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Summary

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# Impact of different fumigants on the quality of perishables

Auswirkungen verschiedener Begasungsmittel auf die Qualität verderblicher Waren

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This paper examines the concerns surrounding the adverse effects of fumigants on the quality of treated perishables. Fumigation is a widely used strategy in the food industry, particularly for exporters, to control insect pests in food commodities under storage. As global trade in perishables continues to expand, the balance between effective fumigation for pest control and preserving product quality becomes increasingly crucial. The selection of an appropriate fumigant is important for a successful export, as the chemical components present in the commodity can interact with the fumigant, leading to changes in flavour, taste, odour, nutritional value, and processing capabilities. Understanding these effects is crucial for optimizing fumigation strategies while maintaining the quality and safety of food commodities. This review provides an overview of the various fumigants used worldwide for fruits and vegetables and evaluates their impact on the quality of treated perishable commodities.

Keywords: Perishables, fumigants, postharvest quality, food quality

#### Introduction

To enhance global horticulture product trade, effective quarantine practices are crucial for preventing the entry of exotic pests into foreign countries. Postharvest pest disinfestation treatments play a vital role in this regard, either before shipping, during transportation, or as emergency treatments upon arrival. Various physical methods, including heat, cold, irradiation, and modified atmosphere, have proven successful in pre-shipment quarantine (Kathpalia et al., 2022). However, fumigation is a practical, easy, and cost-effective treatment to prevent pest infestations in fruits and vegetables. Fumigant applications not only deter spoilage during storage but also eradicate pests in export commodities. Nevertheless, it's important to recognize that fumigation can impact the quality of commodities in different ways. Quality encompasses factors such as edibility, nutritional value, and commercial worth. Understanding the impact of fumigants on product quality is crucial when considering them for post-harvest treatment or quarantine purposes (Kathpalia et al., 2022).

The impact of fumigants on stored product quality varies depending on the specific chemicals used and the frequency of treatments. Key quality parameters include firmness, titratable acidity, pigment content (anthocyanins, chlorophyll, etc.), total soluble solids (TSS), and color parameters like luminosity (L\*), chroma (C), and hue angle (H), representing lightness, brightness, and color tone, respectively. The most common fumigants used for perishables are Methyl Bromide, Phosphine, Methyl Iodide, Nitric Oxide (NO), Carbonyl Sulphide, Ethyl Formate, Sulfuryl Fluoride, Carbon Monoxide, Sulphur Dioxide, HCN etc. The study of the effects of fumigants on perishable quality requires a multidisciplinary approach, involving fields such as entomology, chemistry, biochemistry, and toxicology. Before selecting the fumigant for a specific commodity, the changes in quality in terms of odor, flavor, nutrient quality, taste, etc. must be assessed.

In past years, numerous studies have investigated different fumigants used for post-harvest pest management of stored commodities. Armstrong (1992) provided a comprehensive review of quarantine treatment technologies and practices, including fumigation, heat, or refrigeration treatments to prevent the spread of tephritid fruit flies. Navarro (2006) elucidated the available fumigants for disinfecting stored food commodities and highlighted their global challenges. Plimmer (1977) summarized the major fumigants used for treating grains, vegetables, and fruits and their effect on the quality, while Rajendran (2001) listed various fumigants as alternatives to methyl bromide for stored food commodities. Additionally, Paine et al. (2018) investigated the perceptions of vegetable growers toward the excessive use of pesticides in the Bankura District of West Bengal. Armstrong et al. (2014) conducted a comprehensive literature review to identify viable alternatives to methyl bromide fumigation for New Zealand log exports. Mahajan et al. (2014) examined the current status of postharvest treatments, including the use of fumigants like sulfur dioxide (SO<sub>2</sub>) and nitric oxide (NO) for fresh produce, and emerging technologies aimed at maintaining quality and reducing losses. Zhang et al. (2023) summarized the recent applications of gas fumigation technology, including sulfur dioxide  $(SO_2)$ , ozone  $(O_3)$ , nitric oxide (NO), etc., in postharvest fruit quality management and related biochemical mechanisms.

However, while these studies provide valuable summaries and insights into available fumigants and quarantine practices, this paper aims to contribute to the existing literature by examining the impact of different fumigants on the quality of various fruits and vegetables under varying dosages and experimental conditions.

#### **Methyl bromide**

Methyl bromide has long served as a potent, broad-spectrum fumigant for various stored products including perishables. However, the global phase-out of methyl bromide, mandated by the "Montreal Protocol" due to its ozonedepleting properties, has spurred research on alternative fumigants (Arora et al., 2023).In a study on the Korean strawberry cultivar "Maehyang," methyl bromide (98.5%) at 40 g/m<sup>3</sup> for 3 hours showed no phytotoxic effects and controlled all stages of *Drosophila suzukii*. Combining methyl bromide fumigation at 20 g/m<sup>3</sup> for 3 hours with 1 day of cold treatment (0°C) achieved 100% mortality of all life stages of *D. suzukii* with no fruit damage. Successive application of methyl bromide and cold treatment required a lower dosage of the fumigant for comparable efficacy against *D. suzukii* (Kim et al., 2021).

Three post-harvest treatments combining methyl bromide fumigation (32 g/m<sup>3</sup> for 2.5, 3, or 4 hours) and cold storage periods of 3 or 4 days at 4.4°C and 8.3°C, respectively, were tested on six avocado varieties from Florida. Additionally, a seven-day transit period at 8.3°C was included to simulate the time from pack house to being sold by retailers. The treated avocados exhibited both internal (pulp) and external (skin) damage. The fruit deteriorated rapidly after treatment, showing signs of anthracnose, freezing injury, and abnormal ripening. The damage was attributed to the fumigation, although the six varieties tolerated the cold treatment (Carrillo et al. 2017). Methyl bromide treatment at 48 g/m<sup>3</sup> for 3 hours at 12°C of New Zealand kiwifruit in Japan accelerated fruit softening during storage at 20°C and stimulated respiration, while delaying softening when stored at 0°C. Treated kiwi fruits consistently had lower levels of soluble solids than untreated fruits (Beever & Yearsley, 1987).

For specific Hawaiian crops such as papaya, guava, bell pepper, bitter melon, cucumber, summer squash, string bean, and tomato entering the mainland U.S., methyl bromide fumigation is the approved treatment. The recommended dosage is  $32 \text{ g/m}^3$  for 30 hours at atmospheric pressure and a minimum temperature of  $26.7^{\circ}$ C. In the case of papaya coloration retardation due to methyl bromide, influenced by fruit maturity, dosage, and treatment time noted. A slight change in taste was observed due to retained methyl bromide. Fumigation with methyl bromide also delayed tomato ripening by 3 to 6 days, depending on maturity (Jones, 1940).

In Australia, new clones of Pitaya (Dragon fruit) infested with *Bactrocera* spp. fruit fly were treated with methyl bromide. Main-season fruit from three cultivars (,Golden', ,Venus', and ,Sweety') was exposed to 32 g/m<sup>3</sup> of methyl bromide for 2 hours at 21 °C, followed by ambient temperature storage for a week. Skin color, dry head, and brown brackets increased, while flesh firmness decreased. ,Golden' and ,Venus' fruit had comparable shelf lives after treatment, but ,Sweety' fruit had a longer shelf life (Abdia & Mizrahib, 2012).

Methyl bromide fumigation  $(32/40/48/64 \text{ g/m}^3 \text{ for } 2 \text{ h at } 24/17-22/12-17/12^{\circ}\text{C})$  ensured that U.S. sweet cherry shipments to Japan had no live codling moth (*Cyndia pomo*-

*nella*). The fumigation minimally impacted sweet cherry firmness, except for ,Garnet' cherries, which showed reduced firmness. ,Brooks' and ,Garnet' cherries experienced decrease in soluble solids and titratable acids post-fumigation, with dosage-dependent effects for ,Garnet' cherries. It negatively affected fruit and stem quality for all sweet cherry types, leading to increased visual pitting, especially in ,Brooks' and ,Tulare' cultivars (Hansen et al., 2000).

Fruit fumigation with methyl bromide resulted in darkening of the internal flesh color of "Delicious apples," especially unwaxed apples treated with 48 g/m<sup>3</sup> at 20°C for 2 h. However, ,Golden Delicious' apple internal flesh color was unaffected by 48 g/m<sup>3</sup> at 6°C for 2 h. ,Delicious', ,Golden Delicious', or ,Granny Smith' apples did not lose their firmness or internal color quality after 60 days of storage when fumigated with 32 g/m<sup>3</sup> at 20°C or 56 g/m<sup>3</sup> at 6°C for 2 h (Drake et al.,1988).

## Phosphine

Phosphine is widely employed for insect disinfestation in perishables due to its effectiveness, cost-efficiency, and low potential for leaving residues in treated commodities (Kathpalia et al., 2022). Phosphine stands out as the most extensively employed and recognized fumigant globally for various stored products. It is acknowledged as the preferred chemical for routine grain disinfestation in developing countries, especially in situations where other alternatives, like controlled atmosphere storage, prove to be costly or challenging to implement (Arora et al., 2021). The application of  $1.5 \text{ g/m}^3$  phosphine for 12 or 24 hours at 5°C or 12 hours at 12°C did not impact the quality of lemons, grapefruit, navel and Valencia oranges, and mandarins. Sensory evaluations revealed no reduction in flavor or visual quality (Obenland et al., 2021).

In kiwifruit storage, a 1000 ppm 24/72-hour phosphine treatment at 0-1°C had no detrimental effects on quality, while a higher rate of 3000 ppm resulted in a slight reduction in quality primarily due to low-temperature breakdown. A 36-hour 3000 ppm treatment at 1-3°C caused some increased softness, with no significant decrease in quality. Commercially treated kiwifruit using 2000 ppm for 96 hours at 1°C experienced quality issues and a pronounced metallic/chemical odour upon reaching the market (Jamieson et al., 2012).

In New Zealand, the pure phosphine gas formulation VAPORPH3OS<sup>®</sup>, used with the Horn Diluphos System (HDS) which is an automated system that safely blends pure phosphine with air below its ignition limit, enabling the injection of a phosphine-air mixture into enclosures for fumigation with concentrations up to 10,000 ppm (Tumambing, et al., 2014). It is approved for pest control in cut flowers, apples, and kiwifruit (Jamieson et al., 2012).

Horn et al. (2010) studied postharvest treatment of Chilean exported fruits (kiwifruit, apples, grapes, oranges, plums) using VAPORPH3OS<sup>®</sup> phosphine fumigant (99.3% pure), finding no phytotoxic effects. It was reported that fumigating various orange and lemon varieties with 1,500 ppm phosphine for 24 hours caused no damage (Castro & Gutiérrez, 2009). Klementz et al. (2005) treated table grapes with pure phosphine (VAPORPH3OS<sup>®</sup>) at 2g/m<sup>3</sup> for 48 hours at 0°C, it showed no significant differences in attributes (color, texture, sugar/acid ratio, and juice yield) between treated and untreated samples.

Post-harvest treatment on apples using phosphine

(VAPORPHOS<sup>®</sup>) at 1500 ppm at -0.5°C and +1°C, with dilution using HDS, showed no changes in color, maturity, and fruit condition compared to non-treated fruit. After 6 days, there were no organoleptic changes, and a mild metallic taste disappeared over time but before 6 days, the fruit tasted mildly metallic (Horn et al., 2010). A 48-hour oxygenated phosphine (1.5g/m<sup>3</sup>; 77% purity; QuickPHlo-R granules) fumigation of iceberg and romaine lettuce at 2°C under 60% Oxygen(O<sub>2</sub>) showed brown stains on fumigated Iceberg lettuce, more prevalent in longer treatments (>48 h), with a significant quality difference in the 72-hour treatment for both lettuce types (Liu, 2018).

"Fuji" Apples were fumigated with 0.5, 1.0, and 2.0 g/m<sup>3</sup> Phosphine (equivalent to 25, 50, and 100 g/m<sup>3</sup> of ECO2FUME<sup>TM</sup>) for 72 hours. The fumigated fruits were then transported and stored at  $25 \pm 1^{\circ}$ C for 14 days. In the second test, of 2.0 g/m<sup>3</sup> PH<sub>3</sub> was applied for various fumigation times at a low temperature ( $5 \pm 1^{\circ}$ C). To assess the effects of PH<sub>3</sub> fumigation followed by cold treatment, after 2 g/m<sup>3</sup> PH<sub>3</sub> fumigation for 72 hours, the fumigated fruits were stored at  $3 \pm 2^{\circ}$ C for either 2 or 4 weeks. The fumigated apples were stored for either 4 or 8 weeks prior to evaluating firmness, sugar content, and internal and external color change. Compared to untreated samples, 2.0 g/m<sup>3</sup> of PH<sub>3</sub> applied for 72 hours at either  $5 \pm 1^{\circ}$ C or  $25 \pm$ 1°C had no negative effects on the fruit in terms of firmness, sugar content, weight loss, color change, and flavor (Kim et al., 2022).

'Hass' avocados were treated with Phosphine (ECO-2FUME<sup>®</sup>, 2% Phosphine, 98% CO<sub>2</sub>) at concentrations of 500, 750, and 1,500 ppm for 24, 48, and 72 hours at  $5-6^{\circ}$ C. After treatment, the fruit were stored at  $5^{\circ}$ C for three weeks, then evaluated for external and internal quality after ripening at 20°C. PH<sub>3</sub> treatments did not affect external quality or skin color and only caused minor softening at 24 hours, with no significant changes at 48 or 72 hours (Pidakala et al., 2022).

#### Methyl iodide

To assess the quality tolerance of fresh fruits and vegetables to methyl iodide fumigation, 18 commodities were treated with methyl iodide at 15°C at 30 g/m<sup>3</sup> for 2 hours and at 48.5 g/m<sup>3</sup> for 3 hours. No chemical injury was observed on peach, cherry, strawberry, pumpkin, or tomato. However, clear symptoms of chemical injury were observed on apple, persimmon, grape, pear, banana, melon, asparagus, lettuce, celery, okra, and young soybean (Soma et al., 2007).

For controlling California red scale (*Aonidiella aurantii*) on lemons, tests with Methyl Iodide at dosages of 24, 28, and 32 g/m<sup>3</sup> for 2 hours with 2- and 24-h forced aeration at 21°C immediately after fumigation revealed rind damage increased with higher MI dosage, reducing fruit quality. An effective quarantine treatment involved 26 g/ m<sup>3</sup> for 2 hours followed by 24-hour forced aeration, significantly reducing fruit phytotoxicity (Aung et al., 2004).

Eight apple varieties were fumigated at 20 g/m<sup>3</sup> for 2 hours at 15°C, then stored at 15°C for 5 days or for 3 days at 15°C, 7 days at 5°C, and another 3 days at 15°C. Checks were performed for skin color, flesh decay, and taste. Postharvest, 'Mutsu', 'Shinano Sweet', 'Jonagold', and 'Kinsei' showed no injury. 'Sekaiichi' exhibited light brown skin spots, while 'Fuji' showed watercore breakdown in the flesh (Soma et al., 2023).

#### Nitric oxide

Nitric oxide (NO) fumigation extends postharvest life in fruits and vegetables by inhibiting ethylene biosynthesis. Green bananas treated with the NO donor Sodium Nitroprusside (SNP) at 0.05 mM, stored at 7°C for 15 days, and ripened at 22 °C for 6 days exhibited increased chilling tolerance, delayed ripening, and enhanced firmness, Titratable Acidity (TA), and Total Soluble Solids (TSS) content. Nitric oxide enhanced enzymatic and non-enzymatic the antioxidant system, delaying chlorophyll loss and sustaining fruit quality after cold storage (Wang et al., 2015).

Control of Western flower thrips (Frankliniella occidentalis), was achieved with 2% Nitric Oxide at 5°C for 3h and 1% Nitric Oxide at 2°C for 4h. The treatment when evaluated on different fresh fruits and vegetables, including lettuce, broccoli, pepper, squash, tomatoes, apples, lemons, oranges, peaches, and pears showed no negative impact on the quality of fresh produce when terminated by flushing with nitrogen to dilute Nitric Oxide before exposure to ambient air. However, injuries occurred when flushing with air, allowing Nitric Oxide to react with oxygen to form nitrogen dioxide (Liu, 2016). Liu (2016) fumigated strawberries with 1% Nitric Oxide at 2°C for 4 hours, improving their quality with firmer, brighter, and richer colour compared to the control. Fresh commodities with thick and sturdy skins were more resistant to fumigation than those with thin and delicate skins. In an experiment by Wills et al. (2000), strawberry fruit fumigated in an anaerobic nitrogen atmosphere with Nitric Oxide concentrations ranging from 1 to 4000  $\mu L \ L^{\mbox{--1}}$  for 2h and stored at 20°C or 5°C in air containing 0.1 µL L<sup>-1</sup> ethylene showed a commercially important increase in postharvest life (>50%) at both 20°C and 5°C with Nitric Oxide at 5-10 µL L<sup>-1</sup> after harvest. Zhu & Zhou (2007) dipped strawberries in 1, 5, and 10 µmol L<sup>-1</sup> Sodium Nitroprusside (SNP) aqueous solutions for 2 h at 25°C. The 5 µmol L<sup>-1</sup> concentration increased post-harvest life but decreased ethylene production by inhibiting ACC(1-Aminocyclopropane-1-carboxylate) synthase activity. However, the 10 µmol L<sup>-1</sup> concentration injured the fruit samples.

Loquat fruits (Japanese medlar) fumigated with nitric oxide gas concentrations of 5, 15, 25, 35, and 45  $\mu$ L L<sup>-1</sup> for 2h at 25°C, followed by storage at 5°C, delayed the reduction of TA and TSS content. Nitric Oxide fumigation prevented the increase in fruit firmness and decrease in juice percentage, inhibiting lignification by reducing Phenylalanine Ammonialyase (PAL) and Cinnamyl alcohol Dehydrogenase (CAD) (Mei-zi et al., 2014).

The effect of fumigation with 10, 20, and 30  $\mu$ L L<sup>-1</sup> nitric oxide (NO) was investigated to study its impact on the quality of Yali pears during cold storage. The results showed that nitric oxide not only reduced the peak value of ethylene production rate, maintained higher firmness, soluble sugar, soluble solid content, and starch, but also slowed the degradation of covalent soluble pectin and the accumulation of ionic and water-soluble pectin. Nitric Oxide fumigation also reduced polygalacturonase (PG) and  $\beta$ -Gal activities, delaying the peak of PG activity and preventing softening and ripening of Yali pears (Liu et al., 2011).

Apples treated with 5% Nitric Oxide for 24 h at 2°C under ULO conditions showed improved postharvest quality, with significantly firmer apples compared to the control, attributed to Nitric Oxide's antagonistic effects on ethylene production, delaying ripening and maintaining firmness (Liu et al., 2016). Japanese plums fumigated with

5, 10, and 20  $\mu$ L L<sup>-1</sup> Nitric Oxide gas for 2h at 20°C exhibited reduced respiration and ethylene generation rates during ripening at 21±1°C. The 10 and 20  $\mu$ L L<sup>-1</sup> concentrations delayed the decrease in TA without affecting soluble solids concentration (SSC). Fumigated fruit showed lower chilling injury symptoms (flesh browning and translucency) after 5, 6, and 7 weeks of storage (0 °C) and subsequent ripening for 5 d at 21 ±1 °C (Singh et al., 2009).

Lime fruits treated with 5, 10, and 20  $\mu$ g/L SNP for 1 minute at room temperature and stored at 4°C showed that 5  $\mu$ g/L SNP treatment resulted in the least weight loss and the greatest firmness at the end of storage. Submerging lime fruits in 5  $\mu$ g/L SNP solution yielded high TSS and Ascorbic acid, while 20  $\mu$ g/L SNP slowed Chlorophyllase activity compared to other treatments (Nolpradubphan & Lichanporn, 2016).

'Kensington Pride' mangoes were fumigated with 5, 10, 20, and 40  $\mu$ L L<sup>-1</sup> Nitric Oxide gas for 2 h. The treatments at 20 and 40  $\mu$ L L<sup>-1</sup> suppressed ethylene production, delaying fruit ripening by 2 days and slowing down fruit softening. The 40  $\mu$ L L<sup>-1</sup> dosage exhibited significantly higher pulp cohesion, springiness, and chewiness compared to other doses. Nitric Oxide fumigation also delayed fruit color development but resulted in lower levels of total SSC, total sugars, glucose, and fructose (Zaharah & Singh, 2013).

Pomegranate fruits were submerged in various SNP concentrations (30, 100, 300, and 1000  $\mu$ M) for 2 minutes and then placed at 5°C. The application of 1000  $\mu$ M Nitric Oxide significantly reduced electrolyte leakage and TSS while maintaining antioxidant activity and total anthocyanin levels in pomegranate fruit. However, there was no significant impact of Nitric Oxide treatment on TA, pH of pomegranate juice and chilling injury index (Ranjbari et al.,2016). Pomegranate fruit samples were dipped in NO at 300  $\mu$ M solution for 2 minutes, followed by cellophane wraps (wrapped or unwrapped) improved antioxidant activity, total anthocyanin content, and the a\*(redness) value of aril color and reduced the chilling injury and electrolyte leakage in fruit (Ranjbari et al., 2018).

Fumigating lettuce with, 1%, 2% and 0.5% Nitric Oxide for 3, 8, and 16 hours at 2°C under ultralow oxygen (ULO) conditions ( $\leq$  35ppm O2) proved safe for lettuce quality. This treatment effectively controlled both *Nasonovia ribisnigri* and *Frankliniella occidentalis* in large-scale fumigations of commercially packed lettuce. The study found no adverse impact on external or internal postharvest lettuce quality even after 14 days. Nitric Oxide fumigation emerges as a promising alternative to methyl bromide for postharvest pest management in harvested lettuce (Yang & Liu, 2018).

#### **Ethyl formate**

Ethyl formate (EF), a commonly used and generally regarded as safe food flavouring agent, is a naturally occurring volatile with insecticidal and antimicrobial properties (Zaitoon et al., 2019). It is registered in various countries, including Australia, Switzerland, Italy, the United Kingdom, the United States, Germany, Canada, and New Zealand. VAPORMATE<sup>TM</sup> (16.7 wt.% ethyl formate dissolved in liquid CO<sub>2</sub>) is registered and used in other regions (UNEP, 2010).

For post-harvest control of the grain chinch bug and successful export of South African deciduous fruit, liquid ethyl formate (97% purity) at a minimum concentration of 50g/m<sup>3</sup>

for 1h achieved 100% mortality. Various pome and stone fruit cultivars (Japanese Plum, Nectarines and Pear) treated with a dose range of 50–150g/m<sup>3</sup> ethyl formate for 1h at ambient temperature showed no phytotoxic damage (Smit et al., 2020).

Fumigation of various fruits and vegetables, including bananas, pineapples, strawberries, grapefruits, Satsuma mandarins, squashes, string beans, parsley, and broccoli, with Vapormate<sup>TM</sup> at 75.2 g/m<sup>3</sup> EF and 374.9 g/m<sup>3</sup> CO<sub>2</sub> for 3 h at 15°C, resulted in minimal differences from untreated controls in terms of weight, hardness, color, soluble solids, or flavor. While broccoli displayed no change, slight colour change on the surface of the banana, fumigated parsley underwent a significant colour change accompanied by severe wilting. The colour of fumigated Satsuma mandarins remained unchanged, but the mandarins were softer after 7 days. String beans and broccoli had no adverse impacts on their flavour, however, fumigated parsley had a strong smell (Misumi et al., 2013).

Ethyl formate (97% purity) at the dosage of 10, 20, 30, 40, and 80 g/m<sup>3</sup> 24h at 22–24°C applied to Pink Lady Apples showed no morphological differences compared to untreated apples, demonstrating no adverse effects on colour, texture, or firmness (Agarwal et al., 2015). Similarly, strawberry fruit treated with 0.8% liquid ethyl formate for 2h at 24°C showed no significant differences from control in terms of firmness, color, berry damage, or soluble solids. However, treatment with 1.6 and 2.4% Ethyl Formate resulted in slight to moderate and severe calyx damage, respectively (Simpson et al., 2004).

Table grapes exposed to ethyl formate at concentrations up to 5% for 1 or 2h at 24°C were well tolerated, with the exception of increased rachis browning (Simpson et al., 2007). Navel oranges and lemons exposed to Vapormate<sup>™</sup> at 38 g/m<sup>3</sup> for 1h at 20°C showed no discernible differences in firmness, exterior colour, deterioration, or peel damage compared to untreated control (Pupin et al., 2013). Citrus fruits (Orange, Grapefruit, and Lemon) were treated with 70 g/m<sup>3</sup> of liquid ethyl formate (Fumate, 99%) for 4 h at  $5 \pm 1^{\circ}$ C. There were no significant differences in soluble sugar content, the colour of peel and pulp as measured as L\*a\*b\* values using a colorimeter between the untreated and treated samples after 7-d (lemon and grapefruit) at 15°C and 14-d (orange) storages at 5°C, 5–15°C, and 15°C (Park et al., 2021). Mushroom treated with 35 g/m<sup>3</sup> Ethyl Formate (Fumate<sup>TM</sup>, > 99% purity) + 0.5 g/m<sup>3</sup> Phosphine (ECO2Fume) for 4h at  $> 5^{\circ}$ C showed no phytotoxic damage, weight loss, or colour change (Kwon et al., 2021).

Commercial-scale vacuum fumigation with 0.5% Ethyl Formate for 1h at 60 mm Hg did not cause injury to lettuce, while an increase to 0.9% caused slight injury, with no change in flavor or odour (Stewart & Mon, 1984). Onions fumigated with dosages of 27, 36, 45, and 54 g/m<sup>3</sup> followed by storage at 20°C in a dark room showed no changes in colour, firmness, or rots during storage (Epenhuijsen et al., 2007).

### **Carbonyl sulphide**

Carbonyl Sulphide was tested on Chinese Ya pears at dosages of 30, 60, 90, and 120 g/m<sup>3</sup> for 4h at 25 °C. Dosages exceeding 90 g/m<sup>3</sup> caused surface injury, rendering the fruit unacceptable in the market (Liu et al., 2012).

In experiments with ,Apple' banana, Avocado, Mango, and Papaya using Carbonyl Sulphide (96% purity) at various concentrations (1–6% for banana for 1.5–4 h; 1% and 2% for other fruits for 1–24 h) at 25°C, higher concentrations and

longer exposure times resulted in severe skin injury and delayed flesh softening. For bananas, 4% for 1.5 hours, 2% for 2.5 hours, and 1% for 4 hours did not cause significant damage, but faster softening occurred. In papaya, there was a slight skin injury at 2% after 6 h. Avocado when treated with 2% for less than 4 h showed very slight skin injury (brownred discoloration). Carbonyl Sulphide showed effectiveness for commodities with thick or dry skin, such as nuts, or for controlling surface insects (Chen & Paull, 1998). In nectarines, Carbonyl Sulphide at 20, 40, 60, and 80 g/m<sup>3</sup> for 2 hours at 21°C delayed fruit softening and intensified peel colour, it had no impact on fruit quality, causing brownish spotting lesions over glandular areas (Aung et al., 2001).

#### Carbon monoxide

Carbon monoxide (CO) fumigation at 10µmol/L for 2h reduced lesion diameter in jujube fruit, increased enzyme activities and elevated concentrations of phenolics, flavonoids, lignin, and  $H_2O_2$  (Zhang et al., 2020). Peaches fumigated with 99.99% pure CO at 0.5–10µmol/L for 2 hours prevented firmness and TA loss, decay, and delayed soluble solids content variation. High CO concentrations (20µmol/L) had adverse effects. Appropriate CO dosage improved the fruit quality, nutrition, and antioxidant activity during storage (Zhang et al., 2014).

#### **Sulfuryl fluoride**

Sulfuryl fluoride, a well-known structural fumigant is available as ProFume<sup>®</sup> gas fumigant (99.8% sulfuryl fluoride) for commodity treatments. It was first licenced in 2003 as a broad-spectrum, non-ozone depleting fumigant for rodent, insect pest management (Nead-Nylander & Thoms, 2018). Lemons treated with SF at 10, 20, 40, 80 g/m<sup>3</sup> for 2 h at 21°C. SF at  $\geq$ 40 g/m<sup>3</sup> resulted in 100% red scale mortality but caused commodity phytotoxicity (Aung et al., 2001).

#### **Sulphur dioxide**

Fumigation of blueberries with 28 nLs<sup>-1</sup>L<sup>-1</sup> Sulphur Dioxide (>99% purity), followed by Controlled Atmosphere storage (3%  $O_2$  + 6 or 12%  $CO_2$ ), reduced decay without compromising blueberry quality. High concentrations (24%) of CO<sub>2</sub> caused softening and/or off-flavor. However, Soluble Solids Content, TA, polyphenolic content, and total antioxidant activity remained consistent across all treatments (Cantin et al., 2012).

For controlling blueberry maggot (*Rhagoletis mendax*), Sulphur Dioxide demonstrated dose-dependent effects. Except at the highest concentration (2.2%), parameters like firmness, total soluble solid content, and titratable acidity were mostly unaffected (Abeli et al., 2021)."Red Globe" table grapes treated with low Sulphur Dioxide concentrations (0.20%) at  $1\pm0.5^{\circ}$ C extended shelf life by three months. Decay was inhibited, and key parameters like firmness, weight loss, total soluble solids content, and TA were maintained (Sortino et al., 2017).

Fumigation of Table grapes with 100 ppm SO<sub>2</sub> (1.0%) under ULO conditions with about 30 ppm O<sub>2</sub> and under normal atmosphere at 2°C for 3 and 4 days, effectively controlled mealybugs without adversely affecting fruit quality. (Liu, 2019).

However, Sulphur Dioxide fumigation had undesirable effects on Litchi fruit, causing changes in taste due to increased TA and lower pH. These issues highlight the need for alternative methods to maintain overall litchi fruit quality (Sivakumar & Korsten, 2008).

# Hydrogen cyanide

New Zealand kiwifruit treated with HCN at 1.8 g/m<sup>3</sup> for 30 min at 12°C showed no adverse effect on the fruit quality. It did not influence the fruit softening and respiration rate (Beever & Yearsley, 1987).

tify relevant studies on the impact of fumigants on the quality of perishables. The search included keywords such as "fumigation," "perishables," and "quality," covering articles published up to date. Studies were included if they evaluated the effects of fumigants on the quality attributes of perishables like fruits and vegetables. Data extraction focused on, fumigants used, types of perishables, quality parameters assessed, and experimental conditions.

Details of the list of fumigants tested in different countries and their effects on various fruits and vegetables is given in Table 1 & Table 2.

#### Conclusion

## **Material and methods**

A comprehensive literature search was conducted using PubMed, Scopus, and Web of Science databases to iden-

An ideal fumigant for quarantine or commercial treatment purposes must effectively target pests with minimal commodity phytotoxicity. Therefore, careful selection is crucial to ensure high efficacy against insects without

**TABLE 1:** Summary of the fumigants with the doses and their effect on the quality of the treated fruits.

Name of the Fumigant	Country	Commodity Treated	Dosage/Exposure time/Temperature	Effect on Quality	References
Methyl Bromide	Korea	Strawberry	40 g/m <sup>3</sup> for 3 h at 18 <sup>0</sup> C 20 g/m <sup>3</sup> for 3 h followed by 1 d cold (0 <sup>o</sup> C) treatment	No Phytotoxic effect.	(Kim et al., 2021)
	The USA	Avocado,	32 g/m <sup>3</sup> for 2.5/3/4 h and cold storage periods of 3/4 days at 4.4°C and 8.3°C respectively	Internal (pulp) and external (skin) damage	(Carrillo et al. 2017)
		Рарауа	32 g/m <sup>3</sup> for 30 h at 26.7°C	Retardation in colouring and change in taste in Papaya	(Jones, 1940)
	New Zealand	Kiwifruit	48 g/m <sup>3</sup> for 3 h at 12°C	Accelerated fruit softening at 20 °C and stimulated fruit respiration.	(Beever & Yearsley 1987)
	Australia	Pitaya	32 g/m <sup>3</sup> for 2 h at 21 °C.	Increase in skin colour, dry head, and brown brackets but decrease in firmness of the flesh for few cultivars.	(Abdia & Mizrahib, 2012)
	The USA	Sweet cherries and Apples	32/40/48/64 g/m <sup>3</sup> for 2 h at 24 /17-22/12-17/12°C 32/48/56 g/m <sup>3</sup> for 2 h at 6/12°C	No change in taste, flavour, pitting or bruising but significant increase in stem browning and reduced firmness. Darkening of the internal flesh colour of "Delicious apples"48g /m <sup>3</sup> for 2 h at 20°C. No change in firmness or internal colour quality in apples in other treatments.	(Hansen et al., 2000). (Drake et al.,1988)
Phosphine	The USA	Grapefruit, Navel &Valencia Oranges, Mandarins Avocado	1.5 g/m <sup>3</sup> for 12- 24 h at 5- 12°C 800-1000 g/m <sup>3</sup> for 48 h at 21 °C	No harm to surface and internal quality. Quality affected in some cultivars in avocado.	(Obenland et al., 2021)
	New Zealand	Kiwifruit	1000 ppm 24/72 h at 0-1°C	No detrimental effect	(Jamieson, et al., 2012)
	Zeulund		3000 ppm for 36 h at 1-3°C	Increased Softness	-
			2000 ppm for 96 h at 1°C	Metallic/chemical odour	-
		Avocado	500, 750, and 1,500 ppm (ECO2FUME)for 24/48/72 h at 5–6°C	No effect on external quality; minor softening at 24 h.	(Pidakala et al., 2022).
	Chile	Orange,	1500 ppm for 2 h	No damage	(Castro & Gutiérrez, 2009)
		Kiwifruit, Apples, Grapes, Oranges, Plums, Table grapes	2g/m <sup>3</sup> PH <sub>3</sub> (VAPORPH3OS®) for 24- 48 h at 0°C	No change in colour, texture, sugar/acid ratio and juice yield.	(Horn P. et al., 2010) (Klementz, et al., 2005)
		Apple	1500 ppm at -0.5°C and +1 °C	Change in fruit taste till 6 days which disappeared 6 days after fumigation.	(Horn et al., 2010)
	Korea	"Fuji" Apples	$0.5/1.0/2.0 \text{ g/m}^3$ Phosphine for 72 h 25 ± 1°C / 5 ± 1°C	No adverse effect.	(Kim et al., 2022).
Methyl Iodide	The USA	Peach, cherry, strawberry,apple, grape, pear, banana, melon	30/48.5 g/m <sup>3</sup> for 2/3 h at 15°C	No chemical injury on peach, cherry, strawberry. Chemical injury was observed on apple, grape, pear, banana, melon.	(Soma et al., 2007).
	Japan	Apple	20 g/m <sup>3</sup> for 2 hours at 15°C	Some varieties showed light brown skin spots and watercore breakdown in the flesh.	(Soma et al., 2023).

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# **TABLE 1:** ... continued

NT*4 .* .	China	D	0.05 mM SND:	Learning in thilling to be seen The sect The	(Wesser et al. 2015)
Nitric Oxide	China	Banana	0.05 mM SNP; stored at 7 °C for 15 days	Increase in chilling tolerance, TA and TSS content of the pulp, delay in ripening, but Chlorophyll content maintained.	(Wang et al.,2015)
	The USA	Apples, Oranges, Peaches, Pears, strawberry	1.0% NO for 4h at 2°C	No negative impact on any fruit but rich and bright colour was observed in strawberry fruit with more firmness.	(Liu, 2016)
	China	Strawberry	1.0/5.0/10.0 μmol/L SNP solution for 2 h at 25°C.	5.0 μmol/L increased the post-harvest life & decreased ethylene production 10 μmol/L – toxic to fruit.	(Zhu & Zhou, 2007)
	Australia	Strawberry	5-10 $\mu$ L L <sup>-1</sup> for 2 h at 5/20 °C (in air containing 0.1 ml/L ethylene)	Increased fruit's postharvest life >50%	(Wills et al., 2000)
		Japanese Plum	$5/10/20 \ \mu L \ L^{-1}$ for 2h at 20°C	Reduced respiration and ethylene generation rate in case of plums.	(Singh et al.,2009)
		Mango	$5/10/20/40 \ \mu L \ L^{-1}$ for 2 h	20 and 40 $\mu$ L $\dot{L}^{-1}$ suppressed ethylene production, delayed fruit ripening and delayed fruit color development	(Zaharah & Singh, 2013)
	China	Loquat	5-45 $\mu$ L L <sup>-1</sup> for 2h at 25°C	No change except inhibition of lignification in loquat fruits.	(Mei-zi et al.,2014)
		Yali pears	10/20/30 μL L <sup>-1</sup>	Decreased SSC and soluble sugar content in pears maintaining its firmness and starch level.	(Liu et al., 2011).
	The USA	Apples	5% Nitric Oxide for 24 h at 2°C under ULO conditions		(Liu et al., 2016)
	Iran	Pomegranate	30/100/300/1000 μM SNP for 2 min	Reduced TSS and electrolyte leakage in 1000 $\mu$ M treated fruit.	(Ranjbari et al.,2016)
Ethyl Formate	South Africa	Japanese Plum, Nectarines, Pears	50–150g/m <sup>3</sup> for 1h at ambient temperature	No Phytotoxic damage.	(Smit et al.,2020)
Formate	Japan	Bananas, Pineapples, Strawberry, Grapefruits, Satsuma, Mandarins.	Tog/m <sup>3</sup> EF + 375 g/m <sup>3</sup> CO <sub>2</sub> (Vapormate <sup>TM</sup> ) for 3 h at $15^{\circ}$ C	Slight colour change on the banana surface. Satsuma mandarins were softer after 7 days of fumigation.	(Misumi et al., 2013)
	Australia	Pink Lady Apples	10/20/30/40/80 g/m <sup>3</sup> for 24-h at 22–24°C	No adverse effects on colour, texture, or firmness.	(Agarwal et al.,2015)
	The USA	Strawberry	0.8-2.4% EF for 2h at 24°C	1.6% caused slight to moderate calyx damage but 2.4% caused severe damage.	(Simpson et al.,2004)
		Table grape	5.0 % for 01/02h at 24°C	Well tolerated with initial rachis browning in grapes.	(Simpson et al., 2007).
		Navel oranges	38 g/m <sup>3</sup> (Vapormate <sup>™</sup> ) for 1h at 20°C	No effect on the quality in oranges.	(Pupin et al., 2013)
	Korea	Orange, Grapefruit	70 g/m <sup>3</sup> for 4 h at $5 \pm 1^{\circ}$ C	No effect on quality.	(Park et al., 2021)
Carbonyl Sulphide	China	Ya pears	30/60/90/120 g/m <sup>3</sup> for 4h at 25 °C	Dosage >90 g/m <sup>3</sup> caused surface injury.	(Liu et al., 2012)
	The USA	'Apple' banana	1-4% for 1.5-4 h at 25°C	No skin/flesh damage but early softening. 6% for 12hcaused discoloration of the skin.	(Chen & Paull, 1998)
		Avocado, Papaya, Mango	1-2% for 1-24 h at 25°C	Slight skin injury and discolouration at higher doses.	(Anne et al. 2001)
	China	Nectarine	20/40/60/80 g/m <sup>3</sup> for 2 h at 21°C	Caused brownish spotting lesions over the glandular areas.	
Carbon monoxide	China	Jujube	10µmol/L for 2h	Increase in the activities of resistance-related enzymes, the content of phenolics, flavonoids, lignin, and $H_2O_2$ in Jejube.	
Sulnh	The USA	Peach	0.5–10µmol/L for 2 h 28 nLs <sup>-1</sup> L <sup>-1</sup> Sulphur Dioxide+	Peach showed adverse effects at 20µmol/L. Reduced decay without affecting the quality;	(Zhang et al., 2014) (Cantin, et al., 2012)
Sulphur Dioxide	The USA	Blueberry Table grapes	28 nLs L Sulphur Dioxide+ Controlled Atmosphere 100 ppm Sulphur Dioxide;	Reduced decay without affecting the quality; high $CO_2$ caused off flavour. No effect on quality.	(Cantin, et al., 2012) (Liu YB., 2019)
		I avic grapes	$\leq$ 30ppm O <sub>2</sub> ULO condition) for 3-4d at 2°C	no enect on quanty.	(Liu 1D., 2019)
	Italy	Table grapes	0.20% at 1±0.5°C	Shelf life extended and quality maintained.	( Sortino, et al., 2017).
Hydrogen Cyanide	New Zealand	Kiwifruit	1.8 g/m <sup>3</sup> for 30 min at 12°C	No adverse effect on the quality	(Beever & Yearsley, 1987

compromising treated commodity quality or leaving residues. Methyl bromide, widely used for Quarantine and Pre-shipment purposes, is phased out under Montreal Protocol due to its role in ozone layer depletion. Methyl Iodide does not contribute to ozone depletion and is toxic to insects but harms commodities at high doses. Carbon Monoxide damages fruit quality at high doses. Nitric oxide is environmentally friendly but is expensive and requires a complex fumigation process, involving flushing with Nitrogen gas to establish an ultralow oxygen (ULO) environment before injecting Nitric oxide; and in order to prevent the fumigated goods from being exposed to nitrogen dioxide (may damage perishables), the level of nitric oxide has to be reduced after fumigation. Carbonyl sulfide has a biocidal effect but demands lengthy treatment times and may cause surface injuries at higher concentrations. Moreover, it is recommended to be used for fresh commodities having either thick skin or only requiring the control of surface insects. Cylindered Ethyl Formate has short exposure times and is effective but has limited penetration and high sorption capacity, reducing overall efficacy. Sulfuryl fluoride is an excellent penetrating fumigant effective against various insect life stages but requires longer exposure periods. While it proves to be effective against the adult, pupal, and larval life stages of insects, it exhibits lower activity against the egg stage. Sulphur dioxide is used

for fresh blueberries, grapes, litchi, reducing decay but affects fruit quality and leaves undesirable residues. HCN, used on a limited scale, is not recommended for fruits and vegetables due to its potential to cause damage, including burning, wilting, or discoloration. Phosphine fumigation with some variations like Oxygenated Phosphine Fumigation, low-temperature treatment using pure Phosphine (free from Ammonia) from cylindered sources, has gained popularity over other fumigants. It is inexpensive, easy to apply, poses no environmental risks and leaves no stable residues in the treated commodity. However, determining the optimal dosage and exposure periods for maximum efficacy without adversely affecting produce quality is essential before widespread commercial application.

# **Conflicts of interest**

The author(s) declare that there are no conflicts of interest to disclose.

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**TABLE 2:** Summary of the fumigants with the doses and their effect on the quality of the treated vegetables.

Name of the Fumigant	Country	Commodity Treated	Dosage/Exposure time/Temperature	Effect on Quality	References
Methyl Bromide	Hawaii	Tomato	32 g/m <sup>3</sup> for 30 h at 26.7°C	Retardation in colouring and change in taste in Papaya and delayed ripening in tomato	(Jones, 1940)
Phosphine	The USA	Lemons,	1.5 g/m <sup>3</sup> for 12- 24 h at 5- 12°C	No harm to surface and internal quality.	(Obenland et al., 2021)
	The USA	Lettuce	1.5g/m <sup>3</sup> PH3 + 60% O <sub>2</sub> for 24/48/72 h at 2°C	Increase in brown stains on fumigated Iceberg exposed for ≥48 h	(Liu, 2018).
	Chile	Lemon	1500 ppm for 2 h	No damage	(Castro & Gutiérrez, 2009)
Methyl Iodide	The USA	Lemon	24/ 28/ 32g/m <sup>3</sup> for 2h and 2- and 24-h forced aeration at 21°C.	Rind damage increased with increasing the dosage, Reduced phytotoxicity when aerated.	(Aung et al., 2004)
		Pumpkin, tomato, persimmon, asparagus, lettuce, celery, okra, and young soybean	30/48.5 g/m <sup>3</sup> for 2/3 h at 15°C	No chemical injury on pumpkin, or tomato. Chemical injury was observed on persimmon, asparagus, lettuce, celery, okra, and young soybean	(Soma et al., 2007).
Nitric Oxide	The USA	Lettuce, Broccoli, Pepper, Squash, Tomatoes, Lemons,	1.0% NO for 4h at 2°C	No negative impact on any commodity	(Liu, 2016)
	Thailand	Lime	5, 10 and 20 µg /l SNP for 1 min at Room Temperature	5 ug/l- High total soluble solid (TSS), ascorbic acid and Increased firmness 20 ug/l- Lessened Chlorophyllase activity.	(Nolpradubphan & Lichanporn, 2016)
	The USA	Lettuce	2.0/ 1.0/ 0.5% for 3/8/16 h at 2°C under ULO conditions	No adverse impact	(Yang & Liu, 2018)
Ethyl Formate	Japan	String beans, Parsley, Broccoli	$75g/m^3 \text{ EF} + 375 g/m^3 \text{ CO}_2$ (Vapormate <sup>TM</sup> ) for 3 h at $15^{\circ}\text{C}$	No adverse effect on String beans and Broccoli. The colour of Parsley changed markedly after fumigation, accompanied by severe wilting and a strong smell.	(Misumi et al., 2013)
	The USA	Lettuce	0.5%-0.9% EF for 1 h	Slight injury to lettuce observed with 0.9% EF.	(Stewart & Mon, 1984)
	The USA	Lemon	38 g/m <sup>3</sup> (Vapormate <sup>™</sup> ) for 1h at 20°C	No effect on the quality in Lemons.	(Pupin et al., 2013)
	Korea	Lemon	$70 \text{ g/m}^3 \text{ for 4 h at 5 } \pm 1^{\circ}\text{C}$	No effect on quality.	(Park et al., 2021)
	South Korea	Mushroom	$\begin{array}{c} 35 \text{ g/m}^3 \text{ EF}(\text{Fumate}^{\text{TM}}) + 0.5 \\ \text{g/m}^3 \text{ Phosphine} (\text{ECO2Fume}) \end{array}$	No phytotoxic damage.	(Kwon, et al., 2021)
	New Zealand	Onion	27/36/45/54 g/m <sup>3</sup> EF.	No effect on quality.	(Epenhuijsen et al.,2007)
Sulfuryl fluoride	The USA	Lemon	10/20/40/80 g/m <sup>3</sup> for 2 h at 21°C	SF at $\geq 40$ g/m <sup>3</sup> caused Phytotoxicity.	(Aung et al., 2001)

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