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Modelling CO₂ transfer in foil ripened cheese with CO₂ production
Modelling CO₂ transfer in foil ripened semi-hard Swiss-type cheese
F. Acerbi^a, V. Guillard^{a^a}, M. Saubanere^b, C. Guillaume^a, N. Gontard^a
^aUMR 1208 IATE Agro-polymer Engineering and Emerging Technologies, Montpellier (France),
University of Montpellier, INRA - 2 place Viala - bât. 31, F-34060 Montpellier Cedex 01
^bUMR 5253 - Institut Charles Gerhardt, Montpellier (France), Place Eugène Bataillon, 34090 Montpellier
* corresponding author: valerie.guillard@umontpellier.fr

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Abstract

Eye growth in cheese with intense CO_2 production during ripening mainly depends on CO_2 11 12 production and transfer properties. Despite CO_2 production and diffusion during ripening of 13 semi-hard Swiss-type cheese eyes in such cheeses are considered as important quality parameters, the research concerning key gas production and transfer in cheese remains widely overlooked. In 14 this study, experimentally assessed CO_2 production was coupled with transfer coefficients in a 15 mathematical model in order to predict CO₂ gradients formed inside the cheese during ripening. 16 The permeability coefficient of CO₂ through the multilayer barrier packaging which wraps the 17 cheese during ripening was also included in the model. The presented model was validated by 18 19 assessing the CO₂ concentration in the cheese and its partial pressure in the packaging headspace. CO₂ production rate was found to be the most important input parameter affecting CO₂ gradients 20 formed in cheese during ripening whereas the other input parameters (solubility, diffusivity, 21 permeability) had little effect on the total CO_2 gradient. 22

23

24 Keywords: solubility, diffusivity, permeability, CO₂, cheese ripening

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Nomenclature

25

α	Level of statistical significance				
Α	Surface (m ²)				
Bi	Biot number (non-dimensional)				
br	Bottom rind position of the cheese				
С	Concentration (kg/m ³)				
ch	Relative to cheese				
D	Effective diffusivity coefficient of CO_2 in cheese (m ² s ⁻¹)				
exp	Experimental values				
HS	Packaging headspace				
Ι	Relative to the interface				
j	Relative to a gas specie				
k	External mass transfer coefficient (m/s)				
Κ	Degree in Kelvin, with $K = 273.15 + degree$ in Celsius				
KP	Gas permeability through the packaging film (cm ³ μ m ⁻¹ m ⁻² d ⁻¹ bar ⁻¹)				
1	Cheese thickness (m)				
М	Molar mass (kg/mol)				
р	Partial pressure (Pa)				
P_T	Total pressure (atm)				
Pe	Gas permeability through the packaging film (mol $m^{-1} s^{-1} Pa^{-1}$)				
PAB	Propionic Acid Bacteria				
pred	Predicted values				
PTATN	ratio of phosphotungstic acid soluble nitrogen on total nitrogen (g/100g)				
S or SCO2	Solubility coefficient of CO_2 in cheese (mol m ⁻³ Pa ⁻¹ or mmol kg ⁻¹ atm ⁻¹) or CO_2				
	solubility				
SM	Salt in moisture ratio (g/100g)				
t	Time (s)				
Т	Temperature (K)				
R	Universal gas constant: 8.314 (J mol ⁻¹ K ⁻¹)				
CVRMSD	Coefficient of variation of the root mean squared deviation				
V	Volume (m ³)				
Х	Position in the cheese (m)				
У	Experimental or predicted variable				
μ	average				
$oldsymbol{arphi}$	Mass flow (kg s ⁻¹)				
ν	Production rate (kg $m^{-3} s^{-1}$)				

Relative to the surrounding atmosphere ∞

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27 1. Introduction

In food engineering, mathematical modelling of physical mechanisms such as heat or mass transfer was used for many years to simulate and optimize/control operation units such as drying or salting (Bona et al., 2007; Mayor and Sereno, 2004; Payne and Morison, 1999; Santapaola et al., 2013). More recently these models were coupled to biological ones such as Mickaëlis Menten equation that formalize the aerobic respiration (Ho et al., 2011; Guillard et al., 2012), chemical reaction for oxidation (Bacigalupi et al., 2013) or predictive microbiology models in order to better represent the evolution of the packed food during storage (Chaix et al., 2015).

This modelling approach coupling equations coming from different disciplinary fields was 35 36 recently applied to semi-hard Swiss-type cheese in order to model the eyes' growth during ripening (Laridon, 2014; Laridon et al., 2016). CO₂-source in this type of cheese is propionic acid 37 bacteria (PAB) which means that CO2-production rate and amount in such cheese is much higher 38 39 compared to that of lactic acid bacteria. The ripening of these cheeses includes a step during which cheeses are stored at warm temperature (about 1-2 weeks at 20-25°C) for stimulating the 40 PAB fermentation. During this step, CO_2 is intensively produced, leading to the growth of eyes 41 (Fröhlich-Wyder and Bachmann, 2004). Cheeses are often foil ripened and a plastic packaging is 42 used to wrap the cheeses during the whole ripening period for avoiding excessive loss of gaseous 43 compounds. The modelling approach proposed by Laridon (2014) therefore concomitantly took 44 into account mass transfer of gas (CO₂ produced by bacteria and responsible of eyes' growth), 45 production of the CO_2 and mechanical constraint imposed to cheese paste by this production. 46 47 This model was based on experimentally assessed rheological parameters (stress) and CO₂ production rate in simplified condition, but some input parameters such as CO₂ diffusivity and 48 solubility into the cheese were estimated from the literature and assumed constant throughout the 49 cheese paste and the ripening age. The sensitivity analysis performed by these authors revealed 50

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afterwards the higher influence of CO₂ production and diffusion parameters compared to the
rheological ones in semi-hard cheese (Laridon, 2014).

Faced to the importance of CO_2 diffusion and CO_2 production rate in the ripening of semi-hard Swiss-type cheese, this paper aimed at deepening these two phenomena by coupling them in a mathematical model in order to simulate and predict evolution with time of CO_2 gradients in the cheese paste and in the packed cheese (including CO_2 permeation through the ripening foil). In this purpose, the aim of this study was to develop and experimentally validate in various conditions, mimicking the ripening conditions of Swiss-type cheese, a mathematical diffusionreaction model to predict CO_2 gradients in packed cheeses during ripening.

60

61 **2. Materials and methods**

62 **2.1 Cheese and packaging**

Semi-hard cheese blocks of 1 kg were kindly supplied by a cheese company. The cheeses 63 included about 42% w/w moisture and 26.5% w/w fat, with pH varying from 5.50 to 5.70 from 64 14 to 28 days from renneting. The cheeses used for the model validation without CO₂ production 65 66 (same batch) did not include any intentionally added CO₂ producing bacteria (PAB and heterofermentative lactic acid bacteria or LAB) and was produced from pasteurized milk to avoid any 67 sources of hetero-fermentative LAB or PAB. The cheeses used for the validation with CO₂ 68 production included PAB (10⁶ CFU ml⁻¹ cheese milk) as main source of CO₂ production. They 69 were produced from a second, dedicated batch from pasteurized milk. After brining, all cheeses 70 were packed in a multilayer barrier packaging film made of PE/PVDC/PE. Indicatively, the 71 permeability to CO₂ at 19°C equalled 40000 cm³ μ m m⁻² d⁻¹ bar⁻¹ (Acerbi et al., 2016c). The 72 ripening schedule of all ripened cheeses was as follows: 13°C until 14 days from renneting, 19°C 73

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for 14 days, 2–3 days at 13°C, longer storage at 6°C. The target chemical composition of cheeses
used in this study is described in Table 1.

Cheese blocks were about 15 to 8 cm square in shape (see Supplementary Material A) and were sampled in their core, orthogonally to the interface exposed to headspace/surrounding atmosphere (Figure 1), at least 3 cm away from side rinds, resulting in a cylinder of 8 cm height and about 2 cm of diameter. The sampling region was then cut in thin slices of minimum 0.5 cm of thickness for assessment of chemical composition gradient or CO_2 gradient.

Table 1

- 81
- 82
- 83

84 **2.2** Chemical analyses

The chemical composition (fat, moisture, pH, total nitrogen (TN) and fractions of TN, salt, 85 organic acids) of three cheeses per production was measured, in order to verify that the cheese 86 production was on target. Dry matter and sodium chloride were measured according to the ISO 87 5534 (Anonymous, 2004a) and ISO 5943 (Anonymous, 2006) standards. Total nitrogen (TN), 88 water soluble nitrogen (SN) and phosphotungstic acid soluble nitrogen (PTA-N) were measured 89 90 using Kjeldahl based methods according to ISO 8968-3 standard (Anonymous, 2004b; Bütikofer et al., 1993). The ratio of PTA-N on TN (g/100g) was considered as a good proteolytic indicator. 91 pH and fat content were characterized according to respectively, FD V04-035 (Anonymous, 92 2009) and NF V04-287 (Anonymous, 2002) French standards. Organics acids were assayed using 93 internal method based on high-performance liquid chromatography. 94

95 CO_2 determination in cheese was carried out with the protocol described in Acerbi et al. (2016b). 96 The protocol included a first step where CO_2 was extracted from the cheese sample by immersing 97 it in acidic solution. The extracted CO_2 was then scavenged by a soda solution of known

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- molarity, which was finally titrated with hydrochloric acid. The difference between the initial and
 final soda molarity related to the moles which reacted with CO₂.
- 100 2.3 Microbiology analyses

101 Propionic acid bacteria were enumerated with a method based on the count of the diluted colonies 102 grown on agar plates enriched mainly with sodium lactate and yeast extract after 1 week of 103 incubation at 30°C. The results were expressed in colony-forming unit per gram of cheese (CFU 104 g^{-1}).

105 **2.4 Gas chromatography for headspace analyses**

106 The partial pressure of N_2 , O_2 and CO_2 was measured (resolution: 0.005%) by injecting 10 µl of headspace of cheese packs inside a micro gas chromatography unit including a thermal 107 conductivity detector (MicroGC 3000, SRA Instruments). Homogeneity of the gas composition 108 was ensured by pumping few millilitres of sample gas inside the micro gas chromatography unit 109 before each measurement. The cheese packs were not kept after the analyses because of the too 110 111 low amount of headspace volume. Therefore, new cheese packs produced from the same batch were used for each analysis in order to follow the kinetics of headspace composition during 112 ripening. The gas chromatography unit was previously calibrated with gas bottles of known 113 compositions. At least two measurements were carried out per each sample. 114

115 **2.5 Description of the model**

Evolution of CO_2 partial pressures in the foil packed blind cheese during ripening relies on the interplay of four mechanisms: (1) CO_2 production due to the activity of microorganisms (PAB), (2) gas transport within the cheese paste, (3) gas transfer at the cheese rind/headspace interface and (4) gas transmission through the packaging film. The four described mechanisms are illustrated in figure 1.

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121					
122	Figure 1				
123					
124	2.5.1 Model assumptions				
125	The following assumptions were made in the present mono-directional modelling study:				
126	- The composition of the atmosphere surrounding the packed cheese during ripening is				
127	constant and equals to 78.1% for $N_2,20.9\%$ for O_2 and 0.03% for CO_2 (Widory and				
128	Javoy, 2003).				
129	- Temperature in the packed cheese system and surrounding atmosphere is constant,				
130	without gradients.				
131	- Total pressure of the system is constant and it equals atmospheric pressure (101325 Pa).				
132	- The solubilization of N_2 inside the cheese was considered negligible compared to CO_2 ,				
133	because of its lower solubility in water (about 50 times less soluble than CO ₂ in water at				
134	20°C) (Dean, 1999). O ₂ solubility and diffusivity in the cheese were set to constant values				
135	of 2.5 10^{-9} m ² s ⁻¹ and 1.3 mmol kg ⁻¹ atm ⁻¹ respectively and which correspond to solubility				
136	and diffusivity of the gas in water at 20°C (Chaix et al., 2014).				
137	- The mechanical resistance to deformation of the cheese packaging is not taken into				
138	account in the model. Thus, volume changes according to moles content inside the pack				
139	and total pressure of headspace remains equal to external atmospheric pressure.				
140	Measuring volume changes during experiment has revealed that they are negligible and				
141	that the flexible pouch could easily compensate the small volume change due to its				
142	property of elongation.				

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- For the cheese with salt gradient, the initial NaCl gradient was measured in cheeses
 produced within the same production day and it was considered to remain constant during
 the experiment. Same assumption was used to quantify the proteolytic indicator
 (PTATN).
- Gradients in chemical composition in the cheese from its upper rind to its core are
 symmetric to the gradients from lower rind to the core.
- 149 **2.5.2 Gas balance in headspace**
- 150 The variation of concentration of the gas species *j* in the packaging headspace *HS* depends on the 151 mass flow of gas permeating the packaging film *f* from the surrounding atmosphere φ_{j_f} (kg/s) 152 and the mass flow of the gas species occurring at the interface between the cheese and the 153 headspace φ_{j_I} .
- Assuming that the packaging film does not oppose any mechanical resistance to deformation, when the amount of gas species in the headspace varies, the headspace volume V_{HS} (m³) changes, whereas the total pressure in the headspace P_T remains constant and equal to atmospheric pressure (101325 Pa). The global mass balance of species *j* in the headspace can hence be written as follows:
- 159

$$V_{HS}\frac{dC_{j_{HS}}}{d_t} + C_{j_{HS}}\frac{dV_{HS}}{d_t} = \varphi_{j_f} + \varphi_{j_I}$$
(Eq. 1)

160 where C_{iHS} (kg/m³) is the concentration of the gas in the headspace and t is time (s).

161 Assuming that the gas mixture in the headspace obeys the ideal gas law, $\frac{dv_{HS}}{d_t}$ can be calculated as 162 a pondered sum of the different aforementioned mass flow φ_{j_f} , φ_{j_I} as follows:

163
$$\frac{dV_{HS}}{d_t} = \frac{RT}{P_T} \left(\frac{\varphi_{CO2_f} + \varphi_{CO2_I}}{M_{CO2}} + \frac{\varphi_{O2_f} + \varphi_{O2_I}}{M_{O2}} + \frac{\varphi_{N2_f}}{M_{N2}} \right)$$
(Eq.2)

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166 The concentration of the gas in the headspace $C_{i_{HS}}$ can be calculated according to (Eq. 3)

$$RT \ \sum_{j=\{O_2, CO_2, N_2\}} \frac{C_{j,HS}}{M_j} = P_T = 10^5 Pa$$
 (Eq. 3)

and similarly, for the partial pressure of the gas in the headspace $p_{j_{HS}}$ (Eq. 4),

169
$$p_{j_{HS}} = \frac{C_{j_{HS}}RT}{M_i}$$
 (Eq. 4)

170 **2.5.3 Gas permeation through the maturation foil**

The gas permeation through the packaging film (maturation foil), assuming that the partial pressures in the atmosphere surrounding the cheese are constant, could be conveniently described by the Fick's first law (steady state regime). Therefore, the mass flow φ_f of gases j (N₂, O₂, CO₂) through the packaging film was calculated according to first Fick's law (Fick, 1855) as stated in Eq. 5.

176

$$\varphi_{j_f} = M_j P e_j \, \frac{A_f}{l_f} \left(p_{j_{\infty}} - p_{j_{HS}} \right) \tag{Eq. 5}$$

where Pe_j is the permeability coefficient of the gas j through the film (mol m⁻¹ s⁻¹ Pa⁻¹), l_f is the thickness of the film (m), A_f is the film surface (m²) and $p_{j_{\infty}}$ and $p_{j_{HS}}$ are the partial pressure of the gas j in the surrounding atmosphere (denoted by symbol ∞) and the packaging headspace, denoted by *HS*.

181 **2.5.4 Mass flow at the cheese rind/gaseous interface**

182 The mass flow at the cheese/rind gaseous interface was calculated as follows (Eq. 6):

183

184

 $\varphi_{j_I} = k_j (\frac{M_j A_I}{RT}) (p_{j_{HS,I}} - p_{j_{HS}})$ (Eq. 6) Where k(m/s) is the mass transfer coefficient at the interface between the cheese rind and the

headspace and A_I and $p_{i_{HSI}}$ are the surface at the interface and the partial pressure at the

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immediate vicinity of the cheese surface. The mass transfer coefficient k is calculated according 186 to Eq. 7 187

188

$$kj = \frac{Bi \times D_j}{L} \tag{Eq. 7}$$

Where Bi is the non-dimensional Biot number, assumed to be equal to 10^5 (ratio between 189 diffusivity of CO_2 in air and cheese) (Laridon, 2014), D_i is the diffusivity of CO_2 in cheese (about 190 10^{-10} m² s⁻¹) and L is the characteristic length of the considered material (length of the cheese 191 equalled about 0.008m). 192

Assuming that the gaseous species in headspace are in thermodynamic equilibrium with the 193 194 dissolved species at the cheese surface, the concentration of dissolved gas species *j* at the cheese surface $C_{i_{ch}} = (kg/m^3)$ relates to $p_{i_{HS}}$ according to Henry's law: 195

$$p_{j_{HS,I}} = \frac{c_{j_{ch,x=0}}}{M_j S_j}$$
 (Eq. 8)

Where S_i is the solubility coefficient of the considered gas *j* (mol m⁻³ Pa⁻¹). 197

2.5.5 Gas diffusion inside the cheese paste and CO₂ production 198

The CO₂ diffusion within the cheese paste was represented by making use of Fick's second law of 199 diffusion for the transient state of diffusion and it was coupled to CO₂ production by adding 200 production term v (kg m⁻³ s⁻¹) to Fick's second law, leading to Eq. 9. 201

202
$$\frac{\partial c_{CO2_{ch}}}{\partial t} = D_{CO2} \frac{\partial^2 c_{CO2_{ch}}}{\partial x^2} + v_{CO2}$$
(Eq. 9)

Where $\frac{\partial c_{CO2_{ch}}}{\partial t}$ is the partial derivative of the concentration of CO₂ in the cheese as regard to time, 203 in the direction x (m). x represents the distance from the interface of the cheese rind to headspace 204 and the considered position inside the cheese. x varies from 0 to 8 (cheese thickness in cm). D_{CO2} 205 is the effective diffusivity coefficient of CO_2 in cheese (m²/s). 206

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207 The same equation without the production term was used to model O_2 diffusion within the cheese

208 paste.

209 **2.5.6 Boundary conditions**

210 Equality of flows was considered at the interface between the cheese rind and the headspace:

$$D_{j}\frac{\partial c_{j_{ch}}}{\partial x} = \frac{\varphi_{j_{I}}}{A_{I}} = kj(\frac{M_{j}}{RT})(p_{j_{HS,I}} - p_{j_{HS}}) at x = 0$$
 (Eq. 10)

212 where *j* stands for either CO_2 or O_2 .

213 Since the cheese is pressed on continuous impermeable material during ripening due to gravity,

214 we assumed no diffusion at the cheese bottom rind (br), (x = br):

$$D_j \frac{\partial_{C_{j_{ch}}}}{\partial x} = 0 \text{ at } x = br$$
 (Eq. 11)

Assuming that the food sample was initially in equilibrium with a gas of fixed partial pressure p_{j_0} (Pa), the initial conditions take the form:

215

$$C_{j_{ch}}(x,0) = M_j S_j p_{j_0}(x,0) \quad for \ t = 0$$
 (Eq. 12)

219 **2.5.7 Prediction of model input parameters for different ripening conditions**

The following empirical equation was used in the model for predicting the changes in CO₂ production rate, v_{CO2} (mmol kg⁻¹ d⁻¹) as a function of salt to moisture ratio, SM and temperature, T (Acerbi et al., 2016a):

$$v_{CO2} = 8.527 + 0.0862 \text{ T}^2 - 1.621 \text{ T} + 5.367 \text{ SM} - 0.415 \text{ SM T}$$
 (Eq. 13)

SM (g/100g) is calculated as the percentage of the mass ratio between sodium chloride andmoisture.

The following empirical equation was used in the model for predicting the value of D_{CO2} at different temperatures, *T* salt to moisture ratio, *SM* and *PTATN* (ratio of phosphotungstic acid soluble nitrogen on total nitrogen). The latter coefficient is a ripening indicator related to the

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229	proteolytic phenomena (especially amount of free amino acids) which relates to structure changes		
230	in the cheese during ripening (Acerbi et al., 2016d).		
231	$D_{CO2} = (-0.0428 \text{ T}^2 + 1.3689 \text{ T} - 0.6188 \text{ SM} + 12.2421 \text{ PTATN} - 9.6910) \times 10^{-10}$		
232	(Eq. 14)		
233	The value of S_{CO2} (in mmol kg ⁻¹ atm ⁻¹) was calculated by using a modified version of the		
234	equation given by Acerbi et al. (2016b):		
235	$S_{CO2} = 37.35879 - 0.83414 SM^2 + 4.4619 SM - 0.34768 T $ (Eq. 15)		
236	The modification consisted in the use of a quadratic term for the salt effect instead of a linear		
237	term in the view of more recent results (figure 2).		
238			
239	Figure 2		
240			
241	The value of permeability (KP) of the gas j (O ₂ CO ₂ , N ₂) was estimated at different ripening		
242	temperatures by interpolating the results of permeability coefficients KP given by Acerbi et al.		
243	(2016c) in units cm ³ μ m m ⁻² d ⁻¹ bar ⁻¹ . The <i>KP</i> values were converted into <i>Pe</i> values (mol m ⁻¹ s ⁻¹)		
244	Pa ⁻¹) to be used in the model (Eq. 5).		
245	$KP_{CO2} = -108.03 T^2 + 4551.5 T - 3242.6 $ (Eq. 16)		
246	$KP_{02} = 386.53 T + 6313.6$ (Eq. 17)		
247	$KP_{N2} = 188.78 T + 3422$ (Eq. 18)		
248	2.5.8 Numerical solving and identification procedure		
249	This system of equations governing the coupled diffusion and production of gas in the cheese and		
250	the gas transfer and permeation in the cheese packaging headspace was solved using a dedicated		
251	algorithm "ode15s" developed in Matlab® computing software (The Mathworks Inc., Natick,		

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Mass, USA) and adapted to stiff systems where each of unknown variables may exhibit radically different variation kinetics. This algorithm adjusted automatically the size of the time step used for numerical integration of the equations. To evaluate goodness of fit between experimental and predicted data, the coefficient of variation of the root mean square deviation (CVRMSD) was calculated as follows:

$$CVRMSD = \left(\frac{\sqrt{\frac{(ypred - yexp)^2}{(N)}}}{\mu_{exp}}\right) \times 100$$
(Eq.19)

Where y_{pred} and y_{exp} are respectively the experimental and the simulated residual value, N is the number of experimental measurements and μ_{exp} is the average of the experimental values. CVRMSD enables to compare the quality of the model with other models present in literature. A good quantitative model is considered to have CVRSMD $\leq 10\%$.

262 **2.6 Model validation**

263 The experimental validation was made in three steps of increasing complexity which are264 summarized in Table 1.

 \bullet Firstly, the mono-directional CO₂ diffusion within the cheese and transfer at the cheese rind 265 interface was validated on an old ripened high salted cheese (namely "old cheese") with no salt 266 267 gradient and without CO_2 production (no CO_2 producing bacteria). The cheese was high salted 268 via brining (about 5% NaCl/dm, salt content on dry matter) in order to avoid possible gas production from unwanted microorganisms in such old cheese. The cheese, apart for its upper 269 rind, was fully covered with a gas impermeable membrane (see Supplementary Material A) and it 270 was housed in a controlled temperature cabinet (set at 19°C) with a continuous flow of wet CO₂ 271 (gas supposed to be equilibrated at 100% of relative humidity after bubbling in a flask containing 272 pure water at the temperature of the experiment). After 3 days, the CO₂ dissolved in different 273 positions (e.g. the sample is sliced parallel to the interface) from the upper rind (x=0) to the 274

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bottom rind (x=8) was assessed with the CO_2 determination method described above. Two repetitions were made in order to validate the diffusion phenomenon. For two other repetitions, after 3 days of CO_2 sorption, the cheese samples were then kept 3 days in a continuous flow of wet (100% RH) N₂ (desorption step). The gradient of dissolved CO_2 into the paste after these 3 days of desorption was then assayed as previously described for the sorption step (2 repetitions).

Secondly the coupling of CO_2 diffusion and production was experimentally assessed by using a cheese with PAB and average salt concentration (about 2.5% NaCl/dm, salt on dry matter, in the cheese, namely "young cheese"). This cheese also included a salt gradient due to its younger age (15 days from renneting) when salt is still slowly diffusing from rind to core of the cheese (brined cheese). The same experimental procedure previously described was used, apart for the following: the cheese stayed 1 day at 19°C, before the experiment with the contact of wet CO_2 from upper rind (x=0) started and it lasted for 4.4 days.

The initial CO_2 concentration gradient in the cheese was measured just before the experiment started (i.e. about 9.5 weeks from renneting for the first validation step and 15 days from renneting for the second more complex validation step including CO_2 production). This initial CO_2 gradient is indispensable to parametrize initial conditions in the numerical algorithm.

291 Thirdly, in order to compare the output of gas concentration in the headspace given by the 292 model including permeation phenomenon, gas headspace composition was measured in the 293 headspace of packed cheeses (2 replications). The headspace gas analyses were repeated on 294 different cheeses during ripening (about at 10, 14, 16 ripening days at 19°C).

295

In each case of these aforementioned steps, the model was adapted accordingly to experimental conditions: system of Eq. (6) to (15) for the first and second steps - without the production term in Eq. (9) and related Eq. (13) – and system of Eq. (1) to Eq. (18) for the third, full case.

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300 **2.7. Statistics**

Statistical tests were performed by using R software for statistical computing (R, 2014). Comparisons between the chemical compositions were performed by pairwise comparisons using *t* test with pooled standard deviation. The Holm method for the multiplicity of error was used to adjust the p-value of multiple pairwise comparisons. Different letters were used for denoting significant difference between data sets (level of significance $\alpha = 0.05$, unless stated).

306

307 3. Results and discussion

Our model takes into account experimentally assessed parameters for describing CO₂ production 308 309 and overall transfer in and out a cheese/packaging system during foil ripening. The focus was on the exhaustive description of the gas transport properties in the continuous cheese paste and at its 310 interface with the surrounding atmosphere. We therefore used a model blind cheese (without 311 eyes). We experimentally assessed the following parameters: transport of CO₂ in the cheese paste 312 (effective diffusivity), transfer of CO₂ at the interface between cheese and headspace (solubility), 313 314 oxygen, nitrogen and carbon dioxide transmission rate through the maturation foil (permeability) 315 and CO₂ production rate from the bacteria. The cited parameters were previously assessed in 316 function of the main ripening variables (different temperatures, ripening time, salt content amongst others) (Acerbi et al., 2016a, 2016b, 2016c, 2016d). 317

318

319 **3.1 Compositional analyses**

320 The chemical composition of the cheese without PAB (old cheese – data not shown) was not 321 significantly different (α =0.05) as a function of the position in the cheese, whereas a relevant 322 gradient in PTATN (ratio of phosphotungstic acid soluble nitrogen on total nitrogen) and SM

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323 (salt in moisture ratio) was confirmed from analyses made on cheese with PAB analysed at 15324 and 20 days from renneting (figure 3).

Although the transfer properties of nitrogen components (PTATN) and salt were not experimentally assessed within this study and not included in the model, the initial heterogeneous composition was considered and a linear interpolation was used for predicting the initial composition in all positions of the cheese including PAB. The composition in the position 4 to 8 cm was considered symmetrical to the position 0 to 4 cm.

- 330
- 331
- 332

Figure 3

A relevant gradient in organic acid concentration was found in the cheese with PAB both at 15 333 and 20 days from renneting (figure 4). No propionate and acetate was found in the outer rind (0 334 cm) at 15 days from renneting. The observed delay in PAB fermentation in the outer part of the 335 cheese was probably due to the negative effect of high salt to moisture ratio on the bacteria cells 336 (Guinee, 2004) and it was already demonstrated by Huc et al. (2014) in similar cheeses. The 337 molar ratio between propionate and acetate in the core of the cheese equalled about 2. The ratio 338 of 2 is obtained if PAB convert lactate exclusively via the Fitz pathway (Fröhlich-Wyder and 339 Bachmann, 2004; Piveteau, 1999; Fedio et al., 1994). We can therefore confirm that, in the 340 341 studied cheese, PAB fermented lactate primarily via the Fitz pathway and that probably no other metabolic activity (producing acetate) occurred. 342

- 343
- 344

Figure 4

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The pH of the cheese was measured because pH changes may affect both the solubility of carbon 346 dioxide dissolved in the water phase of the cheese (Chaix et al., 2014) and its diffusivity 347 coefficient due to a different organisation of the casein matrix structure (Lawrence et al., 1987). 348 349 The pH in the studied cheese did not relevantly vary in the considered experimental time (figure 350 5a). The enumeration of PAB cells confirmed the higher metabolic activity observed in the core of the 351 352 cheese (figure 5b). 353 354 Figure 5 355 3.2 Initial CO₂ concentration 356 The initial CO₂ concentration in different positions (from upper to bottom rind) of the cheese was 357 measured in 2 to 3 cheeses produced within the same production batch. Whereas the CO_2 358 distribution was low and rather homogeneous for the old ripened cheese with no intentionally 359 added CO₂ producing bacteria (figure 6a, 3 repetitions), the initial CO₂ gradient was relevant in 360 the cheese with PAB (figure 6b, 2 repetitions). The low and homogeneous initial CO₂ 361 362 concentration observed in the older cheese was expected because this cheese did not contain 363 intentionally added CO_2 producing bacteria, while the CO_2 gradient observed in the cheese with PAB at 15 days from renneting (14 days at 13°C and 1 days at 19°C) reflected the effect of salt 364 gradient on PAB. There is an inhibition of PAB growth (Figure 5b) by the higher salt content 365 close to the rinds with a consequently lower production of CO₂ and propionic acid close to the 366 rinds compare to the core of the product leading to this "bell like curve" for initial CO2 gradient 367 368 in salted cheese with PAB. This evolution of salt content that is spatially-dependant, due to 369 diffusion of salt from the periphery towards the centre of cheeses, has been found in previous

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studies (Huc et al., 2014; Guinee, 2004; Hollywood & Doelle, 1984) and before by Mocquot
(1979), Geurts et al. (1974, 1980) and Pauchard et al. (1980). Therefore, the median value for
initial CO₂ concentration was used (4 mmol/kg) for the model validated for the cheese without
PAB and the real gradient was used as input vector for initial CO₂ concentration for the cheese
with PAB.

375 376 377

Figure 6

378 3.3. Investigating effect of salt content on CO2 solubility

Prior model validation, additional points of solubility of CO₂ within the cheese paste were 379 measured to complete the work of Acerbi et al. (2016b) and obtain more precise S_{CO2} prediction 380 (eq. 15). According to these new values (Figure 2), S_{CO2} increased with light NaCl content, while 381 382 it decreased at very high NaCl content, following a similar behaviour compared to salting in and salting out effect of protein. This phenomenon was ascribed to the possibly higher sorption of 383 CO_2 in highly hydrated protein during salting in phase (Guinee, 2004), while the overall S_{CO2} 384 would decrease due to lower level of protein hydration at high salt concentration (salting out). 385 386 Guinee (2004) suggested that salting out effect of protein in cheese (Mozzarella) may take place for salt to moisture ratio (S/M) higher than 6.3% w/w, which is close to the highest salt level 387 investigated in Figure 2 (about 6.7% S/M). 388

389 3.4 Model validation

The simplest model form describing CO_2 diffusion inside the cheese paste (without PAB and CO_2 production) and the transfer at the cheese rind/gaseous interface (100% CO_2) was successfully validated because the difference between predicted and experimental data was below 10% (figure

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393 7a). Same good validation with a 100% N_2 flux at the cheese rind surface was obtained 394 (CVRMSD < 8%) (see Supplementary Material B).

When increasing the complexity of the model, including CO₂ production rate and considering a 395 396 cheese with salt gradient, the observed error between experimental and predicted data was found higher (30%) (figure 7b). In the latter more complex model, the predicted line was generally 397 underestimating the experimental gradient, leading to a high CVRMSD. The lack of fit of the 398 more complex model could be due to (1) the adoption of a mono-directional model which may 399 400 not be fully appropriate for diffusion in cheeses with gas production and/or (2) underestimations 401 in either the prediction of CO₂ production rate and/or in the initial CO₂ concentration gradient. Underestimation of the CO₂ production rate may be due to the linear approximation used by 402 Acerbi et al. (2016a) to describe the effect of salt content. Indeed, lower salt contents were 403 investigated in the previous work, which provided the predictive equation for CO₂ production 404 rate, compared to the current study. Therefore, effect of high SM ratio is probably not well 405 406 predicted by Eq.13 which was never validated for such SM ratio. This underestimation may be 407 overcome by carrying out more experimental measurements of CO₂ production rate at higher salt content. A possible underestimation of the initial CO₂ concentration gradient in the cheese may 408 be ascribed to natural deviations in metabolic activity of the PAB in different cheeses produced 409 from the same batch. Both hypotheses were confirmed by simulating a 1.7 folds higher CO₂ 410 411 production rate (figure 8) and then, a 2 folds higher initial CO₂ concentration (figure 9). In both cases, the predicted curve fit very well the experimental data. 412

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415

416

Figure 7

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418

Figure 9

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Then, the full model considering permeation through ripening foil in addition to 420 421 solubilisation/diffusion and production of CO₂ within the food was then used to predict the CO₂ partial pressure in headspace. A third set of experiments conducted on cheeses packed in ripening foils were conducted in the objective to validate it. Experimental difficulties arose because gas headspace analysis could not be assessed continuously in the pack (because of too high gas volume injected) therefore only a few experimental points have been collected (See supplementary material C). However, it has been noted that the model tended to underestimate the headspace partial pressure when CO₂ production occurs (in cheese with PAB). But, once again, considering a 1.7 fold higher CO₂ production rate, the prediction fitted better the experimental data. A better fit may also be obtained by reducing the value for CO_2 permeability of the packaging or increasing the initial CO₂ concentration gradient (results not shown). But this 430 hypothesis does not sound well founded and therefore was not applied. The permeability values 431 432 were especially assessed in the conditions encountered in the present work and were therefore considered relevant. 433

3.5 Exploratory analysis of model simulations 434

Simulations were carried by considering the min and max values of 4 parameters in their range of 435 variation (table 2): CO₂ solubility (figure 10a), diffusivity (figure 10b), permeability (figure 10c) 436 437 and production coefficients (figure 10d). During the simulation, only one of the mentioned input parameters was varied from the lowest to the highest value described in Table 2. The boundary 438

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conditions used during these simulations included that the packed cheese was in contact with the 439 atmosphere (20.9% O₂, 0.03% CO₂, 78.1% N₂) from one rind (upper rind) and in contact with a 440 non-permeable support from the below rind (shelf). The range of values for solubility and 441 442 diffusivity was chosen in agreement with the min and max observed in the experimental campaign described by Acerbi et al. (2016b, 2016d). The values for permeability were decided to 443 vary of factor 10 of the predicted value of Equation 16, 17, 18. The value of production rate was 444 decided to vary of 4 units compared to the predicted value of equation 13, because it was 445 446 considered a realistic variation for the different salt contents observed in different positions of the 447 studied cheese at 19°C.

- 448
- 449

Table 2

450

The other input parameters were kept fixed (medium value) as respect of their position. This 451 simplified sensitivity analysis had the goal of highlighting which input parameter had the 452 strongest effect on the output (CO_2 gradients formed in cheese). Logically, changing S_{CO2} led to 453 light differences in CO₂ concentration only close to the gaseous interface (figure 10a) because 454 this parameter only intervenes in the boundary condition at cheese/headspace interface: the lower 455 the solubility, the lower the CO₂ content at the interface. Changing D_{CO2} slightly affected the 456 457 shape of the CO₂ gradient close to the cheese rinds, probably because these positions were characterized by lower v_{CO2} due to the higher salt content (figure 10b) and it affected the overall 458 459 shape of the curve. v_{CO2} showed the highest effect on the CO₂ gradients, from -10 to +20 mmol/kg of difference for the lowest and highest v_{CO2} respectively compared to the median value 460 in the core of the cheese. Concerning the effect of different permeability, the lower the gas 461

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462 permeability of the packaging, the higher was the CO_2 concentration at the cheese rind, but the 463 overall change in CO_2 gradient due to different permeability was negligible.

464

465

466

Figure 10

This paper presents an unprecedented modelling approach that successfully describes the 467 mechanisms of CO₂ diffusion, solubilisation and production by Swiss-type cheese with intensive 468 469 PAB-based CO₂ production and also CO₂ permeation through the ripening foil. All mechanisms 470 were dynamically coupled and experimentally validated permitting to achieve the initial objective of this paper which was to predict evolution with time of CO₂ gradients into the packed cheese. 471 The developed model is the most complete one compare to precedent similar approach of the 472 literature. For instance, the one of Jakobsen and Risbo, (2009), developed for prediction, among 473 others, of the changes in solubilised carbon dioxide in semi-hard cheese packed in modified 474 475 atmosphere packaging, neglected all mechanisms of CO₂ diffusion and production in their 476 approach.

This model could be further used to predict CO_2 gradients into blind cheese or, once coupled with a mechanical model of bubble growth such as the one proposed by Laridon et al., (2014), could be used to predict eye growth in Swiss type cheese and then pilot the ripening step.

480

481 **4. Conclusion**

We presented the first experimentally validated model which couples the phenomena of CO_2 production, solubilisation/diffusion and permeation in a packed cheese system for predicting the CO_2 gradients formed in the cheese during ripening. A three steps validation procedure enabled to build a robust model for a quantitative description of CO_2 gradient formed in a cheese with or

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without CO₂ production by PAB and including the phenomena of CO₂ diffusion in the cheese 486 paste and transfer at the gaseous interface. The model was able to describe the shape of the CO_2 487 gradient formed in the cheese with, nevertheless, less precision when CO_2 production happens. 488 489 This term was probably less accurately characterized for the conditions used in this paper and induces less performant prediction. A simplified sensitivity analysis highlighted CO₂ production 490 as the most important input parameter affecting the CO₂ gradients formed in cheese during 491 ripening. Results presented in this paper represent a solid basis for the description of the most 492 493 important phenomena affecting the quality of cheese with intense CO₂ production during 494 ripening.

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Figure 1: Scheme of the simplified food / packaging system with the four phenomena considered (mono-directional transfer through the headspace/cheese interface, br =cheese bottom-rind)

Figure 2. CO₂ solubility in semi-hard Swiss-type cheese as a function of salt content at 13°C. The point at intermediate NaCl content (1.5% w/w) is added to the ones reported by Acerbi et al. (2016b) and it was measured with same protocol on the same cheese. Different letters a, b c, ...denote significant difference for $\alpha = 0.05$.

Figure 3. (a) PTATN - ratio of phosphotungstic acid soluble nitrogen on total nitrogen and (b) SM - salt in moisture ratio- in different positions of the of the semi-hard Swiss-type cheese with PAB, from rind (0 cm) to core (4 cm) at 15 and 20 days from renneting, representing starting time and ending time of the validation experiment.

Figure 4. Propionate (a) and acetate (b) concentrations in different positions of the semi-hard Swiss-type cheese with PAB at 15 and 20 days from renneting (young cheese).

Figure 5. pH and PAB count in different positions of the semi-hard Swiss-type cheese with PAB at 15 and 20 days from renneting.

Figure 6. Median values for initial CO₂ concentration measured in 9.5 weeks after renneting for old semi-hard Swiss-type cheese without PAB (a) and in 2 weeks after renneting for young semi-hard Swiss-type cheese with PAB (b). Horizontal and vertical error bars represent cheese position used and min and max values for assessed CO₂ respectively.

Figure 7. Experimental (red dots) and predicted (solid line) CO₂ concentration in the semihard cheese without PAB (a) and with PAB (b) CO₂ production after about 4 ripening days at 19°C. Root mean squared error (CVRMSD) is indicated on each figure. Error bars in experimental data represent standard deviations.

Figure 8. Predicted CO₂ gradients in cheese (solid lines) after 1, 2, 3, 4 and 10 days of contact with 100% CO₂, calculated considering 1.7 folds higher CO₂ production rate (19°C). Red

solid line and red error bars correspond to predicted and experimental CO_2 gradient after 4 days of contact.

Figure 9. Predicted CO₂ gradients in cheese (solid or dotted lines) after 1, 2, 3, 4 and 10 days of contact with 100% CO2, calculated considering 2 folds higher initial CO₂ gradient (19°C). Red solid line and red error bars correspond to predicted and experimental CO₂ gradient after 4 days of contact.

Figure 10. Effect of the intensity (low, medium and high, as stated in Table 2, in black, blue and red respectively) of the input parameter CO_2 solubility (a), diffusivity (b) permeability (c) and production rate (d) on the predicted CO_2 gradients in cheese ripened for 4 days at 19°C (age at beginning of ripening equalled 14 days from renneting).

Table 1. Target chemical composition of "old" and "young" cheeses and steps of model

Target Validation step Type of Time Target fat Target salt PAB Target cheese after moisture % absolute % content % pН w/w NaCl/d.m. renneting d.m. **1** CO₂ diffusion only "Old 15 days 42 40 5 % 5.45 No cheese" **2** CO₂ diffusion + "Young 9.5 42 8 2.5 % 5.45 Yes* cheese" production by PAB weeks **3** CO₂ diffusion + production by PAB + CO₂ permeation through ripening foil

validation

*10⁶ CFU ml⁻¹ milk

low	medium	high
25	36	40
1	4	8
4000	44000	440 000
2	4	8
	low 25 1 4000 2	low medium 25 36 1 4 4000 44000 2 4

Table 2. Range of values used in the simulations



Figure 1: Scheme of the simplified food / packaging system with the four phenomena considered (mono-directional transfer through the headspace/cheese interface, br =cheese

bottom-rind)



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4 days of contact.

Highlights

- We proposed the first validated model for the prediction of CO₂ gradient in cheese.
- CO₂ production is the most important parameter affecting CO₂ gradients in cheese.
- A variation of a factor 10 of CO₂ permeability of the packaging did not relevantly affect CO₂ gradients in cheese
- CO₂ permeability of the packaging did not relevantly affect CO₂ gradients in cheese.

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