Environmental Assessment Report

Env-WS03-210820

Methyl bromide and total volatile organic compounds concentrations measured at the Port of Tauranga

Prepared for WorkSafe New Zealand

2020

Report information sheet

Report title	Methyl bromide and total volatile organic concentrations measured at the Port of Tauranga
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Client	WorkSafe New Zealand
Client contract number	Env-WS03- 210820
Date	August 2020
Confidentiality requirement	Confidential (for client use only)
Intellectual property	
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ABSTRACT

AIMS: The scope of this project was to continuously measure the concentrations of methyl bromide and total volatile organic compounds (TVOC) during the ventilation of methyl bromide.

P**LACE:** Port of Tauranga, Mount Maunganui, 21 August 2020.

METHOD: The measurements of methyl bromide and total volatile organic compounds were conducted downwind at the Port of Tauranga. The monitoring stations MS1 and MS2 were located 230 m and 250 m from the ventilated vessel's holds respectively. A mobile Fourier Transform Infrared Spectrometer was utilised to perform methyl bromide measurements in ambient air during the ventilation of four ship's holds. Photo-ionisation devices (PIDs) were used to measure total volatile organic compounds at the same location, ensuring comparable measurements under the same operating conditions.

RESULTS: The results revealed that the 1-hour maximum methyl bromide concentration at MS1 was 0.05 ppm. The 1-hour maximum TVOC concentrations at MS1 were 0.02 ppm and 0.18 ppm in PID 1 and PID 2 respectively. Percent recoveries for methyl bromide (i.e. ratio between TVOC and methyl bromide) were 31% and 331% in PID 1 and PID 2 respectively at the monitoring station MS1. The 1-hour maximum methyl bromide concentration at monitoring station MS2 was 0.12 ppm and higher than the 1-hour TVOC concentrations measured in PID 1 (0.04 ppm) but lower than the 1-hour average concentration in PID 2 (0.45 ppm). The fluctuation of methyl bromide and TVOC were similar during the monitoring period at site MS2 only more marked for PID 2. Percent recoveries for methyl bromide were 331% and 375% in PID 1 and PID 2 respectively at the monitoring station MS2.

CONCLUSION: The concentrations and dispersion of methyl bromide in ambient air were mainly influenced by the wind direction during the ventilation of vessel holds. The 1-hour methyl bromide concentration was low most likely due to the distances from the ventilation area, and operational benefits from ship's holds ventilation. From our observation, the fumigator has greater control (mechanical) of the opening of ship's holds (i.e. emission rate) than during the removal of tarpaulins for log stacks. Ship's holds can be reclosed to control the release fo fumigant and the opening rate are not influenced by wind gust which is a clear benefit when compared to tarpaulins. Further monitoring is recommended at various distances from the ventilated cargo ships to better understand the dispersion of methyl bromide. It is recommended to investigate and compare the different types of enclosures that can be used for fumigation purposes to support best practices.

Table of Contents

List of Figures

List of Tables

1 Introduction

Methyl bromide, also known as bromomethane (CH_3Br) is a fumigant currently used in New Zealand for phytosanitary treatment of pine logs and other commodities (e.g. fruits). Methyl bromide is a very efficient chemical in controlling quarantine pests and is applied when required by the importing country (e.g. logs exported to India). Most (~94%) of the methyl bromide use is on forest products (~94%) fumigated inside tarpaulins and vessel holds, and the remaining proportions are applied on small quantities of exported commodities and imported products at the border, mainly fumigated inside warehouses and containers. Other fumigants can be used depending on the phytosanitary requirements of the importing countries. For example, phosphine can be applied inside ship holds for logs exported to China. The quantity of fumigant applied and the duration of the treatments are defined by the importing countries. The major drawback of hazardous pesticides is their toxicity and the potential to cause serious harm to humans, animals and other living organisms. Methyl bromide is also listed in the Montreal Protocol as a controlled substance with an ozone depleting potential of 0.7, reflecting the high reactivity of bromine with ozone. Therefore, management strategies have been developed and implemented which include, but are not limited to, the establishment of Tolerable Exposure Limits (TELs) that cannot be exceeded, and the establishment of buffer zones to exclude civilians and workers from a risk area.

WorkSafe New Zealand has commissioned Ecocific Limited to undertake real-time monitoring of methyl bromide in ambient air at the Port of Tauranga. This project complements the air quality monitoring using canisters by Air Matters. This project will provide continuous measurements of methyl bromide during ventilation events utilising Ecocific aerial and mobile capability to provide information on the dispersion of chemicals. These results will be made available to Pattle De La More Limited to calibrate and validate a methyl bromide dispersion model, which can be used for future management and decision making.

The aims of this project are:

- To continuously measure and report on the methyl bromide concentrations during the ventilation of methyl bromide post fumigation

- To continuously measure and report on the total volatile organic compounds (TVOC) concentrations during the ventilation of methyl bromide

2 Method

The measurements of TVOC and methyl bromide in ambient air were conducted during the ventilation of four ship holds at 8 Berth of the Port of Tauranga on 21 August 2020. The characteristics of the vented log stacks and weather conditions are presented in Table 1. The size of the vessel holds varied from 7256 m^3 to 9296 m^3.

Table 1. Fumigation characteristics including date, volume and quantity of methyl bromide (Mebr) applied to each log stack, venting time, and atmospheric conditions (wind direction and speed).

21/08/2020	Fumigation		Ventilation		
Log stack ID	Volume (m3)	MeBr (kg)	Vent Time	Wind Direction	Wind Speed (m/s)
Hold 1	7256	523	21:50	267 W	7.2
Hold 2	9262	667	23:08	265 W	3.5
Hold 3	9296	670	0:29	300 WNW	3.8
Hold 4	9284	669	19:48	315 NW	3.4

Two monitoring stations were carefully selected directly downwind from the vented ship's holds (Figure 1). The monitoring station MS1 was located inside the port area at a distance of ~250 m from the vented ship's holds. The monitoring period for MS1 started at 6:45 pm and ended at 10:05 pm. Prior to 9:38 pm, the wind direction was variable from N to WNW direction but dominated by NW wind (Appendix 1). After 9:38 pm, the wind direction was W and therefore, a new monitoring station MS2 was established from 10:23 pm to 1:00 am. The monitoring station MS2 was located inside the Port of Tauranga at a distance of ~230 m. During the monitoring at MS2, the wind was again variable from SW to NW. We acknowledge that both monitoring stations were not always located directly downwind during the ventilation period due to many changes in wind directions. While this monitoring might not represent the worst-case scenario (e.g. light wind from the same direction), it represents a real ventilation event including

changes in natural factors (wind direction and speed) which affect the dispersion and concentrations of methyl bromide.

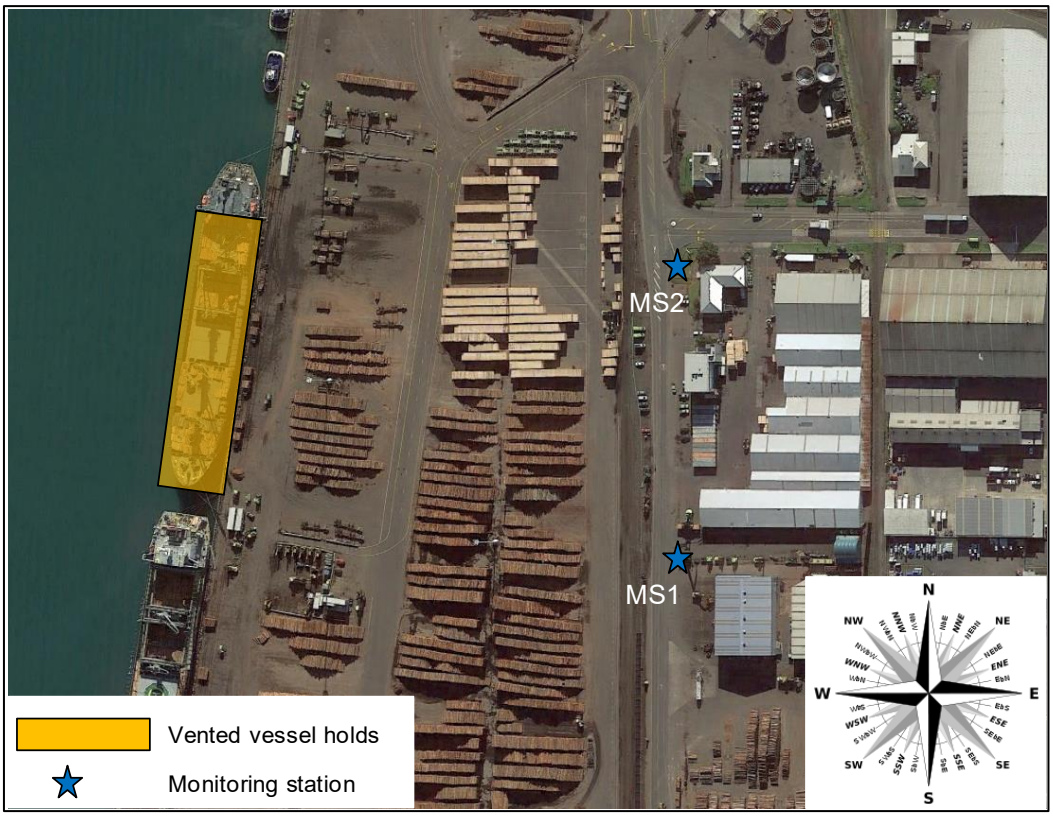


Figure 1. Land cover map of the Port of Tauranga study area with location of the fumigation area (yellow rectangles) and monitoring site (blue star).

The measurements of methyl bromide were collected and analysed by Extractive Fourier Transform Infrared spectroscopy (FTIR) following EPA method 320. This method applies to the analysis of vapour phase organic and inorganic compounds which absorb energy in the mid-infrared spectral region. This method is used to determine compound-specific concentrations in a multicomponent vapour phase sample, which is contained in a closed-path gas cell. The FTIR was zeroed with 99.999% nitrogen (N2) gas (PORTAGAS) prior to sampling and was operated per manufacturer's instructions. The lower detection limit (LDL) for an individual compound is calculated using modified classical least square (CLS) method for analysis. The calculated LDL value for methyl bromide was 0.05 ppm.

Total volatile organic compounds were simultaneously measured using two photo-ionisation devices (PIDs, Table 2) . PID 1 is a Multirae Lite detector which incorporates an air sampling pump. PID 2 is an Ion Cub Science detector which

does not include an air sampling pump and relies on diffuse sampling. The resolution of PID 2 (0.1 ppm) is lower than PID 1 (1 ppm).

Table 2. List of the photo-ionisation devices deployed at the Port of Tauranga.

ID	Brand	Pump	Range (ppm)	Sensitivity (ppm)	Accuracy (ppm)	Resolution (ppm)
PID 1	MultiRae Lite Pumped	Yes	0 - 5000	na	na	1
PID 2	Ion Cub Science	No	0 - 5000	0.001	±5 % display reading	0.1

PID and FTIR measurements were collected at the same location and permitted a direct comparison between methyl bromide and TVOC. A 1-hour running average was calculated when the monitoring was conducted for more than 1 hour. In this case, the maximum 1-hour average was kept for further comparison between TVOC and methyl bromide concentration. The coefficient of determination, R^2, between paired concentration datasets (X_i, Y_i) is calculated by using the below equation:

$$R^2 = \left[\frac{\sum_{i=1}^{n}(X_i-\bar{X})(Y_i-\bar{Y})}{\sqrt{\sum_{i=1}^{n}(X_i-\bar{X})^2}\sqrt{\sum_{i=1}^{n}(Y_i-\bar{Y})^2}} \right]^2$$

R^2 examines the integrity of the linear regression for the paired data set. Its values extend between 0 and 1. These calculations present the proportion of variance for one variable that is expected from the other variable. The recovery rate was calculated by dividing the 1-hour TVOC concentration by the 1-hour methyl bromide concentration for each ventilation event.

3 Result & Discussion

3.1 Monitoring Station 1 (MS1)

3.1.1 The 1-hour average concentration of methyl bromide and TVOC

The concentrations of TVOC and methyl bromide measured during the ventilation of ship's holds at the monitoring station MS1 are presented in Table 3. The 1-hour methyl bromide concentration (0.05 ppm) was higher than the 1-hour TVOC concentration measured with PID 1 (0.02 ppm) but lower than PID 2 (0.18 ppm). The maximum measured methyl concentration (0.43 ppm) was lower than the maximum instantaneous TVOC concentrations measured with PID 1 (0.67 ppm) and PID 2 (0.72 ppm).

Table 3. 1-hour, maximum (max) and minimum (min) Total Volatile Organic Compounds (TVOC) concentrations measured with PID 1 and PID 2, and methyl bromide concentrations measured by FTIR at the monitoring station MS1.

Measured chemicals	methyl bromide	TVOC	
Instrumentation	*FTIR*	*PID 1*	*PID 2*
1h- max average (ppm)	0.05	0.02	0.18
max (ppm)	0.43	0.67	0.72
min (ppm)	0	0	0

3.1.2 Real-time measurements of methyl bromide and TVOC

Figure 2 shows time series data collected by FTIR for methyl bromide, and PID 1 and PID 2 for TVOC during the ventilation of ship's holds. Methyl bromide concentration in the ambient air ranged from non-detectable to a maximum of 0.43 ppm at 9:39 pm. For this monitoring period, the maximum TVOC concentrations in PID 1 (0.67 ppm) and PID 2 (0.72 ppm) were also recorded at 9:39 pm. The first event of methyl bromide (0.34 ppm) was recorded when the ventilation process started. Prior 9:08 pm, TVOC concentrations in PID 1 and PID 2 were lower than methyl bromide and in most cases below the detection limit. After 9:08 pm, TVOC concentrations in PID 2 were higher than methyl bromide.

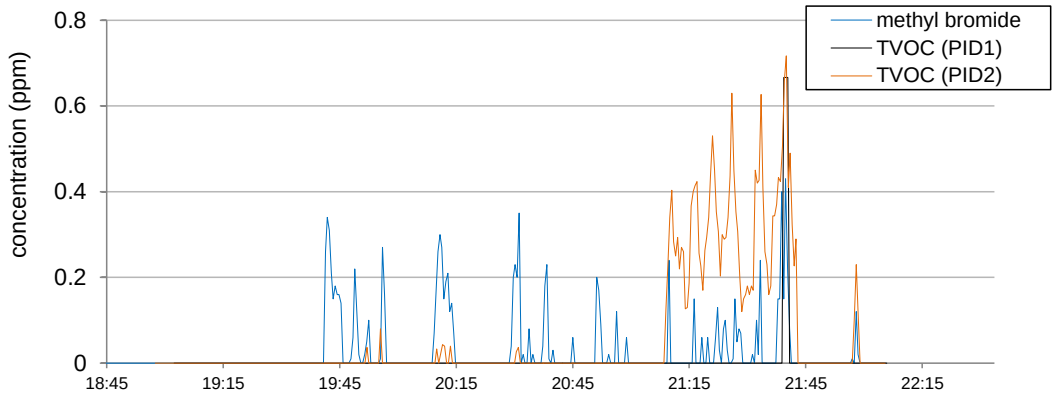


Figure 2. Time series plot comparison of the concentrations of methyl bromide and Total Volatile Organic Compounds (TVOC) measured with PID 1 and PID 2 at the monitoring station MS1.

This result demonstrated that TVOC concentrations showed different fluctuations than methyl bromide attributed to the detection limit for PID 1, and unknown factors for PID 2. Factors affecting the performance of PID 2 could be attributed to weather conditions (e.g. humidity), the presence of chemicals acting as quenching agents and other unknows parameters.

3.1.3 Correlation of Methyl Bromide vs TVOC

Figure 3 illustrates the results of a regression calculation comparing the TVOC and methyl bromide concentrations at 30s intervals. TVOC concentrations measured with PID 1 and PID 2 was not correlated with the methyl bromide measurements demonstrated by the correlation coefficients (R^2<0.1).

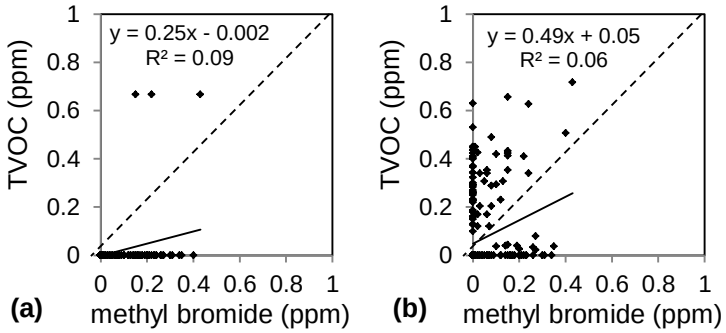


Figure 3. Scatter plot of methyl bromide compared to Total Volatile Organic Compounds (TVOC) measured with PID 1 (a) and PID 2 (b) at the monitoring station MS1. The 1:1 line (- - -) shows identical concentration.

These results demonstrated that the fluctuations in TVOC concentrations measured by PID were not correlated to the changes in methyl bromide concentrations measured by FTIR. PID 1 underestimated the methyl bromide concentration below 1 ppm due to the sensitivity and reporting range of the instrument. PID 2 underestimated the methyl bromide concentrations at the start of the monitoring (6:45 pm – 9:00 pm), and overestimated the concentrations of methyl bromide for the remaining monitoring

3.2 1-hour concentration recovery rate of methyl bromide in PID

The average recovery rate of TVOC in methyl bromide measurements is presented in Figure 4. This calculation permits estimation of the accuracy of the PID over a 1-hour sampling period: i.e. average recovery rate above 100% means that the 1-hour TVOC concentration is higher than the 1-hour methyl bromide concentration.

Percent recoveries for methyl bromide were 31% and 331% for PID 1 and PID 2 respectively. The low average recovery rate in PID 1 was due to the detection limit and reporting of the PID, and the generally lower TVOC values measured when compared to methyl bromide concentrations. The factors responsible for higher readings in PID 2 might be related to the PID technology, the release of

other chemical compounds during ventilation causing interference with the PID sensor, the physiochemical properties of methyl bromide, and/or fluctuations in unknown physical and chemical parameters.

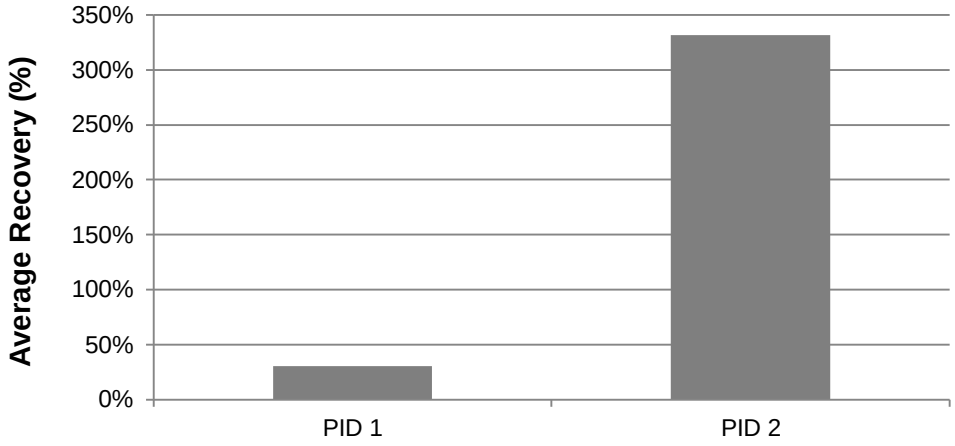


Figure 4. Average recovery of methyl bromide in 1-hour TVOC measurements by PID at the monitoring station MS1.

3.3 Monitoring Station 2 (MS2)

3.3.1 The 1-hour average concentration of methyl bromide and TVOC

The concentrations of TVOC and methyl bromide measured inside the Port of Tauranga area (MS2) during the ventilation of ship's holds are presented in Table 4. The 1-hour methyl bromide concentration (0.12 ppm) was higher than the 1-hour TVOC concentration measured with PID 1 (0.04 ppm) but lower than the 1-hour TVOC concentration measured with PID 2 (0.45 ppm). The maximum measured methyl bromide concentration (0.81 ppm) was lower than the maximum instantaneous TVOC concentrations measured with PID 1 (1.10 ppm) and PID 2 (1.64 ppm).

Table 4. 1-hour, maximum (max) and minimum (min) Total Volatile Organic Compounds (TVOC) concentrations measured with PID 1 and PID 2, and methyl bromide concentrations measured by FTIR at the monitoring station MS2.

Measured chemicals	methyl bromide	TVOC	
Instrumentation	*FTIR*	*PID 1*	*PID 2*
1h- max average (ppm)	0.12	0.04	0.45
max (ppm)	0.81	1.10	1.64
min (ppm)	0	0	0

The historical record of 1-hour average methyl bromide concentration is presented in Appendix 2. The 1-hour methyl bromide concentration was closely related to

the distance from the ventilation area which will be verified during further monitoring. The ventilation of ship's holds seems to provide better control in the release of fumigant than tarpaulins as less pronounce to be influenced by wind gust. Also the opening of ship's holds is mechanically managed in the control room which offers several advantages than tarpaulins fumigation. For example, ship's hold can be close again when levels of fumigant reach safety limits, while log stacks cannot be recovered during the ventilation process.

3.3.2 Real-time measurements of methyl bromide and TVOC

Figure 5 shows time series data collected by FTIR for methyl bromide, and PID 1 and PID 2 for TVOC during the ventilation of ship's holds. Methyl bromide concentration in the ambient air ranged from non-detectable to a maximum of 0.8 ppm at 10:28 pm and 11:21 pm. For this monitoring period, the maximum TVOC concentrations in PID 1 (1.10 ppm) and PID 2 (1.64 ppm) were recorded at 10:33 pm.

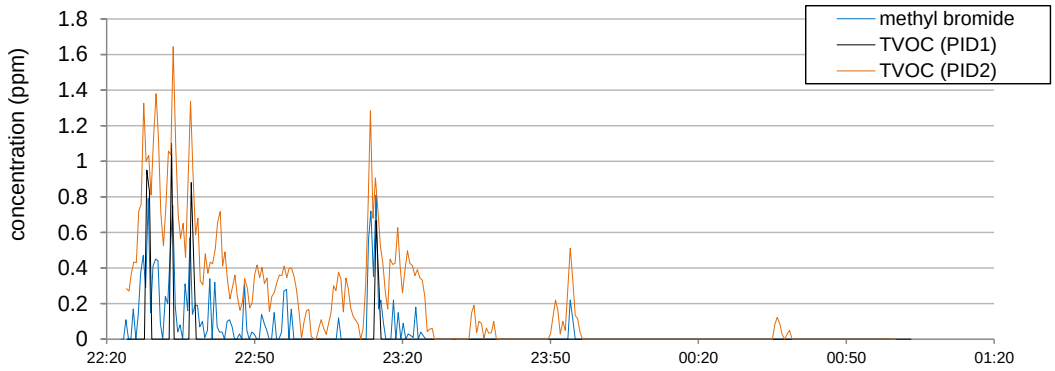


Figure 5. Time series plot comparison of the concentrations of methyl bromide and Total Volatile Organic Compounds (TVOC) measured with PID 1 and PID 2 at the monitoring station MS2.

This result demonstrated similar fluctuations in methyl bromide and TVOC concentrations over small temporal scales. However, TVOC concentrations in PID 2 was continuously higher than methyl bromide.

3.3.3 Correlation of Methyl Bromide vs TVOC

Figure 3 illustrates the results of a regression calculation comparing the TVOC and methyl bromide concentrations at 30s intervals. TVOC concentrations in PID 1 was not correlated with the methyl bromide measurements demonstrated by the low correlation coefficients (R^2=0.24). TVOC in PID 2 showed a moderate correlation with the methyl bromide measurements (correlation coefficient =

0.64), but the linear regression slope of 1.86 indicated that the PID 2 overestimated methyl bromide concentrations.

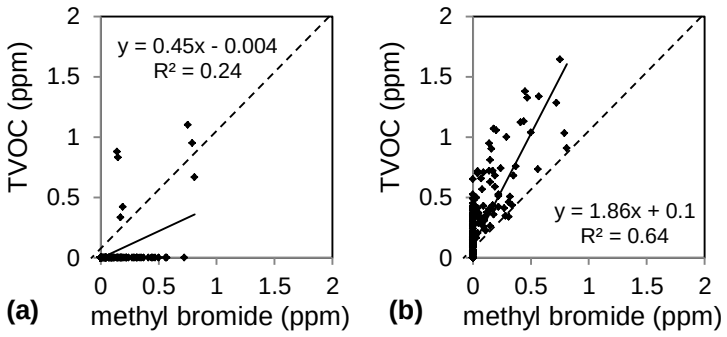


Figure 4. Scatter plot of methyl bromide compared to Total Volatile Organic Compounds (TVOC) measured with PID 1 (a) and PID 2 (b) at the monitoring station MS2. The 1:1 line (- - -) shows identical concentration.

3.3.4 1-hour concentration recovery rate of methyl bromide in PID

The average recovery rate of TVOC in methyl bromide measurements is presented in Figure 4. This calculation permits estimation of the accuracy of the PID over a 1-hour sampling period: i.e. average recovery rate above 100% means that the 1-hour TVOC concentration is higher than the 1-hour methyl bromide concentration.

Percent recoveries for methyl bromide were 33% and 375% for PID 1 and PID 2 respectively. The factors responsible for higher PIDs readings might be related to the PID technology, the release of other chemical compounds during ventilation causing interference with the PID sensor, the physiochemical properties of methyl bromide, and/or fluctuations in unknown physical and chemical parameters.

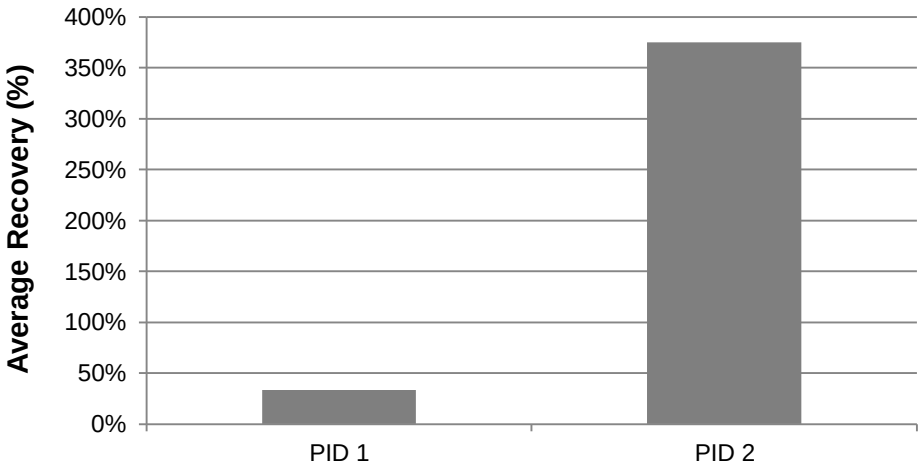


Figure 4. Average recovery of methyl bromide in 1-hour TVOC measurements by PID at the monitoring station MS2.

4 Conclusions

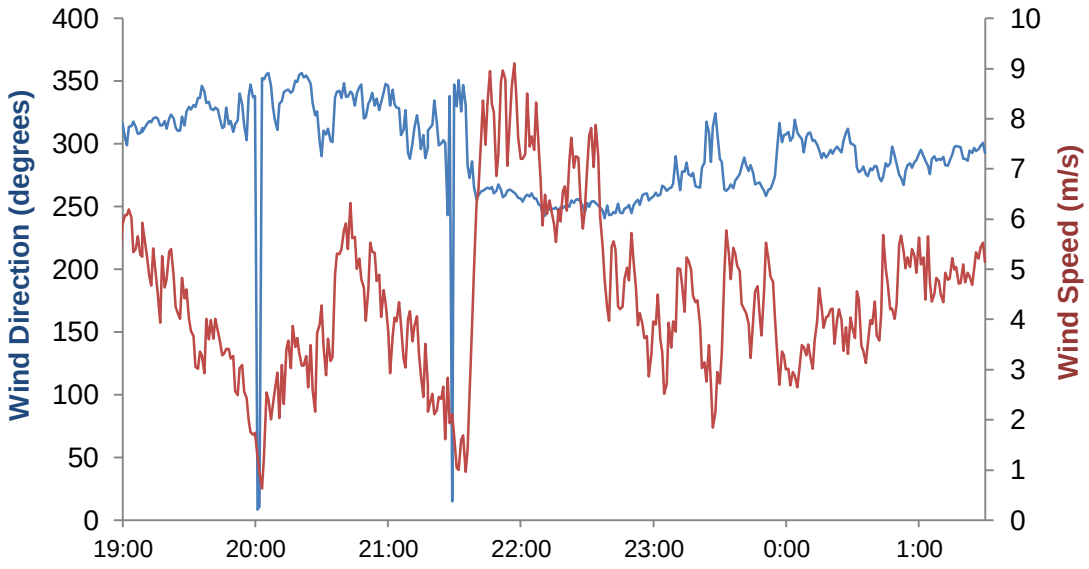
This work presents measurements of TVOC and methyl bromide concentrations collected on 21 August 2020 during the ventilation of four ship's holds at Berth 8 of the Port of Tauranga, New Zealand. Within these tests, TVOC and methyl bromide measurements were simultaneously performed in ambient air at the same location, ensuring that data is acquired and analysed under the same operating conditions. The monitoring was conducted at 2 different locations taking into consideration changes in wind direction. The sampling was conducted at monitoring station MS1 from 6:45 pm to 10:05 pm and at the monitoring station MS2 from 10:23 pm to 1:00 am. TVOC were measured using two different PID and methyl bromide measurements were performed using a FTIR analyser.

The 1-hour maximum concentration for methyl bromide at monitoring station MS1 was 0.05 ppm and higher than the 1-hour TVOC concentrations measured in PID 1 (0.02 ppm) but lower than the 1-hour average concentration in PID 2 (0.18 ppm). The 1-hour maximum concentration for methyl bromide at monitoring station MS2 was 0.12 ppm and higher than the 1-hour TVOC concentrations measured in PID 1 (0.04 ppm) but lower than the 1-hour average concentration in PID 2 (0.45 ppm). The results provided evidence of a linear relationship between methyl bromide obtained by FTIR with the PID 2 at the monitoring station MS2 only. This result was affected by the detection limit for PID 1 and other factors related to the PID technology (e.g. humidity and chemical interference).

From our observation and finding, it appears that the ventilation of ship's holds provides advantages compared to tarpaulins' fumigation which may decrease the risk for fugitive emissions and permit a better control during the ventilation process. For example, the emission rate of methyl bromide during the removal of tarpaulins are prone to be increased during wind gust which directly affects the emission rate of fumigant and concentrations in ambient air. However, the opening rate of ship's holds is not affected by wind gust which might permit better control in the release of the fumigant. Another benefit of ship's holds fumigation is that a reversal process (re-closure) can be conducted at any times when the levels of fumigant in ambient air are close to management limits. This is not practical to recover log stacks with tarpaulins and therefore tarpaulins'

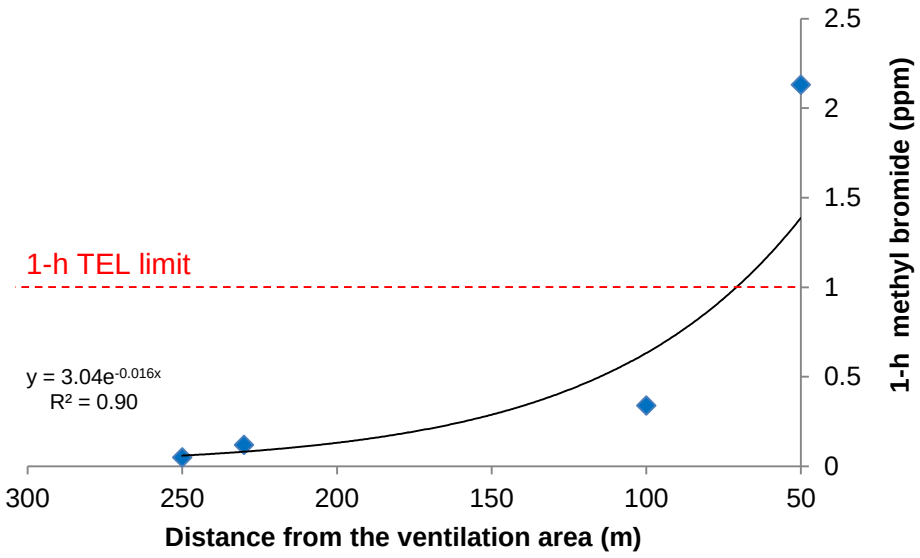
fumigation provides less control in the release of fumigant. We recommend to investigate the benefits and disadvantage of different types of enclosure that can be used to fumigate products, and to undertake further monitoring of vessel holds at different distances (e.g. 50m and 100m) to better understand the dispersion of methyl bromide during the ventilation of ship's holds.

5 Appendix 1: Real-time record of wind direction and speed recorded at berth 8, Port of Tauranga



Data provided by the Port of Tauranga

6 Appendix 2: Historical record of 1-hour average methyl bromide concentrations with distances from the ventilation areas



7 Appendix 3: Historical record of the 1-hour concentration recovery rate of methyl bromide in PID