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Variability in organic carbon reactivity across lake residence time and trophic gradients

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The transport of dissolved organic carbon from land to ocean is a large, dynamic component of the global carbon cycle. Inland waters are hotspots for organic matter turnover, via both biological and photochemical processes, and mediate carbon transfer between land, oceans and atmosphere. However, predicting dissolved organic carbon reactivity remains problematic. Here we present *in situ* dissolved organic carbon budget data from 82 predominantly European and North American water bodies with varying nutrient concentrations and water residence times ranging from one week to 700 years. We find that trophic status strongly regulates whether water bodies act as net dissolved organic carbon sources or sinks, and that rates of both dissolved organic carbon production and consumption can be predicted from water residence time. Our results suggest a dominant role of rapid light-driven removal in water bodies with a short water-residence time, whereas in water bodies with longer residence times, slower biotic production and consumption processes are dominant, and counterbalance one another. Eutrophication caused lakes to transition from sinks to sources of dissolved organic carbon. We conclude that rates and locations of dissolved organic carbon processing and associated CO_2 emissions in inland waters may be misrepresented in global carbon budgets if temporal and spatial reactivity gradients are not accounted for.

Freshwater ecosystems are important conduits for carbon (C) transport[1]; CO_2 emissions associated with organic carbon (OC) mineralisation, and OC burial in lacustrine sediments, represent quantitatively important components of the global C cycle[1-4]. Dissolved organic carbon (DOC), which is the dominant OC fraction in most aquatic ecosystems, can be mineralised through microbial degradation and photochemical breakdown, removed via flocculation, and generated *in situ* via photosynthetic production or heterotrophic processing of particulate OC[4-6]. Several recent studies have highlighted the importance of small, low water residence time (WRT) waterbodies as hotspots of aquatic C cycling[6-9], however the relative importance of different processes in different aquatic systems, and thus their contribution to overall rates of freshwater OC processing, are not well quantified. The apparent turnover time of DOC, quantified as its half-life (T½, i.e. time for concentrations to halve, which should be constant if exponential decay is occurring) varies over several orders of magnitude as a function of assessment method and study system; photodegradation experiments typically suggest T½ values of days to weeks[10-13], with maximal rates observed in fresh samples from high-DOC headwaters. Biodegradation of labile compounds can be similarly rapid[6], but studies based on typical 'humic' DOM suggest T½ values of months to years[14-16]. Lake and catchment budgets give T½ estimates of <1 to >100 years[17-18]. Sharply differing indications of the relative

importance of photochemical and biological processes have been obtained using different methods and/or in different ecosystems, e.g. it has been argued that photochemical processes account for 70-95% of DOC processing in the shallow, unshaded waters of the Arctic[5], whilst another study suggests that microbial processes account for 90% of organic matter consumption in lakes globally[19]. Several studies have concluded that aquatic OC reactivity decreases with transit time, due to selective removal of light-absorbing and bio-available compounds[16,20].

Experimental assessments of DOC turnover necessarily involve a simplification of real-world conditions, for instance using specific compounds, excluding processes (e.g. photodegradation, photosynthesis, sediment-water interactions) or amplifying drivers (e.g. light, temperature) to generate measureable short-term responses. A key constraint of bioassay studies is that they are effectively closed reactors, often conducted in the absence of light, and typically excluding fresh inputs from primary production or terrestrial sources. Whole lake input-output budgets, on the other hand, expose a constantly cycling pool of natural DOC to ambient environmental conditions for a quantifiable time period. Although they present different challenges in disentangling the role of different drivers, we consider that whole lake budgets provide the most realistic indication of turnover rates in natural waters, and thus of the true role of freshwater ecosystems in the global C cycle. For 82 standing waterbodies with DOC budget data (68 lakes and 14 reservoirs from 12 countries, latitudinal range 14° S - 61° N, volumes 10^4 - 10^{13} m^3) we calculated mean WRT, mean DOC output/input ratio (DOC_{out}/DOC_{in}) and T½ for waterbodies acting as DOC sinks (See Methods). WRT ranged from 0.01 to 690 years, and DOC_{out}/DOC_{in} from 0.10 to 2.55 (see Supplementary Information).
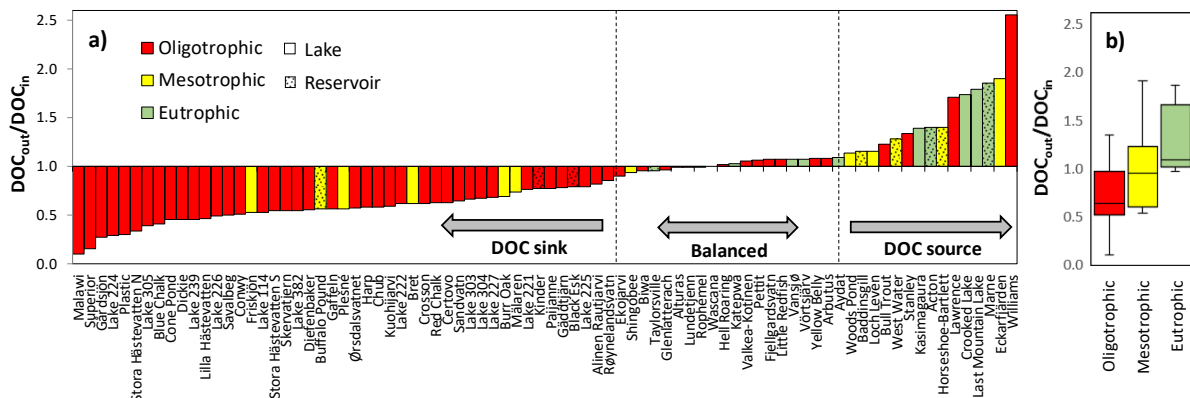
DOC input-output budgets

Of the 82 waterbodies, 48 were annual net DOC sinks (defined as > 10% removal), of which 44 were nutrient-poor (oligotrophic), four moderately nutrient-enriched (mesotrophic) and none highly nutrient-enriched (eutrophic). The two largest lakes, Lake Superior and Lake Malawi, had by far the longest WRTs (170 and 690 years respectively) and greatest net DOC removal (> 80%). The other 46 'sink' sites had T½ values of 0.07 to 19 years. We observed a strong inverse relationship between DOC_{out}/DOC_{in} and ln(WRT) across all DOC sink sites (R^2 = 0.53, p < 0.001; Fig 1a). This relationship produced an even stronger correlation between DOC T½ and WRT, however this is attributable to the use of WRT to calculate T½ (see Supplementary Information). To examine variations in reactivity as a function of WRT we instead compared observed DOC_{out}/DOC_{in} to values that would be predicted if DOC decay followed an average exponential decay function for the dataset (Fig 1a). Residuals (observed-predicted DOC_{out}/DOC_{in}, Fig 1c) were strongly and consistently negative at WRT < 1 year (indicating higher-than-expected DOC removal) and positive (indicating lower-than-expected net DOC removal) in all but one waterbody with WRT > 2.5 years. We found no significant correlation between the residuals of this relationship and any other available physical, hydrological or chemical property of the study sites, suggesting that WRT-related changes in DOC reactivity exert the dominant control on removal rates.

Fifteen waterbodies were net sources of DOC (defined as increase > 10%, Fig 1b), of which 11 were mesotrophic or eutrophic, and 4 oligotrophic. These sites spanned a broad range of inflow and outflow DOC concentrations, from < 2 to > 40 mg l^{-1} (Supplementary Table S4). Again we found a significant (but in this case positive) relationship between DOC_{out}/DOC_{in} and ln(WRT) spanning all lake types (R^2 = 0.49, p = 0.005; Fig. 1c). As for DOC sink lakes, the log-linear relationship implies that net DOC production was not steady over time, but decreased with increasing WRT.
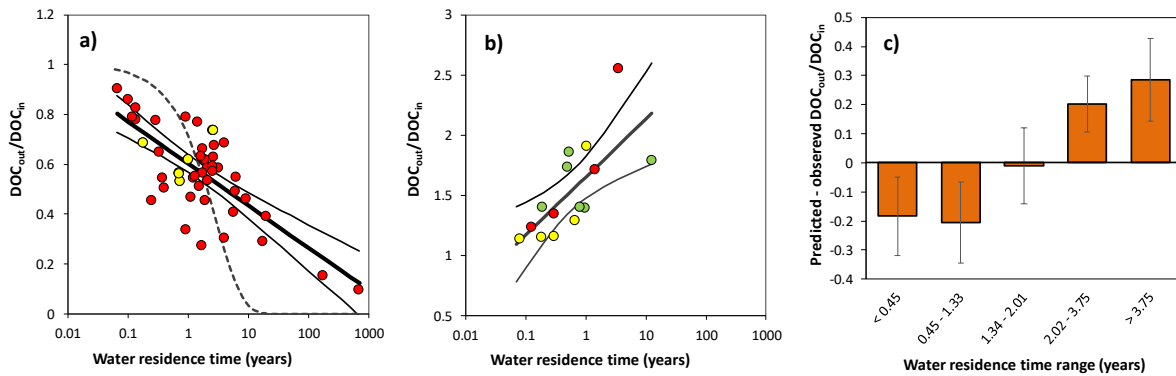
Figure 1*. **Relationships between DOC_{out}/DOC_{in} and WRT for waterbodies acting as a) net DOC sinks and b) net DOC sources**. Red, yellow and green circles represent oligotrophic, mesotrophic and eutrophic waterbodies respectively. Best fit (bold) and 95% confidence intervals (narrow) lines were derived from a linear regression of DOC_{out}/DOC_{in} vs ln(WRT) for each set of waterbodies. The dashed line in (a) shows values of DOC_{out}/DOC_{in} that would be predicted if all DOC sink sites followed an exponential decay curve with an average half-life, and **c)** shows divergence between observed and predicted DOC_{out}/DOC_{in} obtained from this curve, for all DOC-sink sites binned into five equal-sized groups according to WRT.*

The remaining 19 waterbodies were in approximate balance for DOC (change < ±10%). These sites varied in trophic status, however all but four had short WRTs (≤0.5 years) and/or low DOC input fluxes (< 2 g C m^{-2} yr^{-1}), and five had other lakes upstream (Table S4). We infer that net DOC change tends towards zero where opportunities for processing are limited (low inputs, low WRT); where pre-processing has occurred upstream (i.e. WRT of the individual waterbody underestimates true WRT); or where aquatic DOC production and terrigenous DOC consumption rates approach balance.

Figure 2. DOC input-output balance and trophic status of all waterbodies analysed: *a)* *Lakes and reservoirs ranked from low to high DOC_{out}/DOC_{in}, and classified by trophic status; **b)** Boxplot of median (line), quartile (box) and 10th/90th percentile (whisker) values of DOC_{out}/DOC_{in} by trophic status.*

Our results highlight the role of lakes and reservoirs as active zones of OC cycling; 77% of studied sites were 'reactive', in the sense that they acted as either as net sources or net sinks of DOC. The direction of change was strongly influenced by nutrient status: 74% of 57 oligotrophic waterbodies were net sinks, whereas 76% of 25 meso-/eutrophic waterbodies were net sources (44%) or balanced (32%). Across the full dataset, mean DOC_{out}/DOC_{in} was 0.70 (standard deviation ±0.31) in oligotrophic, 0.82 (±0.29) in mesotrophic, and 1.24 (±0.35) in eutrophic systems (Figure 2b). Differences in DOC_{out}/DOC_{in}

were highly significant between oligotrophic and eutrophic sites ($p < 0.001$), and between mesotrophic and eutrophic sites ($p = 0.004$), but non-significant between oligotrophic and mesotrophic sites ($p = 0.23$). Regardless of whether sites were net DOC sources or sinks, the overall rate and magnitude of DOC change was strongly influenced by WRT. For DOC sink sites this is consistent with declining reactivity over time as bio- and photo-labile fractions, and material susceptible to flocculation, are selectively removed. The non-linear relationship suggests that this does not occur evenly over time or space, with reactivity highest immediately following DOC transfer from land to water, and declining rapidly thereafter.

The role of trophic status

While data on net DOC source sites are constrained (n=15) relative to sink sites (n=48), there is a clear tendency towards net DOC production in nutrient-enriched waterbodies, and for declining production rates in longer-WRT systems. Our results are consistent with a previous input-output study of eutrophic ponds[21] which showed DOC production coinciding with nutrient consumption during the growing season. We infer that autotrophic DOC production (e.g. via algal exudation or cell death, sloppy feeding by zooplankton, production by aquatic macrophytes) declines with time as available nutrients are incorporated into biomass and depleted. It is noteworthy that many of the balanced or net-DOC producing oligotrophic lakes had low catchment DOC inputs, a feature generally associated with higher inorganic nutrient levels[22]. Thus, a combination of low availability of terrestrial DOC to degrade, and somewhat higher nutrient levels, may favour net DOC production in these systems despite their low trophic status. It has also been suggested that supersaturation of natural waters with CO_2 from terrigenous sources may stimulate primary production[23]. Given that photodegradation of organic matter liberates CO_2 along with inorganic N and P, the possibility exists of a direct mechanistic link between terrigenous DOC mineralisation (causing CO_2 supersaturation) and aquatic DOC production.

Implications for DOC processing rates

For the subset of sites acting as net DOC sinks, we evaluated the extent to which processing rates occurring under ambient (light-exposed) conditions differed from those obtained under controlled (dark) conditions by comparing our *in situ* results to data from 221 dark incubation bioassays compiled previously[16] to derive estimates of OC decay rate, k (proportional loss per year, related to half-life via $k = \ln(2)/T_{1/2}$). Divergence in fitted k vs WRT for bioassay and input-output data (Fig. 3a) was greatest at short WRT (3 times higher at WRT = 0.02 years), with k values converging at WRT = 1.4 years, beyond which the incubation data suggest higher rates of DOC reactivity than the lake budget data (see Supplementary Information for details). These differences have important implications for the rate of DOC processing through drainage networks, and for the locations where processing occurs; the bioassay data suggest fairly steady but continued DOC removal over time (4% after 30 days, 36% after 1 year, 84% after 10 years). The *in situ* data suggest much higher initial removal, but lower (net) removal over longer periods: 21% within 30 days, 40% after 1 year, and 57% after 10 years (Figure 3b).
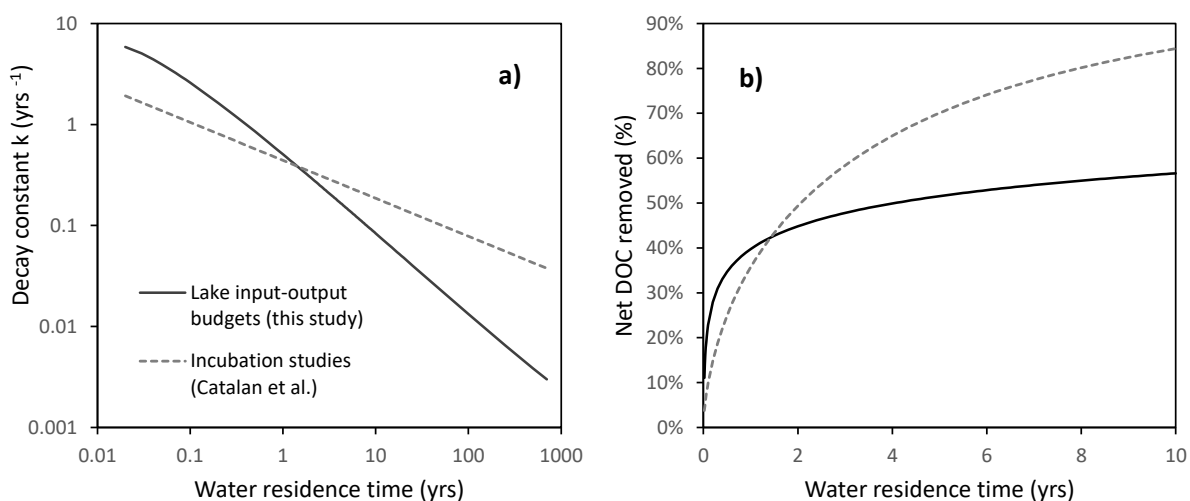
Figure 3. Contrasting relationships between OC processing rates and water residence time obtained from *in situ* and laboratory incubation data: *a) Fitted reaction rate (k) versus WRT based on lake input-output data from this study, and a previous relationship fitted to laboratory dark-incubation data by Catalan et al. (2016)[16]. Relationships are truncated at WRT = 0.02 years, the WRT at which DOC removal exceeds 10% according to our regression analysis (i.e. the threshold removal for sites to be defined as net DOC sinks) and at the maximum WRT in our lake dataset (690 years); **b)** Percentage removal of DOC versus WRT based on the two relationships shown in a).*

The offset between field input-output data and dark bioassay data suggests a vital role of light-driven removal processes (e.g. photodegradation and flocculation, increased bioavailability of photo-modified organic matter, and autotrophic production)[24]. Removal processes dominate in short-WRT systems, where photodegradability of freshly-exposed DOC is maximal, and where previous experimental studies have also suggested extremely high DOM reactivity[10-13]. This is particularly pronounced for headwaters draining peatlands, which are major global sources of surface water DOC[26]. Declining DOC reactivity, and convergence with bioassay-based *k* estimates at higher WRT, can be interpreted as rapid initial loss/modification of the photo-labile DOC fraction, followed by a shift towards biological degradation of the residual DOC pool. Very low rates of net DOC removal at longer residence times, together with evidence of net DOC production in more nutrient-rich lakes, suggest that (under field conditions) *in situ* production increasingly counterbalances removal[25]. Large observed differences between light and dark DOC degradation rates have major implications not only for understanding mechanisms of DOC processing, but also for the locations where processing occurs. For a drainage system with a five year total WRT, our model (incorporating light-driven processes) suggests that 21% of all DOC removal occurs within the first week, 41% within a month, and 77% within a year. The equivalent dark-only figures are 5%, 12% and 51%.

Implications for aquatic carbon cycling

Global C budgets now incorporate freshwater C transport, burial and emission[1,4,9]. A growing number of studies have identified the importance of headwater streams and small lakes[4,7-9,21] but the magnitude and source of CO_2 emissions from these systems remain uncertain[2-3,9]. Global lake area estimates range from 3 to 4 million km^2, with small (< 1 km^2) water bodies comprising a highly uncertain (14-43%) fraction of this total[6-7]. Raymond et al.[9] estimate global stream area at 624,000 km^2, half in first to third-order streams. They estimate that these account for 59% of stream CO_2 emissions, but argue that such large emissions cannot be explained by degassing of CO_2 exported from terrestrial systems alone. Whilst extrapolating from low-WRT lakes to streams is inherently uncertain,

our analysis suggests that the very rapid, primarily photolytic, degradation and transformation of DOC immediately following land-water transfer could contribute significantly to this total flux. Conversely, long-WRT lakes may make a smaller contribution to DOC mineralisation than currently assumed. Nutrient-enrichment is an important confounding factor in the aquatic C cycle, causing lakes to transition from DOC sinks to sources, but again processing rates appear maximal in low-WRT systems.

Overall, our study reinforces the view that low-WRT waterbodies are biogeochemical hotspots, and is among the first to empirically demonstrate the rapidity with which DOC processing rates (both production and consumption) change during the early period of exposure in the water column. This reactivity has arguably been overlooked in previous studies of larger lakes and/or dark-only processes. Our observations provide mechanistic underpinning for a number of other observations, including higher DOC concentrations[27], rates of CO_2 degassing[9,28] and C burial[29] in small versus large water bodies, and the 'chemostatic' stabilisation of DOC concentrations in larger drainage systems[30]. They suggest that extrapolation of process rates from large lakes to short-WRT systems may lead to under-estimation of their biogeochemical significance, unless account is taken of the strongly non-linear relationship between DOC reactivity and WRT, and support a revised calculation of the contribution of small waterbodies to the global C budget.

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Author contributions

CE conceived the study, undertook the initial data analysis and led the writing of the paper. MF and DK contributed to conceptual development and data analysis and wrote sections of the manuscript. FM, ZF and SV provided unpublished data, expert knowledge and ideas, and commented on the text.

Methods

We collated data on the morphology and DOC input-output budgets of a range of waterbodies, including lakes and reservoirs, from a range of literature and several unpublished data sources. In the following method description we refer to 'lakes' for simplicity, but equivalent methods were used for reservoirs. Mean water residence time (WRT) in each lake was calculated as:

$$\text{WRT (years)} = Q_{out} / V_{lake} \qquad\qquad (1)$$

Where Q_{out} is the mean annual discharge from the waterbody (m^3 yr^{-1}) and V_{lake} is lake volume (m^3). In many studies, V_{lake} was not reported directly, but could be derived from reported values for lake area (A_{lake}, m^2) and mean depth (Z, m). In some studies, WRT was reported directly, but one or other of Q_{out} and V_{lake} were not given, in which case the missing parameter was derived from the two reported parameters by rearranging (1). For all sites, areal mean discharge (m yr^{-1}) was calculated as Q_{out} divided by the area of the catchment, $A_{catchment}$, which included the area of the lake. This was used to calculate the discharge into the lake (Q_{in}, m^3 yr^{-1}), if not already reported, by multiplying areal mean discharge by the terrestrial area of the catchment ($A_{catchment} - A_{lake}$).

The calculation of DOC input and outputs varied according to the information provided in the study and the nature of the site. In the simplest case, for lakes dominated by a single large river input (i.e. one draining the majority of the lake catchment area) the mean concentration of DOC in this input was considered representative of all catchment inputs (i.e. the same mean DOC concentration was assumed for unmeasured lake inflows and direct seepage) and scaled up to the full terrestrial catchment area assuming a constant DOC flux per unit area. The total DOC input was then calculated as the mean inflow concentration ([DOC]$_{in}$, g m^{-3}) multiplied by Q_{in}. For lakes with multiple sampled inflows [DOC]$_{in}$ was calculated by weighting the mean concentrations of each inflow according to either gauged water discharge for each inflow (if reported) or alternatively according to subcatchment area. Although DOC input to waterbodies can occur through direct precipitation to the water surface, most studies that measured this flux found that it only contributed a few percent of the total DOC input[31,32]. Because few studies reported rainfall fluxed, we assumed a zero DOC input via this pathway in all studies. Estimates of DOC inputs from emergent macrophytes reported in a number of studies[31-34] were also omitted, as these were considered to comprise part of the in-lake production flux.

In a small number of reported studies, input-output budgets have been constructed for lakes without surface water inflows, based on estimates of seepage inputs[31,34-36] or landscape averaged input fluxes[37,38]. These studies were included in the analysis provided that the estimates were based on direct measurements, e.g. of nearby stream catchments or subsurface inflows. Studies incorporating modelled fluxes[39-41] were omitted in order to avoid circularity. We also excluded short-term (e.g. summer-only) mass-balance studies where changes in internal lake DOC storage were large and uncertain relative to input and output fluxes during the period[42-43], and used multi-year means (treated as single data points) where available. Changes in storage should be negligible for short-WRT systems, and although they could arise lakes with longer WRTs, any errors associated with this should be randomly distributed within the dataset. We were unable to incorporate direct precipitation inputs of DOC to the lake surface in our mass-balance studies, because this term was rarely reported in the source literature. Where reported it was usually a minor term overall, but exceptions are likely where lake:catchment ratios are high, or terrestrial inputs low. By omitting this term we effectively assumed that any DOC deposited on the lake surface was rapidly cycled, and thus did not contribute to measured output fluxes.

In general, reservoirs were treated similarly to natural lake systems in the analysis. However since reservoirs typically exhibit larger fluctuations in volume than lakes, we sought to use or calculate mean values of WRT based on the mean volume of water held within the reservoir during the measurement period, rather than its maximum capacity. One reservoir in France[44] was supplied via a diversion canal and in this case areal mean water and DOC fluxes were calculated relative to the 'effective' catchment area of the reservoir, which was calculated by multiplying the total area of the catchment by the ratio of measured discharge from the reservoir to total catchment discharge. In one study[45,] DOC input-output budgets were reported for a two-reservoir chain, therefore a single combined WRT was calculated for this system.

For all sites, we calculated the ratio of output to input fluxes, DOC_{out}/DOC_{in}. Sites were considered to be acting as DOC sinks if $DOC_{out}/DOC_{in} < 0.9$, and as net sources if $DOC_{out}/DOC_{in} > 1.1$. Sites where outputs fluxes were within 10% of inputs were considered to be in approximate balance. The use of a 10% threshold was practical rather than theoretical, but reflected i) potential errors associated with determination of DOC input and output fluxes, that could lead to sites being erroneously categorised as net sources or sinks if a lower threshold were applied; and ii) increasing instability in calculated DOC reaction rates as the difference between inputs and outputs fell below this threshold.

For systems acting as DOC sinks, we determined DOC 'half-life' (DOC T½) according to the equation:

$$DOC\ T\frac{1}{2} = \frac{ln(2) \times WRT}{-ln\left(\frac{DOC_{out}}{DOC_{in}}\right)} \tag{2}$$

Where DOC_{in} and DOC_{out} are area-normalised DOC input and output fluxes (both expressed in g C m^{-2} yr^{-1} as a function of the total catchment area, including lake area), and DOC T½ and WRT are both expressed in years. The instantaneous decay rate, k, was estimated as $ln(2)/(DOC\ T\frac{1}{2})$. To avoid the possibility of a spurious relationship[46] resulting from WRT being on both sides of the equation, the relationship between k and WRT was estimated as follows. As DOC_{out}, DOC_{in} and WRT are independent measurements, the relationship between DOC consumption and WRT was quantified by simple linear regression, by fitting the following equation to the range of observations:

$$\left(\frac{DOC_{out}}{DOC_{in}}\right) = a + b \times ln(WRT) \tag{3}$$

Prediction intervals for DOC consumption ratios $\widehat{y_0} \pm t_{Crit} \times se$ were estimated as:

$$s.e. = s_{yx} \times \sqrt{1 + \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{SS_x}} \tag{4}$$

Thus, the upper prediction interval for the ratio of DOC_{Out}/DOC_{In} was estimated as:

$CI_{Upper} = a + b \text{ X } ln(WRT) + t_{Crit} \text{ X s.e.}$ (5a)

And the lower prediction interval was estimated as:

$CI_{Upper} = a + b \text{ X } ln(WRT) - t_{Crit} \text{ X s.e.}$ (5b)

DOC half-life was obtained by substituting (3) into (2), giving:

$$DOC\ T\frac{1}{2} = \frac{ln(2) \times WRT}{-ln(a + b \times ln(WRT))} \tag{6}$$

Finally, prediction intervals for T½ were obtained by substituting (5a and b) into (6).

At all sites, in addition to DOC fluxes and WRT, we collated or derived data on catchment and lake surface area, lake volume, mean depth, areal mean discharge and total discharge (see Supplementary Tables). To classify sites according to trophic status we collated available data for a range of nutrient and productivity measures, comprising total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), nitrate (NO_3^-) and chlorophyll-a (Chl-a) concentration. Data reported by the same studies used for DOC flux calculations were used where possible, but obtained from additional sources

where necessary. The most commonly measured parameter, TP, was used to categorise sites into three broad trophic classes, based on threshold values given by Dodds[47]: oligotrophic (TP ≤ 23 µg l^{-1}), mesotrophic (23 < TP ≤ 48 µg l^{-1}) and eutrophic (TP > 48 µg l^{-1}). Where TP was not reported, other measured data plus author site descriptions and aerial imagery (evidence of agriculture and human habitation within the catchment) were used to assign trophic status (see Supplementary Information for details).

In total, we were able to derive annual DOC input-output budgets for a total of 82 waterbodies (68 lakes and 14 reservoirs) on four continents. With one exception, all were located in the Northern Hemisphere, and most were from the cool temperate or boreal zones.

Data sources. All of the data compiled for the analyses presented in this study are available in the Supplementary Information. The majority of data derive from previously published studies (see reference lists). Data from a small number of unpublished studies, and any additional calculations used to derive the values presented in Tables S1 to S4 where these were not reported directly in the original publication (see footnotes in Supplementary Information) are available from the corresponding author on request.

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