Carbon Export from the Raccoon River, Iowa: Patterns, Processes, and Opportunities

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Farmed landscapes are engineered for productivity, and research suggests they contribute a disproportionate share of inorganic C to the Mississippi River and Gulf of Mexico. Here we use alkalinity and total organic C (TOC) measurements collected from the Raccoon River of Iowa to (i) evaluate inorganic and organic C concentrations and export patterns, (ii) compare current trends to historical conditions, and (iii) link C transport processes to current land use management. Export of inorganic C averaged 106,000 Mg per year and contributes 90% of the C flux from the basin. Alkalinity concentrations are unchanged from 1931 to 1944 levels (~53 mg L$^{-1}$ C), but inorganic C loads have doubled due to increasing discharge. Carbonate-rich glacial deposits and agricultural lime provide a large source of inorganic C, and results confirm that alkalinity export in the Raccoon Basin is transport limited. Although fertilization and tillage practices have possibly helped increase C fluxes over the last 70+ yr, the overriding factor on inorganic C export is discharge. Discharge control over C export provides an opportunity for agriculture in terms of quantifying C sequestration for potential C trading. Controlling water flux through soils can limit inorganic C export similar to practices such as reduced tillage and managed rotations.

**Abbreviations:**
- DML, Des Moines Lobe
- DMRWQN, Des Moines River Water Quality Network
- DMRW, Des Moines Water Works
- DOC, dissolved organic carbon
- POC, particulate organic carbon
- SOC, soil organic carbon
- TOC, total organic carbon
- UMB, Upper Mississippi River Basin
and helps regulate the calcium carbonate (CaCO₃) saturation point and pHCO₂ in the oceans (Zeebe and Westbroek, 2003). Alkalinity exported to the oceans from weathering processes can be considered a negative feedback to global warming because atmospheric CO₂ is consumed and the C is stored at the ocean bottom (Berner and Berner, 1996).

Export of alkalinity from the Mississippi River has been examined (Gaillardet et al., 1999; Raymond and Cole, 2003; Raymond et al., 2008). Raymond and Cole (2003) showed that alkalinity export from the Mississippi River increased 59% in the period 1954 to 2001 due to the conversion of noncropped lands to croplands and increased discharge. They further suggested that increased alkalinity loading may be linked to increased N loading (Turner and Rabalais, 1994; Goolsby and Battaglin, 2001), with enhanced soil respiration (Schlesinger and Andrews, 2000) and nitrification (Skiba et al., 1992) producing acids that increase chemical weathering rates.

Spatial variations in alkalinity loading within the Mississippi basin were delineated by Raymond and Cole (2003) into three subbasins: Missouri, Ohio, and Upper Mississippi. The Upper Mississippi Basin (UMB) had the highest portion of land in crops (55%) and contributed 49% of alkalinity to the total flux, even though its portion of total discharge was only 34%. Furthermore, 56% of the alkalinity increase reported for the 1954–2001 period originated from the Upper Mississippi basin. Increased discharge was considered the primary cause of the increased alkalinity flux (Raymond and Cole, 2003).

Farmed landscapes in the UMB are engineered for high levels of productivity (Schilling et al., 2012), and as a result, crops both sequester atmospheric CO₂ and contribute alkalinity to rivers and streams. Reductions in evapotranspiration due to crop production increase discharge and the discharge to precipitation ratio (Gedney et al., 2006; Betts et al., 2007) and increase acceleration of the water budget in the UMB (Schilling, 2005; Zhang and Schilling, 2006). Raymond et al. (2008) estimated that about 52% of the alkalinity flux increase was due to increased discharge not linked to precipitation (i.e., land use factors), ~20% was due to increased precipitation, and ~30% was due to other factors. They point out that lime application to agricultural fields has probably played a role in the increased flux, but examination of the lime application rates and the total U.S. contribution of alkalinity export to the oceans resulting from dissolution of this lime (West and McBride, 2005) implies that this practice is not a major contributor to the increased alkalinity flux from the Mississippi River.

In light of the conclusions reached by Raymond and Cole (2003) and Raymond et al. (2008), subwatersheds within the high-alkalinity export area of the UMB merit examination. In this study, we evaluate C export from the Raccoon River of west-central Iowa, an intensely cultivated area of the American Midwest, and focus attention on alkalinity, the dominant form of C leaving the basin via the river. Our first study objective was to compare inorganic and organic C concentrations and loads to identify relative contributions of C sources. A second objective was to use pre-1945 Raccoon River alkalinity data to compare current patterns with historical conditions. Our third objective involved linking C transport processes in the Raccoon River to land management, climate, and sustainability of current land use practices in the UMB. We conclude by discussing how riverine C export may provide opportunities for C sequestration and trading.

**Methods and Materials**

**Raccoon River Watershed**

The Raccoon River drains a watershed of 9389 km² in west-central Iowa and empties into the Des Moines River at Des Moines, Iowa (Fig. 1). The Des Moines River flows southeast and enters the Upper Mississippi River near Keokuk, Iowa. The North, Middle, and South Raccoon rivers form major tributary branches of the Raccoon. The North Raccoon River flows through the recently glaciated Des Moines Lobe (DML) landform region, which is dominated by low relief and poor surface drainage (Prior, 1991). The geology of the area consists largely of thick pebbly glacial till in flat till plains, clay and peat in depressions, and sand and gravel deposits in major floodplains and moraines. Over half the agricultural land area in the DML has subsurface alkalinity, the dominant form of C leaving the basin via the river. Our first study objective was to compare inorganic and organic C concentrations and loads to identify relative contributions of C sources. A second objective was to use pre-1945 Raccoon River alkalinity data to compare current patterns with historical conditions. Our third objective involved linking C transport processes in the Raccoon River to land management, climate, and sustainability of current land use practices in the UMB. We conclude by discussing how riverine C export may provide opportunities for C sequestration and trading.
drainage (Schilling et al., 2008). The South Raccoon River drains an older pre-Illinoian glacial landscape with higher relief and well developed drainage and is characterized by approximately 1 to 6 m of wind-blown silt (loess) overlying a clay-rich paleosol developed in a dense, fine-grained, weathered glacial till. The Middle Raccoon River drains both of these contrasting landforms. Overall, glacial drift deposits can exceed 100 m thick in the watershed. Low permeable Pennsylvanian (interbedded shale, limestone, and coal) and isolated Cretaceous (sandstone and shale) rocks that underlie the glacial deposits are not a significant water source to streams.

Agriculture is the predominant land use throughout the watershed. Row crops of corn (Zea mays L.) and soybeans (Glycine max (L.) Merr.) comprise about 80% of the basin area (Schilling et al., 2008). In the early 20th century, considerably more land was planted to small grains (primarily oats [Avena sativa L.]) and alfalfa (Medicago sativa L.) compared with the present-day (Haffield et al., 2009). Oat and alfalfa crops were steadily replaced by soybeans over the past 75 yr (USDA NASS, 2009).

Since 1916, annual discharge varies from 0.15 to 5.11 km³ (USGS, 2011). Annual average temperature of seven locations (Guthrie Center, Storm Lake, Carroll, Perry, Jefferson, Des Moines, and Rockwell City) has ranged from 7.9 to 12.4°C, with an average of 9.8°C during the life of the flow gauge. Little or no trend in temperature is apparent since 1951 (0.1°C increase). Annual average precipitation at four locations (Guthrie Center, Storm Lake, Rockwell City, and Des Moines) during the same period ranged from 493 to 1207 mm, with an average of 796 mm (Iowa Environmental Mesonet, 2012).

Water withdrawn from the river for irrigation is negligible because precipitation is adequate for crop production. Withdrawals for industrial or municipal purposes are also insignificant upstream of the Van Meter gauge. A few km downstream of the gauge, the Des Moines Water Works (DMWW) uses the stream as its principal source of supply. Because its watershed is intensely agricultural and its water is a major source of municipal supply, the Raccoon River has been extensively characterized for nitrate N (Lucey and Goolsby, 1993; Schilling and Lutz, 2004; Schilling and Zhang, 2004; Haffield et al., 2009; Jha et al., 2010), sediment (Jones and Schilling, 2011), and bacteria (Schilling et al., 2009) loading.

We obtained near-daily Raccoon River alkalinity data since 1994 and approximately biweekly data for the 1931–1944 period from the DMWW laboratory archives. We also examined organic C data generated by the Des Moines River Water Quality Network (DMRWQN). This data set includes approximately biweekly data for the Raccoon River at Van Meter beginning in 2000. The DMWW sample location (41.57827 N, −93.64971 W) is 5 stream km upstream from the Raccoon confluence with the Des Moines River. The DMRWQN sample location (41.534034 N, −93.95061 W) is 42 stream km upstream of the Raccoon–Des Moines confluence.

Carbon Measurements

At the DMWW laboratory, total alkalinity is quantified by titration with acid to pH 4.5 and reported as mg L⁻¹ CaCO₃. Bicarbonate concentrations for the daily DMWW data were calculated using sample pH and total alkalinity to ensure alkalinity was indeed being exported in this form. For the 2000–2011 period, bicarbonate was 0.982 of total alkalinity, and thus inorganic C was calculated from alkalinity assuming a factor of 2 correction for charge difference between carbonate and bicarbonate (Table 1).

With a few exceptions, DMRWQ grab samples from the river were collected daily at approximately 07:00 h Central Time, Monday through Friday, for the 1994–2011 period and biweekly for the 1931–1944 period. Exceptions include some holidays and days when river ice, floods, or extreme weather prevented collection. Water samples were collected from near the shoreline or from a river intake structure at DMWW’s Fleur Drive Treatment Plant by lowering a sample catcher apparatus into moving river water. After collection, the sample was immediately delivered to the utility’s testing laboratory, where alkalinity and other analyses were conducted that morning.

Total alkalinity was determined using Standard Methods procedure 2320B (APHA, 2005). The frequently turbid river samples were filtered to facilitate visual determination of endpoint. Before 1994, when electronic record-keeping began, alkalinity and other data were carefully recorded by hand in bound books stored in a library at the DMWW treatment plant and imply that staff were using the best available laboratory practices of records management. Review of early Standard Methods (APHA, 1920) editions, which accompany the data books, indicates that alkalinity was quantified by titration since at least 1920. For these reasons, we believe the early DMWW data can be compared favorably with the modern data generated by essentially the same procedure. In the modern era, DMWW laboratory quality control procedures demonstrate a long-term accuracy of 99.2% recovery for known concentration samples and a precision of 0.2% (relative percent difference) for duplicated samples. Duplicate and fortified (samples spiked with a known concentration of the analyte) samples, along with background checks of laboratory-grade water (blanks), are evaluated daily in the DMWW laboratory.

Data for nonanalysis days (weekends and holidays) were extrapolated using values from the measurement days immediately before and after. Daily loads were quantified by multiplying the daily discharge by the concentration. Loads for nonanalysis days were calculated by multiplying the estimated concentration by the actual daily discharge. For early DMWW data (1931–1944), alkalinity loads were calculated by multiplying annual average alkalinity by annual average discharge.

The DMRWQN samples were collected similarly but less frequently. The DMRWQN organic C analysis was conducted using Standard Method procedure 5310B (APHA, 2005), high-temperature combustion, followed by infrared detection of CO₂. Loading of total organic C (TOC) was estimated using the USGS program LOADEST (Runkel et al., 2004). Laboratory quality control procedures for DMRWQN data demonstrate a long-term accuracy of 100.8% recovery for known concentration samples and a precision of 2.1% (relative percent difference) for duplicated samples. Quality control samples are analyzed at a frequency of 10% for the DMRWQN monitoring program.

Results

Inorganic Carbon Concentrations and Loads

From 1994 through 2011, daily discharge of the Raccoon River ranged from 1.9 to 1120 m³ s⁻¹ and averaged 64.3 m³ s⁻¹ (Fig. 2a). Daily river discharge exceeded 600 m³ s⁻¹ in 1998, 2004, 2007, 2008, and 2010, with values greater than...
1000 m$^{-3}$ s$^{-1}$ recorded in 1998 and 2008. In contrast to flow, daily inorganic C concentrations were much less variable (Fig. 2b), with minimum (18.8 mg L$^{-1}$) and maximum (93.6 mg L$^{-1}$) concentrations fluctuating around a mean of 53.8 ± 13.5 mg L$^{-1}$.

Daily inorganic C load exported by the Raccoon River peaked on 15 June 1998, when 3588 Mg of inorganic C was lost from the watershed (Fig. 2c). Daily average inorganic C load was 290 Mg from 1994 to 2011 and totaled 1909,664 Mg for the period. Annual Raccoon River inorganic C load ranged from 13,902 Mg in 2000 to 267,908 Mg in 2010 (Fig. 3) and averaged 106,092 Mg.

Median daily inorganic C loads were substantially less than average values (132.9 Mg d$^{-1}$). Of the total inorganic C mass lost during the 18-yr monitoring period, 13% of the total C was exported during 131 d (2% of the time), and 70% of the C load was exported during the upper 25% of days (Fig. 4). Although daily inorganic C concentrations were negatively related to daily discharge ($p < 0.05$), inorganic C loads were significantly positively related to discharge ($p < 0.001$) (Fig. 5).

Historical DMWW data from 1931 to 1944 ($n = ~24$ per year) showed average annual Raccoon River alkalinity concentrations to be 220 mg L$^{-1}$ (52.9 mg C L$^{-1}$) (Fig. 6). The historical concentrations were similar to the 2000–2011 period, when alkalinity averaged 224 mg L$^{-1}$ (53.8 mg C L$^{-1}$) (Table 1). Average stream discharge was much smaller during the 1931–1944 period (35 m$^3$ s$^{-1}$) compared with the 2000–2011 period (65 m$^3$ s$^{-1}$). The average annual Raccoon River inorganic C export during the 1931–1944 period (58,600 Mg C) was about 56% of that recorded from 2000 to 2011.

### Table 1. Summary of annual inorganic carbon and total organic carbon concentrations and loads in the Raccoon River from 2000 to 2011.

<table>
<thead>
<tr>
<th>Year</th>
<th>Daily flow†</th>
<th>Alkalinity (as CaCO$_3$)‡</th>
<th>Inorganic C§</th>
<th>Measured TOC¶</th>
<th>Total Inorganic C#</th>
<th>Total Organic C††</th>
<th>Inorganic C fraction of total C‡‡</th>
<th>Organic C fraction of total C§§</th>
<th>Ratio Inorganic to organic C¶¶</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>10.0 (10.3)†††</td>
<td>192.6 (44.5)</td>
<td>46.2 (10.7)</td>
<td>5.48 (0.93)</td>
<td>13,901.5</td>
<td>1575.7</td>
<td>0.815</td>
<td>0.185</td>
<td>8.82</td>
</tr>
<tr>
<td>2001</td>
<td>55.9 (79.1)</td>
<td>188.7 (48.4)</td>
<td>45.3 (11.6)</td>
<td>5.45 (1.87)</td>
<td>70,167.7</td>
<td>10,608.8</td>
<td>0.768</td>
<td>0.232</td>
<td>6.61</td>
</tr>
<tr>
<td>2002</td>
<td>31.6 (33.7)</td>
<td>223.1 (56.8)</td>
<td>53.5 (13.6)</td>
<td>4.55 (1.60)</td>
<td>52,418.4</td>
<td>5700.1</td>
<td>0.821</td>
<td>0.179</td>
<td>9.20</td>
</tr>
<tr>
<td>2003</td>
<td>47.0 (87.6)</td>
<td>214.6 (49.9)</td>
<td>51.5 (12.0)</td>
<td>6.08 (2.06)</td>
<td>73,876.2</td>
<td>10,414.5</td>
<td>0.780</td>
<td>0.220</td>
<td>7.09</td>
</tr>
<tr>
<td>2004</td>
<td>59.5 (96.6)</td>
<td>204.9 (47.3)</td>
<td>49.2 (11.4)</td>
<td>6.59 (2.61)</td>
<td>81,776.8</td>
<td>13,080.7</td>
<td>0.758</td>
<td>0.242</td>
<td>6.25</td>
</tr>
<tr>
<td>2005</td>
<td>39.2 (60.8)</td>
<td>206.3 (46.5)</td>
<td>49.5 (11.2)</td>
<td>6.73 (3.07)</td>
<td>59,259.0</td>
<td>7706.1</td>
<td>0.794</td>
<td>0.206</td>
<td>7.69</td>
</tr>
<tr>
<td>2006</td>
<td>28.6 (31.9)</td>
<td>218.2 (54.1)</td>
<td>52.4 (13.0)</td>
<td>5.86 (1.93)</td>
<td>47,630.5</td>
<td>4831.4</td>
<td>0.831</td>
<td>0.169</td>
<td>9.86</td>
</tr>
<tr>
<td>2007</td>
<td>104.5 (119.9)</td>
<td>245.2 (63.6)</td>
<td>58.8 (15.3)</td>
<td>4.17 (1.31)</td>
<td>174,868.5</td>
<td>20,165.1</td>
<td>0.813</td>
<td>0.187</td>
<td>8.67</td>
</tr>
<tr>
<td>2008</td>
<td>111.4 (151.9)</td>
<td>245.1 (55.4)</td>
<td>58.8 (13.3)</td>
<td>5.82 (2.47)</td>
<td>183,912.3</td>
<td>21,372.1</td>
<td>0.811</td>
<td>0.189</td>
<td>8.61</td>
</tr>
<tr>
<td>2009</td>
<td>73.9 (63.8)</td>
<td>247.0 (53.8)</td>
<td>59.3 (12.9)</td>
<td>4.36 (2.97)</td>
<td>137,481.2</td>
<td>10,221.9</td>
<td>0.871</td>
<td>0.129</td>
<td>13.45</td>
</tr>
<tr>
<td>2010</td>
<td>158.1 (164.5)</td>
<td>265.4 (47.9)</td>
<td>63.7 (11.5)</td>
<td>3.64 (0.73)</td>
<td>267,907.9</td>
<td>24,009.2</td>
<td>0.848</td>
<td>0.152</td>
<td>11.16</td>
</tr>
<tr>
<td>2011</td>
<td>56.3 (71.5)</td>
<td>240.2 (44.3)</td>
<td>57.7 (10.6)</td>
<td>3.27 (0.46)</td>
<td>101,115.2</td>
<td>5899.9</td>
<td>0.895</td>
<td>0.105</td>
<td>17.14</td>
</tr>
<tr>
<td>Avg.</td>
<td>64.7 (46.9)</td>
<td>224.3 (5.8)</td>
<td>53.8 (1.4)</td>
<td>5.2 (1.35)</td>
<td>105,359.5</td>
<td>11,298.8</td>
<td>0.823</td>
<td>0.177</td>
<td>9.32</td>
</tr>
</tbody>
</table>

† Average daily flow at the Van Meter USGS gauge.
‡ Average daily total alkalinity as mg L$^{-1}$ CaCO$_3$ generated by the Des Moines Water Works Laboratory.
§ Inorganic C concentration calculated from the total alkalinity (total alkalinity × 0.12 × 2).
¶ Measured total organic C measurements generated by Des Moines River Water Quality Network.
# Summed total of daily loads obtained by multiplying concentration by discharge, with concentrations extrapolated for nonanalysis days.
†† Loads estimated by LOADEST.
‡‡ Inorganic C load divided by sum of Total Inorganic and Total Organic load.
§§ Organic C load divided by sum of Total Inorganic and Total Organic load.
¶¶ Standard deviations of measured values in parentheses.
Of the total C load exported in the Raccoon River from 2000 to 2011, 90.3% was inorganic C, and 9.7% was TOC (Table 1). The fraction of C export for inorganic C varied from 86.2 to 94.5% and was higher during the latter 3 yr of the study period. The average ratio of inorganic to organic C loads was 9.3 for the study period, but this ratio was substantially higher in 2011 (17.1) (Table 1).

**Discussion**

**Sources of Carbon**

Glacially derived deposits in Iowa contain a large proportion of CaCO₃ and CaMg(CO₃)₂ minerals (Ruhe, 1969). In the DML landscape region, through which much of the Raccoon River flows (Fig. 1), calcareous soils formed from the weathering of calcareous parent materials, such as limestone and dolomite, common to the Midwest (Rabenhorst et al., 1991; Prior, 1991; Rogovska et al., 2007). Ruhe (1969) reported the soil CaCO₃ distribution in a typical DML hillslope ranges from 1 to 20% CaCO₃. Similarly, Rogovska et al. (2007) measured soil CaCO₃ as high as 30% with most values <10 to 15%. High values of CaCO₃ are associated with soils having pH >7.5 (Rogovska et al., 2007). Upper soil profiles and well drained areas are often leached of carbonates, which can accumulate in unweathered zones and in low-lying areas. In the Southern Iowa landscape drained by the South Raccoon River, soils are formed in loess and older pre-Illinoian till that were originally calcareous (Kay and Apfel, 1929; Hutton, 1948). The upper horizons of both units (~3–4 m) are typically oxidized and leached of carbonates, but deeper zones are unleached and contain abundant inherited carbonates (Ruhe, 1969; Hallberg, 1978; Kemmis et al., 1981). Loess deposits occasionally contain secondary carbonates as nodules (“loess kindchen”). With a soil matrix dominated by carbonate, alkalinity export is generated when CO₂ encounters the unleached soil profile and carbonate weathering occurs. Simple water flux through calcareous soils leaches inorganic C (White and Blum, 1995; Stumm and Morgan, 1996), so landscapes that produce greater water yield export more alkalinity.

Despite the presence of carbonate-rich soils in Iowa, we cannot ignore the addition of agricultural lime as a potentially important source of inorganic C. Our estimates using available data (R. White, personal communication, 2012) of the average annual inorganic C exported as a result of lime applications in the Raccoon River watershed could be as high as 32,775 Mg, which would represent approximately 31% of the inorganic C export if all of the applied lime-C was lost as riverine bicarbonate export. Lime applications vary considerably across the state and are more important in regions where surface soils have been leached of carbonate minerals. In the Raccoon River basin, lime applications are likely to be more prevalent in the smaller South Raccoon River basin where older loess soils have been leached, compared with the larger North Raccoon where recently glaciated deposits are enriched with carbonates. Furthermore, West and McBride (2005) suggest that as much as 25% of the applied lime-C may be lost back to the atmosphere as CO₂ gas. Finally, reporting of agricultural lime application and consumption is not well monitored, prompting West and McBride (2005) to characterize US agricultural lime consumption data as “suspect.”

Nonetheless, lime application in the Raccoon River should be considered a source of inorganic C in the basin that is available for leaching and transport.

Much of the TOC is derived from allochthonous (SOM, terrestrial plants, litter decomposition) and autochthonous (phytoplankton, benthic algae, macrophytes) sources ubiquitous to the Upper Mississippi River basin (Bianchi et al., 2007; Warrner et al., 2009). Particulate organic carbon (POC), consisting mainly of eroded soil and vegetation debris, has been highly correlated with total sediment flux (Ludwig et al., 1996). In the Raccoon River, recent work indicates that sediment loads have decreased in the river since peaking in the early 1970s (Jones and Schilling, 2011), implying that POC loads may have similarly decreased over the last few decades. Since 1985, annual sediment loads are highly correlated with precipitation.
suggesting that POC export may be largely driven by rainfall runoff patterns. This may explain why the ratio of inorganic:organic C was unusually high in 2011 (17.1) (Table 1). The second half the of year was characterized by dry conditions, which surely reduced surface runoff and the transport of POC relative to inorganic C present in the groundwater and tile water feeding the river. On the other hand, dissolved organic C (DOC) losses can be significant in tile-drained Midwestern watersheds (Royer et al., 2005; Warner et al., 2009). In the North Raccoon River watershed, where more than half of the cropped fields are tile drained (Schilling et al., 2008), DOC may contribute greatly to TOC loads. Contributions of DOC from groundwater (Vidon et al., 2008), tile drains, in-stream sources, and possibly benthic sediments and eroded soils are difficult to differentiate (Warner et al., 2009).

Comparison to Regional Studies

Raymond and Cole (2003) estimated inorganic C export for the entire Mississippi River basin above St. Francisville, Louisiana to be $1.75 \times 10^{13}$ g yr$^{-1}$ for the end of their period of record (2001). They also state that the UMB contributed 0.49 of the total alkalinity flux (i.e., $8.58 \times 10^{12}$ g yr$^{-1}$). This translates to an inorganic C yield for the UMB (above the Missouri River confluence) of $1.93 \times 10^5$ g ha$^{-1}$ yr$^{-1}$. Raymond and Cole (2003) calculated loads by multiplying annual average alkalinity concentrations by annual average discharge from an alkalinity data set that averaged 17 samples per year at St. Francisville. Using the DMWW data set, which averages about 250 samples per year, and calculating annual loads by summing daily loading data, we estimate the average annual inorganic C yield for Raccoon River Basin to be $1.24 \times 10^5$ g ha$^{-1}$ yr$^{-1}$ since 2000. This loading rate is substantially less (0.64) than the UMB inorganic C yield deduced by Raymond and Cole (2003), even though the fraction of cropland in the Raccoon is far higher (0.77 vs. 0.55). The difference could be associated with a lower water yield in the Raccoon River Basin ($2.10 \times 10^5$ m$^3$ yr$^{-1}$) compared with the UMB ($2.67 \times 10^5$ m$^3$ yr$^{-1}$) since 2000. On the other hand, inorganic C yields calculated using the DMWW data are more consistent with Gaillardet et al. (1999) if we apply the 0.49 loading contribution for the UMB used by Raymond and Cole (2003). Gaillardet et al. (1999) estimated inorganic C loading
for the Mississippi to be $1.2 \times 10^{13}$ g yr$^{-1}$, which translates to $1.33 \times 10^{10}$ g ha$^{-1}$ yr$^{-1}$ for the UMB, only slightly larger than the yield of inorganic C we calculate for the Raccoon River Basin. Considering the intensity of crop production in the Raccoon watershed, we expected the yield of inorganic C to be higher in the Raccoon River Basin compared with the UMB. Further work is needed to determine whether differences in inorganic C loading rates among watershed areas is real or an artifact of using difference data sets or methods.

**Land Use, Climate, and Alkalinity Export**

Although much of the focus on alkalinity fluxes has been on discharge, other factors may be contributing. Fertilization is one such factor. An estimated 128,000 Mg yr$^{-1}$ of N inputs enters the Raccoon watershed in the form of chemical fertilizers, animal manures, and legume fixation (Schilling et al., 2008). Nitrogen fertilizer can increase bicarbonate formation and transport through two mechanisms. First, the formation of nitric acid in the soil can result in dissolution of carbonate minerals without consuming atmospheric CO$_2$ (Skiba et al., 1992; Amiotte-Suchet, 1995). This mechanism has been shown to generate 6% of the bicarbonate load in a carbonate-abundant farmed watershed (Semhi et al., 2000). Second, fertilization stimulates soil respiration and thus production of the source of CO$_2$ for chemical weathering (Schlesinger and Andrews, 2000). On the other hand, research has shown that N fertilization can enhance sequestration of soil organic C (Halvorson et al., 2000), primarily through return of crop residues to the soil. Overall, the role of N fertilizer on bicarbonate formation and transport is complex and worthy of future research.

Tillage practices have been implicated in the loss of soil organic C (Doran, 1980; Allmaras et al., 2000; Baker and Griffis, 2005), primarily through soil exposure to oxygen and loss of organic C as CO$_2$ to the atmosphere after oxidation. Losses have also been linked to tile drainage systems (Royer et al., 2005; Warrner et al., 2009). Some estimate that as much as 30 to 50% of the SOM present before cultivation has been lost from soils of the Midwestern United States, including Iowa (Allmaras et al., 2000).

Increased temperatures can also be a factor in C transport through enhanced ecosystem respiration (Griffis et al., 2003; Suyker et al., 2004), and this is true for soils (Bond-Lamberty and Thomson, 2010). However, an examination of climate data (Iowa Environmental Mesonet, 2012) shows only about a 0.1°C increase in average annual watershed temperature since 1951. Increased temperature does not seem to be a major factor for increase C transport in the Raccoon watershed.

Concentrations of alkalinity have changed little, if at all, in the Raccoon River since the 1940s (Fig. 6). Raymond and Cole (2003) deduced a slight increase in concentrations in the UMB, whereas Raymond et al. (2008) indicated that dataset may have been biased by a decade of low flows at the beginning of the record. They found alkalinity flux at average flows increasing substantially, especially in watersheds with annual precipitation >0.6 m yr$^{-1}$. Raymond et al. (2008) demonstrated that the alkalinity flux from portions of the UMB is transport limited and is mildly transport limited in regions where annual precipitation is between 0.5 and 1.0 m yr$^{-1}$, which includes the Raccoon River watershed (0.80 m yr$^{-1}$ since 1900) (Iowa Environmental Mesonet, 2012). In transport-limited systems, soil water is near saturation with resident ions, and increasing inputs of weathering agents does not dramatically affect bicarbonate concentrations. As water throughput increases, however, the added water encounters a reservoir rich in bicarbonate, ready for transport.

It does not appear that alkalinity concentrations have changed appreciably in the Raccoon River in the last 80 yr (52.9 mg L$^{-1}$ C, 1931–1944 vs. 53.8 mg L$^{-1}$ C, 2000–2011). On the other hand, streamflow and baseflow in the Raccoon River increased through the 20th century (Schilling and Libra, 2003; Jones and Schilling, 2011) due to increasing precipitation and land use change from perennial to annual crops. Increasing water flux through carbonate-rich soils has approximately doubled C export from the Raccoon River across the latter half of the 20th century. Alkalinity transport in the Raccoon basin does indeed seem to be transport limited. It is interesting to note that given the increasing intensity of agricultural production, large N inputs, and calcareous soils, alkalinity concentration increases were not observed in the Raccoon River, and the yield of alkalinity from the Raccoon River watershed may be less than the rest of the UMB, according to the UMB estimates of Raymond and Cole (2003).

**Riverine Carbon Flux Compared with Grain Carbon Export**

Baker and Griffis (2005) used eddy covariance and mass balance techniques to determine SOC loss from fields in Southern Minnesota to be about 90 g m$^{-2}$ over a 2-yr period in corn–soybean rotation. Hernández-Ramírez et al. (2011) similarly examined CO$_2$ fluxes in corn–soybean rotations in fields <50 km from the Raccoon River near Ames, Iowa, sharing the same DML landform as the North Raccoon River. Soils are similar to those found in the North Raccoon River watershed (typic Hapludolls) (USDA–NRCS, 2012) (i.e., of the same age and type and formed in the same glacial parent material under prairie vegetation). Carbon dioxide fluxes were monitored using eddy-covariance and soil chambers in adjacent production fields (Hernández-Ramírez et al., 2011). When export of grain C was considered, their corn–soybean rotation showed an apparent decrease in soil C of 104 ± 57 g C m$^{-2}$ yr$^{-1}$ over a period of 4 yr (2004–2007), with the negative flux due almost entirely to the export of grain C. Raccoon River C flux during the same 4-yr period (inorganic and organic C) averaged 10.9 g C m$^{-2}$ yr$^{-1}$. Because only half of the inorganic C load can be linked to SOC (Eq. [1], where one CO$_2$–C originates from the soil and one carbonate-C is liberated from the rock), the riverine export of SOC (linked to both riverine organic and inorganic carbon) is at most 61.1 g C m$^{-2}$ yr$^{-1}$. Hence, loss of SOC via river flux is only about 1/20th the C loss from grain harvest calculated by Hernández-Ramírez et al. (2011). They measured total SOC of their field site as 23,900 g m$^{-2}$ to a depth of 1.2 m. The calculated maximum Raccoon River SOC export of 6.1 g C m$^{-2}$ yr$^{-1}$ translates to only 0.03% of the SOC measured by Hernández-Ramírez et al. (2011). Assuming the soils in the Hernández-Ramírez et al. (2011) study are indeed similar to those in the Raccoon Basin, which seems very likely, we therefore conclude here that loss of SOC via chemical weathering of carbonate minerals and river transport of alkalinity does not seriously threaten the productive sustainability of soils in the Raccoon River watershed.
Opportunity for Agriculture

Sequestration of soil C provides multiple agricultural and environmental benefits. Consideration has been given to the implementation of various C credit trading systems that could provide economic incentives to farmers participating in C sequestration initiatives (Marland et al., 2001a, 2001b). Various strategies have been proposed to reduce loss of SOC, mainly through tillage modifications, residue management, and use of cover crops. Baker and Griffis (2005) examined the use of strip tillage and cover cropping on SOC flux. The cumulative difference between conventional tillage and strip tillage on C sequestration was approximately 10 g m⁻² yr⁻¹. The addition of a spring oats cover crop provided no benefit in the form of C sequestration. They concluded that policies that monetarily stimulate practices to increase SOC may not be especially effective. Halvorson et al. (2002) experimented with tillage, fertilization, and crop rotations in North Dakota and examined their effects on SOC. Their best system improvement, no-till on a wheat-sunflower rotation, improved sequestration of SOC by 23 g m⁻² yr⁻¹. West and Post (2002) found that changing from conventional tillage to no-till sequesters an average of 57 g C m⁻² yr⁻¹ and that enhancing rotation complexity can sequester an average of 20 g C m⁻² yr⁻¹.

We have studied another tile-drained watershed on the DML Landform, Lyons Creek (Schilling et al., 2012), which lies about 50 km east of the Raccoon River watershed. Preliminary data from three tile mains in the Lyons Creek basin show total C (bicarbonate-C plus TOC) yield via tile flow to range from 24 to 39 g m⁻² yr⁻¹. These values from intensively drained cropped fields are similar to those found in the much larger Raccoon River watershed during the same time period (2008–2010, ~23 g m⁻² yr⁻¹) and compare favorably with C sequestration rates from land management practices. This may present an interesting opportunity for agriculture. If farmers can reduce water throughput through engineered and drained systems, most of which are likely transport limited for C export, they may be able to achieve C sequestration rates relatively similar to practices such as reduced tillage and crop rotation complexity. For example, the use of in-line water level control structures (Gilliam et al., 1979; Wesstrom et al., 2001) to manage water flow out of field tiles presents an easy and inexpensive opportunity for farmers to control C loss without operational challenges presented by tillage and crop rotation modification. Furthermore, monitoring C loss through these engineered systems is a simple matter of collecting flow and water quality data, which lends itself well to any C credit trading systems. Managing water flux further offers the benefit of reducing nitrogen and phosphorous export from these hydrologically modified systems (Gilliam et al., 1979; Wesstrom et al., 2001).

Conclusions

The Raccoon River in west-central Iowa has been extensively studied because it drains an intensively cultivated watershed representative of the Corn Belt region of the United States and is frequently monitored as a drinking water supply source. Using near-daily measurements of river alkalinity for a 18-yr period (1994–2011) obtained from DMWW, we report that inorganic C export from the Raccoon River averaged 106,000 Mg per year and contributes 90% of the C flux from the basin. Inorganic C concentrations were relatively unchanged from levels measured more than a half century earlier (~53 mg L⁻¹ C), but loads approximately doubled since the 1931–1944 period due to the effects of increasing discharge on stream loads. Carbonate-rich glacial deposits and agricultural lime provide a large source of inorganic C, and our results confirm that alkalinity export in the Raccoon Basin is transport limited as suggested by Raymond et al. (2008) for many areas in the UMR. In the end, discharge control over C export may provide an opportunity for agriculture. Controlling water flow through soils can limit C export on par with land management practices such as reduced tillage and managed rotations.

Acknowledgments

The authors acknowledge DMWW, Iowa Soybean Association, and Iowa Department of Natural Resources for supporting this research.

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doi:10.3402/j1600-0889.47.issue1.23.


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