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Sorption of propylene oxide by various commodities

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Abstract

Sorption of propylene oxide (PPO) by various commodities was studied at different concentrations during a 4-h exposure at 30 °C. A gas chromatograph was used to determine sorption of PPO applied at concentrations of 24, 49, 82 and 112 mg/l by 1 ± 0.01 kg of narcissus bulbs, wheat, corn and cocoa beans in 2.64-l fumigation chambers. Results showed that for corn and cocoa beans the decrease in concentration during the first hour, that ranged from 40% to 76% of the initial concentration applied, was much greater than that for narcissus bulbs and wheat, which ranged from 25% to 41% of the initial concentration applied. PPO was initially taken up faster by corn and cocoa beans than by narcissus bulbs and wheat. The average sorption rate for each commodity increased with increasing initial concentration. The average sorption rate of PPO by corn and cocoa beans ranged from 14.9 to 48.6 ((mg/kg)/h) which was higher at each concentration than sorption by narcissus bulbs and wheat. In spite of the relatively high rates of sorption, the PPO residues among wheat, corn and cocoa beans immediately following a 4-h fumigation were well below the 300 ppm tolerance. These data show that PPO rapidly desorbed from the commodities under fumigation at 30 °C and at ambient atmospheric pressure.

Keywords: Propylene oxide; Fumigation; Sorption; Narcissus bulbs; Corn; Wheat; Cocoa beans

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1. Introduction

In the wake of legislative regulations designed to phase out the agricultural fumigant methyl bromide (UNEP, 1992, 1995), worldwide efforts have focused on finding suitable alternatives for use as postharvest commodity treatments. Recently, a non-ozone depleting fumigant, propylene oxide (PPO), has been considered as an effective replacement for methyl bromide in some postharvest situations (Creasy and Hartsell, 1999; Griffith, 1999; Isikber et al., 2001). Human health and environmental effects of PPO are reviewed in Meylan et al. (1986). Propylene oxide is a liquid fumigant under normal temperature and pressure (NTP) with a relatively low boiling point (35 °C) and a noticeable ether-like odour (Weast et al., 1986). It is a safe fumigant for use on food as a sterilant because it is quickly converted to non-toxic glycols in the stomach (Griffith, 1999). PPO is an FDA-approved fumigant to control microbial contamination on certain dry food products such as dry and shelled walnuts, cocoa powder and spices (Anonymous, 1980). A disadvantage of PPO is that it is flammable from 3% to 37% volume in air and, therefore, to avoid flammability it should be applied under low pressure or in CO_2-enriched atmospheres.

Griffith (1999) in preliminary tests on some stored-product pests indicated that PPO has insecticidal properties under vacuum conditions as a fumigant, killing all life stages of the confused flour beetle (*Tribolium confusum* (du Val)), the Indian meal moth (*Plodia interpunctella* (Hübner)) and the warehouse beetle (*Trogoderma variable* Ballion). Isikber et al. (2001) compared the relative effectiveness of PPO alone and in combination with low pressure or CO_2 by determining the dosages required for critical mortalities of all life stages of *Tribolium castaneum* (Herbst) at a short exposure time of 4 h. Their study revealed that fumigations with PPO in combination with CO_2 or low pressure (100 mmHg) reduced the LD_{99} of all *Tribolium castaneum* life stages, except eggs, when compared with PPO alone. This implies that 100 mmHg and 92% CO_2 had a synergistic effect on the toxicity of PPO to *Tribolium castaneum*. The 8 + 92% CO_2 formulation greatly broadens the potential applications for PPO because the mixture can be used safely at atmospheric pressure. Zettler et al. (2002) showed that the 8:92% mixture of PPO and CO_2 was effective in controlling postharvest insect pests and a dose of 45 mg/l PPO at 38 °C for 48 h produced complete control of mixed life stages of the following insects: Indian meal moth, *P. interpunctella*; red flour beetle, *Tribolium castaneum*; confused flour beetle, *Tribolium confusum*; warehouse beetle, *Trogoderma variabile*; cigarette beetle, *Lasioderma serricorne* (F.); lesser grain borer, *Rhyzopertha dominica* (F); and saw-toothed grain beetle, *Oryzaephilus surinamensis* (L.).

An understanding of the sorption kinetics of a fumigant on a commodity is important, since the rate of sorption affects the availability of the fumigant that determines the success of the treatment in controlling insects. Sorption varies with the fumigant used, the commodity being fumigated, the duration of exposure, and the temperature and moisture content of the commodity (Banks, 1986). For any successful fumigation, the concentration of fumigant is expected to be maintained at, or above, a given level long enough to kill target organisms. However, concentrations do not remain static during fumigation, they decline through leakage from the system and sorption, either by physical or chemical binding to the fumigation chamber and commodity, or they may be broken down by chemical reaction (Banks, 1986, 1990). In developing fumigation regimes for any commodity, it is necessary to understand these interactions and compensate, where possible, by using either a higher initial dose or by boosting the concentration during the fumigation (Stout, 1983).

Although the 8:92% mixture of PPO and CO_2 is already labelled for use as an insecticidal fumigant for control of stored-product insects by the US EPA and California EPA, there are few or no data on sorption kinetics of PPO; data that are required to define the optimum fumigating conditions. The objective of this study was to determine the sorption characteristics of PPO on various commodities in relation to PPO concentrations.

2. Materials and methods

2.1. Commodities

Hard red winter wheat (*Triticum* spp.) at a moisture content (m.c.) of $11.2 \pm 0.2\%$, Grade no. 2 yellow USA corn for feed (*Zea mays* L.) with m.c. of $11.8 \pm 0.1\%$, Ivory Coast cocoa beans (*Theobroma cacao* L.) at m.c. of $6.3 \pm 0.3\%$ and the Ziva variety of narcissus bulbs (*Narcissus* sp.) at m.c. of $85 \pm 0.3\%$ were used in the tests. The narcissus bulbs were used because quarantine regulations require them to be fumigated with methyl bromide against narcissus flies.

2.2. Fumigation chambers

Test chambers consisted of 2.64-l desiccators, each capped with a ground-glass stopper equipped with entry and exit glass tubing located in the top of the cover. Each entry hole of a ground-glass stopper was equipped with a septum insert for injection of liquid PPO into the fumigation chamber and measuring the change of gas concentrations in the fumigation chamber. Two pieces of Tygon tubing, 5 cm long and 6.2 mm ID, were attached to the glass tubing and sealed with pinch-clamps to avoid gas loss through the septa. A magnetic stirrer placed in the bottom well beneath a wire-mesh disc served to mix the air with the fumigant. The ground-glass lids of the desiccators were sealed in place with high vacuum silicone grease.

2.3. The fumigant

The fumigant was >99% pure liquid PPO that was withdrawn from a sealed vial fitted with a rubber septum, using a gas-tight syringe. PPO was provided by Aberco Inc., USA for experimental purposes.

2.4. Propylene oxide concentration

Concentrations of PPO in the headspace of each desiccator were tested by withdrawing a 15 μl gas sample from the exposure chamber using a 50 μl gas-tight syringe. The gas concentrations of PPO were measured using a Shimadzu 17A GC fitted with an FID (flame ionization detector) and an EC^{TM}-WAX capillary column (30 m length × 0.25 mm ID × 0.25 μm film thickness) run at 170 °C isothermal. During the operation, gas flow rates were 30 ml/min, 50 ml/min, 50 ml/min for helium, hydrogen and air, respectively. Temperatures were 170 °C, 250 °C and 260 °C for column oven, injector port and detector, respectively. Under these conditions, the retention time of PPO was ca. 2.65 min.

2.5. Experimental design and fumigation procedures

Volume, density and the free-space in the fumigation chambers determined for 1 ± 0.01 kg of narcissus bulbs, wheat, corn and cocoa beans are presented in Table 1. The volume occupied by a predetermined weight (1 ± 0.01 kg) of each commodity was measured using the manometric method described by Day (1964). The m.c. of the commodities, except that of narcissus bulbs, was determined using a capacitance moisture meter (Motomco Model 919). The humidity of the narcissus bulbs, was determined by measuring the equilibrium relative humidity (e.r.h.) using a Novasina water activity measuring apparatus. Each commodity weighing 1.0 ± 0.01 kg was placed into a fumigation chamber. Thereafter, the lids of each fumigation chamber were tightly closed using high vacuum silicone grease. Prior to treatment, the fumigation chambers were held for 2 or 3 h for preconditioning of the commodities at 30 °C.

Sorption profiles of PPO were determined for each commodity at four different concentrations of PPO applied over a 4-h period. The calculated volumes of PPO were introduced as a liquid into the desiccators containing the commodities by using a 50 or 250-μl gas-tight syringe. The doses of 24, 49, 82 and 112 mg/l were tested for each commodity. Controls consisting of sealed, empty fumigation chambers were also dosed to determine the "chamber effect" on fumigation concentrations. All exposures were conducted at 30 ± 2 °C and 60 ± 5% r.h. PPO was sampled from the free-space of each chamber to determine the decrease in fumigant concentration due to the sorption.

The PPO residues in wheat, corn and cocoa beans were measured after 4-h fumigations at 30 °C at the dose of 112 mg/l PPO. The levels of PPO residue on each commodity were determined at the end of the fumigation and following a 3-day aeration period. The levels of PPO residue in the commodities were determined by a commercial analytical laboratory service (Aminolab Ltd., Israel) following the analytical method that was a modification of the ASTA analytical method of the Official Methods of Analysis of the AOAC (Anonymous, 2000). For each treatment, approximately 100 g of treated commodity were blended and a 50-g sub-sample was used to render a distillate for analysis. These samples were analysed by gas chromatography with a Shimadzu Model GC-14A with a Porapak P column at 105 °C, injector temperature at 200 °C, and detector temperature at 240 °C. The detector used was a TCD. Retention time was 4.2 min.

Table 1
Volume, density and free-space in the fumigation chamber of 2.64-l determined for 1 ± 0.01 kg of narcissus bulbs, wheat, corn and cocoa beans using the manometric method

Commodity	Volume ± SE (l) ($n = 5$)[a]	Density (kg/l)	Free-space in the chamber (l)
Narcissus bulbs	0.84 ± 0.01	1.19	1.80
Wheat	0.77 ± 0.005	1.29	1.87
Corn	0.86 ± 0.002	1.38	1.78
Cocoa beans	0.73 ± 0.005	1.15	1.91

[a]Number of replicates used in manometric test to determine the volume of the commodity (SE = standard error).

2.6. Data processing and analysis

The amount of PPO in milligram sorbed by the commodity was calculated considering the reduced volume of the free-space due to the mass occupied by the commodities. Therefore, after the volume and particle density of each commodity had been determined using the manometric method, calculations of the amount of PPO in the fumigation chamber were made. The average sorption rate of PPO by each commodity ((mg PPO/ kg of commodity)/h exposure time) during a 4-h exposure was also calculated at four different concentrations of PPO. Average sorption rates were plotted against the initial concentrations of PPO. Thereafter, linear regression analyses were computed to determine the relationship between the sorption rates and the initial concentrations applied. Relationship between sorption of PPO by the commodity and exposure time for each concentration was also determined using linear regression based on sorption (mg PPO/kg commodity) versus exposure time data. All regression analyses on the data were undertaken using the Analysis ToolPak of Microsoft Excel 7.

3. Results and discussion

Free-space concentrations of PPO (mg/l) in the fumigation chamber during 4-h exposures after the application of four doses to 1 kg of narcissus bulbs, wheat, corn and cocoa beans are presented in Figs 1 to 4, respectively. The gas losses observed in the empty fumigation chamber during 4 h of PPO fumigation were minimal (1% or less). In all cases, it became clear that there was an initial rapid decrease in concentrations of PPO during the first hour of exposure followed by a more gradual subsequent drop. The drop in concentrations during the first hour for corn and cocoa beans varied from 40% to 76% of the initial dosage applied, and was much higher than that for narcissus bulbs and wheat, which was from 25% to 41% of the initial dosage applied. This indicates that PPO is initially taken up faster by corn and cocoa beans than by narcissus bulbs and

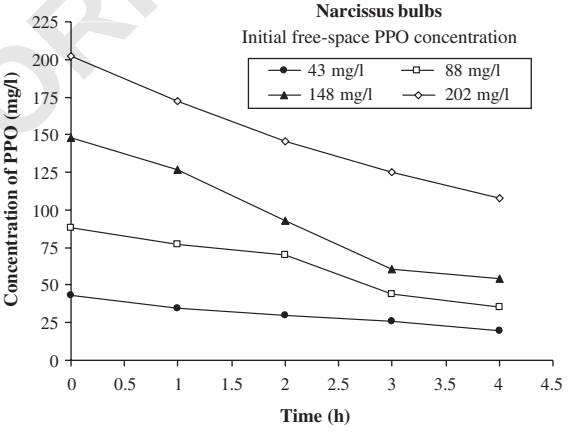

Fig. 1. Free-space concentrations of PPO (mg/l) in a fumigation chamber of 2.64-l (fill ratio: 78.3%) during a 4 h exposure after the application of four doses to 1 ± 0.01 kg of narcissus bulbs at 85% m.c. at 30 °C and 60 ± 5% r.h.

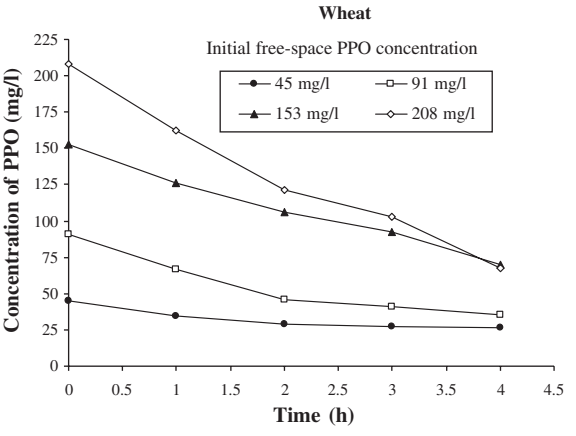

Fig. 2. Free-space concentrations of PPO (mg/l)) in a fumigation chamber of 2.64-l (fill ratio: 46.5%) during a 4 h exposure after the application of four doses to 1 ± 0.01 kg of wheat at 11.2% m.c. at 30 °C and 60 ± 5% r.h.

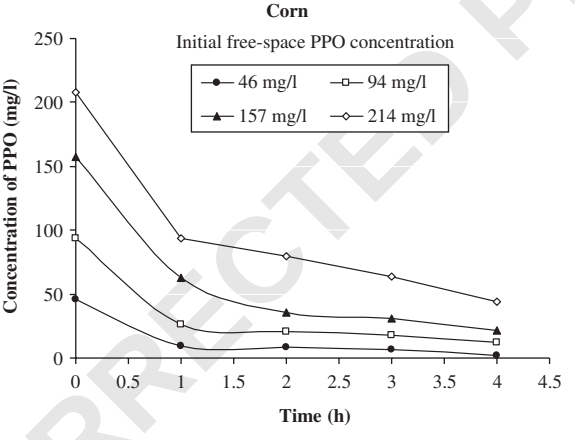

Fig. 3. Free-space concentrations of PPO (mg/l) in a fumigation chamber of 2.64-l (fill ratio: 45.1%) during a 4 h exposure after the application of four doses to 1 ± 0.01 kg of corn at 11.8% m.c. at 30 °C and 60 ± 5% r.h.

wheat. From the figures, it is also clear that the magnitude of the initial dosage of PPO has a great effect on the uptake of PPO by the commodities. Thus, each commodity dosed at different concentrations produced a different pattern of curve showing a high variation with the change in free-space concentrations during the 4-h exposure. In accordance with our results, Zettler et al. (2002) reported that most of the sorption of PPO occurred within the first hours of fumigation but continued throughout the exposure period. They also showed that sorption of PPO throughout the 24-h fumigation was 78%, 95% and 93% for walnuts, raisins and figs, respectively. However, in our study, the sorption of PPO was tested only in the relatively short time of the first 4 h after the release of the fumigant, since PPO has a rapid toxicity to the insects (Navarro et al., 2004).

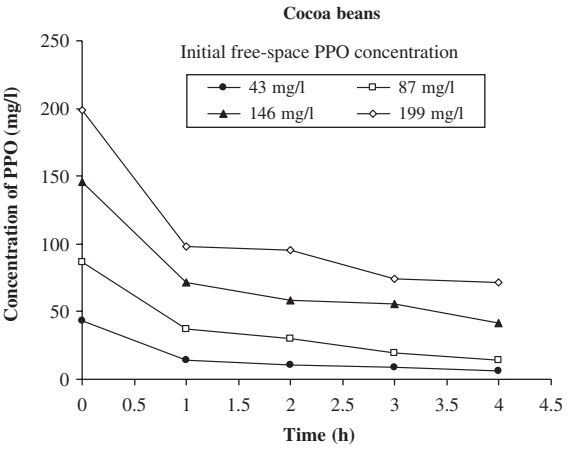

Fig. 4. Free-space concentrations of PPO (mg/l) in a fumigation chamber of 2.64-l (fill ratio: 65.3%) during 4 h of exposure after the application of four doses to 1 ± 0.01 kg of cocoa beans at 6.3% m.c. at 30 °C and 60 ± 5% r.h.

Sorption of PPO (mg PPO/ kg commodity) by narcissus bulbs, wheat, corn and cocoa beans during a 4-h exposure at a dose of 112 mg/l are shown in Fig. 5. Sorption of PPO by all commodities was found to follow a linear relationship during this period ($R^2 = 0.989$ $P < 0.01$, $R^2 = 0.979$ $P = 0.01$, $R^2 = 0.995$ $P < 0.01$, $R^2 = 0.874$ $P < 0.05$ for narcissus bulbs, wheat, corn and cocoa beans, respectively). Banks (1986) described the diffusion/sorption process mathematically as a semi-logarithmic relationship, between concentration and time, which is dependent on the commodity, the fumigant and the fill ratio. However, in this study sorption of PPO did not follow the conventional kinetic laws (Daniels and Alberty, 1963), and thus did not show a logarithmic or semi-logarithmic relationship, since it did not reach steady-state equilibrium due to the short exposure time (4 h). Likewise, Zettler et al. (2002) reported that although the sorption of PPO occurred rapidly, most of it taking place immediately after dosing, it only reached equilibrium after 24 h. In our study, sorption of PPO by the commodities followed a trend similar to that seen with other fumigants on wheat and other commodities (Banks, 1986, 1990); there was an initial rapid sorption during the first hour (> 50% of overall PPO sorption) followed by a more gradual subsequent sorption. This phenomenon for methyl bromide was shown on various commodities by Sinclair and Lindgren (1952), Hayward (1954), Rajendran and Muthu (1978) and Leesch et al. (1979).

Sorption by narcissus bulbs, wheat, corn and cocoa beans after the first hour of exposure was 23.2 (14.4%), 33.1 (22%), 47.2 (33.6%) and 66.4 (40.4%) mg/kg, respectively (Fig. 5), whereas after the 4-h exposure, sorption by narcissus bulbs, wheat, corn and cocoa beans was found to be 74.6 (46.4%), 102.1 (67.7%), 96.4 (68.6%) and 92.3 (56.2%) mg/kg, respectively. A difference in the level of sorption of PPO by the commodities after the first hour of exposure was evident showing a higher initial sorption by corn and cocoa beans than narcissus bulbs and wheat. These findings may be compared with several studies on sorption of other fumigants by wheat, where it was shown that sorption varies in extent according to the type of commodity fumigated, and other factors such as the temperature during and following fumigation, m.c., fumigation concentration and dosage time (Banks, 1986). The results obtained by Berck (1965) indicated that at 27 °C,

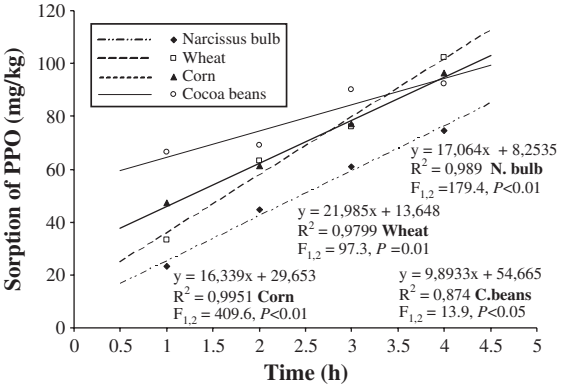

Fig. 5. Relationship between sorption of PPO (mg/l) and time by narcissus bulbs, wheat, corn and cocoa beans at 30°C and 60 ± 5% r.h. during a 4 h exposure at a concentration of 112 mg/l.

sorption of ethylene dibromide, ethylene dichloride and carbon tetrachloride by wheat at 13.5% m.c., after a 4-h exposure was less than 40%, 20% and 5%, respectively. Cherif et al. (1985) reported that at 26 °C, sorption of methyl bromide by wheat at 12% m.c. after a 6 h exposure was less than 70%. It appears, therefore, that PPO tends to be more highly sorbed by wheat than ethylene dibromide, ethylene dichloride and carbon tetrachloride, whilst it is sorbed only slightly more than methyl bromide.

Average sorption rates ((mg/kg)/h) of PPO by narcissus bulbs, wheat, corn and cocoa beans after a 4 h of exposure at four different concentrations are presented in Table 2. Results indicated that differences in the initial concentration of PPO applied had a significant effect on the average sorption rate by the commodities. The average sorption rate of PPO for each commodity increased with increasing initial concentration. Corn had the highest average sorption rate at each concentration, whilst narcissus bulbs had the lowest average sorption rate at all concentrations except at the initial concentration of 82 mg/l (Table 2). It was found that the average sorption rate of PPO by corn and cocoa beans at each concentration was higher than that by narcissus bulbs and wheat. This can be attributed to the different surface area, and physical and chemical properties of the commodities tested. Many studies have shown that for commodities containing high fat content, sorption of the fumigants is enhanced when compared to commodities with low oil content or commodities of a starchy nature (Sinclair and Lindgren, 1958; Punj, 1969; Berck, 1964). Therefore, high sorption of PPO by corn and cocoa beans can be explained on the basis of the oily nature of these commodities.

A plot of the average sorption rates against the initial concentrations gave linear relationships for narcissus bulbs, wheat, corn and cocoa beans, as described by the equations presented in Fig. 6. Using these equations, the sorption by each commodity at 30 °C can be calculated for any given PPO concentration within the range of our tests. Thus, this relationship could be used to predict the amount of PPO that might be sorbed in a commercial scale fumigation facility at various initial concentrations.

The PPO residues in wheat, corn and cocoa beans averaged 173, 157 and 117 ppm, respectively, at the end of the fumigations (Table 1). PPO residues in wheat, corn and cocoa beans after

Table 2
Average ($n = 5$) sorption rate ((mg/kg)/h) of PPO by narcissus bulbs, wheat, corn and cocoa beans during a 4-h exposure at four different concentrations

Concentration of PPO (mg/l)	Mean sorption rate ((mg/kg)/h) ± SE[a]			
	Narcissus bulb	Wheat	Corn	Cocoa beans
24	6.76 ± 0.75	7.14 ± 1.30	17.61 ± 4.74	14.92 ± 3.78
49	12.07 ± 1.19	19.27 ± 2.39	31.24 ± 7.74	26.54 ± 5.38
82	25.12 ± 1.86	22.52 ± 1.44	45.09 ± 7.05	36.60 ± 7.98
112	26.49 ± 1.28	39.87 ± 2.79	48.58 ± 8.03	46.75 ± 9.67

[a]SE = standard error

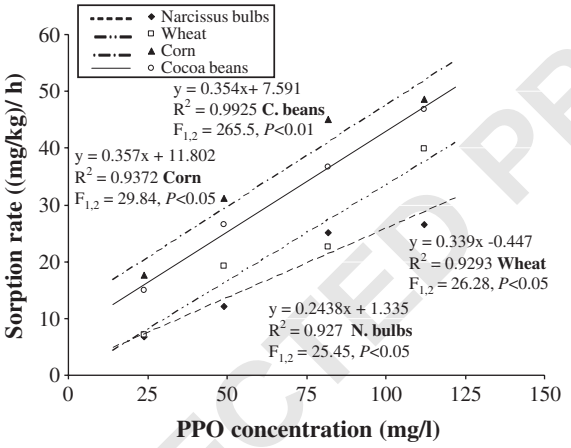

Fig. 6. Sorption rate of PPO ((mg/kg)/h) in relation to the initial concentrations for narcissus bulbs, wheat, corn and cocoa beans during of 4 h exposure.

aeration for 3 days averaged 14, 6 and 8 ppm, respectively. In spite of the relatively high rates of sorption in fumigated commodities, the PPO residues among wheat, corn and cocoa beans immediately following a 4-h fumigation were well below the 300 ppm tolerance determined by US FDA. Following 3 days of aeration, very low residues were detected. These data indicate that PPO rapidly desorbs from the commodity under the experimental fumigation conditions of 30 °C and ambient atmospheric pressure. These data also support those of Zettler et al. (2002), who showed that the PPO residues among almonds, pecans and walnuts immediately after 4-h fumigations with an 8:92% mixture of propylene oxide and carbon dioxide at 38 °C and ambient atmospheric pressure, were below the 300 ppm tolerance and that residues could not be detected following 3 days aeration. With respect to our data, very low levels of PPO residue in the commodities indicate that PPO was physically bound to the commodity and the fumigation chamber, and did not react chemically with components of the commodity. Thus, it is clear that most of the sorption of PPO by the commodity was physical (Table 3).

Table 3
PPO residues (ppm) on wheat, corn and cocoa beans after 4-h fumigations at 30°C and atmospheric pressure with a dose of 112 mg/l PPO

Commodity	Average PPO residue (ppm) in sample during aeration	
	Start	3 days
Wheat	133	14
Corn	157	6
Cocoa beans	117	8

However, although the US EPA and California EPA authorise the use of the 8:92% mixture of propylene oxide and carbon dioxide as an insecticidal fumigant for control of stored-product insects, further study is required in order to define the effects of temperature, relative humidity and moisture content of the commodity on the sorption and desorption rates of PPO so that accurate PPO treatment schedules for postharvest insect pests can be determined.

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