I INTRODUCTION

A  Rivers and Oceanic DOM

The steady state concentration of many dissolved chemical constituents in seawater is dependent on the amount delivered by rivers (Goldschmidt, 1932; Mackenzi and Garrels, 1966). In some cases, since rivers are the major input term, the removal rate of a constituent in the ocean can be indirectly assessed if the riverine term is known. Pioneering work on the radiocarbon age of oceanic dissolved organic matter (DOM) suggested that the riverine input of DOM would be large enough to maintain the steady state age and concentration of oceanic DOM (Bauer et al., 1992; Druffel et al., 1989; Williams et al., 1969). Thus in this case the input rate provided by rivers matched an independent check on the rate of removal, suggesting the source of oceanic DOM could be terrestrial material that aged in the ocean. The importance of rivers to steady state concentrations and chemical character of oceanic DOM motivated oceanographer’s early interest in riverine DOM, which
due to the complexity of the composition of DOM continues to engage researchers.

Early methods for measuring DOM in inland waters were rather crude, often involving measuring the loss on ignition of a vacuum dried sample, attempting to correct for dissolved salts (Hutchinson, 1957). These methods were employed in lacustrine environments more than fluvial systems (Hutchinson, 1957), and were adopted by other studies looking at average river water concentrations globally (Livingstone, 1963). Method improvements in the 1960s involved oxidizing samples to CO₂ and detecting with infrared analyzers (Menzel and Vaccaro, 1964; Vanhall et al., 1963). An early study using these methods on the Amazon River reported concentrations of dissolved organic carbon (DOC) of ~3.5 mg L⁻¹, or 3-4× greater than surface seawater (Williams, 1968).

B Importance of Riverine DOM to Estuarine and Coastal Processes

The flux of riverine DOM from land to ocean is a major source of reduced carbon to marine environments, with biogeochemical cycling in coastal margins near riverine outflows dominated by the influx of terrestrial organic matter and nutrients. DOM can undergo a variety of biogeochemical reactions in river plumes, estuaries, and at the land-ocean interface that ultimately determines both the concentration of DOC and composition of DOM reaching the ocean. Unsurprisingly, the behavior of terrestrial DOM during estuarine mixing is highly variable. Conservative behavior of DOC in numerous estuaries (Abril et al., 2002; Alvarez-Salgado and Miller, 1998; Mantoura and Woodward, 1983) reflects comparatively minor estuarine modification of the terrestrial DOM. In other estuaries, nonconservative behavior at low salinities has been attributed to the removal of specific components of the DOM pool (Benner and Opsahl, 2001; Hernes and Benner, 2003), and DOM composition has been shown to exert a control on the degree of DOC removal (Spencer et al., 2007a). Nonconservative behavior of DOM within estuaries can also result from inputs from sources such as anthropogenic pollution (e.g., the Scheldt and the Tyne), phytoplankton (e.g., Chesapeake Bay and the Mississippi), intertidal areas (e.g., the Sado and the Ems), salt marshes, tributaries (e.g., the Pearl), and desorption from sediments and the flushing of porewaters (e.g., the Tamar and the Gironde) (Abril et al., 1999, 2002; Benner and Opsahl, 2001; Chen and Gardner, 2004; Raymond and Hopkinson, 2003; Spencer et al., 2007b). A number of factors ultimately play into determining how much DOC, and the composition of DOM, exported to coastal waters, including flocculation, adsorption onto suspended sediments, and microbial and photochemical degradation (Hernes and Benner, 2003; Shank et al., 2005; Uher et al., 2001).

Coastal and estuarine microbial communities may be better adapted at consuming terrestrial DOM than riverine microbial communities (Fellman et al., 2010; Stepanauskas et al., 1999; Wikner et al., 1999). Increasing ionic strength also causes biochemical and compositional changes of DOM that can lead to greater bacterial utilization (Dehaan et al., 1987; Kerner et al., 2003). However, Fellman et al. (2010) found no significant difference in DOC utilization using a riverine microbial inoculation added to both river water and river water made up to different salinities with an artificial salt mixture. Marine microbes have the potential for more intensive synthesis of extracellular enzymes with greater diversity, thus allowing them to more effectively metabolize terrestrial DOM (Stepanauskas et al., 1999). Riverine and estuarine microbial communities also show different preferences with respect to degrading various components of the DOM pool (Fellman et al., 2010; Sondergaard et al., 2003). However, some studies have found no significant difference in DOC utilization between marine and freshwater microbial communities (Langenheder et al., 2003; Sondergaard et al., 2003). Coastal regions characterized as receiving elevated riverine DOM
and nutrient inputs with microbial communities that are highly adaptable to shifting physicochemical gradients (e.g., light and salinity) have been deemed hot spots for priming effects on terrestrial DOM (Bianchi, 2011).

Naturally, riverine inputs of DOM impact ocean DOM where inputs are greatest, as is apparent in dissolved lignin phenol (a vascular plant biomarker) concentrations in surface waters. For example, lignin phenol concentrations in Arctic surface waters, a major marine system exhibiting the highest river input to volume ratio, are ~10 times greater than reported for the Atlantic, which are in turn 40% greater than those in the Pacific (Hernes and Benner, 2006). The Arctic Ocean receives ~11% of global riverine discharge into ~1% of the global ocean volume, thus imparting estuarine gradients throughout the Arctic Ocean (McClelland et al., 2012). Similarly, concentrations of dissolved black carbon originating from combustion sources (e.g., wildfires, fossil fuel burning) are elevated in coastal waters likely due to continental runoff (Dittmar et al., 2012b). Riverine DOM has a strong impact on the bio-optical properties of the coastal ocean due to its chromophoric character (CDOM), which in coastal waters dominates the inherent light absorption at ultraviolet and blue wavelengths (e.g., 20-70% at 440 nm; Del Vecchio and Subramaniam, 2004; Mannino et al., 2008). Utilizing satellite imagery, and with appropriate algorithm development, CDOM can trace terrestrial inputs of DOC in coastal regions (Fichot and Benner, 2012; Mannino et al., 2008).

**II LAND TRANSPORT**

With respect to lateral transport of terrestrial material, there are two important fluxes to consider: the mobilization of terrestrial DOM to inland waters and the export of terrestrial and riverine DOM to coastal waters. The latter most interests oceanographers, but the former is important to understanding the amount and character of DOM that ultimately reaches the ocean. In small headwater streams, almost all of the DOC exported is of terrestrial origin (Hynes, 1963; Royer and David, 2005). During transport, however, this material can be removed by heterotrophs (Fisher and Likens, 1972; Sondergaard and Middelboe, 1995), by photo-oxidation (Gjessing and Gjerdahl, 1970; Moran and Hodson, 1994), and by flocculation (Sholkovitz, 1976). Furthermore, autochthonous DOM can be added by algae (Allen, 1956; Baines and Pace, 1991a), wetlands and submerged vegetation (Mulholland and Kuenzler, 1979; Raymond and Hopkinson, 2003), and anthropogenic point sources such as sewage (Griffith and Raymond, 2011).

Wetlands are an important control on the transport of DOM off the terrestrial landscape (Wetzel, 1992). The constant contact of wetland and emergent vegetation with water, and the low oxygen content of soils, result in the transfer of large amounts of OM as DOM into inland waters. River floodplains can also simulate wetlands during flood periods, exporting appreciable DOM (Shen et al., 2012; Tockner et al., 1999). This material is generally modern in age (Mayorga et al., 2005; Raymond and Hopkinson, 2003) and contains a biolabile component (Findlay et al., 1992). It is generally less microbiologically available than phytoplankton exudates and other riverine DOM sources (Mann and Wetzel, 1995; Moran and Hodson, 1994; Wetzel, 1992) but highly photo-reactive (Franke et al., 2012).

Upland ecosystems are increasingly seen as important to drainage network DOM delivery. Fluxes off the landscape during spring runoff in temperate and high-latitude systems can be high when hydrologic flow paths do not interact with wetlands (Laudon et al., 2004). Furthermore the export of DOM from upland systems during large precipitation events is high, and studies which attempt to determine the importance of events are demonstrating a larger lateral transport than previously estimated by studies that have not explicitly sampled events (Raymond and Saiers, 2010).
The largest storms can be responsible for upwards of half of long-term annual average DOC fluxes (Schiff et al., 1998; Yoon and Raymond, 2012), and due to the bypassing of watershed filters, have impacts on inland and coastal carbon fluxes (Bianchi et al., 2013; Klug et al., 2012). The predicted increased proportion of annual rainfall that will be delivered with large events forced by climate change (IPCC, 2012) should therefore significantly impact these lateral fluxes (Jeong et al., 2012; Sebestyen et al., 2009) and coastal ocean processes.

The fraction of terrestrial DOM removed during transport to the ocean is not currently well constrained. DOM from small headwater systems demonstrates a significant biolabile component (Buffam et al., 2001; Fellman et al., 2009a; Holmes et al., 2008; Volk et al., 1997; Wilson et al., 2013b). DOM exported from headwater streams during high-flow events has a high degree of aromaticity and therefore is highly photo-reactive (Fellman et al., 2009a; Vidon et al., 2008); laboratory experiments have confirmed a high degree of photoreactions of riverine DOM (Franke et al., 2012; Gao and Zepp, 1998). The light-absorbing properties of this DOM can influence phytoplankton structure and production by both changing the depth of the photic zone and fractioning the wavelengths of available light (Frenette et al., 2012). Photoreactions are also responsible for the direct loss and transformation of DOM. Most work to date on DOM lability, both from bacteria and sunlight, has been done using laboratory experiments where DOM is incubated over time under controlled conditions. A few studies have directly injected DOM into streams demonstrating a highly biolabile pool and a much larger pool that is conservatively transported (Kaplan et al., 2008). It is, however, difficult to undertake these experiments with DOM that is representative of stream DOM during high-flow periods or in major riverine systems. Lauerwald et al. (2012) assessed the total amount of DOM exported to the oceans from large watersheds and the amount exported from small sub-watersheds, finding that 75% of DOM exported from land makes it to the ocean. The smallest headwater streams are not commonly monitored and therefore were excluded from this analysis. The 25% loss is net, however, due to the addition of autochthonous DOM during transport; the total amount of terrestrial DOM removed has to be >25%.

It is difficult to determine how much autochthonous DOM is added during transport to the coast. Within rivers there can be large additions from submerged and emergent wetlands (Tzortziou et al., 2011; Wetzel, 1992). Phytoplankton also exclude a significant percentage of gross primary production as DOM (Baines and Pace, 1991b), which is often detected in river waters (Massicotte and Frenette, 2011; Raymond and Bauer, 2001a). The light-limited nature of many rivers and short transport times, however, often reduces the importance of authochthonous inputs to low-flow summer periods (Goni et al., 2003; Helie and Hillaire-Marcel, 2006; Roach, 2013), resulting in a low contribution of autochthonous DOM to annual riverine DOM fluxes (Stepanauskas et al., 2005). This outcome might not hold true for large rivers that have high nutrient loadings and large reservoirs (Bianchi et al., 2004). In low-flow rivers with large water withdrawals for drinking water or irrigation, sewage DOM can be detected (Butman et al., 2012; He et al., 2010), making important contributions to heterotrophic processes (Griffith and Raymond, 2011).

A Global Fluxes

Several estimates of global DOC flux from land to ocean via rivers have been made. Early studies grouped DOC and particulate organic carbon (POC) together for a flux of ~0.4 PgC year\(^{-1}\) (Schlesinger and Melack, 1981). Meybeck (1982) grouped a limited number of river DOC measurements into four river classes to estimate a global flux of 0.22 PgC year\(^{-1}\). Meybeck (1993) later improved upon this estimate with measurements from ~40 rivers, reporting a flux of 0.20 PgC year\(^{-1}\). Ludwig et al. (1996) improved upon this using a similar set of riverine DOC measurements but employing an empirical relationship between
DOC flux and discharge, slope and soil C to obtain a flux of 0.21 PgC year\(^{-1}\). Caerwe (2002) used a similar typology to Meybeck but updated the DOC concentrations to obtain a global flux of 0.24 PgC year\(^{-1}\). Dai et al. (2012) used a similar approach, binning measurements from 118 rivers into different types to report a flux of 0.20-0.21 PgC year\(^{-1}\). Aitkenhead and McDowell (2000) binned river DOC fluxes from 164 rivers into biomes to describe a relationship between river DOC flux and soil C:N, then used this relationship to obtain a flux of 0.36 PgC year\(^{-1}\). GlobalNEWS has estimated DOC fluxes based on discharge and wetland extent (Seitzinger et al., 2005). Early estimates from GlobalNEWS, calibrated using measurements from 68 large river systems, had fluxes of ~0.17 PgC year\(^{-1}\) (Mayorga et al., 2010; Seitzinger et al., 2005).

Although the estimates of global river DOC export are in a narrow range, they are still rather coarse. Estimates generally share the same training data taken from a limited number of systems with insufficient temporal sampling (i.e., absent event sampling) required for accurate estimates of DOC fluxes. Some regions, such as the Arctic, are not dealt with well in GlobalNEWS, resulting in inaccurately low fluxes from this region. The estimates also share a similar global discharge data set. Annual variations in discharge, mostly driven by changes in precipitation, are 32,000-41,000 km\(^3\) year\(^{-1}\) or ~25% (Wisser et al., 2010), thus annual variations in riverine carbon fluxes may vary by ~20-30%. Dai et al. (2012) reported a large uncertainty in the annual flux of 30%. Thus advances in global/regional export estimates are still possible.

The top 30 rivers with respect to discharge contribute 51% of the total annual global discharge, with the Amazon providing >18%. These rivers drain 36% of the Earth’s exorheic land surface, providing vast quantities of terrestrially derived DOM to the ocean. In total, these rivers export 90.2 TgDOC-C year\(^{-1}\) as DOC (Table 11.1; Figure 11.1a), or 36% of global DOC flux to the ocean (250 TgDOC-C year\(^{-1}\); Hedges et al., 1997). The Amazon River alone exports DOC at ~27 TgDOC-C year\(^{-1}\) at Obidos (Table 11.1; Moreira-Turcq et al., 2003) or 11% of the total DOC flux to the oceans. However, if downstream major lowland tributaries such as the Tapajos and Xingu Rivers are included (1.50 and 0.95 TgDOC-C year\(^{-1}\), respectively) the total flux for the Amazon is 29.35 TgDOC-C year\(^{-1}\) (Coyne et al., 2005; Moreira-Turcq et al., 2003), 11.7% of the global DOC flux. A number of other major tropical rivers are central to DOC flux as well, with the Congo the second largest exporter (12.4 TgDOC-C year\(^{-1}\); 5% of global total) and the Parana and Orinoco important as well (Table 11.1; Figure 11.1a). The major Russian Arctic rivers, such as the Lena (5.68 TgDOC-C year\(^{-1}\)), Yenisey (4.65 TgDOC-C year\(^{-1}\)), and Ob’ (4.12 TgDOC-C year\(^{-1}\)), support large fluxes of DOC to the Arctic Ocean (Raymond et al., 2007); these fluxes are considerably greater than the next principal rivers (e.g., Amur at 2.50 TgDOC-C year\(^{-1}\) and Mississippi at 2.10 TgDOC-C year\(^{-1}\); Table 11.1; Figure 11.1a).

A number of these major rivers are important point or individual sources (e.g., the Congo to the Atlantic Ocean) while others merge with other substantial rivers at their outlets to the ocean, particularly in deltaic systems, thus representing combined DOM sources to the ocean. For example, the Ganges (1.70 TgDOC-C year\(^{-1}\)) joins the Brahmaputra (1.90 TgDOC-C year\(^{-1}\)) and subsequently the Meghna River (annual discharge = 111 km\(^3\) year\(^{-1}\); Meybeck and Ragu, 1996) before together discharging through the Ganges-Brahmaputra-Meghna delta into the Bay of Bengal. Similarly, the Irrawaddy (0.89 TgDOC-C year\(^{-1}\)) and the Salween (0.23 TgDOC-C year\(^{-1}\)) discharge into the Gulf of Martaban in the eastern Indian Ocean along a similar length of deltaic coast to the Ganges-Brahmaputra (Bird et al., 2008). At the mouth of the Amazon, the Tocantins River also joins the Amazon delta, exporting DOC at 30.47 TgDOC-C year\(^{-1}\) (Table 11.1). Naturally, rivers in the top 30 globally also share deltaic systems with other smaller rivers, for example, the Mississippi (2.10 TgDOC-C year\(^{-1}\)) and the Atchafalaya (1.19 TgDOC-C year\(^{-1}\); Spencer et al., 2013) before entering the Gulf of Mexico.
TABLE 11.1 Discharge, watershed area and DOC fluxes and yields for the top 30 rivers ranked by discharge globally. Discharge and watershed area estimates are from Meybeck and Ragu (1996) if not specified.

<table>
<thead>
<tr>
<th>River Rank by Discharge</th>
<th>River Name</th>
<th>Discharge (km³/yr)</th>
<th>Area (Mkm²)</th>
<th>DOC Flux (TgC/yr)</th>
<th>Global DOC Flux (%)</th>
<th>DOC Yield (gC/m²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Amazon</td>
<td>6590</td>
<td>6.112</td>
<td>26.90d</td>
<td>10.8</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td>Congo</td>
<td>1325a</td>
<td>3.698</td>
<td>12.40b</td>
<td>5.0</td>
<td>3.4</td>
</tr>
<tr>
<td>3</td>
<td>Orinoco</td>
<td>1135</td>
<td>1.100</td>
<td>4.98e</td>
<td>2.0</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>Changjiang (Yangtze)</td>
<td>928</td>
<td>1.808</td>
<td>1.58f</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>Yenisey</td>
<td>673b</td>
<td>2.540b</td>
<td>4.65b</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>6</td>
<td>Lena</td>
<td>588b</td>
<td>2.460b</td>
<td>5.68b</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>7</td>
<td>Mississippi</td>
<td>580</td>
<td>2.980</td>
<td>2.10b</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>8</td>
<td>Parana</td>
<td>568</td>
<td>2.783</td>
<td>5.92b</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>9</td>
<td>Brahmaputra</td>
<td>510</td>
<td>0.580</td>
<td>1.90b</td>
<td>0.8</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>Ganges</td>
<td>493</td>
<td>1.050</td>
<td>1.70b</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>11</td>
<td>Irrawaddy (Ayeyarwady)</td>
<td>486</td>
<td>0.410</td>
<td>0.89f</td>
<td>0.4</td>
<td>2.2</td>
</tr>
<tr>
<td>12</td>
<td>Mekong</td>
<td>467</td>
<td>0.795</td>
<td>1.11*</td>
<td>0.4</td>
<td>1.4</td>
</tr>
<tr>
<td>13</td>
<td>Ob'</td>
<td>427b</td>
<td>2.990b</td>
<td>4.12b</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>14</td>
<td>Tocantins</td>
<td>372</td>
<td>0.757</td>
<td>1.12*</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>15</td>
<td>Amur</td>
<td>344</td>
<td>1.855</td>
<td>2.50f</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>16</td>
<td>St. Lawrence</td>
<td>337</td>
<td>1.780</td>
<td>1.55b</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>17</td>
<td>Mackenzie</td>
<td>316b</td>
<td>1.780b</td>
<td>1.38b</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>18</td>
<td>Zhujiang (Pearl)</td>
<td>280b</td>
<td>0.437</td>
<td>0.40f</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>19</td>
<td>Magdalena</td>
<td>237</td>
<td>0.235</td>
<td>0.47*</td>
<td>0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>Columbia</td>
<td>236</td>
<td>0.669</td>
<td>0.40f</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>21</td>
<td>Salween (Thanlwin)</td>
<td>211</td>
<td>0.325</td>
<td>0.23f</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>22</td>
<td>Yukon</td>
<td>208b</td>
<td>0.830b</td>
<td>1.47b</td>
<td>0.6</td>
<td>1.8</td>
</tr>
<tr>
<td>23</td>
<td>Danube</td>
<td>207</td>
<td>0.817</td>
<td>0.59f</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>24</td>
<td>Essequibo</td>
<td>178</td>
<td>0.164</td>
<td>0.89*</td>
<td>0.4</td>
<td>5.4</td>
</tr>
<tr>
<td>25</td>
<td>Niger</td>
<td>154</td>
<td>1.200</td>
<td>0.53b</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>26</td>
<td>Ogooue</td>
<td>150</td>
<td>0.205</td>
<td>1.25*</td>
<td>0.5</td>
<td>6.1</td>
</tr>
<tr>
<td>27</td>
<td>Uruguay</td>
<td>145</td>
<td>0.240</td>
<td>0.50f</td>
<td>0.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>
DOC yields (i.e., normalization of the carbon load to the watershed area) for the 30 major rivers ranges from 0.4 g C m⁻² year⁻¹ in the Niger to 8.6 g C m⁻² year⁻¹ in the Fly (Table 11.1; Figure 11.1b). At a total DOC flux to the ocean of 250 Tg DOC-C year⁻¹ (Hedges et al., 1997), the average DOC yield from the remaining rivers is 2.15 g C m⁻² year⁻¹, whereas the average DOC yield from the top 30 rivers is 2.3 g C m⁻² year⁻¹. Thus, the major rivers have on average slightly elevated yields in relation to the remaining rivers or, alternatively, the global DOC flux to the oceans is underestimated. If the average DOC yield from the top 30 rivers is applied to the remaining exorheic land surface area that they do not drain, the total DOC flux to the ocean is ~260 Tg DOC-C year⁻¹. A number of recent studies have highlighted DOC fluxes from major global rivers that are elevated in comparison to historic estimates, particularly the major Arctic rivers (Holmes et al., 2012; Raymond et al., 2007; Spencer et al., 2009a). For example, Holmes et al. (2012) note that recent estimates of pan-Arctic riverine flux to the ocean range from 34 to 38 Tg DOC-C year⁻¹, much higher than the value of 2.15 g C m⁻² year⁻¹ for the remaining rivers.

<table>
<thead>
<tr>
<th>River Rank by Discharge</th>
<th>River Name</th>
<th>Discharge (km³/yr)</th>
<th>Area (Mkm²)</th>
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<th>Global DOC Flux (%)</th>
<th>DOC Yield (g C/m²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>Fly</td>
<td>141</td>
<td>0.064</td>
<td>0.55*</td>
<td>0.2</td>
<td>8.6</td>
</tr>
<tr>
<td>29</td>
<td>Kolyma</td>
<td>136</td>
<td>0.650</td>
<td>0.82*</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>30</td>
<td>Pechora</td>
<td>131</td>
<td>0.324</td>
<td>1.66*</td>
<td>0.7</td>
<td>5.1</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td></td>
<td><strong>18553</strong></td>
<td><strong>41.6</strong></td>
<td><strong>90.2</strong></td>
<td><strong>36.1</strong></td>
<td>–</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>36000</strong></td>
<td><strong>116.0</strong></td>
<td><strong>250.0</strong></td>
<td><strong>100.0</strong></td>
<td>–</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.3</td>
</tr>
</tbody>
</table>

*Coynel et al., (2005)  
Holmes et al., (2012)  
Ni et al., (2008) estimates for the whole Pearl Delta  
Moreira-Turcq et al., (2003) estimate for Obidos see section 2.1, for discussion  
Lewis and Saunders (1989);  
Wang et al., (2012);  
Spencer et al., (2013);  
Degens et al., (1991);  
Bird et al., (2008);  
Nakatsuka et al., (2004);  
Cauwet (2002);  
Gordeev et al., (1996);  
Milliman and Farnsworth (2011);  
Vorosmarty et al., (2000) represents the exorheic land mass (87% of the total nonglacierized land mass);  

*Estimated DOC flux: Mekong mean value for DOC concentration data from across the annual hydrograph (2.38 mg/L; range = 1.75 to 3.19 mg/L; Spencer unpublished data) multiplied by annual river discharge data; Tocantins assumed an average DOC concentration of 3 mg/L multiplied by annual river discharge data as no DOC concentration data are currently available but it is described as a clear-water river similar to the Tapajos and Xingu Rivers (Goulding et al., 2003) that have DOC concentrations typically in the 3 to 5 mg/L range (Moreira-Turcq et al., 2003); Magdalena assumed an average DOC concentration of 2 mg/L multiplied by annual river discharge data as no DOC concentration data are currently available but it is an extremely sediment-rich river that typically exhibits low DOC concentrations and estimates for total dissolved solids that are approximately eight-fold higher than the estimated DOC flux (30 x 10⁶ t/yr; Restrepo et al., 2006); Essequibo assumed an average DOC concentration of 5 mg/L multiplied by annual river discharge data as no DOC concentration data are currently available but it is described as a black-water river (Hammond, 2005); Ogooue mean value for DOC concentration of 8.33 mg/L (Cadee et al., 1984) multiplied by annual river discharge data; Fly mean value for DOC concentration of 3.85 mg/L (Alin et al., 2008) multiplied by annual river discharge data.
FIGURE 11.1  DOC fluxes (a) and yields (b) for the top 30 global rivers ranked by discharge. Data from Table 1.
than previous estimates of 18-26 Tg DOC-C year\(^{-1}\). These improved estimates result from higher temporal resolution sampling of the major Arctic rivers (Lena, Yenisey, Ob', Mackenzie, Yukon, and Kolyma), including sampling over the spring freshet. Even these improved DOC flux estimates may be underestimated as the limited data that exist for other northern high-latitude rivers often show higher DOC yields (e.g., the Pechora River; Table 11.1; Gordeev et al., 1996; Lobbes et al., 2000).

Relative to DOC yields from the top 30 rivers, smaller tropical watersheds exhibit higher yields, such as the Fly (8.6 g C m\(^{-2}\) year\(^{-1}\)), Ogooue (6.1 g C m\(^{-2}\) year\(^{-1}\)), and the Essequibo (5.4 g C m\(^{-2}\) year\(^{-1}\); Table 11.1; Figure 11.1b). Major tropical rivers such as the Amazon, Congo, and Orinoco exhibit high yields for DOC (4.4, 3.4, and 4.5 g C m\(^{-2}\) year\(^{-1}\), respectively). The Pechora River displays a high yield (5.13 g C m\(^{-2}\) year\(^{-1}\); Table 11.1; Figure 11.1b), attributable to vast tracts of forest and swamp, including organic carbon-rich soils in the watershed (Gordeev et al., 1996; Tarnocai et al., 2009). Watersheds characterized by elevated DOC yields are important areas for future study in order to improve DOC flux estimates to the ocean.

### B Coastal Vegetation Inputs

The coastal ocean also receives substantial inputs of DOM from fringing wetlands and mangroves. The global areas of salt marshes, mangroves, and seagrasses are estimated at \(\sim 400,000, 200,000, \) and 400,000 km\(^2\), respectively (Jennerjahn and Ittekkot, 2002; McLeod et al., 2011). Although relatively small areas, these systems export a large amount of DOM per unit area due to consistently flooded root systems and direct contact between plants, their detritus, and water. Direct export of DOM from these systems is \(\sim 10-100 \text{ g C m}^{-2} \text{ year}^{-1}\) (Adame and Lovelock, 2011; Barron and Duarte, 2009; Childers et al., 2000; Dame et al., 1991; Dittmar et al., 2006; Gonneea et al., 2004; Happ et al., 1977; Ziegler and Benner, 1999). Using a surface area of 1,000,000 km\(^2\), a global flux of 10-100 Tg DOC-C year\(^{-1}\) is 4-40% of global riverine input. However, a large portion of exported detrital material is transformed to DOM in coastal waters (Dittmar et al., 2006). Remembering that the productivities of these systems are among the highest in the world (Jennerjahn and Ittekkot, 2002), this indirect DOC production in coastal waters could be important. For mangrove forests, the export of litter is \(\sim 100-300 \text{ g C m}^{-2} \text{ year}^{-1}\) (Gong and Ong, 1990; Twilley et al., 1997; Woodroffe et al., 1988), with \(\sim 50\%\) of this exported detritus converted to DOC in coastal waters (Adame and Lovelock, 2011; Dittmar et al., 2006). Data on litter export from other coastal vegetated ecosystems are sparse, but assuming the range for mangroves (50-150 g indirect DOC production m\(^{-2}\) year\(^{-1}\)) holds for these other sites suggests an additional flux of 50-150 Tg DOC-C year\(^{-1}\). Combining the direct and indirect input of DOC from these ecosystems results in a flux that is 24-100% of riverine input. Material exported from salt marshes and mangroves may be particularly important to CDOM input to coastal waters (Clark et al., 2008).

### III RIVERINE DOM COMPOSITION

DOM composition in riverine systems strongly influences DOM’s role in the environment. For example, DOM is a freshwater quality constituent of concern, impacting the formation of carcinogenic and mutagenic disinfection by-products (Chow et al., 2007; Weishaar et al., 2003) as well as the transport and reactivity of toxic substances such as mercury (Aiken et al., 2011; Bergamaschi et al., 2011). Furthermore, riverine DOM composition influences bacterioplankton community structure and function (Crump et al., 2009), so composition data for rivers and streams is of interest to a diverse range of scientists and engineers. To characterize DOM in riverine ecosystems, researchers have focused on bulk properties such as C:N ratios, stable (\(\delta^{13}\)C, \(\delta^{15}\)N) and radiocarbon isotopes (\(\Delta^{14}\)C), optical properties (CDOM absorbance and fluorescence),
as well as biomarkers (e.g., amino acids, carbohydrates, black carbon, and lignin phenols). High-resolution analytical techniques, such as Fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) and advanced nuclear magnetic resonance (NMR) spectroscopy, are now also routinely used to investigate riverine DOM.

Riverine DOM was typically perceived as relatively stable from a geochemical standpoint, representing the degraded remains of vascular plant materials aged in soils (Hedges et al., 1994, 1997). A number of studies have shown however that DOC is predominantly modern and younger than POC and therefore derived from recent plant production (Butman et al., 2012; Mayorga et al., 2005; Raymond and Bauer, 2001b; Raymond et al., 2007; Spencer et al., 2012). Furthermore, the importance of phase history has been highlighted by a number of studies when utilizing biomarkers to assess DOM reactivity (Aufdenkampe et al., 2001; Hernes et al., 2007). For example, the vascular plant biomarker lignin has been used extensively in studies of riverine DOM, and studies have established that degradation of plant tissues leads to increased proportions of oxidized (i.e., acidic) lignin phenols (Opsahl and Benner, 1998), making acid:aldehyde ratios of lignin phenols relative indicators of diagenetic state. In the Amazon River Basin, elevated acid:aldehyde ratios in riverine DOM relative to the ratios in POM has been cited as evidence that DOM is more highly biologically degraded than POM (Hedges et al., 1997). However, Hernes et al. (2007) showed that elevated acid:aldehyde ratios can be produced in DOM through the abiotic processes of dissolution and sorption. Similarly, Aufdenkampe et al. (2001) demonstrated the same process with amino acids, finding that young DOM gains a degraded signature from dissolution and sorption. The apparent degraded biochemical signature of riverine DOM, along with modern radiocarbon ages of DOC, has been reported in systems from the Arctic to the equator (Raymond et al., 2007; Spencer et al., 2008, 2012). As such, physical processes need to be accounted for when interpreting biomarkers in riverine DOM; these findings reconcile earlier reports that apparently stable riverine DOM had little presence in the ocean (Hedges et al., 1997).

A 14C-Age of River DOM

The age of riverine DOM provides information on its sources as well as residence times in the Earth’s carbon cycle. Riverine organic matter pools are made up of complex mixtures of compounds of varying ages. In some instances, age is linked to its reactivity, with young pools being comprised of OM of high nutritional content that is removed quickly, while older pools are highly oxidized and resistant to further degradation (Loh et al., 2008). There are mechanisms such as soil freezing (Goulden et al., 1998), high water levels in wetlands (Laiho, 2006; Oechel et al., 1993), and mineral layer physical protection of OM bound to soils (Keil et al., 1994; Mayer, 1994) that can remove biolabile pools from active cycling. However, these stored pools can be released through disturbance or natural changes in physical conditions, altering the bulk age of the riverine OM (Evans et al., 2007). Finally, there are petrochemical, “14C-dead” sources of DOM that can have a large impact on the river’s DOC ages (Griffith et al., 2009), potentially fueling riverine metabolic processes (Griffith and Raymond, 2011).

There are a growing number of 14C measurements for river DOC. One of the first studies reported ages varying from 1384 years B.P. to modern, with most samples being enriched in bomb carbon (Raymond and Bauer, 2001b). This general trend, a range of riverine DOC ages with a predominance of young ages, has held in subsequent compilations and surveys (Butman et al., 2012; Mayorga et al., 2005; Raymond et al., 2004; Sickman et al., 2010), underscoring the complex nature and multiple sources of river DOM.

These studies provide clues as to the major controls on DOC age. Relatively undisturbed small watersheds demonstrate the propensity for DOM to be young (Longworth et al., 2007). Even in watersheds underlain by shale (Longworth et al.,
and peat (Evans et al., 2007), where one might expect to encounter older DOC, \(^{14}\)C-enrichment dominates. Although there are reports of older DOC with baseflow (Neff et al., 2006; Raymond et al., 2007; Schiff et al., 1997), low-flow periods are inherently less important with respect to fluxes and, therefore, to the average age of DOC exported to the ocean. The dominance of young age is consistent with DOM exported from wetlands and terrestrial systems originating in upper soil profiles (Mayorga et al., 2005). The exception to young DOC can be found in rivers that are rapidly eroding old soil profiles (Masiello and Druffel, 2001) or systems with thawed permafrost or glacier inputs (Hood et al., 2009; Vonk et al., 2013).

Land use and disturbance results in export of aged components. Agricultural watersheds have been shown to export aged DOC (Longworth et al., 2007; Sickman et al., 2010), presumably due to soil disruption and the use of petroleum-based agrochemicals. Disturbance of peatlands also releases older DOC (Moore et al., 2013). The legacy of land use on DOM export can remain for decades (Dittmar et al., 2012a).

Petroleum byproducts make important contributions to riverine DOM. As mentioned, agricultural systems have demonstrated old DOC likely due to agrochemicals (Sickman et al., 2010). One of the first \(^{14}\)C-DOC studies in rivers demonstrated the input of petroleum DOM to rivers from cities (Spiker and Rubin, 1975). Twenty-five percent of DOM in wastewater treatment plants appears to be from petroleum-based household products (Griffith et al., 2009). Glacial streams in both Alaska (Hood et al., 2009) and Europe (Singer et al., 2012) hold old DOC, a fraction of which may be from anthropogenic aerosols (Stubbins et al., 2012) that are bioavailable (Hood et al., 2009; Singer et al., 2012). The potential for human activities to add aged DOC to rivers has been demonstrated in a recent survey of large U.S. rivers (Butman et al., 2012). It appears that the majority of DOM exported to the global ocean from natural ecosystems is young, while human activities inject ancient DOC into riverine systems and the ocean.

**B Microbiologically Reactive Fraction**

Rivers and streams are major sources of \(\text{CO}_2\) to the atmosphere (Aufdenkampe et al., 2011; Butman and Raymond, 2011; Cole et al., 2007; Striegl et al., 2012). The degree to which riverine DOM fuels this efflux is debatable but recent work suggests that biolabile terrestrial DOM is an important source. Firstly, riverine DOM has been shown to be more biolabile in Arctic Rivers in conjunction with an elevated lignin carbon-normalized yield \((\Lambda_s)\) and a modern radiocarbon age (Holmes et al., 2008; Raymond and Oh, 2007; Spencer et al., 2008). Secondly, lignin phenols and a host of other phenolic compounds, largely derived from terrestrial macromolecules, are quickly mineralized in Amazon River water (Ward et al., 2013). The breakdown of these terrestrially derived macromolecules appears to be the primary driver for river-to-air \(\text{CO}_2\) fluxes in the Amazon (Mayorga et al., 2005; Ward et al., 2013). Finally, the emerging view of the utility of biomarkers such as lignin with respect to the information these biomarkers provide is supported from recent studies from the soil organic matter community that highlight environmental factors can mediate molecular structure effects with respect to the long-term persistence of organic matter (Kleber and Johnson, 2010; Schmidt et al., 2011). The inherent ability of specific molecular structures to resist microbial degradation may constrain the use of some historically utilized indicators of chemical stability.

The radiocarbon age of DOC is also a poor predictor of riverine DOM biolability. The most striking example comes from DOC mobilized from Siberian Yedoma permafrost (DOC > 21,000\(^{14}\)C year), which was highly biolabile (34±0.8% decomposed during 14 day incubations under dark, oxygenated conditions at ambient river temperatures) (Vonk et al., 2013). In a similar vein, glacial DOM is both aged and biologically labile (Hood et al., 2009; Singer et al., 2012). Anthropogenic aerosols have been suggested as the source of this aged organic matter, given low levels of
vascular plant-derived compounds and the presence of combustion products commonly found in anthropogenic aerosols (Stubbins et al., 2012). These combustion products were enriched in condensed aromatics, aliphatic compounds, and particularly fatty acids with chain lengths 30+ carbons, which is compatible with a watersoluble organic carbon aerosol source originating from the incomplete combustion of fossil fuels (Stubbins et al., 2012).

These examples do not mean that biochemical composition is not important to DOM biolability but that the influence of composition depends on environmental controls (Schmidt et al., 2011). A number of studies have linked DOM composition and shifts in radiocarbon age to its biolability (Butman et al., 2007; Holmes et al., 2008; Raymond et al., 2007). For example, biodegradation has been shown to preferentially remove specific components of the DOM pool such as amino acids and carbohydrates (Benner and Kaiser, 2011; Volk et al., 1997; Weiss and Simon, 1999). Lignin, for example, is more resistant to biodegradation than other components in plant material such as carbohydrates (Benner et al., 1987). Elevated protein-like fluorescence in DOM, determined in optical assessments, has been linked to elevated biolability (Balcarczyk et al., 2009; Fallman et al., 2009b; Hood et al., 2009; Wickland et al., 2012). Finally, the conventional wisdom suggesting that younger, relatively unaltered DOM should be more easily metabolized by microbial communities has been demonstrated in the Amazon and Arctic rivers (Holmes et al., 2008; Mayorga et al., 2005; Raymond et al., 2007).

DOM composition impacts its biolability but other environmental factors are also at play. For example, the assimilation capability of the ambient microbial community must be taken into account; physicochemical gradients and the potential of priming effects will all impact DOM biolability (Bianchi, 2011). Linking land to ocean, rivers and their receiving estuaries, and coastal waters provide numerous environmental hot spots for DOM biodegradation (e.g., soil porewaters, hyporheic zones, the confluence of rivers with contrasting chemistries, the freshwater-seawater interface, and coastal zones) (McClain et al., 2003; Morris et al., 1978).

### C Photochemically Labile Fraction

Although photochemical mineralization of DOM in rivers and estuaries is typically minimal (Stubbins et al., 2011; White et al., 2010), the material is highly susceptible upon dilution with ocean waters in plumes and coastal waters (Moran et al., 2000; Vodacek and Blough, 1997). Photochemical degradation preferentially removes components commonly utilized to track riverine inputs in the ocean, such as CDOM and lignin phenols, and also enriches DOM δ13C (Benner and Kaiser, 2011; Hernes and Benner, 2003; Opsahl and Benner, 1998; Opsahl and Zepp, 2001; Spencer et al., 2009b).

A typical response of photochemical degradation is observed in a 57-day irradiation experiment of Congo River water (Spencer et al., 2009b; Stubbins et al., 2010; Figure 11.2). Photochemical loss of DOC was slower than of CDOM by photobleaching (Figure 11.2a), consistent with previous studies (Moran et al., 2000; Vähätalo et al., 2010). Lignin phenol concentrations showed a >95% decrease, highlighting the susceptibility of dissolved lignin to photochemical degradation as with past studies (Hernes and Benner, 2003; Opsahl and Benner, 1998; Opsahl and Zepp, 2001). The preferential photodegradation of aromatic compounds such as lignin results in an order of magnitude drop in the DOC-specific absorption coefficient of CDOM at $\alpha_{325} (\alpha_{CDOM}^* [m^2 g^{-1}] = \alpha_{325} m^{-1}/DOC g m^{-3})$ from 1.90 m$^2$ g$^{-1}$ in the initial sample to 0.19 m$^2$ g$^{-1}$ following irradiation (Stubbins et al., 2010). This latter value is within the range reported previously for Atlantic waters (<0.1 to 0.3 m$^2$ g$^{-1}$; Nelson et al., 2007). Similarly, the increase in lignin acid:aldehyde ratios by the end of the irradiation was comparable to previously reported values for marine samples (Hernes and Benner, 2003; 2006; Spencer et al., 2009b). FT-ICR-MS
reveals three fractions based on photoreactivity: (1) photo-resistant, (2) photo-labile, and (3) photo-produced (Figure 11.2b and c; Stubbins et al., 2010). The photo-resistant fraction was heterogeneous, with most molecular classes represented although no condensed aromatics persisted and only a small number of aromatics were present. Overall, irradiation caused a significant drop in the number of molecules identified, a decrease in their structural diversity, and a 90% loss in aromatic compounds. (Stubbins et al., 2010).
As photochemical degradation preferentially removes lignin (Hernes and Benner, 2003; Opsahl and Benner, 1998; Spencer et al., 2009b) and other classes typically defined as stable, such as black carbon, the process likely represents a major sink for these compounds (Stubbins et al., 2010; 2012). Black carbon molecules are particularly resistant to biodegradation (Kim et al., 2006), comprising ~10% of the global riverine flux of DOC to the oceans (Jaffe et al., 2013). Thus photochemistry is exceptionally important in its preferential removal of common tracers of terrestrial DOM. The preferential elimination of the terrestrial signature of riverine DOM via photochemistry is clearly exhibited via FT-ICR-MS, shifting the molecular signature of riverine DOM toward that of marine DOM, thus complicating the tracking of terrestrial DOM in the ocean (Gonsior et al., 2009; Kujawinski et al., 2002; Stubbins et al., 2010).

IV ANTHROPOGENIC INFLUENCES

A Fluxes

Across and within watersheds, DOM fluxes scale with discharge (Meybeck, 1993; Raymond and Oh, 2007). Thus, it is generally accepted that increasing water discharge, due to climate change or land management, will result in higher fluxes. Globally, precipitation is predicted to increase, particularly in wet regions. Many studies are also now demonstrating that the increase in DOC concentration with large discharge events (Schiff et al., 1998) is a common feature in watersheds (Raymond and Saiers, 2010). This is true even for the largest events. Tropical storm Irene in New England, a 500-year storm event, caused stream DOM concentrations to increase such that export of 40% of average annual DOC export occurred in just a few days (Figure 11.3; Yoon and Raymond, 2012). These large events are obviously important to coastal carbon budgets (Bianchi et al., 2013). Thus, it is not only the amount of precipitation, but also the number and size of precipitation events that are important to DOC transfers from land to ocean. The projected increase in the proportion of high rainfall events will likely strengthen the land-ocean DOC connection.

Temperature is also important to DOC fluxes (Figure 11.4). DOC production normalized to discharge is generally higher in warmer months (Wilson et al., 2013a), presumably partly due to temperature controls on dissolution. Many other ecosystem processes important to DOC production, such as microbial degradation, are controlled by temperature, creating indirect links between temperature and DOC export. Increases in DOC production can be offset by temperature modulated increases in evapotranspiration and therefore decreases in discharge, although the interannual variation in evapotranspiration due to temperature is secondary to interannual variation in precipitation in regulating DOC fluxes (Raymond and Oh, 2007). A recent study has argued for an important role between temperature and DOC concentration for watersheds above 43.5°N latitude (Laudon et al., 2012).

Little is known about the influence of land use change on the mass of DOC export. It is well demonstrated that wetlands are hot spots for DOM export off the landscape. This is true for both inland (Junk et al., 2013; Kortelainen, 1993; Mulholland and Kuenzler, 1979; Raymond and Hopkinson, 2003) and coastal wetlands (Jiang et al., 2013; Raymond and Hopkinson, 2003; Tzortziou et al., 2011). Both classes of wetlands continue to be lost to other land uses globally (Dahl, 1990; Junk et al., 2013; McLeod et al., 2011; Waycott et al., 2009). For watersheds of the mid-Atlantic Bight, for instance, wetland cover age has reduced from ~12% to 6% over the past 200 years (Dahl, 1990), presumably resulting in a 20-30% reduction in DOC export to that system (Raymond et al., 2004). The impact of losses of inland marshes and coastal vegetated habitats on lateral transports of DOC is probably significant, but not currently known.

The thawing of permafrost will undoubtedly influence carbon fluxes, although its impact on
DOC fluxes is unclear. Authors have argued for an increase in DOC export from high-latitude watersheds based on both mechanistic (Freeman et al., 2001) and space for time substitution watershed studies (Frey and Smith, 2005). Conversely, the Yukon River demonstrated a decrease in discharge-normalized DOC export over time perhaps due to increases in flow path, residence time,
and terrestrial microbial utilization (Striegl et al., 2005). Tropical peatlands demonstrated a ~30% increase in the flux of DOC, much of it aged, with disturbance (Moore et al., 2013). Thus, ongoing monitoring is required in both Arctic and tropical regions to track the DOC yield responses of these globally significant carbon pools to climate change and anthropogenic impacts such as deforestation and land-use conversion. Numerous rivers in northeastern North America and northwestern Europe are demonstrating changes in DOC concentration (Evans et al., 2005; Findlay, 2005; Monteith et al., 2007). Causes have been suggested to include nitrogen deposition, altered hydrology, and reduced acid rain. Though unmeasured, fluxes have likely increased.

The retreat of glaciers impacts DOM fluxes. Relic glacial water contains low concentrations of DOM, but this material is a net addition to the oceans. Over the 2003-2009 period ~840 km³/year of relic water was added to the world’s oceans (Gardner, 2013). If this flow is considered a river, it is the fifth largest in the world (Table 11.1). Concentrations of DOC in glacial melt water are low (Hood et al., 2009) and therefore the direct contribution to DOC fluxes are low at ~1 TgDOC-C/year⁻¹. Land revegetated after glacier decline, however, exports many times more DOC than the ice-covered landscape (Hood and Scott, 2008); thus, glacial retreat may be resulting in a larger indirect input of DOC. DOM exported from glaciers is also compositionally unique and reactive so coastal regions that receive direct inputs may be impacted (Hood et al., 2009; Singer et al., 2012; Stubbins et al., 2012).

**B Composition**

Riverine DOM composition varies with hydrologic drivers in watersheds from the Arctic to the equator (Amon et al., 2012; Bouillon et al., 2012; Butman et al., 2012; Spencer et al., 2008). Typically at higher discharge, riverine DOM takes on a more terrestrial character due to a shift in sources (i.e., greater surface runoff and leaching of organic-rich soil horizons and surface litter layers), while at lower discharge the increased flow path, residence time, and therefore greater potential for microbial mineralization and physical protection shifts DOM composition to a less...
terrestrial nature (Boyer et al., 1997; McGlynn and McDonnell, 2003; Striegl et al., 2005). These shifts are particularly evident in Arctic rivers which change from very low discharge under-ice to peak spring freshet in a very short time period, leading to extensive leaching of surface organic-rich layers. This thaw and extensive leaching imparts a strong terrestrial signature on riverine DOM during the freshet (e.g., elevated SUVA\textsubscript{254} values, lignin carbon-normalized yields; Figure 11.5). Therefore, the spring flush is a period of high vascular plant-derived and aromatic DOM export in Arctic rivers. After the freshet, SUVA\textsubscript{254} and lignin carbon-normalized yields typically decline due to increased residence time of DOM in contact with subsurface microbial communities and soils; during the summer-autumn period rainfall can increase terrestrial character again alongside increasing discharge due to mobilization of DOM from surface organic-rich layers (Figure 11.5; Spencer et al., 2008, 2009a). With respect to DOM composition in rivers, hysteresis has been reported, with a more terrestrial signature imparted on the rising limb of the hydrograph (e.g., Bouillon et al., 2012; Hood et al., 2006).

Relative inputs from different land cover types are also readily apparent in stream and riverine DOM composition. For example, carbon-normalized vanillyl phenol yields (V) in the Amazon River (0.67 (mg (100 mg OC\textsuperscript{-1})) (Hedges et al., 2001) are elevated compared to the Mississippi (0.44 (mg (100 mg OC\textsuperscript{-1})) (Benner and Opsahl, 2001; Hernes and Benner, 2003) and Arctic rivers (0.13-0.15 (mg (100 mg OC\textsuperscript{-1})) (Lobbes et al., 2000; Spencer et al., 2008), reflecting greater vascular plant inputs derived from the tropical rainforest within the Amazon Basin. The relatively low V in Arctic Rivers is not likely a result of dilution by autochthonous production within these systems as that has been shown to be typically low (Meon and Amon, 2004). Low V in Arctic rivers largely reflects the large inputs from nonvascular sources within these watersheds, such as bryophytes that contain little if any lignin (Spencer et al., 2008). Similarly, the presence of wetlands impacts the terrestrial character of riverine DOM as rivers draining wetland-dominated systems typically contain DOM of greater terrestrial character (e.g., relatively high DOC-specific absorption; Fellman et al., 2009b; Tzortziou et al., 2008).

Riverine DOM composition is impacted by a host of anthropogenic land use and land management practices (Bernardes et al., 2004; Williams et al., 2010; Wilson and Xenopoulos, 2009; Yamashita et al., 2011). Agricultural watersheds export DOM with reduced structural complexity and increased microbial contributions (Wilson and Xenopoulos, 2009), as well as a shifted δ\textsuperscript{13}C signature (Bernardes et al., 2004). One of the most striking impacts of agriculture on DOM composition is the legacy effect of long ceased agricultural practices. Dissolved black carbon continues to be mobilized and exported from Brazil’s Paraiba do Sul watershed despite widespread forest burning having ceased in 1973 (Dittmar et al., 2012b). As major tropical watersheds such as the Amazon and Congo continue to face deforestation and agricultural expansion, much work needs to be undertaken to understand what this means for exported riverine DOM composition and the role this material plays in downstream receiving ecosystems.

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References


REFERENCES


11. RIVERINE DOM


