



# Alternatives to Methyl Bromide Fumigation of Empty Ship Holds

Canadian Leadership  
in the Development of  
Methyl Bromide Alternatives

Canada



Government  
of Canada

Gouvernement  
du Canada

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## **Alternatives to methyl bromide fumigation of empty ship holds.**

**November 1999**

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This publication is also available on the world wide web at  
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Photo credits: Roger Cvasin, Paul Fields, David Mueller and Murray Weightman

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## Acknowledgement

This was truly a collaborative study involving the cooperation of Canadian and American companies, the government of Ontario and various Canadian federal departments. In addition to the numerous direct participants in the study, we would also like to acknowledge the following people: Pierre Beauchamp, Geoff Cutten, Stephen Murch, Noel White and Larry Zettler. The affiliations and coordinates of each of the collaborators are listed in the Appendix B.

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## Foreword

The *Montreal Protocol on Substances that Deplete the Ozone Layer* is a global agreement intended to protect the ozone layer by reducing the production of ozone depleting substances. Developed countries that are signatory to the *Montreal Protocol* - this includes Canada and the United States - must completely phase-out the production and consumption of methyl bromide by the year 2005.

Presently the *Montreal Protocol* exempts the use of methyl bromide for quarantine and pre-shipment purposes. It is essential that pests be controlled from movement between countries. However, as citizens of the planet it behooves all of us to look for effective alternatives to every methyl bromide application.

Judith Moses  
Assistant Deputy Minister  
Policy Branch  
Agriculture and Agri-Food Canada

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## SUMMARY

Although the United Nations *Montreal Protocol on Substances That Deplete the Ozone Layer* presently exempts the use of methyl bromide for quarantine and pre-shipment purposes, many countries question this exemption. There is concern over the increasing use of methyl bromide for quarantine and pre-shipment purposes globally. The cost of methyl bromide has increased in the last few years, and as the phase-out date approaches we expect the price of methyl bromide to continue to increase. To address these concerns the members of the Canadian Industry / Government Working Group on Methyl Bromide Alternatives decided to examine alternatives to methyl bromide fumigation of empty ship holds. We tested three methods of controlling insects in empty ship holds: methyl bromide with recapture, phosphine in cylinders (ECO<sub>2</sub>FUME™) and



The Canadian Trader docked in the Toronto Harbor

controlled generation of phosphine (Horn Generator with magnesium phosphide).

Vials containing adults and eggs of the rusty grain beetle, lesser grain borer, rice weevil and the red flour beetle, common insect pests of stored products, were placed in each of the ship holds. One hold was treated conventionally with 5400 ppm methyl bromide, a second with 500 ppm phosphine using ECO<sub>2</sub>FUME™ as a source of phosphine, and a third hold with 1000 ppm phosphine using the Horn Generator as a source of phosphine. After 32 hours, all treatments controlled 100% of the adults. The phosphine fumigations controlled at least 94% of the eggs after 32 hours, 99% after 48 hours and 100% after 72 hours. Eggs are one of the most difficult stages to control with fumigation. The egg mortality was only slightly higher with phosphine at 1000 ppm compared with 500 ppm.

The temperatures during this trial were warm (highs above 30°C, with an average of 23°C). However, ships often must be fumigated in cooler weather. Phosphine efficacy is reduced more by low temperatures than is methyl bromide. One possible way to overcome the low temperature sensitivity of phosphine would be to preheat the ship before fumigation.

The methyl bromide recapture technique can capture approximately 80-90% of the methyl bromide used, and would add approximately \$CAN 2 000/ 75 kg (160 lb.) of methyl bromide recaptured based on this demonstration project. Larger capacity recapture units would have to be built before this method could be used commercially for ship holds. The advantage to this method compared with others is that there are few regulatory impediments, the captured methyl bromide can be reused, it reduces the human health risks in the vicinity of the fumigation site and it significantly reduces the amount of methyl bromide released to the environment.

Neither ECO<sub>2</sub>FUME™ nor the Magtoxin® Granules (magnesium phosphide formulation for the Horn Generator) are registered in Canada, although the process has begun for Magtoxin®. The main impediment to using phosphine in temperate climates would be the longer exposure periods needed to control insects at low temperatures.

We also examined the corrosiveness of phosphine to metal. Copper strips showed corrosion after exposure to both phosphine treatments. Although phone jacks showed no visible signs of corrosion, a computer held at 500 ppm did stop functioning after 25.5 hours, and

examination revealed that failure resulted from the thinning and overheating of the lead to an integrated circuit chip. However, given the heavy steel construction of ship holds, corrosion as seen in this trial should not be a concern.

In conclusion, each of the three treatments could be used to limit the methyl bromide emissions from ship hold fumigations. These methods presently cost more than methyl bromide treatments, and there are some regulatory issues that would have to be addressed before these methods could be used in ship hold fumigations in Canada.

## Table Headings

- Table 1 The number of grain ships inspected, fumigated, sprayed with insecticide, or re-cleaned in Canadian ports.
- Table 2 The temperatures of ship bulk heads and vials containing insects at three different levels in the holds containing different treatments.
- Table 3 The concentrations of fumigants in the ship holds.
- Table 4 Survival of adults in untreated hold immediately after taken from ship hold.
- Table 5 Survival of adults in untreated hold one week after taken from ship hold.
- Table 6 The number of adults per vial that emerged 5 weeks after vials were exposed to treatments for 32, 48, and 72 hours.
- Table 7 The survival of eggs in treated ship holds as compared to eggs in the untreated ship hold.

## Introduction

The United Nation's has identified methyl bromide as an ozone depleting substance. All developed countries signatory to the *Montreal Protocol on Substances that Deplete the Ozone Layer* (Anon. 1998) must phase-out its use by the year 2005. Although the Montreal Protocol presently exempts the use of methyl bromide for quarantine and pre-shipment (QPS) purposes, many countries question this exemption. There is concern over the increasing use of methyl bromide for quarantine and pre-shipment purposes, as they make up about 22% of the methyl bromide consumed globally. Furthermore, as countries approach the phase-out date and the amount of methyl bromide produced lessens, the price of methyl bromide fumigations for all purposes is expected to increase dramatically. However, it is essential that proven and internationally accepted alternatives exist to meet quarantine and pre-shipment requirements.

The current definition used by the *Montreal Protocol* for quarantine applications is: "...to prevent the introduction, establishment and /or spread of quarantine pests, or to ensure their official control, where official control is that performed by, or authorized by a national plant, animal or environmental protection or health authority." For pre-shipment applications the definition is: "...those applied directly preceding and in relation to export to meet the phytosanitary or sanitary requirements of the importing country or existing phytosanitary or sanitary requirements of the exporting country." Proposed refinements of the definition of pre-shipment would limit it to treatments made 14 days or less before shipment.

Members of the Canadian Industry / Government Working Group on Methyl Bromide Alternatives believed that an investigation into alternatives

for ship hold applications would demonstrate the effectiveness of potential alternatives, reveal whether or not they are currently registered for use in Canada, and would provide data on their associated costs. Furthermore, these techniques may be useful in other situations where methyl bromide is used to control insect infestations.

Canada has a long-standing policy of inspecting all ships before loading grain. The Canadian Grains Act (85-3) does not allow for grain to be loaded into infested vessels. If live stored-product insects are found in ship holds, three possible actions are required depending upon the nature of the infestation; cleaning of the hold, cleaning of the hold followed by a spray of contact insecticide (malathion), or cleaning followed by fumigation. About 1000 ships are inspected each year in Canada with about 2% of them requiring fumigation (Table 1). Methyl bromide is the fumigant of choice because it is a rapid acting insecticide.

An experiment onboard a ship would provide a unique opportunity to simultaneously compare the effectiveness of three alternatives under identical field conditions. The corrosiveness of phosphine was also examined.

Table 1. The number of grain ships inspected, fumigated, sprayed with insecticide, or re-cleaned in Canadian ports<sup>1</sup>. (D. Laidlaw, Canadian Food Inspection Agency, 1999)

Ship Type	Action <sup>2</sup>	Year (1 April - 31 March)						
		92/93	93/94	94/95	95/96	96/97	97/98	98/99
Laker	inspected	76	30	58	-	-	-	81
	sprayed	4	0	0	-	-	-	25
	re-cleaned	17	0	0	-	-	-	39
	fumigated	0	0	0	-	-	-	0
Ocean	inspected	1048	1052	1181	1034	865	1102	959
	sprayed	17	30	5	7	3	22	35
	re-cleaned	470	415	533	299	294	430	393
	fumigated	27	28	25	25	14	19	25
	fumigated (%)	2.6	2.7	2.1	2.4	1.6	1.7	2.5

1. Ports where inspections normally occur are: Quebec, Montreal, St Hyacinthe, Halifax, London, Thunder Bay, Vancouver

2. A remedial action is not necessarily done on the entire ship but may affect one or more of the holds.

## Methods

### The ship

The field trial was conducted onboard the “Canadian Trader,” a 223 metre (730 ft.), lake-going ship designed to carry approximately 29,000 tonnes (6600 ton). Figure 1 describes the dimensions and the layout of the ship. Hold number 1, 4 and 6 were used for the treatments. The “Canadian Trader” was chosen for its similarities in structure and function to ocean-going ships.

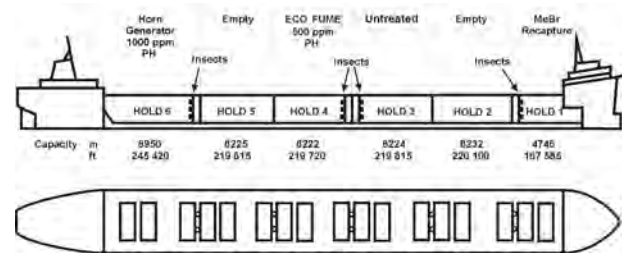
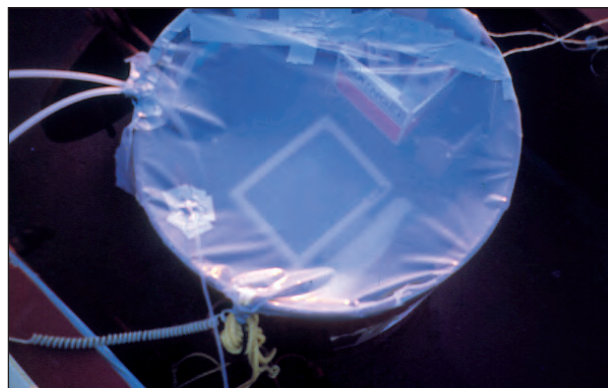


Figure 1: The “Canadian Trader”, size of holds, placement of treatments and deployment of test insects.

### Sealing the holds

At the base of each of the bulkheads (walls) separating adjacent holds were two small tunnels (60 cm x 45 cm, 24 in. x 16 in.) that allow drainage between holds. In the fumigated holds, these tunnels were sealed with 6 mm polyethylene, glue and duct tape. The ship’s steel hatch covers were clamped in place and their edges were sealed with 7-cm-wide (3 in.) duct tape. The manholes were covered with 6 mm (0.25 in.) polyethylene and sealed with duct tape. Tubes for introducing and sampling fumigants were passed through the polyethylene covering the manholes, as were the ropes



Manholes covered with polyethylene and sealed with duct tape

used for retrieving the insect and copper (for corrosion study) samples.

### Pressure testing

Pressure testing is useful to give an indication of the relative level of sealing between holds and to determine the effectiveness of each seal. A high pressure blower (1/2 hp) was used to form a positive pressure of 0.38 kPa (1.5 inches of water) in each test hold. Once pressure was achieved, the blower was turned off, the blower tube sealed and the time to drop from 0.38 to 0.19 kPa was measured. In holds 1, 4 and 6, the pressure dropped by 50% in 6.1, 13.5 and 6.0 minutes, respectively. Initially, the pressure could only be maintained briefly in hold 4, therefore, the drainage tunnels at the base of the hold were resealed and the pressure test redone. These results indicate that there was a tight and secure enclosure by fumigation standards. The Australian pressure testing standards are a half life of five minutes (Banks 1984).



Pressure testing the seals of the ship holds prior to fumigation

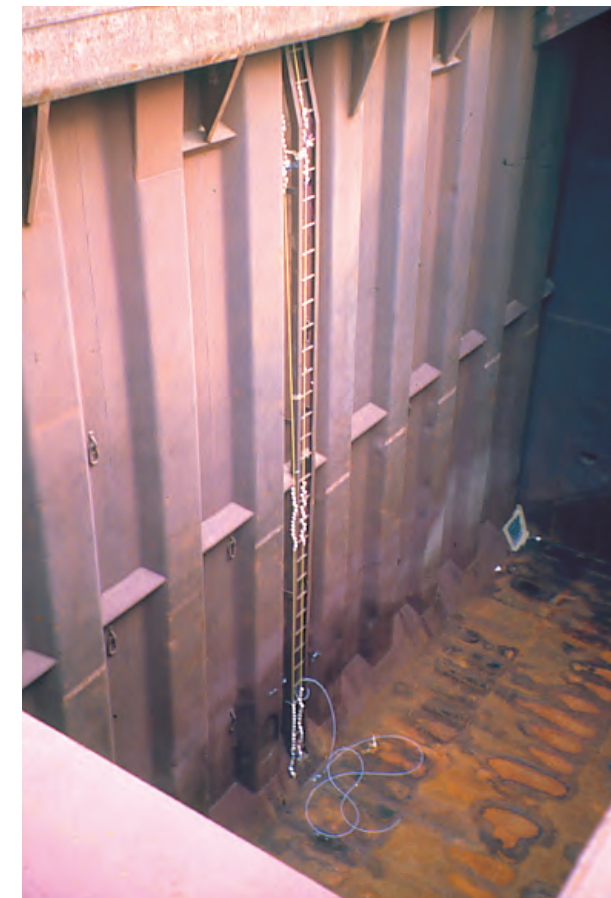
### Treatments

There were three treatments: methyl bromide at approximately 5400 ppm (21 oz/1000 ft<sup>3</sup>) with recapture after one day (hold 1); phosphine at 500 ppm applied using the ECO<sub>2</sub>FUME™ method (hold 4); and phosphine at 1000 ppm applied using the Horn Generator with magnesium phosphide (hold 6). Hold 3 was used as the untreated control. The fumigations were begun between 12:30 p.m. and 12:50 p.m. on Sunday, June 6, 1999.

A Fumigant Gas Analyzer (GO-MAC Instrument Co.) was used to measure the methyl bromide in the ship hold. We used a PortaSens (Analytical Technologies) to measure phosphine in the phosphine treated holds, and a Silo-Chek (Canary Co.) to measure phosphine in the untreated hold. For the boundary line sampling we used a Draeger PAC III, which is sensitive to phosphine at 0.01 ppm. Sampling was done at 6 hour intervals in front of a recycling warehouse which was 11 m (35 ft.) from the ship and 22 m (70 ft.) from ship hold openings. Also the single crew member working on the ship was equipped with a Draeger PAC III during the fumigation. Samples were also taken in the tunnels that were beside the ship holds and above the wing tanks.

### Insect bioassays

Four insects were used in the bioassay: rusty grain beetle (*Cryptolestes ferrugineus* (Stephens)), rice weevil (*Sitophilus oryzae*



Placement of the insects in a ship hold

(L.)), red flour beetle (*Tribolium castaneum* (Herbst)), and the lesser grain borer (*Rhyzopertha dominica* (Fabricius)). Test vials of each species were prepared. Twenty-five mixed aged adults were placed in plastic screen-topped vials containing 10 g of wheat, with 20% being cracked grain, on Wednesday, June 2. The vials were held at 30°C for 24 hours, then transported from Winnipeg to Toronto (approximate temperature 20°C) and placed in the ship holds on Saturday, June 5. This incubation period before treatment enabled females to lay eggs, but was insufficient to allow the eggs to hatch. Consequently, all vials contained both eggs and adults.

Vials were taped to ropes. A set (four species, four replicates/species) was located at the bottom (12 m (36 ft.) from top), mid-way (6 m (18 ft.) from top), and at the top of each hold. Three ropes, each with three sets of vials, were hung from the manhole. One rope was pulled from each hold 32, 48 and 72 hours after the start of the fumigation. For the methyl bromide treatment, there was only one rope that was pulled at the completion of the methyl bromide fumigation (32 hours) For sampling the phosphine treatments at 32 and 48 hours, a cut was made in the polyethylene cover, the rope with attached vials was pulled from the hold and the polyethylene cover was resealed with duct tape.

Temperatures were measured using thermocouple wires connected to a data logger that took temperatures every ten minutes and recorded the mean temperature every hour. Temperatures were taken at six locations in each of the four holds - at the bottom, middle and top positions, attached to the bulkheads, and attached to vials. Relative humidity was measured in hold 4, at the top using a capacitive type RH ± 2% sensor attached to the data logger, and at the bottom using an ACR Smart Reader 2 with temperature and RH sensor ± 4%.



Counting the survival of the insects in each vial

After each rope was removed from a hold, adults were sieved from the wheat from each vial, the survival rates were noted and the adults placed back on clean wheat in new vials. These vials were held at about 20°C in the ship crew quarters until Wednesday, June 9 and then transported to Winnipeg on Friday, June 11 where they were held at 30°C. One week after the insects had been removed from the holds, the number of live and dead adults was reassessed to detect delayed mortality or revival of insects that could have been counted as dead but were in a fumigant-induced stupor. To assess egg survival, the wheat that was held in the holds was placed at 30°C on June 11, and the number of emerged adults counted after five weeks.

#### Corrosion assays

In order to measure the corrosiveness of phosphine to metal, copper samples and electrical components were examined. Copper strips (1 cm x 3 cm, 0.5 in. x 1.25 in.) were cleaned with concentrated hydrochloric acid, weighed and numbered. At the bottom and top levels of each rope a vial containing three copper strips and a male telephone jack connector was attached. Also three 15 m (45 ft.) telephone extension cords, with male and female connectors joined were taped to the end of each rope. At the end of the trials the vials and connectors were sent to Dr. Robert Brigham, a metallurgist, for assay. The copper strips were weighed as received, cleaned with hydrochloric acid to bare metal, dipped in absolute alcohol, dried and reweighed to determine weight

loss. The telephone extension cords were cut, and the resistance across the telephone jack connection was monitored as a function of time generally following ASTM B 539, Test Method C(3). This "dry circuit testing" technique uses a potential of 0.020V and limits the current to 100mA. An EG&G Princeton Applied Research Model 363 potentiostat was used to supply the constant DC voltage and to monitor the resultant current (Brigham 1999).

A 486 mother board was placed at the bottom of hold 6 (1000 ppm phosphine), and recovered at the end of test for examination. A functioning Zenith computer with 512 K of RAM and monitor was placed inside the second manhole of hold 4 (500 ppm phosphine). Power and keyboard cables were passed through the clear polyethylene so that commands could be typed into the computer to determine possible effects from exposure to phosphine.

#### Recapture of methyl bromide

Before hold 1 was sealed, a 0.9 cm (0.38 in.) diameter plastic delivery tube was taped to the top half of the access ladder for the release of methyl bromide. Three recovery hoses, 5 cm (2 in.) in diameter, were inserted into the hold. To optimize recovery, the inlets were spread across the bottom of the hold. The three hoses were connected to the first stage collector that contained a zeolite molecular sieve. The recovery blower was positioned after the collectors to provide for safe recovery. Both the collectors and the blower were on a flatbed truck parked on the dock.



The methyl bromide recapture unit of Cryo-Line Supplies Inc.

In 30 minutes 91 kg (200 lb.) of methyl bromide was released into the hold. After four hours, the hold seals were double checked and an additional 22.5 kg (50 lb.) of methyl bromide was introduced in order to reach the desired concentration (5400 ppm). A fan placed on the bottom of the hold ran for the first six hours of the fumigation to facilitate in distributing the methyl bromide throughout the hold.



Methyl bromide tanks used in the recapture treatment

Methyl bromide recapture was carried out by Cryo-Line Supplies Ltd. of Mississauga Ontario, Canada. It began 24 hours after the start of the fumigation at 1:00 p.m. Monday, June 7. The 25 hp blower powered by a portable generator created 6.8 kPa (2 inches of mercury) of pressure in the hold as it withdrew the air at 470 L/sec (1000 cfm) toward the collectors. After two hours, the recapture was halted for 1.5 hours because of a severe thunderstorm. The recapture process was stopped at 8:30 p.m. when methyl bromide was detected coming out the exhaust of the collector sieves. The concentration of methyl bromide remaining in the ship hold at 9:00 p.m. was 390 ppm, which is less than 10% of the initial concentration. The zeolite in the collector can absorb four to six percent of its weight in methyl bromide. The amount of methyl bromide recovered was determined by weighing the truck and sieve at a commercial weigh scale before and after the recapture.

#### ECO<sub>2</sub>FUME™

ECO<sub>2</sub>FUME™ fumigant gas is a nonflammable, premixed, cylinderized mixture of phosphine and carbon dioxide, and is produced by Cytec Canada Inc. located in Niagara Falls, Ontario, Canada. ECO<sub>2</sub>FUME™ fumigant is a gaseous mixture of 2% phosphine by weight, (2.6% by volume) in carbon dioxide. Phosphine is flammable in air at 1.79% (Bond 1984), but if phosphine is below 2.75% v/v in carbon dioxide, then it is nonflammable in all proportions of air (Pearson 1995).

We used 44 L (1.5 ft<sup>3</sup>) high-pressure cylinders which contain a total of 22.7 kg (50 lb.) of gas; 0.45 kg (1 lb.) of phosphine in 22.23 kg (49 lb.) of carbon dioxide. This size cylinder will fumigate 652 m<sup>3</sup> (23 060 ft<sup>3</sup>) of space at 25°C (77°F) to a concentration of 500 ppm phosphine. Hold 4 being 6220 m<sup>3</sup> (219 720 ft<sup>3</sup>) required 9.5 (22.7 kg.) cylinders of ECO<sub>2</sub>FUME™ to establish the target concentration of 500 ppm.

For this application two manifolds were constructed. Each manifold was capable of attaching four cylinders of ECO<sub>2</sub>FUME™. They were constructed of stainless steel 6mm (1/4 in.) high pressure tubing and fittings and each manifold was equipped with a pressure gauge. A 15-m (45-ft.) length of 6 mm (1/4 in.) copper tubing was attached to the end of each manifold. Copper tubing was selected because of its flexibility, making transportation and installation easy. The two lengths of tubing were run from the cylinder manifolds to the manhole, and were securely attached to the access ladder 2 m (6 ft.) below the manhole top.

ECO<sub>2</sub>FUME™ was chosen for this trial because of its ease and rate of application, and its effectiveness as a fumigant. ECO<sub>2</sub>FUME™ and the Horn Generator / Magtoxin® Granules System are different from traditional phosphine fumigations that use aluminum phosphide or magnesium phosphide in pellets or plates. These solid formulations of phosphine react

with humidity in the air to cause the release of phosphine gas, and hence require more time to reach target concentrations.



The set up of ECO<sub>2</sub>FUME™ cylinders for one of the phosphine treatments.

The first four ECO<sub>2</sub>FUME™ cylinder valves of one manifold were opened to begin the fumigation, but the application rate was reduced to one cylinder at a time. This allowed air to slowly be displaced from the hold and minimize the pressure on the seals. A single cylinder will completely discharge in approximately five minutes. The release of all nine ECO<sub>2</sub>FUME™ cylinders was spaced over a 90-minute period to establish the desired 500 ppm phosphine concentration.

Part of a tenth cylinder of ECO<sub>2</sub>FUME™ was applied 21 hours into the fumigation to top up the phosphine concentration. The balance of this tenth cylinder was added 69 hours into the fumigation. Topping up allowed maintenance of the desired phosphine concentration thereby compensating for the "breathing" of the hold from temperature swings.

#### **Horn Generator / Magtoxin® Granules System**

The Horn Generator is an automated device which is produced by Degesch de Chile. The Horn Generator is a specialized reaction chamber where a high purity magnesium phosphide product reacts with water to produce phosphine. This reaction is carried out under an atmosphere of carbon dioxide. The phosphine / carbon dioxide mixture is then injected through a recirculation system

into the structure to be fumigated. The chemical reactions that occur within the Horn Generator are as follows:



magnesium phosphide + water → phosphine + magnesium hydroxide



magnesium hydroxide + carbon dioxide → magnesium carbonate + water

Degesch Magtoxin® Granules, containing 96% magnesium phosphide as a flowable powder, is designed and formulated specifically for use with the Horn Generator. Granules are supplied in 850g (1.9 lb.) flasks (liberating 411g (0.9 lb.) of phosphine). Applications for pesticide registration for Magtoxin® Granules have been submitted to Canada, the United States and other countries.

After the Horn Generator is activated, it automatically flushes the system with carbon dioxide gas, fills the reaction chamber with water and turns on the recirculation fan. Once these operations are completed, the granules may be manually loaded into the fumigant reservoir inside the instrument. A switch is then activated which automatically transfers the granules to the reactor, and the injection of phosphine into the structure is begun. The Horn Generator is designed to react the contents of one flask of granules in about seven minutes. The transfer lines and reaction chamber inside the Horn Generator must be cleaned after the addition of 21 flasks, (one case of granules). A solution of formic acid is used to wash out the magnesium carbonate. It takes about 30 minutes to clean the Horn Generator, and prepare it for subsequent additions of the granules.

To reach the target concentration of 1000 ppm PH<sub>3</sub>, 24 flasks of Magtoxin® Granules were

used to produce the 9833g (21.6 lb.) PH<sub>3</sub>. The Horn Generator was positioned about 10m (30 ft.) from the manhole used to house gas sampling lines, thermocouple leads and recirculation tubing used for injection and recirculation of phosphine in the hold. The injection tubing was extended to the bottom of the hold, a total length of about 23 m (70 ft.).



The Horn Generator used for one of the phosphine treatments.

The Horn Generator was turned on at 12:40 p.m. on June 6, 1999. After a brief period to fill the reaction chamber with water and flush out the system with carbon dioxide, the addition of granules began at 12:49 p.m. Shortly after granules were added to the reaction chamber, it became apparent that the Horn Generator was not performing up to specifications. The low air flow alarm went off repeatedly, automatically stopping addition of the granules to the reaction chamber. This problem persisted throughout the addition period to the extent that injection of phosphine took almost twice as long as expected. Introduction of phosphine from 24 flasks of granules into the hold was completed at 6:20 p.m. on June 6.

It was subsequently learned that the ship was unable to supply consistent water pressure, and that pressure surges in the water line to the Horn Generator caused water to splash out of the reaction chamber into the pump, thereby retarding the air flow. The pressure drop resulting from the greatly extended length of the injection line from the Horn Generator may have been a contributing factor. A surge protector has been installed on the water inlet line to the Horn Generator. Tests subsequent to the experiment showed that lengthening the recirculating lines had no effect on the air flow rate.

Results

Temperature, relative humidity and gas concentrations

Over the three-day test, temperatures in the ship holds varied between 33°C and 15°C (Figure 2), with an average temperature during the first day of fumigation of 23°C. Vial temperatures were similar to the ship bulk head temperatures. Temperatures were slightly warmer at the top level compare with lower levels (Table 2). Relative humidity varied between 62 and 17% (Figure 2). Both relative humidity sensors gave similar readings, and did not seem to be affected by the phosphine.

Figure 2. The changes in temperature and relative humidity during the ship hold fumigation.

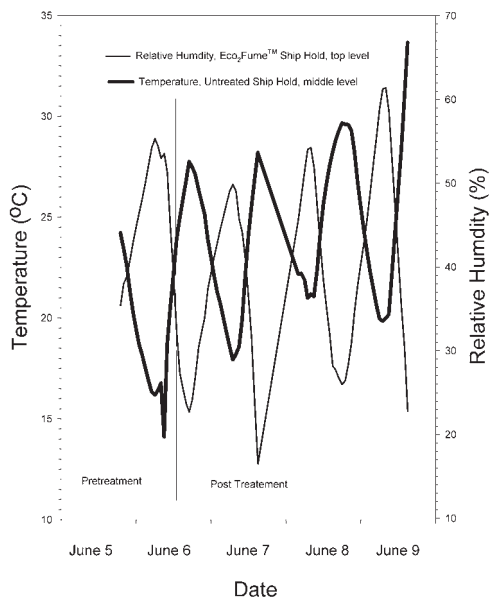


Table 2. The temperatures of ship bulk heads and vials containing insects at three different levels in the holds containing different treatments. This data set used temperatures taken just before treatments were begun, 10:00 a.m. June 5, until 3:00 p.m. June 6.

Place	Level	Temperature (°C) <sup>1</sup>				Average
		Methyl Bromide	Untreated	ECO <sub>2</sub> FUME™ PH <sub>3</sub> 500 ppm	Horn Generator PH <sub>3</sub> 1000 ppm	
Ship Bulk Head	Top	24.5±0.8 a	25.8±0.7 a	25.1±0.7 a	26.3±1.0 a	25.4
	Middle	22.4±0.8 a	23.9±0.6 b	25.1±0.7 a	24.1±0.8 ab	23.9
	Bottom	22.2±0.5 a	22.2±0.4 c	25.1±0.7 a	22.1±0.6 b	22.9
	Average <sup>2</sup>	23.1 y	23.9 zy	24.9 z	24.1 zy	
Vial	Top	23.4±0.5 b	-	-	26.5±1.0 a	25.0
	Middle	24.7±0.8 a	24.1±0.6 a	25.1±0.7 a	23.6±0.8 a	24.4
	Bottom	22.2±0.5 a	22.2±0.4 a	23.4±0.5 a	22.4±0.7 a	22.5
Average	23.4	-	-	24.1		

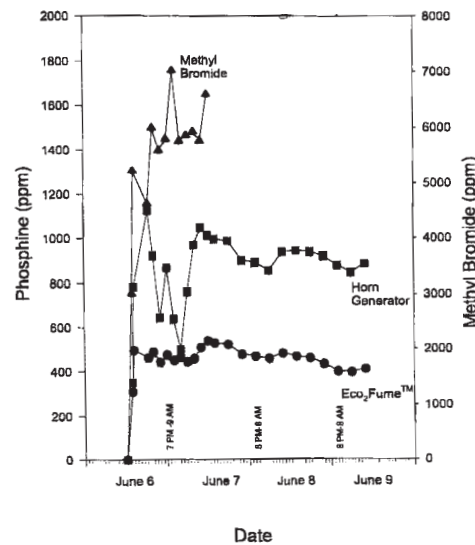
1. For a given treatment-place, means followed by different letters are significantly different, p>0.05, Student-Newman-Keuls Method  
 2. For averages, means followed by different letters are significantly different, p>0.05, Student-Newman-Keuls Method

The target gas concentrations were reached at all three levels after nine hours for methyl bromide (5400 ppm), 1.5 hours for ECO<sub>2</sub>FUME™ (500 ppm phosphine) and 5.5 hours for the Horn Generator (1000 ppm phosphine). Phosphine was detected in the bottom of the control hold, but it never exceeded 10 ppm (Table 3, Figure 3).

Table 3. The concentrations of fumigants in the ship holds. Measurements in gray underestimate true concentrations due to slight vacuum in holds caused by cooling. The target concentrations for methyl bromide treatment was 5400 ppm, for the ECO<sub>2</sub>FUME™ treatment was 500 ppm phosphine and for the Horn Generator treatment it was 1000 ppm phosphine.

Date	Time	Methyl Bromide (ppm)			ECO <sub>2</sub> FUME™ (PH <sub>3</sub> ppm)			Horn Generator (PH <sub>3</sub> ppm)			Control (PH <sub>3</sub> ppm)		
		bot	mid	top	bot	mid	top	bot	mid	top	bot	mid	top
6 June	13:50	10800	8700	700	320	340	275	325	495	230	5	0	0
	14:20	6000	5800	3900	485	500	505	980	1080	300	3	1	0
	18:30	6600	6300	1000	475	480	435	1245	1230	900	2	1	1
	20:00	7300	7300	3400	496	498	476	1060	880	830	0	0	0
	22:00	5800	5500	5500	428	474	430	443	753	741	1	1	1
	24:00	5800	5800	5800	480	480	470	862	858	860	0	0	0
7 June	02:00	6800	7000	7300	464	462	432	614	655	651	0	0	0
	04:00	6000	5500	5800	480	468	454	500+	500+	500+	0	0	0
	06:00	5800	6000	5800	460	448	432	708	774	812	0	0	0
	08:00	6000	5800	6000	454	458	468	957	980	975	1	0	0
	10:00	5800	5500	6000	520	518	489	1059	1032	1054	10	0	0
	12:00	6600	6600	6600	545	530	539	1015	1005	1015	11	1	1
8 June	14:00	-	-	-	520	530	535	1000	1000	985	10	0	0
	18:00	-	-	-	525	530	510	990	990	985	1	1	1
	22:00	-	-	-	475	510	450	900	910	900	1	0	0
	02:00	-	-	-	455	475	480	880	895	905	1	0	0
	06:00	-	-	-	460	470	450	860	860	850	1	0	0
	10:00	-	-	-	500	460	490	940	935	940	1	0	0
9 June	14:00	-	-	-	480	495	430	950	945	940	1	1	1
	18:00	-	-	-	460	470	455	940	940	935	0	0	0
	22:00	-	-	-	430	435	440	930	925	905	1	0	0
	02:00	-	-	-	385	425	395	875	890	875	0	1	0
	06:00	-	-	-	415	400	380	875	860	810	0	0	0
	10:00	-	-	-	440	370	426	880	890	890	4	0	0

Figure 3. The concentrations of fumigants in the ship holds. Measurements in gray underestimate true concentrations due to slight vacuum in holds caused by cooling.



Boundary line air monitoring was conducted throughout the treatment period. Low level phosphine gas readings were taken

every six hours. No detectable levels of phosphine (>0.01 PPM, limit of detectability) were recorded at the boundary lines during the fumigations, including during the aeration. The recycling warehouse was approximately 15 m (47 ft.) from the vessel and 20 m (64 ft.) from the top of the fumigated holds. No phosphine was detected in the ship quarters. The only ship crew member onboard wore a Draeger PAC III at all times and phosphine was never detected during the trial. Low levels of phosphine were detected in the tunnels that ran beside the holds and above the wing tanks. These tunnels were sealed to prevent any further spread of the phosphine. Repair crews had made a 1 m x 2 m (3 ft. x 6 ft.) hole in the side wall of hold 3. This may have been responsible for the leakage of phosphine into the tunnels.

Insect bioassays

After 32 hours, none of the adult insects survived in any of the three fumigation treatments. In the control hold there was at least 98% survival of adults for all species after 32 hours (Table 4). After one week, none of the

Table 4. Survival of adults in untreated hold immediately after taken from ship hold. All adults in the treated holds were dead after 32 hours.

Insects from untreated hold	Level	Survival (%; Average ± SEM)		
		32 hours	48 hours	72 hours
Red Flour Beetle	Top	99±1 a	100±0 a	100±0 a
	Middle	100±0 a	100±0 a	100±0 a
	Bottom	100±0 a	100±0 a	88±3 b
	Average	99.7±0.3	100±0	96±2
Rice Weevil	Top	99±1 a	100±0 a	100±0 a
	Middle	98±2 a	100±0 a	99±1 a
	Bottom	100±0 a	97±2 a	99±1 a
	Average	99±1	99±1	99.3±5
Lesser Grain Borer	Top	98±1 a	99±1 a	98±1 a
	Middle	100±0 a	99±1 a	99±1 a
	Bottom	100±0 a	99±1 a	67±12 b
	Average	99±1	99±1	88±6
Rusty Grain Beetle	Top	99±1 a	100±0 a	96±2 a
	Middle	100±0 a	98±2 a	100±0 a
	Bottom	99±1 a	99±1 a	96±2 a
	Average	99.4±0.5	99±1	97±1

For a given temperature - insect combination, means followed by different letters are significantly different, p>0.05, Student-Newman-Keuls Method

insects from the fumigated holds had revived, and the survival of insects removed from the control hold after 32 hours was not less than 92% for all species, except lesser grain borer which had an average mortality of 69±8% (mean±SEM) (Table 5). Insects from the bottom of the control hold had a lower survival

Table 5. Survival of adults in untreated hold one week after taken from ship hold. None of the adults classed as dead immediately after being removed from the treated holds had revived after one week.

Insects from untreated hold	Level	Survival (%; Average ± SEM)		
		32 hours	48 hours	72 hours
Red Flour Beetle	Top	100±0 a	98±2 a	99±1 a
	Middle	100±0 a	100±0 a	100±0 a
	Bottom	92±3 b	72±3 b	61±9 b
	Average	97±1	90±4	87±6
Rice Weevil	Top	98±2 a	99±1 a	98±1 a
	Middle	99±1 a	100±0 a	99±1 a
	Bottom	93±1 b	82±6 b	78±5 b
	Average	97±1	94±3	92±3
Lesser Grain Borer	Top	88±6 a	90±3 a	78±3 a
	Middle	83±4 a	87±4 a	88±5 a
	Bottom	36±4 b	16±3 b	11±5 b
	Average	69±8	64±10	59±11
Rusty Grain Beetle	Top	94±3 a	97±1 a	94±3 a
	Middle	95±2 a	96±2 a	90±5 a
	Bottom	97±2 a	95±4 a	92±2 a
	Average	95±1	96±1	92±2

For a given temperature - insect combination, means followed by different letters are significantly different, p>0.05, Student-Newman-Keuls Method

rate than those held higher up. This was probably due to the higher concentrations of phosphine, which reached about 10 ppm, at the bottom level as compared with the negligible concentrations at the higher levels (Table 3). There was a slight decrease in survivorship in the untreated hold with the duration of exposure. The survival rate for the lesser grain borer adults was lower than the other test species.

Egg survival was estimated by the number of adults emerging after 5 weeks (Table 6). For the red flour beetle, rice weevil and the lesser grain borer, 11 to 107 adults emerged from

Table 6. The number of adults per vial that emerged after 5 weeks at 30°C. Twenty-five adults were held in vials for 3 days with 20 g of wheat to allow oviposition. Vials were exposed to treatments in ship holds for 32, 48 and 72 hours before the adults were shaken from wheat and the wheat with eggs returned to the vial.

Insect	Level	Exposure Period (hours)	Number of Adults Emerged (Average ± SEM)			
			Methyl bromide	ECO <sub>2</sub> FUME™ PH <sub>3</sub> 500 ppm	Horn Generator PH <sub>3</sub> 1000 ppm	Untreated
Red Flour Beetle	Top	32	0.3±0.3	0±0	0±0	75±2
		48	0±0	0±0	0±0	16±3
		72	-	0±0	0±0	14±2
		Average	0.1±0.1	0±0	0±0	14±2
	Middle	32	0±0	0±0	0±0	13±3
		48	0±0	0±0	0±0	16±2
		72	-	0±0	0±0	9±2
		Average	0±0	0±0	0±0	13±1
	Bottom	32	0±0	0±0	0±0	13±1
		48	0±0	0±0	0±0	13±5
		72	-	0±0	0±0	10±2
		Average	0±0	0±0	0±0	13±1
Rice Weevil	Top	32	0±0	0.8±0.3	0.3±0.3	66±7
		48	0±0	0±0	0±0	69±5
		72	-	0±0	0±0	96±3
		Average	0±0	0.8±0.3	0.3±0.3	68±6
	Middle	32	0±0	4.5±1.0	0±0	88±16
		48	0±0	0±0	0±0	53±14
		72	-	0±0	0±0	73±24
		Average	0±0	1.5±0.5	0±0	71±15
	Bottom	32	0±0	0±0	2.3±1.1	73±5
		48	0±0	0±0	0±0	44±4
		72	-	0±0	0±0	70±10
		Average	0±0	0±0	0.8±0.3	62±6
Lesser Grain Borer	Top	32	0±0	1.0±0.4	1.8±0.9	64±11
		48	0±0	0±0	0±0	129±10
		72	-	0±0	0±0	128±20
		Average	0±0	0.3±0.1	0.6±0.3	107±13
	Middle	32	0±0	9.7±0.9	3.2±1.7	81±4
		48	0±0	0.8±0.8	0.8±0.8	97±16
		72	-	0±0	0±0	105±31
		Average	0±0	3.5±1.2	1.5±0.8	94±16
	Bottom	32	0±0	4.2±1.5	2.2±0.8	64±2
		48	0±0	0.5±0.5	0±0	82±13
		72	-	0±0	0±0	90±16
		Average	0±0	1.7±0.7	0.7±0.3	78±10

each vial held in the untreated hold (Tables 6-8). In the treated holds after 32 hours there were no more than 5 adults emerging per vial. This dropped to no more than an average 0.4 adults per vial after 48 hours into the treatment. There was no emergence from the treated holds after 72 hours. These results are summarized in Table 7. The rusty grain beetle had an average of only 0.1 to 0.3 adults from each vial from the untreated hold, hence it was impossible to estimate the mortality due to fumigation.

### Corrosion assays

Copper strips showed visible corrosion when removed from both phosphine fumigation treatments. There was a linear increase in corrosion with time. More corrosion was

Table 7. The survival of eggs in treated ship holds as compared to eggs in untreated ship hold.

Duration of exposure (hours)	Insect	Survival (%)		
		Methyl bromide	ECO <sub>2</sub> FUMETM PH <sub>3</sub> 500 ppm	Horn Generator PH <sub>3</sub> 1000 ppm
32	Red Flour Beetle	0.9	0.0	0.0
	Rice Weevil	0.0	3.0	1.1
	Lesser Grain Borer	0.0	6.4	3.4
48	Red Flour Beetle	-	0.0	0.0
	Rice Weevil	-	0.0	0.0
	Lesser Grain Borer	-	0.4	0.3
72	Red Flour Beetle	-	0.0	0.0
	Rice Weevil	-	0.0	0.0
	Lesser Grain Borer	-	0.0	0.0

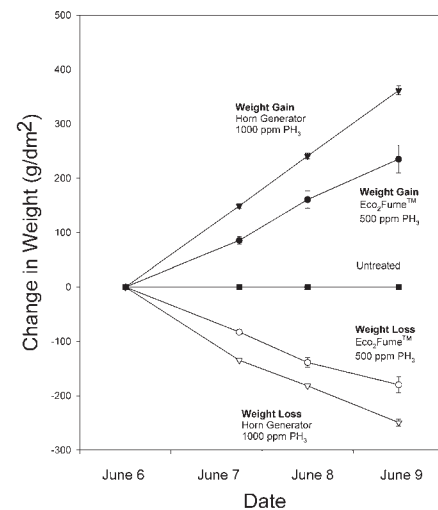
observed at the higher phosphine treatment (1000 ppm) although it did not double the amount of corrosion observed at the lower phosphine treatment (500 ppm) (Figure 4). These results are consistent with laboratory studies (Brigham 1999). There was no significant difference between corrosion at the bottom or top level (two way ANOVA;  $p=0.48$ , for level,  $p>0.001$  for duration) The phone jacks showed no visible signs of corrosion, non-conducting surface deposits or breaking

of circuits due to corrosion. There was no increase in the resistance across the treated phone jacks. The 486 mother board placed in the 1000 ppm hold showed visible deposits on the brass spring connectors. The computer held in the 500 ppm hold for 25.5 hours showed corrosion deposits on the solder coated copper junctions and no longer functioned, however, the high temperatures reached in the hold may also have contributed to the malfunction.

### Recapture of methyl bromide

Eighty-one percent of the 114 kg (250 lb.) of methyl bromide released in the fumigation was recaptured. The recapture system was designed to capture 91 kg (200 lb.) of methyl bromide and it captured 92 kg (203 lb.). The recapturing period spanned approximately 6 hours before the sieve was full, subtracting the 1.5 hours the unit was shut down during the thunderstorm.

Figure 4. The change in Weight ( $\pm$ SEM) of Copper Strips in Untreated Holds with either 500 or 1000 ppm Phosphine



## Discussion

Each of the three treatments could be used to limit the methyl bromide emissions to the atmosphere due to ship hold fumigations. These methods would cost more than the current methyl bromide treatments, and there are some regulatory issues that would have to be addressed before these methods could be used in ship hold fumigations.

### Recapture of methyl bromide

This method would have to be scaled up in order to treat entire ocean-going vessels which have holding capacities ranging from 30 000 to 100 000 m<sup>3</sup> (1 000 000 to 3 500 000 ft<sup>3</sup>). Collectors or sieves can be built to capture 160 kg (350 lb.) of methyl bromide and could be applied during methyl bromide fumigations of containers used for quarantine purposes. A business model developed by Cryo-Line Supplies Ltd. envisages 20 collectors at the Port of Vancouver. The cost of the collector per usage would be \$CAN 1750, assuming each collector would be used twice a month. Each unit is expected to last ten years.

Cryo-Line Supplies Ltd. proposes the following scenario for the recapture of methyl bromide at ports.

1. Each port would have an established area, or recapture dock, with an evacuation system (either a single blower or several smaller blowers) where fumigations with methyl bromide would take place. This would mainly be done for safety reasons, and to reduce costs for the set-up blowers and piping.

2. Containers and ships would be brought to the recapture dock. The piping placed in the chamber, container, or ship would be connected to the stationary network piping via the appropriate number hoses to remove the methyl bromide in the required amount of time.

3. At the end of the fumigation, the methyl bromide would be pulled through the piping and blown through the collectors where it would be trapped.

4. Once filled, the collectors would be exchanged for empty units. The saturated collectors would be transported back to a central plant for methyl bromide reclamation, condensation and re-packing into reclaim cylinders.

5. The methyl bromide would be reprocessed to a standard, and returned to the fumigator for reuse.

There are several advantages to the recapture of methyl bromide:

- Less methyl bromide would be vented to the atmosphere;
- Less of a hazard to workers when opening the fumigated hold or container;
- Recaptured methyl bromide would be available for reuse;
- Clearing ship holds of methyl bromide may be quicker;
- Unlike the other treatments used in this trial, recapture requires no registration from Health Canada;
- Very little change from the present fumigation method is required, other than some additional equipment to be added to the ship hold, container or chamber before sealing.

There are some hurdles to overcome before this method could be used:

- Approvals would have to be gained from the Ministry of Transportation for the movement of the captured methyl bromide.
- Labeling of the reclaimed methyl bromide.
- Ownership of the reclaimed methyl bromide.
- Clarification if reclaimed methyl bromide

falls outside quota allocations.

One way to reduce the amount of methyl bromide to be recaptured and hence the size of the collector required, would be to inflate large balloons inside the hold to reduce the dead space that must be fumigated. These balloons would have to be impermeable to methyl bromide, so that the gas is not diluted below the effective dose required in the ship hold, and the gas could be safely and quickly recaptured after the fumigation. This technique has been used in churches in Germany to reduce the space by 80%, before fumigating with sulfuryl fluoride (Binker 1993).

#### **ECO<sub>2</sub> FUME™**

A ship hold of 6000 m<sup>3</sup> would require 10 cylinders of ECO<sub>2</sub>FUME™ at \$CAN 150/cylinder. The major additional cost compared to a methyl bromide fumigation would be the longer durations needed at low temperature. The demurrage charges for ships at dock are approximately \$CAN 10 000 per day. There is also the additional cost of leaving the ship idle.

The advantage of using ECO<sub>2</sub>FUME™ is that; no methyl bromide would be released into the atmosphere, and it would be faster than fumigating with aluminum phosphide or magnesium phosphide formulations.

There are two main obstacles preventing the use of ECO<sub>2</sub>FUME™ to control insects in empty ship holds. Longer durations are needed for phosphine to work at low temperatures than methyl bromide. The temperatures during this trial were warm, with highs above 30°C. However, ships often must be fumigated in cooler weather. Phosphine efficacy is reduced more by low temperatures than is methyl bromide (Bond 1984). Phillips (1998) showed that at 200 ppm phosphine generated using ECO<sub>2</sub>FUME™ after 24 hours at 5°C gave more than 80% mortality of stored-product adult beetles and but only 15 to 80% mortality for the eggs. A 72-hour exposure was needed to obtain from 75 to 100% mortality of

eggs. The higher concentrations used in this trial would cause some increased mortality even at these low temperatures. However, with phosphine, higher concentrations cannot entirely compensate for shorter durations, i.e., doubling the concentration will not half the time needed for control. Ships are heated for painting, and this technique could be used to preheat ships before a phosphine fumigation, to increase the effectiveness of the treatment. The second obstacle is that ECO<sub>2</sub>FUME™ is not registered in Canada, although Cytec Canada Ltd. has shown interest in registering this product in Canada.

#### **Horn Generator / Magtoxin® Granules System**

As with ECO<sub>2</sub>FUME™, low temperature fumigations would require more time than fumigations done with methyl bromide. The disposal of the magnesium carbonate also has to be addressed. Applications for registration of Magtoxin® Granules intended for use with the Horn Generator have been submitted in Canada, with the support of DEGESCH America, Inc. The cost of a fumigation using the Horn Generator / Magtoxin® Granules System is not available at this time.

#### **Potential use in other applications**

These techniques could be used in other situations where methyl bromide is used to control insects and pathogens. Containers hold everything from manufactured goods to fruits. Some may be fumigated with methyl bromide at export or at import for quarantine or other reasons. Cryo-Line Supplies Ltd. has already demonstrated in the port of Savannah, Georgia that methyl bromide can be recaptured from containers, and they have shown in this trial, it can also be readily recaptured from large volume spaces.

Both phosphine generating methods could be used in conjunction with the heat and carbon dioxide to fumigate food processing plants (Mueller 1993, Marcotte 1996). These fumigation techniques would be more accurate

than the current method which uses aluminum or magnesium phosphide. It would also alleviate the need to re-enter the fumigated structure to add or remove fumigant. Another benefit of the combination method is it uses lower phosphine concentrations (100 ppm) than were used in this study, thereby minimizing corrosion.

The Horn Generator has been used commercially in South America for several years. During this period a wide variety of structures have been fumigated. A number of tests have been conducted in North America. Warehouses (single and multi-floor), chambers, tarpaulins and large-grain silos have been successfully treated.

#### **Other alternatives to empty ship-hold fumigations with methyl bromide**

A thorough cleaning of the holds after unloading grain or any other cargo is an excellent and preferred method to prevent insects from finding food and harborage in the empty ship holds. Modern ship design has greatly reduced the residues of grain left after unloading, making good sanitation easier. This results in fewer insects left in the hold that could infest the next cargo of grain. In 1948 / 1949 of the 517 ships inspected, 8% had to be fumigated because of insects in the empty holds (Monro 1951). Today, about 2% of the inspected ships are fumigated (Table 1).

In the USA and Australia, very few empty grain ships are fumigated with methyl bromide. In the USA, if an infestation is found, the hold is cleaned and sprayed with residual insecticides, cyfluthrin or malathion. There is also less of a concern with insects in the empty ship holds in the USA because grain is often fumigated in transit with phosphine, or is already protected with a residual insecticide on the grain. (L. Zettler, personal communication). In Australia, ships are steam cleaned at sea. If a ship still has insects in its holds, then the ship is turned away. (J. Banks, personal com-

munication). Cleaning is also the most frequent method employed in Canada. In France, methyl bromide has not been used to fumigate ship holds since 1950. Extensive insect infestations in the ship hold are controlled with dichorvos. For limited infestations, the grain is treated with dichorvos at loading or with phosphine after loading (P. Ducom, personal communication).

It is rare that Canadian grain is treated with a residual insecticide, such as malathion or diatomaceous earth, because of Canada's cold winters and because phosphine is used to control infestations at the farm and primary elevators. As grain treated at the farm is diluted with untreated grain, export grain has almost no residual insecticide on the grain. Hence, Canadian grain is susceptible to infestation if insects are present in ship holds at loading. Customers sometimes request that grain be treated with malathion as it is loaded onto the ships, however, most Canadian customers do not want the grain treated with residual insecticides. Fumigation of grain with phosphine in ships is permitted in Canada as it does not leave residues on the grain. This type of treatment would be similar in cost to a methyl bromide fumigation of empty ships, and would also kill any insects that had previously been in the ship. The *Canada Grain Act*, however, does not allow loading grain into infested vessels. Another option would be to turn away the approximately 25 ships that would require a methyl bromide treatment, as is done in Australia.

Finally, sulfuryl fluoride (Vikane) is registered for ship hold fumigations in the USA; however, it is rarely used in ship holds and is mainly used against termites. Sulfuryl fluoride is not very effective against eggs, and requires longer exposures than methyl bromide against other life stages of insects (Bond 1984). It is not registered as a pesticide in Canada.

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**DIRECTION FOR USE**

This product can only be used/applied within the Horn Generator.

It is a violation of the Pest Control Products Act to use this product in a manner inconsistent with its labeling. This product is accompanied by an approved Applicator's Manual. Read and understand the entire labeling. All parts of the labeling are equally important for safe and effective use of this product. Call DEGESCH, America Inc. or Gardex Chemicals Ltd. if you have any questions or do not understand any part of this labeling.

**Refer to the Applicator's Manual for more detailed precautions, recommendations and directions for use.**

**STORAGE INSTRUCTIONS**

1. Store DEGESCH MAGTOXIN® GRANULES in a dry, well-ventilated area away from heat, under lock and key. Post as a pesticide storage area. Do not contaminate water, food or feed by storing pesticides in the same areas used to store these commodities.
2. Do not store in buildings where humans or domestic animals reside. Keep out of reach of children.
3. DEGESCH MAGTOXIN® GRANULES are supplied in gas-tight, re-sealable aluminum flasks.
4. The shelf life of MAGTOXIN® GRANULES is virtually unlimited as long as the containers are tightly sealed.

**DISPOSAL INSTRUCTIONS**

**Do not contaminate water, food or feed by storage or disposal.**

Unreacted or partially reacted MAGTOXIN® GRANULES are acutely hazardous. Improper disposal of excess pesticide is a violation of the Pest Control Products Act. If these wastes cannot be disposed of by use according to the label instructions, contact the manufacturer or distributor for guidance. For specific instruction, see Spill and Leak Procedures in the Applicator's Manual. Some local and provincial waste disposal regulations may vary from the following recommendations. Disposal procedures should be reviewed with appropriate authorities to ensure compliance with local and provincial regulations. Dispose of containers in a sanitary landfill or by other procedures approved by provincial and local authorities. If properly exposed during the fumigation period, spent MAGTOXIN® GRANULES will contain virtually no unreacted magnesium phosphide. This will be a non-hazardous waste. However, incompletely exposed MAGTOXIN® GRANULES will require special care for disposal.

**SPILL AND LEAK PROCEDURES****General Precautions and Directions**

A spill, other than incidental to application or normal handling, may produce high levels of gas and, therefore, attending personnel must wear SCBA or its equivalent when the concentration of hydrogen phosphide gas is unknown. Other NIOSH/MSHA approved respiratory protection may be worn if the concentration is known or found to be less than 15 ppm. Do not use water at any time to clean up a spill of DEGESCH MAGTOXIN® GRANULES. Water in contact with unreacted metal phosphides will greatly accelerate the production of hydrogen phosphide gas which could result in a toxic and/or fire hazard. Wear gloves of cotton or other breathable material when handling metal phosphides.

Return all intact aluminum flasks of MAGTOXIN® GRANULES to original cases or other packaging which has been suitably constructed and marked according to T.D.G.A. regulations. Notify consignee and shipper of damaged cases. If the flasks have been punctured or damaged so as to leak, they must be temporarily repaired with aluminum tape. Transport the damaged flasks, thus sealed, to an area suitable for pesticide storage for inspection. Caution: The punctured flasks may flash upon opening at some later time. Refer to the Applicator's Manual for more detailed Spill and Leak procedures. Further instructions and recommendations may be obtained, if required, from DEGESCH America, Inc. or Gardex Chemicals Ltd.

THIS PRODUCT IS ACCOMPANIED BY AN APPROVED LABEL AND APPLICATORS MANUAL. READ AND UNDERSTAND THE ENTIRE LABELING. ALL PARTS OF THE LABELING ARE EQUALLY IMPORTANT FOR SAFE AND EFFECTIVE USE OF THIS PRODUCT. CALL DEGESCH AMERICA, INC. OR GARDEX CHEMICALS LTD. IF YOU HAVE ANY QUESTIONS OR DO NOT UNDERSTAND ANY PART OF THIS LABELING.

REFER TO THE APPLICATOR'S MANUAL FOR DETAILED PRECAUTIONS, RECOMMENDATIONS AND DIRECTIONS FOR USE.

**Warranty:** Seller warrants that the product conforms to its chemical description and when used according to label directions under normal conditions of use, it is reasonably fit for the purposes stated on the label. Seller makes no other warranty either express or implied, and buyer assumes all risk should the product be used contrary to label instructions.

**RESTRICTED USE PESTICIDE**

**DUE TO ACUTE INHALATION TOXICITY OF HIGHLY TOXIC HYDROGEN PHOSPHIDE (PHOSPHIDE PH<sub>3</sub>) GAS**

For retail sale to and use only by provincially licenced applicators for those uses covered by the applicator's certification or persons trained in accordance with the Applicator's Manual working under the direct supervision and in the physical presence of the provincially licenced applicator. Physical presence means on site or on the premises. Read and follow the label and the Applicator's Manual which contains complete instructions for the safe use of this pesticide.

**DEGESCH MAGTOXIN®**

DEGESCH MAGTOXIN® GRANULES

FOR CONTROL OF PESTS IN STORED GRAIN, PROCESSED FOODS, FEEDS  
AND NON-FOOD COMMODITIES INCLUDING TOBACCO

Active Ingredients: Magnesium Phosphide .....96%  
Inert Ingredients .....4%

KEEP OUT OF REACH OF CHILDREN  
DANGER POISON  
P.C.P.#:

(TO THE USER: If you cannot read English, do not use this product until the label has been fully explained to you).

**STATEMENT OF PRACTICAL TREATMENT**

Symptoms of overexposure are headache, dizziness, nausea, difficult breathing, vomiting and diarrhea. In all cases of overexposure get medical attention immediately. Take victim to a doctor or emergency treatment facility.

**If the gas or dust from magnesium phosphide is inhaled:**

Get exposed person to fresh air. Keep warm and make sure person can breathe freely. If breathing has stopped, give artificial respiration by mouth-to-mouth or other means of resuscitation. Do not give anything by mouth to an unconscious person.

**If magnesium phosphide GRANULES or powder are swallowed:**

Drink or administer one or two glasses of water and induce vomiting by touching back of throat with finger, or if available, syrup of ipecac. Do not give anything by mouth if victim is unconscious or not alert.

**If dust from granules of magnesium phosphide get on skin or clothing:**

Brush or shake material off clothes and shoes in a well-ventilated area. Allow clothes to aerate in a ventilated area prior to laundering. Do not leave contaminated clothing in occupied and/or confined areas such as automobiles, vans, motel rooms, etc. Wash contaminated skin thoroughly with soap and water.

**If dust from granules get in eyes:**

Flush with plenty of water. Get medical attention.

NET CONTENTS:  
850g of GRANULES

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## PRECAUTIONARY STATEMENTS

**HAZARDS TO HUMANS AND DOMESTIC ANIMALS**

**DANGER:** Magnesium phosphide from DEGESCH MAGTOXIN® GRANULES or dust may be fatal if swallowed. Do not get in eyes, on skin or on clothing. Do not eat, drink or smoke while handling magnesium phosphide fumigants. If a sealed container is opened, or if the material comes into contact with moisture, water or acids, these products will release hydrogen phosphide (phosphine, PH<sub>3</sub> which is an extremely toxic gas. If a garlic odour is detected, refer to the Industrial Hygiene Monitoring Section of the Applicator's Manual for appropriate monitoring procedures. Pure hydrogen phosphide gas is odourless; the garlic odour is due to a contaminant. Since the odour of hydrogen phosphide may not be detected under some circumstances, the absence of a garlic odour does not mean that dangerous levels of hydrogen phosphide gas are absent. Observe proper re-entry procedures specified elsewhere in the labeling to prevent overexposure.

**NOTE TO PHYSICIAN**

Magnesium phosphide GRANULES, or dust re-acts with moisture from the air, acids and many other liquids to release hydrogen phosphide (phosphine, PH<sub>3</sub>) gas. Mild exposure by inhalation causes malaise (indefinite feeling of sickness), ringing in the ears, fatigue, nausea and pressure in the chest which is relieved by removal to fresh air. Moderate poisoning causes weakness, vomiting, pain just above the stomach, chest pain, diarrhea and dyspnea (difficulty in breathing). Symptoms of severe poisoning may occur within a few hours to several days resulting in pulmonary edema (fluid in lungs) and may lead to dizziness, cyanosis (blue or purple skin), unconsciousness, and death.

In sufficient quantity, phosphine affects the liver, kidneys, lungs, nervous system and circulatory system. Inhalation can cause lung edema (fluid in lungs) and hyperemia (excess of blood in a body part), small perivascular brain hemorrhages and brain edema (fluid in brain). Ingestion can cause lung and brain symptoms but damage to the viscera (body cavity organs) are more common. Phosphine poisoning may result in (1) pulmonary edema, (2) liver elevated serum GOT, LDH and alkaline phosphatase, reduced prothrombin, hemorrhage and jaundice (yellow skin colour) and (3) kidney hematuria (blood in urine) and anuria (abnormal or lack of urination). Pathology is characteristic of hypoxia (oxygen deficiency in body tissue). Frequent exposure to concentrations above permissible levels over a period of days or weeks may cause poisoning. Treatment is symptomatic.

**PHYSICAL AND CHEMICAL HAZARDS**

Magnesium phosphide GRANULES and partially spent dust will release hydrogen phosphide if exposed to moisture from the air or if it comes into contact with water, acids and many other liquids. Magnesium phosphide is considerably reactive and will liberate gas rapidly. This is particularly true in the presence of liquid water and at higher temperatures. Since hydrogen phosphide may ignite spontaneously at levels above its lower flammable limit of 1.8% v/v, it is important not to exceed this concentration. Magnesium phosphide fumigants should not be stacked or piled up or contacted with liquid water. This may cause a temperature increase, increase the rate of gas production and confine the gas so the ignition could occur.

It is preferable to open containers of magnesium phosphide products in open air as under certain conditions, they may flash upon opening. Containers may also be opened near a fan or other appropriate ventilation which will rapidly exhaust contaminated air. When opening flasks of MAGTOXIN® GRANULES, point the flask away from the face and body and twist the cap off. Although the chances for a flash are very remote never open these containers in a flammable atmosphere. These precautions will also reduce the fumigator's exposure to hydrogen phosphide.

Pure phosphine (hydrogen phosphide) gas is practically insoluble in water, fats, oils, and is stable at normal fumigation temperatures. However, it may react with certain metals and cause corrosion, especially at higher temperatures and relative humidities. Metals such as copper, brass and other copper alloys, and precious metals such as gold and silver are susceptible to corrosion by phosphine. Thus, small electric motors, smoke detectors, brass sprinklers heads, batteries and battery charges, fork lifts, temperature monitoring systems, switching gears, communication devices, computers, calculators and other electrical equipment should be protected or removed before fumigation. Hydrogen phosphide will also react with certain metallic salts and, therefore, sensitive items such as photographic film, some inorganic pigments, etc. should not be exposed.

**Appendix B: Collaborators and Contact List:**

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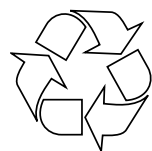
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