



RESEARCH ARTICLE

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Chemical Oxygen Demand as a Measure of Fluvial Organic Matter Oxidation State

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Key Points:

- Chemical oxygen demand can be used to assess the oxidation state (C_{ox}) of fluvial organic matter
- Median C_{ox} of dissolved organic carbon was 0.23 and 0.20 for particulate organic carbon
- Including new estimates of C_{ox} in to the global oxidative ratio gives the annual flux of CO_2 to land (f_{land}) of 1.45 ± 0.1 Gt C/year

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract The oxidative ratio (OR) of the terrestrial biosphere is directly related to the size of the terrestrial biosphere carbon sink. In turn, OR of naturally occurring organic matter can be directly related to the oxidation state of the carbon in naturally occurring organic matter (C_{ox}). Chemical oxygen demand (COD) is a widely measured water quality parameter that has been used as a short-term substitute for the biochemical oxygen demand (BOD). Here, we propose that if the concentration of reduced species is known, then COD measurement can be used to assess the oxidation state (C_{ox}) of fluvial organic C. Using a Bayesian hierarchical modeling approach, this study analyzed 21 years of water quality monitoring across England to calculate C_{ox} of fluvial organic matter. The study showed that (a) COD could not be considered separately from the reduced species (e.g., NH_4) commonly occurring in freshwater water samples, but it was still possible to calculate the C_{ox} of dissolved organic carbon (DOC) and particulate organic carbon (POC). (b) The median C_{ox} of DOC was 0.23 with a 95th percentile range of -0.1 to 0.4 . (c) The median C_{ox} of POC was 0.20 with a 95th percentile range of 0.03 – 0.37 . (d) The estimated C_{ox} in fluvial systems confirms that BOD is decoupled from the production of CO_2 . Including new C_{ox} estimates in the global estimate of OR gives a new median value of 1.059 with a 95th percentile range of 1.047 – 1.071 , giving the annual flux of CO_2 to land (f_{land}) of 1.45 ± 0.1 Gt C/year.

Plain Language Summary Chemical oxygen demand (commonly referred to as COD) is a commonly measured water quality parameter across the globe. COD is measured to assess how much dissolved oxygen that water sample would consume. However, the very way COD is measured means that it is actually measuring the oxidation state of the organic carbon in the water sample. The oxidation state of carbon in natural environments is key to understanding how much carbon dioxide the biosphere can absorb. This study used the routine and widespread measurements of water quality parameters to refine measurement of the annual global terrestrial carbon sink.

1. Introduction

The oxidative ratio (OR) represents the ratio of moles of oxygen (O_2) produced per mole of carbon dioxide (CO_2) fixed by the terrestrial biosphere. The value of OR of an environment is a key parameter in understanding the magnitudes of global carbon sinks. Keeling and Shertz (1992) proposed that the magnitude of global carbon sinks, and more specifically the carbon sinks due to the terrestrial biosphere and the oceans, could be calculated from the relative changes in atmospheric gases. The relative changes of O_2 and carbon dioxide CO_2 concentrations have been used to refine estimates of terrestrial and oceanic carbon sinks of fossil fuel emissions (Keeling et al., 1996; Prentice et al., 2001). Battle et al. (2000) proposed the following equations:

$$f_{land} = -\frac{CS}{OR_{terra}^{global}} f_{fuel} + \frac{1}{k_1 k_2 OR_{terra}^{global}} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} \quad (1)$$

$$f_{ocean} = -\frac{1}{k_1} \frac{d(CO_2)}{dt} - \frac{1}{k_1 k_2 OR_{terra}^{global}} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} - \frac{OR_{terra}^{global} - CS}{OR_{terra}^{global}} f_{fuel} - f_{cement} \quad (2)$$

where f_x = the annual flux of CO_2 (Gt C/year) with x = land, ocean, fuel, or cement; (O_2/N_2) = the molar ratio of atmospheric O_2 and N_2 ; CS = the combustion stoichiometry (1.43; Battle et al., 2000); OR_{terra}^{global} = the oxidative

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ratio of the global terrestrial biosphere; and constants k_1 and k_2 are to convert ppm in the atmosphere to per meg (which is ppm on a molecular basis for oxygen alone) the values are 0.471 and 4.8, respectively. Battle et al. (2000) refer to $OR_{\text{terra}}^{\text{global}}$ as the photosynthetic stoichiometry; this term is also known as α_B in the calculation of the atmospheric potential oxygen (APO; Stephens et al., 1998). The OR is mathematically equivalent to the respiratory quotient (RQ) that is commonly considered in metabolism including aquatic ecosystems (Vachon et al., 2020).

The value of OR has until recently been assumed to be 1.1 (Battle et al., 2000; IPCC, 2007; Keeling et al., 1996; Langenfelds et al., 1999; Prentice et al., 2001; Steinbach et al., 2011) and Keeling and Manning (2014) have dismissed any attempt to update this value as trivial because changes in OR led to only small changes in global flux sizes. In many studies, the value of OR = 1.1 has been assumed to be fixed and invariant for all environments at all times. However, this value is based upon a value from a single study of the biosphere 2 experiment (Severinghaus, 1995) that did not set out to measure an OR value that would be applicable to the global terrestrial biosphere. As an alternative, Worrall et al. (2013) compiled elemental analysis from the literature for whole soil and vegetation data from across the globe to provide a flux-weighted estimate of global OR and found a value of 1.03 ± 0.03 and argued that the present value used by the Intergovernmental Panel on Climate Change (IPCC) represents the 97th percentile of observed values. Although possibly not the major source of uncertainty in Equations 1 and 2, at currently estimated values of f_{land} (1.4 ± 0.8 Gt C/year) then an approximate 10% variation in the estimate of the OR value leads to a 10% change in the value of f_{land} . Similarly, a 0.1 decrease in OR leads to 8% change in the estimate of f_{ocean} . Furthermore, Randerson et al. (2006) have suggested that global OR values may not be at equilibrium but instead responding to ongoing land use change.

The review of Worrall et al. (2013) used data available in the literature and assumed that the major control on OR was the differences between different global soil taxa (e.g., Inceptisols) and between different global biomes (e.g., closed savannah; Olson et al., 2001). Subsequently, the studies of Clay and Worrall (2015a, 2015b) showed no significant difference between soil taxa, at least between mineral soil taxa, and that the significant difference in OR was between simple carbon pools, that is between soil, litter, and vegetation, rather than between sites. Given that the difference in OR is dominated by differences between organic carbon pools, Worrall, Clay, Moody, et al. (2016) used a simple box model to calculate global OR which was based upon the statistical differences in OR found in previous studies. This box model included allowance for soil, litter, and vegetation pools and also included the fluvial organic matter both particulate organic matter (POM) and dissolved organic matter (DOM). Given the box model and the literature values available at the time ($n = 806$), the median value of global OR was 1.034 with an interquartile range of 1.032–1.036. Applying the currently used value of OR (1.1) and leaving all other terms as used in Battle et al. (2000) (Equations 1 and 2), then $f_{\text{land}} = 1.40$ Gt C/year and $f_{\text{ocean}} = 2.11$ Gt C/year. Based upon the box model and the number of OR values available at the time of the Worrall, Clay, Moody, et al. (2016) study, the values of $f_{\text{land}} = 1.49 \pm 0.003$ Gt C/year and $f_{\text{ocean}} = 2.01 \pm 0.004$ Gt C/year, that is, approximately a 6% change in global flux estimates.

Even with subsequent studies measuring and filling gaps in the study of global OR (e.g., Battle et al., 2019), studies have not further considered the role of fluvial organic matter. The current global OR estimate is based upon 806 samples but only 27 samples of DOM and 2 of POM, and these all from one peat-covered catchment (Worrall, Clay, Moody, et al., 2016). Worrall, Clay, Moody, et al. (2016) did show that the OR of DOM was less than 1 implying that accounting for fluvial organic fluxes might be important. In the box model used by Worrall, Clay, Moody, et al. (2016), the values of OR for POM were, because of lack of fluvial organic matter samples, assumed to be that of soil organic matter. Yet in many environments, the fluvial flux of carbon can be the second most important transfer of carbon (Billett et al., 2004). Ciais et al. (2013) estimated the total annual flux of C from soils to rivers, comprising dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and particulate organic carbon (POC), which was estimated by the IPCC to be 1.7 Pg year^{-1} . Of this $\sim 0.2 \text{ Pg}$ is buried in aquatic sediments and $\sim 0.7 \text{ Pg}$ is returned to the atmosphere via gas exchange. The remaining $\sim 0.8 \text{ Pg}$ is transported to the oceans as DIC, DOC, and POC. This fluvial flux is equal to the natural uptake of C by the terrestrial vegetation and similar to the net annual uptake of anthropogenic C by the oceans (2.3 Pg year^{-1}). Therefore, fluvial organic matter is a considerable proportion of the terrestrial carbon cycle and is rapidly turned over to the atmosphere, but it has been underrepresented in the consideration of the oxidation state of the terrestrial biosphere. So, the aim of this study was to use widely available water quality monitoring data to assess OR of fluvial carbon.

2. Approach

The OR represents the ratio of moles of oxygen (O₂) produced per mole carbon dioxide (CO₂) fixed by the terrestrial biosphere and can be directly related to the average oxidation state of carbon in natural organic matter (C_{ox}; Masiello et al., 2008, and equivalent to NOSC; LaRowe & Van Cappellan, 2011).

$$C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]} \quad (3)$$

where [X] = molar concentration of C, H, N, or O.

Assuming that the ultimate source of organic N is N₂, then OR can be calculated from C_{ox}:

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3[N]}{4[C]} \quad (4)$$

The OR has a range of 0–2, with OR of glucose = 1. Therefore, as photosynthesis fixes C at an OR of 1, values of OR > 1 represent organic matter reduced relative to glucose and conversely OR < 1 represents organic matter relatively oxidized compared to that fixed by photosynthesis. Since OR can be calculated from C_{ox}, this study proposes that the C_{ox} of fluvial organic carbon can be calculated for the chemical oxygen demand (COD). The COD is typically expressed as mg O₂/L and is a measure of the oxidative capacity of natural waters including the organic carbon content.

For an organic molecule, C_αH_βO_γN_δ, the number of electrons [e⁻] required to be transferred for complete oxidation to CO₂ is

$$[e^-] = \alpha(4 - C_{ox}) + \beta - 2\gamma + 3\delta \quad (5)$$

Given that COD is measured as mg O₂/L and is measured with dichromate (Cr₂O₇²⁻). Every mole of Cr(VII) or O₂ accepts 4 mol of e⁻, then if COD was based only the reaction with organic matter:

$$[COD] = \frac{\alpha(4 - C_{ox})}{4} + \frac{\beta}{4} - \frac{\gamma}{2} + \frac{3\delta}{4} \quad (6)$$

where [COD] = mol O₂/L. Therefore, C_{ox} is

$$C_{ox} = \frac{1}{\alpha}(2\gamma - \beta - \delta) \quad (7)$$

Therefore:

$$[COD] = \frac{\alpha(4 - C_{ox})}{4} - \frac{\alpha C_{ox}}{4} = \alpha \left(1 - \frac{C_{ox}}{2}\right) [DOC] \quad (8)$$

Since we can calculate [COD] in mol O₂/L, we can express α as mol C/L (i.e., DOC concentration). Furthermore, as we know both [COD] and [DOC], we can calculate C_{ox}. However, there are two problems.

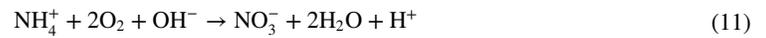
1. COD is measured in unfiltered samples and so DOM is not the only organic matter in the sample, that is, there is POM. However, most commonly and as is the case in England, POM is not monitored; rather it is the concentration of suspended solids (SS) that is monitored. Therefore, Equation 8 can be rewritten to include a contribution from POC:

$$[COD] = \alpha \left(1 - \frac{C_{ox}^{DOC}}{2}\right) [DOC] + \epsilon \theta \left(1 - \frac{C_{ox}^{POC}}{2}\right) [SS] \quad (9)$$

where C_{ox}^{DOC} = C_{ox} (Equation 3) of the fluvial DOC; C_{ox}^{POC} = C_{ox} of the fluvial POC; ε = the stoichiometric constant of the molecular formula of the POM where the stoichiometric formula of POM is defined as (C_eH_fO_gN_h); θ = the proportion of the SS that is organic C.

2. Organic matter is not the only material in natural waters that can be oxidized by dichromate in the COD analysis. COD has three common inorganic interferences:





When expressed as mol O₂/L then:

$$1 \text{ mol N} - \text{NH}_4/\text{L} = \frac{1}{4}[\text{COD}] \text{ to N}_2 \quad (13)$$

$$1 \text{ mol N} - \text{NH}_4/\text{L} = 2[\text{COD}] \text{ to NO}_3 \quad (14)$$

$$1 \text{ mol N} - \text{NO}_2/\text{L} = \frac{1}{2}[\text{COD}] \text{ to NO}_3 \quad (15)$$

$$1 \text{ mol Cl}/\text{L} = \frac{1}{4}[\text{COD}] \text{ to Cl}_2 \quad (16)$$

Therefore, COD should ideally be

$$[\text{COD}] = 4[\text{NH}_4] + 4[\text{Cl}] + 2[\text{NO}_2] + [\text{DOC}] + \theta[\text{SS}] \quad (17)$$

However, given the unknown oxidation state of fluvial organic matter and the potential pathways given by Equations 5–12 means that the measured COD is

$$[\text{COD}] = \eta[\text{NH}_4] + \kappa[\text{Cl}] + \lambda[\text{NO}_2] + \alpha \left(1 - \frac{C_{\text{ox}}^{\text{DOC}}}{2} \right) [\text{DOC}] + \varepsilon \theta \left(1 - \frac{C_{\text{ox}}^{\text{POC}}}{2} \right) [\text{SS}] \quad (18)$$

where η , κ , and λ are the effective stoichiometric constants for NH₄, Cl, and NO₂, respectively.

We propose that, if Equation 18 can be fitted to available water quality data, then we can assess the variation in $C_{\text{ox}}^{\text{DOC}}$ and $C_{\text{ox}}^{\text{POC}}$.

3. Methodology

We propose that Equation 18 can be fitted to available water quality data using a Bayesian hierarchical approach:

$$\begin{aligned} [\text{COD}]_{xt} = & N \left(\alpha_{xt} + \beta_{\text{NH}_4}(\text{Site, Year, Month})[\text{NH}_4]_{xt} + \beta_{\text{NO}_2}(\text{Site, Year, Month})[\text{NO}_2]_{xt} \right. \\ & + \beta_{\text{NH}_4}(\text{Site, Year, Month})[\text{Cl}]_{xt} + \beta_{\text{Cl}}(\text{Site, Year, Month})[\text{Cl}]_{xt} \\ & \left. + \beta_{\text{DOC}}(\text{Site, Year, Month})\Delta[\text{DOC}]_{xt} + \beta_{\text{SS}}(\text{Site, Year, Month})\Delta[\text{SS}]_{xt}, \frac{1}{\sigma^2} \right) \end{aligned} \quad (19)$$

Equation 19 is the multiple linear regression of Equation 18 fitted for each factor level of three factors. The Site factor is the difference between the sites on rivers where there was suitable and sufficient monitoring of the correct collection of determinands (NH₄, NO₂, Cl, DOC, and SS). The Year factor is the difference between the years of sampling and had 22 levels—2000–2021. The Month factor is the difference between months of sampling and has 12 levels one for each calendar month.

Models were fitted using different combinations of the three factors—initially, including the Site factor alone and then adding either or both of the Year and Month factors. The fitting of the Bayesian hierarchical approach was achieved by Markov Chain Monte Carlo (MCMC) simulation to estimate the posterior distribution of the COD using Jags code called from R using the R2Jags library (example R and JAGS code are included in Supporting Information S1). The length of the MCMC chain was 10,000 iterations after 2,000 burn-in cycles with samples saved every 10 cycles and with 3 chains.

Model fit was tested using a number of approaches. First, the adequacy of the MCMC process was assessed using the \hat{R} , the convergence statistic, and values of $\hat{R} < 1.1$ were considered acceptable. If $\hat{R} > 1.1$, then the burn-in process and number of iterations were increased. Second, the 95% credible interval for any factor does not include zero; this is henceforward referred to as being significantly different from zero at a probability of

95%. Similarly, the credible interval is referred to as the confidence interval for ease of understanding for those not so familiar with Bayesian methods. Third, that inclusion of the factor or interaction caused the total model deviance to decrease. Fourth, that the inclusion of an additional factor or interaction decreased the deviance information criterion (DICrit). It is generally true that inclusion of more factors or interactions will decrease the total deviance of a model as the inclusion of a factor, covariate or interaction means greater degrees of freedom for fitting and so the DICrit accounts for the inclusion of more fitting parameters against the additional fit of the model. Fifth, the effective number of parameters (pD) was monitored. It would be expected that as a factor or covariate was added to the model, then the number of effective parameters would likewise increase. If pD did not increase with inclusion of a parameter, then that parameter is having no effect on the model and can be removed. Furthermore, pD should be close to the ideal case, if all parameters are contributing, and so therefore the calculated pD can be expressed as a percentage of the maximum possible—this value can never greater than 100%. Finally, the fit of any model was judged using a posterior prediction check, that is, the output of the model was plotted against the observed values and the fitted line between these two examined. It would be expected that a good fit model would give a 1:1 line between observed and posterior predicted values.

To demonstrate the benefit of the Bayesian hierarchical approach, the analysis was repeated using linear regression based upon the data grouped by the same factors as for Equation 19, that is, Year, Site, and Month, having assessed their significance given the methods described above. Because of the limits of plausible regression analysis, the data, grouped by significant factors, were excluded if there were fewer than four datapoints within the group. Note that this sample size criterion is not a limitation on the Bayesian hierarchical approach.

3.1. Water Quality Data

The study considered river water quality data collected by the Environment Agency (the UK government's environmental regulatory body in England) between the years 2000 and 2021. All data were chosen where the following data were all concurrently available: COD, DOC, NO₂, NH₄, Cl, and SS. Only measurements that were from routine monitoring were included. Data from pollution incidents were excluded because pollution incidents may represent additional sampling at a higher frequency and, given that pollution incidents could represent influx of a specific water type, they could create an unrepresentative bias. The analytical methodology, the methods for harmonizing results across the country, for the HMS sites was prescribed in DoE (1972) and outlined in Simpson (1980). Current procedures are outlined and controlled by the UK Government's Standing Committee of Analysts (<http://standing-committeeofanalysts.co.uk/>). In total, there were 289 sites where there were sufficient data (Figure 1).

3.2. Estimation of Global OR

To determine the value of OR_{terra}^{global} experienced by the global atmosphere based upon new values of C_{ox}^{DOC} and C_{ox}^{POC}, the approach of Worrall, Clay, Moody, et al. (2016) was used and adapted. Worrall, Clay, Moody, et al. (2016) used a method of calculating the OR_{terra}^{global} based upon the weighted sum of the values for 12 global soil taxa (USDA soil taxonomy, Eswaran et al., 1993) and 16 global biomes (Loveland & Belward, 1997; Olson et al., 2001). The approach made an allowance for the speciation of the release of C, that is, the differences due to DOM, POM, CO₂, and CH₄. Where relevant, and practical, inclusion of all pathways in the calculation of ecosystem-scale OR would be beneficial, that is, biomass; litter; soil; fluvial fluxes including both DOM and POM; and gaseous emissions might be as CO₂ and/or CH₄ (a considerable contrast in reduction state).

In many environments, the proportion of the carbon flux that is due to DOM, POM, or CH₄ is very low or negligible, and it is perhaps only in environments with organic soils where all such exchanges are relevant in calculations of ecosystem-scale OR. Because of this, we considered mineral soil environments separately from organic soil environments for OR_{terra}^{global} calculations. For organic soil environments (Histosols, Mollisols, and Gelisols), it was assumed that there were exports of carbon as DOM, POM, and CH₄ in proportion to that predicted by their carbon budget (e.g., Worrall et al., 2012), but that for all other soil orders export via CH₄ or DOM was negligible. We assumed that all soils exported some carbon as particulates (POM); in Histosols, such as peat, where the soil is approximately 100% OM, then the erosion will be 100% organic carbon. However, in mineral soils, the organic carbon content of the particulate flux will be lower, and so will be the fraction of the carbon pool turned over via this mechanism.

Therefore, for organic soil environments:

$$OR_{terra}^{organic} = \varphi_{soil}^{terra} OR_{soil}^{organic} + \varphi_{veg}^{terra} OR_{veg}^{organic} + \varphi_{DOM}^{terra} OR_{DOM}^{organic} + \varphi_{POM}^{terra} OR_{POM}^{organic} + \varphi_{CH_4}^{terra} OR_{CH_4}^{organic} \quad (20)$$

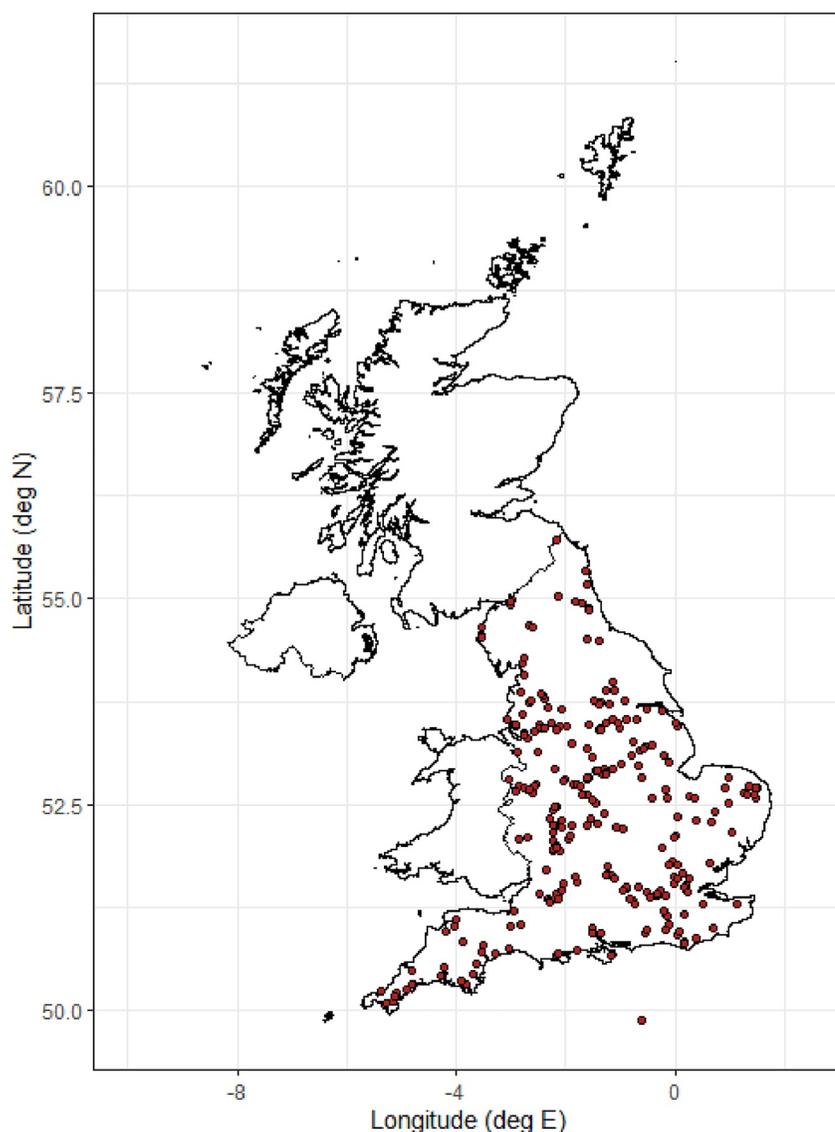


Figure 1. Location of monitoring sites used in this study.

$$\varphi_{\text{soil}}^{\text{terra}} + \varphi_{\text{veg}}^{\text{terra}} + \varphi_{\text{DOM}}^{\text{terra}} + \varphi_{\text{POM}}^{\text{terra}} + \varphi_{\text{CH}_4}^{\text{terra}} = 1 \quad (21)$$

where $\text{OR}_x^{\text{organic}}$ = the OR of the terrestrial biosphere C flux or reservoir from an organic soil environment that is due to DOM, POM, CH_4 , soil, or vegetation; and φ_x^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to DOM, POM, CH_4 , soil, or vegetation flux. The value of $\text{OR}_{\text{CH}_4}^{\text{organic}}$ is 2, by definition from its exactly known molecular formula. Previously, the value of $\text{OR}_{\text{DOM}}^{\text{organic}}$ was based on those reported from the meta-analysis of Worrall et al. (2013) and with the additional analysis of the C_{ox} and OR of DOM from Worrall, Clay, Moody, et al. (2016), however, this was enhanced by data from this study. Values of $\text{OR}_{\text{POM}}^{\text{organic}}$ were added to by values calculated in this study. The values of $\text{OR}_{\text{soil}}^{\text{organic}}$ and $\text{OR}_{\text{veg}}^{\text{organic}}$ were taken and the median and interquartile range of the all the soil and vegetation samples for organic soil environments (Histosols, Mollisols, and Gelisols) based upon the results of Worrall et al. (2013), Clay and Worrall (2015a, 2015b), Worrall, Clay, Moody, et al. (2016), Clay et al. (2018), and from the sources referenced therein. Values of φ_x^{terra} in Equation 21 were taken from the relative fluxes of C as defined by Worrall et al. (2009) and as used in Worrall, Clay, Moody, et al. (2016).

For mineral soil environments:

$$\text{OR}_{\text{terra}}^{\text{mineral}} = \varphi_{\text{soil}}^{\text{terra}} \text{OR}_{\text{soil}}^{\text{mineral}} + \varphi_{\text{veg}}^{\text{terra}} \text{OR}_{\text{veg}}^{\text{mineral}} + \varphi_{\text{POM}}^{\text{terra}} \text{OR}_{\text{POM}}^{\text{mineral}} \quad (22)$$

Table 1
Summary of Water Quality Data Used in This Study

	Concentration (mg/L)	
	Median	95th percentile range
COD	0.75	0.38–2.19
NH ₄	0.0075	0.0024–0.094
Cl	1.45	0.41–6.52
NO ₂	0.0035	0.00052–0.052
DOC	0.47	0.20–1.07
SS	9.23	0.019–92.23

$$\varphi_{\text{soil}}^{\text{terra}} + \varphi_{\text{veg}}^{\text{terra}} + \varphi_{\text{POM}}^{\text{terra}} = 1 \quad (23)$$

where $\text{OR}_x^{\text{mineral}}$ = the OR of the terrestrial biosphere C flux or reservoir from mineral soil environments that is due to POM, soil, or vegetation; and φ_x^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to POM, soil, or vegetation flux. As from previous studies (e.g., Worrall et al., 2013) values of $\varphi_{\text{soil}} = 0.27$ and $\varphi_{\text{veg}} = 0.73$ (based upon the relative fluxes reported by Eswaran et al. [1993] and Olson et al. [2001]) when no other flux of carbon was being considered and then reweighted). In the absence of further information, the value of $\varphi_{\text{POM}}^{\text{mineral}}$ was allowed to vary between 0% and 12% (based upon the POM fluxes reported for the UK; Worrall et al., 2014) for all soil orders other than Histosols, Mollisols, and Gelisols. The value of $\text{OR}_{\text{POM}}^{\text{mineral}}$ was not taken as the same as the soil taxa from which it eroded but rather was based upon the information from this study. The values of $\text{OR}_{\text{soil}}^{\text{organic}}$ and $\text{OR}_{\text{veg}}^{\text{organic}}$ were taken and the median and interquartile range of the all the soil and vegetation samples for soil environments other than those based on Histosols, Mollisols, and Gelisols based upon the results of Worrall et al. (2013), Worrall, Clay, Moody, et al. (2016), Clay and Worrall (2015a, 2015b), Clay et al. (2018), and from the additional calculations carried out as part of this study as described above.

The $\text{OR}_{\text{terra}}^{\text{global}}$ is then calculated as the weighted sum of $\text{OR}_{\text{terra}}^{\text{mineral}}$ and $\text{OR}_{\text{terra}}^{\text{organic}}$:

$$\text{OR}_{\text{terra}}^{\text{global}} = \varphi_{\text{mineral}}^{\text{terra}} \text{OR}_{\text{terra}}^{\text{mineral}} + \varphi_{\text{organic}}^{\text{terra}} \text{OR}_{\text{terra}}^{\text{organic}} \quad (24)$$

$$\varphi_{\text{organic}}^{\text{terra}} + \varphi_{\text{mineral}}^{\text{terra}} = 1 \quad (25)$$

where φ_x^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to either organic or mineral soil environments with values of $\varphi_{\text{organic}}^{\text{terra}}$ and $\varphi_{\text{mineral}}^{\text{terra}}$ based on the relative reservoirs sizes predicted from Eswaran et al. (1993) and Olson et al. (2001).

4. Results

In total, there were 10,130 data where COD, NH₄, Cl, NO₂, DOC, and SS were measured (Table 1). The linear regression of COD against the other variables gave the following best fit equation:

$$[\text{COD}] = \frac{2.77[\text{NH}_4] + 0.018[\text{Cl}] + 1.18[\text{DOC}] + 1.09[\text{NO}_2] + 0.0076[\text{SS}]}{(0.07) \quad (0.0004) \quad (0.01) \quad (0.28) \quad (0.0001)} \quad n = 10, 130, r^2 = 0.95 \quad (26)$$

where the values in the parentheses below the equation are the standard errors in the coefficients. All the terms used in Equation 26 were significantly different from zero at $P < 0.05$ but were not necessarily as expected from Equations 13 to 16. If all NH₄ is oxidized to NO₃ then two COD are required but Equation 26 suggests that NH₄ consumes more COD than expected. Similarly, the presence of NO₂ has a greater impact upon COD than expected from Equation 15. Conversely, the presence of Cl has a lower impact on COD than expected. The coefficient for the SS term in Equation 26 appears small relative to the others but this is the term where the variable is not corrected to mol/L. Given the average POC content of English SS (16%; Worrall et al., 2014), this means that this coefficient would be 0.51. For the DOC, the coefficient value means that the average C_{ox} of the DOC would be -0.09, that is, slightly reduced.

Table 2
Fitting Properties of the Model Combinations Applied

Factors	pD (% expected)	DICrit	Deviance
Site	1,779 (98)	8,675	6,895
Site + Month	1,902 (9)	8,797	6,992
Site + Year	5,143 (13)	12,058	9,584
Year + Month	1,206 (76)	4,723	3,516
Site + Month + Year	172,835 (25)	3,175,117	3,243

Note. The pD is expressed as both its absolute value and the % of that which could be expected if all new parameters included in the model were effective.

4.1. Bayesian Hierarchical Modeling

The fit of the models is given in Table 2. The fit of the Site + Year + Month model (Figure 2b) shows the improvement of prediction from the Site model (Figure 2a). The best fit line for the Site + Year + Month model shows that there was significant overprediction for values up to COD = 10 mg/L.

For 127 out of 289 sites, the value of β_{Cl} was significantly different from zero, that is, 127 sites where including Cl made a difference in the COD. The

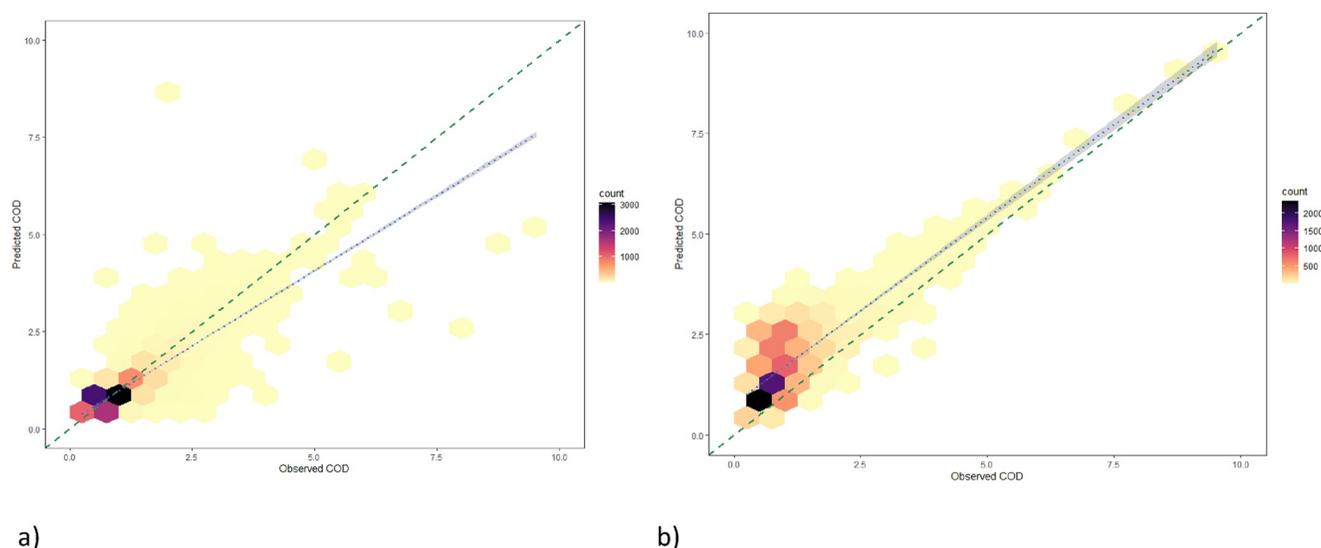


Figure 2. Posterior prediction plots for chemical oxygen demand (COD) given: (a) the Site model and (b) the Site + Year + Month model. The dotted line (· · ·) represents the best fit straight line, and dashed line (- - -) represents the 1:1 line.

median $\beta_{Cl} = 0.08$ and the arithmetic mean = 0.18 with a 95th percentile range of -0.1 to 0.4 . For 4 out of the 127 sites where β_{Cl} was significantly greater than zero the value of $\beta_{Cl} > 0.25$, that is, greater than the value predicted from Equation 26; however, for all of these four sites, the value of β_{Cl} was not significantly different from 0.25. Conversely, most of the 123 sites with $\beta_{Cl} < 0.25$ were significantly lower than 0.25, that is, Cl is not contributing to COD as much as expected.

For β_{NO_2} , there were 169 out of 289 sites where β_{NO_2} was significantly greater than zero, and therefore 169 sites where nitrite is making a significant contribution to COD. The median value of $\beta_{NO_2} = 0.19$, and the arithmetic mean = 0.21 with a 95th percentile range of 0.17 – 0.44 . No value of β_{NO_2} was found to be significantly the same as predicted by Equation 26, that is, although nitrite plays a significant role for many sites, it is not as important as theory would predict (Equation 15).

For β_{NH_4} , there were 173 out of 289 sites where β_{NH_4} was significantly greater than zero, and therefore 173 sites where ammonium is making a significant contribution to COD. The median value of $\beta_{NH_4} = 0.19$, and the arithmetic mean = 0.23 with a 95th percentile range of 0.16 – 0.59 . If it is considered that NH_4 is oxidized to N_2 rather than to NO_3 (Equations 13 and 14), then 15 sites show values of β_{NH_4} significantly greater than the value of 0.25 as expected from Equation 13. At only two sites, the values of β_{NH_4} were significantly lower than 0.25, that is, for most sites oxidation to N_2 was the dominant process.

For β_{SS} , there were 230 out of 289 sites where β_{SS} was significantly greater than zero—this represented 9,760 out of a possible 10,130 samples. The median value of $\beta_{SS} = 0.01$, and the arithmetic mean = 0.014 with a 95th percentile range of 0.005 – 0.042 . Given the range of organic carbon content reported by Worrall et al. (2014; 2.7%–38% OC) then the C_{ox}^{POC} would have a median = 0.20, mean = 0.20, and 95th percentile range 0.03 – 0.37 . Assuming a median organic carbon content of 16%, then the distribution of C_{ox}^{POC} across England shows no distinct spatial distribution of C_{ox}^{POC} values (Figure 3). The pattern of β_{SS} at the study sites does not follow the contemporary pattern of SS concentration or flux across the study catchments (Worrall et al., 2014), that is, β_{SS} does not appear correlated with distribution of SS concentration or flux across the country.

For 87 of the 289 sites, the value of β_{DOC} was not significantly different from zero. For the sites where β_{DOC} was not significantly different from zero, the sample size varied from 2 to 82 with an average sample size of 5. The 202 sites where β_{DOC} could be estimated represented 9,786 samples out of a possible 10,130 samples. The smallest value of β_{DOC} that was significant was 0.01 which we can consider as a detection limit within this study. Given Equation 8 then it was possible to calculate C_{ox}^{DOC} values for 202 sites, where the median $C_{ox}^{DOC} = 0.26$ and the arithmetic mean = 0.23 with a 95th percentile range of -0.1 to 0.4 . Of the 202 sites where C_{ox}^{DOC} could be estimated for 14 of them the value of $C_{ox}^{DOC} < 0$. As with C_{ox}^{POC} the spatial distribution of C_{ox}^{DOC} shows no apparent

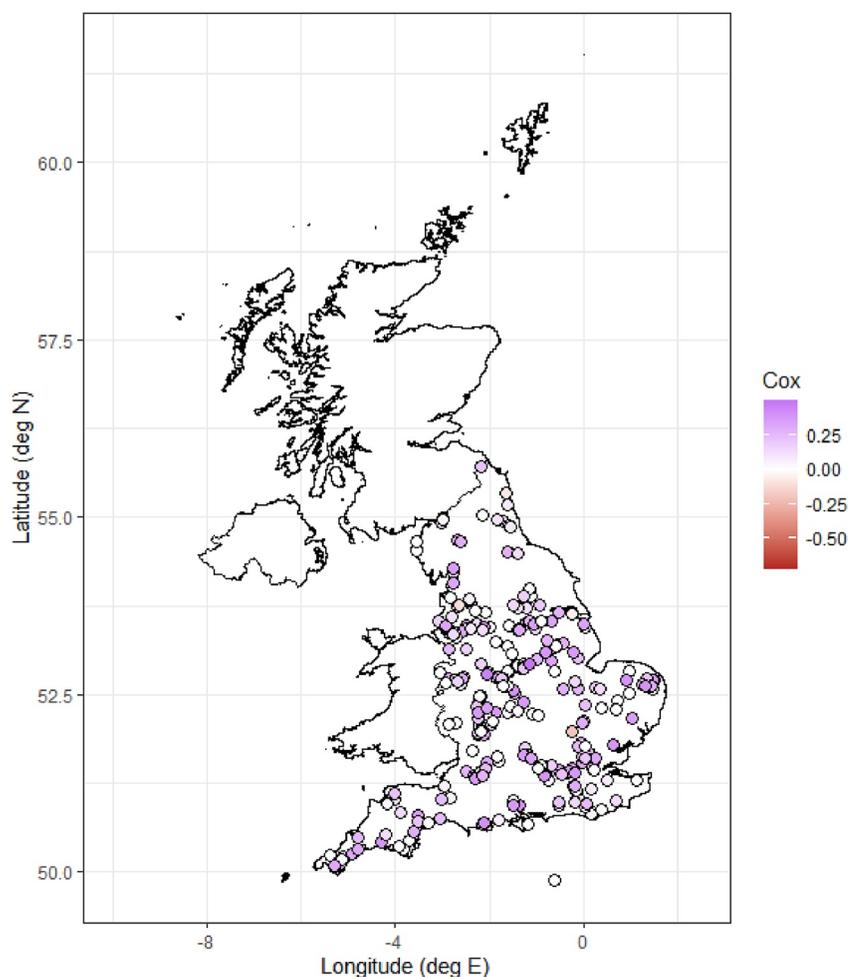


Figure 3. Spatial distribution of the mean Site C_{ox}^{POC} values.

spatial pattern (Figure 4). The pattern of β_{DOC} does not follow the contemporary pattern of DOC concentration or flux across the study catchments (Williamson et al., 2021).

For β_{DOC} , there was a significant trend with time for 23 of the sites over the study period with 6 showing a positive trend and 17 a negative trend. A significant decrease in β_{DOC} represents a significant increase in C_{ox}^{DOC} with the maximum increase being 0.02 over 20 years and the minimum change detected being 0.001 over 20 years. Conversely, the biggest decrease in C_{ox}^{DOC} was 0.006 over 20 years with the smallest detected decrease of 0.001.

For β_{SS} , there was a significant trend with time for 21 of the sites over the study period with 15 showing a positive trend and 6 a negative trend. A significant decrease in β_{SS} represents a significant increase in C_{ox}^{POC} with the maximum increase being 0.1 over 20 years and the minimum change detected being 0.001 over 20 years. Conversely, the biggest decrease in C_{ox}^{POC} was 0.09 over 20 years with the smallest detected decrease of 0.01.

4.2. Calculation of Global OR

Comparing all the measured OR and C_{ox} values for all 1,103 samples from previous studies gives the best fit equation as

$$OR = 1.025 - C_{ox} \quad n = 1,038, r^2 = 0.92 \quad (27)$$

The C_{ox}^{POC} and C_{ox}^{DOC} could be estimated at 202 and 230 sites, respectively, and so the reassessment of the OR_{terra}^{global} was based on 1,507 samples. Given the values of C_{ox}^{POC} in Equation 27 the median $OR_{POM}^{organic} = 0.83$, and the

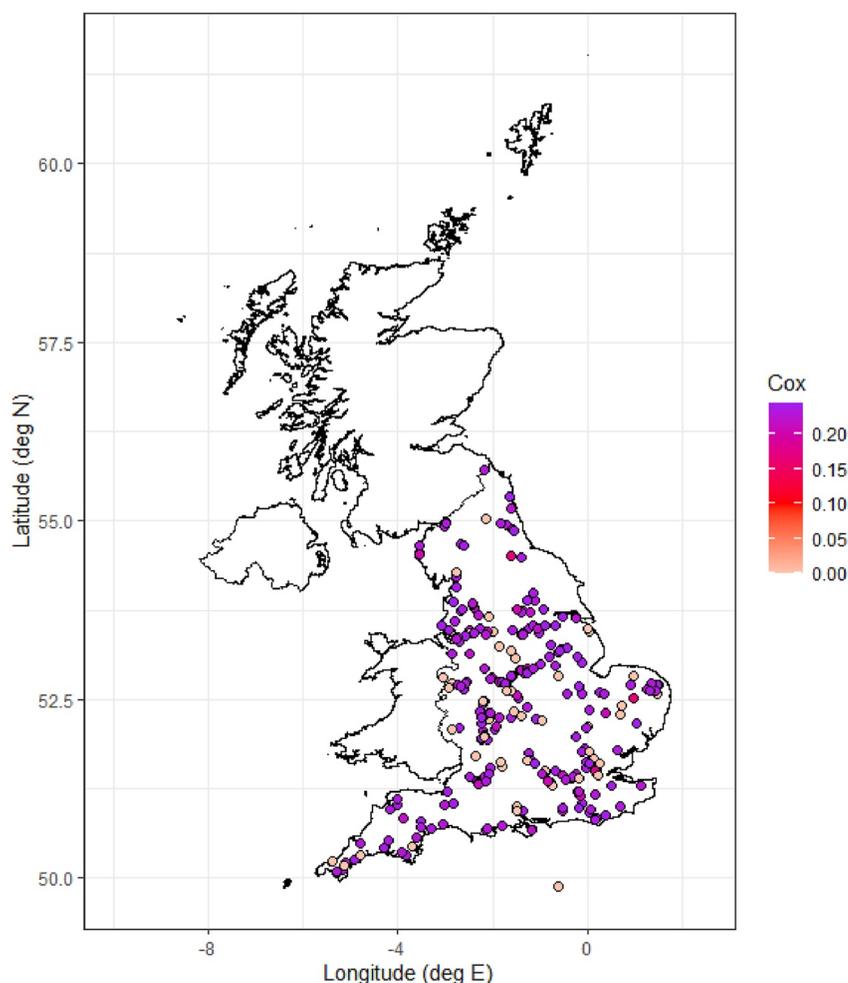


Figure 4. Spatial distribution of the mean Site C_{ox}^{DOC} values.

arithmetic mean = 0.83 with a 95th percentile range of 1.00–0.66. Similarly, for DOC, the median $OR_{DOM}^{organic} = 0.77$ and the arithmetic mean = 0.80 with a 95th percentile range of 1.13–0.63. These updated values and sample size gives a revised OR_{terra}^{global} with a median 1.059 with a 95th percentile range of 1.047–1.073 (Tables 3 and 4). By Equation 1, the revised values of OR_{terra}^{global} the annual flux of CO_2 to land (f_{land}) of 1.45 ± 0.1 Gt C/year.

5. Discussion

The range of C_{ox} values calculated from this study (–0.1 to 0.4) would mean that 1 mol of DOC could consume 0.25 mol of O_2 without any production of CO_2 . Given the relative atomic masses of C and molecular mass of O_2 , then 1 mg C/L DOC would have a biochemical oxygen demand (BOD) of 0.75 mg O_2 /L without any production of CO_2 and would mean that DOC concentration would stay the same, albeit a more oxidized DOC. Similarly, for SS, 1 mol of POC could consume up to 0.175 mol meaning that 1 mg/L of POC could have a BOD 0.525 mg O_2 /L. Therefore, in river water samples where there was just 1 mg/L of both POC and DOC, then the amount of O_2 that could be consumed without production of CO_2 would be 1.225 mg O_2 /L. This result confirms that of Worrall et al. (2021) who showed that BOD was decoupled from DOC concentration and CO_2 production in surface freshwaters. Worrall et al. (2021) assumed a range of C_{ox} of fluvial organic matter of –0.2 to 0.17 based upon values given in Worrall, Clay, Moody, et al. (2016), that is, a smaller range than found in this study. The study of Worrall et al. (2021) proposed that one of the reasons why BOD had been misunderstood was that the oxidation state of C in organic matter, both for dissolved and particulate, had been assumed to be 0. The analysis of Worrall et al. (2021) could neither include nor estimate values of C_{ox} and this meant that the efficiency of the

Table 3

The Range and Median Values of OR for Each of Organic Soil and Mineral Soil Environments Divided by the Significant Organic Matter Types

Environment	Study	Organic matter type	Sample size	Median	95th percentile range
Organic soils	2, 5, 8, 11, 12, 17, 18, 15	Soil	379	1.08	0.97–1.15
	11, 12, 15, 17, 18	Vegetation	144	1.06	0.98–1.13
	12, 17, 18, this study	DOM	237	0.87	0.68–1.07
	12, this study	POM	214	0.85	0.69–1.00
Mineral soils	3, 5, 8, 6, 11, 12, 16, 15	Soil	226	1.10	0.90–1.27
	1, 3, 6, 4, 9, 11, 12, 15, 16	Vegetation	289	1.05	0.98–1.11
	This study	DOM	208	0.87	0.65–1.11
	This study	POM	213	0.84	0.70–1.00

Note. 1 = Hockaday et al. (2009), 2 = Neves-Fernandes et al. (2010), 3 = Masiello et al. (2008), 4 = Olk et al. (1999), 5 = Mao et al. (2000), 6 = Kuz'Menio and Pavlova (1981), 7 = Akranov (1981), 8 = Grishina and Morgun (1985), 9 = Tonoco et al. (2006), 10 = Baldock et al. (2004), 11 = Clay and Worrall (2015a), 12 = Clay and Worrall (2015b), 13 = Worrall, Clay, Moody, et al. (2016) and Worrall, Clay, and MacDonald (2016), 14 = Worrall, Clay, Moody, et al. (2016), 15 = Clay et al. (2018) and this study, 16 = Worrall et al. (2013), 17 = Worrall et al. (2017), and 18 = Worrall, Clay, Moody, et al. (2016).

metabolic process could not be estimated. This study shows that it would be possible to independently estimate freshwater organic matter oxidation states and so future work could now combine the result from this study with the results of Worrall et al. (2021) to estimate metabolic efficiency across river basins. The method used here is in effect a laboratory method for measuring C_{ox} of fluvial organic matter reconstructed from water analysis and not a measure of the in situ behavior of fluvial organic matter. However, in understanding the metabolism of rivers from BOD, Worrall et al. (2021) have shown that any disconnection between O_2 consumption and CO_2 production in part because of the oxidation state of the organic matter but also because energy from oxidation can never be transferred 100% efficiently. Efficiency of energy transfer differs upon the biochemical pathway used. Glucose energy conversion via NADH is 94% efficient, while conversion via ATP is 68% efficient. Lafitte and Loomis (1988) showed that the energy transfer efficiency in plant processes varied between 84% and 89%. If in rivers the BOD is known and the C_{ox} of the fluvial organic matter can be measured independently using the method demonstrated in this study, then the metabolic efficiency of fluvial organic matter can be calculated.

There are number of alternative ways in which the oxidation state of C in natural environment as has been studied—elemental analysis (e.g., Worrall, Clay, Moody, et al., 2016); solid-state NMR (Hockaday et al., 2009); thermogravimetric analysis (Worrall et al., 2017); and Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS; Zhang et al., 2020) although these have only rarely been applied to fluvial organic matter. The overwhelming number of studies and samples used in the calculation of OR_{terra}^{global} and shown in Table 3 are for soils and biomass and not for fluvial organic matter. Using elemental analysis, Worrall, Clay, Moody, et al. (2016) found the C_{ox} of DOM from a first-order peatland stream to be between 0.34 and 0.46. Moody and Worrall (2017) found a range of 0.28–0.65 for fluvial DOM. Moody and Worrall (2021) measured the C_{ox} of fluvial POC as between -0.021 and 0.03.

The RQ (Odum, 1956) has been commonly measured in aquatic ecosystems and as noted above is mathematically equivalent to OR. Many studies of have measured ecosystem metabolism assuming that $RQ = 1$, as this is the perfect glucose metabolism (del Giorgio et al., 2006). Most studies have inferred the RQ from dissolved O_2 consumption by a range of methods (e.g., spectroscopy; del Giorgio et al., 2011). Other studies have measured RQ based upon elemental or measured compositions (e.g., Hedges et al., 2002). Berggren et al. (2012) have noted that very few studies have measured RQ directly by measuring the actual exchange of O_2 and CO_2 and found, across 52 locations in Quebec, an average $RQ = 1.2$. An $RQ = 1.2$ is, assuming a $C/N = 30$ (Clay et al., 2018), a $C_{ox} = 0.7$ (Equation 4), although assumes 100% energy transfer efficiency. The range of approaches taken to measuring and understanding ecosystem respiration has in effect all made at least one assumption

Table 4

The Development of Values of OR_{terra}^{global} From the Publications Used in This Study

Study	Median OR_{terra}^{global}	Uncertainty	Sample size (n)
Worrall et al. (2013)	1.038	1.024–1.052	65
Clay and Worrall (2015b)	1.060	1.056–1.064	703
Clay and Worrall (2015a)	1.056	1.054–1.058	911
Worrall, Clay, Moody, et al. (2016)	1.034	1.032–1.036	983
Worrall, Clay, and MacDonald (2016)	1.040	1.035–1.045	1,162
Clay et al. (2018)	1.060	1.050–1.080*	1,325
This study	1.059	1.047–1.073*	1,910

Note. Uncertainty are as quoted in the individual publications and are the interquartile range except for studies marked * where the uncertainty is the 95th percentile range.

that the approach in this study does not have to make, that is, assumptions that $C_{ox} = 1$; the assumption of 100% efficient energy transfer; and therefore a direct link between O_2 consumption and CO_2 production. These limitations are commonly explicit in ecosystem respiration studies (e.g., Bernhardt et al., 2022) where the assumptions in part direct what the study will be able to measure.

There is evidence from this study that, although for most sites the C_{ox}^{DOC} and C_{ox}^{POC} have not changed significantly over 21 years, there were almost 10% of sites where there was a significant change in C_{ox} . However, while the majority of sites which showed a temporal trend in β_{SS} , showed a significant positive trend (15 out of 21 significant trends were positive from 289 sites), for β_{DOC} , the majority which showed a significant temporal trend had a negative trend (17 out of 23 significant trends were negative from 298 sites). This contrast in the trend between β_{SS} and β_{DOC} suggests that, while C_{ox}^{POC} is decreasing and becoming more reduced, the C_{ox}^{DOC} is increasing and becoming more oxidized. Randerson et al. (2006) suggested that, as a result of dominant land use and vegetation changes across the globe (e.g., deforestation), the terrestrial biosphere would become more oxidized. In this scenario, a cumulative decrease in the OR of net primary production by 0.01 over a period of 100 years would require an increased land carbon sink (f_{land}) of 0.1 Gt C/year to balance global atmospheric O_2 and CO_2 budgets; Randerson et al. (2006) did not consider fluvial organic matter.

We have already observed that spatial distributions of both β_{SS} and β_{DOC} do not match patterns of flux or concentration of both DOC and SS across England (Williamson et al., 2021; Worrall et al., 2014). The significant trends in β_{SS} and β_{DOC} show that the majority of those showing a significant change are in the English midlands and do not follow the spatial patterns of flux and concentration. Furthermore, both SS and DOC concentration and fluxes are known to be decreasing across the UK for non-peat-covered catchments and that this is due to improvements in wastewater treatment (Worrall et al., 2014, 2018). Therefore, at the global scale, we consider the trends to be unclear and so no account of temporal changes in C_{ox}^{DOC} and C_{ox}^{POC} were made in the new estimate of OR_{terra}^{global} given in this study (Table 4).

6. Conclusions

This study has shown that it is possible to estimate the oxidation state of naturally occurring organic matter based upon the measurement of COD. The study showed the following:

1. That to calculate fluvial organic matter oxidation states, it was necessary to include nitrite, ammonium, and chloride concentrations.
2. For DOC, the C_{ox} would have a median = 0.26, mean = 0.23 with a 95th percentile range of -0.1 to 0.4.
3. For POC, the C_{ox} would have a median = 0.20, mean = 0.20, and 95th percentile range 0.03–0.37.
4. The inclusion of the new analysis of fluvial organic matter oxidation states means that the global OR (OR_{terra}^{global}) was recalculated to have a median 1.059 with a 95th percentile range of 1.047–1.073.

A revised value of global OR (OR_{terra}^{global}) gives the annual flux of CO_2 to land (f_{land}) of 1.45 ± 0.1 Gt C/year.

Data Availability Statement

All the data used in this study are publicly available from OpenWims database <https://environment.data.gov.uk/water-quality/view/download/new> (Environment Agency, 2021).

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None.

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