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

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Report information sheet

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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, 09 August 2020.

METHOD: The measurements of methyl bromide and total volatile organic compounds were conducted downwind at the site boundary of the Port of Tauranga. The monitoring station was located ~100 m from the ventilated log stacks. A mobile Fourier Transform Infrared Spectrometer was utilised to perform methyl bromide measurements in ambient air during the ventilation of seven 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 0.34 ppm. The 1-hour maximum TVOC concentrations were 0.12 ppm and 0.27 ppm in PID 1 and PID 2 respectively, and lower than the 1-hour methyl bromide concentration. The fluctuations in methyl bromide and TVOC concentrations during the sampling period were disparate demonstrated by the moderate linear relationship between TVOC and methyl bromide (R^2=0.6). Percent recoveries for methyl bromide (i.e. ratio between TVOC and methyl bromide) were 36% and 79% in PID 1 and PID 2 respectively.

CONCLUSION: The results revealed that the fluctuations of methyl bromide were directly related to the removal of the gas-tight sealants and tarpaulins during the ventilation process. TVOC were generally lower than methyl bromide and this was more marked during the measurements of low levels of methyl bromide (<0.8 ppm). Methyl bromide concentrations were significantly higher during the removal of 1 log stack (DO8), which could be due to a change in atmospheric conditions, the location of the vented log stack and/or the quantity of fumigant remaining inside the enclosure before the ventilation.

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1 Introduction

Methyl bromide, also known as bromomethane (CH_3Br) is a fumigant currently used in New Zealand for the 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 of the methyl bromide is used on forest products (~94%) fumigated inside tarpaulins and vessel holds, and the remaining proportions are applied on small 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 (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 and utilising Ecocific aerial and mobile capability to provide information on the dispersion of the measured 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 seven log stacks at the boundary of the Port of Tauranga on 9 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 540 m^3 to 1346 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).

9/08/2020	Fumigation		Ventilation		
Log stack ID	Covered Volume (m3)	MeBr (kg)	Vent Time	Wind Direction	Wind Speed (m/s)
DO4	1536	185	16:50	267 W	1.5
DO5	1346.4	162	16:30	261 W	7.5
DO6	748.8	90	15:53	281 WNW	4.7
DO7	540	65	15:35	292 WNW	3.6
DO8	640	77	15:06	247 WSW	3.4
DO9	576	70	14:35	235 SW	3.7
DO10	374.79	45	14:18	257 WSW	4.2

A monitoring station was carefully selected directly downwind from the vented log stacks (Figure 1). The monitoring station was located 100 m (DO10) to 110 m (DO4) from the log stacks at the boundary of the Port of Tauranga.

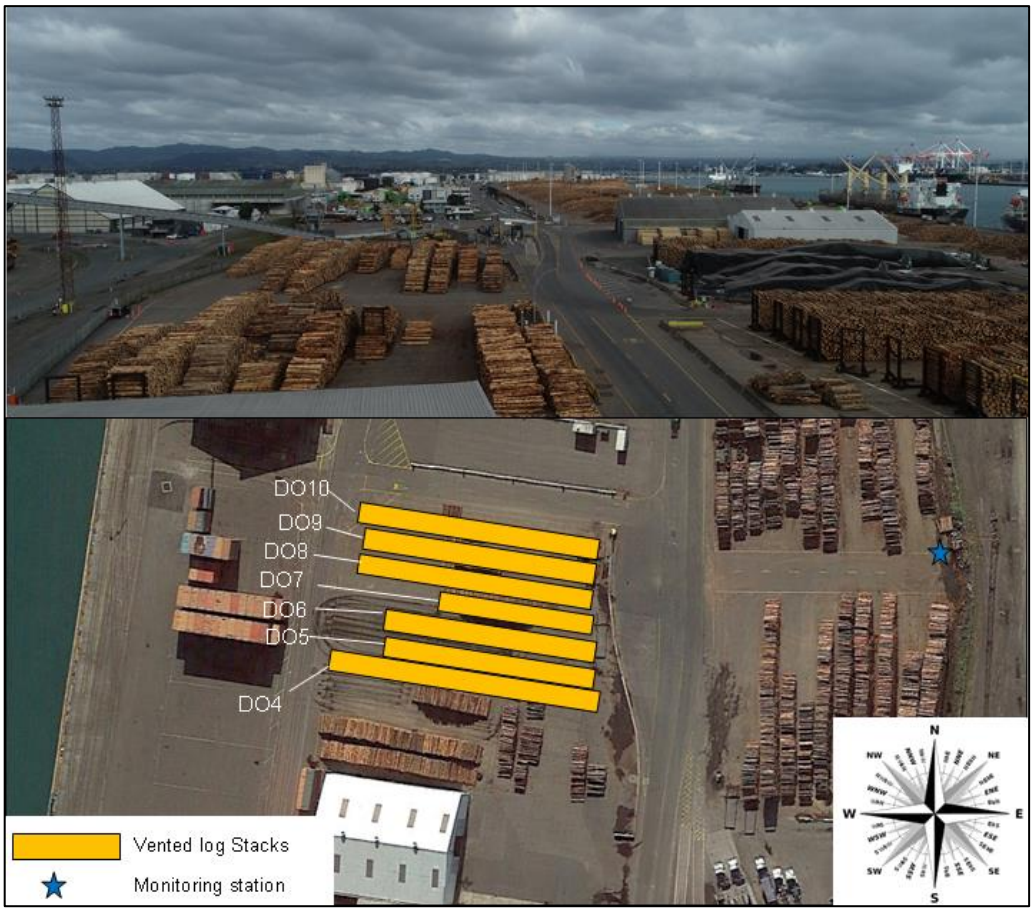


Figure 1. Land cover map of the Port of Tauranga study area with location of the fumigation area (yellow rectangles) and monitoring site (blue star).

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 PID (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 rely 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 equation below:

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

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 at the port boundary during the ventilation of seven log stacks are presented in Table 3. The 1-hour methyl bromide concentration (0.34 ppm) was higher than the 1-hour TVOC concentration measured with PID 1 (0.12 ppm) and PID 2 (0.27 ppm). The maximum measured methyl bromide concentration (4.14 ppm) was higher than the maximum instantaneous TVOC concentration measured with PID 1 (0.12 ppm) but lower than the maximum concentration of 5.09 ppm in PID 2.

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)	0.34	0.12	0.27
max (ppm)	4.14	3.33	5.09
min (ppm)	0.00	0.00	0.00

The historical record using the same instrumentation of 1-hour average methyl bromide concentrations is presented in Appendix 1. The 1-hour methyl bromide concentration at 50 m from the ventilated log stacks (2.13 ppm) was higher than the 1-hour methyl bromide concentration (0.34 ppm) measured at 100 m. Further monitoring will permit to understand better the effects of buffer zones and quantity of methyl bromide vented on the 1-hour methyl bromide levels.

3.1.1 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 seven log stacks. Methyl bromide in the ambient air ranged from non-detectable to a maximum of 4.14 ppm at 15:11 during the ventilation of log stack DO8.

The first increase of methyl bromide (0.36 ppm) and recorded at 13:48 was related to the removal of the sealants (water tubes) around the tarpaulins. The concentrations of methyl bromide increased during the ventilation of all log stacks to reach a value of 0.5–0.8 ppm except for log stack DO8. During the ventilation of log stack DO8, the methyl bromide concentrations increased to 4.14 ppm which was approximately 6 times higher than the maximum concentrations measured for the other vented log stacks. TVOC concentrations measured with PID 1 remained below the detection limit for all vented log stacks except during the ventilation of log stack DO8 (3.33 ppm). This finding was due to the resolution of this PID which is unable to record concentration lower than 1 ppm. TVOC measured with PID 2 responded to 4 ventilation events and generally showed TVOC concentrations lower than methyl bromide, except during the ventilation of log stack DO8 (5.09 ppm). This finding demonstrated that both PIDs did not detect low concentrations of methyl bromide (0-0.8 ppm).

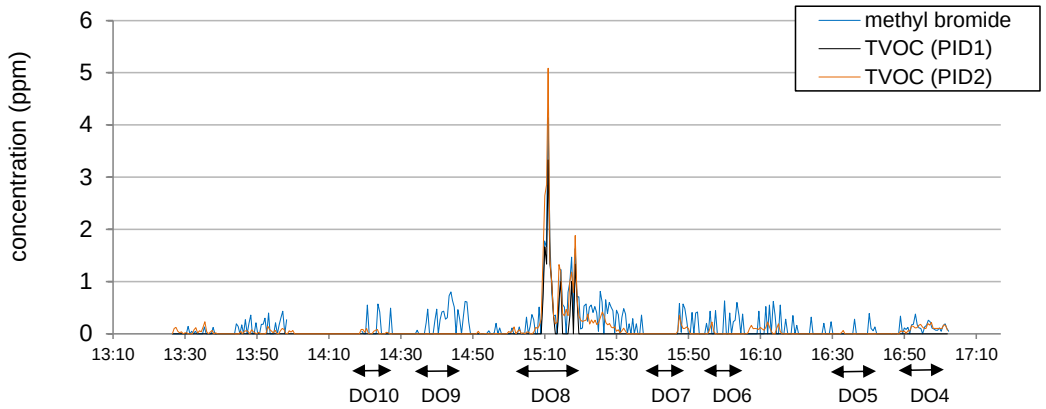


Figure 2. Time series plot comparison of the concentrations of methyl bromide and Total Volatile Organic Compounds (TVOC) measured with PID 1 and PID 2.

This result demonstrated that the fluctuations in methyl bromide were directly related to fumigation activities and especially the removal of gas-tight sealants and 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 DO8 which has a covered volume of 640 m^3. This volume was similar to the adjacent log stacks DO7 and DO9 and therefore it is unlikely that these differences were related to different sizes of enclosure around each stack, but rather affected by local wind patterns influencing the dispersion of fumigant in ambient air.

3.1.2 Correlation of Methyl Bromide vs TVOC

Figure 3 illustrates the results of a regression calculation comparing the TVOC and methyl bromide concentrations at 30 s intervals. The PID 1 showed a moderate correlation with the methyl bromide measurements (correlation coefficient = 0.65), but the linear regression slope of 0.56 indicated that the PID 1 underestimated methyl bromide concentrations. The result displayed similar results for PID 2 with a linear regression slope of 0.90, an intercept of -0.06 ppm, and a correlation coefficient of 0.66.

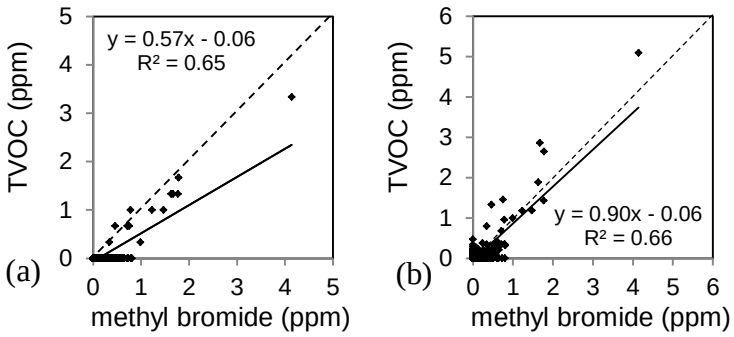


Figure 3. Scatter plot of methyl bromide compared to Total Volatile Organic Compounds (TVOC) measured with PID 1 (a) and PID 2 (b). The 1:1 line (- - -) shows identical concentration.

These results demonstrated that the fluctuations in TVOC concentrations measured by PID were moderately 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 shower a better fit with methyl bromide, however some of the low methyl bromide concentrations events remained undetected by the PID.

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 36% and 79% 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. PID2 had a closer recovery rate with methyl bromide due to a lower detection limit (<1 ppm) but higher TVOC values were recorded during the spike of methyl bromide.

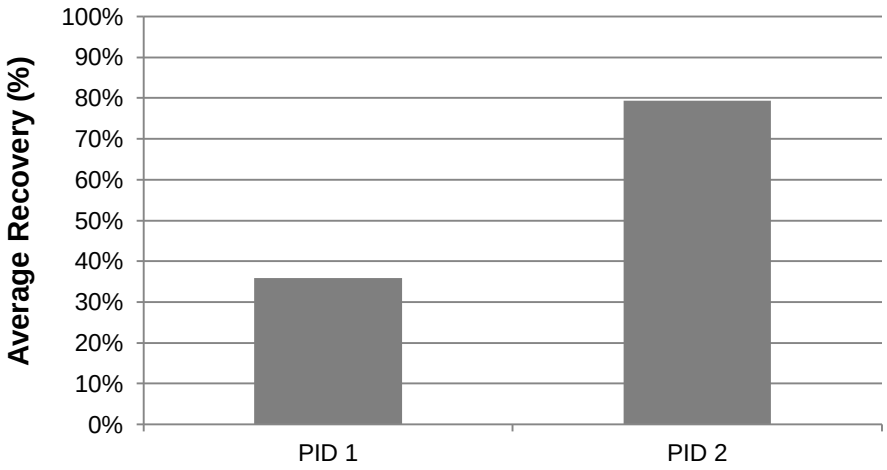


Figure 4. Average recovery of methyl bromide in 1-hour TVOC measurements by PID.

The recovery rate calculated for previous monitoring using the same instrumentation was higher than during the monitoring conducted on 09 August 2020 (Appendix 2). This can most likely be attributed to differences in methyl bromide levels, with higher concentrations measured on 08 August 2020. Further monitoring will permit further explanation of the effects of weather conditions and methyl bromide levels on the accuracy of PIDs to detect and measure methyl bromide.

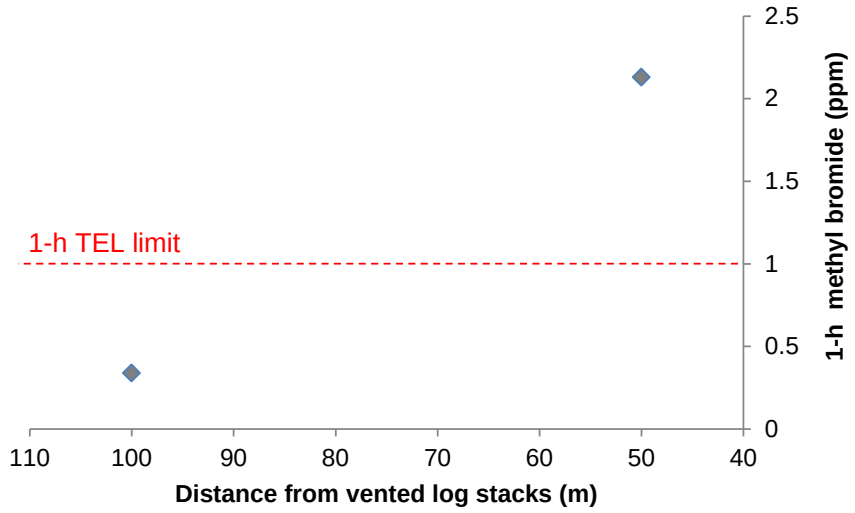
4 Conclusion

This work presents measurements of TVOC and methyl bromide concentrations collected on 09 August 2020 during the ventilation of seven log stacks at the boundary 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. 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 0.34 ppm and higher than the 1-hour TVOC concentrations measured in PID 1 (0.12 ppm) and PID 2 (0.27 ppm). The results revealed that fluctuations of methyl bromide were related to the removal of the gas sealants and tarpaulins. The results provided evidence of a linear relationship between methyl bromide obtained by FTIR with the PIDs. However, TVOC concentrations were generally lower than methyl bromide during the monitoring period, which was more marked during the measurements

of low levels of methyl bromide (<0.8 ppm). Methyl bromide concentrations were much higher during the removal of the cover from log stack DO8 than other log stacks, which could be related to the atmospheric conditions, location of the vented log stacks and/or the quantity of fumigant remaining at the end of the fumigation process.

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



6 Appendix 2: Historical record of the 1-hour concentration recovery rate of methyl bromide in PID