



2018

# Volatile Compounds Assessment Port of Tauranga



## Table of Contents

1 Executive Summary .....	3
2 Introduction .....	4
3 Method .....	6
3.1 Study Area .....	6
3.2 Equipment.....	7
3.2.1 Global Positioning System.....	7
3.2.2 Photo Ionisation Devices .....	7
3.2.3 Canisters and Gauge Flow .....	7
3.3 Chemical Analysis and Data Processing.....	8
4 Result and discussion .....	9
4.1 Port Boundary .....	9
4.2 Buffer Area .....	11
4.3 Proportion of Methyl Bromide in PIDs Measurements.....	12
5 Conclusion .....	13
6 Appendix .....	14

## Glossary

CH <sub>3</sub> Br	Chemical formula of methyl bromide
GPS	Global Positioning System
EPA	Environmental Protection Agency
LOD	Limit of Detection
PIDs	Photo Ionisation Detectors. A device that measures the concentration of total volatile organic compounds by ionizing molecules using high-energy UV light.
PPB	Part per billion (1 ppb = 0.001 ppm)
PPM	Part per million (1 ppm = 1000 ppb)
TELS	Tolerable exposure limits
TVOCs	Total Volatile Organic Compounds
WES	Workplace Exposure Standards

# 1 EXECUTIVE SUMMARY

The concentrations of total volatile organic compounds and methyl bromide have been measured and compared to satisfy the requirement of the clause 5A.4 of General Resource consent number 62719:

“Once a year in March (or as directed by Bay of Plenty Regional Council) General shall carry out ambient air sampling followed by laboratory analysis in combination with PIDs to determine the extent to which background VOCs may influence methyl bromide monitoring results”.

The concentration of total volatile organic compounds measured by photo ionisation devices was 11 times lower than the 1h-TEL prescribed by the Environmental Protection Agency. The concentration of methyl bromide measured by mass spectrometry was 186 times lower than the 1h-TEL prescribed by the Environmental Protection Agency. Methyl bromide represented 2 to 14% of the total volatile organic compounds concentrations measured by PIDs at the Port Boundary.

The concentration of total volatile organic compound was 10 times lower than the 8h-WES prescribed by WorkSafe. The concentration of methyl bromide measured by mass spectrometry was 84 times lower than the 8h-WES. Methyl bromide represented 2 to 17% of the total volatile organic compounds concentrations measured by PIDs within the Buffer Area.

This result confirmed that the usage of PIDs to measure the 1h and 8h averaged methyl bromide concentrations was conservative and granted General with an acceptable safety margin.

## 2 INTRODUCTION

Genera Ltd is the leader in phytosanitary treatments to prevent, minimise and manage the risks from harmful organisms. Eco-friendly treatments have been developed, such as heat treatment for cars. However, most treatments require fumigation and the release of these chemicals (e.g. methyl bromide) to the environment.

The risks associated with the exposure of methyl bromide during ventilation have been assessed by EPA which prescribe minimum buffer zones based on activities and the quantity of methyl bromide used (Appendix- Table 3). Additionally, EPA implement Tolerable Exposure Limits based on 1h and 24h average concentration of methyl bromide to protect the public (Table 1). WorkSafe implement Work Exposure Standards based on 8h average of methyl bromide to protect port workers (Table 1).

**Table 1**

*Tolerable Exposure Limits and Working Exposure Standards for methyl bromide in air*

<b>Compounds</b>	<b>TELs</b>		<b>WES</b>
	1h Av	24h Av	8h Av
Methyl bromide (ppm)	1	0.333	5

This report has been prepared to satisfy the requirement of the clause 5A.4 of the resource consent number 62719:

“Once a year in March (or as directed by Bay of Plenty Regional Council) Genera shall carry out ambient air sampling followed by laboratory analysis in combination with PIDs to determine the extent to which background VOCs may be influencing methyl bromide monitoring results”

The objectives of this report are to:

- Compare the concentration of total volatile organic compounds measured by PIDs with environmental standards.
- Compare the concentration of methyl bromide measured by mass spectrometry with environmental standards.
- Assess and compare the proportion of methyl bromide and other volatile organic compounds with PIDs results.

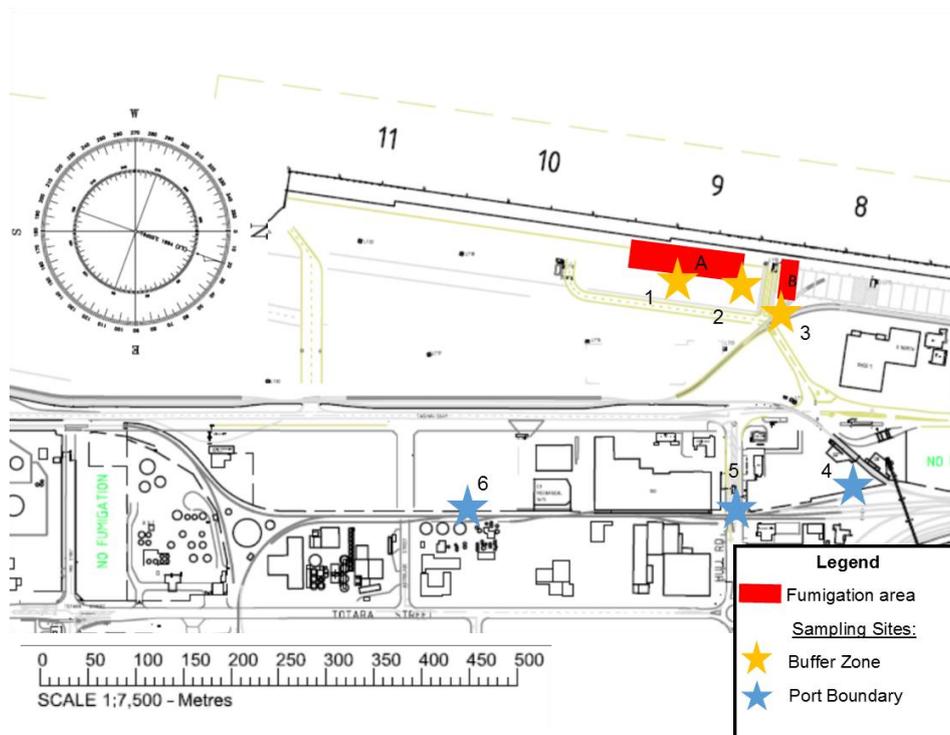
### 3 METHOD

#### 3.1 Study Area

The monitoring of air quality took place at the Port of Tauranga on the 15 March 2018. A total of 6 sites were carefully selected with reference to EPA requirements, accessibility, weather conditions, such as the wind direction and intensity, as well as the distance from the fumigation area (Figure 1). An additional mobile site (Marshaller's vehicle- Site 7) was selected to represent a real life scenario of direct exposure. These sites were grouped into 2 categories which permitted further comparison with relevant environmental guidelines:

- Buffer area: The area inside the Port between the risk area and the port security fence. Port users work within this area. However, the general public are prohibited from this area.
- Port Boundary: The boundary fence which excludes members of the public.

The fumigation included 16 log stacks which represent a total volume of 9115 m<sup>3</sup>. The dosage of methyl bromide was 120 g/m<sup>3</sup>, or 1181 Kg of methyl bromide was applied in accordance with phytosanitary requirements.



**Figure 1**

Land cover map of the Port of Tauranga study area with location of the fumigation area (square) and monitoring sites (stars).

## 3.2 Equipment

### 3.2.1 Global Positioning System



All sampling locations were georeferenced using the GPS Etrex 10. GPS coordinates and associated distance from the fumigation area are presented in Appendix- Table 4.

### 3.2.2 Photo Ionisation Devices



CUB was the PID selected for the measurement of TVOCs during the 2018 environmental survey. This device was selected due to its mandatory deployment for the General Air Monitoring Programme. Additionally, the CUB is the smallest and lightest personal PID gas monitor available and is therefore routinely used by General technicians for personal protection equipment. A total number of 7 CUBs were used to measure the concentration of TVOCs within the Buffer Area and at the Port Boundary. A unique identification number has been attributed to each CUB permitting the georeference of the location and to conduct further data analysis (Appendix- Table 5). The CUBs were collected at the end of the monitoring period. The monitoring was completed when the TVOCs measurements were below 1 ppm for 15 minutes.

### 3.2.3 Canisters and Gauge Flow



Before deployment of the canisters in the field, they were pressurised using a vacuum pump and purified with nitrogen. Canisters were heated in the oven at 70°C and flushed using nitrogen. This process was repeated 3 times to avoid contamination and then subsequently confirmed by a blank sample. Sampling was initiated by attaching the canister to the gauge and continued until a gauge pressure of 0 inch of mercury was achieved. The 1h, 8h and 24h canisters were equipped with a pressure gauge and flow restrictor set for 2, 0.9 and 0.6 ml/min, respectively.

### 3.3 Chemical Analysis and Data Processing

The data generated by the CUBs were downloaded using the software CUB PC. A General air monitoring template was used for the calculation of average concentrations (1h, 8h and 24h) which permitted direct comparison with environmental and health standards.

Air samples were extracted from the canisters in the laboratory to permit further analysis by Syft Technologies, Christchurch. The selected ion flow tube mass spectrometry (SIFT-MS) was used in the detection of 15 volatile organic compounds. SIFT-MS is based on the chemical ionisation of analyte molecules in a sample mixture by mass-selected reagent ions. The limit of detection is usually defined as the minimum concentration that can be detected at a known confidence level and is presented in Table 2.

**Table 2**

*List of chemicals measured in this study and their limit of detection*

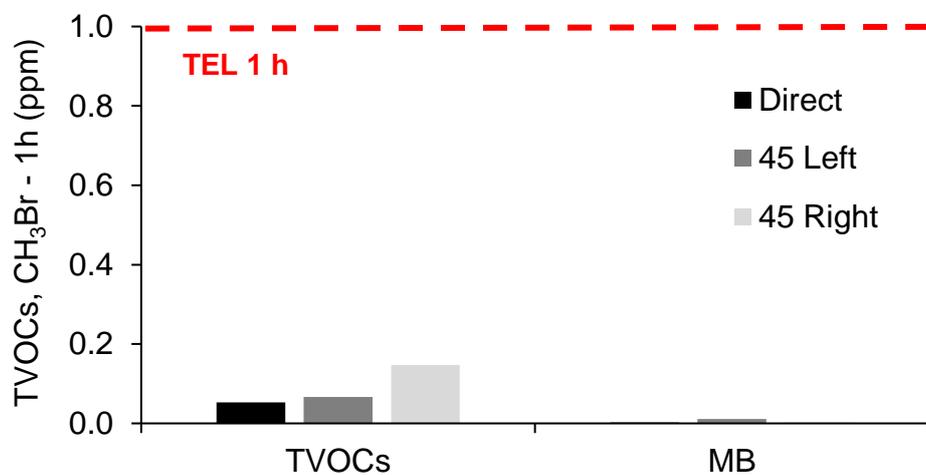
Measured chemicals	Chemical formula	LOD (ppb)
1,2-Dibromoethane (ethylene dibromide) *	CH <sub>2</sub> BrCH <sub>2</sub> Br	5
1,2-Dichloroethane (ethylene dichloride)	CH <sub>2</sub> ClCH <sub>2</sub> Cl	5
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	25
Ammonia	NH <sub>3</sub>	15
Benzene *	C <sub>6</sub> H <sub>6</sub>	5
C2-Alkylbenzenes	-	5
Chloropicrin *	Cl <sub>3</sub> CNO <sub>2</sub>	5
Ethylene oxide	C <sub>2</sub> H <sub>4</sub> O	10
Formaldehyde	CH <sub>2</sub> O	25
Hydrogen cyanide *	HCN	3
Hydrogen phosphide *	PH <sub>3</sub>	3
Methanol	CH <sub>3</sub> OH	10
Methyl bromide	CH <sub>3</sub> Br	5
Styrene *	C <sub>8</sub> H <sub>8</sub>	2
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	3

\*Measurements of these compounds were below the limit of detection in this study

## 4 RESULT AND DISCUSSION

### 4.1 Port Boundary

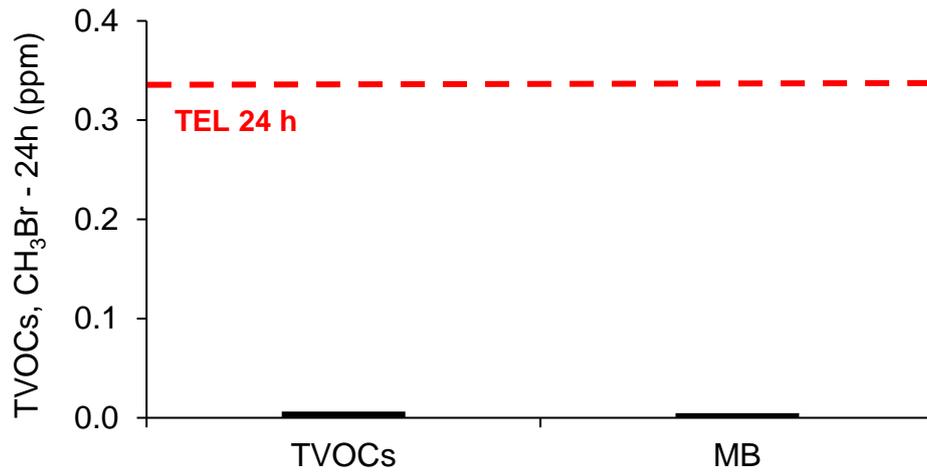
The 1h concentrations of total volatile organic compounds and methyl bromide were compared to the TEL guideline in Figure 2. TVOCs concentrations were 7, 15 and 19 times lower than the TEL and methyl bromide concentration were 90, 388 and 412 times lower than the safety limit. The concentration of TVOCs at the 45° Right site was higher than the site located directly downwind and 45° Left. This difference was most likely due to the manufacturer limitation with concentrations lower than the LOD as well as the presence of other contaminants from unknown sources.



**Figure 2**

*Comparison of the 1h average concentration of TVOCs and methyl bromide at the Port Boundary*

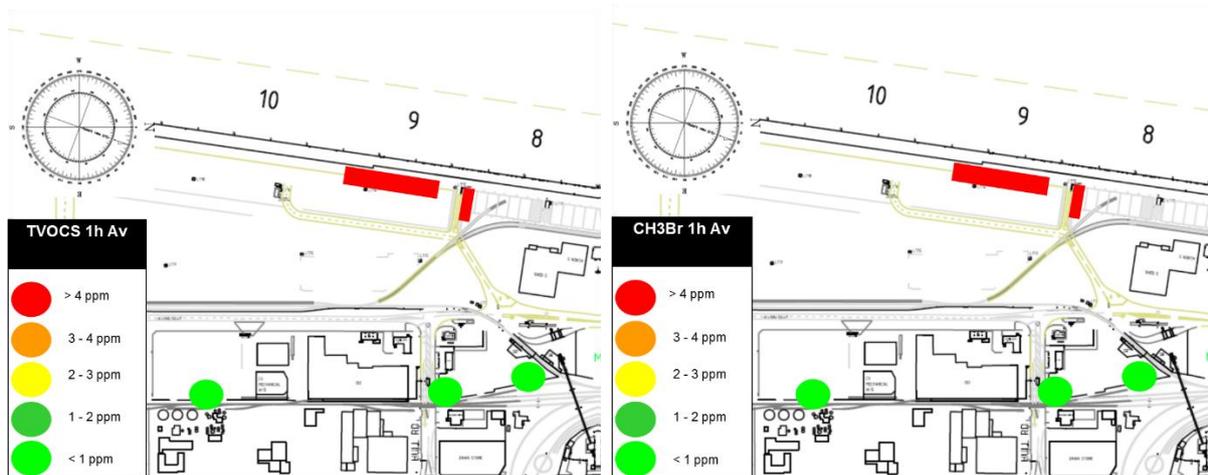
The 24h concentrations of total volatile organic compounds and methyl bromide were compared to the TEL guideline in Figure 3. TVOCs and methyl bromide concentrations were 54 and 73 times lower than the TEL guideline. From this research, Genera complies with the EPA requirements to protect the public from the adverse effects of methyl bromide.



**Figure 3**

*Comparison of the 24h average concentration of TVOCs and methyl bromide at the Port Boundary*

The 1h average concentrations of total volatile organic compounds and methyl bromide for each site were presented in Figure 4. In this research, TVOCs and CH<sub>3</sub>Br concentrations were below 0.2 ppm for all sites. This result confirms that Genera is in compliance with EPA requirements to protect the general public.

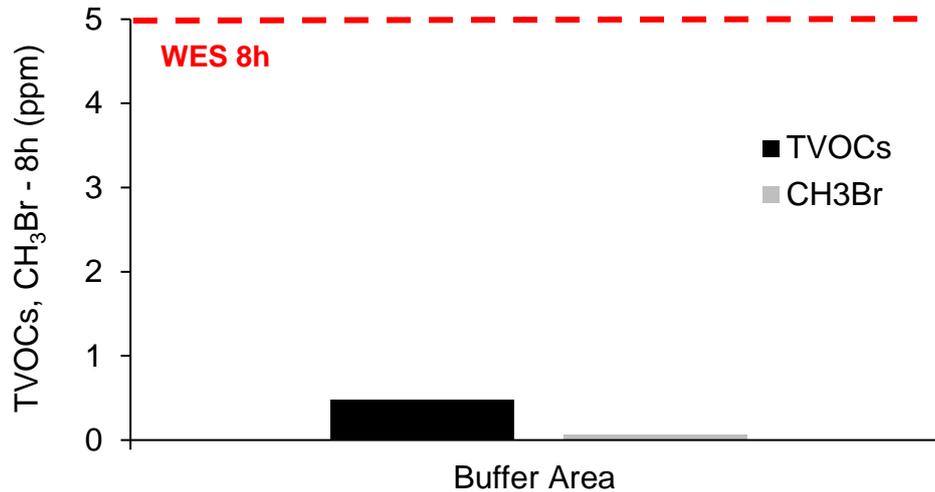


**Figure 4**

*1h average concentration of Total Volatile Organic Compounds and methyl bromide (ppm) at the Port Boundary*

## 4.2 Buffer Area

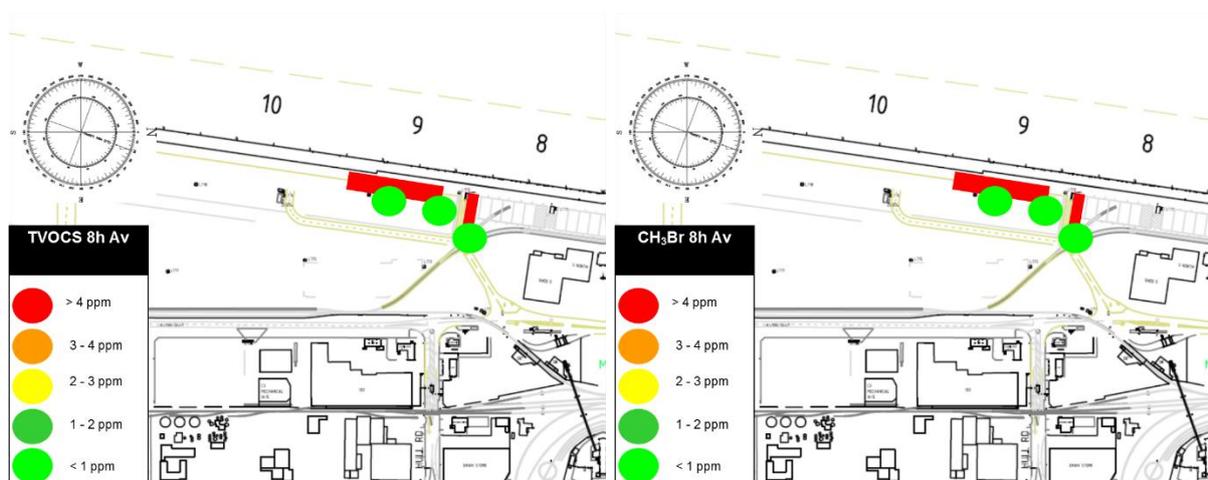
The 8h concentrations of total volatile organic compounds and methyl bromide were compared to the WES guideline in Figure 5. TVOCs concentration was 10 times lower than the WES and methyl bromide concentration was 84 times lower than the safety limit.



**Figure 5**

*Comparison of the 8h average concentration of TVOCs and methyl bromide within the buffer area*

The 8h average concentrations of total volatile organic compounds and methyl bromide for each site were presented in Figure 6. In this research, TVOCs and CH<sub>3</sub>Br concentrations were below 1 ppm for all sites. This result confirms that Genera is in compliance with WorkSafe requirements to protect the port workers.



**Figure 6**

*8h average concentration of Total Volatile Organic Compounds and methyl bromide (ppm) in the Port of Tauranga*

### 4.3 Proportion of Methyl Bromide in PIDs Measurements

The proportion of methyl bromide measured by mass spectrometry at the Port Boundary was compared to the total volatile organic compounds measured by PIDs (Figure 7). Methyl bromide represents 2 to 14% of the TVOCs measured by the PIDs at the Port Boundary. This result confirms that the use of PIDs to measure methyl bromide concentration by Genera is a conservative approach with fumigant concentrations lower than PIDs reading.

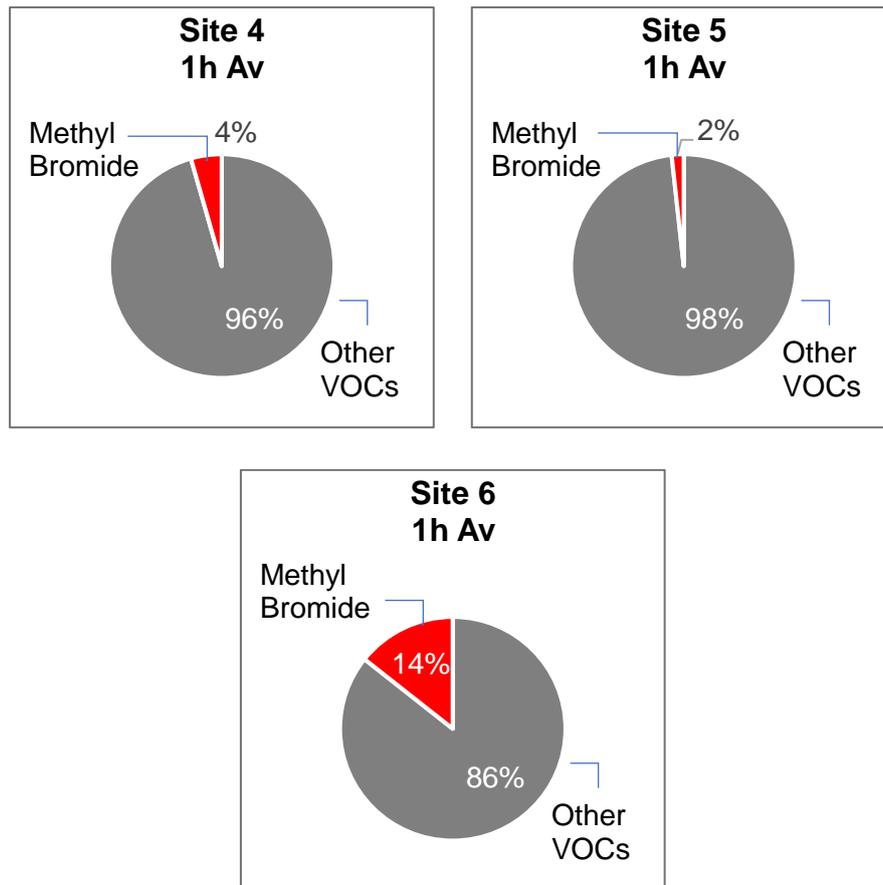
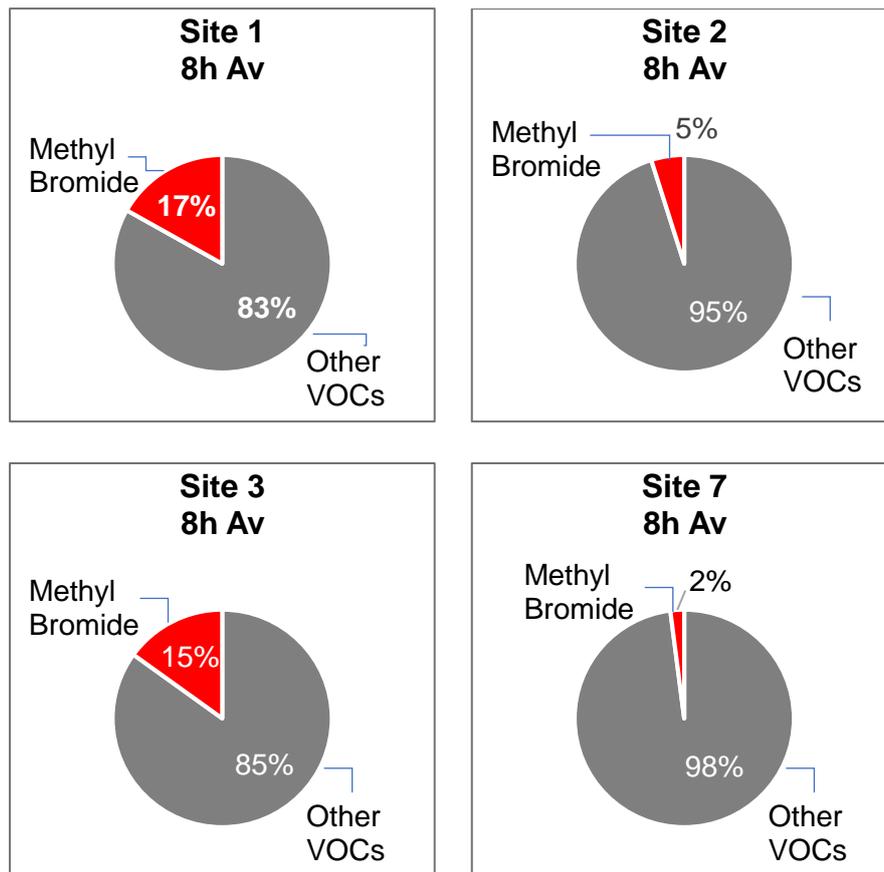


Figure 7 Proportion of methyl bromide (%) measured in PIDs at the Port Boundary

The proportion of methyl bromide measured by mass spectrometry within the Buffer Area was compared to the total volatile organic compounds measured by PIDs (Figure 8). Methyl bromide represents 2 to 16% of the TVOCs measured by the PIDs within the buffer. This result confirms that the use of PIDs to measure methyl bromide concentration by Genera is a conservative approach with fumigant concentrations lower than PIDs reading.



**Figure 8**

*Proportion of methyl bromide (%) measured in PIDs within the Buffer Area and at the Port Boundary*

## 5 CONCLUSION

The concentrations of TVOCs and methyl bromide measured during the 2018 survey were significantly lower than the TEL and WES guidelines. The concentrations of TVOCs and methyl bromide were higher at the monitored safety zone boundary than at the Port boundary. This result can be directly explained by the proximity of these sites with the fumigation area. This result confirms the limitation to use PIDs in the measurement of specific compounds due to detection limit and sensitivity to multiple sources of volatile organic compounds. From this research, it is found that methyl bromide only represented 2 to 17% of the total volatile compounds measured by PIDs.

## 6 APPENDIX

**Table 3**

*Environmental protection agency recommendations on minimum buffer zone*

<b>Use</b>	<b>Minimum BZ</b>
Ships' holds with more than 1,000kg methyl bromide	100-metres
Ships' holds with less than 1,000kg methyl bromide	50-metres
Fumigation under cover	50-metres
Containers total volume over 77m <sup>3</sup> in any 60-minute period	25-metres
Containers total volume less than 77m <sup>3</sup> in any 60-minute period	10-metres

**Table 4**

*Sampling sites characteristics including GPS location coordinates and distances from the fumigation area.*

<b>ID</b>	<b>Location Area</b>	<b>GPS Coordinates</b>	
		<b>Latitude</b>	<b>Longitude</b>
Site 1	Buffer Area	37°39'21.19"S	176°10'58.90"E
Site 2	Buffer Area	37°39'15.96"S	176°11'0.05"E
Site 3	Buffer Area	37°39'15.02"S	176°11'2.56"E
Site 4	Port Boundary	37°39'12.52"S	176°11'6.76"E
Site 5	Port Boundary	37°39'17.59"S	176°11'7.21"E
Site 6	Port Boundary	37°39'28.58"S	176°11'8.52"E
Site 7	Buffer Area	Variable	Variable

**Table 5**

*PIDs and canisters identification for each sampling sites.*

ID	Location Area	Canisters		CUB ID
		ID	Run Time (hour)	
Site 1	Buffer Area	C24	8	TC102633 - C2E7C0B010000
Site 2	Buffer Area	C23	8	TC101667 – CD335D9000000
Site 3	Buffer Area	C25	8	TC101646 – C3F32D9000000
Site 4	Port Boundary	C28	1	TC102634 - C3CAC0B010000
Site 5	Port Boundary	C30	1	TC102759 - CEF9D0B010000
		C32	24	
Site 6	Port Boundary	C20	1	TC102637- CFF8E0B010000
Site 7	Buffer Area	C31	8	TC102633- C2E7C0B010000