



Workplace Group, Occupational Safety and Health Service

Monitoring Report: Use of Methyl Bromide at the Port of Nelson

May 2005

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Quality Assurance Statement	
Workplace Group, Occupational Safety and Health Service	Prepared by: Mike Lewis Occupational Hygiene Specialist, Workplace Group
Monitoring Report: Use of Methyl Bromide at the Port of Nelson	Peer Reviewed By: Derek Stannard, MWH New Zealand Ltd
Project Sponsor: Keith Stewart, Service Manager BSU, Workplace Group	Approved for issue by: Mike Cosman, Manager National Operations, Workplace Group, May 2005

Department of Labour, Workplace Group
Occupational Safety and Health Service
3rd Floor, 203-209 Willis Street
PO Box 27-463
Wellington, New Zealand
PH 04 385 7771
FX 04 382 9159

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1. Background

1.1 Introduction

Residents and businesses adjacent to the Port of Nelson had raised concerns about the potential for exposure to methyl bromide during the fumigation operation undertaken at Shed 2. Some have attributed health concerns to the practice of releasing the fumigant into the general environment, and have described various odours and health symptoms immediately after the covers are removed from the fumigated sawn timber stacks.

Recently, the Regional Public Health Unit have been undertaking a cluster study of motor neuron disease (MND) deaths in Nelson. One goal of the study was to determine whether a causal link could be established between MND and exposure to methyl bromide, and whether the incidence of MND in Nelson has increased against the national average.

Bio-security agreements with export countries dictate that raw logs and sawn pinus radiata timber products are fumigated during the *Arhopalus trisis* (burnt pine beetle) flying season from October to March each year. The adult beetles shelter in the stacks of timber, and if introduced, could cause damage to overseas domestic timber production.

Historically, the fumigation operation had been undertaken in two locations at the Port of Nelson; Shed 2 and the ANZTA shipping store, both positioned at the western and eastern borders of the port respectively.

Occupational Safety and Health were to undertake an assessment of the Shed 2 fumigation operations, however the planned survey was postponed as the operation was moved to Shed 3 after a meeting held at the Port on the 4th of March. (See Figure 3, appendices, page 26)

The move was planned to occur in November 2005, however the timeline was brought forward due to

- a) The withdrawal of the ANZTA Shipping Company from the Port of Nelson; ANZTA undertook parallel fumigation operations at the port. Their withdrawal meant that the two fumigation operations were combined into one location and Shed 2 was identified as no longer suitable for the task due to the increased quantity of timber.
- b) The identified need for more efficient extraction ventilation system to meet the projected increased quantities of methyl bromide now to be used for the fumigation of the combined timber stacks.

As a result, the survey undertaken between the 14th and the 18th of March 2005 was performed on the new Shed 3 location.

It should be noted that due to the changes in the operation, it would be difficult to draw a conclusion from historical factual or anecdotal evidence regarding the possible exposure of workers or others to methyl bromide as a result of the Shed 2 operation.

2. Purpose

To evaluate methyl bromide exposure to workers at the Port of Nelson, from the fumigation operation undertaken at Shed 3.

2.1 Port of Nelson Activities

2.1.1 Sawn Timber Fumigation

The timber is delivered to Shed 3 some 12 to 24 hours prior to shipping. This allows for the fumigation, off-gassing, and uncovering of the timber in time for load-out which must be performed during daylight hours when the beetle is less active and is not attracted to the port lights.

Prior to work, signs are erected to alert port staff and visitors about the fumigation, and expected ventilation date and time.

Polyethylene tubing is placed in the stacks before the timber is covered with a non-permeable plastic sheeting or tarpaulin. Multiple sheets are battened and clipped together to provide a gas tight seal. The edge of the sheeting is weighed down with a water-filled tubing to prevent leakage of methyl bromide. This acts as a physical barrier to the insects in addition to the chemical barrier afforded by an insecticide surface-spray applied at the edges of the sheeting.

Methyl bromide, when compressed, becomes a liquid state and remains so when released from the storage cylinder. To ensure a full conversion from the liquid to the gas phase, the material is heated via a hot water immersed coil. The resulting gas is delivered to the stack via a manifold and polyethylene tubing. The methyl bromide cylinder is weighed pre and post delivery to ensure the correct amount of gas is introduced to the stack. Quantities of 170-280 kg of gas are often required to achieve the under cover concentration of 48gm/m³ (approximately 1000ppm).

The operators detect for leaks or tears in the cover using a halide meter or photo-ionising detector (PID). Holes in the fabric are repaired, and post detection is performed to confirm the presence of a gas tight seal.

The shed is then closed and locked, with signs at the entrances to the building warning of fumigation is in progress. A holding period of 12 – 24 hours is placed on the shed to ensure effective fumigation of the timber.

Once the holding period has passed, and prior to ventilation of the stacks, an exclusion zone of 50 meters is set around Shed 3; the 50-meter exclusion zone is an arbitrary distance that was agreed to in the Port of Nelson users forum, and the Port Code of Practice.

When the immediate area has been cleared of port staff and visitors, fumigation staff enter the shed wearing Self Contained Breathing Apparatus (SCBA).

The water tubing is drained, and the timber is ventilated with the assistance of an extraction fan located at one end of the stack. The fan draws fresh air the full length of the stack, and is exhausted via an 11m high flue into the atmosphere.

When ventilation is completed, the remaining doors of the shed are opened, and the covers are withdrawn from the stack either by hand, or via a forklift.

Gas testing is undertaken using either a Photo Ionization Detector (PID) or colorimetric tubes to determine the residual levels of methyl bromide in the atmosphere inside and immediately adjacent to the shed. The fumigation staff gives clearance for entry by port staff and stevedores only when atmospheric levels are below the agreed standard (currently 5ppm methyl bromide).

The operators wear Full Face Masks with AX methyl bromide canisters or Self Contained Breathing Apparatus during operations where there is a risk of exposure to methyl bromide; i.e. during the gas introduction, leak detection, gas release and post fumigation clearance phases of the operation.

2.1.2 Staggered fumigation.

The common fumigation withholding period and concentration is 12 hours at 48gm/m³ for general export commodities. However, 'sterilisation' fumigation is required for stacks of timber that have been held at the sawmill for an extended period of time. In this case, the stacks are fumigated at 80gm/m³ and withheld for a minimum of 24 hours.

So that both lots of timber are available for a scheduled shipping date, the sterilisation and normal fumigations are staggered. This requires the operator to introduce methyl bromide into the sterilisation stack, then return 12 hours later to conduct the fumigation of the normal export timber stack.

As there is a potential risk of exposure to errant concentrations of methyl bromide in the general shed environment, the operators wear SCBA during the preparation and fumigation of the 12 hour stack; i.e. the process of cover placement, clipping, seal placement, and during the gas introduction phase as mentioned previously.

2.1.3 Raw Timber Fumigation

A similar operation is undertaken at the port for raw logs. The logs that are to be loaded on the ships deck are fumigated under covers whilst those logs to be loaded below deck are typically treated at sea with aluminium phosphide.

This operation falls outside of the scope of the report, and will require a separate assessment at a later date.

2.1.4 Shipping Container Fumigation

Containers are fumigated in-situ. The gas is introduced in a similar manner as the timber stacks, with the containers being sealed for a period of 12 hours prior to the doors being opened and the gas released.

Exclusion zones and warning signs are posted near the containers during the operation.

This operation falls outside of the scope of the report, and will require a separate assessment at a later date.

2.1.5 Storage

When not in use, the methyl bromide cylinders are secured in a container adjacent to the fumigation shed, or on an enclosed and locked trailer. Both the container and trailer have signage alerting to the presence of methyl bromide. Only fumigation staff has access to the container and trailer.

Full cylinders are collected from the Mainfreight depot, and empties returned for shipping and refilling overseas.

The cylinders are under constant supervision during the fumigation process.

2.1.6 Timber Export Volumes

In 2003, the Port of Nelson exported a total of 184,429 m³ of sawn and raw timber to China (111,760) and Australia (72,669)¹.

2.1.7 Usage Rates

Sawn timber is treated at a concentration of 48 gm/m³ for export to Australia; raw logs are treated at a higher rate of 120gm/m³ for the Chinese market.

This equates to approximately 196.41 tonnes of methyl bromide used at the port for the year 2003.

By comparison, the New Zealand's' usage rate is 0.3% of the estimated worldwide tonnage of methyl bromide used (65,304 tones); United States is the majority user at 22,700 tonnes.

3. Methodology

Literature searches were undertaken to determine the toxicity and human health effects of methyl bromide, its worldwide application, production and use, concentrations applied to various commodities prior to export, the method of delivery, and physical characteristics of methyl bromide.

Information was sought from the fumigator (Genera / Nelson Pest Control) regarding their procedures and work practices, withholding and clearance times, and the application of the Port of Nelson Code of Practice.

¹ Glassey, K; Issues Paper for Methyl Bromide, 11 January 2005, Ministry of Agriculture and Fisheries, New Zealand Government.

A site meeting was held between the fumigator, Port of Nelson, the stevedoring services, Port Safety Officer, and Applied Research Services Limited. The meeting outlined the sampling methodology, the location of the ships and port operations relative to Shed 3, and to determine the ventilation start time in order to accommodate the arrival of the car carry ship and the post fumigation load out of timber from Shed 2 and Shed 3 (See Figure 3, appendices, page 26).

A preliminary site visit was conducted to mark the internal and external data set locations, and to map the area (See figure 6, appendices, page 29).

Information was sought from Applied Research Services Limited regarding past sampling and analysis surveys conducted at the Port.

Selected gas detection technologies were assessed for their performance in the field. Their limitations of detection and error ranges were taken into account during the measurement of the methyl bromide, and are discussed further in this report.

The calibration certificates and serial numbers for photo ionization detectors (i.e. ToxiRAE and MultiRAE plus) were inspected and recorded.

4. Risk Assessment

4.1 Methyl bromide

Synonym: Bromomethane

CAS RN No: 74-83-9

UN: 1062

Chemical formula: CH₃Br

Molecular Weight: 94.95

State: liquefied gas, in pressure cylinders

Relative density (air=1): 3.27 (heavier than air)

Calculated relative density during fumigation (air =1): 1.028 (slightly heavier than air)

Evaporation rate: very fast

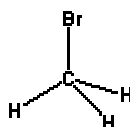


Figure 1. Chemical structure of methyl bromide

A highly toxic fumigant used for soils, grains, silos, mills, warehouses, vaults, ships, buildings, and rail cars, shipping containers, motor vehicles and general commodities². Most commonly used to fumigate against insect pests and rodents under import and export bio security agreements.

² Extoxnet, Extension Toxicology Network, Pesticide Information Profiles, Methyl Bromide; Bromomethane, June 1996

Methyl bromide has 99.5% purity, with hydrogen bromide and water vapour making up the other 0.5%. It is a colourless and odourless liquefied gas, with a chloroform-like odour in high concentrations.

Typically the fumigation rates for export to Australia and Europe range from 48gm/m³ (for 12 hours holding time) for general fumigation to 80gm/m³ (held for 24 hours) for sterilisation. On occasion, a rate of up to 120gm/m³ has been used for markets in China and in America, though these levels are likely to drop after consultation with the source countries has been completed³.

4.2 Sources of Production of Methyl Bromide

Currently three producers account for 71% of the world supply of methyl bromide; these are the Albemarle Group and Great Lakes Chemical Corporation (USA) and the Dead Sea Bromine Company (Israel). Autofina S.A. (France) is currently the only producer of methyl bromide for Western Europe⁴.

World production of methyl bromide has steadily decreased over the years. Bromine (from which methyl bromide is derived) is produced in the following countries (in descending order); United States of America 39%, Israel 38%, China 8%, the United Kingdom 6%, and other countries 9%.

The USA was the leader in the bromine production, accounting for approximately 71% of the worlds total supply in 1973; that figure has steadily dropped over the last few years in attempt to meet the Montreal Protocol for the reduction in ozone depleting halides by 2005.

However extensions for certain agricultural uses of methyl bromide have been granted for some countries until 2015, where there is no technically or economically feasible alternative available for fumigation of commodities.

4.3 Toxicology of Methyl Bromide

Methyl bromide gas is rapidly absorbed by inhalation, and distributed to a number of organ systems, which include the lungs, adrenal glands, kidneys, nasal turbinate, brain, testes and lipid tissue⁵

The central nervous system is a principle target of methyl bromide, with symptoms of nausea, headache, dizziness, lassitude, numbness of the extremities, confusion and feelings of weakness being displayed some 2-12 hours after inhalation. Changes in electroencephalograms (EEG) may be displayed on testing⁶.

³ (<http://www.biosecurity.govt.nz/exports/forests/index.htm>)

⁴ Phyllis A. Lyday; Bromine; U.S. Department of the Interior, U.S. Geological Survey Minerals Information, 14.1 – 14.7. (<http://minerals.usgs.gov/minerals/pubs/commodity/bromine/130498.pdf>)

⁵ International Program on Chemical Safety (IPCS) Health and Safety Guide No. 86, methyl bromide, World Health Organisation, Geneva 1994

⁶ Methyl Bromide Risk Characterization Document, Volume 1 'Inhalation Exposure'. Medical Toxicology, Worker Health and Safety, and Environmental Monitoring and Pest Management Branches, Department of Pesticide Regulation, California Environmental Protection Agency, February 14, 2002.

No severe effects on the nervous system for those exposed to low-level concentrations of methyl bromide over a long period of time have been noted in humans, however animal studies have shown injury can occur⁷.

The half-life of methyl bromide in blood (as the bromine ion) is 2-15 days (average of 12 days) with normal levels in serum or plasma given at <15mg/L. Those exposed typically show levels of up to 80mg/L, with toxic levels estimated at 150 – 400 mg/L. Methanol can also be present as a metabolite.

Methyl bromide is eliminated from the body via the lungs (4-20% as unmetabolised parent compound, and 30-50% and carbon dioxide) and the urinary system (16-40%)⁸.

4.4 Possible Route of Human Exposure

Occupational exposure to methyl bromide occurs principally through inhalation and the gas and dermal absorption of the liquid⁹. Oral ingestion is not a likely source of exposure in the occupational environment.

5. Monitors

5.1 Direct Reading Instruments.

Currently there are three direct reading instruments used to detect the presence of methyl bromide; the Halide Lamp, Photo Ionization Detector and Colorimetric tubes.

5.1.1 Halide Lamps

The halide lamp has been in use for a number of years as a leak detector. The 'lamp' is a butane flame that draws contaminated air into the base of the gas ring, which in turn changes the colour of the flame from blue to shades of green in the presence of halides such as methyl bromide.

The limitation of the instrument is that the colour change in the flame does not occur until the background levels are at or above 30ppm, which is significantly higher than the current Workplace Exposure Standard (WES) of 5ppm. In addition, workers that are red-green colour blind may not detect the subtle colour change in the flame, and misinterpret the absence / presence of the gas as a result.

⁷Health effects, (excerpt from Toxicological Profile for Bromomethane, ATSDR 1992), (<http://www.eco-usa.net/toxics/brometh.shtml>) cited Terr-o-gas 57, Methyl Bromide, Bromomethane; Human Toxicity Excerpts, peer reviewed. (<http://www.frankmckinnon.com/terr.htm>).

⁸ International Program on Chemical Safety (IPCS), Methyl Bromide (PIM 340). INCHEM 11/2/2004. (<http://www.inchem.org/documents/pims/chemical/methbrom.htm>).

⁹ ToxFAQs for Bromomethane (September 1995) (<http://www.atsdr.cdc.gov/tfacts27.html>) cited Terr-o-gas 57, Methyl Bromide, Bromomethane; Human Toxicity Excerpts, peer reviewed. (<http://www.frankmckinnon.com/terr.htm>).

Although an industry standard, the use of the halide lamp for monitoring should be discouraged in favour of more accurate direct reading electronic halide meters.

5.1.2 Photo Ionization Detector (PID)

The PID measures volatile organic compounds (VOC) and other toxic gases in concentrations from as low as parts per billion (ppb). The detector is sensitive to a range of chemicals, and does not typically distinguish one chemical from another.

The PID uses ultraviolet light to ionize the sample gas in positive and negative ions, which are then counted by the detector. The charged particles produce a current that is amplified and displayed on the meter in parts per billion (ppb) or parts per million (ppm)¹⁰.

The particles recombine, and the gas sample exits the meter unchanged, which allows the meter to be used to sample gathering in addition to direct reading measurement.

The meters are fitted with lamps of differing ionization potential (electron volts or eV). The most common lamp used is rated at 10eV and is capable of detecting approximately 230 different compounds, including methyl bromide.

The meter is calibrated against a known concentration of isobutylene, which has a base-line correction factor of 1.00. When measuring a single gas, a specific correction factor is applied to the reading to give an accurate record of the atmospheric concentration. For example, methyl bromide requires a correction factor of 1.70 to be applied to the displayed isobutylene equivalent reading to give the actual concentration in air¹¹.

The difficulty arises when multiple or unknown gases are being measured. No single correction factor can be applied to the mixture, and the reading can only be expressed as a total VOC concentration¹².

The error range of the RAE systems PID against the calibration gas isobutylene is quoted as ± 2 ppm.

5.1.3 Colorimetric tubes.

There is currently no known direct reading meter sensitive to methyl bromide alone. However, direct reading colorimetric tubes (for example Gastec, Kitigawa and Drager) that are specifically sensitive to methyl bromide are available.

The methyl bromide tube is in fact two tubes; a presample filter (for humidity) and the analyte section that gives a 'stain' or colour change in the presence of the desired gas. The methyl

¹⁰ Application Note; RAE systems PID Training Outline.

(http://www.raesystems.com/~raedocs/App_Tech_Notes/App_Notes/AP-000_PID_Training_Outline.pdf).

¹¹ Technical Note (TN-106); Correction factors, Ionization Energies, and Calibration Characteristics. (http://www.raesystems.com/~raedocs/App_Tech_Notes/Tech_Notes/TN-106_Correction_Factors.pdf).

¹² Technical Note (TN-102); Facts about PID Measurements.

(http://www.raesystems.com/~raedocs/App_Tech_Notes/Tech_Notes/TN-102_PID_Facts.pdf).

bromide tube is however cross sensitive to other halides, and may give false positives if refrigerant gases etc are present in the area where sampling is being undertaken.

In addition, most colorimetric tubes have a manufacturers stated error range of between 10-25%. As such, the tubes should essentially be used to determine approximate concentrations of a known atmospheric contaminant, with the results acting as a guide to further investigation rather than a definitive measure¹³.

5.2 Monitor Selection

5.2.1 PID

The instruments of choice were the MultiRae plus (four-gas detector and PID), and the ToxiRae PID. The PID meters gave instantaneous readings, responded to rapid changes in concentration of contaminants, was applicable to a range of VOC present at the workplace, would alarm if concentrations exceeded preset limits, and could datalog the results for later analysis.

All instruments were calibrated against isobutylene, with the ToxiRae having an internal correction factor of 1.70 loaded into the meter for methyl bromide. The MultiRae plus had no correction factor applied, and remained at the isobutylene equivalent of 1.00.

5.2.2 Colorimetric tubes

Colorimetric tubes were used to confirm the presence or absence of methyl bromide in instances where the principle source of contamination could not be readily identified. For example, to give a) an estimation of the residual concentration of fumigant at floor level inside Shed 3 and to b) demonstrate the absence of methyl bromide against the detection of VOC inside a forklift cabin, during the post fumigation timber loadout.

5.2.3 Halide lamp

The halide lamp was not used during the survey due to its lack of sensitivity to low levels of methyl bromide. The fumigation staff used the halide lamp at the initial stages of gas delivery for demonstration purposes only.

5.2.4 Limitations

The limitations of the PID and colorimetric tubes are discussed later in this document.

¹³ California-Arizona Consortium, Labor Occupational Health Program – Hazardous Waste Project, Chapter 3 'Air Monitoring'. University of California, Berkley.

5.2.5 Instruments

Rae Systems ToxiRae model PGM-30, Serial Number 002546.
Calibrated 22/2/2005
Due 22/5/2005
Correction Factor 1.70 (Methyl bromide CH₃Br)
Sensor: Photo Ionisation Detector (PID) for Volatile Organic Compounds (VOC)

Rae Systems ToxiRae model PGM-30, Serial Number 006456
Calibrated 22/2/2005
Due 22/5/2005
Correction Factor 1.70 (CH₃Br)
Sensor: PID / VOC

Rae Systems ToxiRae model PGM-30, Serial Number 006094
Calibrated 15/3/2005
Due 15/3/2005
Correction Factor 1.70 (CH₃Br)
Sensor: PID / VOC

Rae Systems ToxiRae model PGM-30, Serial Number 006086
Calibrated 15/3/2005
Due 15/4/2005
Correction Factor 1.70 (CH₃Br)
Sensor: PID / VOC

Rae Systems MultiRae Plus model PGM50-5P, Serial Number 095 513040
Calibrated 14/3/2005
Correction Factor 1.70 (CH₃Br)
Sensors: Carbon monoxide (CO), PID / VOC, oxygen (O₂).

Rae Systems MultiRae Plus Model PGM50-5P, Serial Number 095 504593
Calibrated 10/2/2005
Due 10/8/2005
Correction Factor 1.00 (isobutylene)
Sensors: CO, PID / VOC, hydrogen sulphide (H₂S), O₂, Lower Explosive Limit (LEL).

5.3 Atmospheric Testing

The monitoring program was divided into three distinct areas of operation; Background VOC Measurement, Fumigation and Gas Release / Ventilation.

5.3.1 Background VOC Measurement.

Background measurements of Volatile Organic Compounds (VOC) were taken in Shed 3 during the loading and placement of the stacks of timber for fumigation.

Of note was the presence of levels of VOC's approaching 70ppm measured near stacks of finished timber products held for storage (See Figure 5, appendices, page 28). It is assumed that the most likely compound is white spirits that is found in the Low Organic Solvent Preservative (LOSP) timber treatment used to protect pine against rot and insect damage.

Anecdotally, a strong solvent smell also was detected around this product and staff experienced slight sensations of light-headedness and stinging eyes.

5.3.2 Fumigation

The shed had three stacks of timber under fumigation. Stacks 1 and 2 were due for a 12 hour fumigation and located to the side, and running the full length, of shed 3. The third smaller stack was due for a 24-hour sterilisation, and was centrally located against the northern wall of the shed. (See Figure 5, appendices, page 28)

All three stacks were due for load out on Wednesday 16 March 2005.

Levels of 0.9 – 22.3ppm were detected around the stacks during gas introduction, with a level of 246ppm found near a tear in the fabric of Stack 3. Once repaired, levels dropped to a background of 17.0ppm.

No gas was detected at the manifold during the delivery to Stack 1. The gas delivery for Stack 2 was conducted from outside of the shed. The gas delivery of Stack 3 had been performed the previous afternoon.

5.3.3 Gas Release / Ventilation.

The three stacks were ventilated the morning of the load out.

Stacks 1 and 2 were forced air ventilated through the use of the extraction fans located at the northern end of the shed, with the inlet plenums at floor level (Figure 4, page 21). The stack covers were placed over the plenum, and held in place with sand bags. The covers were lifted to create an opening of approximately 2.5 meters wide by 1.5 meters at the southern end of the stack to allow fresh air to be drawn in by the extraction fans

The stacks were ventilated for a minimum of 45 minutes before the covers were removed, and the doors opened.

Stack 2 was afforded additional ventilation through the use of two large industrial fans placed at the northern entrances to the shed (See Figure 5, appendices, page 28). The fans blew fresh air into the shed, and down one side of the stack.

Stack 3 was afforded no fan-assisted ventilation. The stack was subject to the previous practice of removing the covers and allowing the gas to escape into the general workplace environment.

Of note was the performance of the extraction fans. The covers were drawn close to the stacks by the suction effect afforded by the fans. It was noted that the plastic covers on the individual packets of timber were also drawn in close to the timber; an effect that the fumigation staff had not witnessed in the Shed 2 operation.

5.3.4 Shed Clearance

VOC measurements were taken of the background environment to give clearance for port workers to the shed as per the agreed code of practice. However, the levels were persistently above the adopted 5ppm standard.

Measurements of VOC were taken inside the cabin of the forklift operating inside Shed 3 after the fumigation. Carbon monoxide, and VOC (principally diesel particulate) were measured at 2.0ppm and 5.1ppm respectively.

Colorimetric tubes were then taken to confirm the presence or absence of methyl bromide in addition to the VOC readings. Nil methyl bromide was detected over two ranges (2-18ppm and 10-100ppm) inside the forklift cabin. The tests were conducted over a 20-minute period with no significant variance in the results being observed.

Levels of 30ppm were detected at floor level during the initial post fumigation forklift operation. Subsequently, the forklifts were allowed access to Shed 3, however pedestrian traffic was prohibited from entry until the background levels of methyl bromide were below 5ppm.

5.3.5 Personal Protective Equipment

Fumigation staff and other personnel afforded access to the Shed 3 used full-face masks with methyl bromide cartridges for errant vapours (e.g. shed inspection once the covers were in place), and Self-Contained Breathing Apparatus (SCBA) for all other operations deemed at risk (e.g. gas introduction, release and cover removal).

Methyl bromide is difficult to absorb onto activated carbon, the principle component of most organic vapour cartridges. The particle is known to migrate through carbon due to its volatile nature, and can show breakthrough after one shift at levels not significantly higher than the WES of 5ppm.

3M have conducted testing of their 60928 methyl bromide cartridge, and have concluded that effluent levels of 1.0ppm are detectable after the filter is exposed to 10ppm for approximately 20 hours. The manufacturer recommends that the cartridge should not be used for longer than one shift, and in levels not exceeding 5ppm.

SCBA systems are not subject to the same exposure limitations; i.e. they have often been used in atmospheres of toxic concentration with little or no concern to the worker regarding an inhalation hazard. However, they are limited by the amount of air that can be stored in a bottle, the fitness of the worker, the respiratory and metabolic rates (exertion) and the potential for leakage of air past the facial seal.

Typically, a bottle can hold enough air for approximately 30 mins of mildly strenuous work, however the time may increase or decrease according to the individual workers' physical characteristics.

5.3.6 Results

Two data sets were taken during the ventilation process: one from inside the shed, the other from outside and at a distance of 6 and 12 meters from the walls. (See figure 6, appendices, page 29).

The arithmetic average PID / VOC results, and ranges of measurement are listed in tables 1 and 2. Corrected results (for methyl bromide CF 1.70) are listed in tables 3 and 4.

	Background Levels	Methyl Bromide introduction	Clips and Battens Removed	Fan Assisted Ventilation	Covers Removed	Timber Transported from Shed
Stack 1	5.5	4.2	1.4	8.4	25.6	0.9
Stack 2	4.5	0.5	1.8	11.5	24.2	0.1
Stack 3	5.5	2.6	1.3	#	146.8	0.1
Outside	0.3	*	*	0.4	0.9	*

* Measurements not taken

Nil ventilation performed on stack 3

Table 1: Averaged VOC results against Shed 3 Activities (ppm).

	Background Levels	Methyl Bromide introduction	Clips and Battens Removed	Fan Assisted Ventilation	Covers Removed	Timber Transported from Shed
Stack 1	3.0 - 17.5	1.9 - 12.5	0.0 - 2.8	1.4 - 12.5	3.5 - 71.1	0.0 - 5.4
Stack 2	2.1 - 8.1	0.5 - 13.1	0.8 - 5.1	4.5 - 16.1	10.2 - 40.7	0.0 - 0.7
Stack 3	5.1 - 21.8	1.3 - 10.4	0.0 - 5.3	#	68.2 - 587.0	0.0 - 0.3
Outside	0.0 - 2.0	*	*	0.0 - 4.4	0.0 - 4.5	*

* Measurements not taken

Nil ventilation performed on stack 3

Table 2: Ranges of VOC measurements for Shed 3 Activities (ppm).

	Background Levels	Methyl Bromide introduction	Clips and Battens Removed	Fan Assisted Ventilation	Covers Removed	Timber Transported from Shed
Stack 1	9.4	7.1	2.4	14.3	43.5	1.5
Stack 2	7.7	0.9	3.1	19.6	41.1	0.2
Stack 3	9.4	4.4	2.2	#	249.5	0.2
Outside	0.5	*	*	0.6	1.5	*

* Measurements not taken

Nil ventilation performed on stack 3

Table 3: Averaged results against Shed 3 Activities corrected for Methyl Bromide (CF 1.70) (ppm).

	Background Levels	Methyl Bromide introduction	Clips and Battens Removed	Fan Assisted Ventilation	Covers Removed	Timber Transported from Shed
Stack 1	5.1 - 29.8	3.2 - 21.3	0.0 - 4.8	2.4 - 21.3	6.0 - 120.9	0.0 - 9.2
Stack 2	3.6 - 13.8	0.9 - 22.3	1.4 - 8.7	7.7 - 27.4	17.3 - 69.2	0.0 - 1.2
Stack 3	8.7 - 37.1	2.2 - 17.7	0.0 - 9.0	#	115.9 - 997.9	0.0 - 0.5
Outside	0.0 - 3.4	*	*	0.0 - 7.6	0.0 - 7.7	*

* Measurements not taken

Nil ventilation performed on stack 3

Table 4: Ranges of measurements for Shed 3 Activities corrected for Methyl Bromide (CF 1.70) (ppm).

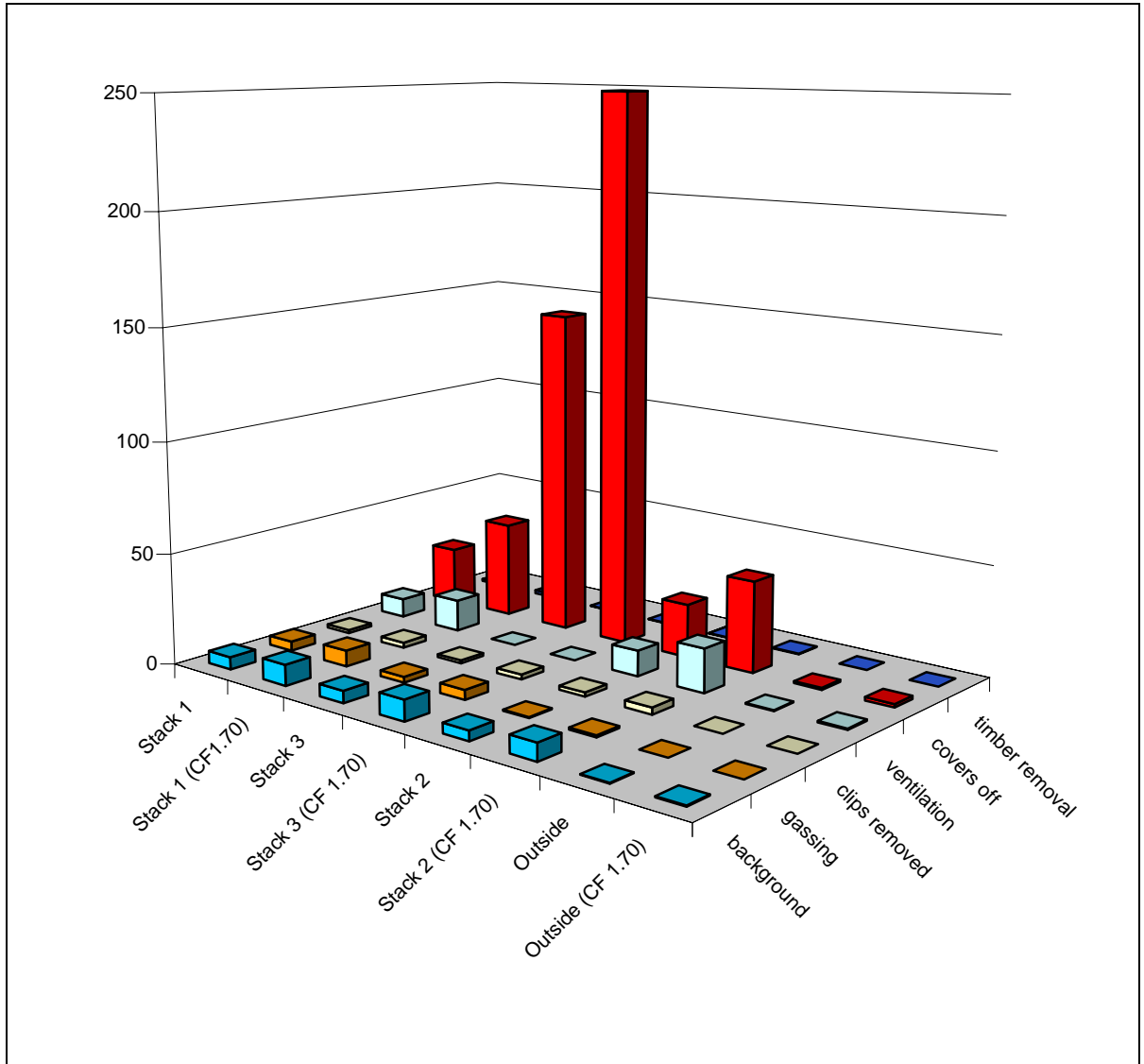


Figure 2: VOC & corrected levels for Methyl Bromide (ppm) against Shed 3 Activities and Sample Locations

5.4 Discussion

Figure 2 displays' more than the graphical representation of data; it gives the approximate relative orientation of the stacks as they were placed in the shed. That is, Stack 3 (the smaller stack) was placed between the two larger stacks that were ventilated using extraction fans prior to the covers being lifted.

The results show that the risk of exposure to VOC's / methyl bromide is low during the gas introduction phase, and when the battens and clips are first removed from the covers. The risk rises during the ventilation of the stacks, and significantly so when the covers are removed.

However, the results do indicate that with the assistance of the extraction fans, the levels of methyl bromide released into the general work environment (i.e. Shed 3) can be reduced up to 160 times less than the initial undercover concentration of 1000 ppm.

Stacks 1 and 2 had been ventilated for a period of 45 mins before the covers were removed; this clearly is not long enough to reduce the levels of *all* VOC's to below the exposure standard applicable to the different solvents present in the timber stacks (including methyl bromide).

However, an increase in the run time of the extraction fans would address this shortfall, and there is every possibility that the levels of residual methyl bromide (and other volatile organics) under the covers could be at or lower than the relevant exposure standard.

Of note, was the existence of the high background levels of VOC's in the shed prior to any fumigation work being undertaken. Levels of between 3.0 – 21.8ppm (with a peak of 127ppm) indicate that other volatile organic compounds were present. A possible and yet unconfirmed source of the VOC's is the timber preservatives and antisap stain chemicals used in the finished pine products, principally the white spirits component of the LOSP treatment.

Port side workers and fumigation staff alike have reported smells akin to that of kerosene or solvents in and around the stacks of timber handled at the port. They have reported immediate symptoms and health effects such as stinging eyes, difficulty in breathing, and tingling of the lips when near timber treated with Low Organic Solvent Preservative (LOSP), Copper Chrome Arsenate (CCA). Similar effects have been reported near glued Laminated Veneer Lumber (LVL) and painted or primed finger jointed fascia board.

The existence of the background VOC's, and persistent levels detected post treatment, may go some way to explaining the 'smells' coming from the timber stacks for a fumigant that otherwise has no odorant properties.

5.4.1 Limitations of Method

The principle limitation is the absence of a singular direct reading device that is sensitive to methyl bromide alone.

Though direct reading colorimetric tubes are available for methyl bromide, they are sensitive to other halides, and often carry an error range in the order of 25-30% resulting in false positives or negatives.

Colorimetric tubes give a 'snap shot' concentration of the contaminant, and as such are not sensitive enough to show peak and trough fluctuations.

They are open to interpretation by the user, who has to estimate the borderline of colour change between the reacted and unreacted analyte in the tube.

That being said, they have some merit as a confirmatory test for the presence or absence of methyl bromide when used in conjunction with a direct reading device sensitive to a range of contaminants such as the Photo Ionization Detector (PID).

The Photo Ionization Detector (PID) has one distinct flaw; it cannot distinguish one ionisable gas from another. If there are multiple contaminants present then the PID can at best give a total gas concentration in isobutylene equivalents (the baseline volatile organic compound from which others are derived).

This was certainly the case at Shed 3. At best there was the likely existence of white spirits (LOSP), diesel particulate, methyl bromide, formaldehyde, paint solvents (toluene, xylene, turpentine) and natural pine oils (pinenes) present during the 4 days of measurement.

Some compounds can be excluded from measurement with the use of lamps with differing ionisation potentials. For example, all the PID's used during the sampling were fitted with 10.6eV (electron volt) lamps, which excluded formaldehyde (present in the glue used with LVL timbers). However this lamp includes diesel, most solvents, and some pinenes, making it difficult to associate the levels of VOC's with methyl bromide alone.

In addition, factors are required to be applied to the readings given by the PID to provide a corrected reading for the chemical being measured. In the instance with the ToxiRAE's, the correction factor of 1.7 was applied at calibration, thus making the unit 'sensitive' to methyl bromide alone. This does not exclude the other VOC's that the meter will read, but allows the user to measure for a known compound without having to make a manual correction to the data as was the case with the MultiRAE plus used inside shed 3.

A point to consider. If the unit is given to an untrained operator, who is told that is 'calibrated' for methyl bromide, and they are not aware that the meter is capable of giving a corrected total gas level, they will assume that the unit is reading for methyl bromide alone. The fact of the matter is that they may very well be reading methyl bromide, but not in isolation, and most certainly not at the levels indicated by the meter.

That being said, the PID is a useful device for performing a trend analysis in real time, and if the operator is confident that the high levels are most likely due to the target analyte alone (as was the case with methyl bromide when the covers were first removed) then the results can be relied upon as an accurate representation of the actual contaminant of interest.

6. Conclusions

Significant changes have been made to the fumigation of sawn and finished pine products at the Port of Nelson (PoN). The Port had recognised the necessity for assisted ventilation of the fumigation sheds, and had installed the two extraction fans firstly in Shed 2, then most recently in Shed 3.

The efficiency of the fans has greatly increased with the endwise orientation of the fans relative to the stacks of timber. The initial assessment of the extraction systems' ability to clear the stacks of methyl bromide and associated VOC's was surpassed by the observed performance during the survey.

Even with limited ventilation run time of 45 mins afforded to Stacks 1 and 2, the results clearly show a significant reduction in residual contaminants compared with Stack 3 (where no ventilation was performed).

The suggestion that high levels of methyl bromide existing some distance away from the shed during gas release, ventilation and cover removal cannot be supported. Levels of contaminant at

up to 12 meters from the doors of the shed show averaged VOC levels of 0.9 ppm, with corrected levels for methyl bromide of between 1 - 5ppm.

Peaks levels of 4.5ppm (VOC) and 7.7 ppm (methyl bromide) were briefly detected at the northeast side of the shed when the covers were first removed. This is not unexpected, given that portable industrial fans located at the northern doors were further ventilating Stack 2.

Caution is needed when interpreting the corrected results for areas not immediately adjacent to the stacks. A high degree of confidence can be applied to the levels of methyl bromide measured after the removal of the covers, and to some large extent, the initial release of the gas when the water seal is drained. The relative concentration of methyl bromide to other VOC's would be high in these instances, given that the gas is captured under the covers, and has not had the chance to dilute into the general atmosphere.

The same degree of confidence could not be applied to the period of time after the covers have been removed, and to the area immediately adjacent to the shed doors. Methyl bromide dissipates quickly into the atmosphere, and as there is a finite concentration of the material, the relative concentration of methyl bromide to VOC would drop significantly. That is, the virtual reservoir of VOC's leaching from the timber exists well after the methyl bromide has dropped to nearly undetectable levels and these could provide a 'false positive' peak above the workplace exposure standard when using a PID alone.

The difficulty is that the PID instruments cannot differentiate between one form of VOC (white spirits for example) and the existence of methyl bromide. There is the distinct possibility that the peak VOC level recorded at the north-eastern door may very well have come from a stack of timber found to be releasing quantities of LOSP vapour (up to 78 ppm) even before fumigation operations commenced.

The exposure to methyl bromide during the entire fumigation operation is well documented and controlled. The reconfiguration of the extraction fans has significantly increased the efficiency of the stack ventilation, which can only improve with some minor engineering improvements.

Finally, an observation on the effectiveness of the 50-meter exclusion zone agreed to in the Port Code of Practice. It is acknowledged that the zone perimeter was set prior to the ventilation process, marked with traffic cones and signs.

The difficulty in maintaining the exclusion zone soon became clear, when port container forklifts required access to refrigerated reefers that were located inside the zone adjacent to the shed. Limiting the traffic during load out of the Maersk Sealand had the potential of attracting significant penalties to the Port of Nelson, and for no apparent benefit regarding the potential exposure of workers to methyl bromide, based on the data to hand.

7. Future Work.

This survey must be placed into context. The data sets were taken during particular meteorological conditions, fumigation quantities, port operations against a single event for ventilation (where the extraction time has since been increased), and where the Shed 3 operations had been instigated less than a week prior to the survey.

Further monitoring is required to gain a comprehensive picture of the performance of the Shed 3 extraction system, and the reduction of methyl bromide in the immediate work environments. These may include plume studies, and flow rates of air in and around the stacks.

In addition, the survey has raised questions regarding the off gassing of timber preservatives into the workplace environment, pre, during and post fumigation, with particular regard to the residual white spirit content in LOSP treated timbers. The potential health risks to port workers and fumigation staff alike needs to be assessed against a robust occupational hygiene survey, targeting the like of LOSP, formaldehyde etc.

The study may include health questionnaires, personal monitoring of port workers and fumigation staff for exposure to VOC, and point source grab samples for analysis by gas chromatography or mass spectroscopy. Measurement of the residual preservative chemicals in pre fumigated timber and the atmospheric concentration of volatile chemicals released pre and post fumigation would be made in addition to the assessment of under cover chemistry during fumigation and the possible interaction of the methyl bromide with the likes of white spirits found in LOSP treated timbers.

Finally, these projects will need to be conducted independent of further surveys into raw log, container, ships hold and commodities fumigation to gain intelligence regarding the fumigation industry as a whole and the duration of exposure of workers and others to methyl bromide under varying operational parameters.

8. Recommendations

8.1.1 Exclusion Zone

In light of the low levels of VOC's measured during the ventilation process, and the difficulties experienced by the general port operations in maintaining the exclusion zone during the fumigant release and stack ventilation, it is suggested that the current exclusion zone of 50 meters be revised after of further atmospheric testing.

Agreement on the zone location and distance from Shed 3, and times to which the exclusion zone is applied during ventilation will need to be reached amongst all port side operators and users, as per the current Port of Nelson Code of Practice.

8.1.2 Stack Ventilation

Fan assisted stack ventilation is to continue in all instances where timber is fumigated in Shed 3. The fumigator has conducted post survey work, and it was found that fan assisted ventilation times in excess of 12 hours have dropped the measured levels of VOC's to practically undetectable.

In light of this work, the minimum ventilation time for individual stacks of timber should not be less than 12 hours, and more, as post ventilation VOC levels dictate.

8.1.3 Flue Height

Industrial ventilation design dictates that exhaust ports for extraction flues are to be at a height of 3 meters or more above the highest point of the adjacent roof. This is to eliminate the potential of building downwash; i.e. contaminants swirling back down into the work area from whence they came.

Furthermore, the exit velocity of the contaminant can be increased through the use of a truncated cone installed at the top of the flue. This will significantly increase the effective plume ejection height to above and away from the immediate port buildings and surrounding areas.

It is recommended that the height of the flue be increased to not less than 3 meters above the highest point of the Shed 3 roof, that an ejection cone be installed at the top of the flue to increase the exit velocity, and that a third flue configuration be installed to ventilate stacks of timber that may be placed on the midline of the shed.

Advice on the specific characteristics of the flue design should be sought from a ventilation engineer.

8.1.4 Shed Clearance

Entry to Shed 3 is prohibited to all personnel (with the exception of the fumigator) whilst the fumigation operation is in progress; this includes the ventilation of the stacks and cover removal.

Only the fumigator or his authorised delegate can issue the shed entry clearance. Preliminary testing of total VOC using a PID is to be augmented with a confirmatory direct reading colorimetric tube test. The operator is to be mindful of the error ranges of both instruments during measurement, and is to make adjustments to the entry time erring on the side of caution.

Shed clearance for entry of port staff and others shall not be given until the averaged levels of VOC's and methyl bromide are at, or below, the relevant Workplace Exposure Standard (WES) for the contaminants.

8.1.5 Personal Protective Equipment

The use of full-face masks and methyl bromide cartridges are to be limited to work where levels of methyl bromide are not likely to exceed 5ppm. Cartridges are not to be used for more than one working shift. Given that methyl bromide will migrate through activated carbon charcoal after exposure, and that it has no odour or warning properties, cartridges are not to be stored for reuse.

For all other operations, Self-Contained Breathing Apparatus (SCBA) are to be used as the primary form of respiratory protective equipment. All staff using such equipment are to be given appropriate training and supervision in the use, care and maintenance of the SCBA and full-face masks.

9. Appendices

9.1 List of Figures

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Figure 6: Approximate locations of internal and external data sets for Shed 3 (Page 29)

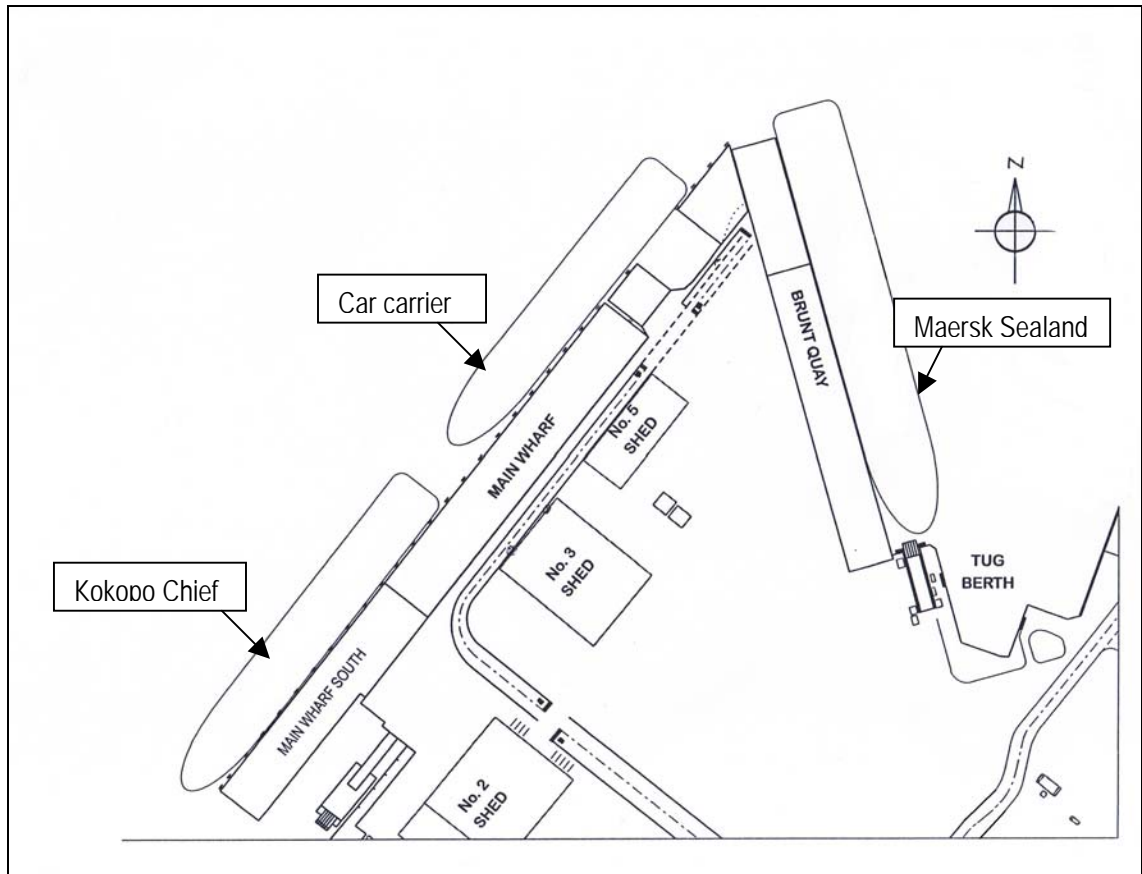


Figure 3: Port Operations 16th of March 2005.

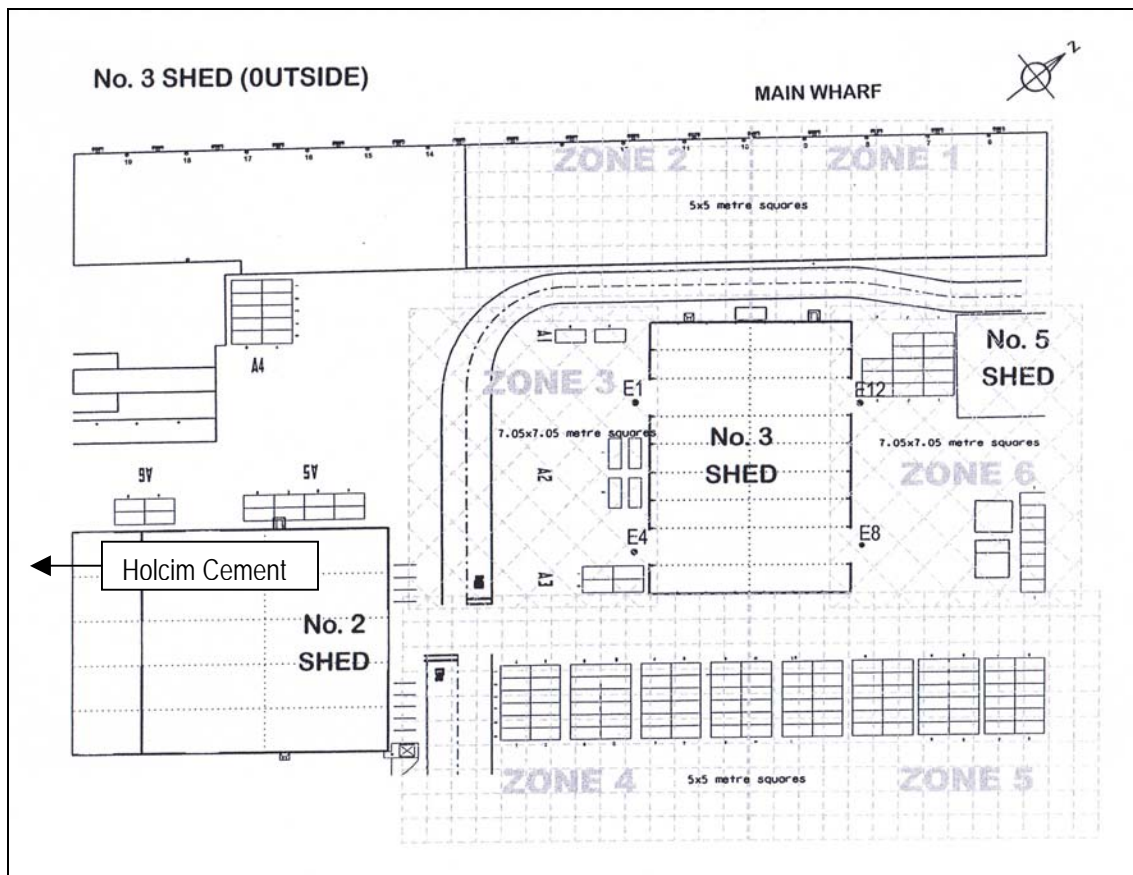


Figure 4: Relative locations of Shed 3 to container storage and Main Wharf.

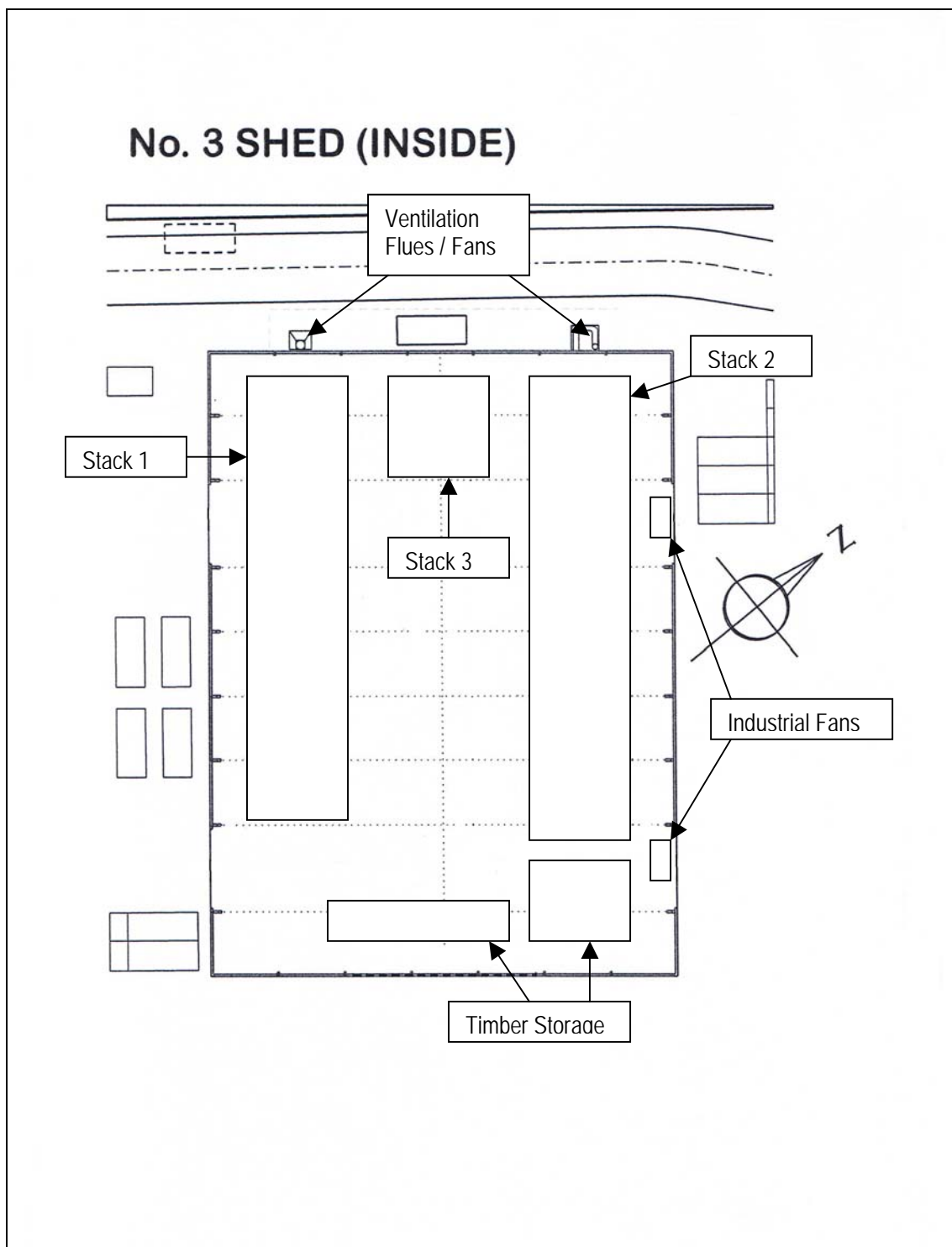


Figure 5: Shed 3 Configuration.

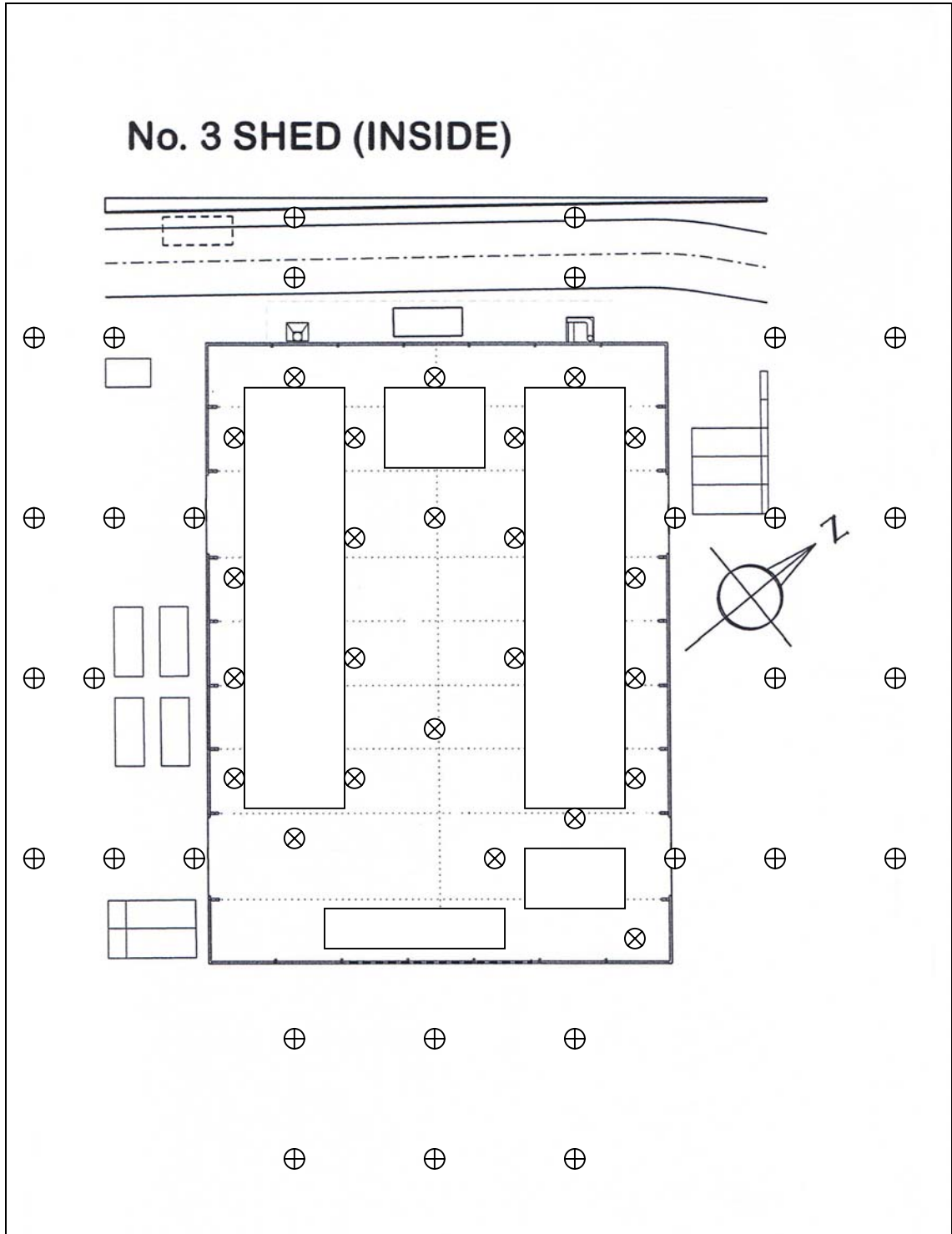


Figure 6: Approximate locations of internal and external data sets for Shed 3

External data sets ⊕

Internal data sets ⊗