Model based leak correction of real-time RQ measurement for dynamic controlled atmosphere storage

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Abstract

A method was developed to correct real-time measurements of the respiratory quotient (RQ) of pome fruit for gas leakage of a cool room. The method is based on a general leakage model that was simplified by performing sensitivity analysis of the contribution of the pressure driven and concentration driven gas transport terms. The analysis showed that pressure driven leakage was dominant over diffusive leakage. The methodology was validated successfully using an empty storage container at 0.4 kPa O₂ and 1.3 kPa CO₂. A sensitivity analysis using virtual storage experiments showed that the error of the RQ estimates with leak correction was 0 %, while without leak correction they increased to above 700 %. Finally, the validated model was successfully implemented in an automated RQ-DCA control system using ‘Braeburn’ apple fruit (*Malus ×domestica* ‘Braeburn’ 2x). RQ estimates without leakage correction were heavily biased when leakage of atmospheric air into the storage container occurred and would lead to erroneous control of the storage atmosphere composition. With the developed leakage correction, RQ measurements were found to be accurate during decreasing as well as increasing atmospheric air pressure.

Keywords

Respiration, Dynamic controlled atmosphere, Air tightness, Model, Gas flow, Apple fruit.

1 Introduction

Controlled atmosphere (CA) storage systems are widely used to preserve quality of apple fruit. During CA storage, fruit are exposed to a decreased O₂ partial pressure, an increased CO₂ partial pressure and a low temperature (Dilley, 2010; Ho et al., 2013). CA storage is intended to slow down respiration and other quality degradation processes that are associated with respiration (Saltveit, 2003; Verboven et al., 2006; Both et al., 2017). Optimal storage conditions are usually determined empirically as to deliver good quality after storage (Peppelenbos, 2003; Wright et al., 2012; Nock and Watkins, 2013). To avoid off-flavor and storage disorders, these optimal storage conditions usually maintain a safety margin relative to the anaerobic compensation point (ACP) – the O₂ concentration at which CO₂ production is minimal. The anaerobic compensation point is the O₂ concentration below which the metabolism of the stored fruit changes from aerobic respiration to fermentation as main energy source, leading to off-flavor and storage disorders (Kader, 1989; Fonseca et al., 2002; Geigenberger, 2003; Franck et al., 2007; Thewes et al., 2015). At O₂ concentrations above the ACP respiration rapidly increases with O₂ concentration, leading to increased quality loss during storage (Burg and Burg, 1965). The safe margin maintained regarding the ACP with conventional CA storage provides an opportunity to improve post-storage fruit quality by further reducing in-cool room O₂ levels and minimizing fruit respiration by storing the fruit as close as possible to – and ideally at the ACP. An additional benefit of storing fruit at low O₂ concentrations, is the reduction of O₂ related storage disorders like superficial scald, which otherwise need to be prevented in a chemical way by treatment with anti-scald agents like diphenylamine (DPA)

and ethoxyquin or the ethylene blocker 1-methylcyclopropene (1-MCP) (DeEll et al., 1996; Blankenship and Dole, 2003; Watkins, 2008; Lurie and Watkins, 2012).

State of the art storage technologies like dynamic controlled atmosphere (DCA) storage, search for the lower oxygen limit (LOL) of the stored produce – which is the lowest O₂ concentration at which the fruit can be stored without developing off-flavor and storage disorders (Wollin et al., 1985; Zanella, 2003). Thereto, in-cool room O₂ concentrations are gradually decreased during storage until low O₂ stress is detected based on real-time measurement of a bio-response of the stored fruit to low O₂ stress (Wolfe et al., 1993). Subsequently, the O₂ concentration is increased again until relief of low O₂ stress, ensuring the produce is being stored at the lowest O₂ concentration possible, and thereby minimizing quality loss (Veltman et al., 2003; Gasser et al., 2008; Wright et al., 2012).

In the past, the most prominent DCA technologies were based on chlorophyll measurements (DCA-CF) and DCA based on measurements of the ethanol content headspace of a small box of sample fruit which is placed inside the cool room (DCS) (Schouten et al., 1997; Prange et al., 2002). More recently, a novel type of DCA storage based on measurements of the respiratory quotient (RQ) of the stored fruit (RQ-DCA) was developed (Delele et al., 2015, Bessemans et al., 2016). The RQ is defined as the ratio of the CO₂ production rate and the O₂ consumption rate of the stored produce (Gran and Beaudry, 1993; Jozwiak and Blanpied, 1993). When aerobic respiration is the main energy source, RQ was found to have a value of about 0.91, 0.91 and 0.90 for ‘Jonagold’, ‘Braeburn’ and ‘Kanzi’ apple fruit respectively (Hertog et al., 2001; Ho et al., 2013). However, when the O₂ concentration approaches zero the fruit metabolism shifts from aerobic respiration to fermentation, resulting in a steep increase in RQ. This increase is therefore a good measure for low O₂ stress (Gran and Beaudry, 1993; Jozwiak and Blanpied, 1993; Yearsley et al., 1997, 1996). RQ-DCA uses real-time estimates of the RQ of the stored fruit in the cool room to alter the CA setpoints continuously throughout

the storage season based on measured changes of gas concentrations (Bessemans et al., 2015; Bessemans et al., 2016; Both et al., 2017, Thewes et al., 2017). Measured changes in CA composition of the cool room atmosphere are mainly caused by consumption of O₂ and production of CO₂ by fruit respiration (Hertog et al., 1998). However, leakiness of the cool room may allow small amounts of atmospheric air to leak inside and vice versa, altering the gas partial pressures of the cool room. Cool room walls may be assumed to be perfectly gastight, but leakage might occur in the seals and seams of the room due to the surface roughness of the materials used (Persson and Yang, 2008). Depending on the surface roughness, elastoplastic properties of the seals and contact pressure, small areas may remain where the seals are not perfectly in contact with the walls (Persson, 2001; Okada et al., 2008). This might result in small percolation channels allowing gas flow between the cool room and environment (Bottiglione et al., 2009,2016; Zhang et al., 2017).

The importance of leakage modelling and its dependence on seal material properties such as surface roughness in cool rooms has been identified (Nahor et al., 2005). Recently, we have shown that obtaining accurate estimates of RQ at low O₂ partial pressures is difficult when the rate of leakage of respiratory gasses reaches the same order of magnitude as the respiration rate of the stored fruit (Bessemans et al., 2016). This leads to biased RQ calculations, while too high leakage rates make it also impossible to reach the desired low O₂ concentrations.

In this work, a leakage model of postharvest storage facilities was developed to compensate in real-time for leakiness in estimates of RQ of fruit under dynamic controlled atmosphere conditions. The method was validated using an empty storage container experiment. The model was implemented in an automated RQ-DCA control system and successfully used in an experiment to compare estimates of RQ with and without leakage correction simultaneously for a batch of ‘Braeburn’ apple fruit (*Malus ×domestica*, ‘Braeburn’ 2x).

2 Materials and Methods

2.1 Storage container

Experiments in this work were conducted in a storage container which was placed in a cool room at 1 °C. The container (0.715 m × 0.515 m × 0.965 m) was made of rigid polypropylene (thickness 1 cm) and consisted of a bottom and top lid with an airlock for gastight sealing. It was connected to an in-house built measuring unit that contained a closed measurement circuit with a pump for continuously circulating the storage atmosphere to a measurement chamber and back to the storage container. The measurement chamber contained a galvanic cell type O₂ sensor (Figaro KE50, Figaro USA), a non-dispersive infrared (NDIR) type CO₂ sensor (GE Telaire T6615-50KF 50000 ppm, TELAIRE, USA) and a digital pressure sensor (MEAS MS5611-01BA03, MEAS, Switzerland). Oxygen and CO₂ sensors were calibrated using two different gas mixtures (Air Products N.V., Belgium) of 0 kPa O₂ and 0 kPa CO₂ and 5 kPa O₂ and 5 kPa CO₂. A photograph and schematic representation of the air lock and the storage container used in the work are shown in Fig. 1.

2.2. Cool room model

The RQ-DCA system in the storage container relies on a generic model of a cool room. It is assumed here that the gas mixture inside the container (volume V) consists only of O₂, CO₂ and N₂ gas with gas partial pressures p_{O_2} , p_{CO_2} and p_{N_2} , respectively. The effect of other gas components on the gas mixture composition is assumed to be negligible. Water vapor is excluded, since it follows from psychrometrics chart that the water vapor partial pressure, in any case, is lower than 0.6 kPa at 1 °C (Talbot and Baird, 1991). The temperature in the container is assumed to be uniform and constant, and the environment is at ambient conditions, with atmospheric O₂, CO₂ and N₂ gas partial pressures given by $p_{O_2,a}$, $p_{CO_2,a}$ and $p_{N_2,a}$.

118 The total atmospheric air pressure is equal to P_a . Changes in gas conditions inside the cool
 119 room are mainly caused by fruit respiration. However, while the wall panels of the cool room
 120 may be assumed to be perfectly gastight, small imperfections in seals and seams of the room
 121 may allow gas flows between the cool room and the environment. Gas flows of O_2 , CO_2 and
 122 N_2 gas are given by q_{O_2} , q_{CO_2} and q_{N_2} , respectively. The rate of change of the number of moles
 123 of the relevant gasses in the cool room is then given by:

$$\begin{aligned}
 \frac{dn_{O_2}}{dt} &= -r_{O_2}(p_{O_2}, p_{CO_2})m + q_{O_2} \\
 \frac{dn_{CO_2}}{dt} &= r_{CO_2}(p_{O_2}, p_{CO_2})m + q_{CO_2} \\
 \frac{dn_{N_2}}{dt} &= q_{N_2}
 \end{aligned} \tag{1}$$

125 with n_i the number of moles of gas component i in the cool room, $\frac{d}{dt}$ the time derivative [s^{-1}],
 126 r_{O_2} the rate of O_2 consumption by the fruit [$mol\ kg^{-1}\ s^{-1}$], and r_{CO_2} the rate of CO_2 production
 127 by the fruit [$mol\ kg^{-1}\ s^{-1}$], that are both dependent on p_{O_2} the partial pressure of O_2 gas in the
 128 cool room [Pa], and p_{CO_2} the partial pressure of CO_2 gas inside the cool room, m the mass of
 129 the stored fruit [kg] and q_{O_2} , q_{CO_2} and q_{N_2} the gas flows of O_2 , CO_2 and N_2 due to leakage
 130 [$mol\ s^{-1}$] where the + sign of q indicates gas flow q from the environment to the cool room.

131 The pressure in the cool room can then be calculated using the ideal gas law:

$$P = \sum_i n_i \frac{RT}{V} \tag{2}$$

133 with P the pressure inside the cool room [Pa], R the universal gas constant [$J\ mol^{-1}\ K^{-1}$], T the
 134 temperature of the air in the cool room [K] and V the free volume of the facility [m^3].

135 The gas fraction of each of the gasses in the cool room and atmosphere is defined as:

$$136 \quad x_i = \frac{p_i}{P}, x_{i,a} = \frac{p_{i,a}}{P_a} \quad (3)$$

137 with x_i the gas fraction of gas component i in the cool room, $x_{i,a}$ the gas fraction of gas
 138 component i in the ambient atmosphere and p_i the partial pressure of component i in the cool
 139 room.

140 **2.3. Leakage model**

141 A leakage model describes the pressure and concentration driven gas transport between cool
 142 room and environment based on mass balances for each of the relevant gasses in the cool room.
 143 The total rate of change of the number of moles of the relevant gasses in the cool room by
 144 leakage is given by:

$$145 \quad \begin{aligned} q_{O_2} &= -k(P - P_a)x_{O_2}^* - \frac{D_{O_2}A}{\delta} \left(\frac{p_{O_2}}{RT} - \frac{p_{O_2,a}}{RT} \right) \\ q_{CO_2} &= -k(P - P_a)x_{CO_2}^* - \frac{D_{CO_2}A}{\delta} \left(\frac{p_{CO_2}}{RT} - \frac{p_{CO_2,a}}{RT} \right) \\ q_{N_2} &= -k(P - P_a)x_{N_2}^* - \frac{D_{N_2}A}{\delta} \left(\frac{p_{N_2}}{RT} - \frac{p_{N_2,a}}{RT} \right) \end{aligned} \quad (4)$$

146 In eq. (4), k represents the leakage constant of the cool room [$\text{mol s}^{-1} \text{Pa}^{-1}$], D_i the diffusivity
 147 of gas component i in air at atmospheric pressure at 274.15 K [$\text{m}^2 \text{s}^{-1}$], A the area of the
 148 leakage of the cool room [m^2], and δ the wall thickness of the cool room [m]. The molar gas
 149 fraction x_i^* is equal to

$$150 \quad x_i^* = x_i H(P - P_a) + x_{i,a} H(P_a - P), \quad (5)$$

151 in which the Heaviside step function H is defined as

$$152 \quad \begin{aligned} H(z) &= 0 \quad z < 0 \\ &= 1 \quad z \geq 0 \end{aligned} \quad (6)$$

153 The first term in the right-hand side of eq. (4) represents pressure driven leakage while the
154 second term represents concentration driven leakage. If the diffusion driven terms can be
155 neglected, eq. (4) can be simplified to:

$$156 \quad \begin{aligned} q_{O_2} &= -k(P - P_a)x_{O_2}^* \\ q_{CO_2} &= -k(P - P_a)x_{CO_2}^* \\ q_{N_2} &= -k(P - P_a)x_{N_2}^* \end{aligned} \quad (7)$$

157 Summation of the equations of eq. (1), using the ideal gas law and assuming that the
158 temperature and the free volume in the cool room are constant, leads to:

$$159 \quad \frac{V}{RT} \frac{dP}{dt} = -r_{O_2}m + q_{O_2} + r_{CO_2}m + q_{CO_2} + q_{N_2} \quad (8)$$

160 Combining eq. (7) with eq. (8) we obtain:

$$161 \quad \frac{V}{RT} \frac{dP}{dt} - m(r_{CO_2} - r_{O_2}) = -k(P - P_a) \quad (9)$$

162 Substitution of eq. (9) in eq. (7) yields the following expression for the leakage gas flows:

$$163 \quad \begin{aligned} q_{O_2} &= \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2})m \right) x_{O_2}^* \\ q_{CO_2} &= \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2})m \right) x_{CO_2}^* \\ q_{N_2} &= \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2})m \right) x_{N_2}^* \end{aligned} \quad (10)$$

164 with

$$x_i^* = x_i H\left(\frac{dP}{dt}\right) + x_{i,a} H\left(-\frac{dP}{dt}\right). \quad (11)$$

Finally, filling in the expressions (10) for the gas flows of O₂, CO₂ and N₂ in eq. (1) yields:

$$\begin{aligned} \frac{dn_{O_2}}{dt} &= -r_{O_2} m + \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2}) m \right) x_{O_2}^* \\ \frac{dn_{CO_2}}{dt} &= r_{CO_2} m + \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2}) m \right) x_{CO_2}^* \\ \frac{dn_{N_2}}{dt} &= \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2}) m \right) x_{N_2}^* \end{aligned} \quad (12)$$

Equation (12) allows one to calculate the changes of number of moles of the relevant gasses in the cool room due to leakage when the rate of change of internal system pressure and respiration rates of the fruit are known. When no fruit is present in the cool room, the change in the number of moles of the relevant gasses is only determined by the leakage of gas, so eq. (12) simplifies to:

$$\begin{aligned} \frac{dn_{O_2}}{dt} &= \frac{V}{RT} \frac{dP}{dt} x_{O_2}^* \\ \frac{dn_{CO_2}}{dt} &= \frac{V}{RT} \frac{dP}{dt} x_{CO_2}^* \\ \frac{dn_{N_2}}{dt} &= \frac{V}{RT} \frac{dP}{dt} x_{N_2}^* \end{aligned} \quad (13)$$

2.4 RQ model

The respiratory quotient (*RQ*) is defined as the ratio of the CO₂ production rate to the O₂ consumption rate. It can be estimated by dividing the change of the CO₂ concentration by that of the O₂ concentration in the cool room during a certain time interval.

Because the ambient CO₂ and O₂ partial pressure are typically smaller and larger than that of the cool room, respectively, leakage causes the RQ to be overestimated and may even become

180 negative. Its estimate can be corrected for the measured changes in respiratory gasses which
 181 are not due to respiration, but due to leakiness of the cool room. We start by rearranging the
 182 last equation of eq. (12), which describes the rate of change of moles of N₂ gas in the room and
 183 contains only information about the leakage:

$$\begin{aligned}
 \frac{dn_{O_2}}{dt} &= -r_{O_2}m + \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2})m \right) x_{O_2}^* \\
 \frac{dn_{CO_2}}{dt} &= r_{CO_2}m + \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2})m \right) x_{CO_2}^* \\
 \frac{1}{x_{N_2}^*} \frac{dn_{N_2}}{dt} &= \left(\frac{V}{RT} \frac{dP}{dt} - (r_{CO_2} - r_{O_2})m \right)
 \end{aligned}
 \tag{14}$$

185 Substitution of the last equation of eq. 14 into the first two equations and using the ideal gas
 186 law leads to:

$$\begin{aligned}
 \frac{V}{RT} \frac{d(x_{O_2}P)}{dt} &= -r_{O_2}m + \left(\frac{V}{RTx_{N_2}^*} \frac{d(x_{N_2}P)}{dt} \right) x_{O_2}^* \\
 \frac{V}{RT} \frac{d(x_{CO_2}P)}{dt} &= r_{CO_2}m + \left(\frac{V}{RTx_{N_2}^*} \frac{d(x_{N_2}P)}{dt} \right) x_{CO_2}^*
 \end{aligned}
 \tag{15}$$

188 Rearrangement to make r_{O_2} and r_{CO_2} subject of the equation yields:

$$\begin{aligned}
 r_{O_2} &= \frac{1}{m} \left(\frac{V}{RTx_{N_2}^*} \frac{d(x_{N_2}P)}{dt} \right) x_{O_2}^* - \frac{V}{RTm} \frac{d(x_{O_2}P)}{dt} \\
 r_{CO_2} &= \frac{V}{RTm} \frac{d(x_{CO_2}P)}{dt} - \frac{1}{m} \left(\frac{V}{RTx_{N_2}^*} \frac{d(x_{N_2}P)}{dt} \right) x_{CO_2}^*
 \end{aligned}
 \tag{16}$$

190 Finally, combining equation eq. (16) and the definition of RQ results in

$$RQ = \frac{r_{CO_2}}{r_{O_2}} = \frac{\frac{d}{dt}(x_{CO_2}P) - \left(\frac{1}{x_{N_2}^*} \frac{d}{dt}(x_{N_2}P) \right) x_{CO_2}^*}{\left(\frac{1}{x_{N_2}^*} \frac{d}{dt}(x_{N_2}P) \right) x_{O_2}^* - \frac{d}{dt}(x_{O_2}P)} \quad (17)$$

Equation (17) is an expression for the instantaneous $RQ(t)$ at a certain time point t and, therefore, is written as a function of the time derivatives describing the instantaneous changes of the partial pressure of O_2 , CO_2 , and N_2 gas in the cool room and total internal pressure. The derivatives in Eq. (17) were calculated by according to a Savitzky-Golay scheme of order 1. In practice, one is often interested in the mean value $\overline{RQ}$ of $RQ(t)$ over a certain time period

$$\Delta t = t_f - t_0:$$

$$\overline{RQ} = \frac{1}{\Delta t} \int_{t_0}^{t_f} RQ(t) dt \quad (18)$$

Finally, estimates of the mean RQ of the fruit without leakage correction $\overline{RQ_0}$ can be obtained from

$$\overline{RQ_0} = \frac{1}{\Delta t} \int_{t_0}^{t_f} RQ_0(t) dt = -\frac{1}{\Delta t} \int_{t_0}^{t_f} \frac{d}{dt} x_{CO_2} \left(\frac{d}{dt} x_{O_2} \right)^{-1} dt \quad (19)$$

The integrals in eqn. (18) and (19) were calculated using the trapezoidal rule.

2.5 Sensitivity analysis

2.5.1 Pressure changes as the main leakage mechanism

To investigate the relevance of the diffusion and pressure driven leakage terms, the model given by equations (1) and (4) was fitted to experimental data obtained from an empty storage container, thus for $r_{O_2} = r_{CO_2} = 0$. Internal pressure as well as atmospheric air pressure were

measured along with gas fractions of O₂ and CO₂ inside the storage container for a time period of 2 h during an increase in atmospheric air pressure. The measured internal container pressure and atmospheric air pressure were used as model inputs. Equation (1) was solved numerically using Matlab R2015b solver ode45 (The Mathworks, Inc., Natick, USA) and the solution was fit to measured gas fractions of O₂ and CO₂ to obtain values for k and A . D_{O_2} and D_{CO_2} were set to $1.6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and $1.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively (Datta, 2002). First, the model containing both concentration and pressure driven leakage terms (eq. (1) and eq. (4)) was fitted to the data. Secondly, a simplified model containing only pressure driven leakage (eq. (1) and eq. (7)) was fit. The relevance of the contributions of the concentration and pressure driven leakage terms to the leakage gas flow was evaluated by statistically testing the goodness of fit of both the full and the simplified model.

2.5.2 *Effect of leak correction on RQ estimate*

To test the effect of leak correction we first fitted a non-competitive inhibition Michaelis-Menten model to respiration data of ‘Braeburn’ apple. We then used this model to simulate virtual storage experiments for different values of RQ and used these data to estimate the RQ using the algorithm outlined above with and without leakage correction.

Fruit (78) were harvested in the orchard of the Experimental Centre of Fruit Growing (pcfruit, Velm, Belgium) in 2007 at the commercial picking date determined by the Flanders Centre of Postharvest Technology (Stage 5 to 6 on the Ctifl starch conversion chart (Ctifl, Paris, France)). Subsequently, fruit were cooled and stored for a period of 21 d at 1 °C preceding CA storage (3 % O₂, 0.7 % CO₂ at 1 °C) until they were used for the experiments. Respiration rate measurements of fruit were conducted using 1.7 L jars as described before (Ho et al., 2013). A full factorial experiment was conducted at 0, 1, 3, 5, 10 and 20 kPa O₂ in combination with 0 kPa CO₂ and a temperature of 5, 10 and 20 °C. The inhibition effect of CO₂ on the respiration

rate was determined at 5, 10 and 20 °C in combination with 10 kPa CO₂. A non-competitive inhibition model as given by Ho et al. (2013) was used to describe the O₂ consumption rate:

$$r_{O_2} = \frac{V_{m,O_2} p_{O_2}}{(K_{m,O_2} + p_{O_2}) \cdot \left(1 + \frac{p_{CO_2}}{K_{mn,CO_2}}\right)} \quad (20)$$

with V_{m,O_2} the maximal O₂ consumption rate [mol m⁻³ s⁻¹], p_{O_2} the O₂ partial pressure [kPa], p_{CO_2} the CO₂ partial pressure [kPa], K_{m,O_2} the Michaelis-Menten constant for O₂ consumption [kPa] and K_{mn,CO_2} the Michaelis-Menten constant of non-competitive CO₂ inhibition of the O₂ consumption rate.

The equation of the CO₂ production rate consists of an oxidative respiration and a fermentation part (Peppelenbos et al., 1996):

$$r_{CO_2} = -RQ_{ox} r_{O_2} \frac{V_{m,f,CO_2}}{\left(1 + \frac{p_{O_2}}{K_{m,f,O_2}}\right)} \quad (21)$$

with RQ_{ox} the RQ at high O₂ partial pressure [-], r_{O_2} the rate of O₂ consumption [mol m⁻³ s⁻¹], V_{m,f,CO_2} the maximal fermentative CO₂ production rate, and K_{m,f,O_2} the Michaelis-Menten constant of O₂ inhibition on fermentative CO₂ production. The temperature effect was described using Arrhenius' law (Hertog et al., 1998). Respiration model parameters were estimated by fitting equations (20) and (21) to the experimental data using a nonlinear least squares regression in Matlab R2015b.

Virtual storage experiments were simulated using eqn. (20) and (21) with RQ values of 1, 1.5, 2 and 2.5. The corresponding O₂ levels were equal to 10.5 %, 3.5 %, 2.3 % and 1.73 %, 2.3 % and 1.73 %.

respectively, and used as initial levels for simulations of storage experiment that lasted 4 h. The initial CO₂ level was set to 2.5 % for all RQ-values. The pressure was assumed to monotonously vary from 101.3 kPa to a range of final positive and negative final pressures relative to the initial pressure. The simulation lasted 4 h and the fruit to cool room volume ratio was 0.16 m³ m⁻³. The temperature was assumed to be 274.15 K. Respiration model parameters that were used are listed in Table 1. The estimation of RQ was based on the initial and final point only because the simulation data were essentially noise free.

2.6 Model validation and real-time application

The simplified leakage model given by eq. (13) was validated using an empty storage container as described in section 2.1. CA conditions were set to typical RQ-DCA conditions of 0.45 kPa O₂ and 1.30 kPa CO₂. Subsequently, CA and temperature control were disabled for a time period of 2 h during which O₂, CO₂ and the total internal pressure P were monitored. N₂ was assumed to be the remaining gas fraction. Measurements were conducted during 2 h of decreasing as well as 2 h of increasing atmospheric air pressure. Equation (13) was used to predict changes in gas partial pressures using measured internal pressure as input. Subsequently, predicted changes in gas composition were compared to measured changes in gas partial pressure.

To compare real-time estimates of RQ with (eq. 18) and without leakage correction (eq. 19), the storage container was loaded with 4 European Packing Standard (EPS) boxes each loaded with 19 ± 0.5 kg of ‘Braeburn’ apple fruit (*Malus × domestica* Borkh. ‘Braeburn’ 2x). Apples were harvested at 01 Oct., 2014, south of Toulouse (France). Unsorted apples were chilled and transported by refrigerated truck to the lab where they arrived on 03 Oct., 2014, having a temperature of 6 °C. Experiments were conducted at 1 °C.

Control of O₂ was conducted according to the RQ-DCA control algorithm discussed previously (Bessemans et al., 2016) using RQ estimates with leakage correction. In brief, the O₂ partial pressure in the storage container was decreased by 0.05 kPa if RQ was smaller than 2. When RQ was larger than 2, the O₂ partial pressure was increased with 0.1 kPa. However, for the control system to take action, the measured RQ had to be valid (Bessemans et al., 2016). If this was not the case, the O₂ setpoint was not adapted. RQ values with leakage disturbance correction were used for O₂ control. Simultaneously with RQ estimates with leakage disturbance correction, RQ estimates without leakage correction were recorded for comparison.

3 Results

3.1 Relevance of concentration and pressure driven leakage terms

Fitting the full leakage model (eq. 4) resulted in an estimated k -value equal to $1.52 \times 10^{-4} \text{ mol s}^{-1} \text{ Pa}^{-1}$. The leakage area A was found to be equal to $6.86 \times 10^{-12} \text{ m}^2$. A strong correlation of 0.999 between the estimated k and A – values was found, indicating that adding the concentration driven term containing A might be unnecessary. Indeed, when using the estimated k and A – values to calculate the pressure and concentration driven gas flows of O₂ and CO₂, the instantaneous pressure driven gas flow was found to be several orders of magnitudes greater than the concentration driven gas flow, $10^{-7} \text{ mol s}^{-1}$ and $10^{-10} \text{ mol s}^{-1}$ for O₂, respectively, and $10^{-6} \text{ mol s}^{-1}$ and $10^{-11} \text{ mol s}^{-1}$ for CO₂, respectively. Also after fitting the simplified leakage model containing only the pressure driven leakage term (eq. 7), a k -value of $1.52 \times 10^{-4} \text{ mol s}^{-1} \text{ Pa}^{-1}$ was obtained. SSE-values and degrees of freedom of fitting both leakage models (3.091×10^{-6} and 237 and 3.090×10^{-6} and 236 respectively), were used to conduct a general statistical test for linear models (Neter *et al.*, 1996). The two-sided F-test delivered an F^* -value of -7.64×10^{-2} , indicating that the simplified model fitted the data equally well as the full model ($\alpha = 0.025$).

297 3.2 Error analysis of RQ estimate

298 Fig. 2 (a) and Fig. 2 (b) show the O₂ and CO₂ consumption and production rate (R_{O_2} and R_{CO_2}
299), respectively, of ‘Braeburn’ apple. Only a small inhibition effect of CO₂ on the respiration
300 rate was observed at all temperatures. The model fits the data well for the investigated
301 temperatures although a rather high variability between measurements of different apples at
302 nearly the same conditions was observed. Values of the Michaelis-Menten constants for O₂
303 consumption (K_{m,O_2}), non-competitive CO₂ inhibition of the O₂ consumption rate (K_{mn,CO_2})
304 and O₂ inhibition on fermentative CO₂ production (K_{m,f,O_2}) were very similar for all
305 temperatures. In contrast, the maximal O₂ consumption rate (V_{m,O_2}) and maximal fermentative
306 CO₂ production rate (V_{m,f,CO_2}) were found to be highly temperature dependent. High values
307 were found at 20 °C while considerably lower values were found at 10 °C and 5 °C. Table 1
308 gives an overview of the estimated model parameters at 1 °C that were used for the virtual
309 experiment.

310 Fig. 3 illustrates the calculated RQ values with (eq. 18) and without leakage correction (eq. 19)
311 based on simulated storage experiments for different internal pressure changes. Fig. 3 (a) shows
312 the result of the analysis for a real RQ value of the stored fruit equal to 1. As indicated by the
313 red line, estimates of RQ without leakage correction method deviated significantly from the
314 real RQ value when the simulated change in internal pressure deviated from 0. The larger the
315 pressure change, the larger the deviation between RQ estimation without leakage correction and
316 the real value of RQ became. During decreasing internal pressure, when leakage occurred from
317 the inside to the environment, deviations between RQ estimation without leakage correction
318 and the real RQ of the stored fruit were smaller compared to the deviations during increasing
319 pressure, when leakage occurred from the environment to the inside. On the other hand, Fig. 3

(a) shows that the RQ estimates with pressure based leakage correction were exactly equal to the real RQ of the stored fruit independently of the measured change in internal pressure. From Fig. 3 (b) to (d), for fruit with increasing RQ, it is clear that the estimation of RQ without leakage correction deviates more and more from the real value of the RQ of the stored fruit, when the real RQ of the fruit increases. In contrast, estimates of the RQ of the stored fruit with pressure based leakage correction are much more stable and useful to estimate the real RQ of the fruit accurately.

3.3 Validation and real-time application of the developed leakage correction

Fig. 4 illustrates the results of the validation experiment using an empty storage container. It shows the measured pressure in the empty storage container (dark green line) and measured atmospheric air pressure (light green line) as a function of time for a time period of 2 h as well as the measured and predicted O₂ and CO₂ partial pressures using the developed leakage correction model during an increase of internal pressure (Fig. 4 a) and during a decrease of internal pressure (Fig. 4 b) at a typical DCA condition of approximately 0.5 kPa O₂ and 1.5 kPa CO₂. Fig. 4 a clearly indicates that the pressure inside the cool room increased when the atmospheric air pressure increased. The internal container pressure increased from 1006.19 hPa to 1009.28 hPa in response to an increase in atmospheric pressure from 1006.7 hPa to 1009.22 hPa in a time period of 2 h. Since the storage container used in the validation experiment contained no fruit, the O₂ partial pressure increased as a function of time from an initial value of 430 Pa to a final value of 490 Pa during the experiment due to an influx of atmospheric air from the environment into the cool room, as shown by the light blue line in Fig. 4 a. The dark blue line shows the predicted O₂ partial pressure in the storage container as a function of time using the developed leakage correction method. The predicted and measured O₂ partial

pressures differed only from each other within the range of the resolution of the sensor used (10 Pa). The CO₂ partial pressure remained constant at 1330 Pa during the time period of 2 h as indicated in Fig. 4 a by the light red line. The dark red line shows the predicted CO₂ partial pressure using the developed leakage model. Here also, the predicted and measured CO₂ partial pressures differed only from each other within the range of the resolution of the sensor used.

In Fig. 4 b, as atmospheric pressure decreased, the pressure inside the storage container decreased from an initial value of 1022.18 hPa to a final value of 1021.50 hPa as a response to a decrease in atmospheric air pressure from 1022.20 hPa to 1021.54 hPa during a time period of 2 h (Fig. 4 b). The O₂ partial pressure in the storage container decreased from a partial pressure of 460 Pa to 450 Pa during the time period of 2 h. The CO₂ partial pressure decreased from a partial pressure of 1010 Pa to 1000 Pa during the time period of 4 h. Also during decreasing pressure the measured and predicted gas composition differed only within the range of the resolution of the sensors

The excellent correlation between measured and predicted O₂ and CO₂ partial pressures in the validation experiment, indicates that the developed leakage model performed well. When comparing the measured changes in O₂ and CO₂ partial pressures during the 2 h of increasing atmospheric pressure, one can see that the change of the O₂ partial pressure was significantly higher compared to that of the CO₂ partial pressure.

Fig. 5 illustrates the real-time application of the leakage correction model to obtain RQ estimates during a time period of 4 d in the storage container loaded with ‘Braeburn’ apple fruit. Fig. 5 a depicts the evolution of internal pressure in the storage container filled with apple fruit as a function of time during a period of 4 d, while b shows the corresponding O₂ setpoint and measured O₂ partial pressure and c the measured RQ values. When the internal pressure remained constant or decreased, the RQ estimates with and without leakage correction were

almost equal, as illustrated by the first four RQ measurements in Fig. 5 c. Subsequently, when atmospheric air pressure increased, the estimated RQ without leakage correction suddenly deviated from the RQ estimate with leakage correction. Depending on the rate of pressure change, the RQ without leakage correction was now negative or larger than the RQ with leakage correction. This is illustrated by the 5th to 7nd RQ measurement, respectively, in Fig. 5 c. Furthermore, one can see that application of the developed leakage correction, delivered RQ estimates during increasing internal pressure with the same RQ value as the RQ value obtained during the previous RQ measurement period while internal air pressure was decreasing as shown in Fig. 5 c by the 7nd and 8th RQ measurement. This confirms that the developed leakage correction is reliable and yields accurate RQ estimates during both decreasing and increasing atmospheric air pressures. At later time points shown in Fig. 5 c, some outlying RQ estimates can be observed. This is not related to the leakage correction methodology itself, but to the limited accuracy of the sensors used and the occurrence of irregularities such as imperfect mixing after control action. The control system was programmed to recognize these invalid RQ values and to neglect them for O₂ control as shown in Fig. 5 b.

Fig. 5 b shows the result of the RQ-DCA control of the O₂ partial pressure in the storage container based on the obtained RQ estimates with leakage correction. Since during the first six RQ-measurements in Fig. 5 b, RQ estimates were below the threshold value of 2, the O₂ partial pressure decreased with 0.05 kPa after each measurement. This led to a gradual increase of the RQ until low O₂ stress was detected by RQ estimates greater than 2 by the 7th and the 8th RQ estimation. The O₂ partial pressure was subsequently increased with 0.1 kPa until the estimated RQ dropped again below 2, indicating relief of low O₂ stress. This process was continuously repeated for a time period of 4 d.

4 Discussion

4.1 *Leakage is a pressure driven process*

Statistical analysis using a general linear test approach (Neter et al., 1996) demonstrated that the diffusion term in the leakage model was negligible compared to the pressure term. This is in line with the approaches used by Bottiglione et al. (2009; 2016) and Zhang et al. (2017). Bottiglione et al. (2016) considered the leakage flow of a fluid through a viscoelastic seal and a hard randomly rough substrate as a laminar flow in a rectangular percolation channel which is pressure driven. They assumed the leakage flow to be proportional to the pressure difference over the seal. Zhang et al. (2017) modelled the leakage flow of lube oil through a metal seal by a computational fluid dynamics (CFD) model using pressure driven laminar flow. The dominance of the pressure driven leakage term over the concentration driven leakage term is plausible by considering the physical nature of concentration and pressure driven processes. As directly shown by Fick's law of diffusion, the rate at which a gas diffuses is proportional to the area of the surface over which the diffusion process takes place and the concentration gradient. The proportionality constant is given by Fick's diffusion coefficient, which is derived from the Maxwell-Stefan diffusion coefficient of gas diffusion in multicomponent mixtures taking into account side effects on diffusion (Bird et al., 2002). Leakage areas found in typical postharvest storage facilities are extremely small. The sandwich panels of which the walls of storage facilities in Belgium are typically constructed can be assumed to be perfectly gastight. However, small leaks may occur in the seams of the rooms or in the sealing of the entrance door by non-perfect contact between the seals and the surfaces to be sealed due to surface roughness of the materials used. According to modern recommendations of gas tightness, leakage areas smaller than $2 \times 10^{-5} \text{ m}^2$ per m^3 storage volume and preferably smaller than $1.5 \times 10^{-5} \text{ m}^2 \text{ m}^{-3}$ are advised (Veltman, 2013). The second parameter determining the rate of diffusion of respiratory gasses in and out of the cool room are the Fick diffusivities for O_2 and CO_2 in air at atmospheric pressure. These diffusivities are typically in the order of magnitude

417 of $10^{-5} \text{ m}^2 \text{ s}^{-1}$. From eq. 4, it follows that the time constant of the diffusion process τ_{diff} (s) is

418 $\tau_{diff} = \frac{\delta}{DA}$. Filling in the diffusivities of O_2 or CO_2 along with the values for A and δ

419 delivers a value of $7.14 \times 10^{13} \text{ s}$. This is a very large value, indicating that the diffusion process

420 is very slow.

421 Pressure differences between the cool room and environment due to changes in atmospheric

422 air pressure create a momentum source, leading to movement of a bulk flow of gas between

423 cool room and environment at a much higher rate. As shown by eq. 7, the rate at which gas

424 exchange between cool room and environment occurs is proportional to the pressure difference,

425 with the k -value [$\text{mol s}^{-1} \text{ Pa}^{-1}$] as a proportionality constant. The time constant of the diffusion

426 process τ_{pres} (s) is given by $\tau_{pres} = \frac{V}{kRT}$. Filling in the volume of the storage container used

427 (0.4 m^3) along with the estimated k -value, gas constant and temperature, yields a value of 1.17

428 s. The time constant of the pressure driven leakage was found to be 13 orders of magnitude

429 smaller, indicating the pressure driven leakage is much faster. Although the results in this work

430 were obtained based on data of small lab-scale storage container, it is realistic to assume that

431 the results hold for large scale commercial rooms. Based on recalculation of the advised air-

432 tightness standards for commercial rooms as formulated in Veltman et al. 2013, the storage

433 container used in this work would have a leakage area A of $6 \times 10^{-6} \text{ m}^2$, leading to a value for

434 τ_{diff} of $1.04 \times 10^8 \text{ s}$ which is still 8 orders of magnitude higher than the value for τ_{pres} of the

435 storage container. Moreover, the increased leakage area implies an increase of leakage channels

436 through which pressure driven gas transport occurs, resulting in a lower value of k and τ_{pres} .

437 As a result, the leakage of the container with commercial standard air tightness would still be

438 a pressure driven process. Finally, assuming the storage space has a cubic shape with side z , it

can be shown that the ratio of the joins of the room L and the storage volume V_{stor} is given by $L/V_{stor} = 12/z^2$. This implies that if the storage volume of the container/room increases (z increases), the ratio L/V_{stor} decreases. As a consequence, for a same degree of filling with stored produce, the effect of leakage on measured changes in gas composition will be smaller for a larger room compared to a smaller room. Therefore, leakage of postharvest storage facilities may be considered to be a pressure driven process.

4.2 Leakage correction improves estimate of RQ

Large errors occur in RQ estimation when leakage of the cool room is not taken into account. Also, the errors were shown to increase with increasing RQ. The large errors found offer a plausible explanation for the highly pressure dependent RQ estimates discussed in our previous work (Bessemans et al., 2016). Also, they explain the high variation in RQ measurements reported in other recent research in the field, where the RQ of stored fruit was estimated based on measured changes in gas partial pressure of O_2 and CO_2 over a time period of 24 h and leakage of the cool room was not taken into account (Brackmann, 2015; Weber et al., 2015; Both et al., 2017).

RQ estimates without leakage correction tend to overestimate the real value of the RQ of the stored fruit, leading to false signals of low O_2 stress of the stored fruit. As a consequence, the O_2 partial pressure in the cool room will be increased. This leads to an increased number of control actions (increased usage of O_2 and N_2 gas) and, therefore, increases the variable cost of RQ-DCA storage. Also, the energy efficiency of RQ-DCA storage will be reduced, since a higher O_2 partial pressure in the cool room increase respiration and thus heat production. Lastly, storing the fruit at a higher O_2 partial pressure might cause suboptimal quality preservation during storage.

4.3 Error on RQ estimate is larger during increasing than decreasing atmospheric pressure

When the atmospheric air pressure increases in time, the cool room is at a small underpressure relative to its environment. Ambient air then flows inside the cool room and may change the internal gas composition significantly. As observed, the effect of the inflow of gas with atmospheric composition into the storage container had a different effect on the O₂ and CO₂ partial pressure. The difference in partial pressure between the inside of the storage container and the environment is much larger for O₂ than for CO₂. Therefore, the effect of inflow of atmospheric air into the storage container has a larger effect on the change in O₂ partial pressure compared to the change in CO₂ partial pressure. Due to the inflow of O₂ rich atmospheric air, the composition of the internal gas mixture will be altered significantly. As a result, large errors will be introduced in RQ estimates.

On the contrary, during decreasing atmospheric air pressure, the cool room is at a small overpressure relative to its environment. Therefore, the gas mixture inside the cool room flows to the outside, and the ambient air cannot affect the composition of the internal gas mixture. As a result, the effect of leakage from the storage environment to the outside on RQ estimates is much smaller than if the leakage occurs in the opposite direction.

Note that eq. 17 describing RQ estimates with leak correction is temperature independent and therefore applicable to storage spaces with and without constant temperature. This is important, because in commercial rooms often temperature is not controlled in a continuous manner, but a differential temperature range is used for controlling the refrigeration system leading to temporal temperature oscillations which are not a problem as such. Yet care is needed when engineering solutions are added to the storage space such as expansion bags which mitigate pressure changes due to temperature oscillations as well as changes in atmospheric air pressure.

To adjust the leak correction method for the effect of pressure mitigation by expansion bags, the leak model needs to be extended with a mathematical model describing the expansion bag using temperature measurement as a model input. This should be part of future research. Alternatively, as an engineering solution to this problem, the storage space may be sealed from the expansion bag using an actively controlled valve during the RQ measurement.

5 Conclusion

A novel method was developed to correct real-time estimates of the respiratory quotient (RQ) of postharvest produce, for leakiness of the storage environment. The method is based on a general leakage model of a confined space that was simplified based on a sensitivity analysis of the contribution of the pressure and concentration driven gas transport terms. The analysis showed that pressure driven leakage was dominant over diffusive leakage. The methodology was validated successfully using an empty storage container at 0.4 kPa O₂ and 1.3 kPa CO₂. The excellent fit between the simulated and measured gas composition indicates that the developed leakage model performed well. A sensitivity analysis using a respiration model of ‘Braeburn’ apple fruit showed that the error of the RQ estimates with leak correction was 0 %, while without leak correction the error increased to above 700 %. Finally, the leakage correction methodology was implemented in an automated RQ-DCA control system using ‘Braeburn’ apple fruit and real-time RQ estimates with and without leakage correction were compared. The effect of leakage from the environment to the storage room on internal gas composition and RQ estimate was much larger than the effect of leakage from the storage environment outside. RQ estimates without leakage correction were heavily biased when leakage of atmospheric air into the storage container occurred and would lead to erroneous control of the storage atmosphere composition. With the developed leakage correction, RQ

509 measurements were found to be accurate during decreasing as well as increasing atmospheric
510 air pressure.

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6 Tables

Table 1: Model parameters of ‘Braeburn’ intact apple fruit respiration model at 274.15 K; the error interval indicates the standard error of the estimated parameter value.

<i>Model</i>	<i>Value</i>	<i>Units</i>
<i>parameter</i>		
V_{m,O_2}	$4.78 \times 10^{-5} \pm$	$\text{mol m}^{-3} \text{s}^{-1}$
	0.43	
E_a, V_{mO_2}	69.9 ± 4.8	kJ mol^{-1}
V_{mfCO_2}	$7.11 \times 10^{-5} \pm$	kPa
	0.43	
E_a, V_{mfCO_2}	65.9 ± 4.3	kJ mol^{-1}
K_{mO_2}	2.78 ± 0.6	kPa
K_{mnCO_2}	192 ± 199	kPa
K_{mfO_2}	1.23 ± 0.24	kPa
RQ_{ox}	0.80 ± 0.06	[-]

530 **7 Figures**

531

532 Fig. 1: (a) Photograph of the storage container, (b) scheme of the water lock of the storage

533 container (cross section) and (c) schematic representation of the storage container and its

534 environment.

535

536

537 Fig. 2: Fit of the developed respiration model of intact 'Braeburn' apple fruit to the measurement
 538 data. R_{O_2} and R_{CO_2} are the specific O₂ and CO₂ consumption and production rate. Each symbol
 539 denotes a measured value on a separate apple fruit. Symbols (+) and (o) represent measurements
 540 with 0 % CO₂ and 10 % CO₂ respectively, while full lines (-) and dashed lines (--) show the
 541 modelled rates at 0 % CO₂ and 10 % CO₂ respectively.

Fig. 3: Estimated values of the RQ of stored apple fruit as a function of pressure changes inside the room. Positive pressure changes indicate gas flow from the environment to the storage room and vice versa. Pressure based leakage correction represented by the green line (RQ) and without pressure based leakage correction represented by the red line (RQ₀) for different real RQ values of the stored fruit equal to 1.0 (a), 1.5 (b), 2 (c) and 2.5 (d).

Fig. 4: Atmospheric (dark green line) and internal container pressure (light green line), measured (dark blue line) and simulated (light blue line) O₂ partial pressures as well as measured (dark red line) and simulated (light red line) CO₂ partial pressures during a time period of 120 minutes with increasing (a) and decreasing (b) atmospheric air pressure during the validation experiment in an empty storage container.

554

555 Fig. 5: Demonstration of the leakage-corrected RQ measurement and control of 'Braeburn' apple
 556 storage: (a) Measured internal container pressure (green line), (b) measured and setpoint O₂ partial
 557 pressures (light blue and dark blue lines respectively and (c) corresponding RQ estimation with

558 (green triangle) and without (red triangle) leakage correction. Outlying RQ measurements that
559 were not considered for O₂ control are marked with a red circle.

560 *Nomenclature*

561			
562	A	Leakage area of the storage facility	[m ²]
563	D_i	Diffusivity of gas component i in air at atmospheric air	
564		pressure and 274.15 K where i may be O ₂ , CO ₂ and N ₂	[m ² s ⁻¹]
565	δ	Thickness of storage facility wall	[m]
566	Δt	Time interval delta t	[s]
567	$H(z) = \begin{cases} 0 & z < 0 \\ 1 & z \geq 0 \end{cases}$	Heaviside function of z	[-]
568	k	Leakage constant of the storage facility	[mol s ⁻¹ Pa ⁻¹]
569	L	Length of the joins of the storage facility	[m]
570	m	Mass of the stored produce inside the storage facility	[kg]
571	n_i	Number of moles of gas component i inside the storage	
572		facility where i may be O ₂ , CO ₂ and N ₂	[mol]
573	p_i	Partial pressure of gas component i in the storage room	
574		where i may be O ₂ , CO ₂ and N ₂	[Pa]
575	$p_{i,a}$	Partial pressure of gas component i in the atmosphere	

576		where i may be O ₂ , CO ₂ and N ₂	[Pa]
577	P	Total pressure inside the storage facility	[Pa]
578	P_a	Atmospheric air pressure	[Pa]
579	q_i	Flow rate of gas component i due to leakage	
580		where i may be O ₂ , CO ₂ and N ₂	[mol s ⁻¹]
581	r_{O_2}	O ₂ consumption rate by fruit respiration	[mol s ⁻¹ kg ⁻¹]
582	r_{CO_2}	CO ₂ production rate by fruit respiration	[mol s ⁻¹ kg ⁻¹]
583	R	Universal gas constant	[J mol ⁻¹ K ⁻¹]
584	R_{O_2}	Measured O ₂ consumption rate by fruit respiration	[mol s ⁻¹ m ⁻³]
585	R_{CO_2}	Measured CO ₂ production rate by fruit respiration	[mol s ⁻¹ m ⁻³]
586	RQ	Instantaneous value of the respiratory quotient	[-]
587	RQ_0	RQ estimate without leak correction	[-]
588	RQ_{ox}	RQ at aerobic conditions	[-]
589	$\overline{RQ}$	Mean value of the respiratory quotient	[-]
590	T	Temperature	[K]
591	t	Time	[s]
592	t_0	Time of the begin of time interval Δt	[s]
593	t_1	Time of the end of time interval Δt	[s]
594	τ_{diff}	Time constant of the diffusion driven leakage process	[s]

595	τ_{pres}	Time constant of the pressure driven leakage process	[s]
596	V	Free volume inside the storage facility	[m ³]
597	V_{stor}	Total volume of the facility	[m ³]
598	V_{m,O_2}	Maximal O ₂ consumption rate	[mol m ⁻³ s ⁻¹]
599	V_{m,f,CO_2}	Maximal fermentative CO ₂ production rate	[mol m ⁻³ s ⁻¹]
600	K_{m,O_2}	Michaelis-Menten constant for O ₂ consumption	[kPa]
601	K_{mn,CO_2}	Michaelis-Menten constant of non-competitive CO ₂	
602		inhibition of the O ₂ consumption rate	[kPa]
603	K_{m,f,O_2}	Michaelis-Menten constant of O ₂ inhibition on	
604		fermentative CO ₂ production	[kPa]
605	x_i	Gas fraction of component i in the storage room	
606		where i may be O ₂ , CO ₂ and N ₂	[-]
607	$x_{i,a}$	Gas fraction of component i in the atmosphere	
608		where i may be O ₂ , CO ₂ and N ₂	[-]

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