REPORT ON THE OUTCOMES OF THE FUMIGANT RISK STUDY

(FOR EXTERNAL RELEASE)

New Zealand Customs Service

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1.0 EXECUTIVE SUMMARY

The New Zealand Customs Service carried out a study to gain a better understanding of fumigant risks posed by import containers and their origin, country of export, and the type of commodity carried. The study was carried out between February and June 2011 at the Port of Tauranga.

Nine fumigants / volatile organic compounds (VOCs) were targeted. These were benzene, chloropicrin, ethylene dibromide, ethylene oxide, formaldehyde, hydrogen cyanide, methyl bromide, phosphine, and toluene.

The study found that at least one of the nine selected fumigants / VOCs was present in 89.7 percent of the air samples collected. In many instances, multiple fumigants / VOCs were detected in a single container. Over 18 percent of the air samples were found to be above the safe reporting level, with some concentrations found to be in excess of 100 times above the safe reporting level. Of the 519 containers sampled, only two containers were observed to display correct fumigant signage on the outside of the container.

The study also found that the types of fumigants and VOCs present inside containers were not just from fumigation or disinfectants, but also from chemicals that were used in the manufacture of the commodities inside. The VOCs are released from the commodities while being shipped. The level of contamination of a specific fumigant or VOC is also related to the type of the commodity and the country of export / origin.

Formaldehyde was the most common fumigant / VOC found inside the sampled containers. It was detected in 87 percent of the air samples collected. Formaldehyde was present in containers from all countries of export sampled, and detected in most of the commodity categories. High concentrations were present in containers that carried new pneumatic tyres for motor vehicles from China and Hong Kong. The average concentration of formaldehyde detected in containers exported from Asia was higher than for other regions.

Toluene was the second most common fumigant / VOC detected. It was present in 31 percent of air samples collected. It was detected in most of the commodity categories, but less frequently detected in foodstuffs. Sixty-four percent of the total detections of toluene were present in containers exported from Australia, and 15 percent in containers from China. On average, the concentration levels of toluene were low, with no detection reported above the safe reporting level.

The other fumigants / VOCs, in order of detection frequency, were: ethylene oxide, methyl bromide, benzene, ethylene dibromide, hydrogen cyanide, phosphine, and chloropicrin. These were detected in less than 5 percent of air samples. Phosphine and hydrogen cyanide were detected at below the safe reporting level, while all other fumigants / VOCs were detected at above the safe reporting level. Chloropicrin was detected in only one container.

2.0 INTRODUCTION AND BACKGROUND

Fumigation of cargo is widely practiced in international shipping. Fumigated goods are often kept in a sealed container for several weeks and exposed to changes in temperature and climate, which may lead to vapours being released. The residual vapours inside the container on opening can be of significance both as an occupational hazard to workers handling the containers and to consumers handling the goods, such as foods. Long-term ill effects on health may develop from exposure to the fumigants[1] and volatile organic compounds (VOCs)[2].

Customs has carried out a study to measure the presence of fumigants / VOCs (type and concentration) inside sealed marine containers imported through the Port of Tauranga between February and June 2011. The purpose of the study is to gain a better understanding of the fumigant risks posed by import containers coming across the New Zealand marine border. Customs deployed a Voice 100 supplied by Syft Technologies Ltd. The Voice 100 can analyse a range of fumigants or VOCs inside the air sample collected from container in one test.

Nine fumigants and VOCs were targeted for the study. The specific chemicals were: benzene, chloropicrin, ethylene dibromide, ethylene oxide, formaldehyde, hydrogen cyanide, methyl bromide, phosphine, and toluene. These chemicals are toxic to human beings through inhalation, skin, or eye contact, and thus pose health and safety risks to people working with containers.

The nine chemicals were calibrated into the Voice 100 at half the lowest threshold limit value (TLV) or Workplace Exposure Standards (WES) [3], and this is reported as the safe reporting level. This conservative approach was considered necessary for this study to allow for error in detection technology and discrepancy during the air sample collecting and testing process.

The analysis focused on identifying the type of fumigants / VOCs, the detection frequency, the concentration above the safe reporting level, the highest concentration detected during the study, and their correlations with the commodities carried inside the containers, and the

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[1] Fumigant is one of a number of techniques that are used to prevent or control insect infestations. Chemicals used as fumigants can exist in gaseous form at a certain temperature and pressure, and in sufficient concentration to be lethal to a given pest organism. Fumigant has acute effects on human health.

[2] VOC is defined to include all organic compounds (substances made up of predominantly carbon and hydrogen) with boiling temperatures in the range of 50-260℃ (excluding pesticides). Substances in the VOC category also include aromatic hydrocarbons (such as benzene, toluene and the xylenes). The VOCs can combine with other substances in the air to form ground-level ozone (smog). Ozone can damage lung tissue, cause respiratory illness, and can have a chronic effect.

[3] TLV is the occupational exposure limit and a reserved term of the American Conference of Governmental Industrial Hygienists (ACGIH). Literature research for this study determined that the TLV level is comparable with other exposure guidelines, such as the acute RELs and New Zealand WES.

Acute or Chronic Reference Exposure Levels (RELs): it is defined as the concentration level at or below which no adverse health effects are anticipated for specified exposure duration (Appendix B).

Workplace Exposure Standards (WES-TWA): it is a term used by the New Zealand Department of Labour. This is based on an eight hour working day and a 40 hour working week. It is designed to protect workers from effects of long-term exposure to toxic chemicals.

countries (regions) of export. Literature research was undertaken to source information on other overseas studies and on the properties, toxicity, sources, applications, and health effects of the nine chemicals.

3.0 METHODOLOGY

Tauranga is a major port where containers containing a wide range of commodities from a number of overseas countries are imported. Australia, China, and the United States are the main countries of origin and export for the imported containers. These three countries account for 77 percent of the total import containers. The proportion of the sampled containers by country of export has reflected the trading pattern of the port.

The majority of air samples were collected from import containers unloaded from vessels at the port and directly loaded onto rail carriages waiting to be railed (MP4) to MetroPort, South Auckland. In addition, air samples were collected from import containers examined at the Tauranga Customs Inspection Facility.

The air samples were collected by a metal probe penetrating between the rubber seals and container doors to a depth of 10 to 25 cm inside the container. One air sample was collected and tested for each container. The container number was recorded, as well as noting whether the container displayed any fumigant signage on the outside of the container. The officers returned with the collected air sample bags, within an hour, to test the samples on the Voice 100. The Voice 100 scanned and analysed the chemicals present in the air sample. The results (type and concentration of chemicals) were then recorded in the system. Syft collected the data from the system and sent it weekly to Customs for analysis. Syft also monitored the calibration and performance of the Voice 100 online to ensure the accuracy and integrity of the results. Further information such as the country of export and type of commodity was sourced from the Customs database.

4.0 ANALYSIS

Over the four months of the study, Customs collected air samples from 519 containers at the Port of Tauranga. These containers were imported from 24 overseas countries and carried on 43 different voyages. Of the total, 497 air samples were valid for analysis.

The study found that 89.7 percent of air samples were contaminated by one of the target fumigants / VOCs, and 18.3 percent were above the safe reporting level. Multiple types of fumigants / VOCs were detected in 34 percent of the air samples collected from the containers.

Formaldehyde and toluene were the most common contaminants present in 87 percent and 31 percent of the air samples respectively. The other fumigants / VOCs were detected in less than 5 percent of the air samples.

Table 1: Fumigant risk study result 1 – Fumigants / VOCs detection

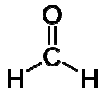
Compounds	Formula	TLV/WES (ppb)	Safe reporting level (ppb)	Detections (frequency)	Above safe report level (frequency)	Highest concentration detected (ppb)
Formaldehyde	CH_2O	300 (Ceiling)	150	431	60	6,562
Toluene	C_7H_8	20,000	10,000	156	0	6,841
Ethylene oxide	C_2H_4O	1,000	500	23	22	9,717
Methyl bromide	CH_3Br	1,000	500	17	8	49,891
Benzene	C_6H_6	500	250	16	8	3,070
Ethylene dibromide	$CH_2Br.CH_2Br$	500	250	10	5	1,066
Hydrogen cyanide	HCN	4,700	2,300	9	0	540
Phosphine	PH_3	300	150	7	0	144
Chloropicrin	Cl_3CNO_2	100	50	1	1	50

Table 2: Fumigant risk study result 2 – Summary of fumigant / VOC detection

Descriptions	Detections (frequency)	Percentage
Total valid air samples	497	
Air samples detected fumigants / VOCs	446	89.7%
Above the safe reporting level	91	18.3%

4.1 Fumigants / VOCs

4.1.1 Formaldehyde (CH_2O)



Formaldehyde is a toxic, volatile and colourless gas with a characteristic pungent odour. It is not only used as a fumigant or disinfectant (formalin), but also has industrial significance, in the synthesis of many compounds.

The formaldehyde found was significant in the sampled import containers for both detection level and concentration level. Formaldehyde was:

- detected in 87 percent of the air samples. Of that, 14 percent were above the safe reporting level, and 27 percent were above the acute REL. At the acute REL, it is likely to cause eye irritation (Appendix B, Table B1)
- detected with the highest concentration of 44 times above the safe reporting level in one air sample. This was from a container imported from China and carried new pneumatic tyres
- detected in import containers from most of the export countries sampled.

The commodities in the sampled containers with higher levels of formaldehyde include: pneumatic tyres, bicycles, plywood, building materials, printing, electronic parts, textiles, handicraft / jewellery (from glue used in the products), dry seed / pet food, insecticide fungicide, disinfectants, and personal effects.

Research has consistently revealed that medium-density fibreboard (MDF) products emit urea-formaldehyde and other VOCs that pose health risks at sufficient concentrations for at least several months after manufacture (Appendix C, Table C1).

In one incidence, a container carrying handmade articles was examined by Customs. Before opening the container, the testing gave a reading of formaldehyde at 600 ppb. The container doors were then opened for natural venting overnight. After 17 hours of natural venting, a second test was carried out and that gave a higher reading at 1,300ppb.

4.1.2 Toluene (C_7H_8)

Toluene is a colourless and water insoluble liquid, with the typical smell of paint thinner. It occurs naturally as a component of crude oil.

Toluene is used in household aerosols, nail polish, paints and paint thinners, lacquers, rust inhibitors, adhesives, and solvent based cleaning agents. Toluene is also used in printing operations, leather tanning, and chemical processes. It has largely replaced benzene as it is less toxic.

In the study, toluene was:

- detected in 31 percent of the air samples
- not detected at above the safe reporting level
- less detected in foodstuffs.

4.1.3 Ethylene oxide (C_2H_4O)

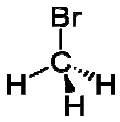
Ethylene oxide (ETO) is a colourless, flammable gas with a faintly sweet odour. Pure ETO is a disinfectant that is widely used in hospitals and the medical equipment industry. It replaces steam in the sterilisation of heat-sensitive tools and equipment, such as disposable plastic syringes.

In the study, the high concentration of ETO was detected in containers that carried equipment for hospitals, medical equipment, and laboratory hygienic ware.

ETO was:

- detected in 4.6 percent of the air samples
- detected above the safe reporting level in 22 out of 23 air samples
- detected in the highest concentration at 19 times above the safe reporting level.

4.1.4 Methyl bromide (CH_3Br)



Methyl bromide is a colourless, odourless, non-flammable gas that is heavier than air. It can penetrate quickly and deeply into materials at normal atmospheric pressure, and therefore, is widely used to fumigate bulk commodities, goods requiring quarantine, stored products, mills, warehouses, and railway cars. At the end of the treatment the vapours dissipate rapidly.

In the study, methyl bromide was:

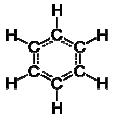
- present in 3.4 percent of air samples
- detected at the highest concentration of 49,891 ppb.

A concentration of 49,891ppb of methyl bromide, 100 times above the safe reporting level, was detected inside a container examined at the Customs facility. Ethylene dibromide (320ppb), formaldehyde (16ppb) and toluene (210ppb) were also detected inside the container. After three hours of forced venting (ram fan), the air inside the container was re-tested and the methyl bromide reading was 970ppb, still above the safe reporting level.

Methyl bromide is a recognised ozone-depleting chemical. It was used extensively as a pesticide until being phased out by most countries in the early 2000s. However, it is still allowed to be used in Australia, New Zealand and many other countries for quarantine purpose.

Eleven out of seventeen detections of methyl bromide were present in containers exported from Australia. The other detections were found in containers from China (3), Thailand (1), the United Kingdom (1), and the United States (1).

4.1.5 Benzene (C_6H_6)



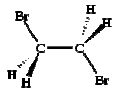
Benzene is a colourless and highly flammable liquid with a sweet smell. Benzene has been widely used as a multipurpose organic solvent. This use is now discouraged due to its high toxicity. Present uses of benzene include as a raw material in the synthesis of styrene, phenol, cyclohexane, aniline, and alkyl benzenes and in the manufacture of various plastics, resins, and detergents. It is used extensively in the tyre and footwear industry.

In the study, benzene was detected:

- in 3.2 percent of the air samples
- above the safe reporting level in half of the detections.

Exposure to benzene may have serious health effects. It is known to be carcinogenic to humans. Exposure to above the acute REL can cause severe problems (Appendix B, Table B1). The USA National Institute for Occupational Safety and Health (NIOSH) recommends that all workers wear special breathing equipment when they are likely to be exposed to benzene at levels exceeding the recommended (8 hour) exposure limit of 100 ppb.

4.1.6 Ethylene dibromide ($CH_2Br.CH_2Br$)



Ethylene dibromide (EDB) is a colourless liquid with a sweet odour. It is more toxic than methyl bromide. It is ranked as the top carcinogenic substance on the Human Exposure / Rodent Potency Index (HERP).

In the study, EDB was detected:

- in 2 percent of the air samples
- above the safe reporting level in half the detections.

EDB has comparatively low volatility (high boiling point and low vapour rate). It is physically absorbed by fumigated materials. Considerable aeration over a long interval is required before the vapours are completely dissipated.

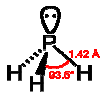
4.1.7 Hydrogen cyanide (HCN)

Hydrogen cyanide (HCN) is a colourless and extremely poisonous liquid that boils slightly above room temperature at 26 °C. Although HCN is easily absorbed by many materials, this action is usually reversible when they are dry. The use of HCN has declined in recent years.

In the study, HCN was

- detected in 1.8 percent of the air samples
- not detected at above the safe reporting level
- detected above the acute RELs in three air samples. At this concentration level severe nervous system problems can occur (Appendix B, Table B1).

4.1.8 Phosphine (PH_3)



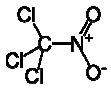
Phosphine is a colourless, flammable, and toxic gas. It is odourless, if pure, but has a highly unpleasant odour like garlic or rotting fish in technical grade samples (presence with substituted phosphine and diphosphine). The gas is kept in metallic phosphides form (usually aluminium or magnesium phosphide) to regulate release of fumigants and suppress flammability.

Phosphine has a low molecular weight, and a low boiling point that diffuses rapidly and penetrates deeply into materials, such as grain or tightly packed materials. Unchanged phosphine does not remain in fumigated commodities in appreciable amounts. It has been widely used in the countries that phased out methyl bromide under the 1989 Montreal Protocol.

In the study, phosphine was:

- detected in 1.4 percent of the air samples
- not detected at above the safe reporting level.

4.1.9 Chloropicrin (Cl_3CNO_2)



Chloropicrin is a colourless highly toxic liquid. Chloropicrin was once used in chemical warfare and is currently used as a soil fumigant. Chloropicrin is difficult to vapourise at ordinary temperatures. Because of its stability, protection requires highly effective absorbents, such as activated charcoal.

Chloropicrin was only detected in one air sample.

4.2 Countries of export by region

The analysis of country of export was carried out by grouping the countries into different regions.

The analysis showed that the detection frequency of fumigants / VOCs above the safe reporting level in the containers from Asia and North America were higher than Australia on average. The average concentration level of formaldehyde present inside the containers from Asia is much higher than the other regions (Appendix A, Table A1).

4.2.1 Australia

Import containers from Australia accounted for 67 percent of the total sample. All of the targeted fumigants / VOCs, except chloropicrin, were detected in containers originating from Australia. The fumigants / VOCs were detected inside 89 percent of the sample containers, and of that, 13 percent were above the safe reporting level.

4.2.2 China / Asia

Fifty-five sample containers (11 percent) were originally exported from China. The fumigants / VOCs were detected present in 90 percent of containers, and of that, 44 percent were above the safe reporting level. Seven target fumigants / VOCs were detected, with chloropicrin and hydrogen cyanide the exceptions.

Containers from Asia (including China) represent 16 percent of the total sample. The fumigants / VOCs were detected present in 87 percent of air samples, and of that, 41 percent were above the safe reporting level. All target fumigants / VOCs were detected.

4.2.3 North America

Fifty-two containers (11 percent of the total sample) were exported from North America (the United States and Canada). The fumigants / VOCs detected were present in 94 percent of the containers, and 21 percent were above the safe reporting level. The targeted fumigants / VOCs, except phosphine, hydrogen cyanide, and chloropicrin, were detected inside the containers.

4.2.4 The other regions

Containers exported from other regions represented 6 percent of the total sample. The fumigants / VOCs detected were present in 94 percent of air samples, and 13 percent were above the safe reporting level. The fumigants / VOCs detected in the containers include benzene, ethylene oxide, formaldehyde, methyl bromide, phosphine, and toluene.

4.3 Commodities

Analysing the relationship between the fumigants / VOCs detected and the types of commodities inside the containers is not easy. A marine container often carries multiple types of commodities that are produced in different countries. It is difficult to then determine the actual source of the fumigant / VOC that was detected.

The type of commodities carried in the sampled containers ranged from Section 1 to 21 of the Tariff (except Section 19/Arms and Ammunition). The descriptions of the goods declared to Customs were grouped into commodities: foodstuffs (21 percent), paper / printing (15 percent), plastics and rubber (13 percent), chemicals (10 percent), furniture / house items (7 percent), equipments (6 percent), machinery / tools (5 percent), and other types of commodities accounted for 23 percent of the total.

Tariff section that presented the highest concentration (on average) of formaldehyde was:

- Section 7: Plastics and articles thereof; rubber and articles; high concentrations were detected in new pneumatic tyres for vehicles from China and Hong Kong

On average, tyres imported from China and Hong Kong recorded a concentration of 2,599 ppb.

Tariff section that presented the highest concentration (on average) of toluene was:

- Section 1: Live animals; animal products (detected in the container carried the coral and shells and powder and waste)

High concentrations of toluene were also detected in the plastics, furniture, and metal categories.

The goods categories with high detection frequency at above the safe reporting level include building / construction materials (40 percent), furniture / house items (35 percent), and plastic / primary and rubber (tyres) (30 percent).

5.0 SUMMARY

The study revealed that the air inside nearly 90% of import containers contained at least one, and often multi types of fumigants and VOCs. Approximately 20% of the containers sampled during the study period were found to contain fumigants / VOCs at above the safe reporting level. The fumigants / VOCs detected were commonly present across most of the commodity categories and countries of export. It is also evident that high concentrations of certain fumigants / VOCs are closely associated with the type of commodity and the country of export / origin. These findings are consistent with findings from similar overseas studies.

It should be noted that the type and concentration levels of fumigants / VOCs found in this study may be specific to the Port of Tauranga. The fumigant type and concentration level might vary at each port as the type and volume of commodity imported through the port and country of export might differ.

The findings from this study confirm that import containers arriving at New Zealand ports may contain vapours of one or more fumigants / VOCs. It is also important to note that the fumigants / VOCs were measured against the safe reporting level in the work exposure standards. People working with containers should also be mindful of the long-term ill effects on health (i.e. carcinogenic substances) that may develop from exposure to some fumigants and VOCs, such as ethylene dibromide.

This study also found that signage alone is not a reliable way to assess a container for its fumigant exposure risk.

6.0 APPENDICES

6.1 Appendix A: Fumigant study results

Table A1: Fumigant risk study result 3 – Country of export

Country of export	Sample size	Detections (%)	Above the safe report level (%)	Formaldehyde concentration detected (average ppb)
Australia	335	89%	13%	61
China	55	91%	44%	390
Other Asia countries	23	78%	35%	527
North America	52	94%	21%	82
Other regions	32	94%	13%	104
Total	497	89.7%	18.3%	121

6.2 Appendix B: Reference exposure level

Table B1: Determination of acute reference exposure levels for airborne toxicants

Chemical Name	REL (µg/m3)	REL (ppb)	Average time(h)	Sp.[1]	Toxicologic endpoints	Severity	Hazard index target organs
Benzene	1,300	400	6	R	Reproductive/developmental	Severe	Reproductive/developmental; Immune system; hematologic system
Chloropicrin	29	4	1	M	Eye and respiratory Irritation	Mild	Respiratory system, eye
Formaldehyde	94	76	1	H	Eye irritation	Mild	Eye, respiratory system, immune system
Hydrogen cyanide	340	300	1	Mk	CNS – serious	Severe	Nervous system
Methyl bromide	3,900	1,000	1	H	CNS- mild (anorexia, nausea, headache;	Mild	Nervous System; respiratory irritation; reproductive/developmental
Toluene	37,000	9,800	1	H	CNS – mild; eye and respiratory irritation	Mild	Nervous system; eye; respiratory system;

1 Species used in key study for REL development: D = dog; GP = guinea pig: H = human; M = mouse; Mk = monkey; R = rat; Rb = rabbit

2 CNS = Central Nervous System.

Table B2: Chronic inhalation reference exposure levels

Chemical Name	REL (µg/m3)	REL (ppb)	Chronic inhalation hazard index target organ system (s)
Benzene	60	18.8	Developmental, hematopoietic system and nervous system
Chloropicrin	0.4	0.06	Respiratory system
Ethylene dibromide	0.8	0.1	Reproductive
Ethylene oxide	30	16.6	Nervous system
Formaldehyde	3	2.44	Eye, respiratory system
Hydrogen cyanide	9	8.14	Cardiovascular system, endocrine system, nervous system
Methyl bromide	5	1.28	Developmental, nervous system, respiratory irritation, respiratory system
Phosphine	0.8	0.57	Alimentary system, cardiovascular system, kidney, nervous/respiratory system
Toluene	300	79.6	Nervous system, eye, respiratory system

Sources: The air toxics hot spots program guidance manual for preparation of health risk assessments by the California Environmental Protection Agency Office of Environmental Health Hazard Assessment. A chronic REL is a concentration level at or below which no adverse health effects are anticipated following long-term exposure. Long-term exposure for these purposes has been defined as 12% of a lifetime, or about eight years for humans.

6.3 Appendix C: Formaldehyde emission rates of several building materials

Table C1: Formaldehyde emission rates of several building materials

Material	Emission rates (micro gms/m2 day)
Medium density fibreboard	17,600 – 55,000
Hardwood plywood panelling	1500 – 36,000
Particle board	2000 – 25,000
UFFI	1200 – 19,200
Softwood plywood	240 – 720
Paper products	260 – 680
Fibre-glass products	400 – 470
Clothing	35 – 570
Resilient flooring	< 240
Carpeting	0 – 65
Upholstery	0 – 7