Linking the dissolved and particulate domain of organic carbon in inland waters

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Key Points:

- Dissolved organic carbon is the dominant form of biomass in inland waters but various 
  processes trigger its aggregation to particles
- The role of organic particles in the global carbon cycle is discussed in context of a recent 
  manuscript published in JGR: Biogeosciences.
Abstract
Organic carbon (OC) in inland waters is found in either dissolved or particulate states, each contributing differently to carbon cycling through state-specific forms of transport, processing and mineralization. Degradation of macroscopic organic material into solutes is the most common transition between these states, yet there is also the potential for dissolved organic carbon (DOC) to aggregate and form particles. This latter process at the soil-stream interface is subject of a new study by Einarsdóttir et al. (2020, https://doi.org/10.1029/2020JG005654) published in this issue. Their findings advance the understanding of the links between the dissolved and the particulate domain of OC with possible implication for long-term OC burial and ecosystem functioning of inland waters.

Plain Language Summary
Lakes and rivers are influenced by their surrounding landscape: Dead biomass releases water-soluble, organic substances that can be washed into surface waters. There, the organic substances are either removed by microorganisms or sunlight, or transported to the oceans. Under some conditions, water-soluble substances stick together and form particles. Particles are no longer transported and sink to the bottom of lakes and rivers, where they can remain for a long time. Recent research, some of it featured in this issue of JGR: Biogeosciences, describes how the organic particles are formed. The involved mechanisms influence the important role of lakes and rivers in the global cycle of carbon.

Main text
Inland waters play a crucial role in the global carbon cycle as they not only transport and process, but also bury large amounts of organic carbon (OC) (Battin et al., 2009; Tranvik et al., 2018). Burial in an inland water body is the net balance of carbon received from terrestrial ecosystems or autotrophic fixation, and lost in mineralization or downstream export. Compared to these in- and ouputs, the burial flux is usually small. However, it constitutes the only mechanism that actively removes carbon from atmospheric circulation for longer timespans (Hanson et al., 2015). It is now clear that lacustrine sediments bury as much OC as the entire ocean floor over the same time, although inland waters occupy a much smaller fraction of the Earth’s surface (1% vs 71% for oceans) (Mendonça et al., 2017).

For OC to settle and be buried in the sediment it must be in the particulate form, for example as part of dead algal biomass, plant detritus, eroded soil particles, microbial exopolymer or attached to mineral surfaces. Particulate OC (POC) is typically a small part of the standing stock of OC in inland waters. POC equals about 10 % of the dissolved fraction (DOC) in lowland rivers but both forms can approach parity in highly erosive environments (Maybeck 1982; Wetzel, 2001). Recent global estimates also confirm a high proportion (mean: 70 %) of dissolved relative to total OC in lakes (Chen et al., 2015; Toming et al., 2020). DOC therefore dominates the flux of OC through the soil-to-ocean continuum, and affects light regime as well as aquatic ecosystem functions such as productivity, nutrient and contaminant transport more directly than POC (Tranvik et al., 2018; Wetzel, 2001). In contrast, for a long time it seemed that DOC contributed relatively little to burial and the POC deposits that formed in inland waters.
Today, multiple lines of evidence suggest that DOC aggregation to POC is widespread in boreal and north-temperate aquatic networks, and contributes strongly to OC sedimentation (Hall et al., 2019; Von Wachenfeldt & Tranvik, 2008). It was recently shown that in some lakes more than half of buried OC bears the signature of terrestrial DOC (Gudasz et al., 2017; Guillemette et al., 2017). Despite this insight, little is known about the processes that act on DOC to form POC, or the functioning and fate of the resultant particles (Figure 1). In the present issue of Journal of Geophysical Research: Biogeosciences, Einarsdóttir and colleagues (2020) present DOC precipitation experiments and illuminate the specific compositional drifts in the resultant (dissolved and particulate) OC pools. The authors conducted their research in boreal Sweden at a mire-stream interface. There, a shift in redox condition triggers OC precipitation, either due to the formation of solid iron (oxy-)hydroxides, or through coagulation and adsorption to purely organic particles. The authors suspected that the growth of the organic particles is supported by microbial exopolymers (EPS, Einarsdóttir et al., 2020). As the POC formation in their assays progresses over multiple days, it is likely that DOC removal in natural waters takes place well beyond the interface and continues during passage of the aquatic network.

Over the course of the experiment about 20% of DOC forms aggregates and is removed from solution, leaving behind a DOC pool that is more hydrophobic (and thus aliphatic) in character. These observations tie in with other recent works that examine how DOC interacts with artificial iron (Fe) phases using high-resolution mass-spectrometry. These studies show that polyphenols and aromatics have a high affinity for Fe surface attachment, and DOC remaining in solution is enriched in aliphatics (Coward et al., 2019; Lv et al., 2016; Sowers et al., 2019). Additionally, the fate of nitrogen (N)-bearing DOC molecules was explored and the authors found that it depended on the precipitation mechanism: More N was recovered from organic than from mineral particles (Einarsdóttir et al., 2020), possibly because binding of N-containing compounds to Fe surfaces is unstable (Coward et al., 2019) and organic particles assembled from remaining compounds after Fe surfaces were covered. It is interesting to speculate if an otherwise reactive portion of the terrestrial DOC escapes decomposition by transferring to the particulate domain soon after entering the aquatic corridor.

It is established that DOC has a high affinity for freshly oxidized iron (Kaiser & Guggenberger, 2000) and that their joint aggregation can act as a vector of OC to sediments (Riedel et al., 2013). Much less clear, however, is under what conditions this process may be reversed. A growing body of work suggests significant amounts of DOC are being mobilized from northern lake sediments (Dadi et al., 2016; Peter et al., 2016, 2017). Because high DOC and Fe fluxes co-occur, it is suggested that the release is driven by reductive dissolution of Fe$^{3+}$ in the sediment (Peter et al., 2016). Accordingly, some DOC is shifting between the dissolved and particulate domain in association with Fe. The prevalence of such a DOC removal-and-release cycle across various ecosystem types is unknown, because it is currently not integrated into the conceptualization of landscape-scale carbon dynamics. An assessment of sediment burial efficiency can determine if settled OC is in fact buried (Hanson et al., 2015; Mendonça et al., 2017; Sobek et al., 2009), but for its calculation, the OC that sediments lose as DOC to overlying waters is either lumped with mineralization (when derived using sedimentation), or ignored altogether (when derived using mineralization). Where Fe and DOC precipitate together, it is likely that removal and release cause hysteresis in the chemical composition of the DOC pool, as DOC modification is not only observed during aggregation but also again during release (Herzsprung et al., 2017). In the case of Einarsdóttir et al. (2020), this may affect the fate of the large amount of Fe$^{3+}$ that is dissolved or colloidal after oxidation (50% of mire-emitted Fe), and
left to travel further with the remaining DOC. Both DOC and Fe are known to influence each other’s properties, as Fe intensifies the color of DOC (Xiao et al., 2013), and DOC affects Fe solubility and redox properties (Daugherty et al., 2017). Therefore, DOC is likely to experience removal-release cycles, thereby changing not only the magnitude and composition of the carbon flux through the aquatic corridor, but also various critical ecosystem properties such as light regime and thermal structure (Bartosiewicz et al., 2019).

Einarsdóttir et al. (2020) expand their results beyond particle formation by also looking at the mechanisms by which particle presence enables further modification of the remaining DOC. Even if mineralization is moderate in the presented setup, it is clear that the presence of organic particles promotes the mineralization of the surrounding DOC. Particles act as “hubs” of microbial activity because they constitute shelters or sheaths of microorganisms, often created by themselves using exopolymers (Wotton, 2007). Throughout their relatively short lifetime (days to weeks in boreal rivers), the active particles stay in a dynamic equilibrium with the dissolved phase, from which they continuously take up DOC as substrate (Attermeyer et al., 2018). Microbial respiration in large rivers measured without such particles can be dramatically underestimated (Ward et al., 2018). Because many mechanistic studies rely on lab-scale assays of respiration, it will be necessary to find approaches to routinely include both dissolved and particulate OC in future experimental setups.

Figure 1 Organic carbon (dissolved or particulate, DOC or POC) derived from terrestrial environments is transferred to and through the interconnected aquatic corridor. OC awaits different fates (arrows) in the dissolved or particulate domain (Hanson et al., 2015; Tranvik et al., 2018). Various mineralization mechanisms oxidize fresh and reactive portions of the OC pool to CO$_2$. A suite of processes links the dissolved and particulate domain through aggregation and disaggregation (white circles). POC from aquatic biomass (macrophytes, zooplankton, algae) is considered fresh and is efficiently mineralized during sediment diagenesis. It is currently unclear if diagenesis of purely organic aggregates affects all POC precursors similarly and can release OC from the sediments (Wotton 2007).

To summarize, a contemporary perspective of carbon in inland waters needs to acknowledge that a suite of mechanisms can aggregate and remove DOC from solution (He et al., 2016), and that this fate may be of equal importance as the more classically considered transport, assimilation and degradation processes (Vachon et al., 2020). DOC-derived particles
are widespread in the interconnected aquatic network, yet it is currently unclear if they withstand diagenesis, or if the protective mechanisms invoked for soil OC are active (Hemingway et al., 2019). While small water bodies (ponds) are known to efficiently store C from the surrounding land (Downing et al., 2008), the strong signature of terrestrial DOC recently found in sediments of northern lakes is surprising and suggests a tighter link between the dissolved and particulate OC pools (Guillemette et al., 2017; Hall et al., 2019; Von Wachenfeldt & Tranvik, 2008). The paper by Einarsdóttir et al. (2020) should inspire new work to better understand the routes of formation and chemical composition of particles derived from DOC, ideally by combining the most advanced analytical approaches for DOC and POC (McCallister et al., 2018). It is time for a deeper integration of the dissolved and particulate domain of OC.

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