SYNTHESIS AND EMERGING IDEAS

Paradigm shifts in soil organic matter research affect interpretations of aquatic carbon cycling: transcending disciplinary and ecosystem boundaries

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Abstract New conceptual models that highlight the importance of environmental, rather than molecular, controls on soil organic matter affect interpretations of organic matter (OM) persistence across terrestrial and aquatic boundaries. We propose that changing paradigms in our thinking about OM decomposition explain some of the uncertainties surrounding the fate of land-derived carbon (C) in marine environments. Terrestrial OM, which historically has been thought to be chemically recalcitrant to decay in soil and aquatic environments, dominates inputs to rivers yet is found in trace amounts in the ocean. We discuss three major transformations in our understanding of OM persistence that influence interpretations of the fate of aquatic OM: (1) a shift away from an emphasis on chemical recalcitrance as a primary predictor of turnover; (2) new interpretations of radiocarbon ages, which affect predictions of reactivity; and (3) the recognition that most OM leaving soils in dissolved form has been microbially processed. The first two explain rapid turnover for terrigenous OM in aquatic ecosystems once it leaves the soil matrix. The third suggests that the presence of terrestrial OM in aquatic ecosystems may be underestimated by the use of plant biomarkers. Whether these mechanisms occur in isolation of each other or in combination, they provide insight into the missing terrestrial C signature in the ocean. Spatially and temporally varying transformations of OM along land–water networks require that common terrestrial source indicators be interpreted within specific environmental contexts. We identify areas of research where collaborations between aquatic and terrestrial scientists will enhance quantification of C transfer from soils to inland water bodies, the ocean, and the atmosphere. Accurate estimates of OM processing are essential for improving predictions

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Springer

of the response of vulnerable C pools at the interface of soil and water to changes in climate and land use.

Introduction

A grand challenge in our understanding of the global carbon (C) cycle is the vulnerability of large organic carbon (OC) pools at the land–water interface to climate change and landscape disturbance (Battin et al. 2009; Raymond and Saiers 2010; Regnier 2013). Large uncertainties surround the quantity of OC mobilized from soils, released to the atmosphere during riverine transport, and delivered to the ocean (Cole et al. 2007; Battin et al. 2009; Aufdenkampe et al. 2011; Raymond et al. 2013). In order to predict C fluxes during transport from land (here defined as terrestrial landscapes, e.g., soils) to the ocean, it is important to address an unresolved question about the fate of plant and soil-derived C in aquatic ecosystems.

The expectation that terrestrial organic matter (OM) should be dominated by lignified (aromatic) plant material or nitrogen-poor, complex soil OM (SOM) with old radiocarbon (^{14}C) ages (Hedges et al. 1997; Raymond and Bauer 2001) has contributed to predictions of low bioavailability or chemical recalcitrance for terrigenous OM. Terrestrial sources dominate OM inputs to fluvial networks and coastal margins, but OM with a terrigenous signature can only be found in trace amounts in the ocean (Hedges et al. 1997; Cole and Caraco 2001; Benner et al. 2005; Aufdenkampe et al. 2011; Bianchi 2011). The paradoxical loss of this recalcitrant terrestrial C in the ocean has been attributed to photodegradation, which is especially effective in breaking down aromatic compounds (Opsahl and Benner 1998; Hernes and Benner 2003; Mayer et al. 2009; Spencer et al. 2009), and more recently to microbial priming (Bianchi 2011) and to the preferential sedimentation of more chemically bioavailable OM, leaving less energetically-favorable terrestrial compounds behind for microbial use (Lalonde et al. 2012).

We propose three further explanations for the aquatic C paradox informed by paradigm shifts in SOM research (Kleber and Johnson 2010; Schmidt et al. 2011). The first two are founded on changing perceptions of the relationship between chemical structure and persistence and between ^{14}C age and reactivity. First, aromatic compounds used as conservative terrestrial biomarkers (e.g., lignin, fire-derived or black C) are not inherently resistant to microbial decay in soils; hence, their decomposition in water is not paradoxical. Second, revised interpretations of ^{14}C ages fueled by new data challenge historical predictions of age and reactivity. Third, the use of plant biomarkers as exclusive indicators of terrigenous OM does not take into account large and often dominant contributions of microbial inputs to SOM. Hence, much OM delivered to aquatic ecosystems may not be identified by common chemical and isotopic methods as coming from a terrestrial source.

As soils are a major contributor of OM to inland water bodies and coastal systems (Raymond and Bauer 2001; Benner et al. 2004; Jaffé et al. 2013), understanding processes controlling SOM transformations and mobilization is important for improving predictions of C turnover during transport from land to the hydrosphere. Here we propose that interpretations of OM source, stability, and age in aquatic ecosystems be reevaluated in the context of a growing consensus in the soils literature that environmental factors mediate the influence of molecular structure on the long-term persistence of OM (Kleber and Johnson 2010; Schmidt et al. 2011). Environmental variables, e.g., climate, soil type and disturbance regime, which in turn affect redox conditions, nutrient availability and decomposer activity, influence the composition of OM accumulating in the soil profile and of dissolved OM (DOM) leached from surface and deep soil horizons. Likewise, changes in environmental conditions along ecosystem boundaries and fluvial networks influence the rate of decomposition of terrestrially derived OM.

Finally, we provide recommendations for enhanced interdisciplinary communication of conceptual and methodological biases, which can help reconcile conflicts in research paradigms among scientific communities. The OM components of interest to aquatic and soils researchers are connected through food webs and biogeochemical cycles (Meyer and Edwards 1990; Heyes and Moore 1992). Better integration of these research communities is critical for improving global C budgets and advancing C cycle science (Hedges and Oades 1997; Grimm et al. 2003; Aufdenkampe et al. 2011).

Reinterpreting recalcitrance and persistence of terrigenous OM

Recent conceptual SOM models characterize OM persistence as a product of multiple environmental factors that vary spatially and temporally, rather than as a function of chemical structure alone, and also recognize the fundamental contribution of microbial residues to long-lived OM pools (Table 1) (Oades 1988; Kleber and Johnson 2010; Schmidt et al. 2011; Gleixner 2013). This paradigm is rooted in some of the earliest work on SOM (for a historical perspective see Kleber and Johnson 2010) and is gaining wider acceptance due to improvements in analytical techniques to characterize OM composition. Growing evidence suggests that molecular structure does not exclusively predetermine environmental behavior, altering expectations of reactivity based on chemical composition. In particular, the use of plant-derived lignin (Hedges and Mann 1979) is constrained by evidence that this aromatic compound is biodegraded in soils (Gleixner et al. 2002; Dignac et al. 2005), vegetation leachates (Pellerin et al. 2012), rivers (Ward et al. 2013), and in marine water (Hernes and Benner 2003). Fractionation of lignin phenols during the processes of solubilization and sorption has also been shown to affect the interpretation of this biomarker in aquatic systems (Hernes et al. 2007; Spencer et al. 2008, 2012b). Here we briefly describe how changing perceptions of the role of chemical structure in controlling SOM decomposition rates (Table 1) can explain the biodegradation of terrigenous OM in marine systems.

Expectations of low bioavailability of aromatic compounds are founded on early work relating chemical SOM extraction products with resistance to decomposition by microbial enzymes and have been influenced strongly by research on humic substances (HS) (Stevenson 1994; Hedges et al. 2000; Hatcher 2004; Paul et al. 2006; Kleber and Johnson 2010). The abundance and old ^{14}C ages of HS in environmental samples contributed to predictions of long-term stability for aromatic compounds. Today, the utility of HS as representative of biological processes occurring in natural soils is questioned (Hayes and Clapp 2001; Schmidt et al. 2011), echoing the early concerns of some of the first chemists experimenting with soils (for a historical review see Waksman 1935; Kleber and Johnson 2010). Current conceptual models highlight the importance of solubility in soil solution rather than molecular complexity in influencing OM bioavailability (Piccolo 2001; Sutton and Sposito 2005; Kleber et al. 2007; Hayes 2009; Kleber and Johnson 2010; Schmidt et al. 2011). An increasing number of studies showing microbial degradation of aquatic HS (Hertkorn et al. 2002; Young et al. 2004; Hayes 2009) also raise uncertainties about the source and behavior of these compounds in aquatic environments.

Predictions of OM persistence due to aromaticity are challenged by highly variable turnover rates for lignin and fire-derived black C observed in terrestrial and aquatic environments (Benner et al. 1990; Baldock et al. 1997; Hernes and Benner 2003; Dignac et al. 2005; Hammes et al. 2008; Mayer et al. 2009; Benner and Kaiser 2011; Stubbins et al. 2012a). Despite expectations from plant litter decomposition studies, lignin does not accumulate preferentially in most soils (Gleixner et al. 2002; Rumpel et al. 2004; Feng et al. 2008; Kögel-Knabner et al. 2008; Carrington et al. 2012). In fact, soils at depth and marine sediments tend to show an abundance of straight-chain aliphatic compounds (Oades 1988; Brocks and Summons 2003; Lorenz et al. 2007), many of which are attributed to microbial synthesis during decomposition.

Contradictions in the persistence of lignin in terrestrial and aquatic environments are, in part, influenced by inconsistent methodologies among research communities, which misidentify different compounds as lignin, in addition to changing paradigms of recalcitrance (Table 1). Plant lignin is an aromatic biopolymer of irregular structure, which confers structural support and resistance to desiccation (Kögel-Knabner 2002). The term lignin has also been attributed to the acid-unhydrolyzable residue (AUR) of a sequential chemical fractionation, which preferentially accumulates in initial stages of litter decomposition and has been used to predict biomass decay rates (Melillo et al. 1989; Ryan et al. 1990). Plant and soil AURs have been shown to contain non-lignin aromatic compounds, e.g., condensed tannins, and non-aromatic compounds, e.g., aliphatic C (see Preston et al. 2009; Hilli et al. 2012). Despite this, aromatic content continues to influence expectations of OM decomposition and lignin is still considered a major component of slow-cycling soil OC pools in models (Parton et al. 1987) that inform current Earth System Models and climate change predictions.

Table 1 Emerging conceptual models of controls on organic matter (OM) persistence in the soils and terrestrial literature influence predictions of aquatic carbon cycling

Historical understanding	Recent findings	Current research paradigm	Implications for aquatic carbon
Recalcitrance of humic substances arises from complex, aromatic structures	OM complexity arises from the micelle-like association of small compounds through polar interactions	Solubility is more important than molecular complexity in determining turnover	Aromatic plant compounds may not be good conservative tracers of terrestrial inputs as they can become degraded in soil before entering the water column; Influence of the environment is important because it determines the degree of lignin and plant decay in soils and the amount delivered to aquatic systems
The acid unhydrolyzable residue (AUR) ("lignin") of litter predicts decay rates; Lignin accumulates in the environment because of its irregular, aromatic structure	AUR is composed of non-lignin aromatic C and non-aromatic C; Lignin does not accumulate in well-aerated environments	Organic compound decay rates vary and are not pre-determined by molecular structure	Lignin may not be a good conservative tracer of terrestrial inputs as it becomes degraded in well-areated soils before entering the water column
Plant-derived aromatic compounds persist in soils because of their recalcitrance	Aromatic C tends to decrease with progressive OM decay in mineral fractions, deep soils, and sediments	Given accessibility and favorable conditions, microbes are omnipotent decomposers	Lignin may not be a good conservative tracer of terrestrial inputs as it can become degraded in soil before entering the water column; Influence of the environment is important because it determines the degree of lignin and plant decay in soils and the amount delivered to aquatic systems
Plant-derived aliphatic compounds persist in soils because of their recalcitrance	Microbial products are dominated by alkyl C	Microbial products make up a large to dominant proportion of SOM	The use of plant biomarkers alone underestimates terrigenous OM. Terrestrial and aquatic microbial OM may be difficult to distinguish, confounding source allocation
Black C is most recalcitrant and persists in soils for millenia	Microbes can break down and assimilate black C and associated nutrients; Black C has been underestimated in river and ocean samples	Black C turnover is affected by environmental properties and characteristics of the black C itself	The persistence of black C is strongly influenced by environmental conditions. Black C will exist in different stages of degradation and is much more mobile than previously thought
OM with millenial radiocarbon ages is recalcitrant	Microbes can respire ancient C, which can respond on annual time scales to disturbance	OM can acquire millenial ages through multiple pathways	OM with old radiocarbon ages can be degraded quickly and does not necessarily imply long-term persistence in the source or receiving ecosystems

This table summarizes historical understanding of OM dynamics, recent findings that have changed our understanding and contributed to current research paradigms about what influences the persistence of OM in the environment and implications for aquatic carbon cycling

Even black C, composed of highly condensed aromatic compounds formed during incomplete combustion of OM and long considered to be one of the least bioavailable components of OM, is susceptible to fungal colonization and degradation by bacteria (Hockaday et al. 2006; Nocentini et al. 2010; Spokas

2010; de la Rosa and Knicker 2011). Variable turnover rates for black C ranging from <100 years to millennia reveal the strong influence of physical and chemical properties of black C and its environment, as well as uncertainties in the methods used to assess decay rates (Brodowski et al. 2005; Keiluweit et al. 2010; Nocentini et al. 2010; Singh et al. 2012). Black C decomposition is accelerated by soil and sediment disturbance, which reduces physical protection from microbial attack and facilitates mobilization to water bodies (Hockaday et al. 2007; Guggenberger et al. 2008), where it becomes vulnerable to biological decay and photodegradation (Stubbins et al. 2012a). Recent observations that dissolved black C can contribute up to 10 % of global riverine dissolved OC (DOC) flux (Jaffé et al. 2013) indicate that black C is much more mobile than previously considered, thus changing perceptions about its reactivity in the environment.

Rather than driven by inherent molecular complexity or aromatic structure, OM persistence in soils is a function of inputs and solubility, the composition and activity of biological decomposers, and properties of the solid and pore matrices. These characteristics interact to influence partitioning between solution and solid states and the rate of decomposition (Fig. 1) (Kaiser and Zech 1999; Marschner and Kalbitz 2003; Dungait et al. 2012; Kaiser and Kalbitz 2012). Matrix characteristics that affect OM turnover include mineralogy, metal concentrations, surface charge and oxidation state of suspended solids and sediments (Fig. 1). Moisture content, temperature, solution chemistry, nutrient concentrations, and oxygen availability affect biological activity in the pores of soils and sediments and within the water column (Fig. 1). Molecular structure can mediate interactions with the physical matrix; e.g., mineral sorption of aromatic compounds may enhance mean residence times (MRTs) of lignin phenols in soil (Kramer et al. 2012), but these same compounds may biodegrade rapidly in the absence of a stabilizing surface. OM transformations can occur at all stages along hydrologic networks from the headwaters to the ocean (Blair and Aller 2012), with rates of decomposition influenced by spatially and temporally variable factors such as bedrock geology, topography, impoundment and weather events which affect water flow rates (Mosher et al. 2010).

Similar processes occur in well-mixed aqueous systems (Hedges and Keil 1999; McKnight et al. 2001)

and in lake and marine sediments (Canfield 1994; Keil et al. 1994; Hedges and Oades 1997; Keil and Mayer 2014). The primary differences between terrestrial and aquatic systems are residence time and the location of chemical reactions. Water residence time in streams and rivers is typically short (days), but can be much longer in lakes and reservoirs (years), whereas bulk SOM MRT is on the order of centuries to millennia, with some components turning over on much shorter time scales.

In aquatic systems, the location of reactions will determine controls on OM turnover. In sediments, nutrient and oxygen availability, and microbial accessibility to OM become important and are controlled by hydrologic exchange and sediment composition. In the water column, solution chemistry and temperature are more important (Hedges and Oades 1997). Further, the interaction between surface waters and groundwater in sediments and stream banks (i.e., the hyporheic zone) create chemical and physical conditions that lead to extremely high processing rates (e.g., Schindler and Krabbenhoft 1998). Transitions from terrestrial to aquatic compartments likely facilitate some of the highest OM turnover rates because of shifts in environmental conditions that influence OM solubility and decomposer activity. For example, northern temperate lakes can turn over approximately 60 % of DOM given water residence times >6 years and cool water conditions (Hanson et al. 2011). Streams and rivers across a diverse range of environments have been shown to be responsible for a major efflux of carbon dioxide (CO_2) to the atmosphere (Richey et al. 2002; Butman and Raymond 2011; Raymond et al. 2013; Wang et al. 2013). The amount to which riverine OM fuels this CO_2 efflux remains unclear but recent studies have shown that the degradation of terrestrially derived OM appears to be an important driver for CO_2 gas fluxes in the Amazon River (Mayorga et al. 2005; Ward et al. 2013). Additionally, others have reported increased bioavailability for riverine DOM in Arctic rivers in conjunction with elevated lignin inputs to the DOM pool and a modern ^{14}C age (Raymond et al. 2007; Holmes et al. 2008; Spencer et al. 2008). These studies support the growing consensus that ecosystem properties (sensu Schmidt et al. 2011) play a fundamental role in determining OM turnover and challenge predictions of bioavailability that rely on molecular structure and age. Next, we discuss how emerging understanding of the factors leading to the
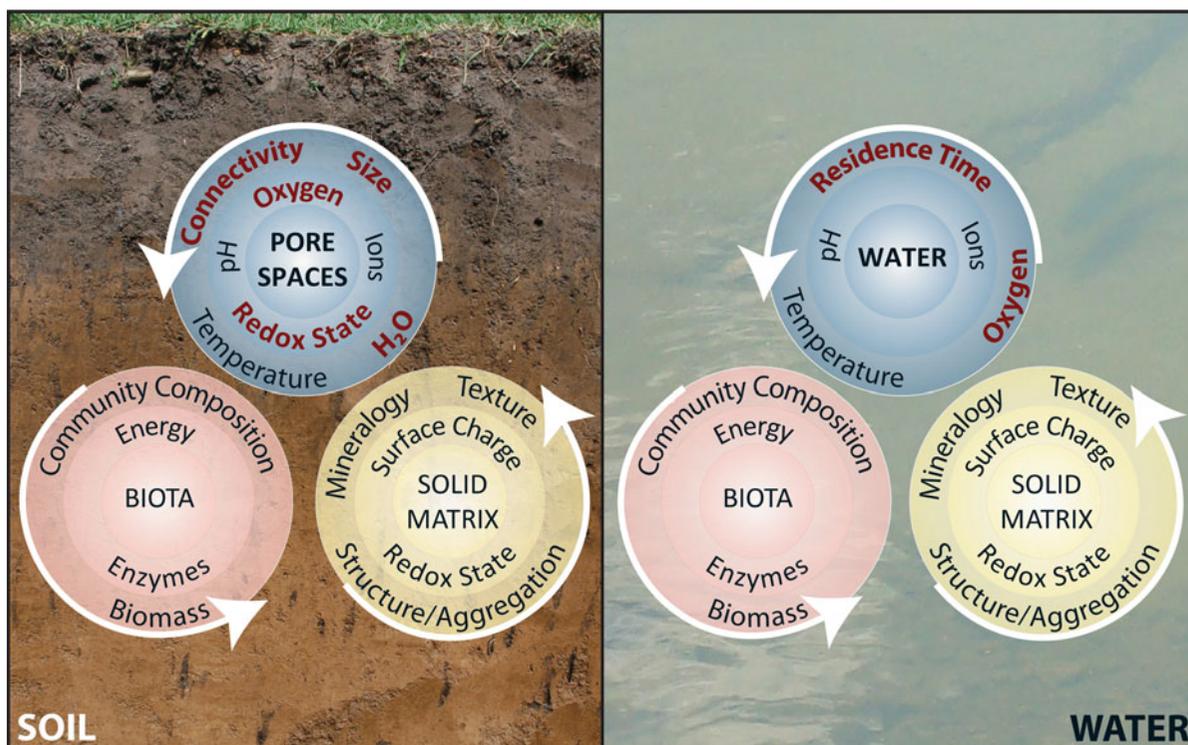
Fig. 1 The persistence of OM in soil and aquatic ecosystems is influenced by interactions between the biomass, composition, metabolic capacity of biological decomposers and OM inputs and by properties of the solid and pore matrices (each represented by *circles*), which control partitioning between solution and solid phases. Solid matrix characteristics affecting OM turnover include mineralogy, texture, structure and aggregation, which interact with properties of the pore spaces to influence surface charge and oxidation state. Temperature, solution chemistry, nutrient and oxygen availability affect biological activity in the pores of soils and sediments and in the water column. Molecular structure can mediate interactions with the physical matrix; e.g., mineral sorption of aromatic compounds may enhance mean residence times of lignin phenols in soil, but these same compounds may biodegrade rapidly in the absence of a stabilizing surface. The primary difference between soils, benthic sediments and the hyporheic zone of streams and rivers are the stability of the structure of the solid matrix and its residence time in the system. In aquatic systems, and less so in soil pores, water residence time is important in influencing the rate of decomposition of OM by affecting interactions between substrate, decomposers and solid surfaces. Different aquatic systems, streams, rivers, lakes and the ocean differ primarily in hydrologic mixing and water residence time. *Arrows around the three circles* (biota, solid matrix and pore spaces or water) indicate interactions between all spheres of influence in determining OM turnover rates. Bold terms in the top circle highlight main differences in properties of the solution in pore spaces and in the water column between soil and water systems. Modified from Schmidt et al. (2011)

accumulation of OM with apparent old ^{14}C ages under different environmental conditions can help interpret the fate of terrestrial OM in aquatic systems.

Reinterpreting predictions of persistence from radiocarbon ages

Spatial and temporal heterogeneity in the mean ^{14}C age of OM in aquatic ecosystems has contributed to uncertainties in estimates of C processing rates and the fate of terrigenous C. An accumulation of data for riverine OM indicate high variability in ^{14}C ages between DOM, most of which is modern, and particulate OM (POM), which can show large differences in age (Raymond and Bauer 2001; Benner et al. 2004; Mayorga et al. 2005; Raymond et al. 2007; Spencer et al. 2012b). Differences in the ^{14}C age of both DOM and POM between the upper and lower reaches of one large temperate river led to estimates that 30–70 % of terrigenous OM with ^{14}C ages >1,000 years was respired within 30 days of transit (Cole and Caraco 2001). In the Gulf of Alaska the proportion of glacial runoff DOC bioavailable to

microbes was found to increase with ^{14}C age, with up to 60 % of DOC with ^{14}C ages of ca. 4,000 years before present readily degraded in 14 day incubations (Hood et al. 2009).

Observations of OM with old ^{14}C ages rapidly decomposing on short timescales (days to <1 year) in the ocean are consistent with evidence that SOM pools with MRTs >1,000 years can respond to disturbance in as little as 5–10 years (Paul et al. 2006; Kleber 2010). Increasing data from both soils and aquatic ecosystems show decoupling between molecular structure and ^{14}C age (Trumbore 2009; Kleber et al. 2011) and between age and reactivity (Hood et al. 2009; Caraco et al. 2010), further challenging expectations of the persistence of land-derived OM with old ^{14}C values in aquatic environments. Below we summarize some of the mechanisms that can contribute to the accumulation of OM with old ^{14}C ages under different environmental conditions.

Organic compounds can acquire long MRTs by various processes that prevent or slow down microbial activity, independent of their molecular structure. In soils, sorption to mineral surfaces and occlusion within micropores inside soil aggregates contribute to temporary protection of OM from complete mineralization to CO_2 (von Lützow et al. 2008; Schmidt et al. 2011). This results in the accumulation of older OM in pools that are less accessible to decomposers and their extracellular enzymes. A disruption of the mechanisms protecting C from mineralization, such as physical disturbance of the soil matrix or a shift in soil moisture, temperature, or pH, can lead to export (Evans et al. 2007; Moore et al. 2013), microbial assimilation or respiration of aged OM (Paul et al. 2006). This state shift can occur within the soil column or as DOM and POM are transported into and throughout the fluvial network. For example, erosion can mobilize rock-derived OM into river drainage systems, exposing formerly protected C pools to degradation and affecting the age of sediments that accumulate downstream (Galy and Eglinton 2011).

Organic matter with long MRTs can also result from recent additions of aged compounds into actively cycling C pools. Microbial recycling and assimilation of OM with old ^{14}C ages can confound interpretations of stability and age. Senescence of OM from long-lived plants and the atmospheric deposition of fossil-fuel C (Stubbins et al. 2012b) can contribute to recent inputs of old C into soil and aquatic systems.

Similarly, the preferential sorption of some microbial residues, such as proteins, to mineral surfaces can result in the incorporation of recent inputs, with both ancient and modern ages, into SOM pools with long turnover times (Kleber et al. 2007; Miltner et al. 2009; Miltner et al. 2012; Gleixner 2013).

Bulk C pool MRTs can be altered by the preferential degradation of select compounds. In an experimental study, photoirradiation caused inconsistent changes in ^{14}C concentrations of suspended OM from river, coastal, and shelf sediments (Mayer et al. 2009), suggesting that old ages and long ^{14}C-based MRTs do not necessarily indicate selective preservation. The age of bulk OM pools can also become increasingly older as recent inputs are selectively oxidized, resulting in a shift in the isotopic composition of OM during diagenetic processes in rivers and marine sediments (Aller et al. 2008; Blair and Aller 2012).

Recent studies have reported assimilation of millennial-aged OM into modern soil and aquatic food webs (Kramer and Gleixner 2006; Caraco et al. 2010; McCallister and del Giorgio 2012). In the subsoil of some riparian forests, 30–100 % of microbial respiration was found to be driven by millennial-aged C (Gurwick et al. 2008). A recent study reported >30 % loss from biological decay during a 14-day incubation of DOC with ^{14}C ages >21,000 years old that was released from permafrost thaw in Siberia (Vonk et al. 2013). Furthermore, when examining controlled mixtures of modern OM and thawed permafrost OM, respiration rates per unit carbon were 1.3–1.6 times higher in waters containing ancient permafrost C, highlighting that this ancient OC was more available for microbial mineralization (Mann et al. 2014). Given that at least over half of the world's belowground OC pool is estimated to be held in northern circumpolar permafrost (Tarnocai et al. 2009), these results highlight the critical need to reassess relationships between age and reactivity and to better understand factors controlling bioavailability of DOC in order to improve predictions of positive feedbacks to climate in a warming world. Respiration of ancient OM to the atmosphere is certainly problematic to C cycle models that assume permanent storage of millennial-aged C.

These and other studies illustrate how interpretations of age and MRT are affected by OM reservoir heterogeneity, as the presence of even a very small proportion of ancient C can greatly skew mean estimates (Torn et al. 2009). Recent conceptual

models of SOM support the long-term persistence and ageing of easily degradable OM when conditions are not favorable for microbial activity. Hence, predictions of OM stability based on interpretations of source and recalcitrance from ^{14}C data must be reassessed if we are to accurately understand OM dynamics across ecosystem boundaries.

Watershed properties can influence the ^{14}C values of POM in rivers delivered to the ocean. Rivers with large loads of POM typically have greater proportions of older OM, representing greater contributions of rock and soil-derived OM, whereas rivers with lower sediment export have greater proportions of recently photosynthesized inputs (Galy et al. 2007; Blair and Aller 2012). Rivers draining mountainous watersheds associated with active margins and rapid physical weathering can also deliver ancient POM (Masiello and Druffel 2001). On the other hand, low-grade rivers with extensive floodplains, characteristic of passive margins, often deliver modern or relatively young C (Blair and Aller 2012). Understanding the source, pathway, and environmental context of C inputs can improve interpretations of variable ^{14}C content of OM in terrestrial and aquatic ecosystems.

Reinterpreting terrestrial source biomarkers

In the previous sections we discussed how changing perceptions of the relationships between molecular complexity, age, and bioavailability can provide insight into the observed missing terrestrial C in the ocean. Additionally, we propose that the persistence of terrestrial OM in aquatic ecosystems is greatly underestimated due to an over-reliance on plant-derived compounds as quantitative indicators of terrestrial inputs. Microbes not only have the capacity to decompose lignin but plants produce variable amounts and types of lignin phenols, which are preferentially degraded in different terrestrial and aquatic environments (Kögel 1986; Benner et al. 1990; Spencer et al. 2009), confounding its use as a conservative tracer. Aquatic macrophytes and some freshwater and marine algae can also synthesize lignin (Martone et al. 2009). The geographic and quantitative importance of algal lignin production still has to be established, but this non-terrigenous source of lignin adds an additional constraint on its use as an unequivocal terrestrial biomarker.

Further contributing to underestimates of terrigenous OM inputs is the increasing recognition that microbes are ubiquitous sources of OM to soils and to aquatic ecosystems via recycling of plant and animal-derived OM and synthesis of new products (Hedges et al. 2000; Ogawa et al. 2001; Jiao et al. 2010; Liang and Balser 2011; Miltner et al. 2012; Gleixner 2013). Most terrestrial inputs to aquatic bodies, especially during, but not limited to, base flow conditions, will have been transformed in the soil by microbial processes, even in cold climates (Feng et al. 2010), and may be unrecognizable as derived from C fixed on land. The capacity of microbes to break down any organic compound, given the right environmental conditions and time, is increasingly recognized (von Lützow et al. 2006; Kögel-Knabner et al. 2008; Schmidt et al. 2011; DeAngelis et al. 2011; Gleixner 2013). Even in anaerobic marine sediments, microbes are estimated to metabolize 30–99 % of deposited OM (Henrichs 1992). Despite the importance of microbial inputs to OM pools, microbial residues remain poorly characterized, especially in aquatic systems.

Organic matter alteration during decomposition constrains the utility of stable C isotopes and soil elemental ratios for distinguishing algal and aquatic macrophyte contributions from terrestrial inputs to aquatic OM, as values for microbially-processed SOM and DOM will approach those of aquatic producers (Meyers 1997; Onstad et al. 2000). Recent plant inputs into streams from direct leaf fall or from overland flow transporting forest floor litter layers have large and variable carbon-to-nitrogen (C-to-N) ratios (40–80), reflecting plant biomass values (McGroddy et al. 2004). In contrast, OM inputs from aerobic mineral soil horizons are characterized by smaller C-to-N ratios and more enriched δ^{13}C values, reflecting preferential loss of C and inputs from N-enriched microbial biomass (Sanderman et al. 2008, 2009; Lambert et al. 2011).

Differences in vegetation, rooting depth, and extent of microbial decomposition can influence depth profiles in soil C-to-N ratios, with implications for DOM export (Fig. 2). In a volcanic soil under tropical rainforest, SOM with unusually large C-to-N ratios accumulated in mineral horizons below 30 cm due to the downward delivery of forest floor POM and DOM via macropore channels (Fig. 2d) (Marin-Spiotta et al. 2011). Here, the largest soil C-to-N ratios occurred where fluctuating redox conditions altered vertical
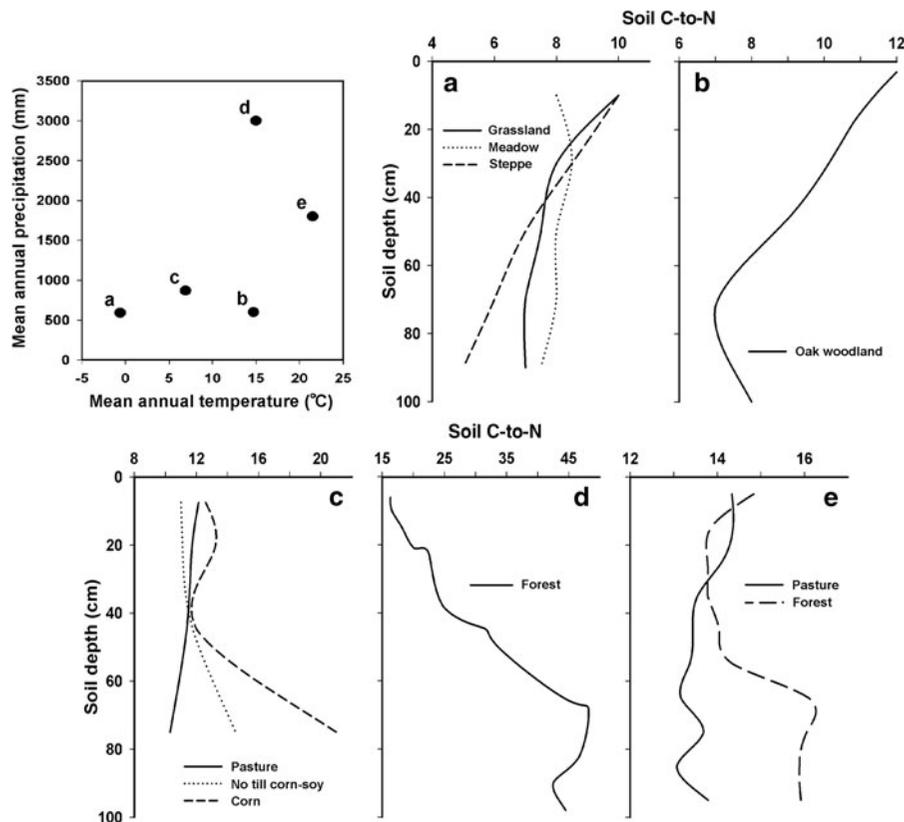
Fig. 2 Soil organic matter (SOM) chemistry can vary horizontally across sites and vertically within soil profiles, which can affect the chemistry of dissolved organic matter (DOM) exported from soils. Depth profiles of soil carbon-to-nitrogen ratios (C-to-N) from sites with different vegetation and soil types along a climatic gradient show this variability: *a* high altitude alpine vegetation in Tibetan plateau (Yang et al. 2010);

b Mediterranean oak woodland on karst (Corvasce et al. 2006); *c* agricultural sites on Mollisols in the U.S. Midwest (Sanford 2012); *d* tropical rainforest on allophanic Andisol in Hawaii (Marin-Spiotta et al. 2011); and *e* subtropical wet forest and pasture on clayey Oxisol in Puerto Rico (Marin-Spiotta et al. 2009)

preferential flowpaths. Differences in hydrology, mineralogy and soil structure led to contrasting patterns of soil elemental ratios in a tropical wet forest soil with lower annual rainfall (Fig. 2e). Although no DOM data is available for the latter site, DOM collected from lysimeters in the mineral soil horizons in the volcanic site also sustained large C-to-N ratios (Marin-Spiotta et al. 2011). The composition of DOM exported from these two forest soils and transported downstream is expected to differ substantially as DOM moving through soils typically closely resembles mineral-associated OM (Sanderman et al. 2008; Sanderman et al. 2009; Lambert et al. 2011; Kaiser and Kalbitz 2012). We highlight this example to show how soil properties can help predict the biochemical composition of stream DOM by influencing its source.

Integrating reinterpretations of OM persistence with environmental source conditions

Emerging conceptual models of how environmental conditions influence the source, composition, and turnover of OM, and thus predictions of its bioavailability and the presence of land-derived C, can explain the loss of conventional terrigenous signatures in aquatic ecosystems. The biochemical and isotopic composition of OM exported from soils through fluvial networks is strongly influenced by long-term environmental factors: climate, seasonality, primary production, topographic position, properties of watershed soils and bedrock geology; and by short-term factors: precipitation events and landscape disturbance affecting microbial processing and hydrologic pathways (Nelson et al. 1993; Kaiser and Zech
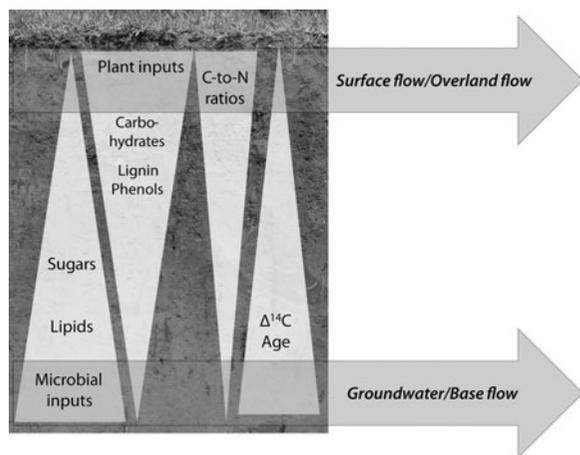
Fig. 3 The chemical composition and age of OM transported from soils into aquatic ecosystems reflects the composition and age of bulk SOM and varies with soil depth and with hydrologic flowpath. Surface soils are enriched in recent, plant-derived OM with larger C-to-N ratios, carbohydrates and lignin concentrations, whereas deeper soil horizons tend to accumulate older, more decomposed OM with a greater contribution of microbially-processed and synthesized compounds and smaller C-to-N ratios. Thus, during base flow or low flow conditions, DOM will reflect inputs from deeper soils, while during peak flow or overland flow, DOM exported from soils will reflect surface SOM. Modified from Kaiser and Kalbitz (2012) and Sanderman et al. (2008)

1997; Striegl et al. 2005; Sanderman et al. 2009; Kaiser and Kalbitz 2012; Stanley et al. 2012). Thus, the environmental controls under which OM is released from soils influence downstream C sources and stocks and should therefore be considered in predictions of aquatic C fluxes.

Recent understanding of the processes leading to the formation of DOM in soils suggests that dynamic exchange occurs between the mineral matrix and OM available for transport to aquatic systems. Soil profiles have been viewed traditionally as chromatographic columns, stripping the more sorptive compounds from solution as water moved down the soil profile. However, increasing evidence indicates that DOM in surface and deeper mineral soils varies substantially with composition of the mineral-associated SOM (Sanderman et al. 2008; Kaiser and Kalbitz 2012). Kaiser and Kalbitz (2012) recently proposed a model where sorption and precipitation, microbial processing, and desorption and dissolution contribute to strong vertical differentiation in the composition and ^{14}C age of mineral-associated SOM and of soil DOM (Fig. 3).

Storm events and hydrologic flowpaths can affect the spatial and temporal heterogeneity of land-derived C transported to fluvial networks and delivered to the ocean. Riverine OM composition has been shown to vary widely with hydrologic drivers in a range of watersheds from the Arctic to the tropics (Spencer et al. 2008, 2010, 2012b; Bouillon et al. 2012). During high-flow conditions, stream DOM can resemble surface soil DOM with large C-to-N ratios, typically increased aromaticity, and contemporary ^{14}C values, indicative of recent or less decomposed plant litter inputs (Fig. 3) (Dai et al. 2001; Sanderman et al. 2009). During low flow, stream DOM resembles deep SOM with older ^{14}C ages, small C-to-N ratios and decreased aromaticity, typical of microbially-processed OM (Fig. 3) (Striegl et al. 2005; Sanderman et al. 2009; Spencer et al. 2010). These differences in hydrologic pathways can contribute to large seasonal variability reported in the biochemical composition and bioavailability of DOM in large rivers from the Arctic to the equator by affecting the source of terrestrial inputs (Holmes et al. 2008; Spencer et al. 2008, 2012b; Wickland et al. 2012).

Landscape position can affect the quantity and composition of DOM produced in soils and transported to streams by influencing drainage and the extent of microbial decomposition of SOM. Well-drained soils, characteristic of those in upland positions, have a greater proportion of more decomposed and microbially-derived OM than soils in lowland positions or with poor drainage, such as wetlands and peatlands, where a greater proportion of plant-derived OM accumulates deeper in the soil profile (Fig. 4). In heterogeneous watersheds, seasonal and storm-driven changes in hydrology can alter the contribution of forested areas and wetlands to stream DOM (Laudon et al. 2011; Lambert et al. 2013). Under low flow conditions, wetland soils contribute greater concentrations of DOC than upland soils, where much OM has been decomposed. During low flow conditions, wetlands in low topographic positions were found to be the primary source of DOC to streams in a boreal Swedish watershed, whereas upland forested soils contributed DOC during high flow conditions due to varying groundwater levels (Laudon et al. 2011). Where most inputs to aquatic systems are dominated by recent plant inputs and less decomposed OM, concentrations of DOC in the absence of new inputs are predicted to decline significantly from the
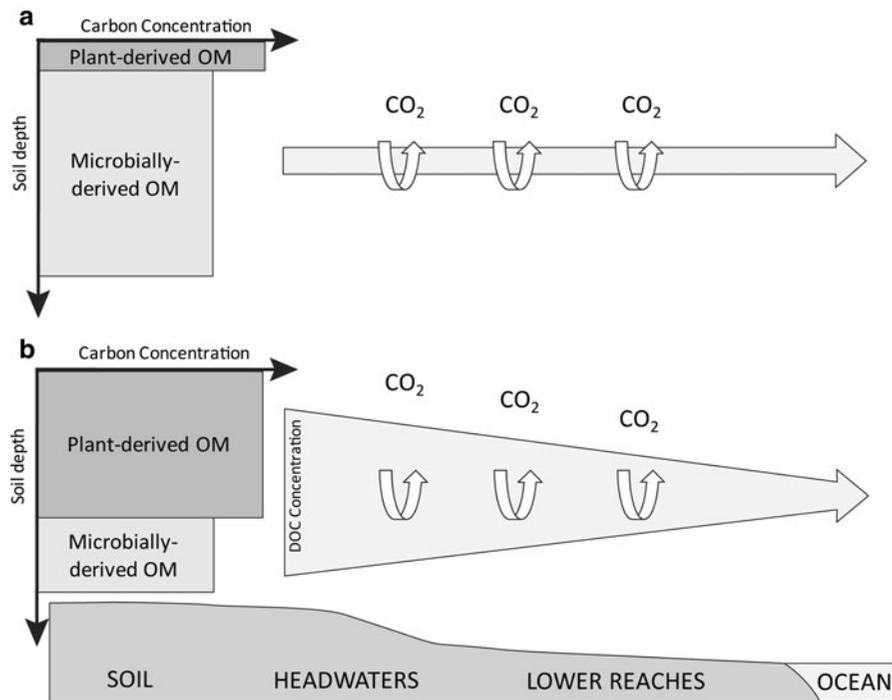
Fig. 4 The persistence of the terrestrial signature of OM transported from soils via rivers to the ocean is influenced by both the concentration of OM at the source and its degree of decomposition, i.e., the relative contributions of plant versus microbial-derived compounds. The properties of DOM and POM exported from soils vary with soil depth, drainage, and topographic position. **a** Well-drained soils in upland positions have a greater proportion of microbially-derived OM down the soil profile. **b** In poorly-drained soils or wetlands at low topographic positions, a greater proportion of less decomposed plant-derived OM accumulates deeper in the soil profile. Concentrations of DOC exported to streams from wetlands will be greater than DOC exported from upland soils but are predicted to decline during transport as most plant-derived OM is consumed. In contrast, DOC concentrations from watersheds dominated by upland soils will vary less during transport to the ocean, as highly processed OM is expected to be a poor energy substrate for downstream productivity

headwaters to the lower riverine reaches, as most plant-derived OM is consumed by aquatic microbial communities (Fig. 4b). On the other hand, where inputs from soils are dominated by microbial inputs (Fig. 4a), concentrations of DOC will vary much less during transport to the ocean, as highly processed OM is expected to be a poor energy substrate for downstream productivity (Kaiser and Kalbitz 2012).

Land use can alter the composition of riverine OM by affecting plant cover, input quantity and source, and degree of microbial transformations (Williams et al. 2010; Stanley et al. 2012). Differences in watershed land cover, in addition to seasonal changes in water flow, can explain variability in OM composition among rivers (Duan et al. 2007; Spencer et al. 2010, 2012a). At the field scale, management practices that alter drainage can leave a strong imprint on the seasonal quantity and chemistry of DOM exported from agricultural landscapes. Stream DOM draining fields with subsurface drainage showed little evidence of a terrestrial signature based on fluorescence indices, because the source was microbially-processed SOM in deep mineral horizons (Dalzell et al. 2011). The use of $\delta^{13}C$ to distinguish terrigenous OM from aquatic production is confounded further in agricultural watersheds and in arid and tropical grasslands dominated by C4 plants, where SOM is enriched in $\delta^{13}C$ compared to soils under C3 plant cover (Bernardes et al. 2004). Variability in isotopic composition of POM derived from highly-processed SOM and under different land cover types can make it indistinguishable from plankton residues in marine sediments (Onstad et al. 2000). Many forested watersheds occur on formerly cultivated land where SOM may exhibit isotopic signatures that result from a legacy of mixed vegetation (Marin-Spiotta et al. 2009). Prior land use

and disturbance can have long-lasting effects on the composition of OM exported to rivers. In a Brazilian watershed, large amounts of black C from historical fires continued to be mobilized during the rainy season 40 years after widespread burning activities ceased (Dittmar et al. 2012), with previously discussed implications for aquatic C dynamics.

Furthermore, landscape disturbance and soil erosion can affect characteristics of both POM and DOM exported from soils. The removal of topsoil and exposure of lower soil horizons can result in the transfer of DOM during high flow conditions that resembles DOM transported during base flow conditions from undisturbed ecosystems. Erosion also increases the amount of POM and mineral-associated OM moving through waterways (Jung et al. 2012), thereby affecting processes controlling OM turnover during transport and the eventual fate of terrestrial C (Berhe and Kleber 2013).

Advancing carbon cycle science at the land–water interface

Emerging paradigms from SOM research on the importance of environmental properties in determining OM turnover provide a framework for reinterpreting the fate of terrestrial C delivered to the ocean. We have proposed that: (1) predictions of OM turnover from molecular structure alone ignore the importance of environmental conditions in controlling decomposer accessibility and activity; (2) old ^{14}C ages do not imply preservation in an unchanged state and are not strong predictors of biological availability; and (3) the use of plant-derived indices likely grossly underestimate terrestrial contributions to aquatic OM as most OM accumulating in soils has undergone some degree of microbial alteration. These changing perceptions on the source, composition, turnover and persistence of OM can improve our understanding of aquatic C cycling.

Rapid decomposition of terrigenous OM in aquatic systems does not support earlier perspectives that inland water channels were passive connectors (pipes) between soils and the ocean (cf., Cole et al. 2007; Aufdenkampe et al. 2011). The decoupling between molecular structure, ^{14}C age, and predictions of SOM persistence is consistent with growing evidence in the aquatic geosciences literature of heterogeneity of OM

composition and age along fluvial networks and of the active role of inland water bodies in the global C cycle (Aufdenkampe et al. 2011). Although recent studies suggest that lakes and rivers actively process OC and can be large sources of CO_2 (Richey et al. 2002; Butman and Raymond 2011; Striegl et al. 2012), most global C models still aggregate soils and inland water bodies (lakes, streams, and rivers) into one land flux to the ocean (Cole et al. 2007; Battin et al. 2009; Tranvik et al. 2009; Aufdenkampe et al. 2011).

Predicting the response of aquatic C pools to climate and land-use change requires the incorporation of new knowledge of OM processing across the soil–water interface. This will be possible only through increased collaborations between aquatic and soil biogeochemists, who predominantly work in isolation of each other (but see Hedges and Oades 1997; Grimm et al. 2003; Spencer et al. 2012b). Carbon cycle science is inherently multidisciplinary. Exchange of new research paradigms is essential for improving estimates of OC turnover in terrestrial and aquatic reservoirs. Below, we suggest specific avenues by which enhanced interdisciplinary communication can be achieved.

Early and targeted educational opportunities are crucial for training C cycle scientists to have an integrated systems perspective that enables them to transcend disciplinary boundaries. In fact, this paper was conceived during a graduate seminar that brought together students from geography, limnology, soil science, botany and forestry. An in-depth historical exploration of methods and conceptual models in this diverse setting accentuated how differences in research paradigms can influence interpretations of literature across disciplines.

Organized symposia provide an effective way to bridge research communities. Select efforts by some societies and small meetings, like the European-funded SOM meeting in Switzerland in October 2012 (Schmidt and Eglinton 2013), are starting to target broader audiences. Annual scientific meetings draw increasingly diverse audiences but could benefit from greater promotion of cross-disciplinary and cross-ecosystem symposia. Too often, SOM sessions run parallel to aquatic biogeochemistry sessions.

Research across the soil–water interface demands innovative funding opportunities and increased collaborations among terrestrial and aquatic scientists to further investigate hydrologic pathways between soils

and headwater stream networks, wetlands, major rivers, and coastal ecosystems. Soil scientists have historically focused on SOM stabilization; although increasing work shows that the exchange between the solid and dissolved phase in soils is a lot more dynamic than originally thought (Kaiser and Kalbitz 2012). More research on the processes leading to OM mobilization at the pedon and landscape scale will benefit models that quantify C transfer across ecosystem boundaries and help identify hotspots of C sources to the atmosphere. For example, a greater understanding of the factors leading to the mobilization of black C from soils to aquatic systems is relevant for improving estimates of global C cycling and downstream trophic dynamics (Jaffé et al. 2013), as well as predictions of the long-term viability of geoengineering C sequestration projects, such as the application of biochar to soils (Masiello and Louchouarn 2013).

New research initiatives, like the international Critical Zone Exploration Network and the U.S.-based Critical Zone Observatories, provide opportunities for measuring hydrologic dynamics and physical, chemical, and biological processes at the interface between land, water, and the atmosphere at the same sites and same temporal and spatial scales as long as they draw diverse groups of scientists. Work across latitudinal and altitudinal gradients can improve quantification of environmental controls on OM biochemical composition and turnover to better inform process-based models.

Similarly, increased collaborations between microbial ecologists and biogeochemists and the development and deployment of improved tools to study decomposition and other process rates in situ are necessary for advancing our understanding of biological controls on C turnover across environmental gradients. Methods that address interactions between OM and its surrounding matrix and include measurements of environmental properties at relevant timescales (e.g., in situ optical sensors; Spencer et al. 2007; Vargas et al. 2010; Pellerin et al. 2012) will enhance predictions of OM processing.

Unprecedented rates of anthropogenic environmental change affect C transfer between the biosphere, lithosphere, hydrosphere, and atmosphere. Increasing temperatures and frequency and severity of precipitation events and landscape disturbance can destabilize ancient terrestrial C pools by accelerating thawing of OM-rich environments and mobilizing large amounts of sediment (Zimov et al. 2006; Guo et al. 2007; Galy and Eglinton 2011; Vonk et al. 2013). Assessment of the implications of these global environmental changes requires accurate knowledge of OM sources and process rates as well as effective communication across scientific disciplines. Increased interdisciplinary exchange between terrestrial and aquatic research communities and integration of emerging paradigms will lead to deeper understanding of environmental controls on the mobilization and decomposition of OM, which is essential for predicting the response of vulnerable OC pools across land–water networks to accelerating global change.

References

Aller RC, Blair NE, Brunskill GJ (2008) Early diagenetic cycling, incineration, and burial of sedimentary organic carbon in the central Gulf of Papua (Papua New Guinea). J Geophys Res 113:F01S09. doi:10.1029/2006jf000689

Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, Alin SR, Aalto RE, Yoo K (2011) Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Front Ecol Environ 9(1):53–60

Baldock JA, Oades JM, Nelson PN, Skene TM, Golchin A, Clarke P (1997) Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. Aust J Soil Res 35:1061–1083

Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ (2009) The boundless carbon cycle. Nat Geosci 2(9):598–600

Benner R, Kaiser K (2011) Biological and photochemical transformations of amino acids and lignin phenols in riverine dissolved organic matter. Biogeochemistry 102(1–3):209–222. doi:10.1007/s10533-010-9435-4

Benner R, Weliky K, Hedges JI (1990) Early diagenesis of mangrove leaves in a tropical estuary: molecular-level analyses of neutral sugars and lignin-derived phenols. Geochim Cosmochim Acta 54(7):1991–2001

Benner R, Benitez-Nelson B, Kaiser K, Amon RMW (2004) Export of young terrigenous dissolved organic carbon from

rivers to the Arctic Ocean. Geophys Res Lett 31:L05305. doi:10.01029/02003GL019251

Benner R, Louchouarn P, Amon RMW (2005) Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic. Glob Biogeochem Cycles 19(2):GB2025. doi:10.1029/2004gb002398

Berhe A, Kleber M (2013) Erosion, deposition, and the persistence of soil organic matter: important considerations and problems with terminology. Earth Surf Proc Land 38:908–912

Bernardes MC, Martinelli LA, Krusche AV, Gudeman J, Moreira M, Victoria RL, Ometto J, Ballester MVR, Aufdenkampe AK, Richey JE, Hedges JI (2004) Riverine organic matter composition as a function of land use changes, Southwest Amazon. Ecol Appl 14(4):S263–S279

Bianchi TS (2011) The role of terrestrially derived organic carbon in the coastal ocean: a changing paradigm and the priming effect. Proc Natl Acad Sci USA 108(49):19473–19481. doi:10.1073/pnas.1017982108

Blair NE, Aller RC (2012) The fate of terrestrial organic carbon in the marine environment. Annu Rev Mar Sci 4:401–423

Bouillon S, Yambele A, Spencer RGM, Gillikin DP, Hernes PJ, Six J, Merckx JR, Borges AV (2012) Organic matter sources, fluxes and greenhouse gas exchange in the Oubangui River (Congo River basin). Biogeosciences 9:2045–2062

Brocks JJ, Summons RE (2003) Sedimentary hydrocarbons, biomarkers for early life. Treatise Geochem 8:63–115

Brodowski S, Amelung W, Haumaier L, Abetz C, Zech W (2005) Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Geoderma 128:116–129

Butman D, Raymond PA (2011) Significant efflux of carbon dioxide from streams and rivers in the United States. Nat Geosci 4:839–842

Canfield DE (1994) Factors influencing organic carbon preservation in marine sediments. Chem Geol 114(3–4):315–329. doi:10.1016/0009-2541(94)90061-2

Caraco N, Bauer JE, Cole JJ, Petsch S, Raymond P (2010) Millennial-aged organic carbon subsidies to a modern river food web. Ecology 91(8):2385–2393. doi:10.1890/09-0330.1

Carrington EM, Hernes PJ, Dyda RY, Plante AF, Six J (2012) Biochemical changes across a carbon saturation gradient: lignin, cutin, and suberin decomposition and stabilization in fractionated carbon pools. Soil Biol Biochem 47:179–190. doi:10.1016/j.soilbio.2011.12.024

Cole JJ, Caraco NF (2001) Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. Mar Freshw Res 52(1):101–110

Cole J, Prairie Y, Caraco N, McDowell W, Tranvik L, Striegl R, Duarte C, Kortelainen P, Downing J, Middelburg J, Melack J (2007) Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. Ecosystems 10(1):172–185

Corvasce M, Zsolnay A, D'Orazio V, Lopez R, Miano T (2006) Characterization of water extractable organic matter in a deep soil profile. Chemosphere 62:1583–1590

Dai KH, Johnson CE, Driscoll CT (2001) Organic matter chemistry and dynamics in clear-cut and unmanaged hardwood forest ecosystems. Biogeochemistry 54(1):51–83. doi:10.1023/a:1010697518227

Dalzell BJ, King JY, Mulla DJ, Finlay JC, Sands GR (2011) Influence of subsurface drainage on quantity and quality of dissolved organic matter export from agricultural landscapes. J Geophys Res 116(G2):G02023. doi:10.1029/2010JG001540

de la Rosa JM, Knicker H (2011) Bioavailability of N released from N-rich pyrogenic organic matter: an incubation study. Soil Biol Biochem 43(12):2368–2373

DeAngelis KM, Allgaier M, Chavarria Y, Fortney JL, Hugenholtz P, Simmons B, Sublette K, Silver WL, Hazen TC (2011) Characterization of trapped lignin-degrading microbes in tropical forest soil. PLoS ONE 6:4. doi:10.1371/journal.pone.0019306

Dignac MF, Bahri H, Rumpel C, Rasse DP, Bardoux G, Balesdent J, Girardin C, Chenu C, Mariotti A (2005) ^{13}C natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France). Geoderma 128(1–2):3–17. doi:10.1016/j.geoderma.2004.12.022

Dittmar T, de Rezende CE, Manecki M, Niggemann J, Coelho Ovalle AR, Stubbins A, Bernardes MC (2012) Continuous flux of dissolved black carbon from a vanished tropical forest biome. Nat Geosci 5(9):618–622. doi:10.1038/ngeo1541

Duan S, Bianchi T, Sampere T (2007) Temporal variability in the composition and abundance of terrestrially-derived dissolved organic matter in the lower Mississippi and Pearl Rivers. Mar Chem 103:172–184

Dungait JAJ, Hopkins DW, Gregory AS, Whitmore AP (2012) Soil organic matter turnover is governed by accessibility not recalcitrance. Glob Change Biol 18(6):1781–1796. doi:10.1111/j.1365-2486.2012.02665.x

Evans CD, Freeman C, Cork LG, Thomas DN, Reynolds B, Billett MF, Garnett MH, Norris D (2007) Evidence against recent climate-induced destabilisation of soil carbon from C-14 analysis of riverine dissolved organic matter. Geophys Res Lett 34:7. doi:10.1029/2007gl029431

Feng X, Simpson A, Wilson K, Williams D, Simpson MJ (2008) Increased cuticular carbon sequestration and lignin oxidation in response to soil warming. Nat Geosci 1:836–839

Feng X, Simpson A, Gregorich E, Elberling B, Hopkins DW, Sparrow AD, Novis PM, Greenfield LG, Simpson MJ (2010) Chemical characterization of microbial-dominated soil organic matter in the Garwood Valley, Antarctica. Geochim Cosmochim Acta 74(22):6485–6498

Galy V, Eglinton T (2011) Protracted storage of biospheric carbon in the Ganges–Brahmaputra basin. Nat Geosci 4(12):843–847. doi:10.1038/ngeo1293

Galy V, France-Lanord C, Beyssac O, Faure P, Kudrass H, Palhol F (2007) Efficient organic carbon burial in the Bengal fan sustained by the Himalayan erosional system. Nature 450(7168):407–410

Gleixner G (2013) Soil organic matter dynamics: a biological perspective derived from the use of compound-specific isotopes studies. Ecol Res. doi:10.1007/s11284-012-1022-9

Gleixner G, Poirier N, Bol R, Balesdent J (2002) Molecular dynamics of organic matter in a cultivated soil. Org Geochem 33(3):357–366

Grimm NB, Gergel SE, McDowell WH, Boyer EW, Dent CL, Groffman P, Hart SC, Harvey J, Johnston C, Mayorga E, McClain ME, Pinay G (2003) Merging aquatic and terrestrial perspectives of nutrient biogeochemistry. Oecologia 442:485–501

Guggenberger G, Rodionov A, Shibistova O, Grabe M, Kasansky OA, Fuchs H, Mikheyeva N, Zrazhevskaya G, Flessa H (2008) Storage and mobility of black carbon in permafrost soils of the forest tundra ecotone in Northern Siberia. Glob Change Biol 14:1367–1381

Guo LD, Ping CL, Macdonald RW (2007) Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. Geophys Res Lett 34(13):L13603. doi:10.1029/2007gl030689

Gurwick NP, McCorkle DM, Groffman PM, Gold AJ, Kellogg DQ, Seitz-Rundlett P (2008) Mineralization of ancient carbon in the subsurface of riparian forests. J Geophys Res 113(G2):G02021. doi:10.1029/2007jg000482

Hammes K, Torn MS, Lapenas AG, Schmidt MWI (2008) Centennial black carbon turnover observed in a Russian steppe soil. Biogeosciences 5(5):1339–1350

Hanson PC, Hamilton DP, Stanley EH, Preston N, Langman OC, Kara EL (2011) Fate of allochthonous dissolved organic carbon in lakes: a quantitative approach. PLoS ONE 6(7):e21884. doi:10.21371/journal.pone.0021884

Hatcher PG (2004) The CHNs of organic geochemistry: characterization of molecularly uncharacterized non-living organic matter. Mar Chem 92(1–4):5–8. doi:10.1016/j.marchem.2004.06.014

Hayes MHB (2009) Evolution of concepts of environmental natural nonliving organic matter. In: Senesi N, Xing B, Huang PM (eds) Biophysico-Chemical Processes Involving Natural Nonliving Organic Matter in Environmental Systems. Wiley, Hoboken, pp 1–39. doi:10.1002/9780470494950.ch1

Hayes MHB, Clapp CE (2001) Humic substances: considerations of compositions, aspects of structure, and environmental influences. Soil Sci 166(11):723–737. doi:10.1097/00010694-200111000-00002

Hedges JI, Keil RG (1999) Organic geochemical perspectives on estuarine processes: sorption reactions and consequences. Mar Chem 65(1–2):55–65. doi:10.1016/s0304-4203(99)00010-9

Hedges JI, Mann DC (1979) Characterization of plant tissues by their lignin oxidation products. Geochim Cosmochim Acta 43(11):1803–1807. doi:10.1016/0016-7037(79)90028-0

Hedges JI, Oades JM (1997) Comparative organic geochemistries of soils and marine sediments. Org Geochem 27(7–8):319–361

Hedges JI, Keil RG, Benner R (1997) What happens to terrestrial organic matter in the ocean? Org Geochem 27(5–6):195–212. doi:10.1016/s0146-6380(97)00066-1

Hedges J, Eglinton G, Hatcher P, Kirchman D, Arnosti C, Derenne S, Evershed R, Kögel-Knabner I, De Leeuw J, Littke R (2000) The molecularly-uncharacterized component of nonliving organic matter in natural environments. Org Geochem 31(10):945–958

Henrichs SM (1992) Early diagenesis of organic matter in marine sediments—progress and perplexity. Mar Chem 39(1–3):119–149. doi:10.1016/0304-4203(92)90098-u

Hernes PJ, Benner R (2003) Photochemical and microbial degradation of dissolved lignin phenols: implications for the fate of terrigenous dissolved organic matter in marine environments. J Geophys Res 108(C9):3291. doi:10.1029/2002jc001421

Hernes PJ, Robinson AC, Aufdenkampe AK (2007) Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". Geophys Res Lett 34:17. doi:10.1029/2007gl031017

Hertkorn N, Claus H, Schmitt-Kopplin P, Perdue EM, Filip Z (2002) Utilization and transformation of aquatic humic substances by autochthonous microorganisms. Environ Sci Technol 36(20):4334–4345. doi:10.1021/es010336o

Heyes A, Moore TR (1992) The influence of dissolved organic carbon and anaerobic conditions on mineral weathering. Soil Sci 154(3):226–236. doi:10.1097/00010694-199209000-00006

Hilli S, Stark S, Willfor S, Smeds A, Reunanen M, Hautajarvi R (2012) What is the composition of AIR? Pyrolysis-GC-MS characterization of acid-insoluble residue from fresh litter and organic horizons under boreal forests in southern Finland. Geoderma 179:63–72. doi:10.1016/j.geoderma.2012.02.010

Hockaday WC, Grannas AM, Kim S, Hatcher PG (2006) Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Org Geochem 37(4):501–510. doi:10.1016/j.orggeochem.2005.11.003

Hockaday WC, Grannas AM, Kim S, Hatcher PG (2007) The transformation and mobility of charcoal in a fire-impacted watershed. Geochim Cosmochim Acta 71(14):3432–3445

Holmes RM, McClelland JW, Raymond PA, Frazer BB, Peterson BJ, Stieglitz M (2008) Lability of DOC transported by Alaskan rivers to the Arctic Ocean. Geophys Res Lett 35:3. doi:10.1029/2007gl032837

Hood E, Fellman J, Spencer RGM, Hernes PJ, Edwards R, D'Amore D, Scott D (2009) Glaciers as a source of ancient and labile organic matter to the marine environment. Nature 462(7276):1044–1100. doi:10.1038/nature08580

Jaffé R, Ding Y, Niggemann J, Vähätolo AV, Stubbins A, Spencer RGM, Campbell J, Dittmar T (2013) Global charcoal mobilization from soils via dissolution and riverine transport to the oceans. Science 340:345–347

Jiao N, Herndl GJ, Hansell DA, Benner R, Kattner G, Wilhelm SW, Kirchman DL, Weinbauer MG, Luo TW, Chen F, Azam F (2010) Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. Nat Rev Microbiol 8(8):593–599. doi:10.1038/nrmicro2386

Jung B-J, Lee H-J, Jeong J-J, Owen J, Kim B, Meusburger K, Alewell C, Gebauer G, Shope C, Park J-H (2012) Storm pulses and varying sources of hydrologic carbon export from a mountainous watershed. J Hydrol 440:90–101. doi:10.1016/j.jhydrol.2012.03.030

Kaiser K, Kalbitz K (2012) Cycling downwards—dissolved organic matter in soils. Soil Biol Biochem 52:29–32

Kaiser K, Zech W (1997) Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. Soil Sci Soc Am J 61(1):64–69

Kaiser K, Zech W (1999) Release of natural organic matter sorbed to oxides and a subsoil. Soil Sci Soc Am J 63(5):1157–1166. doi:10.2136/sssaj1999.6351157x

Keil RG, Mayer LM (2014) Mineral matrices and organic matter. Treatise Geochem Org Geochem 12:337–359

Keil RG, Montlucon DB, Prahl FG, Hedges JI (1994) Sorptive preservation of labile organic matter in marine sediments. Nature 370(6490):549–552. doi:10.1038/370549a0

Keiluweit M, Nico PS, Johnson MG, Kleber M (2010) Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ Sci Technol 44(4):1247–1253. doi:10.1021/es9031419

Kleber M (2010) What is recalcitrant soil organic matter? Environ Chem 7(4):320–332. doi:10.1071/en10006

Kleber M, Johnson MG (2010) Advances in understanding the molecular structure of soil organic matter: implications for interactions in the environment. Adv Agron 106:77–142

Kleber M, Sollins P, Sutton R (2007) A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry 85(1):9–24. doi:10.1007/s10533-007-9103-5

Kleber M, Nico PS, Plante A, Filley T, Kramer M, Swanston C, Sollins P (2011) Old and stable soil organic matter is not necessarily chemically recalcitrant: implications for modeling concepts and temperature sensitivity. Glob Change Biol 17(2):1097–1107

Kögel I (1986) Estimation and decomposition pattern of the lignin component in forest humus layers. Soil Biol Biochem 18(6):589–594

Kögel-Knabner I (2002) The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. Soil Biol Biochem 34(2):139–162

Kögel-Knabner I, Guggenberger G, Kleber M, Kandeler E, Kalbitz K, Scheu S, Eusterhues K, Leinweber P (2008) Organo-mineral associations in temperate soils: integrating biology, mineralogy, and organic matter chemistry. J Plant Nutr Soil Sci 171(1):61–82

Kramer C, Gleixner G (2006) Variable use of plant- and soil-derived carbon by microorganisms in agricultural soils. Soil Biol Biochem 38(11):3267–3278. doi:10.1016/j.soilbio.2006.04.006

Kramer MG, Sanderman J, Chadwick OA, Chorover J, Vitousek PM (2012) Long-term carbon storage through retention of dissolved aromatic acids by reactive particles in the soil. Glob Change Biol 18:2594–2605

Lalonde K, Mucci A, Ouellet A, Gelinas Y (2012) Preservation of organic matter in sediments promoted by iron. Nature 483:198–200

Lambert T, Pierson-Wickmann A-C, Gruau G, Thibault J-N, Jaffrezic A (2011) Carbon isotopes as tracers of dissolved organic carbon sources and water pathways in headwater catchments. J Hydrol 402(3–4):228–238. doi:10.1016/j.jhydrol.2011.03.014

Lambert T, Pierson-Wickmann A-C, Gruau G, Jaffrezic A, Petitjean P, Thibault J-N, Jeanneau L (2013) Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment. Water Resour Res 49(9):5792–5803. doi:10.1002/wrcr.20466

Laudon H, Berggren M, Ågren A, Buffam I, Bishop K, Grabs T, Jansson M, Köhler S (2011) Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. Ecosystems 14(6):880–893. doi:10.1007/s10021-011-9452-8

Liang C, Balser TC (2011) Microbial production of recalcitrant organic matter in global soils: implications for productivity and climate policy. Nat Rev Microbiol 9(1):75. doi:10.1038/nrmicro2386-c1

Lorenz K, Lal R, Preston CM, Nierop KGJ (2007) Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio(macro)molecules. Geoderma 142(1–2):1–10. doi:10.1016/j.geoderma.2007.07.013

Mann PJ, Sobczak W, LaRue M, Bulygina E, Davydova A, Vonk JE, Schade J, Davydov S, Zimov N, Holmes RM, Spencer RGM (2014) Evidence for key enzymatic controls on metabolism of Arctic river organic matter. Glob Change Biol. doi:10.1111/gcb.12416

Marin-Spiotta E, Silver WL, Swanston CW, Ostertag R (2009) Soil organic matter dynamics during 80 years of reforestation of tropical pastures. Glob Change Biol 15(6):1584–1597. doi:10.1111/j.1365-2486.2008.01805.x

Marin-Spiotta E, Chadwick OA, Kramer M, Carbone MS (2011) Carbon delivery to deep mineral horizons in Hawaiian rain forest soils. J Geophys Res 116:G03011. doi:10.01029/02010JG001587

Marschner B, Kalbitz K (2003) Controls of bioavailability and biodegradability of dissolved organic matter in soils. Geoderma 113(3–4):211–235. doi:10.1016/s0016-7061(02)00362-2

Martone PT, Estevez JM, Lu FC, Ruel K, Denny MW, Somerville C, Ralph J (2009) Discovery of lignin in seaweed reveals convergent evolution of cell wall architecture. Curr Biol 19(2):169–175. doi:10.1016/j.cub.2008.12.031

Masiello CA, Druffel ERM (2001) Carbon isotope geochemistry of the Santa Clara River. Glob Biogeochem Cycles 15:407–416

Masiello CA, Louchouarn P (2013) Fire in the ocean. Science 340(6130):287–288. doi:10.1126/science.1237688

Mayer LM, Schick LL, Hardy KR, Estapa ML (2009) Photo-dissolution and other photochemical changes upon irradiation of algal detritus. Limnol Oceanogr 54(5):1688–1698. doi:10.4319/lo.2009.54.5.1688

Mayorga E, Aufdenkampe A, Masiello C, Krusche A, Hedges J, Quay P, Richey J, Brown T (2005) Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers. Nature 436:538–541

McCallister SL, del Giorgio PA (2012) Evidence for the respiration of ancient terrestrial organic C in northern temperate lakes and streams. Proc Natl Acad Sci USA 109(42):16963–16968. doi:10.1073/pnas.1207305109

McGroddy ME, Daufresne T, Hedin LO (2004) Scaling of C:N:P stoichiometry in forests worldwide: implications of terrestrial Redfield-type ratios. Ecology 85:2390–2401

McKnight DM, Boyer EW, Westerhoff PK, Doran PT, Kulbe T, Andersen DT (2001) Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol Oceanogr 46:38–48

Melillo J, Aber J, Linkins A, Ricca A, Fry B, Nadelhoffer K (1989) Carbon and nitrogen dynamics along the decay

continuum: plant litter to soil organic matter. Plant Soil 115(2):189–198

Meyer JL, Edwards RT (1990) Ecosystem metabolism and turnover of organic carbon along a blackwater river continuum. Ecology 71(2):668–677. doi:10.2307/1940321

Meyers P (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org Geochem 27:213–250

Miltner A, Kindler R, Knicker H, Richnow H-H, Kästner M (2009) Fate of microbial biomass-derived amino acids in soil and their contribution to soil organic matter. Org Geochem 40(9):978–985. doi:10.1016/j.orggeochem.2009.06.008

Miltner A, Bombach P, Schmidt-Brücken B, Kästner M (2012) SOM genesis: microbial biomass as a significant source. Biogeochemistry 111(1–3):41–55. doi:10.1007/s10533-011-9658-z

Moore S, Evans CD, Page SE, Garnett MH, Jones TG, Freeman C, Hooijer A, Wiltshire AJ, Limin SH, Gauci V (2013) Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes. Nature 493(7434):660. doi:10.1038/nature11818

Mosher JJ, Klein GC, Marshall AG, Findlay RH (2010) Influence of bedrock geology on dissolved organic matter quality in stream water. Org Geochem 41(11):1177–1188. doi:10.1016/j.orggeochem.2010.08.004

Nelson PN, Baldock JA, Oades JM (1993) Concentration and composition of dissolved organic carbon in streams in relation to catchment soil properties. Biogeochemistry 19(1):27–50

Nocentini C, Certini G, Knicker H, Francioso O, Rumpel C (2010) Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. Org Geochem 41(7):682–689

Oades JM (1988) The retention of organic matter in soils. Biogeochemistry 5(1):35–70. doi:10.1007/bf02180317

Ogawa H, Amagai Y, Koike I, Kaiser K, Benner R (2001) Production of refractory dissolved organic matter by bacteria. Science 292(5518):917–920. doi:10.1126/science.1057627

Onstad GD, Canfield DE, Quay PD, Hedges JI (2000) Sources of particulate organic matter in rivers from the continental USA: lignin phenol and stable carbon isotope compositions. Geochim Cosmochim Acta 64(20):3539–3546. doi:10.1016/s0016-7037(00)00451-8

Opsahl S, Benner R (1998) Photochemical reactivity of dissolved lignin in river and ocean waters. Limnol Oceanogr 43:1297–1304

Parton WJ, Schimel DS, Cole CV, Ojima DS (1987) Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Sci Soc Am J 51(5):1173–1179

Paul EA, Morris SJ, Conant RT, Plante AF (2006) Does the acid hydrolysis-incubation method measure meaningful soil organic carbon pools? Soil Sci Soc Am J 70(3):1023–1035. doi:10.2136/sssaj2005.0103

Pellerin BA, Saraceno JF, Shanley JB, Sebestyen SD, Aiken GR, Wollheim WM, Bergamaschi BA (2012) Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. Biogeochemistry 108(1–3):183–198. doi:10.1007/s10533-011-9589-8

Piccolo A (2001) The supramolecular structure of humic substances. Soil Sci 166(11):810–832. doi:10.1097/00010694-200111000-00007

Preston C, Nault J, Trofymow J (2009) Chemical changes during 6 years of decomposition of 11 litters in some Canadian forest sites. Part 2. 13C abundance, solid-state 13C NMR spectroscopy and the meaning of 'lignin'. Ecosystems 12(7):1078–1102

Raymond PA, Bauer JE (2001) Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. Nature 409(6819):497–500. doi:10.1038/35054034

Raymond P, Saiers J (2010) Event controlled DOC export from forested watersheds. Biogeochemistry 100(1):197–209. doi:10.1007/s10533-010-9416-7

Raymond PA, McClelland JW, Holmes RM, Zhulidov AV, Mull K, Peterson BJ, Striegl RG, Aiken GR, Gurtovaya TY (2007) Flux and age of dissolved organic carbon exported to the Arctic Ocean: a carbon isotopic study of the five largest arctic rivers. Global Biogeochem Cycles 21:4. doi:10.1029/2007gb002934

Raymond PA, Hartmann J, Lauerwald R, Sobek S, McDonald C, Hoover M, Butman D, Striegl R, Mayorga E, Humborg C, Kortelainen P, Dürr H, Meybeck M, Ciais P, Guth P (2013) Global carbon dioxide emissions from inland waters. Nature 503:355–359

Regnier P (2013) Anthropogenic perturbation of the carbon fluxes from land to ocean. Nat Geosci 6:597–607

Richey JE, Melack JM, Aufdenkampe AK, Ballester VM, Hess LL (2002) Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2. Nature 416:617–620

Rumpel C, Eusterhues K, Kogel-Knabner I (2004) Location and chemical composition of stabilized organic carbon in topsoil and subsoil horizons of two acid forest soils. Soil Biol Biochem 36(1):177–190. doi:10.1016/j.soilbio.2003.09.005

Ryan MG, Melillo JM, Ricca A (1990) A comparison of methods for determining proximate carbon fractions of forest litter. Can J For Res 20(2):166–171. doi:10.1139/x90-023

Sanderman J, Baldock JA, Amundson R (2008) Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils. Biogeochemistry 89:181–198

Sanderman J, Lohse KA, Baldock JA, Amundson R (2009) Linking soils and streams: sources and chemistry of dissolved organic matter in a small coastal watershed. Water Resour Res 45:W03418. doi:10.1029/2008wr006977

Sanford GR (2012) Agroecosystem land management and its effect on soil organic carbon stocks and dynamics in the Mollisols of southern Wisconsin. PhD thesis, The University of Wisconsin-Madison, Madison, WI

Schindler JE, Krabbenhoft DP (1998) Dynamics of dissolved organic carbon and carbon gases in the hyporheic zone of a temperate stream. Biogeochemistry 43:157–174

Schmidt MWI, Eglinton TI (2013) Unifying concepts of organic matter cycling in soil, river, and marine environments. EOS 94(15):145

Schmidt MWI, Torn MS, Abiven S, Dittmar T, Guggenberger G, Janssens IA, Kleber M, Kogel-Knabner I, Lehmann J, Manning DAC, Nannipieri P, Rasse DP, Weiner S, Trumbore SE (2011) Persistence of soil organic matter as

an ecosystem property. Nature 478(7367):49–56. doi:10.1038/nature10386

Singh N, Abiven S, Torn MS, Schmidt MWI (2012) Fire-derived organic carbon in soil turns over on a centennial scale. Biogeosciences 9:2847–2857

Spencer RGM, Pellerin BA, Bergamaschi BA, Downing BD, Kraus TEC, Smart DR, Dahgren RA, Hernes PJ (2007) Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). Hydrol Process 21(23):3181–3189. doi:10.1002/hyp.6887

Spencer RGM, Stubbins A, Hernes PJ, Baker A, Mopper K, Aufdenkampe AK, Dyda RY, Mwamba VL, Mangangu AM, Wabakanghanzi JN, Six J (2009) Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. J Geophys Res 114:G03010. doi:10.1029/2009jg000968

Spencer RGM, Hernes PJ, Ruf R, Baker A, Dyda RY, Stubbins A, Six J (2010) Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. J Geophys Res 115:G03013. doi:10.1029/2009jg001180

Spencer RGM, Butler KD, Aiken GR (2012a) Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA. J Geophys Res 117:G03001. doi:10.1029/2011jg001928

Spencer RGM, Hernes PJ, Aufdenkampe AK, Baker A, Gulliver P, Stubbins A, Aiken GR, Dyda RY, Butler KD, Mwamba VL, Mangangu AM, Wabakanghanzi JN, Six J (2012b) An initial investigation into the organic matter biogeochemistry of the Congo River. Geochim Cosmochim Acta 84:614–627. doi:10.1016/j.gca.2012.01.013

Spencer RGM, Aiken GR, Wickland KP, Striegl RG, Hernes PJ (2008) Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska. Glob Biogeochem Cycles 22:GB4002. doi:10.1029/2008gb003231

Spokas KA (2010) Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Manag 1:289–303

Stanley EH, Powers SM, Lottig NR, Buffam I, Crawford JT (2012) Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? Freshw Biol 57:26–42

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions, 2nd edn. Wiley, New York

Striegl RG, Aiken GR, Dornblaser MM, Raymond PA, Wickland KP (2005) A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophys Res Lett 32(21):L21413. doi:10.1029/2005GL024413

Striegl RG, Dornblaser MM, McDonald CP, Rover JR, Stets EG (2012) Carbon dioxide and methane emissions from the Yukon River system. Glob Biogeochem Cycles 26:GB0E05. doi:10.1029/2012gb004306

Stubbins A, Niggemann J, Dittmar T (2012a) Photo-lability of deep ocean dissolved black carbon. Biogeosciences 9(5):1661–1670. doi:10.5194/bg-9-1661-2012

Stubbins A, Hood E, Raymond PA, Aiken GR, Sleighter RL, Hernes PJ, Butman D, Hatcher PG, Striegl RG, Schuster P, Abdulla HAN, Vermilyea AW, Scott DT, Spencer RGM

(2012b) Anthropogenic aerosols as a source of ancient dissolved organic matter in glaciers. Nat Geosci 5(3):198–201

Sutton R, Sposito G (2005) Molecular structure in soil humic substances: the new view. Environ Sci Technol 39(23):9009–9015. doi:10.1021/es050778q

Tarnocai C, Canadell JG, Schuur EAG, Kuhry P, Mazhitova G, ZImov S (2009) Soil organic carbon pools in the northern circumpolar permafrost region. Glob Biogeochem Cycles 23:GB2023. doi:10.1029/2008GB003327

Torn MS, Swanston CW, Castanha C, Trumbore SE (2009) Storage and turnover of organic matter in soil. In: Senesi N, Xing B, Huang PM (eds) Biophysico-chemical processes involving natural nonliving organic matter in environmental systems. Wiley, Hoboken, pp 219–272

Tranvik LJ, Downing JA, Cotner JB, Loiselle SA, Striegl RG, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB, Kortelainen PL, Kutserk T, Larsen S, Laurion I, Leech DM, McCallister SL, McKnight DM, Melack JM, Overholt E, Porter JA, Prairie Y, Renwick WH, Roland F, Sherman BS, Schindler DW, Sobek S, Tremblay A, Vanni MJ, Verschoor AM, von Wachenfeldt E, Weyhenmeyer GA (2009) Lakes and reservoirs as regulators of carbon cycling and climate. Limnol Oceanogr 54:2298–2314

Trumbore S (2009) Radiocarbon and soil carbon dynamics. Annu Rev Earth Planet Sci 37(1):47–66

Vargas R, Detto M, Baldocchi DD, Allen MF (2010) Multiscale analysis of temporal variability of soil CO2 production as influenced by weather and vegetation. Glob Change Biol 16(5):1589–1605. doi:10.1111/j.1365-2486.2009.02111.x

von Lützow M, Kögel-Knabner I, Ekschmitt K, Matzner E, Guggenberger G, Marschner B, Flessa H (2006) Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions—a review. Eur J Soil Sci 57(4):426–445

von Lützow M, Kögel-Knabner I, Ludwig B, Flessa H, Matzner E, Ekschmitt K, Guggenberger G, Marschner B, Kalbitz K (2008) Stabilization mechanisms of organic matter in four temperate soils: development and application of a conceptual model. J Plant Nutr Soil Sci 171:111–124

Vonk JE, Mann PJ, Davydov S, Davydova A, Spencer RGM, Schade J, Sobczak WV, Zimov N, Zimov S, Bulygina E, Eglinton TI, Holmes RM (2013) High biolability of ancient permafrost carbon upon thaw. Geophys Res Lett 40(11):2689–2693. doi:10.1002/grl.50348

Waksman SA (1935) Chemical nature of organic matter or humus in soils, peat bogs and composts. J Chem Educ 12(11):511. doi:10.1021/ed012p511

Wang ZA, Bienvenu DJ, Mann PJ, Hoering KA, Poulsen JR, Spencer RGM, Holmes RM (2013) Inorganic carbon speciation and fluxes in the Congo River. Geophys Res Lett 40(3):511–516. doi:10.1002/grl.50160

Ward ND, Keil RG, Medeiros PM, Brito DC, Cunha AC, Dittmar T, Yager PL, Krusche AV, Richey JE (2013) Degradation of terrestrially derived macromolecues in the Amazon River. Nat Geosci 6:530–533

Wickland KP, Aiken GR, Butler K, Dornblaser MM, Spencer RGM, Striegl RG (2012) Biodegradability of dissolved organic carbon in the Yukon River and its tributaries: seasonality and importance of inorganic nitrogen. Glob Biogeochem Cycles 26:GB0E03. doi:10.1029/2012gb004342

Williams CJ, Yamashita Y, Wilson HF, Jaffe R, Xenopoulos MA (2010) Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. Limnol Oceanogr 55(3):1159–1171. doi:10.4319/lo.2010.55.3.1159

Yang Y, Fang J, Guo D, Ji C, Ma W (2010) Vertical patterns of soil carbon, nitrogen and carbon: nitrogen stoichiometry in Tibetan grasslands. Biogeosci Discuss 7:1–24

Young KC, Maurice PA, Docherty KM, Bridgham SD (2004) Bacterial degradation of dissolved organic matter from two northern Michigan streams. Geomicrobiol J 21(8): 521–528. doi:10.1080/01490450490888208

Zimov SA, Davydov SP, Zimova GM, Davydova AI, Schuur EAG, Dutta K, Chapin FS (2006) Permafrost carbon: stock and decomposability of a globally significant carbon pool. Geophys Res Lett 33:L20502. doi:10.1029/2006GL027484