

The site locations are shown in Figure 1. Site 1 is located at the end of Waitohi Wharf and site 2 is located at the end of Picton Jetty. Security access is required at both sites; this ensures that the sampling equipment is not tampered with during monitoring.

### 4. Monitoring Methodology

During the December fumigation event monitoring at the two sites used Photo-Ionisation Detectors (PIDs) and Gastec tubes. Limitations of this method were the tendency for instrument drift when used for extended periods of time and the relatively high detection limits (for the purpose of ambient monitoring in Picton). For these reasons this method was supplemented with the use of sorbent tubes (USEPA method TO-17 (USEPA, 1999b)) during the January fumigation event. The advantage of this method was the low detection limit and the robustness of the monitor when used for extended periods of time. The disadvantage was the complexity of the method, which requires specialist knowledge and equipment. For the March fumigation event a further method was used replacing the previous two methods. The method uses gas canisters (USEPA method TO-15 (USEPA, 1999a)). In effect this operates in the same way as TO-17 but does not require specialist knowledge or equipment to set up. The use of this method has only just become available in New Zealand although it is a widely used method in Europe and America. The method is described more fully in Appendix 1. Notification of fumigation events can be subject to change at short notice due to changes in the ships schedule. Thus the advantage of using the TO-15 method is that monitoring can be set up relatively quickly without having to rely on the availability of specialists and can be carried out by non-specialists thereby reducing overall costs. Different sizes of canisters are available which allows for long or short durations of sampling. The method also allows for a suite of volatile organic compounds (VOC's) to be analysed for at the same time for minimal extra costs. Photos 1 and 2 show the monitoring equipment used at each of the sites.



Photo 1: Gas canisters (1.4L and 6L)



Photo 2: Vacuum gauge with particulate filter attached

Monitoring was undertaken by Sustainable Environmental Engineering Ltd (SEE Ltd) between the hours of 11pm and 8am from the 31 March to the 1 April. Monitoring equipment was set up prior to fumigation, this included securing the canisters just above ground level (to represent the breathing zone for humans and to assess concentrations at ground level) and ‘flushing’ the valves for 5 minutes each to ensure dilution of the sample did not occur due to ‘clean’ air being present in the valve. The canisters were opened after receipt of a phone call from Port staff to say that venting had begun.

Two canisters were filled at each site covering a period of approximately six and a half hours. Table 1 shows the collection times for each sample. During this time environmental conditions were recorded every 30 minutes at each site using a Kestrel 2500 wind meter. General observations were also made during this time (Appendix 2).

Table 1: Sample collection times for each of the sites.

Site Name	Start of Sampling	End of Sampling	Time period of sample collection
Waitohi Wharf 1	00:31 am	04:05 am	3.57 hrs
Picton Jetty 1	00:41 am	04:22 am	2.35 hrs
Waitohi Wharf 2	04:05 am	06:26 am	3.68 hrs
Picton Jetty 2	04:22 am	06:42 am	2.33 hrs

After the canisters were filled, they were sealed and stored and transported to Hills Laboratories for analysis, the chain of custody is shown in Appendix 3. The canisters were analysed for methyl bromide (bromomethane) in addition to a general suite of volatile organic compounds. It was considered advantageous to perform the additional analysis as it could be carried out at minimal costs and would also aid in the interpretation of the methyl bromide concentrations.

## 5. Results

### 5.1. The fumigation event on the 30<sup>th</sup> March - 31<sup>st</sup> March

Approximately 2200 kg of methyl bromide was used to fumigate logs in ship holds and log stacks under tarpaulin covers. Fumigation began on the 30<sup>th</sup> March, the fumigant then remained under closed covers for 24hrs as is the standard. Venting of the fumigant to the atmosphere began on the 1<sup>st</sup> April at 00:31am. Details of the fumigation event carried out on the 30<sup>th</sup> March 2011 are shown in the Site Evaluation Form in Appendix 4.

### 5.2. The venting event on the 1<sup>st</sup> April

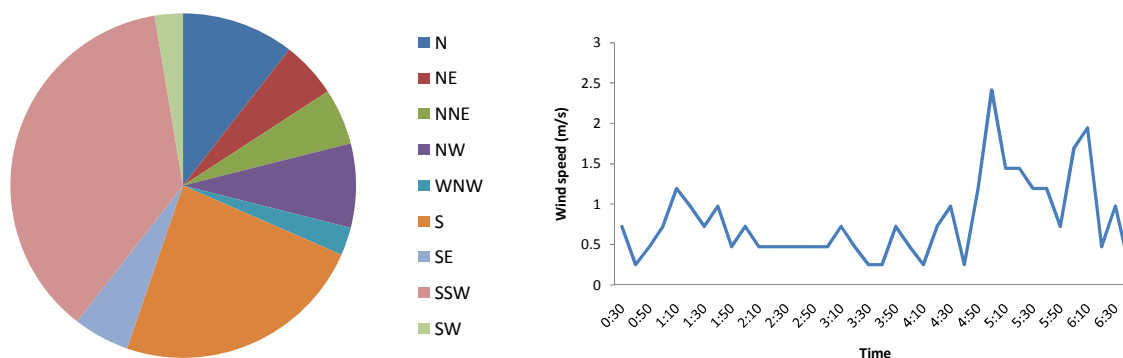
Venting of the logs stacks and ship holds began at 00:31am on the 1<sup>st</sup> April. Wind conditions were calm with a slight NNW breeze. Venting continued until 6.43am on the 1<sup>st</sup> April. There were no problems during venting (pers comm. Patrick Burdon). During venting there was a switch in wind direction from NW to S, wind speed also increased during the venting period.

### 5.3. Field Observations

Field observations were made throughout the venting period. Wind speed and direction were noted approximately every half hour at each of the sites. General observations, such as the arrival and departures of ferries, odours, canister pressure etc were also noted. Field sheets are included as Appendix 2.

### 5.4. Meteorological Data

Port Marlborough operates a meteorological station at Shakespeare Bay and at Waitohi Wharf. Data is collected every minute at Shakespeare Bay and every 10 minutes at Waitohi Wharf. All meteorological data shown has been provided by Port Marlborough. Figure 3 shows wind direction and speed recorded at Waitohi Wharf from 00:30am to 6:40am on the 1<sup>st</sup> April.



**Figure 3: Graphs showing the wind direction and wind speed recorded at Waitohi Wharf from 00:30am to 6:40am**

Wind direction was predominately from the south, wind speed increased from about 4.30am. Figure 4 shows wind rose diagrams showing wind speed and direction recorded at Shakespeare Bay during the approximate time of collection of the two air samples at each site. During the collection of the second air sample at each site the wind was predominantly from the south and wind speed had increased considerably.

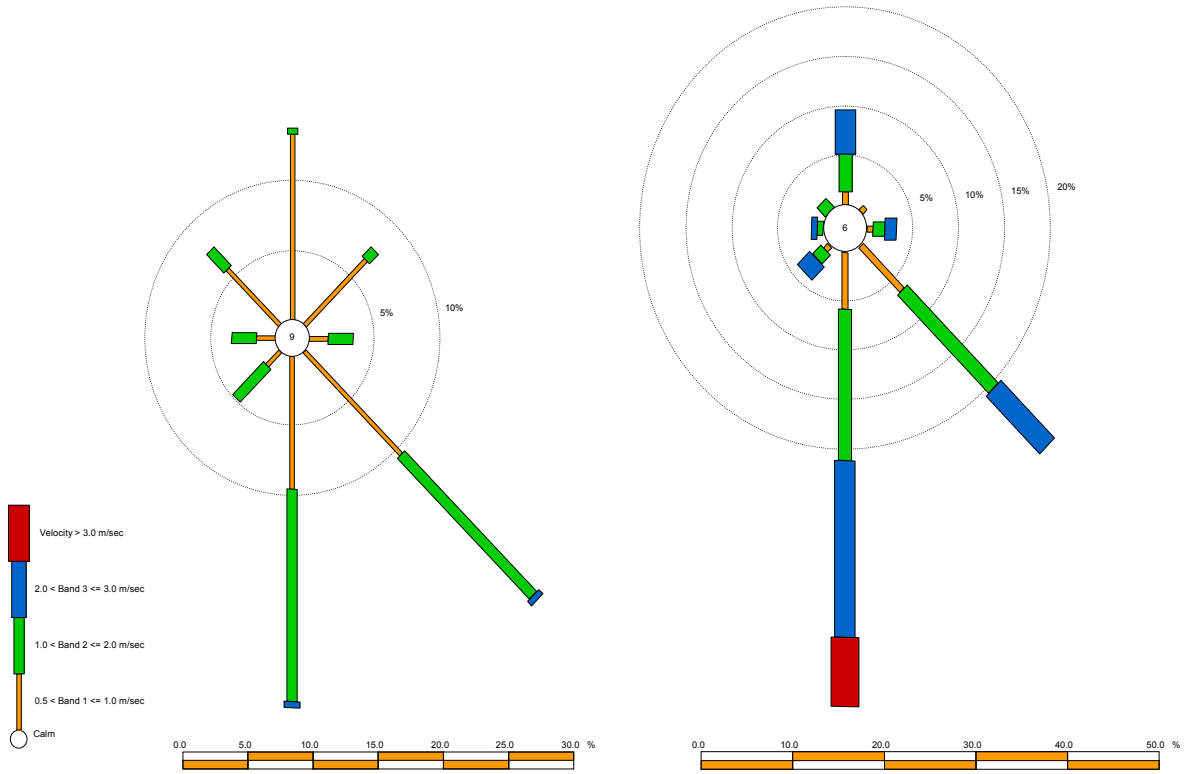


Figure 4: Wind Rose diagrams showing wind speed and direction for Shakespeare Bay from (a) 00:30am to 04:05am and (b) 04:05am to 06:43am. The times approximate the collection time of the air samples at each site.

Appendix 5 shows the complete meteorological conditions recorded at Shakespeare Bay from midnight until 7:00am on the 1<sup>st</sup> April.

Figure 5 shows the temperature during the venting period. The temperature ranged from 10.3°C to 16.6°C, with the lowest temperatures coinciding with low wind speeds in a SSW direction from approximately 01:40am to 04:40am

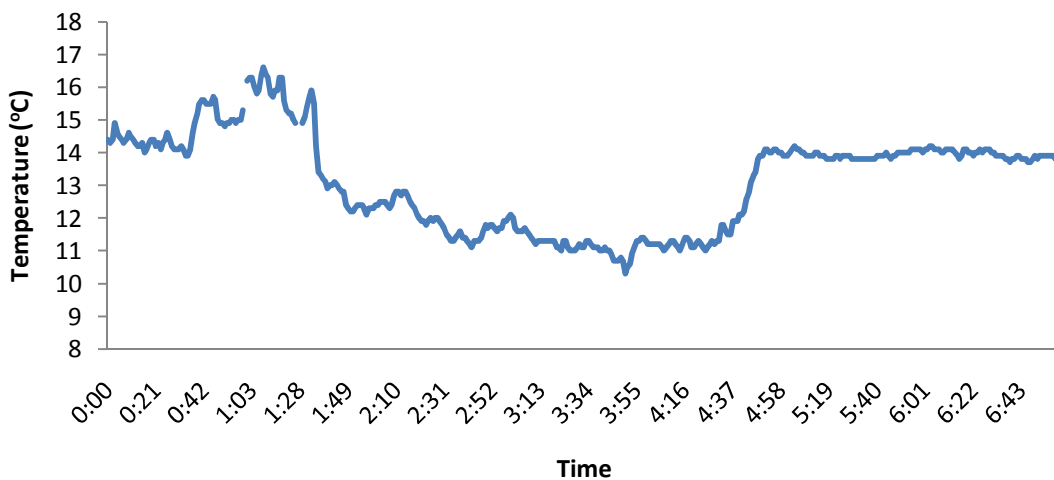


Figure 5: Temperature recorded at Shakespeare Bay from midnight until 6.43am on the 1<sup>st</sup> April.

## 5.5. Results from the TO-15 Monitoring

The Hills Laboratory report is shown in full in Appendix 6. Table 2 summarises the results; all results are expressed as ppbv.

**Table 2: Summary of results**

Parameter	Waitohi Wharf 1	Picton Jetty 1	Waitohi Wharf 2	Picton Jetty 2
Acetone	9	2	12	2
Methyl bromide <sup>†</sup>	1.4	1.2	-	-
Chloromethane	1.5	1.5	0.9	0.8
Dichlorodifluoromethane	0.6	0.6	0.6	0.6
Ethyl acetate	-	-	1.1	-
Heptane	-	-	0.9	-
Hexane	-	-	4.1	-
Isopropyl alcohol	4	-	3	-
Toluene	-	-	3.6	-

The two first samples taken at each site show detectable levels of methyl bromide. Concentrations are very low, 1.4 ppbv at Waitohi Wharf and 1.2 ppbv at Picton Jetty. If it is assumed that all of the sample was collected in one hour (as opposed to the times shown in Table 1), then the estimated 1-hr average concentration is 4.998 ppbv at Waitohi Wharf and 4.416 ppbv at Picton Jetty, the 1-hr standard is 1000ppbv (1ppmv). There were no detectable levels in the second sample taken at each site.

The concentrations measured at each site reflect the weather conditions at the time. Calm conditions with light northerlies at the start of venting would have allowed some gas to drift towards the monitoring sites. The stronger southerly winds during the time of the second samples would have prevented the gas from drifting towards the monitoring sites.

A number of other VOC's were detected in the samples; all of these were detected at very low concentrations and well within any guideline values. There are a number of possible sources for these VOC's including; paints, solvents, coolants, cleaning agents, fuel etc, all of which are commonly used in and around ports.

In general the highest concentrations of VOC's were detected at Waitohi Wharf and with the exception of methyl bromide the highest levels were recorded in the second sample suggesting that Picton harbour (including the ferries and boats docked in the harbour) could be the main source of VOC's obtained in the samples.

## 6. Discussion

The results from the sampling carried out on the 1<sup>st</sup> April are in general agreement with results from previous sampling i.e. concentrations detected are low (up to a 1000 times lower than the standard); concentrations measured at the two sites are dependent on wind speed and direction; additional VOC's detected are likely to be associated with boats and ferries and other activities in Picton harbour. The levels detected at Picton Jetty were only marginally lower than those detected at Waitohi Wharf suggesting that the dispersion of the gas is complex and very dependent of weather conditions at the

<sup>†</sup> Referred to as Bromomethane in the Hills Laboratory report.



time. Dispersion modelling, using data collected to date, would help with understanding the movement of methyl bromide after fumigation events.

## 7. Conclusions

- The TO-15 method is an accurate cost effective way to measure ambient low level concentrations of methyl bromide.
- Concentrations of methyl bromide measured at the two sites are dependent on wind direction, with (relatively) higher concentrations measured when wind direction is in a NW and/or NNW direction i.e. the wind is blowing from Shakespeare Bay towards Picton.
- It is not known how wind speed might affect concentrations at the two sites. Further monitoring under different environmental conditions will help to assess the effect of wind speed on methyl bromide concentrations.
- The likelihood of elevated concentrations of methyl bromide reaching the Picton community is low.

## 8. Recommendations

- Continue with the TO-15 method at the two sites.
- Carry out monitoring at the Port (in collaboration with Port authorities) for a period of two days after the venting of methyl bromide is completed to determine if and at what concentration methyl bromide can be detected at the Port. This will help draw a conclusion as to whether traces of methyl bromide remain in the locality after each fumigation event.
- Continue monitoring each fumigation event for 2011 in order to collect data over a wide range of environmental conditions (i.e. differing wind speeds, wind directions, temperatures) following which an assessment of the data can be carried out to determine if further monitoring is warranted.
- Investigate the use of dispersion models.

## 9. References

ERMA (2010) *Application for the Reassessment of a Hazardous Substance under Section 63 of the Hazardous Substances and New Organisms Act 1996 Name of substances: Methyl bromide and formulated substances containing methyl bromide*. Environmental Risk Management Authority Decision. Application Number: HRC08002. 28 October 2010.

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USEPA (2008) Re-registration Eligibility Decision (RED) for Methyl Bromide. U.S. Environmental Protection Agency, Office of Pesticide Programs, Health Effects Division (7509P). EPA 738-R-08-005.

USEPA (1999a) Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-15. Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS). Second Edition. January 1999. EPA/625/R-96/010b.

USEPA (1999b) Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-17. Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes Second Edition. January 1999. EPA/625/R-96/010b.

## Appendix 1: Summary of TO-15 method (from USEPA, 1999a)

**2.1** The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

**2.2** After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

**2.3** Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

**2.4** To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

**2.5** The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

## Appendix 2: Field Sheets

Field Observations Site Name: WATOHU WHARF

Time (hours)	Comments	Wind Direction (degrees)	Wind Speed (m/s)	Wind Speed Max (m/s)	Rain	Temp. (°C)	Canister Pressure	Barometric Pressure (hPa)
00:30	1 <sup>st</sup> ship hold opened. Interislander docked	305	0.2	1.8	No	15.8	-27.5	1008.6
01:00	Bluebridge ferry arriving + docked	320	0.6	2.3	No	17.8	-25	1008.5
01:30	Interislander + Bluebridge docked. Fumes from ferry. above	200	1.2	2.1	No	15.5	-22	1008.6
01:55	Interislander + Bluebridge docked	200	1.4	1.6	No	14.9	-19	1008.7
02:25	Interislander departed. Bluebridge still docked	200	0.8	0.9	No	14.4	-16	1009.2
02:55	Bluebridge still docked. above from boat/stack	200	1.2	1.6	No	14.8	-12	1009.2
03:25	No ferries	160	0.6	1	No	15.4	-9	1009.7
03:55	CANISTER CHANGED @ 04:05 (low pressure -20)	180	1.5	1.6	No	13.4	-6	1009.6
04:32	LAST COVER REMOVED	—	—	—	—	—	—	—
04:40	Gusty from South	200	1.2	1.3	No	15.7	-17.5	1011.3
05:15	Gusty from South	220	1.6	2.1	No	15.2	-13	1012
05:26	Interislander arriving	—	—	—	—	—	—	—
05:45	Bluebridge arriving	30	2.5	2.8	No	15.7	-10	1013
06:20	Both ferries docked.	40	0.3	0.5	No	16.7	-7	1013
06:26	Interislander leaves	—	—	—	—	—	—	—
06:43	CALL FROM PATRICK - ALL FINISHED	—	—	—	—	—	—	—

Field Observations Site Name: PICTON JETTY

Time (hours)	Comments	Wind Direction (degrees)	Wind Speed (m/s)	Wind Speed Max (m/s)	Rain	Temp. (°C)	Canister Pressure	Barometric Pressure (hPa)
00:41	Ship hold opened @ 00:30 Interislander docked. Fumes visible. Gusty	020	0.8	4.8	No	17.1	-30	1009
01:10	Ferry leaving harbour	320	1.0	2.1	No	15.9	-25	1008
01:40	Very light wind, no ripples on water. Light diesel above	200	0.5	0.6	No	15.9	-23.5	1009.3
02:10	View across to Port shows smoke from ferry drifting to WATOHU WHARF	190	0.8	1.2	No	14.2	-20	1009.4
02:40	Water flat calm	—	0	0	No	15.5	-18	1009.8
03:10	Smoke from ferry going straight up. No ripples. Bluebridge leaving	180	0.3	0.4	No	16.0	-14	1009.8
03:40	—	170°	0.2	0.4	No	15.5	-11	1009.8
04:10	Very still	180	0.4	0.4	No	16.0	-7	1011.2
04:22	CANISTER CHANGED	—	0.3	0.4	No	16.1	-30	1011
04:32	LAST COVER REMOVED	—	—	—	—	—	—	—
05:00	Calm, minor ripples	100	0.9	1	No	16.2	-26	1012.3
05:30	Gusty southerlies	160	1.7	3.2	No	15.7	-23.5	1012.6
06:00	Gusty	140	1.6	3.1	No	15.9	-20	1012.1
06:30	—	140	1.2	1.5	No	15.9	-17	1012.3
06:42	Stopped canister	—	—	—	—	—	—	—

### Appendix 3: Hills Laboratory Chain of Custody.

#### Ambient Air Monitoring: Sampling Methodology USEPA TO-15

Ambient Air Monitoring Equipment Used	1-4 L CANISTERS WITH FLOW RATE VALVE
Method	USEPA TO-15
Laboratory Used	Hills Laboratories
Estimated Duration of Sampling	7 hours
Sample Locations	WATONH WHARF, PICTON JETTY

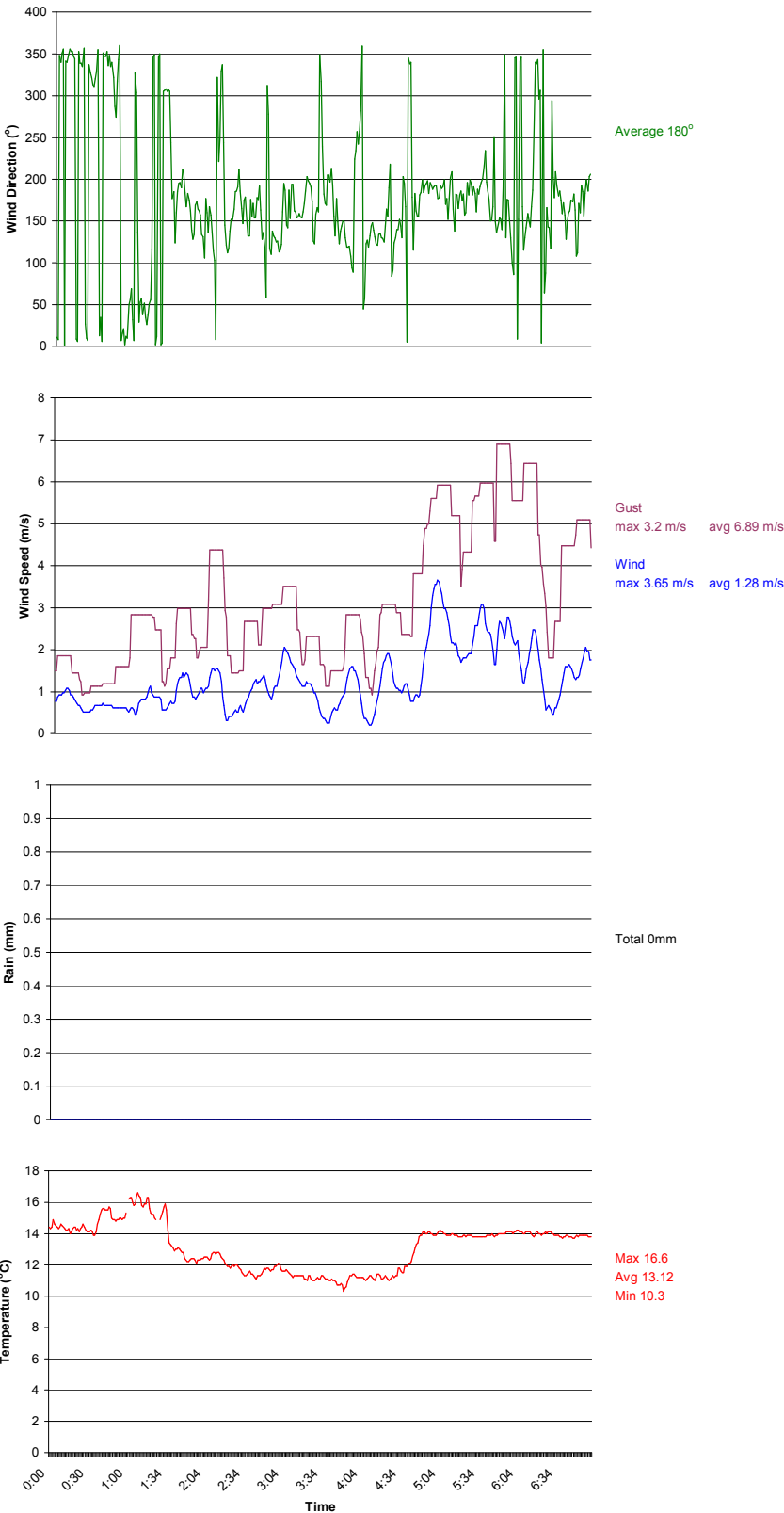
Serial Number of Canister	Date Verified	Date Evacuated	Verified By	Sample ID	Collection Date	Collection Start	Collection End	Collection Time	Collected By	Initial Pressure	Final Pressure	Analysis
513	15/3/11	28/3/11	CB	WATONH 1	1 Apr 11	00:31	04:00	3.5 hrs	SEE LHD	-27.5	-6	Methyl Benzene + VOC suite
510	25/3/11	28/3/11	CB	JETTY 1	1 Apr 11	00:41	04:22	3.5 hrs	SEE LHD	-30	-6	-
00222	15/3/11	28/3/11	CB	WATONH 2	1 Apr 11	04:05	06:30	2 hrs 25 mins	SEE LHD	-21	-5	-
514	25/3/11	28/3/11	CB	JETTY 2	1 Apr 11	04:22	06:15	1 hr 53 mins	SEE LHD	-30	-15	-

## Appendix 4: Site Evaluation Form.

### Methyl Bromide Ambient Air Monitoring: Site Evaluation Form

Site Details (name, location etc.)	Port Marlborough, PICTON
Exporter Details (name, contact person, etc)	Zindia
Fumigator Details (name, contact person, etc)	South Fume, Eric Morrison
Goods under fumigation (name, quantity etc) and location (stacks, holds, containers)	Logs in ships holds and under tarpaulin covers
Fumigant used. Date and time fumigant introduced and quantity	Methyl bromide 30/3/11, 2200kg
Date and time fumigant released	1 Apr 2011 00:31am
Relevant ambient air quality guidelines	ERMA 24hr average = 1ppmv methyl bromide.

# Appendix 5: Meteorological conditions recorded at Waimahara Wharf, Shakespeare Bay on the 1 April 2011



## Appendix 6: Hills Laboratories results



**Hill Laboratories**  
BETTER TESTING BETTER RESULTS

R J Hill Laboratories Limited | Tel +64 7 858 2000  
1 Clyde Street | Fax +64 7 858 2001  
Private Bag 3205 | Email mail@hill-labs.co.nz  
Hamilton 3240, New Zealand | Web www.hill-labs.co.nz

**ANALYSIS REPORT**

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<b>Client:</b> Marlborough District Council	<b>Lab No:</b> 884308	BPV1
<b>Contact:</b> Fleur Tieman	<b>Date Registered:</b> 04-Apr-2011	
C/- Marlborough District Council	<b>Date Reported:</b> 11-Apr-2011	
PO Box 443	<b>Quote No:</b> 44389	
BLLENHEIM 7240	<b>Order No:</b> 42724fti	
	<b>Client Reference:</b> VOCs by USEPA TO-15	
	<b>Submitted By:</b> Fleur Tieman	

Sample Type: Air Sampling Canister 1.4 Litre						
Sample Name:	Waltohi 1 01-Apr-2011 12:31 am	Waltohi 2 01-Apr-2011 4:05 am	Jetty 1 01-Apr-2011 12:41 am	Jetty 2 01-Apr-2011 4:22 am		
Lab Number:	884308.1	884308.2	884308.3	884308.4		
Whole Air Sampling Volatile Compounds						
1,1,1-Trichloroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,1,2,2-Tetrachloroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,1,2-Trichloroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,1-Dichloroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,1-Dichloroethene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,2,4-Trichlorobenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,2,4-Trimethylbenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,2-Dibromoethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,2-Dichlorobenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,2-Dichloroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,2-Dichloropropane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,3,5-Trimethylbenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,3-Butadiene	ppbv	< 2	< 2	< 2	< 2	-
1,3-Dichlorobenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,4-Dichlorobenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
1,4-Dioxane	ppbv	< 2	< 2	< 2	< 2	-
2,2,4-Trimethylpentane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
2-Butanone	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
2-Hexanone	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
4-Ethyltoluene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
4-Methyl-2-pentanone	ppbv	< 0.6	< 0.6	< 0.6	< 0.6	-
Acetone	ppbv	9	12	2	2	-
Allyl chloride	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Benzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Benzyl chloride	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Bromodichloromethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Bromoethene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Bromoform	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Bromomethane	ppbv	1.4	< 0.5	1.2	< 0.5	-
Carbon disulfide	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Carbon tetrachloride	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Chlorobenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Chloroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Chloroform	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Chloromethane	ppbv	1.5	0.9	1.5	0.8	-
cis-1,2-Dichloroethene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
cis-1,3-Dichloropropene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Cyclohexane	ppbv	< 0.5	2.0	< 0.5	< 0.5	-
Dibromochloromethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-

Lab No: 884308 v 1

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Sample Type: Air Sampling Canister 1.4 Litre						
Sample Name:	Waltham 1 01-Apr-2011 12:31 am	Waltham 2 01-Apr-2011 4:05 am	Jetty 1 01-Apr-2011 12:41 am	Jetty 2 01-Apr-2011 4:22 am		
Lab Number:	884308.1	884308.2	884308.3	884308.4		
Whole Air Sampling Volatile Compounds						
Dichlorodifluoromethane	ppbv	0.6	0.6	0.6	0.6	-
Dichlorotetrafluoroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Ethyl acetate	ppbv	< 0.5	1.1	< 0.5	< 0.5	-
Ethylbenzene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Heptane	ppbv	< 0.5	0.9	< 0.5	< 0.5	-
Hexachlorobutadiene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Hexane	ppbv	< 0.5	4.1	< 0.5	< 0.5	-
Isopropyl alcohol	ppbv	4	3	< 2	< 2	-
Methyl tert-butyl ether	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Methylene chloride	ppbv	< 2	< 2	< 2	< 2	-
o-Xylene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
m,p-Xylene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Propene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Styrene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Tetrachloroethene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Tetrahydrofuran	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Toluene	ppbv	< 0.5	3.6	< 0.5	< 0.5	-
trans-1,2-Dichloroethene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
trans-1,3-Dichloropropene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Trichloroethene	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Trichlorofluoromethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Trichlorotrifluoroethane	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Vinyl acetate	ppbv	< 0.5	< 0.5	< 0.5	< 0.5	-
Vinyl chloride	ppbv	< 0.7	< 0.7	< 0.7	< 0.7	-

## SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Air Sampling Canister 1.4 Litre			
Test	Method Description	Default Detection Limit	Samples
Canister Screening activity	US EPA TO-15.	-	1-4
Canisters Dilution activity	US EPA TO-15.	-	1-4
Client returned and pressurised Canister prep	US EPA TO-15.	-	1-4
Whole Air Sampling Volatile Compounds	Whole air analysed by active SPME-GC-MS. US EPA TO-15.	-	1-4

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

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Ara Heron BSc (Tech)  
Client Services Manager - Environmental Division