



Environmental Assessment Report

Env-WS01- 080820

**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
Author	Dr Julien Huteau
Client	WorkSafe New Zealand
Client contract number	Env-WS01- 080820
Date	August 2020
Confidentiality requirement	Confidential (for client use only)
Intellectual property	© Ecocific Limited. All rights reserved. Unless permitted by contract or law, no part of this work may be reproduced, stored or copied in any form or by any means without the express permission of Ecocific Limited.
Disclaimer	The information and opinions provided in the Report have been prepared for the Client and its specified purposes. Accordingly, any person other than the Client uses the information and opinions in this report entirely at its own risk. The Report has been provided in good faith and on the basis that reasonable endeavours have been made to be accurate and not misleading and to exercise reasonable care, skill and judgment in providing such information and opinions. Neither Ecocific, nor any of its employees accept any responsibility or liability in respect of any information or opinions provided in this Report.

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.

PLACE: Port of Tauranga, Mount Maunganui, 08 August 2020.

METHOD: The measurements of methyl bromide and total volatile organic compounds were conducted downwind within the fumigator's risk area at the Port of Tauranga. The monitoring station was located 52 m, 60 m and 66 m from the respective ventilated log stacks. A mobile Fourier Transform Infrared Spectrometer was utilised to perform methyl bromide measurements in ambient air during the ventilation of three tarpaulins- covered log stacks. 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 was 2.13 ppm. The 1-hour maximum TVOC concentrations were 2.38 ppm and 4.01 ppm in PID 1 and PID 2 respectively, and higher than the 1-hour methyl bromide concentration. The fluctuations in methyl bromide and TVOC concentrations during the sampling period were similar demonstrated by the linear relationship between TVOC and methyl bromide ($R^2 > 0.9$). Percent recoveries for methyl bromide (i.e. ratio between TVOC and methyl bromide) were 112% and 188% in PID 1 and PID 2 respectively.

CONCLUSION: The results revealed that the fluctuations of methyl bromide and TVOC were directly related to the removal of tarpaulins during the ventilation process. TVOCs were generally higher than methyl bromide and this was more marked during the higher methyl bromide events. The concentration and dispersion of methyl bromide were mainly influenced by the wind direction. The size of the enclosure and distance between the monitoring station and vented log stacks might be a significant factor, which will be investigated further during the next monitoring events.

Table of Contents

ABSTRACT	iii
List of Figures.....	v
List of Tables.....	v
1 Introduction	1
2 Method	2
3 Result & Discussion.....	4
3.1 The 1-hour average concentration of methyl bromide and TVOC.....	4
3.2 Real-time measurements of methyl bromide and TVOC	5
3.3 Correlation of Methyl Bromide vs TVOC	6
3.4 1-hour concentration recovery rate of methyl bromide in PID	7
4 Conclusions	8

List of Figures

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).....	3
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.	5
FIGURE 3. SCATTER PLOT OF METHYL BROMIDE COMPARED TO TOTAL VOLATILE ORGANIC COMPOUNDS (TVOC) MEASURED WITH PID 1 (A) AND PID 2 (B). THE 1:1 LINE (- -) SHOWS IDENTICAL CONCENTRATION.	6

List of Tables

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).	2
TABLE 2. LIST OF THE PHOTO-IONISATION DEVICES DEPLOYED AT THE PORT OF TAURANGA.	4
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.....	5

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 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. Therefore, management strategies have been developed and implemented which include, but are not limited to, the establishment of Tolerable Exposure Limits (TEs) 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 three log stacks at the Port of Tauranga on 8 August 2020. The characteristics of the vented log stacks and weather conditions are presented in Table 1. The size of the log stacks varied from 1512 m³ to 2196 m³.

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).

08/08/20	Fumigation		Ventilation		
Log stack ID	Covered Volume (m3)	Quantity Mebr (kg)	Ventilation Time	Wind Direction	Wind Speed
DO1	2196	264	16:48	210 SSW	5.7 m/s
DO2	1920	225	16:29	176 S	2.6 m/s
DO3	1512	182	16:03	160 SSE	6.2 m/s

A monitoring station was carefully selected directly downwind from the vented log stacks (Figure 1). The monitoring station was located inside the risk area which is controlled by the fumigator and did not represent the concentrations of methyl bromide at the port boundary. The monitoring station was located at 52 m, 60 m and 66 m away from the log stacks DO3, DO2 and DO1 respectively. The wind turned from SSE to SSW during the ventilation period, and therefore the monitoring station was not located directly downwind during the venting of log stack DO1.

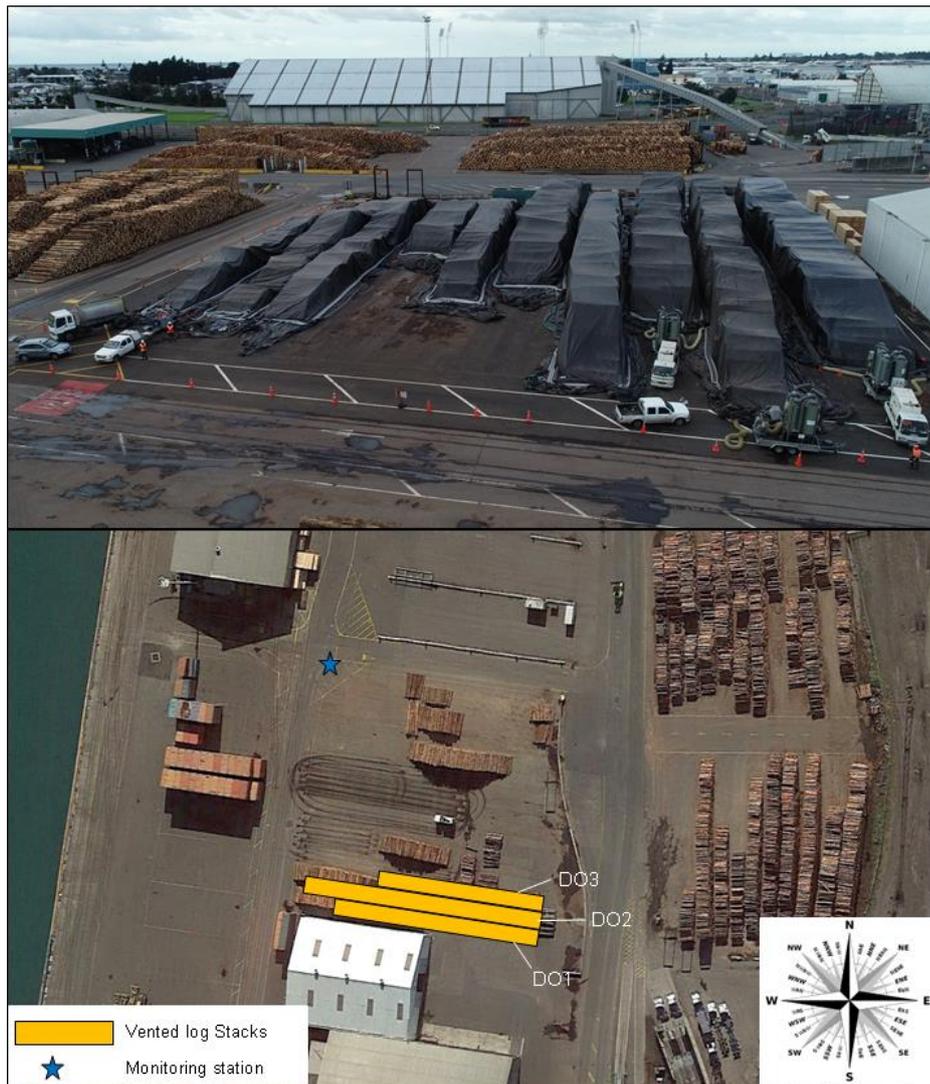


Figure 1. Land cover map of the Port of Tauranga study area with location of the fumigation area (yellow rectangles) and monitoring site (blue star).

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). A correction factor for methyl bromide was applied according to manufacturer's instructions.

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 The 1-hour average concentration of methyl bromide and TVOC

The concentrations of TVOC and methyl bromide measured inside the risk area during the ventilation of three log stacks are presented in Table 3. The 1-hour methyl bromide concentration (2.13 ppm) was lower than the 1-hour TVOC concentration measured with PID 1 (2.38 ppm) and PID 2 (4.01 ppm). The

maximum measured methyl concentration (45.35 ppm) was lower than the maximum instantaneous TVOC concentrations measured with PID 1 (68.33 ppm) and PID 2 (90.73 ppm). This result showed that PID 1 had a lower maximum instantaneous concentration than PID 2 and thus was more accurate for the measurements of a methyl bromide spike.

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.

Measured chemicals	methyl bromide		TVOC	
	Instrumentation	FTIR	PID 1	PID 2
1h- max average (ppm)		2.13	2.38	4.01
max (ppm)		45.35	68.33	90.73
min (ppm)		0.00	0.00	0.04

3.2 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 three log stacks. Two significant methyl bromide events were identified and attributed to the removal of tarpaulins. The ventilation of the last log stack DO1 was not correlated to an increase in methyl bromide concentration due to a slight change in wind direction.

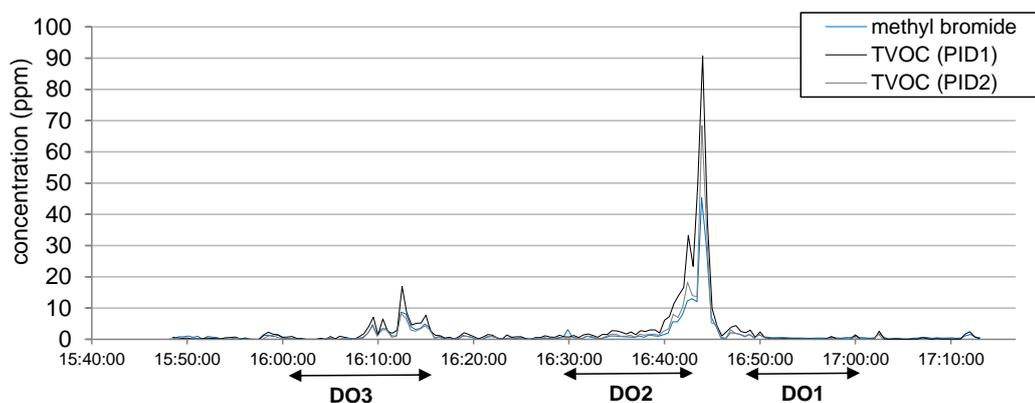


Figure 2. Time series plot comparison of the concentrations of methyl bromide and Total Volatile Organic Compounds (TVOC) measured with PID 1 and PID 2.

The first event of methyl bromide showed a maximum concentration of 5.42 ppm and related to the ventilation of log stack DO3. TVOC concentrations increased to a maximum of 8 ppm and 16.94 ppm for PID 1 and PID 2 respectively. The second event of methyl bromide showed a maximum concentration of 45.35 ppm at 4.44 pm. TVOC concentrations increased to a maximum of 68.33 ppm and

90.73 ppm for PID 1 and PID 2 respectively. TVOC concentrations measured with PID 1 and PID 2 showed similar fluctuations to methyl bromide.

This result demonstrated that the fluctuations in methyl bromide and TVOC concentrations over small temporal scales were directly related to fumigation activities and especially the removal of tarpaulins, with wind direction affecting the dispersion of fumigant in ambient air. Methyl bromide concentrations decreased rapidly after the tarpaulins were removed. The methyl bromide concentrations were higher during the removal of tarpaulin DO2 which could be related to the different sizes of log enclosures. The enclosure for log stack DO2 (1920 m³) was greater than the enclosure for log stack DO3 (1592 m³). However, this finding will need to be confirmed by further monitoring.

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. The PID 1 correlated well with the methyl bromide measurements (correlation coefficient = 0.97), but the linear regression slope of 1.36 indicated that the PID 1 overestimated methyl bromide concentrations. The result shows that PID 2 tracked the methyl bromide measurements well with a linear regression slope of 1.89, an intercept of -0.15 ppm, and a correlation coefficient of 0.90.

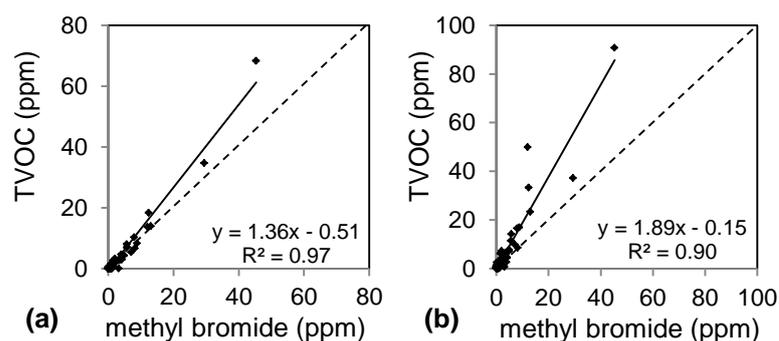


Figure 3. Scatter plot of methyl bromide compared to Total Volatile Organic Compounds (TVOC) measured with PID 1 (a) and PID 2 (b). The 1:1 line (- -) shows identical concentration.

These results demonstrated that the fluctuations in TVOC concentrations measured by PID were correlated to the changes in methyl bromide concentrations measured by FTIR. However, both PIDs demonstrated higher TVOC concentrations which were more marked during the spike of methyl

bromide. This finding could be related to the release of volatile organic compounds other than methyl bromide from the logs such as α pinene and β pinene.

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 112% and 180% 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. Further monitoring will permit better understanding of the main factors responsible for differences between the two sensors.

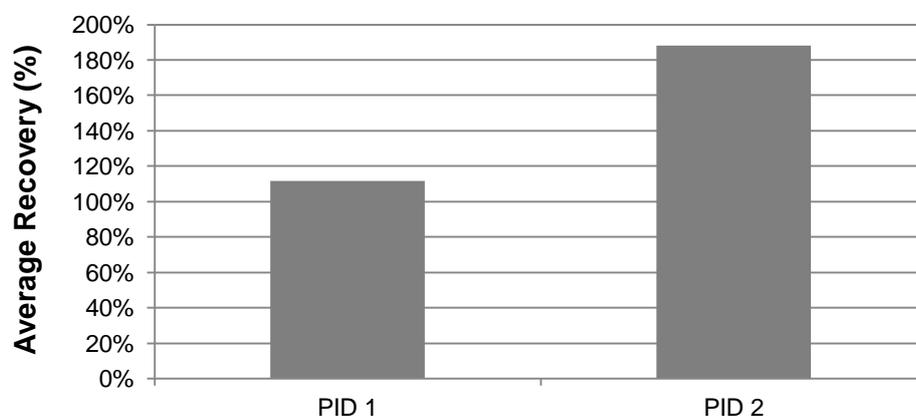


Figure 4. Average recovery of methyl bromide in 1-hour TVOC measurements by PID.

These results showed that PID technology has some limitations in detecting the concentration of a specific chemical compound accurately but still offers conservative management of potential methyl bromide levels.

4 Conclusions

This work presents measurements of TVOC and methyl bromide concentrations collected on 08 August 2020 during the ventilation of three log stacks at 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. 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 was 2.13 ppm and higher than the 1-hour TVOC concentrations measured in PID 1 (2.38 ppm) and PID 2 (4.01 ppm). The results revealed that the fluctuations of methyl bromide were related to the removal of tarpaulins. The results provided evidence of a linear relationship between methyl bromide obtained by FTIR with the PID. However, TVOC concentrations were generally higher than methyl bromide during the monitoring period, which was more marked during the methyl bromide events (spike). Methyl bromide concentrations were higher during the removal of log stack DO2 than during the removal of log stack DO3, which could be related to the different size of the enclosures. Further monitoring will permit better understanding of the specific effect of enclosure' volume on methyl bromide levels during ventilation after fumigation.