

PROPYLENE OXIDE (250)

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EXPLANATION

Propylene oxide is used in agriculture as an insecticidal fumigant and sterilant, to control bacteria contamination, mould contamination, insect infestations, and microbial spoilage of food products as well as to control insects in non-food products. Propylene oxide is also a commercially important industrial chemical finding application as an intermediate for a wide array of products. At the Forty-second Session of the CCPR (2010), it was scheduled for the evaluation as a new compound by 2011 JMPR.

Residue studies were submitted by the manufacturers to support the following commodities: cereal grains (maize and wheat), tree nuts, cocoa, herbs and spices and dried fruit (raisins, figs and prunes).

IDENTITY

Common name Propylene oxide

Chemical name

IUPAC: Methyloxirane

CAS: Methyloxirane

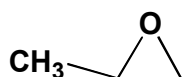
Manufacturer's code numbers: Propylene oxide

CAS number: 75-56-9

Molecular formula: C₃H₆O

Molecular mass: 58.08 g/mol

Structural formula:



Synonyms: 1,2-propylene oxide, epoxypropane, 1,2-epoxypropane, 2,3-epoxypropane, propene oxide, propylene epoxide, methylethylene oxide, methyloxacyclopropane, PPO.

Propylene oxide exists in two optical isomers, and commercial propylene oxide is a racemic mixture.

Formulations Active ingredient content

Fumigant 99.9% propylene oxide

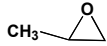
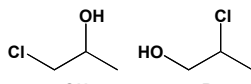
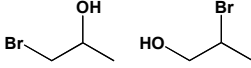
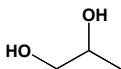
Physical and chemical properties

| Property | Results | Reference |
|------------|-------------------|-----------------------------------|
| Appearance | Colourless liquid | IPCS, 1988; IARC, 1994; ECB, 2002 |
| Odour | Ethereal | IPCS, 1988; ECB, 2002 |

| Property | Results | Reference |
|---|--|-------------------------------------|
| Melting point | -112.16 °C (-112.1 °C to -112.6 °C) | IARC, 1994; ECB, 2002 |
| Boiling point | 33.9 °C–34.3 °C | IARC, 1994; ECB, 2002 |
| Relative density | 0.83 g/L | IARC, 1994; ECB, 2002 |
| Vapour pressure | 59.8 kPa (58.4 kPa–61.2 kPa) | ECB, 2002 |
| Solubility in water | 395–405 g/L (pH = 7) | Warren, 1988; IARC, 1994; ECB, 2002 |
| Solubility in organic solvents (at 20 °C) | Miscible with acetone, benzene, carbon tetrachloride, diethyl ether and methanol. | |
| Henry's law constant | 12.4 Pa m/mole | ECB, 2002 |
| Partition coefficient n-octanol/water | Kow 0.03–0.08 | ECB, 2002; EPA, 2006a |
| Hydrolysis | t _{1/2} = 11.6 days | Koskikallio and Whalley, 1959 |
| Photolysis | Propylene oxide does not absorb solar radiation appreciably at wavelengths greater than 300 nm (it has a maximum absorption at 199.5 nm). Thus direct photolysis does not occur. | ECB, 2002 |

METABOLISM AND ENVIRONMENTAL FATE

Metabolites are given various abbreviations and code numbers in the studies. Structures and abbreviations and codes are shown below.

| Compound | Other identifiers | Structure | Formula | MW | CAS No. |
|----------|---|---|--|--------|------------------------|
| PPO | propylene oxide, methyloxirane, parent |  | C ₃ H ₆ O | 58.08 | 75-56-9 |
| PCH | 1-chloro-2-propanol and 2-chloro-1-propanol, propylene chlorohydrin |  | C ₃ H ₇ ClO | 94.54 | 127-00-4 37493-14-4 |
| PBH | 1-bromo-2-propanol and 2-bromo-1-propanol, propylene bromohydrin |  | C ₃ H ₇ BrO | 138.99 | 19686-73-8 |
| PPG | (±) 1,2-propanediol, propylene glycol |  | C ₃ H ₈ O ₂ | 76.09 | 57-55-6 |

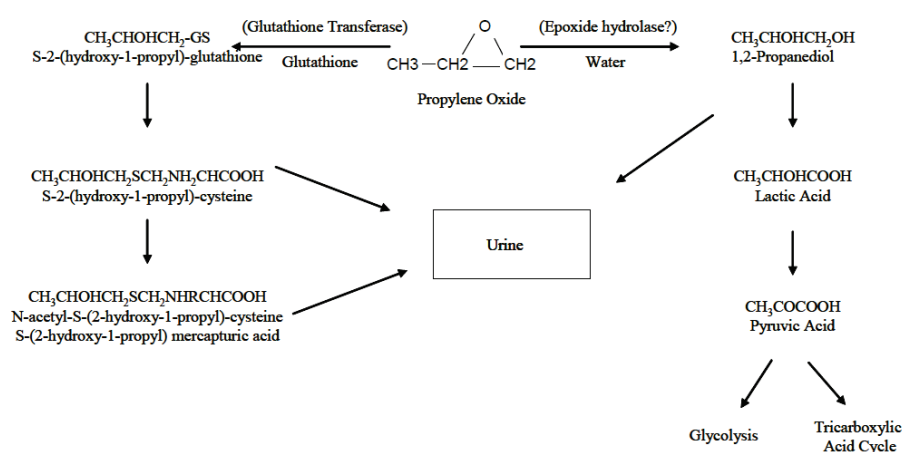
Animal metabolism

The Meeting received studies on the metabolism of [¹⁴C]-labelled propylene oxide in rats. The studies on rats were evaluated by the WHO Core Assessment Group.

Data on livestock metabolism were not provided. PPO is a post-harvest fumigant and sterilant that is used on dried fruits, certain tree nuts, herbs and spices, processed cocoa and edible gums. Livestock are not expected to be exposed to PPO or PCH residues in any feedstuffs. If farm animals were to be exposed to residues of PPO in feed, it would be expected that gastric juice would hydrolyze it to propylene glycol (PPG) as effectively as has been proposed for humans and rats (Patil and Thilagar, 1999).

PPO is metabolized via conjugation with glutathione and hydrolysis by epoxide hydrolase to 1, 2-propanediol (propylene glycol), which is subsequently metabolized to lactic and pyruvic acids. Propylene oxide may also be subject to glutathione conjugation.

The available evidence from the open literature suggests that PCH is widely distributed to tissues, metabolized and excreted following inhalation in animals. Most of the administered radioactivity appears to be excreted in urine as glutathione conjugates. Also, biliary excretion is reported in rats exposed to PCH by inhalation. Following oral exposure, PCH is eliminated as glucuronic acid and glutathione conjugates.



The relative stability of ^{14}C -PPO in human (pH 1.46, 37 °C) and rat gastric juices (pH 4.8, 37 °C) was determined (Patil and Thilagar A 2000). Metabolite profiling was undertaken. The results are summarised below. The only metabolite identified in both systems was PPG. The half-life for decline of PPO residues was approximately 1.9 minutes in human gastric juices and 347 minutes in rat gastric juices.

Table 1 Decay of propylene oxide in human gastric juice and rat gastric juice

| Time (sec) | % Propylene oxide metabolised | |
|------------|-------------------------------|-------------------|
| | Human gastric juice | Rat gastric juice |
| 0 | 0 | 0 |
| 10 | 15.0 | |
| 20 | 18.8 | |
| 30 | 20.5 | 4.2 |
| 40 | 21.4 | |
| 50 | 22.2 | |
| 60 | 20.4 | |
| 90 | – | 5.8 |
| 80 | 32.2 | |
| 100 | 50.6 | |
| 120 | 54.3 | 6.9 |
| 180 | 67.7 | 9.6 |
| 210 | – | 13.0 |
| 240 | 75.4 | 9.0 |
| 300 | 82.8 | 10.5 |
| 480 | 91.2 | |
| 600 | 94.4 | 10.4 |
| 900 | 101.5 | |
| 1200 | 102.3 | 10.8 |
| 2400 | – | 13.6 |
| 3600 | | 17.8 |
| 5400 | | 17.2 |

Plant metabolism

No studies using radiolabelled propylene oxide are available for the post-harvest treatment of plant derived commodities; however, propylene oxide is a simple compound whose chemistry is well understood. The epoxide ring of propylene oxide may open at either of the C-O bonds.

starch in dehydrated potato. It was speculated that the difference between the reactivity of flour and potato starch was due to the nature of the starch, free and partially damaged in flour and sterically hindered within the intact potato cells of dehydrated potato.

The reaction of propylene oxide with starch is the basis for the industrial production of a modified starch (JECFA 1974). Etherification of starch is achieved by reaction with propylene oxide at levels up to 25%. The resultant starch is usually lightly oxidized, bleached or acid modified after etherification. Substitution may amount to a maximum of 40 ether linkages per 100 glucopyranose units if 25% propylene oxide is used, and 4–6 ether linkages per 100 glucopyranose units if 5% propylene oxide is used.

Although all of the main degradation products of PPO (PCH, PBH, PPG) contain an asymmetric carbon there is no information on the relative stereochemistry of the compounds.

Summary of plant metabolism

Based on the similarity in reactions and chemistry between ethylene oxide and propylene oxide and reported degradates from studies with unlabelled PPO it is concluded that in addition to PPO, residues of PPG (free and conjugated), PCH and PBH are formed upon and after postharvest fumigation of plant-based commodities. In fumigated spices that contain salt the PPO will react with chloride ion to form PCH. Similarly, bromide ions present in the material to be fumigated react with PPO to form PBH. Reaction with water present in fumigated samples can produce amounts of PPG. In addition, PPO may react with exposed -COOH, -NH₂, -OH and -SH groups present in natural constituents to give the corresponding hydroxy-propyl compounds.

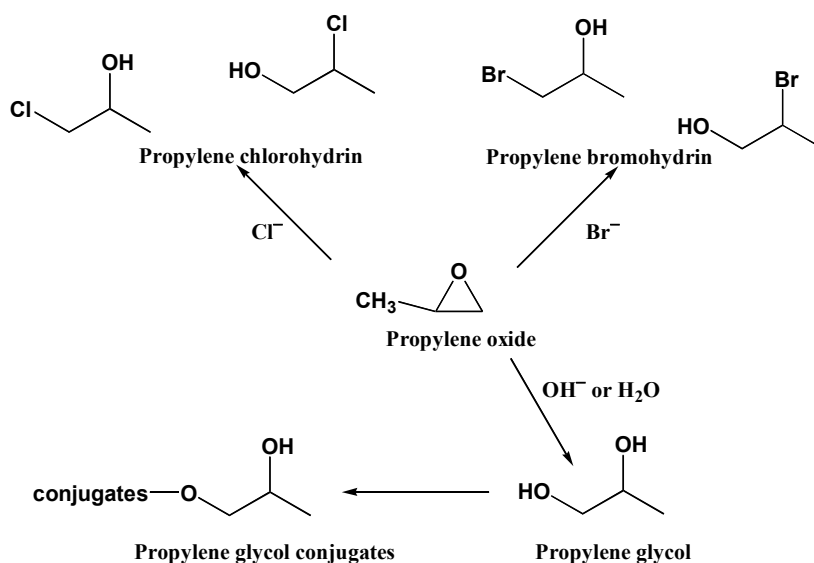


Figure 1 Proposed degradation of propylene oxide in fumigated products

ENVIRONMENTAL FATE

Propylene oxide is a post-harvest fumigant and sterilant and is not expected to be released into the general environment such that significant levels will be found in soil and water. Data on environmental fate are not required and were not provided to the Meeting.

Aqueous hydrolysis

Epoxides such as propylene oxide can degrade in water through hydrolysis and related ionic reactions involving the cleavage of a carbon-oxygen bond. The hydrolysis reaction can be spontaneous (under

neutral conditions), or acid or base catalysed. Bogyo *et al.* (1980) summarised values for the rate constants for the three processes as shown in Table 2.

Table 2 Rate constants for hydrolysis of propylene oxide

| Process | Rate constant (at 25 °C) | Reference |
|------------------------|--|---|
| spontaneous hydrolysis | $6.9 \times 10^{-7} \text{ s}^{-1}$ | Koskikallio and Whalley (1959) |
| acid catalysed | $0.052 \text{ L.mole}^{-1}.\text{s}^{-1}$ | estimated by Bogyo <i>et al.</i> (1980) |
| base catalysed | $8.7 \times 10^{-5} \text{ L.mole}^{-1}.\text{s}^{-1}$ | Koskikallio and Whalley (1959) |

In the environment the major reaction is expected to be the spontaneous process. A number of values have been reported for the rate constant for this process, and these are summarised in Table 3.

Table 3 Rate constants for spontaneous hydrolysis of propylene oxide in water

| Temperature (°C) | Rate constant 10^{-6} s^{-1} | Half-life (days) | Reference |
|------------------|--|------------------|--------------------------------|
| 20 | 0.37 | 21.7 | Nichols and Ingham (1955) |
| 22 | 0.47 | 17.1 | Nichols and Ingham (1955) |
| 25 | ~0.55 | 14.6 | Mabey and Mill (1978) |
| 25 | 0.69 | 11.6 | Koskikallio and Whalley (1959) |
| 25 | 0.68-0.75 | 11.8 - 10.7 | Sato <i>et al.</i> (1985) |

The product of the hydrolysis reaction is PPG which biodegrades rapidly in water.

Photolysis

PPO does not absorb solar radiation appreciably at wavelengths greater than 300 nm (it has a maximum absorption at 199.5 nm). Thus direct photolysis does not occur.

METHODS OF RESIDUE ANALYSIS

The residue analysis described for PPO (ABC 2000a, 2000b, Blinne and Koch 2000a, 2000b, 2000d) was based on methods developed by Woodrow and Seiber (1998) and ABC (1998a). The methodology for the PCH and PBH residue analysis was based on the method developed by ABC (1998b).

Propylene oxide residues in/on pulverized nutmeat samples were quantitated via an automated headspace technique utilizing gas chromatography with flame ionization detection (GC-FID). Samples are ground under cryogenic conditions (liquid nitrogen), transferred to a vial, the vial sealed and the PPO residues desorbed by heating. Powdered samples do not need the grinding step and can be added directly to the vial. The volatilized PPO equilibrates in the headspace of the vial which is then sampled by an automated headspace sampler and injected onto a GC-FID system. Quantitation was achieved by comparison with a calibration curve consisting of fortified matrix samples. It was reported that headspace analysis should occur within 1 hour of sample preparation for nuts or 2 hours for cocoa, herbs and spices. An LOQ of 0.1 mg/kg was attained for most matrices.

Residues of PCH (1-chloro-2-propanol and 2-chloro-1-propanol) and PBH (1-bromo-2-propanol and 2-bromo-1-propanol) are extracted with acetone and quantitated via gas chromatography with electrolytic conductivity detection (GC-ELCD). Where necessary, samples were ground under cryogenic conditions (liquid nitrogen). The powdered samples are extracted with acetone. Residues are quantitated via GC-ELCD. Detector response is not linear over the fortification range and a quadratic model was used for the standard curve. An LOQ of 1 mg/kg has been demonstrated for most commodities.

Results of the method validation are summarized in Tables 4 and 5.

Table 4 Method validation for propylene oxide residues in matrix almonds, onion powder, cocoa powder and raisins

| Matrix | Fortification level (mg/kg) | Residue level (mg/kg) | Recovery (%) | Reference |
|-----------------|-----------------------------|-----------------------|--------------|------------------------|
| Almond, nutmeat | 0.1 | 0.094, 0.11 | 94, 111 | Schrier and Koch, 1998 |
| | 5 | 4.4, 4.9 | 89, 99 | |
| | 10 | 9.2, 9.7 | 92, 98 | |
| | 53 | 49 | 93 | |
| | 105 | 92, 94 | 88, 89 | |
| | 946 | 912, 929 | 96, 98 | |
| Onion powder | 0.1 | 0.106, 0.109 | 106, 109 | Blinne and Koch, 2001 |
| | 5 | 4.88, 4.95 | 98, 99 | |
| | 10 | 10.1 | 101 | |
| | 200 | 193, 200 | 97, 100 | |
| | 1000 | 976, 983 | 98, 98 | |
| | 5000 | 4740, 5120 | 95, 102 | |
| Cocoa powder | 0.1 | 0.0905, 0.113 | 90.5, 113 | Blinne and Koch, 2000c |
| | 5 | 4.59, 4.78 | 91.8, 95.6 | |
| | 10 | 9.78, 10.3 | 97.8, 103 | |
| | 200 | 175 | 87.5 | |
| | 1000 | 941, 968 | 94.1, 96.8 | |
| | 5000 | 5170, 5250 | 103, 105 | |
| Raisins | 0.098 | 0.0819, 0.0883 | 83.6, 90.1 | Blinne 2002 |
| | 9.8 | 8.94, 9.26 | 91.2, 94.5 | |
| | 98 | 98.5, 104 | 101, 106 | |

Table 5 Method validation for propylene chlorohydrin and bromohydrin residues in almonds, onion powder, cocoa powder and raisins

| Matrix | Propylene chlorohydrin | | | Propylene bromohydrin | | | Reference |
|--------------|-----------------------------|-----------------|--------------|-----------------------------|-----------------|--------------|------------------------|
| | Fortification level (mg/kg) | Residue (mg/kg) | Recovery (%) | Fortification level (mg/kg) | Residue (mg/kg) | Recovery (%) | |
| Almond | 0.49 | 0.35, 0.36 | 72, 74 | 0.5 | 0.38, 0.38 | 76, 77 | Schrier and Koch, 1998 |
| | 0.98 | 0.73, 0.79 | 75, 81 | 1 | 0.70, 0.71 | 70, 71 | |
| | 4.9 | 4.2, 4.4 | 86, 90 | 5 | 5.0, 5.3 | 101, 107 | |
| | 9.8 | 8.9, 9.2 | 91, 94 | 10 | 9.8, 11 | 98, 109 | |
| Onion powder | 0.49 | 0.34, 0.41 | 81, 84 | 0.49 | 0.36, 0.36 | 77, 78 | Blinne and Koch, 2001 |
| | 0.99 | 0.82, 0.87 | 82.6, 88.0 | 0.94 | 0.75, 0.78 | 80, 84 | |
| | 9.9 | 9.4, 9.85 | 95.2, 99.7 | 9.36 | 8.2, 8.7 | 88, 93 | |
| | 25 | 24, 24 | 97.6, 98.0 | 23.4 | 21, 21 | 89, 90 | |
| Cocoa powder | 0.45 | 0.48, 0.5 | 107, 110 | | | | Blinne and Koch, 2000c |
| | 0.90 | 0.78, 0.83 | 86, 92 | 0.94 | 0.67, 0.69 | 72, 73 | |
| | 9.0 | 8.2, 8.4 | 90.4, 93.1 | 9.36 | 7.3, 7.9 | 78, 84 | |
| | 23 | 20, 21 | 89.4, 94.7 | 23.4 | 18, 20 | 77, 84 | |
| Raisins | 1.0 | 0.74, 0.99 | 74, 98 | | | | Blinne 2002 |
| | 5.0 | 4.3, 4.8 | 84, 94 | | | | |
| | 25 | 24, 25 | 96, 98 | | | | |

LOQ = Limit of quantification (1 mg/kg).

Values for PCH and PBH each represent the sum of two isomers.

Independent Validation of Residue Methodologies

The analytical methods used to determine PPO, PCH and PCB residues in nutmeats, herbs and spices, and cocoa described for the above studies were later validated in an independent validation study (Simons and Lake, 2001). The validation study used shelled almonds and black pepper as matrices. The validation for PPO was conducted at the LOQ of the method (0.1 mg/kg) and at 300 mg/kg. The halohydrin validation was conducted at the method LOQ (1 mg/kg) and 300 mg/kg. Two validation

trials were carried out for both matrices. The method was successfully validated with all fortification recoveries falling between 70–120% at both quantitation levels in both matrices (Table 6).

Table 6 Recoveries of propylene oxide residues in matrix almonds and black pepper (Simons and Lake, 2001).

| Matrix | Fortification level (mg/kg) | Recovery (%) | | |
|------------------|-----------------------------|--------------|-----|--------|
| | | PPO | PCH | PBH |
| Almonds, shelled | 0.1 | 104 | 79 | 90 |
| | 300 | 89 | 101 | 106 |
| Black pepper | 0.1 | 96 | 77 | 83, 96 |
| | 300 | 105 | 107 | 105 |

Stability of Residues in Stored Analytical Samples

No data were provided on the stability of residues of PPO, PCH, PBH or PPG when samples are stored frozen. In most of the supervised residue trials samples were analysed on the day of collection or soon after in which case the samples were stored at 2 °C or –20 °C until analysis.

USE PATTERNS

Propylene oxide is used as fumigant and sterilant to control bacterial and mould contamination, insect infestations, and microbial spoilage of food products (tree nuts, spices, dried fruits and cocoa beans and powder), either as an end-use product alone or in mixtures with carbon dioxide. As it is a liquid at room temperature, fumigations are carried out at elevated temperatures but less than 52 °C and exposure times of up to 48 hours. Additionally PPO is flammable at concentrations in air of between 1.7 and 37% and is therefore used under conditions of reduced pressure. To enable fumigations at atmospheric pressure a non-flammable mix with carbon dioxide is used (8% PPO with 92% CO₂).

Table 7 Registered uses of propylene oxide on commodities in the US

| Commodity | Type | Rate (g ai /L chamber) | Temp ^a (°C) | Flush ^b | Degas and post fumigation interval |
|---|------|---------------------------------|------------------------|--------------------|--|
| Inshell and processed nutmeats (except peanuts) | Fum | 2.0 for < 6 hours | < 52 | 4× | 28 days @ 25 °C or 35 °C prior to shipment or until residues PPO < 300 mg/kg |
| Processed spices ^d | Fum | 2.0 for < 12 hours | < 52 | 4× | 48 hours @ ≥ 25 °C prior to shipment or until residues PPO < 300 mg/kg |
| Cocoa bean and cocoa powder | Fum | 2.0 for < 4 hours | < 52 | 4× | 48 hours @ ≥ 25 °C prior to shipment or until residues PPO < 300 mg/kg |
| Figs | Fum | 0.2 ^c for < 48 hours | < 52 | 4× | 48 hours @ ≥ 25 °C prior to shipment |
| Prunes | Fum | 0.2 ^c for < 48 hours | < 52 | 4× | 48 hours @ ≥ 25 °C prior to shipment |
| Raisins | Fum | 0.2 ^c for < 48 hours | < 52 | 4× | 48 hours @ ≥ 25 °C prior to shipment |

^a temperature for fumigation treatment

^b number of volumes of fumigation chamber that must be replaced with air or inert gas

^c must be used in combination with an inert gas, 8% PPO and 92% inert gas.

^d US EPA Crop Subgroup 19B. Spice subgroup: Allspice; anise (seed); anise, star; annatto (seed); caper (buds); caraway; caraway, black; cardamom; cassia (buds); celery (seed); cinnamon; clove (buds); coriander (seed); cilantro (seed); cumin; dill (seed); fennel, common; fennel, Florence (seed); fenugreek; grains of paradise; juniper (berry); lovage (seed); mace; mustard (seed); nutmeg; pepper, black; pepper, white; poppy (seed); saffron; and vanilla.

[OR US EPA Crop group Herbs and Spices: Allspice, Angelica, Anise (anise seed), Anise, star, Annatto (seed), Balm (lemon balm), Basil, Borage, Burnet, Camomile, Caper buds, Caraway, Caraway, black, Cardamom, Cassia bark, Cassia buds, Catnip, Celery seed, Chervil (dried), Chive, Chive, Chinese, Cinnamon, Clary, Clove buds, Coriander (cilantro or Chinese parsley) (leaf), Coriander (cilantro) (seed), Costmary, Culantro (leaf), Culantro (seed), Cumin, Curry (leaf), Dill (dill weed), Dill (seed), Fennel (common), Fennel, Florence (seed), Fenugreek, Grains of paradise, Horehound, Hyssop, Juniper berry, Lavender, Lemongrass, Lovage (leaf), Lovage (seed), Mace, Marigold, Marjoram (includes sweet or annual marjoram, wild marjoram or oregano, and pot marjoram), Mustard (seed), Nasturtium, Nutmeg, Parsley (dried), Pennyroyal, Pepper, black, Pepper, white, Rosemary, Rue, Saffron, Sage, Savory, summer and winter, Sweet bay, Tansy, Tarragon, Thyme, Vanilla, Wintergreen, Woodruff, Wormwood. The EPA also noted that items such as dried onions, dried garlic, and dehydrated vegetables are included in ASTA definition of spices. As a consequence the EPA also established tolerances for these items.]

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised trials for PPO on the following commodities:

| Commodity | Table No. |
|-------------------------------------|-----------|
| Cereal grain | 8 |
| Tree nuts—supervised trials | 9 |
| Tree nuts—commercial scale trials | 10 |
| Cocoa | 11 |
| Herbs and spices | 12 |
| Dried fruit (raisins, figs, prunes) | 13 |

Where duplicate samples from an unreplicated fumigation were taken at each sampling time and were analysed separately, the mean of the two analytical results was taken as the best estimate of the residues in the product and the means are recorded in the tables. When residues were not detected they are shown as below the LOQ (e.g., < 0.01 mg/kg). Residues and fumigation rates have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. Those results included in the evaluation are underlined.

Conditions of the supervised residue trials were generally well reported in detailed fumigation reports. The post-fumigation interval (PFI) is assumed to start at the end of the fumigation period and includes the period when the fumigation chamber is flushed with air.

Cereal grain

In laboratory scale experiments Isikber *et al* (2004, 2005) studied residues of PPO residues in wheat and corn grain and cocoa beans fumigated with PPO in a small scale chamber (2.6 l). The commodities were treated at 0.112 g ai/l at 30 ± 1 °C for four hours and at reduced pressure. At the end of the fumigation period the commodities were held at ambient temperature for off-gassing. The levels of PPO residue in the commodities were determined by a commercial analytical laboratory service following the analytical method that was a modification of the ASTA analytical method of the Official Methods of Analysis of the AOAC (Anonymous, 2000). PCH and PBH were not analysed in this study. Samples were dispatched for analysis at the time of collection (Isikber pers comm.).

Table 8 Residues in cereal grain after post-harvest fumigation with propylene oxide

| Matrix (year) | Application rate (g ai/L) | Off-gassing (°C) | PFI (days) | Residue (mg/kg) | | | Reference |
|-----------------------------------|------------------------------|---------------------|------------|-----------------|-----|-----|------------------------------------|
| | | | | PPO | PCH | PBH | |
| Winter wheat | 0.112×4h | 25–30 | 0 | 133 | – | – | Isikber <i>et al</i> 2004, 2005 |
| Hard red #2 (2004) | | | 3 | 14 | – | – | |
| Grade No 2 | 0.112×4h | 25–30 | 0 | 157 | – | – | Isikber <i>et al</i> 2004, 2005 |
| Yellow corn for feed (2004) | | | 3 | 6 | – | – | |

Wheat $11.2 \pm 0.2\%$ moisture; corn $11.8 \pm 0.1\%$ moisture

Tree nuts

In laboratory scale experiments, Schrier and Koch (1998) fumigated almonds (8.1 kg), pecans (5.9 kg) and walnuts (5.7 kg) nutmeat with PPO (2.08 g/L) for 6 hours at 52 °C. Nuts were packed into cardboard containers (30 × 30 × 18 cm) and the fumigation chamber (28.4 L) loaded to 50% capacity (nut volume/chamber volume = 50%). Following fumigation under vacuum the chamber air was replaced four times to remove excess PPO followed by off-gassing at either 25 °C or 35 °C for

various intervals. Air flow through during this period was approximately $\frac{1}{3}$ of oven volume per minute. Samples were generally analysed on the same day as collected although occasionally retained samples stored at $-20\text{ }^{\circ}\text{C}$ were used. Analysis for PPO was by an automated headspace technique utilising GC-FID (LOQ 0.1 mg/kg). Propylene halohydrins were measured by GC-ELCD (LOQ 1 mg/kg). The almonds and walnuts were fumigated with methylbromide two to three months prior to PPO treatment. Some pecans may have been exposed to a chlorine wash and dried prior to packaging and PPO fumigation.

Muhareb *et al.* (2006) fumigated almonds using a laboratory scale vacuum chamber (28.4 L vacuum desiccator). Shelled and unshelled almonds (4.5 kg) were placed in unlined cardboard boxes and fumigated with PPO at 0.5 g ai/L for 4 hours at $32\text{--}40\text{ }^{\circ}\text{C}$ under reduced pressure. At the end of the fumigation period the chamber air was replaced four times and the nuts off-gassed at either 24 or $38\text{ }^{\circ}\text{C}$. Sorption of PPO during fumigation was estimated to be 61–76% for shelled almonds ($C \times T = 0.54\text{--}0.63\text{ g h}$) and 78–79% for inshell almonds ($C \times T = 0.54\text{ g h}$). PPO was analysed using GC-FID according to the American Spice Trade Association method 26.0 “Propylene Oxide Analysis-Distillation Method Ethylene Oxide” as modified by DFA (Heuser and Scudamore 1969). The LOQ was 5 mg/kg. Samples were analysed on the same day as collection (pers commun). The analysis results for in-shell almonds include the shell unless otherwise specified.

Danyluk *et al.* (2005) treated almonds in a commercial facility using standard industry operating procedures. The almonds were loaded into bins (900 kg) or cardboard boxes (22.7 kg) and warmed to $43\text{--}49\text{ }^{\circ}\text{C}$ prior to fumigation. The bins were $137 \times 130\text{ cm}$ and lined with a 1.25 mm thick non-perforated polyethylene plastic bag and were reported to be typical of bins used by the almond industry. Bins or pallets of boxes were loaded into a five-bin capacity fumigation chamber, the chamber sealed and heated to $48\text{ }^{\circ}\text{C}$ for fumigation under reduced pressure at a PPO concentration of 0.5 g ai/L for four hours. At the end of the fumigation period the chamber was flushed four times with air over a 2.5 hour period. The pallets were then either moved to a chamber maintained at $38\text{--}43\text{ }^{\circ}\text{C}$ to continue off gassing (ventilation) and then moved to a room maintained at $15\text{--}18\text{ }^{\circ}\text{C}$ for a further three days (tempering) or moved directly to the tempering room for a period of five days. Analysis for PPO was by GC-FID, LOQ not specified.

Allred *et al.* (2001) studied residues of PPO on almonds, pecans and walnuts following fumigation under reduced pressure in laboratory scale chambers (28.4 L) at 0.05 g ai/L. Approximately 6.8 kg of in-shell almonds (Peerless), pecans (50:50 mix Western and Wichita varieties) and walnuts (Hartley) were placed separately into cardboard cartons ($23 \times 29 \times 29\text{ cm}$) and fumigated for 48 hours at $38\text{ }^{\circ}\text{C}$ and 0.05 g ai/L. At the end of 48 hours the samples were forced air aerated for 30 minutes at $38\text{ }^{\circ}\text{C}$ and then maintained at $30\text{ }^{\circ}\text{C}$ with the air flushed continuously (2.5 volumes per minute) for three days. Samples were analysed on the same day as collection. Almond nuts were shelled prior to analysis by GC-FID. Sorption of PPO during fumigation was estimated to be 97% for in-shell almonds ($C \times T = 0.19\text{ g h/L}$), 99% for in-shell pecans ($C \times T = 0.11\text{ g h/L}$) and 99% for inshell walnuts ($C \times T = 0.18\text{ g h/L}$).

In another study, almonds, pecans and walnuts were fumigated with a mixture of propylene oxide (PPO) and CO_2 (8%:92% w/w) in 28.4 L chambers (Zettler *et al.* 2002). Fumigations were conducted at normal atmospheric pressure at $38\text{ }^{\circ}\text{C}$ for 48 h. Fumigation using a rate of 0.045 g ai/L at $38\text{ }^{\circ}\text{C}$ resulted in more than 97% sorption in almonds, pecans and walnuts. A 24-h fumigation of walnuts, raisins and figs using a rate of 0.075 g/L at $26.7\text{ }^{\circ}\text{C}$ resulted in 78, 95 and 93% sorption. The rate of PPO sorption into walnuts, raisins and figs was independent of PPO fumigation rate for the concentration range 0.0125–0.1 g ai/L.

Isikber *et al.* (2005, 2006) fumigated almonds, peanuts and walnuts (1 kg) in fumigation chambers of 2.64 L capacity for 4 hours at $30\text{ }^{\circ}\text{C}$ and atmospheric pressure with a dose of 0.112 g/L PPO and at $60 \pm 5\%$ relative humidity.

Table 9 Residues in tree nuts after post-harvest fumigation with propylene oxide

| Matrix (Year) | Application rate (g ai/L) | Off-gassing (°C) | PFI (days) | Residue (mg/kg) | | | Reference |
|---|------------------------------|---------------------|---------------|-----------------|------|-------|------------------------------|
| | | | | PPO | PCH | PBH | |
| Almonds, shelled whole (1998) ^a | 2.08× 6 h | 25 | 0 | 3580 | 6.25 | 11.9 | Schrier and Koch, 1998 |
| | | | 6 | 1150 | – | – | |
| | | | 7 | – | 5.38 | 9.24 | |
| | | | 13 | 759 | 4.02 | 4.26 | |
| | | | 17 | 542 | – | – | |
| | | | 22 | 379 | –1 | – | |
| | | | 28 | 273 | 3.04 | 1.66 | |
| | | | 44 | 125 | 4.88 | 2.03 | |
| Almonds, shelled whole (1998) ^a | 2.08× 6 h | 35 | 0 | 3290 | 7.59 | 16.5 | Schrier and Koch, 1998 |
| | | | 6 | 667 | – | – | |
| | | | 7 | – | 5.91 | 6.33 | |
| | | | 13 | 347 | 3.55 | 1.91 | |
| | | | 17 | 215 | – | – | |
| | | | 22 | 102 | – | – | |
| | | | 28 | 95.5 | 2.93 | 0.986 | |
| | | | 44 | 35.3 | 2.65 | 0.757 | |
| Almond shelled whole (2006) | 0.5× 4 h | 24 | 0 | 960 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | 426 | | | |
| | | | 5 | 82 | | | |
| | | | 9 | 16 | | | |
| | | | 15 | 5.4 | | | |
| | | | 26 | 3.0 | | | |
| | | | 42 | < 1.9 | | | |
| Almond shelled whole (2006) | 0.5× 4 h | 24 | 0 | 975 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | 465 | | | |
| | | | 5 | 91 | | | |
| | | | 9 | 19 | | | |
| | | | 15 | 6.0 | | | |
| | | | 26 | 2.2 | | | |
| | | | 42 | < 1.9 | | | |
| Almond shelled whole (2006) | 0.5× 4 h | 38 | 0 | 1021 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | – | | | |
| | | | 5 | 55 | | | |
| | | | 9 | 10 | | | |
| | | | 15 | < 1.9 | | | |
| | | | 26 | < 1.9 | | | |
| Almond shelled whole (2006) | 0.5× 4 h | 38 | 0 | 1188 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | – | | | |
| | | | 5 | 57 | | | |
| | | | 9 | 11 | | | |
| | | | 15 | 2.2 | | | |
| | | | 26 | < 1.9 | | | |
| | | | 42 | < 1.9 | | | |
| Almonds (in shell) (2006) ^b | 0.5× 4 h | 24 | 0 | 566 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | 238 | | | |
| | | | 5 | 201 | | | |
| | | | 9 | 58 | | | |
| | | | 15 | 66 | | | |
| | | | 26 | 16 | | | |
| | | | 40 | 27 | | | |
| | | | 61 | 17 | | | |
| | | | 82 | 11 | | | |
| | | | 82 shell | 26 | | | |
| 82 nmt | < 1.9 | | | | | | |
| Almonds (in shell) (2006) ^b | 0.5× 4 h | 24 | 0 | 352 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | 195 | | | |
| | | | 5 | 204 | | | |

| Matrix (Year) | Application rate (g ai/L) | Off-gassing (°C) | PFI (days) | Residue (mg/kg) | | | Reference |
|---|------------------------------|---------------------|----------------|-----------------|------|------|--|
| | | | | PPO | PCH | PBH | |
| | | | 9 | 44 | | | |
| | | | 15 | 57 | | | |
| | | | 26 | 18 | | | |
| | | | 40 | 28 | | | |
| | | | 61 | 33 | | | |
| | | | 82 | 10 | | | |
| Almonds (in shell) (2006) ^b | 0.5×4 h | 38 | 0 | 495 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | 139 | | | |
| | | | 5 | 49 | | | |
| | | | 9 | 21 | | | |
| | | | 15 | 25 | | | |
| | | | 26 | 7 | | | |
| | | | 40 | 8 | | | |
| | | | 61 | 11 | | | |
| Almonds (in shell) (2006) ^b | 0.5×4 h | 38 | 0 | 498 | | | Muhareb <i>et al.</i> , 2006 |
| | | | 1 | 144 | | | |
| | | | 5 | 86 | | | |
| | | | 9 | 21 | | | |
| | | | 15 | 26 | | | |
| | | | 26 | 6 | | | |
| | | | 40 | 13 | | | |
| | | | 61 | 13 | | | |
| Pecans nutmeat pieces (1998) ^a | 2.08×6 h | 25 | 0 | 3720 | 22.8 | < 1 | Schrier and Koch, 1998 |
| | | | 6 | 373 | – | – | |
| | | | 12 | 171 | 11.6 | < 1 | |
| | | | 18 | 71.2 | – | – | |
| | | | 22 | 45.0 | – | – | |
| | | | 27 | 36.7 | 8.22 | < 1 | |
| Pecans nutmeat Pieces (1998) ^a | 2.08×6 h | 35 | 0 | 3820 | 23.3 | < 1 | Schrier and Koch, 1998 |
| | | | 6 | 234 | – | – | |
| | | | 12 | 54.3 | 9.87 | < 1 | |
| | | | 18 | 22.5 | – | – | |
| | | | 22 | 13.7 | – | – | |
| | | | 27 | 12.4 | 7.21 | < 1 | |
| Walnuts nutmeat Pieces (1998) ^a | 2.08×6 h | 25 | 0 | 1670 | 6.12 | 4.73 | Schrier and Koch, 1998 |
| | | | 6 | 876 | – | – | |
| | | | 12 | 542 | 9.42 | 5.57 | |
| | | | 18 | 392 | 8.43 | 6.36 | |
| | | | 22 | 254 | – | – | |
| | | | 27 | 209 | 7.42 | 7.89 | |
| Walnuts nutmeat pieces (1998) ^a | 2.08×6 h | 35 | 0 | 1720 | 6.29 | 3.45 | Schrier and Koch, 1998 |
| | | | 6 | 536 | – | – | |
| | | | 12 | 471 | 7.71 | 3.60 | |
| | | | 18 | 264 | 8.03 | 2.87 | |
| | | | 22 | 171 | – | – | |
| | | | 27 | 81.1 | 6.76 | 2.40 | |
| Almond Nonpareil 23/25 (2005) | 0.5×4 h | 25 | 0 | 490 ± 190 | | | Danyluk <i>et al</i> 2005 ^e |
| | | 38–43 | 2 ^c | 240 ± 30 | | | |
| | | + 15–18 | 5 ^c | 90 ± 40 | | | |
| Almond Nonpareil 23/25 (2005) | 0.5×4 h | 28 | 0 | 410 | | | Danyluk <i>et al</i> 2005 |
| | | 38–43 | 2 ^c | 260 | | | |
| | | + 15–18 | 5 ^c | 130 | | | |
| Almond Nonpareil 23/25 (2005) | 0.5×4 h | 31 | 0 | 600 ± 70 | | | Danyluk <i>et al</i> 2005 |
| | | 38–43 | 2 ^c | 370 ± 40 | | | |
| | | + 15–18 | 5 ^c | 110 ± 10 | | | |
| | | 15–18 | 2 ^d | 335 | | | |

| Matrix (Year) | Application rate (g ai/L) | Off-gassing (°C) | PFI (days) | Residue (mg/kg) | | | Reference |
|---|------------------------------|---------------------|----------------|-----------------|-------|--------|------------------------------------|
| | | | | PPO | PCH | PBH | |
| | | 15–18 | 5 ^d | 210 | | | |
| Almond Nonpareil 23/25 (2005) | 0.5×4 h | 34 | 0 | 480 ± 10 | | | Danyluk <i>et al</i> 2005 |
| | | 38–43 | 2 ^c | 300 | | | |
| | | + 15–18 | 5 ^c | 120 | | | |
| | | 15–18 | 2 ^d | 360 | | | |
| | | 15–18 | 5 ^d | 260 | | | |
| Almond Mission 27/30 2005 | 0.5×4 h | 33 | 0 | 620 | | | Danyluk <i>et al</i> 2005 |
| | | 15–18 | 2 ^d | 440 | | | |
| | | 15–18 | 5 ^d | 340 | | | |
| Almond Nonpareil 23/25 (2005) | 0.5×4 h | 28 | 0 | 520 ± 80 | | | Danyluk <i>et al</i> 2005 |
| | | 38–43 | 2 ^c | 370 | | | |
| | | + 15–18 | 5 ^c | 250 | | | |
| | | 15–18 | 2 ^d | 340 | | | |
| | | 15–18 | 5 ^d | 290 | | | |
| Almond Mission 27/30 (2005) | 0.5×4 h | 33 | 0 | 590 | | | Danyluk <i>et al</i> 2005 |
| | | 15–18 | 2 ^c | 480 | | | |
| | | 15–18 | 5 ^c | 420 | | | |
| Almond Mission 27/30 (2005) | 0.5×4 h | 32 | 0 | 850 | | | Danyluk <i>et al</i> 2005 |
| | | 38–43 | 2 ^c | 230 | | | |
| | | + 15–18 | 5 ^c | 190 | | | |
| | | 15–18 | 2 ^d | 335 | | | |
| | | 15–18 | 5 ^d | 300 | | | |
| Almond Mission 27/30 (2005) | 0.5×4 h | – | 0 | 885 | | | Danyluk <i>et al</i> 2005 |
| | | 38–43 | 2 ^c | 460 | | | |
| | | + 15–18 | 5 ^c | 210 | | | |
| | | 15–18 | 2 ^d | 560 | | | |
| | | 15–18 | 5 ^d | 640 | | | |
| Almond (in shell) (2001) | 0.05×48 h | – | 0 | 23 | | | Allred <i>et al</i> 2001 |
| | | 30 | 3 | < 5 | | | |
| | | – | 0 | 56 | | | |
| | | 30 | 3 | < 5 | | | |
| Pecan (in shell) (2001) | 0.069×48 h | – | 0 | 249 | | | Allred <i>et al</i> 2001 |
| | | 30 | 3 | < 5 | | | |
| | | – | 0 | 18 | | | |
| | | 30 | 3 | < 5 | | | |
| Walnut (in shell) (2001) | 0.053×48 h | – | 0 | 72 | | | Allred <i>et al</i> 2001 |
| | | 30 | 3 | < 5 | | | |
| | | | | PPO | PCH | PPG | |
| Walnuts pieces (rerun) (1995) ^f | 2.4×4 h | 28 | 0 | 1749.5 | 68.0 | 1481.7 | Poole <i>et al</i> 1995 |
| | | | 4 | 1013.3 | 39.5 | 1243.8 | |
| | | | 10 | 871.7 | 40.0 | 1224.0 | |
| | | | 14 | 628.0 | 41.5 | 1208.7 | |
| | | | 17 | 778.0 | 30.3 | 1239.7 | |
| Pecan pieces (rerun) (1995) ^f | 2.4×4 h | 28 | 0 | 4673.6 | 77.3 | 1435.3 | Poole <i>et al</i> 1995 |
| | | | 4 | 1916.2 | 34.3 | 1759.0 | |
| | | | 10 | 1452.5 | 39.0 | 1817.0 | |
| | | | 14 | 1087.0 | 27.0 | 3632.8 | |
| | | | 17 | 1504 | 49.0 | 1602.0 | |
| Pecans whole (rerun) (1995) ^f | 2.4×4 h | 28 | 0 | 47.3 | 102.3 | 214.8 | Poole <i>et al</i> 1995 |
| | | | 4 | 1694.5 | 82.0 | 240.0 | |
| | | | 10 | 100.3 | < 20 | 273.7 | |
| | | | 14 | 226.0 | < 9.5 | 225.3 | |
| | | | 17 | 260.0 | 22.3 | 232.5 | |
| Almond nutmeat (2003) | 0.112×4 h | 25–30 | 5h | 46 | | | Isikber <i>et al</i> 2005, 2006 |
| | | | 3 | < 2 | | | |
| Peanut nutmeat (2003) | 0.112×4 h | 25–30 | 5 h | 111 | | | Isikber <i>et al</i> 2005, 2006 |
| | | | 3 | 8 | | | |

| Matrix (Year) | Application rate (g ai/L) | Off-gassing (°C) | PFI (days) | Residue (mg/kg) | | | Reference |
|--------------------------|------------------------------|---------------------|---------------|-----------------|-----|-----|------------------------------------|
| | | | | PPO | PCH | PBH | |
| Walnut nutmeat (2003) | 0.112× 4 h | 25–30 | 5 h | 80 | | | Isikber <i>et al</i> 2005, 2006 |
| | | | 3 | 26 | | | |
| Almond nutmeat (2002) | 0.045× 48 h | ambient | 0 | 56 | | | Zettler <i>et al</i> 2002 |
| | | | 3 | < LOD | | | |
| Pecan nutmeat (2002) | 0.045× 48 h | ambient | 0 | 249 | | | Zettler <i>et al</i> 2002 |
| | | | 3 | < LOD | | | |
| Walnut nutmeat (2002) | 0.045× 48 h | ambient | 0 | 72 | | | Zettler <i>et al</i> 2002 |
| | | | 3 | < LOD | | | |

^a Schrier and Koch (1998) almonds 7% moisture, 830 mg Cl/kg, 92 mg Br/kg; pecans 4% moisture, 316 mg Cl/kg, 47 mg Br/kg; walnuts 3% moisture, 4080 mg Cl/kg, 190 mg Br/kg.

^b for analysis of samples of in-shell nuts, the nuts were ground whole and include the shell.

^c nuts maintained at 38–43 °C to continue off-gassing (ventilation) and then moved to a room maintained at 15–18 °C for a further three days (tempering)

^d nuts moved directly to the tempering room (15–18 °C) for a period of five days

^e Danyluk *et al* = shelled whole almonds

^f Study should not be used for estimation of maximum residue levels. The study was submitted to demonstrate the formation of PPG during fumigation.

nmt = nutmeat

Results for commercial scale fumigation of almonds were reported by Ludwig and Graham (2006). Almonds were fumigated under reduced pressure with PPO shortly after harvest according to a standard protocol, fumigation temperature 49–51 °C, PPO 0.5 g/L for 4 hours, air wash (4–14 times), held at 38–43 °C for 2 days or above 15 °C for 5 days. Samples were collected at different intervals after fumigation. Almonds were contained in field bins (FB22, *ca* 900 kg) or cardboard boxes (50# = 50 lbs = 22.7 kg), the latter were stacked on pallets for fumigation. Fumigated nuts from Blue Diamond, a major California almond producer, were degassed at ambient temperature for a maximum of 43 days after treatment and then placed in cold storage. Residues were variable, because there were different treatment and storage regimes and the same lots were not analysed sequentially; lots representing different storage intervals were sampled at the same time. Samples were analysed on the same day as collection or stored overnight at -27 to -30 °C prior to analysis.

Additional samples were collected from four different processors. The treatment protocol required off-gassing at 38–43 °C for at least 2 days or ambient temperature (but > 15 °C) for at least 5 days. Samples which had been off-gassing for less than 14 days were shipped on ice to prevent further off-gassing during transportation. Once received by the laboratory, samples were stored at -26.5 °C and analysed within a week of receipt (*pers comm*).

Table 10 Residues in almonds (shelled, whole unless stated otherwise) after commercial post-harvest fumigation with propylene oxide

| Matrix ^a | | Application rate (g ai/L) | Fumigation temp (°C) | PFI (days) | Residue (mg/kg) | | | Reference |
|----------------------|------------------------|------------------------------|-------------------------|---------------|-----------------|-----|-----|----------------------------|
| | | | | | PPO | PCH | PBH | |
| Blue Diamond data | container ^b | | | | | | | |
| Whole raw N/G | FB22 | 0.5× 4h | 49–51 | 4 | 140 | | | Ludwig & Graham 2006 |
| Whole raw | FB22 | 0.5× 4h | 49–51 | 5 | 200 | | | |
| Whole raw | FB22 | 0.5× 4h | 49–51 | 5 | 130 | | | |
| Whole raw | FB22 | 0.5× 4h | 49–51 | 6 | 69 | | | |
| Ne Plus 25/27 | FB22 | 0.5× 4h | 49–51 | 7 | 140 | | | |
| Whole raw | FB22 | 0.5× 4h | 49–51 | 7 | 120 | | | |
| Whole raw | FB22 | 0.5× 4h | 49–51 | 10 | 66 | | | |
| Whole raw | FB22 | 0.5× 4h | 49–51 | 11 | 66 | | | |
| Butte 25/27 | FB22 | 0.5× 4h | 49–51 | 13 | 54 | | | |
| Butte 25/27 | FB22 | 0.5× 4h | 49–51 | 13 | 26 | | | |

| Matrix ^a | | Application | Fumigation | PFI | Residue (mg/kg) | | | Reference |
|---------------------|--------------------------------|---------------|------------|--------|-----------------|-----|-----|-----------|
| | | rate (g ai/L) | temp (°C) | (days) | PPO | PCH | PBH | |
| Nonpareil 16/18 | 50# | 0.5× 4h | 49–51 | 15 | 66 | | | |
| Nonpareil 16/18 | 50# | 0.5× 4h | 49–51 | 15 | 71 | | | |
| Butte 25/27 | FB22 | 0.5× 4h | 49–51 | 16 | < 25 | | | |
| California 20/22 | 50# | 0.5× 4h | 49–51 | 17 | 73 | | | |
| Butte 25/27 | FB22 | 0.5× 4h | 49–51 | 19 | 33 | | | |
| Butte 25/27 | FB22 | 0.5× 4h | 49–51 | 19 | 18 | | | |
| Nonpareil16/18 | 50# | 0.5× 4h | 49–51 | 26 | < 25 | | | |
| Whole Raw | FB22 | 0.5× 4h | 49–51 | 29 | 53 | | | |
| California 23/25 | 50# | 0.5× 4h | 49–51 | 30 | 28 | | | |
| Nonpareil 20/22 | 50# | 0.5× 4h | 49–51 | 30 | 38 | | | |
| California 20/22 | 50# | 0.5× 4h | 49–51 | 30 | 51 | | | |
| Carmel 22/24 | 50# | 0.5× 4h | 49–51 | 32 | 12 | | | |
| Carmel 22/24 | 50# | 0.5× 4h | 49–51 | 32 | 36 | | | |
| Mission 27/30 | 50# | 0.5× 4h | 49–51 | 34 | 46 | | | |
| California 25/27 | FB22 | 0.5× 4h | 49–51 | 35 | 54 | | | |
| Mission 27/30 | 50# | 0.5× 4h | 49–51 | 36 | < 25 | | | |
| Nonpareil 20/22 | 50# | 0.5× 4h | 49–51 | 40 | 67 | | | |
| Carmel 22/24 | 50# | 0.5× 4h | 49–51 | 41 | 40 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 43 | 42 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 43 | 34 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 43 | < 25 | | | |
| Nonpareil18/20 | 50# | 0.5× 4h | 49–51 | 43 | 23 | | | |
| Nonpareil18/20 | 50# | 0.5× 4h | 49–51 | 43 | 33 | | | |
| Nonpareil18/20 | 50# | 0.5× 4h | 49–51 | 43 | < 25 | | | |
| California 20/22 | 50# | 0.5× 4h | 49–51 | 44 | 29 | | | |
| Nonpareil 20/22 | 50# | 0.5× 4h | 49–51 | 57 | 22 | | | |
| Carmel 22/24 | 50# | 0.5× 4h | 49–51 | 64 | < 25 | | | |
| Non Pareil 18/20 | 50# | 0.5× 4h | 49–51 | 64 | < 25 | | | |
| Nonpareil 20/22 | 50# | 0.5× 4h | 49–51 | 67 | < 25 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 74 | 22 | | | |
| Butte 27/30 | 50# | 0.5× 4h | 49–51 | 75 | 37 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 93 | 47 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 94 | < 25 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 95 | < 25 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 103 | < 25 | | | |
| Nonpareil 18/20 | 50# | 0.5× 4h | 49–51 | 106 | 43 | | | |
| Mission 32/34 | 50# | 0.5× 4h | 49–51 | 270 | < 25 | | | |
| Processor data | Sample ^c /processor | | | | | | | |
| Nonpareil 22/24 | 2/B | 0.5× 4h | 49–51 | 0 | 233 | | | |
| Nonpareil 22/24 | 3/B | 0.5× 4h | 49–51 | 0 | 491 | | | |
| Whole raw | 21/C | 0.5× 4h | 49–51 | 0 | 499 | | | |
| Whole raw | 1/A | 0.5× 4h | 49–51 | 1 | 512 | | | |
| Whole raw | 22/C | 0.5× 4h | 49–51 | 3 | 173 | | | |
| Nonpareil 20/22 | 30/D | 0.5× 4h | 49–51 | 9 | 149 | | | |
| Whole raw | 31/A | 0.5× 4h | 49–51 | 14 | 30.9 | | | |
| Nonpareil 18/20 | 4/B | 0.5× 4h | 49–51 | 15 | 26.2 | | | |
| Nonpareil 20/22 | 5/B | 0.5× 4h | 49–51 | 15 | 17.7 | | | |
| Nonpareil 18/20 | 6/B | 0.5× 4h | 49–51 | 15 | 19.2 | | | |
| Whole raw | 32/C | 0.5× 4h | 49–51 | 15 | 18 | | | |
| Nonpareil 20/22 | 29/D | 0.5× 4h | 49–51 | 20 | 55.2 | | | |
| Nonpareil 20/22 | 28/D | 0.5× 4h | 49–51 | 20 | < 2 | | | |
| Nonpareil 27/30 | 27/D | 0.5× 4h | 49–51 | 26 | < 2 | | | |
| Whole raw | 33/A | 0.5× 4h | 49–51 | 27 | 2.4 | | | |
| Whole raw | 34/C | 0.5× 4h | 49–51 | 30 | 8.7 | | | |
| Natural 12/8 | 26/D | 0.5× 4h | 49–51 | 32 | 99.9 | | | |
| Mission 25/27 | 10/B | 0.5× 4h | 49–51 | 33 | 14.6 | | | |
| Natural meal | 25/D | 0.5× 4h | 49–51 | 33 | 11.3 | | | |

| Matrix ^a | | Application | Fumigation | PFI | Residue (mg/kg) | | | Reference |
|---------------------|------|---------------|------------|--------|-----------------|-----|-----|-----------|
| | | rate (g ai/L) | temp (°C) | (days) | PPO | PCH | PBH | |
| Mission 25/27 | 15/B | 0.5× 4h | 49–51 | 33 | < 2 | | | |
| Mission 25/27 | 16/B | 0.5× 4h | 49–51 | 33 | < 2 | | | |
| Carmel | 24/D | 0.5× 4h | 49–51 | 39 | < 2 | | | |
| Natural fine diced | 23/D | 0.5× 4h | 49–51 | 42 | 21.5 | | | |
| Nonpareil 20/33 | 9/B | 0.5× 4h | 49–51 | 43 | 11.4 | | | |
| Nonpareil 20/22 | 14/B | 0.5× 4h | 49–51 | 43 | < 2 | | | |
| Nonpareil 20/22 | 19/B | 0.5× 4h | 49–51 | 43 | < 2 | | | |
| Whole raw | 35/C | 0.5× 4h | 49–51 | 45 | < 2 | | | |
| Nonpareil 20/22 | 7/B | 0.5× 4h | 49–51 | 61 | < 2 | | | |
| Nonpareil 20/22 | 8/B | 0.5× 4h | 49–51 | 61 | < 2 | | | |
| Nonpareil 20/22 | 12/B | 0.5× 4h | 49–51 | 61 | < 2 | | | |
| Nonpareil 20/22 | 11/B | 0.5× 4h | 49–51 | 72 | < 2 | | | |
| Nonpareil 20/22 | 13/B | 0.5× 4h | 49–51 | 72 | < 2 | | | |
| Nonpareil 20/22 | 17/B | 0.5× 4h | 49–51 | 72 | < 2 | | | |

^a Almond nut sizes are given as the number of nuts per 28.35 g (1 oz), e.g. 18/20 = 18 to 20 nuts per 28.35 g.

^b FB22 = 900 kg field bin; 50# = 50 lb (22.7 kg) cardboard boxes

^c Samples 1, 31, 33: 6 × air wash, off-gassing for 3 days at 43 °C, 2 days at 27 °C and storage for 9 days at 10–16 °C
Samples 2,3: 5 × air wash, no liner in bin

Samples 4, 5 6: 5 × air wash, no liner in carton, off-gassing for 4 days at 38 °C, 11 days at 18 °C.

Samples 7–17, 19: 5 × air wash, no liner in carton, off-gassing for 4 days at 38 °C and storage at 10–16 °C

Samples 7–17, 19: 5 × air wash, no liner in carton, off-gassing for 4 days at 38 °C and storage at 10–16 °C

Samples 21: 5 × air wash, plastic lined wood bin

Samples 22, 32, 34: 5 × air wash, plastic lined wood bin, off-gassing for 3 days at 29–32 °C

Samples 35: 5 × air wash, plastic lined wood bin, off-gassing for 3 days at 29–32 °C, storage for 42 days at 13–18 °C

Samples 23–30: 6 × air wash, off-gassing for 3 days

Cocoa

In laboratory scale experiments described earlier under cereal grain, Isikber *et al.* (2004, 2005) studied residues of PPO residues in cocoa beans fumigated with PPO in a small scale chamber (2.6 L).

Blinne and Koch (2000c) fumigated cocoa powder (5.6% moisture content) using 2.06 g ai/L in a small scale chamber (28.4 L) operating at 51.7 ± 2 °C for four hours and at reduced pressure. The other conditions were the same as in Blinne and Koch (2001) reported below for spices. Samples were typically not stored but were analysed (PPO) or extracted (PCH, PBH) on the same day as collection.

Table 11 Residues in cocoa beans after post-harvest fumigation with propylene oxide

| Matrix (year) | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|--|---------------|-------------|--------|-----------------|------|------|---------------------------------|
| Country | rate (g ai/L) | (°C) | (days) | PPO | PCH | PBH | |
| Cocoa beans (Ivory Coast) ^a | 0.112 × 4h | 30–35 | 0 | 117 | – | – | Isikber <i>et al</i> 2004, 2005 |
| | | | 3 | 8 | – | – | |
| USA 2000 Cocoa Powder | 2.06 × 4h | 25 | 0 | 221 | 13.4 | 10.5 | Blinne and Koch, 2000c |
| | | | 2 | 136 | 12.5 | 9.62 | |
| | | | 6 | 69.2 | 9.41 | 8.53 | |
| | | | 12 | 27.7 | 4.93 | 4.27 | |
| | | | 16 | 18.8 | – | – | |
| | | | 22 | 9.55 | 6.16 | 4.84 | |
| | | | 30 | 5.86 | 3.53 | 2.36 | |
| | | | 40 | 3.84 | 4.68 | 3.11 | |
| USA 2000 Cocoa Powder | 2.06 × 4h | 35 | 0 | 221 | 13.4 | 10.5 | Blinne & Koch, 2000c |
| | | | 2 | 71.8 | 11.6 | 8.73 | |
| | | | 6 | 13.4 | 9.24 | 7.83 | |
| | | | 12 | 2.97 | 5.72 | 4.23 | |

| Matrix (year) | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|---------------------------|------------------|-------------|--------|-----------------|------|-------|-------------------------|
| Country | rate (g ai/L) | (°C) | (days) | PPO | PCH | PBH | |
| | | | 16 | 2.16 | – | – | |
| | | | 22 | 1.34 | 4.15 | 2.19 | |
| | | | 30 | 1.13 | 2.49 | 1.48 | |
| | | | 40 | 0.78 | 2.51 | 1.45 | |
| | | | | PPO | PCH | PPG | |
| USA 1995 | 2.4 × 4h | 28 | 0 | – | – | 280.0 | Poole <i>et al</i> 1995 |
| Cocoa powder ^b | | | 4 | – | – | – | |
| | | | 10 | – | – | 457.7 | |
| | | | 18 | < 5 | 25.0 | 757.3 | |

^a cocoa beans 6.3 ± 0.3% moisture.

^b Study should not be used for estimation of maximum residue levels. The study was submitted to demonstrate the formation of PPG during fumigation.

Herbs and spices

Blinne and Koch (2001) studied residues of PPO and propylene halohydrins in herbs and spices fumigated under reduced pressure with PPO in a small scale chamber (volume 28.4 L). Herbs and spices (3.44 kg onion powder, 3.22 kg black pepper, 3.32 kg garlic powder, 0.955 kg dried basil, 2.9–3.2 kg chilli powder) were treated at 2.08 g ai/L (and chilli powder 0.44 g ai/L) at 51.7 ± 2 °C for 12 hours and at reduced pressure. The chamber load factor was approximately 50%. The system was flushed with air four times at the end of the fumigation period and the herbs/spices placed in off-gassing chambers and held at 25 ± 2 or 35 ± 2 °C for the off-gassing period. Air flow through the oven during this period was approximately 1/3 of oven volume per minute. Sample analysis was generally conducted within a day of sample collection. PPO analysis was by head-space sampling with GC-FID (LOQ 0.1 mg/kg). Propylene halohydrins were analysed by acetone extraction and GC-ELCD (LOQ 1 mg/kg).

Poole *et al.* (1995) studied PPO residues on various dried commodities. Samples were fumigated under reduced pressure at a commercial facility and at 2.4 g ai/L at a temperature not exceeding 52 °C. The PPO was divided into four equal amounts and added sequentially to the fumigation chamber with a 30 minute interval between additions. Fumigation times were 12 hours for dried commodities (basil, chilli pepper, dill, marjoram, sage, celery seed, mustard seed, orange peel, parsley, peppercorns, turmeric, onion and garlic), 12 hours for fresh commodities (celery seed, chilli pepper, mustard seed, orange peel, peppercorns and poppy seed), 24 hours for gums (guar, xanthin), 4 hours for nutmeat (almonds and walnuts) and 4 hours for cocoa powder. On completion of fumigation, the chamber flashed with air four times and the fumigated products stored at ambient temperature until sampling at various post-fumigation intervals. The experimental protocol suggests analysis for PPO residues occurred soon after sampling with samples stored at 2 °C prior to processing. Analysis for PPO was by head-space sampling with quantitation by GC-FID (LOQ 5 mg/kg), propylene chlorohydrin and propylene glycol analysis was by acetone extraction of samples with quantitation by GC-FID (LOQ 5 mg/kg for each). The study was submitted to demonstrate the relative levels of PPO, PCH and PPG rather than for use in estimation of maximum residue levels. A number of deficiencies were identified in the study that make it unsuitable for maximum residue estimation. For example, no details of the interval between sample collection and analysis are available, nor storage conditions or actual fumigation records to verify dose, some samples were re-run due to problems with scheduling analyses and matrix problems were encountered for ground mustard and cocoa.

Table 12 Residues in herbs and spices after post-harvest fumigation with propylene oxide

| Country | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|----------|-------------|-------------|--------|-----------------|-----|------|------------------|
| Year | rate | (°C) | (days) | PPO | PCH | PBH | |
| Matrix | (g ai/L) | | | | | | |
| USA 2001 | 2.08 × 12 h | 25 | 0 | 32.1 | 107 | 1.03 | Blinne and Koch, |
| Onion | | | 2 | 15.2 | – | – | 2001 |

Propylene oxide

| Country | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|---------------------------|---------------|-------------|--------|-----------------|------|------|-----------------------|
| Year Matrix | rate (g ai/L) | (°C) | (days) | PPO | PCH | PBH | |
| Powder | | | 7 | 9.05 | 42.4 | < 1 | |
| | | | 12 | 7.60 | 38.8 | < 1 | |
| | | | 21 | 4.54 | – | – | |
| | | | 30 | 3.65 | 31.2 | – | |
| USA 2001 Black pepper | 2.08× 12 h | 25 | 0 | 250 | 910 | 11.8 | Blinne and Koch, 2001 |
| | | | 2 | 93.3 | – | – | |
| | | | 7 | 55.1 | 322 | 3.82 | |
| | | | 12 | 42.9 | 215 | 1.08 | |
| | | | 21 | 23.7 | 168 | < 1 | |
| | | | 30 | 12.9 | 200 | – | |
| | | | 40 | – | 112 | – | |
| USA 2001 Garlic Powder | 2.08× 12 h | 25 | 0 | 218 | 500 | 1.14 | Blinne and Koch, 2001 |
| | | | 4 | 147 | – | – | |
| | | | 7 | 117 | 338 | < 1 | |
| | | | 13 | 72.4 | 192 | < 1 | |
| | | | 21 | 35.8 | 384 | – | |
| | | | 31 | 20.7 | 126 | – | |
| | | | 40 | – | 192 | – | |
| USA 2001 Dried basil | 2.08× 12 h | 25 | 0 | 372 | 6670 | 14.6 | Blinne and Koch, 2001 |
| | | | 4 | 164 | – | – | |
| | | | 7 | 107 | 1860 | 4.50 | |
| | | | 13 | 60.3 | 1080 | 2.15 | |
| | | | 21 | 31.5 | 627 | 1.46 | |
| | | | 31 | 19.4 | 384 | < 1 | |
| | | | 40 | – | 359 | – | |
| USA 2001 Celery seed | 2.08× 12 h | 25 | 0 | 126 | 474 | 15.7 | Blinne and Koch, 2001 |
| | | | 4 | 68.8 | – | – | |
| | | | 6 | 45.5 | 161 | 6.36 | |
| | | | 13 | 43.3 | 124 | 4.67 | |
| | | | 21 | 28.5 | – | – | |
| | | | 29 | 21.4 | 62.5 | – | |
| | | | 40 | – | 2860 | 22.9 | |
| USA 2001 Chilli Powder | 2.08× 12 h | 25 | 0 | 18.7 | 2860 | 22.9 | Blinne and Koch, 2001 |
| | | | 4 | – | – | – | |
| | | | 7 | 0.63 | 1690 | 14.1 | |
| | | | 13 | 0.44 | 1110 | 10.7 | |
| | | | 20 | – | 800 | 7.8 | |
| | | | 29 | – | 357 | 3.4 | |
| | | | 40 | – | 239 | 2.5 | |
| USA 2001 Chilli Powder | 2.08× 12 h | 35 | 0 | – | – | – | Blinne and Koch, 2001 |
| | | | 4 | – | – | – | |
| | | | 7 | 0.24 | 760 | 8.77 | |
| | | | 13 | 0.23 | 586 | 6.41 | |
| | | | 20 | – | 224 | 3.46 | |
| | | | 29 | – | 58.1 | < 1 | |
| | | | 40 | – | 2.55 | < 1 | |
| USA 2001 Chilli Powder | 0.44× 12 h | 25 | 0 | 1.52 | 572 | 6.41 | Blinne and Koch, 2001 |
| | | | 4 | 0.20 | – | – | |
| | | | 7 | 0.15 | 254 | 3.97 | |
| | | | 13 | – | 223 | 3.76 | |
| | | | 21 | – | 112 | 2.01 | |
| | | | 29 | – | 86.5 | 1.80 | |
| | | | 40 | – | – | – | |
| USA 2001 Chilli Powder | 0.44× 12 h | 35 | 0 | – | – | – | Blinne and Koch, 2001 |
| | | | 4 | 0.13 | – | – | |
| | | | 7 | < 0.1 | 197 | 3.25 | |
| | | | 13 | – | 94.9 | 1.97 | |
| | | | 21 | – | 27.0 | < 1 | |
| | | | 29 | – | 18.7 | < 1 | |
| | | | | | | PPO | |

| Country | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|---|------------------|-------------|--------|-----------------|--------|---------|-------------------------|
| Year Matrix | rate (g ai/L) | (°C) | (days) | PPO | PCH | PBH | |
| USA 1995 Celery seed ^a | 2.4 × 12 h | 28 | 0 | 269 | 849.5 | 194.8 | Poole <i>et al</i> 1995 |
| | | | 4 | 106.5 | 988.5 | 287.5 | |
| | | | 10 | < 8.7 | 913.3 | 197.3 | |
| | | | 18 | < 5 | 840.5 | 501.3 | |
| USA 1995 Mustard seed ^a | 2.4 × 12 h | 28 | 0 | 199.3 | 25.3 | 12.7 | Poole <i>et al</i> 1995 |
| | | | 4 | 50.0 | < 5 | 26.3 | |
| | | | 10 | < 9.3 | < 10 | 35.5 | |
| | | | 18 | < 6.5 | < 5 | 62.8 | |
| USA 1995 Poppy seed ^a | 2.4 × 12 h | 28 | 0 | 892.0 | 53.5 | 217.8 | Poole <i>et al</i> 1995 |
| | | | 4 | 210.5 | 53.0 | 234.0 | |
| | | | 10 | 46.7 | 47.0 | 161.7 | |
| | | | 18 | 27.5 | 44.7 | 786.4 | |
| USA 1995 Xanthan Gum ^a | 2.4 × 24h | 28 | 0 | < 5 | N/G | 584.0 | Poole <i>et al</i> 1995 |
| | | | 4 | 28.0 | N/G | 560.0 | |
| | | | 10 | < 5 | N/G | 525.3 | |
| | | | 18 | < 5.7 | N/G | 738.8 | |
| USA 1995 Guar gum ^a | 2.4 × 24h | 28 | 0 | < 28 | N/G | 45.5 | Poole <i>et al</i> 1995 |
| | | | 4 | 19 | N/G | 93.0 | |
| | | | 10 | < 5 | N/G | 46.7 | |
| | | | 18 | 7.8 | N/G | 121.3 | |
| USA 1995 Chilli Powder ^a | 2.4 × 12 h | 28 | 0 | 1460.0 | 1257.7 | 5577.0 | Poole <i>et al</i> 1995 |
| | | | 4 | 109.0 | 1350.5 | 5084.0 | |
| | | | 10 | 33.0 | 1164.0 | 6439.3 | |
| | | | 18 | 13.3 | 847.0 | 9841.0 | |
| USA 1995 Whole pepper (rerun) ^a | 2.4 × 12 h | 28 | 0 | 73.0 | 194.3 | 1401.8 | Poole <i>et al</i> 1995 |
| | | | 4 | 124.0 | 273.0 | 5657.5 | |
| | | | 10 | 81 | 225.3 | 3429.5 | |
| | | | 14 | 96.3 | 133.4 | 1736.5 | |
| | | | 17 | 92.5 | 122.5 | 3614.7 | |
| USA 1995 Orange peel ^a | 2.4 × 12 h | 28 | 0 | 267 | 318.5 | 2631 | Poole <i>et al</i> 1995 |
| | | | 4 | 106.5 | 237.5 | 1725.8 | |
| | | | 10 | < 8.7 | 277.7 | 1889.3 | |
| | | | 18 | < 5 | 219.7 | 2574.8 | |
| USA 1995 Onion (minced, dried) ^a | 2.4 × 12 h | 28 | 0 | 25.0 | 115.7 | 97.3 | Poole <i>et al</i> 1995 |
| | | | 4 | < 21.4 | 86.8 | 132.5 | |
| | | | 10 | < 26 | 181.5 | 128.0 | |
| | | | 18 | < 5 | 95.7 | 344 | |
| USA 1995 Garlic (granulated, dried) ^a | 2.4 × 12 h | 28 | 0 | 45.8 | 88.3 | 373.8 | Poole <i>et al</i> 1995 |
| | | | 4 | 33.8 | 326.8 | 280.0 | |
| | | | 10 | 28.3 | 213.7 | 240.0 | |
| | | | 18 | 15.0 | 65.5 | 320.5 | |
| USA 1995 Basil Leaf (dried) ^a | 2.4 × 12 h | 28 | 0 | 532.0 | 5601.0 | 1901.8 | Poole <i>et al</i> 1995 |
| | | | 4 | 303.3 | 3592.5 | 3337.7 | |
| | | | 10 | 383.0 | 2428.0 | 3340.0 | |
| | | | 18 | 195.5 | 3125.7 | 3679 | |
| USA 1995 Dill seed ^a | 2.4 × 12 h | 28 | 0 | 77 | 1983.5 | 13757.0 | Poole <i>et al</i> 1995 |
| | | | 4 | 15.8 | 1874.3 | 2958.5 | |
| | | | 10 | 94.3 | 1830.0 | 3331.3 | |
| | | | 18 | 74 | 1431.0 | 2060.0 | |
| USA 1995 Marjoram (rerun) ^a | 2.4 × 12 h | 28 | 0 | 867.5 | 907.3 | 4504.5 | Poole <i>et al</i> 1995 |
| | | | 4 | 788.0 | 2291.3 | 6667.3 | |
| | | | 10 | 648.0 | 826.3 | 4831.3 | |
| | | | 14 | 628.7 | 1622 | 3356.5 | |
| | | | 17 | 572.0 | 867.3 | 12361 | |
| USA 1995 Parsely Flakes ^a | 2.4 × 12 h | 28 | 0 | 140 | 678.0 | 1350.2 | Poole <i>et al</i> 1995 |
| | | | 4 | 41.7 | 1515.0 | 791.8 | |
| | | | 10 | 46.0 | 926.7 | 738.7 | |
| | | | 18 | 14.8 | 944.2 | 555.0 | |

| Country | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|---|---------------|-------------|--------|-----------------|--------|---------|-------------------------|
| Year Matrix | rate (g ai/L) | (°C) | (days) | PPO | PCH | PBH | |
| USA 1995 Ground Pepper ^a | 2.4 × 12 h | 28 | 0 | 1090 | 1544.0 | 9568.0 | Poole <i>et al</i> 1995 |
| | | | 4 | 917.7 | 2025.0 | 11187.8 | |
| | | | 10 | – | – | 2949.0 | |
| | | | 14 | 330.3 | 2374.0 | – | |
| | | | 18 | < 5 | 1259.0 | 1129.0 | |
| USA 1995 Ground celery seed ^a | 2.4 × 12 h | 28 | 0 | 114 | 1488.0 | 2763 | Poole <i>et al</i> 1995 |
| | | | 4 | 32.0 | 1218.5 | 1166.0 | |
| | | | 10 | – | – | – | |
| | | | 14 | < 8.5 | 1668.5 | 1480 | |
| | | | 18 | < 5 | 1139.7 | 1134 | |
| USA 1995 Ground sage ^a | 2.4 × 12 h | 28 | 0 | < 5 | 718.7 | 3505.5 | Poole <i>et al</i> 1995 |
| | | | 4 | < 5 | 941.7 | 3526.0 | |
| | | | 10 | – | – | 1804 | |
| | | | 14 | < 5 | 723.8 | – | |
| | | | 18 | < 5 | 511.3 | 3399.0 | |
| USA 1995 Turmeric ^a | 2.4 × 12 h | 28 | 0 | 607.7 | 1046.0 | 1170.7 | Poole <i>et al</i> 1995 |
| | | | 4 | 199.8 | 1014.3 | 1457.0 | |
| | | | 10 | 202.7 | 619.0 | 1597.5 | |
| | | | 14 | 240.8 | 784.0 | 1414.5 | |
| | | | 17 | 165.0 | 821.0 | 1552 | |
| USA 1995 Ground mustard (rerun) ^a | 2.4 × 12 h | 28 | 0 | 154.3 | 30.0 | 459.0 | Poole <i>et al</i> 1995 |
| | | | 4 | 173.8 | 47.5 | 244 | |
| | | | 10 | 101 | 49.0 | 1943.0 | |
| | | | 14 | 103.3 | 46.3 | 606.7 | |
| | | | 17 | 144.0 | 54.7 | 517.0 | |

^a Study should not be used for estimation of maximum residue levels. The study was submitted to demonstrate the formation of PPG during fumigation.

Dried fruit

In laboratory scale experiments Blinne (2002) studied residues of PPO and propylene chlorohydrins in dried fruit fumigated with PPO at atmospheric pressure in a small scale chamber (volume 28.4 L). The PPO fumigant was not introduced directly into the fumigation chamber, but rather was added to a CO₂ atmosphere to form a PPO/CO₂ mixture in the chamber. Dried fruit (6.8 kg raisins, 3.73 kg figs, 4.2 kg prunes) were treated at 1.6 to 2.0 g ai/L at 27 ± 2 °C for 48 hours and at reduced pressure. The chamber load factor was approximately 50%. The system was flushed with air four times at the end of the fumigation period and the fruit placed in off-gassing chambers and held at 25 ± 2 °C for the off-gassing period. Samples were analysed on the same day as collection. PPO analysis was by head-space sampling with GC-FID (LOQ 0.1 mg/kg). Propylene chlorohydrins were analysed by acetone extraction and GC-ELCD (LOQ 1 mg/kg) for raisins and figs. The acetone extraction was replaced by an accelerated solvent extraction step for the analysis of prunes.

Table 13 Residues in dried fruits after post-harvest fumigation with propylene oxide

| Country | Application | Off-gassing | PFI | Residue (mg/kg) | | | Reference |
|---------------------|---------------|-------------|--------|-----------------|------|-----|--------------|
| Year Matrix | rate (g ai/L) | (°C) | (days) | PPO | PCH | PBH | |
| USA 2002 Raisins | 1.58 × 48 h | 25 | 0 | 0.845 | 4.31 | – | Blinne, 2002 |
| | | | 4 | < 0.1 | 3.16 | – | |
| | | | 7 | < 0.1 | – | – | |
| | | | 17 | – | 1.48 | – | |
| USA 2002 Figs | 2.0 × 48 h | 25 | 0 | 2.05 | 2.79 | – | Blinne, 2002 |
| | | | 2 | 0.376 | 2.30 | – | |
| USA 2002 Prunes | 2.0 × 48 h | 25 | 0 | 1.54 | 1.08 | – | Blinne, 2002 |
| | | | 2 | < 0.1 | 0.96 | – | |

FATE OF RESIDUES IN STORAGE AND PROCESSING

When volatilization was precluded, a combination of high temperature and prolonged time in cooking did not appreciably alter the propylene chlorohydrin content of food, but when volatilization was possible, the chlorohydrin content was reduced 50 percent by cooking (Wesley *et al.* 1965). When propylene chlorohydrin was added to a standard ground laboratory rat diet, 20 minutes of mixing in an open mixer at room temperature resulted in a 65 percent decrease in the propylene chlorohydrin content (USFDA 1969).

RESIDUES IN ANIMAL COMMODITIES

By-products from tree nuts (e.g., almond hulls and shells) can be incorporated into feeding rations for ruminant livestock (cattle and sheep) (Velasco *et al.* 1965; MacLachlan 2006). However, livestock are not given feedstuffs from commodities treated by PPO, and thus, are not exposed to PPO residues. Therefore, no data on residues in animal commodities are included here.

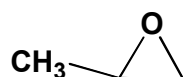
As early as the 1950s, propylene glycol (PG), by drenching or feeding, has been shown to effectively treat ketosis in dairy cows due to its glucogenic property (Johnson 1954, Nielsen and Ingvarsten 2004).

Residue and Analytical Aspects

Propylene oxide is used in agriculture as an insecticidal fumigant and sterilant to control bacteria contamination, mould contamination, insect infestations, and microbial spoilage of food products as well as to control insects in non-food products. Propylene oxide is also a commercially important industrial chemical finding application as an intermediate for a wide array of products. At the Forty-second Session of the CCPR (2010), it was scheduled for evaluation as a new compound by 2011 JMPR.

Residue studies were submitted by the manufacturers for support of the following commodities: cereal grains (maize, wheat), tree nuts, cocoa, herbs and spices, dried vegetables (onion and garlic) and dried fruit (raisins, figs and prunes).

Propylene oxide is methyloxirane.



The following abbreviations are used for the metabolites discussed below:

PPO = propylene oxide

PCH = propylene chlorohydrin, (1-chloro-2-propanol and 2-chloro-1-propanol)

PBH = propylene bromohydrin, (1-bromo-2-propanol and 2-bromo-1-propanol)

PPG = 1,2 propanediol

Animal metabolism

No data for livestock are available on the absorption following oral dosing with propylene oxide. However, data from rats on other routes of administration enable conclusions on the metabolism of PPO to be made. Two metabolic pathways are suggested: 1) conjugation with glutathione via glutathione epoxide transferase; 2) hydrolysis by epoxide hydrolase to 1,2-propanediol (propylene glycol, PPG). PPG can be excreted as such or metabolized to lactic and pyruvic acid. Propylene oxide is a direct alkylating agent that forms DNA (N-2-hydroxypropyl-guanosine, N-2-hydroxypropyl-guanosine) and protein adducts (hemoglobin alkylation at the cysteine, histidine or valine) residues. Assuming a 100% alveolar absorption and first-order kinetics, a half-life of 40 minutes was estimated

for the elimination of PPO in rats. Under *in vitro* conditions, the half-life of PPO in human gastric juice (pH 1.46 and 37 °C) is approximately 1.9 minutes while in rat gastric juice (pH 4.8) it is 347 minutes.

Plant metabolism

Limited data were available of the metabolism of propylene oxide in plants and fumigated plant-based commodities. The Meeting concluded, based on the similarity in reactions and chemistry between ethylene oxide and propylene oxide and reported degradates from studies with unlabelled PPO, that in addition to PPO residues of PPG (free and conjugated), PCH and PBH are formed upon and after postharvest fumigation of plant-based commodities. In commodities that contain salt the PPO will react with chloride ions to form PCH. Similarly, bromide ions present react with PPO to form PBH. Reaction with water present in fumigated samples can produce PPG. In addition, PPO may react with exposed -COOH, -NH₂, -OH and -SH groups present in natural constituents to give the corresponding hydroxy-propyl compounds.

Environmental fate

Propylene oxide is a post-harvest fumigant and sterilant and is not expected to be released into the environment such that significant levels will be found in soil and water. In addition, PPO is hydrolysed in water at 25 °C with a half-life of 10.7 to 14.6 days. The rate of hydrolysis is increased in the presence of acid or base. Propylene oxide is not expected to be present or persist in the environment.

Analytical methods

Methods are available for the analysis of PPO and PCH in plant commodities. Samples are ground under cryogenic conditions (liquid nitrogen), transferred to a vial, the vial sealed and the PPO residues desorbed by heating. Powdered samples do not need the grinding step and can be added directly to the vial. The volatilized PPO equilibrates in the headspace of the vial which is then sampled by an automated headspace sampler and injected onto a GC-FID system. Quantitation was achieved by comparison with a calibration curve consisting of fortified matrix samples. It was reported that headspace analysis should occur within 1 hour of sample preparation for nuts or 2 hours for cocoa, herbs and spices. An LOQ of 0.1 mg/kg was attained for most matrices.

Residues of PCH (1-chloro-2-propanol and 2-chloro-1-propanol) and PBH (1-bromo-2-propanol and 2-bromo-1-propanol) are extracted with acetone and quantitated via gas chromatography with electrolytic conductivity detection (GC-ELCD). Detector response is not linear over the fortification range and a quadratic model was used for the standard curve. An LOQ of 1 mg/kg has been demonstrated for most commodities.

Stability of pesticide residues in stored analytical samples

No data were provided on the stability of residues of PPO, PCH, PBH or PPG when samples were stored frozen. In most of the supervised residue trials samples were analysed on the day of collection or soon after, in which case the samples were stored at 2 °C or -20 °C until analysis.

Definition of the residue

Following fumigation, the major components of the residue observed in trials are PPO, PCH, PBH and PPG. In nuts and cocoa PCH and PBH were present at levels that are about 10% of the PPO level while PCH levels were the same or much greater than PPO in spices and dried fruit. Levels of PPG were about the same as those of PPO in nuts but much greater than PPO in cocoa and spices. PBH residues were similar in magnitude relative to PCH residues in almonds, pecans, walnuts and cocoa powder but much lower in herbs and spices.

The Meeting considered that although PPG was often present at the highest concentration, PPG is much less toxic than PPO and PCH and is not required to be included in the residue for dietary risk assessment. The residues of concern for dietary risk assessment are PPO, PCH and PBH. Based

on differences in toxicological effects, PPO and PCH/PBH are assessed separately and the residues are not combined for estimation of dietary risk exposure.

The Meeting recommended that the residue definition for plant and animal commodities, for compliance with MRLs should be propylene oxide.

The Meeting recommended that the residue definition for plant and animal commodities, for dietary risk assessment should be propylene oxide, propylene chlorohydrins and propylene bromohydrin. Propylene chlorohydrin and propylene bromohydrin to be considered separately from propylene oxide.

The log K_{ow} of propylene oxide (log K_{ow} 2.9, pH 7) suggests that PPO is likely to be borderline fat soluble however, the predicted distribution of residues in the rat study suggested the residues are not fat soluble⁵.

Definition of the residue (for compliance with MRL): *propylene oxide*.

Definition of the residue (for estimation of dietary intake): propylene oxide, propylene chlorohydrin and propylene bromohydrin. Propylene chlorohydrin and propylene bromohydrin to be considered separately from propylene oxide.

The residue is not considered fat soluble.

Results of supervised trials on crops

Residue trials, including data from published scientific papers, were available for the use of PPO on: cereal grains, tree nuts, spices and herbs, dried garlic, dried onion, cocoa beans and dried fruit. No GAP was available to assess trials on cereal grains and these trials are not considered further.

Residues are reported below for PPO with corresponding values for PCH reported in brackets. During fumigation almost all the PPO is absorbed by the commodity being fumigated, at least for initial fumigation chamber PPO concentrations in the range 0.0125 to 0.1 g ai/L. The load ratio (volume occupied by material for fumigation to total chamber volume) may have an influence on the final residues. In the residue trials the load was generally 50% capacity. Factors important in determining residues of the related fumigant ethylene oxide are also likely to be relevant to propylene oxide. Important factors include: the total amount and concentration of propylene oxide, the composition of the treatment mixture, temperature, the type of commodity and its moisture content, pH, permeability, and particle size, and the method of packaging as well as aeration and storage conditions after treatment.

Tree nuts

Data were available from supervised trials on almonds, pecans and walnuts in the USA. The GAP of the USA is for fumigation of tree nuts at 2 g ai/L for up to six hours and a post fumigation interval (PFI) of 28 days if off-gassing at 25 °C otherwise the product can be released if residues have declined to below 300 mg/kg. Residues in tree nuts from trials in the USA matching GAP were: 273 (PCH 3.0) for shelled almonds, 37 (PCH 8.2) mg/kg for pecan pieces and 209 (PCH 7.4) mg/kg for walnut pieces.

To be able to estimate a maximum residue level according to the use pattern, sufficient trials are required to estimate a maximum level or to be confident that residues remain below 300 mg/kg at 28 days or more of off-gassing at 25 °C. The number of trials that comply with maximum GAP are too few to estimate a maximum residue level. The Meeting also noted that data from commercial fumigations where shelled almond nuts were fumigated at a lower rate suggest PPO residues in almonds decline rapidly during the first 15 days of off-gassing and only slowly thereafter. If

⁵ Csanády GA, Filser JG (2009) A Physiological Toxicokinetic Model for Inhaled Propylene Oxide in Rat and Human with Special Emphasis on the Nose. Toxicology Sciences 95: 37–62. (tissue:blood partitionratios; fat:blood 1.06, muscle:blood 0.84)

proportionality were to apply to fumigation, the commercial results also suggest residues of PPO may be higher than 300 mg/kg at PFIs of greater than 28 days. The Meeting considered the data inadequate to estimate maximum residue levels for PPO and PCH in tree nuts.

Dried fruit

Data were available from supervised trials on dried fruit in the USA.

The GAP of the USA is for fumigation of figs, prunes and raisins at 0.2 g ai/L for up to 48 hours and off-gassing at ≥ 25 °C for 48 hours prior to shipment. No trials complied with GAP.

Herbs and Spices

Data were available from supervised trials on a variety of dried herbs, spices as well as dried vegetables in the USA. The GAP of the USA is for fumigation of processed spices at 2 g ai/L for up to 12 hours and off-gassing at ≥ 25 °C for 48 hours prior to shipment with earlier release possible if residues of PPO are less than 300 mg/kg. Clarification was sought from the US EPA regarding the commodities covered by processed spices in the US. The term processed spices is applied to herbs and spices as well as dried onions and dried garlic. Residues in black pepper complying with GAP were 93 (PCH not reported) mg/kg while those in onion powder were 15.2 (PCH not reported) mg/kg. Residues of PPO in an additional trial on celery seed sampled at 4 rather than 2 days after fumigation were 69 (PCH not reported) mg/kg while day 0 residues in the same trial were 126 (PCH 474) mg/kg. Residues in dried basil sampled at day 4 rather than day 2 after fumigation were 164 (PCH not reported) mg/kg and on day zero 372 (PCH 6670) mg/kg.

To be able to estimate a maximum residue level according to the use pattern, sufficient trials are required or to be confident that residues remain below 300 mg/kg after off-gassing at 25 °C for 48 hours. The Meeting considered whether or not the available data provided confidence that residues at a post fumigation interval of 48 hours would be below 300 mg/kg. Account was taken of trials conducted in 1995 that were not adequate to resolve questions over their use for estimation of maximum residue levels but did show a large variation in residues of PPO in treated spices, dried vegetables and dried herbs and that residues at 48 hours after fumigation may exceed 300 mg/kg. The Meeting concluded the small number of supervised residue trials that comply with GAP were not sufficient to estimate a maximum residue level for herbs and spices, for dried garlic and dried onion or for dried chilli powder.

Cocoa Powder

The GAP of the USA is for fumigation of cocoa beans and cocoa powder at 2 g ai/L for up to 4 hours and off-gassing at ≥ 25 °C for 48 hours prior to shipment with earlier release if residues of PPO are less than 300 mg/kg. The residues of PPO for supervised trials conducted on cocoa powder that complied with GAP of the USA are: 71.8 (PCH 11.6) and 136 (PCH 12.5) mg/kg. The Meeting considered two trials as insufficient for the purposes of estimating maximum residue levels.

Animal feedstuffs

No animal feed items were considered by the current Meeting.

Fate of residues during processing

No data is available on the effect of processing on the nature of residues.

Residues in animal commodities

No animal feed commodities were considered at by the current Meeting. No data were supplied for the transfer of residues from feed to foods of animal origin. Propylene oxide is degraded to PPG in the stomach such that should livestock be exposed, no residues are anticipated to transfer from feed to tissues, milk or eggs.

FURTHER WORK OR INFORMATION

Desirable

Additional trials conducted according to GAP to support estimation of maximum residue levels.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with MRL): *propylene oxide*

Definition of the residue (for estimation of dietary intake): *propylene oxide, propylene chlorohydrin and propylene bromohydrin*. Propylene chlorohydrin and propylene bromohydrin to be considered separately from propylene oxide.

The residue is not considered fat soluble.

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