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DEVELOPMENT OF ASSESSMENT TOOLS OF PACKAGE/ PRODUCT SYSTEMS FOR A SUSTAINABLE FOOD CHAIN

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DEVELOPMENT OF ASSESSMENT TOOLS OF PACKAGE/PRODUCT SYSTEMS FOR A SUSTAINABLE FOOD CHAIN

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Abstract

Post-harvest life of fresh produce is limited due to high metabolic activity and microbial spoilage. Modified atmosphere packaging (MAP) has proven to be one of the most effective techniques to extend the shelf life of fresh produce commercially. Obtaining of an optimum concentration of oxygen and carbon dioxide inside the package depends upon the product properties, the environmental conditions of the cold chain, the permeable film, some of which are subjected to natural variability during the food distribution chain. This variability may generate produce that is out of specification that will lead to food waste. Uncertainty analysis of this problem may lead to relevant interventions to prevent these losses.

The hypothesis of this work was to create a mathematical model that predicts key quality factors for MAP packaged fresh products in the supply chain distribution, which will help to assess the food losses in relation to quality thresholds. The model developed simulated the respiration rate as function of O_2 and CO_2 concentration and produce temperature using Michaelis-Menten equations. The exchange of gases (O_2, CO_2) and water vapour between the fruit surface, package atmosphere and external atmosphere was modelled taking into account the process of transpiration and condensation. In the transpiration model, the fresh produce surface was assumed to be perfectly saturated and the energy of respiration was used to evaporate surface water. Temperature changes in the headspace due to metabolic heat, convective heat transfer and heat exchange by gas transmission through the package were accounted for. The quality attributes of fresh produce included weight loss and colour change (L, a, and b values) for mushroom, from *Botrytis* and its fermentative activity for strawberry and weight loss and spoilage for tomato.

These conditions were simulated for real and variable i) export cold chain and ii) retail display storage to evaluate the effect of cold chain variability (temperature and relative humidity) on the quality of fresh produce and associated waste generation. The prediction of propagation of biological variance on the quality of fresh produce during storage was obtained using a mathematical model. Sensitivity analysis of the stochastic MAP model pointed out the influence of input parameters on the quality of fresh produce. The conclusions of the study showed that the toolbox developed is able to interpret cold chain data: 1) mathematical prediction of quality; 2) simulation of cold chain conditions allowing for different variability components; 3) estimation of waste generation kinetics based in all quality criteria and thresholds; 4) sensitivity analysis to identify the most sensitive technological parameters; and 5) identification of interventions that affect the benchmarked technological parameters.

Declaration

I declare that this thesis which I now submit for examination is entirely my own work and has not been taken from the work of others, save to the extent that such work has been cited and acknowledged within the text of my work. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in any submission.

This thesis was prepared according to the regulations for postgraduate study by research of Technological University Dublin and has not been submitted in whole or in part for another award in any institute.

The work reported on in this thesis conforms to the principles and requirements of the Institute's guidelines for ethics in research.

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Kompal Joshi   **Date**

Acknowledgement

Nomenclature

a_w	Water activity of fresh produce
A_c	Surface area of produce (m^2)
A_{p1}	Surface area of packaging film (m^2) ($D_1 x D_2$)
A_{p2}	Surface area of package bottom (m^2) ($D_1 x D_2$)
A_{p3}	Surface area of package walls (m^2)
A_p	Total surface area of package (m^2)
CA	Controlled atmosphere packaging
C_a	Air humid air (J kg^{-1} K^{-1})
C_s	Specific heat of produce (J kg^{-1} K^{-1})
E_{O_2,CO_2}	Activation energy of rate constant (J mol^{-1})
d_c	Equivalent diameter of produce (cm)
d_H	Diameter of perforation (mm)
$D_1 x D_2 x D_3$	Dimensions of package (cm)
$D_{i,air}$	Diffusion coefficient of I = O_2, CO_2, H_2O in air (m^2 s^{-1})
h_p	Convective heat transfer coefficient on produce surface (J h^{-1} m^{-2} K^{-1})
k_s	Spoilage rate constant
K_a	Air-film mass transfer coefficient (kg m^{-2} s^{-1} Pa^{-1})
K_s	Skin mass transfer coefficient (kg m^{-2} s^{-1} Pa^{-1})
K_t	Transpiration coefficient (kg m^{-2} s^{-1} Pa^{-1})
K_{mO_2}	Michaelis-Menten constant in O_2 consumption (% O_2)
K_{mCO_2}	Michaelis-Menten constant in CO_2 evolution (% O_2)
K_{mico_2}	Michaelis constant for inhibition of O_2 consumption (%) where $i = c$: competitive and u: uncompetitive
$K_{mc_{i_f}}$	Michaelis constant for competitive inhibition of fermentative $CO2$ production by either $i= O2$ or $CO2$ (%)
L_f	Thickness of packaging film (m)
LSODE	Livermore Solver for Ordinary Differential Equations
m_{pr}	Rate of water permeation through film (kg sec^{-1})

MAP	Modified Atmosphere Packaging
m_w	Water vapour flux (kg m^{-2} s^{-1})
M_{con}	Condensation rate on commodity (kg s^{-1})
M_{wcon}	Condensation rate on package walls (kg s^{-1})
M_i	Molar mass of species (i = O_2, CO_2, H_2O, C)(kg mol^{-1})
N	Spoilage
N_o	Initial spoilage of batch
N_{max}	Maximum spoilage
N_h	Number of perforations
p_i	Partial vapour pressure inside package (Pa)
p_c	Partial vapour pressure at commodity surface (Pa)
p_o	Partial vapour pressure outside package (Pa)
p_s	Saturated vapour pressure (Pa)
P_{atm}	Atmospheric pressure =101325 Pa
P_i	Film permeability to species (i = O_2, CO_2 , H_2O) (mL m m^{-2} h^{-1} atm^{-1})
$P_{i\ ref}$	Reference permeability of film to i = O_2 , CO_2 , H_2O (mL m m^{-2} h^{-1} atm^{-1})
Q_{con}	Condensation heat released due to commodity (J s^{-1})
Q_{wcon}	Condensation heat near the packaging walls (J s^{-1})
Q_r	Respiration heat (J h^{-1})
Q_{tr}	Evaporative heat transfer due to transpiration (J s^{-1})
r_{CO_2}	CO_2 production rate (mol kg^{-1}s^{-1})
$r_{CO_{2f}}$	CO_2 production rate (mol kg^{-1}s^{-1})
r_{O_2}	O_2 consumption rate (mol kg^{-1}s^{-1})
R	Gas constant (8.314 J mol^{-1} K^{-1})
Rel_{MR}	Relative metabolic rate
RQ	Respiratory Quotient
R_h	Radius of perforation (m)
RH	Relative humidity inside package (%)
RH_O	Relative humidity outside package (%)
t	Time (s)
t_r	Transpiration rate (kg m^{-2} h^{-1})
T_i	Temperature inside package (K)

T_o	Temperature outside package (K)
T_s	Temperature of produce surface (K)
T_{ref}	Produce reference temperature (K)
V_b	Bulk volume of produce (m^3)
V_f	Free volume in headspace (mL)
V_{mO_2}	Maximum O_2 consumption rate (mL kg^{-1} h^{-1})
V_{mCO_2}	Maximum CO_2 evolution rate (mL $kg^{-1}h^{-1}$)
VPD	Vapour pressure deficit (Pa)
W_a	Weight of dry air (kg)
W_s	Weight of produce (kg)
W_l	Weight loss
$[CO_2]_i$	CO_2 concentration inside package (%)
$[CO_2]_o$	CO_2 concentration outside package (%)
$[O_2]_i$	O_2 concentration inside package (%)
$[O_2]_o$	O_2 concentration outside package (%)
Greeks	
α	Heat conversion factor
ϵ	Porosity
λ	Latent heat of vaporization (J kg^{-1})
ρ_b	Bulk density of produce (kg m^{-3})

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Chapter 1.   Introduction

1.1.   Background

The global production of fruits in 2010 was 608 million tonnes, with China being the largest producer (122 million tonnes), followed by India (75 million tonnes). The European total fruit production in that year was 68 million tonnes, with Spain ranked first (15 million tonnes). Total global production of vegetables in 2010 was 1044 million tonnes, and China, India and US are the leading producers (539, 100 and 35 million tonnes respectively). The 2010 EU vegetables production reached 94 thousand tonnes, with Italy as leading producer (14 thousand million tonnes), followed by Spain (12 million tonnes) and France (5.5 million tonnes) (FAO, 2014). In Ireland, the farm gate value of the horticulture industry was worth €433 million in 2016, the 4th highest sector in terms of gross agricultural commodity output value – behind beef, dairy and pigs. Within the horticulture food output, mushrooms accounted for €122 million, potatoes €87 million, field vegetables €73 million, protected fruit €38 m, protected vegetables €30 million and outdoor fruit €11 million. The retail fresh produce market was worth €1.5 billion in the year ending March 2017, with vegetables accounting for €570 million, fruit €735 million and potatoes €195 million. Fruit and vegetables combined represent 15.7% of the average grocery shopping basket (Stiofán Nutty, 2017).

Fruits and vegetables are important commodities for developing countries to diversify their exports. International trade of fruits and vegetables has increased drastically in the past decades. The increase in health awareness and demand for convenience foods have accelerated year round consumption of fresh fruits and vegetables. Around 88% consumers are willing to pay more for foods with healthy

1

attributes (Nielson, 2015). The challenge to fulfil the year round demand of fresh produce, difference in natural climate and growing conditions between countries are the main driving force for trade (Dolan and Humphrey, 2000; Kader, 2002). To meet the demands of a continuously growing market is a challenge for industries. There exists a need for development of suited postharvest preservation technologies for fresh fruits and vegetables (Kader and Rolle, 2004).

Over the last decades, there has been a 56% increase in the production of mushrooms worldwide. The global market has been valued at $29,427.92 million in 2013. China, USA and the Netherlands are the leading producers, accounting for 60 % of the world's production. Fresh mushrooms export accounts to 0.014 to 0.482 million tonnes. EU mushroom production is about 27% of the world's production. In the EU, UK followed by Germany are the largest importers of fresh mushrooms (Wakchaure, 2011). Tomato is most grown vegetable crop in the world; annual production is 152 million tons with a value of $74.1 billion. The total growth has increased by 35 % over the last 10 years. The US was the world's largest strawberry producer followed by Turkey, Spain, Egypt and Korea. The total value of strawberry produced in 2014 was $2.4 billion. The total production was reported as 1.4 million tonnes in 2014 which represents 30% of the world's production (Tabatabaie and Murthy, 2016). The estimated worth of strawberry grown in Ireland is €74.3 million. The growers produce about 7700 tonnes of fresh strawberries per annum. The most popularly grown cultivar is the Dutch variety *Elsanta* (Slawski, 2016).

The mushroom industry is one of the largest horticultural sector in Ireland, where the total mushroom production is estimated to be worth €173 million. There is also steady growth observed in both volume and value in mushroom market. *Agaricus bisporus* (button) mushroom continue to be the most valued mushrooms at around 60 % followed

by Chestnut mushrooms. Eight percent of mushroom produced in Ireland is exported each year. Ireland has one of the most important mushroom export markets with sales remaining steady each year (Bia, 2015). Strawberries (*Fragaria × ananassa)* and tomatoes (*Solanum lycopersicum*) come under the protected crops category in Ireland as they require a controlled climatic environment to produce an adequate commercial yield. The soft fruit industry in Ireland is valued at € 100 million. The berry sector is one of the most challenging, rewarding and profitable sectors. Strawberry is the dominant produce, covering 50% of the berry market in Ireland. In 2014, the annual production of fresh strawberry reached around 7000 tonnes, valued at 37 million euros/year (Bia, 2015; DAFM, 2014). Strawberries are experiencing significant growth and producers are exploring export possibilities (Stiofán Nutty, 2017). Tomato is another important horticultural crop in Ireland as it is ranked as the third top three vegetable markets. In 2011, 4663 tonnes of tomato were produced, worth € 9.1 million. Ireland accounts for 3.9% of the total production in EU, with a production area of 10 hectares in 2012. In Ireland the retail fresh produce market was worth €1.5bn in the year ending March 201,7 with vegetables accounting for €570m, fruit €735m and potatoes €195m. Fruit and vegetables combined represent 15.7% of the average grocery shopping basket (DAFM, 2014).

1.2. Food losses in the supply chain

Food loss is ascribed to food rejected from the supply chain at primary production, processing and distribution steps. The exact definition of food waste is still debatable. According to FAO (Food and Agriculture Organization of the United Nations), it can be defined as the mass of food wasted in the part of food chains leading to edible products going to human consumption. Food waste in the UK is defined by WRAP (Waste and Resources Action Programme) as "any food or drink produced for human consumption

that has, or has had, the reasonable potential to be eaten, together with any associated unavoidable parts, which are removed from the food supply chain" (Manzocco et al., 2016).

The EU accepted the definition of waste by the FUSION programme: "any food, and inedible parts of food, removed from the food supply chain to be recovered or disposed (including composed, crops ploughed in/not harvested, anaerobic digestion, bio-energy production, co-generation, incineration, disposal to sewer, landfill or discarded to sea" (Fusion, 2016).

Food losses are generally categorised as those that occur during storage, transport or wholesale, at retail or consumer level. Food losses can be quality related, such as reduced nutrient value and undesirable changes to taste, texture, or colour, or quantity related, as measured by decreased weight or volume (Buzby and Hyman, 2012). One third of the food produced in the world (around 1.3 billion tonnes) for human consumption is lost or wasted. Per capita waste by consumers is between 95-115 kg/year in Europe and North America, while in sub-Saharan Africa, South and South eastern Asia food waste amounts between 6-11 kg/year (FAO, 2016). It is estimated that, depending on crops and countries, between 25% and 50 % of fruits and vegetables are wasted along the supply chain (Mena 2011). Worldwide postharvest losses of fresh produce in developed countries range from 2-23 % and can be as high as 5-50 % in developing countries (Kader, 2004). These losses can be due to effects in different steps of the food chain:

1) Agricultural production

Postharvest losses at farm level can be due to crop becoming affected by disease, microbial contamination, seasonal calamities, and mechanized harvesters. Failure to meet the minimum quality standard is also one of the reasons. Data from the UK indicates that 20-40% of crops are not harvested as they are not meeting retail quality standards. Instead

of being redirected to other useful purpose, this food is wasted despite its nutritional value (Adam, 2015).

2) Processing/packaging

At processing level losses can occur due to handling damage, deterioration, improper packaging, and infestation. The waste percentages for processed products are 0.59 times those of the fresh food for distribution waste, and only 0.2 times those of fresh food for consumption waste (Kummu et al., 2012).

3) Distribution/transport

Losses and damage of perishable goods during transportation are substantial snd s global issues. Limited infrastructure, improper transportation and handling are some of the main reasons for losses of fresh produce during transit. Failure to manage the required temperature can lead to weight loss, appearance degradation and microbial spoilage. Due to the variety of products and their different temperature requirements, the allocation of products to the appropriate refrigerated facilities is complex (Aung and Chang, 2014)

4) Retail

Retail contributes to a greater proportion of total losses in the cold chain. Some of the reasons contributing to losses in retail are appearance, large pack sizes, expired products, goods on offer, damaged and spoiled goods (Kader, 2004). Produce which do not reach retail stores within one third of their defined shelf life are often rejected by the retail stores, thus causing loss of good eating quality and nutritious produce (Adam, 2015). Around 2-12 % of losses of fresh fruit and vegetables at retail level have been reported (Buzby and Hyman, 2012; Killeen Davis, 2015). In the USA, the loss observed at supermarkets in 2005-06 were estimated to be 9.8 % for strawberry, 12.7 % for mushrooms and 13.2 % for tomatoes (Buzby et al., 2009). Fig 1.1 provides some of the causes leading to food loss and waste at each step of the supply chain. Food waste at

refrigerated distribution and retail represent significant losses of money, energy and resources invested throughout the supply chain. Around 20% of perishables are lost worldwide due to lack of appropriate refrigeration infrastructure (Defraeye et al., 2015). Improper temperature and relative humidity levels inside refrigeration chambers and during retail display is one of the main reasons contributing to fruit and vegetable quality loss and hence increased waste at the consumer level (Nunes et al., 2009). Industrialized regions generate both higher per capita food loss and per capita food waste by consumers as compared to the developing countries (Siu, 2014).

5) Consumer

Consumer attitude (e.g. fresh products consumption, taste preferences, attention towards healthy diets) and the excessive amount of incoming goods (e.g. inconvenient packaging, unplanned purchase) often represent the root causes of food waste (Manzocco et al., 2016). Other factors explaining household food waste are household size and composition, household income, household demographics and household culture. Household food waste is driven by inadequate storage, consumer's high expectation of cosmetic standards of food and low price of food relative to disposable income. Increasing urbanisation disconnects people from how food is grown, which can lead to further food waste (Parfitt et al., 2010). Per capita waste by consumers is between 95-115 kg/year in Europe and North America, compared to only 6-11 kg/year in sub Saharan Africa, South and South East Asia (Gustavsson et al., 2011).

<table>
<tr>
<td>

Farm
- Damage by insects and environmental conditions.
- Difficulty prediciting number of buyers/customers leads to overplanting.

</td>
<td>

Packaging/ Processing
- Outgrading of produce due to minimal quality standards.
- Inefficiency during tranporting or processing.

</td>
<td>

Distribution/ Retail
- Damaged or inappropriate packaging.
- Over stocking due to difficulty estimating sales.
- Inadequate storage techniques, and technical malfunction.

</td>
<td>

Consumer
- Inadequate storage, technical malfunction and mishandling.
- Lack of knowledge and awareness about food labelling.
- Socio demographic and seasonal factors.

</td>
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Fig 1.1 Causes of food loss and waste at the farm, processing, retail and consumer levels in the food supply chain.

1.3. Reducing food waste

Reducing postharvest losses starts from the field and ends with the consumer, as educating people and raising awareness on food loss can provide world with adequate supply of wholesome food (Aulakh and Regmi, 2013). The World Food Congress in 1974 highlighted the importance of reducing food waste to increase food availability. An expert consultation on food loss prevention in perishable crops, mainly covering fruit and vegetables. was held in Rome in 1980 (Rolle, 2006). Efforts have been made to adopt new policy frameworks and legislation to reduce food waste. In 2011, FAO published a report assessing the global food waste, which highlighted the significant environmental and economic impact of food waste. Food waste endangers global food security and causes environmental concerns (Nations, 2013).

The first step towards an efficient management of food wastage is to adopt a more sustainable production and consumption approach to tackle food loss and waste throughout the supply chain. Quality standards are one of the main drivers of waste

generation (EC, 2008). Resulting from the negative implication of out grading, the European Commission has relaxed the rules of marketing standards for 26 fruits and vegetables in 2009. Marketing standards were retained for certain fresh commodities, however products not fulfilling the criteria are labelled accordingly to be distinguishable from the EU classification (Adam, 2015).

The main aim of the management of a fresh product cold chain distribution system is to extend the shelf life of fresh produce while maintaining the nutritional quality, ensuring its safety and retaining desired sensory characteristics until consumed by the consumer. Cold chain distribution has made international trade of fresh fruits and vegetables possible, where refrigeration is complimented with other technologies to assure their quality and safety (Kader, 2003; Kuo and Chen, 2010). Fruits and vegetables remain as living tissue until the time they are consumed or cooked. All living tissues respire, which has a profound effect on the shelf life of fresh produce. Cooling the fresh produce in general can slow down many undesirable changes taking place in them. Reducing the respiration rate can slow down senescence and prolong the shelf life of fresh produce. Modified Atmosphere Packaging (MAP) together with refrigeration storage and distribution has a significant impact on the quality of fresh produce and is thus are effective intervention to extend shelf life (Defraeye et al., 2015). However, the addition of packaging material and the sensitivity of this intervention to temperature fluctuations present a challenge to the future of the fruit and vegetable industry. New solutions of sustainable packaging (e.g. biodegradable packaging, retailer size packaging and absence of individual packaging) are proposed to improve the sustainability of this industry and reduce waste (Williams et al., 2012). This will be discussed in the sections below.

1.3.1. Packaging as a tool to reduce food waste

Packaging enhances, protects and surrounds the product all the way from processing, transportation and handling to storage. The goal of food packaging is to contain and protect food in a cost-effective way, meet industry and consumer desires, to maintain food safety and exert minimal environmental impact. Effectively designed packaging can reduce the waste generated during supply and will lessen the impact on the environment. The use of particular kind of packaging is driven by the requirements during different points of the supply chain, which will support the development of an improved packaging system (Marsh and Bugusu, 2007).

Food packaging protects food from external influences (physical, chemical and biological) and retards product deterioration, maintains quality and provides safe food. Well-developed packaging provides a physical barrier and cushioning of delicate commodities such as fruits and vegetables. Chemical protection against environmental influences, such as gases (O_2, CO_2), moisture and light protects against to undesirable reactions (Mattos et al., 2012). However, in some certain cases some level of permeability is desired as per the requirement of the fresh produce (Marsh and Bugusu, 2007). Packaging also provides protection against microbial contamination by providing conditions that can kill or reduce the microbial growth rate (Brown et al., 2011). Packaging has also played an important role in enhancing the image of the produce and development of fast pace consumer retailing. This in turn has also created demand for development of different packaging as required by the individual produce to reduce waste during retail.

Packaging also controls the loss of water vapour, which is an important factor contributing to quality loss, and control of flux of gases, which helps in building up an optimal atmosphere within the headspace (Torrieri et al., 2009). Although there is no

substitute for maintaining effective cold chain conditions throughout the postharvest handling system, packaging can help in the temperature management of the produce with the aim of shelf life extension. The factors that should be considered when developing or sourcing a packaging to extend the shelf life of fresh produce are: 1) Understanding the properties of the fresh produce and 2) Determining the atmospheric conditions to which the packed product will be exposed (Kader and Rolle, 2004). Some of the existing packaging technologies successfully used to extend shelf life and maintain quality of fresh produce are Controlled atmosphere (CA) packaging, Modified atmosphere packaging (MAP), Active packaging, and intelligent packaging (Kader, 1980; Kader et al., 1989; Labuza and Breene, 1989; Mattos et al., 2012; Pesis et al., 2000).

1.3.2. Relevance of losses to the sustainability of the fresh food production and distribution industry

Food waste must be tackled if the food industry is to meet the demand of the growing population within a sustainable framework. From the industry perspective, food waste represents significant loss of money and other resources invested throughout the supply chain. Moreover, the negative impact of fresh produce loss on the environment cannot be ignored as it affects the sustainability of the industry (Akkerman et al., 2010; Parfitt et al., 2010). Food waste at the point of consumption costs on average of US $1,600 for a family of four in the United States and £680 annually for an average household in the United Kingdom (Lipinski et al., 2013). Environmentally, food waste represents an unnecessary greenhouse gas emission and misuse of water and land resources. Food loss and waste annually consume around 24 % of the total water used for agriculture, which is around 173 billion cubic meters of water. If the food supply chain losses were halved, an extra one billion people could be provided with an adequate food supply and critical natural resources can preserved (Kummu et al., 2012).

Storage and packaging processes have significant greenhouse gas implications. For decades, the main reason for greenhouse gas has been packaging materials and use of recycled alternatives, rather than a reduction of food losses. The designing of new packaging solutions to lower fresh produce losses would substantially reduce environmental impact (Williams and Wikström, 2011). In a life cycle assessment study done in Japan for packed tomatoes, it was observed that the environmental load for MAP is greater compared to normal packaging due to the of the use of OPP films. However, MAP was found to be a more suitable method for long distance transport over that of short distance (Roy et al., 2008). A Life Cycle Impact Assessment (LCIA) performed by Siracusa et al. (2014) showed that for MAP a lower amount of water is required when compared to equivalent thermal processes. The US Environmental Protection agency found that approximately 31% of the municipal solid waste is represented by packaging related materials, including glass, metal, plastic and paperboard. Plastic contributes to 11.8% of the total waste (Marsh and Bugusu, 2007). Alternative packaging systems are an efficient method to reduce the environmental burden of packaging. The use of recyclable plastic and biodegradable plastic has been shown to reduce the environmental burden. Therefore, the best scenario to obtain a sustainable food supply chain is the use of modified atmosphere packaging along with low-impact packaging system.

To minimise fresh produce losses during the distribution chain and maximise the shelf life, an understanding the biological and environmental factors that affect the postharvest deterioration is important as it will define the generation of out of specification products (Arah et al., 2015).

Chapter 2. Review of literature

2.1. Parameters governing losses of fresh produce in the supply chain

As fresh produce moves through the distribution supply chain, a number of factors leads to losses produced such as improper handling, microbial spoilage, inappropriate storage techniques. The factors leading to degradation of quality and thus producing waste in supply chain are presented Fig 2.1 (Gustavsson et al., 2011; Harvey, 1978).
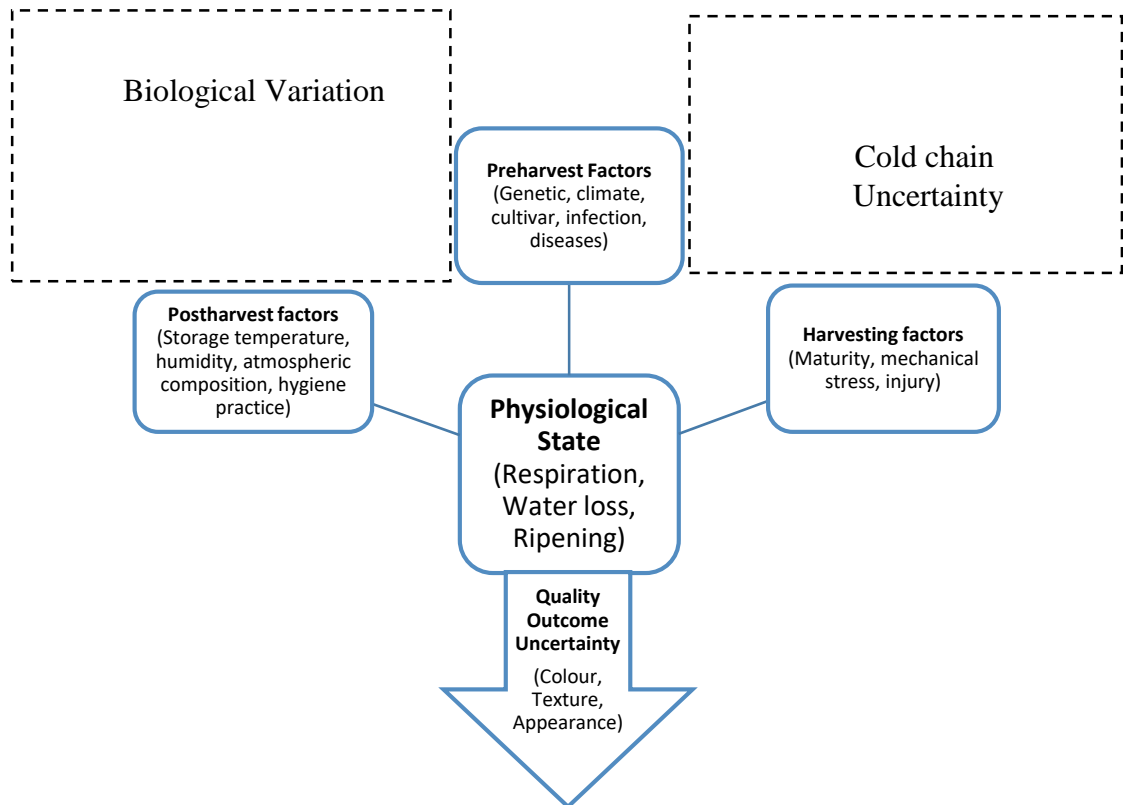
Fig 2.1 Schematic represenation of factors affecting the quality of fresh produce

2.2. Biological variation

Fresh food supply chain deals with living tissues that slowly change with time and are a source of biological variance. Fresh produce behaviour is inherently affected by

biological variability. Biological variance is a result of various sources of variability. In every batch of fresh produce variation exists in its properties or attributes, which directly or indirectly affects the characteristics of fresh produce and therefore its quality (Hertog et al., 2007a). The correct interpretation of the postharvest behaviour requires awareness of the different sources of variation present. The primary production industry efforts to tackle variation aim to keep it to a minimum. Sorting and grading is used in food processing industry to minimise the effects of product variance ascribed to external quality attributes and to minimise variation of storage conditions. The variability issue can be better understood by the following example, Caleb (2012) reported the respiration rate of Pomegranate (*Punica granatum* cv. Acco) to be R_{O_2}= 8.55 ml/kg h and R_{CO_2}= 11.10ml/kg h and the respiration rate of Pomegranate (*P. granatum* cv. Herskawitz) at the same temperature was found to be R_{O_2}= 8.74 (ml/kg h) and R_{CO_2}= 11.50 (mL/kg h). On researching the availability of literature data on respiration rate parameters for strawberries (Table 2.1), it can be observed that each provider and variety has different values. Variability can be observed as well for the same varieties of strawberry.

Biological variability is ascribed to variations in batches, climate and time of harvest. As reducing the rate of respiration of fresh produce affects postharvest quality, designing packaging that is optimal to the specific cultivar is important to reduce food waste. In tomatoes, for instance, biological variation becomes discernible from the changes in their initial colour through harvest. The initial colour at harvest can be used as a measure of biological age (Hertog, 2004). The preservation of colour towards the end of the supply chain is important for consumer acceptability.

In a large lot of produce, there exists a lot of variance in maturity. Whenever a smaller batch is drawn the batch will have individuals with different maturity levels. If all produce was harvested at the same biological age the variation at harvest would be

negligible (Hertog et al., 2004a). Generally, the behaviour of an individual object is ignored and the main focus is on averaged batch behaviour based on large sample sizes. Not taking individual product behaviour into account while modelling the quality changes can lead to an inefficient estimation of means and misleading conclusions (Hertog and others 2007).

Understanding the changes in quality attributes of fresh produce is of utmost importance to achieve the highest quality end product desired by the consumer with respect to complete cold supply chain. For this, more insight is required in modelling the quality degradation and variability propagation through the postharvest supply chain.

2.2.1. Cold chain variation

During supply chain distribution the two most important factors causing variability is the environmental temperature and relative humidity to which the fresh produce is exposed to. Maintaining ideal conditions during storage is very important for preserving the quality of fresh produce, which will reduce losses during the supply chain (Garvan, 2007; Gwanpua et al., 2015).

Effect of temperature variability

Temperature is the most important environmental factor that influences the shelf life of fresh produce. All the physiological reactions and pathological deteriorations taking place in fresh produce are controlled by temperature. Reducing temperature influences all metabolic responses driven by enzymes. Low temperature during handling, transportation and storage is the most effective method of postharvest preservation as it reduces the rate of respiration and transpiration (Jobling, 2000; Lee et al., 1995).

Table 2.1 Range of values of respiration rate parameters found in the literature for strawberry

Produce and type of respiration rate		Respiration parameters			Reference
		V_m (mol kg^{-1} h^{-1})	K_m (kPa)	K_i (kPa)	
Strawberry *F. × ananassa* Duchesne	O_2 consumption	4.4×10^{-4}	0.99	8.80	An et al., (2009)
	CO_2 consumption	2.78×10^{-4}	1.79	8.07	
Strawberry (*cv. Elsanta*)	O_2 consumption	8.712×10^{-4}	1.2	51	(Geysen et al., 2005)
	CO_2 consumption	6.3×10^{-4}	0.14	53	
Strawberry (*cv. Elsanta*)	O_2 consumption	9.72	2.63 (%)	-	(Hertog et al., 1998)
	CO_2 consumption	18	0.50 (%)	0.056 (%)	
Strawberry (cv. San andreas)	O_2 consumption	85.6 (ml kg^{-1} h^{-1})	8.6 (%)	25.2 (%)	(Barrios et al., 2014)

The rate of respiration increases as temperature increases, and the extent of increase depends upon the cultivars and species (Hui and Evranuz, 2015). The deterioration rate generally is associated to the respiration rate and increasing temperature. Accordingly, the shelf life increases as temperature reduces. However, temperature lower than the optimal storage temperature for some commodities can lead to physiological injuries. Fruits and vegetables undergo tissue damage, discoloration, decay, loss of ripening ability and wilting when stored below their optimal storage

temperature. The shelf life of strawberry at 0^0C is around 2 weeks and at room temperature (20^0C) it reduces to 3-4 days (Gol et al., 2013).

The physical or physiological change induced by exposure to low temperature together with the subsequent expression of characteristic symptoms is commonly termed as 'chilling injury'. Some of the most commonly recognised symptoms of chilling injury are: cellular changes, altered metabolism, reduced plant growth, surface lesions, water soaking of tissue, internal discoloration, increased susceptibility to decay, failure to ripen and loss of vigour (Wang, 1990).

The development of most chilling symptoms is often mediated by environmental factors. For example, corn suffers severe injury when exposed to sunlight while chilling. Chilling injury also appears on some produce when they are exposed to higher temperatures. During cold storage, darkening of the mesocarp and browning of the pulp are some of the chilling injury symptoms exhibited by avocadoes (Pesis et al., 2002). Tomatoes affected by chilling injury shows slow and abnormal ripening, blotchy colour development and increased rate of respiration and ethylene production. Green mature tomato fruit stored at 13^0 C for more than 2 weeks and red fruit stores at 10^0 C for 1 week, leads# to lesser quality loss in terms of colour loss, firmness and shelf life (Wang, 1990). In a study by Pesis et al., (2000) CA of 5kPa of carbon dioxide and 10kPa of oxygen were effective in reducing the peel colour development and chilling injury symptoms in mangoes. Also, MAP storage with moderate relative humidity eliminated the chilling injury symptoms of red spots around lenticels in mango ('Kensington') stored at 12^0 C.

The most successful means to avoid chilling injury is to refrain from exposing commodities to temperatures below their critical threshold. Temperature conditioning or acclimation, achieved by lowering the temperature to slightly above the chilling range,

has proven to be effective for many commodities, including sweet potato, cucumber, tomato and banana (Jackman et al., 1988).

Temperature also affects the quality of fresh produce by influencing weight loss. The driving force for water loss from fresh produce is the difference in the amount of water present on the produce surface and the air surrounding the commodity. Weight loss as low as 5 % of produce can affect the quality appearance of strawberries (Kader, 2003). Temperature has a direct influence on the partial pressure of water vapour in the air surrounding the commodity. Thus, reducing temperature can effectively reduce the driving force and hence reduce water loss (Burton, 1982; Hui and Evranuz, 2015). In leafy vegetables water loss can lead to wilting and shrivelling causing it to be less appealing. In fresh fruits and vegetables, water loss can lead to tissue softening during storage, which is a limiting factor for consumer acceptability (Vigneault et al., 2009). Javanmardi and Kubota (2006) determined the weight loss of tomatoes during postharvest storage at different temperatures and reported weight loss of 0.49 % when stored at 12^0 C and for 5^0 C was 0.15 % per day and when produce was stored at room temperature (26^0 C) the weight loss was significantly higher at a rate of 0.68% per day for 7 days storage.

Temperature also affects the sensitivity of the produce to ethylene. At higher temperature, fresh produce is more sensitive to ethylene than at low temperature (Lee et al., 1995). Initially, physical changes are caused by chilling injury which can then lead to secondary responses including increases in respiration rates (Hui and Evranuz, 2015).

Effect of Relative humidity variability

Fresh fruits and vegetables contain sizeable amount of water. Since most of the water in fresh produce is free water, there will be continuous loss of water to the surrounding atmosphere. Therefore, it is important to consider relative humidity as a main

factor in the postharvest storage of fresh produce (Mishra and Gamage, 2007). The driving force for water loss from produce to its surroundings is the difference in water content between both. Exposure of fresh produce to a low humidity atmosphere can lead to transpiration, which will induce weight loss and shrivelling. At a temperature when the ambient relative humidity is the same as the humidity of the fresh produce, the driving force for water loss is reduced. However, even at 100% relative humidity weight loss can be observed due to the difference in temperature between the produce surface (attributed to the heat of respiration) and the air surrounding the package. For example, weight loss of 0.4-0.5 % when grapefruit was stored at 30 % RH was reduced to 0.3% at 90% (Alférez and Burns, 2004). The effect of relative humidity on quality decay of strawberry is more pronounced when the storage temperature is higher (Shin et al., 2007). High relative humidity helps reduce the rind breakdown of many varieties of citrus fruits (Techavises and Hikida, 2008).

However, exposure to very high humidity can cause condensation on the produce and packaging. As temperature is reduced, it is easier to generate air with high humidity. At lower temperature, fluctuations in temperature can lead to condensation. Free water on the surface of produce is favourable for microbial growth, which reduces shelf life (Hui and Evranuz, 2015). Thus, the ideal conditions need to be maintained by finding a balance between the rate of water vapour transfer from produce to surroundings through a permeable packaging film. Optimum conditions for the storage of fruit is 85-90% and 90-98% for most vegetables (Rahman, 2007).

2.2.2. Modelling of Modified Atmosphere Packaging System

Mathematical modelling is a tool for studying the relationships between system and process parameters and simulated outcomes. It is a flexible research method that

minimizes the number of experiments required to determine the influence of process parameters on product quality and safety (Smith and del Olmo, 2013).

Integrative mathematical modelling is an area of research that combining information into mathematical equations to predict the impact of various factors on food quality. It can also be used to aid packaging design in the food cold chain (Sousa-Gallagher et al., 2013; Sousa-Gallagher and Mahajan, 2013). Fig 2.2 shows a schematic diagram of the mathematical modelling approach followed in this thesis.

```
                        ┌─────────────────────┐
                        │ Problem Definition  │
                        └─────────────────────┘
                                  ↓
                        ┌─────────────────────┐                    Data
         Theory         │ Mathematical Model  │  ←──────
                        └─────────────────────┘          ┌──────────────────┐
                                  ↓                       │ Cold      Chain  │
  ┌──────────────────┐   Problem solving tools:          │ Variability:     │
  │ • Fruit Physiology│   Computers, Statistics,          │ RH          and  │
  │ • Heat Transfer  │    numerical methods.             │ temperature      │
  │ • Mass Transfer  │            ↓                       │                  │
  │ • Quality        │   ┌─────────────────────┐         │ Product          │
  └──────────────────┘   │ Numerical or Graphical│        │ Variability:     │
                        │      Results        │         │ Initial quality and│
                        └─────────────────────┘         │ respiration   rate │
                                  ↓                       │ parameters.      │
                        ┌─────────────────────┐         └──────────────────┘
                        │ Variability Assesment│
                        └─────────────────────┘
                                  ↓
                        ┌─────────────────────┐
                        │  Model Validation   │
                        └─────────────────────┘
                                  ↓
                        ┌─────────────────────┐
                        │   Implementation    │
                        └─────────────────────┘
```

Fig 2.2 Schematic diagram of the mathematical modelling approach used

Fig 2.3 shows the schematic diagram of a modified atmosphere packaging (MAP) system. MAP system is a dynamic system in which the metabolic processes within the fresh produce, package environment and external environment drive the transport

processes within the system. The fresh produce is enclosed in a protective tray covered with a permeable packaging film. The packages are usually stored in cold store or ambient conditions. If the relative humidity inside the package is high and the water vapour permeation rate in the film is low, condensation on the produce's surface and package's walls can occur, leading to microbial contamination. Condensation of water vapour on the package's walls can hinder its permeability properties, resulting in unfavourable modified atmosphere conditions. Low humidity can lead to transpiration damage, high water loss and shrivelling of the fresh produce surface (Techavises and Hikida, 2008). In addition, freshly harvested fruit or handled fruit show an increase in gas exchange rates (Kader and Saltveit, 2003).

2.2.3. Mass transfer

A basic law of physical science is the mass conservation law. It states that mass can neither be created nor be destroyed (Bird, 2002). Hence, the mass of material entering a process must be equal to the mass leaving the process. A simple mass or material balance equation is based on the following equation:

$$Input = Output + Accumulation \qquad\qquad 2.1$$

In the case of the steady flow of fluids, the accumulation rate will be zero. Thus, the input rate will be equal to the output rate. Molecular transport refers to the transfer of individual molecules across a fluid by means of random movement. The diffusion of gas molecules of CO_2, O_2, N_2, H_2O through the packaging film and the accumulation or depletion in the head space of modified atmosphere packaging are affected by the respiration rate of the fresh produce and the permeability of the MAP film. The water

vapour exchange rate in MAP is very important as it affects the relative humidity inside the package.

Transport of gases

The respiration process leads to consumption of oxygen and production of carbon dioxide. This continuous production and consumption creates various concentration gradients in the MAP system, and these gases are transferred from the system to its surroundings.

Each fresh fruit and vegetable are a complex biological system, which contributes to the uncertainties associated to mathematical predictions. The total production of carbon dioxide is partly due to the oxidative respiration and to fermentative metabolism (Hertog et al., 2001). Within fruits, there exists a continuous system of intercellular spaces. The gases within this intercellular network are referred to as internal atmosphere of the fresh produce. Gas exchange takes place between the internal atmosphere and the individual cells, where gases are consumed or produced, and the external atmosphere through produce-surface diffusion. Respiratory Quotient (RQ) is defined as the ratio of CO_2 produced and O_2 consumed during respiration (Barbosa et al., 2011; Kader et al., 1989). RQ is affected by CO_2 fixation, incomplete oxidation and storage conditions. At high O_2 levels, aerobic respiration prevails. In this case, the RQ depends on the type of substrate being consumed, and its value remains close to the unity. When the O_2 concentration is low, fermentation can occur develop and increase RQ. As fermentation increases, the CO_2 production increases in relation to the O_2 consumption. Besides the effect of O_2 on respiration and fermentation, CO_2 is also known to inhibit gas exchange in some fresh produce. In climacteric produce, a respiration burst can be observed when fruit starts to ripen.
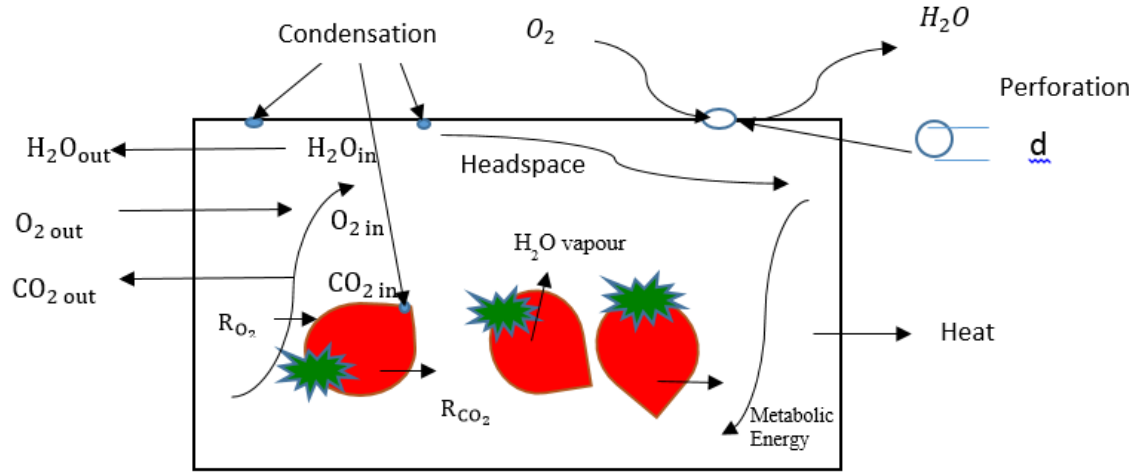
Fig 2.3 Modelling of fluxes of a MAP system (Sousa-Gallagher et al., 2013)**.**

Gas exchange is considered a function of O_2 and CO_2 levels. An additional driving force is the effect of atmospheric composition surrounding the product. The driving force for diffusion is a result of the difference in partial pressure for CO_2 and O_2 between the produce's surface and the external atmosphere generated by gas exchange. The largest resistance to the gas diffusion from the external environment to the fresh produce is offered by the produce's skin (Hertog et al., 2001).

$$\begin{pmatrix} Rate\ of\ O_2 \\ accumulation\ in\ the \\ package\ atmosphere \end{pmatrix} = \begin{pmatrix} Rate\ of\ O_2 \\ permeation\ through \\ packaging\ film \end{pmatrix} - \begin{pmatrix} Rate\ of \\ respiratory\ O_2 \\ consumption \end{pmatrix} \quad 2.2$$

$$\begin{pmatrix} Rate\ of\ CO_2 \\ accumulation\ in\ the \\ package\ atmosphere \end{pmatrix} = \begin{pmatrix} Rate\ of \\ respiratory\ CO_2 \\ production \end{pmatrix} - \begin{pmatrix} Rate\ of\ CO_2 \\ permeation\ through \\ packaging\ film \end{pmatrix} \quad 2.3$$

The gas permeation through the film was considered as a series model between film and perforation permeations:

$$\begin{pmatrix} Rate\ of\ gas \\ permeation\ through \\ packaging\ film \end{pmatrix} = \begin{pmatrix} Rate\ of\ gas \\ permeation\ through \\ permeable\ film \end{pmatrix} + \begin{pmatrix} Rate\ of\ gas \\ permeation\ through \\ perforations \end{pmatrix}$$

2.4

Transport of water vapour

The internal atmosphere of fruits and vegetables may be considered to be fully saturated with water. The diffusion of water vapour from the produce to the atmosphere behaves similarly to CO_2 and O_2 diffusion. Water loss is driven by the difference in partial pressure for water vapour between the fruit and the external atmosphere. Water loss is an important issue related to the quality of fresh produce. Moisture transpires continuously from the surface of the commodity during postharvest handling and storage. Moisture loss governs the weight loss, shrivelling and texture loss and is also responsible for generating conditions that can lead to microbial growth in the package (ASHRAE, 2001; Becker et al., 1996).

Transpiration of water from the commodity's surface is driven by the water vapour pressure difference between the commodity and the atmosphere surrounding it. As the fresh produce's surface is considered to be saturated, the water pressure at the commodity's surface is equal to the saturated vapour pressure (Becker and Fricke, 1996a).

Evaporation of water vapour takes place from the produce's surface, when the vapour pressure is higher than that of the atmosphere surrounding the commodity. The solutes present in the cell sap lowers the vapour pressure of the sap. However, the cell membrane is semi-permeable, which restricts the movement of solutes out of the cell.

Liquid exposed to evaporation has low solute concentration but higher vapour pressure (Becker and Fricke, 1996b). Evaporation is an endothermic process as it tends to cool down the surface of the produce, whereas respiration increases the temperature of the commodity's surface, raising the vapour pressure and increasing transpiration.

At any given temperature the air can hold only a certain amount of water vapour, above which the water vapour condenses to form liquid water. Condensation of water droplets occurs on any surface that has temperature below the dew point of air (McHard et al., 1991).

$$\begin{pmatrix} Rate\ of\ moisture \\ accumulation\ in \\ package\ headspce \end{pmatrix} = \begin{pmatrix} Rate\ of \\ moisture\ loss \\ from\ fruit \end{pmatrix} - \begin{pmatrix} Rate\ of\ moisture \\ permeated\ through \\ packaging\ film \end{pmatrix}$$

$$- \begin{pmatrix} Rate\ of\ moisture \\ condensation\ on \\ fruit\ surface \end{pmatrix} - \begin{pmatrix} Rate\ of\ moisture \\ condensation\ on \\ packaging \end{pmatrix} \qquad 2.5$$

$$\begin{pmatrix} Rate\ of\ moisture \\ permeated\ through \\ packaging\ film \end{pmatrix} = \begin{pmatrix} Rate\ of\ moisture \\ permeated\ through \\ permeable\ film \end{pmatrix} + \begin{pmatrix} Rate\ of\ moisture \\ permeated\ through \\ perforation \end{pmatrix}$$

$$2.6$$

2.2.4. Heat Transfer

In an ideal mathematical model of a MAP system, all forms of heat transfer (conduction, convection, radiation, evaporation and condensation) would be identified. As the product is cooled down, the heat from the produce is transferred to its surface by conduction. From the produce's surface, heat is transferred to the surrounding atmosphere by convection and by evaporation of water vapour. Heat transfer from produce to produce

is possible by conduction or radiation. If the package is unventilated, diffusion and unforced convection are the dominant heat transfer phenomenon within the package's atmosphere. Heat transfer to the packaging wall occurs by convection, conduction or condensation of water vapour. In case of perforation, heat transfer takes place through the perforations.

$$\begin{pmatrix} Rate\ of\ energy \\ accumulation\ in \\ package\ atmosphere \end{pmatrix} = \begin{pmatrix} Rate\ of\ convective \\ heat\ transfer\ at \\ the\ fruit\ surface \end{pmatrix} + \begin{pmatrix} Rate\ of\ evaporative \\ heat\ loss\ at\ fruit \\ surface \end{pmatrix} -$$

$$\begin{pmatrix} Rate\ of\ heat\ transfer\ due\ to \\ permeation\ of\ water\ vapour \\ through\ perforations\ in\ film \end{pmatrix} + \begin{pmatrix} Rate\ of\ heat\ conduction \\ through\ packaging\ walls \end{pmatrix} \qquad 2.7$$

2.3. Existing research to model quality of fresh produce

The ability to predict the point at which fresh produce has reached the end of its shelf life is important to industry for trade and export. The factors determining the loss of fresh produce include microbiological, physical and chemical factors, the processing method used, the packaging and the environment surrounding the produce (Kilcast and Subramaniam, 2000). The most obvious attribute perceived by the consumer for the quality of fresh produce is the sensory properties. Quality of produce is subject to its external appearance attributes such as colour, shape, texture, smell and flavour (Brosnan and Sun 2004; Vigneault and others 2009). Most commonly observed physical deteriorative changes taking place in fresh produce are mechanical damage and shrivelling. These attributes are highly influenced by the postharvest management and storage conditions. Kinetic modelling of chemical and biological phenomena studies the changes in time of those properties, which can be captured in a mathematical model containing kinetics parameters and possibly rate constants. In many cases, those rate

constants have a temperature dependence characterised by activation energies. In this way, modelling food quality attributes means modelling kinetic changes in the quality of food over time (Van Boekel, 2008).

The changes in the fresh produce quality properties represent the behaviour of the produce in its environment. In the case of packed produce, dynamic modified atmosphere package mathematical models describe the changes in the environment in which it is stored (e.g., MAP). The interaction between packaging material and the environment affects the environment inside the package, which ultimately affects produce quality. For non-packed produce, the environmental conditions at successive time points are taken into account (Sloof et al., 1996).

While it is possible to model all the changes that take place in a MA package at all levels, such a model will be difficult to operate as it needs to be fully parametrised. The mathematical model can be optimised depending upon the specific issue that needs to be addressed (Hertog and Banks, 2003). Some significant models that have been used to assess modified atmosphere packaging are mentioned below:

i) Fishman et al, (1996) developed a mathematical model for perforation mediated MAP for mango (cv. Keitt), taking into account the respiration and transpiration rate. Michaelis-Menten equations have been applied to describe the respiration rate as a function of O_2 concentration. Fick's law of diffusion was used to describe the flux of water vapour through the fruit surface. The model comprised a theoretical analysis of gas permeation through the perforated film. This was aimed at optimizing the storage conditions for mango fruit.

ii) Hertog et al. (1999) modelled the keeping quality of strawberry (cv. *Elsanata*) packed under modified atmosphere. The quality change rate was dependent upon the temperature and metabolic rate of strawberry. Michealis-Menten equations were used to

model the gas concentration in the package as a function of concentration of gases (O_2 and CO_2) and temperature. The calibrated model was used to optimise package and transport conditions.

iii) A respiration-transpiration model was developed by Song et al. (2002), which described simultaneous respiratory and transpiratory behaviour of MAP-packed blueberry (*Vaccinium corymbosum* L.). The respiration rate was modelled using a Michaelis-Menten-type respiration model. The model was based on heat and mass transfer balances accounting for respiration and transpiration. The heat balance took into account the internal heat, external heat, latent heat of moisture vaporization and sensible heat for increasing the produce's temperature. The mass balance considered the amount of water and gases produced and consumed by the fresh produce and the moisture and gases permeated through the film. The model aimed at designing an ideal MAP system for blueberry storage. The results indicate that the existing commercial films cannot control the relative humidity within the headspace below 100 %.

iv) Techavises and Hikida (2008) developed a mathematical model to simulate O_2, CO_2, N_2 and H_2O vapour exchanges in a modified atmosphere package with macroscopic perforations. Fick's first law of diffusion was used to model the gas and water vapour exchanges through the polymeric film and the perforations. Gas and water vapour exchange through a permeable package depends on the combination of rate of respiration and transpiration by the produce and on the permeation of the film and perforations to gas and water vapour exchange. An empirical equation was used to predict the effective permeability of a thin macroscopic perforation as a function of perforation diameter. The MAP model along with the effective permeability model yielded a good prediction of gas concentration and RH.

v) A complete mathematical model of perforation mediated modified atmosphere packaging was developed by Rennie and Tavoularis (2009a), considering respiration, transpiration, condensation, heat transfer and diffusive transport of gases. The computational domain was divided into four subdomains: the ambient storage environment, the perforations, the layer of fresh produce, and the package headspace. The model used Michaelis-Menten equations to predict the fresh produce's respiration rate. The temperature of the gas mixture and the temperature of surface of commodity was modelled using the energy balance equation. Transport of oxygen, carbon dioxide, nitrogen and water vapour were modelled employing the Maxwell- Stefan equations coupled with Darcy and Navier-Stokes equations. The general and fundamental approach to the model development allowed it to be employed for the modelling of storage conditions.

vi) Xanthopoulos et al. (2012) developed a space and time-dependent mathematical model to predict the headspace concentration of gases (O_2, CO_2, N_2 and H_2O) in perforated MA packed strawberries. The model included the mass transport mechanism (transpiration, respiration and diffusive transport). The respiration rate was modelled using the Michaelis-Menten equation, considering uncompetitive inhibition of CO_2 for O_2 production rate and the combination of an oxidative and fermentative process for CO_2 production rate. The transpiration rate was modelled using water vapour pressure deficit between the surface of produce and its surroundings as the driving force. The Maxwell-Stefan diffusion equation was used to calculate the mass fraction of gases in the headspace.

Table 2.2 Existing modified atmosphere packaging mathematical model

Model	Model description	Reference
MAP model for perforation mediated packaging.	Michaeles-Menten equation to describe respiration rate, Fick's law of diffusion for transpiration rate	Fishman et al., (1996)
Spoilage of strawberry packed in MAP	Spoilage of strawberry depending on temperature and relative metabolic rate.	Hertog et al., (1999)
Respiration-Transpiration model	Michaeles-Menten equation to model respiration rate and heat and mass transfer balances to determine temperature change in package.	Song et al., (2002)
MAP model to predict gas concentration and RH	Fick's law of diffusion to model gas and water vapour exchange to predict effective permeability across packaging film.	Techavises and Hikida, (2008)
Overall MAP mathematical model	Michaeles-Menten equation for respiration rate, transpiration, condensation, heat transfer and diffusive transport of gases.	Rennie and Tavoularis, (2009b, 2009a)
Changes in quality of mushroom packed in MAP	Space and time dependent mathematical model to predict gases (O_2, CO_2, N_2 and H_2O) for packed strawberries.	Oliveira et al., (2012)

vii) A mathematical model was developed for button mushrooms (*A. bisporus*) to design an optimal packaging system and predict its shelf life. The Weibull model was

used to predict the kinetics degradation of quality parameters as a function of time.(Oliveira et al., 2012).

These mathematical models have helped in designing optimal packaging scenarios for different fresh fruits and vegetables based on their characteristics aiming at an extended shelf life. However, they fail to take into account the variability associated with the fresh produce and the storage conditions. Modelling this variability will help quantify losses and the causes behind them, in a way that interventions can be introduced to reduce waste in the supply chain.

2.3.1. Existing tools to assess losses in supply chain

Mathematical modelling packaging and quality attributes

Frisbee (Food Refrigeration Innovations for Safety, Consumer's Benefit, Environmental Impact and Energy Optimization) software was developed as a tool for assessing the quality and safety of produce, energy use and global warming impact of refrigeration technologies along the cold chain (Gwanpua et al., 2015) (http://frisbee-wp2.chemeng.ntua.gr/coldchaindb/index.php). Different areas of expertise are required to develop a mathematical tool that account for losses in the supply chain. Such areas are cold chain sustainability, food refrigeration operations, food microbiology, food quality, postharvest technology, energy modelling and software development. Frisbee can be used by consumers, retailers, logistics companies and manufactures of refrigeration equipment to evaluate their cold chain. The software produces a time-temperature history that simulates real cold chain conditions and the predicts product quality in term of its shelf life at different stages of the cold chain. Shelf life is estimated by taking into account the impact of process variables and technology on the quality of fresh produce, energy consumption and impact of refrigeration system on global warming

TAILORPACK is another free decision system software used to design adequate packaging for fresh produce in the supply cold chain from production to retail. This mathematical model is built on mass balances between the gas exchange flux through the packaging film and O_2 consumed and CO_2 produced through respiration. (http://www.tailorpack.com/#, UMR IATE, France). The model is based on the Michaelis-Menten equation for respiration of produce and Fick's law for gas transfer, as mentioned in Cagnon et al. (2013). The tool can be run in two modes as available on the website: optimization and simulation. The headspace gas (O_2 and CO_2) concentration is simulated when the permeability characteristics of the film are provided. In the case of optimization, the optimal atmosphere for storage is obtained by simulation and the packaging's optimal permeability is predicted (Cagnon et al., 2013).

Another user-friendly software called PACKinMAP is used for designing MAP for fresh produce and minimally processed fruits and vegetables. The software can simulate perforation-mediated packaging and polymeric packaging films with macro perforations. To achieve the optimal atmosphere inside the package, it simulates the O_2 and CO_2 concentration for different combinations of film, area and thickness to determine the best packaging film. The objective is to obtain a suitable packaging film for a given product, its area and thickness, filling weight and equilibrium gas composition at isothermal and non-isothermal conditions. It accurately simulates the evolution of atmosphere composition for any type of temperature regime, simulates the conditions of real life distribution chains and tests the packaging's ability to withstand temperature abuse (Mahajan et al., 2007).

NextGenPack (Next Generation of Advanced Active and Intelligent Bio-based Packaging for Food) is an advanced system that uses the concept of active, intelligent and sustainable food packaging to develop eco-friendly innovative packaging for fresh,

minimally processed food and convenience food. It is used to design active and intelligent packaging. Mathematical equations that model mass transfer are coupled with a shelf life model to serve as a decision support tool. It also determines the efficacy, stability, safety, environmental impact and cost-effectiveness of the packaging (http://nextgenpack.eu/). Van Bree et al.(2010) developed a user-friendly software simulation tool that can be used to select or compare different packaging films with regard to their sensitivity to the product and the target shelf life. It simulates the oxygen concentration in the package's headspace over time according to the temperature profile. To model the consumption of O_2, the Michealis-Menten equation has been used. The effect of different packaging films, thickness, temperature and headspace volume on the concentration of oxygen (O_2) is simulated.

The gap in the present knowledge of tools to optimise MAP packaging should take into account the variability associated to it at every step in the supply cold chain. By evaluating the losses at each step, it will design possible interventions to prevent losses. There is a possibility to develop further the present state of the art by conducting a Life Cycle Analysis, which will help find sustainable solutions for reducing waste in the cold supply chain.

Table 2.3 Summary of existing tools to access losses

Tools for predicting losses	Brief description	Process modelled	Reference
Frisbee (Food Refrigeration Innovations for safety, consumer's benefit, environment impact and energy optimization)	A tool for assessing product quality and safety, energy use, and global warming impact of refrigeration technologies along the cold chain	Heat transfer model. Kinetic model for quality evolution, Energy use ad global warming impact assessment.	Gwanpua et al., (2015)
TAILORPACK	A tool to select the viability of the selected packaging.	O_2 and CO_2 partial pressure in headspace, permeability through film, respiration of fresh produce	Cagnon et al., (2013)
PACKinMAP	A tool to analyse the adequacy of various packaging systems to generate modified atmosphere for each packaged fresh whole/fresh cut product	O_2 and CO_2 concentration in headspace, permeability through film,	Mahajan et al., (2007)
NextGenPack (Next Generation of Advanced Active and Intelligent Bio-based Packaging for Food)	A tool for developing packaging and determine the efficacy, stability, safety, environmental impact and cost-effectiveness of the packaging.	Mass transfer model and shelf life assessment.	Pant et al., (2017, 2018)Bibi et al., (2017)
Software simulation tool for packaging and storage.	To predict the headspace oxygen concentration in different packaging configurations and storage conditions	Permeability through packaging, O_2 concentration in headspace	Van Bree et al., (2010)

Metabolic Profiling in postharvest supply chain

Metabolomics approaches are effective ways to investigate food quality and safety based on identification and quantification of characteristic metabolites (Cheng et al., 2015). This analysis can be targeted or untargeted. Targeted analyses focus on a specific group of intended metabolites, it is important for assessing the behaviour of a specific group of compounds in the sample under determined conditions. The metabolite profile of products meeting minimum quality standards can be used as a baseline for quality acceptance (Cevallos-Cevallos et al., 2009). Samples obtained during the different steps in supply chain can be used to compare with the baseline to determine the acceptability of the batch. Many quality parameters can be quantified using predictive models on sample metabolite profiles making it cost effective and time saving alternative to existing quality analyses. Metabolomics have the capacity to become single all parameters analysis tool (Kushalappa et al., 2008).

The major cause of quality loss in mushroom is colour which causes reduction in market value. Mechanical damage triggers the browning process within mushroom tissues changing the metabolic state of the mushroom. Chemometric tools were successfully applied to GC/MS data to predict damage in mushrooms. GC/MS coupled with chemometric methods have the ability to predict damage in mushrooms, with specific metabolites highlighted as possible markers of damage. Those markers could be used to further develop chemical sensors of early damage in production and export of mushrooms (O'Gorman et al., 2012).

Organic acids are important components in tomatoes that strongly influence their taste and overall quality. The metabolic profiling approach followed by Gemma characterized compositional changes occurring in tomato fruit during pre-harvest fruit development and ripening, and the subsequent postharvest shelf life. Changing the balance between organic

compounds like sugar, acids and glutamic acid will directly affect taste perception. Changes in the texture of the produce is due to the biochemical changes taking place in the cell wall (Oms-Oliu et al., 2011).

Significant advancements have been made to identify thousands of chemicals in fresh produce, to exploit its full potential there are still a significant number of chemicals that are yet to be identified. A further use case of this can be analysing the headspace gases to determine the chemical composition of the organisms that cause spoilage of fresh produce.

2.4. Variability and uncertainty assessment of the effect of cold chain in shelf life

In every batch of fresh produce some variation in properties are present, this variation affects the characteristics of fresh produce directly or indirectly. This change in the behaviour of fresh produce can lead to problem in handling and storing. The magnitude of variation in produce and the magnitude of batch needs to be calculated to predict the behaviour of fresh produce (Tijskens et al., 2003). Currently the horticulture industry is not capable of differentiating their postharvest interventions to an extent where biological variance can be taken into account. The dynamics of quality change and propagation of biological variance through the postharvest chain is required. Different sources causing biological variation needs to be identified and assessed. Not taking individual product behaviour into account while modelling can lead to inefficient estimation of means and misleading conclusions (Hertog et al., 2007b). Modelling variability provides a base to screen different products for fixed effect (cultivars, growers, and growing conditions) and also taking into account the full range of external influences observed. Finding the variation magnitude provides a base to screen different groups for fixed effects (cultivars, growers and growing conditions). This modelling approach can be applied to a single step or to the whole supply chain (Hertog et al., 2007).
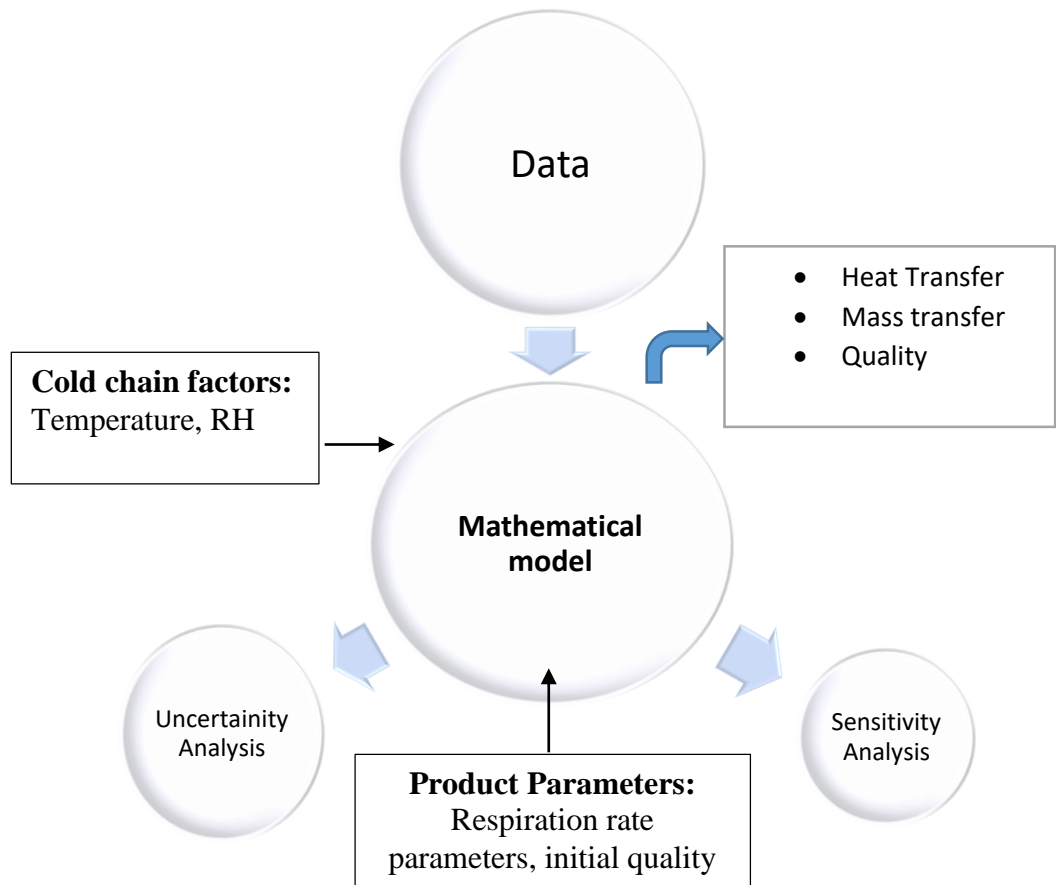
Fig 2.4 Approach followed to model, evaluate and access the cold chain scenario

Several techniques have been used to model variability in quality along postharvest chain (Hertog et al., 2004a, 2007b; Gwanpua et al., 2014; Duret et al., 2015). Mathematical models were developed by Hertog et al., (2004b) to interpret postharvest batch behaviour describing colour change as a function of time and temperature for tomato fruit, propagation of biological variance to analyse the experimental data on stem growth of Belgian endive (Hertog et al., 2007d) . Gwanpua et al., (2014) developed a model to cover the mechanisms involved with the loss of green background colour in apples, which can be extended to other fresh produce similar to those developed in the model. Including biological variance enhances the understanding of batch dynamics and it will prove to be of great commercial value to industries. (Hertog et al., 2004b). This

approach can potentially help models to optimise the operational quality of chain taking into account the quality of fresh produce including complete range of variance present (Hertog et al., 2007).

2.5. Modelling variability in distribution supply chain

Researches have modelled variability in the supply chain using a combination of stochastic and deterministic models to describe what they have called biological age variability. Biological variance is propagated in the dynamic quality change models to predict its effect during the postharvest supply chain. One of the main drivers for this is the demand for non-destructive measuring techniques that allow monitoring the individual produce over time (Hertog et al., 1999). Driven by the data reported on individual objects, several authors have started including biological variance into their statistical data (Aguirre et al., 2008; Gwanpua et al., 2014; Hertog, 2004, 2002; Tijskens and Evelo, 1994). After the identification of the source of variation, it can be linked to the quality property of the fresh produce. The changes in characterisations of fresh produce can be used to predict the divergent behaviour of batches while in supply chain. This information can be used to design sustainable supply chain with least waste produced.

To the best of our knowledge, no research has considered the relative importance of different variability components (both product and cold chain) in quantitative terms. Such assessment can help to elucidate how variability influences quality and ultimately the generation of waste in the food distribution chain.

2.5.1. Existing variability models

Several authors have used different techniques to model variability of changes in quality along postharvest chains (Hertog et al. 2004; Hertog et al. 2007; Gwanpua et al. 2014; Duret et al. 2015) (Table 2.2). Talasila et al. (1994) developed a mathematical

model to predict the frequency distribution of O₂ partial pressure in modified atmosphere packaging of fresh produce, which predicted that small variation in O₂ uptake and film permeability can cause large variations in the package's O₂ concentration.

Schouten et al, (2002) developed a mathematical model for chlorophyll breakdown and synthesis of chlorophyll during the storage of cucumbers. Baudrit et al. (2009) modelled variability propagation in weight loss during cheese ripening . The change in the colour of tomatoes during storage was modelled using the logistic function (Tijskens et al., 2003).

$$col = col_{min} + \frac{col_{max} - col_{min}}{1 + e^{-k(t + \Delta t)}} \qquad\qquad 2.8$$

Where, col represented colour, k was the rate constant for the colour development. The dependence of rate constant on the temperature (K) was modelled using Arrhenius' Law, Δt was the maturity at the harvest. Where, col_{min}, col_{max} represented the minimum and maximum colour values respectively. The rate constant k was same for all the individual produce in a batch, Δt is stochastic variable with a different value of individual produce at harvest.

Iqbal et al. (2009) studied the impact of respiration rate parameters on the concentration of oxygen and carbon dioxide concentration in the package headspace.. A model was developed for the loss of firmness in apple as a result of pectin breakdown by degrading enzymes as shown in Eq. 2.9 (Duret et al., 2015a).

$$\frac{dP}{dt} = -k_{pect}[P][E_{pect}] \qquad\qquad 2.9$$

Where, $[P]$ is the amount of unhydrolyzed pectin, k_{pect} is the rate constant of pectin breakdown and $[E_{pect}]$ normalised concentration of pectin degrading enzyme.

The variability models presented above are directed towards the effect of one source of biological variation. Integrating these models along with other packaging, quality degradation models to create an overall mathematical model can predict the losses in the supply chain.

Table 2.4 Quality parameters that are affected by the biological variance

Uncertainty	Produce	Reason	Reference
Colour	Tomato	Initial colour at harvest is not always uniform.	Hertog et al., (2004a)
	Jonagold apples		(Gwanpua et al., 2014)
	Avocado		Hertog, (2002)
L, a, b value	Mushroom		Aguirre et al., (2008)
Stem growth	Belgian endive	Large variation in terms of size of chicory head and length of stem.	Hertog et al., (2007c)
Shrivel	Apple	Due to different structural variation, individual apples have different values of water vapour permeation	Hertog, (2002)
Stress crack development	Corn grains	Size of the grain leading to different length of diffusion pathway of water vapour	Hertog, (2002)
Firmness	Apples, mushroom	Initial firmness at harvest is not always uniform.	Duret et al., (2015a; Mohapatra et al., (2010)
Weight	Mushroom	Initial weight is not uniform	Aguirre et al., (2008)

2.6.   Sustainable supply chain

Sustainable food chains refer to those that provide healthy, safe produce to the consumers in response to the market demand. They should operate within the biological limits of the natural resources to be able to achieve high standards of environmental performance by reducing energy consumption (Smith, 2008). For obtaining a long term sustainable food chain in developing countries, investments in advanced postharvest handling systems can reduce food losses generated throughout the supply chain. In developed countries, the problem lies at the retail, distribution and household level (Kader 2004; Parfitt and others 2010).

In the context of fresh food with short shelf life, losses can be reduced by predicting changes in quality of fresh produce and thus ensuring that the product reaching the consumer is of the highest quality. Reducing the waste produced at every step in the distribution cold chain is an important factor in terms of sustainability. Improving sustainable performance requires changes in the whole supply chain, not only at the point where the problem occurs. Efficient supply chains need to be tailored according to the specific characteristics of the fresh produce. Innovative technologies throughout the fresh food supply chain, particularly in relation to packaging, that takes into account uncertainties caused by biological factors have higher potential to ensure produce quality and therefore reduce losses (Hertog et al., 2011).

There is a need to design more robust and sustainable supply cold chains in order to reduce waste and create a sustainable supply chain. Designing optimal MA packaging for fresh fruits and vegetables based on their characteristics is helpful in reducing the waste produced due to short shelf life.   To take into account the effect of biological uncertainty on the quality of fresh produce and the losses associated with it, mathematical

models considering uncertainty propagation during simulation will provide a prediction associated with an uncertainty component. When accounting for the uncertainties associated with the supply of fresh produce, the information gap can be filled. Such approaches can be adopted to predict the waste produced in the distribution supply chain of fresh produce packed in modified atmosphere packaging. This will enable us to design interventions to reduce food waste and create a more sustainable supply chain.

2.7.　　Aim and Objectives

The main aim of this work is the development of an efficient simulation model for the quality assessment of produce packed in modified atmosphere packaging during the supply cold chain of three perishable products: mushrooms, strawberry and tomatoes. With this purpose, the following objectives have been setup:

- To model the oxygen consumption and carbon dioxide production rate of mushroom, strawberry and tomato as function of O_2 and CO_2 concentration in the package's headspace and its dependence on temperature.

- To model the heat and mass transfer processes that affect shelf life in modified atmosphere packaging (MAP).

- To identify different design and environmental factors that may have a significant effect on the modified atmosphere package.

- To assess the effect of the known variability/uncertainty sources on the quality and/or safety of these produces.

- To identify the relative importance of different elements in the cold chain associated to the decay in quality and shelf life in order to search for further optimisations.

- To propose and validate interventions that may improve shelf life and/or prevent waste.

Chapter 3.   Impact of variability on quality of mushrooms in MAP during distribution cold chain

The findings of this chapter were published in Joshi et al. (2018)

3.1.   Introduction

Mushrooms are a highly perishable produce because of the absence of a cuticle to protect them from mechanical damage, microbial attack and quality loss. The susceptibility of mushroom to microbial attack and enzymatic browning is ascribed 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, which also responds to the emerging consumer demand for convenience and quality. MAP alters the atmosphere inside the package, it relies on transfer of gases through the packaging film, resulting in an atmosphere rich in CO2 and deficient in O2 (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). A concentrations of CO_2 higher than 12 % can result in quality degradation due to browning, while a O_2 concentration lower than 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, therefore the 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.

The quality characteristics of mushroom are visual appearance, colour, freshness, microbial growth and weight loss (Aguirre, 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 by 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).

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 biological variance and ignoring these biological variances can lead to misleading conclusions.

Natural variability of mushrooms

All fresh produce possesses a large inherent variability. Management of biological variability is challenging to industry. The variability is controlled as much as possible by sorting and grading the product after harvest (Hertog et al., 2004b). A batch of produce is defined as all the individual produce sharing growth history implying same harvest date, grower and cultivar. Variation during storage would be negligible if all the produce was harvested at the same biological age (Hertog, 2002). This would make deciding the acceptability of batch easy as all produce would show the same quality characteristics. However, mushrooms are not harvested with such homogeneity, therefore some items will degrade sooner.

Biological variation is a combination of biological properties that differentiate individual units of a batch. Attribute variation directly or indirectly affects the quality of a produce, rendering it unacceptable during distribution (Tijskens et al., 2003). Keeping the storage conditions constant during storage and distribution will help eliminate the biological variability.

The main objective of this study was to develop a model for studying the effect of MAP design parameters on produce quality to find the waste generated during distribution. The effect of cold chain factors (temperature and relative humidity) and biological factors on the quality of mushroom packed in modified atmosphere during the distribution supply was assessed. A sensitivity analysis was carried out to quantify the effect of biological parameters on the shelf life.

The major challenge is to develop a predictive model that takes into account the uncertainty of the predicted results (Hertog et al., 2007d). Biophysical properties of the

skin, mass transfer coefficient, initial colour coordinates (L, a and b) and respiration rate parameters were analysed as variables affecting the quality of mushroom in the 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 changes in quality and loss during the distribution supply chain.

3.2.   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.

3.2.1.   Model hypothesis

- The material and energy balances arising from MAP packaging of mushrooms may be described using a compartmental model and lumped transfer coefficients.

- 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.

- Package walls are impermeable and perforated film was permeable to O_2, CO_2, N_2 and H_2O.

- Packaged produce and the gases inside package are in thermal equilibrium.

- The surface of the mushroom was assumed to be saturated (water activity≈1).

- 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.

- 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).

3.2.2. Mass Balance

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 was 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.

$$V_f \frac{d[O_2]_i}{dt} = 100 \times \left[\frac{A_{p1} P_{O_2} P_{atm}}{L_f} \left[\frac{[O_2]_o}{100} - \frac{[O_2]_i}{100} \right] - W_s r_{O_2} \right] \qquad 3.1$$

$$V_f \frac{d[CO_2]_i}{dt} = 100 \times \left[\frac{A_{p1} P_{CO_2} P_{atm}}{L_f} \left[\frac{[CO_2]_o}{100} - \frac{[CO_2]_i}{100} \right] + W_s r_{CO_2} \right] \qquad 3.2$$

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.

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. 3.3.

$$\frac{dm_{pr}}{dt} = \left[\frac{P_{H_2O} A_p (p_i - p_o)}{L_f} \right] \left[\frac{0.018 P_{atm}}{R T_s} \right] \qquad 3.3$$

When the water vapour pressure inside the package (P_i) is less than or equal to the saturated vapour pressure (P_s), the moisture is permeated from the film to its surroundings. Inversely, when P_i is higher than the saturated vapour pressure, condensation will occur and the latent heat of condensation will rise the produce's temperature.

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)**)**

$$\frac{dHR}{dt} = \frac{t_r - m_{pr}}{W_a} \qquad\qquad 3.4$$

The relative humidity in the headspace can then be estimated as the ratio of the humidity ratio inside the package at any time (eq. 3.4) to the humidity ratio of saturated water vapour (HR_{sat}) at the same temperature eq. 3.5 (Becker et al., 1996).

$$HR_{sat} = \frac{0.62198 p_s}{(P_{atm} - p_s)} \qquad\qquad 3.5$$

3.2.3. Heat Balance

The temperature of surface of produce and gases surrounding it in headspace was 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.

$$Q_r W_s + Q_{con} + h_p A_p (T_o - T_i) = Q_{tr} + W_s C_s \frac{dT_s}{dt} + W_a C_a \frac{dT_s}{dt} \qquad 3.6$$

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

$$\frac{dT_s}{dt} = \frac{Q_r W_s + Q_{con} + h_p A_p (T_o - T_i) - Q_{tr}}{W_s C_s + W_a C_a} \qquad\qquad 3.7$$

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. 3.8 (Becker and Fricke, 1996b; Fonseca et al., 2002).

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2816kJ \qquad\qquad 3.8$$
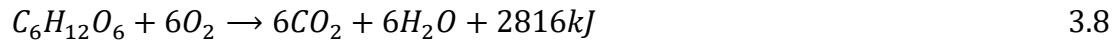
Respiration Rate

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., 2009b; Lu et al., 2013).

$$r_{O_2} = \frac{V_{mO_2}[O_2]}{K_{mO_2} + (1 + [CO_2]/K_{iO_2})[O_2]} e^{\left(\frac{-E_{O_2}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right)} \qquad\qquad 3.9$$

$$r_{CO_2} = \frac{V_{mCO_2}[O_2]}{K_{mCO_2} + (1 + [CO_2]/K_{iCO_2})[O_2]} e^{\left(\frac{-E_{CO_2}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right)} \qquad\qquad 3.10$$

The parameters used in calculation of r_{O_2}, r_{CO_2} are given in Table 3.1 and Table 3.3. 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, 2009b).

$$Q_r = \frac{2816}{6} \times \frac{r_{O_2} + r_{CO_2}}{2} \times \alpha \times W_s \qquad\qquad 3.11$$

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 was 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. 3.12.

$$P_i = P_{i\,ref} + \frac{\pi R_h^2 \times D_{i,air}}{(L_f + R_h)} \times N_h \qquad\qquad 3.12$$

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.

3.2.4. 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. 3.13, 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.

$$VPD = (a_w - RH)p_s \qquad 3.13$$

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 (m_w) is expressed as the product of the transpiration coefficient and water vapour pressure deficit as eq. 3.14 (Becker et al., 1996; Xanthopoulos et al., 2012).

$$m_w = VPD \times K_t \qquad 3.14$$

The transpiration rate (t_r) is product of the water vapour flux (m_w) and the surface area of the commodity(A_c) eq. 3.20.

$$t_r = m_w A_c \qquad 3.15$$

$$K_t = \frac{1}{\left(\frac{1}{K_s} + \frac{1}{K_a}\right)} \qquad 3.16$$

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 eq. 3.23 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);

$$p_s = 0.041081186T_s^3 - 32.43188T_s^2 + 8567.5269T_s - 757070.1 \qquad 3.17$$

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.

$$Q_{tr} = \lambda\, t_r \hspace{9cm} 3.18$$

3.2.5. 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. 3.19 (Jalali et al., 2017; Rennie and Tavoularis, 2009b)

$$M_{con} = \begin{cases} K_a(p_{i-}\, p_c)\delta A_c\,, & if\,(p_i > p_c) \\ 0 & otherwise \end{cases} \hspace{3cm} 3.19$$

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

$$A_c = d_c \times W_s{}^b \hspace{9cm} 3.20$$

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.

$$M_{wcon} = \begin{cases} K_a(p_{i-}\, p_s)\delta A_w\,, & if\,(p_i > p_s) \\ 0 & otherwise \end{cases} \hspace{3cm} 3.21$$

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

$$Q_{con} = \lambda \times (M_{con} + M_{wcon}) \hspace{7cm} 3.22$$

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

$$K_a = 2 \times D_{H_2O} \times \frac{M_{H_2O}}{d_c \times R \times T_s}$$ 3.23

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

$$\lambda = (3151.37 + (1.805 \, T_s) - (4.186 \, T_s)) \times 1000$$ 3.24

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

$$h_p = \frac{0.59 A_{p1}\left(\frac{T_i - T_o}{D_1}\right)^{0.25}}{A_p} + \frac{1.32 A_{p2}\left(\frac{T_i - T_o}{D_2}\right)^{0.25}}{A_p} + \frac{1.42 A_{p3}\left(\frac{T_i - T_o}{D_3}\right)^{0.25}}{A_p}$$ 3.25

3.2.6. 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).

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.

$$\frac{dq}{dt} = kq^n \tag{3.26}$$

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. 3.26.

$$k_L = (8.283477 \times 10^{-5}T_s) + (-7.181884 \times 10^{-4}RH) + \tag{3.27}$$

$$(-1.258058 \times 10^{-5}T_s\,RH) + (-2.278137 \times 10^{-5}T_s{}^2) +$$

$$(7.816388 \times 10^{-5}RH^2)$$

The mixed effect model estimated batch-to-batch and inside-batch variability components that are integrated in Table 3.3.

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.

$$\frac{dw}{dt} = m_{pr} + r_{CO_2} W_s M_C \qquad\qquad 3.28$$

3.3. Stochastic Simulation and Sensitivity Analysis

On the basis of the mathematical models developed in section 3.2, 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 3.1. 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).

3.3.1. Uncertainty assessment

1) Assessment of the impact of cold chain variability on waste production

A simulation scenario considering average product characteristics without variation and a variable cold chain was used to assess the importance of different transport and retail conditions. The history of export of four international cold chains between Ireland and the United Kingdom were used, comprising temperature and relative humidity data, including the production farm, the packaging house, international haulage, retail storage and arrival to the retail shop. This data was originally collected as part of a research innovation project in collaboration with industry. The data was collected using temperature and relative humidity dataloggers (XSense®, BT9 Intelligent Supply Chain Solutions, UK) with a logging frequency of 10 minutes. The experimental data 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 (Fig 3.1).

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 over 85 premises spread through the 26 counties in the Republic of Ireland, including open and close refrigerated cabinets in a supermarket, a deli shop and a butcher outlet in each county (Fig 3.2).

a)

b)
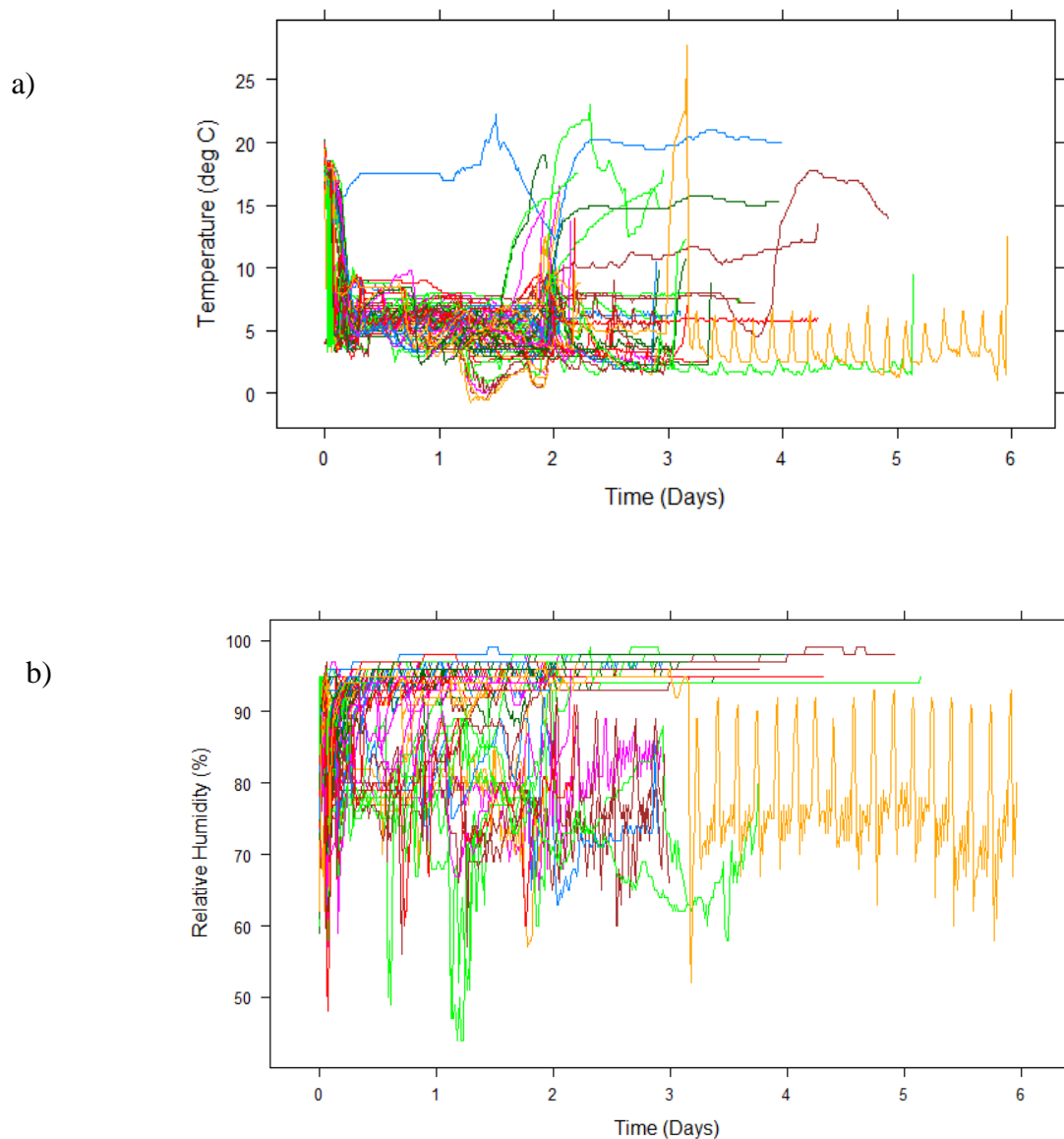
Fig 3.1 Export cold chain profile: a) Temperature and b) Relative humidity.

56

a)

b)
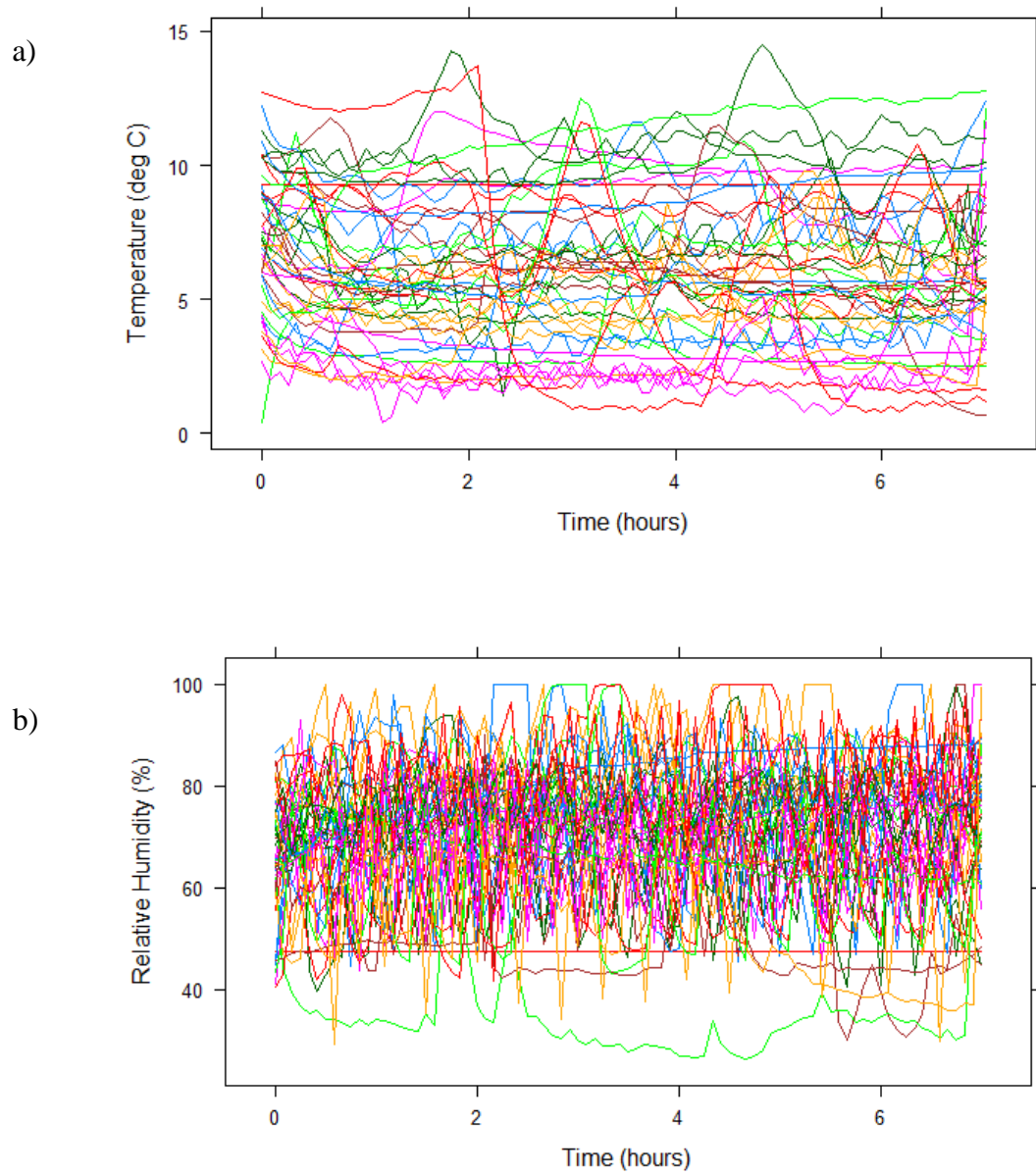
Fig 3.2 Retail cold chain profile: a) Temperature and b) Relative humidity.

The factors leading to uncertainty in the cold chain were the air temperature and the relative humidity variation. Fig. 3.1 shows the temperature and relative humidity export cold chain profile used in the study. Fig. 3.2 is the retail cold chain profile for temperature and relative humidity used in the study. The mathematical model was

simulated against these cold chain profiles to study the effect of cold chain uncertainty on the quality of produce. The results are presented in the following section.

2) Assessment of the effect of product variability on waste production

A simulation scenario considering full product variability and constant storage conditions was used to assess the relative effect of different product variability sources. The storage conditions tested involved:

- An ideal storage temperature of 4°C and relative humidity 80%.

- An abuse cold chain composed of the following steps: 1/2h packaging at 8 °C followed by transportation at 4 °C up to 1 day, followed by retail storage including 4h at 20 °C, followed by 1 day at 8 °C, and finalised by retail shop 4h at 20 °C 21h at 8°C

The product parameters responsible for the variability are presented in Table 3.1. The results in Section 3.5 shows the uncertainty due to the product parameters uncertainty on the quality parameters of strawberry.

3) Combined assessment of product and cold chain uncertainty effect on waste

This study contributes to the identification of the relative influence of different parameter uncertainties and the interventions that can be designed to maintain the quality and reduce the waste in supply chain. A sensitivity analysis was also carried out to access the effect of individual parameters on the produce quality, as explained in the next section.

3.4.   Validation Experiment

Mushroom trays (250g of white, closed cup, 2.5 - 4 cm in diameter) packaged in micro-perforated polypropylene film (8 perforations per package) were supplied by Monaghan Mushrooms Ltd. Samples were stored in an environmental chamber under abuse condition (Section 3.3.1) and ideal condition in a refrigerator (at 3 °C) for 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.

Table 3.1 Properties of package, film and produce

Parameter	Value
a_w	0.99
ρ_b (kg m^{-3})	561
C_s (J kg^{-1}K^{-1})	3990
$D_1 \times D_2 \times D_3$ (cm^3)	$11.9 \times 16 \times 5.8$
d_c (cm)	4
d_H (micron)	150
N_h	8
L_f (m)	33.9×10^{-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}

Source: (Borchert et al., 2014; Iqbal et al., 2009a; Lu et al., 2013; Mahajan et al., 2008; Rux et al., 2015; Simón et al., 2010)**.**

3.5. Results

3.5.1. Validation of the mathematical model

The model parameter estimates in Table 3.1 were used to compare the experimental and predicted results. The integrated mathematical model was used to simulate the quality conditions during the distribution supply chain. The experimental data used for validation were retrieved from a study by DIT and Monaghan Mushrooms Ltd. 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> 86 are classified as good quality and 80-85 as fair quality (González-Fandos et al., 2000) and < 70 would be generally rejected by the consumers (Kim et al., 2006). These L value thresholds were used as indicators to calculate the losses during the supply chain.

The mathematical model was able to predict the changes in L values during the distribution chain. The grey ribbon in Fig. 3.3 represents the uncertainty margins of 5% and 95% percentiles pertaining to the variable. It shows the experimental data with 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, regardless of the temperature simulations were done at abusive conditions (4^0, 8^0, 20^0 C). When simulated at the ideal storage temperature of 3^0 C the change in L value was between 95 and 89 Fig 3.3.

The weight variation was not large when the mushrooms are stored at 3°C. The change in moisture content of mushroom for the different temperatures (4^0, 8^0, 20^0 C) in Fig 3.4a with the experimental data falling in the predicted interval. Similar results were obtained at the ideal temperature (3^0 C) Fig. 3.4b. This shows the weight of mushroom was preserved in the packaging acting as a barrier.
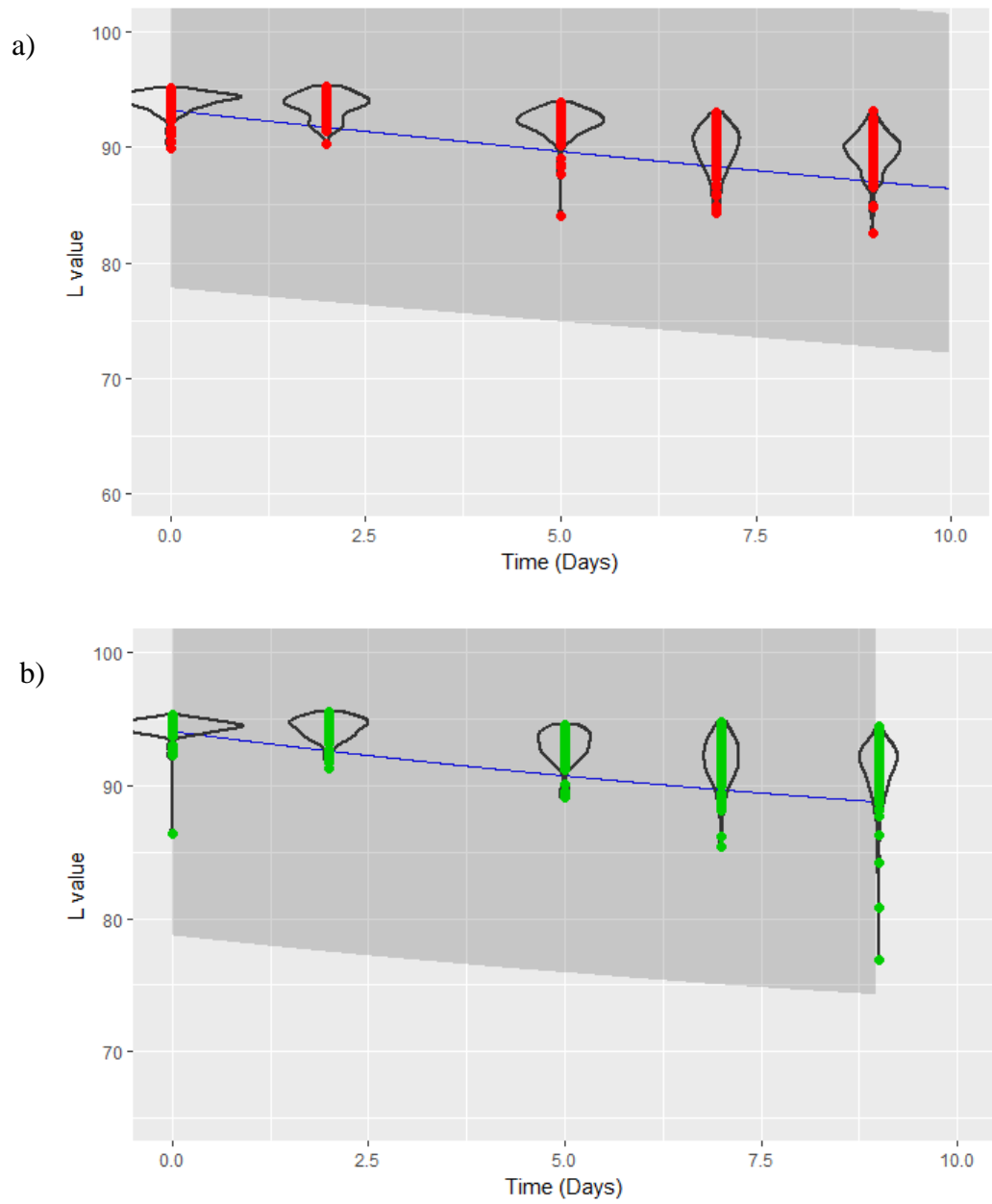
Fig 3.3 Comparison of Lvalue model predictions with experimental data points at (a) different abusive temperature conditions(4ºC, 8ºC and 20ºC) (red points) and (b) ideal temperature (green points).

a)

b)
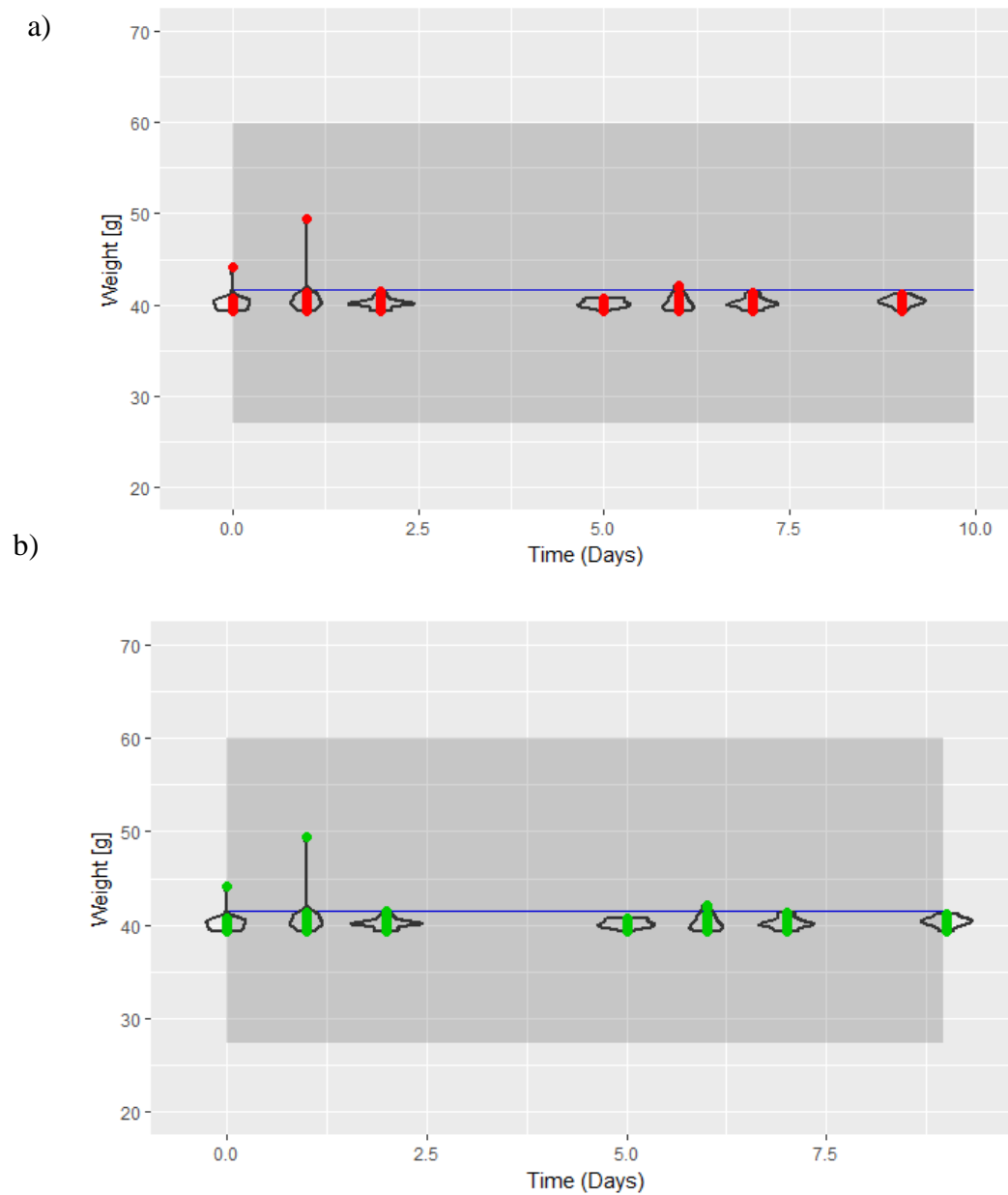
Fig 3.4 Comparison of weight of mushroom model predictions with experimental data points at (a) different abusive temperature conditions: (a) 4ºC, 8ºC and20ºC) (red points) and (b) ideal temperature (green points)

The comparison between experimental and predicted results are presented in form of bias factor and accuracy factor. A bias factor lower than one indicates that a model, in general, 'fail-safe'.

Table 3.2 – Bias and accuracy factors for the comparison between simulated and experimental data.

		Bias Factor	Accuracy Factor
L value	Abuse	0.9503	1.0598
	Ideal	0.9833	1.0388
Weight	Abuse	0.9687	1.0406
	Ideal	0.9916	1.0187

3.5.2. Cold chain variability assessment

The integrated mathematical model and the quality model presented in section 3.2 were used to simulate the quality conditions of mushrooms during the distribution supply chain. The governing ordinary differential equations were used to simulate the changes in gas concentration, temperature and relative humidity in the package headspace (eq 3.1 and 3.2).

Variations in the respiration rate of mushroom causes change in the concentration of O_2 and CO_2 in the package's headspace. CO_2 rises in the headspace from 0.03% up to 15%, while the O_2 concentration decreases from 21% to 2% (Fig. 3.5a) when simulated against the export cold chain profile. These results are in agreement with Cliffe-Byrnes and O'Beirne (2007) where O_2 concentration changes from 20 to 2 % when mushrooms were stored at 5 different temperatures (4^0, 8^0, 10^0, 13^0 and 16^0 C) representing abuse cold chain. 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. 3.5c shows the weight loss observed during the supply chain. The typical kinetic quality change (L value) during

the distribution supply chain in Fig. 3.5d. Jiang et al (2011) reported a drop in L values around 81.8 after 8 and 78.1 12 days storage respectively at 4^0 C in MAP, after which the product exceeds the threshold for acceptable quality for *Agaricus bisporus*.

a)
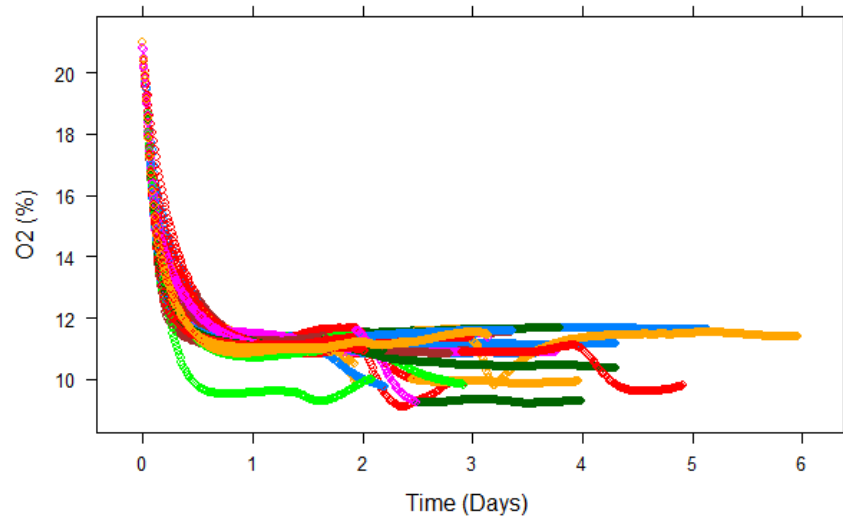
b)
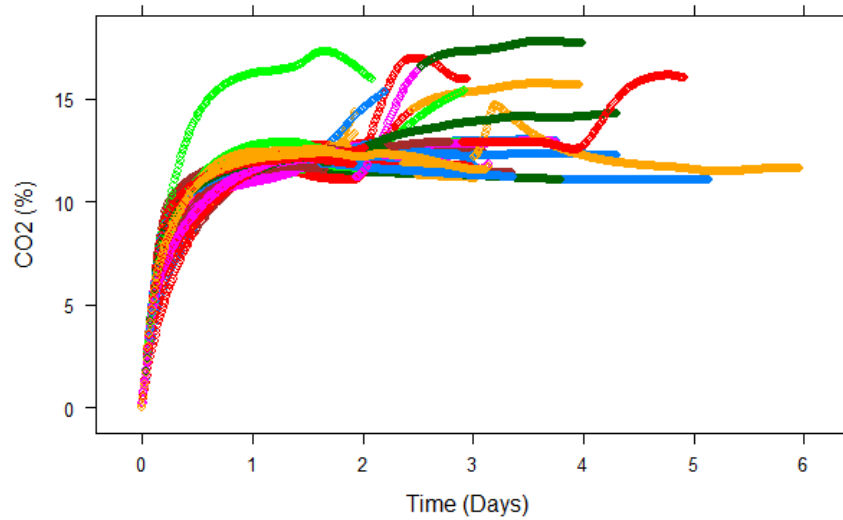
c)
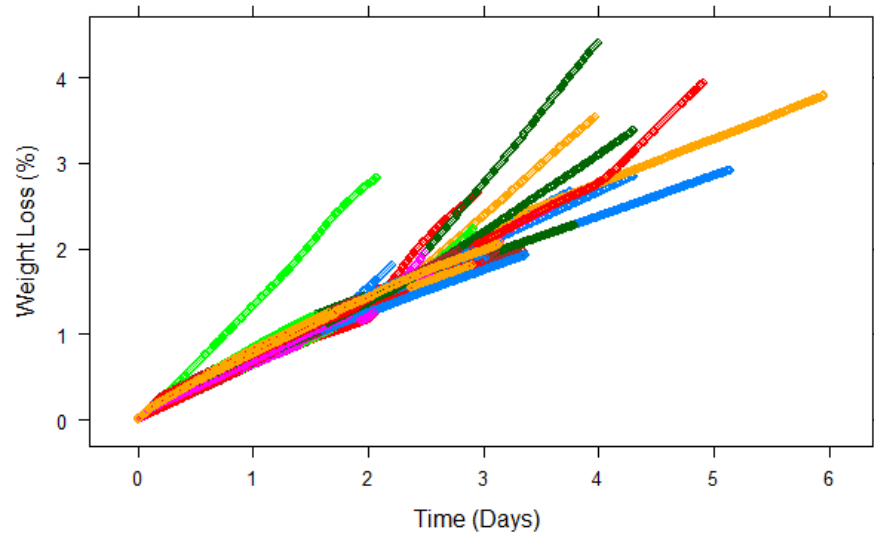
d)
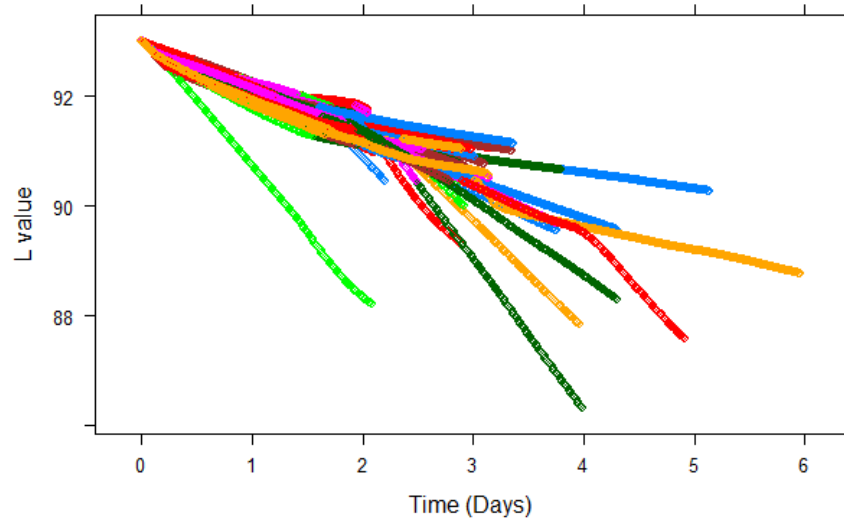
Fig 3.5 Prediction of the effect of cold chain variability parameters on: (a) O2 in the package's headspace, (b) CO2 in the package's headspace, (c) weight loss and (d) L value during the distribution supply chain.

3.5.3. Product variability assessment

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. For quality the biological variability was described by the initial colour values (L, a, b value), initial weight of the produce and the skin mass transfer coefficient (Table 3.3).

Table 3.3 – Estimated parameters and 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	8.5×10^{-3} (cm h^{-1})

The mathematical model was used to simulate and predict the effect of input product parameter uncertainty on the quality of mushroom. The time domain for simulation was 7 days at (3^0, 7^0, 15^0C). The optimal storage condition for mushroom 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 in Fig. 3.6a. The rate at which the propagation of the biological variation

increases depends directly on temperature. The variation observed at 15^0 C was larger than that in the other temperature.

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 3^0C and 7^0C as evident from Fig. 3.6b. However, anaerobic conditions are observed at 15^0 C after 5 days. Weight loss in mushrooms was mainly caused by transpiration of water from the mushroom's surface and CO_2 loss through respiration Eq 3.15. Greater weight loss was observed when the produce was stored at higher temperatures, this was due to an increase in transpiration and respiration rate of mushroom Fig. 3.6c. The effect of product parameters variation on weight loss in mushroom was not observed. Maximum weight loss of 2.47% was noted after 16 days of MAP storage at 4^0 C (Jiang et al., 2011). Roy et al (1995) reported a 3% of weight loss (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 was observed for the L value as evident from Fig. 3.6d. Based on the results obtained, the following conclusions can be reached. Lower temperatures during the supply chain distribution are preferred as the associated variation is lower, therefore the produce quality is better retained and losses during the distribution chain are reduced.

a)
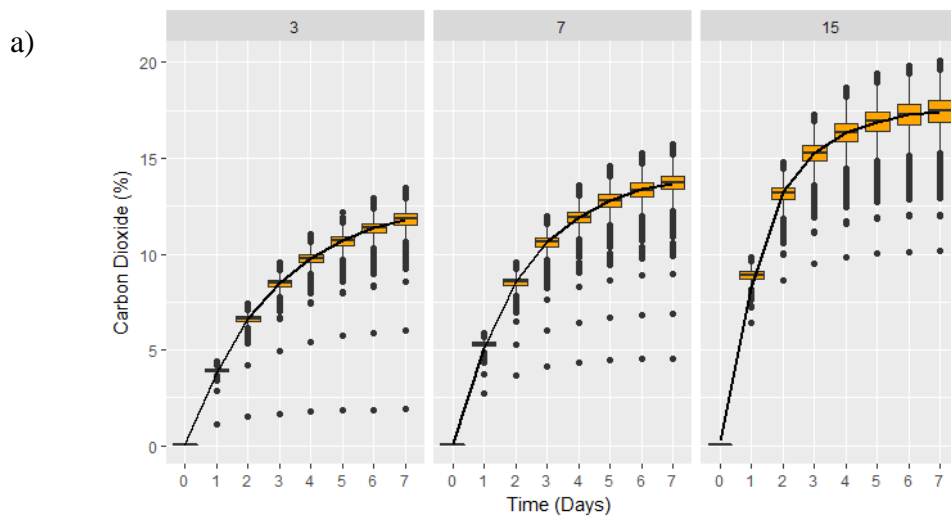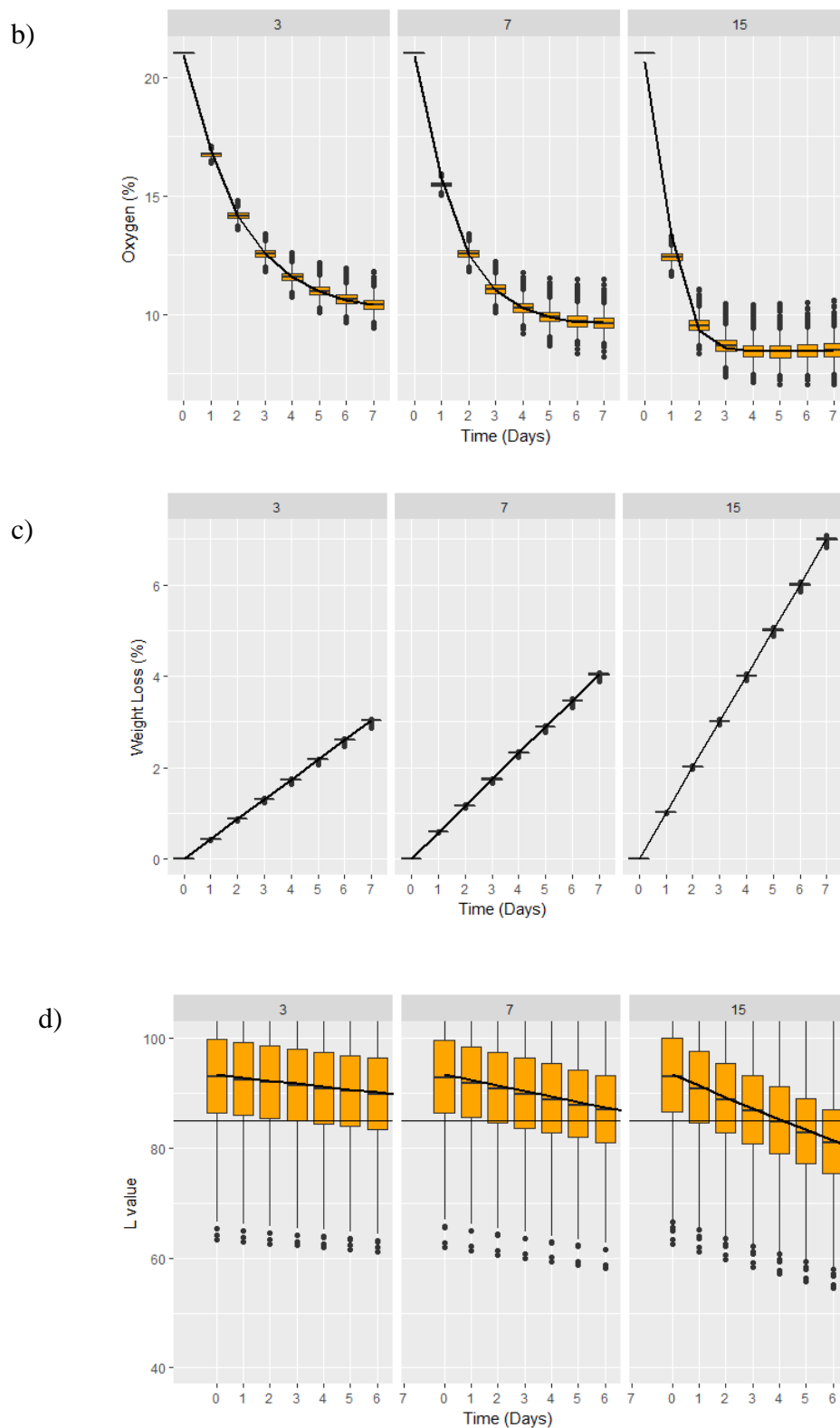
Fig 3.6 Propagation effect of product parameters on: (a) carbon dioxide concentration, (b) oxygen concentration, (c) weight loss and (d) L value of mushrooms stored at different temperatures (3, 7 and 15ºC) in the cold chain.

3.5.4. Comparing the importance of variability on mushroom quality

The relative frequency was plotted against storage time for different characteristics of the produce to compare the effect of variability due to cold chain parameters (RH and Temperature) and product parameters (Table 3.3). The concentration of gases (O_2 and CO_2) in the headspace of the package are influenced by the product variability parameters, as evident from Fig 3.7a&b. For the L-value, the main influence was ascribed to the product parameters Fig 3.7c. This result was in accordance with the general practice in postharvest technology of mushrooms, which includes grading and sorting of the produce before packing to reduce the variability associated to the effect of the storage/distribution supply chain. The weight loss was influenced by the cold chain parameters Fig 3.7d. The temperature and relative humidity during storage influenced the rate of moisture loss during the distribution supply chain. A relatively small weight loss of 3-6 % in fruits and vegetables is sufficient to cause wilting, shrivelling and dryness. As a consequence, it causes a great deal of economic loss (Nunes et al., 2009).

a)

b)

c)

d)
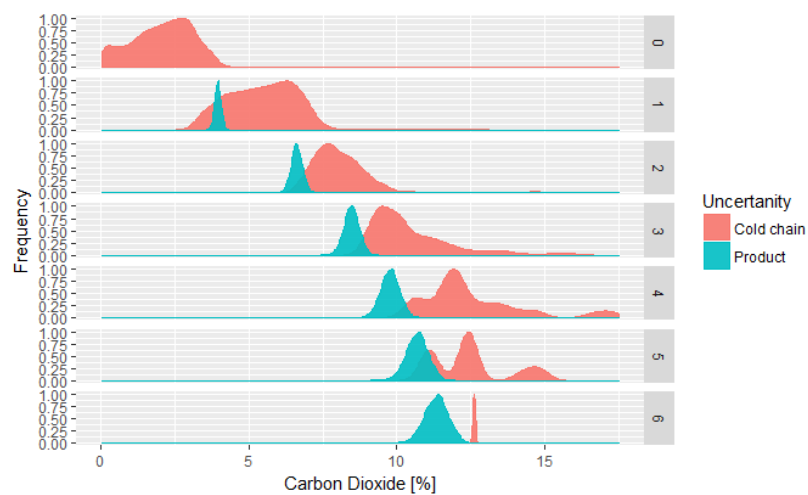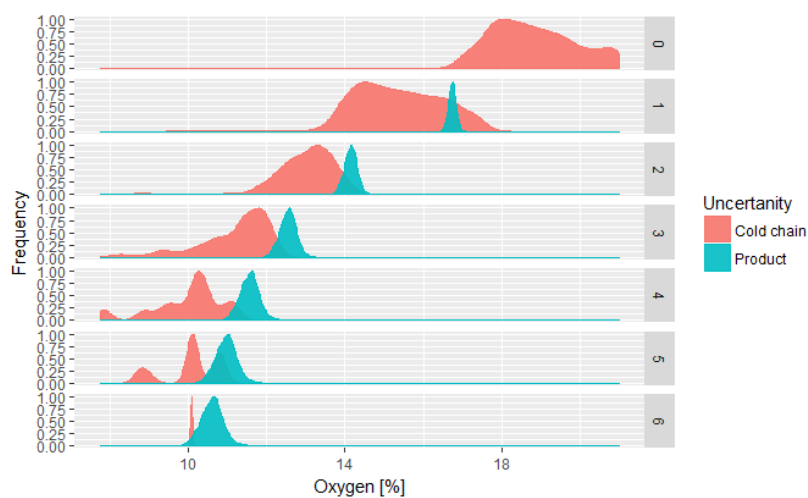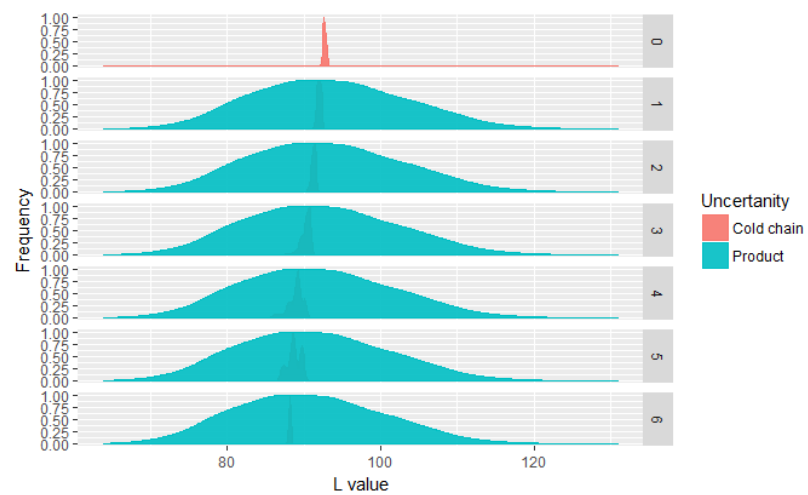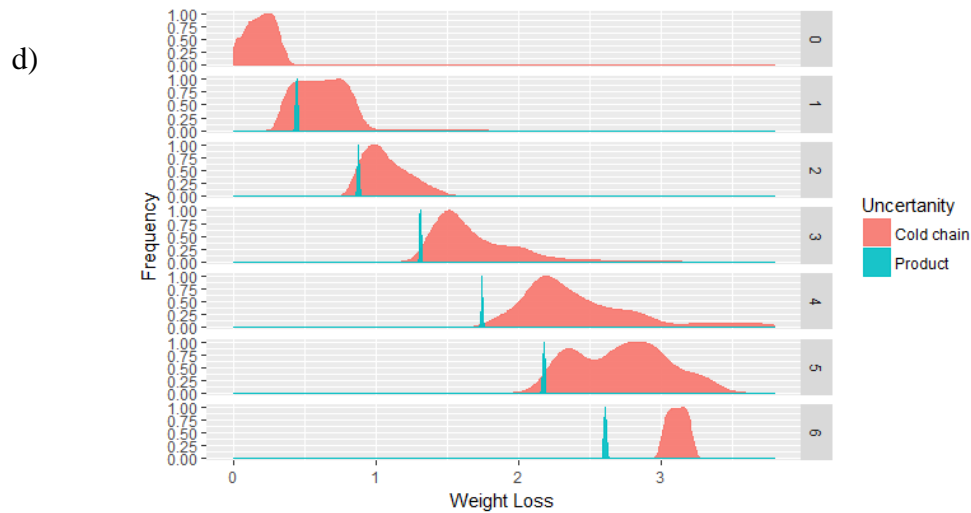
Fig 3.7 Comparison of the effect of cold chain parameters and product parameters on (a) CO2 concentration in the package's headspace, b) O2 concentration in the package's headspace, c) L value and d) weight loss observed during the distribution supply chain.

3.5.5. Sensitivity analysis

Uncertainty analysis usually accompanies a sensitivity analysis to quantify 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 sensitivity analysis for the L value coordinate shows that initial L value has 100% contribution towards the variability Fig. 3.8b. The results of the sensitivity analysis of CO_2 indicates that the Michaelis-Menten respiration rate constants have the highest impact on the concentration of CO_2 in the headspace (90%). The results of the sensitivity analysis of the weight loss are presented in the Fig. 3.8c. The activation energy rate constant depends on temperature have the highest impact on the weight loss of mushroom

in the supply chain. Along with respiration rate parameters it contributes to 90% of the variability. Some variability was observed due to interactions between parameters such as skin mass transfer coefficient and initial weight of mushroom. To tackle the weight loss of mushroom, the intervention should target the cold chain variations (temperature and relative humidity) and should be managed throughout the supply chain.

a)

b)

c)
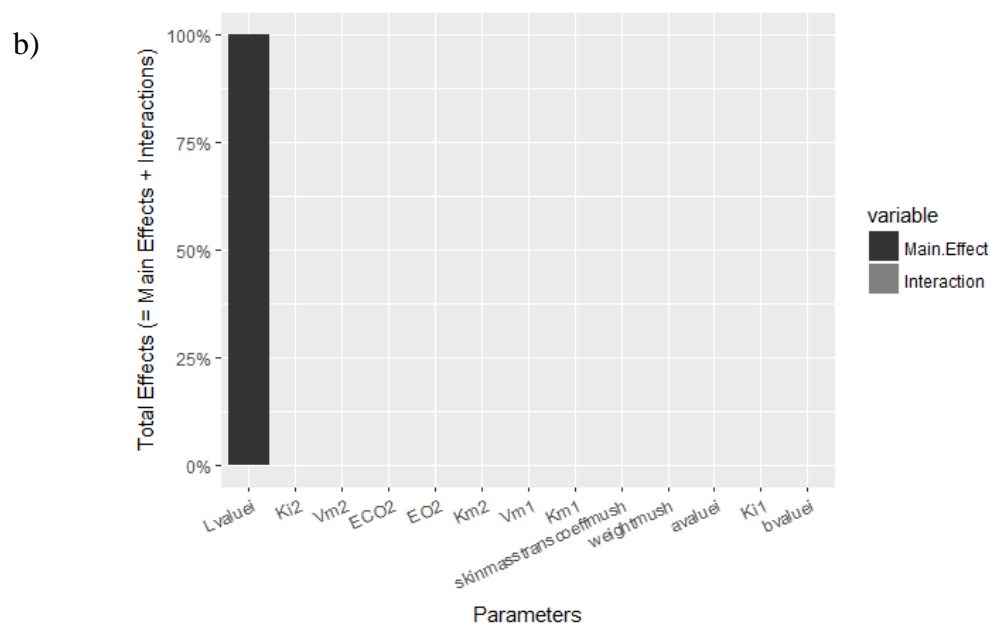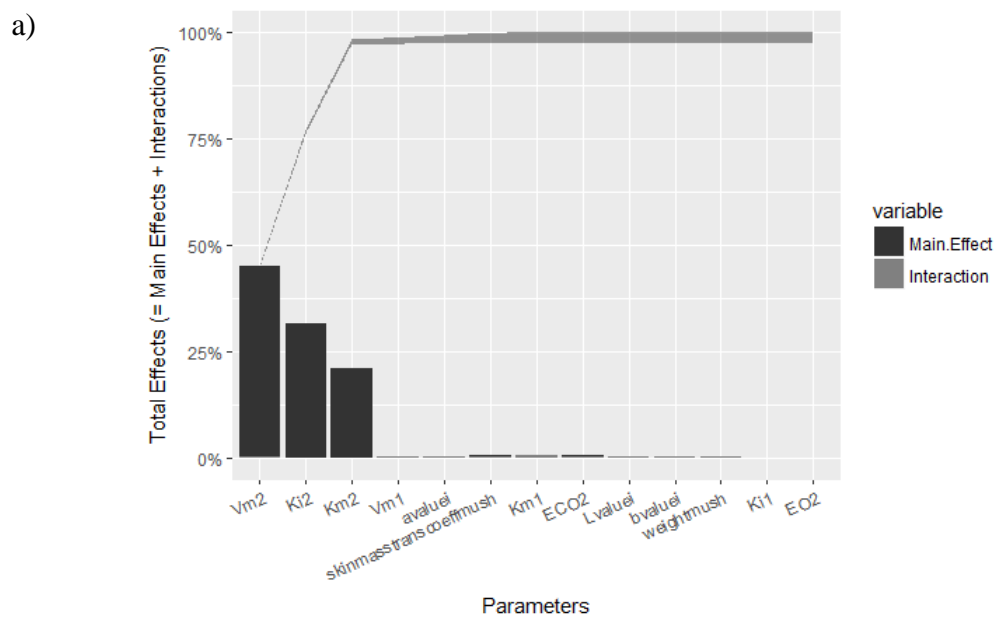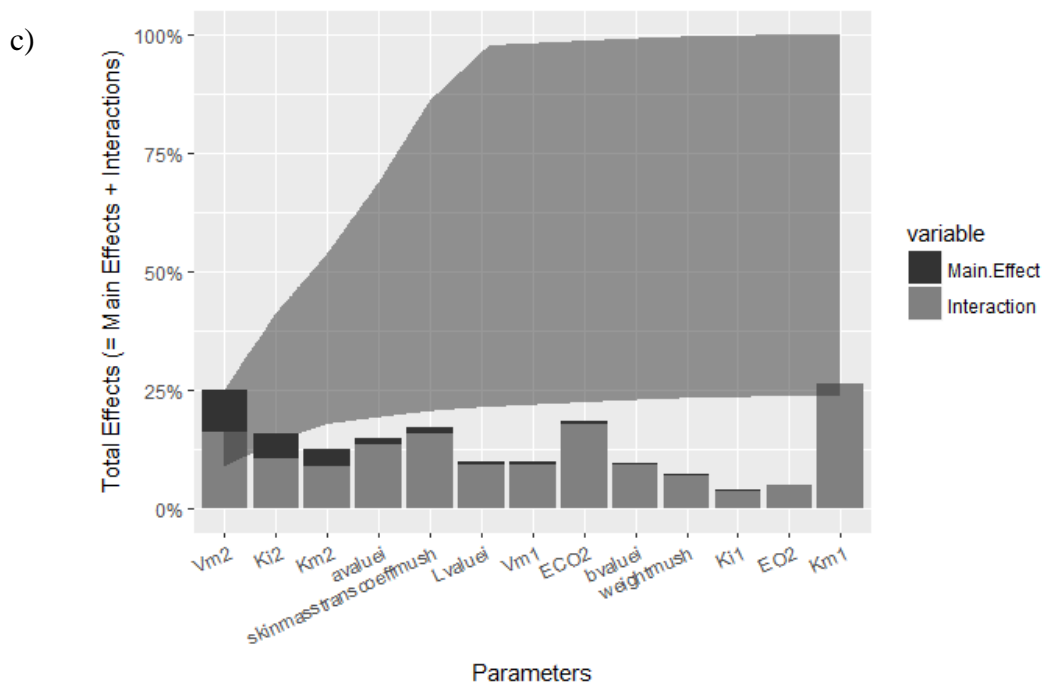
Fig 3.8 Lowry plots of the sensitivity analysis: (a) CO2, (b) L value and (c) weight loss.

*The total effect of the main parameter is given in black, while any first order interactions with other parameters is represented in grey as a proportion of the variance. The ribbon represents the variance due to parameter interactions, the cumulative sum of main effect is represented by the lower line and the sum of total effect by the upper line.

3.5.6. Waste generation during the supply chain

Quality characteristics of mushroom are the visual appearance, colour, freshness, microbial growth and weight loss (Aguirre, 2008). The main processes leading to waste generation in modified atmosphere packed mushroom are browning and textural changes. Texture changes can be attributed to weight loss due to moisture loss (Lukasse and

Polderdijk, 2003). Despite the postharvest efforts, such as grading and packaging, the losses due to natural variability cannot be explained.

Conditional density plot
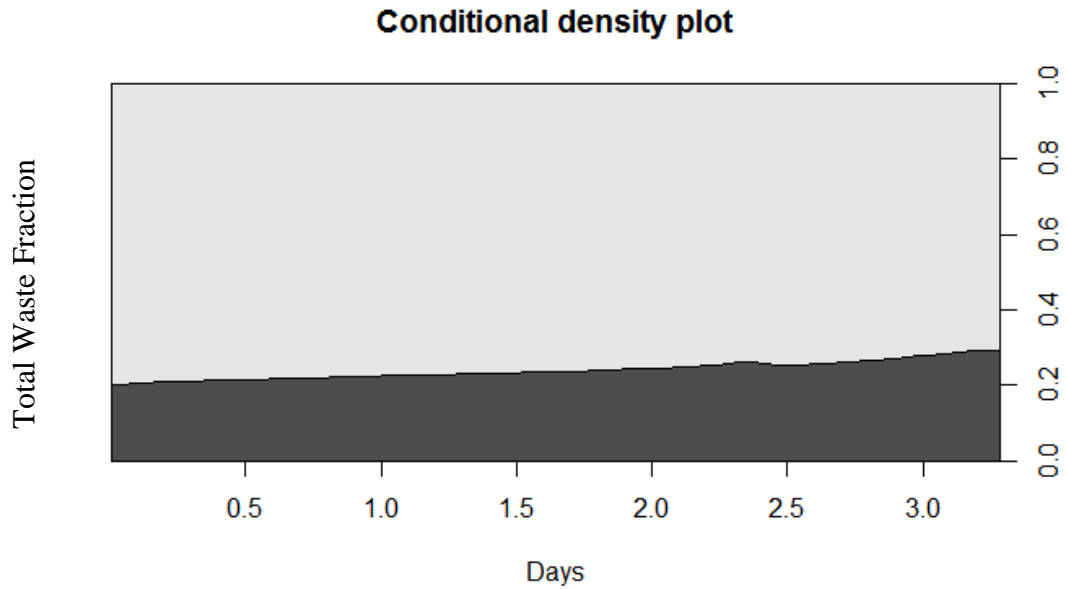
Fig 3.9 Conditional density plot for the estimation of total waste generated in the mushroom supply chain.

Fig. 3.9 shows the total losses observed in the mushroom export supply chain due to quality degradation. The mushroom quality levels that fall below the acceptability threshold were used to calculate the losses observed in the supply chain. The quality threshold for mushrooms was L=85 for colour and 5% for weight loss. There exists a direct relationship between the initial L-value and the losses observed in the supply chain Fig. 3.10. Higher initial L-values are able to maintain the quality associated to colour, leading to less losses during the supply chain. If all the mushrooms were of same higher initial quality, the initial variation introduced in the batch of fresh produce would be reduced, leading to less waste generation in supply chain.

Abuse Conditions
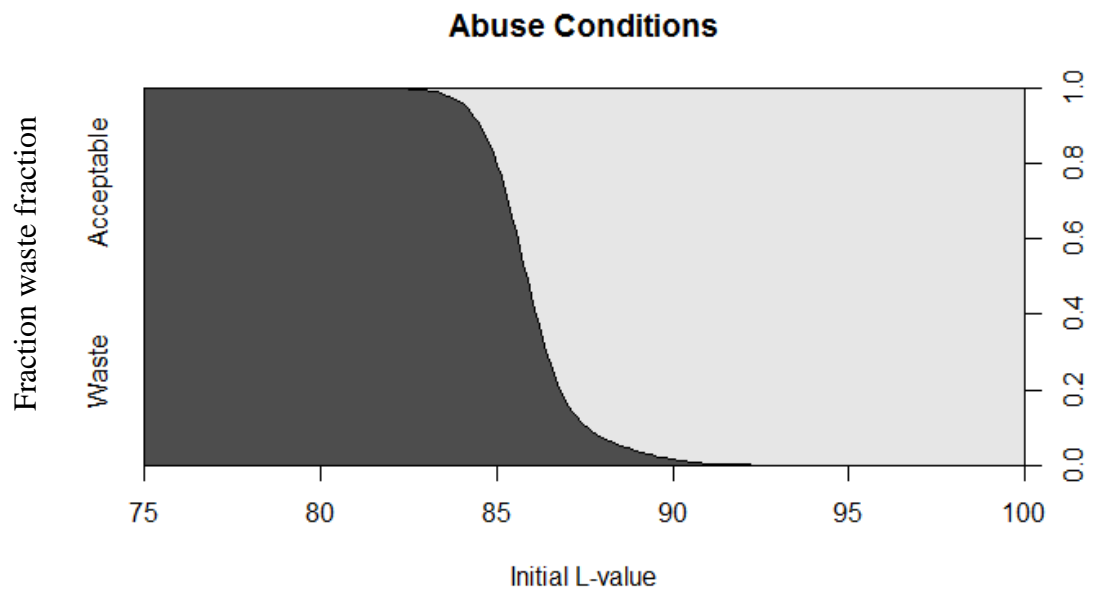
Fig 3.10 Conditional density plot for estimation of the effect of initial L-value on the generation of waste during the supply chain.

3.6. Conclusions

Mushrooms are an attractive food product with a growing global market as observed from increases in production and consumption. However, due to the perishable nature of mushroom, its distribution is challenging. A mathematical model was developed to predict the change observed in the quality of mushrooms packed in modified atmosphere during storage. The model integrates mass transfer processes, including transpiration, transport of gases (O_2, CO_2) and heat transfer, such as respiration heat, convection through produce into its surroundings, transpiration heat and heat of condensation. The comparison between the 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, a sensitivity analysis was performed which explained the effect of the main parameters and the interactions between the parameters. Regarding the threshold values of weight loss and L coordinate, the total waste during the cold chain can be

calculated. This calculation considers the uncertainty (cold chain and product parameters), can account for the specified goal (headspace gas concentration, quality) and provide viable solutions (packaging design, storage conditions, product selectivity) for a high quality end product.

Chapter 4.   Predicting quality attributes of strawberry packed under modified atmosphere throughout the cold chain

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The findings of this chapter were published in (Joshi et al., 2019)

4.1.   Introduction

Strawberries are highly perishable in nature with high metabolic rate and thus have short shelf life. The major limiting factor of the quality of strawberries is spoilage due to *Botrytis* infection. The tissue of strawberry deteriorates through natural senescence during the food distribution chain and *Botrytis* develops due to tissue softening as a result of over ripening (Hertog et al., 1999). Other limiting factors to strawberry shelf life are appearance, texture and taste, which are affected by decay and weight loss during the supply chain. The most effective intervention to extend the shelf life is to use low temperature storage (Sanz et al., 2000). Packaging is another important technique to extend the shelf life of perishable fruit to facilitate a longer transportation distribution (Caner et al., 2008). The storage quality can be further improved by using modified atmosphere packaging (MAP) and altering the concentration of gases surrounding the fresh strawberry (Geysen et al., 2005; Zhang et al., 2003).

MAP has been used to increase and preserve the shelf-life of produce, while also responding to the emerging consumer demand for convenience and quality. The design of optimal MAP for a specific produce depends on the characteristics of the produce, permeability of the packaging film and dependence on external factors such as temperature and relative humidity (Zagory and Kader, 1988). Apart from extending the

shelf life of strawberries it maintains the quality characteristics firmness, prevents weight loss and microbial spoilage (Caner et al., 2008; Larsen and Watkins, 1995; Pelayo et al., 2003).

Sources of uncertainty in postharvest distribution of strawberries

Managing uniform quality of produce is a tedious task due to the many sources of variability, inherent biological variation and fluctuation occuring in storage conditions (Duret et al., 2015b). Postharvest management aims at controlling the variation as much as possible by sorting and grading the product at different stages of the postharvest chain (Hertog et al., 2009a). Identifying and quantifying different sources of variance in the experimental data and assigning uncertainties to the parameter values and error provides better interpretation of the postharvest behaviour (Aguirre, 2008; Hertog et al., 2007b). Biological variation has been previously studied by including this variation in the quality change model, estimating the initial variation ("harvest age") and using it to assess the effect throughout the postharvest chain (Hertog et al., 2009b). Over the last decade models explaining biological variation in fresh produce have been developed (Duret et al., 2015b; Gwanpua et al., 2014; Hertog et al., 2007d, 2004b).

In a MAP gas exchange kinetic model, the uncertainty can also be estimated at the respiration models of strawberries. Michaelis-Menten inhibition constants for O_2 consumption (Km_{O_2}) and fermentative CO_2 production ($Kmc_{O_2(f)}$), the reference rate constant of maximum oxygen consumption (Vm_{O_2}) and maximum carbon dioxide production ($Vm_{CO_2(f)}$) and the activation energy rate that have been experimentally assessed will have an associated uncertainty, conventionally in the form of a standard error (Hertog et al., 1999).

When describing the kinetics of weight loss in a packaged produce, the fruit skin mass transfer coefficient (K_s) is one of the main source of product variation due to the

structural variation in the skin of individual fresh produce along with the initial spoilage of the batch (N_0) (Hertog et al., 1999). The statistical values of these parameters are presented in Table 4.2.

The objective of this study is to predict the quality of strawberry in the supply cold chain. The assessment of the effect of cold chain variability and product variability on the quality of strawberry will help estimate the waste generated. A sensitivity analysis was carried out to quantify the effect of different parameters and design an intervention that will reduce losses in the supply chain.

4.2. Materials and Methods

In the model, we took into account the dynamic processes occurring in the MA package using differential equations that contemplate the aspects mentioned below (Jacxsens et al., 2002; Sousa-Gallagher and Mahajan, 2013):

- The diffusion of gases (O_2, CO_2) and H_2O vapour through the packaging film.

- Respiration of fresh produce, which continuously change the concentration of gases inside the headspace of package.

- Moisture loss from the fresh produce to external atmosphere using Fick's diffusion. Condensation of water inside the package.

- Quality of packed fresh produce during the distribution cold chain.

- Heat transfer inside the package to calculate the change in temperature inside it.

These points are discussed in detail in the following sections.

4.2.1. Model hypothesis

- CO_2 production is a combination of oxidative and fermentative production, the oxidative consumption is proportional to the O_2 evolution and the fermentative production follows the Michaelis-Menten equations.

- The temperature of the surface of commodity (T_s) is equal to the temperature of air surrounding the commodity (T_i).

- The surface of the commodity is assumed to be perfectly saturated condition.

- The metabolic energy released by produce, large part of it (80-100 %) is dissipated as heat.

- 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.

- The quality of strawberry is described as weight loss due to transpiration and by *Botrytis* spoilage as modelled by (Hertog et al., 1999).

4.2.2. Mathematical Model development

The mathematical model takes into account the heat and mass transfer balances due to the metabolic behaviour of strawberry and the transport phenomenon across package (Table 4.1). The assumptions used in the mathematical model and sub model to describe respiration- transpiration of strawberry and gas transport across package. The influence of these on the quality of strawberry during distribution chain is estimated.

4.2.3. Transpiration

The driving force for transpiration is a water vapour deficit between the commodity and the surrounding gas. For transpiration to take place, the water vapour partial pressure in the headspace must be lower than the saturated vapour pressure, while the water vapour pressure at the commodity's surface must be greater than the partial vapour pressure in the gas mixture in the headspace (Xanthopoulos et al., 2012).

Transpiration is caused due to vapour pressure deficit VPD (Pa) between the produce surface and the surrounding atmosphere. VPD is the function of difference in the amount of moisture in air and the amount of moisture air can hold when it is saturated (Becker et al., 1996).

$$VPD = (a_w - RH)p_s \qquad\qquad 4.1$$

It is assumed that water activity of strawberry is ($a_w \sim 0.99$).

Saturated water vapour pressure at the surface of commodity can be calculated using following equation (Rennie and Tavoularis, 2009b) based on saturated water vapour pressure data from ASHRAE (1997).

$$p_s = 0.041081186T_s^3 - 32.43188T_s^2 + 8567.5269T_s - 757070.1 \qquad\qquad 4.2$$

Transpiration occurs when water vapour pressure at the surface of commodity exceeds the water vapour pressure of the headspace of package (Becker et al., 1996; Xanthopoulos et al., 2012).

$$m_w = VPD \times K_t \qquad\qquad 4.3$$

Transpiration rate (kg m^{-2}h^{-1}) is product of water vapour flux (m_w) and the surface area of the commodity(A_c)

$$t_r = m_w A_c \qquad\qquad 4.4$$

$$K_t = \frac{1}{\left(\frac{1}{K_s} + \frac{1}{K_a}\right)} \qquad\qquad 4.5$$

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

$$Sh = \frac{K_a d_c}{D_{H_2O,air}} \qquad\qquad 4.6$$

For convective mass transfer from commodity spherical in shape, (Becker et al., 1996) recommended Sherwood-Reynolds-Schmidt correlation of the following form to be used.

$$Sh = 2.0 + 0.552\, Re^{0.53} Sc^{0.33} = \frac{K'_a\, d_c\, R\, T_s}{D_{H_2O,air}\, M_{H_2O}} \qquad\qquad 4.7$$

It is assumed, there is negligible flow around the commodity ($Re \approx 0$). Therefore, air film mass transfer coefficient can be calculated as:

$$K_a = 2 \times \frac{D_{H_2O-air}\, M_{H_2O}}{d_c\, R\, T_s} \qquad\qquad 4.8$$

4.2.3.1. *Transpiration Heat*

The process of transpiration requires energy for evaporation of moisture from surface of produce, this process cools down the commodity. Evaporative heat transfer rate (Q_{tr}) is a product of latent heat of vaporization (λ) and transpiration rate (t_r).

$$Q_{tr} = \lambda\, t_r \qquad\qquad 4.9$$

4.2.4. Relative humidity in headspace

The concentration of water vapour inside the package is dependent on the rate of water vapour transfer from the moisture sources to moisture sinks within the package. The main moisture sources in the package is water transpired from the surface of fresh produce (t_r) and the main source of moisture sink is permeation of water vapour through the film (m_{pr}) (Becker et al., 1996; Jalali et al., 2017).

The amount of water vapour in the headspace is calculated using humidity ratio which is the ratio of mass of water vapour in headspace to mass of dry air in the headspace of package (kg/kg).

$$\frac{dHR}{dt} = \frac{t_r - m_{pr}}{W_a} \qquad\qquad 4.10$$

Relative humidity is calculated as ratio of humidity ratio inside the package (HR) to the humidity ratio of saturated water vapour (HR_{sat}) (Jalali et al., 2017; Song et al., 2002).

$$HR_{sat} = \frac{0.62198 P_s}{(P_{atm} - P_s)} \qquad 4.11$$

$$RH = \frac{HR}{HR_{sat}} \qquad 4.12$$

4.2.5. Condensation

In perforation mediated packaging condensation rate is seldom modelled in MAP, due to near saturation conditions and non-uniform or fluctuating temperature within the package, condensation can occur on the commodity surface or inside of package film and walls. It is assumed that the water vapour condensed on the surface of commodity does not penetrate the skin of fresh produce. For condensation to take place the partial pressure of water vapour should be greater than the saturated water vapour pressure (Jalali et al., 2017; Joshi et al., 2018; Rennie and Tavoularis, 2009b).

$$M_{con} = \begin{cases} K_a(P_{H_2O-} P_c)\delta A_c, & if(P_{H_2O} > P_s) \\ 0 & otherwise \end{cases} \qquad 4.13$$

The corresponding rate of release of heat due to condensation on the surface of commodity is Q_{con} calculated as:

$$Q_{con} = \lambda M_{con} \qquad 4.14$$

The rate of condensation on package wall (M_{wcon}) is calculated similarly using air film mass transfer coefficient (K_a).

$$M_{wcon} = \begin{cases} K_a(P_{H_2O-} P_s)\delta A_w, & if(P_{H_2O} > P_s) \\ 0 & otherwise \end{cases} \qquad 4.15$$

The heat released during condensation (Q_{wcon}) heats up gases in atmosphere near wall.

$$Q_{wcon} = \frac{\lambda M_{wcon}}{A_w} \qquad\qquad 4.16$$

4.2.6. Quality

The quality of fresh produce is determined by the overall characteristics (appearance, texture, flavour and nutritive value) of fresh produce (ElMasry et al., 2007). The perception of quality is highly subjective and depends on consumer and number of qualitative factors. Quality of fresh produce in general is often described using a chemical kinetic model (Merts, 1996). The main attributes of quality in strawberries is weight loss and spoilage.

4.2.6.1.   *Weight loss*

The amount of water vapour transpired from the surface of fruit (t_r) and carbon loss due to respiration accounts for the weight loss.

$$\frac{dW_l}{dt} = t_r + M_c r_{CO_2} W_s \qquad\qquad 4.17$$

4.2.6.2.   *Spoilage*

The inhibition of spoilage in strawberry in modified atmosphere is assumed to be the result from inhibitory effect of gas composition on gas exchange in strawberry. When the gas exchange is inhibited the overall metabolic rate and the ripening rate will be inhibited resulting in a slower spoilage rate (Hertog et al., 1999). (Tijskens and Polderdijk, 1996) used relative metabolic rate (eq. 4.18), which represents a ratio of the actual respiration rate under any gas conditions to the respiration rate under normal air conditions (21% O_2, 0.03% CO_2) at the same temperature. In the case of strawberries fermentative activities are taken into account in the respiration model therefore the gas exchange is expressed in terms of CO_2 production.

$$Rel_{MR} = \frac{r_{CO_{2(f)}}([O_2],[CO_2],[H_2O],T_s)}{r_{CO_2}(21\%\ O_2, 0.03\% CO_2, T_s)} \qquad\qquad 4.18$$

The spoilage of strawberry due to *Botrytis*, in terms of percentage of strawberry affected can be described by the following ordinary differential.

$$\frac{dN}{dt} = Rel_{MR} \times k_s \times N \times \left(\frac{N_{max}-N}{N_{max}}\right), initiate\ at\ N_0 \qquad\qquad 4.19$$

Where, N_{max} is maximum spoilage (100%), k_s is the spoilage rate constant which depends on the temperature according to Arrhenius equation. The value of activation energy associated with the spoilage rate constant is mentioned in table 4.2.

1   **Table 4.1 Equations used in the mathematical model**

Process	Equation	Reference	Eq. no.
Respiration	$$r_{O_2} = \frac{Vm_{O_2}.[O_2]}{Km_{O_2}.\left(1+\frac{[CO_2]}{Kmc_{CO_2}}\right)+[O_2].\left(1+\frac{[CO_2]}{Kmu_{CO_2}}\right)}$$ $$r_{CO_2(f)} = \frac{Vm_{CO_2(f)}}{\left(1+\frac{[O_2]}{Kmc_{O2(f)}}+\frac{[CO_2]}{Kmc_{CO2(f)}}\right).Km_{CO_2(f)}+1}$$ $$r_{CO_2} = RQ_{ox}.r_{O_2} + r_{CO_2(f)}$$	Strawberry respiration rate follow uncompetitive type inhibition. The CO_2 production is a combination of oxidative and the fermentative process (Hertog et al., 1999; Song et al., 2002)	4.20 4.21 4.22
Respiration heat	$$Q_s = \frac{2816}{6} \times \frac{r_{O_2} + r_{CO_2}}{2} \times \alpha \times W_s$$	α is conversion factor of respiration energy dissipated as heat. The literature suggests the value of α has a range between 0.8-1.0 (Burton, 1982). For 100% conversion of respiration energy as heat $\alpha =1$ (Song et al., 2002)	4.23
Mass Balance			
Gas exchange in package	$$\frac{d[O_2]_i}{dt} = 100 \times \left(\frac{A_p p_{O_2} P_{atm}}{L_f}\left[\frac{[O_2]_o}{100}-\frac{[O_2]_i}{100}\right]-W_s r_{O_2}\right) \times \frac{1}{V_f}$$ $$\frac{d[CO_2]_i}{dt} = 100 \times \left(\frac{A_p p_{CO_2} P_{atm}}{L_f}\left[\frac{[CO_2]_o}{100}-\frac{[CO_2]_i}{100}\right]+W_s r_{CO_2}\right) \times \frac{1}{V_f}$$	The mass balance of gas components in the package is represented by ordinary differential equations (Song et al., 2002). As the package initially contains air, initial conditions (t=0) becomes $[O_2]_i$=21.0%, $[CO_2]_i$=0.03%	4.24 4.25
Permeability	$$p_{O_2,CO_2,H_2O} = p_{O_2,CO_2,H_2O \ ref} + \frac{\pi R_h^2 \times D_{i,air}}{(L_f + R_h)} \times N_h$$	Permeability is a function of permeability of film and the number and size of perforations.	4.26

Water permeation through film	$\frac{dm_{pr}}{dt} = \left[\frac{p_{H_2O}A_p(P_i - P_o)}{L_f}\right]\left[\frac{0.018P_{atm}}{RT_s}\right]$	The driving force of permeation of water vapour from the headspace of package to surrounding is the water vapour pressure difference.	4.27
Heat Balance			
Temperature headspace of package	$Q_s + Q_{con} + h_pA_p(T_i - T_o)$ $\qquad = Q_{tr} + W_sC_s\frac{dT_s}{dt} + W_aC_a\frac{dT_s}{dt}$ $\frac{dT_s}{dt} = \frac{Q_s + Q_{con} - h_pA_p(T_i - T_o) - Q_{tr}}{W_sC_s + W_aC_a}$	The heat is generated by respiration and heat is transferred in headspace due to convection, transpiration and condensation. This ODE is used to estimate the temperature of the fresh produce (Lee et al., 1996)	4.28 4.29

2

4.3. Numerical Simulations of the ODE system

To estimate the effect of input parameter uncertainty on the prediction of concentration of gases and effect on quality during the cold chain distribution, Monte Carlo simulations were performed to simulate three scenarios:

1) A distribution scenario where temperature and relative humidity are varying with the cold chain data.

The history of export of four international cold chains between Ireland and the United Kingdom was used, comprising temperature and relative humidity data, including the production farm, the packaging house, international haulage, retail storage and arrival to the retail shop. This data was originally collected as part of a research innovation project in collaboration with industry, described in detail in Joshi et al. (2018). The data was collected using temperature and relative humidity dataloggers (XSense®, BT9 Intelligent Supply Chain Solutions, UK) with a logging frequency of 10 minutes. The experimental data 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 (Fig 4.1).

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 over 85 premises spread through the 26 counties in the Republic of Ireland, including open and close refrigerated cabinets in a supermarket, a deli shop and a butcher outlet in each county (Fig 4.2).

a)
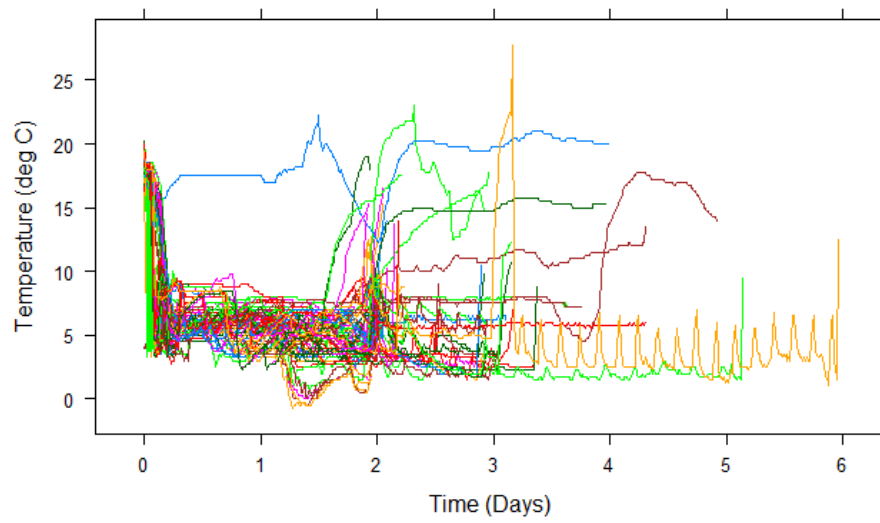
b)
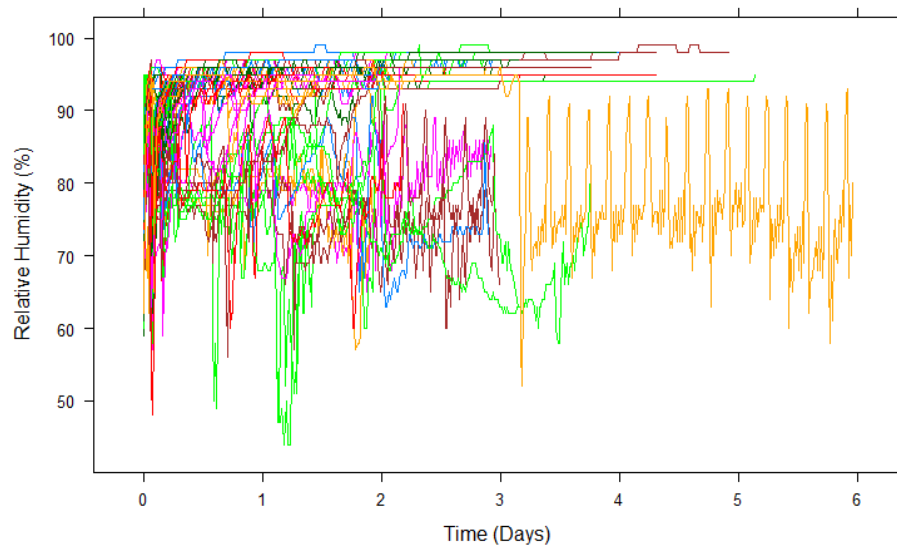
Fig 4.1 Export cold chain profile: a) Temperature and b) Relative humidity.

a)

b)
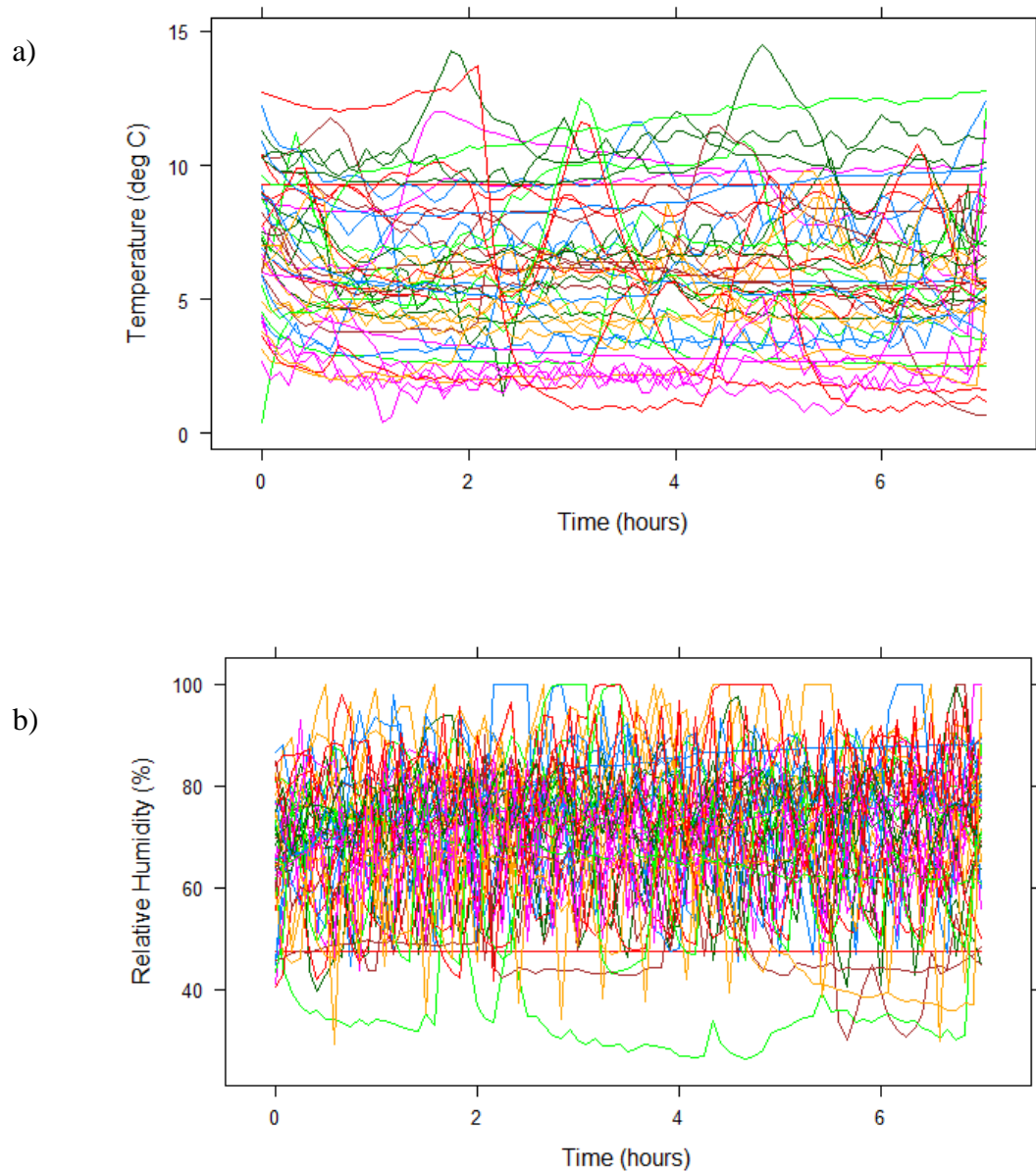
Fig 4.2 Retail cold chain profile: a) Temperature and b) Relative humidity.

2) A distribution scenario with an ideal cold storage temperature (4°C). and relative humidity (80%) and with variable product properties, as specified in Table 4.2.

3) A distribution scenario considering the joint uncertainties of 1) and 2).

The value of product parameters used in the model are in table 4.2. The ordinary differential model was solved using the deSolve library (Soetaert et al., 2010) using the

lsoda solver on R 3.4.3 (R Development Core Team, 2008). All the plots 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).

4.3.1. Assessment of the impact of cold chain on quality in cold chain

A simulation scenario considering average product characteristics without variation and a variable cold chain temperature and relative humidity profile was used to assess the importance of different transport and retail conditions. This simulation scenario used cold chains of 3 and 6 days of temperature and relative humidity export profiles from the study (Joshi et al. 2018). The mathematical model was simulated against these cold chain profiles to study the effect of cold chain uncertainty on the quality of strawberry results are presented in the following sections.

Table 4.2 Parameter estimate and their standard error for strawberry Source: ([*]Becker et al., 1996; Hertog et al., 1999)

Parameter	Value	Standard error (SE)
$Vm_{O_2,ref}$ (µmol kg^{-1}sec^{-1})	0.27	0.010
$E_{aVm_{O_2}}$ (J mol^{-1})	74826	3451
$Vm_{CO_2(f)ref}$ (µmol kg^{-1}sec^{-1})	0.50	0.22
$E_{aVm_{CO_2(f)}}$ (J mol^{-1})	57374	14400
Km_{O_2} (%)	2.63	0.274
Kmc_{CO_2}	$+\infty$	-
Kmu_{CO_2}	$+\infty$	-
$Kmc_{O_2(f)}$ (%)	0.056	0.041
$Kmc_{CO_2(f)}$	$+\infty$	-
$Km_{CO_2(f)}$ (%)	1	-
K_s [*](kg m^{-2} sec Pa)	13.6 x 10^{-9}	4.8
$k_{s,ref}$ (day^{-1})	0.60	0.045
Ea_s (J mol^{-1})	70108	7056
N_0 (%)	0.83	0.10

4.3.2. Assessment of product variability on waste production

A simulation scenario considering full product variability and constant storage conditions was used to assess the relative effect of different product variability sources. The storage conditions tested involved:

- An ideal storage temperature of 4^0C and relative humidity 80%.

- An abuse cold chain composed of the following steps: 2 hours of packaging at 8^0C followed by retail storage for up to 1.5 day at 4^0C, transportation at 8^0C for 1 day and retail shop storage at 4^0C for 3 days.

    The product parameters responsible for the variability are presented in Table 4.2. The results showed the uncertainty due to the product parameters uncertainty on the quality parameters of strawberry.

To further investigate the effect of individual product parameter, a sensitivity analysis was performed using a main and first order interactive effects model excluding time. The results are presented using a Lowry plot (McNally et al., 2011)

4.3.3. Combined assessment of product and cold chain uncertainty effect on waste

The combined assessment of cold chain uncertainty and product uncertainty. This study contributes to the identification of the relative influence of different parameter uncertainties and the interventions that can be designed to maintain the quality and reduce the waste in supply chain. A sensitivity analysis was also carried out to access the effect of individual parameters on the produce quality, as explained in the next section.

Sensitivity analysis

The input parameters of the sensitivity analysis are shown in Table 4.2. The results of the sensitivity analysis were presented using a Lowry plot (McNally et al., 2011) . The total effect of the main parameters is presented in black and any first order interactions

with other parameters was represented in grey. The ribbon represents the variance due to parameter interactions, while the cumulative sum of the main effects and the sum of the total effects is indicated by the lower line and upper line, respectively.

Estimation of waste generation

The losses observed in the strawberry cold supply chain are ascribed to weight loss and spoilage. The simulation results of product variability were used to calculate the waste generated based on the industrial thresholds. Conditional density plots were used to illustrate the waste produced in the strawberry supply chain.

Table 4.3 Properties of packaging film, produce and other conditions used in the model

Parameter	Value	Reference
$P_{O_2\ ref}$ (m^3m $h^{-1}m^{-2}$Pa)	8.5×10^{-14}	(Xanthopoulos et al., 2012)
$P_{CO_2\ ref}$ (m^3m $h^{-1}m^{-2}$Pa)	2.8×10^{-13}	(Xanthopoulos et al., 2012)
$P_{H_2O\ ref}$ (m^3m $h^{-1}m^{-2}$Pa)	4.5×10^{-13}	(Xanthopoulos et al., 2012)
ρ_b (kg m^{-3})	600	(Xanthopoulos et al., 2012)
ϵ	0.27	(Xanthopoulos et al., 2012)
a_w	0.99	(Xanthopoulos et al., 2012)
C_s (kJ kg^{-1} K^{-1})	4	(ASHRAE, 2006)
$[CO_2]_i$ (%)	0.03	(Song et al., 2002)
$[O_2]_i$ (%)	21.0	(Song et al., 2002)
M_{O_2} (kg mol^{-1})	0.032	(Bird, 2002)
M_{CO_2} (kg mol^{-1})	0.044	(Bird, 2002)
M_{H_2O} (kg mol^{-1})	0.018	(Bird, 2002)
R (J $K^{-1}mol^{-1}$)	8.314	(Bird, 2002)
P_{atm} (Pa)	101325	(Bird, 2002)
ρ_{O_2} (kg m^{-3})	1.43	(Siracusa, 2012)
ρ_{CO_2} (kg m^{-3})	1.98	(Siracusa, 2012)
T_{ref} (^{0} C)	10	(Hertog et al., 1999)
N_H	4	Experimental
d_c (m)	0.03	Experimental

4.4. Validation

Strawberry (150g, 3-5 cm diameter) were purchased from local wholesale fruit market Dublin, Ireland and packaged in an industry standard perforated polypropylene LDPE film (4 perforations) and were stored in either ideal conditions (4^0 C) or abuse condition (1/2 day in packaging facility at 8 ºC followed by transportation at 4 ºC up to 2 days, followed by retail storage including 4h at 20 ºC, followed by 2 days at 8 ºC, and finalised by retail shop 4h at 20ºC 2 days at 8 ºC) for a period of 10 days.

A chitosan solution (1.5 %) was prepared by dissolving chitosan (Sigma-Aldrich Ltd., UK, medium molecular weight, 75-85% deacetylated) in distilled water containing 1% glacial acetic acid using a magnetic stirrer. After complete dissolution 0.2% Tween 80 (Sigma-Aldrich Ltd., UK) was added to the solution. The pH of the solution was adjusted to 5.2 with 1N NaOH (Sigma-Aldrich Ltd., UK) (Petriccione et al., 2015). A second sample of the same batch of strawberries was immersed in chitosan solution for 60s then allowed to dry for 1 hour in air dryer at room temperature and stored in the same conditions as above.

Strawberries were visually examined on regular intervals during storage period. The fruits showed surface mycelia growth or bacterial lesions were considered decay. Results were expressed as percentage of spoiled fruits. Weight loss was expressed as percentage loss of initial weight (Han et al., 2004).

4.5. Results and discussions

4.5.1. Cold chain variability assessment

The mathematical model presented in section 4.2 was used to simulate the effect of cold chain variation on the changes in the concentration of gases in the headspace and quality of strawberry. The governing ODE (eq. 4.20 and 4.22) were used to obtain the concentration of carbon dioxide and oxygen package's headspace. The results presented

in Fig 4.3 were simulated in contrast with the export cold chain. The creation and maintenance of optimal atmosphere inside the modified atmosphere package depends on the product's respiration rate and on the permeability of the films, both of which are dependent on temperature. At very low oxygen concentration (<2%), anaerobic respiration is initiated in the tissue, which shortens the shelf life. However, the results obtained from the simulations showed there was no anaerobic condition was observed in the package.
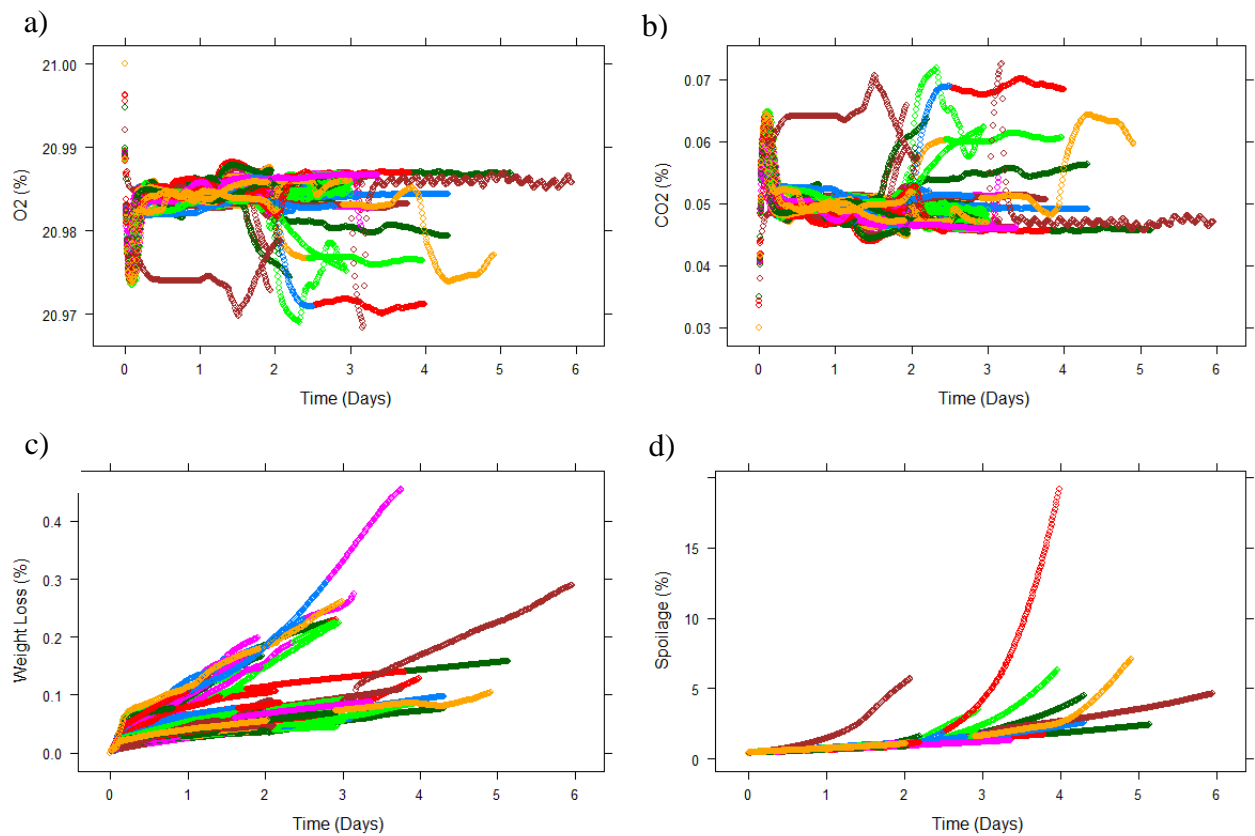
Fig 4.3 Simulation results of average (a) oxygen concentration and (b) carbon dioxide concentration in the headspace of packages (c) weight loss observed and (d) spoilage against the cold chain profile.

Temperature fluctuations and their effect on the atmosphere inside the package had a major effect on strawberry quality. The spoilage increased with higher

95

temperatures, however the effect of MA was also evident. A linear effect of CO_2 concentration on spoilage was. At 0% CO_2, 1.72 % spoilage was observed, versus to 0.87% spoilage at 18% CO_2 (Kader, 1986). At higher CO_2 concentration (20-80%), a clear inhibition occurred. At these extremely high levels of CO_2, fungal growth is indeed inhibited in strawberries (Ke et al., 1991). The amount of water vapour in the headspace of the package was estimated using Fick's diffusion and psychometric equations to calculate the relative humidity inside the package. The results showed that the package is saturated (RH=100%) during storage Fishman et al. (1996) obtained similar results for MAP of mango, and Song et al. (2002) obtained similar experimental and predicted results of relative humidity saturating rapidly during storage.

Weight loss as a result of transpiration and carbon loss due to respiration was directly dependent on temperature (Fig 4.3c). Sanz et al. (2000) reported weight loss of 3.53% in control packages and 0.9% in micro-perforated packages towards the end of storage (7 days). The barrier in the movement of water vapour through the film and perforations leads to less weight loss. The spike in spoilage (>5%) after 2 days of storage was attributed to the result of abusive temperature profile. A linear effect of CO_2 concentration was observed on spoilage: 1.72 % spoilage at 0% CO_2 and 0.87% spoilage at 18 % CO_2 (Kader, 1986).

4.5.2. Scenario analysis

4.5.2.1.   Effect of Perforations

The changes observed within the package was predicted by model with 0, 4, 8 and 12 perforations Fig 4.4. The change in number of perforations leads to change in the transmission of film to gases and water vapour. More the number of perforations the atmosphere within the package becomes sensitive to the ambient atmospheric conditions. The change observed in the relative humidity in the package (Fig 4.4a) is due to the

change in the driving force for permeation of water vapour through the film. In case of no perforations the RH inside the package was more than 100% which can cause spoilage in the supply chain. More perforation in the package reduces the relative humidity in the headspace and maintains the quality of fresh produce.
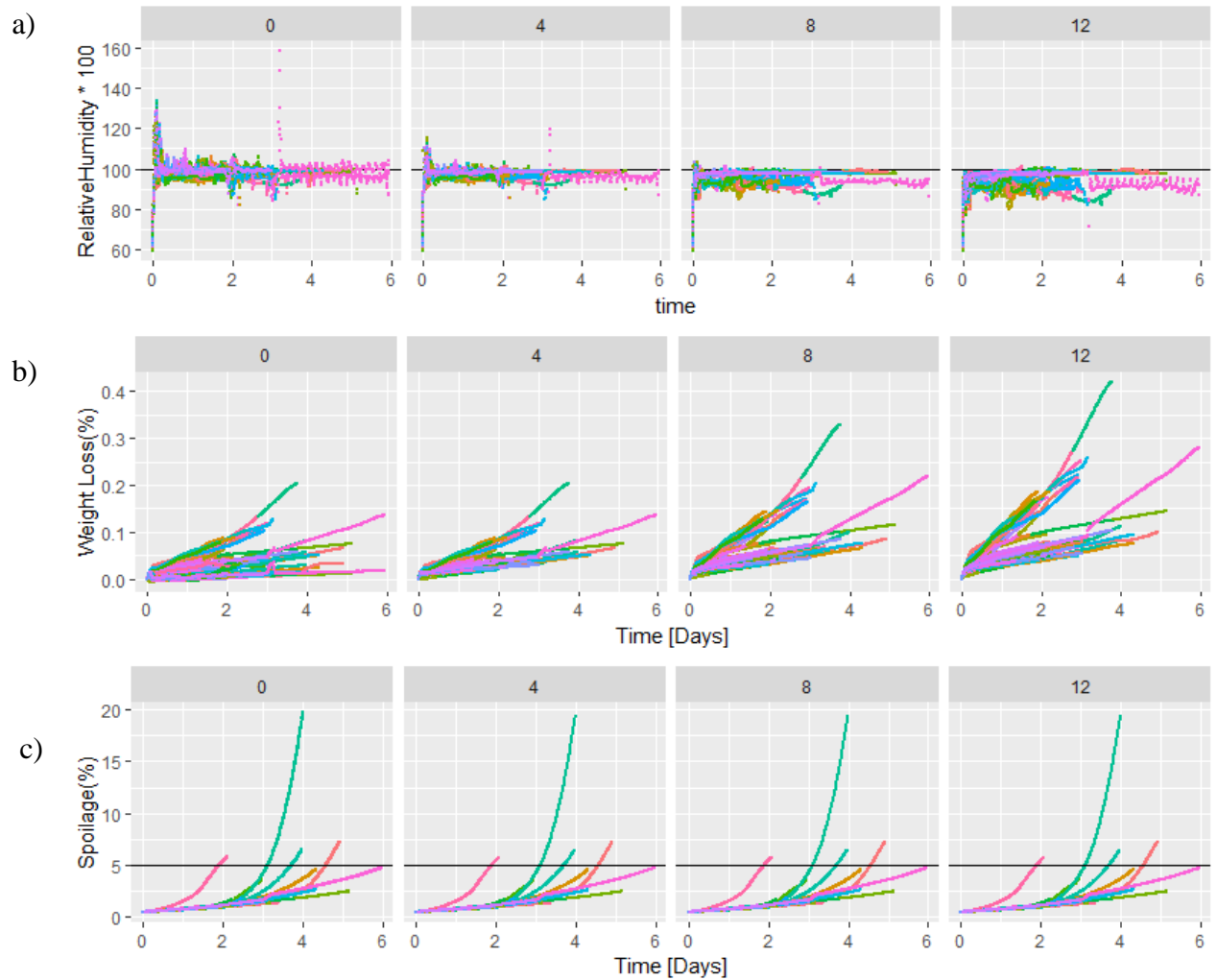
Fig 4.4 Effect of number of perforation (0,4,8 and 12) on the a) Relative humidity in the headspace, b) weight loss (%) c) spoilage (%)

The increase in number of perforation leads to increase in the permeable area. More area for transmission exhibits higher fruit weight loss which was more evident as the storage continues (Fig 4.4b). 0 and 4 perforation showed weight loss less than 0.1% during

storage where for 12 perforations weight loss was more than 0.3%. Spoilage does not seem to show much difference with the change in the number of perforations.

4.5.3. Product variability assessment

Knowledge of the impact of biological variation on quality within a batch is very important to assure a uniform quality in the cold chain. could the variability assessment aid the prediction of factors responsible for quality deterioration during storage. The model developed in this study can help find the effect of variability on the quality parameters. (Hertog et al., 1999). The results obtained are estimates of the values expected due to the variability in the product parameters. The dimensions used are shown in Table 4.3. Fig 4.5 shows the propagation of product parameters on the quality characteristics of strawberry at different storage temperatures (4, 8 and 20°C). From fig 4.5, it is observed that the variation was directly dependant on temperature, where the higher temperatures have higher associated variation.

a)
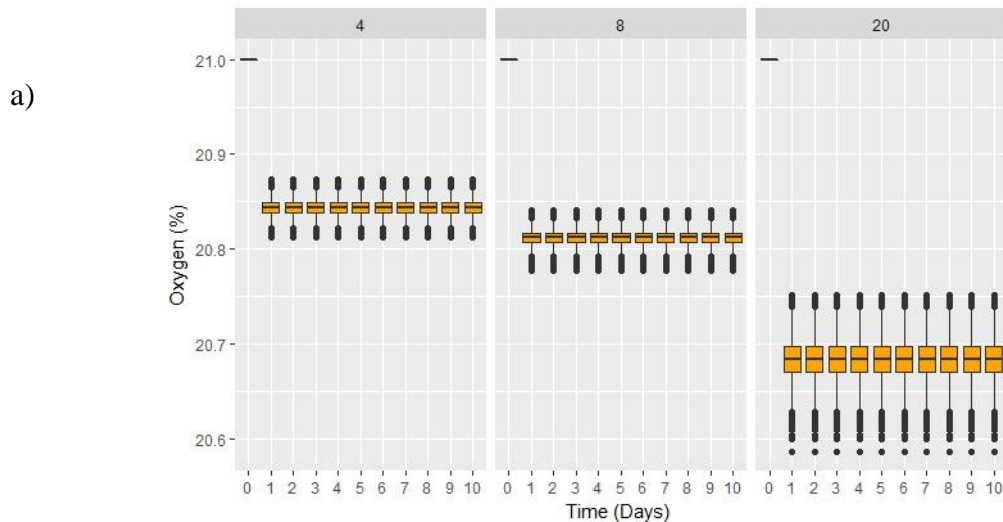
b)
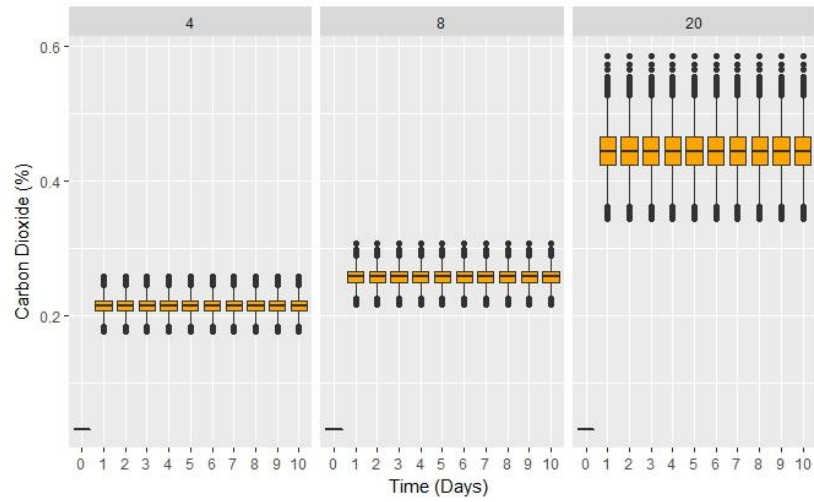
c)
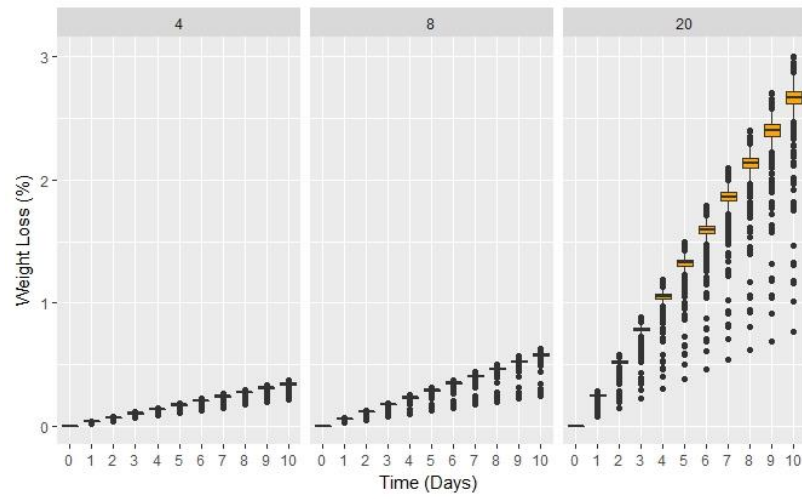
d)
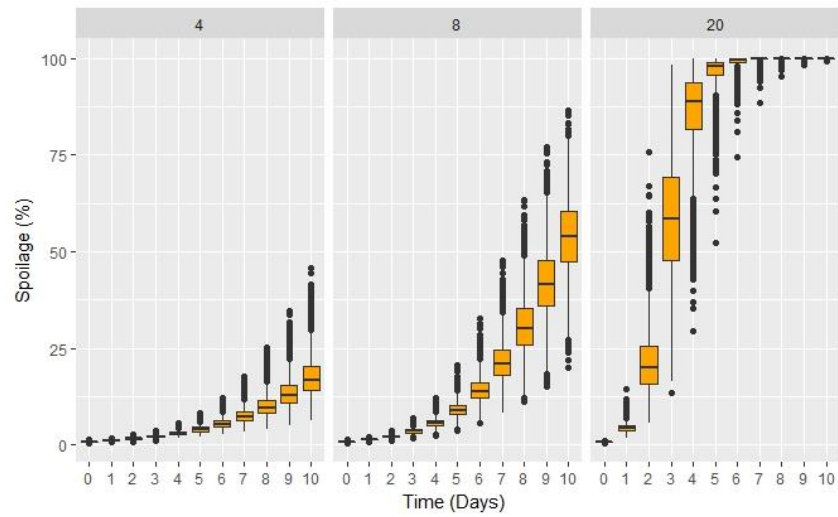
Fig 4.5 Propagation of product parameter variability observed in (a) concentration of oxygen (b) carbon dioxide in headspace (c) weight loss and (d) Spoilage observed in strawberry packed in modified atmosphere 15 days storage at 4^0 C and 80% RH.

$Vm_{O_2,ref}$ and $Vm_{CO_2(f)ref}$ are the respiration rate parameters which are directly dependant on temperature. The increase in temperature resulted in increase in the respiration rate. Geysen et al. (2005) reported the effect of temperature on the activation energy of maximum O2 consumption. The weight loss of strawberry constantly increased with time and higher weight loss was observed at higher temperatures. Strawberries have no protective skin which leads to higher weight loss due to transpiration The uncertainty associated with weight loss due to the product parameters was lower. As the storage temperature increased, the variability also increased, as evident from Fig 4.5c. The weight loss was lower than 0.5% at 4°C in 10 days, whereas at 20^0C the weight loss reached 2.7%. Spoilage increased with storage temperature, as shown in Fig 4.5d. Spoilage was lower than 15% in 10-day storage, around 37% at 8°C, 100% spoilage at 20°C in 6 days. The effect of CO_2 on spoilage could be explained by the effect of CO_2 on the respiration rate. Hertog and co-authors (1999) showed that *Botrytis* inoculated fruits displayed an inhibitory effect of CO_2 on spoilage levels below 20%, which was strongly batch dependant.

4.5.4. Comparing the effect of variability on strawberry quality

The uncertainty associated with cold chain variability (temperature and relative humidity) and the variation associated with biological product parameters were compared by plotting kernel density plots for each food chain distribution day and for each of the scenarios. Fig 4.6 a&b show how the concentration of gases in the package's headspace is dependent both on cold chain and product variability. The second peak observed in the fig 4.6 was the result of abusive storage temperature ($>10^0$C). Variations at the 4th day of distribution in CO_2 and O_2 concentrations seems to be largely cold chain dependent, however by day 6 the cold chain variation has reduced below the variation of the product.

a)
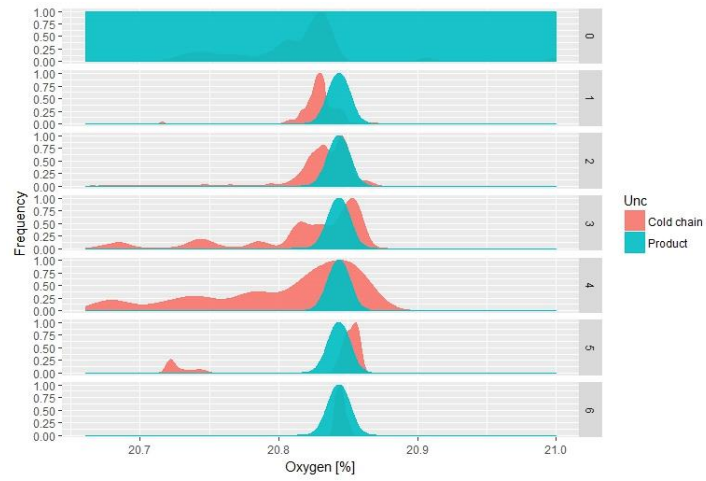
b)
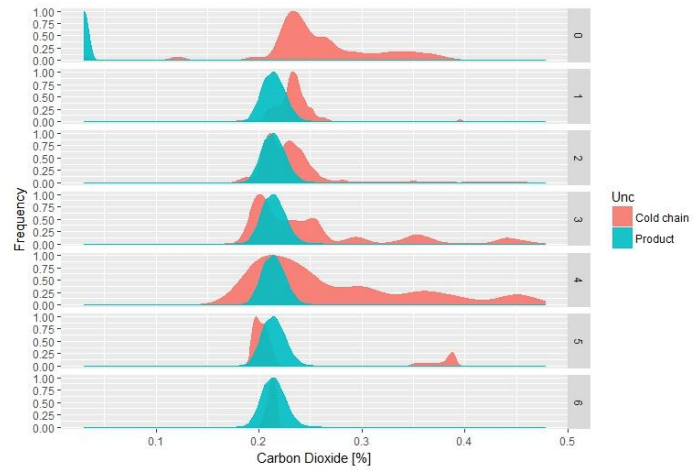
c)
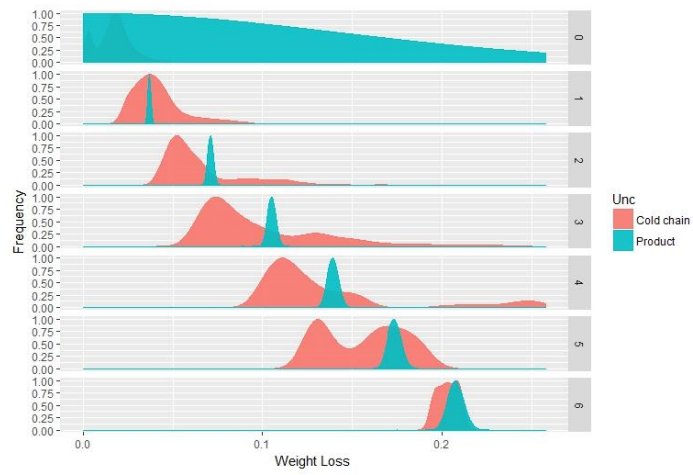
d)
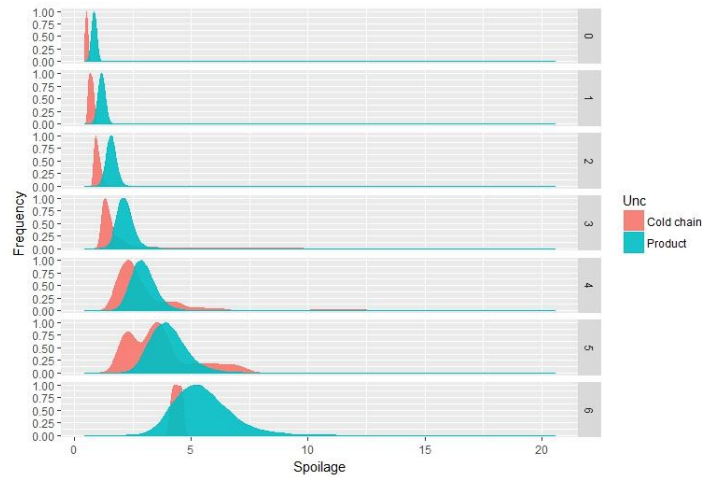
Fig 4.6 The effect of cold chain uncertainty (green) and product parameter uncertainty (orange) on the (a) oxygen concentration (b) carbon dioxide concentration in headspace (c) weight loss during storage (d) Spoilage of strawberry. Each subplot within (a), (b), (c) and (d) represents the simulated variation in a given distribution day

The weight loss showed dependence on the cold chain factors and storage temperature and relative humidity. Strawberries stored at $1^{\circ}C$ showed less than 1% weight loss in 8 days, versus 8% at $20^{\circ}C$ in 4 days, which exceeds the acceptable limit (Nunes et al., 1998). The spoilage rate (Fig 4.6d) was most influenced by the cold chain factors at the start of storage, but product uncertainty had a more prominent impact later during storage. Strawberries have been found to be colonised by the fungus *B. cinerea* before packaging, with the fungal infection increasing with storage time and inadequate storage conditions (Almenar et al., 2007). The initial spoilage (N_0) is a value representing initial ripening stage or sensitivity of strawberry to *Botrytis* infection (Hertog et al., 1999). From Fig 4.6c and Fig 4.6d it was evident that the cold chain conditions (temperature and relative humidity) need to be controlled in order to minimise the product's weight loss. Nevertheless, in the case of spoilage the product parameters are the main cause of variability that need to be controlled to extend the shelf life.

4.5.5. Sensitivity Analysis

Sensitivity analysis was performed to study the results of variation and how it could be apportioned qualitatively and quantitatively to different sources of variation in the model input (Kader and Saltveit, 2003). The result of the sensitivity analysis (SA) on the weight loss of packed strawberry are presented in Fig 4.7a. The most important parameters contributing to the 90% of the variability were a combination of respiration rate parameters ($RQ_{ox}, Vm_{O_2,ref}, K_{mO_2}$), skin mass transfer coefficient (K_s) and the activation energies associated with ($E_{aVmO_2}, E_{aVm_{CO_2}(f)}$). Main effects interactive effects between the product parameters had an important impact on variability. This result suggests that controlling the respiration rate of the fresh produce and reducing the mass transfer through their skin can help reduce losses during the supply chain.

a)

b)

c)
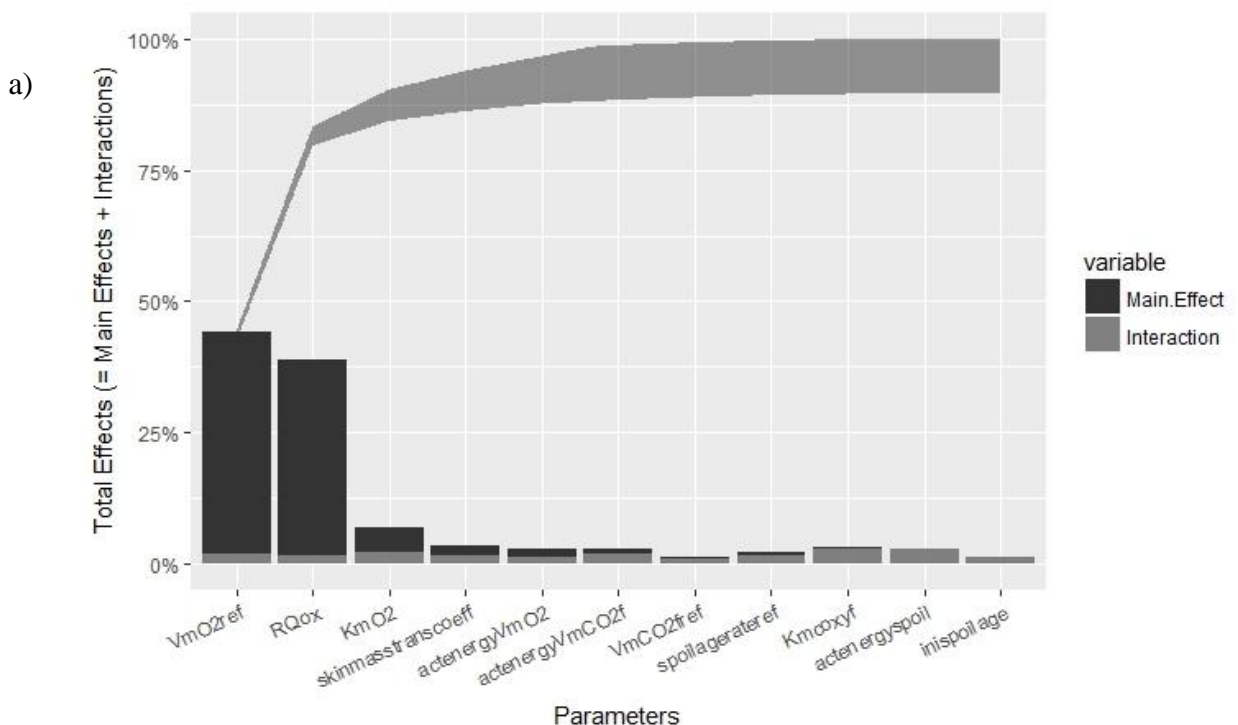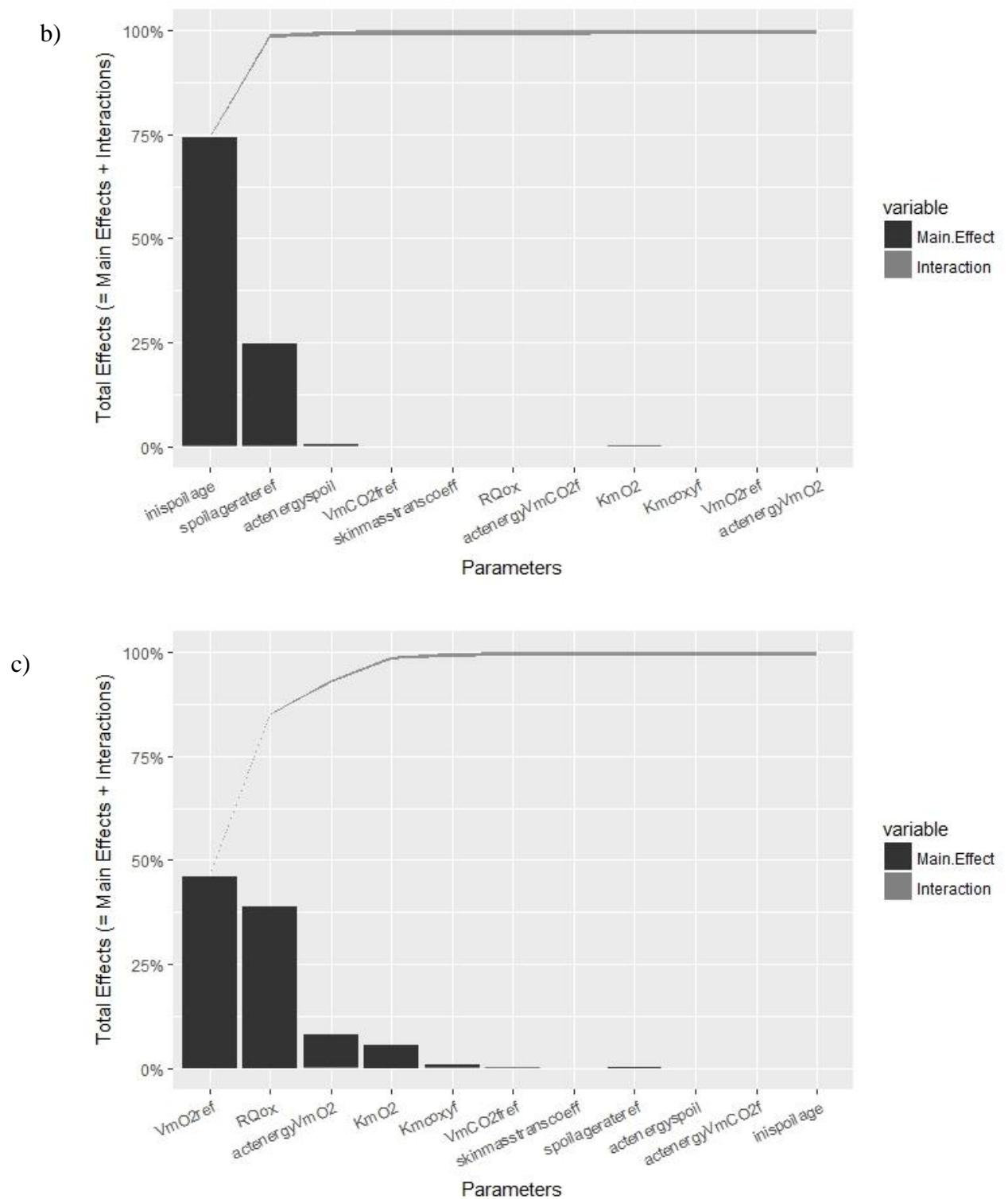
Fig 4.7 Lowry plot for the effect of product parameters on the a) weight loss b) spoilage, c) CO₂

Identification of an effective intervention

The sensitivity analysis of strawberry spoilage indicates that the most important parameters contributing to 90% of the variability are initial spoilage and spoilage rate constant ($k_{s,ref}$) (Fig 4.7b). Thus, the waste due to spoilage can be reduced by ensuring a good initial quality of strawberry and by controlling the spoilage rate during the supply chain. The product parameters contributing to the concentration of CO_2 in the package's headspace were $Vm_{O_2,ref}, RQox$ and $E_{Vm_{O_2,ref}}$ (Fig 4.7c). As these parameters contributed to 90% of the variability, a waste reduction would be achieved by controlling them.

4.5.6. Validation experiment

The input model parameters from Table 4.2 and 4.3 are used to compare the experimental and predicted results presented in the Fig 4.8. The experimental data comprises strawberry stored at ideal temperature ($4^{\circ}C$) and abusive temperatures (4, 20, $8^{\circ}C$) for 10 days, in order to simulate real life supply chain conditions. Weight loss, colour, firmness and spoilage were measured at 1, 3, 5, 7 and 10 days. The grey ribbon represents the uncertainty margins of 5% and 95% percentiles ascribed to variability.
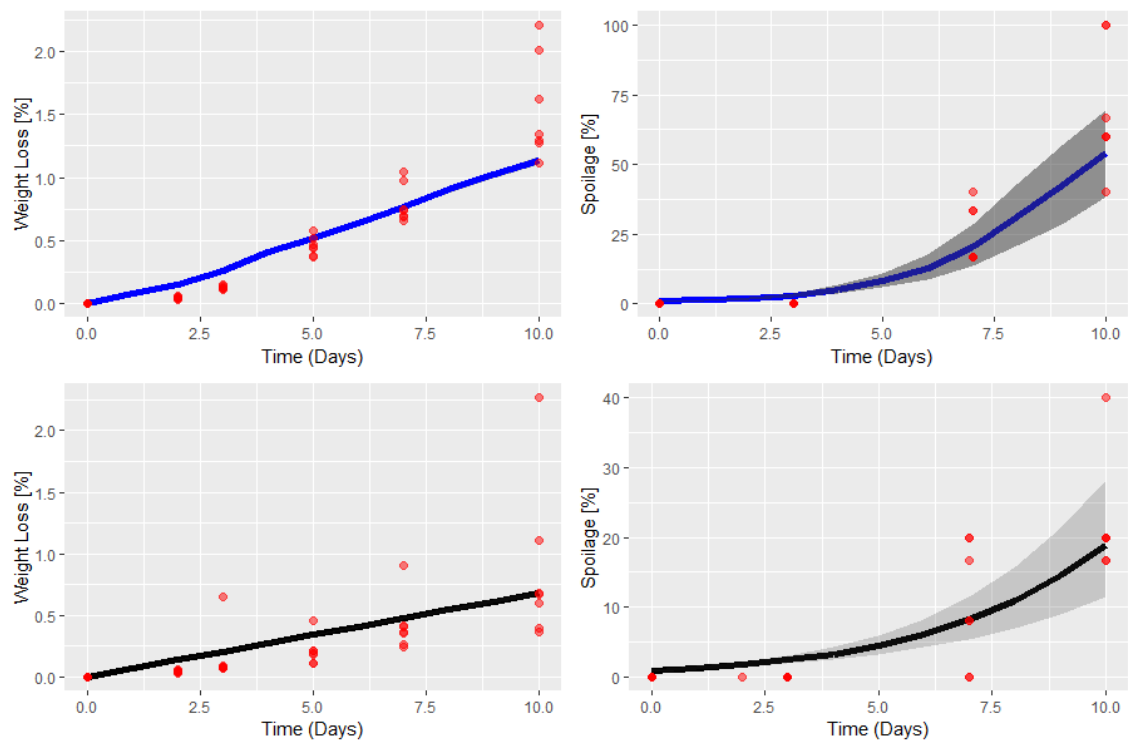
Fig 4.8 Comparison of model predictions with the experimental data (points) at different storage conditions ((4, 8, 200 C) (a, b) and at ideal temperature (40C) (c,d) a) weight loss b) spoilage at (4, 8, 200 C) , c) weight loss and d) spoilage at (40C).

There was less variability associated with the weight loss due to the product parameters uncertainty also evident from fig 4.5c. Cold chain parameters are responsible for the weight loss variability during the distribution chain of strawberry (Fig 4.6c). At abusive storage conditions the weight loss goes up to 2 % and was less than 1% in ideal conditions. Spoilage was highly variable and were more dependent on product uncertainty parameters (Fig. 4.5d). At abusive conditions spoilage goes up to 75% and in ideal supply chain conditions the spoilage was 20%. The experimental results fall in the grey ribbon showing a good agreement with the prediction. The results of bias and accuracy are presented in the Table 4.4.

Table 4.4 Results of bias and accuracy factor in the model validation of strawberry quality according to the cold chain conditions.

		Bias Factor	Accuracy Factor
Control	Abuse	0.899	1.108
	Ideal	0.903	1.097
Coating	Abuse	0.875	1.347
	Ideal	0.884	1.279

4.5.7. Waste generation estimation during the supply chain

Fig 4.9 shows the total waste estimation throughout the strawberry supply chain, as a combination of waste due to weight loss and spoilage. Threshold values were used to calculate the waste – weight loss≥5%, when fruits start to shrivel and become unmarketable), and 5% spoilage. Significant amounts of out-of-specification product yielding to waste appear from day 2 of distribution; by the end of day 3, approximately 10% of all product would be potentially unsuitable for consumption, leading to waste generation.
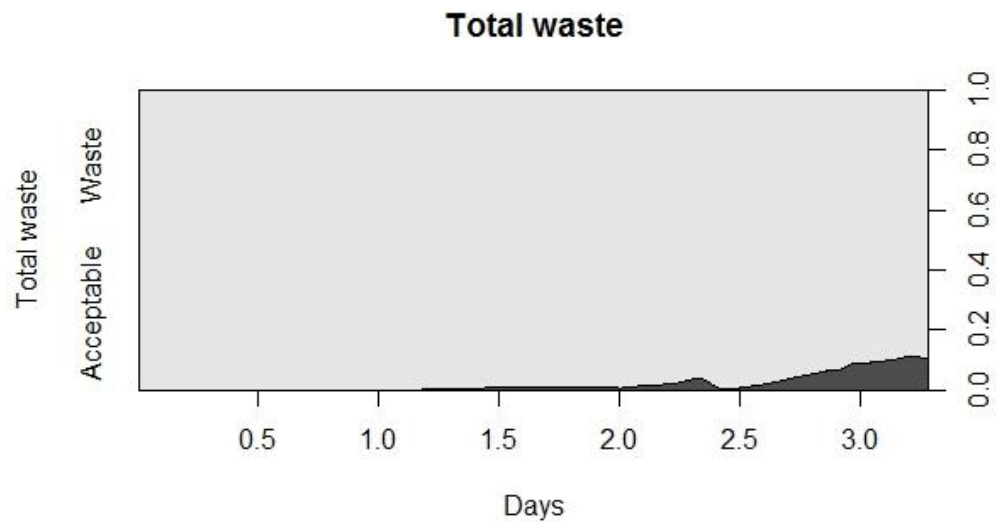
Fig 4.9 Conditional density plot of total waste generated in the strawberry supply chain.

4.6. Conclusions

A mathematical model was developed to predict the concentration of gases (O_2, CO_2) and water vapour in the packaging headspace. The model takes into account the heat and mass transfer processes occurring in MAP, such as respiration, transpiration condensation and transport of gases through the permeable film. The kinetic behaviour of fresh produce was modelled with respect to the cold chain conditions and product parameters. The effect of cold chain variability and product variability on the quality of fresh produce was assessed. Weight loss was shown to be influenced by the cold chain factors like temperature and humidity. In contrast, spoilage was initially impacted by the cold chain factors, but product variability becomes prominent towards the end of storage. The results of the sensitivity analysis showed that control of the respiration rate and skin mass transfer would help reduce the waste produced the during supply chain. The model validation showed that the model was a good fit to the experimental data.

Chapter 5.   Impact of cold chain attributes and product parameters on waste generation of packaged tomato in cold supply chain

5.1.   Introduction

Among horticultural produce tomato is the second most grown crop worldwide. Tomato is also rich in vitamins and minerals and are an essential part of human diet (de Castro et al., 2005). Tomato is a perishable, climacteric commodity whose quality is a composite of appearance (colour, decay), firmness, flavour and nutritional value (Kader, 1984). Postharvest losses observed in tomato quality are generally caused by physical damage and exposure to abusive storage conditions (temperature and RH). Inadequate storage temperature influences the colour uniformity and ripening of tomato. This deteriorates the quality and restricts the shelf life, and leading to product losses (Gil et al., 2002; Pinheiro et al., 2013; van der Vorst et al., 2011).

Low temperature storage can retard the changes due to ripening. Tomatoes are also susceptible to chilling injury, therefore too low storage temperature can lead to pitting, uneven ripening and fungal spoilage (Geeson et al., 1985). Storage of tomatoes stored at temperatures from 12 to 20^0 C and under low oxygen atmosphere can delay ripening (Kader, 1984). The potential of polymeric films to create a modified atmosphere for extending the shelf life of tomato has been extensively researched. MAP with 3 % O_2 and 1% CO_2 have been reported as optimum conditions to avoid anaerobic respiration

and maintaining quality. However 3% O_2 and 5% CO_2 were reported as optimal MA environment for mature green tomatoes (Nakhasi et al., 1991).

The need for transportation of tomatoes over long distances renders MAP associated with low storage temperature a most promising and inexpensive method to extend their shelf life. To minimise the losses related to postharvest deterioration, it is important to understand the biological and environmental factors that lead to quality decay. Biological factors associated with the deterioration of quality are the produce's respiration rate, ethylene production and action, compositional change, mechanical injury, physiological disorder and pathological breakdown (Kader, 2004). Edible coatings have been proven a beneficial technique to manage the quality deterioration of tomato. Chitosan, for instance, prevents spoilage due to its antifungal activity. Edible coatings are also known to contribute to the creation of a modified atmosphere and to reduce weight loss during transportation and storage (Casariego et al., 2008).

A model to predict gas concentration (O_2 and CO_2) and colour development of ripening tomatoes packed in polymeric packages has been developed by (Yang and Chinnan, 1988). The respiration rates were modelled using a polynomial function and the hunter colour ratio was used to predict the colour change during ripening. (Cameron et al., 1989) used Fick's law to obtain the flux of gases (O_2 and CO_2) through the film. Schouten et al. (2007) modelled the change in colour and firmness of tomato during storage. In an integrated mathematical modelling system, all these equations may be employed to build a model able to predict the effect of temperature and packaging properties on the quality of the tomato (Jacxsens et al., 2002). Most of the input parameters of these integrative models will have an associated uncertainty, which can be very important for the assessment of the final quality of a product in variable industrial

conditions. To design a food system which will extend the shelf life and reduce waste, all these uncertainties should be considered (Hertog, 2002).

The objective of this study was to develop a mathematical model to predict the behaviour of tomato in packaging. Heat and mass transfer principles associated to physiological processes (respiration, transpiration, condensation) were used to build the model. The model predictions were simulated based on real cold chain conditions to study the effect of cold chain uncertainty on tomato quality. The product uncertainty was studied separately at different storage temperature scenarios. The effect of cold chain and product uncertainty components were compared to the fate of quality of tomato during the cold chain. A sensitivity analysis was performed to quantify the influence of product parameters and cold chain variability on tomato quality. This approach enabled to benchmark the most effective product/package properties in reducing waste losses, which then helped identify potential interventions that may influence those product/process parameters. The simulation results were then compared with the experimental data to validate the model.

5.2. Materials and Methods

5.2.1. Model hypothesis

- CO_2 production is a combination of oxidative and fermentative production, the oxidative consumption is proportional to the O_2 evolution and the fermentative production follows the Michaelis-Menten equations.

- The temperature of the surface of commodity (T_s) is equal to the temperature of air surrounding the commodity (T_i).

- The surface of the commodity is assumed to behave as perfectly saturated condition for water transport.

- A large part (80-100 %) of the metabolic energy released by the produce is dissipated as heat.

- 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.

- The quality of tomato is described as weight loss due to transpiration and spoilage model by (Hertog et al., 1999; Tijskens and Polderdijk, 1996).

5.2.2. Mathematical Model development

The mathematical model took into account

- the heat and mass transfer balances due to the metabolic behaviour of tomato and the transport phenomenon across the package.

- The assumptions used in the mathematical model and sub model to describe respiration- transpiration of tomato and gas transport across package.

- The influence of these on the quality of tomato during the distribution chain.

5.2.3. Mass Balance

The transport of oxygen and carbon dioxide in the package was modelled using a mass balance for the two gases

$$V_f \frac{d[O_2]_i}{dt} = 100 \times \left(\frac{A_p P_{O_2} P_{atm}}{L_f} \left[\frac{[O_2]_o}{100} - \frac{[O_2]_i}{100} \right] - W_p r_{O_2} \right) \qquad 5.1$$

$$V_f \frac{d[CO_2]_i}{dt} = 100 \times \left(\frac{A_p P_{CO_2} P_{atm}}{L_f} \left[\frac{[CO_2]_o}{100} - \frac{[CO_2]_i}{100} \right] + W_p r_{CO_2} \right) \qquad 5.2$$

5.2.3.1.   *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 5.3.

$$\frac{dm_{pr}}{dt} = \left[\frac{P_{H_2O}A_p(p_i-p_o)}{L_f}\right]\left[\frac{0.018P_{atm}}{RT_S}\right] \qquad\qquad 5.3$$

When the water vapour pressure inside the package (p_i) is less than or equal to the saturated vapour pressure (P_s), the moisture is permeated from the film to its surroundings. Inversely, when p_i is higher than the saturated vapour pressure, condensation will occur and the latent heat of condensation will rise the produce's temperature.

5.2.3.2.   *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)

$$\frac{dHR}{dt} = \frac{t_r-m_{pr}}{W_a} \qquad\qquad 5.4$$

The relative humidity in the headspace can then be estimated as the ratio of the humidity ratio inside the package at any time Eq. 5.4 to the humidity ratio of saturated water vapour (HR_{sat}) at the same temperature Eq. 5.5 (Becker et al., 1996).

$$HR_{sat} = \frac{0.62198p_s}{(P_{atm}-p_s)} \qquad\qquad 5.5$$

5.2.4. Heat Balance

The temperature of surface of produce and gases surrounding it in the headspace was assumed to be uniform. The major source of heat generation inside the MAP was the

metabolic processes by fresh produce and heat was transferred in the headspace due to convection, transpiration and condensation. Thus, the overall energy balance in the package was written as follows.

$$Q_r W_s + Q_{con} + h_p A_p (T_o - T_i) = Q_{tr} + W_s C_s \frac{dT_s}{dt} + W_a C_a \frac{dT_s}{dt} \qquad 5.6$$

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

$$\frac{dT_s}{dt} = \frac{Q_r W_s + Q_{con} + h_p A_p (T_o - T_i) - Q_{tr}}{W_s C_s + W_a C_a} \qquad 5.7$$

5.2.5. Metabolic process

Respiration is a metabolic process which provides energy for the biochemical processes occurring. The oxygen and carbon dioxide respiration rate were calculated using:

$$r_{O2} = \frac{V_{m_{O_2}} \cdot [O_2]}{(Km_{O_2} + [O_2]) \cdot (1 + \frac{[CO_2]}{Kmn_{CO_2}})} \qquad 5.8$$

$$r_{CO2} = RQ \, r_{CO2} \qquad 5.9$$

The respiration rate also acts as an indicator of the shelf life of fresh produce. During this process energy is generated, part of which is released as heat Eq. 5.10 (Becker and Fricke, 1996b; Fonseca et al., 2002).

$$C_6 H_{12} O_6 + 6 O_2 \longrightarrow 6 CO_2 + 6 H_2 O + 2816 kJ \qquad 5.10$$
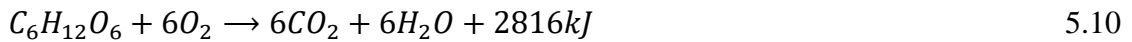
5.2.5.1. *Transpiration*

Water vapour pressure deficit VPD (Pa) between the produce surface and the surrounding atmosphere causes transpiration from the surface of produce (Xanthopoulos et al., 2012). Vapour Pressure Deficient (VPD) is the function of difference in the amount of moisture in air and the amount of moisture air can hold when it is saturated (Becker et al., 1996).

$$\text{VPD} = (a_w - RH)p_s \qquad\qquad 5.11$$

It is assumed that water activity of fresh produce surface is ($a_w \sim 0.99$).

Saturated water vapour pressure at the surface of commodity could be calculated using eq. 5.12 (Rennie and Tavoularis, 2009b) based on the saturated water vapour pressure data from ASHRAE (1997).

$$p_s = 0.041081186T_s{}^3 - 32.43188T_s{}^2 + 8567.5269T_s - 757070.1 \qquad 5.12$$

Transpiration occurs when water vapour pressure at the surface of commodity exceeds the water vapour pressure of the headspace of package (Becker et al., 1996; Xanthopoulos et al., 2012).

$$m_w = VPD \times K_t \qquad\qquad 5.13$$

The transpiration rate (kg m^{-2}h^{-1}) is the product of water vapour flux (m_w) and the surface area of the commodity (A_c)

$$t_r = m_w A_c \qquad\qquad 5.14$$

$$K_t = \frac{1}{\left(\frac{1}{K_s} + \frac{1}{K_a}\right)} \qquad\qquad 5.15$$

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

$$Sh = \frac{K_a d_c}{D_{H_2O,air}} \qquad\qquad 5.16$$

In order to estimate the convective mass transfer from an spherical commodity (Becker et al., 1996) recommended the following Sherwood-Reynolds-Schmidt correlation.

$$Sh = 2.0 + 0.552\, Re^{0.53} Sc^{0.33} = \frac{K'_a\, d_c\, R\, T_s}{D_{H_2O,air}\, M_{H_2O}} \qquad\qquad 5.17$$

It was assumed that there was a negligible flow around the commodity ($Re \approx 0$). Therefore, the air film mass transfer coefficient could be calculated as:

$$K_a = 2 \times \frac{D_{H_2O-air} \, M_{H_2O}}{d_c \, R \, T_s} \qquad\qquad 5.18$$

Transpiration Heat

The process of transpiration requires energy for the evaporation of moisture from the surface of the produce, with the corresponding cooling down of the commodity. The evaporative heat transfer rate (Q_{tr}) is a product of the latent heat of vaporization (λ) and the transpiration rate (t_r).

$$Q_{tr} = \lambda \, t_r \qquad\qquad 5.19$$

5.2.5.2.   *Relative humidity in headspace*

The concentration of water vapour inside the package is dependent on the rate of water vapour transfer from the moisture sources to moisture sinks within the package. The main moisture sources in the package is water transpired from the surface of fresh produce (t_r) and the main source of moisture sink is permeation of water vapour through the film (m_{pr}) (Becker et al., 1996).

The amount of water vapour in the headspace was calculated using the humidity ratio which is the ratio of mass of water vapour in headspace to mass of dry air in the headspace of package (kg/kg).

$$\frac{dHR}{dt} = \frac{t_r - m_{pr}}{W_a} \qquad\qquad 5.20$$

Relative humidity was calculated as ratio of humidity ratio inside the package (*HR*) to the humidity ratio of saturated water vapour (*HR$_{sat}$*) (Becker et al., 1996; Jalali et al., 2017; Song et al., 2002).

$$HR_{sat} = \frac{0.62198 P_s}{(P_{atm} - P_s)} \qquad\qquad 5.21$$

$$RH = \frac{HR}{HR_{sat}}$$
5.22

5.2.5.3. *Condensation*

In perforation mediated packaging condensation rate is seldom modelled, a common phenomenon due to near saturation conditions within the package and non-uniform or fluctuating temperature during storage, distribution, sale and consumption. Condensation can occur on the commodity surface or inside of package film and walls. It is assumed that the water vapour condensed on the surface of commodity does not penetrate the skin of fresh produce. For condensation to take place the partial pressure of water vapour should be greater than the saturated water vapour pressure (Jalali et al., 2017; Joshi et al., 2018; Rennie and Tavoularis, 2009b).

$$M_{con} = \begin{cases} K_a(P_{H_2O-} P_c)\delta A_c, & if(P_{H_2O} > P_s) \\ 0 & otherwise \end{cases}$$
5.23

The corresponding rate of release of heat due to condensation on the surface of commodity was Q_{con} calculated as:

$$Q_{con} = \lambda\, M_{con}$$
5.24

λ, is the latent heat of vaporization estimated by eq 5.25.

$$\lambda = (3151.37 + (1.805\, T_s) - (4.186\, T_s)) \times 1000$$
5.25

The rate of condensation on package wall (M_{wcon}) was calculated similarly using air film mass transfer coefficient (K_a).

$$M_{wcon} = \begin{cases} K_a(P_{H_2O-} P_s)\delta A_w, & if(P_{H_2O} > P_s) \\ 0 & otherwise \end{cases}$$
5.26

The heat released during condensation (Q_{wcon}) heated up the atmosphere near the package wall.

$$Q_{wcon} = \frac{\lambda M_{wcon}}{A_w}$$
5.27

5.2.6. Quality

The quality of fresh produce is generally associated to the overall characteristics (appearance, texture, flavour and nutritive value) (ElMasry et al., 2007). The perception of quality is highly subjective and depends on consumer and on a number of qualitative factors. Quality of fresh produce in general is often described using chemical kinetic models (Merts, 1996). Some of the main attributes of quality in tomatoes is weight loss and spoilage.

5.2.6.1. *Weight loss*

The amount of water vapour transpired from the surface of fruit (t_r) and carbon loss due to respiration were used to estimate the product weight loss.

$$\frac{dW_l}{dt} = t_r + M_c r_{CO_2} W_s \qquad\qquad 5.28$$

5.2.6.2. *Spoilage*

Species of *Botrytis* have been reported as one of the common pathogens associated with postharvest diseases of tomato (Etebu et al., 2013). There are two components of the spoilage model used by Hertog for strawberries: Rel_{MR} and logistic rate spoilage model (Hertog et al., 1999). The relative metabolic rate (eq 5.29), which is ratio of the actual respiration rate under any gas conditions to the respiration rate under normal gas conditions (21% O_2, 0.03% CO_2) at the same temperature is used to show the effect of MAP and temperature control on the spoilage of fresh produce.

$$Rel_{MR} = \frac{r_{CO_{2(f)}}([O_2],[CO_2],[H_2O],T_s)}{r_{CO_2}(21\% \, O_2, 0.03\% CO_2, T_s)} \qquad\qquad 5.29$$

The spoilage model for tomato was a classic logistic model dependent on a number of intrinsic product parameters and the Rel_{MR}.

$$\frac{dN}{dt} = Rel_{MR} \times k_s \times N \times \left(\frac{N_{max}-N}{N_{max}}\right), initiate \, at \, N_0 \qquad\qquad 5.30$$

N_{max} is maximum spoilage (100%), k_s is the spoilage rate constant which depends on the temperature according to Arrhenius equation.

$$k_s = k_{s,ref} \cdot e^{\frac{Ea_s}{R_{gas}} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T_s}\right)}$$ 5.31

5.3.   Numerical Simulations of the ODE system

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).

To estimate the effect of input parameter uncertainty on the prediction of concentration of gases and effect on quality during the cold chain distribution, Monte Carlo simulations were performed to simulate three scenarios:

5.3.1.   Uncertainty assessment

1. Assessment of cold chain on waste production

A simulation scenario considering average product characteristics without variation and a variable cold chain was used to assess the importance of different transport and retail conditions. This simulation scenario used a cold chain of 3 and 6 days chosen on a random basis among on cold chain data used. The temperature and relative humidity record during the export of four international cold chains between Ireland and the United Kingdom was used, comprising temperature and relative humidity data, including the production farm, the packaging house, international haulage, retail storage and arrival to the retail shop. This data was originally collected as part of a research innovation project in collaboration with industry, described in detail in Joshi et al. (2018). The data was collected using temperature and relative humidity dataloggers (XSense®, BT9 Intelligent Supply Chain Solutions, UK) with a logging frequency of 10 minutes. The experimental

data comprised 4 export chains including at least 3 retail storage and arrival to 3 shops with 3 replicates extending from 3 to 6 days.

The study from Garvan (2007) was conducted throughout the summer of 2007 over 85 premises spread through the 26 counties in the Republic of Ireland, including open and close refrigerated cabinets in a supermarket, a deli shop and a butcher outlet in each county. The mathematical model was simulated against these cold chain profiles to study the effect of cold chain uncertainty on the quality of tomato and the results are presented in section 5.4.

a)

b)
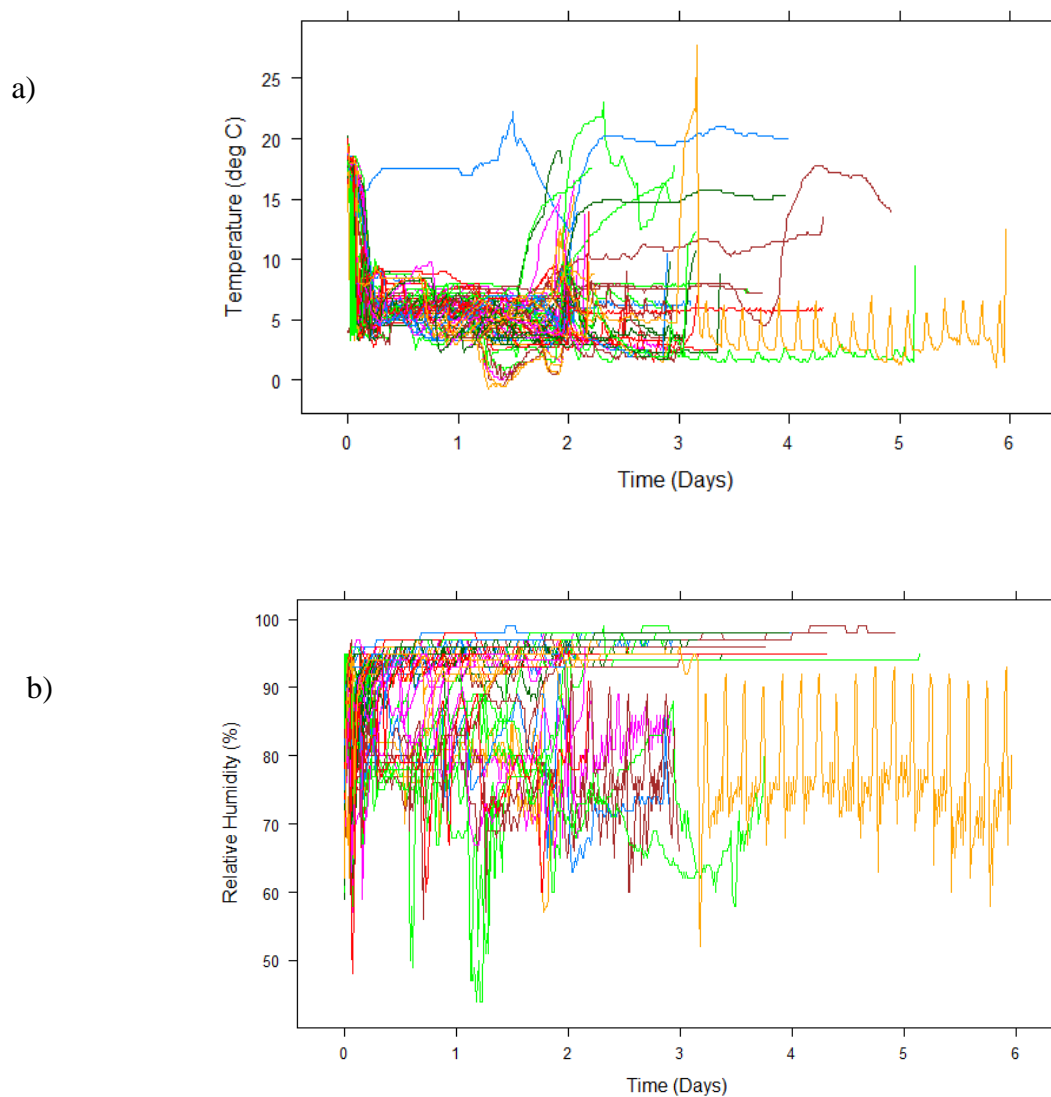
**Fig 5.1 Export cold chain profile: a) Temperature and b) Relative humidity.**

a)

b)
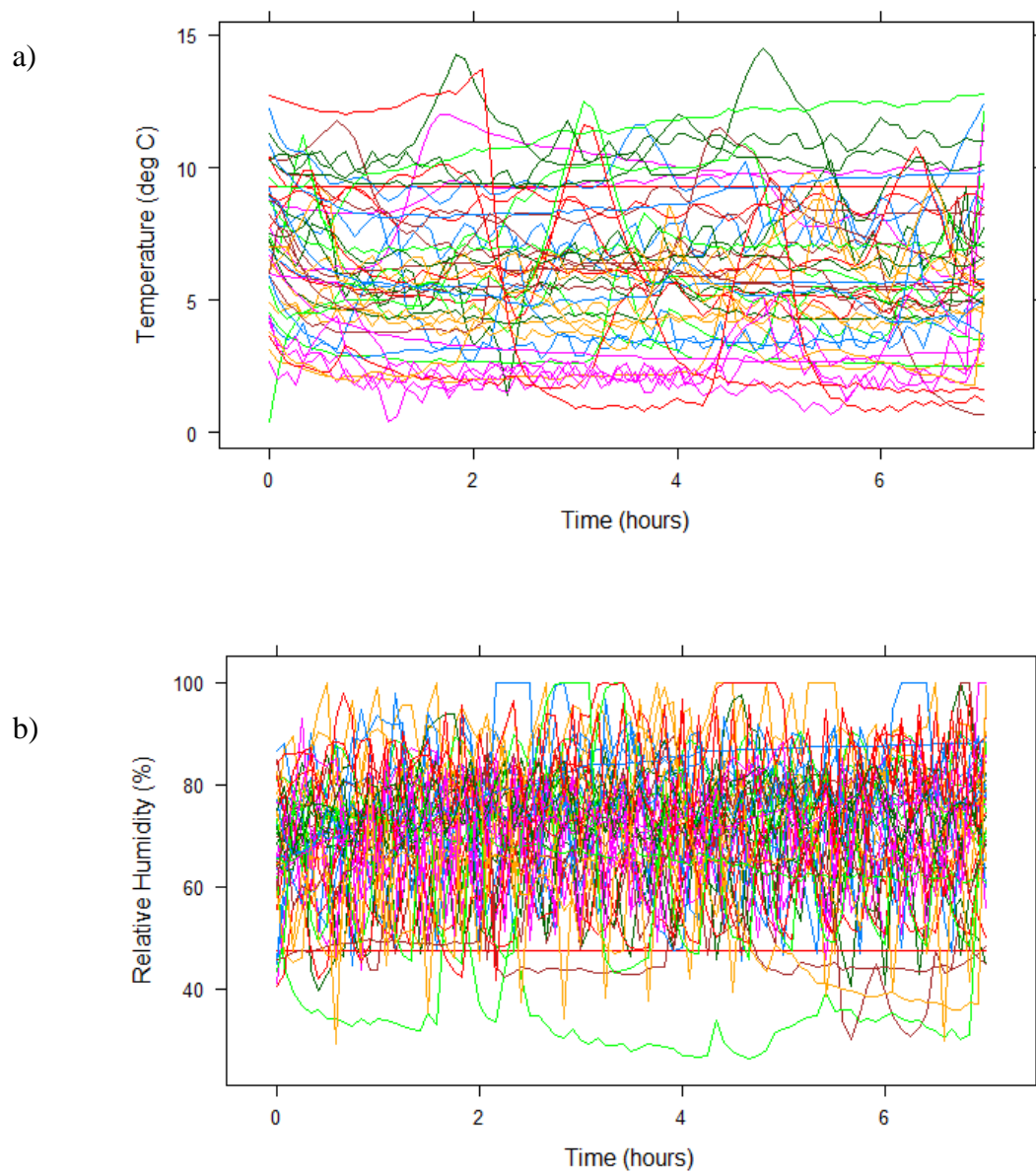
Fig 5.2 Retail cold chain profile: a) Temperature and b) Relative humidity.

2. *Assessment of product variability on waste production*

The product parameters responsible for variability are presented in table 5.1. The storage conditions tested involved

1) An ideal storage temperature of 4^0 C and relative humidity 80%.

2) An abuse cold chain that was composed of the following steps: 2 hours of packaging at 8^0 C followed by retail storage for upto 1 and half day at 4^0 C followed by the transportation at 8^0 C for 1 day and finalised by 4^0 C of retail shop for 3 days.

The product parameters responsible for variability are presented in table 5.2. The results shows the uncertainty due to the product parameter uncertainty on the quality parameters of tomato.

3. Combined assessment of product and cold chain uncertainty effect on waste

In the following section the combined assessment of cold chain uncertainty and product uncertainty was done. This contributed to identification of the influence of different parameter uncertainty and the interventions that can be designed to maintain quality and reduce the waste in supply chain. A sensitivity analysis was completed to understand the effect of individual parameters on the quality explained in next section.

5.3.2. Validation Experiment

Tomatoes packaged in perforated polypropylene LDPE film (4 perforations) were stored in ideal storage condition (4^0 C) and abuse storage condition imitating the abusive cold supply chain conditions (1/2 day in packaging facility at 8 ℃ followed by transportation at 4 ℃ up to 2 days, followed by retail storage including 4h at 20 ℃, followed by 2 days at 8 ℃, and finalised by retail shop 4h at 20℃ 2 days at 8 ℃) for period of 10 days (Joshi et al., 2019).

A chitosan solution (1.5 %) was prepared by dissolving chitosan in distilled water containing 1% glacial acetic acid using a magnetic stirrer. After complete dissolution 0.2% Tween 80 was added to the solution. The pH of the solution was adjusted to 5.2 with 1N NaOH (Petriccione et al., 2015). Tomatoes were then immersed in chitosan solution for 60s, allowed to dry for 1 hour in air dryer at room temperature and then stored as mentioned above.

Produce was visually examined on regular intervals during storage period. Tomatoes showed surface mycelia growth or bacterial lesions were considered decay. Results were expressed as percentage of spoiled produce. Weight loss was expressed as a percentage of the loss of initial weight (Han et al., 2004).

Sensitivity analysis

Sensitivity analysis is the study of how variation in a risk assessment output can be apportioned, qualitatively or quantitatively to different sources of variation (McNally et al., 2011). The input parameters mentioned in table 5.2. Sensitivity analysis using a main and first order interactive effects model excluding time were analysed using a Lowry plot (McNally et al., 2011).In a Lowry plot the main parameter effect displayed in black and the sum of all first order interactive effects with other parameters is displayed in grey. The thickness of the ribbon added in the plot represents the variance due to parameter interactions, the cumulative sum of main effect being lower line and the sum of total effect the upper line.

5.4.   Results and discussions

5.4.1. Cold chain variability

The integrated mathematical model mentioned in the section above was used to simulate the quality parameters of tomatoes during the distribution supply chain. The governing ordinary differential equations were used to simulate the changes in gas concentrations, temperature, relative humidity in the headspace and quality changes (weight loss and spoilage) based on the supply chain profile.

Table 5.1 Properties of packaging film, produce and other conditions used in the model

Parameter	Value	Reference
ρ_b (kg m^{-3})	490	(Cameron et al., 1989)
ϵ	0.27	(Xanthopoulos et al., 2012)
a_w	0.99	(Xanthopoulos et al., 2012)
C_s (J kg^{-1} K^{-1})	4020	(ASHRAE, 2006)
$[CO_2]_i$ (%)	0.03	(Song et al., 2002)
$[O_2]_i$ (%)	21.0	(Song et al., 2002)
M_{O_2}(kg mol^{-1})	0.032	(Bird, 2002)
M_{CO_2}(kg mol^{-1})	0.044	(Bird, 2002)
M_{H_2O}(kg mol^{-1})	0.018	(Bird, 2002)
R (J K^{-1}mol^{-1})	8.314	(Bird, 2002)
P_{atm} (Pa)	101325	(Bird, 2002)
ρ_{O_2} (kg m^{-3})	1.43	(Siracusa, 2012)
ρ_{CO_2}(kg m^{-3})	1.98	(Siracusa, 2012)
T_{ref} (^{0} C)	10	(Hertog et al., 1999)
RQ_{ox}	0.8	(Hertog et al., 1998)
d_H(m)	0.0035	Experimental
N_H	3	Experimental
d_c(m)	0.01	Experimental
D$_1$xD$_2$xD$_3$(cm)	22x16.5x3	Experimental
$P_{O_2\,ref}$ (ml h^{-1}m^{-2}atm)	4200	Experimental
$P_{CO_2\,ref}$(ml h^{-1}m^{-2}atm)	20000	Experimental
$P_{H_2O\,ref}$(g h^{-1}m^{-2})	6	Experimental

Changes in the respiration rate of tomato during storage caused a variation in the concentration of O_2 and CO_2 in the package's headspace. The CO_2 concentration increased in the headspace, while the O_2 concentration decreased when simulated against the export cold chain profile in Fig 5.1. The package atmosphere was slightly modified from the initial atmosphere. This gas exchange dynamic was observed for LDPE packaging with perforations. The results obtained by Charles et al. (2003) are in agreement with the present simulations.
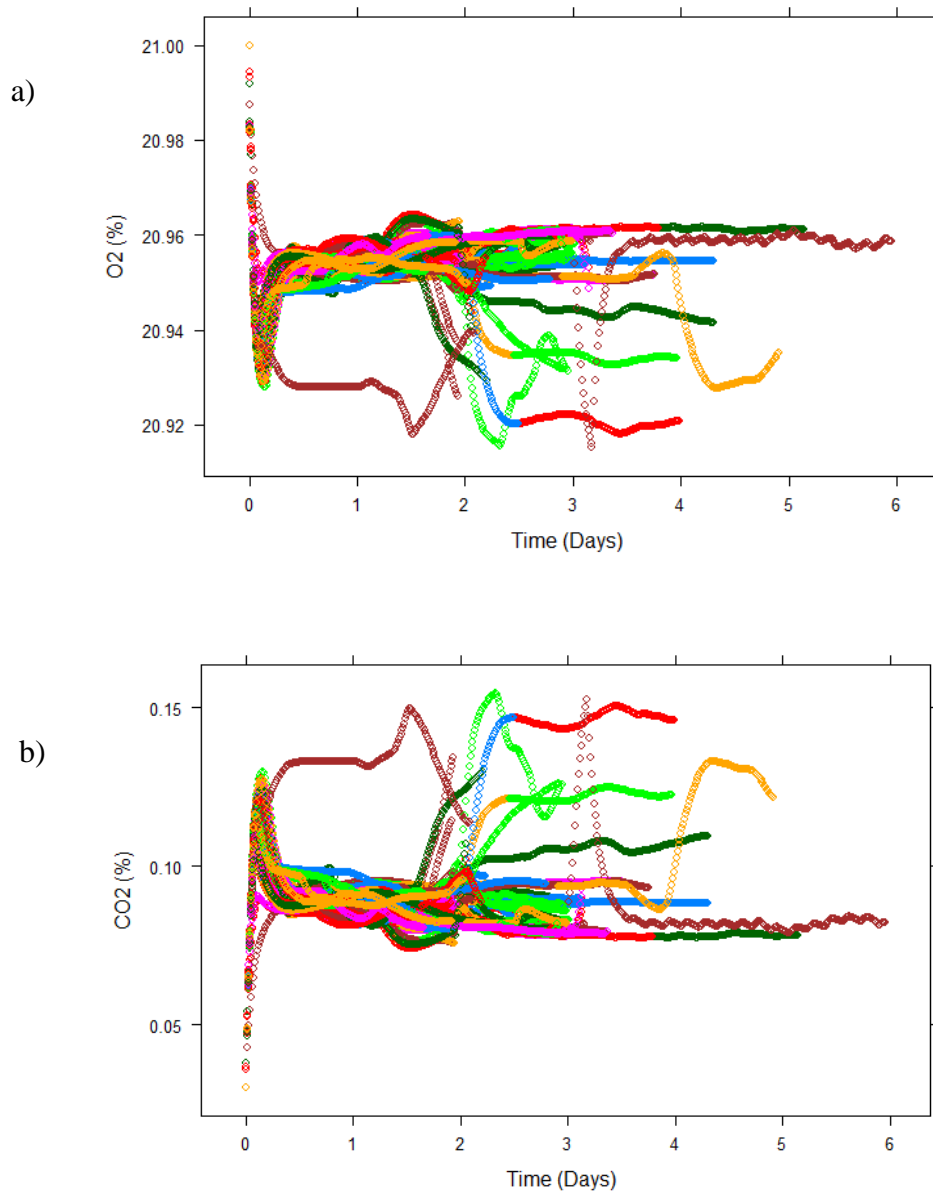
Fig 5.3 Effect of cold chain parameters on the concentration of gases in headspace a) O₂ and b) CO₂

Fig 5.4a shows the weight loss observed during the supply chain. Storage temperature had significant effect on the weight loss due to transpiration thus reducing the quality and inducing losses in supply chain. In this modified packed tomato weight loss observed was only 0.16% in 6 days. Geeson et al. (1985) observed 0.11 % of weight

loss after every week of storage with an acceptable threshold for weight loss is 5%. The spoilage of fresh produce below 10% falls in the acceptable limit for commercial packaging of fresh produce (Hertog et al., 1999). Some cold chain shows higher spoilage which may be a result of abusive storage temperature.

a)

b)
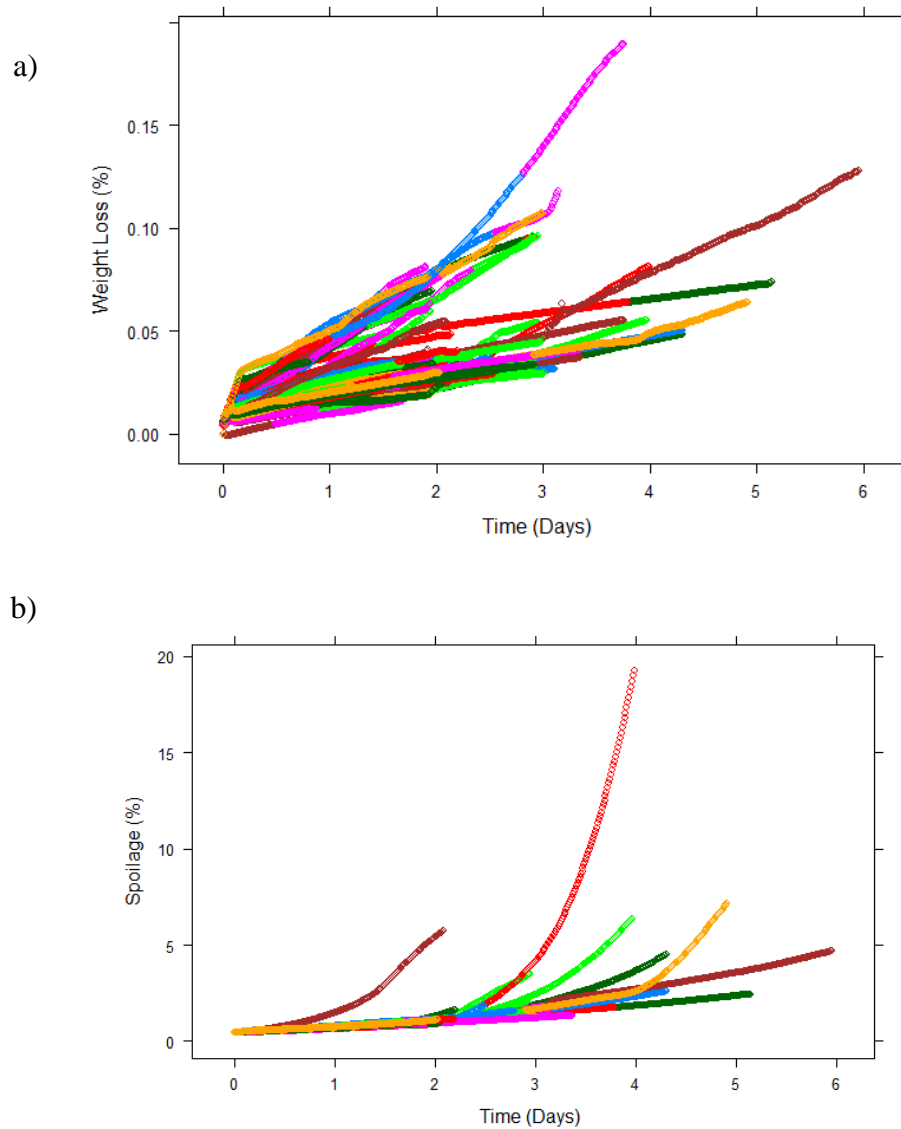
Fig 5.4 Effect of cold chain variability on the quality characteristics a) weight loss and b) spoilage.

5.4.1.1.　　　　　*Scenario analysis*

Effect of Perforations on the fate of tomato quality criteria

Based on these storage profile simulations were carried out for film with permeability (Table 5.1) and the number of perforation ranging from 0, 4, 8 and 12. An increase in the number of perforation led to an increase in the overall transfer area. The transfer area for 0, 4, 8 and 12 perforations was 0, 2.826×10^{-5}, 5.652×10^{-5} and 8.478×10^{-5} m^2 respectively. The larger the transmission area, the more the package became sensitive to the ambient atmosphere conditions. Fig 5.5 shows the changes associated to the increase in the number of perforations.

The package without perforations saturated within a few hours of storage, which was attributed to the low water vapour transmission of the packaging film. The perforations increased the transmission area, meaning that the perforations lower the humidity in the headspace (Fig 5.5b). Spoilage in tomatoes was not affected by the number of perforations, spoilage was more influenced by the storage condition in this case.

The driving force for the permeation of water vapour from the headspace of the package to its surrounding is the water vapour pressure difference. An increase in the number of perforations led to a lower H_2O permeability as there was no barrier for the transport, which explains the higher weight loss, as evident in Fig 5.5c.
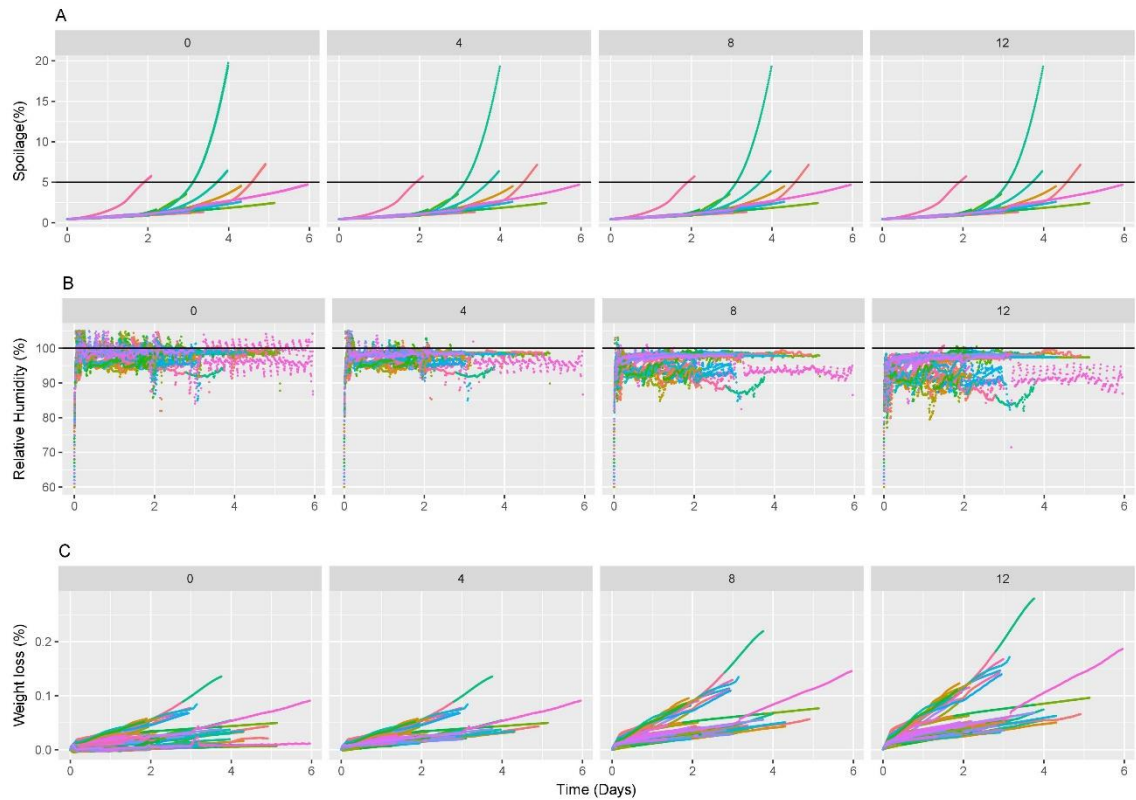
Fig 5.5 Effect of number of perforation on the A) spoilage B) change in relative humidity in headspace and C) weight loss of produce.

5.4.2. Product variability assessment

Fig 5.6 a&b shows the propagation of product parameter uncertainties on the headspace concentration of carbon dioxide. Large variations were observed, which increases throughout the storage. Similar results were obtained for oxygen concentration in the headspace. The variability associated to the concentration of gases in the headspace was high, with the Michaelis-Menten respiration rate parameters and respiration quotient are being the main factors contributing to the variability in the concentration of gases in the headspace.

Weight loss was found to be directly dependant on the difference in the water vapour pressure between the environment and inside of the fruit. The average weight loss observed towards the end of the 15 days-transport and storage simulation was around 5%. The variability associated with the weight loss was higher towards the end of storage. The

median spoilage observed at the end of a simulation (15 days) was above 50%. The variability observed in tomato spoilage was a higher that that found with strawberries at the same storage temperature making tomato a more complex product to handle and to devise new interventions for waste reduction in supply chain (Joshi et al., 2019).

Table 5.2 Constants for Michaelis-Menten equation for respiration rate of tomato The standard error (S.E.) are expressed as a percentage, relative to the estimated value. ($T_{ref}=10^0$ C) Source: (Hertog et al., 1998)

Parameter	Estimated value
$V_{mO_2,ref}$ (μmol kg^{-1} sec^{-1})	0.122 (11)
E_{O_2} (J mol^{-1})	67338 (2.8)
Km_{O_2} (%)	23.2 (19)
Kmc_{CO_2} (%)	21.3 (33)
Kmu_{CO_2}(%)	7.85 (23)
$Vm_{CO_2(f),ref}$ (μmol kg^{-1} sec^{-1})	0.0817 (8.3)
E_{CO_2} (J mol^{-1})	65159 (6.1)
$Kmc_{O_2(f)}$ (%)	1
$Kmc_{CO_2(f)}$(%)	1.37 (18)
$Km_{CO_2(f)}$ (%)	6.49 (14)
RQ_{ox}	0.8

a)

b)

c)
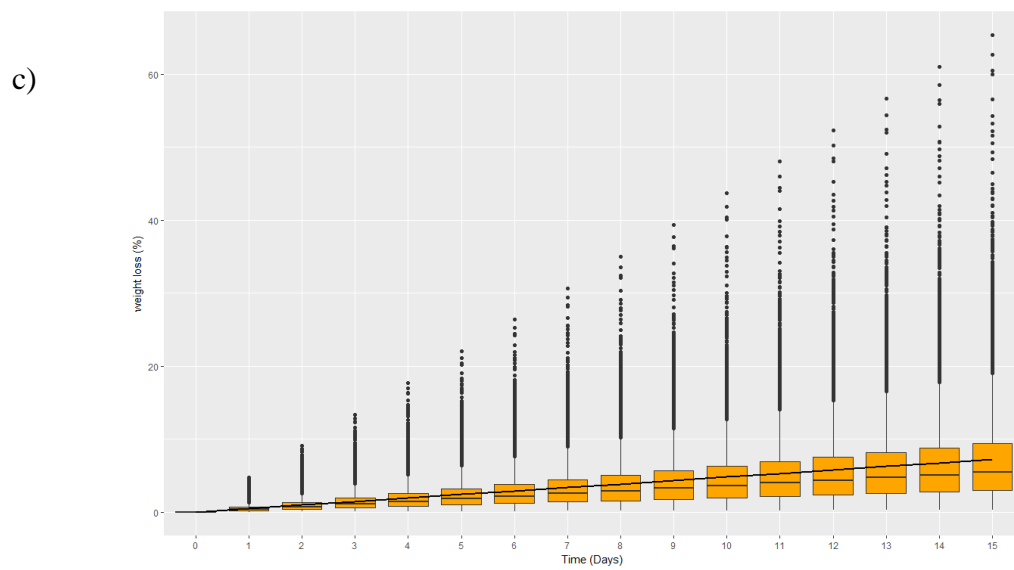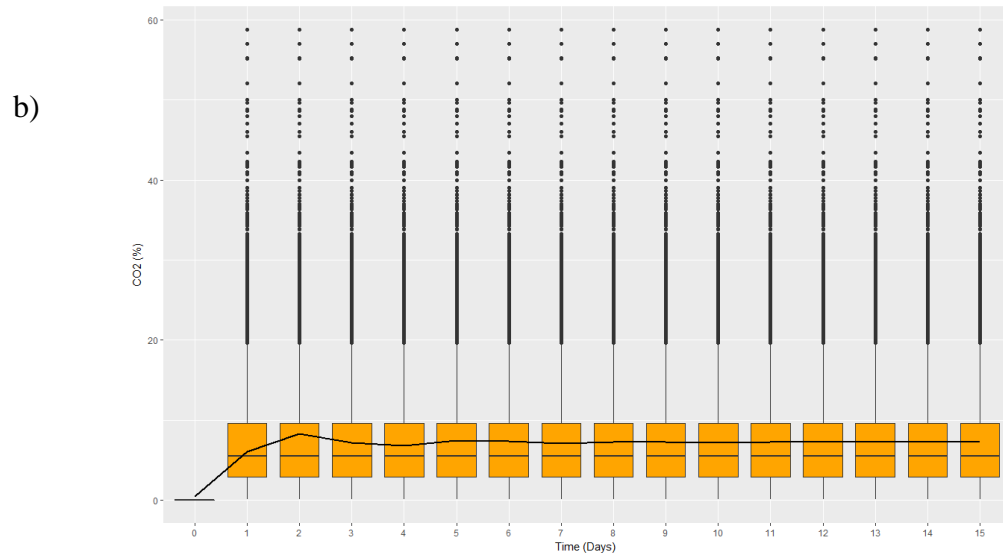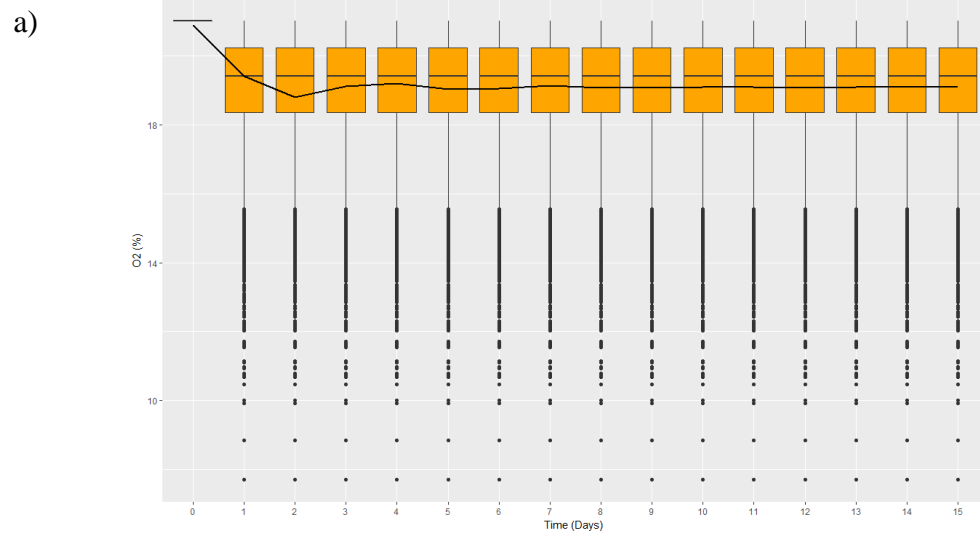
d)
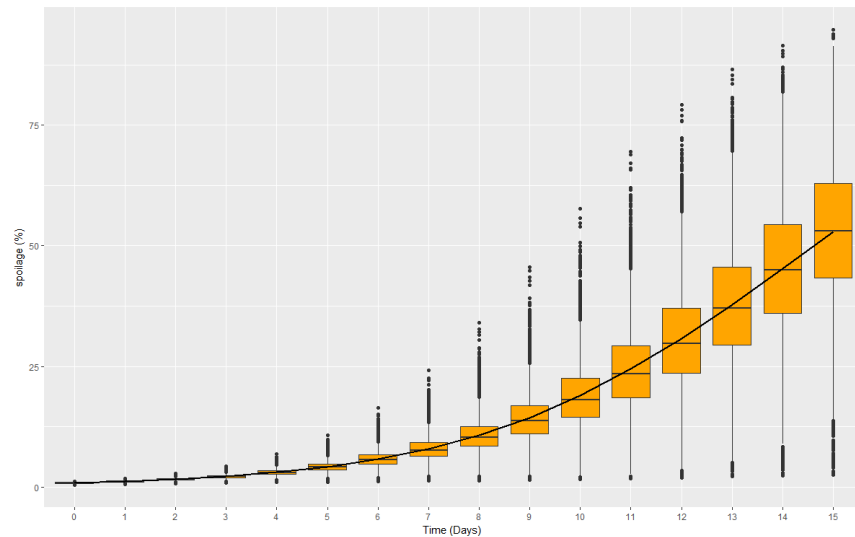
Fig 5.6 Propagation of effect of product parameters variability on the a) oxygen concentration (b) carbon dioxide concentration in the headspace c) weight loss and d) spoilage at 80% RH and 4^0 C storage temperature.

5.4.3. Comparing the importance of product and cold chain variability on tomato quality

The comparison of the frequency distribution between the two aforementioned scenarios was used to compare the relative importance of cold chain variability factors and the product parameter variation (Fig 5.7). Product parameters had more influence on the oxygen and carbon dioxide concentration in the headspace of the package, as evident from Fig 5.7 (a and b). The Michaelis-Menten respiration parameters had an associated variability, which influenced the respiration rate, thereby changing the concentration of gases in the headspace.

Weight loss in tomato during the distribution supply chain seemed to be influenced by product parameters (Fig 5.7 c). This finding indicated that in order to prevent weight loss of tomato during the supply chain, product parameters such as the respiration rate should be controlled by interventions. The cold chain parameters and product parameters

had similar influence on spoilage of tomato at the start of storage and towards the end product parameter was dominant as evident in Fig 5.7d. The results suggest that a possible intervention that can control all the elements of both product and cold chain uncertainty sought to be used to reduce waste in supply chain.

a)

b)

c)

d)
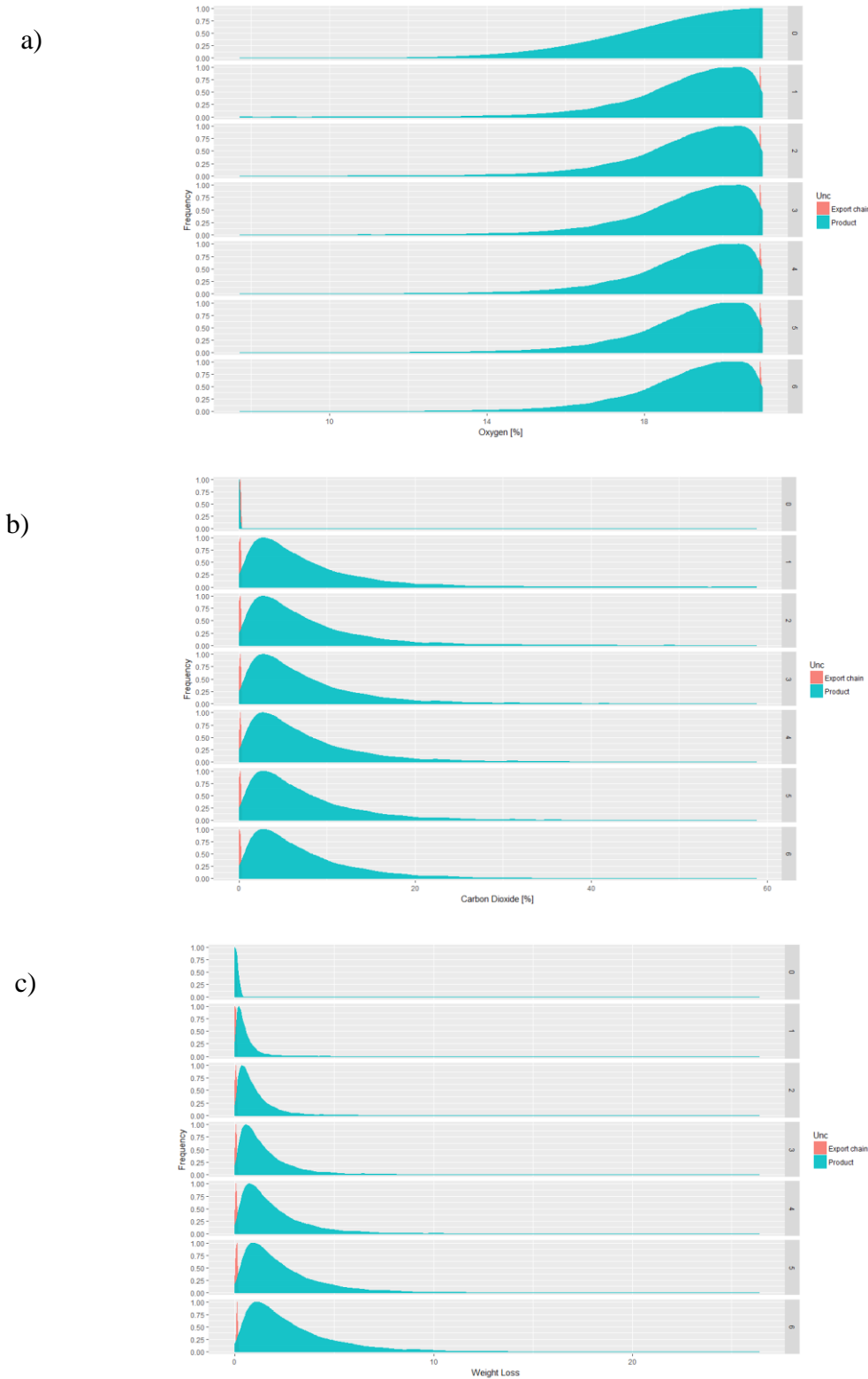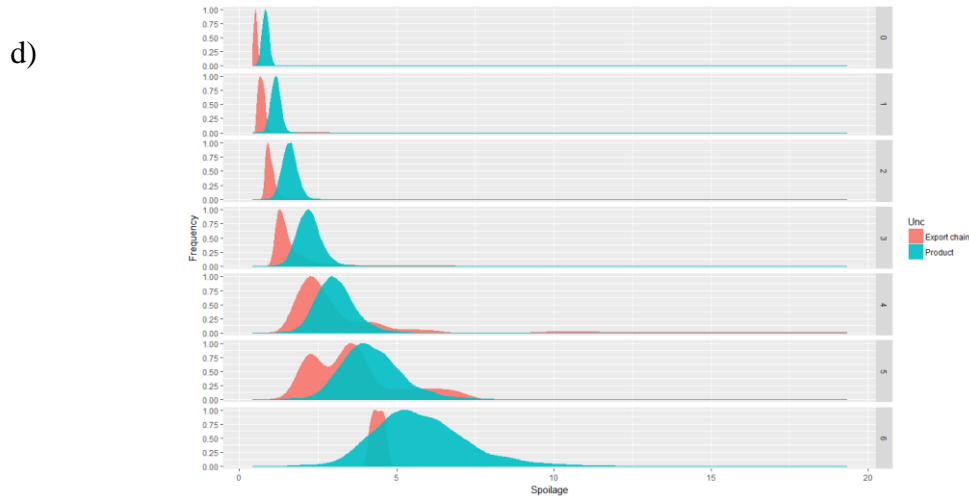
Fig 5.7 The effect of cold chain factors (temperature and relative humidity) and product parameter uncertainty on the (a) oxygen concentration (b) carbon dioxide concentration in headspace (c) weight loss (d) Spoilage during a simulated 6 days storage.

5.4.4. Sensitivity analysis

Uncertainty analysis usually accompanied by sensitivity analysis quantifies the contribution of each input parameter to the output parameters (Duret et al., 2015b). A sensitivity analysis was performed to study the quantitative and qualitative effects of different sources of variation in the model input (Kader and Saltveit, 2003). The results for the weight loss sensitivity in Fig 5.8a show that just over 75% of the initial variability was due to the main effect of the respiration rate parameters $V_{mO_2,\text{ref}}$ (maximum oxygen rate consumption) and RQ_{ox} (respiratory quotient) and Km_{O_2} and 25% to the interaction between these parameters. This showed that the weight loss was the property most influenced by the respiration rate parameters, confirming the results from Fig 5.7c. Controlling the product parameter variability will help manage the weight loss in the supply chain. Weight loss in strawberry was influenced by the main effect of respiration rate parameters and respiratory quotient (Joshi et al., 2019). Whereas in mushroom the

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main effect from respiration rate parameter and skin mass transfer coefficient and interactive effect between these parameters influence the weight loss (Joshi et al., 2018).

In the case of spoilage, the variability was caused by a number of parameters, as a combination of the effect of main parameters and the interaction between them. The main effect due to initial spoilage, spoilage rate constant and O_2 consumption rate was evident and interaction between respiration rate parameters was observed (>60%), with a high interation part (>20%). The results of sensitivity analysis of spoilage in strawberry spoilage showed more than 90% variability due to initial spoilage and spoilage rate constant. Therefore, designing intervention to reduce food waste in that case was easy to tackle.

A total of 75% of the variability in the O_2 concentration in the headspace was ascribed to the maximum O_2 consumption rate ($Vm_{O_2,ref}$). The remaining variability was a combination of Km_{O_2} and RQ_{ox}. The results of the sensitivity analysis were used to determine the parameters responsible for the variability and the interventions that can be designed along with the packaging to reduce the waste produced in the cold chain.

a)
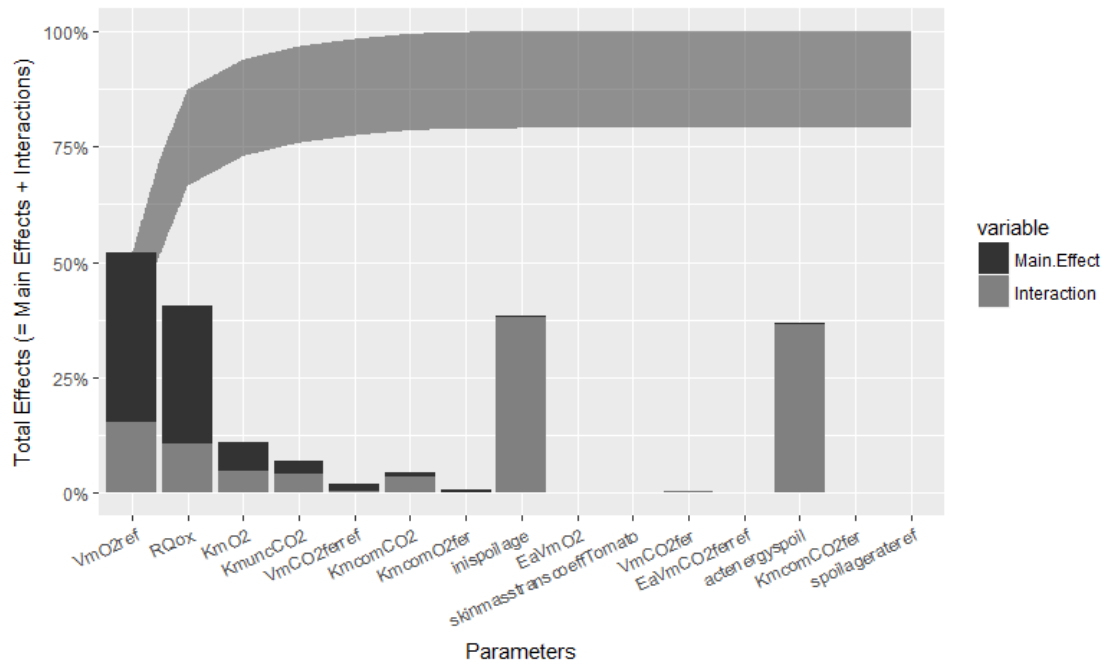
b)
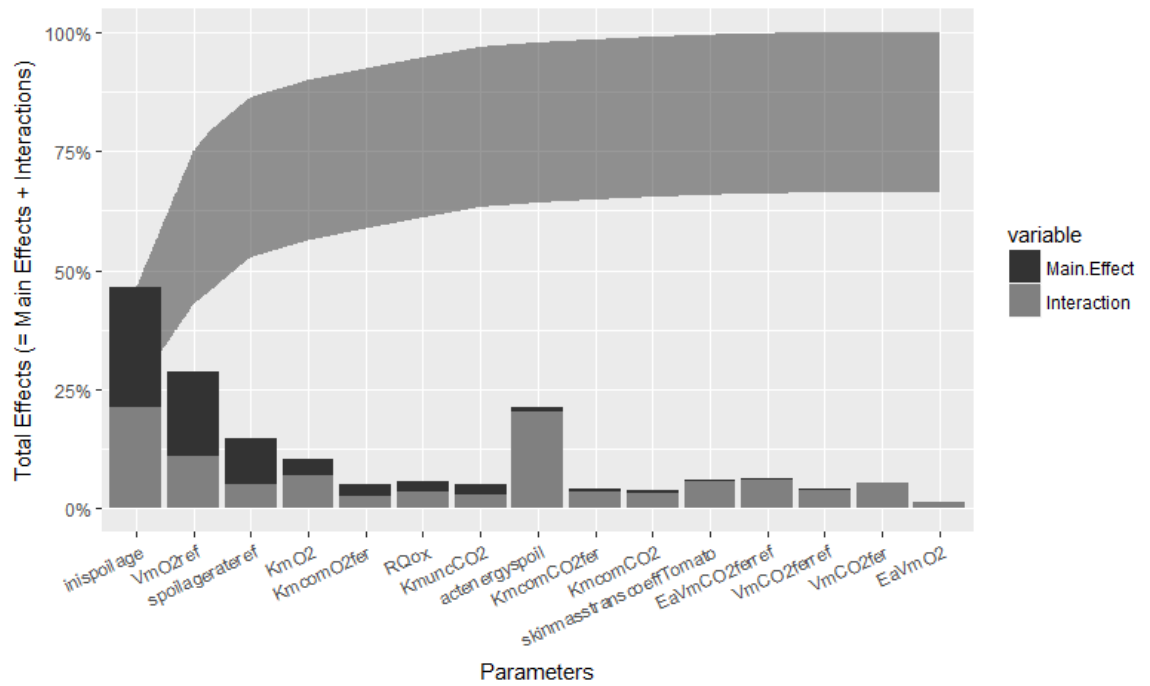
c)
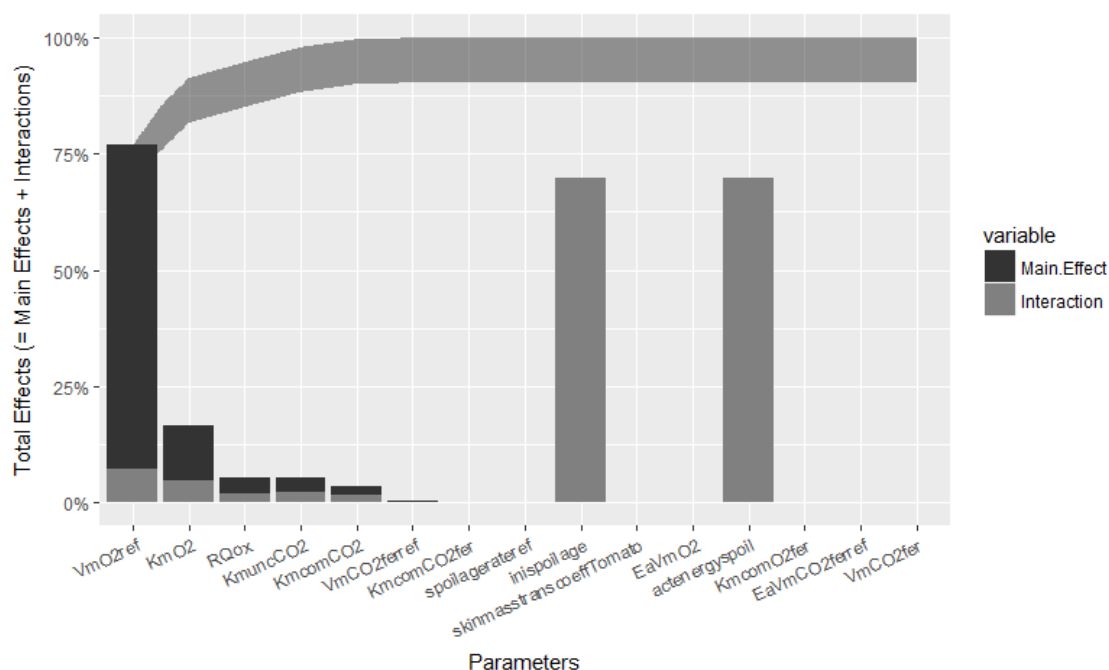
Fig 5.8 Lowry plots from the sensitivity analysis (*The total effect of main parameter given in black and any first order interaction with other parameters is grey given as a proportion of variance. The ribbon represents variance due to parameter interactions, the cumulative sum of main effect is lower line and the sum of total effect is upper line a) weight loss, b) spoilage and c) oxygen concentration.

5.4.5. Experiment validation

Tomatoes treated with chitosan and packed tomatoes without treatment were stored at the ideal storage condition (4°C) and at variable temperature (with parts of the experiment at 4, 8 and 20°C), mimicking abusive supply chain conditions in order to simulate a real life supply chain. The storage temperature profile is described in Section 5.32. The weight loss observed in the packed tomatoes stored at variable temperature was 0.8 % after 15 days of storage, while chitosan-coated tomatoes showed 18.75% less weight loss as compared to the control. When stored at the ideal temperature, a weight loss of only 0.2% was observed in the control and 0.18% in the chitosan-coated tomatoes.

The variability associated with the product parameters was high, as seen in Fig 5.6. The grey ribbon represents the uncertainty margins of 5% and 95% percentiles associated to the prediction variability. The experimental data values are shown as points. The spoilage observed at the end of the storage under ideal conditions was around 20%, and similar results were obtained from the experimental data fig 5.10. At abusive storage conditions, the spoilage was predicted to be 25% and the variability associated with the experimental values fell into the grey ribbon pertaining to the associated variability.

a)
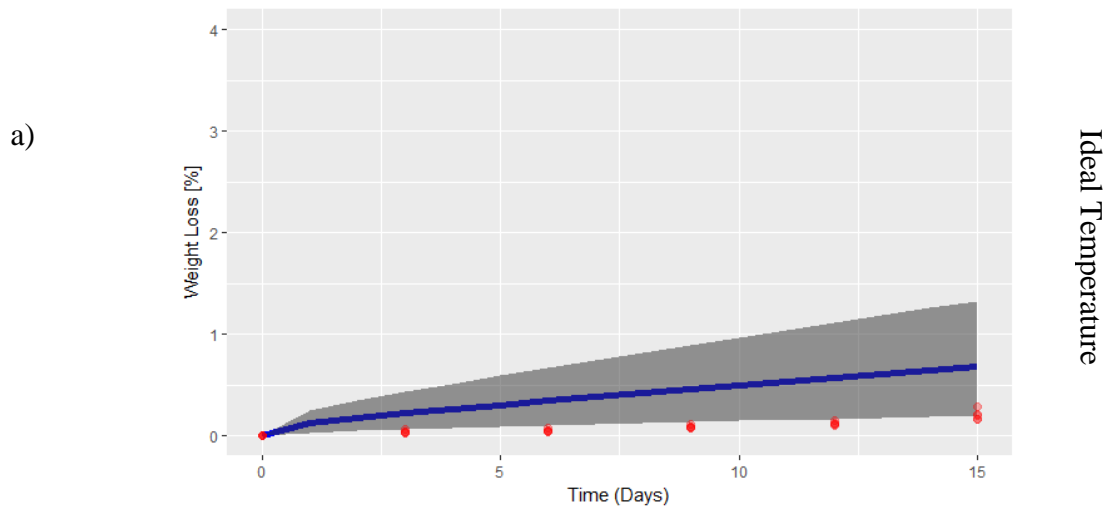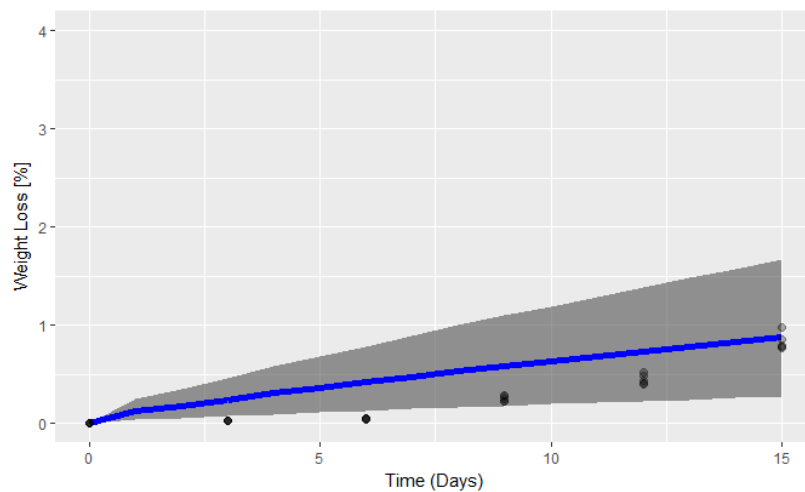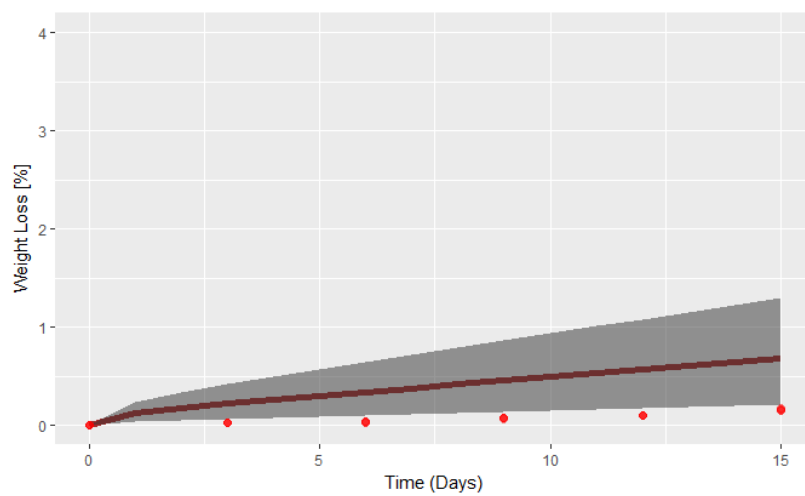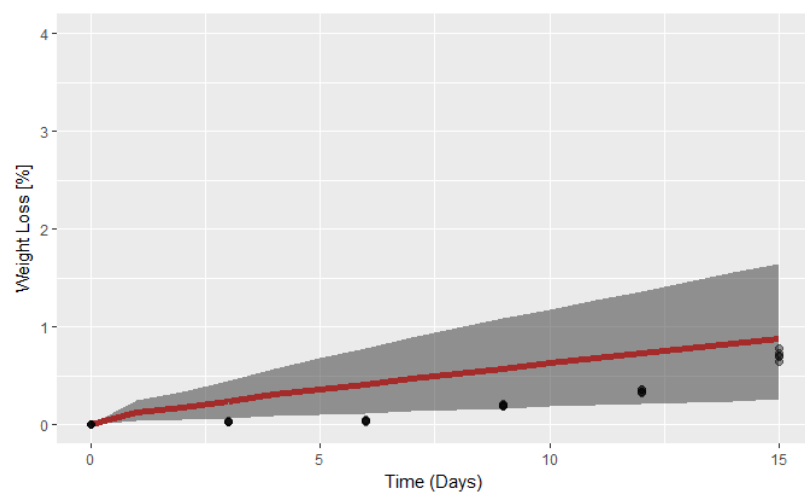
Fig 5.9 Comparison of experimental data with the mathematical model predictions of weight loss in tomatoes without coating a) stored at 4^0C (ideal) b) stored at 4, 20, 8^0C (abusive) and with 1% chitosan coating c) stored at 4^0C (ideal) d) stored at 4, 20, 8^0C (abusive).

At abusive variable temperature, the spoilage observed in the control was around 50%, versus 20% in the chitosan-coated fruits due to chitosan's antimicrobial effect. Under ideal storage conditions, no spoilage was observed until day 12. Towards the end of storage, 8% spoilage was found for the control and 3.5% the chitosan-coated tomatoes. El Ghaouth et al. (1992) observed that the first signs of fungal development appeared after 2 days of storage in the control fruit, while signs of infection were visible only after 10 days at 20°C in the coated fruit. The variability associated with the spoilage at abusive storage temperature was higher.

a)

b)

Abusive Temperature
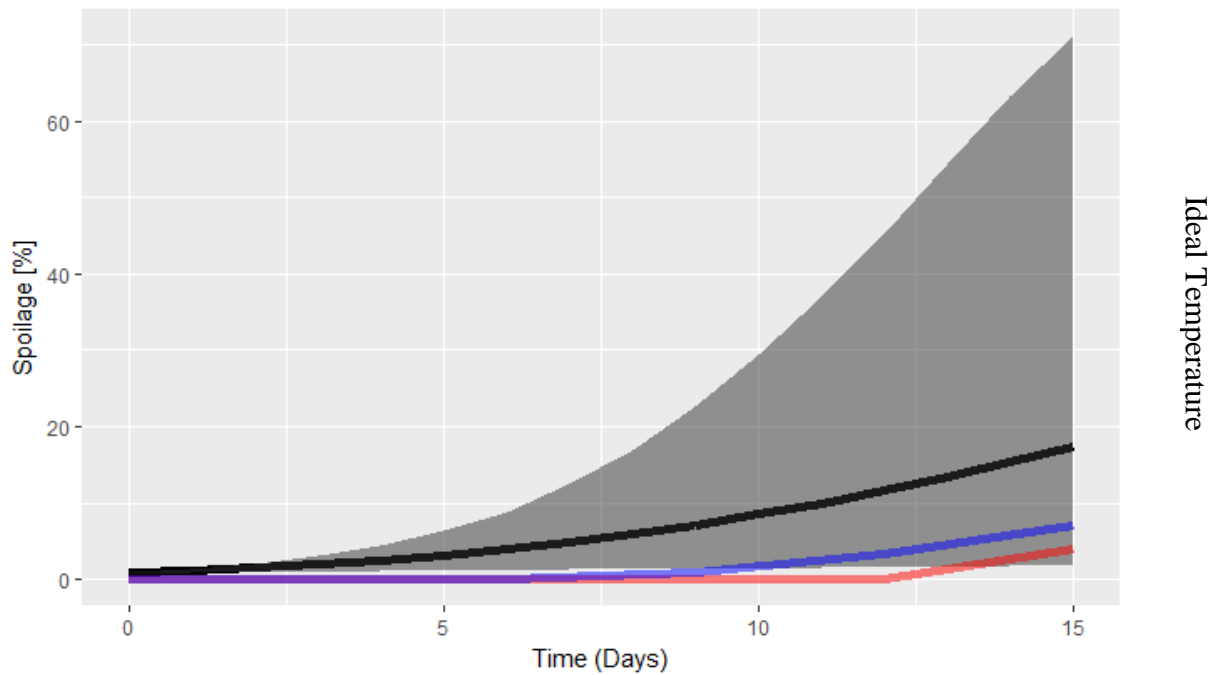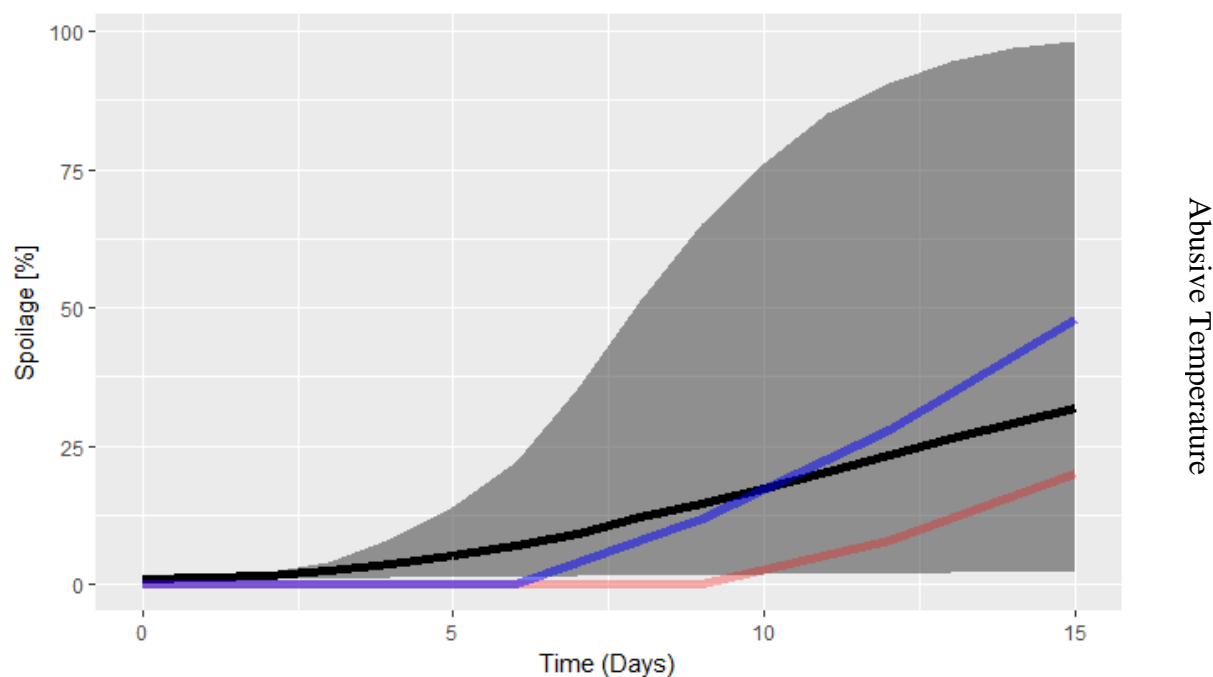
Fig 5.10 Comparison of experimental data with the mathematical model predictions of spoilage in tomatoes a) stored at 4⁰C with 1% chitosan coating (red) control (blue) and b) and stored at 4, 20, 8⁰C with 1% chitosan coating (red) control (blue).

The accuracy and bias factor's closeness to a value of 1 is an effective and practical measure of predictive model validity. The results from the bias and accuracy factor related to the comparison between experimental and predicted results in Table 5.3. The results indicate that the mathematical model would be overestimating the waste in abuse conditions, especially in the non-coated tomatoes. The model is a better fit for coated tomatoes in abuse and ideal conditions.

Table 5.3 Results of bias and accuracy factor of mathematical model validation

		Bias Factor	**Accuracy Factor**
Control	**Abuse**	0.647	3.785
	Ideal	1.0348	1.5809
Coating	**Abuse**	0.9359	3.2627
	Ideal	1.0607	1.7806

5.4.6. Waste Estimation during supply chain

The total waste produced throughout the supply chain due to weight loss and spoilage can be seen in Fig 5.11a. The total waste observed at the end of the cold supply chain of packaged tomato was around 10% - weight loss contributed to around 8% losses and spoilage 2%. Weight loss was therefore, main cause of waste generation in the tomato supply chain. Chitosan coating was used as an intervention to prevent the losses generated in the supply chain. The waste generation results are shown in Fig 5.11b. The total waste produced by chitosan-coated packed tomatoes at the end of the supply chain was 7%. The study of Joshi elucidated through sensitivity analysis the high dependence of mushroom waste production on the variability of single item (initial L value, related to the whiteness of the mushroom (Joshi et al., 2018). This is an ideal situation as it indicates a clear policy that will reduce waste. The same study on strawberries arrive in this case to the conclusion that the variability of one phenomena (spoilage rate at reference temperature in the case of spoilage and a complex relation of respiration and mass transfer properties in the case of weight loss) was the dominant element in the shelf life and generation of waste. While not as evident as the mushroom study, this provided indication of the type of intervention that would reduce waste as well with at least one quality criteria variability clearly defined. In the case of the present study tomato waste production through the food distribution chain the Lowry plots indicate that both weight loss and spoilage variability are affected by the different parameters in a complex manner, with a large importance of interactions. This complex relationship makes that improvement through interventions was more difficult to achieve compared to the previous problems. The complex relationship with a high weight of interactions between variability and the parameters may reduce the effectiveness of the proposed intervention as it may have a favourable effect on some groups of parameters and a negative effect on others.

As chitosan acts a barrier that reduces the water loss through the skin, other than exhibiting antifungal properties, it was able to reduce the waste attributed to spoilage. Thus, introducing further intervention along with packaging associated with low temperature storage can improve tomato quality and lower the waste generation in the supply chain.

a)

No Coating

b)

Coating
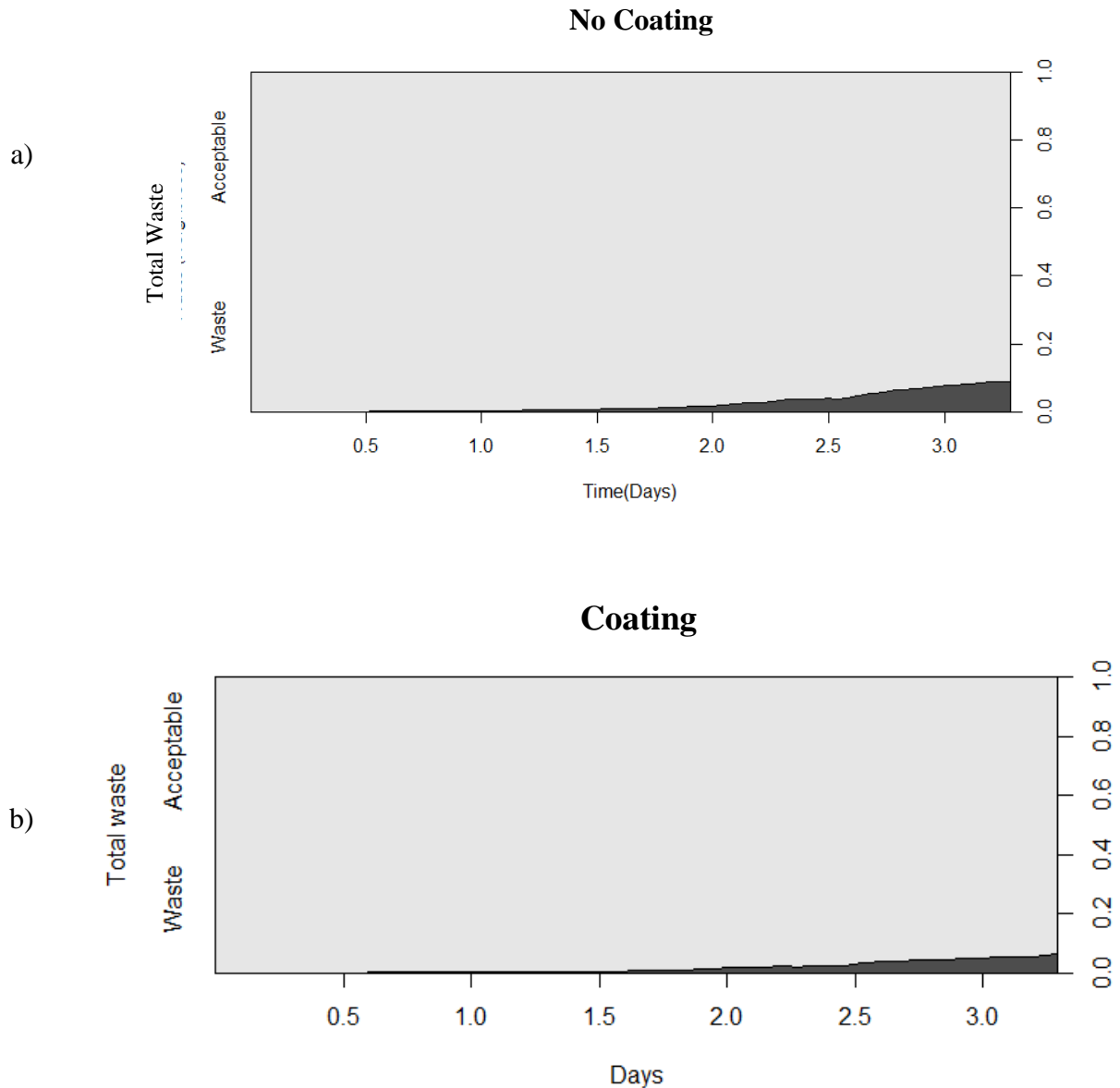
Fig 5.11 Conditional density plot for the estimation of total waste generated due to a) weight loss and b) spoilage

5.5. Conclusion

A mathematical model was developed to predict the concentration of gases (O_2, CO_2) and water vapour in the packaging headspace. It considers the heat and mass transfer processes taking place in the packaging, such as respiration, transpiration condensation and transport of gases through the permeable packaging film. The kinetic behaviour of tomato was modelled with respect to the cold chain conditions and product parameters. The effect of cold chain variability and product variability on the quality of tomato was assessed. Weight loss was influenced by the product parameter uncertainty and spoilage had equal influence from cold chain parameters and product parameters. The important factors associated with product parameter variability were quantified using sensitivity analysis. Weight loss was found to be influenced by the respiration rate parameters and spoilage was influenced by interactive effect of initial spoilage and respiration parameters. Therefore, designing an intervention process to inhibit these parameters was difficult because targeting reduction of parameter effect might influence other parameters hence not warranting reduction of variability and waste in supply chain. The results from an experimental validation of a proposed intervention to target those factors, coating with chitosan, indicated that while experimental results are within the model uncertainty band, the prediction presents some bias and further improvement is needed for the implementation of this methodology with tomatoes.

Chapter 6. Conclusions

6.1. Methodology

This work focused on developing and demonstrating a methodology to identify interventions to reduce food waste in the supply chain through predictive modelling tools. While loss/waste is largely unavoidable, waste due to inefficiencies or poor handling in the supply chain is not. This is where packaging and technology interventions can play an important role, for example by reducing losses in transit and handling or by extending food shelf life.

While the results of this study point to elements of improvement in the cold chain distribution is noteworthy that storage and distribution will not improve the quality of a product, it will rather only delay the spoilage. Introducing a new technology hurdle (multiple small interventions) may ensure that the quality of the fresh produce is maintained for longer, however temperature control is the most important parameter to retain quality at all stages of the supply chain, including transportation, retail and consumer. Fresh produce stored at low temperature ensure maximum shelf life and produces less waste.

The most relevant contribution of this work are:

- A mathematical model to simulate the fate of a modified atmosphere packaged horticultural product was developed that considered:

- The prediction of O_2, CO_2 and H_2O in perforation mediated packaging for fresh produce during MAP. The model incorporated water loss from the fresh produce driven by the difference of partial pressure for water vapour between the fruit surface and the external atmosphere. The water activity of the fresh produce surface was considered to be 1.0 (100%), assuming it to be fully water saturated.

The heat balance across the MAP system was used to calculate the temperature of the commodity and at the surrounding atmosphere, it includes the metabolic activity in fresh produce which is the main source of heat in MAP. Evaporation of water vapour from the produce's surface requires energy and cools down the produce and condensation of water vapour on the packaging film and surface of the fresh produce leads to release of heat. Weight loss, loss of color and spoilage were used as parameters to access the loss of quality.

- The effect of product variability on the fresh produce was assessed and compared with the effect of the variation arising from a typical export chain between a farm in Ireland and a supermarket shop in the UK.

- The total resulting variation of the quality criteria associated to the produce was then assessed against technological thresholds to assess the amount of out-of-specification (ie. waste) generated during the distribution chain.

- A sensitivity analysis (considering main and interactive effects) of the total variation of the system was used to identify the model parameters that could be targeted by directed interventions.

6.1.1. Validation of the methodology

The case studies chosen to demonstrate and assess the methodology were the production and export from IE to the UK of mushroom, strawberry and tomato because of their economic importance to the Irish economy.

Case Study 1- Mushroom

- The mathematical predictions were compared to the experimental data to validate the model. The experimental results fell within the uncertainty margin. The value of the bias and accuracy factors indicates that a model was, in general, 'fail-safe'.

- The product parameters (respiration rate, initial quality and skin mass transfer) used to assess the effect of product uncertainty on mushroom quality were obtained from the literature. The results of product uncertainty show that higher storage temperature led to a larger variability. Mushroom stored at optimal temperature, 3°C, resulted in a 12.5% rise in the CO_2 level and a drop around 10% in the O_2 level The weight loss observed was lower than 3% and the L-value maintained above the threshold limit of 82 during the 7 day-storage.

- While comparing the effect of cold chain variability and product uncertainty on the individual parameters, it was observed that the gases (O_2 and CO_2) in the package were influenced by the cold chain variability. The L-value was strongly impacted by the product parameters and the weight loss was highly influenced by the cold chain parameters.

- Further investigation was done to study the effect of product parameters on the quality parameters of mushroom. The results of the sensitivity analysis for the L-value showed that the initial L-value was the single major contributor towards colour variability. Thus, designing an intervention that controls the initial colour will reduce the waste in cold supply chain. The sensitivity analysis related to the CO_2 concentration indicated that the Michaelis-Menten respiration rate constants had the highest impact (90%) on the concentration of CO_2 in the headspace. The parameters leading to variability on weight loss were a combination of main effect of product parameters and interaction between product parameters.

- The waste produced during the supply chain was calculated based on quality thresholds. Waste generation was considered whenever the mushroom quality fell below the acceptability threshold. The total waste produced in the export cold chain due to quality degradation was estimated at 30%. The comparison between

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the initial L value and the waste produced showed that a higher initial L value (above 93) resulted in considerable lesser waste generation in the cold chain.

Case Study 2 – Strawberry

- The effect of product parameters on the quality attributes of strawberry showed that higher temperatures increased the variability. The effect of variability on the concentration of gases (O_2 and CO_2) was evident from the start of storage. The variability related to weight loss was low at 4^oC, but became high at higher temperature (20^oC), resulting in around 2.8% weight loss at the end of the distribution. There was a similar increase in the variability related to spoilage at higher temperatures: at 20^0C 100% spoilage was observed on the 5th day of storage. This confirmed that control of storage temperature is the most important parameter in the in avoidance of waste in strawberry export.

- The effect of cold chain variability and product variability on the quality parameters was compared. Product parameters had more evident effect on the concentration of gases in the package's headspace. In the case of weight loss, the cold chain uncertainty had higher influence than the product parameter uncertainty. These results were similar to those for mushroom. For spoilage, the cold chain and product parameter variability had similar effect at the start of the storage, but the product parameter uncertainty became more dominant towards the end of storage. The comparison of the effect of cold chain and product variability helped to assess possible interventions to reduce waste efficiently.

- A sensitivity analysis was performed to study the effect of product parameters in detail. The effect of product variability on weight loss was a result of main effect of respiration rate parameters and skin mass transfer coefficient. However, in the case of spoilage 90% of the variability was ascribed to the initial spoilage and

spoilage rate. For the concentration of CO_2 in the package, the respiration rate parameters ascribe to 90% of the variability.

- A validation experiment using an intervention identified through the sensitivity analysis and a control showed that the model was able to predict strawberry quality in terms of weight loss and contamination. The results indicated that the model is a good fit for strawberries in abuse and ideal conditions.

- Waste produced in the export cold chain was calculated as the sum of spoilage and weight loss. The mathematical model was used solved based on the export cold chain profile, with quality parameters (spoilage and weigh loss) above the threshold considered as waste. A weight loss of around 10% was observed in the cold chain.

Case Study 3 – Tomato

- At constant temperature and relative humidity profile the effect of product parameter uncertainty showed large variation on the concentration of gases (O_2 and CO_2) in the headspace. The variation on the weight loss is higher as compared to the gas concentration in packaging and increases throughout the 15 days storage profile. Similar results of variation increasing towards the end of storage were observed for spoilage. The results of product variations showed 50% spoilage of tomatoes at the end of storage.

- A comparison between cold chain variation and product parameter variation was done to define which uncertainty has more influence on the parameters responsible for the waste production in the cold chain. The gases (O_2 and CO_2) in the package are influenced by the product parameters. In case of mushroom cold chain parameters (relative humidity and temperature) influenced the gas concentration in headspace whereas, for strawberry both cold chain parameters

and product parameters has similar influence. The variability in weight loss of tomato was influenced by the product parameters and results from mushroom and strawberry showed cold chain parameters influencing weight loss in supply chain. In case of spoilage, the variability due to the cold chain and product variability had the same influence at the start of the supply, but the product variability exerted higher influence towards the end of storage. Similar results were observed in strawberry. The comparison between cold chain variability and product variability was able to identify the cause of variability in the supply chain and the interventions can be designed around it to reduce waste in supply chain.

- To further investigate the effect of product variability on the quality parameters, sensitivity analysis was done. The results from the weight loss showed that 90% of the initial variability was the result of main effect of maximum oxygen rate consumption and respiratory quotient and interaction with other parameters. Results from mushroom showed little effect from main parameters and was mostly interaction between different product parameters. However, for strawberry variability was result of main effect of product parameters. For spoilage in tomato, the variability was caused by a combination of main effect of parameters (initial spoilage, respiration rate parameters), and the interaction between different parameters. However, for strawberry the results showed initial spoilage and spoilage rate reference contributing to nearly 100% variability thus designing a process that inhibits this will reduce waste in supply chain but in tomato its not straightforward as targeting the reduction of a parameter effect might influence (via the interactive effect) other parameters, hence not warranting a reduction of variability and waste.

- The results indicated that the mathematical model would be overestimating the waste in abuse conditions, especially in the non-coated tomatoes. The model was a better fit for coated tomatoes in abuse and ideal conditions.

- The waste produced in the supply chain was considered the result of weight loss and spoilage. The mathematical model was simulated based on the export cold chain profile, and threshold values were used to calculate the waste generated in the supply chain. The total waste observed in the cold supply chain of packed tomato was around 10%, where weight loss contributed to around 8% losses and spoilage 2%. The total waste related to chitosan coated packed tomatoes was 7%. Introducing another intervention along with packaging and low temperature storage can improve the quality of tomato and produce less waste in the supply chain.

6.2. General conclusion

This work presents a novel contribution to the design of packaging for the preservation of fresh goods in MAP, by taking into consideration the conditions of the cold chain and proposing a simulation framework that can predict the produce shelf life, and quantify the waste generation and the sensitivity to different product or cold chain technological parameters. Those, in turn, can help to quantify the effect of different candidate interventions and assist in the selection of the most appropriate ones, which can then be tested and validated. To the best of our knowledge no previous attempt to complete this approach has been taken, although several groups have worked in different areas of this problem.

The present work demonstrates this methodology with three case studies that show the different approaches needed to manage postharvest waste generation in a cold chain.

- Variability affecting the quality of the product (and the waste associated to losing it) maybe arising from either the cold chain conditions or from the inherent biological product diversity, requiring different corrective measures.

- While shelf life is a multi-criteria problem, one main quality property, as it was in the case of mushroom colour, may dominate the whole cold chain distribution. In this case easy to interpret criteria of original product tolerances can be easily inferred from the simulation results. It was shown that in the present conditions, high colour specification, specially above 93 in L value, would result in a significant cut of waste generation.

- Sensitivity analysis aided to identify the water transfer processes as of importance in the loss of quality and to direct the search for an intervention that could affect the surface water transfer coefficient in the two other cases. While this was the case for tomato and strawberry, it would not be expected that a different MAP design or a different crop would yield the same results as weight loss in other crops may have a higher dependence on respiratory parameters and therefore be more dependent on the film properties, or indeed other quality parameters such as microbial spoilage may come into play.

- Three validation experiments showed the feasibility of this approach, which showed to produce unbiased predictions of the quality through different cold chains with a reasonable precision, showing the applicability of uncertainty analysis in this scenarios.

- The results presented in this thesis point to the applicability of the approach to other packaged food products.

As seen from the results the variability has shown to affect the quality of fresh produce packed in modified atmosphere packaging. It is important to take into account the

variability caused by the product and the cold chain factors when designing a robust sustainable cold supply chain. Taking into account the effect of variability reduces the losses observed in the supply chain due to quality degradation. Altering the normal packaging to modified atmosphere packaging extend the shelf life and reduce the overall impact on the environment. Further introducing another intervention such as coating the fresh produce reduces the waste produced in supply chain. The total environmental impact of the cold supply chain can be reduced by reducing the waste produced throughout the supply chain. The comparison between different case studies has shown that different produce requires different intervention methods. The results from mushroom showed that colour was influenced by the initial L value thus designing an intervention that will maintain the initial colour will reduce the waste produced in the supply chain. Sensitivity analysis results on quality parameters of strawberry showed that effect of few main parameters (respiration rate parameters and skin mass transfer coefficient) was responsible for causing variability. To restrain these parameters strawberry was coated with chitosan which showed reduction in waste in strawberry. Lastly for tomato the variability depends on main effect and interactive effect of multiple parameters, which arises the complication in designing possible intervention to reduce waste.

6.3. Future recommendations

A mathematical model that can assess new sources of variability and calculate waste produced in supply chain based on the fresh produce batches grown in different seasons and cultivars.

Waste produced at the consumer level would give a more accurate representation of the waste generation at the end of the supply chain.

Furthermore, managing the end point variation in cold supply chain at different end point (3-4-5 days) and estimating the waste generated at each of those end points of the supply

chain. The connection of the simulations presented here with a Life Cycle Analysis of the production, transportation and consumption levels would enable to assess environmental impact of interventions in the distribution chain, helping to ensure the sustainability of the produce supply chain.

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