

## Quantifying Nitrate Flux during Storm Events

J. S. Herman<sup>1</sup>, A. L. Mills<sup>1</sup>, G. M. Hornberger<sup>1</sup>, A. C. Sofranko<sup>2</sup>, and M. S. Olson<sup>3</sup>

<sup>1</sup>Program of Interdisciplinary Research in Contaminant Hydrogeology, Department of Environmental Sciences, University of Virginia, P.O. Box 400123, Charlottesville, VA 22904-4123; PH (434) 924-7761; FAX (434) 982-2137; e-mail:

[jherman@virginia.edu](mailto:jherman@virginia.edu)

<sup>2</sup>Department of Civil and Environmental Engineering, University of California-Berkeley, Berkeley, CA 94720-1710; e-mail: [annasofranko@gmail.com](mailto:annasofranko@gmail.com)

<sup>3</sup>Department of Civil, Architectural and Environmental Engineering, Drexel University, 3141 Chestnut St, Philadelphia, PA 19104; e-mail:

[mira.s.olson@drexel.edu](mailto:mira.s.olson@drexel.edu).

### Abstract

Excess nitrate, mainly due to agricultural fertilizers, is a common problem in the surface water and groundwater of the Coastal Plain of the eastern United States. Baseflow conditions have been studied in an effort to understand nutrient loading to coastal waters, but there are many unanswered questions pertaining to nitrate flux during storm events. An automated stream sampler was deployed to collect water from a stream on the Eastern Shore of Virginia, USA, whenever stream stage rose following a rainfall event. Baseflow nitrate concentrations were typically 2.0-2.2 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>, and concentrations decreased rapidly with the onset of precipitation. Slightly in advance of peak discharge, the typical streamwater concentration was reduced to approximately 0.2-0.4 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>. Streamwater nitrate concentrations slowly returned to pre-storm levels after the discharge level returned to baseflow. Even though the nitrate concentration of surface water decreased during storms, the average storm nitrate flux was approximately a factor of 3 times greater than the average base flow nitrate. Large quantities of nitrate were quickly transferred during storms due to the large volume of water with low nitrate concentrations flowing in the stream. Insights to nutrient management, particularly considering rates of biological uptake of nitrate, are supported by this more complete understanding of the dynamic flux of streamwater nitrate to coastal waters.

## Introduction

Nitrogenous fertilizers are widely used in agriculture throughout the United States to improve crop yield, but the fertilizers also contaminate surrounding water supplies with dissolved nitrate. On the Eastern Shore of Virginia, almost 50% of the land use is in crop production (Reay et al., 2001), and fertilizers and manures are commonly applied to the soil surface. Impacted by direct surface-water runoff and by discharge of groundwater and soil water, the streams draining these agricultural areas carry high nitrate concentrations. In particular, the sandy soil in this region, by allowing rapid infiltration and subsurface flow, facilitates the transport of nitrate from upland fields into streams.

High nitrate concentrations lead to eutrophication, an over-enrichment of a body of water with nutrients, which results in excessive growth of aquatic plants and depletion of dissolved oxygen in the water. When the algae die and decompose, the reduction in dissolved oxygen in the water column has subsequently killed many fish. Algal blooms have occurred in the Chesapeake Bay and coastal waters when there are excess nutrients, particularly nitrate, in the water. Therefore, eutrophication disrupts the ecological balance and produces an environment which does not readily support aquatic life (Winter et al., 1998).

In the hydrogeological setting of the Coastal Plain of the eastern United States, groundwater typically discharges to low-gradient streams that may carry the dissolved nitrate flux to coastal lagoons and bays where nutrient-supported algal blooms degrade water quality and impact aquatic life. Steady state, baseflow conditions have been studied with a view toward understanding nutrient loads in surface waters, but there are many unanswered questions pertaining to nitrate flux during storm events. Whereas discharge records indicate that the majority of annual freshwater discharge from small coastal watersheds occurs during storms, much less is known about the dynamics of nutrient discharge. This study sought to quantify the transient nitrate flux associated with storm events.

## Methods

### Field Site

Cobb Mill Creek (Fig. 1) is located near the town of Oyster on Virginia's Eastern Shore, the southern end of the Delmarva Peninsula located between the Chesapeake Bay and the Atlantic Ocean. This is an intensely cultivated region of unconsolidated, sandy Coastal Plain deposits [Mixon, 1985]. Cobb Mill Creek is underlain by sandy sediment interbedded with a thin silty layer that is rich in organic material. Cobb Mill Creek is a second-order, low-gradient (over a stream length of 2.9 km, the streambed elevation drops 10.7 m), groundwater-dominated creek that drains a low-relief, 4.8 km<sup>2</sup> watershed at the Anheuser-Busch Coastal Research Center (ABCRC) of the University of Virginia. The field site has been extensively characterized for agricultural nitrate contamination and active biogeochemical conditions in the streambed sediments [Galavotti, 2004; Gu et al., 2007].

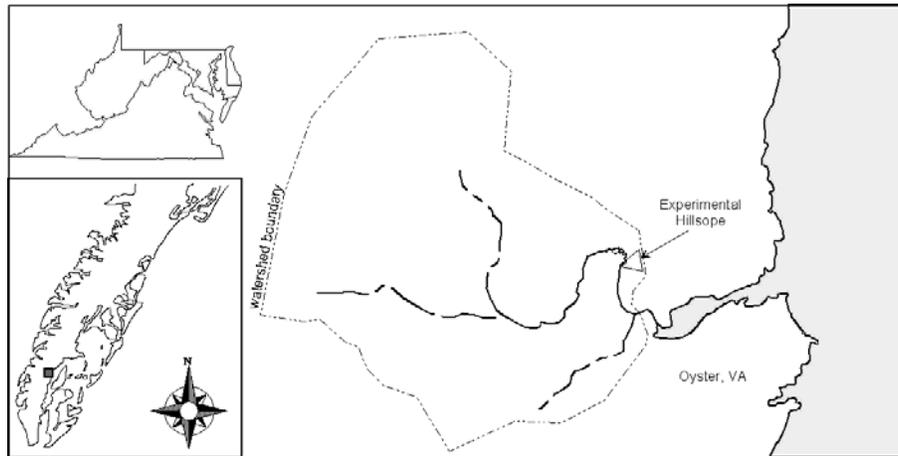


Figure 1. Location of experimental watershed drained by Cobb Mill Creek near the town of Oyster on the Eastern Shore of Virginia. Stream samples were collected adjacent to the position labeled “Experimental Hillslope.”

### Stream Sampling

A sensor, a pump, tubing, 24 collection bottles, a battery, and a programmable interface comprised an automatic, stage-activated sampler. The sensor was suspended slightly above the water level in the stream, the tubing was placed mid-depth in the stream, and the rest of the equipment was placed on level ground on the streambank. The sampler was programmed to begin collection when the stream stage rose with the onset of a rain event and to collect a new sample after a given time interval, either 1 or 2 hours, for a total of 24 samples. The samples were then refrigerated soon thereafter to inhibit any change to the chemical composition of the water samples.

### Chemical Analyses

Samples were brought to the laboratory within 24 hours of the end of a storm event. From each sample bottle, water was immediately filtered through 0.45  $\mu\text{m}$  Millipore filters and split into three separate glass centrifuge bottles with screw-on plastic caps. The triplicates of each water sample were analyzed for chloride, nitrate, and sulfate by ion chromatography. Samples were re-analyzed if the concentration of nitrate for one of the triplicates differed by more than 0.05 standard deviation. In the rare case that the second chemical analysis also yielded poor reproducibility, the values from the run with a smaller standard deviation were used. The average of the concentrations of the triplicate samples was used for further data analysis.

## Results

Only a brief lag time of a few hours separated the onset of precipitation from an increase in stage (Fig. 2). With almost no lag, the concentration of nitrate in Cobb Mill Creek decreased sharply as discharge began to increase due to precipitation during a storm event. Baseflow nitrate concentrations were typically  $2.0\text{--}2.2\text{ mg NO}_3^- \text{-N L}^{-1}$ , and concentrations decreased rapidly with the onset of precipitation. Slightly in advance of peak discharge, the typical streamwater concentration was reduced to approximately  $0.2\text{--}0.4\text{ mg NO}_3^- \text{-N L}^{-1}$ . As the rain stopped and discharge began to decrease, the concentration of nitrate increased slowly. Streamwater nitrate concentrations slowly returned to pre-storm values after the discharge returned to baseflow levels.

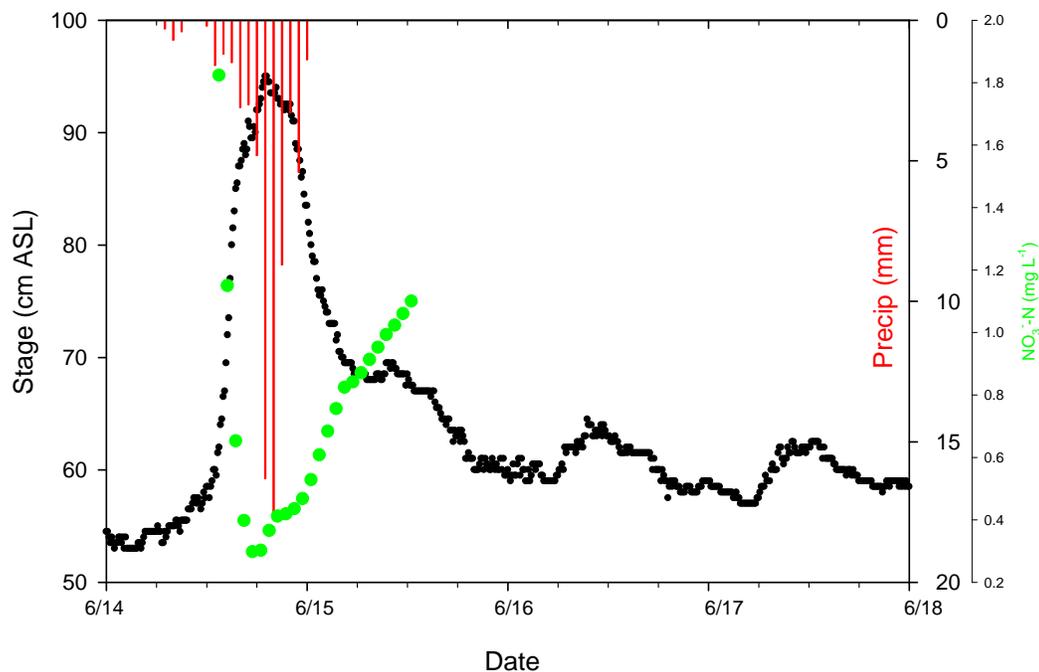


Figure 2. Complete storm hydrograph for storm starting on June 14, 2006. Shown are stage (cm above sea level), nitrate concentrations ( $\text{mg NO}_3^- \text{-N L}^{-1}$ ), precipitation (mm; note that the amount of precipitation is plotted with reverse y-axis values where a large rainfall is represented as a bar extending a greater distance from the top of the plot to the bottom).

## Discussion

Even though the nitrate concentration of surface water decreased during storms, the average storm nitrate flux was approximately a factor of 3 times greater than the average base flow nitrate flux due to the large volume of water discharged during a storm. Large quantities of nitrate were quickly transferred during storms due to the

large volume of water draining the coastal watershed. Even with very low nitrate concentrations in the streamwater, the increased flux of water carried with it a significant load of nitrate to the seaside lagoon. Insights to nutrient management are supported by this more complete understanding of the dynamic flux of streamwater nitrate to coastal waters.

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