NUTRIENT LOADING PATTERNS ON AN AGRICULTURALLY IMPACTED STREAM SYSTEM IN HUNTINGDON COUNTY PENNSYLVANIA OVER THREE SUMMERS

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ABSTRACT: Spruce Creek and Warrior's Mark Run, located in Huntingdon County of Central Pennsylvania, were studied from 2002 to 2004 to determine the effects of agricultural practices on water quality. These two creeks are tributaries to the Juniata River which feeds the Susquehanna River. The summers of 2002, 2003, and 2004 represent different hydrologic conditions of the Spruce Creek watershed, which allowed for testing of nutrient fluctuations under a variety of hydrologic conditions. Land use varies along the banks of these streams; a concentrated animal feeding operation is located near the banks of Spruce Creek, while Warrior's Mark Run has much traditional agriculture located near its banks.

Headwater samples of Warrior's Mark Run contain low nitrate concentrations (0.44-0.89 mg/L), whereas the water samples from all other sampling sites have higher nitrate concentrations (>8.0 mg/L). Overall, the total nitrate loads are higher on Spruce Creek than Warrior's Mark Run. Nitrate is present in the stream system regardless of the amount of rainfall, and tends to increase as discharge decreases. This could indicate that nitrate enters the system through baseflow.

Within this stream system, phosphate behaves differently than nitrate. Generally, Spruce Creek exhibits a higher phosphate load than Warrior's Mark Run. Phosphate concentrations seen in the headwaters of Warrior's Mark Run are similar to the other sampling locations along this stream, indicating that the bedrock is potentially a source for this nutrient. In contrast to nitrate concentrations, the phosphate concentrations increased during large discharge events. This signifies that phosphate is likely associated with particulates derived from surface runoff due to rain events.

Turbidity typically increases with elevated discharge, as well as with increases in phosphate levels. This suggests that an input of phosphate into the stream system may be associated with an input of particulates, which will raise turbidity. Conversely, nitrate concentrations vary with increasing turbidity.

INTRODUCTION

With the increasing rate of urban and agricultural growth in the United States, many surface waters are becoming polluted due to nutrient overloading, which can lead to eutrophication (Paerl 1996; Anderson et al. 2002). Consequences of this process include algal blooms and anoxia in the system, as well as fish kills (Rosemond et al. 1993; Correll 1999; Dodds and Welch 2000). Stream monitoring programs have been implemented across the country to monitor water quality and quantity, as it is necessary to monitor these systems to better understand the source and transport of nutrients (Karr 1999; Gouveia et al. 2000).

High levels of growth-limiting nutrients like nitrate and phosphate can adversely affect stream biota and water quality (Webster et al. 1995; Correll 1998; Dodds and Welch 2002; Ha et al. 2003). While many point and non-point sources exist for these nutrient species, agriculture is typically the main source (Moog and Whiting 2002). Although these nutrients may not directly affect fish (Hrubec et al. 1996; Miltner and Rankin 1998), nitrate and phosphate enhance the growth of algae, which in turn will stress the biological oxygen supply. Fish and other organisms in a stream rely on oxygen to survive, and populations decline if there is an insufficient supply (Rabalais 2002; Davies et al. 2004).

Agriculture is a common practice in Pennsylvania, especially in the Susquehanna River Watershed. This watershed is of special interest because it empties into the Chesapeake Bay, which is known to receive large influxes of nutrients (Officer et al. 1984; Krupnick et al. 1998). Around the Chesapeake Bay area, non-point source pollution has become the largest contributor of nutrient pollution, as most environmental legislation focuses on point source pollution (Yoder and Rankin 1998; Boesch et al. 2001). Therefore, quantifying nutrient loads from non-point source pollutants in first and second order streams is important in helping to determine the overall nutrient load that will flow into the Chesapeake Bay.

Spruce Creek, whose waters flow to the Chesapeake Bay, is one of the many spring-fed, second order, limestone streams in central Pennsylvania. This stream is approximately seven miles long, and its waters provide an exceptional habitat to the large rainbow and brown trout for which it is known. Over the years, those who live along its banks and those who frequent its waters have noticed a dramatic decline in the quality of Spruce Creek's fishery. The suspected reason for this decline in quality is nutrient loading from the agriculture located on the banks of Spruce Creek and its tributaries. In particular, there is a concentrated animal feeding operation (CAFO) found along the banks of Spruce Creek that is thought to influence its water quality. A CAFO is defined by the Environmental Protection Agency (EPA) as an "operation which stables or confines and feeds or maintains for a total of 45 days or more in any 12-month period more than 700 mature dairy cattle" (USEPA 2002).

Downstream from the CAFO there is a tributary to Spruce Creek, called Warrior's Mark Run, as illustrated in **Figure 1.** Along Warrior's Mark Run, there is an abundance of traditional agriculture. These typical farming practices, which tend to be smaller in scale, do not fall under CAFO regulations. It is possible that this traditional agriculture along Warrior's Mark Run is also contributing significant nitrate concentrations to Spruce Creek.

This study focused on quantifying nutrient concentrations at various locations from the headwaters of Spruce Creek to its confluence with the Little Juniata River in order to identify nutrient sources within this stream system.

MATERIALS AND METHODS

Sampling Procedures

During the course of the study, nine sampling sites along Spruce Creek and Warrior's Mark Run were established in order to best capture an overall nutrient profile of the stream system (Fig. 1). During 2002, only sites 1, 2, 3, and 9 on Spruce Creek were sampled until it was speculated that Warrior's Mark Run might also be contributing nutrients to the stream system, as there is a significant increase in nutrients downstream from the confluence of these two streams. In 2003, sampling sites 4, 5, 6, and 7 along Warrior's Mark Run were added, as well as site 8 on Spruce Creek. All sampling locations were specifically chosen in order to determine where nutrients were entering the streams. Site 1 was chosen as a generally unaffected site, as it is upstream from the CAFO. Downstream from site 1 are sites 2, 8, and 9. Site 2 is directly downstream from the CAFO, and sites 8 and 9 are downstream from both the CAFO and the confluence of Spruce Creek and Warrior's Mark Run. Sites 7 and 6 represent the two agriculturally impacted branches of Warrior's Mark Run. Downstream from the confluence of these two branches are sites 5, 4, and 3. All three of these sites are downstream from agriculturally impacted areas, and are surrounded by agriculture as well. Site H1 was chosen to represent the agriculturally unaffected headwaters of Warrior's Mark Run, but was only sampled occasionally during the summer of 2004.

During the summers of 2002, 2003, and 2004, water samples were collected five days a week between the end of May and the beginning of August, and two days a week during the remaining months. From May through August, the time of sampling was kept constant, with sampling beginning at 9:00 am and ending at 11:00 am. From late August to early May, sampling generally began between 1:00 or 2:00 pm and ended between 3:00 or 4:00 pm. It has been found that stream water quality is strongly related to diurnal variations (Fogle 2002), therefore sampling times were kept consistent to ensure that varied times of sampling did not affect the results.

Parameters measured in the field include temperature, total dissolved solids, and discharge. Temperature and total dissolved solids measurements were collected using a HACH Sension5 portable meter, and discharge was

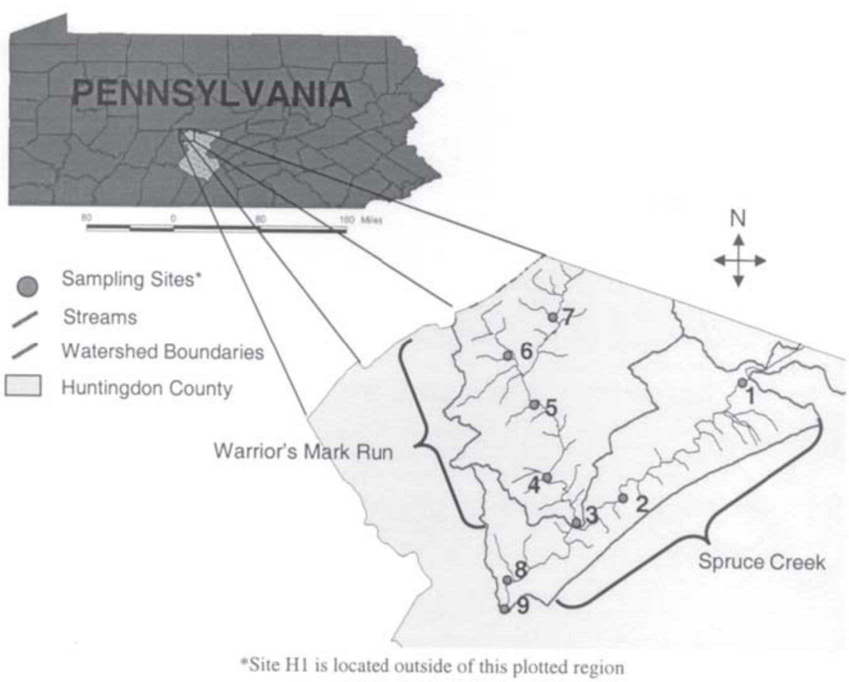

Figure 1. Map of Spruce Creek and Warrior's Mark Run in relation to Huntingdon County and the state of Pennsylvania. Sampling sites are numbered along the segments of each stream.

calculated using data collected from a Global Water FP101 flow probe. Water samples were collected using 250 mL glass bottles and were kept in a cooler until they were tested, which was generally 2 to 3 hours after collection.

Laboratory Procedures

All water samples were analyzed in the laboratory for pH, turbidity, nitrate as NO_3^--N, and phosphate as PO_4^{3-}. pH was measured using a HACH Sension1 portable meter (HACH a 2000). Turbidity was measured using the HACH DR2000 direct reading spectrophotometer (HACH d 2003). Nitrate was measured using the HACH DR2000 with a cadmium reduction method (HACH c 2003) and ion chromatography (Dionex IC1000). Phosphate was measured using the HACH DR2000 with a sulfuric acid reduction method (HACH b 2003) and ion chromatography. All concentrations obtained through the HACH method were corrected using the data from the Ion Chromatograph (IC), so that our reported values were consistent (Phillips et al. 2006). Errors for all analyses are reported at the 2σ level and were determined by measuring the variation of the standard run 12 times during one analytical session. For further clarification of testing methods, see HACH Water Analysis Handbook 2nd Edition.

DATA AND RESULTS

Hydrologic Profile

As can be seen for site 1, which is typical of all sampling sites, the summers of 2002, 2003, and 2004 were significantly different in terms of hydrologic conditions **(Fig. 2a)**. The summer of 2002 was characterized by drought conditions in the region, and the lack of rainfall correlates with low discharge on Spruce Creek. Based on data from nearby State College, PA, no measurable precipitation fell on the area during June, July, and August (Weather Underground 2005). Accordingly, maximum discharge was well below 150 cfs, and the average discharge for this summer was around 34 cfs. The hydrograph for the summer of 2002 shows a gradual recession of baseflow due to these dry conditions.

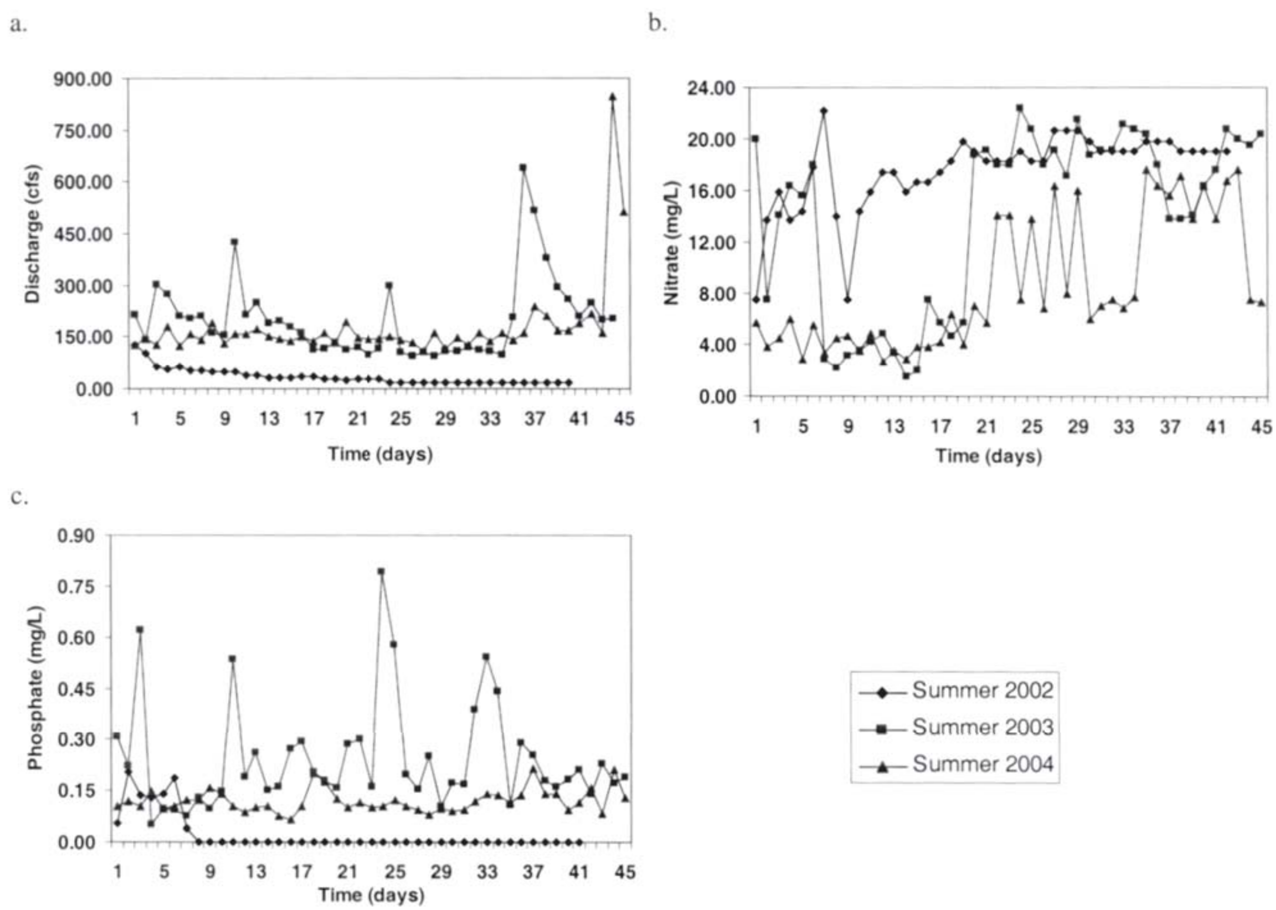

Figure 2. Plots of measured stream parameters collected during the months of May through August 2002 through 2004. A) Discharge in cubic feet per second at site 1, located on Spruce Creek, for the summers of 2002, 2003, and 2004. B) Nitrate concentrations in milligrams per liter at site 1, located on Spruce Creek, for the summers of 2002, 2003, and 2004. C) Phosphate concentrations in milligrams per liter at site 1, located on Spruce Creek, for the summers of 2002, 2004, and 2004.

The summer of 2003 was a wetter summer, with steady precipitation leading to high stream flow levels. Precipitation data from State College shows that the area received 14.6 total inches of precipitation in June, July, and August of 2003 (Weather Underground 2005). Stream discharges were therefore considerably higher than in the summer of 2002; maximum discharge was as high as 650 cfs, and average discharge was around 201 cfs.

The summer of 2004 was a median between the wet and dry summers. Precipitation data show 9.0 inches of precipitation in June, July, and August (Weather Underground 2005); stream discharges were accordingly between those encountered in the summers of 2002 and 2003. Discharges ranged from 125 to 225 cfs and the average discharge for this summer was about 155 cfs.

Average discharge rates for each site from 2003 and 2004 are shown in **Table 1**, although 2002 is unrepresented due lack of data at sites 4, 5, 6, 7 and 8 during this time period.

Nutrient Profiles

The highest and lowest nitrate concentrations for each sampling site varied from summer to summer, as seen in **Table 2.** Even through nitrate concentrations varied by day, all concentrations are higher than the EPA EcoRegion XI standard for stream water (USEPA 2000).

Average nitrate concentrations varied between sites on each stream as shown in Table 1, though concentrations are slightly higher on Warriors Mark Run than Spruce Creek. During the summer of 2002, low discharges, with an average of 34 cfs, coincided with high nitrate concentrations, with an average of 17.77 mg/L (Figs. 2a and b, respectively). During the summer of 2003, highly variable discharge rates, ranging from 100 to 650 cfs, caused nitrate concentrations to fluctuate between 1.55 and 22.36 mg/L with an average of 13.99 mg/L. The summer of 2004 shows a moderate variability in the discharge rate, ranging from 125 to 225 cfs, and a roughly daily fluctuation in the nitrate concentration between 2.66 and 17.57 mg/L with an average of 8.56 mg/L.

Average phosphate concentrations decrease downstream, with Warrior's Mark Run exhibiting higher concentrations than Spruce Creek, as seen in Table 1. Phosphate concentrations correlate with low discharge for the summer of 2002, with the average concentration being below the detection limit of our analytical method (Fig. 2c). The summer of 2003 showed a high degree of variability for both discharge rates and phosphate concentrations, which varied between 0.05 and 0.8 mg/L. During the summer of 2004, there were moderate fluctuations in discharge and phosphate concentrations, with phosphate ranging from 0.05 to 0.25 mg/L with an average of 0.12 mg/L.

Table 1. Average turbidity, total dissolved solids, and nitrate and phosphate concentrations measured for all sampling sites on Spruce Creek and Warrior's Mark Run for the summers of 2002, 2003 and 2004, and average discharge for all sampling sites on Spruce Creek and Warrior's Mark Run for the summers of 2003 and 2004.

Site	Average Discharge (cfs)	Average Turbidity (FTU)	Average TDS (mg/L)	Average Nitrate Concentration (mg/L)	Average Phosphate Concentration (mg/L)
Spruce Creek Sites					
1	189.38	11.65	189.38	11.27	0.18
2	221.55*	10.97	182.21	12.80	0.16
8	--	10.65	182.14	12.05	0.15
9	--	10.13	179.97	12.51	0.15
Warriors Mark Run Sites					
7	19.07	17.88	186.38	15.45	0.21
6	8.59	12.15	208.72	14.65	0.20
5	41.11	16.49	205.84	18.09	0.22
4	78.41	9.69	167.46	8.78	0.18
3	82.14	9.55	180.00	11.71	0.18

*Discharge data was recorded at site 2 only during 2003

Table 2. The highest and lowest nitrate concentrations (mg/l) measured for all sampling sites on Spruce Creek and Warrior's Mark Run for the summers of 2002, 2003, and 2004.

Site	Summer '02 Highest Nitrate Concentration in mg/L	Summer '02 Lowest Nitrate Concentration in mg/L	Summer '03 Highest Nitrate Concentration in mg/L	Summer '03 Lowest Nitrate Concentration in mg/L	Summer '04 Highest Nitrate Concentration in mg/L	Summer '04 Lowest Nitrate Concentration in mg/L	EPA Ecoregion XI Standard in mg/L
1	22.21	7.48	22.36	3.10	17.58	2.66	0.31
2	42.02	8.58	28.63	3.52	19.44	2.64	0.31
8	-	-	-	-	19.56	3.54	0.31
9	35.56	8.58	29.28	2.66	19.56	2.88	0.31
3	21.42	5.72	28.17	3.52	15.87	1.1	0.31
4	-	-	22.77	3.10	14.15	1.56	0.31
5	-	-	37.66	4.21	29.28	5.09	0.31
6	-	-	36.73	3.54	21.96	3.32	0.31
7	-	-	35.33	3.77	19.56	3.99	0.31

To determine if the phosphate concentrations observed in these streams are dissolved or adsorbed to particulates, undigested water samples were analyzed using an IC. These tests resulted in phosphate concentrations that were below the detection limit of the instrument, indicating that the phosphate detected in the sulfuric acid reduction method, which involves digestion of the samples, were adsorbed to particulates.

Over these three summers, turbidity levels generally decreased downstream on Spruce Creek and Warrior's Mark Run, as shown in Table 1. Warriors Mark showed higher levels of turbidity than Spruce Creek. Turbidity levels tend to increase during sharp increases in the hydrograph **(Fig. 3)**, which typically signifies a rain event. **Figure 4** illustrates the relationship between turbidity and nutrient concentrations. Nitrate concentrations vary at increasing turbidity levels, while phosphate concentrations tend to increase.

Effects of CAFO and Traditional Agriculture on Nutrient Loading

Traditional agriculture and CAFO agriculture add nutrients to the Spruce Creek and Warrior's Mark Run stream systems in different capacities. Spruce Creek, which flows alongside a CAFO, and Warrior's Mark Run, which is surrounded by traditional agriculture, vary in their nutrient concentrations and the total load of nutrients flowing through them.

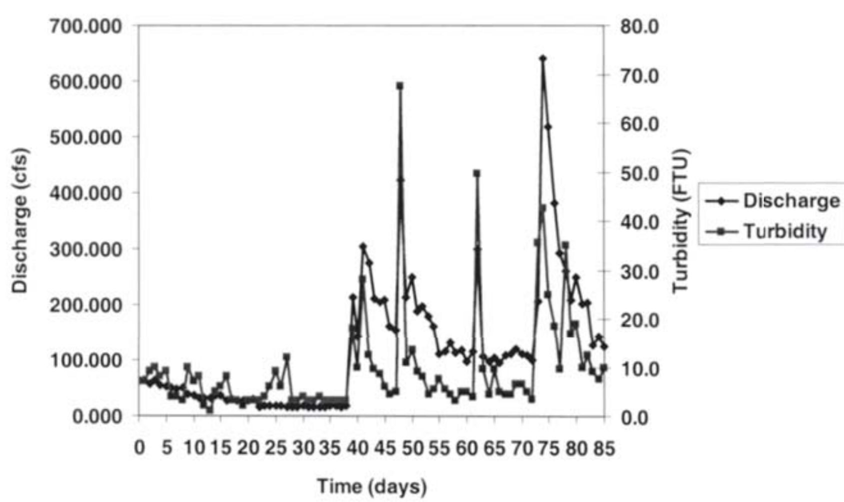

Figure 3. Plot of turbidity (Formazin) versus discharge (cfs) measreud at site 1, located on Spruce Creek, for the summer of 2003.

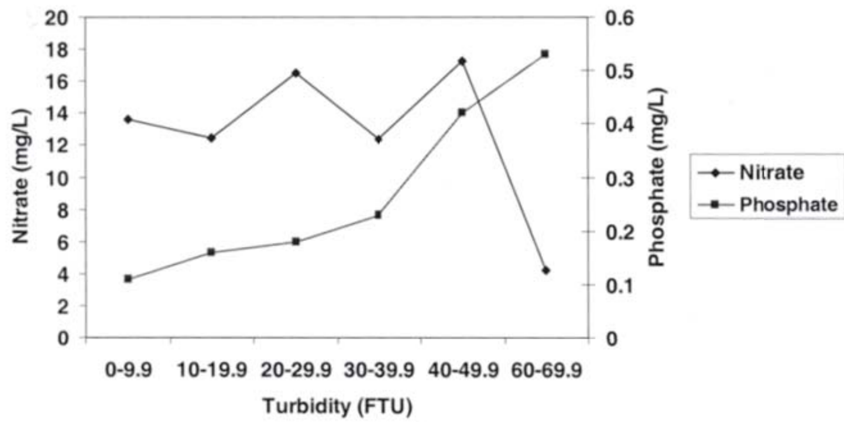

Figure 4. Ranges of turbidity (Formazin) and the average nitrate and phosphate concentrations (mg/l) that correspond with those turbidity ranges at site 1, located on Spruce Creek, for the summer of 2003.

Table 3. This table summarizes the average discharge (cfs) to the total daily nitrate and phosphate loads (kg/day) for the summer of 2003 on the headwaters of Warrior's Mark Run (no agriculture), Warrior's Mark Run (traditional agriculture), and Spruce Creek (CAFO agriculture).

No Agriculture Sites	Average Discharge (cfs)	Nitrate Load (kg/day)	Phosphate Load (kg/day)
H1	2*	2.98*	0.51*
Traditional Agriculture Sites			
7	19.07	774.80	9.92
6	8.59	315.28	4.39
5	41.11	1857.39	23.02
4	78.41	1628.62	33.01
3	82.14	2337.40	34.91
CAFO Agriculture Sites			
1	141.30	5301.10	85.53
2	135.84	6939.29	86.00

*Data was recorded at site H1 only during 2004

Warrior's Mark Run generally has higher concentrations of nutrients (Table 1), while Spruce Creek has higher overall nutrient loads (**Table 3**). Table 3 also illustrates that the total load of nitrate and phosphate moving through the stream system typically increases downstream from each site. The only exception is that the nitrate load decreases slightly between sites 5 and 4 while the phosphate load increases greatly between these two areas.

The Warrior's Mark Run headwater samples consistently contain a lower concentration of nitrate than the Warrior's Mark Run stream water samples (**Table 4**), while phosphate concentrations of the headwaters are similar to those of the stream waters (**Table 5)**. Table 3 shows that the total load of nutrients for each headwater sample is low when compared to the rest of Warrior's Mark Run.

DISCUSSION

There are many possible sources for nitrate and phosphate within the Spruce Creek watershed. Typical sources of nitrate within stream water include septic tanks, leach pools, refuse dumps, animal feed lots, fertilizers, municipal and industrial wastewater, urban drainage, atmospheric deposition, underlying bedrock, and decaying plant debris (Viney et al. 2000). Within the Spruce Creek watershed, the possible sources are septic tanks, animal feed lots, fertilizers, and atmospheric deposition. While the weathering of rocks may be a source of nitrate in other locations (Holloway and Dahlgren 2001), water interaction with bedrock in stream bottoms an unlikely source of nitrate. The rock units that underlie these streams are limestone (Coburn, Loysburg, Axemann, Stonehenge, Warrior Run, and Pleasant Hill Formations) and dolomite (Bellfont, Nittany, and Gatesburg

Table 4. This table provides a comparison of nitrate concentrations (mg/l) on Warrior's Mark Run headwater samples with Warrior's Mark Run stream samples for three days in the summer of 2004.

Nitrate Concentrations (mg/L) on Warrior's Mark Run			
Site	**6/8/2004**	**6/22/2004**	**7/29/2004**
H1	0.89	0.44	0.44
7	5.54	17.17	7.53
6	4.43	13.78	7.53
5	5.54	20.37	17.98
4	2.22	6.42	13.78
3	3.52	6.82	7.92

Table 5. This table provides a comparison of phosphate concentrations (mg/l) on Warrior's Mark Run headwater samples with Warrior's Mark Run stream samples for three days in the summer of 2004.

Phosphate Concentrations (mg/L) on Warrior's Mark Run			
Site	**6/8/2004**	**6/22/2004**	**7/29/2004**
H1	0.06	0.11	0.06
7	0.13	0.25	0.15
6	0.11	0.24	0.19
5	0.09	0.20	0.16
4	0.10	0.13	0.13
3	0.09	0.12	0.14

Formations), with an occasional shale (Reedsville and Juniata Formations) or sandstone unit (Bald Eagle and Juniata Formations). These rocks do not have the chemical composition necessary to add significant concentrations of nitrate to the stream system.

Typical sources of phosphate within a stream system include animal wastes, animal feed, fertilizers, sewage, detergents, weathering of rocks or minerals, and road salts used in winter (Viney et al. 2000; Bennett et al. 2001; Pant et al. 2002). For the Spruce Creek watershed, the possible sources include animal wastes, fertilizers, weathering of rocks or minerals, and sewage. The weathering of the Bald Eagle sandstone and conglomerate could be adding phosphate to Warrior's Mark Run, as it contains phosphatic minerals (Castle and Byrnes 2005). This rock unit underlies the majority of Warrior's Mark Run, and they are the rocks from which the headwaters originate. Because the headwaters are found in a forested area with no agriculture, this would indicate that the phosphate concentrations seen in the headwaters are likely derived from the Bald Eagle sandstone and conglomerate. Phosphate concentrations increase downstream from the headwaters, which indicates that agriculture is likely a supplementary source of this nutrient as the waters flow from their source.

Of the possible sources of nutrients in this watershed, agriculture is the most likely source, as farms are the most prominent feature that borders both streams. Many studies across the United States have determined that agriculture is the main cause of non-point source nutrient inputs to stream systems (Neary et al. 1989; Staver and Brinsfield 2001). Additionally, there are few houses around these streams, indicating that septic tanks will not be a significant source of either nitrate or phosphate, and atmospheric deposition would not be able to deliver either nutrient to the streams in the quantities observed. Therefore, it is likely that the nitrate in this stream system originates from agricultural sources, while the source of phosphate is more likely a combination of agriculture and local bedrock.

In order to ensure a healthy stream system, nitrate levels for ambient water should be 0.31 mg/L or less (USEPA 2000). No measured nitrate concentrations in Spruce Creek or Warrior's Mark Run were at or below this level during the summers of 2002, 2003, or 2004. The only exception is the headwaters of Warrior's Mark Run, which consistently contain lower nitrate concentrations than the downstream waters. This indicates that there is a significant source of nitrate directly downstream from the headwaters, which is likely agricultural in nature.

The different forms of agriculture in the Spruce Creek Watershed can influence the nutrient budget of this system in different manners. Given their large size and intensive land use, CAFOs should provide a significantly greater impact to the nutrient load than traditional agriculture. While Spruce Creek flows through a CAFO and Warrior's Mark Run is surrounded by traditional agriculture, both streams have elevated levels of nutrients. However, the total load of nutrients flowing through Spruce Creek is much higher than that of Warrior's Mark Run. The reason for this variation is that Spruce Creek, with its larger discharge, is able to dilute its total nitrate and phosphate loads to concentrations that are comparable to those on Warrior's Mark Run. This indicates that the agriculture along Spruce Creek is indeed contributing a larger total nitrate load into the stream system than Warrior's Mark Run, even though the streams have comparable nutrient concentrations.

Different temporal patterns seen in nitrate and phosphate concentrations may be due to differences in the process of stream entry for each nutrient. Nitrate, a highly soluble species, leaches easily into groundwater (Puckett 1994; Cepuder and Loiskanl 2000) and tends to enter a stream through baseflow. Phosphate has a low solubility (Berka et al. 2000) and therefore adsorbs to particulates before it can enter the groundwater. Most phosphate in stream systems is adsorbed to particulate matter (GSWQMP 2002), which indicates that most phosphate enters stream systems through overland flow (Sharpley et al. 1999). Previous studies have found that phosphate concentrations in stream bottom sediments will increase as overland flow from manure-amended agricultural fields is added to the stream system (McDowell 2003).

This study supports previous research that suggests that nitrate enters the system through groundwater inputs, whereas phosphate enters the system through overland flow. Nitrate is present in the system regardless of discharge, but phosphate appears to enter most noticeably during increases in discharge and turbidity. Increases in phosphate that coincide with increases in turbidity suggest that these species are adsorbed to suspended sediment particles and will increase the total load of nutrients within the stream system (Stalnacke et al. 2003). Increases in turbidity typically indicate a rain event that is capable of suspending sediments in the water entering the stream from overland flow; these particular sediments are likely the source for phosphate added to the stream system during high turbidity events.

Conclusions and Implications

The water quality of the Spruce Creek stream system is impaired; nutrient concentrations in the water are too high to sustainably support a trout population (Miltner and Rankin 1998). Implementation of Best Management Practices (BMPs) along Spruce Creek and Warrior's Mark Run could help to reduce the effects of agricultural pollution in these coldwater stream systems (Wang et al. 2002). An easier and less expensive alternative to a BMP would be to employ woody draws, which are small drainage areas covered by trees and shrubs, to lessen runoff and other agricultural inputs (Qiu et al. 2002).

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