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Silicate weathering and CO_2 consumption within agricultural landscapes, the Ohio-Tennessee River Basin, USA

S. K. Fortner[1], W. B. Lyons[2,3], A. E. Carey[3], M. J. Shipitalo[4], S. A. Welch[2,3], and K. A. Welch[2]

[1]Department of Geology, Wittenberg University, P.O. Box 720, Springfield, OH 45501, USA
[2]Byrd Polar Research Center, The Ohio State University, 1090 Carmack Road, Columbus, OH 43210, USA
[3]School of Earth Sciences, The Ohio State University, 125 South Oval Mall, Columbus, OH 43210, USA
[4]United States Department of Agriculture-Agricultural Research Service, P.O. Box 488, Coshocton, OH 43812, USA

Correspondence to: S. K. Fortner (sfortner@wittenberg.edu)

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Abstract. Myriad studies have shown the extent of human alteration to global biogeochemical cycles. Yet, there is only a limited understanding of the influence that humans have over silicate weathering fluxes; fluxes that have regulated atmospheric carbon dioxide concentrations and global climate over geologic timescales. Natural landscapes have been reshaped into agricultural ones to meet food needs for growing world populations. These processes modify soil properties, alter hydrology, affect erosion, and consequently impact water-soil-rock interactions such as chemical weathering. Dissolved silica (DSi), Ca^{2+}, Mg^{2+}, NO_3^-, and total alkalinity were measured in water samples collected from five small (0.0065 to 0.383 km^2) gauged watersheds at the North Appalachian Experimental Watershed (NAEW) near Coshocton, Ohio, USA. The sampled watersheds in this unglaciated region include: a forested site (70+ year stand), mixed agricultural use (corn, forest, pasture), an unimproved pasture, tilled corn, and a recently (<3 yr) converted no-till corn field. The first three watersheds had perennial streams, but the two corn watersheds only produced runoff during storms and snowmelt. For the perennial streams, total discharge was an important control of dissolved silicate transport. Median DSi yields (2210–3080 $kg\,km^{-2}\,yr^{-1}$) were similar to the median of annual averages between 1979–2009 for the much larger Ohio-Tennessee River Basin (2560 $kg\,km^{-2}\,yr^{-1}$). Corn watersheds, which only had surface runoff, had substantially lower DSi yields (<530 $kg\,km^{-2}\,yr^{-1}$) than the perennial-flow watersheds. The lack of contributions from Si-enriched groundwater largely explained their much lower DSi yields with respect to sites having baseflow. A significant positive correlation between the molar ratio of (Ca^{2+} +Mg^{2+})/alkalinity to DSi in the tilled corn and the forested site suggested, however, that silicate minerals weathered as alkalinity was lost via enhanced nitrification resulting from fertilizer additions to the corn watershed and from leaf litter decomposition in the forest. This same relation was observed in the Ohio-Tennessee River Basin where dominant landuse types include both agricultural lands receiving nitrogenous fertilizers and forests. Greater gains in DSi with respect to alkalinity losses in the Ohio-Tennessee River Basin than in the NAEW sites suggested that soils derived from younger Pleistocene glacial-till may yield more DSi relative to nitrogenous fertilizer applications than the older NAEW soils. Because silicate weathering occurs via acids released from nitrification, CO_2 consumption estimates based on the assumption that silicate weathers via carbonic acid alone may be especially over-estimated in fertilized agricultural watersheds with little baseflow (i.e. 67 % overestimated in the corn till watershed). CO_2 consumption estimates based on silicate weathering may be as much as 20 % lower than estimates derived from carbonic acid weathering alone for the Ohio-Tennessee River Basin between 1979–2009. Globally, this may mean that younger landscapes with soils favorable for agriculture are susceptible to fertilizer-enhanced silicate weathering. Increases in silicate weathering, however, may be offset by shifts in hydrology resulting from agricultural land management practices or even from soil silica losses in response to repeated acidification.

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1 Introduction

Human activities, which exert an ever-increasing influence on the Earth's surface, include altering the quantity and quality of our water resources and accelerating soil loss (Wagener et al., 2010; Wilkinson and McElroy, 2006). Changes in landuse activities, especially the conversion of pristine landscapes into agricultural ones, affects both the timing and magnitude of river flows and their water quality (Barnes and Raymond, 2009; Gordon et al., 2010, Gordon et al., 2008; Raymond et al., 2008). The conversion of natural into agricultural ecosystems has increased more than six-fold from the 1700s to the 1990s (Pongratz et al., 2008). This in turn has led to changes in hydrologic flow paths, increased erosion and soil loss, and enhanced fluxes of nutrients due to applications of fertilizer and manure (Turner and Rabalais, 2003, Zhang and Schilling, 2006). Conventional agricultural practices (e.g. tilling, removing crop residues, grazing) disturb the uppermost soil horizon, decrease infiltration and evapotranspiration and increase surface runoff (Gordon et al., 2008; Logan et al., 1991). Arable lands have depleted extractable silica with respect to forested landscapes, perhaps resulting from erosion of surface soil via tilling practices (Clymans et al., 2011). In the Scheldt River Basin, Europe, converting forested landscapes into long-term agricultural ones (>250 years) has decreased the baseflow export of total silica (i.e. dissolve and amorphous) to the ocean by two to three orders of magnitude (Struyf et al., 2010). This loss has been attributed to the erosion of the soil pool of amorphous silica, ultimately lowering silica released (Struyf et al., 2010). Yet the initial loss of amorphous silica from conversion to agricultural landuse sends a pulse of silica from soil into watersheds (Clymans et al., 2011). Earlier studies suggested that agricultural landuse alters water storage properties on the landscape potentially altering dissolved silica (DSi) yields (Collins and Jenkins, 1996; Conley et al., 2000; Jenkins et al., 1995). More work is needed to evaluate the response of silicate yields to changing landuse through both base and stormflow conditions. In addition, watersheds with different crop types, management practices and geologic characteristics need to be evaluated so that changes in silica yields with landscape alteration can be better constrained.

The relation between silicate weathering and agricultural landuse varies with the geologic characteristics. In western France, small-scale (<0.12 km^2) Paleozoic-aged granitic lithologies with tilled and manured agricultural fields had DSi yields similar to other non-agricultural temperate and tropical catchments (Pierson-Wickmann et al., 2009b). In the Chesapeake Bay, USA, elevated DSi concentrations were associated with increased cropland in the unconsolidated sand, clay, and gravel of the Coastal Plain, but not with the primarily crystalline lithologies in the Piedmont (Jordan et al., 1997; Liu et al., 2000; Weller et al., 2003). Agricultural landscapes in the crystalline gneiss, schist and calc-silicates in the Middle Hills of Central Nepal had elevations in base cations, silica, and fertilizer-associated ions with respect to their forested counterparts (Collins and Jenkins, 1996; Jenkins et al., 1995) and greater silicate weathering rates (West et al., 2002). While biology, hydrology, lithology, and soil age may be controls of silicate yields from croplands, yields may also relate to chemical weathering interactions with ongoing applications of chemical fertilizers and manure that generate acid via nitrification and to acid-neutralizing lime applications (Barnes and Raymond, 2009; Perrin et al., 2008; Pierson-Wickmann et al., 2009a, b). In the calcareous lithologies of southwest France, acid production from the application of acid-generating N-fertilizers has enhanced the rate of carbonate mineral weathering relative to forested landscapes (Perrin et al., 2008). In unlimed agricultural granitic catchments in western France, soil acidification has increased the export of basic cations and enhanced saprolite (i.e groundwater) weathering (Pierson-Wickmann et al., 2009a). The application of N-fertilizers in China has increased the export of H^+ more than an order of magnitude beyond that attributable to acid rain deposition (Guo et al., 2010). Although silicate mineral weathering via nitrification has not been calculated for agricultural landscapes, it has been shown that in some forested landscapes nitrification can enhance the weathering of silicates (Berthelin et al., 1985). It has been postulated that the addition of N-fertilizers may weather silicate minerals and hence, not release HCO_3^- as with weathering via carbonic acid (Barnes and Raymond, 2009) Therefore, calculations of CO_2 consumption associated with silicate mineral weathering must be carefully made in the presence of fertilizers.

Between 1953 and 2001 bicarbonate fluxes in the Mississippi River have increased (Raymond and Cole, 2003; Raymond et al., 2008). This observation, coupled with an increase in discharge not associated with increased precipitation, has been postulated to result from an increase in cropland relative to forested areas (Raymond et al., 2008). During approximately the same time period, there was no increase in the flux of DSi to the Mississippi River, and no relation found between percent cropland and DSi (Donner, 2003; Goolsby et al., 1999). In North America, increases in bicarbonate alkalinity are primarily attributed to agricultural liming practices (Moosdorf et al., 2011a, Oh and Raymond, 2006; Raymond et al., 2008; West and McBride, 2005). Increases may also relate to greater plant productivity releasing organic acids and CO_2 that in turn increases soil weathering rates (Raymond and Cole, 2003). In the Ohio River Basin, watersheds with >5 % agricultural area exported more than 3.4 times the HCO_3^- compared to those with <5 % agricultural area (Barnes and Raymond, 2009; Oh and Raymond, 2006). While inorganic carbon exports are clearly tied to chemical applications (liming) more work is needed to understand the influence of fertilizer applications. The overall lack of correlation between DSi and NO_3^- observed throughout the Mississippi River Basin (Goolsby et al., 1999) may be reflective of the distinct interrelation between added fertilizers with varying subbasin lithologies or hydrological alteration.

Our objective was to evaluate the role of agricultural landuse practices on silicate weathering by focusing on very small watersheds. This included examining the influence of landuse on hydrology and silicate weathering and examining potential silicate weathering via N-fertilizers and manures. We did not distinguish between abiotic (e.g. mineral weathering only) and biotic (e.g. stored and released from plants) silicate pools. Small watersheds ($<0.39\,km^2$) with distinct landuse types were selected for this study including forest, tilled corn and no-till corn, unimproved pasture, and mixed landuse including one-third tilled corn. An initial goal was to evaluate whether till versus no-till practices generate distinct silicate weathering yields and how these yields compared with other landuse types. Hydrologic distinctions between landuse types were evaluated along with DSi yields. Another goal of this study was to estimate the potential affects of N-fertilizer applications on silicate weathering rates. This required an examination of losses of alkalinity, or increases in the (Ca^{2+}+Mg^{2+})/alkalinity ratio, along with calculating silicate weathering via nitrification using median DSi and NO_3^- concentrations. To understand hydrochemical controls of silicate weathering on agricultural land, our findings from NAEW watersheds were compared to results from the Ohio-Tennessee River Basin ($526\,000\,km^2$). For all sites, annual DSi yields and CO_2 related to silicate weathering were evaluated; this included a subtraction of DSi associated with ammonium in fertilizer generating nitric acid.

2 Site description

2.1 North Appalachian Experimental Watershed (NAEW), Ohio

The small watershed experimental sites were selected from long-term hydrological monitoring sites at the United States Department of Agriculture- Agricultural Research Service (USDA-ARS) NAEW at 40°22′ N and 81°41′ W near Coshocton, Ohio, USA (Fig. 1). These watersheds were established in the 1930s and have well-documented land management histories (Owens et al., 2010, 2008). This region of southeastern Ohio was not glaciated during the Pleistocene epoch, and consists of shallow, well-drained residual soils with silt loam surfaces derived from Pennsylvanian-aged shales and interbedded sandstones (Kelley et al., 1975; Owens et al., 2008). High-resolution modeling of geology and DSi yields in United States suggests that sedimentary rocks (both carbonaceous and siliciclastic) release the greatest amount of DSi with respect to other lithologies (Jansen et al., 2010). The NAEW soils are predominantly comprised of aluminosilicates and contain less than 5 % carbonates (Eckstein et al., 2007). Geochemical modeling indicates

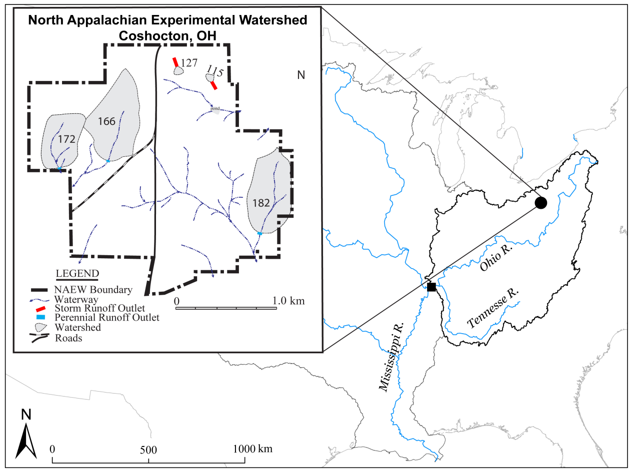

Fig. 1. Map of the USDA North Appalachian Experimental Watershed (NAEW) watersheds, Ohio, shown with respect to the Ohio-Tennessee River subbasin of the Mississippi-Atchafalaya River Basin. NAEW watersheds include: WS 115 Corn No-Till, WS 127 Corn Till, WS 166 Mixed-Use, WS 172 Forest, and WS 182 Unimproved Pasture.

soil waters are supersaturated with respect to kaolinite, illite, and gibbsite, however groundwaters are undersaturated with respect to these phases (Eckstein et al., 2007). Calcite and dolomite, however, were undersaturated in both soil and groundwaters though are important to precipitation acid-neutralization (Eckstein et al., 2007).

The size, present landuse, and total mineral N and manure applications onto each sampled watershed between 1980–1999 and 2000–2009 are shown in Table 1. Lime ($CaMgCO_3$-dolomite), K and P mineral applications are not detailed in this study, whether the sites had these applications or not. Since 2008, watershed (WS) 115 has been a no-till corn with applications of inorganic N-fertilizers and N-rich manure and throughout its 70-year history. WS 127 has been a disk-tilled corn watershed since 2006 and has had N-fertilizer and manure applications throughout its 70-year history. Of the two corn watersheds examined, WS 127 has a steeper slope than WS 115. Slopes range from 2–18 % in WS 127 compared to 2–12 % in WS 115 (Kelley et al., 1975). WS 166 is a mixed-landuse site that rotates among pasture, tilled corn, and hay, and portions have been grazed continually since 1976. Additionally, one-third of WS 166 is forested, with trees surrounding part of the stream channel. This site has also had ongoing N-mineral applications, but no manure has been applied. Like WS 166, WS 182 has been grazed for more than 30 years. There have been no chemical applications to this watershed in the last 40 years (Table 1). WS 172 has been forested for more than 70 years with no chemical applications. Prior to reforestation, WS 172 was <30 % forested and mostly composed of pasture and, to a lesser extent, abandoned farmland. This watershed is also the steepest of the watersheds examined, with slopes typically more than 15 %. Sites 166, 172, and 182 have permanent streams associated with them and hence have baseflow. The two corn watersheds, WS 115 and 127, only have overland flow during storm runoff.

2.2 The Ohio-Tennessee River Basin

The NAEW sites are part of the larger Ohio-Tennessee River Basin (Hydrologic Unit 03612500, The Ohio River at Dam 53 near Grand Chain, Illinois), which covers an area of $\sim$526 000 km^2 and flows into the Mississippi River Basin at 37°12′ N, 89°02′ W (Fig. 1). Three-quarters of the total discharge in the Ohio-Tennessee River Basin is from the Ohio River (Oh and Raymond, 2006). Furthermore, the Ohio-Tennessee River Basin contributed between 33 and 57 % of the total annual flow of the Mississippi-Atchafalaya River Basin between 1979 and 2005 (calculated from Aulenbach et al., 2007).

Oh and Raymond (2006) report that landuse for the Ohio River Basin is primarily forest and agriculture (croplands and pasture and range) with reductions in croplands with respect to pastures occurring in recent decades. Monthly and annual nutrient loads have been calculated for the Mississippi River Basin and its subbasins as a part of this long-term monitoring program to understand hypoxia in the Gulf of Mexico (Aulenbach et al., 2007). The heavily fertilized Ohio-Tennessee River Basin has a higher average nitrate yield (505 $kg\,km^{-2}\,yr^{-1}$) compared to the entire Mississippi-Atchafalya Basin (300 $kg\,km^{-2}\,yr^{-1}$) (Turner and Rabalais, 2004). DSi contributions to the Mississippi-Atchafalaya are high relative to discharge for the Ohio-Tennessee River Basin compared with other major tributaries to the Mississippi River (Aulenbach et al., 2007; Goolsby et al., 1999). The geology of the Ohio-Tennessee River Basin is primarily Paleozoic in age and sedimentary in composition, dominated by lithologies include dolomite, limestone, dolostone, shale and siliclastic rocks (King et al., 1974). A new high-resolution study of the United States shows that both carbonaceous and siliclastic sedimentary lithologies are responsible for yielding substantial DSi (Jansen et al., 2010). While these sedimentary lithologies are distinct in their mineralogy, they both yield similar rates of DSi per unit flow (Moosdorf et al., 2010). Yet the northwestern one-fifth of the Ohio-Tennessee River Basin is overlain by till of mixed lithologies from the Wisconsinan and pre-Illinoian Glaciations and these recently glaciated areas have correspondingly younger soils that are more readily weathered than older landscapes (Buol et al., 1997; Oh and Raymond, 2006).

3 Methods

Water samples were collected from mixed use, forested, and unimproved pasture (watersheds 166, 172, and 182) one to three times a month during October 2008–February 2010. Sampling from these sites occurred primarily during baseflow. Because the two corn watersheds, WS 115 and WS 127, have no baseflow, they were sampled only during storm runoff. Runoff from these sites was collected during December 2008–February 2010. Grab samples were manually collected immediately below the weirs at the perennial flow sites, while flow-proportional samples were automatically collected from the sites with only runoff using Coshocton Wheel samplers immediately below H flumes (Brakensiek et al., 1979). These hydrologic measurements can be used to understand instantaneous discharge as well as total storm volumes. Stormflow volumes were estimated for sites with baseflow (WS 166, WS 172, WS 182) by subtracting the amount of baseflow from the total flow.

Sample collection bottles were 1 liter Nalgene® low-density polyethylene (LDPE) bottles that had been rinsed with deionized water (DIW) prior to use. Upon return to the laboratory at The Ohio State University, aliquots were separated for chemical analyses. Approximately 30 ml of each sample was filtered through a 0.4 µm Nuclepore® filters into DIW-rinsed 60 ml LDPE bottles to analyze for dissolved silica (DSi). DSi was analyzed colorimetrically using a Skalar San++ Continuous Flow Analyzer® and the molybdenum blue method. Major cations and anions in filtered samples were analyzed using a Dionex 120 Ion Chromatograph® and the methods described in Welch et al. (1996). We report only Ca^{2+}, Mg^{2+}, and NO_3^- here. All concentrations were more than three times instrument detection limits. Major ion concentrations in NAEW stream samples were corrected for the concentrations found in precipitation by subtracting the 2009 annual precipitation concentration averages measured at Delaware, Ohio, as part of the National Trends Network in the National Atmospheric Deposition Program (NADP, 2010). A subtraction was performed rather than normalizing the data based on ratios to a conservative constituent recognizing that the agricultural fields had cation and anion additions from fertilizers (e.g. K^+ and Cl^- from potash). Additionally, non-fertilizer associated SO_4^{2-} is associated with pyrite weathering from a coal seam in the groundwater and not the surface soil region (Eckstein et al., 2007). Precision of DSi and NO_3^- measurements was better than 5 % based on standards run as samples and replicate samples. Total alkalinity was measured in triplicate by titration using Hach© Method 8203 (Hach, 2008). All three measurements were within 10 % of their mean concentration. Based on the circumneutral pH of these waters, we assume that alkalinity is approximately equivalent to the bicarbonate concentration.

Specific discharge, discharge normalized to area, was determined to compare between watersheds. The differences in hydrology and DSi yields among NAEW watersheds were evaluated using the procedures outlined as following. Total and cumulative storm flows (i.e. baseflow subtracted) were compared to evaluate the hydrologic distinctions among watersheds. DSi yields were compared among all watersheds

Table 1. Watershed area, landuse during study period, N-fertilizer and manure applications* during 1980–1999 and 2000–2009 for NAEW watersheds.

Watershed	Area (km^2)	Landuse	N Fertilizer Application ($kg*10^3\ km^{-2}$)	Manure Application ($kg*10^3\ km^{-2}$)
			1980–1999: 139.1	1980–1999: 5400 (40 loads)
115	0.0065	No-till Corn	2000–2009: 54.7	2000–2009: 1600 (12 loads)
			1980–1999: 48.2	1980–1999: 4700 (36 loads)
127	0.0067	Disk-tilled Corn	2000–2009: 70.2	2000–2009: 4000 (31 loads)
		Grazed	1980–1999: 490.7	None
166	0.321	Pasture/Corn/Forest	2000–2009: 104.8	
172	0.177	Forest	None	None
		Grazed Unimproved		None
182	0.383	Pasture	None	None

*Manure mass is estimated from number of loads and may vary due to differences in water saturation.

with baseflow and the two corn sites with stormflow only. For the watersheds with perennial streams, DSi yields were calculated on a per storm basis by multiplying total storm discharge by the associated measured concentration and dividing by the watershed area. For the stormflow only watersheds, DSi yields were calculated based on instantaneous discharge by multiplying instantaneous discharge by the associated measured concentration and dividing by the watershed area. Annual DSi yields could then be calculated for all watersheds based on their relation to specific discharge (storm and instantaneous) and the associated linear regression. These yields were compared to yields from the Ohio-Tennessee River Basin calculated from USGS area-normalized load estimates (Aulenbach et al., 2007). The USGS loads used for this calculation were determined using USGS LOADEST that uses daily element concentrations and flow data to determine their relation and selects a best-fit model to approximate annual loads (Runkel et al., 2004).

Comparisons were made to assess the relation between silicate weathering and losses of alkalinity [increasing molar ratio of (Ca^{2+}+Mg^{2+})/alkalinity] potentially associated with application of nitrogenous fertilizers (Barnes and Raymond, 2009). This relation and the relation of median DSi concentrations to median NO_3^- concentrations, was used to understand silicate weathering behavior for the NAEW watersheds and the Ohio-Tennessee River watershed. The Ohio-Tennessee River Basin DSi, NO_3^-, total alkalinity, Ca^{2+}, and Mg^{2+} data were retrieved from a USGS database, http://waterdata.usgs.gov/nwis, all of these constituents were available for 1959–1962, and 1985–2010. For NAEW sites and the Ohio-Tennessee River Basin maximum CO_2 consumption from silicate weathering was calculated based on the assumption that silicate minerals were weathered by carbonic acid releasing silicic acid (i.e. DSi) (Berner, 1995). Additionally, minimum CO_2 consumption from silicate weathering was calculated assuming that all NO_3^- resulting from nitrification went toward weathering silicate minerals. For this calculation, only the DSi not weathered by NO_3^- is associated with carbonic acid weathering and hence CO_2 consumption.

4 Results

4.1 NAEW area-normalized flow conditions

All watersheds experienced their highest total monthly flows in December through March (Fig. 2a) with almost no storm flow in May, June, July, and August (Fig. 2b). Results from an ANOVA two-factor test without replication revealed that the forested watershed (WS 172) and the mixed land use (WS 166) and unimproved pasture site (WS 182) did not all have statistically similar average monthly flow and monthly flow variation ($\propto = 0.05$, $p = 0.0296$, $F = 5.86$, $F_{crit} = 4.60$). Cumulative differences between total flow and stormflow only were compared throughout the entire sample period (Fig. 3). Total cumulative flow for perennial streams (WS 166, WS 172, WS 182) were more than 25 % greater than the tilled corn (WS 127) and more than double the total flow observed in the no-till corn (WS 115) during the 14-month sampling interval. Overall the tilled corn, WS 127, had the highest cumulative storm flow (252 mm) during our sampling period. In fact, its cumulative storm flow was more than six times greater than the forested WS 172 (42 mm). More than 87 % of the flow from the forested watershed occurred as baseflow. The cow-trampled, unimproved pasture, WS 182, had the second highest cumulative storm flow (139 mm) followed by the no-till corn, WS 115 (115 mm). In WS 182, 67 % of the total cumulative flow occurred as baseflow. Mixed landuse WS 166 had total cumulative storm flow (76 mm) more similar to the no-till corn (WS 115) than the forested (WS 172). However, unlike the corn (WS 115), most (77 %) of the cumulative flow in WS 166 was from baseflow.

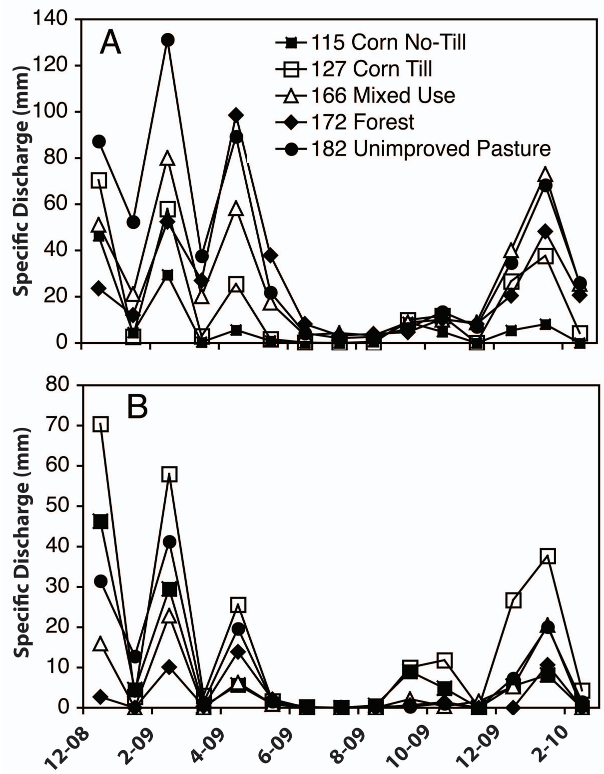

Fig. 2. Specific discharge (mm) by month for **(A)** total flow and **(B)** stormflow from December 2008–February 2010 for NAEW watersheds.

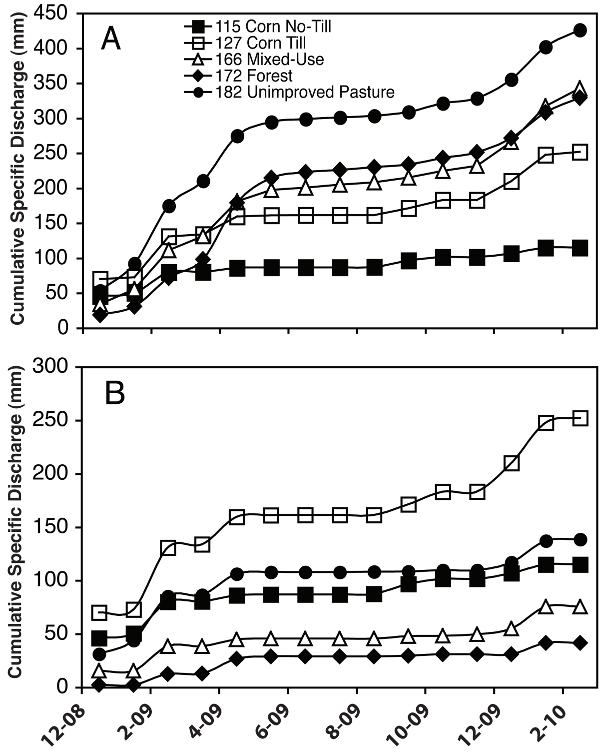

Fig. 3. Cumulative specific discharge (mm) for **(A)** total flow and **(B)** stormflow from December 2008–February 2010 for NAEW watersheds.

Because the tilled corn (WS 127) had more than twice the cumulative stormflow of the no-till corn (WS 115), it was necessary to consider whether those differences were driven by the differences in tillage. Relative differences in runoff from WS 115 compared to WS 127 have not changed noticeably since WS 115 was converted no-till in 2008 (Fig. 4). This may suggest that a response to tillage practices had not yet occurred.

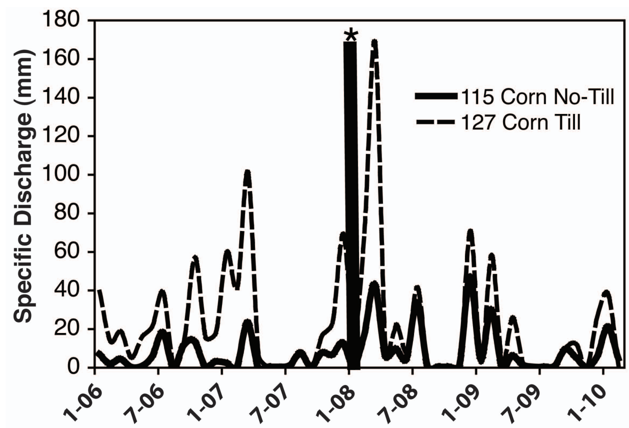

Fig. 4. Monthly discharge (mm) for corn watersheds 115 and 127 during January 2006–February 2010. WS 115 becomes no-till watershed in 2008.

4.2 Dissolved Si yields for NAEW sites

DSi yields for the two corn watersheds are compared with specific discharge (Fig. 5). For both watersheds, a two-tailed t-test shows that DSi yields have a significant positive correlation ($\propto = 0.05$) with specific discharge (WS 115: $n = 18$, $r = 0.877$, $p < 0.01$; WS 127: $n = 21$, $r = 0.767$, $p < 0.01$). Overall the tilled corn (WS 127) had greater specific discharge and higher mean DSi yields than did the no-till corn (WS 115). For both watersheds, the storm yielding the highest DSi was not associated with the greatest storm discharge. There was more variation between discharge and in DSi yield for WS 127 than WS 115. For both sites, however, the overall relation of DSi with discharge suggested that changes in flow control relative DSi yields.

Samples from perennial flowing streams in WS 166, WS 172, and WS 182 were collected as grab samples and so only instantaneous DSi yields were calculated for these sites (Fig. 6). As with the proportional flow samples from the two corn watersheds, instantaneous DSi yields increased with discharge. To compare among all sites, the DSi yields were divided by specific discharge to calculate the average DSi

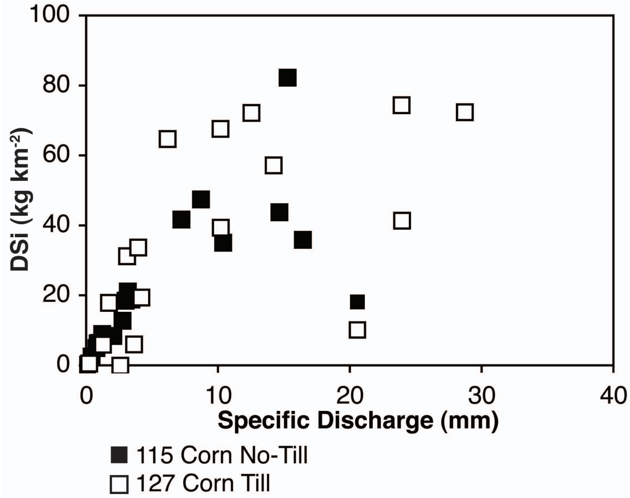

Fig. 5. Dissolved silica yields from corn watersheds 115 and 127 for individual storms plotted with specific discharge (mm) associated with individual storms.

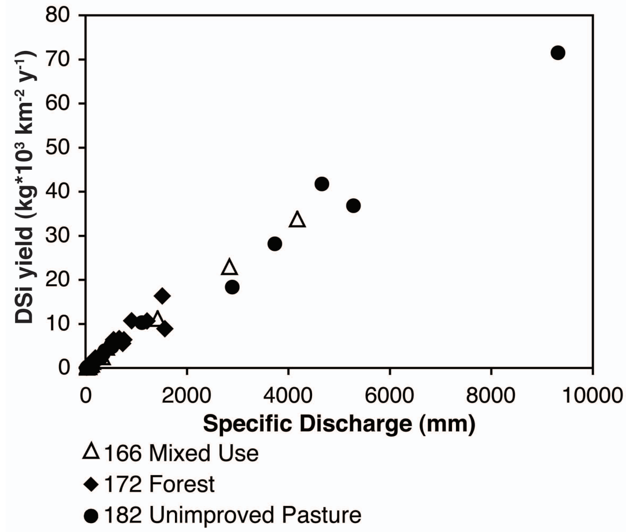

Fig. 6. Dissolved silica yields for discreet sampling events from WS 166, WS 172, and WS 182 plotted with instantaneous annual specific discharge (mm).

per mm of flow each year (Table 3). The two cornfields with no baseflow had DSi yield to specific discharge ratios (0.057, 0.052 kg mm^{-1} a^{-1}) that were less than the other sites ($\geq$0.080 kg mm^{-1} a^{-1}). A chemical mass balance performed using yields from both cornfields and all perennial sites showed that DSi yields are 39–50 % lower in stormflow (i.e. surface runoff) than in baseflow. This means that DSi yields from the two corn watersheds are as much as 37 % lower than the forested site per mm of flow.

4.3 DSi in relation to chemical applications in the NAEW and in the Ohio River Basin

NAEW sites with liming applications also had applications of mineral N-fertilizers and N-rich manure. The relations among Ca^{2+}+ Mg^{2+}, DSi, NO_3^-, and alkalinity can be used to illustrate how agricultural chemical applications can affect silicate weathering. In the tilled corn watershed (WS 127), the range of Ca^{2+} and Mg^{2+} concentrations was similar to the no-till corn watershed (Table 2). DSi had a greater range 0.1–180 µM in the tilled corn and the maximum NO_3^- concentration (3120 µM) was more than an order of magnitude greater than the maximum observed in the no-till watershed (110 µM). Median concentrations of DSi were slightly lower (<104 µM) in the stormflow only corn watersheds (WS 115, WS 127) than in the watersheds with perennial streams (>131 µM).

5 Discussion

5.1 Hydrology of agriculturally managed landscapes

Of the NAEW watersheds studied, the agriculturally managed watersheds generated far more storm runoff per area than the forested watershed. Of the perennial stream sites, the forested watershed had the least stormflow, suggesting a higher percentage of recharge. The lack of hydrologic difference after the conversion of WS 115 from a tilled corn to a no-till corn watershed is likely because in only 2 years, this site had not yet developed well-defined macroporosity and soil structure associated with some long-term no-till practices. Conversion of agricultural practices does not always result in immediate shifts in soil conditions that affect hydrologic routing (Johnson-Maynard et al., 2007). Given that all of the investigated land management types are found in similar soils, the present hydrologic differences between these two corn watersheds may be related to differences in their slopes. Most of WS 115 has a slope between 2 and 6 %, with a maximum of 12 %, while most of WS 127 had a slope between 6 and 18 % (Kelley et al., 1975). Runoff typically increases in croplands with greater slopes (Ekholm et al., 2000). Slope, however, does not explain major differences among croplands and forested watersheds, because the forested WS 172 had the steepest slope, but the lowest cumulative runoff. Greater precipitation interception, effective soil cover, and improved infiltration generally reduce runoff in forested areas with respect to altered landscapes, especially during more intense storms (Calder, 1992; Fohrer et al., 2001). Activities like grazing and tilling reduce infiltration

Table 2. Ranges and (median) concentrations of DSi, NO_3^-, Ca^{2+}, Mg^{2+}, and Alkalinity. The number of samples (n) only include those that were collected for all constituents on the same dates throughout the October 2008–February 2010 sample period.

Watershed	n	DSi (µM)	NO_3^- (µM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Alkalinity* (mM)
WS 115	13	36–123 (92)	9–110 (38)	0.06–0.36 (0.29)	0.09–0.38 (0.26)	0.51–1.15 (0.86)
WS 127	13	0.1–180 (103)	3–3120 (189)	0.12–0.93 (0.42)	0.13–1.01 (0.45)	0.61–3.93 (1.11)
WS 166	11	106–171 (132)	8–155 (41)	0.13–1.23 (0.51)	0.14–0.96 (0.39)	0.53–2.55 (1.25)
WS 172	14	27–199 (148)	0.1–47 (15)	0.10–1.20 (0.46)	0.10–0.61 (0.26)	0.34–3.83 (0.89)
WS 182	12	89–162 (132)	0.8–125 (22)	0.26–1.06 (0.67)	0.14–0.50 (0.24)	0.38–2.00 (0.73)

*Alkalinity estimated as equivalent to HCO_3^-.

and increase surface runoff (Asner et al., 2004; Gilley et al., 1996; Gordon et al., 2008; Logan et al., 1991).

5.2 The relation of silicate weathering to hydrology and its implications

Chemical fluxes in agriculturally managed landscapes are largely related to surface applications (e.g. liming, fertilizer and manure applications), but are controlled primarily by changes in discharge (Basu et al., 2010; Raymond et al., 2008). Similarities between DSi yields and flow for all perennial watersheds (i.e. forests and mixed use) suggested that small differences in relative contributions of storm or base flow do not affect DSi yielded per equivalent discharge. The perennial NAEW watersheds had between 67 and 87 % baseflow contributions. The stormflow only corn watersheds had DSi yields that were as little as two-thirds of the DSi yield from the perennial flow sites (Table 3). This is consistent with previous findings from across the United States where mean stream DSi concentrations (baseflow+stormflow) were 18 % less than mean groundwater DSi concentrations (Davis, 1964). Similarly, DSi loads were lower in less permeable coastal watershed in North Carolina, USA, that had lower baseflow contributions than in the adjacent watershed with more permeable cover (Loucaides et al., 2007). Total flow recorded at the Ohio River at Metropolis, Illinois (∼30 km upstream from the downstream-most Ohio-Tennessee River Basin station at Grand Chain, Illinois) increased by 9.2 % during 1940–2003, with approximately proportional increases in both base and storm flow (Zhang and Schilling, 2006). Overall shifts in Ohio River DSi yields through this time period are unlikely to have a strong relation to changes in percent baseflow. An Anova Two Way statistical test performed without replication revealed that mean DSi loads normalized to flow were not statistically different ($\alpha = 0.05$, $p < 0.05$) for the Ohio-Tennessee River Basin for each three decadal ranges of sampling (1980–1989, 1990–1999, 2000–2009) (calculated from Aulenbach et al., 2007). Other tributaries of the Mississippi River, however, have experienced appreciable increases in relative baseflow contributions (Zhang and Schilling, 2006).

Table 3. Mean DSi yield (kg km^{-2} yr^{-1}) divided by specific discharge (mm km^{-2}) for NAEW watersheds to calculate average annual DSi yield per mm flow, n = number of samples.

Site	n	Ratio (kg mm^{-1} yr^{-1})
WS 115 Corn No-Till	18	0.057
WS 127 Corn Till	21	0.052
WS 166 Mixed-Use	14	0.080
WS 172 Forested	15	0.091
WS 182 Unimproved Pasture	20	0.090

For example, total annual streamflow in the Cedar River at Cedar Rapids, Iowa increased by more than 100 % between 1940 and 2003 in response to greater baseflow resulting from the conversion of seasonal vegetation to annual vegetation (i.e. soybeans) (Zhang and Schilling, 2006). Similarly, the Iowa River at Wapello, Iowa (05465500), which is fed primarily by the Cedar River, experienced mean decadal flow increases of >40 % during 1980–1990 and 1990–2000 while DSi yields increased by > 90 % (calculated from Aulenbach et al., 2007). Such DSi increases suggest that landuse conversions altering hydrologic pathways are a major influence of silicate-weathering rates. Low mechanical weathering, however, can be associated with lower DSi concentrations (Roy et al., 1999).

Landuse also influences the amount of silica taken-up and returned to the landscape by biomass (Alexandre et al., 1997; Derry et al., 2005; Sommer et al., 2007) and in agricultural landscapes some silica could exit the system with the removal of the crops. In the Hubbard Brook Experimental Forest DSi yields increased for up to 20 years after forest harvesting and the decay of associated remains (Conley et al., 2008). Hence, in the NAEW sites, with more time and further hydrologic evolution there could be greater differences in overall DSi yields between distinct landuse types. Future runoff projections have already been projected to increase DSi yields throughout North America by 12.8 % (Moosdorf et al., 2011b). It is unclear how these projections for DSi yields might be affected by increased agricultural landuse. What is known is that long-term (>250 years) agricultural sites in the Scheldt watershed have substantially lower baseflow yields of silica (mostly DSi) than long-term forested sites (Struyf et al., 2010). Our study, therefore, suggests the importance of evaluating silica yields through varying time scales and through both base and stormflow conditions. Losses in baseflow yields of Si in croplands may be balanced by gains in Si weathered by fertilizers in surface runoff.

5.3 Effects of nitrogen fertilizer/manure applications on silicate weathering

Of the NAEW agricultural watersheds, only the tilled corn had significant positive correlation between (Ca^{2+} + Mg^{2+})/alkalinity and DSi (Fig. 7). This, coupled with the overall greater concentrations of NO_3^- in the tilled corn (WS 127) with respect to other agricultural watersheds, may be indicative of NH_4^+ enhanced weathering of silicates (Eq. 1) and carbonate minerals (Eq. 2) as a result of nitrification of N fertilizers (Barnes and Raymond, 2009).

$$2NH_4^+ + 4O_2 + CaSiO_3 -> 2NO_3^- + H_2O + Ca^{2+} + H_4SiO_4 + 2H^+ \quad (1)$$

$$NH_4^+ + 2O_2 + CaCO_3 -> NO_3^- + H_2O + 2Ca^{2+} + 2HCO_3^- + H_2O \quad (2)$$

In soils, NH_4^+ in nitrogeneous fertilizer and manure produces protons (H^+) that can oxidize silicate minerals and release base cations and silicic acid (H_4SiO_4) from silicate minerals.

Furthermore, HCO_3^- released from soil and lime weathering is titrated via H^+ thereby releasing CO_2 into the atmosphere. This results in losses of alkalinity with respect to base cations (Berthelin et al., 1985; Gandois et al., 2011; Perrin et al., 2008). Losses of alkalinity have been evaluated previously by examining the relationship between Ca^{2+} + Mg^{2+} and alkalinity (Barnes and Raymond, 2009; Perrin et al., 2008). When losses occur, the (Ca^{2+} + Mg^{2+})/alkalinity ratio increases (Barnes and Raymond, 2009). Specifically, ammonium oxidation leads to the weathering of silicate and carbonate minerals and the generated acid transforms bicarbonate into CO_2 (Barnes and Raymond, 2009). To understand the relation between silicate weathering and weathering associated with losses of alkalinity due to nitrification released acid, (Ca^{2+} + Mg^{2+})/alkalinity ratios were plotted versus DSi concentrations for all watersheds (Fig. 7). Only the forested (WS 172) and tilled corn (WS 127) have a significant positive correlation (α=0.05, $p < 0.05$) between (Ca^{2+} + Mg^{2+})/alkalinity ratios and DSi (Fig. 7). The (Ca^{2+} + Mg^{2+})/alkalinity ratio also had a significant positive correlation (α=0.05, $p < 0.05$) with DSi in the Ohio-Tennessee River Basin.

As with the tilled corn site (WS 127) the forested location (WS 172) had a significant positive linear relation between (Ca^{2+} + Mg^{2+})/alkalinity versus DSi. In the corn watershed, this is likely to related to nitrogenous fertilizer applications as described above. The response in the forested site, however, may be indicative of other processes enhancing nitrification-released acids. For example, leaf litter decomposition has been shown to enhance nitrification-associated silicate weathering in mature temperate forests (Berthelin et al., 1985). The relation between nitrification and chemical weathering in forested sites probably depends on the dominant tree cover and resulting litter decomposition. In the Pacific Northwest enhanced nitrification occurred beneath a 50 year-old stand of red alder, which generated greater exchangeable cation loads than a neighboring Douglas fir stand with lower rates of nitrification (Van Miegroet and Cole, 1984). As mentioned, deforestation at Hubbard Brook Experimental Watershed in New Hampshire, USA resulted in short–term increases in the export of DSi (Conley et al., 2008), at the same time rates of denitrification increased (Likens, 2004). Therefore, it is possible that denitrification processes in forested sites also enhance silicate weathering.

DSi concentrations in the Ohio-Tennessee River Basin also had a significant positive relation with (Ca^{2+} + Mg^{2+})/alkalinity. The geochemical similarity between the larger basin and the tilled NAEW corn field and forested watershed is not surprising considering that the Ohio-Tennessee River Basin is dominantly composed of agricultural lands and forests (Oh and Raymond, 2006). The distinction is that the weathering of DSi occurs at a slightly (∼10 % and 30 %) greater rate with respect to losses of alkalinity in the Ohio-Tennessee River Basin than in the NAEW corn and forested watersheds, respectively. While this may relate somewhat to differences in sampling strategies and/or scale, it likely also relates to differences in landscape age. The NAEW watersheds overlie Paleozoic-aged sediments similar to much of the Ohio-Tennessee River Basin but the NAEW sites are not overlain by Pleistocene glacial till. Unglaciated portions of Ohio, including where the NAEW is located, have soils depleted in exchangeable cations with respect to their younger counterparts derived from recent glacial till (Buol et al., 1997). N-fertilizers may have a greater impact on silicate weathering rates in the younger soils and lithologies in the Ohio-Tennessee River Basin. Chemical weathering rates are related to landscape age (Riebe et al., 2004) and laboratory experiments suggest not simply mineral dissolution (White and Brantley, 2003). Soils derived from the young glacial moraines have greater weathering rates than older landscapes (Taylor and Blum, 1995). In the Chesapeake Bay region, increases in silicate weathering in croplands relative to non-croplands were found in the Coastal Plain but no trends were observed in the Piedmont (Liu et al., 2000). Landscape age, and hence previous exposure to weathering agents, may explain this as Coastal Plain sediments were derived from Pleistocene glacier flooding and ocean uplift, while the Piedmont is much older and ranges from Proterozoic to Paleozoic in age.

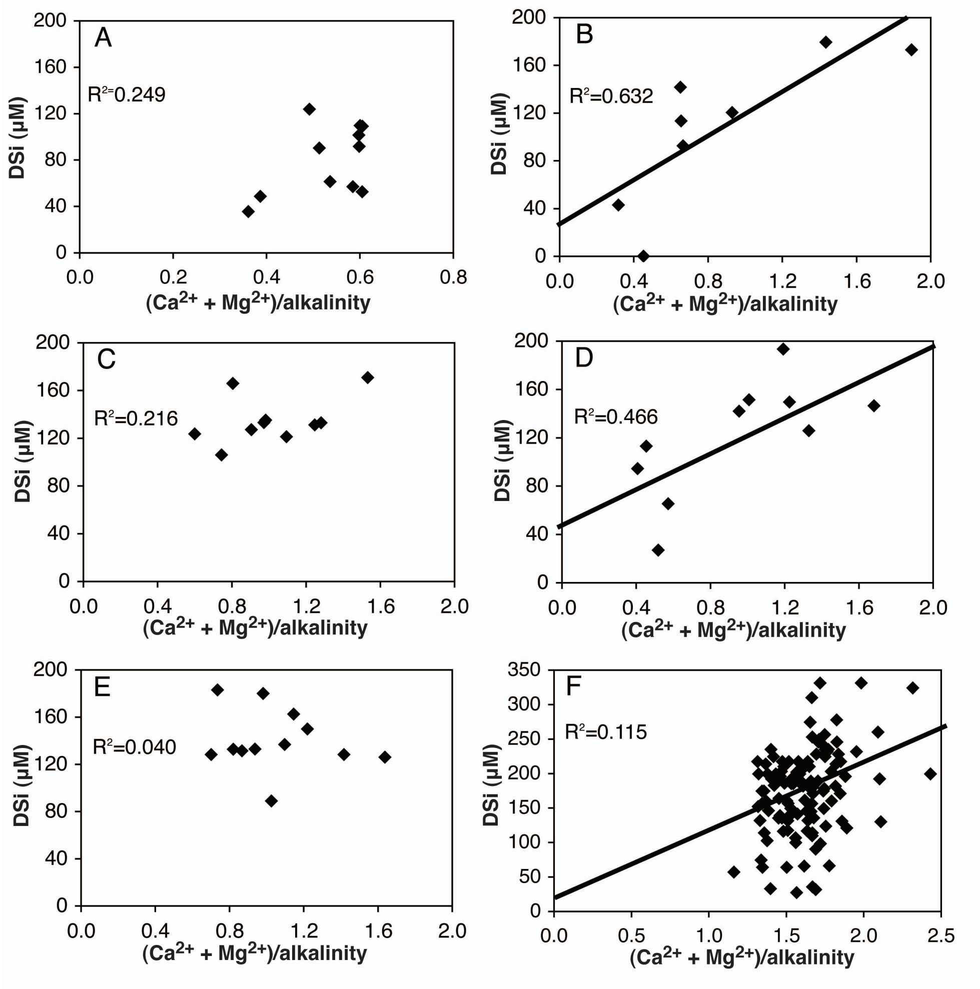

Fig. 7. (Ca^{2+}+ Mg^{2+})/alkalinity molar ratios vs. DSi concentrations for NAEW watersheds: **(A)** 115 Corn No-Till, **(B)** 127 Corn Till, **(C)** 166 Mixed-Use, **(D)** 172 Forest, **(E)** 182 Unimproved Pasture, and **(F)** the Ohio-Tennessee River Basin. Significant (α = 0.05) linear correlations are shown with a black line.

There was greater variability in DSi concentrations observed in the Ohio-Tennessee River Basin than in the NAEW sites (Fig. 7). This might be related, in part, to the greater number of samples or greater time span of sampling for the Ohio-Tennessee River Basin, thus affecting the magnitude of hydrogeochemical response. Yet, the large-scale of the Ohio-Tennessee River Basin may be subject to greater biogeochemical processing than observed at smaller scale. For example, throughout the Mississippi River Basin and its major tributaries diatom production, which affects the uptake of both DSi and NO_3^-, may be enhanced upstream of dams (Goolsby et al., 1999). Spatial and temporal variations in spring rainfall might also affect N-leaching from agricultural watersheds (Donner and Scavia, 2007) and hence the interaction of N with silicate minerals. Furthermore, some soils within the larger watershed might have greater sensitivity to other acids, like sulfuric, delivered via fossil fuel burning. However, in spite of these scaling differences, both the small-scale NAEW sites and the Ohio-Tennessee River suggest that nitrogenous fertilizer applications are important to the weathering of silicate minerals.

5.4 Silicate weathering yields and CO_2 consumption

The weathering of silicate minerals regulates atmospheric CO_2 concentrations and global temperatures over geologic timescales (Berner, 1995; Raymo and Ruddiman, 1992; Walker et al., 1981). Enhanced rates of silicate weathering by carbonic acid decrease atmospheric CO_2 concentrations and, hence cooling occurs from lowered greenhouse gas effects. Little work has examined silicate weathering or the associated CO_2 consumption associated with agricultural land management (Liu et al., 2000; West et al., 2002). Yet, understanding the affects of landscape alteration on silicate weathering rates is critical to evaluating the role of human activities on the global biogeochemical cycles of silica and carbon.

Table 4. Potential Silicate Weathered via Fertilizer (PSWF) calculated from Eq. (3). Total annual DSi yield for NAEW sites and the Ohio-Tennessee River Basin (DSi and NO_3 from Aulenbach et al., 2007). Maximum CO_2 consumption if all DSi is weathered via carbonic acid. Minimum CO_2 consumption = Maximum-PSWF.

Sites	DSi (μM)	$NO_3/2$ (μM)	b* (μM)	DSi-b (μM)	PSWF (μM)	DSi yield (kg km^{-2} yr^{-1})	Max CO_2 flux (mol*10^3 km^{-2} yr^{-1})	Min CO_2 flux (mol*10^3 km^{-2} yr^{-1})
WS 115 Corn No-Till	92	19	−9	101	21	370	26	20
WS 127 Corn Till	103	94.5	27	76	70	520	37	12
WS 166 Mixed-Use	132	20.5	101	31	4.8	2210	157	152
WS 172 Forested	148	7.5	50	98	5.0	2730	194	188
WS 182 Unimproved Pasture	132	11	159	0	0	3080	219	219
Ohio Tennessee River Basin	181	37.5	10	171	35	2560	182	147

*b intercept shown on Fig. 7.

Silicate weathering yields for the NAEW sites were calculated based on 2008 total annual flow using a linear best-fit regression (Table 4). Maximum CO_2 consumption rates were calculated based on the assumption that silicate minerals weathered in carbonic acid release one mole of DSi with two moles of CO_2 consumed (Edmond and Huh, 1997; Goldsmith et al., 2008). Cation charge balance equations were not used to estimate CO_2 consumption rates from silicate weathering given that agricultural sites were loaded with lime (Ca^{2+}, Mg^{2+}), potash (K^+, Cl^-) and manure. Recall that 1 mole of DSi is weathered in association with 2 moles of NO_3^-. The potential silicate weathered by via fertilizer (Eq. 3) is hence:

$$\text{PotentialSilicateWeatheredbyFertilizer} = [(NO_3)/(2) * (DSi - b)]/DSi \quad (3)$$

Therefore, minimum CO_2 consumption rates were estimated by subtracting the potential silicate weathered by fertilizer from the maximum CO_2 consumption (Table 4). These estimates may be low given that silica may be retained in natural impoundments along the watershed (Triplett et al., 2008), however, we suspect little silica removal from harvest, given the negligible concentration of silica in feed corn (Lanning et al., 1980).

Note, for this calculation, it was assumed that all NO_3^{-*} (* precipitation subtracted) released corresponds to silicate minerals weathered by NH_4^+ oxidation. In the N-fertilizer weathering of silicates two moles of NO_3^- are released in association with one mole of DSi released. The exception was the DSi not associated with losses of alkalinity or the y-intercept from the plots of (Ca^{2+}+Mg^{2+})/alkalinity versus DSi. This correction accounts for alkalinity lost to other non-precipitation sources of acid that might weather silicate minerals. DSi yields and NO_3 yields used to understand the relation between DSi and NO_3 in the Ohio-Tennessee River Basin were calculated by area normalizing annual loads reported in Aulenbach et al., 2007. The DSi unaffected by nitrogenous fertilizer applications was determined from the y-intercept in the (Ca^{2+}+Mg^{2+})/alkalinity versus DSi graph created with the downloaded USGS data for The Ohio River at Dam 53 near Grand Chain, Illinois (Fig. 7).

For the perennial streams in the NAEW, annual silicate yields (2210–3080 kg km^{-2} yr^{-1}) and maximum associated CO_2 consumption rates (1.57–2.19*10^5 mol km^{-2} yr^{-1}) were similar to those calculated for the entire Ohio-Tennessee River Basin (Aulenbach et al., 2007) (Table 4). However, silicate weathering yields (370, 520 kg km^{-2} yr^{-1}) and maximum CO_2 consumption rates (≤3.7*10^4 mol km^{-2} yr^{-1}) were substantially lower for the two corn watersheds than in the watersheds with perennial streams. As previously discussed, the lower DSi yields for the two corn watersheds are thought to result from the lack of Si-enriched baseflow contributions to these sites. Soil silica depletions noted in temperate agricultural landscapes (Clymans et al., 2011) may also be related to enhanced losses of Si from fertilizer-enhanced weathering.

As previously noted, water routing differences are responsible for the greater DSi yields in the NAEW sites with baseflow compared to those without baseflow. However, natural nitrification processes in the forested site (WS 172) and N-fertilizer enhanced nitrification (WS 115, WS 127, WS 166) also affects the reactions controlling silicate weathering, and hence the DSi produced. Although the no-till corn (WS 115) yielded the lowest median DSi, the tilled corn (WS 127) with greater NO_3^- concentrations had less silicate weathering associated CO_2 consumption because of its greater weathering via nitrogenous fertilizer. Furthermore, both fertilized corn watersheds had a greater percentage of potential weathering of silicate minerals via acids produced from N fertilizers than the other NAEW sites. The lack of baseflow in the NAEW corn sites may enhance the exchange of nitrogenous fertilizers and therefore, the oxidation and release of protons with surface soils.

Calculations of minimum potential CO_2 consumption for the mixed-use watershed (166) also reflected minimal N-fertilizer additions to this landscape. Less than 4 % of the DSi produced is associated with NH_4^+ oxidation/weathering, corresponding to a decrease in CO_2

consumption of ∼$5.0^{*}10^{3}$ mol km^{-2} yr^{-1}. While losses of alkalinity corresponded to increased silicate weathering in the forested site, there was a substantial amount of DSi not solubilized through the nitrification process. Minimum CO_2 consumption that included the affects of nitrification, therefore, was only ∼$5.0^{*}10^{3}$ mol km^{-2} yr^{-1} less than the maximum ($1.94^{*}10^{5}$ mol km^{-2} yr^{-1}) estimated CO_2 consumption.

NAEW watersheds with perennial flow had similar DSi yields and associated maximum CO_2 consumption to the Ohio-Tennessee River Basin. Furthermore, minimum CO_2 consumption associated with silicate weathering in the Ohio-Tennessee River Basin ($1.47^{*}10^{5}$ mol km^{-2} yr^{-1}) was similar to the mixed-use NAEW watershed ($1.52^{*}10^{5}$ mol km^{-2} yr^{-1}). However, this may not simply reflect similarities in landuse types. Firstly, baseflow represents approximate two-thirds of the Ohio-Tennessee River Basin total flow (Zhang and Schilling, 2006) and it composes three-quarters of the total flow in the NAEW mixed-use site. Secondly, DSi increased at a greater rate in association with losses of alkalinity in the Ohio-Tennessee River Basin than in any of the NAEW sites. DSi weathering and associated CO_2 consumption are likely controlled by hydrologic routing and N-fertilizer applications. Routing differences may have a greater affect on DSi yielded from older lithologies where surface soils are especially depleted in weatherable minerals with respect to the regolith. Even the depth of groundwater exchange is important to DSi weathering for older lithologies. A Precambrian granitic watershed in Shenandoah National Park, Virginia, USA had greater available silica for weathering at greater depths within the groundwater zone (Scanlon et al., 2001). But as previously noted, N-fertilizers may be especially effective in weathering silicate minerals in younger soils and lithologies, hence explaining why silicate weathering in the Ohio River Basin may be up to 20 % affected by nitrogenous fertilizers. It is also important to note that while nitrogenous fertilizer enhances weathering response, repeated fertilizer applications likely deplete soil silica pools through time.

6 Conclusions

Hydrologic conditions, especially the amount of baseflow relative to total flow, are a major determinant of silicate weathering yields. NAEW sites with no baseflow had DSi yields that were substantially lower than sites with baseflow. While deforestation immediately increases DSi yields over short time periods (Conley et al., 2008), through time the conversion of forest to traditionally managed agricultural landscapes (e.g. tilled croplands) leads to increases in the relative contributions of silica-depleted surface water with respect to total discharge thereby reducing DSi yields. Our results also suggest that hydrologic and geochemical responses associated with routing may lag behind landuse changes.

Silicate weathering in corn watersheds that solely had surface runoff was enhanced by the application of nitrogenous fertilizers but DSi yields were still far lower than watersheds that had baseflow (with or without N-fertilizer applications). However, clearly the application of nitrogenous fertilizers enhances silicate weathering. Greater rates of DSi weathered associated with alkalinity loss in the larger Ohio-Tennessee River Basin compared with all NAEW sites suggest that soil age is probably important in the reactivity of silicate minerals to weathering agents. The younger soils derived from the glacial till-covered portion of the Ohio-Tennessee River Basin are likely more responsive to nitrogenous fertilizers than the older NAEW soils derived from unglaciated material. In fact, reactions with nitrogenous fertilizers potentially generated up to 20 % of all DSi yielded from the Ohio-Tennessee River Basin between 1979 and 2009. Silicate yields are sensitive to landuse-induced alterations in hydrology (e.g relative contributions of baseflow) and N fertilizer applications. Finally, because of the interaction of fertilizer with soil minerals, CO_2 consumption calculations associated with silicate weathering need to consider applications of fertilizers. This consideration becomes even more important as the global application of fertilizers continues to grow (Pongratz et al., 2008). Future research is needed to understand if soil silica pools are lowered in response to enhanced weathering from fertilizers. In addition, more work is necessary to classify how distinct lithologies and landscape age relate to silicate response to fertilizer applications. Our results suggest that some agricultural landuse types that shift toward less baseflow may enhance fertilizer weathering of silicates.

Supplementary material related to this article is available online at: http://www.biogeosciences.net/9/941/2012/bg-9-941-2012-supplement.pdf.

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