Riverine Response of Sulfate to Declining Atmospheric Sulfur Deposition in Agricultural Watersheds

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Abstract
Sulfur received extensive study as an input to terrestrial ecosystems from acidic deposition during the 1980s. With declining S deposition inputs across the eastern United States, there have been many studies evaluating ecosystem response, with the exception of agricultural watersheds. We used long-term (22 and 18 yr) sulfate concentration data from two rivers and recent (6 yr) data from a third river to better understand cycling and transport of S in agricultural, tile-drained watersheds. Sulfate concentrations and yields steadily declined in the Embarras (from ~10 to 6 mg S L⁻¹) and Kaskaskia rivers (from 7 to 3.5 mg S L⁻¹) during the sampling period, with an overall ~23.1 and ~12.8 kg S ha⁻¹ yr⁻¹ balance for the two watersheds. There was evidence of deep groundwater inputs of sulfate in the Salt Fork watershed, with a much smaller input to the Embarras and none to the Kaskaskia. Tiles in the watersheds had low sulfate concentrations (<10 mg S L⁻¹), similar to the Kaskaskia River, unless the field had received some form of S fertilizer. A multiple regression model of runoff (cm) and S deposition explained much of the variation in Embarras River sulfate (R² = 0.86 and 0.80 for concentrations and yields; n = 46). Although atmospheric deposition was much less than outputs (grain harvest + stream export of sulfate), riverine transport of sulfate reflected the decline in inputs. Watershed S balances suggest a small annual depletion of soil organic S pools, and S fertilization will likely be needed at some future date to maintain crop yields.

Core Ideas
- Riverine sulfate in agricultural watersheds responds to atmospheric deposition inputs.
- Agricultural sulfur budgets suggest annual depletion of organic S pools.
- Tile drains respond quickly to agricultural sulfate inputs.

Atmospheric deposition of sulfur (S), primarily from SO₂ emissions from coal combustion, was a major environmental issue of the 1980s and 1990s. The United States spent about $600 million studying the environmental impacts of added atmospheric S deposition to ecosystems through the National Acid Precipitation Assessment Program (NAPAP), authorized by Congress under the Acid Precipitation Act of 1980 (Russell, 1992). When Congress enacted Title IV as part of the Clean Air Act Amendments in 1990, S deposition began a slow decline due to decreasing SO₂ emissions in the eastern United States, which are now only about 20% of what they were in the 1970s (USEPA, 2015a). This decline has been clearly documented in the measured decrease in sulfate deposition by the National Atmospheric Deposition Program/National Trends Network monitoring of wet deposition (NADP, 2015). There have been many studies documenting the recovery of ecosystems (Burns et al., 2011), including forests (Lawrence et al., 2015; Likens et al., 1996) and lakes in the northeastern United States (e.g., Waller et al., 2012). There have been continuing questions about sulfate release from southeastern watersheds where previous sulfate adsorption led to soil storage of added atmospheric S (Rice et al., 2014).

Early on in NAPAP it was recognized that acidic deposition had little impact on crop production, and studies in Illinois on corn and soybeans ended quickly (Banwart et al., 1987; Porter et al., 1987). However, S is an important macronutrient in plants (Dick et al., 2008), and decreasing atmospheric deposition of S has led to concerns about S deficiencies in crop plants in the midwestern United States (e.g., Dick et al., 2008; Fernández et al., 2012; Sawyer et al., 2011). We have long recognized that direct uptake of atmospheric SO₂ and S deposition could be important to crop S uptake (e.g., Dick et al., 2008; Hoeft et al., 1972). Most soil S is in organic forms, and mineralization and release of sulfate is an important process in agricultural soils (Dick et al., 2008; Eriksen, 2009).

Farmers are now showing interest in S fertilizers in the upper Midwest, although most crop trials do not show a response to S fertilizers on fine-textured soils high in organic matter at this time (Fernández et al., 2012). However, a few sites low in soil organic matter did show a small response to S fertilization across Illinois (Fernández et al., 2012). Superphosphate (0–20–0) fertilizers used to contain about 12% S because sulfuric acid was

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doi:10.2134/jeq2015.12.0613
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Supplemental material is available online for this article.
Received 21 Dec. 2015. Accepted 14 Mar. 2016.
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used to acidulate rock phosphate. Triple superphosphate (0–46–0) fertilizers mostly eliminated S from P fertilizers (<3% S), and the ammoniated phosphate fertilizers (monoammonium phosphate and diammonium phosphate) now typically used have little S (Robert Hoeft, personal communication, 2015; Pioneer, 2015). Locally in east-central Illinois, ammonium sulfate fertilizer (6–0–0–6) from Archer Daniels Midland Company is used by a limited number of farmers around the Decatur, IL, area as a solution applied in the late fall or winter (Gentry et al., 2000). For watersheds in this region this is a source of S, although its use is limited in scope because it was first made available in 1993 and is not widely distributed. Therefore, most agricultural fields in the upper Midwest currently receive little S from fertilizers, and inputs from atmospheric deposition are greatly decreased, yet harvested S is increasing due to increasing crop yields. Tile drainage facilitates leaching of sulfate from soils, which is the other major output from fields, in addition to grain harvest (Dick et al., 2008).

In watersheds throughout the world, a source of river water sulfate can also be from deep groundwater where deposits of S minerals such as pyrite and gypsum are released (e.g., Schlesinger and Bernhardt, 2013). However, even in a New Jersey watershed where sulfate was primarily from groundwater (80%), declining S deposition inputs were thought to be the reason for decreasing river sulfate concentrations (Sun et al., 2014).

The effect of declining atmospheric S deposition on stream sulfate concentrations and loads in tile-drained agricultural watersheds and the overall S balance of agricultural watersheds has not been studied in midwestern agricultural areas. Therefore, the objectives of this study were (i) to construct input and output S balances in tile-drained agricultural watersheds in the Corn Belt, (ii) to examine long-term trends in riverine sulfate concentrations and loads, and (iii) to determine the effect of atmospheric S deposition on both the watershed balances and stream sulfate concentrations.

**Materials and Methods**

**Site Description**

This study used data from three watersheds in east-central Illinois (Supplemental Fig. S1), each defined by a USGS gaging station located at the outlets: the upper Embarras River (USGS site no. 03343400 near Camargo, 481 km²), the Lake Fork of the Kaskaskia River (USGS site no. 05590800 near Atwood, 386 km²), and the Salt Fork of the Vermillion River (USGS site no. 03336900 near St. Joseph, 347 km²). We have sampled these locations since June 1993 (Emballas), October 1996 (Kaskaskia), and March 2010 (Salt Fork), and there are many previously published studies on various aspects of the watersheds, including various maps (e.g., David et al., 1997, 2015, 2016; Gentry et al., 2007, 2014; Royer et al., 2006). The landscape of each of these watersheds is flat (<2% slopes) with soils that are poorly or very poorly drained Mollisols that were formed when this area was a wet tall grass prairie. Drummer is the dominant soil series (fine-silty, mixed, superactive, mesic Typic Endoaquolls), and it requires tile drainage for crop production. Therefore, each watershed is characterized by older random tile systems, combined with newer pattern drainage systems, typically at a 1 to 1.5 m depth. Land use in each watershed is dominantly row crop agriculture (>90%), typically under a corn (Zea mays L.) and soybean (Glycine max (L.) Merr.) rotation, with almost no animal production. Annual precipitation is about 100 cm, with approximately 10 cm as snow.

**Riverine and Tile Sampling**

We had available long-term river flow and sulfate concentration data sets for these watersheds, of varying lengths. For the Embarras River at the gaged outlet, we collected 1194 water samples from 1993 through the end of the 2015 water year. For the Kaskaskia River, we collected 1271 samples from 1996 through 2015, and for the Salt Fork, 345 samples were collected from 2010 through 2015. Water samples were collected weekly to daily, depending on flow, and we attempted to sample all high flow periods (>28 m³ s⁻¹) on a daily basis. River samples were filtered (0.45 µm pore size) and analyzed for sulfate by ion chromatography ( Dionex). We used linear interpolation to estimate a sulfate concentration for every daily discharge value to determine daily and annual loads. We also obtained monthly sulfate data for the Embarras River at Camargo from 1962 through 1971, sampled and measured by the Illinois State Water Survey (Harmeson and Larson, 1969; Harmeson et al., 1973), and data collected by Illinois EPA sampled on a 6-wk-interval basis from 1979 through 1993 (USEPA, 2015b). Again, linear interpolation was used to estimate daily sulfate concentrations that were combined with measured USGS flow data. The analysis of the 1962 through 1993 data was used to obtain annual flow-weighted sulfate concentrations and to calculate annual yields. Trends in sulfate concentration in the Kaskaskia and Embarras Rivers during our sampling period were assessed using the Seasonal Kendall test from the USGS that performs the Mann–Kendall trend test for individual seasons of the year, which we defined as four seasons, as well as on annual flow-weighted means (Helsel et al., 2006).

In the Salt Fork watershed, there are two separate subwatersheds that merge 1.6 km above the USGS gauge site (Supplemental Fig. S1). We also collected water samples from both of these subwatersheds (the Upper Salt Fork Ditch and Spoon River) on the same days as the St. Joseph gauge site. During 2012–2014, nine water samples were collected along the length of the Spoon River subwatershed at 1- to 3-km intervals and one from the largest headwater tributary, for a total of 10 locations. Each year, samples were collected once at these locations during the spring tile flow period and a second time in summer when there was no tile flow. In the Embarras River watershed during 1999–2000, water samples were collected 18 times from 17 locations throughout the watershed to determine the pattern of sulfate concentrations in the river system (locations shown on a map in David et al. [2003]). All major tributaries were sampled. Again, for both the Salt Fork and Embarras River sampling, sulfate was determined by ion chromatography.

To examine sulfate in tile drainage in these watersheds we used data from a variety of fields; details are provided in the supplemental material. Four tiles in a biofuel study in the Embarras River watershed had sulfate concentrations monitored from 2008 through 2015 (Smith et al., 2013; Zeri et al., 2011), and we also analyzed sulfate in an additional three tiles located in fields in the center of the Embarras River watershed and 10 tiles distributed throughout the Salt Fork watershed from 2011 to 2015. These latter 13 tiles drained fields with corn and soybean.
production. Water samples from tiles were collected using both grab samples and ISCO automatic samplers during high flow periods, and flow was determined using pressure transducers and data loggers. All sulfate concentrations were measured with ion chromatography.

Sulfur Budget

Annual S budgets for the Embarras and Kaskaskia watersheds were estimated using the riverine sulfate export determined above, along with atmospheric deposition inputs, crop fertilization, and crop harvest. Wet deposition of sulfate for 1980 through 2015 was from the Bondville, IL, site of the National Atmospheric Deposition Program, which was located between the two watersheds, just outside the borders of each (NADP, 2015). Dry deposition of S was estimated as 50% of wet (33% of total deposition), based on measured dry deposition S values from the USEPA Clean Air Status and Trends Network (CASTNET) Bondville, IL, site (USEPA, 2015c). To estimate S deposition before 1980, we used data on SO$_2$ emissions for the United States available in Smith et al. (2011). We regressed 1980 to 2005 SO$_2$ emissions from Smith et al. (2011) versus our Bondville, IL, total S deposition estimates. The resulting linear equation had an $R^2 = 0.70$ and was used to predict 1962 through 1979 S deposition values for the Embarras River watershed.

Most crops in Illinois do not receive S fertilizers, but ammonium sulfate from the Archer Daniels Midland Company is used on some fields in the Embarras and Kaskaskia watersheds. To estimate these inputs of S, we used Illinois Department of Agriculture fertilizer tonnage reports for Champaign, Douglas, and Piatt Counties where ammonium sulfate sales are reported (Illinois Department of Agriculture, 2015). Fertilizer sales of ammonium sulfate for Champaign and Douglas counties were summed each year and assumed to be applied to the Embarras River watershed. The same was done for the Kaskaskia River watershed, using the ammonium sulfate sales for Piatt County. Crop harvest of S was from annual corn and soybean harvests for Champaign, Douglas, and Piatt Counties each year (USDA–NASS, 2015) and then scaled to each watershed using the fraction in corn and soybean of the total area for each watershed. The concentration of S in harvested corn and soybean grain (dry mass basis) was estimated at 0.10 and 0.34% of dry mass, respectively (Avila-Segura et al., 2011; Batal et al., 2011; Karlen et al., 2015; Masters et al., 2016).

Linear Regression Modeling

We used multiple linear regression using SAS v. 9.3 to predict annual flow-weighted Embarras River sulfate concentrations and annual riverine yields (kg S ha$^{-1}$ yr$^{-1}$) from 1962 through 2015 (except for the 1972 to 1978 water years, where no data were available; $n = 46$ yr), with two variables: (i) water yield and (ii) atmospheric deposition of S. Plots of predicted versus modeled sulfate concentrations and yields in the final models are shown in the supplemental information. Model residuals were tested for normality of distribution using the Anderson–Darling $A^2$ test. Final model results are given in Supplemental Table S2. Initial modeling work also used estimates of S in phosphorus fertilizers from 1962 on and from ammonium sulfate from 1993 on, either by year or moving averages of 1 to 3 yr, but this variable was not found to be significant. There was some S in the superphosphate and triple superphosphate used until about 1973 in the area (Illinois Department of Agriculture, 2015) and then again after 1993 in the ammonium sulfate applied in this region.

Results

Riverine and Tile Sulfate

Sulfate concentrations were greatest in the Salt Fork River, followed by the Embarras and then the Kaskaskia Rivers (Fig. 1). Daily and annual flow-weighted sulfate concentrations had a significant decreasing trend using the seasonal Kendall test ($p < 0.001$) in the Embarras and Kaskaskia Rivers during our sampling periods (Fig. 1 and 2). Sulfate concentrations were greatest during low flow periods each year (typically summer to fall) and decreased with increasing flow (Fig. 3). The pattern was different among the three rivers, with the sulfate concentration in the Salt Fork decreasing the most with flow, followed by the Embarras. The Kaskaskia had much lower variation with flow. Annual riverine sulfate yields varied from 1.7 to 47.2 kg S ha$^{-1}$ yr$^{-1}$ in the three watersheds and increased with water yields (Fig. 4). The same pattern in yields was observed as in concentrations, with Salt Fork > Embarras > Kaskaskia for a given water yield.

Tile sulfate concentrations (seven tiles monitored in the Embarras watershed and 10 monitored in the Salt Fork) reflected...
whether the field had received some type of S fertilizer. For the 10 tiles monitored in the Salt Fork watershed, tiles without S fertilizers were typically <10 mg S L\(^{-1}\), with the South tile the lowest at 2 mg S L\(^{-1}\) (Fig. 5). Tiles A and B, as well as tile C in 2013, had much greater concentrations (20–40 mg S L\(^{-1}\)) due to an application of bed ash, a calcium carbonate and sulfate material applied by the farmer on these fields. The two fields that received animal manure (M East and West) also had larger concentrations of sulfate (about 15–20 mg S L\(^{-1}\)). In the biofuel tiles that received no S fertilizers, concentrations were about 6 mg S L\(^{-1}\) during 7 yr of measurement and showed a steady decline (Supplemental Fig. S2), with little variation among crop type. Finally, in the Embarras River watershed tiles from K West and K East and BR1 were all <10 mg S L\(^{-1}\) (Supplemental Fig. S3).

**Watershed Sulfur Budget and Regression Modeling**

The greatest S input to the Embarras and Kaskaskia watersheds was atmospheric deposition of S, which was about 7 kg S ha\(^{-1}\) yr\(^{-1}\), with a smaller fertilizer input of about 4.7 kg S ha\(^{-1}\) yr\(^{-1}\) (Table 1). Grain harvest in the two watersheds was about 9 kg S ha\(^{-1}\) yr\(^{-1}\), with stream exports of 26.7 and 15.6 kg S ha\(^{-1}\) yr\(^{-1}\) for the Embarras and Kaskaskia watersheds, respectively. The overall S balance was −23.1 and −12.8 kg S ha\(^{-1}\) yr\(^{-1}\) for the Embarras and Kaskaskia watersheds during the 22- and 18-yr measurement periods, respectively. Atmospheric deposition inputs of S steadily declined at the NADP Bondville, IL, station from 1980 through 2015 (Fig. 6). In the early 1980s, deposition inputs were about 12 to 14 kg S ha\(^{-1}\) yr\(^{-1}\) and declined to about 5 kg S ha\(^{-1}\) yr\(^{-1}\) after 2010.
To expand our sulfate concentration data, we used previously published reports from the 1960s and 1979 through 1993 (Fig. 7). Flow-weighted sulfate concentrations were greatest during the 1960s (after increasing from 1962 through 1965), were lower but steady in the 1980s, and have declined since 1990. Multiple regression models with water yield and deposition had $R^2$ values of 0.86 and 0.80 for concentration and yield, respectively (Supplemental Table S1). Plots of measured and predicted sulfate values and residual plots indicated that both models were robust and fit the observed data well (Supplemental Fig. S4 and S5).

**Discussion**

**Riverine Sulfate Patterns and Controls**

Sulfate concentrations in tiles from corn and soybean fields that have not received S fertilizers had a similar concentration as the Kaskaskia River during the past 10 yr (about 5 mg S L$^{-1}$). The greater concentration of sulfate in the Embarras and Salt Fork Rivers compared with the Kaskaskia River was likely due to sulfate inputs from groundwater. During the 1999 and 2000 synoptic sampling in the Embarras watershed, sulfate concentrations increased from southwest to northeast (9.1–21.9 mg S L$^{-1}$), indicating that high sulfate groundwater was entering the river system from the northeast section of the watershed. In the Salt Fork watershed, the Spoon River subwatershed had much greater low flow sulfate concentrations than the Upper Salt Fork Ditch subwatershed, whereas at moderate to higher flows the concentrations were similar (Supplemental Fig. S6). In addition, sampling along the Spoon River from the origin to just above the confluence with the Upper Salt Fork Ditch showed that sulfate concentrations were quite low until 9.3 km downstream, where they increased about 20 mg S L$^{-1}$ during spring flows and 40 mg S L$^{-1}$ during the summer under low flow (Table 2). This clearly reflects a groundwater sulfate source in these two watersheds.

Both the Embarras and Kaskaskia River sulfate concentrations significantly decreased during our sampling period. The long-term concentrations and yields from 1962 on in the Embarras River, combined with the regression model results, indicate a strong control of atmospheric S deposition. Therefore, the Kaskaskia and Embarras Rivers have anthropogenic controls on sulfate, with the Embarras also having some mineralogical control. The Salt Fork is strongly under mineralogical control during low flow periods, and our data were not extensive enough to determine if there was anthropogenic control during high flow periods. These results are similar to Sun et al. (2014), who determined that there were both types of controls in their New Jersey watersheds.

**Table 1.** Average S inputs (wet and dry atmospheric deposition, fertilizer) and outputs (grain harvest, stream export) for the Embarras River watershed at Camargo, IL, for 1994 to 2014 and Lake Fork of the Kaskaskia River watershed at Atwood, IL, for 1998 to 2014. The overall long-term balance of S is also given.

<table>
<thead>
<tr>
<th></th>
<th>Embarras</th>
<th>Kaskaskia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inputs</td>
<td></td>
<td></td>
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<tr>
<td>Atmospheric deposition</td>
<td>7.5</td>
<td>7.1</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>4.6</td>
<td>4.9</td>
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<tr>
<td>Outputs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain harvest</td>
<td>8.5</td>
<td>9.2</td>
</tr>
<tr>
<td>Stream export</td>
<td>26.7</td>
<td>15.6</td>
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<tr>
<td>Balance</td>
<td>-23.1</td>
<td>-12.8</td>
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Fig. 6. Estimated atmospheric deposition inputs of S at Bondville, IL, from 1962 through 1979 (red) and measured wet and dry deposition from 1980 through 2015 water years (black).

Fig. 7. Embarras River at Camargo, IL, grab sample sulfate concentrations from 1962 through 2015 (black circles) and annual flow-weighted concentrations for the same period (red circles). Also shown are linear regression modeled flow-weighted sulfate concentrations in green triangles. Data before 1994 from Harmeson and Larson (1969), Harmeson et al. (1973), and USEPA (2015b).

Table 2. Sulfate concentrations from grab samples at sites along the Spoon River of the Salt Fork watershed during the spring (tile flow period) and summer (no tile flow, groundwater inputs only) of 2012 to 2014 ($n = 3$).

<table>
<thead>
<tr>
<th>Distance from source</th>
<th>Sulfate-S</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Spring</td>
</tr>
<tr>
<td>km</td>
<td>mg S L$^{-1}$</td>
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<tr>
<td>2.2</td>
<td>5.3</td>
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<tr>
<td>3.8</td>
<td>8.1</td>
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<td>4.4</td>
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<td>6.8</td>
<td>6.8</td>
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<td>9.3</td>
<td>24.2</td>
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<td>11.0</td>
<td>28.5</td>
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<td>13.1</td>
<td>28.8</td>
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<tr>
<td>21.0</td>
<td>21.4</td>
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<tr>
<td>23.2</td>
<td>16.2</td>
</tr>
</tbody>
</table>
We did not find any relationship of fertilizer inputs of S (either as incidental additions in P fertilizers before 1973 or from ammonium sulfate from 1993 on) with stream concentrations in the Kaskaskia and Embarras Rivers. This supports the result that declining atmospheric deposition is leading to the decline in stream water sulfate concentrations.

An interesting observation is that for both the Embarras and Kaskaskia watersheds, atmospheric deposition of S was much less than stream export, yet there was a clear and strong response to deposition in both watersheds. Sun et al. (2014) had a similar conclusion, where atmospheric deposition only accounted for about 20% of sulfate in stream water, the rest likely from the dissolution of gypsum or oxidation of pyrite. If we assume all deposition was transported in stream water during the 2004–2014 water years, 29 and 67% of the sulfate was from atmospheric deposition in the Embarras and Kaskaskia Rivers, respectively. It is likely the strong mineralogical control of sulfate in the Salt Fork and weaker control in the Embarras is due to the oxidation of pyrite. This eastern region of Illinois has long had coal mines based on the large resource present, although none is located in any of our studied watersheds (Louchios et al., 2013). However, it is still likely that the Salt Fork (and Spoon River in its lower reach) and northeastern part of the Embarras are receiving sulfate from oxidized pyrite commonly found with coal deposits, which are found at various depths throughout this area (Illinois State Geological Survey, 2015).

In the Kaskaskia and Embarras watersheds, with a predominantly agricultural land use, we measured a clear response in stream water sulfate to declining deposition of S. This was evident in both watersheds and was supported by the multiple regression model developed with data back to 1962 for the Embarras watershed. Declining sulfate in streams and lakes has been documented in the northeastern United States (e.g., Waller et al., 2012), but we are not aware of any studies in the midwestern United States that have evaluated streams draining agricultural watersheds. In some aspects this is surprising, given that deposition inputs are much less than outputs (grain harvest + riverine sulfate export), particularly for the Embarras watershed.

**Sulfur Balance in Agricultural Watersheds**

Our S balances in both the Embarras and Kaskaskia watersheds suggest much larger outputs than inputs. Given that the Embarras watershed has some contribution of sulfate from deep groundwater, the ~12.8 kg S ha⁻¹ yr⁻¹ balance in the Kaskaskia is likely more reflective of what the agricultural balance is with current deposition inputs. That the stream sulfate concentrations in the Kaskaskia River were also similar to tiles from fields with no history of S fertilizers is also supportive of this watershed having no other S sources. This suggests that current agricultural practices, with little S fertilization, are likely depleting soil S pools. Mollisols in these watersheds have large amounts of organic matter, where David et al. (2009) measured 175 Mg C ha⁻¹ in the top meter of 18 cultivated fields in similar soils of Illinois. Assuming a C/S ratio of 70 from Kirkby et al. (2011) or 85 from Dick et al. (2008), the S pool would be about 2000 to 2500 kg S ha⁻¹ in the top meter of soil. Most soil S is in organic forms (Eriksen, 2009), and it is likely that mineralized S is providing what the crop needs (Dick et al., 2008; Kim et al., 2013). Dick et al. (2008) estimated that a typical soil with a soil organic S turnover rate of 2% might release 5.3 kg S ha⁻¹ for each 1% of organic C in the top 20 cm. Soils in our watersheds typically have about 3% organic C in the top 20 cm, for a mineralization rate of 15.9 kg S ha⁻¹ yr⁻¹. This is about equal to the S balance in the Kaskaskia watershed (Table 1), suggesting that net mineralization of S from soil organic matter likely balances the observed net loss.

In the long-term, a net soil depletion of 12 to 16 kg S ha⁻¹ yr⁻¹ (about 0.6% of the soil S pool each year) is not sustainable, and corn and soybeans will likely respond to S fertilization at some point in the future, a conclusion also reached by Dick et al. (2008) in their review paper. Most S fertilization trials in Illinois have not found a response in corn and soybeans to S additions on fine-textured soils (Fernández et al., 2012). Some S deficiency symptoms have been documented on medium- and fine-textured soils in Minnesota and Iowa, however, suggesting that in soils low in organic matter and with little atmospheric deposition, crops will respond to S fertilization (Rehm, 2005; Sawyer et al., 2011). Sulfate concentrations in some of our monitored tiles were as low as 2 mg S L⁻¹ and may suggest fields where corn and soybeans responsiveness to S fertilization should be evaluated.

When S fertilizers or amendments containing S (bed ash, ammonium sulfate, manure) were added to fields in these watersheds, there was a rapid and large increase in soluble sulfate, and tile concentrations greatly increased. This likely also increased S availability to crop plants, although leaching and transport through tile drainage might limit how long the additional S is retained in these soils. A steady decrease in sulfate concentrations in tiles A and B was measured during the 5 yr after the addition of 319 kg S ha⁻¹ (Fig. 5). Tiles A and B had cumulative sulfate losses of 228 and 285 kg S ha⁻¹ for 2012–2015 (flow was not gaged in 2011), indicating that most of the added sulfate was lost through tile flow. However, there is some uncertainty about the amount of S in the bed ash that was added. The pattern of tile sulfate leaching is quite similar to chloride losses from these same tiles in response to potash additions, as discussed in David et al. (2016), and shows how rapidly soluble and poorly retained anions can be transported from agricultural soils through tile drainage systems. This also suggests that there is little available sulfate retention capacity in these soils.

**Conclusions**

Rivers draining two agricultural watersheds in the midwestern United States have responded to decreased atmospheric deposition of S, with clear decreases in sulfate concentrations. Both the Kaskaskia and Embarras watersheds, where deposition inputs were small compared with outputs (grain harvest + stream export), had declining riverine sulfate concentrations after decreases in atmospheric inputs. Sulfur balances indicate a net depletion of soil organic S pools in these agricultural watersheds. With increasing crop yields and continued S leaching via tile drainage, it is likely at some point in the future the dominant crops, corn and soybean, will respond to S fertilization.

**Acknowledgments**

The authors thank intern José Zavala for field sampling in the Spoon River watershed. This article is based on research partially supported by the National Institute of Food and Agriculture, USDA, under Agreement No. 2011-039568-31127, the National Atmospheric Deposition Program through HATCH Project ILLU-875-935, and the Energy Biosciences Institute.