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Key Points:

- Watershed size imposes a primary control on the Damköhler number (Da) for dissolved organic carbon (DOC) uptake in global river networks
- The Da for DOC uptake in tropical river networks is 2–6 fold that in temperate and the Arctic river networks
- Damming and climatic warming significantly enhance the Da for DOC uptake in global river networks

Supporting Information:

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

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Global Controls on DOC Reaction Versus Export in Watersheds: A Damköhler Number Analysis

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Abstract The relative capacity for watersheds to eliminate or export reactive constituents has important implications on aquatic ecosystem ecology and biogeochemistry. Removal efficiency depends on factors that affect either the reactivity or advection of a constituent within river networks. Here, we characterized Damköhler number (Da) for dissolved organic carbon (DOC) uptake in global river networks. Da equals the advection to reaction timescale ratio and thus provides a unitless indicator for DOC reaction intensity during transport within river networks. We aim to demonstrate the spatial and temporal patterns and interplays among factors that determine DOC uptake across global river networks. We show that watershed size imposes a primary control on river network DOC uptake due to a three orders of magnitude difference in water residence time (WRT) between the smallest and largest river networks. DOC uptake capacity in tropical river networks is 2–6 times that in temperate and the Arctic river networks, coinciding with larger DOC removals in warm than in cold watersheds. River damming has a profound impact on DOC uptake due to significantly extended WRTs, particularly in temperate watersheds where most constructed dams are situated. Global warming is projected to increase river network DOC uptake by ca. 19% until year 2100 under the RCP4.5 scenario.

Plain Language Summary Dissolved organic carbon (DOC) transported by river networks is either removed during transport or exported to downstream receiving basins. The capacity for river networks to remove DOC is determined by the relative balance between its transport and reaction timescales. Damköhler number measures the transport to a reaction timescale ratio and provides a common framework for evaluating the spatial and temporal variations in DOC uptake across global river networks. We show that large river networks have higher DOC uptake because of orders of magnitude longer advection time than in small river networks. Tropical river networks have higher DOC uptake than temperate and the Arctic river networks because of higher reaction rates in warm than in cold watersheds. Damming significantly prolongs water advection and increases DOC uptake within river networks. Global warming is also projected to increase river network DOC uptake because of enhanced DOC uptake rates under a warmer climate.

1. Introduction

Terrestrial materials transported by river systems are either exported to terminal receiving basins or removed during downstream transport (Cole et al., 2007; Ensign & Doyle, 2006) via processes, including particulate sedimentation, in situ photo-/biological transformation, or surface degassing. The relative balance between within-river removal and export of these materials has important implications for biogeochemistry and ecology in both rivers (Battin et al., 2008; Raymond et al., 2013) and downstream receiving water bodies (Bauer et al., 2013; Maavara, Akbarzadeh, & Van Cappellen, 2020). The temporal dimension of river networks being either a reactor or an exporter of terrestrial materials is illustrated by the pulse-shunt concept (Raymond et al., 2016), which describes the phenomenon where high-discharge events allow moments for quick pulse/shunting of dissolved organic matter (DOM) through headwaters/small rivers and enhanced export to downstream systems. The temporal alternations of rivers between reaction and export are also illustrated by the concept of river network saturation (RNS; Wollheim et al., 2018), where supply of a constituent surpasses its demand (or removal), resulting in a breakthrough of the constituent from river networks and high exports during high-discharge events. Despite the importance of these earlier works, research that nourished these conceptual developments originated predominantly from temporal observations within small temperate watersheds (0.1–230 km^2) (Acuña and Tockner, 2010; Casas-Ruiz et al., 2017; Dhillon and Inamdar, 2013; Raymond and Saiers, 2010; Wilson et al., 2013;

Yoon & Raymond, 2012) and lacked a spatial perspective across watershed size or climate conditions. Both conceptual frameworks account for downward shifts of within-network uptake in response to higher discharge in larger watersheds (400–200,000 km^2) (Raymond et al., 2016; Wollheim et al., 2018), implying a key spatial constraint on watershed export (Bertuzzo et al., 2017). However, this was not illustrated across watersheds of contrasting reaction rates and/or physical conditions. Given that context, we propose that current research lacks a global geographical context, quantifying how reaction versus export varies across watersheds of different sizes or climate regions due to the lack of a common framework unifying these dynamics.

From a perspective of river network modeling, the efficiency of constituent removal at the watershed/river network scale depends on the amount of time a reactive constituent stays within the system before export, here parameterized as surface water residence time (WRT), assuming negligible delays between transport of the constituent and water. Previous work has identified WRT as a key hydrologic and biogeochemical modulator for aquatic system removal efficiency (Casas-Ruiz et al., 2017; Evans et al., 2017; Maavara, Chen, et al., 2020; Vollenweider, 1975), constituent composition and reactivity (Catalán et al., 2016; Evans et al., 2017; Mari et al., 2007), and autotrophic community dynamics (Obertegger et al., 2007). At the mesoscopic scale, temporary hydraulic retention or residence within land/aquatic functional units of the aquatic "macrosystem" (e.g., hyporheic zones or floodplains) has also been suggested to be critical and linked to constituent removal efficiency in these biogeochemical "hotspots" (Harvey et al., 2019; Marzadri et al., 2017; Newcomer et al., 2018; Zarnetske et al., 2011), which allows for a later-stage scaling-up of these processes at larger spatial scales and/or across time. Despite its apparent significance in watershed biogeochemistry and aquatic ecology (Hosen et al., 2021), plus straightforwardness in calculation (Worrall et al., 2014), surface WRTs have rarely been characterized within or across river networks at broad geographical scales. This was partly due to unavailability of global discharge or flow velocity data sets (Lin et al., 2019) that allows for consistent seasonal characterization of surface WRTs over millions of river/stream reaches and across watersheds. While recently modeled for some regional river systems (Brinkerhoff et al., 2021), this lack of a consistent global residence time database, in practice, has impeded a broad-scale perspective of cross-region watershed removal or export, given that WRT is a necessary parameter.

Constituent removal efficiency depends further on reaction rate, which is often a function of aquatic constituent reactivity, microbial community, kinetic responses to concentration, temperature, and other factors. For a specific reaction and assuming no other significant limitations (e.g., by light or nutrients; Bernhardt et al., 2018), microbial production and respiration are affected by temperature with rates of these processes increasing by a factor of 2–3 for every 10°C increase in temperature (Follstad Shah et al., 2017; Mao & Li, 2018; Peierls & Paerl, 2010; Raymond & Bauer, 2000; Wickland et al., 2012). Though temperature-induced variations in aquatic reaction rate are widespread and important (Follstad Shah et al., 2017; Yvon-Durocher et al., 2010), how they interact with hydrology and the broadly varying WRTs of river networks is largely unknown in terms of shaping the landscape of watershed biogeochemistry and removal/export across climate regions and seasons. Temperature must also be accounted for when determining aquatic ecosystem responses to climate change (Yvon-Durocher et al., 2010, 2011).

Reaction rate in a river is measured either as a volumetric or areal rate (mass length^{-3} (or length^{-2}) time^{-1}), an uptake velocity (length time^{-1}), turnover length (length), or simply a per time constant (time^{-1}) (Catalán et al., 2016; Ensign & Doyle, 2006; Mineau et al., 2016; Stream Solute Workshop, 1990). Conceptually and mathematically, all reaction rates can be transformed to a characteristic reaction timescale that corresponds to a specific system-wise removal efficiency (e.g., $t_{1/2}$ or half turnover time that corresponds to a removal efficiency of 1/2) after accounting for the dimension or standing stock of the constituent in the system (Catalán et al., 2016; Marzadri et al., 2017; Zarnetske et al., 2012). This timescale, coupled with the characteristic advection timescale of the reaction system (i.e., WRT), provides a common, unitless indicator (i.e., Damköhler number or Da) based on which the relative reaction intensity in river systems can be evaluated.

In this analysis, we adopted the concept of Da as a common framework and evaluated the spatial and temporal variations of constituent removal in river systems worldwide. The concept was first introduced in the early twentieth century in chemical engineering to describe reaction efficiencies of flow-reaction systems (Rehage & Kind, 2021). We used dissolved organic carbon (DOC) as an illustrative reactive constituent, considering its core role in river biogeochemistry and ecology (Kaplan & Cory, 2016). Depending on the angles of approach, the Da can have different formulations in aquatic studies (Marzadri et al., 2021; Wollheim et al., 2018). In cases where both the advection and reaction timescales are known, the Da is essentially expressed as the advection-to-reaction

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timescale ratio of the chosen reaction system (unitless, Equation 3 in Section 2). A Da above 1 often refers to a reaction-dominated system, whereas below 1 an advection-dominated system (Rehage & Kind, 2021). Another feature of the Da is its direct translation to a reaction efficiency, given known reaction kinetics (e.g., zero, first, or second order). For instance, under the assumption of first-order kinetics (i.e., reaction rate responds linearly to reactant concentration), the reaction efficiency for reactant to pass through a system can be described as an exponential relationship with Da (i.e., $R = 1 - \exp(-\mathrm{Da})$) (Rehage & Kind, 2021; Wollheim et al., 2018).

The best use of the Da depends further on reaction systems with clearly defined boundaries that allow an advection timescale to be calculated (Marzadri et al., 2017). In this analysis, Da was calculated as a watershed/river network property instead of a reaction site or storage zone property as in many earlier studies that involved Da calculations (Harvey et al., 2019; Zarnetske et al., 2012) to provide a perspective on how the watershed/river network as a whole varies in reaction/export across space and time. We accounted for hydrology-induced spatial and temporal variations in river network advective transport and the temperature effect in the calculation of the Da. Applying the same concept, we also examined how river damming and global warming affect watershed DOC uptake considering their impacts on either WRT (Vörösmarty et al., 1997) or uptake rate (Maavara et al., 2017) in river systems. Through this practice, we aim to provide a unified view for and demonstrate factors that shape the global landscape of river networks as reactors/exporters of reactive terrestrial materials.

2. Materials and Methods

2.1. Instream Water Residence Time

In this analysis, both estimates for instream WRTs and river network Da for DOC uptake were based on the GRADES (Global Reach-Level A Priori Discharge Estimates for SWOT) river networks (Lin et al., 2019). GRADES river networks start channelization at an area threshold of 25 km^2. A total of ~2.9 million individual flow lines and nine stream orders (SO) (Strahler) were depicted for the global river networks. To delineate watersheds for the GRADES river networks, we utilized topological relationships describing connectivity of all GRADES flow lines. Watersheds, defined as those that export to oceans, were delineated by first locating the outlet (i.e., a flow line with no downstream reaches) and then identifying all upstream flow lines and associated unit catchment areas. The unit catchment areas were then fused to form a single watershed (Python Rasterio, version 1.1). A total of 59,958 watersheds were delineated, ranging in area from 10 to >3 million km^2. These watersheds form the basis for the current analysis.

GRADES provides reconstructed daily discharge estimates (year 1979–2014) for each river reach (Lin et al., 2019). We used annual and monthly mean discharges from the GRADES to estimate WRTs corresponding to these timescales (i.e., monthly or annual). WRT at a single river reach was calculated as length (m) divided by flow velocity (m s^{-1}) at the river reach. Flow velocity was estimated using a hydraulic geometry formulation of the Manning's equation after imposing a rectangular river channel (Equation 1; Dingman, 2007),

$$V = \left(\frac{S^{0.3}}{n^{0.6} W_b^{0.4}} \right) Q^{0.4} \quad (1)$$

where V is flow velocity (m s^{-1}), S channel slope (unitless), W_b (m) bankfull width of the reach, and Q (m^3 s^{-1}) annual/monthly discharge from GRADES. Bankfull widths for the GRADES river networks were from Lin et al. (2020). A uniform Manning's n (0.03) was assumed.

WRT at the river network scale was estimated by routing reach-scale annual/monthly WRTs through the river network. We applied a discharge-weighted algorithm for the routing where cumulative WRTs from all joining upstream reaches were weighted by their respective reach discharge, plus the independently estimated (i.e., reach length divided by flow velocity) advection time at the downstream reach, to obtain an average, cumulative WRT at the downstream reach (Equation 2; Hosen et al., 2021).

$$t_{ri} = \frac{\sum Q_j t_{rj}}{\sum Q_j} + t_i \quad (2)$$

where t_{ri} and t_{rj} (hr) were cumulative WRTs at the downstream reach i and the jth joining reach, respectively, Q_j water discharge at the jth joining reach (m^3 s^{-1}), and t_i the advection time at the single downstream reach i.

We joined 6,767 dams from the HydroLakes database (Messager et al., 2016) to the GRADES river networks. This dam database, which is the same as GRanD (the Global Reservoir and Dam database) (Lehner et al., 2011), is complete for dams with reservoirs 10 km^2 or larger, and additionally includes reservoirs to 0.1 km^2 in area. These dams were distributed in a total of 1,295 watersheds. The HydroLakes database provides annual WRT estimates for each included single reservoir (calculated from statistically modeled reservoir volumes and outflow discharge). To estimate reservoir contribution to river network WRTs at the annual timescale, we replaced WRT at natural GRADES river reaches where HydroLakes reservoirs are situated with HydroLakes reservoir residence times for the river network scale routing. Reservoir WRT was calculated as the difference between the routed WRT with reservoir contribution and without. Reservoir contribution to river network WRT was only estimated at the annual timescale, considering only annual reservoir WRTs were available from HydroLakes (Messager et al., 2016).

2.2. River Network Damköhler Number Calculation

In this analysis, monthly Da for DOC uptake was calculated for each of the 59,958 watersheds as the ratio between monthly river network WRTs (t_r, hr) and a temperature-dependent characteristic reaction time for aquatic DOC uptake (t_s, hr) in the system.

$$Da = \frac{t_r}{t_s} \tag{3}$$

The characteristic reaction time (t_s) quantifies the time needed for DOC uptake in a river system (Rehage & Kind, 2021). A Da above 1 means that the system is reaction dominated, whereas a Da below 1 means the system is export dominated. Depending on the understandings of whether riverbed or water column processes dominate DOC uptake in river systems, t_s can be formulated differently (Marzadri et al., 2021). In cases where riverbed processes dominate the uptake (e.g., in small rivers/streams), reaction rate is often expressed as an uptake rate per unit area of stream bottom (U, in unit of mass $area^{-1}$ $time^{-1}$) (Stream Solute Workshop, 1990; Wollheim et al., 2006). Uptake velocity (v_f) is defined consequently as the concentration (C, in unit of mass $volume^{-1}$) normalized areal uptake rate (i.e., $v_f = U/C$). Uptake velocity (v_f) has a unit of length per time and can be thought of as a vertical velocity at which solute (e.g., a reactive DOC molecule) is transferred through the water column to a reactive sediment/water interface (Stream Solute Workshop, 1990). The ratio between water column depth (d, m) and v_f therefore defines a characteristic time needed for the transfer (i.e., $t_s = d/v_f$). The Da for a river system can thus be approximated by the following equation.

$$Da = \frac{t_r/24}{d/v_f} \tag{4}$$

where d (m) is a characteristic water column depth for the watershed and v_f (m d^{-1}) is the DOC uptake velocity. For d, we used discharge-weighted mean reach water column depth as an approximation to the mean watershed water column depth (Equation 5). By accounting for all river reaches, this formulation accounted for shallower depths (thus more efficient uptake) (Wollheim et al., 2006) at numerous small river reaches and allowed d to increase as watershed increases in size (or larger watersheds have deeper d) (Bertuzzo et al., 2017).

$$d = \frac{\sum Q_i d_i}{\sum Q_i} \tag{5}$$

where Q_i and d_i were discharge and water column depth at the ith river reach within a river network, respectively.

To determine a t_s or v_f suitable to scale DOC uptake at the watershed scale is difficult, considering the large methodological difficulties in measuring DOC uptake in actual river networks (Fellman et al., 2009; Lutz et al., 2012) and the vast spatial and temporal variations in DOC v_f both within and across river systems (Bott & Newbold, 2013; Mineau et al., 2016; Munn & Meyer, 1990). In practice, constrained by complex and irreplicable molecular compositions, DOM uptake at the reach scale is often evaluated via whole-system simple molecule (e.g., acetate, glucose, and arabinose) or organic leachate addition experiments where added surrogate solute concentration is monitored at multiple distances down experimental reaches of small rivers (Stream Solute Workshop, 1990). Calculated DOC spiraling characteristics from solute addition experiments (median v_f: 3.2 m d^{-1}) however suggest solute elimination within short downstream advection distances (0.9 quantiles: 0.01–1.7 km)

(Table S1 in Supporting Information S1). We suggest that simple molecules or organic leachates represent a highly reactive fraction of the DOM reactivity continuum and overestimate actual DOC uptake in river networks (Mineau et al., 2016). DOC υ_f derived from solute addition experiments is thus not suitable to scale DOC uptake at actual watershed scales (Lv et al., 2019).

In this analysis, we have chosen a υ_f (0.038 m d^{-1}) derived from a best model fit to hierarchically sampled DOC concentrations along a medium-sized (400 km^2) river network (the Ipswich River, USA; Wollheim et al., 2015) to scale Da for instream DOC uptake in global river networks. This υ_f corresponds to a balance between total river network DOC gains (e.g., via terrestrial input or autochthonous production) and losses (e.g., via photo-/microbial oxidation) and thus measures net DOC removal within the river network (Wollheim et al., 2015). Importantly, the υ_f yields a global DOC removal efficiency that matches the magnitude of global river network CO_2 emission from heterotrophic respiration (Battin et al., 2008; Raymond et al., 2013) (see Section 4). We recognize large uncertainty in applying a single temperature-dependent υ_f to whole river network DOC cycling (e.g., inability to account for spatial and temporal variations in aquatic DOC reaction rate; see Section 4) (Bertuzzo et al., 2017; Lv et al., 2019; Raymond et al., 2016; Wollheim et al., 2018). We argue that since the aim of the analysis is to illustrate the impacts of watershed hydrologic conditions and temperature-dependent instream microbial processing on spatial and temporal variations in river network DOC uptake, this υ_f offers sufficiently accurate DOC uptake for Da calculation at the watershed scale.

To account for the effects of temperature on uptake and Da, the υ_f was assumed to work at an ambient water temperature of 15°C and was scaled up with temperature according to the Arrhenius law (Equation 6; Montagnes et al., 2008).

$$\upsilon_{f,T} = \upsilon_f \theta^{\frac{T-15^\circ C}{10^\circ C}} \tag{6}$$

where $\upsilon_{f,T}$ is the uptake velocity at the temperature T. An Arrhenius coefficient (θ) of 2 was used in this analysis (Follstad Shah et al., 2017; Mao & Li, 2018; Wickland et al., 2012).

Monthly air temperature for watersheds was estimated by overlapping the GRADES watersheds with a global land surface air temperature data set (World Climate Version 2.0) (Fick & Hijmans, 2017). The monthly air temperature was then converted to water temperature using a simple equation from Raymond et al. (2013) (Equation 7). The relationship derived from an analysis of coupled water and air temperatures from the GLORICH database (Hartmann et al., 2014) and R^2 for the relationship was 0.65 (Raymond et al., 2013).

$$T_w = 0.67T_a + 7.45 \tag{7}$$

where T_w and T_a are water and air temperatures (°C), respectively. Temperature was bottomed at zero degree Celsius for water. A test against direct measurements at 366 river gauging stations worldwide (United Nations Environment Programme, 2019) shows that the simple calculation predicted sufficiently reliable monthly water temperatures for global watersheds (Figure S1 in Supporting Information S1, $R^2 = 0.8–0.93$).

3. Results

3.1. Surface Water Residence Time

Surface WRT ranges from less than 1 hr to more than 3 months (2,232 hr) for global river networks (with a watershed area of 10–>10^6 km^2) (Figure 1a). WRT scales closely with watershed size (Figure 2a). The longest WRTs are found in large watersheds, draining interiors of major continents and shorter WRTs in small watersheds, draining coastal areas or isolated islands (Figure 1a). In terms of SO, median WRT for SO 1 watersheds is 6 hr, about 1 day (23 hr) for SO 2 watersheds, about 10 days (230 hr) for SO 5 watersheds, and over a month (760 hr) for watersheds of SO 7 and above (Figure 1b and Table 1). Using discharge at watersheds' outlet as a weight, a mean "age" for the total exported water from global watersheds could be estimated. This age, corresponding to the mean residence time of surface waters in global river networks, is 908 hr (or 38 days), close to those of SO 7 and 8 watersheds (767–1,396 hr), suggesting the importance of the world's large watersheds in determining the mean surface WRT of land-exported waters.

In addition to system size, WRT also scales negatively with water runoff (or specific discharge) across watersheds (Figure 2c). For instance, for SO 5 watersheds (0.95 quantile drainage area: 2,440–38,000 km^2), median WRT in

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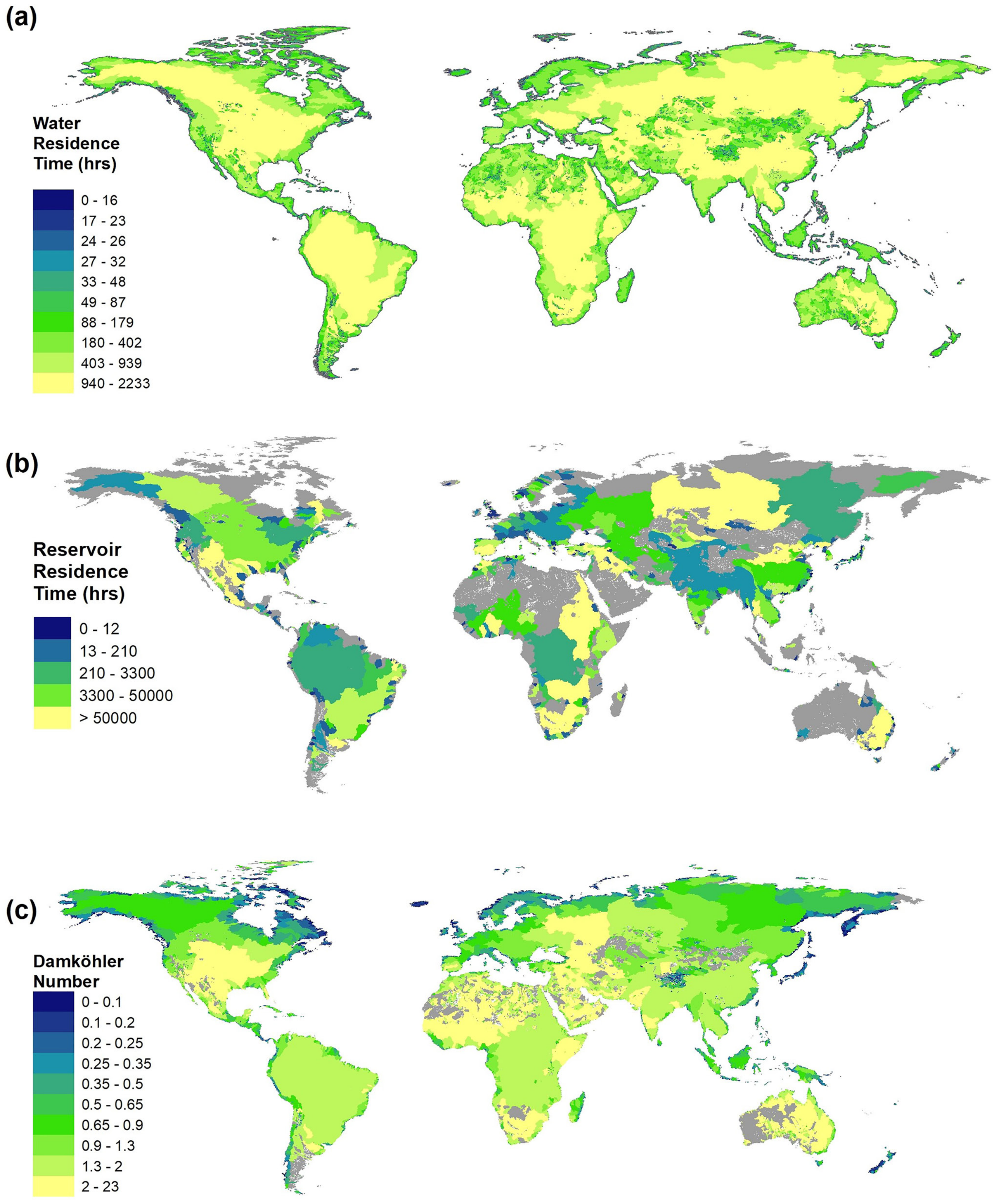

Figure 1. Maps showing water residence time in (a) global river networks and (b) reservoirs and (c) Damköhler number calculated at mean annual discharge and water temperature.

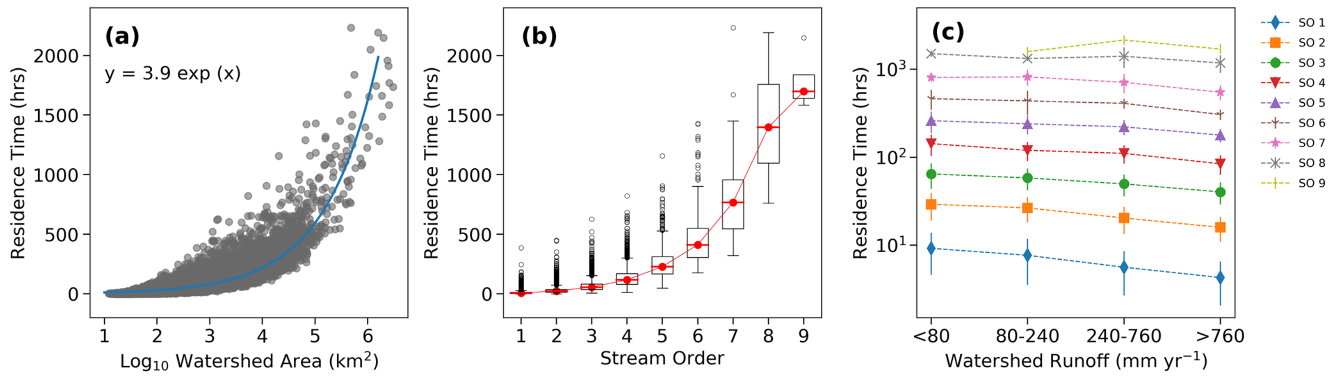

Figure 2. Surface water residence times in global river networks and their relationship with (a) watershed size, (b) stream order, and (c) water runoff from watersheds.

watersheds of the highest runoff class (>760 mm yr^{-1}) is only 68% that of the lowest runoff class (<80 mm yr^{-1}) (176 vs. 260 hr). The effect of watershed runoff is also apparent in a direct comparison of the largest watersheds (Table S2 in Supporting Information S1). As an illustration, the Amazon has the largest watershed area (over 3 million km^2, 1,730 hr), but the longest WRT is found in the Yellow River, a semiarid river with a watershed area of only 16% that of the Amazon (0.48 million km^2, 2,160 hr). In addition, while the Yellow and Mekong are comparable in watershed size (0.48 vs. 0.42 million km^2), WRT in the Mekong (which flows partly through tropical Southeast Asia) is only 75% of the Yellow River (1,670 vs. 2,160 hr).

3.2. Damköhler Number

Da calculated for river network DOC uptake spans over five orders of magnitude (from <0.001 to >90; the 0.90 quantiles are 0.01–3.2; Figure 1c), suggesting highly variable river network DOC uptake across watersheds. The smallest Da (e.g., <0.5; and thus export-oriented systems) is found in small river networks (SO 1–3) (Figures 3a and 4), draining coastal watersheds or off-continent islands (Figure 1c). These systems make up the largest percentage among the global watersheds (∼93%) but a rather small fraction (∼12.3%) of the total global water discharge (∼47,000 km^3 yr^{-1}) (Lin et al., 2019) because of their small drainage size (e.g., ∼95% are <1,000 km^2) (Table 1). These watersheds are also found at all latitudes (Figure 1c) despite the large temperature gradient along the altitude (e.g., mean annual air temperature from <5°C in the high latitudes to >25°C in the tropics).

The Da for more than half of SO 7–9 watersheds is larger than 2, suggesting uptake dominance in these largest river networks. These watersheds make up 46% of the global land surface area, and summed discharge from these watersheds (∼25,100 km^3 yr^{-1}) is more than half (54%) of the total global water discharge (Table 1). In terms of

Table 1
Global Watershed Area, Annual Discharge, Stream Network Length, and Annual Water Residence Times by Watershed Stream Order

Stream order	No. of watersheds	Watershed area (km^2)	Annual discharge (km^3)	Stream network length (km)	Annual water residence time (hr)	
					Mean ± SD	Median (range)
1	32,616	66 ± 1,128	0.04 ± 0.1	9 ± 10	10 ± 12	6 (0.03–386)
2	15,658	299 ± 6,405	0.1 ± 0.2	48 ± 40	30 ± 25	23 (0.4–449)
3	7,365	942 ± 7,399	0.4 ± 0.8	205 ± 152	68 ± 48	55 (6–627)
4	2,943	3,827 ± 33,493	1 ± 3.	839 ± 608	137 ± 84	117 (10–822)
5	1,009	15,915 ± 117,353	6 ± 12	3,602 ± 2,715	258 ± 133	227 (47–1,157)
6	276	49,375 ± 42,073	22 ± 37	15,753 ± 13,473	468 ± 229	411 (176–1,431)
7	64	219,103 ± 185,081	75 ± 121	61,302 ± 45,577	805 ± 338	767 (322–2,233)
8	23	1,041,948 ± 719,893	419 ± 349	296,721 ± 160,466	1,435 ± 395	1,396 (761–2,191)
9	4	2,348,999 ± 530,711	2,658 ± 2,861	752,162 ± 254,567	1,782 ± 252	1,697 (1,584–2,147)

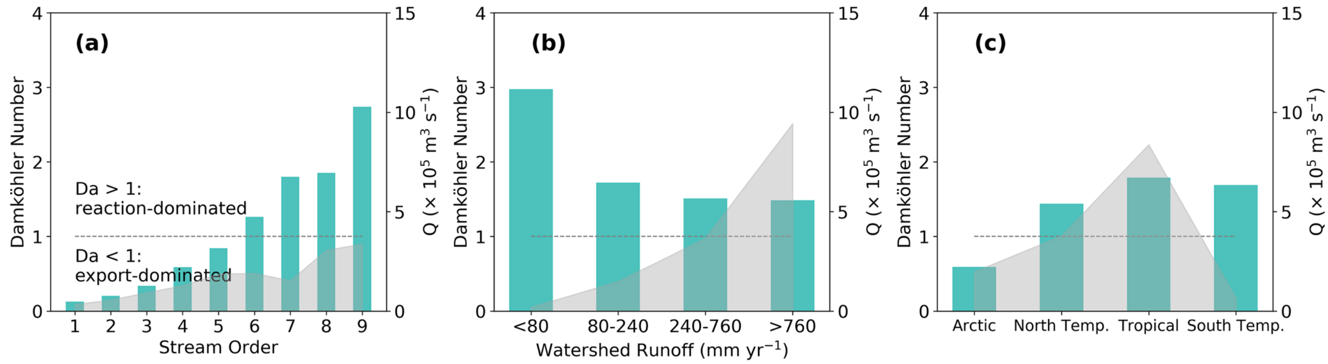

Figure 3. Damköhler number (Da) for dissolved organic carbon uptake in global river networks by (a) stream order, (b) watershed runoff, and (c) latitudinal. Shaded areas show total water discharge from watersheds of each subgroup. Dashed line shows Da = 1.

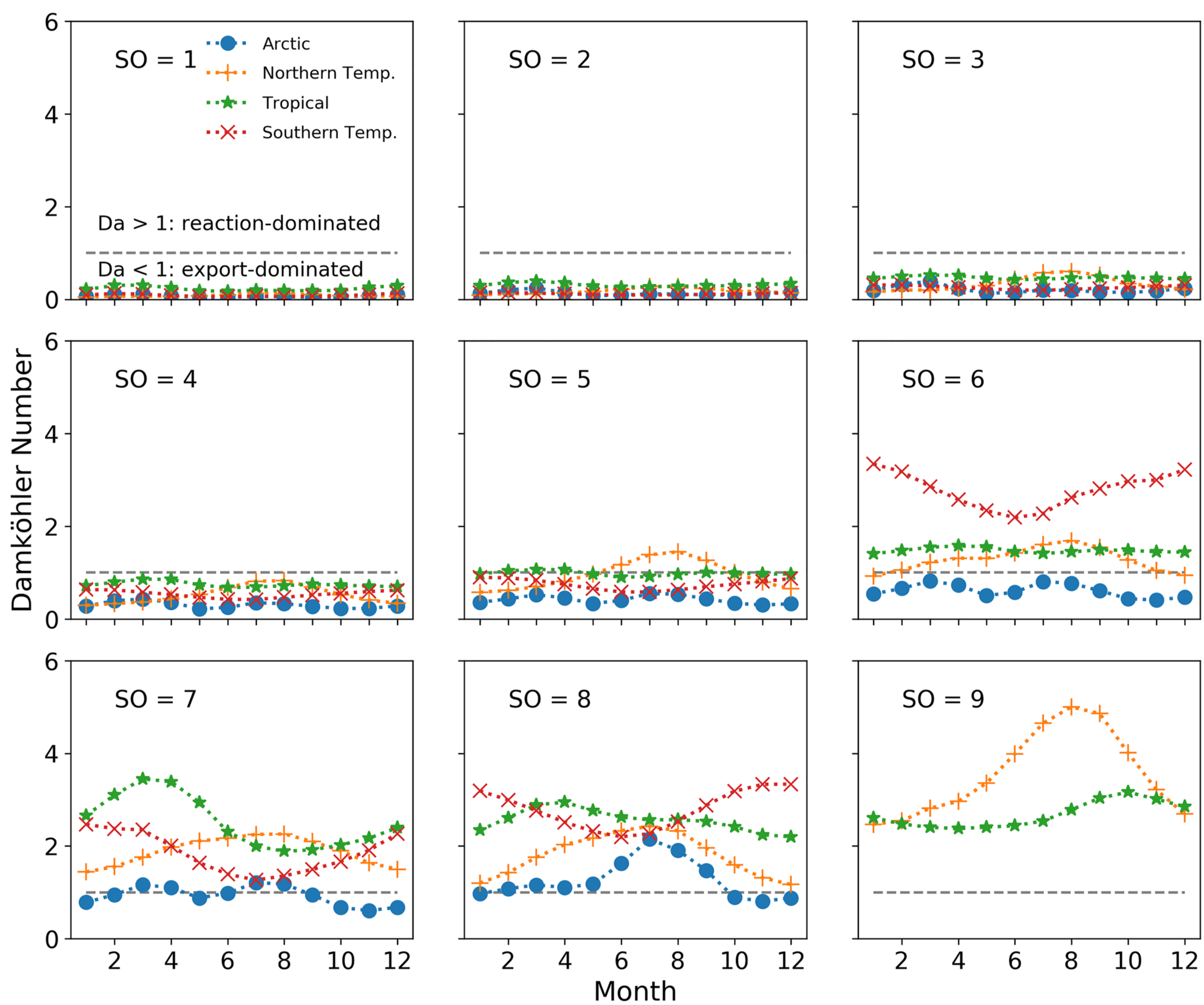

Figure 4. Monthly Damköhler number for dissolved organic carbon uptake in global river networks by stream order and climate region. Dashed line shows Da = 1.

SO, Das are 0.15–0.4 for SO 1–3 watersheds, 0.6–1.3 for SO 4–6 watersheds, and 1.8–2.8 for SO 7–9 watersheds (Figure 3a). Da turns above 1 between SO 5 and 6 (or 9,300–38,000 km^2 in watershed area), implying that watersheds turn from export-to reaction-dominated systems in terms of DOC uptake at the same SO. Despite large seasonal variations, large watersheds (e.g., SO 7–9) in temperate and tropical regions are primarily reaction-dominated systems as suggested by Da above 1 in all seasons (Figure 4).

Besides in large watersheds, high Da (e.g., 3–23) are also found in arid basins of Sahara, central Asia, southwestern US, and central Australia (Figure 1c), suggesting these watersheds are reaction dominated. The Da is 3.25 for the lowest watershed runoff class (<80 mm yr^{-1}), ~2 times that in river systems of higher runoff (i.e., >80 mm yr^{-1}) (Figure 3b). Despite high Da, total water discharge from arid watersheds is only ~1.3% of the global total discharge.

Across climate regions, Das are highest for tropical rivers (absolute latitude of watershed outlet is below 23.5°; 1.82), intermediate in temperate rivers (23.5°–56°; 1.48–1.74), and lowest in the Arctic rivers (above 56°; 0.61) (Figure 3c). Total water discharge is 58%, 29%, and 13% of the global total for tropical, temperate, and the Arctic watersheds, respectively. In contrast to high Da in temperate and tropical river systems, Da in the Arctic rivers are low (e.g., less than 1) only until the largest watersheds (SO 8) (Figure 4), suggesting export dominance in most Arctic rivers.

3.3. Damming Effect

For a total of 1,295 watersheds found to be associated with at least one reservoir, WRT ranges from 6 hr to >53 years in comparison to 1 hr to 93 days under natural flows in these watersheds (Figures 1b and 6a). Damming thus substantially extends the time that water stays in these watersheds by 1–86,800 times. By SO, WRTs in the regulated watersheds are 4.7–823 times as long as under natural flows and the changes are most significant in small watersheds (e.g., 125–823 times in SO 1–3 watersheds) (Figure 6b). This translates to an enhancement in Da of 141–2,944 times from 0.08 to 2.7 under natural flows to 13–232 under dammed conditions (Figure 6c). Damming therefore transforms natural rivers to systems of high processing capacities, assuming the same substrate uptake rate in reservoirs as in natural rivers (Wollheim et al., 2015). Along the latitude, enhancement in Da by river damming is most significant in northern and southern temperate watersheds where most reservoirs are found (Figure 5c).

3.4. Global Warming Effect

Evaluating on an annual basis, over 98% of the global watersheds had seen an increase in temperature (averaging 0.63°C) between the year 1900 and 2006, which causes an increase in river network Da for DOC uptake of ~4.9% in magnitude at the global scale (Figure 7a). Under future climate changes, all watersheds will experience temperature increase and the estimated Da increases by the year 2100 are 19% and 42% under the RCP4.5 and RCP8.5 scenarios, respectively (Figures 7b and 7c). In line with the projected temperature changes, Da increases are more pronounced in the Arctic and northern temperate rivers. For example, Da increases under the RCP4.5 scenario are 18%, 18%, 10%, and 7% for the Arctic, northern temperate, tropical, and southern temperate rivers, respectively, and 55%, 34%, 23%, and 17%, respectively, under the RCP8.5 scenario. These Da increases imply enhanced instream DOC uptake in global river networks under future climate changes.

4. Discussion

4.1. DOC Cycling and Measurements in River Networks

DOC cycling in river networks involves multiple processes that contribute simultaneously to its gains/losses within rivers (Battin et al., 2008; Bernhardt et al., 2018; Kaplan & Cory, 2016). In situ photooxidation (Maavara et al., 2021) and biotic mineralization (del Giorgio & Pace, 2008; Raymond & Bauer, 2000) are the two main processes contributing to permanent DOC removal and CO_2 emission from river systems. The magnitude of DOC removal rate in river networks is however difficult to quantify due to the complex interplays among multiple biotic/abiotic processes that contribute to DOC concentration variations in spatially distributed river networks (Lv et al., 2019; Wollheim et al., 2015). Characterization of river network DOC removal is also hindered by complex DOM compositions that preclude replication and realistic DOC uptake rate quantification via simple

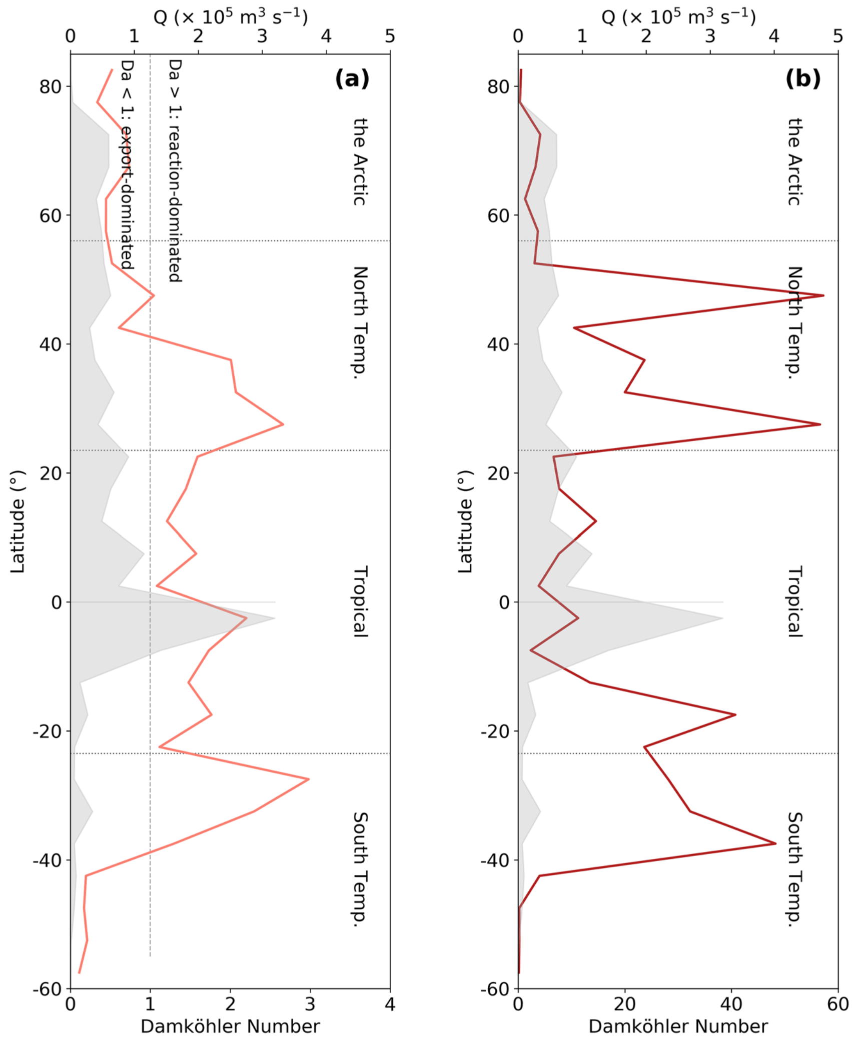

Figure 5. Latitudinal variations in Damköhler number for dissolved organic carbon uptake in (a) natural river networks and (b) river networks with the damming effect added. Shaded areas show latitudinal variations in water discharge from global watersheds.

solute addition experiments at river reaches (Mineau et al., 2016; Stream Solute Workshop, 1990). Bottle river/stream water photooxidation and/or microbial incubation experiments (i.e., bioassays) provide opportunities for bulk DOC reactivity quantification in an isolated and controlled setting (del Giorgio & Pace, 2008). Bioassays are however problematic because the more important benthic/hyporheic removals in real river network settings are not accounted for (Harvey et al., 2019; Newcomer et al., 2018).

In Table S1 in Supporting Information S1 and Figure 8, we compared DOC spiraling characteristics measured from reach-scale solute addition experiments and bulk photooxidation/bioassay experiments. Median DOC υ_f measured from 152 individual simple molecule or organic leachate addition experiments was 3.2 m d^{-1} (0.9 quantiles: 0.9–22 m d^{-1}). The υ_f suggests a characteristic reaction time (t_r) of ~0.3 hr (0.9 quantiles: 0.03–9.7 hr) (Figure 8) or a characteristic uptake length of 3.7 km (0.9 quantiles: 0.27–40 km) (Table S1 in Supporting Information S1). These DOC spiraling characteristics suggest quick elimination of the added surrogate solutes within water advection timescales even of the smallest watersheds (e.g., 6 hr in SO 1 watersheds, Table 1). Mineau et al. (2016) tried to reconcile the solute addition-derived stream DOC υ_f by accounting for DOC reactivity under ambient conditions. The resultant DOC υ_f (0.37 m d^{-1}) was one order of magnitude lower than measured from stream solute addition experiments. However, runoff DOC concentration required to balance the removal rate was high (14.8 in comparison to 4.3 mg L^{-1} in typical headwater streams) (Mineau et al., 2016), suggesting that the ambient DOC υ_f may still represent an overestimate. We suggest simple molecules or organic leachates

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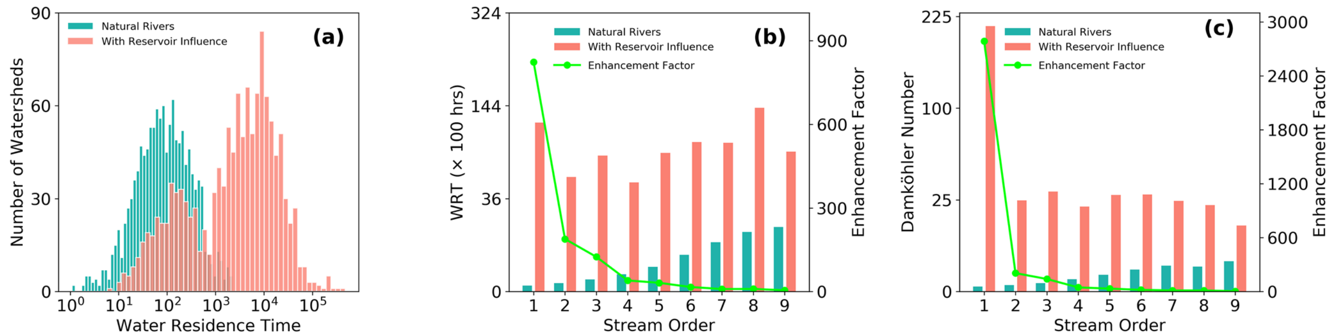

Figure 6. Annual water residence time (a, b) and mean Damköhler number (c) for dissolved organic carbon uptake in reservoir-affected watersheds.

represent a highly labile fraction and rapidly consumed within the heterogeneous aquatic DOM mixtures (Lutz et al., 2012). In addition, high-solute uptake can also result from assimilatory biotic uptake, transformation, or adsorption (Munn & Meyer, 1990) and does not correspond solely to DOC mineralization.

In contrast to rapid removals suggested from solute addition experiments, median DOC t_s calculated from 90 dark bioassays (as the inverse of first-order decay coefficient or k) was five orders of magnitude higher than that measured from reach solute addition experiments (11,100 hr vs. 0.3 hr) (Figure 8). The bioassay t_s was also fivefold the longest WRT found for river networks (2,232 hr, see Section 3). The bioassay t_s thus implies limited DOC reactivity or removal even in the largest river networks (Da <0.2), probably because the method significantly underestimates in situ DOC uptake by accounting for processing only within water columns (del Giorgio & Pace, 2008). DOC t_s measured from 20 combined photooxidation/bioassays were comparatively much lower (median: 314 hr) (Figure 8), indicating quicker mineralization when considering in situ photo- and biotic oxidations together. Particularly, photodegradation is a widely recognized process that promotes microbial breakdown (Allesson et al., 2016; Lu et al., 2013) though either photo- or microbial oxidation alone is insignificant for DOC removal in river networks (del Giorgio & Pace, 2008; Maavara et al., 2021). DOC υ_f chosen for Da scaling in this analysis (0.038 m d^{-1}, corresponding of a t_s of 720 hr or WRT of a 6–7 order river network) (Wollheim et al., 2015) falls between DOC uptake determined from the solute addition and dark bioassay methods (Figure 8). Slightly slower turnover in comparison to that suggested from photooxidation/bioassays (720 hr vs. 314 hr) results likely from the fact that the model-derived DOC spiraling characteristics (υ_f or t_s) (Wollheim et al., 2015) accounted for in situ autochthonous DOC production in real river networks.

The large discrepancy in DOC uptake measured from different methods highlights incompleteness in current understandings of DOC cycling in river networks (Bernhardt et al., 2018; Raymond et al., 2016). Nonetheless, our choice of υ_f yields reasonable instream DOC removal at the global scale. Under this υ_f, global river network DOC removal efficiency was ~65% (as a discharge-weighted mean removal efficiency across global watershed; corresponding to a Da of 1.05 under the first-order reaction kinetics). Considering total DOC export by global river networks is ~0.21 Pg C yr^{-1} (Ludwig et al., 1996), total instream respiratory DOC loss would be at a magnitude of ~0.6 Pg C yr^{-1}. This value corresponds to a third of total CO_2 emitted from global river networks (1.8–2.0 Pg C yr^{-1}) (Liu et al., 2022; Raymond et al., 2013) and within the empirical range of estimated DOC metabolism contribution to CO_2 emission in typical river systems (15%–50%) (Battin et al., 2008; Hotchkiss et al., 2015; Ward et al., 2013). We however recognize rarity of system-wise DOC removal estimates (Wollheim et al., 2015) and the limitations in describing the complex issue of river network DOC cycling as a single υ_f or Da (see Section 4.5). The work is however valuable as it provides a means to examine the variability of DOC removal versus export across watersheds at broad geographical scales.

4.2. Watershed Controls on DOC Removal and Export

The analysis identifies watershed size to be a primary factor determining the relative balance between DOC removal and export in river networks. This effect is best illustrated by a comparison of Da in river networks at the two ends of the watershed size continuum (Figures 3 and 4). Drainage area of the largest watersheds (i.e., SO 7 and plus) is typically >3,000–50,000 times as large as the smallest watersheds (e.g., SO 1), which results in a difference in river network WRT of typically 100–300 times and a difference in Da of 12–20 times. The large difference

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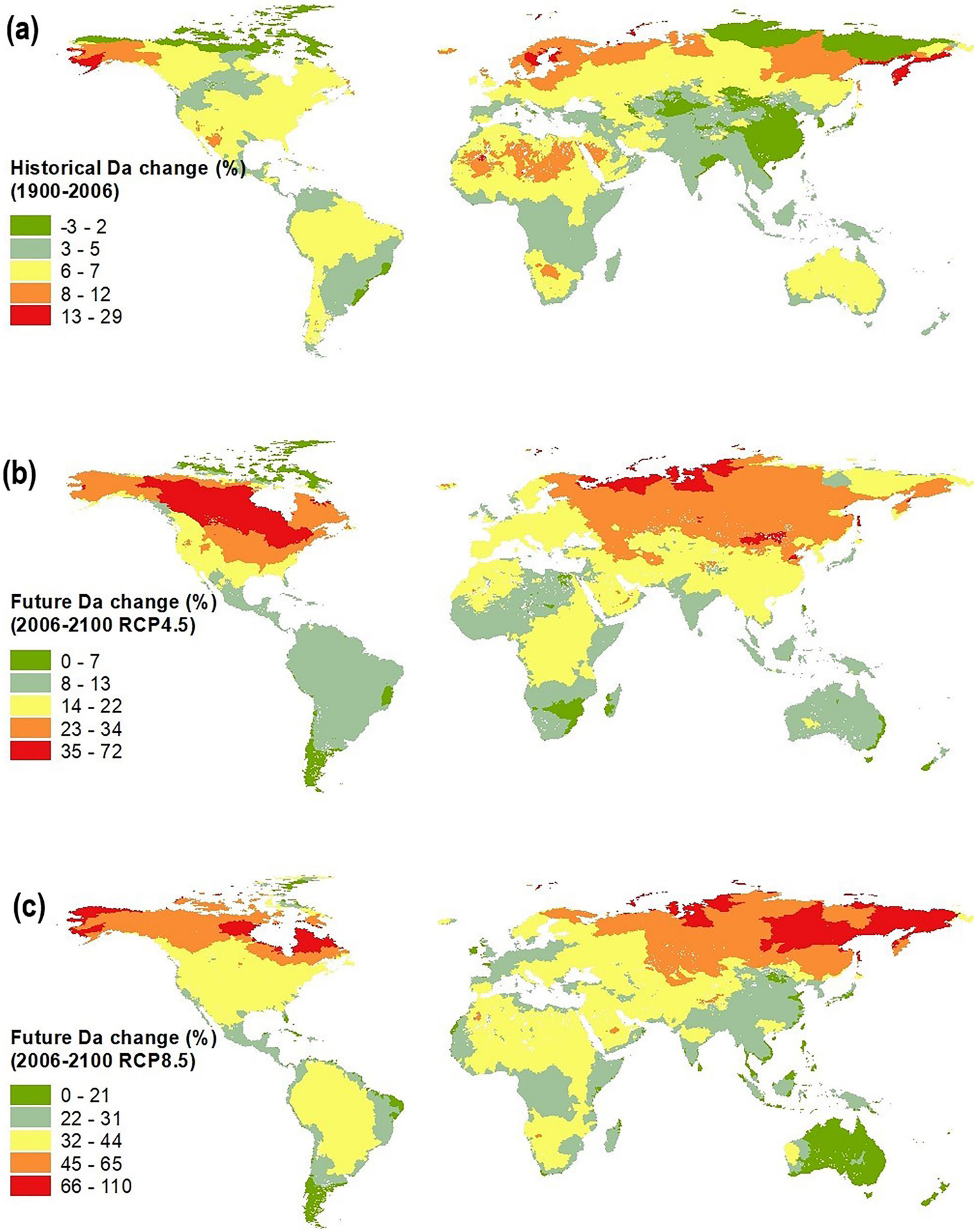

Figure 7. Historical (a) and projected (b, c) Damköhler number changes for dissolved organic carbon uptake in global watersheds. Historical Damköhler number change is calculated based on the temperature difference between the average of the years 1900–1910 and the years of 2006–2016.

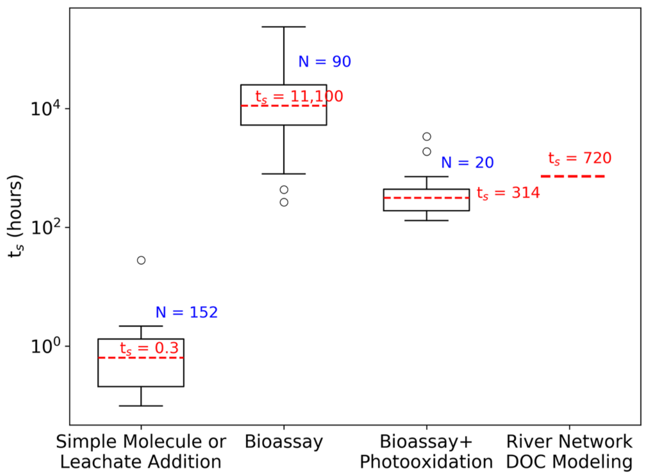

Figure 8. Characteristic reaction timescales for dissolved organic carbon (DOC) uptake (t_s) determined from simple molecule or leachate addition experiments, bioassay/photooxidation experiments, and a river network DOC cycling modeling work (Wollheim et al., 2015). Data are from published literature (see Table S1 in Supporting Information S1). For conversion methods from original reported literature data, see annotations to Table S1 in Supporting Information S1. A high t_s indicates low uptake rate.

in watershed size and river network WRT thus imposes a physical constraint on DOC removal in the smallest versus largest watersheds. For instance, a 20°C temperature difference (i.e., close to the largest seasonal or latitudinal water temperature difference) would cause a fourfold change in Da (Equation 6). This change however wound not make low-ordered stream networks (with Da <0.25, making up 66% of SO 1–3 river networks) reaction-oriented systems. This physical constraint therefore determines the smallest river networks (SO 1–3) to be predominantly export-oriented systems (Da << 1) in line with observations that suggest effective river organic carbon exports by small mountainous watersheds (Hilton et al., 2011) and the largest river networks (SO 7–9) reaction-oriented systems (Da >1) across seasons and the latitude (Figures 1c and 4) though latitudinal and seasonal variations within each SO are also significant (Figure 4).

The turn from export-to reaction-oriented systems at ca. SO 5–6 for global watersheds (Figures 3 and 4) is important as it implies a clear difference in the amount and quality of DOC exported by river networks of different sizes to receiving basins. While small watersheds principally export terrestrial DOC in less altered forms, large watersheds export highly processed DOC that preserves less terrestrial compositional signals (Hosen et al., 2021). The analysis further suggests that this turn can occur at variable watershed sizes across the geographic regions. In general, drier and warmer watersheds become reaction-oriented at a smaller watershed size than wetter and colder watersheds (Figure 4).

On temporal scales, high-discharge events are suggested to induce large exports due to enhanced DOC concentration and shortened WRT that limit within-network removal (Raymond et al., 2016; Yoon & Raymond, 2012). The analysis suggests this phenomenon is also subject to the watershed size effect. For instance, a high-discharge event of 10 times as large as the base flow would increase flow velocity by a factor of ~2.5 (Equation 1) and decrease instream WRT correspondingly by ~60%. Therefore, assuming the same reaction rate (or reaction timescale t_r, Equation 3) for DOC, river networks with Da between 1 and 2.5 are most prone to the high-discharge effect. This corresponds roughly to medium-sized river networks (SO 5–7), which alternate between reaction- and export-oriented systems with flow and seasonal temperature changes (Figure 4). In contrast, the smallest river networks remain export-oriented and the largest river networks reaction-oriented under high flows.

In large watersheds where high-discharge-induced DOC transport does not end up being exported, hot spots for DOC uptake perpetuate to downstream ecosystems within the river networks. The progressive saturation in river network uptake capacity and quick transfers of DOC through headwaters and small rivers under high discharge and increased loads have been described as the "shunting" effect within the pulse-shunt framework (Raymond et al., 2016) or "spatial saturation" under the RNS concept (Wollheim et al., 2018). These concepts underscore the capacity for large river networks to process legacy constituents leaked from upstream river networks, a capacity that small river networks do not possess.

4.3. Latitudinal and Seasonal Changes

The temperature effect causes a DOC uptake gradient along the latitude (Figures 3–5). The analysis suggests high DOC removal capacity in tropical rivers, which is overall two times as large as that in temperate rivers and 4–6 times as large as that in high-latitude rivers in terms of Da (Figures 3–5). Therefore, enhanced DOC uptake due to higher temperatures is more pronounced though higher discharge in tropical river networks works to shorten instream residence times and reduce removal. High DOC removal is in line with quick DOC turnover (Mayorga et al., 2005) and large CO_2 emission (Richey et al., 2002) in tropical river networks. In contrast, the Arctic rivers are identified as export-oriented systems where main export dominance can be found in systems of up to the 7th SO (Figures 3 and 4).

Temperature-induced Da change across seasons is more pronounced in medium-sized to large (SO 6–9) river networks in temperate and the Arctic regions (Figures 4 and 5). We propose that temperate and the Arctic rivers are characterized by much greater seasonal variations in temperature and DOC uptake rate than tropical rivers (e.g., 0°C–23°C vs. 23°C–25°C), which cause larger seasonal Da changes than in tropical rivers. Additionally, longer WRTs in large watersheds allow for more sufficient DOC processing (Lv et al., 2019; Wollheim et al., 2018) and have an enlarged and more pronounced temperature effect in large (SO 6–9) than in smaller river systems. Variations in Da among geographical regions are also observable. For example, SO 6 watersheds in southern temperate regions exhibit significantly higher Da than in other climatic regions (Figures 4 and 5). We suggest that a larger percentage of arid/semiarid watersheds in this area (e.g., in central/western Australia) is responsible for the elevated Da, considering that arid/semiarid river systems also feature longer retention times and thus higher processing capacity (Figure 1). This reinforces the idea of a combined effect of hydrology and aquatic biogeochemistry in shaping the riverine DOC cycling landscapes across global watersheds.

4.4. The Impact of River Damming and Global Warming

We note the significant impacts of river impounding and climate warming on WRT and/or DOC uptake in river networks (Figures 6 and 7). Dam-induced water residence extension in river networks has also been described by the concept of river water "aging" (Vörösmarty et al., 1997). The magnitude of damming-induced river water aging depends highly on the number and spatial distribution of constructed dams and therefore the completeness of dam database matters. Evaluating based on a total of 746 large reservoirs (capacity >0.5 km^3), Vörösmarty et al. (1997) arrived at a mean river water aging of 31 days (or 744 hr) for global watersheds or 58 days (1.392 hr) for regulated watersheds alone. Here, estimating based on the HydroLakes database that includes all reservoirs >10 km^2 in area and additional reservoirs to 0.1 km^2 (Messager et al., 2016), we suggest a mean river water aging by dams of 237 days (5,687 hr) for global watersheds or 371 days (8,908 hr) for regulated watersheds alone. Therefore, river damming has increased water aging by approximately seven times since its first evaluation ~24 years ago (Vörösmarty et al., 1997). More significant water aging and reservoir impacts on river network DOC uptake are anticipated with the ongoing and planned dam constructions on the world's rivers (Zarfl et al., 2015). We acknowledge systematic regime shifts associated with these changes and under climate change (Maavara, Chen, et al., 2020; Maavara et al., 2017) and future research needs on this.

4.5. Caveats and Limitations

The main limitation of using a single, temperature-dependent v_f or t_s to describe DOC removal is its inability to account for the significant spatial and temporal variability in DOC reactivity and complex DOC cycling dynamics in real river networks (Wollheim et al., 2015). First, aquatic DOC composition is known to vary dramatically in rivers of different sizes, watershed compositions, and geographic regions (Kaplan & Cory, 2016) and cause significant variations in in situ aquatic DOC reactivity. This effect is however difficult to account for considering current technical difficulties in quantifying in situ DOC reactivity (Mineau et al., 2016). Second, terrestrial landscapes are heterogenous in terms of DOC supply to river networks and therefore the within-network location of terrestrial DOC sources (e.g., wetlands) matter in terms of allochthonous DOC input and removal in river networks (Lv et al., 2019; Wollheim et al., 2015). The spatial heterogeneity in terrestrial DOC supply was however not accounted for by discharge-weighted WRT estimates in this analysis (Equation 2), which implicitly assumed spatially uniform input from terrestrial landscapes. Third, rivers of different sizes or hydrogeomorphic configurations are expected to possess different DOC metabolic capabilities (Battin et al., 2008). This variability was not accounted for by a v_f designed to respond solely to temperature in this analysis (Equation 6). Fourth, the single v_f also did not account for within-network variations in autochthonous DOC production, particularly in impounded waters where autochthonous production strengthens and aquatic DOC dynamics alters (Maavara, Chen, et al., 2020).

Despite the limitation, the Da analysis allows us a unified view of riverine DOC reaction variability across broad spatial scales. One main value of the current analysis is the common framework for scaling DOC removal and the hydrologic advection timescales that are necessary for a quantitative assessment of the magnitude of DOC removal in global river networks. We suggest that future river network DOC modeling work takes into consideration the hydrologic and biogeochemical perspectives for quantitative evaluations of DOC cycling in river networks. We however acknowledge that the current analysis lacks a full spatially resolved DOC data set necessary for quantitative DOC budget assessments in global river networks. Efforts are also needed for a full disentangling of the complex DOC reaction rate variations in river networks.

We also note the operational nature in defining river networks as reaction- or export-oriented systems using a conventional Da cutoff of 1 (Rehage & Kind, 2021). This Da corresponds to a high removal efficiency (63%) under the first-order reaction kinetics assumption and suggests a transition from export- to reaction-oriented river networks at around SO 5–6 for DOC uptake. Using 0.1 as the cutoff, which corresponds to a removal efficiency of ∼10% instead, only the smallest (e.g., first order) river networks would be classified as export-dominated systems. Furthermore, Da and river network removals are highly sensitive to the magnitude of v_f (Bertuzzo et al., 2017; Lv et al., 2019; Wollheim et al., 2018). Therefore, export-dominated river networks defined in terms of DOC uptake may be highly reactive systems in terms of the cycling of other constituents with orders of magnitude higher uptake (e.g., nitrogen or phosphorous) (Wollheim et al., 2018). Therefore, the DOC-based classification of reaction- or export-oriented river networks should be interpreted in a relative sense and within the context of a targeted constituent.

5. Conclusion

The concept of Da relates the reaction to advection timescales of reactive constituent transport and provides a common framework for evaluation of river network removal/export across space and time. In this analysis, we viewed watersheds/river networks as unit reaction systems and evaluated factors that affect their reaction efficiency across watersheds and seasons. We demonstrate that the watershed size imposes a primary control on river network reaction due to a difference in WRT of >3 orders of magnitude. Hydrology or temperature-induced seasonal variations in reaction (or export) are more pronounced in medium-sized watersheds, suggesting that these watersheds are more transitional between reactors and exporters across seasons or hydrologic variations. Temperature-induced latitudinal variations in reaction are also significant, where tropical river systems are two times more efficient than temperate river systems and 4–6 times more efficient than the Arctic river systems. Assessing under the same framework, river damming has a profound effect on river network reaction, considering significantly extended WRTs especially for small watersheds. Global warming is projected to increase reaction by ca. 19% until year 2100 under the RCP4.5 scenario. We conclude that river network reaction/export is controlled together by watershed size, constituent reactivity, and spatiotemporal variations in hydrology and temperature.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The GRADES (Global Reach-Level A Priori Discharge Estimates for SWOT) river networks and daily discharge data sets are accessible via https://www.reachhydro.org/home/records/grades. Monthly water residence time and Damköhler number estimates for DOC cycling in global watersheds are available via Dryad at https://doi.org/10.5061/dryad.2v6wwpzqv.

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