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Stream nitrate and DOC dynamics during three spring storms across land uses in glaciated landscapes of the Midwest

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Summary Many studies have investigated nitrate and dissolved organic carbon (DOC) export mechanisms during storms in forested mountainous to hilly catchments. However, the number of studies across land uses in artificially drained landscapes of the Midwest remains relatively small despite the importance of nitrate and carbon losses to streams on water quality in this region. This study investigates water, nitrate, and DOC delivery (timing) to streams during storms, and the mechanisms (flowpaths) affecting nitrate and DOC flushing trajectories during three spring storms in an agricultural watershed and a mixed land use watershed in glaciated landscape of the Midwest. Hydrograph separation techniques using oxygen-18 isotopes of water and the analysis of major cation flushing trajectories were used to determine the flowpath associated with the export of nitrate and DOC in each watershed. Higher anthropogenic N inputs in the agricultural watershed are associated with higher stream nitrate concentration during storms, while DOC concentration in streams across land uses is mainly influenced by storm characteristics/discharge. In both watersheds, DOC concentration quickly increases and decreases with discharge. In the mixed land use watershed, the peak in nitrate is consistently delayed relative to the peak in DOC; however, nitrate peaks vary in relation to discharge in the agricultural watershed. The comparison of the nitrate/DOC concentration patterns to the concentration patterns of major cations during the storms studied suggests that

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DOC is likely exported via a combination of overland flow and preferential flow through soil macropores in both watersheds. Data suggest nitrate is exported with groundwater, either as tile-drain flow or subsurface flow to the streams. Results also indicate that the connectivity between nitrate/DOC reservoirs and the stream is an important control mechanism on the timing of delivery of nitrate and DOC to the stream in the watersheds studied. Finally, results indicate that even in agricultural watersheds where tile-drain flow is an important contributor to stream flow during storms, there is not necessarily a consistent export mechanism for all solutes. These results underscore the need for further studies investigating the relative importance of matrix flow, overland flow and macropore flow at the watershed scale in order to fully understand event scale processes controlling the transport of solutes to streams in glaciated landscapes of the Midwest under various land use conditions.

Introduction

Understanding the processes controlling nitrate and dissolved organic carbon delivery to streams is important as both stream nitrate and organic carbon concentrations are critical components of the nitrogen and carbon cycles at the continental scale. For instance, excess nitrogen concentration in rivers and streams has been linked to the eutrophication of coastal waters (e.g. Chesapeake Bay and Gulf of Mexico) (Goolsby et al., 2000; Royer et al., 2006) and has been shown to have negative effects on human and ecosystem health (Martin et al., 1999). Similarly, dissolved organic carbon (DOC) dynamics in streams has been linked to acidification processes (Wigington et al., 1996), and to heterotrophic productivity and respiration in small streams, which is important in influencing rates of C cycling and short term CO_2 outgasing (Dalzell et al., 2005). Research has shown that most nutrient and carbon losses generally occur during precipitation events (Boyer et al., 1997; Royer et al., 2006), and that flowpaths that dominate during storm events generally determine the resulting surface water chemistry during and after the event (Bonell, 1993). Nevertheless, much uncertainty remains on the processes controlling the delivery of nitrate and DOC to streams during storms. For instance, in the Adirondack Mountains of New York, McHale et al. (2002) found that nitrate concentration peaked before the peak discharge during one storm and after discharge during another storm. In an agricultural watershed 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 stormflow. Similarly, Inamdar et al. (2004) indicated that nitrate concentration does not necessarily follow discharge during summer storms in two forested catchments of the Adirondacks Mountains, New York, and that nitrate typically precedes the peak in discharge. Welsch et al. (2001) observed staggered nitrate and DOC concentration peaks during summer storm events in a forested catchment in New York, and Hangen et al. (2001) indicated that DOC typically peaks after the peak in discharge in a forested catchment in the Black Forest Mountains of Southwest Germany. On the other hand, Hornberger et al. (1994) and Boyer et al. (1997) indicated that DOC concentration typically peaked prior to discharge on the rising limb of the snowmelt hydrograph and then quickly decreased as snowmelt continued in forested mountainous catchments of Colorado.

This variability in the timing of nitrate and DOC delivery to streams depending on location and seasons has been related to differences in the mechanisms controlling the delivery of these solutes to streams. Inamdar et al. (2004) attributed the early peak in nitrate concentration to the displacement of till water with high nitrate concentration. On the other hand, Creed and Band (1998) indicated that the nitrate peak during storms in an Ontario forested watershed is due to the flushing of nitrate from near surface soil layers, while Hill et al. (1999) found that throughfall was the main source of nitrate in a northern Ontario forested catchment. Similarly, the difference in the timing of DOC delivery to streams depending on location and season suggests that the mechanisms controlling DOC delivery to streams are variable.

Research therefore suggests that nitrate and DOC flushing trajectories in forested catchments are affected by season (snowmelt vs. summer) and the geomorphological characteristics of the catchments studied (Black Forest Mountains vs. Catskills Mountains vs. Ontario vs. Rocky Mountains). However, research is lacking on the processes controlling the flushing behavior of nitrate and DOC during storms in non-forested glaciated landscapes, such as in agricultural or mixed land use watersheds of the Midwest. Many studies looked at nutrient export in Midwestern watersheds (Vanni et al., 2001; Coulter et al., 2004; Royer et al., 2006) and have shown that in agricultural landscapes of the Midwest where approximately 50% of agricultural land is artificially drained (Zucker and Brown, 1998), tile drains and preferential flow through soil macropores are primary pathways for agricultural-chemical transport to streams (Shaffer et al., 1979; Smettem et al., 1983; Edwards et al., 1989; Li and Ghodrati, 1994; Baker et al., 2006; Royer et al., 2006). Nevertheless, these studies do not focus on the mechanisms controlling nitrate and DOC delivery to streams at a high temporal resolution during storms. Understanding event-scale mechanisms controlling nitrate and DOC delivery to streams is critical as most nutrient and carbon losses occur during storms (Boyer et al., 1997; Royer et al., 2006; Dalzell et al., 2007) and excess nutrient losses from Midwestern states such as Ohio, Indiana, and Illinois have been linked to the development of an anoxic zone in the Gulf of Mexico (Goolsby et al., 2000; Royer et al., 2006). In partic-