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IMPACT OF COLD CHAIN AND PRODUCT VARIABILITY ON QUALITY ATTRIBUTES OF MODIFIED ATMOSPHERE PACKED MUSHROOMS (*Agaricus bisporus*) THROUGHOUT DISTRIBUTION

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ABSTRACT

An integrated mathematical modelling approach was followed to model the heat and mass transfer processes taking place in modified atmosphere packaged mushrooms and its effect on the quality throughout distribution supply chain was simulated. The model equations were solved to obtain the concentration of gases (O_2, CO_2) and H_2O in the headspace of the package. The change in the quality (colour and weight loss) during the distribution supply chain were monitored. The simulation results are in agreement with the experimental data.

The model can study the effect of biological parameters and cold chain parameters on the quality of mushroom. Weight loss is influenced by the cold chain parameters whereas product lightness (L) value is influence by the product uncertainty parameters. Sensitivity analysis was performed to quantify the effect of individual parameters on the quality of mushroom.

Using this integrated model the changes in the quality of MAP mushroom during the supply chain can be predicted and the losses can be assessed at each step.

1. Introduction

Mushrooms are highly perishable produce because of the absence of a cuticle to protect them from mechanical damage, microbial attack and quality loss. Susceptibility of mushroom to microbial attack and enzymatic browning is due to its high respiration rates and high moisture content (Aguirre et al., 2008; Oliveira et al., 2012). The shelf life of mushroom at ambient temperature is 1-3 days. Managing the supply chain is challenging as its quality deteriorates significantly over time at rates dependent on temperature and relative humidity (Blackburn and Scudder, 2009). Modified atmosphere packaging (MAP) is a postharvest technique used to increase the shelf-life of fresh produce, it also responds to the emerging consumer demand for convenience and quality. MAP alters the atmosphere inside package, it relies on transfer of gases through packaging film which leads to atmosphere rich in CO_2 and deficient in O_2 (Oliveira et al., 2012).

Modified atmosphere packaging of mushrooms accompanied with low temperature storage is effective in extending the shelf life and retards quality changes (Cliffe-Byrnes and O'Beirne, 2007). Concentrations of CO_2>12 % can result in quality degradation due to browning and concentration of O_2<1% leads to anaerobic respiration resulting in off flavour production and susceptibility to microbial contamination (Kim et al., 2006; Tano et al., 2007; Villaescusa and Gil, 2003). The optimum conditions reported for shelf life extension of mushroom is 2.5 – 5% CO_2 and 5-10% O_2 stored at 2^0 C (Ares et al., 2007). The use of microperforated films has been widely reported to prevent the accumulation of CO_2 and depletion of O_2 within the package and prevention of condensation. Temperature has a major effect on the rate of metabolic processes taking place in mushroom, its dependence on respiration rate and permeability should be taken into account for designing an ideal MA package (Charles et al., 2005). Mushrooms have high sensitivity towards relative humidity because they lack a barrier against diffusion. Saturated in-package conditions can lead to condensation on the produce surface and walls which can favour microbial growth and browning (Oliveira et al., 2012; Roy et al., 1995). Thus, water permeable films are recommended to be used for packaging mushrooms to reduce waste due to spoilage during the distribution chain.

Quality characteristics of mushroom are visual appearance, colour, freshness, microbial growth, weight loss (Aguirre et al., 2008). Quality evolution is predominately affected by the storage conditions including temperature and relative humidity. The main processes leading to waste generation are browning and textural changes. Texture changes can be caused from the weight loss due to moisture loss (Lukasse and Polderdijk, 2003). Weight loss observed in open mushroom punnets stored at 5^0 C is averaged at 4 % per day (Mahajan et al., 2008).

All fresh produce possesses a large inherent variability. Management of its biological variability is challenging for industries. The variability is controlled as much as possible by sorting and grading the product after harvest (Hertog et al., 2004). During storage the individual produce shows the same generic behaviour, however the variation can be observed due to the time zero from which the product is being observed. Variation during storage would be negligible if all the produce was harvested at same biological age (Hertog, 2002). This would make deciding upon the acceptability of a batch easy as all produce will show same quality characteristics. However, mushrooms are not harvested with such homogeneity therefore some items will degrade sooner than the others.

Distribution supply chain refers to a sequence of activities performed in order to deliver the highest quality fresh produce from the farm to the consumer (Tijskens et al., 2001). During the distribution supply chain the environmental conditions and the product itself has the potential to influence its quality. Management of uniform quality throughout the distribution supply chain is strenuous as mushrooms are affected by the biological variance and ignoring these biological variances can lead to misleading conclusions. The major challenge is to develop a predictive model that takes into account the uncertainty of the predicted results (Hertog et al., 2007). Biophysical properties of the skin, mass transfer coefficients, initial value of colour (L, a and b value), respiration rate parameters have been identified as variables affecting the quality of mushroom in cold chain supply (Mahajan et al., 2008; Sastry and Buffington, 1983). Understanding the mechanism and dynamics of variation will eventually result in better prediction of the changes in the quality and losses observed during distribution supply chain.

Thus, the main objective of this study was to develop a model to study the effect of MAP design parameters on product quality and to assist in identifying where the waste is generated during distribution. To assess the effect of the cold chain factors (temperature and relative humidity) and the biological factors on the quality of mushroom in modified atmosphere packaging during distribution. Sensitivity analysis was performed to quantify the effect of biological parameters on the quality of mushroom.

2. Mathematical model

Mathematical modelling captures the useful properties of a food system. In this section, we outline the governing ordinary differential equations and other equations that describe the metabolic activity (respiration, transpiration), the transport of gas taking place through permeable films and perforations, dimensions of a package and changes in quality (L, a and b value, browning index and weight loss) during storage.

2.1. Model hypothesis

1. The material and energy balances arising from MAP packaging of mushrooms may be described using a compartmental model and lumped transfer coefficients.
2. O_2 consumption and CO_2 production due to respiration may be described by a Michalies-Menten type model with uncompetitive inhibition of CO_2.

3. Package walls are impermeable and perforated film is permeable to O_2, CO_2, N_2 and H_2O.
4. Packaged produce and the gases inside package are in thermal equilibrium.
5. The surface of the mushroom is assumed to be saturated (water activity≈1).
6. Condensation of water may occur in the product or the package when the free volume air relative humidity reaches 100% using a saturated surface model.
7. The quality of the mushroom colour maybe described using the temperature and relative humidity model from (Aguirre et al., 2008) together with the relative extension approach from (Hertog, 2002).

2.2. Mass Balance

2.2.1 Gas exchange in package

The quantities of gases change dynamically in the headspace of the package during storage. The mass balance of gas components in the package is represented by ordinary differential equations (Song et al., 2002). This model includes the convective gas transfer through the packaging film including perforations and concentration of gas inside and outside of the package and the rate of O_2 consumption and CO_2 production. (Oliveira et al., 2012) used this model for MAP packaging of fresh sliced mushroom.

$$V_f \frac{d[O_2]_i}{dt} = 100 \times \left[\frac{A_{p1} P_{O_2} P_{atm}}{L_f}\left[\frac{[O_2]_o}{100} - \frac{[O_2]_i}{100}\right] - W_s r_{O_2}\right] \quad (1)$$

$$V_f \frac{d[CO_2]_i}{dt} = 100 \times \left[\frac{A_{p1} P_{CO_2} P_{atm}}{L_f}\left[\frac{[CO_2]_o}{100} - \frac{[CO_2]_i}{100}\right] + W_s r_{CO_2}\right] \quad (2)$$

As the package initially contains air, initial conditions (t=0) becomes $[O_2]_i$= =21.0%, $[CO_2]_i$=0.03% and V_f (ml) free volume is the difference between the pack volume and bulk volume of mushroom.

2.2.2. Film water permeation

The driving force of water vapour permeation from the headspace of the package to the surrounding is the water vapour pressure difference (Becker and Fricke, 1996a) . The rate of water permeated from the headspace of package through the film can be calculated using Eq. (3).

$$\frac{dm_{pr}}{dt} = \left[\frac{P_{H_2O}A_p(p_i - p_o)}{L_f}\right]\left[\frac{0.018P_{atm}}{RT_s}\right] \quad (3)$$

2.2.3. Humidity Ratio

The humidity ratio can be calculated from the mass balance to water vapour in the package headspace, considering the transpiration rate t_r of the product, the water permeated through the film m_{pr} and the total mass of headspace air (Jalali et al., 2017; Song et al., 2002))

$$\frac{dHR}{dt} = \frac{t_r - m_{pr}}{W_a} \quad (4)$$

Using Eq. (4), the relative humidity in the headspace can then be estimated as the ratio of the humidity ratio inside the package at any time (eq. 4) to the humidity ratio of saturated water vapour (HR_{sat}) at the same temperature Eq. (5) (Becker et al., 1996).

$$HR_{sat} = \frac{0.62198p_s}{(P_{atm} - p_s)} \quad (5)$$

2.3. Heat Balance

The temperature of surface of produce and gases surrounding it in headspace is assumed to be uniform. The major source of heat generation inside the MAP is respiration heat by fresh produce and heat is transferred in headspace due to convection, transpiration and condensation. Thus, overall energy balance in the package is written as follow.

$$Q_rW_s + Q_{con} + h_pA_p(T_o - T_i) = Q_{tr} + W_sC_s\frac{dT_s}{dt} + W_aC_a\frac{dT_s}{dt} \quad (6)$$

This equation can be simplified to obtain rate of temperature change inside package (T_s).

$$\frac{dT_s}{dt} = \frac{Q_rW_s + Q_{con} + h_pA_p(T_o - T_i) - Q_{tr}}{W_sC_s + W_aC_a} \quad (7)$$

2.3.1. Metabolic process

Respiration is a metabolic process which provides energy for the biochemical processes occurring. The respiration rate also acts as an indicator of the shelf life of fresh produce, with mushrooms having a relatively high respiration rate and thus a short shelf life. MAP reduces the respiration rate of produce, increasing shelf life and maintaining quality (Cliffe-Byrnes and O'Beirne, 2007). During this process energy is generated, part of which is released as heat (Eq. 8) (Becker and Fricke, 1996b; Fonseca et al., 2002).

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2816\text{kJ} \qquad (8)$$

2.3.1.1. Respiration Rate

In this work O_2 consumption rates (r_{O_2}) and CO_2 production rates (r_{CO_2}) are calculated from the Michaelis-Menten enzyme kinetics model with uncompetitive type CO_2 inhibition. The rate of CO_2 production and O_2 consumption is a function of temperature, thus temperature dependence is studied using Arrhenius equation (Iqbal et al., 2009; Lu et al., 2013).

$$r_{O_2} = \frac{V_{mO_2}[O_2]}{K_{mO_2}+(1+[CO_2]/K_{iO_2})[O_2]} e^{\left(\frac{-E_{O_2}}{R}\cdot\left(\frac{1}{T_s}-\frac{1}{T_{ref}}\right)\right)} \qquad (9)$$

$$r_{CO_2} = \frac{V_{mCO_2}[O_2]}{K_{mCO_2}+(1+[CO_2]/K_{iCO_2})[O_2]} e^{\left(\frac{-E_{CO_2}}{R}\cdot\left(\frac{1}{T_s}-\frac{1}{T_{ref}}\right)\right)} \qquad (10)$$

The parameters used in calculation of r_{O_2}, r_{CO_2} are given in Table 1. The rate of O_2 consumption and rate of CO_2 production are not equal thus average of these values is used to estimate the heat of respiration (Q_r). This energy is used for the basic functions of cell but also a large component is used in evaporative water vapour from the surface of the commodity. The heat of respiration can be calculated from following equation (Rennie and Tavoularis, 2009).

$$Q_r = \frac{2816}{6} \times \frac{r_{O_2}+r_{CO_2}}{2} \times \alpha \times W_s \qquad (11)$$

The chemical reaction indicates for every 6 moles of CO_2 produced, 2816 kJ heat is generated. α is conversion factor of respiration energy dissipated as heat (ranging between 0.8 to 1.0) (Song et al., 2002). In this work it is assumed that all the respiration heat produced is dissipated as heat thus $\alpha = 1.0$.

Permeability

Film permeability is governed by the number and size of the film's perforations. The theoretical model is derived from the assumption that low molecular weight mass exchange at steady state conditions is given by two parallel mass fluxes-one related to permeation through the matrix Eq. (12)

$$P_i = P_{i\,ref} + \frac{\pi R_h^2 \times D_{i,air}}{(L_f + R_h)} \times N_h \qquad (12)$$

Where, P_i is the permeability of the film to (i=O_2, CO_2 and H_2O), $P_{i\,ref}$ is the reference value of permeability of film to (i=O_2, CO_2 and H_2O) at reference temperature, R_h is the radius of the perforation (m), $D_{i,air}$ is diffusivity of (i=O_2, CO_2 and H_2O) in air ($m^2 sec^{-1}$), N_h is number of perforations.

2.3.2. Transpiration

Transpiration is an important physiological process which has an adverse effect on mushroom quality, influencing weight loss, appearance and texture. The factor which contributes to transpiration is the vapour pressure deficit VPD (Pa) Eq. (13), between the produce surface and the surrounding atmosphere (Xanthopoulos et al., 2012). VPD is the function of the difference in the amount of moisture in the air and the amount of moisture air can hold when it is saturated.

$$VPD = (a_w - RH)p_s \qquad (13)$$

In the above equation water activity ($a_w \sim 1$) of the fresh produce is assumed and RH is relative humidity of the atmosphere surrounding the product.

Transpiration sets in when water vapour pressure at the surface of the commodity exceeds the water vapour pressure of the headspace in the package. Water vapour flux ($\mathrm{m_w}$) is expressed as the product of the transpiration coefficient and water vapour pressure deficit as Eq. (14) (Becker et al., 1996; Xanthopoulos et al., 2012).

$$\mathrm{m_w = VPD \times K_t} \tag{14}$$

The transpiration rate (t_r) is product of the water vapour flux (m_w) and the surface area of the commodity(A_c) Eq. (20)

$$t_r = m_w A_c \tag{15}$$

$$K_t = \frac{1}{\left(\frac{1}{K_s} + \frac{1}{K_a}\right)} \tag{16}$$

Here, K_t is the transpiration coefficient (kg m^{-2}s^{-1}Pa^{-1}) which is constant for the specific commodity, K_s (kg m^{-2}s^{-1}Pa^{-1}) is the skin mass transfer coefficient obtained from literature (Becker et al., 1996), K_a (kg m^{-2}s^{-1}Pa^{-1}) is the air film mass transfer coefficient calculated from equation 23 using the Sherwood-Reynolds-Schmidt correlations (Becker et al., 1996).

The saturated water vapour pressure (p_s) is calculated from the following equation at the surrounding air temperature(T_s);

$$p_s = 0.041081186 T_s^3 - 32.43188 T_s^2 + 8567.5269 T_s - 757070.1 \tag{17}$$

For transpiration to take place energy is required to evaporate water from surface of the produce which in turn cools the product. It is assumed that all the energy required for transpiration is provided by the heat of respiration.

$$Q_{tr} = \lambda\, t_r \tag{18}$$

2.3.3. Condensation

Due to near saturation conditions in the package and non-uniform temperature, condensation can occur on surface of the produce, the package film and walls. It is assumed that the water condensed on the surface of the produce does not penetrate its skin. The rate of condensation on the surface of commodity M_{con} (kg sec^{-1}) was calculated using Eq. (19) (Jalali et al., 2017; Rennie and Tavoularis, 2009)

$$M_{con} = \begin{cases} K_a(p_i - p_c)\delta A_c\,, & if\,(p_i > p_c) \\ 0 & otherwise \end{cases} \tag{19}$$

Where, A_c can be calculated as following assuming an equivalent spherical shape (Mahajan et al., 2008).

$$A_c = d \times W_s{}^b \tag{20}$$

The rate of condensation on the walls and film of package M_{wcon} can be calculated similarly using the air film mass transfer coefficient (K_a). Where A_w is inside surface area of the package.

$$M_{wcon} = \begin{cases} K_a(p_i - \mathrm{p}_s)\delta A_w\,, & if\,(p_i > p_s) \\ 0 & otherwise \end{cases} \tag{21}$$

And rate of heat release due to condensation raises the temperature of air surrounding fresh produce and determined using;

$$Q_{con} = \lambda \times (M_{con} + M_{wcon}) \tag{22}$$

Where, K_a is air film mass transfer coefficient. The Sherwood-Reynolds-Schimidt correlation is used to estimate the value of K_a.

$$K_a = 2 \times D_{H_2O} \times \frac{M_{H_2O}}{d_c \times R \times T_s} \tag{23}$$

The latent heat of vaporisation λ (J kg^{-1}) is estimated using;

$$\lambda = (3151.37 + (1.805\,T_s) - (4.186\,T_s)) \times 1000 \tag{24}$$

The convective heat transfer coefficient (h_p) is estimated by using the natural convection of air (Song et al., 2002).

$$h_p = \frac{0.59 A_{p1}\left(\frac{T_i - T_O}{D_1}\right)^{0.25}}{A_p} + \frac{1.32 A_{p2}\left(\frac{T_i - T_O}{D_2}\right)^{0.25}}{A_p} + \frac{1.42 A_{p3}\left(\frac{T_i - T_O}{D_3}\right)^{0.25}}{A_p} \tag{25}$$

2.4. Quality

The quality of fresh produce is determined by the overall evaluation of various characteristics of the individual product. Perception of quality is subjective and depends largely on qualitative factors. To be able to predict the development of these quality characteristics as a function of storage time is highly desirable in order to support optimisation. The quality of fresh produce is generally determined by the overall characteristics (appearance, texture, flavour and nutritive value) of fresh produce (ElMasry et al., 2007).

2.4.1. Colour in mushrooms

Consumers consider the appearance of fresh produce into consideration as a primary criterion, with colour a key factor. Changes in colour occur due to various biochemical processes taking place in the produce over time. Browning of mushroom reduces the quality and is a limiting factor for its shelf life (Aguirre et al., 2008).

One of the major roles in modelling the quality in supply chain is the dynamics of quality degradation. Quality degradation of produce is dependent on storage time (t), temperature, and various constants such as the activation energy and gas constant.

$$\frac{dq}{dt} = kq^{n} \tag{26}$$

Where, q is the quality parameter and k is rate of degradation depending on environmental conditions like temperature, n is the power factor is the order of reaction (n will have value 0 or 1, zero order or first order reactions) leading to linear or exponential quality decay (Aiello et al., 2012; Rong et al., 2011).

A linear mixed effect model is used to model the effect of temperature and relative humidity on the apparent first order rate constant of the L value of mushroom caps. The kinetic dependence with time is studied using eq. 26.

$$k_L = (8.283477 \times 10^{-5} T_s) + (-7.181884 \times 10^{-4} RH) + (-1.258058 \times \tag{27}$$

$$10^{-5}\mathrm{T_s}\,\mathrm{RH}) + \left(-2.278137 \times 10^{-5}\mathrm{T_s}^{2}\right) + (7.816388 \times 10^{-5}\mathrm{RH}^{2})$$

The mixed effect model estimated batch-to-batch and inside-batch variability components that are integrated in Table 2.

2.4.2. Weight loss

Transpiration of water vapour from the surface of produce is one of the major contributor to weight loss observed in fresh produce. Carbon loss through gas exchange also contributes to weight loss in fresh produce as they continue respiring throughout storage. Here, we have assumed the weight loss (w) to be equal to the amount of water permeated from the film (m_{pr})and carbon loss during respiration.

$$\frac{dw}{dt} = m_{pr} + r_{CO_2} W_s M_C \qquad (28)$$

Stochastic Simulation and Sensitivity Analysis

On the basis of the mathematical models developed in section 2, stochastic simulations were developed to analyse the effects of biological and cold chain variability on the quality characteristics of mushroom. The values of parameters used in our model to solve ordinary differential equations are shown in Table 1. All simulations were carried using the R 3.4.3 (R Development Core Team, 2008). The ODE model was integrated using the deSolve library (Soetaert et al., 2010) using the *lsoda* solver. All figures were produced using the ggplot2 library (Wickham, 2009). Sensitivity analysis using a main and first order interactive effects model excluding time were analysed using a Lowry plot (McNally et al., 2011).

2.5. Cold chain variability

The history of export of four international cold chains between Ireland and the United Kingdom, comprising temperature and relative humidity data including the production farm, the packaging house, international haulage, retail storage and arrival to the retail shop. The data was collected using temperature and relative humidity dataloggers (XSense®, BT9 Intelligent Supply Chain Solutions, UK) with a logging frequency of 10 minutes and comprised 4 export chains including at least 3 retail storage and arrival to 3 shops with 3 replicates extending from 3 to 6 days depending on the different conditions.

In order to simulate the sales conditions cold chain data for the retail display scenario were added to this study. The study from Garvan (2007) was conducted throughout the summer of 2007 including 85 premises spread through the 26 counties in the Republic of Ireland, including open and close refrigerated cabinets with a supermarket, a deli shop and a butcher outlet in each county.

2.6. Validation Experiment

Mushroom trays (250g of white, closed cup, 2.5 - 4 cm in diameter) packaged in microperforated polypropylene film (8 perforations per package) were supplied by Monaghan Mushrooms Ltd. Samples were stored in an environmental chamber under abuse condition (1/2h packaging at 8 ºC followed by transportation at 4 ºC up to 1 day, followed by retail storage including 4h at 20 ºC, followed by 1 day at 8 ºC, and finalised by retail shop 4h at 20 ºC 21h at 8 ºC) and ideal condition in a refrigerator (at 3 ºC) for a 7 days period

Mushroom tissues colour was measured using a Hunter colorimeter in the L*, a*, b* scale (Colour Quest XE Hunter Lab, VA, USA). 30 measurements were taken per punnet. Three punnets were analysed per treatment and day. Moisture content was determined following the AOAC methods (32.1.02 and 32.1.03) (Lee, 1995). Photographic evidence of initial day and 7 days storage can be inspected in the highlights section.

3. Results

3.1. Validation of the mathematical model

The model parameter estimates in Table 1 and 2 are used to compare the experimental and predicted results. The integrated mathematical model mentioned in section 2 is used to simulate the quality conditions during the distribution supply chain. The experimental data used for validation mimicked the results of an average and an abuse cold chain of recorded cold chain information. The mushrooms were stored in commercial packaging at different temperatures simulating abuse conditions at (4^0, 8^0, and 20^0 C) and at ideal temperature of 3^0 C for 9 days. Mushroom colour was measured using the L value and the moisture content was measured using the AOAC methods. The mushrooms with L value>86 are classified as good quality and 80-85 as fair quality (González-Fandos et al., 2000). Those with L values less than 70 would be generally rejected by consumers (Kim et al., 2006). These L-value threshold values are used as indicators to calculate the losses during the supply chain.

The mathematical model (section 2) was able to predict the changes in L values during storage. The grey ribbon in the Fig. 1 represents the uncertainty margins of 5% and 95% percentiles pertaining to the variable. It can be observed from figure that the experimental data with the variation falls in the prediction interval obtained from the simulation. Throughout the simulated cold chain, L value remains between the acceptable limits within 82-95, even though the product was stored at different temperatures (4^0, 8^0, 20^0 C) Fig.1(a). When simulated at the ideal temperature of 3^0 C the change in L value was between 95 and 89 Fig.1(c). The bias and accuracy factors of the L value prediction were and respectively. The change in moisture content of mushroom for the different temperatures (4^0, 8^0, 20^0 C) is shown in Fig.1(b). with the experimental data falling in the predicted interval. Similar results were obtained at the ideal temperature (3^0 C) (Fig. 1(d)). This shows the weight of mushroom is preserved in the packaging.

3.2. Cold chain variability assessment

The integrated mathematical model mentioned in section 2 is used to simulate the quality conditions during the distribution supply chain. The governing ordinary differential equations are used to simulate the changes in gas concentration Eq. (1 and 2), temperature Eq. (7) and relative humidity Eq. (4, 5) in the headspace of an ideally designed modified atmosphere pack and changes in quality are simulated against the supply chain conditions Fig. 2.

Changes in the respiration rate of mushroom causes changes in the concentration of O_2 and CO_2 in the headspace of package. CO_2 rises in the headspace of package, O_2 concentration decreases from 21% to 12% (Fig. 2(a)) and CO_2 concentration increases from 0.03% to <10% when simulated against the export cold chain profile (Fig. 2(b)). These results are in agreement with (Cliffe-Byrnes and O’Beirne, 2007) where O_2 concentration changes from 20 to 2 % when mushrooms are stored at 5 different temperatures (4, 8, 10, 13 and 16^0 C) representing abuse temperature. The relative humidity inside the package saturates within a few hours of storage. Similar results were obtained by (Rux et al., 2015) in mushrooms, (Song et al., 2002) for blueberry and (Fishman et al., 1996) for mango stored in MAP. Fig. (2(c)) shows the weight loss observed during the supply chain. The typical kinetic change of quality (L value) during the distribution supply chain is shown in Fig. 2(d). The variability decreases towards the end of storage. (Jiang et al., 2011) reported that the L value decreased to 81.8 and 78.1 after 8 and 12 days storage respectively at 4^0 C in MAP, after which the product passes the threshold for acceptable quality for *Agaricus bisporus*.

Sources of variability

The main sources of biological variability associated with mushroom are the Michaelis-Menten respiration parameters and the activation energy parameters associated with these constants (Table 1). For quality the biological variability is described by the initial colour values (L, a, b value), initial weight of the produce and the skin mass transfer coefficient (Table 1).

3.3. Product variability assessment

The mathematical model is used to simulate and predict the effect of input product parameter uncertainty on the quality of mushroom. The time domain for simulation is 7 days at (3^0, 7^0, 15^0C). The optimal storage guide for mushroom storage to maximise its quality and shelf life is 1-3^0 C and as high RH as possible (Aguirre et al., 2008). The effect of product parameter variation on the CO_2 concentration at different temperatures of storage is presented in Fig. 3(a). The rate at which the propagation of the biological variation increases depends directly on temperature. The variation observed at 15^0 C is larger than observed in other cases. In the case of O_2 the variation increases with increase in temperature, with similar results observed for CO_2. Anaerobic conditions are not observed at 3^{0}C and 7^{0}C as evident from Fig. 3(b). However, anaerobic conditions are observed at 15^0 C after 5 days.

Weight loss in mushrooms is mainly caused by transpiration of water from surface of mushroom and CO_2 loss through respiration Eq. (28). More weight loss is observed when mushrooms are stored at higher temperatures, which is due to the increase in transpiration and respiration rates Fig. 4(a). The effect of product variation on weight loss in mushroom was not found. The maximum weight loss of 2.47% was noted after 16 days MAP storage at 4^0 C (Jiang et al., 2011). (Roy et al., 1995) reported weight loss of 3% (120 g) and 4.5% (50 g) in packages after 9 days storage when stored at 12 ^{0}C. The maximum variation due to product parameters is observed for the L value as evident from Fig. 4(b). With increase in temperature the variation increases and the acceptability threshold is thus crossed at 15^0 C in both cases of weight loss and L value. Based on these results a lower temperature during the supply chain distribution is preferred as the variation associated with it is less, to retain the quality of mushroom and to reduce the losses during distribution chain.

3.4. Comparing the importance of variability components on quality kinetics of Mushroom under distribution conditions

Relative frequency is plotted against the time of storage for the different characteristics of the produce to compare the effect of variability due different sources (Table 2). The concentrations of gases (O_2 and CO_2) in the headspace of the package are influenced by the product variability parameters as evident from Fig. 5(a) and (b). For the L-value the main influence observed is from the product parameters Fig. 5(c). This result is in agreement with the general practice in postharvest technology of mushroom which includes grading and sorting of produce before packing to reduce variability on how product is affected by storage/distribution supply chain. To obtain the final product with the highest L value, the initial value of the product should be higher. In the case of weight loss in mushrooms it is influenced by the cold chain parameters Fig. 5(d). The temperature and relative humidity during storage will influence the rate of moisture loss during the distribution supply chain. Relatively small weight loss of 3-6 % in fruits and vegetables is sufficient to cause wilting, shrivelling and dryness. In addition to this it causes significant economic losses (Nunes et al., 2009).

3.5. Sensitivity analysis

Uncertainty analysis usually accompanies sensitivity analysis which quantifies the contribution of each input parameter to the output parameters (Guillard et al., 2012). Sensitivity analysis is performed to study the results of variation and how it can be apportioned qualitatively or quantitatively to different sources of variation in the model input (Kader and Saltveit, 2003).

The result of sensitivity analysis for L value shows that initial L value as 100% contributor towards the variability Fig. 5(a). The results of sensitivity analysis of CO_2 indicate the Michaelis-Menten respiration rate constants to have the highest impact on the concentration of CO_2 in the headspace (90%). The results of sensitivity analysis of weight loss are presented in the Fig. 5(b). The activation energy rate constant which are dependent on temperature have highest impact on the weight loss of mushroom in supply chain. Along with respiration rate parameters it contributes to 90% variability. Some variability was observed due to the interactions between the parameters like skin mass transfer coefficient and initial weight of mushroom. To tackle the loss of weight of mushroom, the cold chain variations (Temperature and Relative humidity) should be managed throughout supply chain.

4. Conclusions

A mathematical model is developed to predict the change observed in the quality of mushroom packed in modified atmosphere packaging during storage. The model integrates mass transfer processes including; transpiration, transport of gases (O_2, CO_2) and heat transfer process like respiration heat, convection through produce into surroundings, transpiration heat and heat of condensation. The comparison of effect of biological parameters (respiration rate parameters and initial quality) and the cold chain parameters (relative humidity and temperature) on the quality of mushroom was observed. To quantify the effect on the biological parameters, sensitivity analysis was performed which explained the effect of the main parameters and the interactions between the parameters. In terms of colour change of the mushroom, the initial L value variation showed to be the most contributory factor to variations during distribution and cold chain, while the weight loss depended on a larger number of process and product parameters.

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Nomenclature

a_w	Water activity of fresh produce	P_i	Film permeability to species (i=O_2, CO_2 , H_2O) (ml m $m^{-2}h^{-1}atm^{-1}$)
A_c	Surface area of produce (m^2)	$P_{i\,ref}$	Reference Permeability of film to i= O_2 , CO_2 , H_2O (ml m $m^{-2}h^{-1}atm^{-1}$)
A_{p1}	Surface area of packaging film (m^2) $(D_1 x D_2)$	Q_{con}	Condensation heat released due to commodity (Js^{-1})
A_{p2}	Surface area of bottom of package (m^2) $(D_1 x D_2)$	Q_r	Heat of respiration (J h^{-1})
A_{p3}	Surface area of walls of package (m^2)	Q_{tr}	Evaporative heat transfer due to transpiration (Js^{-1})
A_p	Total surface area of package (m^2)	r_{CO_2}	CO_2 production rate (mol $kg^{-1}s^{-1}$)
C_a	Humid heat of air (J $kg^{-1}K^{-1}$)	r_{O_2}	O_2 consumption rate (mol $kg^{-1}s^{-1}$)
C_s	Specific heat of produce (J $kg^{-1}K^{-1}$)	R	Gas constant (8.314 J $mol^{-1}K^{-1}$)
E_{O_2,CO_2}	Activation energy of rate constant ($Jmol^{-1}$)	R_h	Radius of perforation (m)
d_c	Equivalent diameter of produce (cm)	RH	Relative humidity inside package (%)
d_H	Diameter of perforation (mm)	RH_O	Relative humidity outside package (%)
$D_1 x D_2 x D_3$	Dimensions of package (cm)	t	Time (s)
$D_{i,air}$	Diffusion coefficient of i=O_2, CO_2, H_2O in air (m^2s^{-1})	t_r	Transpiration rate (kg $m^{-2}h^{-1}$)
h_p	Convective heat transfer coefficient on produce surface ($Jh^{-1}m^{-2}K^{-1}$)	T_i	Temperature inside package (K)
K_a	Air film mass transfer coefficient (kg $m^{-2}s^{-1}Pa^{-1}$)	T_o	Temperature outside package (K)
K_s	Skin mass transfer coefficient (kg $m^{-2}s^{-1}Pa^{-1}$)	T_s	Temperature of surface produce (K)
K_t	Transpiration coefficient (kg $m^{-2}s^{-1}Pa^{-1}$)	T_{ref}	Produce reference temperature (K)
K_{mO_2}	Michealis constant in O_2 consumption (% O_2)	V_b	Bulk volume of produce (m^3)
K_{mCO_2}	Michealis constant in CO_2 evolution (% O_2)	V_f	Free volume in headspace (ml) (
K_{iO_2}	Inhibition constant in O_2 consumption (% CO_2)	V_{mO_2}	Maximum O_2 consumption rate (ml $kg^{-1}h^{-1}$)
K_{iCO_2}	Inhibition constant in CO_2 evolution (% CO_2)	V_{mCO_2}	Maximum CO_2 evolution rate (ml $kg^{-1}h^{-1}$)
L_f	Thickness of packaging film (m)	VPD	Vapour pressure deficit (Pa)
m_{pr}	Rate of water permeation through film (kg sec^{-1})	W_a	Weight of dry air (kg)
M_{con}	Condensation rate on commodity (kgs^{-1})	W_s	Weight of produce (kg)

M_{wcon}	Condensation rate on package walls (kgs^{-1})	$[CO_2]_i$	CO_2 concentration inside package (%)
M_i	Molar mass of species (i= O_2, CO_2, H_2O, C)(kg mol^{-1})	$[CO_2]_o$	CO_2 concentration outside package (%)
N_h	Number of perforations	$[O_2]_i$	O_2 concentration inside package (%)
p_i	Partial vapour pressure inside package (Pa)	$[O_2]_o$	O_2 concentration outside package (%)
p_c	Partial vapour pressure at commodity surface (Pa)	Greeks	
p_o	Partial vapour pressure outside package (Pa)	α	Heat conversion factor
p_s	Saturated vapour pressure (Pa)	ϵ	Porosity
P_{atm}	Atmospheric pressure =101325 Pa	λ	Latent heat of vaporization (J kg^{-1})
		ρ_b	Bulk density of produce (kg m^{-3})

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Table 1 Properties of package, film and produce (Borchert et al., 2014; Iqbal et al., 2009; Lu et al., 2013; Mahajan et al., 2008; Rux et al., 2015; Simón et al., 2010)

Parameter	**Value**
a_w	0.99
ρ_b (kg m^{-3})	561
C_s (J kg^{-1}K^{-1})	3990
D_1xD_2xD_3(cm^3)	11.9 × 16 × 5.8
d_c (cm)	4
d_H (micron)	150
N_h	8
L_f (m)	33.9x10^{-6}
M_{O_2}	0.032
M_{CO_2}	0.044
M_{H_2O}	0.018
ϵ	0.2595
W_s (kg)	0.250
P_{CO_2ref}(mL.m.m^{-2}h^{-1})	16.12× 10^{-13}
P_{O_2ref}(mL.m.m^{-2}h^{-1})	5.66× 10^{-13}
P_{H_2Oref} (mL.m.m^{-2}h^{-1})	4.32× 10^{-14}

Table 2 Parameter estimate and the standard error associated (Aguirre et al., 2008; Iqbal et al., 2009b; Mahajan et al., 2008). L value$_i$, a-value$_i$, b-value$_i$ initial values, $()_b$ standard deviation associated with batch variability $()_s$ standard deviation associated with sample variability.

Parameter	**Value**
V_{mO_2}	63.64±1.13 (mL kg^{-1} h^{-1})
E_{O_2}	54.38±1.07 (kJ mol^{-1})
K_{mO_2}	4.09±0.285 (%)
K_{iO_2}	38.60±5.03 (%)
V_{mCO_2}	54.68±1.19 (mL kg^{-1} h^{-1})
E_{CO_2}	56.04±1.44 (kJ mol^{-1})
K_{mCO_2}	3.18±0.296 (%)
K_{iCO_2}	57.90±13.53 (%)
L-value$_i$	93 $(0.008)_b(0.007)_s$
a-value$_i$	0.77 $(0.9)_b(-)_s$
b-value$_i$	10.6 $(1.57)_b(2.4)_s$
K_s	8.5 x10^{-3} (cm h^{-1})

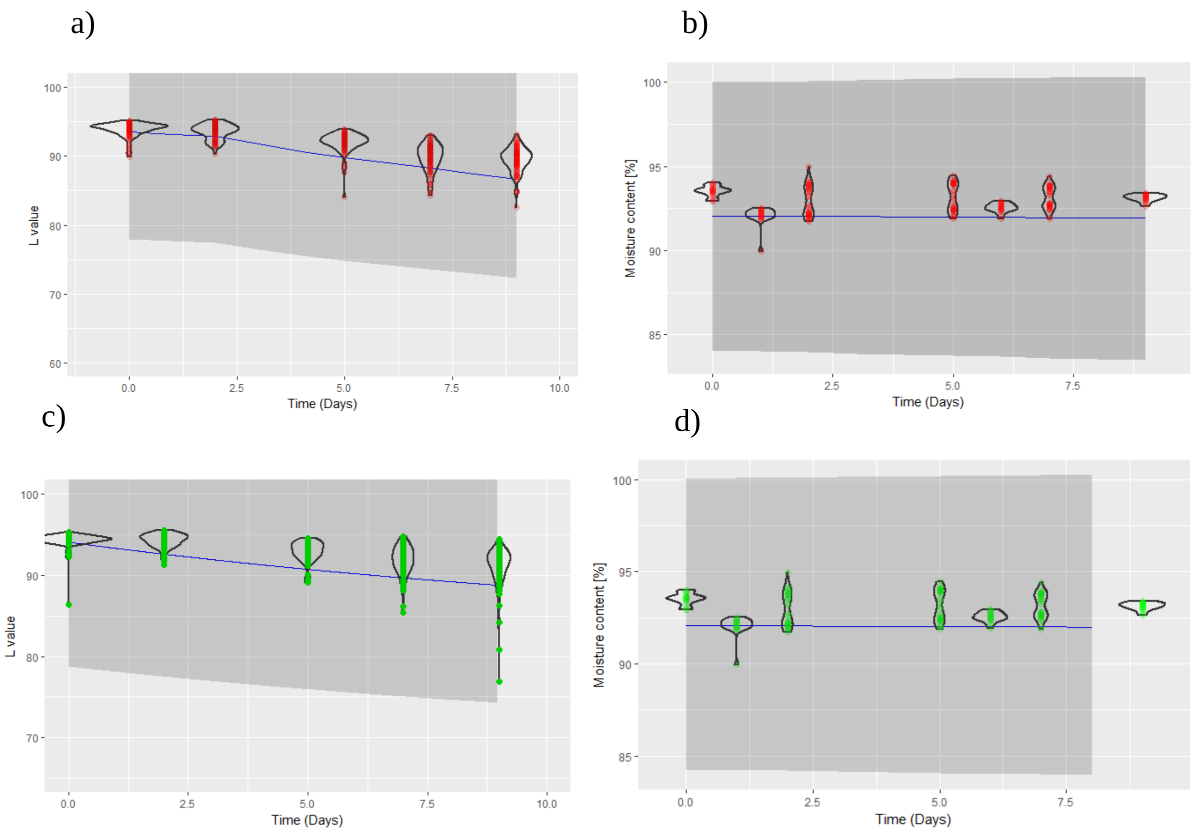


Fig. 1. Comparison of model predictions with the experimental data (points) at different temperature conditions (4, 8, 20^0 C) (red points) and at ideal temperature (3^0C) (green points) a) Change of L value over time and b) Moisture content (% w/w) of mushroom at (4, 8, 20^0 C), c) Change of L value over time and d) Moisture content (% w/w) of mushroom at (3^0C). The black line contour in each of the experimental levels indicates the distribution of the experimental data as a violin plot.

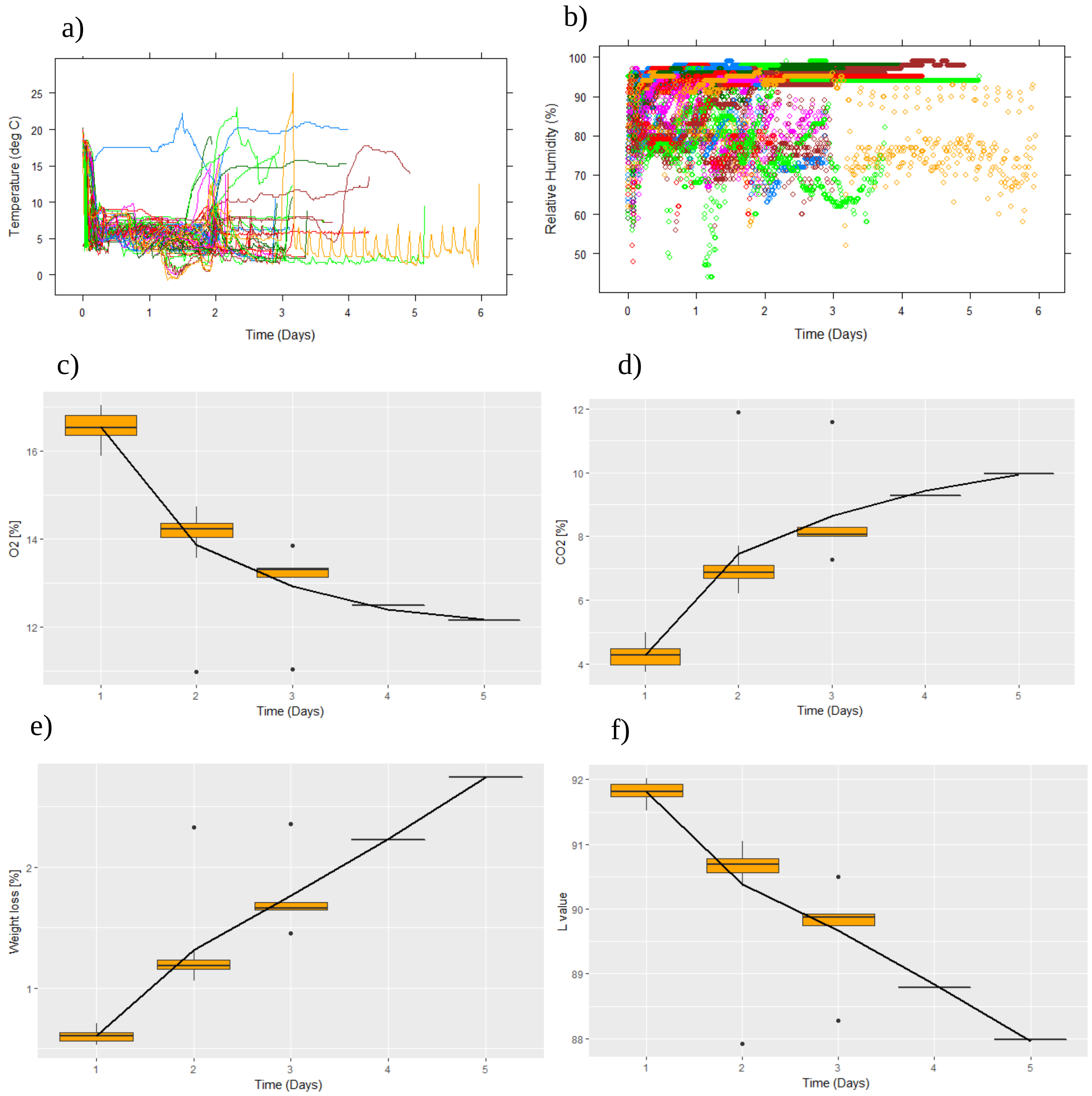


Fig. 2. Prediction of the effect of a) temperature and b) relative humidity cold chain variation on c) O_2, d) CO_2 in the headspace of package, e) weight loss and f) change in L value during supply chain.

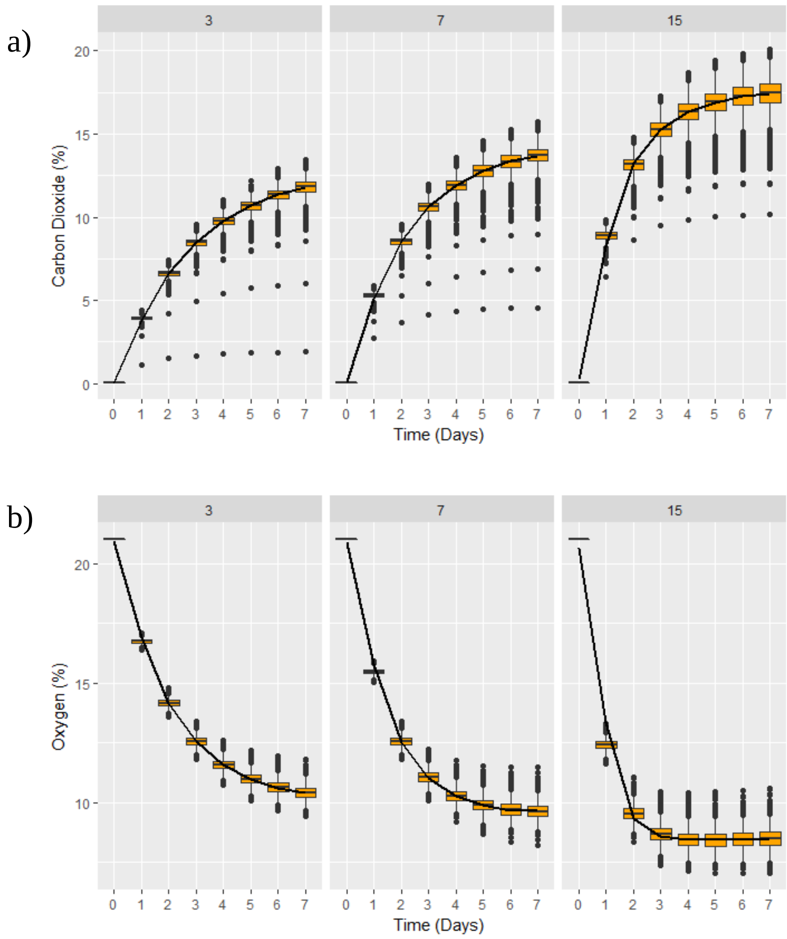


Fig. 3. Propagation of effect of product parameters on the a) carbon dioxide concentration (b) oxygen concentration of mushroom tray packaging stored at different temperature (3, 7, 15 ^{0}C) in cold chain.

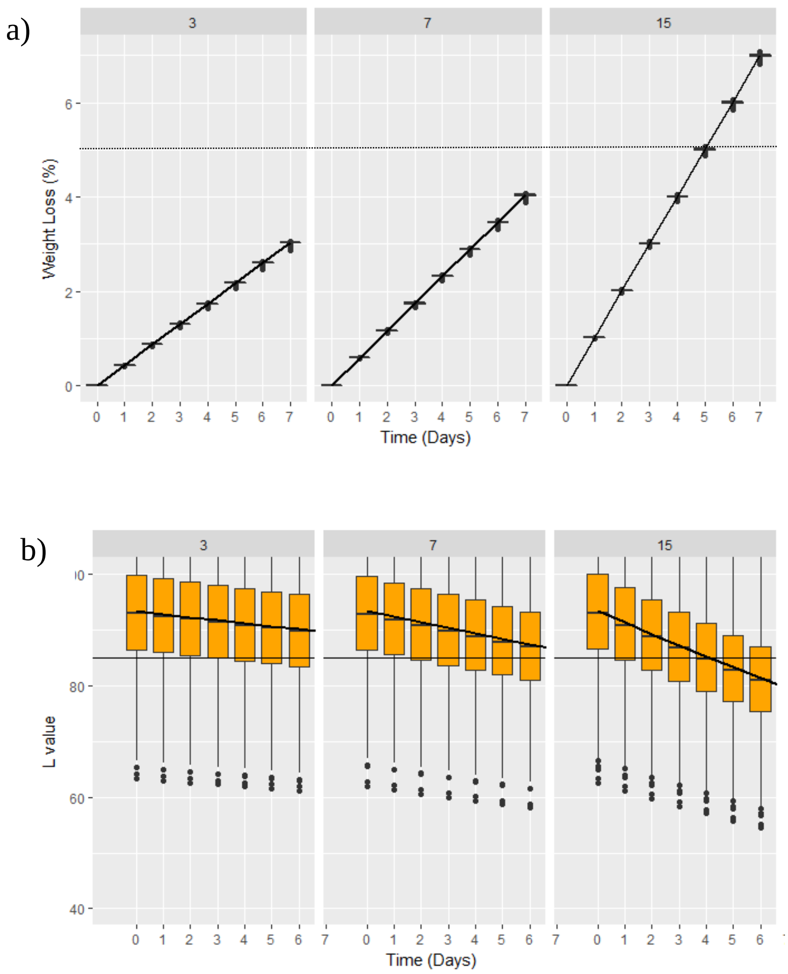


Fig. 4. Propagation of effect of product parameters on the a) weight loss (b) L value of tray packed mushroom stored at different temperature (3, 7, 15 ^{0}C) in cold chain.

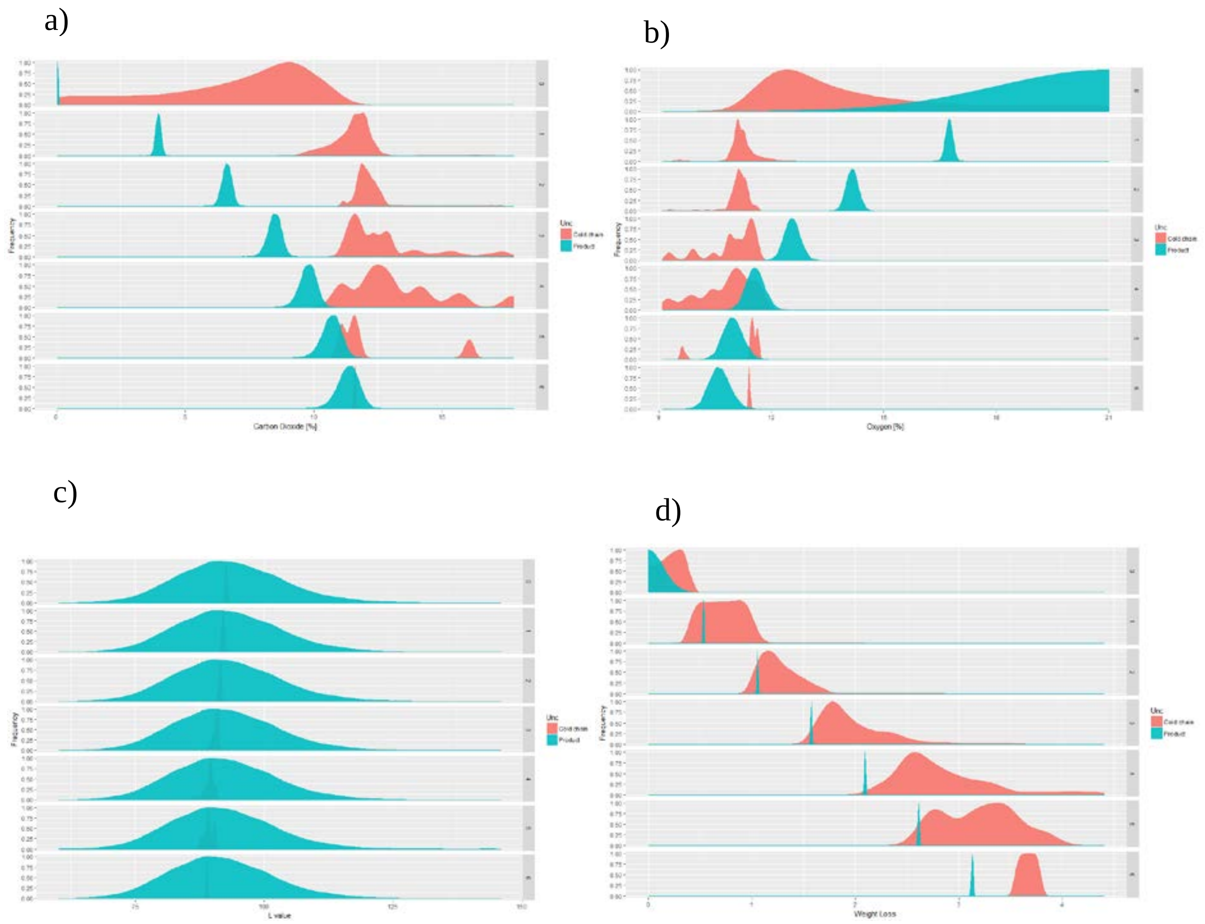
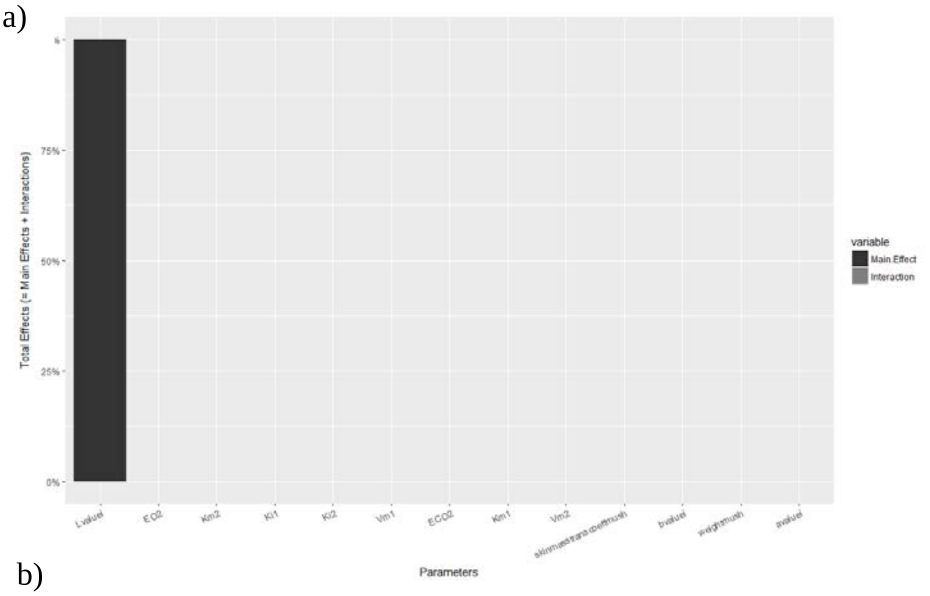


Fig. 5. Comparison of the effect of cold chain parameters and product parameters on the a) CO_2, b) O_2 concentration in the headspace of package, c) L value and d) weight loss observed during distribution supply chain. Each subplot provides a kernel density distribution estimate arising from either the cold chain (pink) or product variability (blue) from day 0 (initial conditions) to day 6 of storage indicated in the right hand facet.

a)



b)

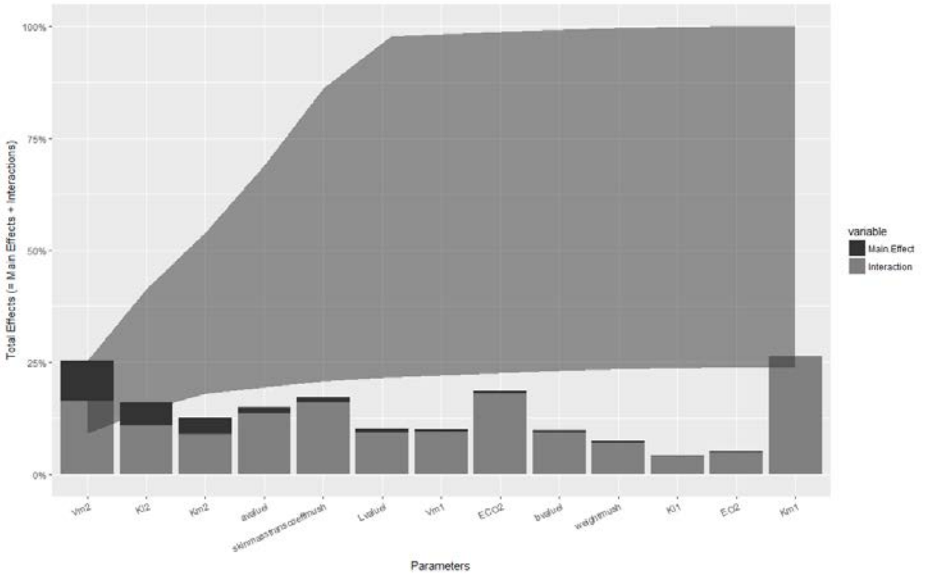


Fig. 6. Lowry plot for sensitivity analysis (The total effect of main parameter given in black and any first order interaction with other parameters is grey given as a proportion of variance. The ribbon represents variance due to parameter interactions, the cumulative sum of main effect is lower line and the sum of total effect is upper line) (a) L value and (b) weight loss.