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Assessing baby leaf kale (*Brassica oleracea*) waste production mitigation in the transition to sustainable packaging with the application of silicon through an integrative model of quality

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ABSTRACT

This research builds a mathematical modelling to assess food waste production when designing sustainable packaging solutions integrated with an agricultural intervention in kale production. The model utilizes experimental data obtained from simulated retail and distribution storage conditions to assess the probability of the product to be found out of technical specification and becoming waste. The packaging design was made using a system of differential equations describing the gas exchanges inside the packaging. The waste was estimated fitting linear mixed effect models to the postharvest experimental data, accounting for the variability between and within groups. A field experiment with kale treated with silicon during growth as a bio stimulant was used with the aim to make the product more resilient to packaging conditions. The Kale was then packaged in polylactic acid and oriented polypropylene for postharvest testing. Technological thresholds that indicate out-of-specification product were used to estimate the percentage of product that would likely end up as food waste. In total 7.2% of the product was found to be out of specification with the PLA film after 7 days. Silicon treatment was able to reduce this value to negligible, demonstrating the ability of agricultural interventions to facilitate sustainable packaging and reducing food waste in horticultural products.

1. Introduction

Plastic food packaging for perishable products is a major cause of plastic waste production, but at the same time is an invaluable instrument to manage shelf life and reduce food waste. As the sustainability of horticultural packaging and distribution has become a subject of research, inventory methods, such as LCA study (Kikuchi and Kanematsu, 2020) (Wikströ et al., 2014), have been used to assess the impact of this production. Often in this type of calculation the final use, and thus its effect on food waste production is neglected, leading to the possibility of miscalculating the overall effect of the use of different materials on the environmental impact (Wikströ et al., 2014) (Conchedda and Nicola Tubiello, 2020). Food waste production is accountable for the 8–10% of the global greenhouse gas emissions (De Luca and Rigillo, 2022), while the agricultural sector is accountable for 17%, and for the use of 70% of freshwater (Conchedda and Nicola Tubiello, 2020) (Programme, 2020). Horticultural products are environmentally expensive to produce (Moshtaghian et al., 2021), and the use of a more sustainable packaging material could potentially lead to underperformance during postharvest, potentially increasing food waste production and the environmental impact (FAO, 2019) (Hellali and Korai, 2023).

Horticultural product may become waste during its shelf life due to quality and safety parameters, with both affected by multiple subjective and objective criteria (Steele, 2004) (Moschopoulou et al., 2019) (Ishangulyyev et al., 2019). The identification of thresholds that define when a specific property associated with quality or safety of a product reach unacceptability can be a complex task. The overall acceptability of a product is a combination of legislation, consumer habits, and the

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standards of the industry. However, food and postharvest technology research and industry practice has managed to identify several "technological" thresholds that are used in retail and distribution to assess the product and accept/reject lots which are highly correlated to this acceptability (Hellali and Korai, 2023) (Nicoli, 2012) (Meiselman and Cardello, 2003) (Li et al., 2022). Failure of one of these quality or safety parameters is sufficient to dictate the unmarketability of the product in retail and distribution, leading to the worst-case scenario, where all the energy spent making both packaging and product is lost (Ishangulyyev et al., 2019) (Lei et al., 2022). Furthermore, there are other "hidden quality" parameters for which there are no clear thresholds, but that still contribute to the overall quality acceptance of a specific product lot in retail and distribution.

Equilibrium modified atmosphere (EMAP) is a widely employed packaging technology of fresh horticultural products (Li et al., 2022) (Czerwiń et al., 2021). While some MAP packaging may require a flush step to obtain an initial composition different from the atmospheric one (Linus Opara et al., 2019), EMAP starts with the atmospheric gas composition and uses the natural respiration rate of the product, the permeability of the film and the free volume of the package to obtain the desired steady state gas composition during the storage period (Lei et al., 2022) (Jacxsens et al., 2001) (Czerwiń et al., 2021).

Oriented polypropylene (OPP) is one of the most used films for food packaging of horticultural products due to its low price and permeability proprieties compatible with a wide range of crops (Calhoun, 2010). Polylactic acid (PLA) (Ranakoti et al., 2022) is currently one of the few compostable films with commercial application in MAP (Angelin Swetha et al., 2023) (Fordham and Hadley, 2003), as it is already being mass produced and has good mechanical properties. The higher economic cost and permeability proprieties that may not suit some fresh products are barriers in the adoption of PLA in horticulture (Jim Jem and Tan, 2020), however the use of an agricultural bio stimulant has proven effective to improve the suitability of PLA in horticultural products (Giordano et al., 2024).

Kale (*Brassica oleracea)* is a curly leafed crop extensively growth for human consumption, rich in vitamins (Bergh, 1993) (Antonio Pellicer et al., 2020). The ability to be cultivated in a wide range of temperatures, from 258 K to warm summer temperature, makes it an option also for autumn animal grazing (Fordham and Hadley, 2003). Kale leaves are sold either separately or in fresh product mixes as minimal processed food, with the use MAP together with refrigerated storage as the main technologies ensuring the shelf life of the product. The main quality factors affecting the shelf life of kale leaves are colour change, weight loss and the disruption of the structure of the leaves that lead to a loss of crispness.

Silicon supplementation during cultivation has proven to be effective in slowing down the respiration rate of spinach, and thus making the plant able to retain its quality parameters for a longer period of time (Savvas and Ntatsi, 2015) (Obyedul Kalam Azad et al., 2021) (Grankina et al., 2021). One of the challenges that needs to be assessed when employing silicon supplementation is the possible interactions between the bio stimulant and the uptake of metals of the plant.

Mathematical modelling has the potential to be used in combination with a reduced number of experiments to evaluate and compare the effect of different packaging solutions or other mitigation strategies on food waste production (Coffigniez et al., 2021) (Gonzá et al., 2009) (Sousa-Gallagher and Mahajan, 2013). The mathematical models used for packaging design are based gas exchanges between the product, the free packaging space and the external storage atmosphere (Giordano et al., 2024). The food waste and rejection during retail and distribution is affected by batch heterogeneity (Albornoz and Cantwell, 2016). The heterogeneity of a product may arise from different factors (variations in cold chain, human subject assessment), however, one of the main contributors is the biological product variation inherent to fresh agricultural production (Raak et al., 2017). The use of mixed effect models to study the data of the experiment provides the possibility to model the variability between and within the groups (production batches), and thus to have a better understanding of the effect of the different combinations of treatment and packaging on the shelf life of the product, accounting for product variability (Harrison et al., 2018).

The main aim of this work is to assess if the use of silicon as a bio stimulant could improve the resistance of kale leaves and facilitate the transition to a PLA based sustainable packaging. This was achieved by of the use experimentation to study the effect that the different combinations of Silicon treatment and film had on the postharvest quality criteria and then employing linear mixed effect models to assess waste production.

2. Materials

2.1. *Brassica oleracea (baby leaf kale)*

The Gorilla green kale variety was used, with incised and frilly leaves, mild flavour, and good resistance to mildew. It can be grown in different types of soil, and it has a good yield The seeds were sown the July 5, 2021 and harvested by hand shears on the 3 of August, 29 days after sowing, with the kale being just within the threshold of baby leaf. The planting density was typical of commercial a production, with a spacing of 25 cm. The harvested leaves had a SPAD of 38 ± 2, turgor potential of 4 ± 1.5 MPa, and electrolyte leakage of 2 ± 1 μS.

2.2. *Packaging films*

Two packaging films were used, the polylactic acid film employed was NATIVIA® NTSS Environmental, a PLA Certified DIN EN 13432 with a specified thickness of 30 μm, a heat seal range of 358–413 K, oxygen permeability of 730 $cm^3\ m^{-2}\ d^{-1}$ (23 °C - 0% RH) ASTMD3985, and water vapor permeability of 270 $g\ m^{-2}\ d^{-1}$ (38 °C - 90% RH) ASTM F1249. The oriented polypropylene film utilized was Vibac CT Heat Sealable Coextruded Film with a thickness of 30 μm, an optimal heat seal temperature of 378 K, oxygen permeability of 1300 $cm^3\ m^{-2}\ d^{-1}$ (23 °C - 0% RH) ASTM D3985, and water vapor transmission rate of g m-2 d-1 (23°C-85% RH) ASTM F1249.

2.3. *Metal analysis*

Metal analysis employed a Microwave Accelerated Reaction System (Model MARS 6,CEM Corporation,U.S.). The digestion of the samples was performed in Nitric acid and TraceSELECT, for trace analysis, ≥69.0 % (Honeywell Fluka, U.S.). For ICP-MS analysis an Agilent 7900 was used, with a VWR Chemicals Aristar (Belgium) Multi element quality control calibration standard for ICP-MS 21 components 100 mg L^{-1}.

2.4. *Silicon treatment*

YaraVita (U.K.) ACTISIL, with stabilized orthosilicic acid as its silicon source, and Engage Agro Europe (U.K.) Ltd Sentinel, comprising a blend of silicon and salicylic acid were used. The concentrations tested were 0.04 mL $L^{-1}\ m^{-2}$ and 0.02 mL $L^{-1}\ m^{-2}$ for YaraVita, and 0.02 mL $L^{-1}\ m^{-2}$ for Sentinel. The results of a control ICP-MS analysis of the bio stimulants showed a silicon concentration of 805.173 mg Si kg^{-1} for a density of 1.137 g mL^{-1} for YaraVita, and1121.995 mg Si kg^{-1} with a density of 1.060 g mL^{-1} for Sentinel. The treatment consisted in two foliar applications based on product recommended application rates per area. The rate for Sentinel consisted in a total solution coverage of 40 mL per m^2. Each experimental plot measured 1.4 m by 5.4 m, with a total area of 30 m^2 across four replicated plots. A total of 1200 mL of solution was applied per treatment in the plot using a 5 L knapsack sprayer, calibrated at 138 kPa, which delivered 300 mL of solution for each of the 4 plots. Application of the two treatments of Yara was performed following the same procedure. Rainwater was used for the production of all the solutions, with control getting only rainwater.

Table 1
Summary of the mixed effect models results.

	Oxygen	Carbon dioxide	Weight loss	Electrolyte leakage	Turgor	SPAD	DeltaE
(intercept)	20.851 (0.251)***	−0.119 (0.239)	0.097 (0.091)	1.764 (0.223)***	3.221 (0.198)***	43.527 (1.562)***	2.555 (0.325)***
Day:FilmPLA:TreatmentControl	−2.749 (0.303)***	2.23 (0.260)***	1.098 (0.107)***		−0.247 (0.055)***	−2.044 (0.851)*	0.180 (0.106)
Day:FilmOPP:TreatmentControl	−3.129 (0.303)***	2.357 (0.260)***	1.176 (0.107)***		−0.247 (0.055)***	−2.177 (0.850)*	0.557 (0.106)***
Day:FilmPLA: TreatmentTreatment 1	−3.129 (0.303)***	2.438 (0.260)***	0.688 (0.107)***		−0.233 (0.055)***	−2.380 (0.850)***	0.017 (0.106)
Day:FilmOPP: TreatmentTreatment 1	−2.512 (0.303)***	2.117 (0.260)***	0.638 (0.107)***		−0.098 (0.055)	−3.602 (0.850)***	0.168 (0.106)
Day:FilmPLA: TreatmentTreatment 2	−2.226 (0.303)***	1.911 (0.260)***	0.682 (0.121)***		−0.136 (0.055)*	−2.323 (0.887)**	−0.052 (0.117)
Day:FilmOPP: TreatmentTreatment 2	−3.215 (0.303)***	2.37 (0.260)***	0.522 (0.107)***		0.049 (0.061)	−1.319 (0.850)	0.061 (0.106)
Day:FilmPLA: TreatmentTreatment 3	−1.948 (0.303)***	1.755 (0.260)***	0.802 (0.107)***		−0.031 (0.055)	−2.548 (0.850)**	−0.072 (0.106)
Day:FilmOPP: TreatmentTreatment 3	−3.240 (0.303)***	2.276 (0.260)***	0.602 (0.107)***		−0.097 (0.055)	−2.252 (0.850)**	0.257 (0.106)*
FilmPLA:TreatmentControl:Dayˆ2	0.253 (0.303)***	−0.184 (0.041)***	−0.075 (0.017)***		0.120 (0.055)	0.119 (0.105)	
FilmOPP:TreatmentControl:Dayˆ2	0.199 (0.048)***	−0.124 (0.041)**	−0.132 (0.017)***			0.112 (0.104)	
FilmPLA:TreatmentTreatment 1: Dayˆ2	0.326 (0.048)***	−0.224 (0.041)***	−0.047 (0.017)**			0.316 (0.104)**	
FilmOPP:TreatmentTreatment 1: Dayˆ2	0.143 (0.048)**	−0.139 (0.041)***	−0.068 (0.017)***			0.504 (0.104)***	
FilmPLA:TreatmentTreatment 2: Dayˆ2	0.237 (0.048)***	−0.185 (0.041)***	−0.043 (0.019)*			0.299 (0.112)**	
FilmOPP:TreatmentTreatment 2: Dayˆ2	0.277 (0.048)***	−0.191 (0.041)***	−0.052 (0.017)**			0.108 (0.104)	
FilmPLA:TreatmentTreatment 3: Dayˆ2	0.111 (0.048)*	−0.114 (0.041)**	−0.074 (0.017)***			0.306 (0.104)**	
FilmOPP:TreatmentTreatment 3: Dayˆ2	0.246 (0.048)***	−0.150 (0.041)***	−0.060 (0.017)***			0.207 (0.104)*	
AIC	658.9	617.232	354.473	308.933	340.079	623.602	488.465
BIC	717.328	675.664	412.42	316.626	371.102	677.187	519.488
Log Likehood	−310.45	−289.616	−158.236	−151.466	−159.039	−292.801	−2.33233
Num. obs.	160	160	156	96	124	124	124
Num.groups: Block	4	4	4	3	4	4	4
Var:Block (Intercept)	0	0.044	0.002	0.108	0.052	0.845	0.029
Var:Residual	2.164	1.592	0.268	1.318	0.589	5.138	2.193

Table 2
MANOVA analysis of differences in metals concentration between Silicon supplementations. Significant differences can be analyzed by the F value statistic as well as the p value of the Pillai test.

Metal	F value	Pr (>F)
Cd	1.412	0.245
Si	2.09	0.107
B	4.932	0.003**
Na	1.64	0.186
Mg	1.091	0.357
Al	3.3	0.024*
K	3.003	0.034*
Ca	2.582	0.058
Ti	2.61	0.056
Cr	0.215	0.885
Mn	1.7	0.173
Fe	2.152	0.01
Co	2.72	0.049*
Ni	3.565	0.017*
Cu	1.03	0.383
Zn	2.45	0.069
As	10.913	3 e−6***
Mo	8.055	8 e−5***
Pb	3.811	0.013*

3. Methods

3.1. Field experiment

Kale variety Gorilla was cultivated to commercial standards in an Irish agricultural field in County Meath. The kale was sown in situ on July 3, 2021. The experiment was set up in the field using a randomised block design comprising four replicates divided into 16 plots. Treatments included silicon foliar applications from the two proprietary plant products, and rainwater applied to control plots. On the 4th August, all kale samples were harvested using hand shears.

3.2. Design of kale E-MAP packaging

The design of the EMAP packaging for the kale was performed using a mathematical model coded in R (RStudio, 2022) with the aim of optimizing the evolution of concentration of gases during the seven day storage scenario. The respiration rate of kale was modelled using a Michaelis-Menten uncompetitive inhibition kinetic (Peppelenbos and van't Leven, 1996). The model was designed assuming a constant respiration rate quotient (RQ) for the production between O_2 and CO_2 production (Thompson and Bishop, 2016), with isotherm conditions inside the packaging and water activity saturation on the surface of the product. The initial gas concentration in the package was atmospheric and the optimal selected was the center of the optimal window of 1–3% O_2, 15–20% CO_2 (Fonseca et al., 2005). Furthermore, condensation

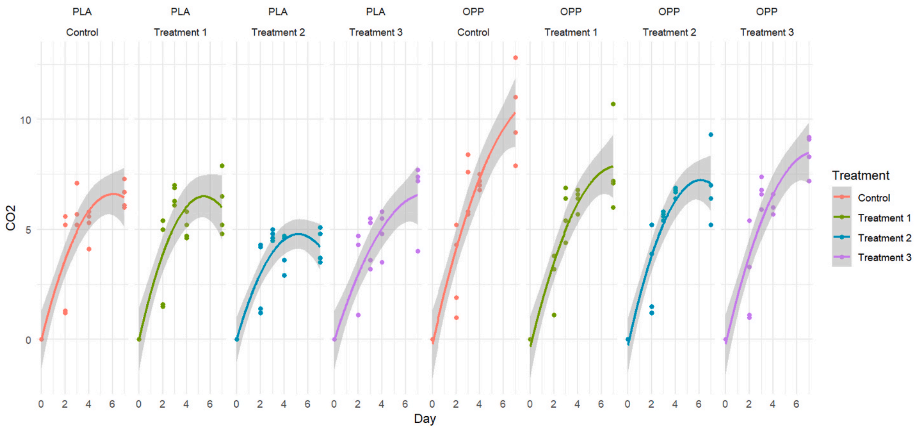

Fig. 1. CO_2 concentration determination and kinetic modelling inside the different packages (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against Control on a seven days storage experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

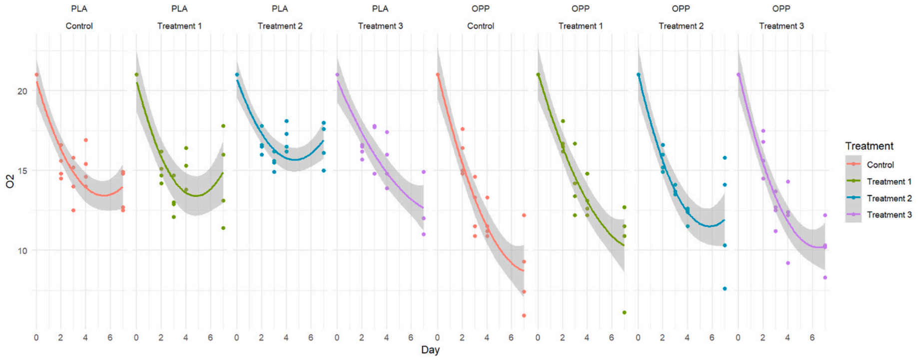

Fig. 2. O_2 *concentration* determination and kinetic modelling *inside the* different *packages* (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against Control on a *seven day storage* experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

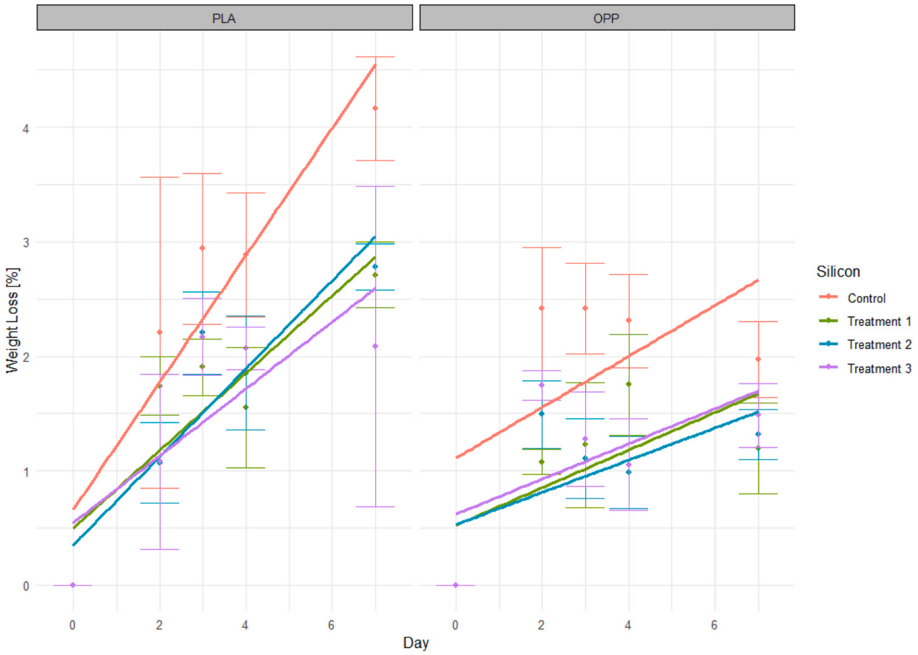

Fig. 3. *Weight loss* kinetics and modelling *inside the* different *packages* (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against Control on a *seven days storage* experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

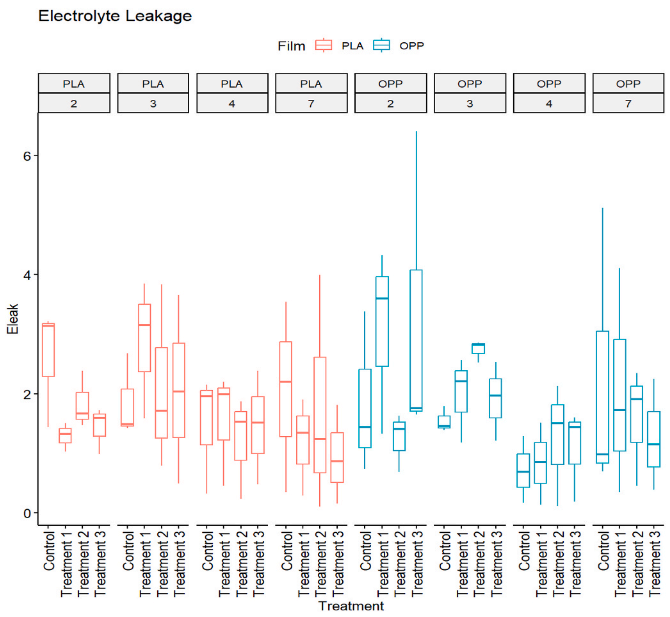

Fig. 4. *Electrolyte leakage* kinetics (Days 2, 3, 4 and 7) *inside the* different *packages* (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against the Control. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

inside the package was considered possible with a humidity value of 100% and the energy produced by respiration was considered as converted in heat.

The MAP model consisted of the following equations:

$$V_f * \frac{dCO_2}{dt} = \left(A.p * pCO_2 * \frac{P.atm}{L.f} * 0.01\ \left(CO_{2,O}. - CO_2\right) + W.s * r.CO_2 \right) * 100 \tag{1}$$

Equation (1) (Song et al., 2002) describes the evolution of CO_2 inside the package during the storage time. $A.p$ = permeable area [cm^2], $p.CO_2$ = CO_2 permeability coefficient [mL cm^{-1} h^{-1}], $P.atm$ = atmospheric pression [atm], $L.f$ = thickness of the film [cm], $CO_{2,O}.$ = external CO_2 concentration [%], CO_2 = Packaging CO_2 concentration [%], $W.s$ = weight of the product [kg], $r.CO_2$ = CO_2 respiration rate of the product [[mL kg^{-1} h^{-1}], and V_f = free volume of the package [mL].

$$V_f * \frac{dO_2}{dt} = \left(A.p * p.O_2 * \ \frac{P.atm}{L.f} * 0.01\ \left(O_{2,O} - O_2\right) + W.s * r.O_2 \right) * 100 \tag{2}$$

Equation (2) (Song et al., 2002) describes the evolution of CO_2 inside the package during the storage time. $p.O_2$ = permeability coefficient of the film to O_2 [mL cm^{-1} h^{-1}], $P.atm$ = atmospheric pression [atm], $O_{2,O}$ = concentration of O_2 outside the package [%], O_2 = concentration of O_2 inside the package [%], $r.O_2$ = O_2 respiration rate of the product [mL kg^{-1} h^{-1}].

$$r.O_2 = \frac{O_2 * V.mO_2}{(K.mO_2 + O_2)} \tag{3}$$

Equation (3) (Saenmuang et al., 2012) use the Michaelis-Menten model to describe the respiration rate of oxygen concentration over time. O_2 = concentration of O_2 inside the package [%], $V.mO_2$ = maximum O_2 consumption rate [mL kg^{-1} h^{-1}], $K.mO_2$ = Michaelis-Menten constant for O_2 consumption [% O_2]

$$r.CO_2 = RQ * r.O_2 \tag{4}$$

Equation (4) describes the respiration rate of CO_2 as a quotient of equation (3). RQ = respiration quotient, $r.O_2$ = equation (3).

The respiration model parameters (Vm, Km, RQ) were obtained by measuring the change in atmosphere composition in a closed respirometer using sealed glass jars of 1 L containing 50g of kale. Once the parameters of the specific kale respiration were identified, a packaging dimensions for 100g of kale were optimised. Because kale storage steady state was not reached in 7 days of the shelf life scenario, the packages were designed so that an atmosphere composition during the simulation of gas atmosphere at a storage scenario would be as close as possible to the center of the optimal storage window (Fonseca et al., 2005) by minimizing the Euclidean distance between the simulation and the center of the optimal MAP storage window. A penalty in the objective function was included if a certain packaging design fell under fermentative or carbon dioxide toxicity levels (O_2 below 2% or CO_2 over 20%). The constraints in the optimization parameters were established by the limits of dimensions and thickness of the film in line with the size

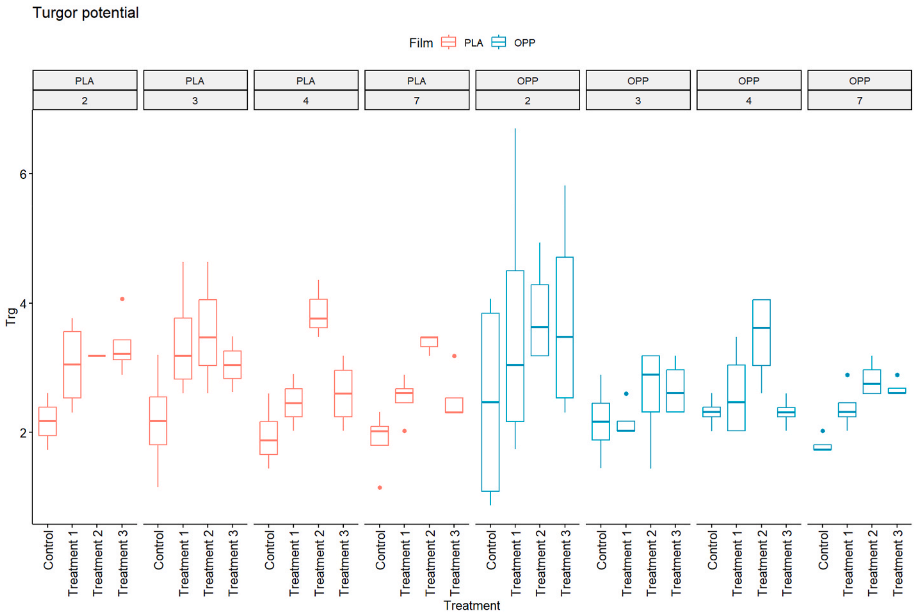

Fig. 5. Turgor potential [MPa] kinetics (Days 2, 3, 4 and 7) *inside the* different *packages* (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against the Control. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

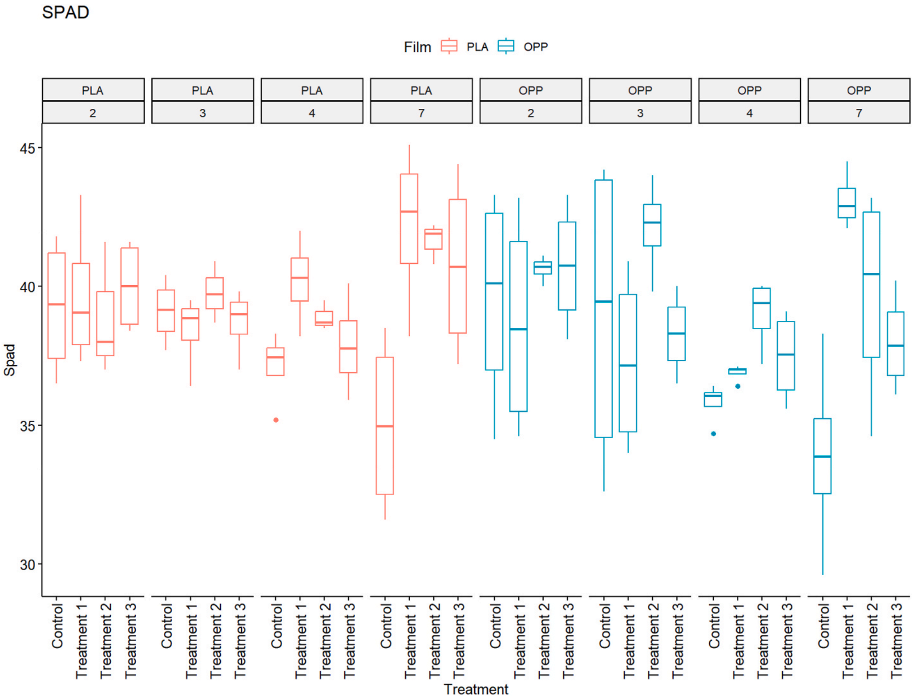

Fig. 6. Chlorophyl content kinetics (Days 2, 3, 4 and 7) *inside the* different *packages* (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against the Control. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

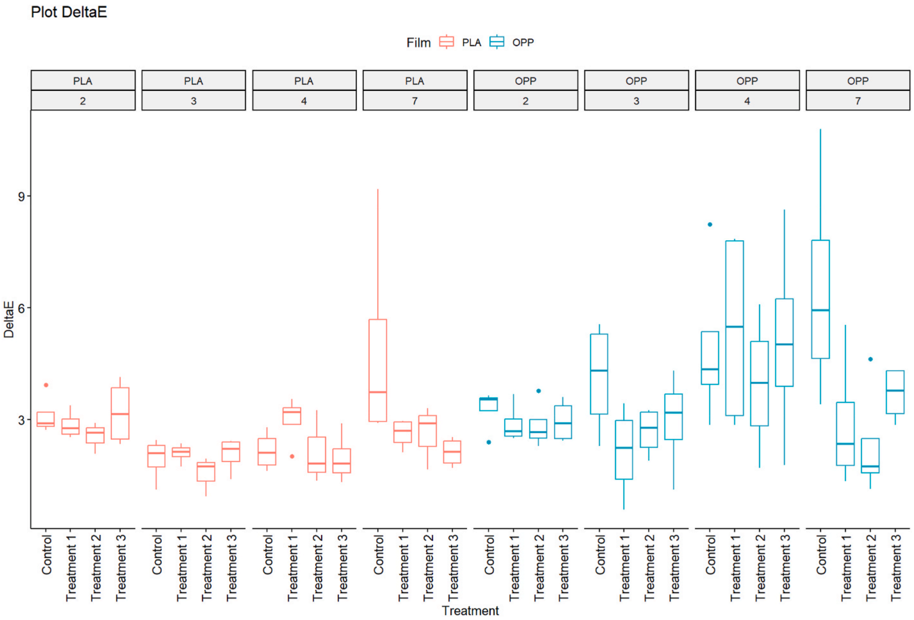

Fig. 7. Colour (DeltaE) kinetics (Days 2, 3, 4 and 7) inside the different packages (PLA and OPP) of Kale subject to Silicon (Treatment 1, 2 and 3) against the Control. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

commonly used by producers commercially. The BFGS optimization algorithm in R was used (RStudio, 2022), and the ODE model was simulated using the lsoda algorithm DeSolve library (Hindmarsh and Petzold, 2005).

3.3. Packaging production and kale packaging

The fresh harvested kale was delivered to the research laboratory and packaged on the same day. For each production batch 60 bags were produced with the optimised 20 × 26 cm dimensions, and a free volume of 250 mL. The 100 g of product was weighed with a Kern (Germany) ABS 220 N scale (precision of 0.1 mg). The bags were sealed using an impulse sealer Optimax (U.K.) mod. Pacplus 400HCT.

3.4. Storage studies

The temperature condition of the storage cold room was 90% RH and a temperature of 276 K. Control of qualitative properties and spoilage was carried out on day 2, 3, 4, and 7.An Ametek (U.S.) Dansensor CheckPoint 3 equipped with single use perforation needles was used to

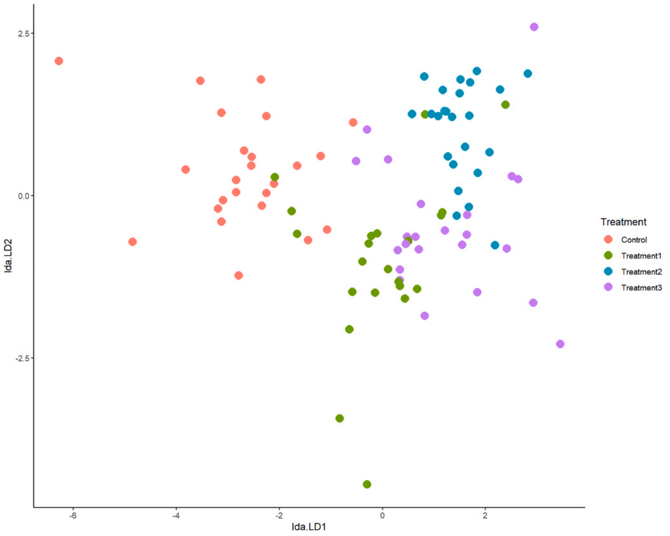

Fig. 8. Scatter plot of the first two linear discriminant analysis dimensions of the inverted MANOVA model relating metal concentrations to Si supplementation.

perform the analysis of the atmosphere composition of each package during the seven days. The kale weight loss percentage was measured using a Kern ABS 220 N scale (Readout [d] = 0.1 mg).

3.5. Water activity and turgor potential analysis

Water activity (a_w) was measured with an ACQUALAB model Series 3 TE METER Group (U.S). The turgor potential, as proposed by (Krishnan et al., 2004), was used to assess the integrity of the plant cell structure. The turgor potential was calculated as follows (Luard and Griffin, 1981),:

$$\Psi_{w=RT\ \ln\ (a_w/\upsilon)} \tag{5}$$

$$\Psi_{w=}\Psi_s+\Psi_p+\Psi_m \tag{6}$$

Where the molar volume of water υ is 101.325 Pa (18 0.048 mL mol^{-1}), Ψ_w is the water potential, Ψ_s is the osmotic potential, Ψ_p is the turgor potential, and Ψ_m is the matrix potential (Beecher et al., 2001a).

The methodology to estimate the postharvest turgor potential was a modification of the one used for mushrooms by Beecher (Beecher et al., 2001a). Disks with a diameter of 2 cm were extracted from the central region of the leaves within a cold room. Initial water activity readings were taken from these fresh samples. Subsequently, the disks were subjected to a freezing temperature of 193 K for 4 h followed by thawing at 294 K. This thawing process led to the rupture of plant tissue cells, resulting in a reduction of the turgor potential to 0. A second round of measurements was carried out on the thawed samples, and the turgor potential was determined as the disparity in water potential between the two samples (n = 5).

3.6. Electrolyte leakage analysis

(EL) is employed in postharvest research as an indicator of cellular state (Camposa et al., 2003) (Kimberly and Sokorai, 2005) (Rolny et al., 2011). Kale squares, measuring 1 × 1 cm, were obtained from the central part of the leaf, submerged in ultra-pure water, and subjected to conductivity assessment using an MRC INE-DDSJ-318 conductivity meter. The initial reading (e0) was recorded after 15 min. Subsequently, the samples underwent gentle agitation on an orbital shaker (Stuart SSL1) for 3 h to facilitate electrolyte leakage (e1). Finally, the samples were boiled for 15 min to disrupt cellular structure, and a reading of electrical conductivity was taken to determine the total electrolyte content (et). The electrolyte leakage was then obtained by the equation:

$$EL = \frac{100\ (e_1 - e_0)}{e_t} \tag{7}$$

With e_0 the value of electrolyte leakage after 5 min, e_1 the value of electrolyte leakage after 180 min, and e_t the value of electrolyte leakage after boiling.

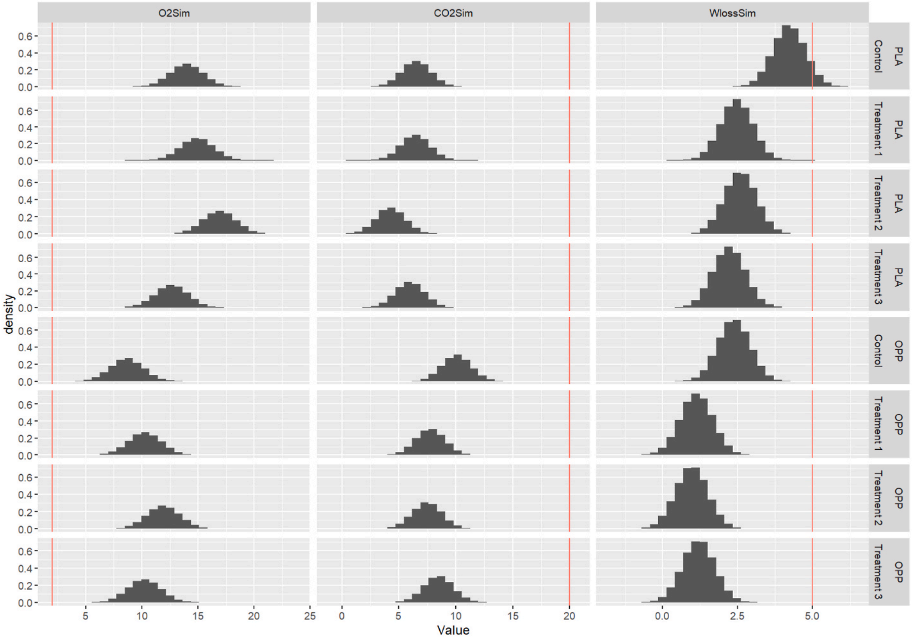

Fig. 9. Histogram of the predicted O_2 (O2Sim) CO_2 (CO2Sim) and Weight loss (WlossSim) distributions after 7 days postharvest stored with OPP or PLA flim and subject to Silicon Treatment 1, 2 and 3 against a control. The vertical red line indicates the technological threshold used to identify the quantile of the distribution that is outside-specification (<2% O_2 >20% CO_2 and >5% weight loss). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

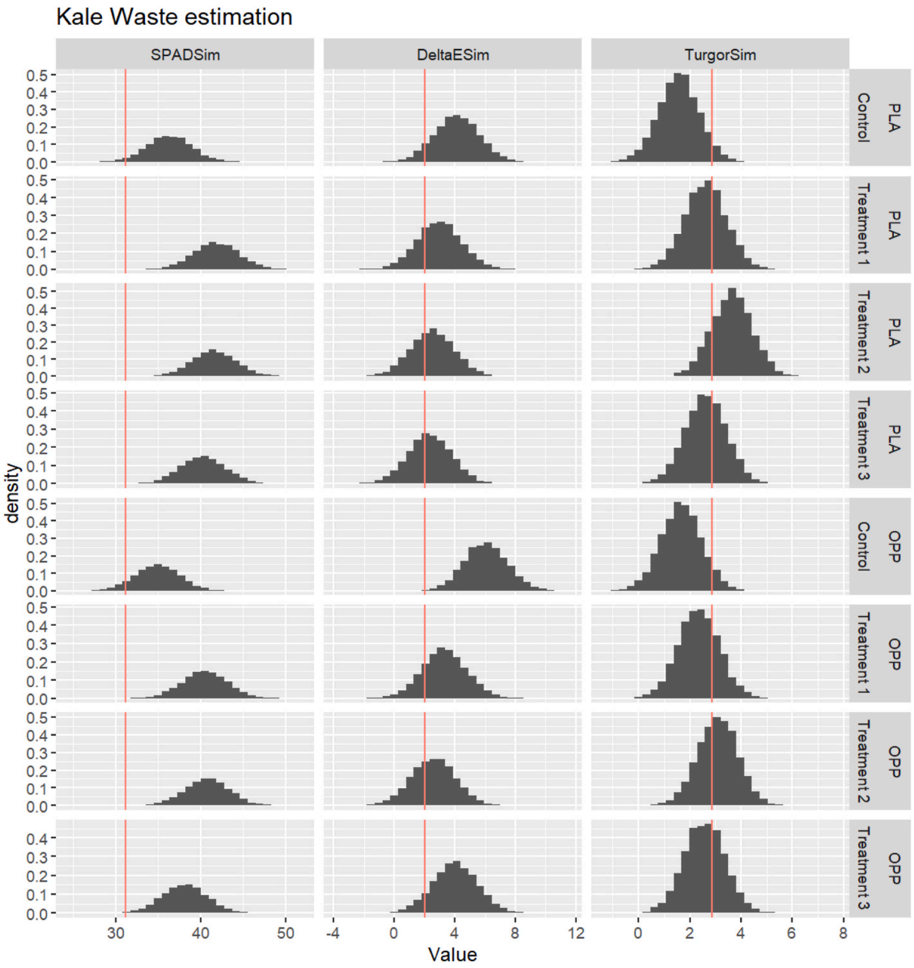

Fig. 10. Histogram of the predicted SPAD (SPADSim) DeltaE (DeltaESim) and Turgor (TurgorSim) distributions after 7 days postharvest stored with OPP or PLA flim and subject to Silicon Treatment 1, 2 and 3 against a control. The vertical red line indicates the technological threshold used to identify the quantile of the distribution that is outside-specification (10% variation for SPAD, DeltaE and Turgor). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.7. Kale colour testing

Ten leaves were collected from each package and stored in a dark container to avoid chlorophyll degradation. Colour changes were evaluated using a Colorimeter CR10 plus (Konica Minolta, Japan), by comparing the initial average leaf color on day 0 with measurements recorded on days 2, 4, and 7 ($n = 10$). The leaf surface colour was assessed at multiple points and represented in the CIE Lab color scale. Additionally, the total colour change (ΔE) was calculated using the CIE76 color difference formula, where L is the colour brightness ranging from 0 (completely black) to 100 (completely white), a represents the position on the green (negative) to red (positive) axis, and b represents the position on the blue (negative) to yellow (positive) axis.

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \tag{8}$$

3.8. Soil plant analysis development (SPAD) analysis

The chlorophyll concentration was assessed using the SPAD-502 Plus (Konica Minolta, Inc.), which measures leaf absorbance in the red and near-infrared regions (Konica Minolta Optics, 2012) following the methodology described in the EnMAP Field Guides (Süß et al., 2015).

3.9. ICP-MS

Metal analysis was carried out in accordance with the methodology described previously (CEM, 2018). In summary, samples from each batch were collected and stored in sterile plastic containers at 193 K. Fresh product weighing 0.5 g was freeze-dried, resulting in an average weight loss of 90% from the original. The dried samples were then placed in digestion vessels containing 10 mL of nitric acid. After swirling, the mixture was allowed to rest for approximately 15 min before sealing the vessel. The digestion process involved heating for 25 min followed by cooling for 15 min. The final samples were diluted to 50 mL with ultra-pure water. Plasticware was exclusively used when handling ICP-MS samples to prevent silicon contamination, and the plasticware was cleaned with 5% HNO_3. The diluent for running ICP-MS consisted of 2% nitric acid +0.5% HCl, with a calibration solution of stock 500 ppb. Various elements within the crops were compared, with a particular attention on silicon and heavy metals. The potential impact of silicon treatment on crop concentrations and any differences in levels of Cd, Si, B, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, and Pb between the treated and control samples were analyzed.

3.10. Estimation of waste in a 7-day simulated retail and distribution scenario

Linear mixed effect models (Meteyard and Davies, 2020) were used to fit the quality property kinetics and then simulations from those models were used to estimate the amount of product out-specification, where a threshold could be defined. The models for each property in Table 2 were chosen from a series of candidate models by using the Akaike and Bayesian information criteria (AIC, BIC) together with the logarithm of the likelihood as model discrimination criteria.

One thousand simulations using those estimated models were used to create a simulated scenario of the packaged kale after 7 days of storage. The quantile of the simulated population that exceeded a level of O_2 lower than 3%, or CO_2 above 20 %, or a Weight Loss over 5% was considered as quantification of products that would become food waste. Simulations were performed using the R software (www.r-project.org, version 4.2.2).

4. Results

The evolution of the atmosphere composition inside the packages during the storage time can be seen in Figs. 1 and 2. A significant difference between films and treatments ($p < 0.05$) can be observed. The differences in gas permeability between packages resulted in a higher concentration of O_2 and a lower concentration of CO_2 in the PLA film even after the optimised package configuration. This could be considered positive, as it would cause a delay in reaching unfavourable atmosphere conditions. Only some of the samples of the control seemed to reach higher value of $CO_{2,}$ while the treatment showed a positive effect in slowing down the respiration rate, in particular treatment 2 (see Table 2).

Fig. 3 shows how the use of PLA film resulted in a higher water loss from the product and Table 2 shows a significant effect for the films and treatments ($p < 0.05$). The weight loss due to the use of PLA was partially compensated by the effectiveness of the film in lowering the respiration rate and reducing the product metabolism. This could be due to the kale leaves having a more resistant structure compared to other green leafy vegetables (Woro Lestari and Rosyidah, 2022) The positive effect of the treatments in reducing the weight loss was evident in the two packaging films. In the case of PLA, it allowed a weight loss comparable with the control OPP, despite PLA having a higher water permeability.

The electrolyte leakage kinetics (see Fig. 4) showed no effect of the films and with no significant differences between treatments or films (see Table 2). The levels of electrolyte loss seemed to remain almost constant, indicating a good cellular integrity of the kale.

The kinetics of the turgor potential (Fig. 5) were in agreement with those of the electrolyte leakage. The starting value constantly decreased over time, thus during its shelf life in packaging, the kale lose intracellular water, but not to such level as to trigger the need to import extracellular water into it. Neither the Silicon intervention or the packaging seemed to affect the change with time of the Turgor, with only Treatment 1 in OPP showing a faster reduction of turgor with time (see Table 2).

The study of the evolution of the SPAD (Fig. 6) showed some significant differences between films and treatments ($p < 0.05$) (see Table 2). However, Fig. 6 shows no visible evidence of yellowing or discolouration. This result is encouraging regarding the possibility of using PLA as more sustainable packaging solution for kale.

The colour change (Fig. 7) reflect in part the results of the SPAD reading. There was a bigger variation in the colour change of OPP packaged kale in comparison with those with PLA. This could be a result of the higher metabolic activity of the kale. A significant difference ($p < 0.05$) was observed between packaging and treatments, indicating a positive effect of the treatments in reducing colour changes, especially in the end of shelf life (see Table 2).

The interaction of the silicon treatment with the potential uptake of metals by the kale is presented in Fig. 8 and Table 1. The linear discriminant analysis of the results (Fig. 8) showed differences in the concentrations of metals between groups, with the control treatment well separated from the treatments. The LDA analysis of the data resulting from the ICP-MS showed the presence of a difference in the metal concentration between batches, suggesting again some level of intrinsic variability in the uptake of metals. Also, the difference in metal concentration didn't result in any safety concern, with all the levels being well under the threshold of concern for human health.

4.1. *Food waste production*

The food waste production 7 day scenario simulation for quality properties with a threshold are presented in Fig. 9, while Fig. 10 shows "invisible" quality, for which an unambiguous threshold is more difficult to be determined. The concentration of carbon dioxide, oxygen and weight loss was used for total waste estimation. The gas concentrations in Fig. 9 did not reach toxicity levels in either of the packaging film levels, however a positive effect of the silicon was showed, with treatments showing population distributions further away from the threshold than the control. It may be possible to further optimize the dosage of Silicon and the packaging design to prevent waste, possibly even reducing its dimensions, thus saving material. The weight loss, on the other hand, show a 7.23% of product out of specification in the case of the use of PLA without treatment. All the silicon treatments were able to reduce the out of specification percentage to negligible levels in a seven day storage scenario.

In Fig. 10, thresholds of 10% change from the initial value of SPAD, delta E and Turgor potential were selected with the aim of compare the potential beneficial effect of the Silicon treatment on the potential food waste production of the two different MAP films. This, however, is just an arbitrary value and more studies would be necessary to identify how large the variation in these parameters must be to have an unsellable product. The simulation of the SPAD distribution on a 7 day scenario estimated 8.2% out of specification product for OPP under control conditions and 0% with silicon treatment. In the case of PLA the same trend was observed, with a change of the estimation of waste from 2.7% in the control to 0 in the Silicon treatments. Silicon treatment improved the simulated waste in colour change in OPP packages by 35% and 30% in PLA packages applying treatment 2. The Turgor potential potential waste was improved with Silicon treatments by 25% in OPP packaging and 30% in the case of PLA ones.

5. Discussion

The transition from traditional film packaging to compostable solutions for fruits and vegetables is proving difficult to implement in the market, both for economic reasons and for the limitations in maintaining adequate shelf life (Michaliszyn-Gabry et al., 2022) (Ocicka et al., 2023) (Shaikh et al., 2021). The approach to overcome some of the limitations of the material through the use of agricultural interventions could facilitate the pathway towards a more circular economy. The experimental results and the simulations of the control samples of the two film packages showcase the gap of the transition between OPP and PLA based packaging. OPP films for the horticultural industry are designed and commercially selected for its ability of maintain the quality of the product, and especially in avoiding weight losses. The main limitation to the use of the PLA film is the water vapor permeability and the high hygroscopicity, which risks higher weight losses than OPP. The simulated food waste production related to a weight loss was 7.23% in PLA bags, as opposed to OPP which was negligible. Further optimization of the water permeability of the PLA film could reduce this disparity (Chin Tze Seng et al., 2020).

The ability of PLA packages to maintain a modified atmosphere was to be comparable with the OPP solution. Increasing the thickness of the PLA film could to reduce the water permeation to more desired levels, however it may introduce the risk of inadequate atmosphere conditions, industrial processing complications, and higher costs. In comparison, the silicon treatment proved to be effective in reducing the water loss of the samples, probably due to its ability to induce changing in the mobility of the stomata and thus to its conductance (Vandegeer et al., 2021). This hypothesis is supported also by the differences in gas composition between control and treatment samples as result of the lower respiration rate, in which the stomata play a role as well. The SPAD and colorimetric analysis had very little difference between all the samples, indicating that both packaging solutions were able to keep an overall good visual quality during the storage period studied. The electrolyte leakage and turgor potential remained almost constant during the experiments, showing only a small degree of variation. This could be attributed to the resistant structure of the kale leaves, where a loss of intracellular water does not need to be compensated by drawing water from the extracellular matrix.

The ICP-MS analysis showed the presence of some difference in the metals uptake between treated and untreated samples, but the overall concentration of metals remained below any levels of concern for human consumption. This difference should be explored in a future work under controlled growth conditions.

The analysis of the data through mixed effect modelling, presented in Table 2, showed consistency in highlighting the positive effect for all the parameters for which clear technological thresholds exist. The difference in weight loss appeared to be the critical factor affecting the waste production between the two films. The use of the silicon treatment decreased kale waste value by 35% in the case of PLA for the best-case scenario, with similar results to the product packaged in OPP without treatment. The overall positive effect of the treatment is evident in the reduction of food waste production, especially regarding the effect on weight loss observed in the case of use of PLA.

6. Conclusions

The use of a silicon bio stimulant as an instrument to improve the physiological response of kale through postharvest and storage has proved to be an effective strategy to facilitate the transition to more sustainable packaging solutions for the implementation of circular economy. Furthermore, the result of this study underscores the potential of bio stimulants not only to improve postharvest physiology but also to reduce food waste, which is a significant issue in the fresh produce industry. By mitigating the adverse effects associated with the higher water vapor permeability and hygroscopic nature of PLA films, the application of the silicon treatment offered a possibility for overcoming one of the main barriers to the adoption of compostable packaging in the horticultural sector. The ability of the silicon treatment to lower the product's respiration rate, possibly by affecting stomatal conductance resulted in an overall improvement of the physiological integrity of the kale leaves. Waste due to weight loss was reduced from reduced from 7.23% to 0% when using a silicon treatment in PLA packaging. This, integrated with a specific intervention in the design phase of the PLA packaging and optimization in the permeability, makes feasible the compostable packaging of kale leaves, having a food waste production of the same magnitude of the traditional polyolefin films.

CRediT authorship contribution statement

Francesco S. Giordano: Methodology, Investigation, Formal analysis, Writing – original draft. **Andrew Reynolds:** Methodology, Investigation, Writing – review & editing. **Catherine M. Burgess:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Lorraine Foley:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Jesus M. Frias:** Conceptualization, Formal analysis, Writing – review & editing, Supervision, Resources.

Declaration of competing interest

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Data availability

Data will be made available on request.

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