Factors affecting release of ethanol vapour in active modified atmosphere packaging systems for horticultural products

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Abstract: The active modified atmosphere packaging (active MAP) system, which provides interactive postharvest control, using ethanol vapour controlled release, is one of the current interests in the development of active packaging for horticultural products. A number of published research work have discussed the relationship between the effectiveness of ethanol vapour and its concentration in the package headspace, including its effect on postharvest decay and physiological controls. This is of importance because a controlled release system should release and maintain ethanol vapour at effective concentrations during the desired storage period. A balance among the mass transfer processes of ethanol vapour in the package results in ethanol vapour accumulation in the package headspace. Key factors affecting these processes include ethanol loading, packaging material, packaged product and storage environment (temperature and relative humidity). This article reviews their influences and discusses future work required to better understand their influences on ethanol vapour release and accumulations in active MAP.

Keywords: modified atmosphere packaging, ethanol vapour controlled release, active packaging, horticultural products

INTRODUCTION

A current and increasing trend in the development of active packaging systems for horticultural and food products is the employment of controlled release of gas-phase antimicrobial agents, e.g. ethanol [1-3], essential oils [4, 5], 2-nonanone [6] and hexanal [7-9]. Although these volatiles have generally-recognised-as-safe (GRAS) status, only ethanol vapour has been utilised industrially. Examples of ethanol vapour controlled release systems are Antimold Mild® and Negamold® sachets commercialised by the Freund Industrial Co. (Japan). Ethanol vapour controlled release systems are reportedly incorporated into modified atmosphere packaging (MAP) systems for horticultural products, such as grape [1, 10, 11], tomato [12, 13], fresh-cut apple [14], sweet cherry
[2] and fresh-cut papaya [15]. MAP containing active systems such as controlled release and O₂ scavenging can be designated ‘active MAP’ [16]. The application of an ethanol vapour controlled release system imparts antimicrobial activity and delay changes of postharvest quality by inhibiting ethylene synthesis and action [12], minimising discoloration and senescence [10, 13], thereby enhancing aroma [1, 2, 15, 17].

The release and accumulation of ethanol vapour at effective levels in the package headspace is the main purpose for which the ethanol controlled release system is designed, and these can technically be affected by a number of factors, including ethanol loading in the controlled release system, packaging film and storage environment. The aim of this review is to provide understanding of key factors and their influences on ethanol vapour release and accumulation in the active MAP.

**CONFIGURATIONS OF ETHANOL VAPOUR CONTROLLED RELEASE SYSTEMS**

Ethanol vapour controlled release systems that have been reported are developed in two key configurations: sachet and paper pad (Table 1). Sachet refers to a small packet containing a carrier which is pre-equilibrated with ethanol. The carriers contained in the sachet are usually porous adsorbents with a high specific surface area, such as those based on silica, which ensures that sufficient amounts of agents are available to be delivered within the desired time frame. Paper-based materials such as filter paper and newspaper are also utilised as carriers (Table 1). The ethanol-containing carriers developed for Antimold Mild® are reportedly called ethanol powder, due to their small and fine structures. This sachet material governs the release rate of ethanol vapour from the sachet to the package headspace. The material of Antimold Mild® is a paper/ethyl vinyl acetate copolymer for regulating ethanol vapour release [11, 18]. The paper-pad release system utilises paper as an ethanol carrier, which is technically soaked with ethanol liquid (Table 1). Unlike sachets, the paper pads are exposed to the environment with no physical barrier to limit ethanol vapour release. The ethanol left on the pad, compared to the sachet, should decrease at a faster rate.

Both controlled release configurations are extensively used in active MAP due to their convenience, as they can be added to the packages along with the product and conveniently removed from the packages and discarded at the end of the storage period. However, the use of sachets may pose a low probability that the packaging material properties will be compromised, especially the physical/mechanical properties. There are concerns among consumers about sachets inside packages in regard to the misuse of sachets such as fear of ingestion, spillage of sachet content into food causing adulteration of the food product, and ‘foreign component’ in the package [19].

**FACTORS AFFECTING ETHANOL-VAPOUR RELEASE AND ACCUMULATION IN PACKAGE HEADSPACE**

The release of ethanol vapour and its subsequent accumulation in the package headspace at an effective concentration level is desirable for controlling postharvest decay and physiological changes. The phenomenon can be affected by factors involving mass transfer processes in the sachet, the packaged horticultural product and the type of package. Figure 1 diagrammatically illustrates a concept model of the key mass transfer processes for release and accumulation of ethanol vapour in active MAP. The diagram is adapted from the model package reported by Bai et
Table 1. Examples of ethanol-vapour controlled release systems and their reported applications for horticultural products

<table>
<thead>
<tr>
<th>Ethanol-vapour controlled release system</th>
<th>Horticultural product</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration</strong></td>
<td><strong>Carrier</strong></td>
<td><strong>Trade name</strong></td>
</tr>
<tr>
<td><strong>Sachet</strong></td>
<td>Ethanol powder</td>
<td>Antimold-Mild(^\text{®})</td>
</tr>
<tr>
<td><strong>Sachet</strong></td>
<td>Ethanol powder</td>
<td>Antimold-Mild(^\text{®})</td>
</tr>
<tr>
<td><strong>Pad</strong></td>
<td>Paper</td>
<td>-</td>
</tr>
<tr>
<td><strong>Sachet</strong></td>
<td>Filter paper</td>
<td>-</td>
</tr>
<tr>
<td><strong>-</strong></td>
<td>Paper wick(^2)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Sachet</strong></td>
<td>Ethanol powder</td>
<td>Antimold-Mild(^\text{®})</td>
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<td>Antimold-Mild(^\text{®})</td>
</tr>
<tr>
<td><strong>Pad</strong></td>
<td>Filter paper</td>
<td>-</td>
</tr>
<tr>
<td><strong>Pad</strong></td>
<td>Newspaper sheet</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Commercialised by Freund Industrial Co. Ltd, Japan
2 Immersed in ethanol

Figure 1. Conceptualisation of key mass transfer processes of release of ethanol vapour in a model clamshell package with enclosed sachet and sweet cherries simplified as one-dimensional transport (adapted from Bai et al. [2]). The Antimold Mild\(^\text{®}\) was attached to the top lid of the clamshell and sweet cherries were packaged into the clamshell.
al. [2]: an incorporation of Antimold Mild® sachet into a clamshell package containing intact sweet cherry. Ethanol vapour is carried on a porous adsorbent and is continuously desorbed from it into the sachet atmosphere (simplified as one-dimensional mass transport) before crossing the sachet film into the package headspace \( (r_{sc}^{EtOH}) \). Ethanol vapour can both pass through the packaging material from the internal headspace to the storage environment \( (r_{pk}^{EtOH}) \) and interact with the product \( (r_{p}^{EtOH}) \). The dynamic balance of the rates of these processes determines the net rate of accumulation of ethanol vapour in the package headspace \( (r_{pkhs}^{EtOH}) \). The key factors involved in the mass transfer processes (Figure 1) are reviewed and presented as follows.

Load of Ethanol on Carrier

Different loads of ethanol on carriers has different release and accumulation effects in the package headspace. Suzuki et al. [18] reported a linear relationship between the mass of ethanol on the carrier (3-12 g ethanol powder) and the peak concentration and accumulation pattern of ethanol vapour delivered from Antimold Mild® into the headspace of perforated PE bags containing broccoli branchlets at 20°C for 5 days. The peak release and quasi steady-state of ethanol concentration was reported for the 12g-sachet (Figure 2-I). Similarly, Smith et al. [25] reported higher peaks of ethanol vapour released from the Ethicap® type E1 (4 g ethanol powder), compared to type E1 (1 g ethanol powder) in the headspace of a high ethanol vapour barrier pouch at 25°C for 16 days (Figure 2-II; data on the 7th day of E1+a w 0.85 was not reported). In the study of Thompson seedless grape, Lurie et al. [1] reported that paper impregnated with ethanol with a loading ratio of 8 ml\( \text{EtOH}/\text{kg}_\text{fruit} \) could apparently generate a higher initial peak and quasi steady-state concentration than a loading ratio of 4 ml\( \text{EtOH}/\text{kg}_\text{fruit} \) (Figure 2-III). In a study on Red Globe table grape, Candir et al. [11] reported highest ethanol concentration measured in the headspace of a non-perforated bag (ZOEpac) containing Antimold Mild® with 8 g ethanol powder, in comparison to Antimold Mild® with 6 g and 3 g ethanol powder (Figure 2-IV). Recently Utto et al. [15] reported that the kinetic release rate and level of ethanol vapour concentration at 10°C are dependent on the ethanol load (0.5, 1.0 and 1.5g) on the filter paper.

The information noted above indicates that the higher the ethanol loading is on the carrier, the higher the release peak becomes and, most likely also, the higher the quasi steady-state concentration in package headspace results. This is explained by the differences in the system capacity of the sachet, which is in proportion to the mass of ethanol adsorbed. The extent of change in the ethanol vapour concentration is a function of the reciprocal of the system capacity [26], and therefore the slowest change in the vapour concentration in the sachet headspace, which is in equilibrium with ethanol adsorbed on the carrier, would occur in the system with the highest loading of ethanol. This causes the slowest change of concentration gradient across the sachet after the onset of release, thus resulting in the highest initial peak concentration and a slow depletion of ethanol vapour from the package headspace leads to a high quasi steady-state concentration. It can be noted that in Figure 2 the quasi steady-state concentrations of ethanol vapour developed in the long term storage, i.e. 2-4 months, become comparable regardless of ethanol loading.
Ethanol vapor concentration (µL L⁻¹)  

**Figure 2.** Changes in ethanol vapor concentration in the atmosphere of bags containing: (I) broccoli branchlets and varying mass of ethanol powder (3, 6 and 12 g) [17]; (II) *a*ₜₐₜ-adjusted potato dextrose agar plates and Ethicap® (type E₁: 1g ethanol powder and type E₄: 4g ethanol powder) [25]; (III) Thomson seedless grape and paper pad containing ethanol with 4 and 8 mlEtOH/kg fruit loading ratios [1]; (IV) Red Globe table grape and Antimold Mild® with varying mass of ethanol powder (3, 6 and 8 g) [11]

**Packaging Material**

Ethanol vapour released into the package headspace will permeate through the packaging material in accordance with the ethanol vapour concentration gradient between package headspace and environment. A high-barrier plastic film can accordingly minimise ethanol vapour permeation through the film, and a high vapour concentration can be achieved (Figure 2-II). Ethanol vapour released shows varied concentrations, and often there are high initial concentration peaks (Figure 2). Under such concentrations, the permeability to ethanol vapour of non-perforated films are likely to be concentration-dependent [27-29]. Miyauchi et al. [30] reported the concentration-dependent characteristic of ethanol-vapour permeability in polypropylene (PP), polyvinylidene chloride (PVC) and a multi-layer film (comprised of nitrocellulose, polyethylene terephthalate (PET) and aluminium layers). During the initial release, high vapour concentration can increase film permeability to ethanol vapour. High permeant concentrations tend to interact with film, thus leading to changes in its polymeric structure, which may increase free volume and facilitate permeation of the permeance through the film [27-29]. The rate of ethanol vapour permeation from the headspace to the immediate environment should then be increased, with consequent reduction in the concentration level of ethanol vapour accumulated in the package headspace. This may affect the efficiency of microbial or physiological control by ethanol vapour.

In addition to the non-perforated films, there are reports on using perforated films for packaging [11, 18]. Perforations physically facilitate and stimulate the permeation of gas and vapour
through the film, thus effectively increasing film permeability. Ethanol vapour concentration in the perforated package headspace subsequently becomes lower than that in the non-perforated one. Candir et al. [11] reported lower concentrations (36-44 µL.L⁻¹) in the headspace of perforated LDPE, compared to those of non-perforated bags (84-198 µL.L⁻¹). The lower ethanol vapour concentration accumulated in the perforated bags, however, may provide a benefit to the design of active MAP in relation to consumers’ aroma perception of fermented ethanol vapour. High ethanol vapour concentrations may be considered ‘foreign’ and it may cause consumers to reject the product. Bai et al. [2] reported that the odour of ethanol vapour at 9-26 µL.L⁻¹ could be perceived after opening the clamshells containing cherry with an ethanol-vapour controlled release sachet. Although lowering ethanol vapour concentration in the package headspace may be achieved by the perforated film, it is important that the lowered concentration in the headspace has to be within the level at which ethanol vapour is effective for antimicrobial and/or physiological control.

**Storage Environment (Temperature and Humidity)**

An increase in storage temperature reportedly stimulates the release or desorption of adsorbed particles from the carrier, resulting in a high concentration accumulated in the package headspace. Bai et al. [2] reported that concentration peaks of ethanol vapour at 1°, 10° and 20° C were approximately 12, 23 and 27 µL.L⁻¹ respectively, which is consistent with the findings of Candir et al. [11]. A high concentration of ethanol vapour in the package headspace at high storage temperature can provide better control of microbial proliferation, especially during postharvest handling when temperature fluctuations (likely temperature increase) are not uncommon [31-33].

Packaging film permeability is also well known for its temperature dependence [34]. Miyauchi et al. [30], for example, reported that there is a clear relationship between storage temperature (29-40°C) and film permeability to ethanol vapour. Increasing temperature may be considered an additional effect on the high concentration accumulated at the release peak. High temperature can increase film permeability to ethanol vapour, thus stimulating the rate of ethanol vapour permeation from the headspace to the immediate environment and lowering the ethanol vapour concentration in the package headspace.

In addition to storage temperature, relative humidity reportedly can affect the ethanol vapour release rate. Smith et al. [35] reported that a high relative humidity can affect the equilibrium condition by stimulating the release of ethanol from Antimold Mild®. The effect of relative humidity on the release process is assumed to be due to the competition for active adsorption sites through the displacement of adsorbed molecules by water vapour [25]. Given a reasonable porosity and water vapour permeability of controlled-release sachet material, high relative humidity developed in modified atmosphere packages containing fresh-cut horticultural products can be utilised for stimulating ethanol vapour release from the sachet, thus potentially providing better control of microbial proliferation under the high humidity developed in the package headspace.

However, if the sachet material is a hydrophobic plastic film, for example LDPE film, which is a good water vapour barrier, the high humidity accumulated in the package headspace will have a minimal effect on the release of ethanol vapour from the sachet [15]. High humidity accumulated in the package headspace of modified-atmosphere packages can, however, stimulate fungal decay and overcome the antifungal activity of the released ethanol vapour. In a study of Red Globe grape [11], Antimold® 80 (with 8g ethanol powder) placed in a non-perforated LDPE box liner reportedly did no give an effective antifungal activity compared to that in a perforated (6-mm holes) LDPE liner.
due to the high relative humidity accumulated in the non-perforated liner. Similar findings on the effect of high humidity on antifungal activity of ethanol vapour were reported in other grape cultivars including ‘Superior’ [36], ‘Reliance’ and ‘Saturn’ [37]. It was remarked that the humidity level accumulated in the package headspace has to be controlled in order to maintain the antifungal activity of ethanol vapour released from the sachet.

Packaged Product

The interaction between ethanol vapour and the packaged product can evidently lower the concentration of ethanol vapour in the package headspace [2]. Similar evidence was reported for other volatile compounds including hexanal, nonanal and hexyl acetate [38, 39]. Whilst there are no reported studies for ethanol vapour, interactions between hexanal vapour and fresh-cut apple [40] and intact tomato [41] are reportedly concentration- and temperature-dependent. Given similar characteristics, interactions between ethanol vapour and products hypothetically should increase under a high storage temperature and ethanol vapour concentration, and these should rapidly decrease the concentration in the headspace. This assumption is supported by the study of Bai et al. [2], who reported that there was a sharp decrease in headspace concentration of ethanol vapour from ca. 27 to 13 μL·L⁻¹ at 20°C within 48 hr while the reduction time frame of ethanol vapour concentration at 10°C was 240 hr.

Interactions between ethanol vapour and the products may stimulate metabolism such as the respiration rates of tomato [42] and potato [43], and the biological conversion of ethanol vapour to acetaldehyde, which causes browning in grape [1]. Stimulation of respiration rate may cause high O₂ consumption and CO₂ production, which may affect the modified atmosphere developed in the package headspace as a result of the balance between respiration rate and rate of permeation of O₂ and CO₂ through the packaging film [44, 45]. However, ethanol vapour released in active MAP reportedly has no effect on the modified-atmosphere condition in packages containing sweet cherry [2], grape [1] and fresh-cut papaya [15] (Table 2). Similarly, Serrano et al. [46] reported that antifungal volatiles (eugenol, thymol and menthol) released from saturated gauze did not alter the levels of O₂ and CO₂ in plastic bags containing sweet cherry.

Such minimal effects of the vapour of ethanol or other volatiles released from the essential oils may be attributed to the developed modified-atmosphere conditions, which slow down metabolic processes in horticultural products [47] and consequently limit their interactions with the volatiles. In the study on intact tomato [7], continuous hexanal vapour treatment (40-70 μL·L⁻¹) reportedly increased respiration rate up to 50% during a 7-day storage at 20°C. In their subsequent work [41], however, the effect of hexanal vapour treatment on the respiration rate became minimal under a modified-atmosphere condition (10% O₂ and 5% CO₂ (v/v)). However, a significant effect of the antifungal eucalyptol volatile on the modified atmosphere was evident, as seen in the study of Serrano et al. [46]. This volatile was reported to increase the oxidative metabolism of cherry, thus causing a large change in the modified-atmosphere condition (ca. 7% O₂ and 3.5% CO₂) compared to that developed under eugenol, thymol and menthol volatiles (11-12% O₂ and 2-3% CO₂). Such information suggests that the design of active MAP has to take into account the change in modified-atmosphere condition by the volatile released.
Table 2. Modified atmosphere conditions developed in package headspace in which vapour of ethanol and other volatiles accumulated

<table>
<thead>
<tr>
<th>Product</th>
<th>Storage temperature (ºC)</th>
<th>Package</th>
<th>Controlled release system</th>
<th>Modified atmosphere condition a</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape</td>
<td>0</td>
<td>(1) Xtend® plastic liner</td>
<td>Active vapour</td>
<td>(1) 8% CO₂ and 12% O₂</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) Polyethylene</td>
<td></td>
<td>(2) 2% CO₂ and 15-18% O₂</td>
<td></td>
</tr>
<tr>
<td>Sweet cherry</td>
<td>10</td>
<td>Polystyrene clamshell</td>
<td>Steady-state concentration (µL·L⁻¹)</td>
<td>14-18</td>
<td>[2]</td>
</tr>
<tr>
<td>Papaya</td>
<td>10</td>
<td>LDPE bag</td>
<td>Ethanol</td>
<td>0.01-0.06</td>
<td>[15]</td>
</tr>
<tr>
<td>Grape</td>
<td>0</td>
<td>Nonperforated LDPE (ZOEpac)</td>
<td>Ethanol</td>
<td>84-198</td>
<td>[11]</td>
</tr>
<tr>
<td>Sweet cherry</td>
<td>1</td>
<td>Oriented polypropylene (OPP)</td>
<td>Eugenol, Thymol, Menthol</td>
<td>Not reported</td>
<td>[46]</td>
</tr>
</tbody>
</table>

a Reported not significantly different between bags with and without controlled release sachet
b On the last storage day of 7-week storage trial, an upsurge of ethanol vapour from ca. 640 to ca. 900 µL·L⁻¹ was reported.

CONCLUSIONS

This review provides information on key factors, viz. ethanol loading, packaging material, packaged product and storage environment (temperature and relative humidity), affecting the release of ethanol vapour in active MAP. The conceptual model representing the key mass transfer processes of the packaging system assists understanding of how these factors influence the processes. The design of active MAP to achieve effective ethanol concentration is complicated by interactions among packaging components, which are mainly the controlled release system, the packaging film and the product, thus resulting in changes of ethanol vapour concentration. This concentration importantly should be at a level at which it does not cause negative sensory responses from consumers whilst still providing effective control on the packaged product.

More studies should be conducted in order to understand the effects of simultaneous changes made to multiple factors influencing ethanol vapour release since most work reported has only manipulated a single factor. The understanding would assist packaging technologists and engineers to properly design components of active MAP to suit the packaging requirements of products and the shelf life desired. Mathematical models appropriately developed and validated could be utilised to optimise packaging designs through information obtained from the simulations. At the present time there are no available mathematical models reported for the design of ethanol-vapour release in active MAP.

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