On the rate of adsorption of carbon dioxide by food grains

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Abstract

Carbon dioxide is central to several applications in stored grains postharvest technology. For example, insects that infest stored food grains can be controlled by enriching the intergranular atmosphere with carbon dioxide. A second application relies on the fact that organisms, such as insect pests and fungi, produce carbon dioxide which can be detected and used as an indicator of grain spoilage. If controlled atmospheres and spoilage detection systems are to be optimised it is essential that mathematical models of the sorption of carbon dioxide by grains are developed. This requires the formulation of reliable expressions for the rate at which grain kernels adsorb and desorb carbon dioxide. It is customary to measure the rate of sorption by observing the rate at which the pressure of carbon dioxide decreases in a constant-volume system. Many of the published studies of the rate of sorption have shortcomings. For example, several researchers terminated their experiments before they had attained a steady state, and consequently any extrapolations of their data were problematic. In contrast, a steady state was attained in several published studies, but the data are too exiguous during the important early stages of sorption to enable detailed mathematical models to be formulated. This study quantifies some of the issues concerning experimental methods used to measure the rate of adsorption of carbon dioxide by food grains. It is essential that mathematical models of sorption of carbon dioxide are developed that account for arbitrarily changing conditions. The correlations reported in the literature fail to achieve this. Three mechanistic models of sorption are suggested, and experiments are outlined that will enable them to be validated and further refined.

Key words: Carbon dioxide, sorption, model. empirical, mechanistic, lumped parameter, diffusion

NOMENCLATURE

c	Concentration of carbon dioxide, kg/m^3
C	Mass fraction of adsorbed carbon dioxide, $\mathrm{kg_{CO_2}/kg_{grain}}$
C_e	Mass fraction of adsorbed CO$_2$ in equilibrium with surrounding atmosphere, $\mathrm{kg_{CO_2}/kg_{grain}}$
$C_{e,p}$	Mass fraction of adsorbed CO$_2$ in equilibrium with atmosphere in pores, $\mathrm{kg_{CO_2}/kg_{grain}}$
c_G	Concentration of carbon dioxide, kg/m^3
C_∞	Mass fraction of adsorbed CO$_2$ at the steady state, $\mathrm{kg_{CO_2}/kg_{grain}}$
$\mathcal{D}_{ads}$	Diffusivity of CO$_2$ through grain kernels with mass fraction adsorbed as driving force, m^2/s
$\mathcal{D}_{eff}$	Effective diffusivity of CO$_2$ through grain kernels with gaseous concentration as driving force, m^2/s
k_e	Partition constant relating mass fraction of sorbed CO$_2$ and pressure, $\mathrm{kg_{CO_2}/(kg_{grain}.\,Pa)}$
K_e	Partition constant, $\mathrm{(kg_{CO_2,adsorbed}\ /kg_{grain})\cdot(m^3_{pores}/kg_{CO_2,adsorbed})}$
k_p	Rate constant in lumped parameter model, 1/s
k_{p1}	Parameter in double exponential equation for the pressure of CO$_2$
k_{p2}, k_{p3}	Parameter in double exponential equation for the pressure of CO$_2$, 1/s
$k_{r,p}$	A notional rate constant for adsorption of CO$_2$ from the internal pores of grain kernels, 1/s
m_{CO_2}	Mass of CO$_2$ adsorbed in experiments to measure rate of sorption, kg
m_g	Mass of grain in experiments to measure rate of sorption, kg
M	Moisture content of grains, wet basis, $\mathrm{kg_{H_2O}/kg_{wet\ grain}}$
p	Partial pressure of CO$_2$ in the intergranular atmosphere surrounding grain kernels, Pa
p_0	Partial pressure of CO$_2$ in the intergranular atmosphere when experiments are initiated, Pa
p_∞	Partial pressure of CO$_2$ in the intergranular atmosphere when system is at steady state, Pa
r	Radius of grain kernels, m
R_{CO_2}	Gas constant of carbon dioxide, J/(kg.K)
t	Time, s
T	Temperature, K
V	Volume of gas in the apparatus, m^3

Greek letters

$\propto$	Empirical parameter in Cofie-Agblor et al.'s (1995) model of sorption, 1/s
β	Empirical parameter in Cofie-Agblor et al.'s (1995) model of sorption
γ_1	Empirical parameter in equation for $\propto$, 1/s
γ_2, γ_4	Empirical parameters in equation for $\propto$ and β.
γ_3	Empirical parameter in equation for β, 1/K
ε_p	Void fraction of the pores within a grain kernel
ρ_s	Density of grain kernels, kg/m^3

INTRODUCTION

Stored grains are susceptible to attack by insects, mites, moulds and other biota. Insects can be controlled by fumigation, but species that infest stored grains are becoming resistant to phosphine, a widely used and inexpensive fumigant (Nayak, et al., 2020). Carbon dioxide is an effective alternative to phosphine provided its concentration throughout a grain store exceeds 35% for more than 15 days and the temperature is maintained at a minimum of 20°C

(GRDC, 2017). Constantin et al. (2020) have observed strains of *Cryptolestes ferrugineus* (Stephens) (Laemophloeidae: Coleoptera) that are strongly resistant to phosphine are susceptible to mixtures of carbon dioxide and phosphine. For example, they showed that in an atmosphere comprising 30% CO_2 the LC_{50} and $LC_{99.9}$ of phosphine can be reduced 8-fold and 2.8-fold respectively.

Carbon dioxide, heat and water are liberated when biota such as insects and fungi respire. Importantly, the speed at which carbon dioxide is transported by air currents is about 1000 times that of heat and 100,000 times that of moisture (Thorpe, 2001). As a result, hot spots generated by moulds and insect pests are likely to be detected much more quickly by measuring the concentrations of CO_2 in grain stores rather than by measuring increases in temperature which may be much more localised. This has prompted the idea that increases in carbon dioxide concentrations can be used as an indicator of grain spoilage (Kaushik and Singhai, 2019; Lutz and Coradi, 2022). However, concentrations of CO_2 fluctuate diurnally (Ileleji et al., 2006), and they vary temporally and spatially throughout grain stores. These factors render the interpretation of CO_2 concentrations in grain stores problematic.

Changes in the temporal and spatial distribution of the concentration of CO_2 throughout grain stores are incessant. Some changes are driven by a combination of external forces such as the speed and direction of the wind, ambient temperature and solar radiation. Design factors such as the number and placement of roof vents, leaks in the fabric of the grain store, and entry and egress of air through aeration fans and ducts contribute to variation in CO_2 concentrations. Internal factors such as the temperature and moisture content of the grains, the presence of insects and fungi and the type and integrity of the grains (e.g. the fraction of broken grains) also contribute to the concentration and distribution of CO_2.

A plethora of factors influences the concentration and distribution of carbon dioxide in grain stores. Some factors are external and depend on the weather, others depend on the state of the grain, and other factors result from the design and condition of the fabric of the grain store.

THE IMPORTANCE OF MECHANISTIC MODELS OF SORPTION

The above discussion leads us to an important conclusion, namely: intergranular[1] concentrations of carbon dioxide in grain stores vary stochastically. At any location within a grain store the concentration increases or decreases because of forces external to the silo, and over which grain store managers have no control. It is therefore essential to develop mechanistic models of sorption that are capable of responding to arbitrarily changing conditions.

There is a pressing need to formulate mechanistic models of the sorption of carbon dioxide by food grains

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[1] In this work *intergranular* refers to properties that occur in the pores external to, and between, grain kernels. The dimensions of these pores are of a similar order of magnitude to those of the individual grain kernels. *Intragranular* refers to properties that occur within kernels.

Some issues with previously published studies

Previous authors have published correlations that describe the rate of sorption carbon dioxide by food grains and seeds, but the correlations are experiment-specific. The results apply to systems that contain fixed amounts of grains and a fixed volume of gas. Systems with a number of initial concentration of carbon dioxide have been investigated.

In principle, such experiments are able to provide results that may be used to develop generalised models of sorption, but most research in this area has been compromised for one or more of three reasons:

(i) The experiments have been terminated before they have reached a steady state[2] or equilibrium.
(ii) Insufficient data are collected during the early stages of experiments when the rate of sorption is high.
(iii) The empirical expressions developed to describe the rate of sorption are experiment-specific, and they cannot be used as components of mathematical models of grain storage systems.

It is important to know the amount of carbon dioxide adsorbed at the steady state at which stage the mass fractions of carbon dioxide in the intergranular pores and the grain kernels are in equilibrium. It is demonstrated in this work that when empirical data gained from many published experiments are extrapolated, the values of the equilibrium mass fraction of carbon dioxide are unreliable. This difficulty is important because steady-state values of the amount of sorbed carbon dioxide provide information on the sorption isotherm.

Three problems with many published works: The experiments have been terminated too early, measurements were not always made during early stages of sorption, and the results were experiment-specific, hence not general.

Some experimental studies on the sorption of carbon dioxide have extended to the steady state, but this is often at the expense of insufficient data being collected during the important early stages of sorption. As a result, it is not possible to derive an accurate mathematical model of sorption.

Researchers have presented mathematical expressions that describe the rate that carbon dioxide is adsorbed by grains, but they are experiment-specific. They apply only to cases in which there is a step change in the concentration of intergranular carbon dioxide at the start of the experiments. The results cannot be applied to situations in which the intergranular concentration of carbon dioxide varies in an arbitrary manner, as occurs in practice. Furthermore, the published results are dependant on the experimental apparatus such as its volume, mass of grain treated and the initial partial pressure of carbon dioxide. The first two shortcomings listed above preclude the data from being used to develop mechanistic models that are accurate.

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[2] In this work we use the term 'steady state' to imply that the system has reached an equilibrium condition. However, the term 'steady-state' is adopted when it is used as an adjective as in 'steady-state value' which implies that the value pertains at a steady state, and it is not a steady (unchanging) state value.

THE LITERATURE ON SORPTION EXPERIMENTS

We shall now consider in more detail published data on the rate of sorption of carbon dioxide by food grains. Cofie-Agbor et al. (1995) pioneered a method of determining the rate of sorption of carbon dioxide in a constant volume system held at fixed temperatures. The first experiments considered the rate of sorption by wheat, and subsequent publications by a number of authors (Cofie-Agblor et al. 1995, 1998; Navarro, 1997, Jian et al. 2014, Iturralde-Garcia et al. 2019) studied a wide range of grains including oats, barley, canola and chickpeas.

The basis of the dynamic method of measuring the rate of sorption of carbon dioxide is to place a mass, m_g, of grains into a sealed system in which the gas volume is V. When the experiments are initiated the pressure p_0 of carbon dioxide is known, and after an elapsed time, t, the pressure is measured to be p. The ideal gas law implies that

$$(p_0 - p)V = m_{CO_2} R_{CO_2} T \tag{1}$$

in which R_{CO_2}, 188.9 J/(kg K), m_{CO_2}, and T are the gas constant for carbon dioxide, the mass of carbon dioxide that has been adsorbed, and the absolute temperature respectively. The mass fraction, C, of sorbed CO_2 is

$$C = \frac{m_{CO_2}}{m_g} \tag{2}$$

which is calculated at various times throughout the experiment.

Cofie-Agblor et al. (1995, 1998) fitted their experimental data to an equation of the form

$$C = C_\infty\left(1 - \exp(-\alpha t^{\beta}\right) \tag{3}$$

in which C_∞ is the equilibrium mass fraction of carbon dioxide adsorbed by the grain as the time, $t \rightarrow \infty$, and $\propto$ and β are functions of moisture content, M (wet basis), and temperature, T. At a temperature of 20°C the relationship between C_∞ and M is given by

$$C_\infty = 3.316M^{-0.804} \tag{4}$$

and the effect of grain moisture content on $\propto$ and β when the temperature of wheat is 20°C was determined by Cofie-Agblor et al. (1995) to be

$$\alpha = \gamma_1 exp(\gamma_2 T) \tag{5}$$

and

$$\beta = \gamma_3 + \gamma_4 T \tag{6}$$

where $\gamma_1, \gamma_2, \gamma_3$ and γ_4 are empirical constants.

Cofie-Agblor et al. (1995) collected data on wheat during the first 60 hours of sorption, but they did not allow the system to reach a steady state. Because $\propto$, β and C_∞ are free parameters it is difficult to obtain accurate values of them that apply over a time scale that ensures an approach to equilibrium. The problem is that the variables interact with each other to ensure the best fit to experimental data. It would be more appropriate to obtain values of C_∞ when equilibrium is approached and then separately obtain values of $\propto$ and β.

It is important to take sufficient measurements to ensure the system has approached equilibrium. In this way C_∞ can be measured directly, instead of being estimated simultaneously with $\propto$ and β.

Navarro (1997) carried out experiments that were similar to those of Cofie-Agblor et al. (1995) Not only did he make measurements of the degree of sorption of carbon dioxide by wheat over sufficiently long periods of time for his experiments to reach a steady state, but he also collected data over the first three hours. He collected sufficient data for mechanistic models of sorption to be formulated and tested, although Navarro (1997) fitted only an empirical model to his first three hours of data.

Jian et al. (2014) measured the rate at which canola adsorbs carbon dioxide under a constant pressure. In this case the mass fraction, C_e, at the surface of the seeds is constant and $C_e = C_\infty$ when $t \geq 0$. When the experiments are initiated at $t = 0$ the mass fraction of adsorbed carbon dioxide is zero, i.e. $C = 0$. Jian et al. (2014) were motivated to determine the elapsed time, t_E, at which the mass fraction of carbon dioxide adsorbed by the seeds had reached 97% of its final value. They achieved this by fitting Eqn (7) to their data to obtain values of the constant k_p,

$$C = C_\infty\left(1 - \exp\left(-k_p t\right)\right) \tag{7}$$

When $C/C_\infty = 0.97$ it follows that

$$\exp\left(-k_p t\right) = 0.03 \tag{8}$$

and by taking natural logarithms of both sides of the this equation we find that $t_E = -\ln(0.03)/k_p$. Jian et al. (2014) did not present their values of k_p, nor did they suggest that Eqn (7) implies a mechanistic model of sorption.

A possible contradiction

In their study of the sorption of CO2 by chickpeas, Iturralde-Garcia et al. (2019) appear to fit their data to an equation of the form Eqn (3), but they make use of Jian et al.'s (2014) criterion, Eqn (8), to estimate the time for the chickpeas to reach 97% saturation. This would be a contradiction. When Eqn (3) is used to calculate t_E the correct expression is $t_E = \sqrt[\beta]{-\ln(0.03)/\alpha}$.

MASS TRANSFER DRIVING FORCES ARE CENTRAL TO MECHANISTIC MODELS

When stored food grains are suddenly exposed to an atmosphere that has a high concentration of carbon dioxide the rate of sorption is initially high. This is because the gradient of the mass fraction of CO_2 within the grain kernels or seeds is very high in the vicinity of their outer surfaces. Furthermore, geometry dictates that the region near the surface comprises a high mass fraction of the grain substrate. For example, in the case of a sphere that has radius R, the material contained between $0.9R$ and R comprises 27% of all of the material in the sphere. Hence, two factors contribute to the rapid increase in the mass fraction of adsorbed carbon dioxide immediately after grains have been exposed to carbon dioxide, namely large mass transfer driving forces, and the solid substrate comprises a high volume fraction in the vicinity of the surface.

> It is important to take a sufficient number of measurements during the early stages of sorption processes.

> The rate of sorption is governed by concentration gradients of carbon dioxide at the outer surface of grain kernels.

A lumped parameter model

In chemical engineering parlance a lumped parameter model is one in which spatially highly resolved driving forces are disregarded, and they are replaced with averaged, or lumped values (Rasmussen et al. 2014). One such model of the rate of sorption of carbon dioxide is proposed by Smith et al. (2001), and it is expressed as

$$\frac{\partial c_G}{\partial t} = k_p(c - c_G) \tag{9}$$

in which k_p is a rate constant, c_G and c are the concentrations of carbon dioxide within the grain kernels and the intergranular pores, respectively. In this case, the mass transfer driving force is the difference between the average concentrations of carbon dioxide at the surface and that inside the kernels. Smith et al. (2001) do not state explicitly the algebraic relationship between the concentration of carbon dioxide, c_G, in the intragranular pores (i.e. pores within the grain kernels) and the mass fraction, C, of CO_2 sorbed by the solid substrate. However, it is inferred that

$$C = K_e c_G \tag{10}$$

in which K_e is a partition function that Smith et al. (2001) assumed to be a constant. They assign a value to K_e that is accurate to within an order of magnitude. At the outer surface of the grain kernels the mass fraction of carbon dioxide, C_e, in equilibrium with the carbon dioxide in the intergranular pores is given by

$$C_e = K_e c \tag{11}$$

The change in partial pressure of carbon dioxide is measured at discrete times throughout the experiments, and the mass fraction of carbon dioxide that is adsorbed is calculated by means of Eqns (1) and (2). It is therefore convenient to define a second partition constant, k_e, such that

$$C_e = k_e p \tag{12}$$

This implies that when the partial pressure of carbon dioxide is p the equilibrium mass faction adsorbed at the surface of grain kernels is C_e.

When equations (10) and (11) are substituted into Eqn (9) we may write

$$\frac{\partial C}{\partial t} = -k_p(C - C_e) \tag{13}$$

which is analogous to an equation used to predict the rate of drying of food grains (Jayas et al 1991), but in that case the mass transfer driving force is the difference between the moisture content at the outer surface of the grains and the average kernel moisture content.

In a grain store the partial pressure of carbon dioxide varies with time in an arbitrary way, hence the mass fraction of carbon dioxide adsorbed by grains at any location is determined by integrating Eqn (13) numerically.

Diffusion models

We have noted that mechanistic models generally include a mass transfer driving force, and that sorption is most rapid after a step change occurs in the intergranular concentration of carbon dioxide. The lumped parameter model satisfied both of these criteria, but it fails to respond sufficiently quickly during the early stages. This is because the model does not capture the steep intragranular concentration gradients adjacent to their outer surfaces.

It is hypothesized that diffusion-based models can account for (a) the rapid rate of sorption that occurs immediately after a step change in the concentration of intergranular carbon dioxide. This is because the concentration gradient, hence the mass transfer driving force, is high near the wall of the kernels, and (b) arbitrary changes in CO_2 concentration in the intergranular pores.

Yamamoto and Mitsuda (1980) summarise the factors that govern the rate of sorption of carbon dioxide by a number of food grains. They conclude that the process is one in which carbon dioxide diffuses through pores within the grain kernels and seeds, whence it is physisorbed by the solid substrate. The fact that the rates and degrees of adsorption and desorption are similar, but not identical, supports the view that carbon dioxide is loosely bound, or physisorbed rather than chemisorbed. As noted above, near the outer surface of the grains the concentration gradient of carbon dioxide is very high when the kernels are subjected to a step change in the concentration of intergranular carbon dioxide. Since the rate of mass transfer by diffusion is deemed to be proportional to the concentration gradient, It is hypothesised that diffusion-based models may be able to capture the high rate of sorption during the early stages of the process. Furthermore, it is anticipated that diffusion-based models are able to respond accurately to arbitrarily changing intergranular concentrations of carbon dioxide.

A simple approach may be to consider that the mass transfer driving force within the grain kernels is the gradient of the mass fraction of adsorbed carbon dioxide, and it is expressed as

$$\frac{\partial C}{\partial t} = \mathcal{D}_{ads}\left(\frac{2}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2}\right) \tag{14}$$

in which $\mathcal{D}_{ads}$ is an effective diffusion coefficient, and r is the radius of a notionally spherical grain kernel. The assumption that the driving force is the gradient of the mass fraction of adsorbed carbon dioxide is analogous to that used by Wei et al. (2019) to model the rate at which grain kernels dry. In their case they used the mass fraction of adsorbed water, scilicet, the moisture content expressed on a dry basis.

A second approach may be to assume that carbon dioxide diffuses as a gas through the intragranular pores and it is adsorbed by the solid substrate. This is in keeping with the mechanism proposed by Yamamoto and Mitsuda (1980). The governing equations as

$$\frac{\partial c}{\partial t} = \mathcal{D}_{eff}\left(\frac{2}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right) - \frac{\rho_s\left(1-\varepsilon_p\right)}{\varepsilon_p}\frac{\partial C}{\partial t} \tag{15}$$

where ε_p is the void fraction of the intragranular pores, $\mathcal{D}_{eff}$ is the effective diffusivity of gaseous carbon dioxide through the pores within the kernels, and ρ_s is the density of the solid substrate. Carbon dioxide in the pores is adsorbed from the pores by the solid substrate at a rate, $\partial C/\partial t$, expressed by

$$\frac{dC}{dt} = -k_{r,p}\left(C - C_{e,p}\right) \tag{16}$$

in which $k_{r,p}$ is a rate constant that is determined by fitting an integrated form of Eqn 16 to experimental data. In this case $C_{e,p}$ is analogous to C_e in Eqn (6), but it is the mass fraction of carbon dioxide adsorbed at the surface of the internal pores of the grain kernels.

FITTING EMPIRICAL EQUATIONS TO EXPERIMENTAL DATA

The objective of this section is to demonstrate that, although we may be able to fit empirical models to a limited range of experimental data, there are problems with extrapolating the results to a steady state. In this work, we shall fit three different purely empirical models to Cofie-Agblor et al's (1995) sorption data and we obtain three different values of C_∞. This is because the experiments were terminated prematurely, and the correct value of C_∞ therefore remains unknown. The models we shall examine are:

1. Cofie-Agblor et al.'s (1995) model in which $\propto$, β and C_∞ are determined by fitting Eqn (3) to the data measured at a particular temperature and two grain moisture contents.
2. Cofie-Agblor et al.'s (1995) model in the case when values of $\propto$, β and C_∞ are calculated using the correlations proffered by the authors, namely Eqns (3), (4), (5) and (6).
3. A model in which the variation in the measured values intergranular pressures of carbon dioxide are fitted to a double exponential equation of the form

$$p = k_{p1}\big(p_\infty + (p_0 - p_\infty)\exp(-k_{p2}t)\big) \\ +\big(1 - k_{p1}\big)\big(p_\infty + (p_0 - p_\infty)\exp(-k_{p3}t)\big) \qquad (17)$$

in which the fitted parameters are k_{p1}, k_{p2}, k_{p3} and p_∞. Thorpe (unpublished) found that Eqn (17) provides an excellent fit to Navarro's (1997) data. Significantly, in the latter case the steady-state pressure, p_∞, could be measured directly because the experiments were allowed to run to equilibrium . Navarro (1997) also presents highly resolved data garnered during the early stages of adsorption.

Navarro (1997) carried out his studies on sorption of carbon dioxide by wheat with a moisture content of 12.9% (w. b.) at temperatures of 15°C, 20°C, 25°C, and 30°C. It is considered useful to compare values of the partition constant, k_e, defined by Eqn (12) that arise from Cofie-Agblor et al.'s (1995) and Navarro's (1997) experimental results. To this end, values of k_e were calculated using all three models adumbrated above using Cofie-Agblor et al.'s (1995) data on the sorption of carbon dioxide by wheat with moisture contents of 12% and 14% at 20°C, and the moisture-weighted value calculated when M = 12.9% and compared with that determined from Navarro's (1997) work.

The partition constant, k_e, is an intrinsic property of the type of grain under consideration. As such, it should have a fixed value at a given temperature. It should be independent on the experimental procedure used to estimate it.

RESULTS

When Cofie-Agblor et al.'s (1995) experimental data were fitted to Eqns (3) and (17) using the Nelder and Mead (1965) simplex method the parameters presented in Table 1 were estimated.

The parameters $\propto$, β and C_∞ calculated by means of the correlations presented by Cofie-Agblor et al.'s (1995) for sorption of carbon dioxide by wheat at a temperature of 20°C are shown in Table 2. C_∞ is calculated from Eqns (1) and (2) when $p \rightarrow p_\infty$, ie.e at the steady state.

Figure 1 shows three fits to Cofie-Agblor et al.'s experimental data on the sorption of carbon dioxide by wheat with a moisture content of 12% (w.b.). It is clear that the relationship given by Eqn 3 and computed using the correlations given by Eqns (4), (5) and (6) is the least accurate model. This is reasonable because the values of $\propto$, β and C_∞ are themselves found from correlations of results obtained at moisture contents of 12%, 14%, 16% and 18%. In passing, it may have be more accurate (if less-user friendly) to have presented a series of three piecewise linear interpolation functions between the values of the parameters determined at each of the moisture contents. The parameters would have been accurate at each of the four moisture contents considered.

Table 1. Parameters determined by fitting Equation 3 and Equation 17 to Cofie-Agblor et al.'s (1995) data in the case of wheat at 20°C

Parameter	**Moisture content, % w. b.**	
	12%	14%
$\propto$	0.18098	0.20497
β	0.48477	0.52107
C_∞	4.1818×10^{-4}	4.4151×10^{-4}
k_e	4.1279×10^{-9}	4.0971×10^{-9}
k_{p1}	2.3541×10^{-3}	2.8114×10^{-3}
k_{p2}	4.0595×10^{-4}	2.8823×10^{-4}
k_{p3}	1.2739×10^{-5}	1.5887×10^{-5}
p_∞	8.7465×10^{4}	8.6580×10^{4}
$C_\infty{}^*$	3.2180×10^{-4}	3.4236×10^{-4}
Double exp. k_e	3.6791×10^{-9}	3.9543×10^{-9}

Table 2. Values of $\propto$, β and C_∞ calculated using Cofie-Agblor et al.'s (1995) correlations, and k_e is found by making use of C_∞ in Eqn 4. The values pertain to the sorption of carbon dioxide by wheat at a temperature of 20°C.

Parameter	**Moisture content, % w. b.**	
	12%	14%
$\propto$	0.1653	0.2570
β	0.4620	0.5114
C_∞	4.497×10^{-4}	3.973×10^{-4}
k_e	5.4875×10^{-9}	4.7179×10^{-9}

In contrast, Eqn (3) proposed by Cofie-Agblor et al. (1995) provides a good fit to the data when $\propto$, β and C_∞ are fitted specifically to the data obtained when the moisture content is 12%. The double exponential model based on Eqn 17 is also observed to afford an accurate fit to the empirical data. These qualitative observations are supported by the mean errors between the modelled and calculated mass fractions of CO_2 sorbed shown in Table 3. It is seen that the errors are 4.5032, 6.4475, 1.9455 (all $\times\ 10^{-6}$) in the cases of Cofie-Agblor et al.'s (1995) equation parameters when they are fitted, correlated or estimated using the double exponential equation respectively.

A similar situation is observed in Figure 2 when the moisture content is 14%. The application of correlations to calculate $\propto$, β and C_∞ is seen to give rise to the largest error, namely 15.363×10^{-6} as given in Table 3. In the case the Cofie-Agblor et al. (1995) model provides a better fit to the data than the double exponential equation, and the errors are 2.1068×10^{-6} and 2.8796×10^{-6} respectively.

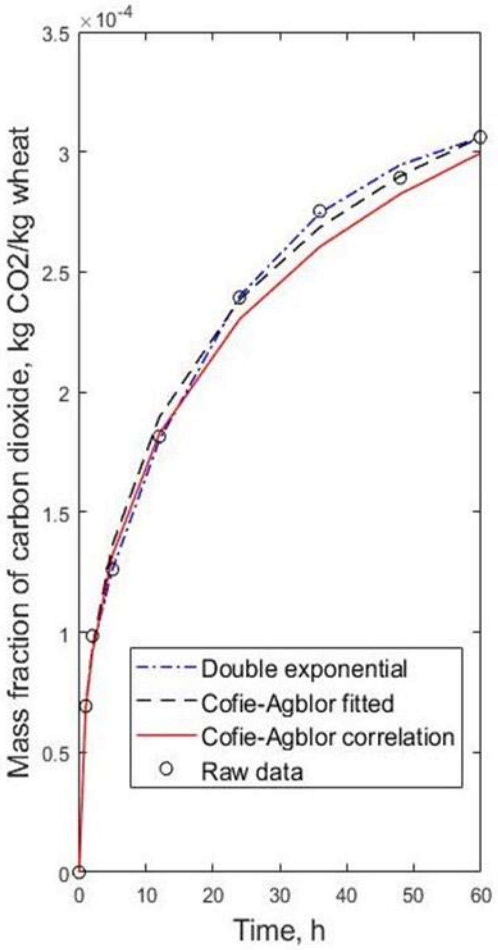

Figure 1. The fits of the double exponential equation and Cofie-Agblor et al.'s (1995) equation when $\propto$, β and C_∞ are adjusted so they fit the experimental data, and when they are calculated by means of correlations, Eqns (4), (5) and (6). The fit to the double exponential Eqn (17) is also shown. The data apply to wheat with a moisture content of 12% at a temperature of 20°C.

Table 3. The mean errors between the measured and fitted data for 12% and 14% moisture content grain at a temperature of 20°C

Model	**Mean error ×10^{-6}**	
	12%	14%
Cofie-Agblor : Fitted to data	4.5032	2.1068
Cofie-Agblor: Correlations	6.4475	15.363
Double exponential	1.9455	2.8796

Uncertainties associated with extrapolating data

A marked difference between the Cofie-Agblor et al. (1995) and double exponential model can be observed in Figures 1 and 2. It is this:

> After 60 hours the predicted *rate* of sorption of carbon dioxide is greater when using the Cofie-Agblor et al. (1995) equations than are estimated by the double exponential model.

This suggests that the Cofie-Agblor et al. (1995) equations will predict higher steady-state mass fractions of carbon dioxide than the double exponential equation. This prediction is corroborated by the data presented in Tables 1 and 2 in which it can be seen that in the case of 12% moisture content wheat that the steady-state value of the mass fraction, C_∞, of sorbed CO_2 is 4.1818×10^{-4} when Cofie-Agblor et al.'s (1995) equation is fitted to experimental data. In contrast, the double exponential equation predicts 3.218×10^{-4}. When correlated values are used in the Cofie-Agblor et al. (1995) equation it is estimated that $C_\infty = 4.497\times10^{-4}$. When the moisture content of the wheat is 14% the double exponential equation again predicts the lowest value of the steady-state mass fraction, C_∞, of sorbed carbon dioxide, namely 3.4236×10^{-4}.

Same data: three reasonably accurate models and three different estimates of the steady-state mass fraction, C_∞. Beware of extrapolation.

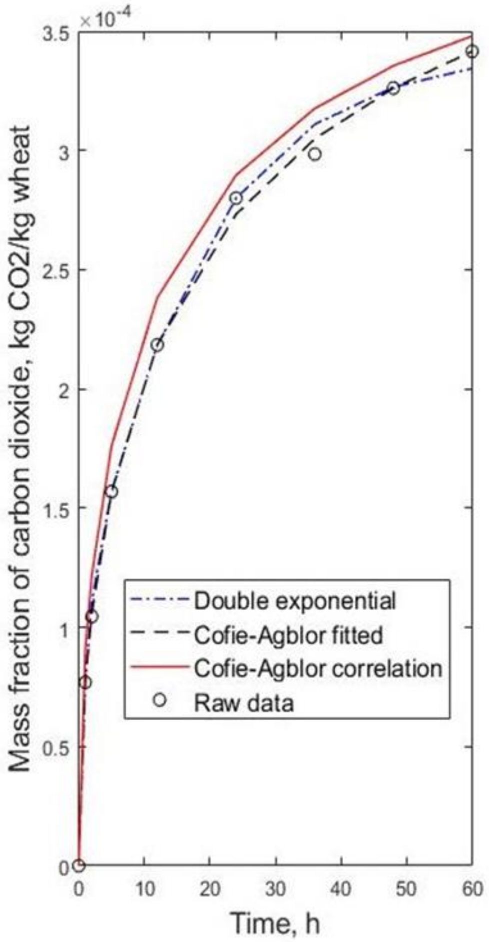

Figure 2. The fits of the double exponential equation and Cofie-Agblor et al.'s (1995) equation when $\propto$, β and C_∞ are adjusted so they fit the experimental data, and when they are calculated by means of correlations. The data apply to wheat with a moisture content of 14% at a temperature of 20°C.

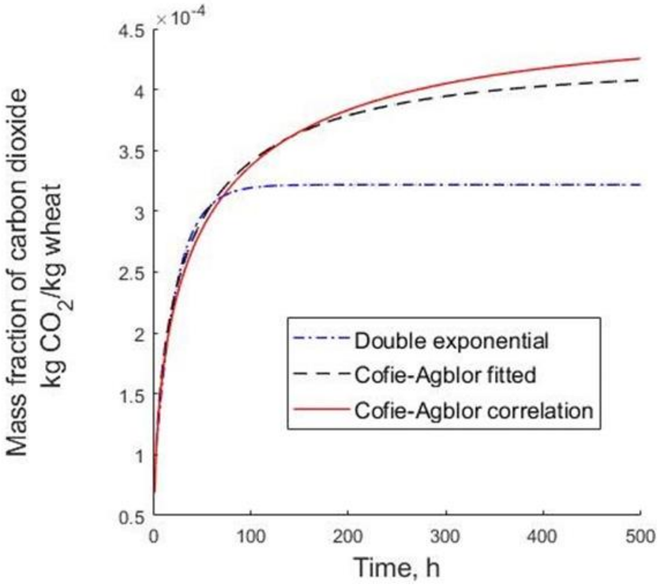

Figure 3. When the data are extrapolated to an elapsed time of 500 hours it can be seen that neither of the two versions of the Cofie-Agblor et al. (1995) models (i.e. those with $\propto$, β and C_∞ obtained by fitting Eqn (3) to raw data, or being determined by correlation Eqns (4), (5) and (6)) approaches the steady state in 12% moisture content wheat. However, the double exponential model suggests that the steady state is closely approached after about 100 hours.

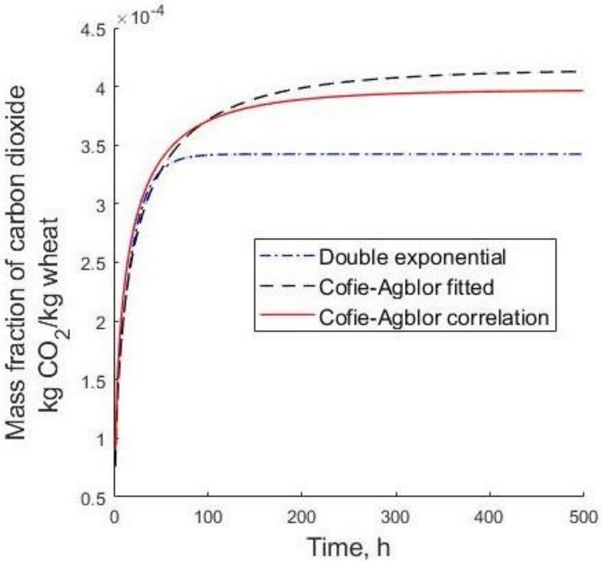

Figure 4. . When the data are extrapolated to an elapsed time of 500 hours it can be seen that neither of the two versions of the Cofie-Agblor et al. (1995) models approaches the steady state in 14% moisture content wheat. However, the double exponential model suggests that the steady state is closely approached after about 150 hours.

The uncertainties of predicting steady-state mass fraction, C_∞, of sorbed carbon dioxide that arise when terminating equations prematurely are graphically illustrated in Figures 3 and 4. It is observed in Figure 3 that the Cofie-Agblor et al. (1995) model, Eqn (3), fails to predict that a steady-state mass fraction of sorbed CO_2, C_∞, will have been achieved in 12% moisture content wheat after an elapsed time of 500 hours. This is the case whether or not the parameters $\propto$, β and C_∞ are determined by fitting the raw data to Eqn (3), or if they are calculated bt means of the correlation Eqns (4), (5) and (6). This compares with an elapsed time of about 100 hours predicted by the double exponential model.

A similar situation occurs when considering wheat that has a moisture content of 14%, but in this case, Figure 4 shows that the Cofie-Agblor et al.'s (1995) model with parameters fitted to the experimental data predicts the highest steady-state value of the sorbed carbon dioxide.

NAVARRO'S (1997) DATA AND A NON-LABORATORY-SPECIFIC RESULT

We have noted that Navarro (1997) measured the rate of sorption of CO_2 by wheat that had a moisture content of 12.9%. In particular, he measured the degree of sorption at 30 minute intervals during the first 3 hours of his experiments. He subsequently measured the degree of sorption at approximately 24 hour intervals until an elapsed time of 190 hours. It is significant that after about 100 hours the sorption process was very close to completion. Thorpe (unpublished) found that the double exponential model fits Navarro's (1997) data over the entire range.

The partition constant, k_e, is a grain-specific quantity that is independent of the experimental set up used to measure its value. Using Navarro's 1997 data, Thorpe (unpublished) calculated the value of k_e in wheat with a moisture content of 12.9% to be 4.31×10^{-9}. The linearly weighted values of k_e presented in Table 1 when fitting a double exponential function is 4.11×10^{-9} which is gratifyingly close to that obtained by Thorpe's (unpublished) analysis of Navarro's (1997) work.

The partition constant, k_e, has a grain-specific value that is, in principle, experiment-independent. The values of k_e determined when fitting the double exponential function to both Navarro's (1997) and Cofie-Agblor et al.'s (1995) data yield values of 4.31×10^{-9} and 4.11×10^{-9} respectively, and which are satisfyingly close.

DISCUSSION

If this work has a subtext it is this: Researchers in the discipline of stored grains postharvest technology are advised to carry out their work in an intellectual framework that facilitates their results being applied.

Modelling the stored grains ecosystem is a multidisciplinary activity. Thorpe (2010) has pointed out the dangers of viewing grains postharvest technology as a closed discipline.

In the case of the sorption of carbon dioxide a suitable intellectual framework is multiphysics, which has the power to simulate the behavior of any type of grain, in any environment, provided the physical data are available

(Thorpe, 2010). When formulating models of the sorption of carbon dioxide by food grains sorption isotherms and rate equations are required. Over the decades White (1992), Thorpe (2010) and Jian and Jayas (2012) have remarked on the importance of a multidisciplinary approach to grains postharvest technology. Such an approach is required to develop general models of sorption that consider phenomena such as:

(i) The effects of hysteresis on the adsorption and desorption of carbon dioxide by grain kernels and seeds.
(ii) Mechanisms of diffusion of carbon dioxide within grain kernels
(iii) Isotherm data.
(iv) The formulation of computer-based models of the grain eco-system.

An overarching aim should be to formulate expressions that can be incorporated into mechanistic mathematical models of the stored grain ecosystem. Thorpe (2008, 2010) points out that commercially available multiphysics software can be readily modified to account for biological and chemical phenomena such as the population dynamics of insects, the rate of decay of chemical pesticides applied to grain, the transport of fumigants around grains stores and the response of the stored grains ecosystem to aeration, drying and so on.

> Commercially available multiphysics software can be easily modified to account for biological and chemical phenomena that occur in grain stores. Before the behavior of carbon dioxide in stored grains can be simulated, we require rate equations that describe the adsorption and desorption of CO_2 by grain kernels.

In this work, we have noted the likely errors associated with extrapolating data. It is natural for stored grains technologists to carry out research on grain under conditions that are met in practice, and under which insects, say, are likely to be their most fecund. However, it is not only these commonly encountered conditions that are of interest, but also extrema. This is because insect control might be achieved at the extremes, i.e. at low or high temperatures, both of which are inimical to the growth of insect populations. Hence, further work on the adsorption and desorption of carbon dioxide by food grains should be carried out over a wide range of moisture contents and temperatures. Because conditions in grain stores vary with time it is important to carry out experiments in which the intergranular concentration of carbon dioxide varies non-monotonically with time, possibly in a cyclical manner. This would help to devise mechanistic models of sorption.

> It is important to explore conditions at extrema, because these are often the ones of most interest for controlling the quality of stored grains. Furthermore, by gathering data at the extremes one is more likely to avoid the dangers of extrapolation.

CONCLUSIONS

The spatial and temporal distributions of carbon dioxide in grain stores are driven by a number of diverse forces. If comprehensive models of the behavior of carbon dioxide are to be developed it is essential to formulate equations that govern the rate at which it is sorbed. Experiments have been published that report the rates of sorption of carbon dioxide by food grains and seeds, but several of the experiments display weaknesses, namely:

i) Insufficient meausrements were taken to develop reliable models during the early stages of sorption by grain kernels.
ii) Not all experiments approached the steady state. This compromised the formulation of accurate mathematical models of sorption. It also resulted in a loss of information that contributes to the establishment of sorption isotherms.
iii) Although experimentalists have proposed expressions and correlations that fit their results, most of their expressions are experiment-specific. This limits their use.

To highlight problems associated with extrapolating experimental data Cofie-Agblors (1995) results were fitted to three empirical expressions. However, their experiments were terminated after 60 hours by which time they had failed to reach a steady state. Importantly, even though the three expressions fitted their data quite well, it is found that the steady-state values of the amount of carbon dioxide adsorbed by wheat exhibited considerable variation.

It is found that a double exponential function of time not only provides an accurate fit Cofie-Agblor et al.'s (1995) data, but the time for adsorption of carbon dioxide to approach a steady state is similar to that observed by Navarro (1997). As a result, it has been possible to quantify a partition coefficient that is wheat-specific, and therefore potentially useful.

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