

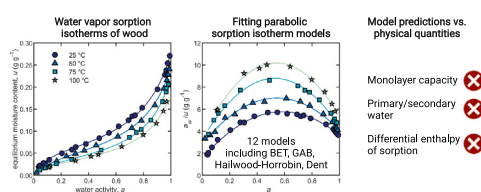
Common sorption isotherm models are not physically valid for water in wood

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HIGHLIGHTS

- Physical quantities predicted by common sorption isotherm models are evaluated.
- 12 sorption isotherm models include BET, GAB, Hailwood-Horrobin, and Dent.
- Fit to reliable sorption isotherm data for water in wood at 4 temperatures.
- Monolayer capacity, primary/secondary water, and enthalpy of sorption are predicted.
- Model predictions are inconsistent with independently measured physical quantities.

GRAPHICAL ABSTRACT



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ABSTRACT

Sorption isotherm models are frequently used to understand the interactions of water with cellulosic materials. Many commonly used models, such as the Guggenheim-Anderson-de Boer, Hailwood-Horrobin, and Dent isotherm models, are based on idealized physical systems. In the scientific literature, these models are often used to predict properties of wood such as the monolayer capacity, which is a representation of the number of available sorption sites in the material. Reporting such properties assumes that an idealized system adequately represents actual wood-water interactions. These models can be reduced to the same form, where the ratio of water activity, a_w , to equilibrium moisture content (EMC), is a second-order polynomial function of a_w . Here we review twelve models that have a parabolic form, fit these models to high quality water vapor sorption isotherm data for wood at multiple temperatures, and calculate physical properties from the model parameters. Moreover, variability in model predictions arising from measurement uncertainties in a_w and EMC values is propagated using a Monte Carlo method. Predicted physical properties are tested against independently measured values of hydroxyl accessibility, relative amounts of primary and secondary water, and enthalpy of sorption. None of the models accurately predicts any of the physical properties, even when the reported measurement uncertainties are increased by a factor of three. Therefore, it must be concluded that parabolic sorption isotherm models are not valid for water in wood cell walls.

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1. Introduction

Water vapor sorption is fundamental to the behavior of wood and affects nearly all its properties. Therefore, the interaction of wood with water is important for all applications of wood products. Dry wood exposed to humid air will absorb water vapor until equilibrium is reached with the surrounding environment. The relation between equilibrium moisture content (EMC) of the wood and water activity (i.e., relative humidity) of the environment at a given temperature is described by the water vapor sorption isotherm. This has been an essential part of wood science for over a century [1–3]. For nearly as long, the scientific discussion in the field has focused on the fundamental mechanisms governing the wood-water equilibrium state and the sorption process towards this state [4–13].

Wood consists of three dominant biopolymers (cellulose, hemicelluloses, and lignin) assembled into a porous material with a hierarchical structure, i.e., a high degree of order at different length scales. It is thus not surprising that the interaction between water and wood is complex. For instance, water absorption in wood involves a range of physicochemical phenomena that may affect the equilibrium state or sorption process. These include the mechanics of the cell wall as it swells upon water absorption [14], thermal processes as water molecules change from the vapor state to the absorbed state [15], diffusion of water molecules into the solid cell walls [16], glass transition of the amorphous biopolymers that are plasticized by water [16], and hydrogen bonding between water molecules and sorption sites on the biopolymers [17,18]. In addition, water sorption in wood exhibits hysteresis in both the hygroscopic range and the over-hygroscopic (capillary) range [19–21]. Further influential factors include the relative proportions of ordered cellulose, amorphous cellulose, hemicelluloses, and lignin, and the amounts of mineral ions and extractives in the wood cell wall [22–27]. The understanding of these phenomena continues to be improved as new insights are gained, in part as a result of the development and refinement of experimental techniques and analytical tools. Important for the advancement of our knowledge is the critical assessment of existing theories and hypotheses. Such evaluation should naturally take into account the growing body of experimental data, some of which was unavailable when the original theories or hypotheses were first formulated or applied in the field of wood science.

For the analysis and interpretation of wood-water interactions, sorption isotherm models play an important role. These models describe the EMC as a function of the environmental conditions, i.e., temperature and water activity. A large number of sorption isotherm models exist in published literature. For instance, van den Berg and Bruin [28] review 77 different models while several more models have been published in the last decades since that review. Many sorption isotherm models are purely empirical and useful for predicting EMC in specific environments; several of these have been evaluated for goodness of fit to water vapor sorption data for wood [2,29–31]. However, a range of models are derived from theories describing the sorption process in an idealized physical system.

The most commonly used sorption isotherm models for water in wood are the Dent model [32], the Guggenheim-Anderson-de Boer (GAB) model [33–35], and the Hailwood-Horrobin (HH) model [36]. Their popularity stems in part from the good fit to experimental sorption data they provide [4,29,37]. All three of these models can be re-arranged by algebraic transformation into an expression where the ratio of water activity a_w to EMC is given by a second-order polynomial function of a_w , as seen in Eq. (1) [38,39].

$$\frac{a_w}{u} = C + Ba_w + Aa_w^2 \quad (1)$$

where a_w is water activity ($0 \leq a_w \leq 1$), u is equilibrium moisture content expressed as the mass ratio of water to dry wood (g g^{-1}), and A , B , and C are fitting parameters. We refer to models having this form as “parabolic sorption isotherm models”. Their similar mathematical form

implies that they provide exactly the same fit to experimental data [38]. The Dent, GAB, and HH models as well as other parabolic sorption isotherm models are based on physical theories describing either adsorption of vapor on an idealized surface or absorption of vapor in an idealized polymer. In the wood science literature, these models are often fitted to water vapor sorption data not only for empirical prediction but also for physical interpretation. Hereby, it is tacitly assumed that their idealized physical systems adequately represent the real physical system. Derived physical quantities, such as the monolayer capacity and the relative amounts of primary and secondary water, have been widely reported for water in wood [37,40–63]. Similarly, these physical quantities are often reported in the food science literature based on fitting specific sorption isotherm models to water vapor sorption data for various foods [64–69]. Primary water (also called “monolayer water” in the literature) describes water molecules interacting directly by hydrogen bonding with specific sorption sites in the porous solid material, whereas secondary water (also known as “multilayer” or “poly-layer” water) describes water molecules hydrogen bonding with other water molecules but not directly with sorption sites [4]. The amount of primary water that would fully occupy all sorption sites is called the “monolayer capacity” and is related to a hypothetical “internal surface area” available for water sorption within the material. In the HH model, this parameter is derived from the number of sorption sites available, since the model describes sorption as a solution phenomenon in an idealized polymeric system rather than multiple layers on a solid surface.

The idealized physical systems assumed by parabolic sorption isotherm models are inconsistent with wood-water interactions. For example, the majority of models assume sorption occurs at a planar, inert, homogeneous solid-gas interface; however, this assumption would result in an unrealistically high surface energy and it ignores the phenomena of intermolecular hydrogen bonding in biopolymers and water sorption between polymer molecules [70,71]. Furthermore, none of these models includes a description of the glass transition, the mechanics of hygro-expansion, or sorption hysteresis. The complexity of the wood-water equilibrium state is therefore poorly represented by the idealized physical systems described above. However, the popularity of sorption isotherm models for deriving physical parameters for water in wood illustrates the widespread assumption that these models can in fact provide fundamental insights about wood-water interactions.

Previous studies have questioned the validity of model derived physical parameters based on independently measured values using other experimental techniques. For instance, the models have been shown to significantly underpredict the number of sorption sites in wood [72]; the predicted relative amounts of primary and secondary water at different temperatures have been shown to contradict the model assumptions [39,72]; and the models have been shown to give incorrect predictions of the enthalpy of sorption [29]. These critiques have been recognized recently in several studies which suggest that the interpretation of derived physical parameters needs further investigation [73, 74]. In retrospect, the previous critical evaluations of the Dent, GAB, and HH models [29,39,72] had significant limitations. Importantly, the analyses were not conducted using the most reliable experimental sorption isotherm data. The critiques of the HH model by Simpson [29] and Willems [72] were based on fitting the model to historic sorption data from the Forest Products Laboratory. An investigation of the origins of this dataset [2] found that it could not be considered reliable for scientific purposes (despite its utility for many practical applications). The critique of Zelinka et al. [39] relied on data from Kelsey [75]. In a subsequent review of the literature, which identified the most reliable water vapor sorption measurements for wood at three or more temperatures based on the measurement protocol, the operational definition of sorption equilibrium, and inherent measurement uncertainties, Zelinka et al. [76] found that the Kelsey [75] dataset could not be recommended for testing sorption isotherm models.

The objective of this study is to conduct a comprehensive analysis of

Table 1

Overview of parabolic sorption isotherm models from the literature. The parameters u , u_m and a_w denote the equilibrium moisture content, the monolayer capacity, and the water activity, respectively. The other parameters are model specific parameters corresponding to an idealized physical system. Further information on the models and the physical pictures behind them is provided in the [Supplementary Material](#).

#	Original source	Sorption isotherm model	Parabolic equation
1	Anderson [34], var. 1	$\frac{u}{u_m} = \frac{c_0 k a_w}{(1 - k a_w)(1 + (c_0 - 1)k a_w)}$	$\frac{a_w}{u} = \frac{1}{c_0 k u_m} + \frac{(c_0 - 2)a_w}{c_0 u_m} + \frac{(1 - c_0)k a_w^2}{c_0 u_m}$
2	Anderson [34], var. 2	$\frac{u}{u_m} = \frac{c_0 a_w}{(1 - j a_w)(1 + (c_0 - 1)a_w)}$	$\frac{a_w}{u} = \frac{1}{c_0 u_m} + \frac{(c_0 - j)a_w}{c_0 u_m} + \frac{(1 - c_0)j a_w^2}{c_0 u_m}$
3	Anderson and Hall [77], var. 1	$\frac{u}{u_m} = \frac{c_0 a_w}{(1 - j a_w)(1 + (c_0 - j)a_w)}$	$\frac{a_w}{u} = \frac{1}{c_0 u_m} + \frac{(c_0 - 2j)a_w}{c_0 u_m} + \frac{j^2 - j c_0 a_w^2}{c_0 u_m}$
4	Anderson and Hall [77], var. 2	$\frac{u}{u_m} = \frac{c_0 k a_w}{(1 - j k a_w)(1 + (c_0 - j)k a_w)}$	$\frac{a_w}{u} = \frac{1}{c_0 k u_m} + \frac{(c_0 k - 2j k)a_w}{c_0 k u_m} + \frac{(j k)^2 - j k c_0 k a_w^2}{c_0 k u_m}$
5	Brunauer et al. [78]	$\frac{u}{u_m} = \frac{c_0 a_w}{(1 - a_w)(1 - a_w + c_0 a_w)}$	$\frac{a_w}{u} = \frac{1}{c_0 u_m} + \frac{(c_0 - 2)a_w}{c_0 u_m} + \frac{(1 - c_0)a_w^2}{c_0 u_m}$
6	Cassie [79]	$\frac{u}{u_m} = \frac{a_w}{(1 - a_w)(\beta + (1 - \beta)a_w)}$	$\frac{a_w}{u} = \frac{\beta}{u_m} + \frac{(1 - 2\beta)a_w}{u_m} + \frac{(\beta - 1)a_w^2}{u_m}$
7	de Boer [35]	$\frac{u}{u_m} = \frac{k K_0 a_w}{(1 - K_0 a_w)(1 + (k - 1)K_0 a_w)}$	$\frac{a_w}{u} = \frac{1}{k K_0 u_m} + \frac{(k - 2)K_0 a_w}{k K_0 u_m} + \frac{-(k - 1)K_0^2 a_w^2}{k K_0 u_m}$
8	Dent [32]	$\frac{u}{u_m} = \frac{b_0 a_w}{(1 - b_1 a_w)(1 + b_0 a_w - b_1 a_w)}$	$\frac{a_w}{u} = \frac{1}{b_0 u_m} + \frac{(b_0 - 2b_1)a_w}{b_0 u_m} + \frac{(b_1 - b_0)b_1 a_w^2}{b_0 u_m}$
9	Gascoyne and Pethig [80]	$\frac{u}{u_m} = \frac{1}{a_0 b_0 a_w} \left(\frac{1 + K_2 a_w}{1 + K_1 a_w} \right)$	$\frac{a_w}{u} = \frac{1}{a_0 b_0 u_m} + \frac{(a_0 - 2b_0)a_w}{a_0 b_0 u_m} + \frac{(b_0 - a_0)a_w^2}{a_0 b_0 u_m}$
10	Guggenheim [33]	$\frac{u}{u_m} = \frac{1}{K_2(1 - K_1 a_w)(1 + K_1 K_2 a_w)}$	$\frac{a_w}{u} = \frac{1}{K_2 u_m} + \frac{K_2 a_w}{K_2 u_m} + \frac{(K_1 - K_2)K_1 a_w^2}{K_2 u_m}$
11	Hailwood and Horrobin [36]	$\frac{u}{u_m} = \frac{K_2(1 - K_1 a_w)(1 + K_1 K_2 a_w)}{K_1 K_2 a_w}$	$\frac{a_w}{u} = \frac{u_m(1 + K_1 K_2)(1 + K_2)}{K_1 K_2(1 + K_2)} + \frac{u_m(1 + K_1 K_2)(1 + K_2)a_w}{K_1 K_2(1 + K_2)} - \frac{K_1^2 K_2^2 a_w^2}{u_m(1 + K_1 K_2)(1 + K_2)}$
12	Langmuir [81] var. VI	$\frac{u}{u_m} = \frac{\sigma_1 K_1 a_w}{1 + (\sigma_1 - 2\sigma_2)K_1 a_w + (\sigma_2^2 - \sigma_1 \sigma_2)K_1^2 a_w^2}$	$\frac{a_w}{u} = \frac{1}{u_m \sigma_1 K_1} + \frac{(\sigma_1 - 2\sigma_2)K_1 a_w}{u_m \sigma_1 K_1} + \frac{(\sigma_2^2 - \sigma_1 \sigma_2)K_1^2 a_w^2}{u_m \sigma_1 K_1}$

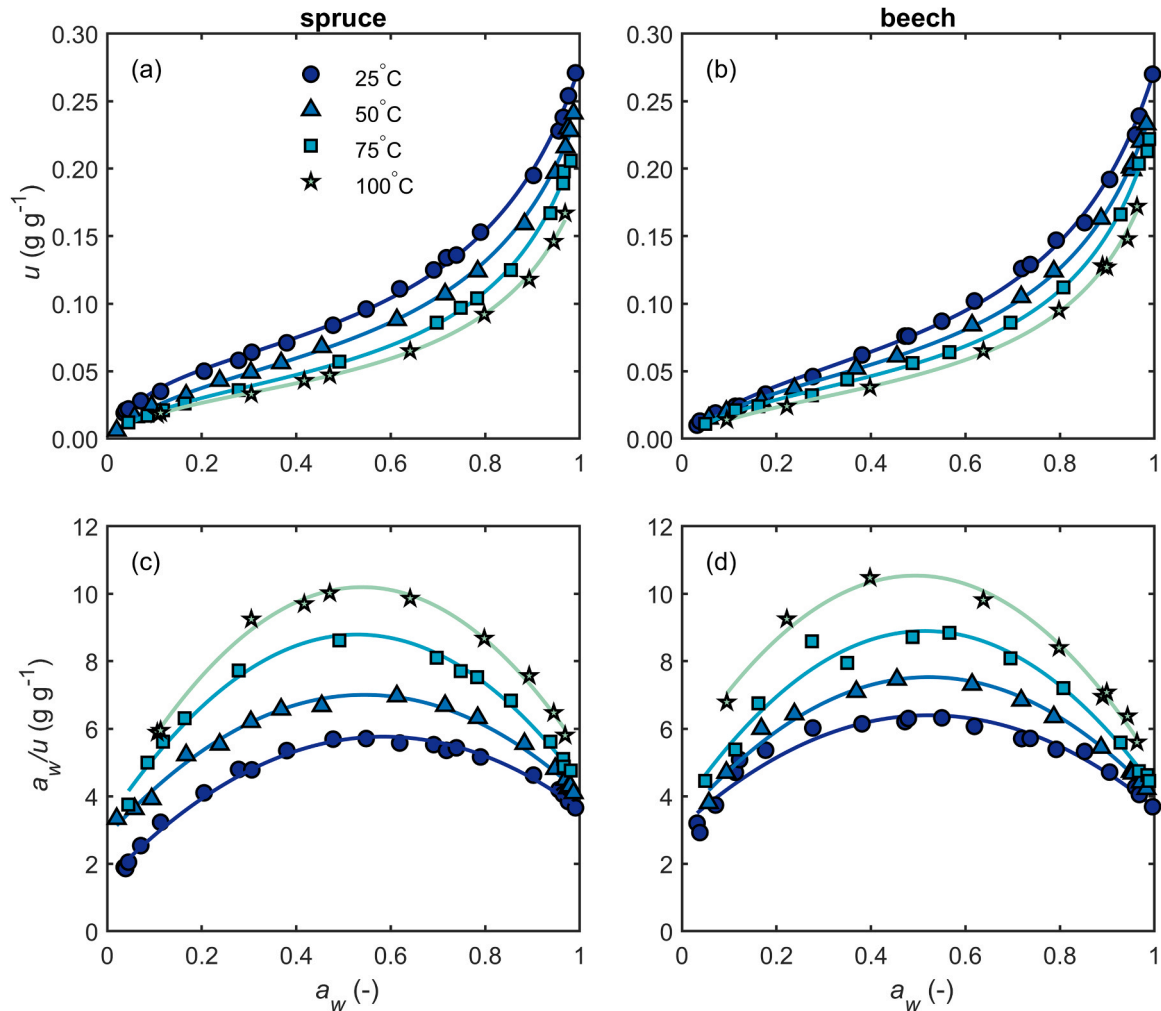


Fig. 1. Experimental sorption isotherm data for (a) spruce and (b) beech from Weichert [82] showing equilibrium moisture content, u , as a function of water activity, a_w , at four temperatures. The same data is then plotted in the bottom row (c,d) as a_w/u vs. a_w to illustrate the parabolic fits to these data.

the physical parameters describing water in wood derived from parabolic sorption isotherm models. Although the physicochemical phenomena mentioned previously, such as the mechanics of hygro-expansion in wood cell walls and the glass transition of amorphous polymers, are intimately linked to water sorption, none of the parabolic sorption isotherm models incorporates these phenomena. We therefore limit our analysis to physical quantities within the purview of the models. Given that the parabolic sorption isotherm models omit important phenomena and make assumptions that are unrealistic for water in wood, we hypothesize that these models are unable to describe the wood-water equilibrium state, despite their popularity and widespread use to do exactly that. To test this hypothesis we use the most reliable sorption data identified in previous work [76] to derive physical parameters from 12 different theoretical parabolic sorption isotherm models, including the Dent, GAB, HH, and Brunauer-Emmett-Teller (BET) models, and assess the validity of model predictions against independently measured physical quantities from other experimental techniques. Since all experimental data have some degree of measurement uncertainty, we introduce a Monte Carlo method as a novel tool to propagate this uncertainty into the derived physical parameters.

2. Methods

2.1. Literature search and model selection

The selection of sorption isotherm models is based on the compilation of 77 of these models by van den Berg and Bruin [28], out of which 63 are theoretically or partially theoretically based. By algebraic transformations 12 of the 63 theoretically based models could be transformed to a parabola.

2.2. Algebraic rearrangement into a consistent form

The twelve sorption models that were identified as parabolic from the literature search were then converted into a format equivalent to Eq. (1), as presented in Table 1. The full details of the algebraic transformation of the various sorption isotherm models are given in the Supplementary Material.

While the parabolic expression in Eq. (1) is commonly used to fit the models to sorption isotherm data, most isotherms are typically written so that ratio of the total moisture content u , to the monolayer capacity, u_m , is a function of a_w . We include this mathematical expression as well for easy comparison between models. It should be noted that several of the models, namely 1, 3, 7, and 10, are identical, and are collectively known as the Guggenheim-Anderson-de Boer (GAB) model, which is typically written as:

$$\frac{u}{u_m} = \frac{c_0 k a_w}{(1 - k a_w)(1 + (c_0 - 1)k a_w)} \quad (2)$$

where c_0 and k are parameters corresponding to an idealized physical system. As shown in the Supplementary Material, models 5 and 6 have constrained fitting parameters and therefore do not produce the same fit as the rest of the listed models.

2.3. Fitting models to experimental data

Typically, the derivation of thermodynamic sorption parameters requires fitting models to experimental sorption data at multiple temperatures levels. Zelinka et al. [76] recently evaluated 27 publications with sorption data collected on wood at three or more temperatures over the last 100 years and identified only three data sets that they recommended for use in developing and testing sorption isotherm models. Reasons for not recommending other data sets were lack of stringency in attaining equilibrium, large uncertainty in measurement of EMC, instability in temperature and relative humidity conditions, or

Table 2

Mathematical expressions for the monolayer capacity (u_m) for the various parabolic sorption isotherm models described in the Supplementary Material. The expressions are given based on the parameters A , B , and C from the general parabolic sorption isotherm (Eq. 1). The parameter Z can be calculated from A , B , and C and is given in Eq. (3). Please note that expression IV is based on the constrained parabolic fit with different values of B and C .

Designation	Monolayer capacity	Model ^a
I	$u_m = 1/(BZ + 2CZ^2)$	9
II	$u_m = 1/(B + 2CZ)$	1, 3, 4, 7, 8, 10, 11, 12
III	$u_m = 1/(B + C + CZ)$	2
IV	$u_m = 1/(B + 2C)$	5, 6

^a See Table 1.

insufficient reporting of experimental details. Of the three recommended data sets, the data of Weichert [82] shown in Fig. 1a and b spans the widest range in temperature and was selected for this study.

The absorption measurements of Weichert [82] include eight data sets, for both spruce and beech wood at 25, 50, 75 and 100 °C. Each set was fit to a parabola (Eq. 1) as illustrated in Fig. 1c and d with $y = a_w/u$ and $x = a_w$ using the *polyfit* function in MATLAB [83]. This function implements a least-squares algorithm to fit a polynomial to (x,y) data, in this case of order 2, thereby identifying the parameters A , B , and C . This method was used for the 10 models that have three independent parameters.

Given that the models of Brunauer et al. [78] and Cassie [79] have two independent parameters rather than three, we used two different approaches. In the first approach, each dataset was fit to a constrained parabola with $y = a_w/u$ and $x = a_w$ allowing only B and C to vary, with $A = -(B + C)$. For this case *polyfit* was not robust, so MATLAB's *fit* function was used, which implements a nonlinear least-squares curve fitting algorithm for the custom function $y = -(B + C)x^2 + Bx + C$. In the second approach, the data were linearized with $y = a_w/[u(1 - a_w)]$ and $x = a_w$. Each set was fit to a line using *polyfit* (order = 1) for data points in the range $0.05 \leq a_w \leq 0.35$, following the recommendation of Brunauer et al. [78].

2.4. Evaluation of model predictions

To evaluate the model predictions, physical quantities were calculated from the fitting parameters. In this paper, we first compare the monolayer capacity predicted by the models with the hydroxyl accessibility measured using deuterium exchange. Second, we compare the relative amounts of primary and secondary water predicted by the models with two distinct populations of sorbed water in wood cell walls identified by 2D low-field NMR and quasielastic neutron scattering (QENS). Although it is not yet known how these populations differ in terms of their physicochemical environment within cell walls, both techniques differentiate between sorbed water that interacts more intimately with the cell walls (more constrained in NMR, faster QENS dynamics), and loosely sorbed water (less constrained in NMR, slower QENS dynamics). Finally, we compare the differential enthalpy of sorption as a function of moisture content predicted by the models to calorimetric measurements and values derived from the sorption data using the Clausius-Clapeyron equation. Details on the three physical quantities predicted by the models are given in the following sections.

2.4.1. Monolayer capacity

The monolayer capacity can be calculated from the model fit parameters (A , B , and C in (Eq. 1)). Expressions for the model fit parameters are given in Table 2; the parameter Z naturally arises from the parabolic nature of the isotherms and can be calculated from A , B , and C :

$$Z = \frac{-B + \sqrt{B^2 - 4AC}}{2C} \quad (3)$$

Table 3

Mathematical expressions for primary water (u_1) and secondary water (u_2) for the different sorption isotherm models. Both types of water are given relative to the total moisture content, u .

Designation	Primary water	Secondary water	Model ^a
V	$\frac{u_1}{u} = 1 - Za_w$	$\frac{u_2}{u} = Za_w$	1, 2, 7, 8, 10
VI	$\frac{u_1}{u} = 1 - a_w$	$\frac{u_2}{u} = a_w$	5
VII	$\frac{u_1}{u} = \frac{(B + CZ)(1 - Za_w)}{B + 2CZ}$	$\frac{u_2}{u} = \frac{CZ + (BZ + CZ^2)a_w}{B + 2CZ}$	11

^a See Table 1.

Table 4

Equations for molar enthalpy of sorption of primary and secondary water from isotherm models fit to data at a single temperature.

Designation	Primary water	Secondary water	Model ^a
VIII	$\Delta H_1(T) = -RT \ln\left(\frac{B}{C} + 2Z\right)$	$\Delta H_2(T) = -RT \ln(Z)$	1, 7
IX	$\Delta H_1(T) = -RT \ln\left(\frac{B}{C} + 2\right)$	$\Delta H_2(T) = 0$	5

^a See Table 1.

Table 5

Equations for molar Gibbs energy of sorption of primary and secondary water from isotherm models.

Designation	Primary water	Secondary water	Model ^a
X	$\Delta G_1(T) = -RT \ln\left(\frac{B}{C} + 2Z\right)$	$\Delta G_2(T) = -RT \ln(Z)$	1, 8
XI	$\Delta G_1(T) = -RT \ln\left(\frac{B}{C} + 2\right)$	$\Delta G_2(T) = -RT \ln(Z)$	11

^a See Table 1.

For the twelve models in Table 1, there are four different expressions of the monolayer capacity (see Supplementary Material for mathematical derivations).

The monolayer capacities predicted by the models are compared with experimental data (at room temperature) for hydroxyl accessibility using deuterium exchange. In these experiments, wood is exposed to an excess of D₂O and the number of accessible hydroxyl groups in the wood cell wall (sorption sites) can be determined by the increase in dry mass. Deuterium exchange measurements have been performed on both spruce and beech, although there is more available literature data for spruce [84–87].

2.4.2. Relative amounts of primary and secondary water

The partitioning between primary and secondary water varies across the different parabolic sorption isotherm models. The models are classified into three groups given in Table 3 (see Supplementary Material for mathematical derivations). The symbols u_1 and u_2 denote the equilibrium moisture content (g g⁻¹) of primary and secondary water, respectively. The values predicted by the models are compared with experimental data from QENS [88] and 2D low-field NMR [89].

2.4.3. Differential enthalpy of sorption

Several of the original papers describing parabolic sorption isotherm models in Table 1 relate model parameters to thermodynamic quantities, such as enthalpies or free energies. To facilitate comparison with measured values, we derive the differential enthalpy of sorption for these models as a function of moisture content, from the contributions of primary and secondary water.

First, a subset of the models equates certain parameters to enthalpies of primary and secondary water, as listed in Table 4. At a given temperature, the BET, Anderson, and de Boer models (1, 5, and 7 in Table 1) assume that the enthalpy of each type of water is independent of moisture content. The equations for the molar enthalpy of sorption are

summarized in Table 4, where $\Delta H_1(T)$ refers to primary water (relative to pure liquid water) and $\Delta H_2(T)$ refers to secondary water (relative to pure liquid water). These model values can be identified directly by fitting sorption data at a single temperature. Mathematical derivations are given in the Supplementary Material.

Second, we consider models that equate parameters to Gibbs energies of primary and secondary water, as listed in Table 5. At constant temperature, the Anderson, Dent, and HH models (1, 8, and 11 in Table 1) assume that the molar Gibbs energy of each type of water is independent of moisture content. The expressions for the molar Gibbs energy of sorption are summarized in Table 5, where $\Delta G_1(T)$ refers to primary water (relative to pure liquid water) and $\Delta G_2(T)$ refers to secondary water (relative to pure liquid water). Anderson [34] states that the thermodynamic parameters could represent either enthalpy or free energy, hence the expressions in both Tables 4 and 5.

The molar enthalpy of sorption for primary and secondary water can be determined from the temperature dependence of the respective ΔG values [29,32]. After a given isotherm model has been fit to experimental vapor sorption data acquired at multiple temperatures, the value of ΔH for each type of water can be determined from the slope of a plot of $\Delta G/T$ versus $1/T$. Details are given in the Supplementary Material.

The differential enthalpy of sorption, $\Delta_{\text{sorp}}h$ (J mol⁻¹) or $\Delta_{\text{sorp}}h$ (J g⁻¹), is the difference in enthalpy between water in wood at equilibrium moisture content u and pure liquid water at the same temperature. The differential enthalpy of sorption is also known as the net isosteric heat of sorption (but opposite in sign). For each sorption isotherm model, the differential enthalpy of sorption as a function of moisture content can be expressed in terms of the contributions of primary and secondary water:

$$\Delta_{\text{sorp}}h(u) = \Delta h_1 \frac{du_1}{du} + \Delta h_2 \frac{du_2}{du} \quad (4)$$

$$\frac{du_1}{du} = \frac{du_1}{da_w} \frac{da_w}{du} \quad (5)$$

$$\frac{du_2}{du} = \frac{du_2}{da_w} \frac{da_w}{du} = 1 - \frac{du_1}{du} \quad (6)$$

Eq. (4) was previously given by Skaar [4] for the model of Dent [32], but the details of the derivation were not presented. We provide the mathematical derivation in the Supplementary Material.

The differential enthalpy of sorption was also directly calculated (without the need for a parabolic fit) from the Weichert [82] sorption isotherm data using the Clausius-Clapeyron equation. In this method, the natural logarithm of the water activity required to achieve a specified moisture content is plotted versus inverse absolute temperature. The differential enthalpy of sorption for a given equilibrium moisture content u can be calculated by:

$$\Delta_{\text{sorp}}h(u) = - \left. \frac{R}{M_w} \frac{\partial \ln(a_w)}{\partial \left(\frac{1}{T}\right)} \right|_u \quad (7)$$

where R is the gas constant (8.31446 J mol⁻¹ K⁻¹), M_w is the molar mass of water (18.01528 g mol⁻¹), and T is the absolute temperature (K). Therefore, the differential enthalpy of sorption calculated from the Clausius-Clapeyron equation uses the exact same sorption isotherm data as the parabolic models listed in Tables 4 and 5. It should be noted that the Clausius-Clapeyron derivation requires interpolation between measured data, which is often obtained from a fit using a parabolic sorption isotherm model. However, the differential enthalpy of sorption can be determined by any appropriate method of interpolation. In the Supplementary Material the interpolation for Eq. 7 is done by linearization, cubic spline fit, and a parabolic fit, and the derived differential enthalpy of sorption does not vary appreciably between these methods. In addition to values derived from the sorption data using the Clausius-

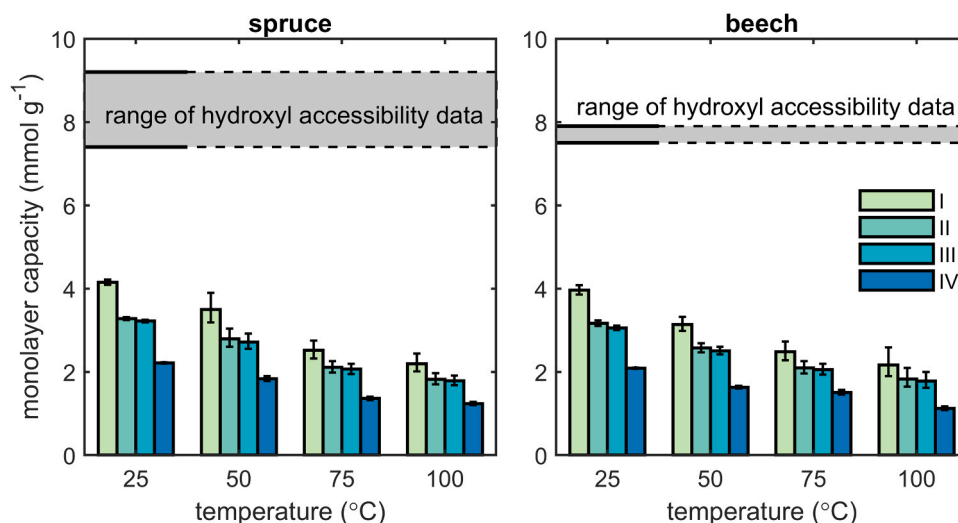


Fig. 2. Predicted monolayer capacity based on fitting models to sorption data for spruce and beech as a function of temperature compared to experimental hydroxyl accessibility data. The four model designations (Roman numerals) refer to Table 2. Error bars were calculated from Monte Carlo simulations accounting for sorption measurement uncertainty (see Supplementary Material).

Clapeyron equation, the model predictions are also compared to sorption calorimetric measurements by Nopens et al. [15]. The “differential enthalpy of sorption” used in this study is equivalent to the “mixing enthalpy” used by Nopens et al.; both are defined relative to pure liquid water and both use the sign convention that an exothermic process has a negative change in enthalpy.

2.4.4. Estimation of uncertainty in predicted physical quantities

The sorption isotherm models yield a prediction of each physical quantity that depends on the fit of the model to the data. It is useful to understand the range of potential values stemming from uncertainty in the measured water activity and equilibrium moisture content. The uncertainty in water activity is governed by the temperature stability during the experiment and the calibration accuracy of the manometer used for measuring water vapor pressure in the vacuum sorption apparatus [76]. Similarly, for the Weichert [82] data, the uncertainty in EMC is determined by the accuracy of the instrument used for measuring specimen mass. Each data point is therefore associated with uncertainties in two dimensions and propagating these to the model fit parameters cannot be done directly.

Uncertainties in predicted physical quantities were estimated using a Monte Carlo simulation method, which created multiple new datasets based on the reported measurement uncertainty in a_w and u . Each new dataset was developed from a Latin hypercube sample [90] using the MATLAB *lhsdesign* function to sample the space between $x - \Delta x$ and $x + \Delta x$, where Δx is the uncertainty in a_w (assuming the measurement uncertainty was uniformly distributed). Similarly, *lhsdesign* sampled the space between $u - \Delta u$ and $u + \Delta u$, and a new associated y value ($y = a_w/u$) was calculated for each x . Each measured data point was sampled N times to generate N sets of simulated data points. Each set was fit as described previously to identify the parameters A , B , and C (Eq. 1). Predicted physical quantities were calculated for each set of fitting parameters. The distributions of model predictions were approximately normal in some cases but were asymmetric in other cases. While it is typical to report a 95% coverage interval (excluding the lowest 2.5% and the highest 2.5% of values, roughly corresponding to $\mu \pm 2\sigma$ for a normal distribution), in this study we selected a 98% coverage interval. The mean values are reported and error bars are thus selected based on the 1st percentile and 99th percentile values. For all cases $N = 10^4$ simulated datasets were fit. We found that increasing N to 10^6 did not appreciably change the uncertainty in model parameters or model predictions (see Supplementary Material).

The measurement uncertainty in the Weichert [82] data is appreciably smaller than most other studies in the literature [76]. Therefore, we included Monte Carlo simulations with tripled uncertainty to also derive model predictions based on measurement uncertainties that are more common in the literature. The details of these simulations and the predictions can be found in the Supplementary Material.

3. Results and discussion

3.1. Monolayer capacity

Fig. 2 shows the predicted monolayer capacity for the four model designations in Table 2 at four different temperatures for beech and spruce wood from the data of Weichert [82]. At 25 °C, the predicted values fall between about 2 and 4 mmol g⁻¹. Although the monolayer capacities appear to be similar across the models, their predictions vary by 18–24% around the grand mean, excluding the models with constrained fitting parameters, i.e., the BET and Cassie models (5 and 6, respectively, in Table 1). This variation in monolayer capacity predictions is caused solely by the different thermodynamic assumptions across models and not data or curve fitting, since these were calculated from the same parabolic fit to sorption isotherm data of the highest quality.

The monolayer capacities predicted from the models are compared with experimental data (at room temperature) for hydroxyl accessibility in Fig. 2. The hydroxyl accessibility measurements are much (2–5 times) higher than the monolayer capacity values predicted by the parabolic sorption isotherm models. Even for a tripled measurement uncertainty, the error bars designating the span from the 1st to the 99th percentiles do not cover the experimentally determined hydroxyl accessibility (see Fig. S5 in the Supplementary Material).

From Fig. 2 it is clear that the mean values of the monolayer capacity greatly under-predict the hydroxyl accessibility of the wood cell wall. In fact, the difference between the model predictions and measured values is worse than it appears in Fig. 2. The experimentally determined hydroxyl accessibility is lower than the actual concentration of water-accessible hydroxyls because not all of the accessible hydroxyls on cellulose microfibrils can be deuterium exchanged [91]. Thybring et al. [84] have estimated that the amount of this underestimation in Norway spruce is 0.7 mmol g⁻¹.

Finally, it should be noted that the models predict a different monolayer capacity at each temperature. While experimental data on

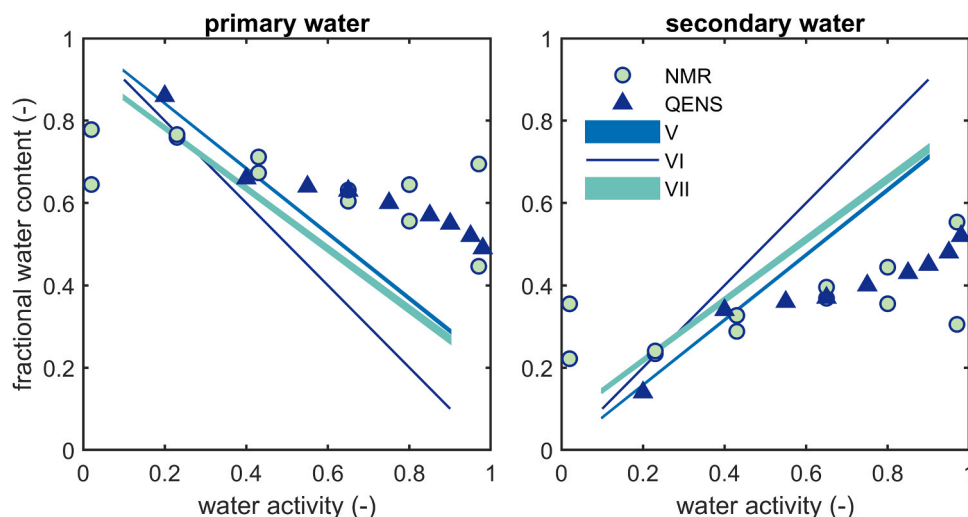


Fig. 3. Predicted fraction of primary (left) and secondary water (right) as a function of water activity based on fitting models to sorption data for spruce at 25 °C. Roman numerals refer to Table 3. Experimental data for more confined and less confined sorbed water in Douglas fir from 2D low-field NMR relaxometry [89] and water with fast and slow dynamics from quasielastic neutron scattering (QENS) on loblolly pine [88] are included for comparison.

hydroxyl accessibility of wood cell walls only exist at room temperature, it is worth noting that there is no physical reason why there should be fewer available hydroxyls at higher temperatures. In other words, the fact that the monolayer capacity decreases with increasing temperature is contrary to the physical picture behind the models. In fact, even Guggenheim [33] criticized the BET model for predicting a temperature dependent monolayer capacity, despite the fact that his own model also contains this dependence.¹

While the wood material differs appreciably from the planar surfaces for which the BET and GAB models were derived, it is unlikely that the number of sorption sites decreases with increasing temperature. If anything, one may expect the number of sorption sites to increase because as the temperature increases, the polymers will have more molecular motions and thus free volume [16]. This free volume could potentially result in more sorption sites becoming available. As an example of this, the accessibility of sorption sites in the polymer Nylon 6 has been found by deuterium exchange to increase with increasing temperature [92].

In summary, the monolayer capacity predictions from parabolic sorption isotherm models are inconsistent with measured data and the temperature dependence of wood polymers. These predictions, though often reported, cannot be physically correct.

3.2. Relative amounts of primary and secondary water

In Fig. 3 we compare the amounts of primary and secondary water predicted by the models to the results of 2D low-field NMR and QENS measurements. Although the techniques are quite different and are measuring different characteristics of water in wood cell walls, they yield similar partitioning between the two types of water, especially when the water activity is between 0.2 and 0.8. On top of these measurements, we plot (as lines) the predictions for primary and secondary water from the parabolic sorption isotherm models. Visually, it appears that the model predictions do not match the measured data for $a_w > 0.5$.

¹ Guggenheim's words: "According to the model for which all these formulae have been derived we expect the parameter v_m to be independent of the temperature. We must mention here that Brunauer has expressed the contrary view that v_m varies at the two thirds power of the density of the liquid adsorbate. The author is completely at a loss to understand this view. All the B.E.T. formulae have been derived, and can only be derived, from a model of the surface having a definite number N_s of adsorption sites."

Even for a tripled measurement uncertainty, the 1st to the 99th percentile span of the model predictions does not match the measured data (see Fig. S6 in the Supplementary Material).

Therefore, it must be concluded that the predicted amounts of primary and secondary water from the models do not match the populations of water that have been measured experimentally in wood cell walls. It should be noted that the 2D low-field NMR and QENS measurements did not directly associate these two populations of water with primary and secondary water predicted by isotherm models. However, if multiple populations of water can be measured in wood cell walls, then this should be captured by the sorption isotherm models. Because the predicted fractions of primary and secondary water do not match measured values, one must conclude that the physical systems presented by the models cannot describe the state of water in wood cell walls.

3.3. Differential enthalpy of sorption

The differential enthalpy of sorption derived by the Clausius-Clapeyron equation, Eq. (7), from the temperature dependency of the sorption data is plotted in Fig. 4a. Although the derivation involves interpolation between data points to arrive at enthalpy values at specific moisture contents, the derivation was stable to the choice of interpolation method (linear, cubic spline, parabolic fit) as seen in Fig. S7 in the Supplementary Material. Fig. 4a also plots experimentally determined values of the differential enthalpy of sorption from sorption calorimetry by Nopens et al. [15]. These data of Nopens et al., taken on beech and pine, are direct measurements of the heat released by the sorption process starting from the dry condition. A good correspondence is seen in Fig. 4a between the differential enthalpy of sorption derived by Eq. (7) and the sorption calorimetric measurements. These experimental results (via Clausius-Clapeyron Eq. 7) are compared with the model predictions of the differential enthalpy of sorption (via parabolic fits and Eq. 4) in Fig. 4b and c. From these figures it is clear that the parabolic sorption isotherm models greatly underestimate the differential enthalpy of sorption that is derived directly from the temperature dependence observed in the sorption isotherm data.

The models that predict the differential enthalpy of sorption from sorption data at a single temperature (Fig. 4b and Table 4) exhibit lower variability than the models that derive it from the temperature dependence of the Gibbs energy (Fig. 4c and Table 5). Thus, even though the latter models utilize the same temperature dependence of the sorption data as the Clausius-Clapeyron derivation with Eq. 7, they are unable to

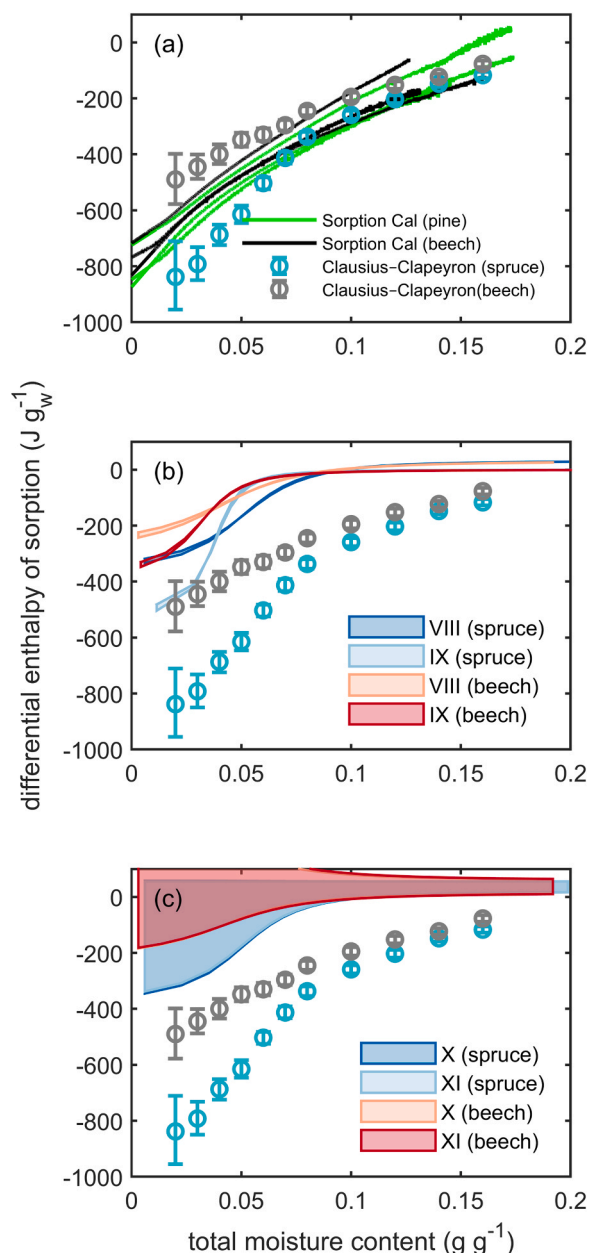


Fig. 4. Differential enthalpy of sorption vs. total moisture content. (a) Experimental data from sorption calorimetry [15] and derived from the data of Weichert [82] with the Clausius-Clapeyron equation, Eq. (7), using linear interpolation between data points. Multiple lines for sorption calorimetry represent replicates. (b) Model predictions calculated directly from fits to the data of Weichert [82] at 25 °C. Roman numerals refer to Table 4. (c) Model predictions calculated from fits to the data of Weichert [82] using the Gibbs energy at four temperatures. Roman numerals refer to Table 5. Shaded regions in (b) and (c) represent the range from 1st to 99th percentile values.

predict the differential enthalpy of sorption. In fact, the span in predictions of the latter models is so wide that the 99th percentile values are positive, as shown in Fig. 4c. When the measurement uncertainty is tripled, the variability of both types of models increases (see Fig. S8 in the Supplementary Material). Under these large uncertainty conditions, the 1st percentile values of the model predictions derived from the Gibbs energy come in range of the values derived by Eq. 7 and experimentally measured. At the same time, however, the 99th percentile values extend far above zero, reaching (positive) values in the range of 480–760 J g_w^{-1} at low moisture contents, making the predictions essentially worthless. This illustrates the sensitivity of these model predictions to

measurement uncertainty.

For many years, it has been known that some discrepancies in thermodynamics existed between sorption isotherm models and measured data. For example, Simpson [29] compared the differential enthalpy of sorption from various sorption isotherm models against measured data and found that the models, in general, under-predicted the enthalpy in the dry state. However, the analysis of Simpson [29] did not examine the trends in the differential enthalpy of sorption as a function of moisture content. The data presented in Fig. 4 provide a much more convincing argument that these models cannot correctly predict the differential enthalpy of sorption. Not only are the magnitudes of the model predictions incorrect, but the moisture content dependence of the models does not follow the same trends as measured data. Therefore, it must be concluded that the models do not yield meaningful information about the thermodynamics of the water sorption process in wood.

4. Conclusions

Sorption isotherm models have previously been derived based upon an idealized physical system representing vapor adsorption on a solid surface or vapor absorption in polymeric materials. In the literature these models have often been applied to predict physical quantities related to wood-water interactions. Several of the most popular models used in wood science, namely the Guggenheim-Anderson-de Boer, Hailwood-Horrobin, and Dent sorption isotherm models, can be rearranged into the same mathematical form using algebraic transformations. While mathematically equivalent, these models predict (1) different monolayer capacities, (2) different relative amounts of primary and secondary water, and (3) different values for the differential enthalpy of sorption. It logically follows that at most one of these models can be physically valid. However, we compared the model predictions against independently measured values of these three properties and in all cases the model predictions were far from measured values. Furthermore, we used a Monte Carlo method to propagate the uncertainties in the sorption isotherm data, yet still found that the range of model predictions were outside of the range of measured data. This uncertainty analysis clearly rejects the commonly cited explanation of “data quality” for the disagreement between predicted values and experimental measurements. Thus, the data and analysis presented in this work thoroughly show that physical quantities predicted by parabolic sorption isotherm models are not valid for water in wood cell walls.

This work highlights the need for physical models that correctly account for molecular sorption sites; distinct populations of sorbed water; and the heat of interaction between moisture and wood, which varies non-linearly with moisture content. Additionally, valid physical models would elucidate the role of moisture-induced swelling, glass transition of amorphous polymers, and the phenomenon of sorption hysteresis.

The approach developed in this study is broadly applicable for testing sorption isotherm models for natural polymeric materials such as wood, plant-based foods, and textiles, as well as synthetic polymers.

CRediT authorship contribution statement

Emil E. Thybring: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Visualization, Writing – original draft, Writing – review & editing. **Charles R. Boardman:** Methodology, Formal analysis, Software, Validation, Writing – original draft, Writing – review & editing. **Samuel L. Zelinka:** Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Samuel V. Glass:** Conceptualization, Methodology, Investigation, Formal analysis, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2021.127214.

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