Biophysical controls on organic carbon fluxes in fluvial networks

Metabolism of terrestrial organic carbon in freshwater ecosystems is responsible for a large amount of carbon dioxide outgassing to the atmosphere, in contradiction to the conventional wisdom that terrestrial organic carbon is recalcitrant and contributes little to the support of aquatic metabolism. Here, we combine recent findings from geophysics, microbial ecology and organic geochemistry to show geophysical opportunity and microbial capacity to enhance the net heterotrophy in streams, rivers and estuaries. We identify hydrological storage and retention zones that extend the residence time of organic carbon during downstream transport as geophysical opportunities for microorganisms to develop as attached biofilms or suspended aggregates, and to metabolize organic carbon for energy and growth. We consider fluvial networks as meta-ecosystems to include the acclimation of microbial communities in downstream ecosystems that enable them to exploit energy that escapes from upstream ecosystems, thereby increasing the overall energy utilization at the network level.

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Fluvial networks link multiple components of the landscape, including soils and groundwater, with the atmosphere and the oceans. Each year streams and rivers of the world transport, transform or store nearly 2 Pg of terrestrial organic carbon (Box 1), a quantity that represents a large fraction of the global annual terrestrial net ecosystem production[1–4] (see Box 2 for a glossary of terms). Most of the respired carbon originates from terrestrial vegetation and is initially stored in soils where turnover times can range from years to centuries[5]. This has led to the conventional wisdom that fluvial carbon is processed and refractory. Recent estimates of CO_2 outgassing from streams and rivers[3,4,6–8] contradict this perception, and suggest that land-derived organic carbon is an important integrator of terrestrial and aquatic ecosystem processes that fuel the net heterotrophy of fluvial ecosystems. This raises the question: how can organic carbon be oxidized during its route from continents to oceans given transit times in fluvial ecosystems of days to weeks relative to extended residence times in soils?

To address this question we have developed a conceptual model that integrates recent progress from geosciences[9], microbial ecology[10] and biogeochemistry[7,8,11–16] and describes how microorganisms adapt to the structure and dynamics of the geophysical world. The ensuing microbial processes exert control over net heterotrophy in and CO_2 outgassing from fluvial networks, and ultimately influence global carbon fluxes. Our core concept is that the efficiency with which streams, rivers and estuaries retain and oxidize organic carbon rests on the evolution of microbial physiological capacities in response to geophysical opportunities that involve extending the residence time of organic molecules in transport. Of course, direct contact between microbes and their substrates is essential, so geophysical opportunities involve transport rates, and microbial capacities involve reaction rates. Transport rates primarily reflect physical or geophysical constraints (for example, geomorphology, hydrologic connectivity), whereas reaction rates reflect the evolution of microbial pathways (for example, metabolic diversity). Further, because our focus is on microbial metabolism of dissolved organic carbon (DOC) (Box 1) from headwater streams to estuaries, our concept also draws on advances in fluvial network theory, DOC molecular-level chemistry and microbial biogeography.

GEOPHYSICAL OPPORTUNITIES IN FLUVIAL CHANNELS

Fluvial channels and networks are optimized for transport of water and sediments[17], but we begin by asking whether they also provide opportunities for the transformation of terrestrial DOC. Transformation requires contact with biologically active surfaces, and increased fluxes, storage and hydrologic retention of substrates, nutrients and oxygen favour microbial growth; similar processes also regulate chemical transformations associated with surfaces. This section highlights how storage and retention change and offer

Box 1 DOC and POC

Terrestrial net ecosystem production (NEP) can enter aquatic ecosystems as dissolved organic carbon (DOC) and particulate organic carbon (POC). Both phases form a continuum along physical, chemical and biological properties and with continuous interactions (for example, lysis, aggregation). Revised carbon fluxes of the major world rivers identify the flux of terrestrial DOC (0.25 Pg C y^{-1}) as the largest transfer of reduced carbon from the land to the ocean with POC export estimated at 0.18 Pg C y^{-1} (ref. 1).

The movement of DOC and POC through fluvial networks is fundamentally different. DOC travels with the water, whereas POC is subject to gravitational settling, hydrodynamic lift and drag forces. As a result, POC transport occurs as a series of discrete events. POC deposited in sediments can remain immobile for prolonged periods of time, but is subject to rapid mobilization and pulsed transport during high flow.

The bulk of POC in transport under low flow has traditionally been considered old, typically small (<20 µm diameter) and of low metabolic availability and nutrient content. Recent research is redressing this perception and now shows that a fraction of this material is important to net ecosystem metabolism. Fresh and labile POC is expected to be consumed quickly and locally without significant transport downstream.

Despite the metabolic relevance of POC, DOC is the most important intermediate in global carbon cycling. In fact, only low-molecular-weight compounds (500–1,000 daltons) are transported through the microbial cell membrane and subsequently subject to metabolism. Microbial extracellular enzymes thus have to hydrolyse POC first, and the resulting DOC molecules can be subject to microbial metabolism.

multiple and repeated opportunities for DOC transformation in streams, rivers and estuaries.

Published studies from temperate, tropical, semi-arid and Arctic streams and rivers show a broad downstream trend of declining in-stream storage volumes and storage times with increasing discharge (Supplementary Information, S1). Discharge shapes channel geomorphology (for example, width, depth, slope) and bed topography through fluvial networks as described by downstream hydraulic geometry[17], and is thus likely to control reach-scale storage dynamics (Fig. 1). For instance, flow over morphological features ranging in size from ripples and dunes to meanders and pool-riffle sequences controls surface–subsurface fluxes, whereas sediment characteristics (for example, hydraulic conductivity) control the resistance to exchange[18,19]. Recent research has highlighted the fractal relationship between topography, surface–subsurface fluxes and subsurface storage across a very wide range of scales (from bedforms to continents), and suggests topographic control of storage dynamics as a general phenomenon[20]. Furthermore, tracer experiments reveal that the channel friction factor predicts reach-scale storage and retention[20] and thus constitutes an alternative downstream predictor of geophysical opportunity related to subsurface storage (Fig 1).

In high-gradient streams, rough, coarse and highly permeable streambeds create opportunities for subsurface retention and storage under low flow conditions, and exchange with the surface water is frequent (see Supplementary Information S1 for further discussion). In contrast, low-gradient streams and rivers are generally depositional environments and less topographically constrained than high-gradient streams. During low flows, fine-grained sediments accumulate, clog interstitial spaces and reduce bed roughness, all

of which, by extension, reduce the potential for surface–subsurface fluxes, storage and retention in larger rivers (Fig. 1). However, the few studies performed with conservative tracers in larger rivers suggest unexpected surface–subsurface exchange[21], probably induced by meanders and other large-scale morphological features. Further, the downstream decline of in-stream storage in these ecosystems is offset by alternative storage and retention allocated to stream surface components such as debris dams and most notably over-bank storage in floodplains (Fig. 1). Flood pulses can generate considerable lateral interactions with the fringing floodplains, resulting in long-term retention between flood pulses but with less frequent exchange relative to smaller streams.

Estuaries constitute the terminal interface of the fluvial network and the ocean. They have unique hydrodynamics with bi-directional tidal flows and complex circulation patterns that result in broad ranges and spatial distributions of residence times within single systems[22]. Of particular interest is the estuarine turbidity maximum (ETM), where solutes flocculate as rivers mix with seawater, particles accumulate (up to 1 kg m^{-3}) and particle residence times can increase from days to weeks[23]. In many estuaries, river flows connect to tidal flats and intertidal wetlands, habitats that greatly increase storage and retention. A variety of mechanisms ranging from tidal pumping to small-scale bioirrigation[24] can generate substantial surface–subsurface fluxes in these ecosystems, with similar effects to those described for streams.

MICROBIAL LIFESTYLES AND CAPACITY

How do microorganisms respond to these downstream shifts in geophysical opportunities? We suggest that enhanced metabolic capacity in fluvial networks results from microbial attachment to surfaces — either as biofilms on the riverbed or as aggregates suspended in the water column (Fig. 1) — elaboration of three-dimensional architectures, and shifts in community composition. Biofilms typically dominate microbial life in ecosystems with high sediment-surface-area to water-volume ratios and high downstream transport, such as in headwaters or tidal flats. Where lower surface-area to water-volume ratios coexist with extended surface residence times — as in larger rivers, reservoirs, floodplain lakes and estuarine drown valleys — there are opportunities for microorganisms to develop as suspended aggregates. Attachment extends the residence time of microorganisms relative to the transport of water and solutes and enhances the potential for metabolism of substrates and formation of consortia. Aggregates and biofilms have comparable structure–function coupling, and we consider them as analogous lifestyles with community compositions and physiological capabilities often differing from their free-living counterparts[25–27] and adapted to the prevailing geophysical opportunities.

Biofilms and aggregates develop multiple strategies to increase biomass and activity and yet cope with hydrodynamic constraints. For instance, microbially extruded extracellular polymers form complex architectures with channel networks that facilitate solute supply and waste removal, and thereby establish and sustain chemical gradients. The three-dimensional architecture of biofilms creates retention zones, and the resulting spatial proximity of DOC storage with cellular activity benefits the community in a high-throughput ecosystem[10]. Biofilms can produce filamentous streamers that extend access to regions with higher solute transport and fluxes while retaining surface attachment and fostering perseverance in favourable locations. Similarly, advective solute transfer through pores and channels may be sufficient to satisfy biochemical reactions within aggregates[25,28,29], thus increasing growth rates by enhanced solute replenishment and overcoming a rate-limiting step in low-turbulence environments. Enzymatic dissolution of aggregates, which produces plumes enriched in DOC and nutrients as aggregates sink[25,29], can often be higher than substrate uptake itself. These plumes can support abundant and active free-living cells[25,29] that, together with the aggregates themselves, structure the water column.

Application of molecular methods reveals a gradual succession of microbial community composition along longitudinal gradients in headwaters[30,31], large rivers[32] and estuaries[23]. Essentially, these studies show that microbial community composition shifts from headwaters with populations provisionally attributed to freshwater and terrestrial habitats to estuaries dominated by marine bacterioplankton. Similarly, longitudinal changes in bacterioplankton activity also revealed a downriver increase in total bacterial carbon demand in the tidal Hudson River[33]. The drivers of community level changes are far from certain, yet the above observations collectively suggest that microbial communities acclimate to the changing resources within a fluvial network and increase their metabolic capacity.

NET HETEROTROPHY IN FLUVIAL ECOSYSTEMS

We analysed 130 published whole-ecosystem measurements of gross primary production (GPP) and respiration (R) in streams, rivers and estuaries, and used these to calculate net ecosystem production (NEP = GPP – R) (see Table 1 in Supplementary Information S2). Negative values of NEP indicate net heterotrophy, as ecosystem GPP is augmented by terrestrial organic subsidies that microorganisms respire. Overall, our estimate of global fluvial respiration from headwaters through estuaries equals 2.16 Pg C y^{-1} and represents a global net heterotrophy of 0.63 Pg C y^{-1}. These estimates are conservative as stream and river surfaces are difficult to quantify and probably underestimated, respiration within fringing floodplains is not included, and tropical systems are under-represented. Thus, it is not surprising that the estimates are lower than the extrapolations from large rivers[3,6–8], where outgassing from the Amazon alone is estimated at 0.3 Pg C y^{-1}. Nevertheless, even our conservative estimate shows that fluvial net heterotrophy is significant on a global scale[2,3] and underscores the metabolic performance of fluvial ecosystems.

R declines and NEP increases (that is, net heterotrophy declines) from headwaters through rivers and into the estuaries as the respiration of organic matter subsidies declines relative to GPP (Table 1). These data are consistent with predictions from the River Continuum Concept[34], though we have extended the fluvial network to include the transition to estuaries. Metabolic performance (as R) is highest in headwaters where most of microbial biomass and metabolic processes are associated with streambed surfaces, and continuous surface–subsurface exchanges ensure replenishment of nutrients, substrates and oxygen, and the removal

Box 2 Glossary

Biofilms are microbial accretions enclosed in a matrix formed of extracellular polymeric substances and are attached to surfaces. They form the bulk biomass in most aquatic ecosystems where they drive central ecosystem processes.

The *channel friction factor* is a dimensionless measure of roughness in channels. It is a function of water velocity and channel morphology, which change regularly in the downstream direction.

Downstream hydraulic geometry[18] describes downstream changes in channel geomorphology (depth, width, slope) and current velocity as a function of discharge. It is derived from hydraulic conditions (continuity, hydraulic friction and sediment transport) and energy statements (equal power per unit area, equal power per unit length).

Epixylic refers to biofilm growth on woody debris.

The *Flood Pulse Concept*[38] (FPC) adds an explicit lateral dimension to the central postulate of the River Continuum Concept (RCC). It focuses on the flood pulse (monomodal or polymodal, predictable or not) that connects the river channel to the floodplains and that is the main driving force for the river–floodplain ecosystem. The FPC predicts that the bulk of riverine biomass derives directly or indirectly from production within floodplains and not from upstream subsidies.

Hydrologic retention is the average time that water and solutes spend in storage per unit of downstream transport.

Net ecosystem production (NEP) is a central concept in carbon-cycling research and is the imbalance between gross primary production (GPP) and ecosystem respiration (R).

River Continuum Concept[34] (RCC) is a mainstay in fluvial ecology. It predicts downstream changes in organic-matter dynamics, ecosystem metabolism, and invertebrate community structure in response to changes in channel geomorphology and terrestrial subsidies. For instance, net heterotrophy of fluvial ecosystems is predicted to decrease downstream as channels widen, allowing both solar radiation and primary production to increase relative to respiration. POC, a major focus of the RCC, is thought to be generated locally and in upstream tributaries, and to interact with the streambed to contribute significantly to the metabolism along the river continuum. The interplay of POC processing, storage and downstream leakage is predicted to maximize energy use along the river continuum. The RCC did not cover much of DOC dynamics and microbial ecology, which, at the time of its publication, were young disciplines.

The *Spiralling Concept* provides a framework and mathematical tools to evaluate the strength of linkages that result from upstream contributions of material and energy to downstream ecosystems as predicted by the RCC. The Spiralling Concept describes the cycling of materials as they are removed from the water, become transiently incorporated into biomass and are released back to the water. The length of a spiral corresponds to the average distance an atom travels downstream during one cycle through the water and biota. The spiralling length depends on how quickly cycling occurs, but also on the retentiveness of the ecosystem, or the degree to which the downstream transport of materials is retarded relative to that of water. It thus translates into ecosystem efficiency to retain and transform materials, where the components of retentiveness translate into geophysical opportunity and the biota into capacity.

Storage refers to the temporary delay in downstream movement of water and solutes that results from water exchange between the channel and storage zones.

Suspended aggregates are of microbial origin and often initiated by algal cells. They are formed by microbial cells, their extracellular polymeric substances and by various non-living particles. Depending on turbulence, ionic strength and the available building blocks, suspended aggregates can reach multimillimetre size (for example, river, lake and marine 'snow').
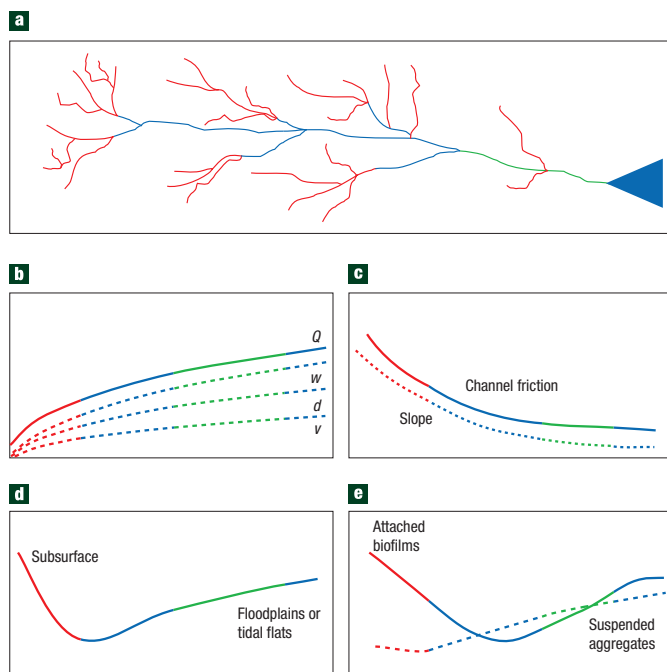
Figure 1 Heuristic concept of downstream changes of channel geomorphology, geophysical opportunity and microbial lifestyles. **a**, Fluvial network including an estuary. **b**, Channel width (*w*), water depth (*d*) and current velocity (*v*) change predictably with discharge (*Q*) as described by downstream hydraulic geometry. **c**, Channel friction shifts downstream as a result of decreasing slope and roughness due to the accumulation of fine-grained sediments. **d**, These downstream shifts translate into a re-allocation of geophysical opportunities for hydrologic storage and retention from predominantly subsurface to surface components. **e**, Consequently stable surface area per water volume decreases, which favours development of attached biofilms in streams, tidal flats and the development of suspended aggregates in rivers, floodplains, reservoirs and drowned estuaries.

of metabolic wastes. The establishment of chemical gradients along the resulting flowpaths provides niches for diverse microbial communities[35], providing opportunities for populations to express their physiological potential and process a broad range of organic molecules. Furthermore, the cross-scale interplay of the porous structures, hydrodynamic exchanges, and chemical and biological gradients in the streambed and its biofilms enhance metabolic performance in streams.

The decrease of stable surface area per water volume explains the decreased metabolism in the larger rivers, especially when current velocities are sufficient to wash out suspended algae and bacteria before they become established as active planktonic communities.

There are no data that partition respiration between riverbed and water column, or even between a river and its floodplain. Although both the riverbed[23,36] and the water column[37] certainly contribute to metabolism in larger rivers, floodplains can be a significant driver of river ecosystem metabolism[38,39]. The flood pulse connects floodplains and rivers, but the hydrologic connectivity is neither continuous nor frequent. Moreover, although the physical and temporal extent of river–floodplain interactions, habitat diversity, and diverse suspended[26] and often epixylic[40] communities contribute to the heterotrophy in rivers, little quantitative information is available on the functional relevance of aggregates suspended in rivers or the attached biofilms along subsurface flowpaths that connect rivers and their floodplains.

Estuarine respiration and notably net heterotrophy decline (that is, NEP increases) relative to streams and rivers, which puts the role of estuaries in terrestrial carbon cycling[41,42] into perspective (see Supplementary Information S2). We tentatively attribute this reduced metabolism to the combined effects of increased DOC recalcitrance following fluvial processing, increased primary production (for example, marshes), and seasonally decreased residence times coupled with low temperatures in many temperate estuaries where riverine discharges are highest in late winter and early spring. Nevertheless, an important driver of estuarine metabolism is the continuous physical mixing at the freshwater/saltwater interface that generates a unique physical and chemical environment. Flocculation and particle entrapment coupled with extended residence time in the ETM certainly influence estuarine metabolic efficiency. For instance, microbial particle transformation can contribute 90% to total bacterial carbon production[43]. Coupled chemical and physical processes in the ETM also induce particle sedimentation, storage and further processing on the sea floor. However, the balance between DOC removal via metabolism versus flocculation and sedimentation still needs to be established[42]. Tidal sediments also contribute to estuarine metabolism with benthic communities respiring on average 24% of the organic inputs from the water column[41]. Advective flow[24] delivers particles and solutes to the sediments, where a rich and active microbial community[44] can sustain high metabolism.

META-ECOSYSTEMS AND THE UPSTREAM LEGACY

Having outlined the metabolic efficiencies within individual ecosystems, we now consider how entire fluvial networks, from headwaters to estuaries, function as meta-ecosystems[45]. Meta-ecosystems are sets of ecosystems spatially connected by flows of energy and materials, which in streams and rivers are explicitly described in the River Continuum and Spiralling concepts[46]. In a meta-ecosystem, each ecosystem functions simultaneously as a sink for and source of material spirals such that the different ecosystems fulfil different functions[45]. Downstream ecosystems are thus structured to exploit energy that escapes upstream ecosystems, implying that ecosystem metabolic efficiency relative to supply increases as

Table 1 Gross primary production (GPP), respiration (R) and net ecosystem production (NEP) in streams, rivers and estuaries as determined from whole-ecosystem metabolism measurements (see Supplementary Information S2), and global estimates of respiration and net heterotrophy.

Ecosystem	GPP (g C m^{-2} d^{-1})	R (g C m^{-2} d^{-1})	NEP (g C m^{-2} d^{-1})	Global R (Pg C y^{-1})	Global net heterotrophy (Pg C y^{-1})
Streams (n = 62)	1.95 ± 0.38 (0.04–15.0)	5.14 ± 0.51* (0.78–21.7)	−3.19 ± 0.41* (−15.6–6.7)	0.51	0.32
River (n = 37)	2.42 ± 0.27*† (0.15–6.08)	4.08 ± 0.39* (0.55–9.44)	−1.66 ± 0.29*† (−5.49–4.26)	0.44	0.18
Estuaries (n = 31)	3.14 ± 0.41‡ (0.72–10.4)	3.53 ± 0.32 (0.83–7.58)	−0.39 ± 0.20‡ (−2.98–2.86)	1.20	0.13

Given is the mean ± s.e., and the minimum and maximum in brackets. Ecosystems with the same superscript are not statistically different (α = 0.05, one-way analysis of variance with a Scheffe post-hoc test, data were log-transformed). Rivers were defined as running waters with a discharge >500 l s^{-1} or larger than 5th order. Global stream and river surface area were estimated at 0.275 and 0.295 10^6 km^2, respectively (Wilfred M. Wollheim personal communication); the global surface estimate of 0.94 x 10^6 km^2 for estuaries is from ref. 42 (see Supplementary Information S2).

individual ecosystems are aggregated in the continuum. For instance, storms elevate DOC exports from headwaters; flood pulses transfer this subsidy onto floodplains, where microorganisms receive a 'second chance' to transform DOC over an extended residence time. The putatively high metabolic efficiency of rivers and estuaries at a network level thus raises the question of what network processes enable the degradation of molecules that are already processed and apparently recalcitrant?

In a fluvial network, headwaters receive most of the terrestrial DOC because of their drainage length, density[17], and interdigitation within the landscape. The first step in subjecting soil organic carbon to microbial transformation in headwaters is the removal of chemical and physical preservation[47]. Disintegration of soil aggregates, pH alteration of organomineral complexes and tertiary molecular structures, and certainly water activity figure among the chief removal processes. Novel high-resolution geochemical tools show that stream microorganisms dramatically alter terrestrial DOC, including humic substances and lignin[11–13]. Upstream sources and their processing thus impart a novel composition to organic molecules in transit, and the DOC in a given downstream ecosystem is a legacy of prior metabolic activities[48]. Evidence that DOC is metabolized continuously throughout fluvial networks has been reported from the Amazon basin[7,8] and large temperate rivers and estuaries[14–16]. In the Amazon, for instance, the metabolism of young organic carbon from plant sources accounts for most of the CO_2 outgassing, but is augmented by the processing of older organic carbon previously protected within soils[8]. Isotopic and biomarker analyses at the microbial cell level provide further evidence of the contribution of aged terrestrial DOC to the net heterotrophy in rivers and estuaries[14–16].

The metabolism of DOC exported downstream is further promoted by photolysis, co-metabolism, shifts in microbial community composition, and DOC aggregation. Downstream changes in channel morphology and residence time foster these ecological shifts. Photomineralization produces CO_2, and when oxidation is not complete, photolysis either enhances or reduces the biodegradability of the remaining DOC[49]. Timescales for photochemical oxidation in natural sunlight range from days to weeks in rivers — probably sufficient to transform DOC in transit. Increased solar radiation as the canopy opens downstream can also augment the production of organic carbon from marsh plants, macrophytes and algae, providing significant support for microbial biomass in large temperate rivers and estuaries[14,15]. In suspended aggregates, algal exudates of labile organic compounds may enhance the transformation of recalcitrant DOC through priming or co-metabolism[50]. As environmental conditions shift along large rivers and estuaries, the change in microbial communities, documented above, enhances the metabolic capacity to transform recalcitrant DOC through complementary resource use by a diverse and changing community. Finally, sedimentation of aggregated DOC increases both the residence time and the contact of organic carbon with reactive zones in rivers and estuaries.

FUTURE PROSPECTS

Past decades have seen exciting strides in microbial ecology and biogeochemistry of distinct ecosystems. The global dimension of biogeochemical processes now requires the integration of both ecosystems and disciplines. Tropical and Arctic ecosystems should receive more attention given their predicted sensitivity to climate change and involvement in global carbon cycling. Future work will most certainly be driven by better dialogue between terrestrial and aquatic sciences, and an integration of microbial ecology and biogeochemistry at the terrestrial/aquatic interface. Microbial ecologists must increasingly appreciate the coupled physical, chemical and biological processes that control microbial community structure and function, and seek avenues to link microorganisms to ecosystem functioning. For instance, the

physical processes that regulate residence time distributions of solutes and microorganisms must be better understood to adequately assess long-term average carbon transformation over large scales. Microbial consortia that putatively facilitate the degradation of recalcitrant compounds need more attention, as does DOC photochemistry in fluvial ecosystems. These combined efforts clearly require rooting in fluvial network theory so that microbial and accompanying biogeochemical processes observed locally are scaled appropriately to arrive at accurate predictions of global phenomena. This is a challenging task, but in the face of global change, a necessary endeavour.

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Author contributions

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