Baseflow Nitrate in Relation to Stream Order and Agricultural Land Use

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Management of agricultural nonpoint-source pollution continues to be a challenge because of spatial and temporal variability. Using stream order as an index, we explored the distribution of nitrate concentration and load along the stream network of a large agricultural watershed in Pennsylvania—the East Mahantango Creek Watershed and two of its sub-watersheds. To understand nitrate concentration variation in the stream water contributed from ground water, this study focused on baseflow. Impacts of agricultural land use area on baseflow nitrate in the stream network were investigated. Nitrate concentration showed a general decreasing trend with increasing stream order based on stream order averaged values; however, considerable spatial and temporal variability existed within each snapshot sampling. Nitrate loads increased with stream order in a power function because of the dominant effect of stream flow rate over the nitrate concentration. Within delineated sub-watersheds based on stream orders, positive linear functions were found between agricultural land use area percentage and the baseflow nitrate concentration and between agricultural drainage area and the nitrate load. The slope of the positive linear regression between the baseflow nitrate concentration and percent agricultural land area seems to be a valuable indicator of a watershed’s water quality as influenced by agricultural practices, watershed size, and specific physiographic setting. Stream order seems to integrate, to a certain degree, the source and transport aspects of nonpoint-source pollution on a yearly averaged basis and thus might provide a quick estimate of the overall trend in baseflow nitrate concentration and load distribution along complex stream networks in agricultural watersheds.

Knowledge of the spatial distribution of key watershed variables can enhance the understanding of watershed heterogeneity and physical responses at different scales (Hornberger and Boyer, 1995). Among diverse watershed variables, stream order is of particular interest in this study. Investigations on stream-ordering system initiated by Horton (1945) and later refined by Strahler (1957) led to the widely known Horton’s laws of drainage composition. In essence, stream order is a measure of the position of a stream in a hierarchical tributary network. A watershed can be labeled with an order number corresponding to the stream order within its boundary. Stream channel geometry based on stream order also presents insights of self-organizing of river network evolution, reflecting fractal characteristics, sediment transport, and landscape processes (Rodriguez-Iturbe and Rinaldo, 1997). Therefore, a stream-ordering scheme provides a relative scale index that might shed light on watershed processes. A fractal scaling relationship of stream number, stream length, and drainage area to stream order has been well recognized (Horton, 1945; Leopold et al., 1964; Rodriguez-Iturbe and Rinaldo, 1997). However, the relationship between water quality and stream order is yet to be developed (Gupta and Waymire, 1998).

Limited efforts have been made to explore nutrient concentrations or loads in stream water as related to stream order. Few such relevant studies, as summarized herein, suggest that stream order is a potentially valuable indicator of stream water quality. Böhlke and Denver (1995) reported a decreasing nitrate concentration downstream during baseflow in two agricultural watersheds in the Atlantic Coastal Plain, USA. Meybeck (1998) studied water and particulate chemistry (nutrients, major ions, and heavy metals) in the Seine watershed of France at 10 key positions (from the first-order stream to the eighth-order stream at the river mouth). He found that nitrate maximum occurred in small agricultural streams, but phosphate maximum was located at the most downstream stations. In studying the spatial distribution of stream water composition, Hutchins et al. (1999) suggested that the degree of the variability may show some relationship with stream order and land use. When attempting to demonstrate a link between perturbations to the terrestrial phosphorus (P) cycle, the delivery of P to waters, and biological impact, Edwards et al. (2000) indicated that the ecoregion concept combined with stream order would integrate spatial and temporal aspects of gradient, land use,
flow velocity, and water quality. Alexander et al. (2000) reported that nitrogen loss rate in streams declined rapidly with increasing channel size in their SPARROW analysis of 374 monitoring stations in the USA, suggesting that surface water travel time through smaller tributaries (lower-order streams) is a major determinant of their downstream transport to marine systems. Meybeck (2001) reported that daily sediment transport decreased within higher-order stream in a French river. A marked upstream–downstream gradient of contamination was observed that showed major discrepancies between least sensitive elements (cobalt, barium, arsenic) and most sensitive elements (cadmium, mercury, zinc) in the river sediment. Peterson et al. (2001) found that headwater streams played a disproportionately large role in nitrogen (N) transformation on the landscape despite their relatively small dimensions. The importance of lower-order streams in contributing nitrate to stream channel network has also been reported by Gburek and Folmar (1999a) and Lin et al. (2001).

Landscape variables affect water quality in stream and ground waters by altering chemical loads, sediment transport, and hydrological processes (Karr and Schlosser, 1978; O'Neil et al., 1997; Basnyat et al., 1999). These variables could explain a high percentage of total variation in N, P, and sediment yield (Hunsaker et al., 1992; Bolstad and Swank, 1997; Jones et al., 2001). For example, 87% of the variation in total nitrate yield could be explained by landscape metrics (O’Neil et al., 1997). The most significant indicators of the landscape were the amount of agricultural land use, riparian forests, and atmospheric nitrate deposition in a watershed (Jones et al., 2001). Land use is a landscape variable that is largely controlled by human interests but is also often dictated by topography, soil conditions, and climate. Changes of land use by human activities could lead to higher nitrate concentration in streams or aquifers than that of natural background. High nitrate loss to surface and ground waters caused by high percentage of agricultural land use have been widely reported (e.g., Boyer and Pasquarell, 1996; Gburek and Folmar, 1999a; Lin et al., 2001; Coulter et al., 2004). The percentage of cropland in a watershed has been suggested to linearly correlate with nitrate concentration in stream water (Gburek and Folmar, 1999a; Schilling and Libra, 2000; Lin et al., 2001; Schilling and Spooner, 2006).

Ground water and surface water are fundamentally interconnected with multiple hydrological processes (Winter et al., 1998). Nonpoint source pollutants that infiltrate into deeper soil or enter streams can be carried into aquifers by the exchange process between ground water and surface water or vadose zone water. Vice versa, pollutants contained within ground water discharge can have a significant impact on surface water quality (Winter et al., 1998; Harvey et al., 2003; Vanni et al., 2001). During baseflow (also called “low flow,” i.e., when ground water discharge dominates stream flow), high nitrate concentration resulting from agricultural land use can be detected from surface water quality monitoring (Boyer and Pasquarell, 1996; Vanni et al., 2001). Gburek and Folmar (1999a) reported that high nitrate discharge in shallow fracture layer in the East Mahantango Creek Watershed significantly leads to high nitrate concentration in streams during baseflow.

Many previous studies of watershed water quality have focused on headwater streams of small catchments or on specific monitoring sites in large river basins. Sampling schemes were generally snapshots (e.g., one-time sampling), which may not interpret the spatial and temporal variations of water quality from a whole watershed perspective over a longer period (Wayland et al., 2003). Understanding nutrient variability and their relations to land use in different orders of streams may provide insights regarding water quality spatial and temporal variation in stream networks. Therefore, the objectives of this study were (i) to investigate the quantitative relationship between stream order and stream nitrate concentration and load during baseflow and (ii) to examine agricultural land use impacts on stream nitrate in a large agricultural watershed (from the first-order to the fifth-order streams) through a year-round baseflow monitoring. The overall yearly trend reported in this study provides an assessment of the snapshot measure, when linked to stream order and agricultural land use area, in estimating nutrient concentration and load in different sizes of watersheds.

Materials and Methods

Study Watershed

The East Mahantango Creek Watershed is located in the Ridge and Valley Physiographic Province of east-central Pennsylvania, USA (Fig. 1). The drainage basin area is 423.6 km², with an altitude dropping from 550 m in the east to 110 m in the west. The main geological formations are sandstones with interbedded sedimentary rocks (Berg and Dodge, 1981). The climate is temperate and humid with an average annual precipitation of 1090 mm. Agricultural land use dominates in this watershed, with 57% for crops, 35% for forests, and 5% for pastures. Point-source pollution was insignificant in this watershed owing to the absence of a large sewage system and other point sources (Gburek and Folmar, 1999a; Lindsey et al., 2001). Within this watershed, a sub-watershed, called WE-38, has served as a research watershed for the USDA-Agricultural Research Services’ Pasture System and Watershed Management Research Unit since the 1960s. Another sub-watershed adjacent to WE-38, labeled as PA-01, was selected in this study for comparison purpose with the WE-38. Further details of the watershed under study can be found in Pionke et al. (1996) and Lindsey et al. (2001).

Stream Order System, Sub-watershed Delineation, and Watershed Land Use

Derived from the USGS national hydrography datasets (1:24,000), the stream network was used to determine the stream orders for all stream segments within the watershed using the Horton-Strahler method (Strahler, 1957). A total of 218 first-order streams, 48 second-order streams, 11 third-order streams, two fourth-order streams, and one fifth-order stream were identified in the entire stream network of the East Mahantango Creek Watershed.

Eleven quads (7.5 minutes) of the 10-m resolution digital elevation model of the USGS national elevation dataset were processed (including format conversion, emerging, and
smoothing) using ArcGIS 8.2 (Environmental Systems Research Institute, Redlands, CA). With the hydrology extension in ArcGIS 8.2, sinks were found and filled first, and then flow directions were generated based on the filled digital elevation model data. Outlets of different order streams were used to delineate the sub-watersheds based on stream order.

Land use coverage for the entire East Mahantango Creek was obtained from the USGS National Land Cover Dataset, which was based on the Landsat 5 TM imagery (1992) with a spatial resolution of 30 m (Vogelmann et al., 2001). Agricultural land use percentage (including crop and fallow land, pasture, and hay) was calculated as total agricultural land area within a sub-watershed divided by total sub-watershed area.

**Water Quality Monitoring and Analysis**

The protocols from the National Field Manual for the Collection of Water Quality Data (USGS, 1997) were followed for water sampling in this study. Approximately biweekly sampling was conducted to monitor baseflow stream nitrate at 31 representative sites distributed throughout the watershed (Fig. 1). The monitoring sites included nine first-order streams, eight second-order streams, six third-order streams, four sites at two fourth-order streams, and four sites along the fifth-order stream channel (Fig. 1). Due to the similarity of topography, geology, and land use in the lower-order streams in the East Mahantango Creek Watershed, most sampling sites of lower-order streams were located in the two focused sub-watersheds, WE-38 and PA-01. The other sites for higher-order streams were distributed along the main channel network. A total of 17 samplings were conducted at these 31 sites during baseflow from May 2003 to April 2004. To monitor nitrate concentration in stream water contributed from ground water, this study focused on baseflow sampling. No significant thawing or precipitation within 3 d is required for baseflow status in the East Mahantango Creek Watershed, based on an empirical relationship developed by Linsley et al. (1975): $D = 0.827A^{0.2}$, where $D$ is the number of days between the storm peak and the end of overland flow, and $A$ is the drainage area in square kilometers. In our study watershed, $A = 423.6 \text{ km}^2$, and $D = 2.77$ d. In this study, baseflow samplings were conducted during a period when there was no significant thawing or precipitation within at least 4 d. Real-time flow data at a USGS gauge near the outlet of the watershed (located at the fifth-order stream) were used to assist in judging baseflow conditions in the watershed (Fig. 2), where almost all sampling was conducted when the stream flow rate at the watershed outlet was below approximately 10 $\text{ m}^3 \text{ s}^{-1}$. To monitor nitrate loads more closely at different order streams, four gauging stations within the East Mahantango Creek were used in our sampling: the FD-36 gauge on a first-order stream, the WE-38 gauge on a third-order stream, the Klingertown gauge on a fourth-order stream, and the USGS gauge located on a fifth-order stream (Fig. 1). Nitrate loads were
calculated by multiplying flow rate and nitrate concentration. For each sampling, grab samples were collected from all 31 sites within a period of 4 h. We used a specially designed bailer for sampling mixed water samples in large streams. Samples were kept on ice until analysis in the laboratory. After water samples were filtered to autosampler vials through 0.45-μm filters, nitrate was analyzed by the Ion Chromatograph (Dionex Company, Sunnyvale, CA). Autosampler vials were set for wash with mill-Q water, and five standard concentrations (0.1, 1, 5, 10, and 15 mg L⁻¹ nitrate N) were run to develop a standard curve. To ensure quality assurance and quality control, about 10% of samples were randomly replicated for analysis. The standard concentrations after a mill-Q water wash were also randomly inserted to a sample queue.

Nitrate and flow data collected during a sustained baseflow on 13 July and 14 July 1998 for a large portion of the East Mahantango Creek (Lindsey et al., 2001) were re-analyzed with stream order in this study. All 26 sampling sites by Lindsey et al. (2001) were located at the upstream of the Klingerstown gauge, including five first-order streams, nine second-order streams, nine third-order streams, and three fourth-order streams. Wading measurement with a pygmy current meter and a Flo-Mate model 2000 portable water flowmeter (Marsh-McBirney, Inc., Frederick, MD) were used for flow measurements in that study (Lindsey et al., 2001). Five synoptic baseflow water quality samplings in the WE-38 conducted from July 1997 to May 1999, plus one collected in September 1990 (Gburek and Folmar, 1999a), were included for further analysis in this study to investigate their relationships to stream order.

Results and Discussion

Nitrate Concentration in Relation to Stream Order during Baseflow

Averaged nitrate concentration during baseflow over the year-round approximately biweekly sampling showed a general declining trend with increasing stream order in the East Mahantango Creek Watershed, although considerable variation existed within each sampling (Fig. 3). Lower-order streams (e.g., the first- and second-order streams) tended to have higher nitrate concentrations than higher-order streams (e.g., the fourth- and fifth-order streams) on the basis of stream order averaged values. One major reason for such a higher nitrate concentration in the low-order streams was higher discharge from shallow ground water that contained higher nitrate concentration caused by higher agricultural land use in headwater catchments. This observation was supported by the studies of Pionke and Urban (1985) and Gburek and Urban (1990). In contrast, several factors combined to contribute to the lower nitrate concentrations in higher-order streams. First, there is a general trend of reduced agricultural land use area in the higher-order sub-watersheds of the East Mahantango Creek Watershed, although the difference among the five stream orders was not statistically significant (Fig. 4). This general trend would imply reduced sources of nitrate to streams in higher-order sub-watersheds. Second, discharge of ground water in higher-order sub-watersheds tends to come from deeper aquifers that have lower nitrate concentration, as suggested by Pionke and Urban (1985), Gburek and Urban (1990), Böhlke and Denver (1995), and Lindsey et al. (1997). Third, higher nitrate concentration from lower-order streams would be diluted downstream in higher-order streams. A fourth reason is nitrate depletion during in-stream transport through processes such as denitrification in the riparian and hyporheic zones and nitrate consumption by phytoplankton (Cooper, 1990; Burns, 1998; Grimaldi and Chaplot, 1999). Thus, increased in-stream processes in higher-order streams would further reduce nitrate concentration downstream during the baseflow periods.

Significant variations of nitrate concentration in different order streams were noticeable (Fig. 3). The reasons for such variation include (i) a high degree of land use variability within each stream order (Fig. 4 and 5), particularly in headwater areas, where two extreme scenarios were encountered in this study (i.e., 94.14% agricultural use and 92.21% forestry in some first-order sub-water-
Nitrate Concentration in Relation to Agricultural Land Use Area

Nitrate concentration was positively related to agricultural land area percentage in a nearly linear function in this study (Fig. 5). This result was in agreement with previous studies reported by Gburek and Folmar (1999b) and Lindsey et al. (2001). Similar linear relationships between stream nitrate concentration and agricultural land use area have also been reported in other states of the USA, such as West Virginia (Boyer and Pasquarell, 1995), Kentucky (Taraba et al., 1996), and Iowa (Schilling and Libra, 2000). Gburek and Folmar (1999b) developed a simple model for the WE-38 using weighted land uses to predict nitrate concentration in the stream: NO$_3$–N (mg L$^{-1}$) = [1 (%forest) + 8 (%crop rotation) + 10 (%pasture) + 20 (%corn) + 30 (%animal)]/100. Agricultural land use area percentages in this equation (including rotation, pasture, row crops, and animal) were dominant variables influencing water quality. Lindsey et al. (2001) simplified the above model using only three land use variables of forest, row crop, and pasture. Our regression equations shown in Fig. 5 contained an overall percentage of agricultural land area within each sub-watershed that included cropland, fallow, and pasture/hay lands. Using such an overall agricultural land area percentage in lieu of detailed separation of row cropland from other agricultural land uses can provide an easier prediction of stream nitrate concentration without the constraint of detailed land use area distribution (which may be difficult to obtain, especially for large watersheds). In addition, fallow and pasture/hay lands are potential nitrate source areas and therefore should be considered for predicting nitrate in the watershed.

We observed the slope value of the positive linear regression between baseflow nitrate concentration and agricultural land area percentage to decrease with increasing watershed size (Fig. 5). Figure 5a includes the dataset collected from all five orders of streams during this study, and Fig. 5b contains a separate sampling set by Lindsey et al. (2001) that was limited to within the fourth-order streams in the East Mahantango Creek Watershed and another sampling set by Gburek and Folmar (1999a) for the WE-38 only (the first- to third-order streams). The slopes of the three regressions shown in Fig. 5 decreased from 0.15 for the third-order WE-38 to 0.12 for the fourth-order sub-watershed and to 0.10 for the entire fifth-order watershed. Such a trend suggests that agricultural land area percentage tends to have more pronounced impact on stream water quality in lower-order stream areas. As watershed size (and stream order) increases, the watershed system “damping” tends to increase. Schilling and Libra (2000) summarized linear regressions of nitrate concentration and row cropland percentage for different sizes of watersheds (from 0.1 to 237,000 km$^2$) in the midwestern USA and found that the slope of nitrate concentration versus row crop percentage decreased from 0.14 to 0.07 with increasing watershed size. Another interesting observation in this study is that, if we force the intercept of the linear regression to be that of the forestry watershed average (0.47 in this study [see Fig. 5a], which could be interpreted as the watershed’s background nitrate concentration), then the slope for all three regressions shown in Fig. 5 for the Mahantango Creek Watershed would be almost identical (i.e., 0.10). This suggests that the slope of nitrate concentration (mg L$^{-1}$) vs. agricultural land area (%) relationship can serve as a comparative indicator of nitrate output during baseflow among different agricultural watersheds within similar climatic regimes. Besides watershed size (and stream order), other factors, such as hydrogeology, geomorphology, and the type of agriculture, influence this slope value. For example, Boyer and Pasquarell (1995) reported the slope of linear regression of median nitrate concentration with percent agricultural land area to range from 0.19 to 0.25 in Karst springs in an extensively grazed area in West Virginia, suggesting that animal agriculture has a greater impact per percent increase in agricultural land area in Karst watershed.

Averaging over the entire year of our monitoring dataset, baseflow nitrate concentration in this study showed a linear relationship with agricultural land area (y = 0.69 + 0.10x; $r^2 = 0.55$) and stream order (y = 7.90 – 0.69x; $r^2 = 0.36$), but with opposite trends (Fig. 3 and 5). This could be partially explained by an overall decreasing trend of agricultural land area percentage with increasing stream order in the watershed studied (Fig. 4). With added links to in-stream processes and travel distance, stream order seems to reflect, to a certain degree, a combined effect of source and transport aspects of nonpoint-source pollution, hence achieving a higher yearly-averaged regression $r^2$ (0.76) with baseflow nitrate concentration.
than that with agricultural land area percentage alone ($r^2 = 0.55$). We are aware that in some other areas agricultural land use area percentage may increase with increasing stream order because of the tendency of steeper landforms (poorly suited to agriculture) to occur closer to watershed divides (i.e., in lower-order stream areas). Thus, the observed stream order relationships in this study may not hold everywhere. Nevertheless, the generic nature of a stream-ordering scheme would allow a wider application of stream order in examining watershed processes in relation to water quality in different portions of a hierarchical stream tributary network.

**Nitrate Loads in Relation to Stream Order and Agricultural Land Use Area**

Based on stream flow and water quality data collected in the 1990s, nitrate loads increased with increasing stream order in a power function (Fig. 6). Seasonal effects changed total loads of nitrate but did not change the power function relationship between nitrate loads and stream order (Fig. 6b). Nitrate loads obtained from our four gauging stations (representing four different order streams) from May 2003 to April 2004 also showed a power function relationship with stream order (Fig. 7). Such a relationship was apparently dominated by the impact from stream flow rate or, equivalently, drainage area because they both had a power function relationship with stream order (Fig. 7b). Because nitrate loads were calculated as the product of flow rate and nitrate concentration and because stream flow rate varied much more significantly from the first-order to the fifth-order streams than that of baseflow nitrate concentration, the load distribution along the stream network was controlled by the flow rate rather than the nutrient concentration. Lower nitrate loads in headwater streams were due to lower flow with smaller drainage area, although nitrate concentration tended to be higher than that in higher-order streams in the watershed in this study.

In terms of contributing area of agricultural land and nitrate loads, their relationship is nearly linear for the East Mahantango Creek Watershed as a whole and for its sub-watershed WE-38 (Fig. 8). The power function relationship of drainage area and stream order, as suggested in the Horton’s laws (Horton, 1945), implies that a linear relationship between agricultural drainage area and nitrate loads is expected because nitrate loads and stream order also display a power function relationship in this watershed. Compared with drainage area, stream order is simpler to determine and can provide well defined sub-watershed area and the location in the complex stream network, whereas drainage area is more continuous and varies considerably depending on the targeted stream segment or sampling site. In addition, stream order is a simple variable in the hierarchical tributary network that might enable quick prediction of relative nutrient concentration, load, stream flow, and landscape features across different sizes of watersheds.

**Summary**

The results of this study suggest that stream order, as indicated in earlier work, might quantitatively integrate the effects of source and transport factors controlling diffuse pollution. Stream order in this study showed the general trend of baseflow nitrate concentration and load distribution along the tributary stream network in the East Mahantango Creek Watershed, USA. An overall inverse relationship was observed between baseflow nitrate concentration and stream order using stream order averaged values; however, considerable spatial and temporal variations existed within each stream order during each
snapshot sampling, owing to the variability in agricultural land area, manure application rate, stream flow regime change, and seasonal or diurnal fluctuations. The general decreasing trend of baseflow nitrate concentration with increasing stream order is explained by the reduced nitrate sources (e.g., decreased agricultural land area percentage) and increased in-stream processes, including dilution effect. In contrast, a power function relationship was observed between nitrate loads and stream order in the study watershed, owing to the dominant effect of stream flow rate that increased with stream order in a power function manner. Nitrate loads can also be estimated by the contribution area of agricultural land use through a simply linear function. Nevertheless, compared with drainage area, the simpler index of stream order might enable quick estimate of relative nutrient concentration, load, stream flow, and landscape features across different sizes of watersheds. Further studies are needed to explore nonpoint-source pollutant distribution in various watershed stream networks and how in-stream processes may alter such distribution. Although watershed specificity might exist, the generic nature of a stream-ordering scheme might provide wider implications for enhanced understanding of watershed processes as related to water quality along a hierarchical stream tributary network.

This study found that the slope of the linear regression between baseflow nitrate concentration (mg L$^{-1}$) and percent agricultural land area (%) is a useful indicator of the degree of agricultural impacts on water quality in a given watershed. Such a slope varies with watershed size (and stream order) and

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**Fig. 6.** Nitrate loads in different order streams in (a) the East Mahantango Creek Watershed and (b) the WE-38 sub-watershed. Error bars indicate 1 SD. The regression analysis in (a) was performed with averaged nitrate load for each stream order. (Data from Lindsey et al., 2001; Gburek and Folmar, 1999a.)
the type of watershed and its related landscape features, such as the type of agriculture, hydrogeology, and climate.

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