

THE EFFECT OF LOW CONCENTRATIONS OF CARBON DIOXIDE
ON THE PENETRATION OF PHOSPHINE THROUGH WHEAT

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Abstract

Aluminum phosphide was applied with and without CO₂ (dry ice) to the top of 4.15m towers containing soft red winter wheat. Dosages were calculated on the total volume of the towers to produce theoretical concentrations of 1.74g PH₃/m³ and 5% (v/v) CO₂. Concentrations of PH₃ and CO₂ were determined periodically during the 6-day experiments. When CO₂ was applied with aluminum phosphide, phosphine penetrated the column of wheat faster and accumulated in higher concentrations than when aluminum phosphide was applied alone. The effects of the CO₂ were more pronounced as the depth in the column increased. At the end of the exposure time, concentrations of phosphine were more evenly distributed when CO₂ was applied with the aluminum phosphide.

Introduction

Fumigation has been a major chemical control technique for many years to eliminate insect infestations from stored products. Recently, environmental factors have greatly influenced our choice of chemicals to control insects and have resulted in the loss of many fumigants today. In an effort to maximize the efficiency while reducing the amount of chemical that is used for insect control, research has focused on ways to use fumigants in a more efficacious manner. Early research on mixtures of hydrogen cyanide with other volatile compounds was conducted by Pratt et al. (1935). In fact, the toxicity of methyl bromide, which is one of the primary fumigants in use today, was discovered when Le Goupil (1932) tried mixing it with various fumigants to reduce their flammability. He quickly realized that the methyl bromide was more toxic to the insects than the original fumigants.

Other studies have centered on mixtures of fumigants with various non-reactive gases such as carbon dioxide (CO₂) and nitrogen. Cotton (1930) investigated the use of carbon dioxide with fumigants and concluded that carbon dioxide might increase the toxic effects of the fumigants by satisfying the sorptive properties in commodities when it is used with the fumigants. Cotton and Young (1929) and Cotton (1932) studied the uses of carbon dioxide to stimulate respiration which resulted in the increased toxicity of some fumigants. Cotton (1932) concluded that carbon dioxide did not increase the toxicity of hydrogen cyanide to insects. Jones (1938) was able to show that

the concentration of CO₂ was a factor in increasing the toxic effect of methyl bromide and other fumigants to the red flour beetle, Tribolium castaneum (Herbst). For methyl bromide, CO₂ had the most effect at concentration below 40%. Recently, Desmarchelier (1984) showed that a low concentration (25%) of carbon dioxide increased the toxicity of phosphine to some stored product insects but not to others. In a study of the effect of CO₂ on the toxicity of phosphine to diapausing larvae of the Khapra Beetle, Trogoderma granarium Everts, El-Lakwah et al. (1989) found that CO₂ had a negative effect on the toxicity of phosphine at short exposure times (18 to 24 hr) but a positive effect at longer exposure periods (48 to 72 hr). Rajendran and Muthu (1989) were able to show that CO₂ did increase the toxicity of phosphine to Tribolium castaneum Herbst. Kashi and Bond (1975) showed that concentrations of CO₂ ranging from 1 to 50% potentiated the toxic effects of phosphine to adults of Sitophilus granarius (L) and Tribolium confusum (duVal). All of these studies have concentrated on the effects carbon dioxide on the toxicity of fumigants to insects.

Calderon and Carmi (1973) recognized the penetration properties carbon dioxide and applied it with methyl bromide to determine if the toxic properties methyl bromide and the penetration properties of carbon dioxide could be combined. Their results showed that carbon dioxide, where added to the methyl bromide, greatly increased the penetration rate of the methyl bromide in large bins.

Our experience in developing methods for the in-transit fumigation of grain on ships using phosphine has led us to believe that some method to distribute phosphine quickly in deep masses of grain would be highly desirable (Gillenwater et al. 1981, Zettler et al. 1984, Leesch et al. 1986, and Leesch et al. 1990). Pursuing these thoughts, we decided to determine if carbon dioxide affected the penetration of phosphine in vertical towers.

Materials and Methods

Two identical towers were constructed by welding five, 208-liter (55-gallon) steel drums together to form a tower which was 4.4m in height (Figure 1). Each tower was filled with U. S. Grade No. 1 soft red winter wheat to within 10cm of the top. After loading, a steel lid equipped with a gasket was secured to the top of each tower. The top port shown in Figure 1 was used to introduce the carbon dioxide and aluminum phosphide to the top surface of the grain. Based upon the total volume (1.15m³), an amount of dry ice was added to half of the test towers along with the aluminum phosphide to achieve a 5% (v/v) theoretical concentration of CO₂. In all cases, aluminum phosphide was added to achieve a dosage of 1.74g PH₃/m³. Thus for these towers, 235g dry ice and 2 Phostoxin^(R) tablets-R were used in each tower.

Temperatures in the grain were not controlled but were the result of ambient surrounding temperatures in the warehouse. Temperatures were recorded at each depth of grain in the center of the column. Depths to be observed in the column of grain were established at 0, 0.8, 1.8, 2.6, 3.5, and 4.1m from the top of the grain mass. At each point, a stainless steel probe (6.35mm outer diam. x 3.25mm inside diam.) with a pointed end was inserted into the

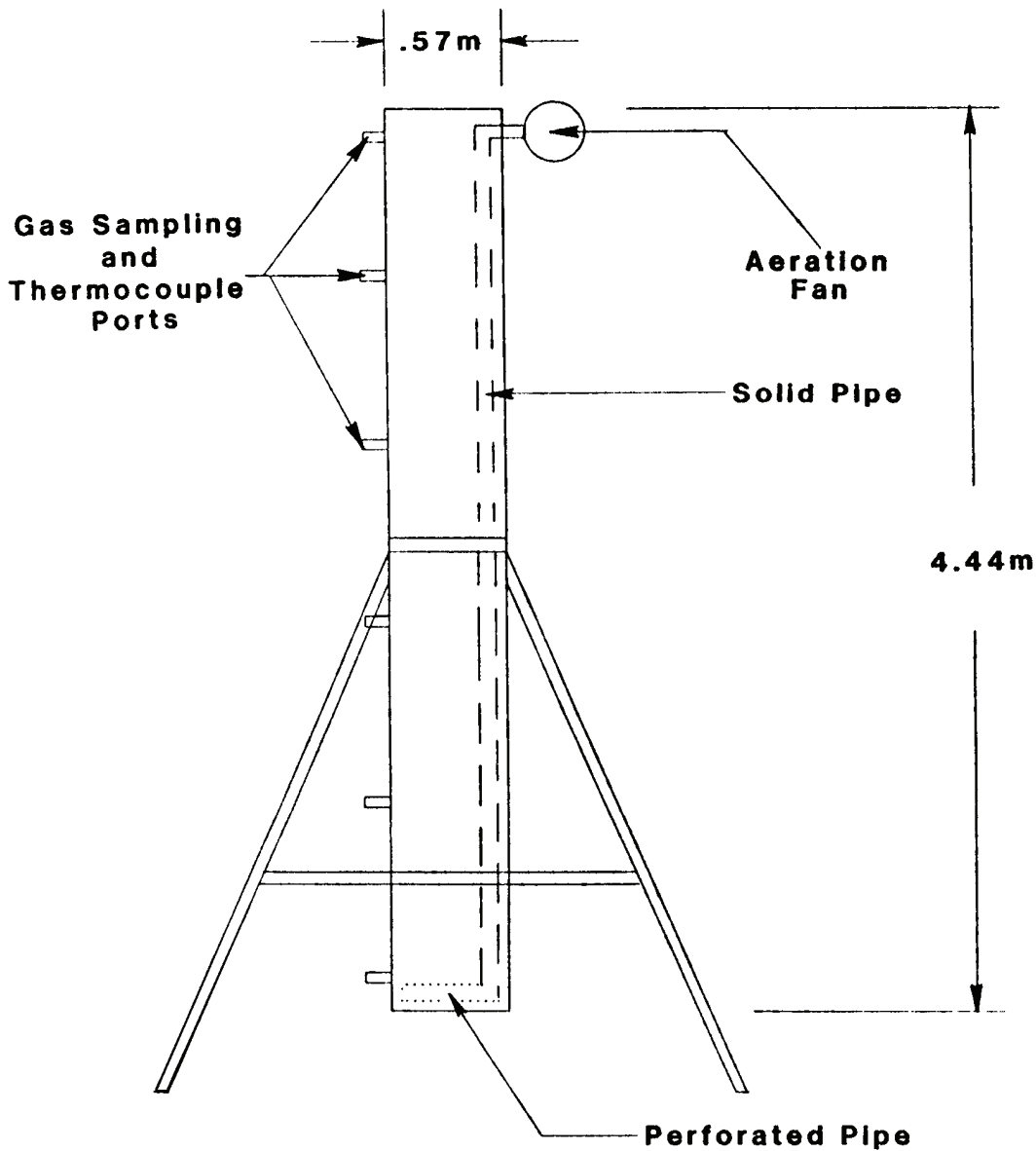


Figure 1. Diagram of the towers used to evaluate the penetration of phosphine applied with or without carbon dioxide.

center of the column of wheat. Also, a thermocouple probe was placed in a second tube at each point and inserted to the same depth in the wheat as the concentration-measuring probe. Both probes were held in place by a two-holed rubber stopper fitted into the wall of the tower.

Temperatures were recorded and gas concentrations determined at designated times for 6 days. Temperatures were taken on a YSI Scanning Telethermometer model 47 (Yellow Springs Instrument Co., Inc. Yellow Springs, Ohio), phosphine concentrations were determined with Draeger gas detection tubes (models 0.1/a and 50/a from National Draeger Co. Pittsburg), and carbon dioxide concentrations were determined using Draeger gas detection tubes (model carbon dioxide-1% from National Draeger Co.). Carbon dioxide concentrations were also verified with a Gow-Mac gas analyzer model 20-600 (Gow-Mac Instrument Co. Bridgewater, New Jersey).

Wheat was loaded into each tower and allowed to equilibrate before the first series of tests began. After each set of tests, a fan was connected to the inside pipe shown in figure 1 and the top removed so that air was pushed up through the wheat for at least 48 hrs to remove any phosphine and carbon dioxide before initiating another test. Each test was begun by sealing the top on each tower and applying the dry ice, if part of that test, through the top fan port. Immediately, the 2 tablets of aluminum phosphide inside a 40-mesh monel cage (2cm in diam. by 8cm long) mounted on a rubber stopper, was inserted into the fan port so that the stopper sealed the port. Means of the 4 replicates with carbon dioxide were compared with the 4 replicates with phosphine alone using the paired t-test procedure of SAS Institute (1988).

Results and Discussion

The results of the tests are shown in Figure 2. As the depth of the sampling point increased from the point of application, the effect of the presence of CO₂ was increasingly evident. Very little difference was seen at the 0- and 0.9-meter depths between the applications with and without CO₂. In fact, the applications with CO₂ at the end of the fumigation were lower in phosphine concentration than those without CO₂. This is because the phosphine in the applications with CO₂ was more evenly distributed downward in the towers.

The apparent differences in the concentrations during the first 3 days are seen at the 1.8- and 2.6-meter depths. Although no significant differences were present at the 1.8-meter depth, a definite trend can be seen. At the 2.6-meter depth, differences were significant after 3 days and at the end of the fumigation. Concentrations began to decline at both of these depths between 3 and 6 days because the phosphine was continuing to move down even at the end of the fumigation. In contrast, the concentrations in the applications without CO₂ were still climbing at the end of the fumigation because the distribution of the fumigant downward was slower.

Finally, the significant differences in the concentration of phosphine with time are evident at the 3.5- and 4.1-meter depths as shown by the standard errors of the means shown in Figure 2. The concentrations of PH₃ were higher after 2 days and continued to be higher than the applications without CO₂ throughout the tests. The difference in the concentrations between the two applications continued to increase until the experiments were terminated after 6 days.

PHOSPHINE CONCENTRATION (PPM)

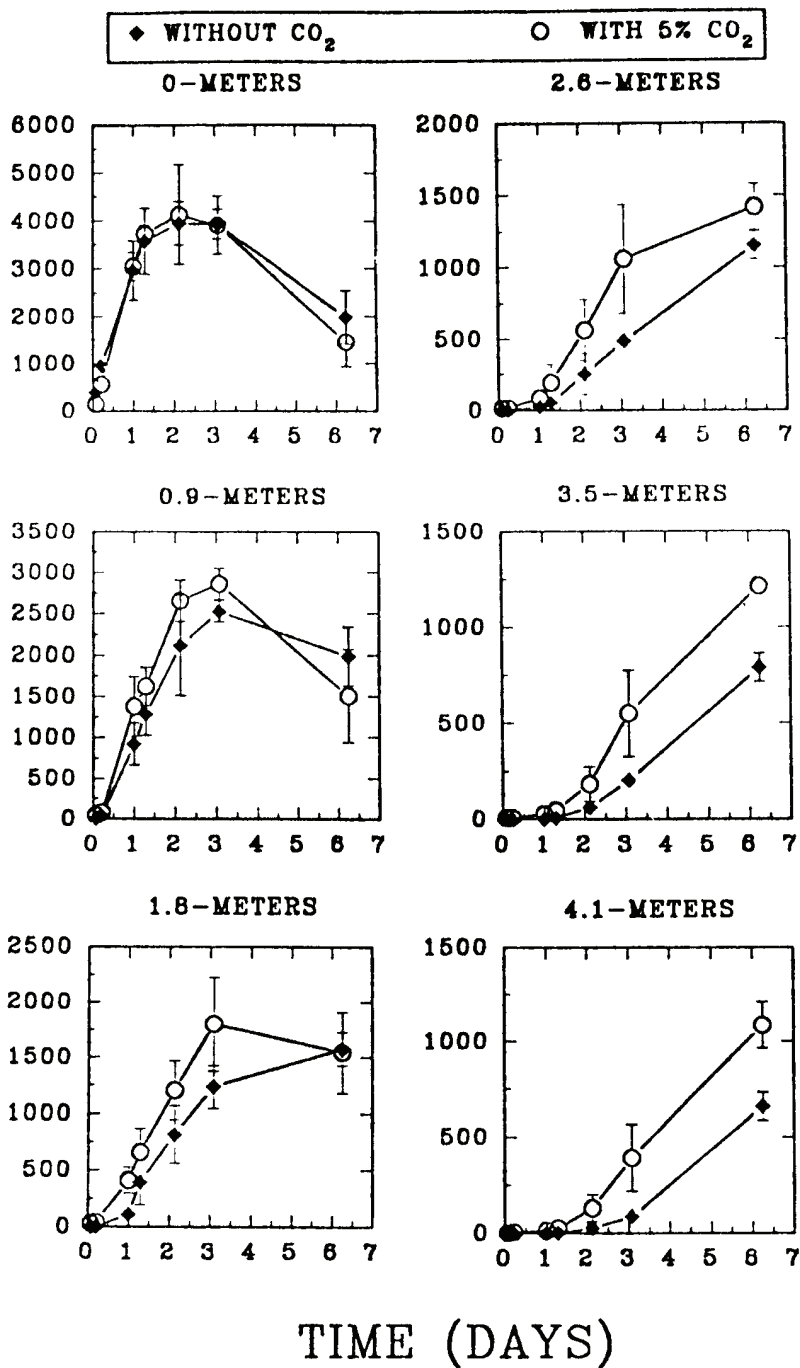


Figure 2. The concentrations of phosphine at various depths in the towers after the application of aluminum phosphide either with or without carbon dioxide.

Figure 3. The difference in phosphine concentration between applications with or without carbon dioxide at various depths throughout the exposure.

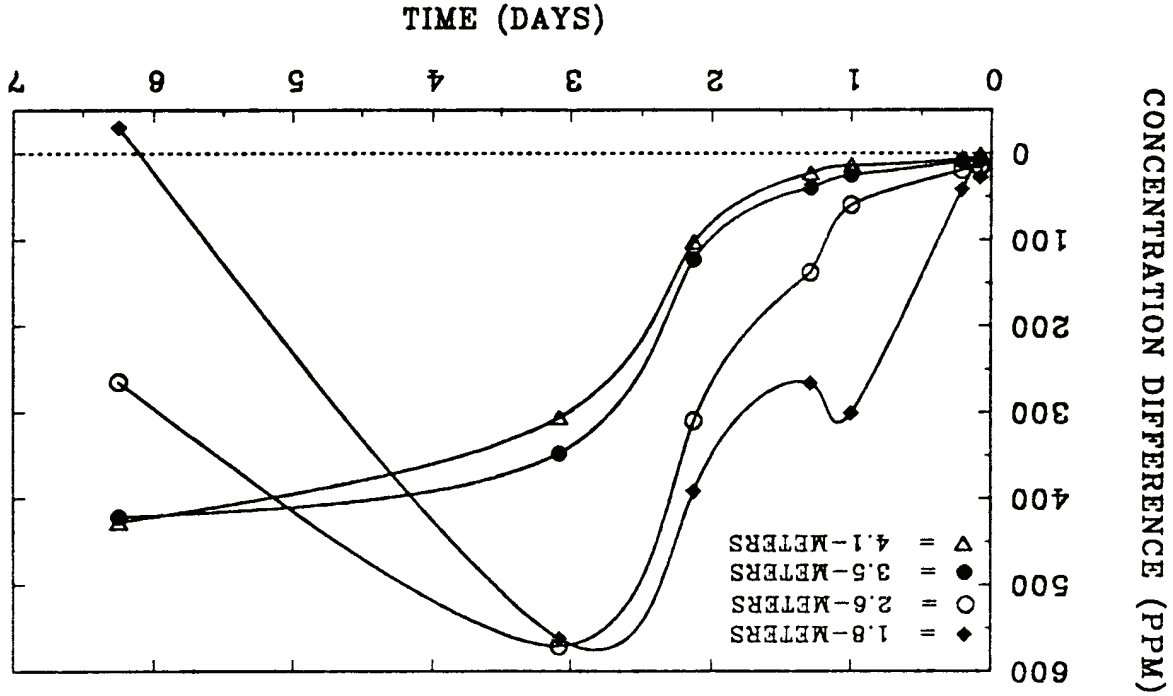
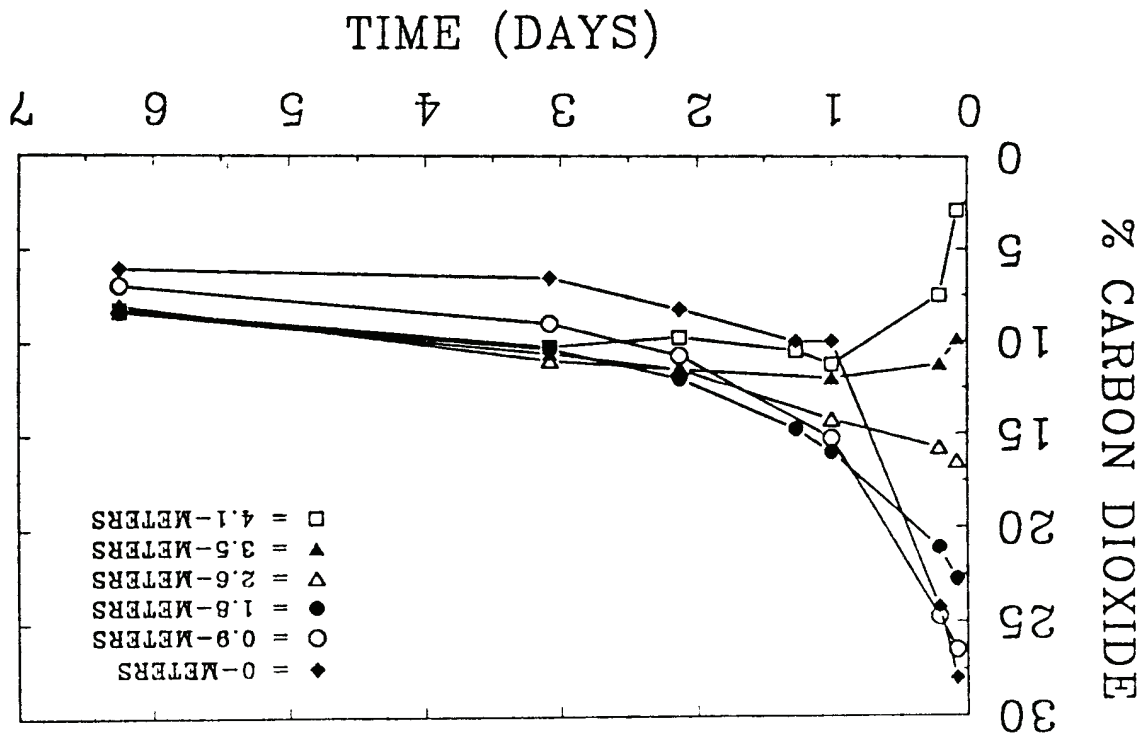


Figure 4. The concentration of carbon dioxide at various depths in the towers after the concomitant application with aluminum phosphide.



It is of interest that at the end of the tests, the distribution of PH_3 was much more even in the towers when CO_2 was applied with the PH_3 . At the end of the fumigations, concentrations of PH_3 from the top to the bottom of the towers ranged from 1990 to 660ppm, and 1510 to 1090ppm for the applications without and with CO_2 , respectively. This clearly indicates a better downward distribution of the PH_3 when it is applied with CO_2 . The trends of the results can be seen in Figure 3 which shows the differences in concentration with time between the applications made with CO_2 and without CO_2 . The peak difference in concentration occurs later as the depth increases beginning with the 1.8-meter depth. This figure also shows that at the end of the fumigation, the concentration difference for the bottom 3 depths was similar. The difference at the 1.8m depth was negative at the end of the fumigation indicating that more phosphine was still at the higher depths when PH_3 was applied alone.

In those tests where CO_2 was applied with the phosphine, the concentrations of CO_2 were evenly distributed vertically in the towers within 24hr as shown in Figure 4. At the 24hr reading, the concentrations at all points ranged from 10 to 17% and after 48hr the concentrations ranged from 8 to 12%. After the initial application, the surface concentration rapidly dropped and remained the lowest concentration throughout the fumigations. There are two reasons for this; first, the carbon dioxide in the surface penetrated rapidly downward and second, the surface gas was more susceptible to leakage around the lid of the towers as compared with the other positions. If we ignore the surface position, the range of concentrations at any time are drastically reduced. The mean concentration for the entire experiment remained at about 10% with a slow decrease due to sorption of the CO_2 and possibly some leakage.

From these studies on the effects of CO_2 on the penetration of PH_3 , it can be concluded that the concomitant application of CO_2 with the fumigant causes a faster penetration of the PH_3 through the wheat mass. This effect could be used to speed the distribution of phosphine in silos and ship's holds or in any application where penetration through a deep mass of material is essential for a successful fumigation.

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**LES EFFETS DES BASSES CONCENTRATIONS DE DIOXYDE DE CARBONE
SUR LA PENETRATION DE LA PHOSPHINE A TRAVERS LES STOCKS DE BLE EN
VRAC**

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RESUME

Du phosphore d'aluminium a été déposé, avec et sans CO₂ (neige carbonique) au sommet de plusieurs tours de 4,15 m contenant du blé tendre " hard red winter". Les doses ont été étudiées en partant du volume total des tours afin d'obtenir des concentrations théoriques de 1,74 g de PH₃/m³ et 5 % (v/v) CO₂. Les concentrations de PH₃ et de CO₂ ont été mesurées périodiquement pendant l'expérience qui a duré 6 jours. Les résultats montrent que lorsque le CO₂ était déposé avec le phosphore d'aluminium, la phosphine résultante pénétrait plus vite à travers la colonne de blé et s'accumulait à des concentrations plus élevées que lorsque le phosphore d'aluminium était déposé seul. D'autres études entreprises sur une plus large échelle sont en cours, afin de savoir si cette combinaison de dioxyde de carbone et de phosphine peut être commercialisée.