A new method of using low levels of phosphine in combination with heat and carbon dioxide

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Abstract

A combination of low levels of phosphine (65–100 ppm), heat (32–37°C), and carbon dioxide (4–6%) were used in three mills in the United States. Fumigations were carried out for 24 hours. Multiple species of stored-product insects in various life stages were used as bioassays. A corrosion study was conducted with copper and electronic equipment. A penetration study was conducted with 2 and 3 m deep tubes filled with wheat flour. All insect bioassays were retained for 30 days. A 100% insect mortality within bioassays was achieved in 24 hours or less. This method of fumigation holds promise as a replacement for methyl bromide fumigations in flour mills and similar structures.

Introduction

The purpose of the study was to evaluate the use of combination treatments to effectively control given populations of stored-product insects. Insects are stressed by the increased levels of carbon dioxide and heat. This allows lower levels of phosphine to be more effective in shorter periods of time.

History

Fumigations with inert gases and methyl bromide have been performed since 1929. The famous stored-product entomologist R.T. Cotton is noted for the work and patented a combination method. More recently, the Australians have performed numerous experiments with carbon dioxide and phosphine on commodities in sealed structures. The Israelis patented a method in 1979 for using four parts carbon dioxide with one part methyl bromide in grain storages. Carmi and Leesch have shown that carbon dioxide is effective in moving an atmosphere of phosphine deeper into the grain mass.

Mueller states in 'The Mallis Handbook of Pest Control' (7th ed.) that there are several ways to produce insect stress including: 1) decreasing oxygen concentration, 2) increasing carbon dioxide levels, or 3) increasing temperature. It has been published that insect respiration can be increased by 50% by increasing carbon dioxide levels to 3%. Insect respiration increased 300% when carbon dioxide levels were raised to 5%.

Materials and Methods

Fumigants

Fumigants for this study were produced from Degesch FUMI-CEL™ and Degesch FUMI-STRIP™, a magnesium phosphide formulation in a solid plate form. Each plate generates 33 g of hydrogen phosphide (phosphine) gas. These formulations have advantages over standard aluminium phosphide formulations in that gas is generated more rapidly. A minimum concentration of 100 ppm can be achieved in 7 hours at 32°Cand 50% r.h. This compares to 11 hours with aluminium phosphide at the same tested dosage rates and conditions.

Dosage

A dosage rate of 6.6 g/1000 cu. ft. was initially used to treat each location. One gram of phosphine produces 25 ppm in 1000 cu. ft. The theoretical maximum concentration for the dosage rate was 165 ppm. Conventional fumigations with phosphine would have concentrations between 850 and 1500 ppm. Each of the three locations showed peak phosphine concentrations of more than 50% of the theoretical maximum concentration. These concentrations were representative of properly sealed buildings.

The first location (Mill #I) was a two storey, 60000 cu. ft. feed mill at Purdue University in West Lafayette, IN. The second location (Mill #2) was a six storey, 181000 cu. ft. flour mill in Honolulu, HI. The third location (Mill #3) was a six storey, 300000 cu. ft. flour mill in Frankenmuth, MI. All fumigations were carried out during the summer of 1993.

Carbon Dioxide

During the first combination fumigation at Purdue University (Mill #I), a total of 37 fifty pound steel cylinders of carbon dioxide were used during the fumigation. Use of cylinders was cumbersome and more expensive than larger vessels.

Carbon dioxide must be vaporised from a liquid to a gaseous state. Gas temperatures should range from 70–90°F or 20–30°C when entering the building. Special hoses and regulators are required when working with 40°F liquid carbon dioxide. Advanced knowledge of how to control and release this inert gas is necessary. Even though carbon dioxide is inert, it can be very deadly. Oxygen levels are decreased when carbon dioxide enters a building. Carbon dioxide should be treated as a hazardous fumigant similar to methyl bromide and phosphine.

Heat

Frequently mills and similar facilities have heating systems that maintain a content temperature in the building. The Purdue University location utilised electric heaters to maintain a 100°F (38°C) temperature (± 2°C). The Hawaiian Flour Mill (Mill #2) had no heating system. No heaters were available on the island of Oahu.

The ambient temperature of the flour mill was 30–31°C, temperatures necessary for the combination techniques. A steam boiler was used to heat radiators in the building and an additional steam coil-type 125000 BTU heater was utilised to enhance heating capacity. Outdoor temperatures during the Michigan fumigation (Mill #3) reached 4°C or 40°F. The other two fumigations (Mill #1 and Mill #2) were performed on warm summer days.

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Results

Test Insects

Mill #1

Test insects were placed in four locations at the Purdue Feed Mill. Four species of insects were utilised. These included: Angoumois grain moth *(Sitotroga cerealella),* red flour beetles *(Tribolium castaneum),* warehouse beetles *(Trogoderma variable),* and rice weevils *(Sitophilus oryzae).* Eggs, larvae, pupae, and adults were placed in 250 mL plastic containers.

Two groups of 36 containers were placed on the first floor and two groups of 36 containers were placed on the second floor.

Test insects were retrieved from the fumigated mill beginning 20 hours after the start of fumigation. Test insects continued to be retrieved every 4 hours until 48 hours after the start of fumigation. Adult and larval stages were evaluated for all sampling intervals. All insect stages were dead starting 20 hours into the fumigation. All of the containers were taken to the lab at Purdue University and incubated for 30 days in a growth chamber. No insect activity was observed after 30 days. Control insects remained alive throughout the evaluation period.

Mill #2

Two species of stored-product insects were placed as bioassays in the flour mill fumigation in Hawaii; red flour beetles *(Tribolium castaneum)* eggs, larvae, pupae, and adults (Indiana strain and Hawaii strain), and rice weevil *(Sitophilus oryzae)* adults. A total of 150 insect cages with 10 or more insects per cage were placed on the 6 floors. Insect cages were placed approximately one meter above the floor. Insect cages were retrieved from the building beginning 13 hours after the start of fumigation. All insects within bioassays and retrieved at the 13 hour interval were dead. All insects retrieved from the flour mill at 24 hours after the start of fumigation were also dead. These insects were incubated in Hawaii and Indianapolis for 30 days with no activity observed. All indoor and outdoor insect control groups were alive 48 hours after the fumigation start and 87% were alive after 30 days.

Mill #3

During the Michigan flour mill fumigation, 3 species of stored-product insects were used in bioassays: red flour beetle eggs, larvae, pupae, and adults, rice weevil adults, and Indianmeal moth eggs *(Plodia interpunctella).*

Insect cages were placed on each floor and controls were maintained as described previously. Over 150 cages were placed in the mill with 10 or more insects per cage.

Insect canes were retrieved from the building twelve hours after the start of the fumigation. All adult and larval specimens were dead twelve hours from the beginning of the fumigation. All insects retrieved from 12– 24 hours after the start of fumigation were subsequently dead. All specimens were held at room temperature. No insect activity was observed for any stage of the three stored-product insects tested. Controls from outdoor cages and indoor cages remained alive.

Penetration Study

Phosphine and carbon dioxide are excellent penetrating gases. Phosphine is a more effective penetrator than methyl bromide. Twelve 6 inch diameter × 6 ft long PVC pipes were capped and permanently sealed on one end. Insect cages were placed in the bottom of these long tubes. Each tube was subsequently filled to a 3-foot level with wheat flour and insect cages were placed at that level. Flour was again added to the remaining 3 feet and tubes were filled completely. A 1.4 ml polyethylene bag was secured with tape over the open end of each tube. Two tubes were placed on each of 6 floors of the (Mill #2) Hawaiian Flour Mill (HFM).

Five flour-filled tubes were retrieved from the flour mill 24 hours after the start of the fumigation. Carbon dioxide and phosphine levels were measured with a Draeger tube and levels were found to be equal to the ambient concentration of the fumigated mill. Phosphine levels under polyethylene bags were 50 ppm, the carbon dioxide levels were 3%. Test insects at 3 feet and 6 feet were evaluated. All adults and larvae were dead. Eggs and pupae were incubated for 30 days.

The remaining 6 tubes were retrieved 48 hours after the start of fumigation. To affect a kill on test insects, gases had to penetrate the 1.4 mL polyethylene bag, permeate 3–6 feet of flour and inside polyethylene bioassay tubes and kill egg larvae, pupae, and adult insect specimens. Insects in control groups remained alive. After 30 days, insects in polyethylene vials positioned at the bottom of 6 foot flour tubes showed some survival in the first instar larvae stage. Some eggs had survived this penetration study.

The study was taken one step further in Michigan (Mill #3). Two 5-foot and one 10-foot tube similar to those described above were placed in the fumigated mill. All stages of insects were positioned at 10-foot, 5-foot, and I-foot levels within tubes. A 1.4 mL polyethylene bag was placed over one 5- foot tube. No bags were placed over the remaining tubes.

Observations 12 hours after the start of fumigation indicated that insects at the bottom of the 5-foot tube without a plastic bag were dead. After 24 hours the test insects at the bottom of the 5-foot tube with bag and 10-foot tube were dead. The immature stages were incubated for 30 days. No survivors appeared after 30 days. This fumigation was about 4°C or 10°F warmer than the Hawaiian study. The gas concentrations were nearly the same.

Corrosion Study

One negative characteristic of phosphine is that under certain conditions it can cause corrosion of precious metals and coppers. Many items should be removed from buildings to be fumigated when possible. Often it is impossible to remove items that could be affected by high levels of phosphine and high humidity.

Phosphine produced from magnesium phosphide or aluminium phosphide can generate phosphoric acid. When phosphoric acid and sufficient moisture are combined on precious metals, a mild acid is formed and corrosion occurs. With severe corrosion, instruments will often fail. Corrosion management is necessary when phosphine is to be used in fumigating buildings that contain printed circuits, and sensitive equipment.

Heat and carbon dioxide will lower humidity within a facility. Samples of wheat from the Mill #3) dropped from 13–11% moisture during the fumigation process, while moisture in the flour mill dropped 12% (56% vs. 44%).

By managing large peaks in phosphine gas levels, levels of H_3PO_4 can also be managed. Phosphine levels should remain in a range from 50–100 ppm with the need for magnesium phosphide fumigant to be physically removed when levels reach 150 ppm. Magnesium phosphide can be easily added or removed from buildings to achieve these target levels. Proper safety precautions are necessary.

A new method of evaluating corrosion was developed for this test. New copper pennies where placed throughout the structures to determine severity of corrosion with combination fumigation techniques. Each penny was labelled with a number and weighed prior to fumigation. Pennies were located randomly throughout each structure and placed vertically on-edge. Some pennies were suspended from ceilings with fishing line at various heights. Solid blocks of steel and copper where placed within the Purdue Feed Mill during fumigation.

Results of the corrosion study revealed small weight gains of each of the pennies. Average weight gains of 0.0009 grams for the 10 pennies in the Michigan study and average weight gains of 0.0040 grams were observed for 31 pennies in the Hawaiian study.

Electron microscope scans revealed no traces of phosphorus or other elements (except inherent impurities) on the two steel samples placed on the first and second floors of the feed mill. No traces were found in the copper sample (apart from impurities) placed on the second floor of the mill. The copper sample placed on the first floor, did show a treatment effect of about 8% phosphorus contamination (average of two readings) due to phosphine gas treatment.

Although this information is preliminary, future comparisons should allow for ratings of corrosion potential and a determination of the method's viability.

A ten-penny corrosion test is planned for each future fumigation. Average percent weight gains should be a factor that will help with corrosion management assessment programs.

Cost

Real costs of a fumigation are related to shutdown time. Many mills and processed food operations cannot afford shutdowns longer than 24 hours.

The costs of carbon dioxide are offset by reduced costs for magnesium phosphide. Additional costs for equipment rental (vaporiser and vessel) also exist. Permanent installation of such equipment would be relatively simple. Additional costs for heat would be determined by outdoor temperatures and how well a building is sealed and/or insulated. Additional steam coils or electrical heaters could be installed if necessary.

It is difficult to determine the specifics of a building without studying it extensively during the first few combination fumigations. This will require many around-the-clock gas readings throughout the building. After experience is gained in stabilising and maintaining levels of phosphine within the proper range, combination fumigations can be very successful and cost-effective.

Conclusion

The future of the fumigation business is unclear. Dozens of fumigants have been removed from the market during the past decade. Methyl bromide has been identified as a serious ozone depletion with an Ozone Depletion Potential (ODP) of 0.7. The Clean Air Act in the United States declares that any product with an ODP of 0.2 or greater will be eliminated in due course. The Montreal Protocol's 120 plus signature countries are discussing similar retribution. There may be a day in the near future when phosphine could be the only conventional fumigant available.

With this uncertainty, alternatives are needed to eliminate insects from structures. Methyl bromide provides several advantages in that it acts quickly (24-hours or less), is inexpensive, and causes minimum damage to contents of structures, although it is a less aggressive penetrator than phosphine, it provides for effective kill of pests.

A Combination Method of fumigation using maintained lower levels of phosphine, moderate heat, and higher carbon dioxide levels for a 24-hour periods in sealed structures has potential for replacing many methyl bromide applications within mills and similar structures.

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