Amounts, isotopic character, and ages of organic and inorganic carbon exported from rivers to ocean margins: 2. Assessment of natural and anthropogenic controls

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Riverine exports of carbon (C) and organic matter (OM) are regulated by a variety of natural and anthropogenic factors. Understanding the relationships between these various factors and C and OM exports can help to constrain global C budgets and allow assessment of current and future anthropogenic impacts on both riverine and global C cycles. We quantified the effects of multiple natural and anthropogenic controls on riverine export fluxes and compositions of particulate organic C, dissolved organic C, and dissolved inorganic C for a regional group of eight rivers in the northeastern U.S. Potential controls related to hydrogeomorphology and regional climate, soil order, soil texture, bedrock lithology, land use, and anthropogenic factors were analyzed individually, collectively, and at scales of both local and regional influence. Factors related to hydrogeomorphology and climate, followed in importance by land use and anthropogenic factors, exhibited the strongest impacts on riverine C exports and compositions, particularly at smaller localized scales. The effects of hydrogeomorphology and climate were primarily related to volumetric flow, which resulted in greater exports of terrestrial and total C. Principal anthropogenic factors included impacts of wastewater treatment plants (WWTPs) and river impoundments. The presence of WWTPs as well as anthropogenic use of carbonate-based materials (e.g., limestone) may have substantially increased riverine C exports, particularly fossil C exports, in the study region. The presence of nuclear power plants in the associated watersheds is also discussed because of the potential for anthropogenic 14C inputs and subsequent biasing of aquatic C studies utilizing natural abundance 14C.


1. Introduction

Present-day riverine export of carbon (C) and organic matter (OM) has been linked to diverse natural and anthropogenic factors [see, e.g., Moosdorf et al., 2011; Alvarez-Cobelas et al., 2012; Lauerwald et al., 2012]. Discharge and runoff, for example, appear to be among the dominant controls of riverine C and OM fluxes, with exports of particulate organic C, dissolved organic C, and dissolved inorganic C (POC, DOC, and DIC, respectively) increasing under conditions of greater hydrologic flow [e.g., Meybeck, 1982; Bluth and Kump, 1994; Ludwig et al., 1996; Moosdorf et al., 2011; Alvarez-Cobelas et al., 2012; Lauerwald et al., 2012]. Other identified natural controls on riverine C and OM exports fall under the general categories of watershed geomorphology, lithology, and pedology. Riverine exports of POC tend to increase with watershed relief and slope because of greater mechanical erosion [Ludwig et al., 1996; Blair et al., 2003], whereas exports of DOC tend to increase in watersheds of relatively flat terrains, because of longer water residence times along OM-rich surface and shallow subsurface flowpaths [Clair et al., 1994; Ludwig et al., 1996; Mulholland, 1997; Frost et al., 2006; Wilson and Xenopoulos, 2008; Lauerwald et al., 2012]. In contrast, riverine DIC exports appear to be relatively unaffected by watershed geomorphology [Clair et al., 1994; Moosdorf et al., 2011]. The underlying lithology of watersheds may also have a significant impact on the amounts and sources of C and OM exported by rivers. Exports of DIC, for example, are typically greater in regions with carbonate-rich rock types
(e.g., limestones, dolomites) [Meybeck, 1993; Bluth and Kump, 1994; Clair et al., 1994; Pawellek and Veizer, 1994; Baker et al., 2008; Moosdorf et al., 2011]. Additionally, lithologies rich in either inorganic C (IC) or organic C (OC; e.g., shales and other sedimentary rocks) have been implicated in greater proportional contributions from fossil DIC and fossil POC, respectively [Pawellek and Veizer, 1994; Raymond et al., 2004; Leithold et al., 2006; Longworth et al., 2007; Zhang et al., 2009].

Pedologically, watersheds with greater abundance of OC-rich soils tend to export more DOC [Ludwig et al., 1996; Hope et al., 1997a; Aitkenhead et al., 1999; Lauerwald et al., 2012]. Catchments dominated by soil orders such as Spodosols (also known as Podsolos) and particularly Histosols have also demonstrated higher DOC export [Alvarez-Cobelas et al., 2012], presumably reflecting the higher soil OC (SOC) contents in these soil orders [Kern, 1994; Tarnocai, 2000]. In contrast, DOC export is reduced in watersheds having more clay-rich soils and hence higher adsorption capacities for DOC [Nelson et al., 1993; Lauerwald et al., 2012].

Riverine C and OM exports are also increasingly under anthropogenic control [e.g., Meybeck and Vorosmarty, 1999; Meybeck, 2003]. Alteration of the associated landscape through cultivation, urbanization, and other modified land uses has been shown to generally increase riverine exports of POC [Kao and Liu, 1996; Hope et al., 1997b] and DIC [Clair et al., 1994; Oh and Raymond, 2006; Baker et al., 2008; Raymond et al., 2008; Barnes and Raymond, 2009; Zeng and Masiello, 2010; Moosdorf et al., 2011] but decrease exports of DOC [Cronan et al., 1999; Alvarez-Cobelas et al., 2012; Lauerwald et al., 2012; but see also Wilson and Xenopoulos, 2008; Sickman et al., 2010]. Observed increases in riverine exports of both total and aged POC are primarily linked to accelerated soil erosion with cultivation [Kao and Liu, 1996; Hope et al., 1997b; Raymond et al., 2004; Longworth et al., 2007], as presumably deeper and physically protected aged SOC becomes exposed to erosional forces with tillage [e.g., Ewing et al., 2006]. In contrast, cultivation has been observed to frequently result in a net decrease in riverine DOC export [Cronan et al., 1999; Alvarez-Cobelas et al., 2012; Lauerwald et al., 2012], which may be due to both a depletion of total SOC and a reduction in litter biomass following cultivation [e.g., Post and Mann, 1990; Amundson, 2001; Guo and Gifford, 2002]. Exports of total and aged DIC have been associated with human use of carbonate-based materials in both construction [Baker et al., 2008; Barnes and Raymond, 2009; Zeng and Masiello, 2010; Moosdorf et al., 2011; Zeng et al., 2011] and agricultural [Clair et al., 1994; Oh and Raymond, 2006] activities.

Other anthropogenic impacts on riverine C and OM exports include wastewater treatment and river impoundment. Wastewater effluent can contribute to riverine OC and IC loads either indirectly, by stimulating autochthonous (i.e., internal) production of riverine OC through nutrient inputs [e.g., Gücker et al., 2006; Carey and Migliaccio, 2009; Zeng et al., 2011], or directly through input of wastewater OC [Gücker et al., 2006; Sickman et al., 2007; Barnes and Raymond, 2009; Griffith et al., 2009; Zeng et al., 2011]. The impact of impoundment on riverine POC exports has been found to be more variable because of the opposing effects of particle settling [Soltero et al., 1973; Webster et al., 1979; Stanford and Ward, 1983; Grobbelaar and Toerien, 1985; Vosshall and Parker, 1985; Perry and Perry, 1991] and enhanced autochthonous production [Spence and Hynes, 1971; Grobbelaar and Toerien, 1985; Vosshall and Parker, 1985; Kendall et al., 2001; Sullivan et al., 2001]. DOC also has been observed to both increase, presumably through mineralization of enhanced autochthonous production within impoundments [Stanford and Ward, 1983; Perry and Perry, 1991], or show no net change [Soltero et al., 1973]. Impoundment effects on riverine DIC loads range from enhanced degassing and calcite precipitation, to increased autochthonous production and subsequent remineralization [Whalen et al., 1982; Grobbelaar and Toerien, 1985; Wachniew, 2006; Wang et al., 2011].

Both natural and anthropogenic factors are also expected to impact the composition of exported riverine C and OM by altering the relative source contributions. Proportions of allochthonous (i.e., terrestrial) versus autochthonous (i.e., aquatic) C in rivers, for example, have been shown to vary in response to discharge [Webster and Meyer, 1997] and anthropogenic activities such as agriculture, wastewater treatment, and road construction [Oh and Raymond, 2006; Barnes and Raymond, 2009; Zeng et al., 2011]. Other studies have determined that the aged (i.e., derived from fossil C or old SOC) versus modern fractions in river C may be controlled by factors such as lithology [Pawellek and Veizer, 1994; Raymond et al., 2004; Leithold et al., 2006; Longworth et al., 2007; Zhang et al., 2009] and human use of fossil OC and IC materials [Spiker and Rubin, 1975; Barnes and Raymond, 2009; Sickman et al., 2010; Zeng and Masiello, 2010; Zeng et al., 2011].

Despite significant advances in our understanding of the natural and anthropogenic factors affecting C and OM inputs to rivers, there still remains considerable uncertainty in the relative importance of these controls on riverine C and OM composition and exports from land to the coastal ocean. Addressing this uncertainty requires studies that evaluate the effects of multiple controls simultaneously. To date, only a small number of studies have attempted such a comprehensive approach [e.g., Ludwig et al., 1996; Moosdorf et al., 2011; Alvarez-Cobelas et al., 2012; Lauerwald et al., 2012]. In this second paper of a two-part series, we analyze the natural and anthropogenic factors influencing riverine OC and IC exports, including the proportions of allochthonous and aged OC and IC, for a regional group of eight northeastern U.S. rivers discharging to a common ocean margin, the Middle Atlantic Bight [see also Hossler and Bauer, 2013]. Potential controlling factors were grouped into six general categories (i.e., hydrogeomorphology and regional climate, soil order, soil texture, bedrock lithology, land use, and additional anthropogenic factors) and assessed at both a localized scale (i.e., hydrologic subbasin) and a broader, regional scale (i.e., hydrologic subregion). The primary goal of this study was to establish which classes of controls, as well as specific factors, dominated regional riverine OC and IC exports, and whether the effects of these controls were localized or integrated over broader regions.
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Table 1. Hydrogeomorphic and Climatic Characteristics of the Rivers Sampled in This Study and Their Associated Watersheds*

<table>
<thead>
<tr>
<th>River</th>
<th>Area (km²)</th>
<th>Length (km)</th>
<th>Slope b</th>
<th>Relief c</th>
<th>Discharge d</th>
<th>Velocity b</th>
<th>Runoff b</th>
<th>Precip d</th>
<th>Temp d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subbasin</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Connecticut</td>
<td>28,164</td>
<td>18,935</td>
<td>29.9</td>
<td>1429</td>
<td>591</td>
<td>0.31</td>
<td>66.1</td>
<td>113.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Hudson</td>
<td>31,457</td>
<td>19,019</td>
<td>20.6</td>
<td>1226</td>
<td>583</td>
<td>0.31</td>
<td>58.5</td>
<td>111.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Delaware</td>
<td>17,333</td>
<td>10,658</td>
<td>19.4</td>
<td>1013</td>
<td>436</td>
<td>0.31</td>
<td>79.3</td>
<td>114.0</td>
<td>8.2</td>
</tr>
<tr>
<td>Schuylkill</td>
<td>4,860</td>
<td>3,091</td>
<td>13.1</td>
<td>542</td>
<td>105</td>
<td>0.29</td>
<td>68.1</td>
<td>116.0</td>
<td>10.3</td>
</tr>
<tr>
<td>Susquehanna</td>
<td>70,632</td>
<td>50,501</td>
<td>11.9</td>
<td>472</td>
<td>84</td>
<td>0.29</td>
<td>44.8</td>
<td>104.7</td>
<td>11.2</td>
</tr>
<tr>
<td>Potomac</td>
<td>2,893</td>
<td>1,182</td>
<td>14.1</td>
<td>478</td>
<td>33</td>
<td>0.28</td>
<td>35.8</td>
<td>102.7</td>
<td>12.3</td>
</tr>
<tr>
<td>Pamunkey</td>
<td>3,015</td>
<td>1,203</td>
<td>8.8</td>
<td>317</td>
<td>28</td>
<td>0.25</td>
<td>29.0</td>
<td>108.2</td>
<td>13.3</td>
</tr>
<tr>
<td>Roanoke</td>
<td>1,318</td>
<td>1,194</td>
<td>1.3</td>
<td>87</td>
<td>12</td>
<td>0.25</td>
<td>29.8</td>
<td>115.8</td>
<td>15.0</td>
</tr>
</tbody>
</table>

| Subregion |            |             |         |          |             |            |          |          |        |
| Connecticut | 28,164     | 18,935      | 23.1    | 1429     | 591         | 0.31       | 66.1     | 113.5    | 6.4    |
| Hudson   | 31,457     | 19,019      | 14.4    | 1226     | 583         | 0.31       | 58.5     | 111.3    | 7.1    |
| Delaware | 17,333     | 10,658      | 12.5    | 1013     | 436         | 0.31       | 79.3     | 114.0    | 8.2    |
| Schuylkill | 4,860      | 3,091       | 12.0    | 542      | 105         | 0.29       | 68.1     | 116.0    | 10.3   |
| Susquehanna | 70,632    | 50,501      | 9.8     | 472      | 84          | 0.29       | 44.8     | 104.7    | 11.2   |
| Potomac  | 2,893      | 1,182       | 10.2    | 478      | 33          | 0.28       | 35.8     | 102.7    | 12.3   |
| Pamunkey | 3,015      | 1,203       | 6.4     | 317      | 28          | 0.25       | 29.0     | 108.2    | 13.3   |
| Roanoke  | 1,318      | 1,194       | 4.5     | 87       | 12          | 0.25       | 29.8     | 115.8    | 15.0   |

*Watershed drainage area, stream length, slope, relief, mean annual discharge, velocity, runoff, precipitation, and temperature are representative of each hydrologic subbasin (i.e., localized area drained by the river upstream of the sample locale, the eight-digit hydrologic unit code) and subregion (i.e., the entire area drained by the river upstream of the sample locale, usually the four-digit hydrologic unit code; see Table S1). See also section S3 for further description of the data.

2. Materials and Methods

2.1. Study Area

[9] The eight river systems investigated in the present study included the Connecticut, Hudson, Delaware, Schuylkill (a tributary of the Delaware), Susquehanna, Potomac, Pamunkey, and Roanoke (see Figure S1 and Table S1 in section S1 of the auxiliary material). The rivers covered a range of hydrogeomorphologies, soil types, underlying mineralogies, land uses, and other anthropogenic features (Tables 1–3 and sections S1 and S2; see also section S3 for a description of drainage area characterization methodologies).

2.2. Sample Collection and Processing

[10] Details of sample collection and processing can be found in Hossler and Bauer [2012]. Briefly, each river was sampled at approximately 3–4 month intervals between 2005 and 2007 at the point farthest downstream that was both accessible by small boat and above the reach of tidal influence. Surface water samples (~0.1 m depth) were collected near the midpoint of each river and filtered through prebaked Whatman quartz fiber filters (QFF; 0.8 μm nominal pore size). Note that one caveat to our sampling strategy is that by collecting surface water samples (although common practice) as opposed to width- or depth-integrated samples, we have likely underestimated the C pools, particularly the POC fraction [Curtis et al., 1979; Martin et al., 1992; Raymond et al., 2007]. Another potential source of sampling bias is the small number of sampling events per river (i.e., 7); however, we did capture a representative range of hydrologic conditions [Hossler and Bauer, 2013, Figure S3], including several high discharge events which are estimated to contribute to the majority of riverine C export [see, e.g., Raymond and Saiers, 2010]. In a trade-off with finer-scale sampling within a single river, this study focused on sampling a spectrum of rivers within a single region.

[11] The POC was considered to be that fraction collected directly on the QFF filters while the DOC was considered the filtrate. Samples for DIC were collected directly from the rivers using gas-tight syringes, then injected immediately into gas-tight glass serum bottles that were presparged with ultrahigh-purity N₂ gas and fixed with saturated HgCl₂ (0.2% v/v).

[12] Following acidification to remove inorganic carbonates, POC and DOC samples were oxidized to CO₂ (by sealed tube combustion and high-energy UV irradiation, respectively), then purified and quantified on a vacuum extraction line [Sofer, 1980; Bauer et al., 1992; Druffel et al., 1992; see also Hossler and Bauer, 2012]. DOC concentrations were also analyzed independently by high-temperature catalytic oxidation. DIC samples were acidified to pH 2 with phosphoric acid and sparged to extract the CO₂ gas which was then purified and quantified on a vacuum extraction line [Sofer, 1980; Druffel et al., 1992; see also Hossler and Bauer, 2012]. Aliquots of CO₂ were collected in sealed Pyrex tubes and analyzed for 13C and Δ14C at the National Science Foundation-Arizona Accelerator Mass Spectrometry (AMS) Facility.

2.3. Total, Allochthonous, and Aged C

[13] Total (i.e., allochthonous and autochthonous, aged and modern) riverine POC, DOC, and DIC export fluxes
were calculated for each watershed as the multiple of the sample concentration and mean daily discharge (discharges obtained from the U.S. Geological Survey water data [http://waterdata.usgs.gov/nwis]; see also section S3) for each sample collection date. The total C export fluxes were then normalized by upstream watershed area (i.e., converted to areal yields) for size-independent statistical analyses. For the allochthonous and aged C contributions to POC, DOC, and DIC exports, we first estimated fractional contributions from six potential sources for POC and DOC (i.e., modern C₃ plant material (C₃ OC), modern C₄ plant material (C₄ OC), slow-turnover soil OC (slow SOC; turnover time 5000 years), passive-turnover soil OC (passive SOC; turnover time 25 years), and fossil OC; turn-over time 60 years) and four potential sources for DIC (i.e., modern atmospheric CO₂ exchange, carbonate dissolution, POC remineralization, and DOC remineralization) using a time-varying isotope mixing model (see Hossler and Bauer [2012] for details). Using these estimated source contributions, we then estimated the allochthonous proportions of (a) the POC and DOC pools to be the C₃ OC, C₄ OC, slow SOC, passive SOC, and fossil OC contributions; and (b) the DIC pools to be the dissolved carbonates, remineralized allochthonous POC, and remineralized allochthonous DOC contributions. We considered aged C to be anything older than ~60 years (note that following convention in radiocarbon dating, we define AD 1950 to be the year delineating aged and modern [Stuiver and Polach, 1977]), which included passive SOC and fossil OC for POC and DOC and dissolved carbonates and aged fractions of remineralized POC and DOC for DIC [see also Hossler and Bauer, 2013].

2.4. Statistical Analysis

[14] We were first interested in comparing the relative importance of six overarching classes of controlling factors, at scales of both hydrologic subbasin and hydrologic subregion (i.e., local and regional, respectively; see Tables S1 and 1–3), on (1) POC, DOC, and DIC exports; (2) contributions from allochthonous C to POC, DOC, and DIC exports; and (3) contributions from aged C to POC, DOC, and DIC exports (Table S2). To accomplish these comparisons, we used Procrustes analysis—a multivariate statistical method to compare the similarity between two or more data sets (e.g., riverine C exports with bedrock lithology) [Gower, 1971; Peres-Neto and Jackson, 2001]. Although commonly used in morphometric analyses [see, e.g., Bookstein, 1996], Procrustes analysis has only recently been proposed as a potentially powerful analytical tool to explore relationships among multiple sets of variables within ecology and biogeoscience studies [Peres-Neto and Jackson, 2001]. The premise of Procrustes analysis is that a set of samples can be represented by a configuration in each multivariable space (e.g., a “C exports” configuration and “bedrock lithology” configuration). One configuration (e.g., bedrock lithology) is then rigidly translated, rotated, and scaled (i.e., superimposed) to best align with the reference configuration (e.g., C exports). The degree of concordance between the two configurations can then be quantified by a correlation-like
The Procrustes statistic \( r \) impacts such as agriculture or urbanization) (Tables 1–3).

Anthropogenic factors other than land use (e.g., wastewater treatment plants, impoundments; i.e., bedrock lithology, (5) land use, and (6) additional anthropogenic factors (e.g., wastewater treatment plants, impoundments) affect volumetric flow), (2) soil order, (3) soil texture, (4) regional climate (i.e., hydrologic parameters describing volumetric flow and basic environmental parameters likely to affect volumetric flow), (2) soil order, (3) soil texture, (4) bedrock lithology, (5) land use, and (6) additional anthropogenic factors (e.g., wastewater treatment plants, impoundments; i.e., anthropogenic factors other than land use impacts such as agriculture or urbanization) (Tables 1–3).

Procrustes analysis requires that the data sets be of the same dimensions. To achieve this end, it is common to first ordinate each data set by principal component analysis (PCA), which effectively reduces larger multivariable data sets into lower dimensional data sets with preservation of the main patterns of variation [Hotelling, 1933; Peres-Neto and Jackson, 2001]. Before performing the PCA ordinations, data sets were first merged one-to-many to preserve any-to-many controlling factors aligned with the measures of C export and composition. We also used Pearson correlation between specific variables (e.g., total DOC export with subregional soil order, subbasinal soil order). Variables were transformed as necessary for normal distribution, then centered and scaled to unit variance. The first two principal components from each PCA ordination were then compared by Procrustes analysis.

We were also interested in determining important specific parameter relationships and achieved this by evaluating the Procrustean superimpositions to see which individual controlling factors aligned with the measures of C export and composition. We also used Pearson correlation between specific variables (e.g., total DOC export with subregional discharge). The Pearson correlation statistic is also denoted by the symbol \( r \) and can range from –1 to 1. Significance was determined by resampling with replacement \( (n = 1000) \).

To control for cumulative error rates across the multiple tests of significance evaluated for the Procrustean and Pearson correlations, we used the false discovery rate (FDR) methodology of Benjamini and Hochberg [1995]. This methodology compares the significance of each correlation to a critical value based on the a priori significance level (e.g., \( \alpha = 0.05 \)) and the total number and rank of the hypotheses being tested. We evaluated each correlation coefficient at the significance levels of \( \alpha = 0.05 \) and \( \alpha = 0.01 \).

### Table 3. Land Use and Additional Anthropogenic Features in the Watersheds of the Present Study

<table>
<thead>
<tr>
<th>River</th>
<th>Percent Land Use*</th>
<th>Power Plants*</th>
<th>Impoundments*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AGR</td>
<td>URB</td>
<td>FOR</td>
</tr>
<tr>
<td>Subbasin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Connecticut</td>
<td>10</td>
<td>30</td>
<td>47</td>
</tr>
<tr>
<td>Hudson</td>
<td>17</td>
<td>16</td>
<td>52</td>
</tr>
<tr>
<td>Delaware</td>
<td>35</td>
<td>13</td>
<td>43</td>
</tr>
<tr>
<td>Schuylkill</td>
<td>37</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Susquehanna</td>
<td>60</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Potomac</td>
<td>46</td>
<td>17</td>
<td>34</td>
</tr>
<tr>
<td>Pamunkey</td>
<td>28</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td>Roanoke</td>
<td>28</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>Subregion</td>
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<td>Schuylkill</td>
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<tr>
<td>Pamunkey</td>
<td>28</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td>Roanoke</td>
<td>22</td>
<td>7</td>
<td>59</td>
</tr>
</tbody>
</table>

*Summary of anthropogenic features in the watersheds of the eight rivers sampled in this study. Only select properties are described (the complete listing of land use and additional anthropogenic factors assessed in this study can be found in Table S3). See also section S3 for further description of the data.

*Percent of watershed area under land use: agriculture (AGR), urban (URB), forest (FOR), wetland (WET).

*Number of power plant units in watershed area: nuclear (NUPP), coal, oil, gas; FFPP is the total number of coal, oil, and gas power plants (note that some power plants utilize more than one energy source so will count once toward FFPP and may count more than once toward coal, oil, or gas).

*Number of wastewater treatment plants (WWTP) in watershed area.

*Number of impoundments (total or large) in watershed area. Large impoundments are defined by the World Commission on Dams as equal to or greater than 15 m in height, or between 5 and 15 m in height with storage capacity equal to or greater than 3 × 10^6 m^3.

\[ r \] determined from the residual sum-of-squares. The Procrustes statistic \( r \) can range from 0 to 1 (with 1 indicating perfect concordance) and can be tested for significance by randomization (i.e., PROTEST) [Jackson, 1995; Peres-Neto and Jackson, 2001]. The controlling factor categories of interest were (1) hydrogeomorphology and regional climate (i.e., hydrologic parameters describing volumetric flow and basic environmental parameters likely to affect volumetric flow), (2) soil order, (3) soil texture, (4) bedrock lithology, (5) land use, and (6) additional anthropogenic factors (e.g., wastewater treatment plants, impoundments; i.e., anthropogenic factors other than land use impacts such as agriculture or urbanization) (Tables 1–3).
correlating specific factor (POC: driven primarily by catchment area, which was the strongest effect for the remainder of the analyses, but wished to make note of the significance of catchment size as a dominant control of total C exports.

[20] Area-normalized fluxes (i.e., areal yields) of total POC, total DOC, and total DIC from the eight rivers correlated significantly with all potential controlling factors. Not too surprisingly, absolute C fluxes correlated most strongly with the factor class of subregional hydrogeomorphology and climate (r = 0.58, p = 0.001; not shown). This relationship was driven primarily by catchment area, which was the strongest correlating specific factor (POC: r = 0.37, p = 0.006; DOC: r = 0.54, p = 0.001; DIC: r = 0.67, p = 0.001; not shown) among all potential specific factors (i.e., regardless of factor class). As this effect is expected to be primarily one of scale (i.e., bigger watersheds have greater exports [see, e.g., Mullholland, 1997; Seo et al., 2008]), we removed the size-effect for the remainder of the analyses, but wished to make note of the significance of catchment size as a dominant control of total C exports.

[21] Subregional land use correlated most strongly with areal C yield (r = 0.59, p = 0.001; Table 4). This relationship was driven primarily by an increase in areal DIC yield with urban land use (r = 0.63, p = 0.001; Table S4), as well as an increase in areal OC yield with wetland land use (Figures 1a and 2a). Other studies have observed increased DIC exports in more urban areas, presumably from weathering of limestone-based construction materials [Baker et al., 2008; Barnes and Raymond, 2009; Zeng and Musiella, 2010; Moosdorf et al., 2011; Barnes and Raymond [2009], for example, estimated that urban development (along with agricultural land use) increased DIC export by 60–380 % over native forest land use based on streams sampled in the Connecticut River watershed. The relationship between OC exports and wetland land coverage has also been demonstrated in several river-based studies, which have reported higher DOC exports (or higher concentrations of DOC) from watersheds containing greater proportions of OC-rich wetlands and peatlands [Hope et al., 1997b; Raymond and Hopkinson, 2003; Raymond et al., 2004; Baker et al., 2008; Wilson and Xenopoulos, 2008; Mattsson et al., 2009; Lauerwald et al., 2012]. In this study, POC and DOC areal yields were not significantly correlated to wetland coverage by Pearson correlation (r = 0.11 (p = 0.4) and r = 0.21 (p = 0.2), respectively), but these relationships were supported by the Procrustes analysis, which compares the overarching patterns in land use to areal C yields (Figure 1a).

[22] The relationship between areal C yield and soil texture—both subbasinal (r = 0.56, p = 0.001) and subregional (r = 0.53, p = 0.001; Table 4)—suggested an increase in areal OC yield with greater abundance of organic-based soils and an increase in areal IC yield with greater abundance of fine-textured mineral-based soils (Figure 1a). These relationships were also evident through Pearson correlations (see Table S4). The relationship between areal OC yield and organic-based soil coincided with the observed increase in areal OC yield with greater wetland coverage. The indicated relationship between areal IC yield and soil texture, however, was not straightforward. Coarse-textured soils are expected to have deeper subsurface flow and subsequently greater export of DIC [e.g., Johnson et al., 2006]—such a relationship is apparent in the analysis of controlling factors for allochthonous C contributions (see section 3.2). This opposing pattern suggests that the increase in areal DIC yield with greater abundance of fine-textured soils must be driven primarily by an increase in autochthonous DIC. Autochthonous C sources for DIC include atmospheric CO2 exchange and remineralization of autochthonous POC and autochthonous DOC. It does not seem likely that soil texture would impact atmospheric CO2 exchange, which leaves the remineralization of autochthonous POC and autochthonous DOC. One suggested mechanism is that the finer-textured soils export more nutrients such as phosphorus [see, e.g., Kyllmar et al., 2006], supporting increased algal growth in-stream and ultimately increased areal DIC yield via remineralization. The fact that there is not a similar observable increase in areal OC yield with finer soil texture may be attributable to greater response of areal OC yield to
other controlling factors acting independently of soil texture (e.g., proportion of OC-rich soils). We also cannot rule out entirely the possibility that the relationship between DIC areal yield and soil texture is coincidental and derived from other underlying gradients.

[23] The relationship between areal C yield and subbasinal hydrogeomorphology and climate ($r = 0.551, p = 0.001$; Table 4) was driven primarily by an increase in areal C yield with greater runoff and precipitation (Figure 1a). The importance of factors such as runoff and precipitation to OC and IC exports has been observed in several previous studies [Meybeck, 1982, 1993; Bluth and Kump, 1994; Clair et al., 1994; Hope et al., 1997a; Mulholland, 1997; Moosdorf et al., 2011; Alvarez-Cobelas et al., 2012; Lauerwald et al., 2012] and may be attributable to increased denudation and removal of terrigenous C materials with increased hydrologic flow [e.g., Bluth and Kump, 1994; Mulholland, 1997]. However, such a relationship—particularly with runoff—is not unexpected since areal yield is the product of concentration and runoff [Mulholland, 1997; Gaillardet et al., 1999; Lauerwald et al., 2012] (note that such a relationship is also referred to as spurious correlation [Kenney, 1982]). Indeed, for the eight rivers of this study, log-log plots of areal C yield versus runoff have slopes near unity (Figure S9) indicating a direct scaling between areal C yield and runoff (i.e., C concentrations are invariable relative to runoff) [Gaillardet et al., 1999]. The observed relationships between runoff and precipitation and areal C yield do suggest, however, that wetter climates will have higher areal C yields.

[24] Increased areal yields of riverine DIC also coincided with ruggedness of watershed terrain (e.g., greater relief, steeper slope; Figure 1a). Areal yields of riverine POC and DOC, however, were unaffected by watershed terrain as indicated both by the Procrustes superimposition (Figure 1a) and Pearson correlations (Table S4). Relief and slope effects on C exports in previous studies have been mixed, with reports of direct effects on POC [Blair et al., 2003], inverse effects on DOC [Clair et al., 1994; Ludwig et al., 1996; Mulholland, 1997; Frost et al., 2006; Wilson and Xenopoulos, 2008; Lauerwald et al., 2012], and indeterminate or no effects on DIC [Clair et al., 1994; Moosdorf et al., 2011].

[25] Following subbasinal hydrogeomorphology and climate, soil order was the next dominant controlling factor for riverine POC, DOC, and DIC areal yields both subbasinally and subregionally ($r = 0.55$ ($p = 0.001$) and $r = 0.54$ ($p = 0.001$), respectively; Table 4). Typically, when soil is considered as a factor in C export, it has been in the con-
Figure 2. Conceptual model of the dominant factors controlling (a) riverine areal yields of total POC, total DOC and total DIC, (b) allochthonous C proportional contributions to areal C yields, and (c) aged C proportional contributions to areal C yields in the eight temperate rivers examined in the present study. In each subfigure, the four dominant factor classes (e.g., “subregional land use”) are indicated by the larger boxes with dashed borders; Procrustes correlations are provided in the upper right corners. Dominant factors within each class are indicated by the smaller enclosed boxes with solid borders; significant single factor Pearson correlations are provided in parentheses above the connecting arrows. Strongly correlating single factors (or a small subset of factors; e.g., fossil IC lithology) outside of the dominant factor classes are also indicated (smaller boxes with solid borders outside of any larger boxes, and with the Pearson correlation in parentheses above the connecting arrow). Special notes regarding either the class of factors as a whole or single factors are indicated in italics; a “???” notation indicates theoretical uncertainty in the relationship. Some relationships were not apparent through Procrustes or Pearson correlations, but were supported by other lines of evidence (see section 3.4); these relationships are indicated by dotted arrows and “(?)” notation.
text of SOC availability and linked to greater DOC export [Ludwig et al., 1996; Hope et al., 1997a; Aitkenhead et al., 1999; Lauerwald et al., 2012]. However, the relationship observed in the present study was that of increased C export for younger soils (i.e., Entisols and Inceptisols; Figure 1a and Table S4). Since SOC content is expected to be similar between the younger and older soils (e.g., compare Entisol and Ultisol SOC content in Kerr [1994]), the likely explanation for the observed relationship had to do with soil depth and horizon development (Figure 2a). As soils age, bedrock weathering and OM inputs deepen the soil profile and increase the depth to bedrock [e.g., Richter and Markewitz, 1995]. Bluth and Kump [1994], in their review of river chemistry across various basaltic catchments, observed that thick, more highly weathered soils (e.g., Ultisols) created a barrier to DIC flux by reducing water percolation through the soil and subsequent dissolution of bedrock carbonate, in contrast to thin, less-weathered soils (e.g., Entisols or Inceptisols). Also occurring during soil genesis is the formation of distinct layers (e.g., A horizon, B horizon) along the soil profile [e.g., Richter and Markewitz, 1995]. Older soils (e.g., Ultisols) have well-developed B horizons which readily adsorb DOC leached from upper, SOC-rich O and A horizons, thus reducing subsequent DOC exports [McDowell and Wood, 1984; Hope et al., 1994; Richter and Markewitz, 1995; Neff and Asner, 2001].

[25] The various primary factors controlling areal C yields for the eight rivers of the present study are summarized in Figure 2a. Factors such as runoff and precipitation and soil development impacted both OC and IC areal yields, with higher total areal C yields in catchments with wetter climates and shallow, less developed soils (e.g., Entisols and Inceptisols). Additionally, OC areal yields were higher in catchments with greater proportions of wetlands or OC-rich soils, while DIC areal yields, with higher total areal C yields in catchments with wetter climates and shallow, less developed soils (e.g., Ultisols). Also occurring during soil genesis is the formation of distinct layers (e.g., A horizon, B horizon) along the soil profile [e.g., Richter and Markewitz, 1995]. Older soils (e.g., Ultisols) have well-developed B horizons which readily adsorb DOC leached from upper, SOC-rich O and A horizons, thus reducing subsequent DOC exports [McDowell and Wood, 1984; Hope et al., 1994; Richter and Markewitz, 1995; Neff and Asner, 2001].

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3.2. Allochthonous C Contributions to Riverine POC, DOC, and DIC Exports

[25] The proportional contributions of allochthonous C to total riverine POC, DOC, and DIC exports in the present study correlated significantly with all factor classes (Table 4), but there was a range in correlation strength. The strongest correlating factor class was subbasinal anthropogenic factors (r = 0.83, p = 0.001; Table 4), with gradients of increasing fossil fuel power plant (FFPP) density and decreasing impoundment density coinciding with greater proportional allochthonous C contributions to POC, DOC, and DIC (Figure 1b). Density of FFPPs, as a single factor, was among the strongest correlates for allochthonous DIC (r = 0.78, p = 0.001; Table S4 and Figure 2b). To our knowledge, such a relationship has not been previously documented. One possible explanation is that acid deposition in the vicinity of FFPPs [e.g., Galloway et al., 1984; Bouwman et al., 2002] results in more rapid weathering of soil and rock carbonates and release of DIC [e.g., Kilham, 1982; Li et al., 2008]. Density of impoundments, as a single factor, correlated negatively with allochthonous POC (r = −0.78, p = 0.001; Table S4 and Figure 2b). This effect is expected to be primarily indirect through an increase of autochthonous POC [e.g., Grobbelaar and Toerien, 1985; Vosshall and Parker, 1985; Kendall et al., 2001; Sullivan et al., 2001], as river impoundment creates conditions that favor phytoplankton growth such as slower moving, less turbid water [Soballe and Kimmel, 1987; Sullivan et al., 2001]. Surprisingly, the gradient of WWTP density was counter to the gradients of allochthonous POC, DOC, and DIC (Figure 1b and Table S4). This pattern was unexpected based on examples from the literature of significant contributions of WWTP effluent (i.e., an allochthonous source) to riverine POC, DOC, and DIC exports [Gücker et al., 2006; Sickman et al., 2007; Barnes and Raymond, 2009; Griffith et al., 2009; Zeng et al., 2011], as well as the positive correlation observed between WWTP density and DIC areal yield in this study (Figure 1a, Table S4, and section 3.1). As discussed in section 3.1, however, the impact of WWTPs on riverine C loads may be primarily through stimulation of autochthonous production due to high nutrient loads in WWTP effluent [e.g., Gücker et al., 2006; Carey and Migliaccio, 2009].

[25] Several studies have linked hydrogeomorphic characteristics such as stream discharge and relief with allochthonous C contributions to POC [Kao and Liu, 1996; Raymond and Bauer, 2001; Blair et al., 2003], total OC [Webster and Meyer, 1997], and DIC [Finlay, 2003]. In the present study, subbasinal hydrogeomorphology and climate was also a dominant class factor for riverine export of allochthonous C (r = 0.71, p = 0.001; Table 4). Specifi-
cally, allochthonous C contributions to total DOC and DIC exports increased with precipitation while allochthonous C contributions to total POC exports increased with decreasing runoff (Figures 1b and Table S4). The relationship between allochthonous POC and runoff, though also significant by Pearson correlation ($r = -0.64, p = 0.001$; Table S4), was contrary to expectation: terrigenous POC typically increases with runoff because of accelerated erosion (assuming most of the runoff is surficial) [Raymond and Bauer, 2001; Blair et al., 2003; Kao and Liu, 1996]. The underlying cause for this unexpected relationship, however, could be attributed to subbasinal density of impoundments and subregional urban land use—both of which tended to be higher in sites with more subbasinal runoff ($r = 0.82$ ($p = 0.05$) and $r = 0.86$ ($p = 0.03$), respectively (not shown); see also Tables 1 and 3); and were negatively correlated to allochthonous POC ($r = -0.78$ ($p = 0.001$) and $r = -0.82$ ($p = 0.001$), respectively; Figure 2b and Table S4).

[30] Land use at the subregional scale also impacted allochthonous C contributions to riverine C exports ($r = 0.70, p = 0.001$; Table 4), with allochthonous DOC and DIC contributions increasing under forest and wetland land use, and allochthonous POC contributions decreasing under urban land use (Figure 1b). The positive correlation between allochthonous DOC and wetland land use ($r = 0.57, p = 0.001$; Table S4 and Figure 2b) was consistent with the observed increase in DOC areal yield with greater proportion of wetland land use and organic-based soils (Figure 1a and Table S4) and corroborated the several river-based studies also reporting higher DOC exports from watersheds with greater proportions of OC-rich wetlands (i.e., allochthonous C sources) [Hope et al., 1997b; Raymond and Hopkinson, 2003; Raymond et al., 2004; Baker et al., 2008; Wilson and Xenopoulos, 2008; Mattsson et al., 2009; Lauerwald et al., 2012].

[31] Allochthonous DIC correlated positively with forest land use and negatively with agricultural land use ($r = 0.75$ ($p = 0.001$) and $r = -0.67$ ($p = 0.001$), respectively; Table S4 and Figure 2b). These relationships ran counter to previous observations reported in the literature of increased DIC export under agricultural land use because of bicarbonate release from liming (i.e., an allochthonous C source) [Clair et al., 1994; Oh and Raymond, 2006]. Possibly for the six rivers in this study, the observed effect of land use on the proportion of allochthonous DIC was hydrologically mediated, with native land cover (e.g., forest; Figure 2b) slowing storm runoff and increasing infiltration and groundwater flow [Harbor, 1994], thereby promoting dissolution of soil and rock carbonates [Finlay, 2003]. Note also that in contrast to DIC areal yield, there was not a strong gradient of increasing allochthonous DIC with greater urban land use (compare Figure 1a and Figure 1b). The lack of this relationship is likely due to the exclusion of the most and least subregionally urban watersheds (i.e., Schuylkill and Pamunkey, respectively; Table 3) in the six river subset. This suggests that in the absence of a strong urban factor the proportion of allochthonous-derived DIC is controlled by a gradient of forest land use. (Another possibility is that the relationship between urban land use and DIC areal yield was driven by both allochthonous- and autochthonous-derived DIC (i.e., no change in the proportion of allochthonous-derived DIC), which has also been suggested to explain the contrasting relationships observed for DIC areal yield and allochthonous DIC with soil texture and WWTP density; see also section 3.1.)

[32] For POC, the increase in allochthonous contributions with decreasing urban land use was also significant by Pearson correlation ($r = -0.82, p = 0.001$; Table S4) and likely related to an indirect effect of urban land use favoring autochthonous POC production through enhanced N and P loading [e.g., Glandon et al., 1981; Brett et al., 2005; Walsh et al., 2005; Mallin et al., 2009] (Figure 2b). For the six study rivers, subregional urban land use also correlated with greater subbasinal density of impoundments ($r = 0.95, p = 0.004$ (not shown); see also Table 3) which had a similar indirect negative effect on allochthonous POC.

[33] Subregional soil texture was the next most important control on riverine export of allochthonous C ($r = 0.68, p = 0.001$; Table 4), with allochthonous C contributions to DOC and DIC exports increasing with proportion of coarse-textured soils in the six study rivers (Figures 1b and Table S4). The effect of texture on allochthonous DOC contributions was likely due to differences in adsorption capacity: adsorption capacities tend to be smaller in coarse-textured soils (e.g., sandy loams; see also Table 2), leaving more DOC available to be exported from soil solution to streams [Nelson et al., 1993; Remington et al., 2007]. In contrast, the effect of soil texture on allochthonous DIC contributions was attributable to hydraulic properties of the soils. Coarse-textured soils have higher hydraulic conductivities [Rawls et al., 1998] which promote subsurface flow and transport of DIC from soils to streams [Johnson et al., 2006].

[34] Figure 2b aggregates the controlling factors of principal importance for allochthonous C contributions to total POC, DOC, and DIC exports in the present study. Two dominant factors (both anthropogenic) were the presence of impoundments, which decreased allochthonous contributions to POC, and fossil-fuel consumption, which increased allochthonous contributions to DIC (although the reason for the latter relationship is uncertain). Natural environmental factors related to soil permeability and precipitation impacted terrigenous inputs to both riverine DOC and DIC, while land use factors variously affected allochthonous C contributions through nutrient inputs (e.g., POC), OC-richness (e.g., DOC), and infiltration (e.g., DIC).

### 3.3. Aged C Contributions to Total Riverine POC, DOC, and DIC Exports

[35] Almost all of the class factors correlated significantly with the proportional contributions of aged C to total riverine POC, DOC, and DIC exports in the present study (Table 4), but similar to the correlations with allochthonous proportional contributions, there was a range in correlation strength. Hydrogeomorphic factors had the greatest impact on the contribution of aged C to total riverine POC, DOC, and DIC exports, operating at both subregional and subbasinal scales ($r = 0.78$ ($p = 0.001$) and $r = 0.65$ ($p = 0.001$), respectively; Table 4). In particular, hydrologic volume was a significant regulator of both aged OC and aged IC inputs—a relationship which was also apparent through examination of Pearson correlations (Table S4). Aged C contributions to POC export fluxes, for example, increased with stream dis-
charge (Figure 1c). This relationship at the subregional scale was the strongest specific factor correlation for aged POC ($r = 0.79$, $p = 0.001$; Table S4 and Figure 2c). Similar relationships have been observed in other studies and may be attributed to greater mechanical weathering of OC-rich rock with greater volumetric flow [e.g., Kao and Liu, 1996; Blair et al., 2003]. Runoff (as a specific factor) correlated positively with aged C contributions to both DOC and DIC (e.g., aged DOC versus subregional runoff: $r = 0.51$, $p = 0.001$; aged DIC versus subregional runoff: $r = 0.72$, $p = 0.001$; Table S4 and Figure 2c), likely reflecting greater chemical weathering of OC-rich and IC-rich rock with greater volumetric flow.

[36] Also of high importance for aged C contributions to riverine C exports in the present study were subbasinal and subregional additional anthropogenic factors ($r = 0.68 (p = 0.001)$ and $r = 0.52 (p = 0.001)$, respectively; Table 4). Previous river-based studies have observed increases in aged C contributions to DIC under anthropogenic impacts attributed to road construction [Zeng and Masiello, 2010; Zeng et al., 2011], liming of agricultural fields [Oh and Raymond, 2006], and wastewater effluent [Zeng et al., 2011]. For the six rivers not impacted by anthropogenic $^{14}$C in the present study, aged DIC correlated strongly with WWTP density subregionally and subbasinally (single factor basis: $r = 0.73 (p = 0.001)$ and $r = 0.68 (p = 0.001)$, respectively; see also Figures 1c and 2c and Table S4). This relationship may be attributed both to WWTP inputs of aged OC [Griffith et al., 2009; Zeng et al., 2011] which can be remineralized to aged DIC, and to the presence of aged DIC constituents in WWTP effluent. Sodium bicarbonate, for example, which is manufactured from limestone through the Solvay process, is present in a wide variety of products which eventually contribute to the waste stream: animal and human food additives, pharmaceuticals, detergents [Lakhanisky, 2002]. WWTP density also correlated positively with aged POC at the subbasinal scale ($r = 0.51, p = 0.002$; Figures 1c and 2c and Table S4), but did not correlate with aged DOC either subregionally or subbasinally (Table S4). For aged DOC, however, the relationship could have been obscured by the Susquehanna River which had a large number of WWTPs (Table 3) but was estimated to have no aged DOC component (Table S2). Excluding the Susquehanna River samples resulted in stronger positive correlations at both scales (subregional: $r = 0.45$, $p = 0.01$; subbasinal: $r = 0.54$, $p = 0.002$; not shown).

[37] Aged DIC also increased with river impoundment density based on the Procrustes analysis (Figure 1c) as well as Pearson correlations ($r = 0.50 (p = 0.002)$ and $r = 0.66 (p = 0.001)$, subregionally and subbasinally respectively; Table S4 and Figure 2c). In contrast, previous studies regarding aged DIC and river impoundments have suggested decreased aged C contributions to DIC with impoundment because of conditions favoring autotrophy and atmospheric gas exchange (i.e., modern DIC sources) [Zhang et al., 2009; Zeng et al., 2011]. The best explanation that we can suggest for the relationship observed in the present study is a rise in water table behind the river impoundments, which would permit greater contact time between subsurface flow and bedrock, thus promoting dissolution of bedrock carbonates. Aged DOC also correlated positively with impoundment density in the present study (subregional: $r = 0.56$, $p = 0.001$; subbasinal: $r = 0.51$, $p = 0.001$; Figures 1c and 2c and Table S4), which could likewise be explained by greater dissolution of both fossil OC and old SOC with a rising water table—but this is speculative.

[38] In the present study, factors related to either hydrogeomorphology and climate (e.g., Table 1) or additional anthropogenic activities (e.g., Table 3) exhibited the strongest control of allochthonous contributions to total riverine POC, DOC and DIC exports (e.g., Figure 2b), and in particular, aged contributions to the C exports (e.g., Figure 2c). Aged C contributions to exports of riverine POC, DOC and DIC related primarily to hydrogeomorphologic and climatic factors relevant to mechanical and chemical erosion (e.g., stream discharge, runoff). However, of nearly equal importance were effluent inputs from WWTPs as sources of aged DOC, DIC, and possibly DOC; and river impoundment density, which correlated positively with aged DOC and DIC, although the mechanism for this relationship is uncertain (Figure 2c).

[39] In summary Figure 2c, we additionally highlight two significant relationships between aged C contributions and controlling factors from among the remaining factor classes. Several previous studies have observed increased aged C exports from watersheds with fossil C-rich lithologies [Pawellek and Veizer, 1994; Raymond et al., 2004; Longworth et al., 2007; Zhang et al., 2009]. While the lithology factor class was not particularly strong in this study (Table 4), there were significant positive correlations between fossil OC-rich rock types and aged DOC and between fossil IC-rich rock types and aged DIC (Figure 2c and Table S4). Aged DIC also correlated significantly with urban land use (subregional: $r = 0.69$, $p = 0.001$; subbasinal: $r = 0.47$, $p = 0.002$; Figure 2c and Table S4). As suggested for DIC areal yield (section 3.1 and Figure 1a), this relationship may be attributable to weathering of limestone infrastructure in urban areas [e.g., Baker et al., 2008; Zeng and Masiello, 2010]. Potential impacts of both urban and agricultural limestone use are further explored in section 3.4.
of further analyses addressing the likely impacts of these anthropogenic activities. We also briefly discuss the influence of nuclear power plants (NUPPs) which, though not expected to alter riverine C exports, could greatly affect C export age and source estimates.

3.4.1. Wastewater Treatment Plants and Riverine C and OM

[41] Griffith et al. [2009] analyzed effluent from 12 WWTPs in the lower Hudson River and Connecticut River watersheds and observed an average POC concentration of 4.9 mg L\(^{-1}\) and DOC concentration of 8.7 mg L\(^{-1}\), with estimated fossil OC contributions of 14% and 25%, respectively. For DIC, the average concentration was 18.1 mg L\(^{-1}\) for wastewater effluent sampled from six treatment plants within the Connecticut River watershed (fossil C contributions, however, were not estimated) [Barnes and Raymond, 2009]. Using these measurements and total WWTP design flow for each watershed subregion (see section S3), we estimated annual total POC, DOC, DIC, and aged POC and DOC exports attributable to wastewater discharge (Table S5).

[42] Total WWTP-derived exports were highest for the Susquehanna River, the largest river and watershed subregion, which annually exported an estimated 4.3 Gg yr\(^{-1}\) of WWTP-derived POC, 7.6 Gg yr\(^{-1}\) of WWTP-derived DOC, and 15.8 Gg yr\(^{-1}\) of WWTP-derived DIC, on average (Table S5). However, in terms of proportion to total riverine C exports, the Schuylkill River received the greatest contribution from wastewater effluent, with WWTP-derived C contributing an estimated 100% to exported POC, 30% to DOC, and 7% to DIC. Across all eight rivers, WWTP effluent contributions to POC, DOC, and DIC exports averaged 15%, 8%, and 4%, respectively. These loadings compared to previous estimates for several U.S. rivers [Sickman et al., 2007; Barnes and Raymond, 2009; Griffith et al., 2009], suggesting that while WWTP contributions to riverine C exports across broader regions may be relatively small, for individual rivers, particularly those with small discharges and high WWTP densities (e.g., the Schuylkill River; Tables 1, 3, and S5), the within-stream WWTP C loads and impacts could be substantial. Also to be considered is the typically continuous flow exhibited by WWTP effluent [Carey and Migliaccio, 2009] which may result in varying significance when contrasted with temporal variations in riverine POC, DOC, and DIC fluxes [Andersen et al., 2004; Kolpin et al., 2004; Sickman et al., 2007; Carey and Migliaccio, 2009]. For the rivers of the present study, C fluxes were smallest during the summer months with characteristically low discharge [Hossler and Bauer, 2013, Figures 4 and S2], hence WWTP contributions would be expected to have greater significance during this season. These potentially seasonal effects are indicated in Figure 2a.

[43] Nearly half of the aged POC exports in the Potomac River and all of the aged DOC exports in the Susquehanna River could potentially be accounted for by WWTP effluents alone (Table S5). Across the combined six rivers for which aged riverine C estimates were available (i.e., excluding the Schuylkill and Pamunkey Rivers), WWTP effluent contributed approximately 18% to aged POC exports and 33% to aged DOC exports. These percentages were ~1.2 and ~4.1 times higher than for the WWTP contribution to total POC and total DOC, respectively, suggesting that the WWTP impact was more significant as a source of aged riverine C than as a source of total riverine C.

3.4.2. Agricultural Liming and Riverine DIC

[44] Oh and Raymond [2006] estimated that 17% of annual bicarbonate flux in the Ohio River basin of the mid-western U.S. could be attributed to agricultural liming (i.e., the application of crushed limestone and dolomite to soil). Following their general approach, we estimated the component of DIC flux attributable to agricultural liming for the eight northeast U.S. rivers of this study (details of the calculations can be found in section S4). Based on the annual mean agricultural lime (aglime) application rate of ~35 Mg km\(^{-2}\) for cropland in the northeast U.S. and an approximate 46,992 km\(^2\) of agricultural land drained by the eight rivers of this study, the estimated annual application was 1.6 Tg of calcium carbonate (Table S6). This amount of aglime is expected to release 130–260 Gg yr\(^{-1}\) of C annually (Table S6; see also section S4), or 7–25% of the estimated annual DIC export for the eight study rivers combined [Hossler and Bauer, 2013]. Half of the aglime C flux would derive directly from the applied calcium carbonate (i.e., fossil C; see section S4), hence aglime-derived C could account for 20–100% of the aged DIC export from the study region [Hossler and Bauer, 2013, Tables 2 and S2].

[45] Of further consideration is the amount of limestone (and a minor amount of dolomite) consumed annually for construction of roads and buildings. Given a mean annual consumption rate for crushed limestone in the eastern U.S. of ~130 Mg km\(^{-2}\) and a total drainage area of 208,316 km\(^2\) for the eight rivers of the present study, an additional 26 Tg of calcium carbonate was expected to have been consumed annually for construction of new infrastructure in the eight river study region (Table S6; see also section S4). This limestone usage would result in the release of ~20–30 Gg yr\(^{-1}\) of C (half derived directly from the limestone, and hence fossil), with another ~830–1130 Gg yr\(^{-1}\) potentially leaching from the approximately 1020 Tg of existing (i.e., prior to the beginning of this study in 2005) limestone-based infrastructure in the region of study (Table S6 and section S4). While these estimates are only approximate, it is apparent that limestone-based infrastructure can also be a significant source of riverine DIC and may be driving the positive correlations observed between urban land use and both DIC areal yield and aged DIC in this study (Figures 2a and 2c). Several previous studies have likewise observed higher DIC concentrations and exports in more urban areas [Baker et al., 2008; Barnes and Raymond, 2009; Zeng and Masiello, 2010; Moosdorf et al., 2011].

3.4.3. Nuclear Power Plants as a Source of “New” \(^{14}\)C in Watershed and Aquatic C Studies

[46] Exceptionally elevated \(^{14}\)C signatures of POC, DOC, and DIC were measured in two of the eight rivers in the present study (see, e.g., Figure S11, as well as Figure 2 and Table S1 in Hossler and Bauer [2013]). Therefore, the potential impact of NUPPs on the \(^{14}\)C content of these C pools must be considered (see also section S5 for a discussion of other potential \(^{14}\)C sources). Within the Schuylkill River and Pamunkey River watersheds, \(^{14}\)C signatures of up to 1958/\(^{129}\)C were measured from the riverine C samples collected during the present study, which to our knowledge are the most \(^{14}\)C enriched values for any river yet studied.
For perspective, the maximum $\Delta^{14}C$ signatures observed for the remaining six sites were 49$\%$ for POC, 105$\%$ for DOC, and 102$\%$ for DIC (Figure S11; see also Figure 2 in Hoessler and Bauer [2013]). It is also worth noting that the $\Delta^{14}C$ signature of atmospheric CO$_2$ was around 56$\%$ at the time of the study [Turnbull et al., 2008], while the maximum atmospheric CO$_2$, $\Delta^{14}C$ signature was $\sim$90$\%$ near the height of atmospheric nuclear weapons testing in the 1950s and 1960s [Levin et al., 1985].

[47] The possibility that NUPPs located upstream of the Schuylkill and Pamunkey sample sites were the source of the extremely enriched $\Delta^{14}C$ signatures (e.g., Figure S5) was therefore investigated (see also section S5 for a more thorough discussion of this topic). While NUPPs were likewise located upstream of two other sample sites (i.e., the Connecticut and Susquehanna Rivers), only the Schuylkill and Pamunkey Rivers showed evidence of radiocarbon contamination in the riverine C samples. One possible reason for this discrepancy is that only the NUPPs within the Schuylkill and Pamunkey were releasing significant amounts of $^{14}C$-containing materials or that radiocarbon signatures stemming from the NUPP emissions became much more diluted in the larger Connecticut River and Susquehanna River watersheds (see section S5). If the latter case is correct, then we can expect that we have consequently underestimated the proportion of aged C exports from the Connecticut and Susquehanna watersheds.

[48] Use of natural abundance $^{14}C$ isotope analyses has been growing in Earth and aquatic studies as a means to make inferences on the ages (and sometimes recalcitrance) of carbonaceous materials, to track C flow through ecosystems, and to identify and quantify sources contributing to bulk C pools. As such, the possibility of radiocarbon contamination from extraneous sources (e.g., NUPPs; see also section S5) needs to be kept in mind in order to avoid, or at least qualify, potentially biased results.

4. Synthesis and Summary

[49] For the eight northeast U.S. rivers of the present study, each of the six factor classes analyzed correlated significantly with areal C yields, allochthonous C contributions, and aged C contributions, and often with similar correlation strengths, attesting to the complexity of relationships affecting the export and composition of riverine C. However, one emerging generality was the predominance of hydrogeomorphology and climate, which ubiquitously impacted areal C yields and composition (Figure 2). The influence exerted by hydrogeomorphology and climate seemed primarily related to volumetric flow, with increased precipitation and runoff resulting in greater areal C yields and more terrestrial C contributions. Also of broad importance were anthropogenic factors and land use (Figure 2). Among the anthropogenic factors analyzed, presence of WWTPs and impoundments were significant determinants of allochthonous C and aged C contributions to riverine POC, DOC, and DIC exports. The potential impact of WWTPs on C export composition, as well as on total C export flux, was further strengthened by a separate analysis of WWTP effluent POC, DOC, and DIC loads to the eight study rivers. A similar series of estimates likewise demonstrated the potential significance of anthropogenic limestone/dolomite use to riverine DIC exports, a relationship which also emerged from the positive correlations observed between urban land use and both DIC areal yield and aged DIC.

[50] In addition, two of the eight rivers studied (the Pamunkey and Schuylkill) exhibited clear evidence of present-day anthropogenic $^{14}C$ inputs, with the most likely explanation being nuclear reactor emissions in these watersheds. While the levels of $^{14}C$ in these two rivers were extraordinarily elevated, these findings further highlight the potential for lower level reactor emissions in other watersheds and rivers. In such systems, $^{14}C$ levels might appear to be within the “norm” for bomb or pre-bomb $^{14}C$ levels, but may still be elevated above $^{14}C$ levels that would be encountered in the absence of nuclear reactors. These factors collectively underscore the significance of anthropogenic activities to riverine and global C cycles and their study, both currently and in the future.

[51] A final generality regarding both the quantities and compositions of C exports was that factors tended to exert stronger influence on smaller scales, i.e., subbasinal effects were more important than subregional effects. Anthropogenic factors, in particular, were often equally or more important at localized scales in the present study. This observation appears at odds with the common perception of rivers as integrators of the surrounding landscape [e.g., Richey, 1983; Karr, 1998; Richey, 2006], but merely suggests a weighted integration with more local effects having greater import. In almost all cases, the factor classes correlated significantly to the three C measures at both subbasinal and subregional scales.

[52] Improving our understanding of environmental controls on riverine C exports is important for several reasons. First, relationships between environmental factors and riverine C exports can be used to constrain global C budgets [e.g., Ludwig et al., 1996; Moosdorf et al., 2011; Lauerwald et al., 2012]. There are a growing number of publicly available geospatial databases (see, e.g., section S3) that could be used to calculate riverine C exports across broader scales once reliable relationships have been established. This approach may be advantageous over direct measurement of riverine C exports, which can be costly to collect in terms of both time and money.

[53] Second, in our now anthropogenically modified world, exploring the effects of natural and anthropogenic factors can help assess the impact of our behaviors on C export fluxes and compositions [e.g., Meybeck, 2003; Meybeck and Vörösmarty, 2005]. Based on the present study, anthropogenic practices such as wastewater treatment, river impoundment, and use of carbonate-based materials are substantially affecting the total export flux, allochthonous C composition, and aged C composition of riverine POC, DOC, and DIC.

[54] Third, as anthropogenic impacts intensify, a better understanding of these relationships can help predict future scenarios. Climate change models, for example, predict regions of greater precipitation and regions of lesser precipitation, depending on location [IPCC, 2008]. As supported in both the literature and the present study, precipitation and discharge are primary determinants of riverine C flux, and it is therefore expected that riverine C exports and C cycling in general will be altered accordingly.
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References


Hosler and Bauer: Environmental Controls of Riverine Carbon


