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NITROGEN, PHOSPHORUS AND CARBON DYNAMICS IN A THIRD-ORDER STREAM OF THE US MIDWEST

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ABSTRACT. Excess nitrogen, phosphorus and carbon exports (NPC) from agricultural land of the US Midwest affect coastal eutrophication and water quality throughout the Mississippi River basin. However, little is known about the processes regulating NPC dynamics during storms in large third-order streams (> 200 km^2) in this region. The objectives of this study were to determine stream nitrate (NO_3^-), ammonium (NH_4^+), total organic nitrogen (TON), dissolved organic carbon (DOC) and total phosphorus (TP) concentration dynamics (timing, export pathways) during storms in Upper Eagle Creek Watershed (UECW); a large (274 km^2) third-order watershed representative of agro-ecosystems of the US Midwest. Ammonium, TON, DOC and TP were primarily exported via overland flow or preferential flow to tile drains through soil macropores, and more than 72% of variations in TON and TP concentrations (45% for DOC, 42% for NH_4^+) could be explained by variations in stream discharge regardless of seasons. Although NO_3^- was primarily exported via subsurface flow, no consistent concentration patterns as a function of flow were observed between storms. Variations in antecedent moisture conditions and N availability with seasons affected NH_4^+ and NO_3^- export patterns along with precipitation characteristics and stream response to precipitation. NPC concentration patterns as a function of flow in UECW were generally "smoother" than at smaller scales (< 20 km^2) suggesting that scale may play an important role in the development of stream solute concentration patterns. Further research is underway to fully understand the effect of scale on NPC export patterns in streams in the US Midwest.

Keywords: Watershed, nitrogen, phosphorus, carbon, precipitation, scale

Excess nitrogen (N) export from agricultural land in the Mississippi River Basin (MRB) has been shown to significantly contribute to the development of large areas of hypoxic bottom water in the Gulf of Mexico every summer (Royer et al. 2006). Excess nitrate in fresh water, if ingested, can also be toxic to infants and it can contribute to freshwater eutrophication (Martin et al. 1999; Tedesco et al. 2005). States like Illinois, Iowa and Indiana contribute more N (1801–3050 Kg N/km^2/yr) to the Mississippi River than any other state in the MRB (Goolsby et al. 2000; Alexander et al. 2008). Further, nitrogen wet atmospheric deposition in the Midwest and in Indiana in particular is one the highest in the nation (500–700 kg N/km^2/yr) (NADP 2008), making Indiana a hot spot of N contamination in the MRB. Phosphorus (P) export from agricultural watersheds of the US Midwest can also be significant (Royer et al. 2006) and contribute to algae blooms in streams and freshwater reservoirs (Tedesco et al. 2005). Recent research in the Louisiana coastal waters also indicates that P might play a more important role than previously thought in the development of the Dead Zone every summer in the Gulf of Mexico (Alexander et al. 2008). Organic carbon (OC) and dissolved organic carbon (DOC) in particular are also important to water quality. For instance, the quantity and quality of OC and the processing and transport of this carbon influence heterotrophic productivity and respiration in lotic systems, which is important in influencing the rates of C cycling and short term CO_2 outgassing (Dalzell et al. 2005).

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Most NPC exports occur during episodic high flow periods (Boyer et al. 1997; Royer et

al. 2006; Inamdar et al. 2004; Hood et al. 2006; Dalzell et al. 2007; Vidon et al. 2008). Indeed, Royer et al. (2006) showed that 50% of annual nitrate exports and 80% of annual phosphorus exports occurred during high flow conditions that represented less than 10% of the time for three agricultural watersheds in Illinois, USA. Similarly, Dalzell et al. (2007) showed that 71–85% of annual DOC load occurred at high flow (20% of the time) in 2002 and 2003 in a central Indiana watershed, USA. It is therefore critical to thoroughly understand the processes regulating concentration patterns of nitrogen (nitrate, ammonium, total organic nitrogen), carbon (dissolved organic carbon) and phosphorus in streams during storms in agroecosystems of the US Midwest. This will increase our ability to accurately estimate solute loading, determine total maximum daily loads for regulatory purposes, and inform model development in a region of the country responsible for disproportionally high NPC exports to streams in the MRB.

Research has also shown that nitrogen and carbon dynamics can be extremely variable from one setting to another (Vanni et al. 2001; Welsch et al. 2001; Inamdar & Mitchell 2006; Hood et al. 2006; Wagner et al. 2008). Some studies have shown that DOC typically peaked with or slightly after the peak in discharge in some forested catchments (Hangen et al. 2001; Inamdar et al. 2004) while others reported that DOC typically peaked prior to the peak in discharge on the rising limb of the snowmelt hydrograph in forested mountainous catchments of Colorado (Hornberger et al. 1994; Boyer et al. 1997). Inamdar et al. (2004) showed in two forested catchments in the Adirondack Mountains, New York, that the peak in nitrate concentration typically preceded the peak in discharge, while in Ohio, Vanni et al. (2001) found that some storms produced a decrease in nitrate concentration during stormflow while other storms exhibited an increase in nitrate concentration with flow. Although many studies have investigated phosphorus dynamics in streams (Kronvang et al. 1997; Johnes & Heathwaite 1998; McDowell & Wilcock 2004; Royer et al. 2006), very little information is available on P dynamics at a high temporal resolution (5–10 hours) during precipitation events even though most particulate phosphorus losses occur during storms (Ellison & Brett 2006; Royer et al. 2006).

With the exception of a few studies (Vanni et al. 2001; Vidon et al. 2008; Wagner et al. 2008), most studies on NPC dynamics in streams during storms also take place in forested mountainous to gently rolling landscapes (Creed & Band 1998; Hangen et al. 2001; Welsch et al. 2001; Inamdar et al. 2004; Inamdar & Mitchell 2006). With a dominance of poorly-drained soils, the common use of artificial drainage and a large percentage of agricultural land dominated by corn and soybean crop, the hydrology of the upper Midwest is clearly unique and the export patterns of nitrogen, phosphorus and carbon are likely to be different from those observed in other regions of the country. Identifying the flowpaths by which various forms of nitrogen, phosphorus and carbon are exported to streams during storms as well as identifying NPC concentration patterns during storms as a function of flow is therefore critical to fully understand the processes regulating NPC delivery to streams during storms in this region of the country.

Further, with the exception of the Vanni et al. (2001) study, most studies investigating NPC dynamics in streams during storms at a high temporal resolution generally all take place in small (< 15 km^2) first or second-order watersheds (Hook & Yeakley 2005; Inamdar & Mitchell 2006; Inamdar 2007; Poor & McDonnell 2007; Inamdar & Mitchell 2008; Wagner et al. 2008; Vidon et al. 2008). Although research focusing on first and second-order watersheds is essential to identify primary hydrological controls on NPC exports to streams, research focusing on larger watersheds (> 200 km^2, $> 3^{rd}$ order) is also important to identify large scale processes (Bianchi et al. 2004; Dalzell et al. 2007). Large scale studies are also often highly relevant to watershed managers as management decisions are often made at the county or state level.

Considering the critical need for studies documenting NPC dynamics in large (third order and higher) streams at a high temporal resolution in artificially drained landscapes of the Midwest, the objectives of this study were to 1) determine the export pathways of nitrate, ammonium, organic nitrogen, dissolved organic carbon and phosphorus in streams during storms in Upper Eagle Creek Watershed (UECW); a large (274 km^2) third-order watershed near Indianapolis, Indiana, that is repre-

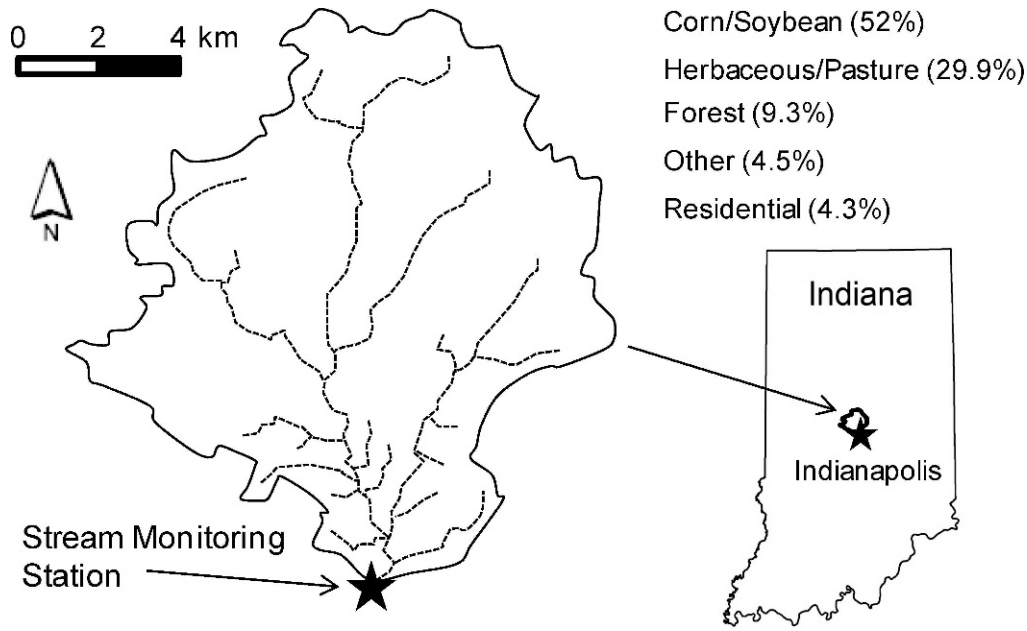

Figure 1.—Location of Upper Eagle Creek Watershed (UECW) (274 km^2) in Central Indiana, USA. Land use is also indicated.

sentative of agro-ecosystems of the US Midwest; 2) identify differences (if any) in solute concentration patterns across storms; and 3) determine how these patterns relate to previously published NPC export patterns in smaller watersheds. Finally, determine the implications of these findings for watershed management.

To address these objectives, we monitored NPC concentrations, along with sulfate, chloride and cation concentration export patterns in UECW for two storms in December 2007/January 2008 and for three consecutive storms over a 14-day period in May 2008. This approach using traditional hydrological methods (discharge, precipitation characteristics), along with sulfate, chloride and cation concentration patterns for a total of five storms over a six-month period allowed us to shed light onto the processes regulating NPC export patterns in large watersheds of the upper Midwest.

METHODS

Site description.—Upper Eagle Creek Watershed (UECW) (274 km^2) is part of the larger Eagle Creek Watershed (ECW) (420 km^2) in central Indiana, USA (Fig. 1). Indiana has a temperate continental and humid climate. The mean annual temperature for central Indiana is 11.7 °C with a mean January temperature of 3.0 °C and a mean July temperature of 23.7 °C. The long term average annual precipitation (1971–2000) in ECW is 105 cm (NOAA 2005). Precipitation is relatively evenly distributed throughout the year, which typically precludes the need for irrigation in summer time. Average stream discharge nevertheless varies with seasons owing to higher evapotranspiration in summer months. Highest stream discharge is observed in March while the lowest discharge typically occurs in September (Clark 1980). Topography is nearly flat with slope angles mainly between 1–2% with steeper areas of 2–6% slopes (Waldrip & Roberts 1972). Soils in ECW generally belong to the Crosby-Treaty-Miami association and are poorly drained, deep, and nearly level to gently sloping silt loams and silty clay loams (USDA 1974).

Land use in UECW is dominated by agriculture (52%) followed by herbaceous (29.9%), forest (9.3%), high and low density development (4.3%) and other land uses (roads or open water) (4.5%). Approximately 90% of nitrogen applied as fertilizer each year is applied on corn in the spring at an average rate of 165 kg N/ha/yr (Tedesco et al. 2005). Wet atmospheric deposition rates of nitrate and ammonium are approximately 2–3 kg N/ha/yr and 3–4 kg N/ha/yr, respectively (NADP 2008).

Nitrogen fixation rate by soybean is estimated at approximately 84 kg N/ha/yr (Russelle & Birr 2004). Only minimal amounts of nitrogen based fertilizer (1% of fertilizer input) are applied on soybean every year (2.2 kg N/ha/yr) (Tedesco et al. 2005). The remaining 9% of N fertilizer applied in ECW each year is generally applied on residential lawns at an estimated rate of 97 kg N/ha/yr (David & Gentry 2000). Nitrogen fixation by pastured areas is estimated at 15 kg N/ha/yr (David & Gentry 2000). Phosphorus is also applied in the watershed with approximately 76% of phosphorus applied on corn at a rate of 80 kg/ha/yr (58 kg/ha/yr on soybean) (Tedesco et al. 2005). Potash (K_2O) is applied in ECW at an estimated rate of 140 kg/ha/yr on corn and 124 kg/ha/yr on soybean (Tedesco et al. 2005).

METHODS

Five storms (1, 2, 3A, 3B, 3C) were monitored for this study. Storms 1 and 2 occurred in December 2007 and January 2008 after an unusually dry summer and fall period. Storms 3A, 3B and 3C were three consecutive storms over a 14-day period in May 2008. Although precipitation characteristics (total amount, intensity, duration) at one point cannot accurately represent precipitation for the entire watershed (274 km^2), we report daily precipitation recorded at Eagle Creek Airpark located approximately 12 km from the outlet of UECW to illustrate general precipitation patterns for the study period. Although discharge is affected by many variables (land use, vegetation development stage, evapotranspiration…), we use variations in discharge before each storm as indicators of changes in antecedent moisture conditions. Discharge was measured at a 15-minute interval at the outlet of UECW by the US Geological Survey (stream monitoring station #03353200). For each of the storms studied, water samples were collected in the stream using automated samplers (ISCO 6712). Sampling intervals ranged from 5–10 h and were calculated based on historical discharge data to collect samples at a higher temporal resolution on the rising limb and peak of the hydrograph than the falling limb. Thirteen samples were collected for Storm 1, 7 for Storm 2 and 45 for Storms 3A, 3B and 3C. Equipment failure prevented the collection of a larger number of samples for Storm 2. Following Storm 2, two large events occurred in February and March; however, high flow conditions and/or freezing temperatures prevented equipment repairs until early April. Collected water samples were analyzed for nitrate (NO_3^-), ammonium (NH_4^+), total Kjeldahl nitrogen (TKN), total phosphorus (TP), dissolved organic carbon (DOC), major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}), chloride (Cl^-) and sulfate (SO_4^{2-}). Samples to be analyzed for DOC, TP and TKN were collected in 500 ml ISCO PropPak bottles with LDPE liners containing 2 ml of 11N sulfuric acid. All other samples were collected in non-acidified 500 ml ISCO PropPak bottles with LDPE liners. Upon return to the laboratory, all samples (except samples for TP and TKN analysis) were filtered using Whatman GF/F 0.7 μm filters and refrigerated until analysis within 48 h of collection (TKN, TP, DOC, cations) or frozen until analysis (NO_3^-, NH_4^+, Cl^-, SO_4^{2-}). Nitrate, NH_4^+, Cl^-, and SO_4^{2-} were analyzed using standard colorimetric methods using a photometric analyzer (AquaKem 20 – ESTA-nalytical) (Clesceri et al. 1998). TKN was measured using the standard Kjeldahl Method (EPA method 351.4) and total organic nitrogen (TON) calculated as TKN minus NH_4^+. Total phosphorus was determined using EPA standard method 4500 PE consisting of a strong acid and persulfate digestion analyzed colorimetrically using the ascorbic acid-molybdate blue method. Dissolved organic carbon was determined using a persulfate oxidation to CO_2 and an OI Analytical DOC/DIC analyzer interfaced to an IRMS. Major cation concentrations were determined by ion chromatography using a Dionex DX500 Ion Chromatograph with a CS15 column and 11N sulfuric acid eluent. Triplicate analysis of 10% of all samples and analysis of check standards every 10 samples was performed to assess measurement error and check for accuracy and precision of measurement techniques.

For each of the storms studied, the start of the event was defined when a perceptible rise in discharge was observed after precipitation started (Inamdar & Mitchell 2006). The end of the event was defined when discharge returned to pre-event values or when a subsequent event started, whichever occurred first (Inamdar & Mitchell 2006). Seven-day, 30-day and 90-day antecedent precipitation for each event was calculated by computing total precipitation (cm) in the seven, 30 and 90 days

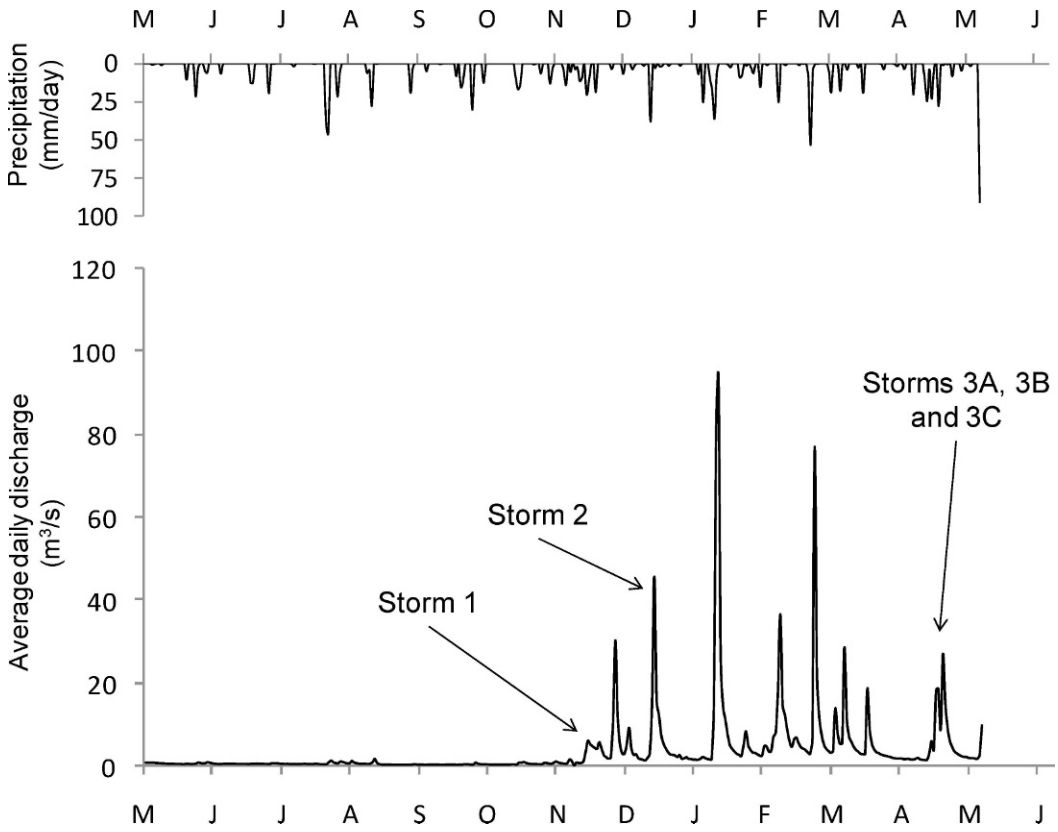

Figure 2.—Daily precipitation and average daily discharge at the outlet of Upper Eagle Creek Watershed (UECW) between May 2007 and May 2008.

preceding the events using weather station data, respectively. The runoff ratio for each storm is the ratio of total discharge for the event expressed in millimeters (discharge normalized by area) divided by the bulk precipitation for the event, also expressed in millimeters. The time to peak is defined as the time between the start of the rising limb and the peak in discharge (Poor & McDonnell 2007). Maximum discharge recurrence intervals were calculated for each of the storms studied based on long-term discharge data obtained from the US Geological Survey. SigmaPlot 11.0 was used for statistical analysis. Data were tested for normality and equal variance, and *t*-tests were used to determine significant differences between groups if normally distributed. Significance levels of differences between non-normally distributed data were determined using Mann-Whitney Rank Sum Tests.

RESULTS

Storm characteristics and watershed hydrological response to storms.—The summer and fall of 2007 were characterized by a dry weather pattern for central Indiana (60% below normal, NOAA 2005), with no significant discharge events occurring in UECW between 31 May and 1 December 2007 (Fig. 2). During this time period, the average runoff ratio was 0.06 (Fig. 3). Following Storm 1 (11–14 December), the runoff ratio for the December 2007–May 2008 period was one order of magnitude higher at 0.60 (Fig. 3). Although Storm 1 was the second smallest of the storms studied (after Storm 3A) with a maximum discharge of 0.365 mm/hr (Table 1), it represents the first significant discharge event after a drier than normal summer/fall period (Fig. 2).

Average bulk precipitation varied between 2.5 and 4.2 cm depending on the storm

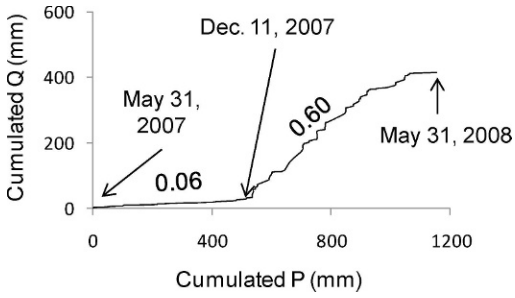

Figure 3.—Double mass curve showing cumulated precipitation (cumulated P) *vs.* cumulated discharge (cumulated Q) between May 2007 and May 2008. Numbers indicate runoff ratios for the May–December 2007 period and the December 2007–May 2008 period.

(Table 1). With the exception of Storm 2 for which 7-day antecedent precipitation was much smaller (0.4 cm) than for any of the other storms, 7-day antecedent precipitation for the other storms varied between 3.2 cm for Storm 3A and 6.6 cm for Storm 3C. Thirty and 90-day antecedent precipitations for each of the storms studied were within 27% and 14% of the average 30 and 90-day antecedent precipitations for all the storms. Baseflow in the hours preceding each storm was one order of magnitude lower for Storm 1 than for any of the other storms (Table 1). Baseflow is not reported for Storms 3B and 3C because the stream did not return to baseflow until the end of Storm 3C (Fig. 2). Mean stormflow and peak discharge were highest for Storm 2. For Storms 3A, 3B and 3C, peak discharge progressively increased from Storms 3A to 3C, however, mean stormflow was lower for Storms 3C than 3B owing to a longer falling limb. During Storms 3A, 3B and 3C, the runoff ratio was low during Storm 3A (0.12) and then increased to 0.56–0.58 for Storms 3B and 3C. The time to peak progressively decreased from 27.7 h for Storm 3A to 8.4 h for Storm 3C (Table 1).

Chloride, sulfate and major cation concentration patterns..—Mean SO_4^{2-}, Cl^-, Mg^{2+}, Na^+, K^+, and Ca^{2+} concentrations during Storms 1, 2, 3A, 3B and 3C are shown in Table 2. Mean SO_4^{2-} and Cl^- concentrations were significantly ($P < 0.008$) higher for Storm 1 than for Storms 2, 3B or 3C, but no significant differences in mean SO_4^{2-} ($P = 0.592$) or Cl^- ($P = 0.171$) concentrations were observed between Storms 1 and 3A (Table 2). Similarly, mean Na^+ concentrations were significantly higher ($P < 0.015$) for Storm 1 and 3A than Storms 2, 3B and 3C. Mean Ca^{2+} and Mg^{2+} concentrations were significantly different between Storm 1 and Storms 2 and 3A ($P < 0.007$) but not significantly different to mean Ca^{2+} and Mg^{2+} concentrations for Storms 3B or 3C ($P > 0.065$). Mean K^+ concentration during Storm 1 was significantly different than mean K^+ concentrations during Storms 3A and 3C ($P < 0.013$), but not significantly different from mean K^+ concentrations during Storms 2 and 3B ($P > 0.118$).

Detailed concentration patterns (max, min, timing) for SO_4^{2-}, Cl^-, Mg^{2+} and K^+ are shown on Figs. 4 and 5 for Storms 1, 2, 3A, 3B and 3C. Because Na^+ and Ca^{2+} concentration patterns were similar to those of Mg^{2+}, only Mg^{2+} concentration patterns are shown. For

Table 1.—Storm characteristics and Upper Eagle Creek watershed hydrological response to precipitation for Storm 1 (11–14 December 2007), Storm 2 (8–11 January 2008) and Storms 3A, 3B and 3C (8–22 May 2007).

	Storm 1	Storm 2	Storm 3A	Storm 3B	Storm 3C
Bulk precipitation (cm)	4.1	4.2	3.3	2.5	4.0
7-day antecedent precipitation (cm)	4.8	0.4	3.2	4.0	6.6
30-day antecedent precipitation (cm)	11.3	8.1	6.5	9.0	9.7
90-day antecedent precipitation (cm)	24.7	27.0	25.8	28.7	31.2
7-day antecedent discharge (mm/h)	0.022	0.046	0.019	0.033	0.110
30-day antecedent discharge (mm/h)	0.010	0.067	0.038	0.040	0.046
90-day antecedent discharge (mm/h)	0.005	0.025	0.110	0.084	0.086
Mean stormflow (mm/h)	0.113	0.245	0.054	0.204	0.106
Peak discharge (mm/h)	0.365	0.962	0.092	0.451	0.622
Baseflow (mm/h)	0.007	0.037	0.017	n/a	n/a
Runoff ratio	0.42	0.73	0.12	0.58	0.56
Time to peak (h)	68.4	17.5	27.7	14.0	8.4

Table 2.—Mean stream sulfate (SO_4^{2-}), chloride (Cl^-) and major cation (Mg^{2+}, Na^+, K^+, Ca^{2+}) concentrations for Storm 1 (11–14 December 2007), Storm 2 (8–11 January 2008) and Storms 3A, 3B and 3C (8–22 May 2007) in Upper Eagle Creek watershed. Numbers in parenthesis indicate standard deviation.

	Storm 1	Storm 2	Storm 3A	Storm 3B	Storm 3C
$SO4^{2-}$ (mg/L)	41.03 (+/−15.19)	23.71 (+/−6.75)	35.57 (+/−5.52)	22.30 (+/−4.44)	26.51 (+/−8.77)
Cl− (mg/L)	45.73 (+/−40.36)	24.73 (+/−5.88)	45.28 (17.75)	24.91 (+/−6.02)	25.37 (+/−6.35)
Mg^{2+} (mg/L)	17.01 (+/−3.36)	12.48 (+/−2.28)	22.97 (+/−2.30)	16.07 (+/−2.69)	18.65 (+/−5.04)
Na^+ (mg/L)	25.87 (+/−29.47)	12.89 (+/−3.19)	22.67 (+/−4.66)	11.63 (+/−3.32)	13.06 (+/−4.20)
K^+ (mg/L)	3.02 (+/−0.36)	3.27 (+/−1.46)	2.41 (+/−0.27)	2.87 (+/−0.56)	2.50 (+/−0.61)
Ca^{2+} (mg/L)	62.95 (+/−9.76)	48.06 (+/−7.73)	73.95 (+/−5.42)	56.1 (+/−8.41)	65.28 (+/−15.92)

Storms 1 and 2, Mg^{2+}, Cl^- and SO_4^{2-} concentrations showed a quick decrease in concentration on the rising limb of the hydrograph with a progressive return to pre-event concentration levels on the falling limb of the hydrograph. For Storm 1, lowest concentrations occurred along with the peak in discharge for SO_4^{2-} and slightly after the peak in discharge for Mg^{2+} and Cl^-. Similar Cl^-, Mg^{2+} and SO_4^{2-} concentration patterns were observed for Storms 3A, 3B and 3C, with a decrease in concentration with each successive peak in discharge, and a progressive return to baseflow concentrations on the falling limb of each storm hydrograph. For Storms 2, 3A and 3C, K^+ concentrations typically increased with flow and maximum K^+ concentrations occurred slightly after the peak in discharge. Although maximum discharge for Storm 3C was higher than for Storm 3B, maximum K^+ concentration was reached during Storm 3B. No large variations in K^+ concentration were observed for Storm 3A.

Nitrogen, phosphorus and carbon concentration patterns.—Mean NO_3^-, NH_4^+, TON, TP and DOC concentrations for Storms 1, 2, 3A, 3B and 3C are shown in Table 3. Table 3 also shows the average percentage of inorganic nitrogen in total nitrogen (% Inorganic N) for each of the storms studied. Mean NO_3^- concentration during Storm 3B was significantly higher ($P < 0.012$) than for any of the other storms. On the other hand, mean NO_3^- concentrations during Storms 2 and 3A were significantly lower ($P < 0.007$) than during any of the other storms studied. Mean NH_4^+ concentration was significantly ($P < 0.004$) higher for Storm 3B than for Storms 3A or 3C and below detection limit (0.04 mg N/L) for Storms 1 and 2. Mean TON concentrations were highest for Storm 2 but not significantly higher ($P > 0.05$) than for Storms 1 or 3B. Mean TON concentration for Storm 2 was nevertheless significantly higher ($P < 0.001$) than for Storms 3A or 3C. Mean DOC and TP concentrations were highest for Storm 2 and lowest for Storms 3A and 3C. The percentage of inorganic N in total nitrogen (% Inorganic N) was lowest for Storm 2 and highest for Storms 1, 3B and 3C (Table 3).

Detailed concentration patterns for NO_3^-, NH_4^+, TON, TP and DOC are shown for Storms 1, 2, 3A, 3B and 3C on Figs. 6 and 7. Ammonium concentrations were below detection limit (0.04 mg N/L) for Storms 1 and 2 and are therefore only shown for Storms 3A, 3B and 3C. Figures 6 and 7 also show the variation in the proportion of inorganic nitrogen in total nitrogen (% Inorganic N) for each of the storms studied. Nitrate concentration patterns were not consistent across storms. An increase in NO_3^- concentration with flow from approximately 2 mg N/L to 5 mg N/L was observed for Storm 1, but a dilution pattern was observed for Storm 2. For Storms 3A and 3B, NO_3^- concentrations showed an initial decrease in concentration on the rising limb of the hydrograph and then a sharp increase on the falling limb of the hydrograph to levels higher than before the storm started. For Storm 3C, a similar pattern was observed, although NO_3^- concentrations did not reach levels as high as they did after Storm 3B. Overall, maximum nitrate concentrations were reached after Storm 3B in spite of a higher maximum discharge for Storm 3C. Maximum NH_4^+ concentrations were also reached during Storm 3B; however, NH_4^+ concentration for Storms 3B and 3C typically increased with discharge, peaked slightly after the peak in discharge and then progressively returned to pre-storm levels on the falling limb of the storm hydrograph. No

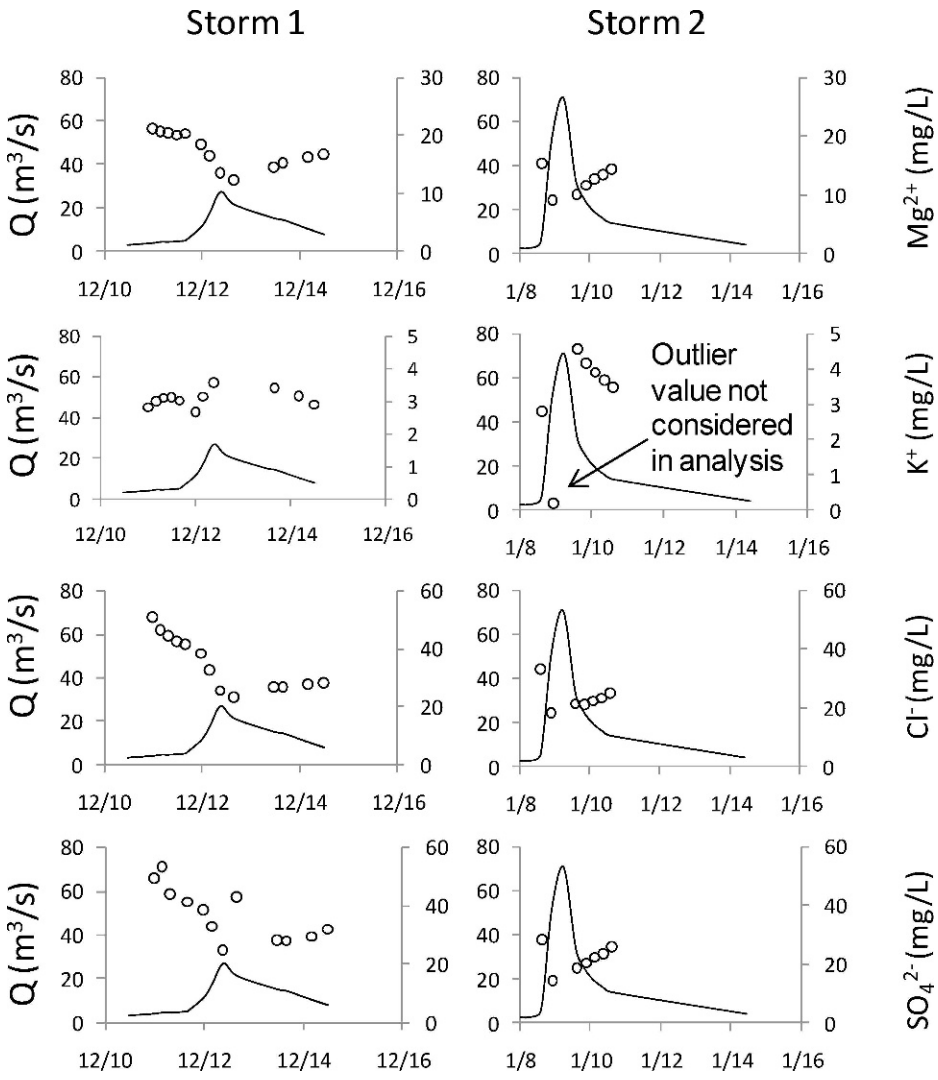

Figure 4.—Discharge (Q) and stream magnesium (Mg^{2+}), potassium (K^+), chloride (Cl^-) and sulfate (SO_4^{2-}) concentrations for Storm 1 (11–14 December 2007) and Storm 2 (8–11 January 2008) in Upper Eagle Creek watershed. Solid line indicates discharge, open circle indicates solute concentration.

clear concentration or dilution patterns were observed for NH_4^+ during Storm 3A. For all the storms studied, TON concentration sharply increased with flow, peaked with discharge and then progressively returned to baseflow levels on the falling limb of the hydrograph. Unlike NH_4^+, maximum TON concentration during Storms 3A, 3B and 3C was reached during the highest peak in discharge (3C).

"Patterns of % Inorganic N" showed significant inter-storm variations. For instance, "% Inorganic N" remained between 73–81% of total nitrogen during Storm 1 and did not show a clear increasing or decreasing pattern as a function of flow. Conversely, a significant drop (from 52% to 21%) in the proportion of inorganic N in total N was observed as discharge increased during Storm 2. This decrease in "% inorganic N" was followed by a progressive return to pre-storm levels on the falling limb of the hydrograph. Although NH_4^+ and TON concentrations typically increased with flow, "% Inorganic N" patterns during Storms 3A, 3B and 3C were similar to NO_3^- concentration patterns owing the dominance of the nitrate form of N in total N for these storms (Table 3).

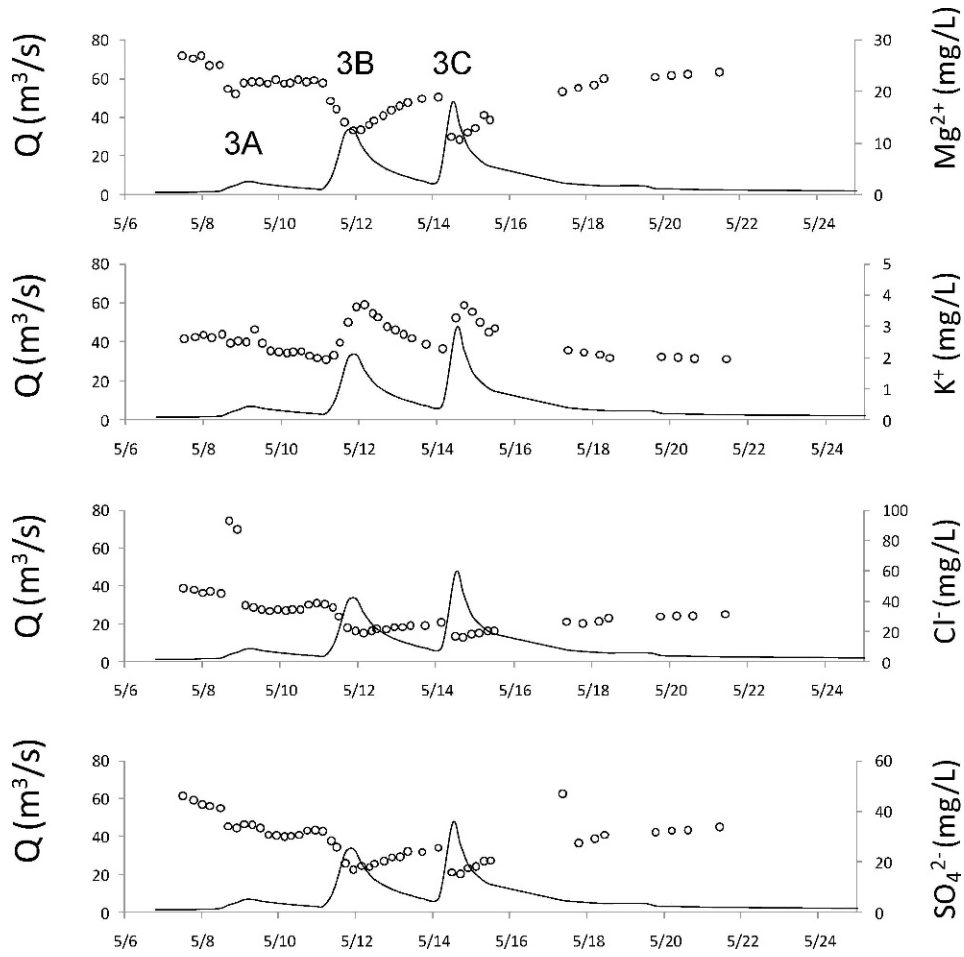

Figure 5.—Discharge (Q) and stream magnesium (Mg^{2+}), potassium (K^{+}), chloride (Cl^{-}) and sulfate (SO_4^{2-}) concentrations for storms 3A, 3B and 3C (8–22 May 2007) in Upper Eagle Creek watershed. Solid line indicates discharge, open circle indicates solute concentration.

Total P concentration patterns were consistent across all storms and indicated a clear increase in TP concentration on the rising limb of each storm hydrograph followed by large decreases in TP concentrations to pre-storm levels on the falling limb of each storm hydrograph. Total phosphorus peaked slightly before the peak in discharge for Storms 2, 3A

Table 3.—Mean stream nitrate (NO_3^{-}), ammonium (NH_4^{+}), total organic nitrogen (TON), percentage of inorganic nitrogen in total nitrogen (% Inorganic N), total phosphorus (TP) and dissolved organic carbon (DOC) concentrations for Storm 1 (11–14 December 2007), Storm 2 (8–11 January 2008) and Storms 3A, 3B and 3C (8–22 May 2007) in Upper Eagle Creek watershed. Numbers in parenthesis indicate standard deviation. (BDL = Below Detection Limit).

	Storm 1	Storm 2	Storm 3A	Storm 3B	Storm 3C
NO_3^{-} (mg N/L)	3.79 (+/−1.27)	2.83 (+/−0.44)	2.24 (+/−1.62)	5.04 (+/−1.38)	3.79 (+/−0.86)
NH_4^{+} (mg N/L)	BDL (<0.04)	BDL (<0.04)	0.09 (0.04)	0.25 (+/−0.16)	0.09 (0.07)
TON (mg N/L)	1.48 (+/−0.67)	2.12 (+/−0.79)	0.93 (+/−0.28)	1.49 (+/−0.52)	0.98 (+/−0.78)
% Inorganic N	71.94 (+/−7.45)	48.94 (+/−15.42)	62.71 (+/−17.37)	77.34 (+/−7.39)	77.85 (+/−10.18)
TP (mg/L)	0.28 (+/−0.20)	0.54 (+/−0.37)	0.09 (+/−0.06)	0.30 (+/−0.17)	0.25 (+/−0.22)
DOC (mg/L)	5.17 (+/−1.04)	6.20 (+/−0.86)	3.18 (+/−1.13)	5.47 (+/−1.45)	4.35 (+/−1.42)

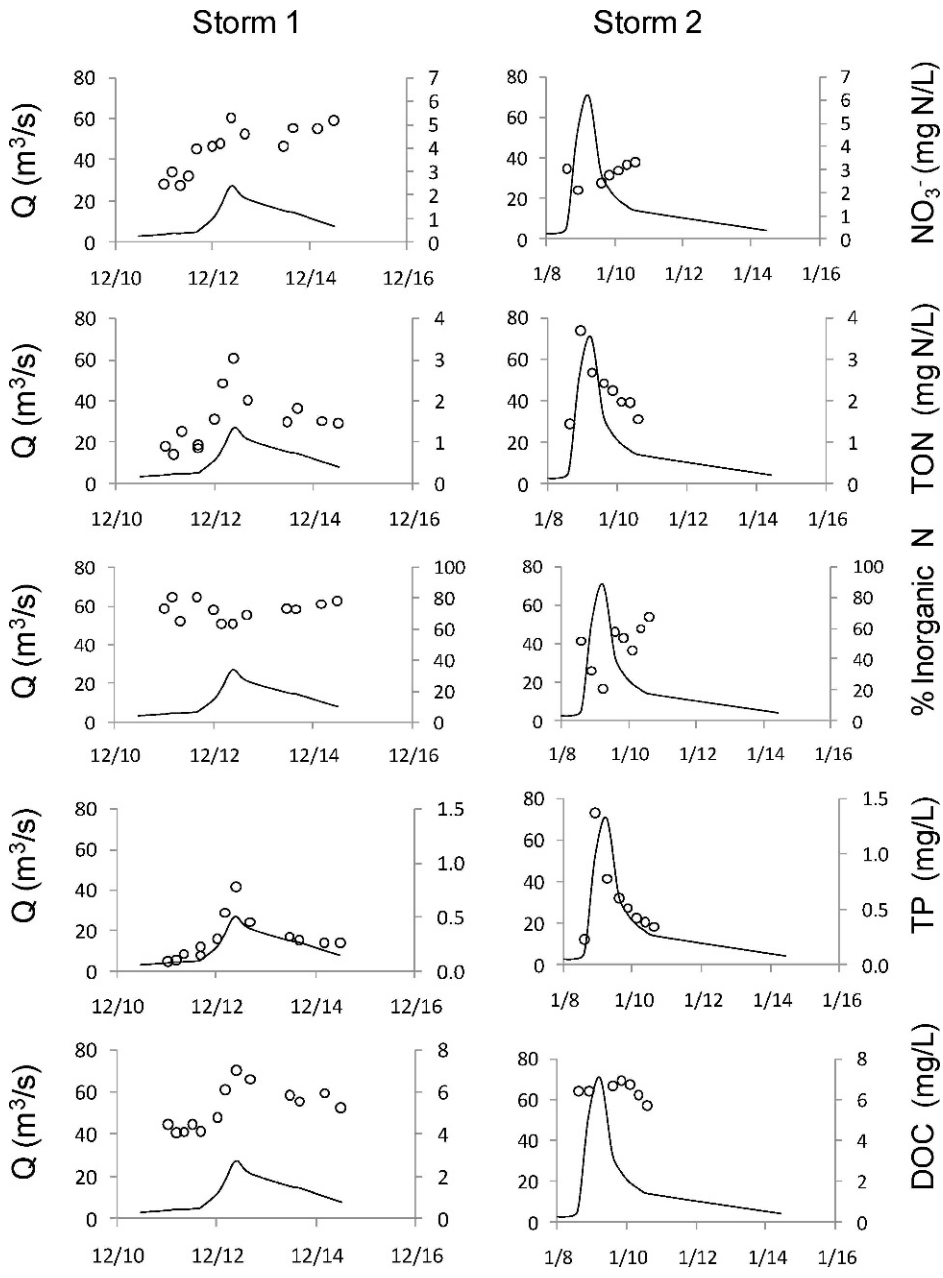

Figure 6.—Discharge (Q) and stream nitrate (NO_3^-), total organic nitrogen (TON), percentage of inorganic nitrogen in total nitrogen (% Inorganic N), total phosphorus (TP) and dissolved organic carbon (DOC) concentrations for Storm 1 (11–14 December 2007) and Storm 2 (8–11 January 2008) in Upper Eagle Creek watershed. Solid line indicates discharge, open circle indicates solute concentration.

and 3B, and with the peak in discharge for Storms 1 and 3C. Dissolved organic carbon concentrations typically increased with flow and peaked with the peak in discharge for Storms 1, 3A, 3B and 3C, with the exception of Storm 2 for which DOC did not show a clear increasing or decreasing pattern with changes in flow conditions. The highest DOC concentration (7.4 mg/L) during Storms 3A, 3B and 3C was reached during Storm 3B, even though maximum discharge occurred during Storm 3C.

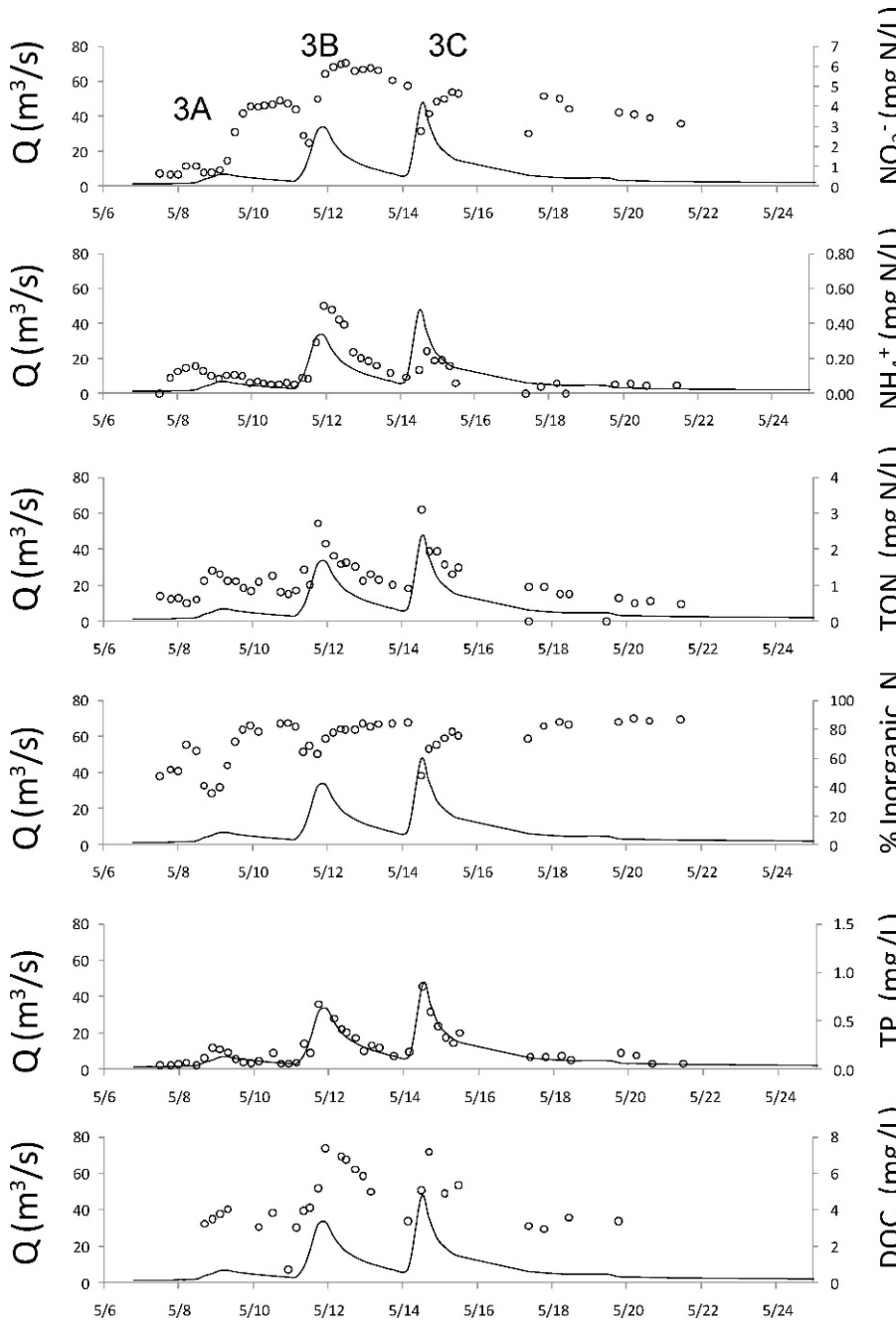

Figure 7.—Discharge (Q) and stream nitrate (NO_3^-), ammonium (NH_4^+), total organic nitrogen (TON), percentage of inorganic nitrogen in total nitrogen (% Inorganic N), total phosphorus (TP) and dissolved organic carbon (DOC) concentrations for Storms 3A, 3B and 3C (8–22 May 2007) in Upper Eagle Creek watershed. Solid line indicates discharge, open circle indicates solute concentration.

DISCUSSION

Processes regulating N, P, and C exports during storms.—Differences in NO_3^- and DOC, TP, NH_4^+ and TON concentration patterns during the storms studied suggested differences in the processes regulating the export of these solutes at the watershed scale (Figs. 6, 7) (Inamdar et al. 2004; Wagner et al. 2008). TON, NH_4^+, TP and DOC concentrations typically increased and decreased with discharge with maximum concentrations occurring around peak flow. This pattern is consistent with TON, NH_4^+, TP and DOC being primarily exported via quick transport processes such as overland flow or preferential flow to tile drains via macropore flow (Stone & Wilson 2006; Wagner et al. 2008; Vidon et al. 2008). Indeed, in a smaller nearby watershed (10.9 km^2), Wagner et al. (2008) showed that DOC concentrations peaked with the peak in discharge and that the maximum contribution of new water to the stream (overland flow + macropore flow + precipitation) occurred at/or around peak flow for a variety of storms. Stone & Wilson (2006) also showed that macropore flow contributions to tile drain flow, which is a major contributor to stream flow in our watersheds, were highest around peak flow for two storms in an agricultural watershed near Indianapolis, Indiana.

Chloride, SO_4^{2-} and cation data are also consistent with TP, DOC, NH_4^+ and TON being exported to streams primarily as overland flow and/or preferential flow to tile drains through soil macropores. Indeed, potassium (K) concentrations presented a similar pattern to TP, DOC, NH_4^+ or TON (Figs. 4, 5). Significant amounts of potash (K_2O) are applied to the soil surface in UECW (see methods) suggesting that potassium is likely to be exported along with overland flow in this watershed. Others have also associated an increase in K^+ concentration in stream water to overland flow contribution to streams (Hood et al. 2006; Vidon et al. 2008). Conversely, TP, DOC, NH_4^+ and TON concentration patterns tend to be inversely related to Mg^{2+}, Cl^- and SO_4^{2-} concentration patterns (Figs. 4, 5). High magnesium concentration in groundwater is common in this region of the country where Mg^{2+} rich glacial till is widespread (Tedesco et al. 2005). Many studies indicate that magnesium is typically exported via groundwater flow and that dilution trends in magnesium concentrations are often indicative of the dilution of Mg^{2+} rich groundwater by Mg^{2+} poor event water (precipitation, overland flow) during storms (Reid et al. 1981; Elwood & Turner 1989; Kahl et al. 1992; Hill 1993; Hood et al. 2006). A drop in stream magnesium concentration as flow increases in UECW is therefore consistent with a dilution of groundwater by low magnesium event water (precipitation, overland flow, macropore flow). Sulfate and Cl^- are highly soluble and typically associated with subsurface flow, which is consistent with the observed decrease in SO_4^{2-} and Cl^- concentrations during the storms studied.

Unlike NH_4^+, TON, DOC and TP, NO_3^- concentration patterns varied from storm to storm (Figs. 6, 7). For Storm 1, NO_3^- concentration progressively increased with flow and remained high on the falling limb of the hydrograph (Fig. 6). Storm 1 was the first major discharge event following a drier than normal period (Figs. 2, 3; Table 1). It is possible that NO_3^- accumulated near the soil surface in the weeks or months preceding Storm 1 owing to a lower than normal water table and the development of conditions unusually favorable to nitrification. Such phenomenon has been observed by Cirmo & McDonnell (1997) in a riparian zone in New York, where water table drawndown led to the development of conditions favorable to nitrification in a riparian zone where denitrifying conditions generally dominated. This subsequently caused the flushing of high NO_3^- concentration water during the first storm following this dry period. Poor & McDonnell (2007) also found elevated stream NO_3^- concentrations following a dry period in an agricultural catchment in Oregon.

For Storm 2, nitrate concentrations showed a dilution pattern with lowest NO_3^- concentrations occurring around peak flow (Fig. 6). This is consistent with NO_3^- being primarily exported as subsurface flow and nitrate rich groundwater being diluted by nitrate poor event water (overland flow, precipitation, macropore flow) as flow increases during Storm 2. For Storms 3A, 3B and 3C, which occurred in May following application of large amounts of N based fertilizers in spring in UECW (see materials and methods), there was a progressive increase in NO_3^- concentration throughout the storms with short-lived decreas-

es in NO_3^- concentration around peak flow. This is consistent with a large NO_3^- pool available for flushing throughout Storms 3A, 3B and 3C. Similar NO_3^- concentration patterns showing an initial NO_3^- concentration decrease with peak flow and then a delayed NO_3^- concentration peak after the hydrograph peak were observed for a series of storms in the Padez catchment (42.1 km^2) in Slovenia (Rusjan et al. 2008). The authors attributed these concentration patterns to variably saturated source areas and a large nitrate pool available for flushing in the soil profile.

Together, these results suggest that NO_3^- is mainly exported via subsurface flow regardless of the storm, but also revealed a lack of consistent NO_3^- concentration patterns between storms. Considering the size of the watershed, it was not possible to accurately measure variations in soil nitrate concentration with season throughout the watershed to directly quantify the impact of drought or fertilizer application on soil N concentration; however, data suggest that seasonal variations in the size of the soil NO_3^- pool available for flushing in the watershed was likely an important variable regulating observed NO_3^- export patterns in UECW. The lack of consistent NO_3^- export patterns from storm to storm for the storms studied is consistent with results reported by others in ago-ecosystems of the US Midwest (Vanni et al. 2001; Wagner et al. 2008). It is often assumed that NO_3^- flushing in agro-ecosystems of the US Midwest is a relatively simple process because of the importance of subsurface drainage in regulating water and NO_3^- fluxes in the subsurface; however, results suggest that NO_3^- export processes in this region of the country may be more complex than initially thought, and that further research on primary hydrological controls (antecedent moisture conditions, soil texture, macropore flow, NO_3^- availability…) regulating NO_3^- exports at the watershed scale is needed.

Inter-storm variability in N, P, C concentration patterns.—As indicated above, the larger NO_3^- concentration for Storm 1 than for Storm 2 is consistent with the availability of a larger nitrate pool for flushing before Storm 1 than Storm 2 owing to the development of conditions unusually favorable to nitrification leading to the progressive accumulation of nitrate near the soil surface. For Storms 3A-3C, maximum NO_3^- concentration was reached during Storm 3B in spite of a higher discharge during storm 3C. This suggests a progressive exhaustion of the pool of NO_3^- available for flushing during the 14-day period covered by Storms 3A, 3B and 3C (Fig. 7). Overall, NO_3^- concentration was poorly correlated to discharge (Pearson correlation coefficient $\rho_{xy} = 0.09$) and NO_3^- availability was likely a critical factor in determining NO_3^- flushing behavior at the watershed scale. In particular, variations in antecedent moisture conditions (e.g., antecedent discharge, Table 1) and N availability (conditions favorable to nitrification, timing of fertilization) with seasons were likely explanations for observed changes in NO_3^- export patterns along with precipitation characteristics and stream response to precipitations.

Higher NH_4^+ concentrations for Storms 3A, 3B and 3C than during Storms 1 or 2 are likely due to the application of anhydrous ammonia as fertilizer in the spring (Tedesco et al. 2005). Nevertheless, although Storm 3C was larger than Storms 3A or 3B in terms of total precipitation and maximum discharge (Table 1), maximum NH_4^+ concentrations were reached during Storm 3B (Fig. 7). This suggests a progressive exhaustion of the pool of NH_4^+ available for flushing during Storms 3A through 3C.

Unlike NH_4^+, maximum TP and TON concentrations were larger with each successive peak in discharge during Storms 3A, 3B and 3C, suggesting that TP and TON availability was unlikely to be the primary factor limiting TP and TON export at the watershed scale during the spring storms studied. Of the five storms studied, mean TP and TON concentrations were highest for Storm 2 (Table 3). Bulk precipitation, mean storm flow, maximum storm flow and runoff ratio were also highest for Storm 2 (Table 1). This is consistent with a larger amount of overland flow occurring during Storm 2 than for any of the other storms. When all the storms are lumped together, the Pearson correlation coefficient (ρ_{xy}) between TP and discharge is 0.91 ($P < 0.01$) and 0.85 ($P < 0.01$) for TON versus discharge. This indicates that more than 72% of variations in TON or TP can be explained by variations in discharge regardless of season.

Although DOC was also significantly positively correlated to discharge ($\rho_{xy} = 0.67$, $P <$

0.01), maximum DOC concentration during Storms 3A, 3B and 3C was reached during Storm 3B in spite of Storm 3C being the largest of the three. Like for NH_4^+, this suggests a progressive exhaustion of the DOC pool available for leaching during the three successive spring storms studied here (Fig. 7).

The mean percentage of inorganic N in total N (% Inorganic N) varied from 49–78% depending on the storm (Table 3) and generally presented a similar variation pattern as NO_3^- (Figs. 6, 7). The dominance of inorganic N (mainly NO_3^-) in total N in streams during storms in this part of the country is consistent with large in-stream nitrate loads and large input of inorganic N to agricultural fields (David & Gentry 2000; McIsaac et al. 2002; Royer et al. 2006). In their study of N dynamics in three watersheds in Ohio varying in scale from 12 to 129 km^2, Vanni et al. (2001) reported that NO_3^- was generally the dominant form of N, with NO_3^- representing between 70–87% of total N on an annual basis depending on the year. The slightly higher proportion of NO_3^- in total N in the Vanni et al. (2001) study can be explained by the fact that they looked at the relative importance of NO_3^- in total N in annual fluxes, as opposed to focusing on storms only, which are periods during which the relative importance of organic N relative to nitrate increases (Figs. 6, 7).

Impact of watershed scale on NPC concentration patterns & implications for water quality management.—Although the impact of scale on stream flow is a well documented phenomenon (Dunne & Leopold 1978; Pazzaglia et al. 1998, Dingman 2002), little information is available on the effect of scale on solute dynamics. Wagner et al. (2008) investigated NO_3^-, DOC and cation dynamics for three spring storms in an agricultural watershed (10.9 km^2) located just a few kilometers south west of UECW (274 km^2). In the Wagner et al. (2008) study, NO_3^- concentrations showed no clear increasing or decreasing patterns as a function of flow during storms. In addition, background variations in nitrate concentrations before and after each storm were high and often as high as variations associated with variations in discharge (Fig. 8). Although NO_3^- concentration patterns as a function of flow were also variable from storm to storm in UECW, background variations in NO_3^- concentrations were small and of a lesser magnitude than any variation in concentration associated with changes in flow conditions during the five storms studied (Fig. 6 and 7). This suggests that as scale increases, a ''smoothing'' effect occurs. At the plot scale, NO_3^- concentration variations as a function of flow are often extremely variable and background variations in NO_3^- concentrations are sometime larger than any variation in nitrate concentration associated with flow (Vidon unpubl. data). We propose that the large inter-storm variability in nitrate concentration as a function of flow at the plot scale or small watershed scale (Fig. 8) is responsible for the lack of consistent relationship between NO_3^- concentration and flow observed at larger scales. However, the increased smoothness of NO_3^- concentration patterns as scale increases suggests that an averaging effect occurs as many first-order streams with a diversity of NO_3^- concentration patterns mix and contribute to form the NO_3^- concentration patterns observed in larger watersheds like UECW.

A similar phenomenon is observed for Mg^{2+}. A comparison of Mg^{2+} concentration patterns during storms in UECW (Figs. 4, 5) with those obtained by Wagner et al. (2008) (Fig. 8) indicates that Mg^{2+} concentration patterns in UECW are also smoother than in the smaller watershed studied by Wagner et al. (2008). This suggests that a similar averaging or ''smoothing'' effect is occurring for Mg^{2+} and NO_3^-. Interestingly, a clear smoothing effect is not observed for DOC as scale increases (Figs. 6–8). Vanni et al. (2001) also did not report a clear smoothing effect for nitrate, particulate P or total N as scale increases; however, the range of scale represented in the Vanni study (12–129 km^2) is smaller than between UECW (274 km^2) and the Wagner study (6.7–10.9 km^2). Research by Inamdar & Mitchell in a series of glaciated forested catchments in New York State ranging in scale from 0.016–6.96 km^2 also brings some light on the impact of scale on solute export patterns (Inamdar & Mitchell 2006; Inamdar 2007; Inamdar & Mitchell 2008). A careful analysis of the chemographs reported by the authors for SO_4^{2-} (Inamdar & Mitchell 2008), NH_4^+ (Inamdar 2007), and NO_3^- and DOC (Inamdar & Mitchell 2006) revealed contrasting results. Nitrate and DOC concentration patterns, and to a lesser extent NH_4^+ concentration patterns, were often smoother at the outlet of the larger

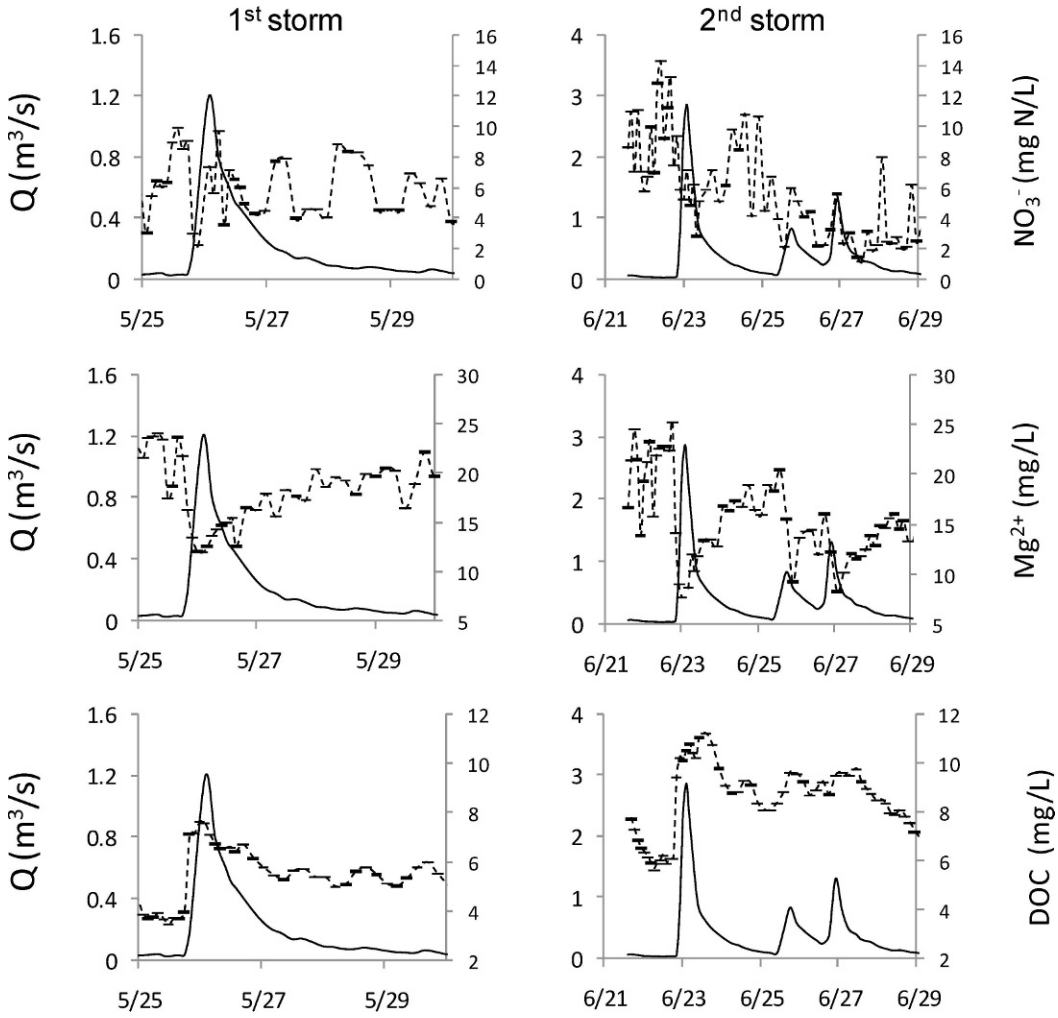

Figure 8.—Discharge (Q) and stream nitrate (NO_3^-), magnesium (Mg^{2+}), and dissolved organic carbon (DOC) concentrations in a small agricultural watershed (10.9 km^2) a few kilometers south west of UECW for two storms in May and June 2006 (Adapted from Wagner et al. 2008).

catchment than in smaller ones. However, this was not clearly observed for sulfate.

Although more research needs to be conducted to fully understand why and how scale affects solute export in a variety of geomorphic settings, an initial analysis of published data suggests that scale may play an important role in the expression of solute concentration as a function of flow. On the other hand, scale may not affect all solutes in a similar way, and scale thresholds above which an effect on solute concentration patterns is observed may be different from one area to another. Regardless, the effect of scale on solute flushing patterns as a function of flow has significant implications for watershed management. Understanding how various solute concentration patterns vary in relation to discharge at various scales is critical to the development of accurate solute export models. Such work, as well as the identification of scale thresholds above which certain export mechanisms are buffered or not fully expressed in solute concentration patterns is also key to constrain the scale of application of a variety of solute export models such as SPARROW (Smith et al. 1997) or SWAT (Santhi et al. 2006; Gassman et al. 2007). Fully understanding how solute concentration patterns change with scale can also help optimize sampling strategies when only a limited number

of samples are collected for monitoring purposes (Vidon et al. 2009). Indeed, Vidon et al. (2009) showed that the precision and accuracy of solute load calculations in streams is affected not only by the sampling frequency, but also by each solute concentration pattern as a function of flow (i.e., dilution or concentration pattern, noisiness of concentration signal). This aspect of solute dynamics as a function of flow is especially important for the development of total maximum daily load regulations when accurate solute load estimates must be established often based on a limited number of data points.

Further research is underway to fully characterize how scale, from the plot scale (i.e., subsurface drainage flow, overland flow) to the larger 4th order watershed (2000 km^2), affects NPC dynamics in the Midwest region of the United States. We believe that this work is critical to further constrain the range of application of a variety of solute export models and to characterize how scale affects the expression of primary hydrological controls on NPC exports at the watershed scale.

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