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ENVIRONMENTAL STUDIES

Precision and bias of carbon storage estimations in wetland and mangrove sediments

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Peaty sediments in coastal wetlands play an important role in the sequestration of atmospheric carbon dioxide and its belowground storage. Sediment cores are used to quantify organic matter (OM) density, estimated by multiplying the bulk density of a core segment by its OM fraction. This method can be imprecise, as repeated samples often differ widely. Recent studies have shown that sediment bulk density and OM fraction are not independent but tightly related by a function called the ideal-mixing model. Thus, the bulk density of the sediment can be directly estimated from its OM fraction. Statistical theory and simulations demonstrate that the high variance in the product estimation of OM density is the result of error propagation in the product of two functionally related variables with independent errors. Estimating OM density in wetland sediments using the ideal-mixing model is more precise than the traditionally used product estimate, especially in highly organic sediments.

INTRODUCTION

In recent years, a large number of studies have highlighted the importance of peaty sediments in coastal lagoons, especially under mangrove forests, for the sequestration of atmospheric CO_2 and subsequent storage as organic matter (OM) buried in the sediments. The relevance of this process in the balance of atmospheric greenhouse gasses and the mitigation of climate change is potentially very high. To assess buried carbon storage, sediment cores are often used to quantify the carbon density (i.e., the mass of carbon in a unit volume of sediment) of a given sediment layer. Carbon density (CD) in a core segment is estimated by multiplying the bulk density (b) of the core segment times the relative carbon content of the sample, also known as carbon fraction (1). Carbon fraction (c) can be estimated with an elemental analyzer (provided carbonates are removed first by HCl fumigation), or by estimating OM fraction (o) by loss-on-ignition, i.e., the percentage mass that is lost after high-temperature treatment in a muffle furnace. Both values can be converted if a conversion factor has been calibrated for those sediments, whose value in mangroves is usually close to 2.2 (2). Thus, $\widehat{CD} = bc$, or, alternatively, $\widehat{CD} = bo/2.2$. Conversely, the density of OM (OD) is estimated as

$$\widehat{OD} = bo \tag{1}$$

Most studies estimating carbon stocks in coastal wetlands, or "blue carbon," multiply the bulk density of the core by its OM fraction to obtain an estimate of OD.

Recent studies (2–6), however, have found that in wetland and tropical mangrove sediments, bulk density and OM fraction are not independent but, rather, tightly related by a mathematical function that has been well known in soil science for over half a century (7, 8) and called by some researchers (4–6) the "ideal-mixing model." The name derives from the model's central assumption of "ideal mixing" implying that, in a binary mixture of different particle types, each particle type does not disturb the packing of the other particle type (9). The ideal-mixing model describes an inverse functional relationship between soil bulk density and OM fraction, under the assumptions that (i) the bulk densities

of pure OM and pure mineral matter are constant and that (ii) in a mixture, the volumes occupied by the organic and mineral components are additive (7, 8). If the OM fraction, i.e., the relative mass of OM in a mangrove sediment sample, is defined as o (a proportion that varies between 0 and 1), then the relative volume occupied by OM in a sample is o/δ_p, where δ_p is the self-packing density of pure OM in grams per cubic centimeter. It follows that the relative mass of mineral particles in the sample will be equal to $(1 - o)$, and hence, the relative volume occupied by mineral particles in the sample is $(1 - o)/\delta_m$, where δ_m is the self-packing density of pure mineral sediments. The sum of both components $[o/\delta_p + (1 - o)/\delta_m]$, expressed in cm^3/g, will give an estimate of the volume occupied jointly by the two fractions in a mixture of 1 g. The inverse of this calculated joint volume will yield an overall estimation of the apparent density of the sediment sample containing a proportion o of pure OM and a proportion $1 - o$ of inorganic sediments so that the equation for the ideal-mixing model becomes

$$b_{\text{mix}} = \frac{1}{\left(\frac{o}{\delta_p}\right) + \left(\frac{1-o}{\delta_m}\right)} \tag{2}$$

where b_{mix} is the estimated bulk density of the sample. This equation can also be written as

$$b_{\text{mix}} = \frac{\delta_p \delta_m}{\delta_m o + \delta_p (1 - o)} \tag{3}$$

Because this model assumes that sediment bulk volume equals the summed bulk volumes of organic and mineral components, it also assumes that peat accumulation in the sediment creates a volume expansion of the sediment equal to its own bulk volume (8). Although this hypothesis may not hold strictly in agricultural soils, where soil structure and compaction may vary as a result of farming activities like tilling or trampling by grazing animals, the model has been used with success in large, continental-scale datasets of marshlands and peatlands (2, 4, 5).

One of the most attractive aspects of the ideal-mixing model is that it only has two parameters to be estimated for the fitted function, δ_p and δ_m, which correspond to the bulk, self-packing densities

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of pure peat and pure mineral sediments, respectively. These parameters have a simple and direct ecological interpretation and can be obtained from the literature for the estimation of stored carbon in mangrove sediments. The close relationship between OM fraction and bulk density can be seen in Fig. 1A, for a pooled dataset of mangroves in the Caribbean and Pacific coasts of Mexico and Panama, known as "Costa's dataset" (2). The model, fitted by nonlinear methods, explained 86% of the variation in the data ($r^2 = 0.86$). Likewise, Morris et al. (4) reported a similarly high fit ($r^2 = 0.73$) for the ideal-mixing model on a large dataset of coastal wetlands in the conterminous United States. Similarly, after testing four alternative models, Crnobrna et al. (6) found that the ideal-mixing model produced the best fit (according to the Akaike information criterion) to the relationship between OM fraction and bulk density in tropical peatland soils of the upper Amazon Basin. Although various other empirical functions have been tried to fit this relationship (3, 4, 6), the ideal-mixing assumptions seem to yield, in all published cases, the model providing the best fit in wetland sediments.

The ideal-mixing model in Eq. 3 shows the relationship between bulk density and the OM fraction in the sediment, used as a
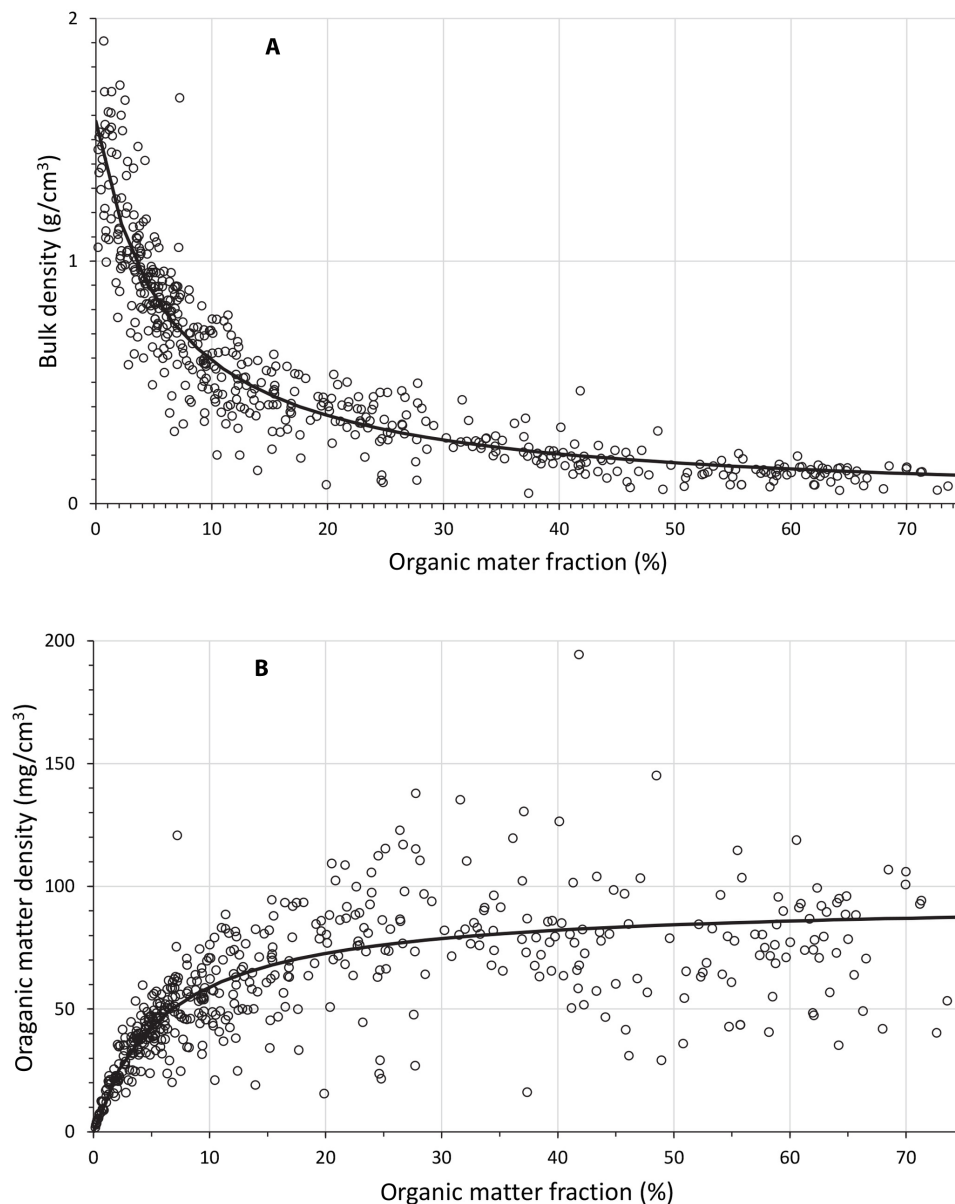

Fig. 1. Propagation of errors in OM density estimation. Gravimetric bulk density measurements yield statistical estimates of total carbon density that are strongly heteroscedastic and show a large dispersion of the data in sediments rich in OM. (**A**) Bulk density versus OM fraction in 496 sediment cores from mangroves in the Caribbean and the Pacific coasts of Panama and Mexico [see (2) for details]. OM fraction predicted 86.1% of the total variation in the bulk density data ($r^2 = 0.861$). (**B**) Despite the close functional relationship between bulk density versus OM fraction, the relationship between OM fraction and OM density (the product of bulk density × OM fraction) showed a high dispersion between the predictions of the ideal-mixing model (black line) and the values calculated using gravimetric estimates of bulk density ($r^2 = 0.315$).

predictor. It is feasible, however, to solve Eq. 3 for OM fraction (o) and perform the opposite calculation, i.e., to estimate the OM fraction of the sediment using the core's gravimetric bulk density as a predictor. Solving Eq. 3 for o, the OM fraction, we get

$$o_{\text{mix}} = \frac{\delta_p(\delta_m - b)}{b(\delta_m - \delta_p)} \qquad (4)$$

where o_{mix} is the OM fraction in the sample estimated from bulk density through the ideal-mixing model. Because the two parameters, bulk density and OM fraction, are so closely related, the latter can conceivably be used to calculate the former or, alternatively, bulk density can be used to estimate OM fraction. Thus, the OM density of the sediments can be calculated in three alternative ways: (i) using the product of both estimated parameters ($\widehat{OD} = b.o$), (ii) using only the estimated OM fraction and calculating bulk density from Eq. 3 ($\widehat{OD} = b_{\text{mix}}.o$), or, alternatively (iii) using only the estimated bulk density and calculating OM fraction from Eq. 4 ($\widehat{OD} = b.o_{\text{mix}}$). We will call these three alternative estimations of OM density (i) the product estimation, (ii) OM fraction estimation, and (iii) the bulk density estimation.

The last two procedures can be written in terms of the ideal-mixing model (Eqs. 3 and 4) to obtain the full equations predicting OM density as a sole function of OM fraction

$$\widehat{OD} = \frac{\delta_p \delta_m \, o}{\delta_m o + \delta_p (1 - o)} \qquad (5)$$

Alternatively, using Eq. 4, it can be estimated as a function of bulk density

$$\widehat{OD} = \frac{\delta_p(\delta_m - b)}{(\delta_m - \delta_p)} \qquad (6)$$

It is interesting to note that, although the ideal-mixing model (Eq. 3) fits the relationship between bulk density and OM fraction very well ($r^2 = 0.861$; Fig. 1A), the OM density values calculated using the product estimation show a poor fit against the OM fraction estimation ($r^2 = 0.315$; Fig. 1B). If the three estimates for Costa's dataset are compared pairwise, some noteworthy patterns can be found (Fig. 2): (i) The slope of the three estimates does not differ significantly from 1 (i.e., the identity function $y = x$). (ii) Pairwise comparisons involving the product estimate have a much higher dispersion than the bulk density estimate plotted against the OM fraction estimate. (iii) Last, the high dispersion in the data points when using the product estimation is not distributed uniformly but tends to be larger in highly organic sediments.

The strong heteroscedasticity (unequal distribution of variances) in the product estimate is conspicuous. The increasing variance of the model residuals with increasing OM fraction in the sediment when using the product estimation of OM density seems to be a serious problem in the assessment of blue carbon densities in coastal wetlands because it increases the experimental error in those sediments that contribute most to the quantification of buried carbon.

The fact that bulk density and OM fraction in mangrove sediments can be so tightly related and yet the product of the two can show such high dispersion in the data when used to predict carbon density (a simple product of both bulk density and OM fraction) may

seem, at first glance, somewhat perplexing. Why is it that two functionally related variables, with independent random errors, increase their dispersion so noticeably when multiplied together? Two possible hypotheses can be proposed to explain this phenomenon. An initial, or null, hypothesis is that wetland sediments are intrinsically highly variable and the high dispersion of the product estimate of OM density reflects a true feature of the sediment samples. An alternative hypothesis is that the high variability observed in OM density samples using the product estimate is the result of sample-error propagation in the statistical product, a conjecture explored (but not demonstrated rigorously) by Sternberg-Rodríguez et al. (2). If this second hypothesis was true, then it would support the use of the ideal-mixing model—a simple, one variable estimator of OM density—over the traditionally used product estimate and could, in turn, transform the way we measure OM density in wetland sediments globally for carbon sequestration and storage estimates.

In this study, we will test the hypothesis that the high variance of the residuals in the product estimate of OM density when compared to the estimates derived from the ideal-mixing model is the result of the way the propagation of errors operates when calculating the product of two functionally related variables with independent random errors. To test this, we will analyze error propagation in the three different procedures that can be used to estimate OM density in wetland sediments: (i) the product estimation (Eq. 1), (ii) the OM fraction estimation (Eq. 5), and (iii) the bulk density estimation (Eq. 6). The propagation of errors for each estimate will be analyzed using two alternative and independent approaches: (i) statistical theory derivations and (ii) numerical simulations.

The theoretical estimation of error propagation is based on Cramér's theorem (10), which states that, given a function F used to calculate the value of a result variable w from two predictor variables x and y, then the variance of w can be calculated from the partial derivatives of F with respect to x and y multiplied by the variances of y and x (see Materials and Methods for a detailed description of the procedure). Cramér's derivation is still the most robust and commonly used approach for the calculation of error propagation in engineering and for instrumentation (11–13).

RESULTS

Propagation of errors using statistical theory
Propagation of errors in the product estimation of OM density
The traditionally used product estimation of OM density is calculated as $\widehat{OD} = bo$. Its partial derivatives are $\partial OD/\partial b = o$, and $\partial OD/\partial o = b$. Following Cramér's theorem, we can apply these derivatives to Cramér's equation (see text S1) to get the following

$$\text{st. err.} (\widehat{OD}) = \varepsilon \, \widehat{OD} \, \sqrt{2(1 + r_{bo})} \qquad (7)$$

where r_{bo} is the correlation coefficient between b and o, and ε is the relative error, or error coefficient, of the sample (i.e., the ratio between the standard error of the sample and its expected value). For simplicity, we are assuming that the relative error of both variables b and o is the same. A full derivation is provided in text S1.

That is, the relative error of calculating OM density through the multiplication of bulk density and carbon fraction is larger than ε, the relative error of each of the intervening variables. This multiplicative effect of the error propagation is buffered in low-carbon sediments by the negative correlation between b and o because, as shown in Fig. 1,
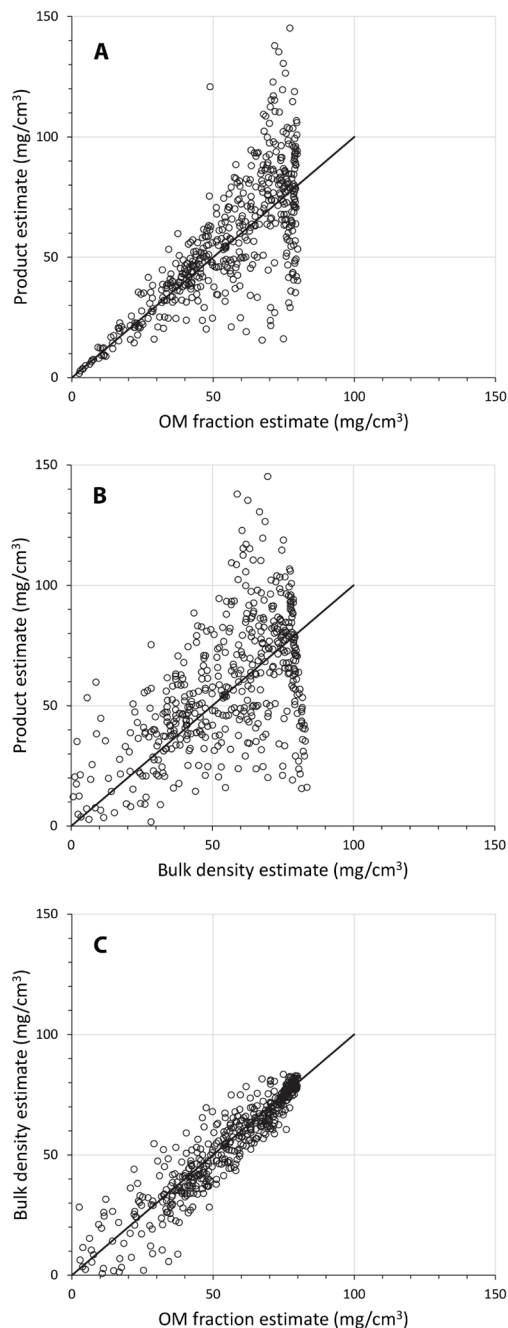
Fig. 2. Dispersal of errors in three alternative estimators of OM density. Pairwise comparisons of the three OM density estimators show the increased dispersion in the estimated values when using the product model: (**A**) product versus OM fraction estimates ($r = 0.75$), (**B**) product versus bulk density estimates ($r = 0.54$), and (**C**) bulk density versus OM fraction estimates ($r = 0.93$). In all three cases, the slope of the major axes fitted to the data cluster did not differ significantly from that of the identity function, marked as a black line, indicating that the three models do not differ in their mean expected values but differ in their residual variation, a measure of precision. A slope test on the residual-versus-predictor regression showed strong and positive heteroscedasticity in plot A ($t = 9.66$, df 494, $P < 0.0001$), suggesting that precision in the product estimation decreases with increasing OM in the sediment. In contrast, both for the OM fraction and the bulk density estimates, precision increased significantly toward the peatier sediments ($t = 9.76$, df 494, $P < 0.0001$ and $t = 6.78$, df 494, $P < 0.0001$, respectively).

at this extreme of the gradient, bulk density and OM fraction have a strong negative slope (with a correlation coefficient in our dataset of $r \cong 0.8$). However, for peaty sediments, with o values larger than 20%, the ideal-mixing model curve becomes near horizontal and the correlation coefficient between bulk density and OM fraction becomes very low, so that in peaty sediments st. err. $(\widehat{OD}) \cong \sqrt{2}\, \varepsilon\, \widehat{OD}$.

Propagation of errors in OM fraction estimation of OM density
If the bulk density of the sediment is estimated from the OM fraction o, then the formula for OM density becomes $OD = b_{mix}\, o$. In this method, the bulk density (b_{mix}) is estimated through the ideal-mixing model (eq. 3). As shown in text S2-a, using the quotient rule, the derivative with respect to o, the predictor variable, is

$$\frac{\partial OD}{\partial o} = \frac{b_{mix}^2}{\delta_m} \tag{8}$$

Now, incorporating this derivative into Cramér's error propagation model, we get (see text S2-b)

$$\text{st. err.}\,(\widehat{OD}) = \varepsilon\, \frac{b_{mix}}{\delta_m}\, \widehat{OD} \tag{9}$$

Note that, as the sediment decreases in OM fraction, its bulk density b_{mix} also decreases because the bulk density of peat-rich sediments is much lower than that of mineral sediments. Thus, the theory predicts that the precision of the ideal-mixing model estimate will increase in OM-rich sediments.

Propagation of errors in bulk density estimation of OM density
Let us now recall Eq. 6, a univariate function that predicts the sediment's OM density solely from its bulk density. The derivative of this equation with respect to b (see text S3-a) is

$$\frac{\partial OD}{\partial b_g} = \frac{-\delta_p}{\delta_m - \delta_p} \tag{10}$$

Inserting this derivative into Cramér's error propagation model (text S3-b), we get

$$\text{st. err.}\,(\widehat{OD}) = \varepsilon\, \frac{b}{\delta_m - b}\, \widehat{OD} \tag{11}$$

In this case, as in the previous one, as sediments become more organic (i.e., when $b \to \delta_p$) the term $\frac{b}{\delta_m - b}$ decreases and the error diminishes. Inversely, as sediments become less organic (i.e., when $b \to \delta_m$), the term $\frac{b}{\delta_m - b}$ increases, and the error expands rapidly.

Precision of the estimators
We have analyzed error propagation in three alternative methods of estimating OM density in a sediment core. The first one, product estimation, uses two sample parameters: bulk density multiplied by OM fraction. The other two methods estimate OM density using only a single parameter from the core sample, either OM fraction or bulk density: The second method estimates OM density by means of OM fraction only, using the ideal-mixing model as a predictor of bulk density. Last, the third method estimates OM density using the core's bulk density as a predictor and calculates OM fraction as a function of bulk density, also using the ideal-mixing model.

The error functions for the three methods (i.e., Eqs. 1, 5, and 6) are plotted together in Fig. 3 as a function of OM fraction, i.e., the "peatiness" of the sediment. The theory predicts that the dispersion
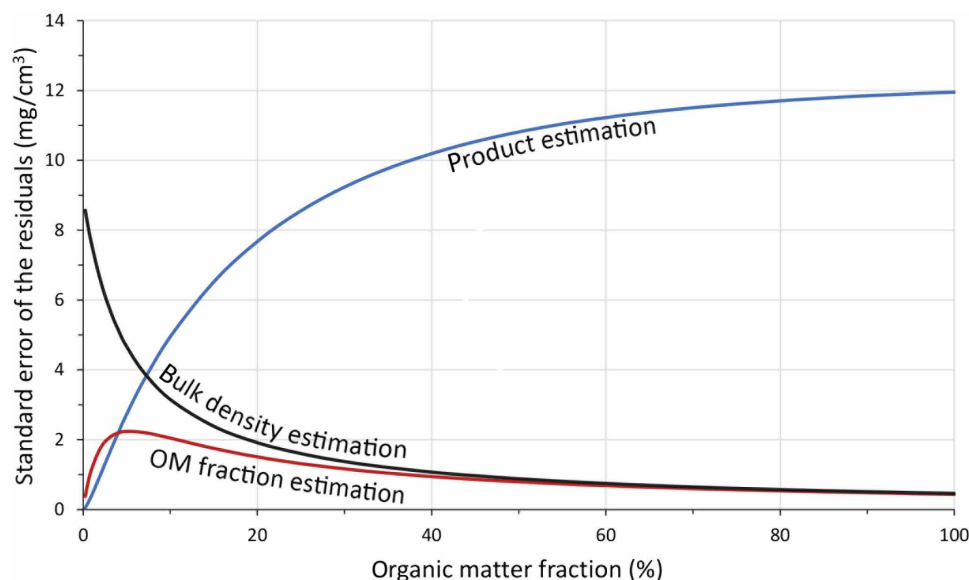
Fig. 3. Theoretical error dispersal in three alternative estimators of OM density. Error functions for the three estimation methods plotted as a function of OM fraction: The predicted dispersion of the residuals increases monotonically in the cross-product model (blue line). Using bulk density alone as a predictor (black line) gives lower errors than the product model for peaty sediments, but its relative error increases rapidly in low-OM sediments. The lowest errors, overall, were predicted when using OM fraction as the predictor of OM density.

of the residuals will increase monotonically in the product estimate, the two-variate model most commonly used in blue carbon computation, as the OM fraction increases. Using bulk density alone as a predictor will give lower errors than the product model for peaty sediments but, when OM fraction is lower than 10%, its relative error will increase rapidly and become much higher than that of the product model. Overall, the lowest errors in peaty sediments were given by the single-variate estimation using OM fraction as the predictor of OM density. Note in the figure, however, that in mineral sediments with less than 4% OM fraction, the theory predicts that the product estimate will work as well as, or slightly better than, the ideal-mixing model estimate based on OM fraction.

These analytical results confirm the empirical findings of Sternberg-Rodríguez *et al.* (*2*) in the sense that estimating OM (or carbon) in peaty wetlands using only OM fraction provides more precise estimations than the product estimation method and opens the door to estimating carbon storage in sediment data that contains OM or carbon fraction but no reliable bulk density estimate.

Numerical simulation

Three approaches were used to calculate the OM density on each core using three different numerical simulations: (i) The first method estimated OM density (OD) using the simple cross-product of the sample's OM fraction × its gravimetric bulk density ($\widehat{OD} = b\,o$). (ii) The second method estimated $\widehat{OD}$ using only the sample's OM fraction and estimating bulk density through the ideal-mixing model, as in Eq. 5. (iii) The last method estimated $\widehat{OD}$ using only the sample's bulk density and estimating the OM fraction through the inverse ideal-mixing model, as in Eq. 6.

In all simulations, the ideal-mixing model fit was used assuming the true values of the parameters had been estimated accurately: $\delta_p = 0.085$ and $\delta_m = 1.65$ g/cm³, i.e., the same parameter values used to generate the simulated sampling data. In the following section,

the problems that arise in the estimation process when these values are not accurately known will be discussed. The results of the three models (Fig. 4) agreed well with the analytical derivations. Although the simulated bulk density followed a close relationship to the OM fraction (Fig. 4A), the dispersion of the residuals was high in the product estimation, which multiplies the estimated bulk density by the estimated OM fraction (Fig. 4B). With this method, the simulated estimate of OM density becomes very imprecise in highly organic, peaty sediments. The estimate based on bulk density only (Fig. 4D) gave lower errors than the product model, especially in peaty sediments, but in low OM fraction sediments, its error increased rapidly. The lowest residual errors around the predicted values, and hence the highest precision, were observed when using the OM fraction as the single predictor of OM density (Fig. 4C).

For statistical comparison of the three graphs (Fig. 4, B to D), the value of each point was decomposed into three variance elements: (i) the sum of the squared differences between each replicate and the mean of the core (i.e., the within core error or "pure error" in statistical terms) (*14*), (ii) the sum of squares of the difference between the mean of each core and the predictions of the ideal-mixing model (i.e., the "lack of fit" error) (*14*), and (iii) the sum of squares of the differences between the predictions of the ideal-mixing model and the overall mean OM density of the whole dataset (the model fit). The results (Table 1) show that (i) the total variance of the simulated data is much higher in the product estimation than in the single-variable estimations and that (ii) the pure error term, or variation between replicates of the same sample, is also much higher in the product estimation, confirming both the predictions of the theory and the trends observed in the graphs.

Accuracy and precision of the estimates

Precision is a measure of how close repeated measurements are to each other. Highly precise measurements are closer together than
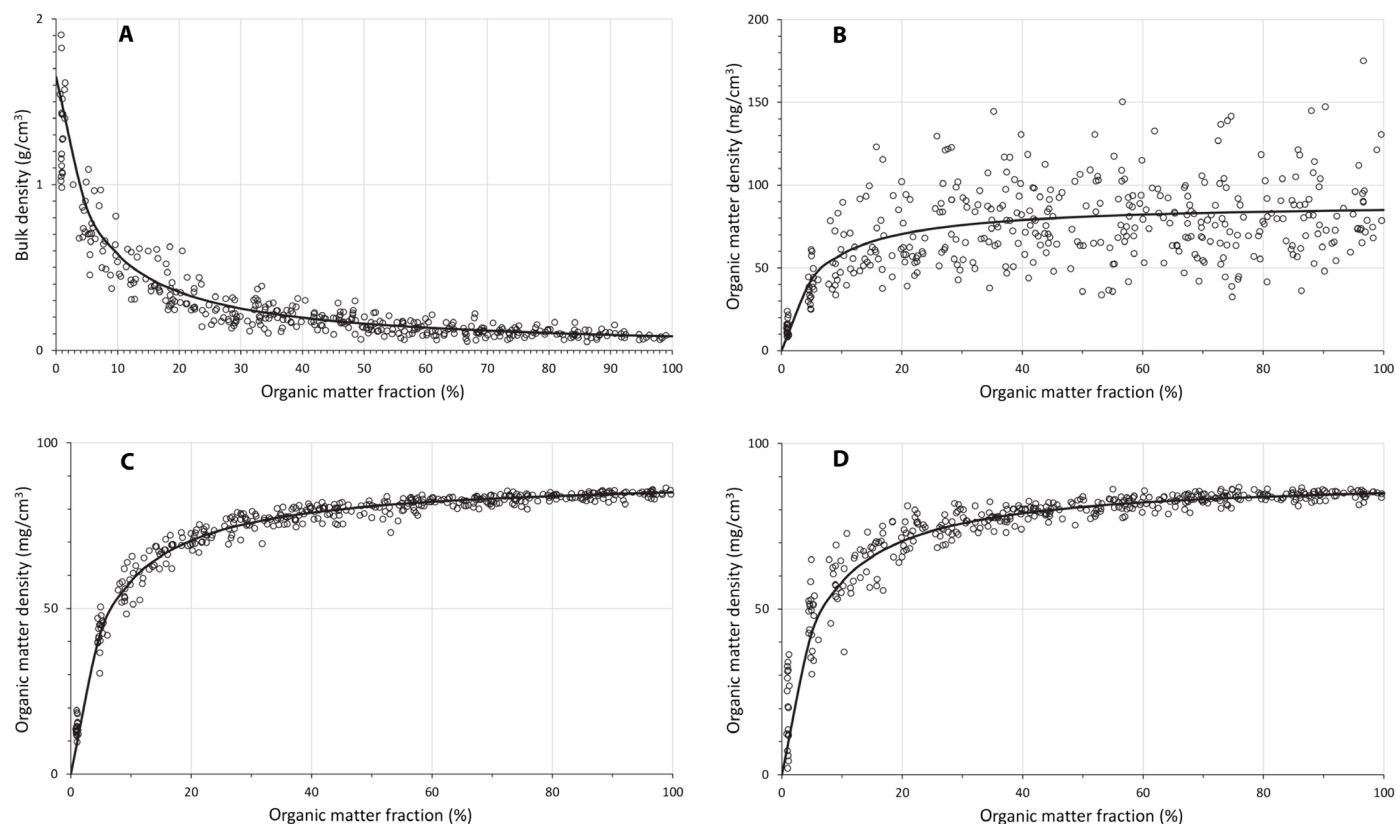
Fig. 4. Numerical simulation of error propagation. Simulated sampling corroborates the error distribution of both observed data and analytically predicted errors. (**A**) Bulk density versus OM fraction in 420 simulated sediment cores ($r^2 = 0.921$). (**B**) Carbon density, calculated as the product of simulated bulk density × simulated OM fraction, showed a high dispersion between the predictions of the ideal-mixing model (black line) and the values calculated using gravimetric estimates of bulk density ($r^2 = 0.303$). (**C**) The dispersion in the simulated data when using only OM fraction as a predictor decreased markedly, showing a high precision of the estimates throughout the range of OM fraction values ($r^2 = 0.976$). (**D**) When using only simulated gravimetric bulk density as a predictor of OM density, the fit to the model was also high ($r^2 = 0.922$) but the dispersion of the estimates increased in sediments low in OM.

Table 1. Decomposition of variances. Sum-of-squares decomposition of the model data is depicted in Fig. 4 (B to D) (see text for a description of how each source of variation was calculated). Because the ideal-mixing model is nonlinear, the variances are only approximately additive, i.e., the total sum of squares is close, but not identical, to the sum of the three sources of variation.

	Cross-product		OM fraction		Bulk density	
	Sum of squares	Proportion of variation	Sum of squares	Proportion of variation	Sum of squares	Proportion of variation
Model	0.1191	0.367	0.1191	0.982	0.1192	0.929
Lack of fit	0.0075	0.022	0.0001	0.001	0.0006	0.005
Pure error	0.2069	0.621	0.0021	0.017	0.0085	0.066
Total	0.3614	-	0.1222	-	0.1291	-

low-precision measurements. The variance of repeated samples, or the sum of the squared residuals of a model, is a measure of statistical precision: the lower the variation, the higher the precision of the estimator. Clearly, of the three methods explored for the calculation of OM density, the single-variable estimation using OM fraction represents the most precise approach. Accuracy, on the other hand, assesses whether a series of measurements are correct on average. It relates to the central tendency, or expected value, of a large number of

measurements and not to their dispersion. If the expected value of the estimates differs from the true value, then the measure is considered inaccurate or biased. Of the three methods used, the two single-variable predictors of OM density depend critically on the a priori estimation of the two parameters of the ideal-mixing model: δ_p, the bulk density of pure peat, and δ_m, the bulk density of pure mineral sediments. Thus, the accuracy of the estimate of total OM and total carbon based on the ideal-mixing model depends very

strongly on the accuracy with which the model parameters δ_p and δ_m are estimated.

The impact of under- or overestimating the ideal-mixing model parameters δ_p and δ_m can also be evaluated analytically following Crámer's theorem (*11*) as was done for the random sampling errors. Calculating the partial derivatives of $\widehat{OD}$ with respect to the ideal-mixing parameters δ_p and δ_m, and plugging these derivatives into Cramér's equation (text S4-a and -b), we can calculate the relative bias (ε_{OD}) in the estimation of $\widehat{OD}$ given certain systematic errors (ε_m and ε_p) in the parameters δ_p and δ_m

$$\varepsilon_{OD} = \frac{\widehat{OD}}{\delta_m}\left(\frac{1-o}{o}\right)\varepsilon_m + \frac{\widehat{OD}}{\delta_p}\varepsilon_p \tag{12}$$

This expression is plotted in Fig. 5A, assuming a 10% bias in the estimates of both δ_p and δ_m. If the relative error of the estimation is the same for both parameters $\varepsilon_m = \varepsilon_p = \varepsilon$, then the equation becomes (text S4-c)

$$\varepsilon_{OD} = \varepsilon\left[\frac{\widehat{OD}}{\delta_m}\left(\frac{1-o}{o}\right) + \frac{\widehat{OD}}{\delta_p}\right] \tag{13}$$

It can be shown (see text S4-d) that the term in parentheses equals one for any value of $\widehat{OD}$, so that the relative error in the estimate of $\widehat{OD}$ is equal to, but never larger than, the bias error in the estimation of δ_p and δ_m.
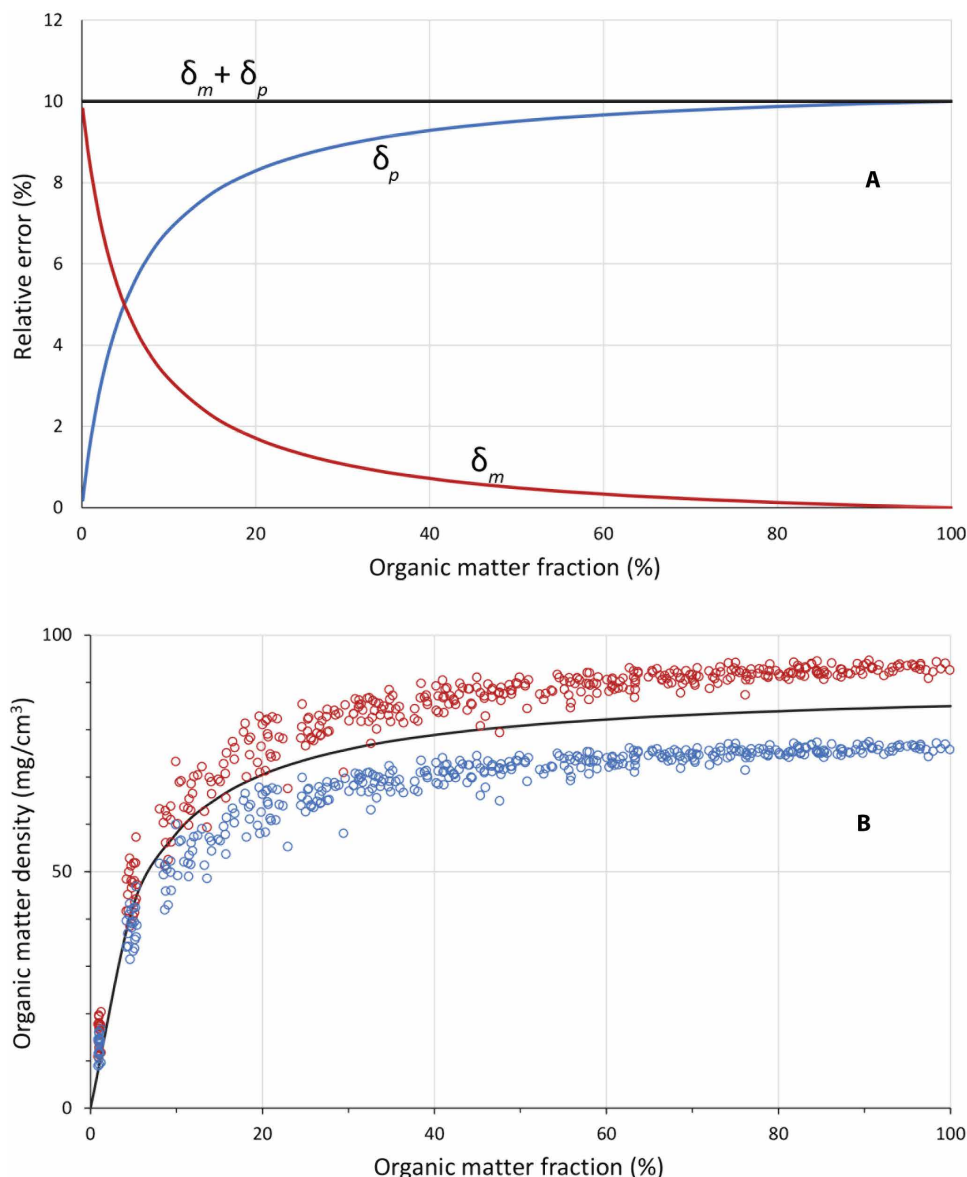

Fig. 5. Precision and bias of the ideal-mixing model. (**A**) Analytically derived relative bias (systematic error as a proportion of the OM density value) given a 10% systematic error in the estimation of the ideal-mixing model parameters δ_p (blue line) and δ_m (red line). The black line shows the additive effect of both errors occurring simultaneously. (**B**) Simulated deviation of the OM density estimates given a 10% overestimation of both δ_p and δ_m (red dots) or a 10% underestimation of both parameters (blue dots).

DISCUSSION

Sediment bulk density and OM fraction are not independent variables; rather, they are narrowly associated by the ideal-mixing model, an inverse nonlinear relationship that depends on two parameters: the self-packing density of OM (δ_p) and the self-packing density of mineral sediments (δ_m). Because of this relationship, the ideal-mixing model provides an alternative to the traditional product estimation of carbon density in wetland and mangrove sediments. As demonstrated in this study, the product estimation commonly used to calculate OM (or carbon) density in sediment can be very imprecise because of the way sampling errors propagate in the product of two variables with independent random errors. Using the product method, repeated sampling of the same core can yield widely different results simply as a result of error propagation in the product of bulk density × OM fraction. In contrast, the estimation of OM density using the ideal-mixing model shows a much higher precision; repeated sampling of the same core will consistently yield similar results, especially in peaty or highly organic sediments.

Apart from the analytical and numerical results shown here, the high precision of the single-variable estimators, especially the OM fraction estimation, can be empirically tested using a simple spreadsheet. Let us assume, for example, a sediment core with an OM fraction $o = 0.40$ (or 40% OM) and a bulk density $b = 0.23$ g/cm^3, with parameter values for the ideal-mixing model $\delta_m = 1.6$ g/cm^3 and $\delta_p = 0.1$ g/cm^3. The product estimate of OM density (Eq. 1) will be 0.092 g/cm^3. Using the ideal-mixing model, the OM fraction estimate (Eq. 5) and the bulk density estimate (Eq. 6) will both estimate 0.091 g/cm^3, very close to the product value. Now, let us assume that the OM fraction has an overestimation error of 10%, so now $o = 0.44$. The product estimate will yield 0.1012 g/cm^3, exactly 10% larger than the true value, but the OM fraction estimate will yield 0.0926 g/cm^3, only 1.3% larger than the true value. If we now assume an overestimation error of 10% for both OM fraction and bulk density, then the product estimate will yield an error of 21%, while the single-variable estimators will yield errors of 1.32% for the OM fraction estimator and −1.68% for the bulk density estimator. That is, the ideal-mixing model tends to dampen any error in the measurement of the predictor variables, especially in peaty sediments. The reason for this lies in the very low slope of the OM density curve when plotted against the OM fraction. Above 30% OM fraction, as the proportion of OM increases, the bulk density decreases and the total carbon density tends to remain relatively constant, around 0.9 g/cm^3. This pattern was first noticed by Holmquist *et al.* (*5*), who noted that, in peaty sediments, as average bulk density increased, average OM fraction decreased, such that the two patterns offset each other and average carbon mass varied little.

This study demonstrates that because of the way statistical errors propagate in the traditionally used product method (multiplying bulk density by OM fraction estimates), the alternative and simpler one-variate ideal-mixing model will yield substantially more precise results. The ideal-mixing model, additionally, has potentially a higher degree of universality because it can allow researchers to use existing databases containing sediment OM or carbon fraction even if no bulk density estimates have been included.

Throughout this study, we have assumed that bulk density and OM fraction samples were measured with similar errors (ε). However, it is well known in soil science that the determination of bulk density from soil core samples is costly, difficult, and time-consuming, and the error in estimating bulk density from standard cores is around four times larger than the error observed in bulk densities estimated from carefully extracted large-diameter sample rings (*15*). Because of the high error and methodological difficulties involved in the accurate estimation of bulk density, soil scientists often resort to estimating it indirectly using a series of empirical functions known as pedotransfer functions (*15*). Because of the large errors involved in the estimation of bulk density from soil cores, it is likely that in reality, the relative errors of the bulk density estimates are larger than those of the OM fraction estimate. If this was the case, then eliminating the need for a bulk density estimate in the calculation of blue carbon stocks would add a strong additional element in favor of the use of the ideal-mixing model.

The results presented here, however, depend critically on the existence of a strong and predictable relationship between OM fraction and bulk density. This relationship has been explored in at least five studies in highly organic sediments (*2*–*6*) and found to be robust, but clearly, more research is needed to confirm its universality. The central assumption of the ideal-mixing model, as proposed by its original developer W. A. Adams (*7*), implies "that the bulk volume of a soil containing organic matter approximates to the summed self-packing volumes of the mineral and organic components." Empirically, published studies have shown this to be generally correct, but, apart from trampling and compaction potentially induced by human activities, other factors could also conspire to break the relationship, such as dissolved organic carbon loss from a site or fine-grained mineral sediment transport into the site. Furthermore, it must be also noted that all the currently published studies using the ideal-mixing model in wetland sediments have been done in mature wetland ecosystems and mangrove forests where, presumably, a relatively stable rate of biomass growth and soil accretion has been attained. Little is known about this relationship in recently restored wetlands, as newly accreted soils with high OM contents require some time for compaction to take place. Researchers using this method in such sites should test the fit of the model to their own OM and bulk density data. Further research may add important information to confirm the universality of the ideal-mixing model. Last, sample depth per se could potentially have an impact on compaction (thus affecting bulk density), as deeper sampling points will have a larger sediment column above them. For sediment samples less than 1 m deep, two studies (*2*, *5*) found no significant effect when testing the ideal-mixing model for an additional effect of depth on the predicted bulk density values. This, of course, does not entirely rule out that deeper samples may show a detectable effect of depth on bulk density, which becomes relevant when assessing stocks at depths greater than 1 m.

Although beyond the scope of this study, it must be noted that there is still considerable uncertainty and potential variability associated with the quantification of OM or organic carbon. There is a risk of losing carbon in the form of CO_2 during the drying of highly peaty samples. If an elemental analyzer is used to measure total carbon, then inorganic forms of carbon need to be eliminated by HCl fumigation; otherwise, the amount of organic carbon in the sample may be seriously overestimated and the ideal-mixing model relationship may be lost. If estimating OM is through loss-on-ignition methods, sizeable errors can be introduced in the OM estimate from incorrect oven temperature, burn time, or individual sample size, as well as clay content-dependent correction factors for structural water loss (*16*). Further research comparing the relative errors and uncertainties in

bulk density and OM fraction estimates could add important points of refinement to the ideal-mixing model approach.

Despite its higher precision, estimating OM density (or carbon density) with the ideal-mixing model is prone to sampling bias. Because the model depends on the parameters δ_p and δ_m (the self-packing density of OM and mineral sediments, respectively), the estimation is sensitive to under- or overestimations of δ_p in highly organic sediments. However, as shown in the preceding section, the bias in the estimation of OM density will never be higher, in relative or proportional terms, than the bias in the estimation of the parameters. The published values for δ_p range from 0.081 to 0.098 g/cm^3 with a mean value of 0.088 g/cm^3, while the published values for δ_m range from 1.575 to 1.990 g/cm^3 with a mean value of 1.745 g/cm^3 (*2–5*). Thus, taking some conservatively low estimates of the self-packing densities of pure peat and pure mineral sediments, say, of 0.08 g/cm^3 for δ_p and 1.6 g/cm^3 for δ_m, to plug into the ideal-mixing model equation will yield very precise and conservative estimations of OM and/or carbon stored in the sediment.

The dilemma in choosing between the two-variate product estimation of OM density against the single-variate prediction using the ideal-mixing model highlights the difference between the statistical concepts of precision and accuracy. Because of error propagation, the product estimation is very imprecise, but because of the need for two external parameters, the ideal-mixing model prediction can be biased if the parameters are not estimated accurately. In quantitative terms, however, the bias of the ideal-mixing model is relatively low compared to the increased precision the model can achieve, and this bias can be managed by choosing realistic and slightly conservative values for the two intervening parameters: the self-packing density of pure peat (δ_p) and that of pure mineral sediments (δ_m).

As a conclusion, some practical recommendations can be offered for practitioners interested in assessing OM density in coastal wetlands for purposes such as quantifying blue carbon stocks, estimating atmospheric CO$_2$ sequestration in coastal ecosystems, calculating emissions inventories of greenhouse gasses, and performing restoration initiatives in mangroves and coastal lagoons. In previous studies with mangrove sediments (*2*), we have found that the conversion of OM fraction to carbon fraction can be approximated by dividing OM fraction by a factor of 2.2. This value, however, could vary in other wetland sediments or even in other mangroves. If OM fraction, estimated through loss-on-ignition, is used to estimate carbon fraction, then this relationship must be verified. Overall, it seems clear that estimating OM or carbon density in wetland sediments using the ideal-mixing model is more precise (and much simpler) than the traditionally used product estimate, especially in undisturbed sediments. In disturbed or heavily trampled sediments, it is advisable to take first a few samples measuring both OM fraction and bulk density, to fit the ideal-mixing model to the two variables and, using this preliminary data cluster, then estimate the self-packing density of pure peat (δ_p) and pure mineral sediments (δ_m), as well as analyzing the statistical fit of the model under these conditions. Using either the OM fraction or carbon fraction as a single and precise estimator of carbon density in coastal sediments can yield precise results; however, incorporating more paired OM fraction and bulk density sample points into published data repositories will certainly increase the ability of the scientific community to understand the dynamics of carbon and substrate density properties in mangrove sediments. Last, it is important to note again that the ideal-mixing model opens the possibility of revisiting sediment data repositories for different regions of the world, even if they lack bulk density estimates. This may allow the incorporation of large amounts of data into our current knowledge of carbon stocks in coastal wetlands, a group of ecosystems of immense importance in the global balance of atmospheric greenhouse gasses.

MATERIALS AND METHODS
Analytical calculation of error propagation
Cramér's theorem (*10*) states that, given a function F used to calculate a result variable w from two predictor variables x and y, so that $w = F(x, y)$, then the variance of w can be calculated from the partial derivatives of F with respect to x and y multiplied by the standard error of x and y, so that

$$\text{var}(\widehat{w}) = \left(\frac{\partial F}{\partial x}\right)^2 \frac{\sigma_x^2}{n} + \left(\frac{\partial F}{\partial y}\right)^2 \frac{\sigma_y^2}{n} + 2\frac{\partial F}{\partial x}\frac{\partial F}{\partial y}\frac{\sigma_{xy}}{n} \qquad (14)$$

Following Cramér's derivation, the derivatives with respect to their predictor variables (*o* and *b*) were calculated for each of the three models used to estimate OM density in wetland sediments. These derivatives were then plugged into Cramér's equation to calculate how the variances of the predictor variables propagated onto the variance of OM density ($\widehat{OD}$).

Numerical simulation of error propagation
The theoretical derivations on the propagation of errors were tested numerically using a Monte Carlo simulation approach. A numerical database for 21 simulated cores was constructed, each core coming from a simulated "site" with decreasing amounts of OM fraction at 5% intervals from 1 to 100% peat (100, 95, 90, … 15, 10, 5, and 1%), to cover all the range of possible OM fractions observed in wetland sediments. Using the ideal-mixing model, the theoretical bulk density for each level of OM fraction was calculated. Within each core, 20 simulated resamples (or repeated samples) were taken assuming that, even if sampling was perfect, each sample could differ slightly from the rest because of heterogeneity in the sediment. Thus, random variation, or "white noise," was added to the values of OM fraction and bulk density in the simulated cores, assuming a coefficient of variation (i.e., SD relative to the mean) of 0.1, or 10%, within each core. To prevent negative values in the randomization, a Gamma distribution was used, which will behave as a Normal distribution when the mean is high, but will acquire an asymmetrical shape when the mean is low, being bound only to the realm of positive real numbers. Thus, a vector of OM fraction and a vector of bulk densities were constructed, each of length 420 (21 levels of OM × 20 repeat samples within each vector). These vectors were considered the statistical population data, containing the "true" data.

The two vectors were then sampled by adding random variation to each repeated measure. As before, a Gamma distribution was used to maintain the randomized statistics within the realm of positive numbers, assuming, in this case, a coefficient of variation of 0.2 (20%) induced on both measures by sampling error. The result was a sample vector of OM fraction and a sample vector of bulk densities, each also of length 420, but departing from the true data as a result of the generated random sampling errors. These latter vectors were considered the statistical sample data.

The OM density on each core was then calculated using three different approaches: (i) The first method was the traditionally used estimation of OM density ($\widehat{OD}$) using the simple cross-product of the sample's OM fraction × its gravimetric bulk density ($\widehat{OD} = b\,o$). (ii) For the second method, $\widehat{OD}$ was calculated using only the sample's OM fraction and estimating bulk density through the ideal-mixing model as in Eq. 5. (iii) For the last method, $\widehat{OD}$ was calculated using only the sample's bulk density and estimating the OM fraction through the inverse ideal-mixing model, as in Eq. 6. In all simulations, the ideal-mixing model was fitted assuming that the true values of the parameters ($\delta_p = 0.085$ and $\delta_m = 1.65$ g/cm^3) had been estimated accurately, i.e., the same parameter values used to generate the sampling data. Last, by repeating the simulations with different values of δ_p and δ_m, the sensitivity of the ideal-mixing model estimation to the errors in the estimation of the two parameters was evaluated.

Supplementary Materials

This PDF file includes:
Text S1 to S4

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