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A method for describing equilibrium moisture content of forest fuels

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The isothermal adsorption and desorption of water vapor by forest fuels is represented with a two-parameter model based on an exponential relationship between Gibbs free energy change and equilibrium moisture content. The model is applied to five sets of sorption data in the literature to illustrate goodness of fit. Two of the data sets are well reproduced by the model; description of the remaining data is less satisfactory. Whether the deviations are due to experimental factors or a deficiency in the model is not determined. At constant temperature, hysteresis ratios tend to increase as percent relative humidity increases.

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Les isothermes d'adsorption et de désorption de la vapeur d'eau pour les combustibles forestiers sont représentés par un modèle à deux paramètres dérivé d'une relation exponentielle entre le changement d'énergie libre de Gibbs et la teneur en humidité à l'équilibre. Le modèle a été vérifié en l'appliquant à cinq ensembles de données de sorption tirés de la bibliographie. Il s'avère adéquat dans deux cas alors que, dans les trois autres, il est moins satisfaisant. Il reste à savoir si les écarts rencontrés sont attribuables à des facteurs expérimentaux ou à une faiblesse du modèle. À température constante, les rapports d'hystérèse tendent à augmenter avec l'accroissement de l'humidité relative.

[Traduit par le journal]

Introduction

Numerous studies have been made of the equilibrium adsorption and desorption of water vapor by various cellulosic materials, including wood and textiles (Stamm and Loughborough 1935; Anderson and McCarthy 1963). Simpson (1973) used a nonlinear regression technique to show that a number of theories of multilayer, or sigmoidal, adsorption can describe sorption data for wood. Similar relationships are obtained for forest fuels (Van Wagner 1972; King and Linton 1963). Simard (1968) mathematically described the equilibrium sorption of moisture by forest fuels with a set of three regression equations applicable to three distinct ranges in relative humidity. A single equation involving five regression constants has been used by others (Van Wagner 1972; Anderson *et al.* 1978).

Curves relating forest fuel equilibrium moisture content to relative humidity at constant temperature (called sorption isotherms) are part of the American (NFDRS) and Canadian systems of fire-danger rating (Deeming *et al.* 1977; Van Wagner 1974). In both of these systems, equilibrium moisture content is an indicator of the moisture content of fine surface fuels (Van Wagner 1975). However, the NFDRS fine fuel moisture relationships are based on data for wood (Deeming *et al.* 1977). Information is needed for improving estimates of fuel moisture in the surface litter through which most forest fires spread.

An illustration of the need for estimation accuracy is given

by Anderson *et al.* (1978). They point out that an estimate of moisture content 3–4% below the actual moisture content can cause a 100% error in the NFDRS ignition component, and thus adversely affect a control unit's plan of action. This difference of 3–4% can be due to sorption hysteresis² or differences in fuel species (Van Wagner 1972). Because of uncertainties caused by hysteresis and fuel differences, there is a need to refine estimates of equilibrium moisture content for various fuels, and to note differences in sorption owing to these effects. This paper reports a model sorption isotherm that can be used in research studies to describe sorption data for forest fuels. Comparisons are made between model values and experimental moisture content data reported by others to demonstrate the utility of the model and goodness of fit. In addition, there is discussion of the variability in the sorption model parameters and in ratios of adsorption moisture content to desorption moisture content at several values of relative humidity and constant temperature. These ratios are hereafter called hysteresis ratios. Sorption differences caused by temperature differences have been described briefly by Anderson *et al.* (1978); they are not considered in the present study.

Methods

The model for describing the experimental data has been used to

²This term refers to the fact that the amount of water held by forest fuels at a given temperature and relative humidity depends on the direction from which equilibrium is approached.

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TABLE 1. Isotherm parameters computed from data for sorption of water vapor by several forest fuels at constant temperature according to [1]

Fuel and sorption type	Temperature (°C)	A	B	r ²	Maximum residual in m ^o
Slash pine					
Adsorption	26.7	4.745	-15.495	0.971	0.0160
Desorption		5.176	-14.379	0.991	0.0109
Southern red oak					
Adsorption	26.7	4.644	-13.730	0.961	0.0204
Desorption		4.898	-11.652	0.976	0.0206
Wiregrass					
Adsorption	26.7	4.585	-16.690	0.974	0.0144
Desorption		4.673	-13.893	0.982	0.0150
Hardwoods					
Adsorption	26.7	5.481	-21.412	0.994	0.0060
Desorption		5.357	-16.630	0.993	0.0072
Ponderosa pine					
Adsorption	23.9	5.130	-20.697	0.999	0.0018
Desorption		5.252	-18.353	0.999	0.0018

^aAbsolute values are given here.

represent sorption data for wood and cotton (Nelson 1983). A key to the model's utility is the approximately exponential relationship between the change in Gibbs function of the adsorbed water and equilibrium moisture content. The change in Gibbs function, denoted here by ΔG , is a thermodynamic variable which represents the change in free energy taking place when a unit mass of liquid water is adsorbed by a mass of cellulosic material so large that the moisture content of the material remains essentially unchanged (Stamm and Loughborough 1935). Units for ΔG are cal/g (1 cal = 4.1868 J). The exponential relationship may be expressed in linear form as

$$[1] \quad \ln \Delta G = A + B m = \ln \Delta G_0 + B m$$

where m is the fractional moisture content (g/g) on an oven-dry weight basis, B is a constant with units of reciprocal m , and A is the value of $\ln \Delta G$ when $m = 0$. Generally, [1] applies over a range in relative humidity from about 10 to 90% for sorption by wood and cotton, and similar behavior occurs for forest fuels. The sorption isotherm is obtained by eliminating ΔG between [1] and the thermodynamic relation

$$[2] \quad \Delta G = - \frac{RT}{M} \ln \frac{H}{100}$$

where R is the universal gas constant (1.987 cal/mol K), T is absolute temperature (K), M is the molecular weight of water (18 g/mol), and H is percent relative humidity. Use of [2] involves the assumption that water vapor is an ideal gas. The isotherm is

$$[3] \quad m = \frac{1}{B} \ln \left(- \frac{RT}{M \exp(A)} \ln \frac{H}{100} \right)$$

where A and B must be evaluated from sets of m and H data at a constant value of T . Variation in A and B with T is not considered here.

Sorption data reported in the literature were used to test the model. Moisture content at selected values of H were scaled from graphs of isotherms reported by Blackmarr (1971) for needles of slash pine (*Pinus elliotii* Engelm.), leaves of southern red oak (*Quercus falcata* Michx.), and wiregrass (*Aristida* spp.). Data of Van Wagner (1972) for litter of Canadian hardwoods (representing average values for trembling aspen (*Populus tremuloides* Michx.) and sugar maple (*Acer saccharum* Marsh.)) were obtained in a similar manner. Actual values of m and H for ponderosa pine (*P. ponderosa* Dougl. ex Laws.) needles were taken from a report by Anderson *et al.* (1978).

The data were used in [1] and [2] to evaluate constants A and B by linear regression. These constants were substituted into [3] and values of m from the equation plotted against H . The experimental data also

were plotted for purposes of comparison. Residuals (defined as the experimental m minus the model m) were computed to indicate the goodness of fit.

In addition, hysteresis ratios were examined for each set of experimental data by dividing the adsorption moisture content by the desorption moisture content (at fixed H) for all available values of H . H ranged from about 10 to 90%.

Results

Sorption isotherm parameters for the fuels studied are given for both adsorption and desorption (Table 1). The values of r^2 indicate that more than 90% of the variability in $\ln \Delta G$ from [1] is explained by variation in m . The isotherm parameters A and B vary for adsorption and desorption within a given fuel type. Generally, this variation is due to hysteresis. However, the Van Wagner (1972) data for hardwoods show A for adsorption exceeding that for desorption. Such a result is not usually observed and may be due to experimental difficulties or approximations made in development of the model. Absolute values of the maximum residual for each data set also are shown in Table 1. The model does not describe the data for southern red oak well. Residuals of 2% moisture content are noted for this fuel type. Relatively large errors are associated with the data of Blackmarr (1971) reported in this study. These errors may be due to deviations from [1] or to some experimental factor.

Adsorption and desorption isotherms associated with the parameters in Table 1 are shown in Fig. 1. In most cases, the large errors in modeling the slash pine and red oak data appear to be about the same as error introduced by neglecting hysteresis effects. However, modeling of the hardwoods and ponderosa pine data is better, as indicated by lower residuals (Table 1).

The model curves in Fig. 1 tend to intersect the H axis at nonzero values of H . This failure to pass through the origin is caused by the tendency of ΔG in [2] to approach infinity as H approaches zero, whereas the finite value of A in [1] gives finite values of ΔG when $m = 0$. This inconsistency in the model equations causes deviations from the experimental values for m , as is evident in Fig. 1. However, for practical purposes, $m = 0$ when $H = 0$.

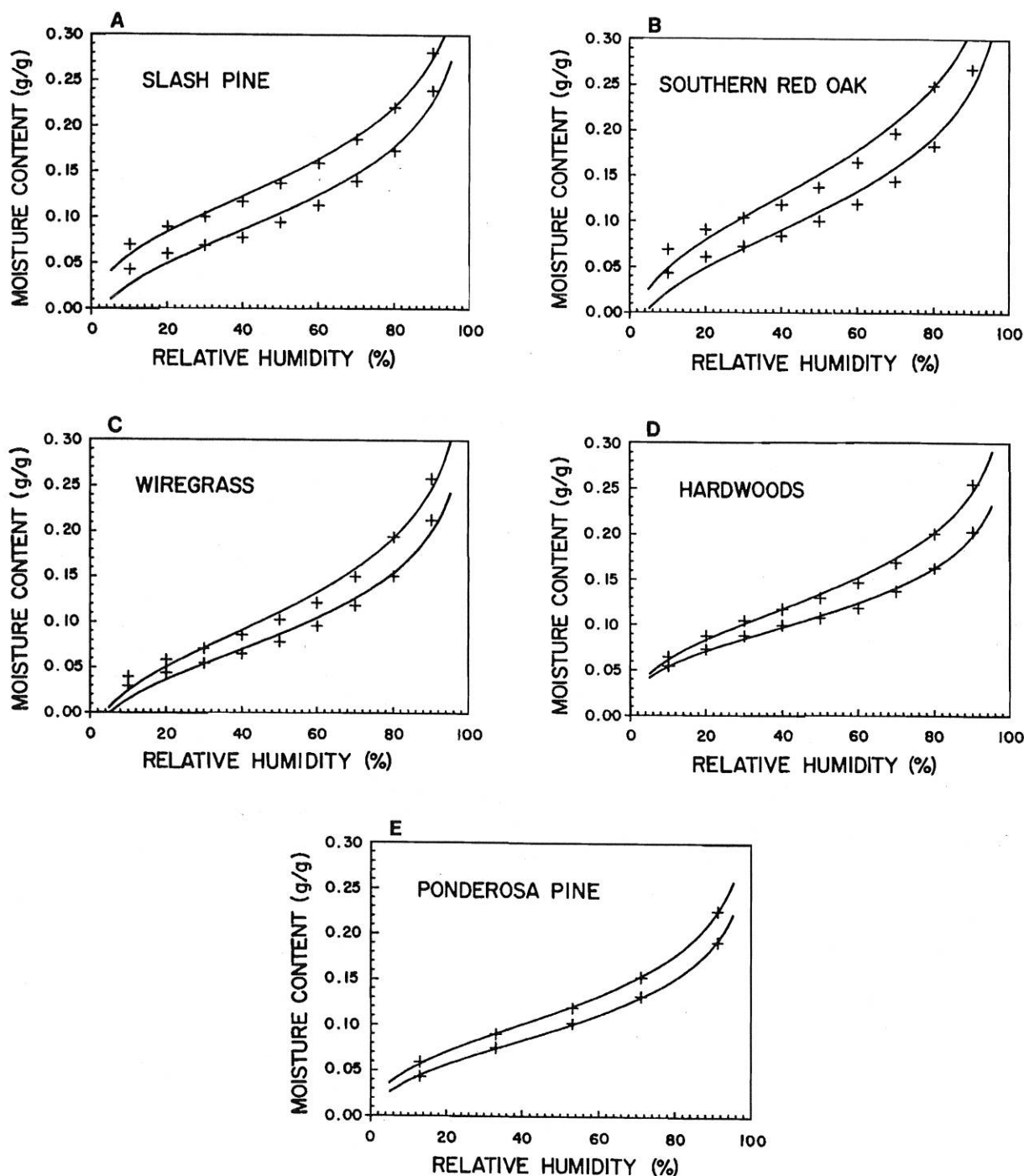


FIG. 1. Model representation of adsorption and desorption data for five forest fuels and temperatures given in Table 1. Upper curves are for desorption and lower curves for adsorption. The line represents model calculations; + represents experimental data.

The experimental sorption data were used to investigate variation in hysteresis ratio with H . Except for hardwood litter, the results in Table 2 indicate that the ratio increases as H increases. This result was noted earlier by Anderson *et al.* (1978). Hysteresis ratios for the hardwoods are roughly constant up to $H \approx 50\%$ and then begin to decrease. Stamm (1964) found that hysteresis ratios for wood, cotton, and other cellulosic materials increase gradually from about 0.80 to 0.85 as H increases from 10 to 95%. For the forest fuels of this study, the increase is much more pronounced. A possible explanation is that these fuels contain extractives which are more strongly

hygroscopic than those of wood and the other materials. However, this has not been demonstrated.

Application of the model

According to [3], two parameters must be known to describe a set of adsorption or desorption data at a fixed temperature. A useful application of the model is the mathematical representation of a number of data points or estimation of missing values when only two or three data points are available. First, temperature and relative humidity data are used in [2] to obtain values of ΔG . Next, $\ln \Delta G$ values and their corresponding mois-

TABLE 2. Experimental hysteresis ratios as affected by relative humidity for sorption of water vapor by several forest fuels

Fuel type	Relative humidity (%)								
	10	20	30	40	50	60	70	80	90
Slash pine	0.612	0.674	0.690	0.665	0.689	0.710	0.751	0.784	0.852
Southern red oak	0.623	0.670	0.699	0.712	0.730	0.726	0.733	0.733	0.817
Wiregrass	0.746	0.754	0.775	0.759	0.762	0.788	0.787	0.777	0.825
Hardwoods	0.844	0.833	0.840	0.847	0.829	0.809	0.814	0.811	0.795
Ponderosa pine ^a	0.769	0.802	0.818	0.828	0.836	0.842	0.848	0.853	0.860

^aHysteresis ratios are based on model values of moisture content instead of experimental values to facilitate comparisons over a range in H from 10 to 90%.

ture content are substituted into [1] for evaluation of the parameters A and B . If only two data points are available, the two algebraic equations can be solved. If a number of points are available, A and B can be determined either by linear regression or inspection of a plot of the data according to [1]. Substitution of A and B into [3] gives a mathematical representation of the data.

Discussion

The isothermal sorption of water vapor by litter of several forest fuels has been described using a two-parameter model. Some of the sorption data are reproduced well by the model, but other data are not. It is likely, however, that the model can provide useful estimates of equilibrium moisture content for work in forest fire behavior and fire danger rating.

The large variability in the sorption parameters of Table 1 and the hysteresis ratios of Table 2 was not expected. Some of the differences may be attributed to varying amounts of oils, waxes, or other extractives in forest fuels which could cause variations in sorption characteristics. Also, there is uncertainty whether moisture content was determined when the samples were in equilibrium with their environments. The values of A and B in Table 1 indicate that grouping of fuel types according to values of these sorption parameters may not be feasible. Also, the large changes in hysteresis ratios with changes in relative humidity shown in Table 2 seem to preclude use of a constant ratio for computing adsorption equilibrium moisture content from desorption values. However, the present tests cover a limited number of fuels and were obtained by different experimental methods. These tentative conclusions concerning sorption model parameters and hysteresis ratios should be verified on a large number of fuels with the same experimental method; they do not detract from the model as a means of fitting experimental data with a mathematical expression.

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