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NITROGEN IN SURFACE WATERS AND GROUNDWATER AT EKU'S MEADOWBROOK FARM

By

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Undergraduate Thesis

May 2017

ABSTRACT

Agricultural activities often contaminate watersheds with excess nutrients leading to poor water quality and eutrophication. Eastern Kentucky University's Meadowbrook Farm, contributes dissolved nitrogen into the Muddy Creek watershed. To assess the concentrations of dissolved nitrogen compounds, we sampled waters draining from the Farm as springs, runoff, and subsurface pipe drainage as well as Muddy Creek on six days from May to August 2016 under a variety of weather conditions. We measured dissolved nitrate (NO₃-) and ammonium (NH₄+) using standard colorimetric methods and spectrophotometry with an accuracy of ~0.1 mg/L.

Nitrate was the dominant nutrient contaminant, whereas ammonium was often absent in water samples. Nitrate levels were usually <2 mg/L in surface waters. Springs and some tributaries exhibited the largest nitrate values generally ranging from 7.0 to 14.3 mg/L. Ammonium displayed sporadic concentration spikes between 2.0 and 4.3 mg/L.

Dissolved nitrogen concentrations responded to rainfall. We saw a general decrease of nitrogen concentration during dry periods, especially in Muddy Creek and an increase in nitrogen concentration under wetter conditions. Springs maintained high nitrogen concentrations regardless of different rainfall conditions.

We compared our nitrogen measurements from Meadowbrook Farm to national values. For surface waters, the median nitrate concentration was 2.7 mg/L, lower than the national median (3.8 mg/L), whereas ammonium values were 0.2 mg/L, higher than the national median (0.1 mg/L). In groundwater, we found the median nitrate concentration was 3.9 mg/L, higher than the national median (3.4 mg/L), whereas the median ammonium concentration was 0.05 mg/L, higher than the national median (0.02 mg/L).

INTRODUCTION

Since the passage of environmental legislation in the late twentieth century, water contamination has mostly shifted from industrial point sources to urban and agricultural non-point sources. Agricultural activities often contaminate watersheds with excess nutrients leading to poor water quality and eutrophication—conditions of excess growth of algae—which also diminishes dissolved oxygen concentrations and decreases ecosystem diversity. Eastern Kentucky University's Meadowbrook Farm in Madison County Kentucky, which raises both crops and livestock, is no exception. Farm activities contribute dissolved nitrogen (nitrate, NO₃-; and ammonium, NH₄+) from fertilizers and animal waste into neighboring Muddy Creek via springs, runoff in tributaries, and subsurface tile drains.

Meadowbrook Farm

Meadowbrook Farm is situated in the eastern part of Madison County, Kentucky (Fig. 1). The Farm is generally bound by Meadowbrook Road to the west and by Muddy Creek to the south and east. The Farm mainly raises crops (corn and soybeans) and dairy and beef cattle. The dairy complex (DC) consists of a holding barn, a milking facility, and surrounding pasture. Other areas of the Farm are used for crops and pasture, and are periodically rotated.

Meadowbrook Farm can be separated into three general areas. The southern and western area of Meadowbrook Farm is drained by a runoff channel and flows south next to Meadowbrook Road and enters Muddy Creek at tributary 0W. The central area of Meadowbrook Farm contains a group of smaller runoff channels draining the central fields forming the Big Runoff Channel (BRC; Fig 1). The BRC flows southeast and

enters Muddy Creek at tributary 5W. The milking complex and pig sheds are situated on this subwatershed and manure effluent is collected in ponds, dubbed the pig (PL) and cow lagoons (CL). The northern area of Meadowbrook Farm does not contain a merging network of streams but consists of tributaries associated with springs, such as spring 6 and tributary 11W and springs 2 through 4 and tributary 7W. Several tributaries (1E, 6E, 9E, 13E, and 41E) drain the northern area of the farm. Tributaries 1E through 14E drain into Muddy Creek from off-farm areas to the east of the Farm.

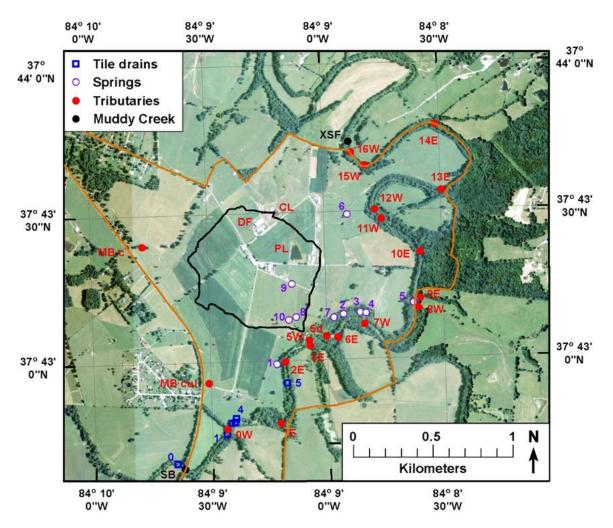


Figure 1. Map of Meadowbrook Farm with all sampling sites labeled. Springs, tributaries, tile drains, and Muddy Creek samples are labeled as white circles, red circles, blue squares, and black circles, respectively. The boundary of Meadowbrook Farm is show with an orange line. The black line outlines the subwatershed of the Big Runoff Channel. The dairy complex (DF), cow lagoon, and pig lagoon (PL) are also shown.

Local Geology

Most of the Farm area is underlain by the Devonian New Albany Shale (Fig. 2). Muddy Creek exposes the underlying Silurian Crab Orchard Formation which consists of claystone, shale, and dolomitic limestone. Most of the springs on the Farm property are sourced from the contact between the Boyle Dolomite and the underlying Crab Orchard Formation

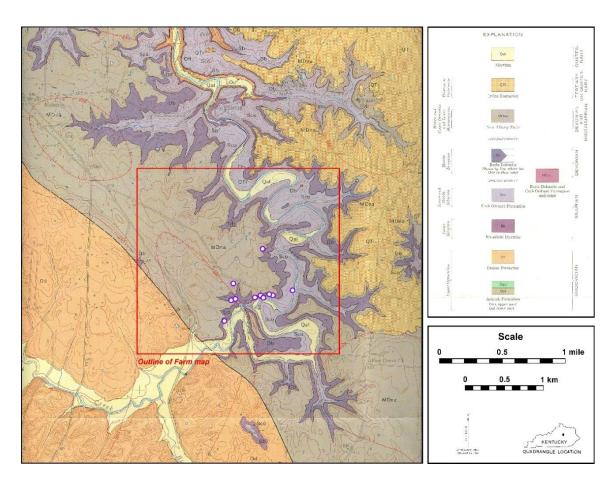


Figure 2. Geologic map of a portion of the Moberly Quadrangle (Green 1968). Note springs rising out of the Boyle Dolomite as shown by the white circles. The red outline of the Meadowbrook Farm map (Fig 1).

Project Objectives

The project's objectives were: (1) to determine the relative concentrations of dissolved nitrogen compounds in different sample types; (2) to identify any consistent sources of dissolved nitrogen; (3) to find any connection between dissolved nitrogen levels and rainfall events; (4) and to compare the nitrogen data to national data to put the magnitude of any contamination into context.

METHODS

Sampling Strategy

To determine dissolved nitrogen levels in surface and groundwater at Meadowbrook Farm, we established sampling stations on the Farm and along Muddy Creek (Figure 1, Tables A1, A2). A list of the sampling stations (Table A1) and their GPS coordinates (Table A2) are included in the Appendix. Twenty-eight of these sampling stations occur in tributaries draining Meadowbrook Farm and off-farm areas to the east to monitor dissolved nitrogen contributions to Muddy Creek. Twelve sampling stations were established in Muddy Creek between the furthermost upstream (station SB) and downstream (station XSF) locations, generally at tributaries. Muddy Creek sampling stations were established to ascertain any potential contribution in dissolved nitrogen from the Farm. We also established sampling stations at eight springs and at six tile drains to determine dissolved nitrogen contribution via groundwater. We also collected water samples from the cow and pig lagoons as they are potential sources of dissolved nitrogen compounds.

Sampling

We collected water samples on six different sampling days (May 24, June 17, June 24, July 8, July 27, and August 18) under a variety of rainfall conditions during the summer of 2016 (Fig. 3). Rainfall data were collected from the weather station on Meadowbrook Farm (ELST) to study the effect of rainfall on nitrogen concentrations. The weather station is operated by the Kentucky Mesonet (www.kymesonte.org).

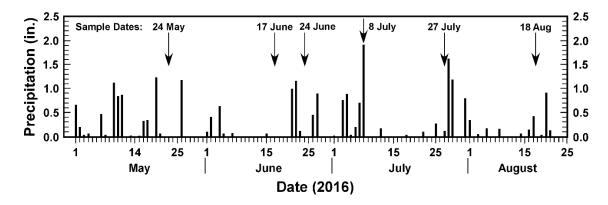


Figure 3. Rainfall data from the Kentucky Mesonet website and labeled sampling dates during the summer of 2016 field season.

Sampling Techniques

We used standard water sampling techniques as, described by Borowski et al. (2012) and Clesceri et al. (2012). Water samples were collected in 60-ml syringes, passed through a 0.45 µm filter, acidified to a pH of ~2 with concentrated H₂SO₄, stored in 20-ml borosilicate vials, and refrigerated until laboratory analysis, which typically occurred one to two days after sampling.

Laboratory Analysis

We measured dissolved nitrogen as ammonium and nitrate via colorimetric spectrophotometry with an accuracy and precision of \pm 0.1 mg/L. Nitrate was measured via the cadmium reduction method (Hach, 1986), and ammonium was measured via the sodium hypochlorate method established by Solorzano (1969) and as modified by Gieskes et al. (1991).

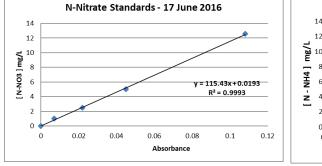
The cadmium reduction method measures both dissolved nitrate (NO_3^-) and nitrite (NO_2^-) but nitrate is the predominant component (Eaton et al., 2005). Standards with concentrations of 0.0 to 12.6 mg/L N-NO₃⁻ were made for nitrate.

The sodium hypochlorate method measures both dissolved ammonium (NH_4^+), and ammonia ($NH_3NH_4^+$), but ammonium is the predominant compound. Standards with concentrations of 0.0 to 12.7 mg/L $N-NH_4^+$ were made for ammonium.

The nitrate and ammonium standard solutions were used to construct linear calibration curves via least squares regression. The correlation coefficient (r²) values from the calibration plots used for each day's samples ranged from 0.9539 - 0.9997 (Table 1); typical standard curves are shown in Figure 4.

Table 1. Compiled r^2 values from the calibration plots used to calculate the concentrations from the six sampling days during the summer of 2016.

	Sampling Day					
Nitrogen Compound	24-May	17-Jun	24-Jun	8-Jul	27-Jul	18-Aug
NO ₃ -	0.9938	0.9993	0.9951	0.9964	0.9539	0.9825
$NH_4{}^+$	0.9987	0.9997	0.9960	0.9990	0.9748	0.9946



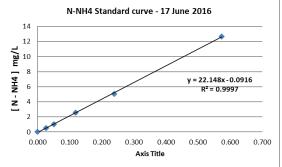


Figure 4. Typical calibration curves for nitrate and ammonium showing best-fit parameters and r2 values.

RESULTS

Nutrient Data

Dissolved nitrate, ammonium, and total dissolved nitrogen values are tabulated and graphically compiled in the Appendix (Table A3, Fig. A1). Overall, nitrate was the dominant dissolved nitrogen compound with concentrations typically <2 mg/L N-NO₃ but with the highest values ranging from 7.1 to 14.3 mg/L N-NO₃ (Table A3, Fig. A1). Nitrate concentrations in water samples from different sources were generally about the same with the exception of springs which typically displayed higher nitrate concentrations.

Ammonium values generally ranged between 0.0 and 0.5 mg/L with high concentration spikes sporadically occurring between 2.0 and 4.3 mg/L (Table A3, Fig A1). The majority of water samples contained 0 mg/L N-NH₄⁺ in ammonium.

Table 2. General concentration ranges of dissolved nitrogen compounds for different sampling categories

	Sampling Category						
	Tile Drains	Springs	Eastern Tributaries	Western Tributaries	Big Runoff Channel	Western Runoff	Muddy Creek
N-NH ₄ ⁺ (mg/L)	0.0-0.5	0.0-0.7	0.0-1.1	0.0-1.1	0.0-1.0	0.1-0.7	0.0-1.0
$N-NO_3^-$ (mg/L)	0.3-3.6	2.5-14.3	0.0-5.4	0.0-4.6	0.0-7.1	0.0-5.4	0.0-3.2
N-NO ₃ - + N-NH ₄ + (mg/L)	0.3-4.1	2.5-14.3	0.0-5.5	0.0-4.6	0.0-8.1	0.0-4.5	0.0-3.9

Rainfall

The summer can be divided into three general weather categories: dry, normal, and rainy conditions (Fig. 3). There was a period of normal weather from May 24, the first sampling day, to June 6. Then, the first dry period ensued until June 21, including the sampling day on June 17. A rainy period started on June 22 and lasted until July 8, and we sampled during that period on June 24 and July 8. The second dry period lasted from July 9 to July 27, another sampling day. Slightly drier than normal weather conditions continued through August 18, the final sampling day.

DISCUSSION

Dissolved Nitrogen in Tributaries and Runoff

The highest nitrate values consistently occur in samples from the Big Runoff Channel, from springs, and from tributaries fed by springs. The Big Runoff Channel (Tributary 5W) collects surface water from the central portion of the farm and often exhibits larger values and ranges of dissolved nitrogen. Nitrogen concentrations in the Big Runoff Channel are up to 8.2 mg/L, which is almost two times higher than the highest values from the western Meadowbrook drainage channel and most western tributaries (Table 2). This indicates that the Big Runoff Channel and the central area of

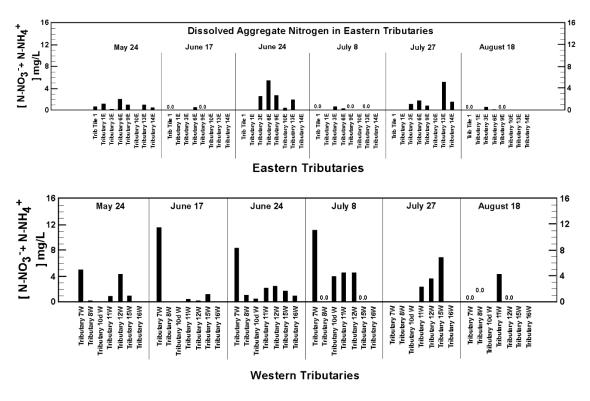


Figure 5. Comparison of dissolved nitrogen values within eastern and western tributaries over the six sampling days. Although aggregate dissolved nitrogen values are presented here, nitrate is the predominant dissolved nitrogen species.

the Farm was the significant source of dissolved nitrogen to the Muddy Creek watershed from the Farm.

Other tributaries (7W, 6E, and 13E) were consistent sources of nitrogen contamination as well. Tributary 7W is likely connected to springs 2, 3, and 4, which generally have the highest dissolved nitrogen values from the Farm apart from the Big Runoff Channel (Fig. 5). Tributaries 6E and 13E displayed larger aggregate nitrogen values than the other eastern tributaries and are consistent sources of dissolved nitrogen (Fig. 5).

The Effect of Rainfall

Rainfall episodes affect dissolved nitrogen concentrations. Runoff samples typically had higher nitrogen concentrations after rainfall events. For example, total dissolved nitrogen significantly increased from normal conditions on June 17 in runoff samples as compared to wetter conditions on June 24 (Fig. 6).

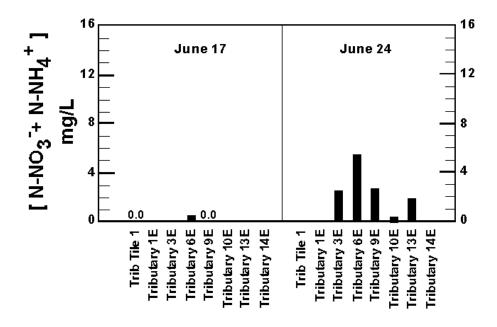


Figure 6. Comparison of dissolved total nitrogen in eastern tributaries on June 17 and June 24.

Rainfall and nitrogen data indicate dissolved nitrogen transport surges in surface waters during heavy rainfall events as seen in the Big Runoff Channel. On normal conditions during May 24 and dry conditions on June 17, dissolved nitrogen levels in the Big Runoff Channel were generally low (Fig. 7). During wetter conditions on June 24, the Big Runoff Channel exhibited significantly higher dissolved nitrogen levels in surface waters (Fig. 7). Because the Big Runoff Channel predominantly drains surface water from the central area of the farm, the most significant episodes of nitrogen contamination from the Farm may occur from surface waters during storm events.

Dissolved nitrogen concentrations in Muddy Creek track those of eastern tributaries. For example, the average total nitrogen concentrations in eastern tributaries and Muddy Creek decreased in dissolved nitrogen concentrations over the dry period extending from June 8 to June 21. Total nitrogen values in Muddy Creek decreased from low values on May 24 to mostly zero on June 17 (Fig. 8). Over the dry period, eastern tributaries either cease to flow or decrease in dissolved total nitrogen values. This trend indicates Muddy Creek's dissolved nitrogen concentration is likely controlled to some extent by eastern tributaries.

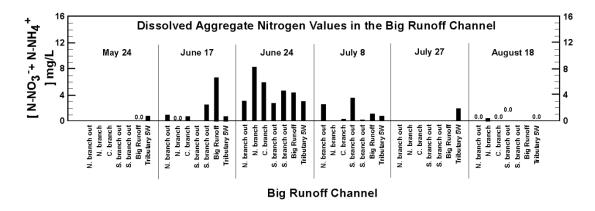


Figure 7. Comparison of dissolved total nitrogen in the Big Runopff Channel on each sampling day.

Interestingly, dissolved nitrogen values increased in western tributaries on June 17 and on July 27. This may be due to springs being the sources for many western tributaries (Fig. 8). However, there are instances where dissolved nitrogen decreases during wetter conditions.

For example, sampling day July 8 occurred during a relatively rainy period (Fig. 3) but exhibited very low nitrogen values for all samples except for the springs, two BRC samples, and four western tributary samples (7W, 10d, 11W, and 12W) (Fig. 9, Fig. A4). These 4 western tributary samples have possible connections to springs (Fig. 1). The decrease in nitrate values over the rainy period from June 24 to July 8 indicate most of the dissolved nitrogen was transported off the fields during the rainy period before July 8, reducing the nitrogen present in the water on that later sampling day (Fig. 8).

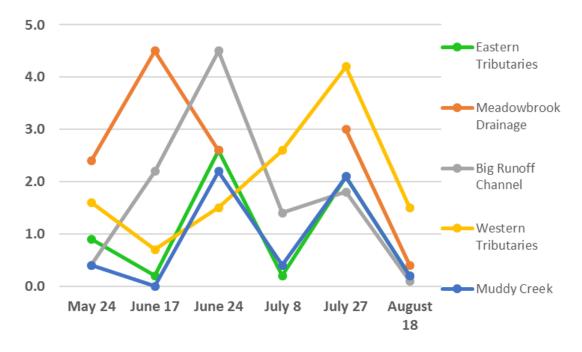


Figure 7. Comparison of averaged values from surface drainage: eastern tributaries, Meadowbrook Road drainage, Big Runoff Channel, western tributaries, and Muddy Creek. Tributary 7W was an anomaly and was omitted from the western tributary category

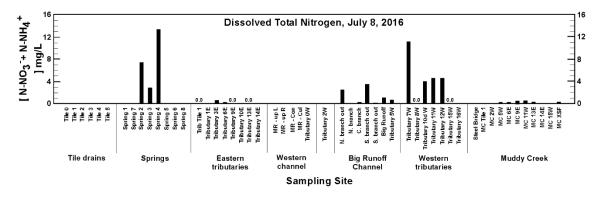


Figure 9. Dissolved nitrogen from Farm stations on July 8.

Dissolved Nitrogen in Spring Water

Certain springs maintained high nitrogen concentrations independent of rainfall conditions. Ammonium concentrations increased in the springs transitioning from the dry period to the rainy period from June 17 to June 24 (Figs. 3, 10).

During the drought conditions on June 17, ammonium values were low in the springs perhaps because the soil retained ammonium, as ammonium absorption by soils has been observed (Bartholomew 1965). During heavier rainfall conditions before and after June 24, perhaps ammonium was flushed from the soil into the groundwater. Since the ammonium values surged on June 24, two to three days after the first heavy rains, this suggests groundwater emanating from the springs may have short residence times. Nitrate concentrations from spring samples decreased slightly from June 17 to June 24. Nitrate is likely more mobile than ammonium and can leach into groundwater via soil infiltration without being adsorbed by soil constituents (Freeze and Cherry 1979).

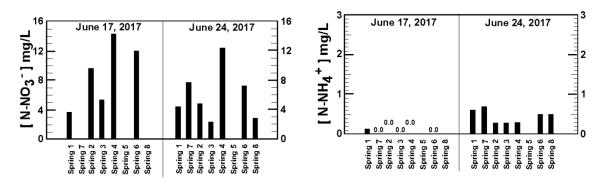


Figure 10. Comparison of ammonium and nitrate values within springs from June 17 (dry) to June 24 (wet).

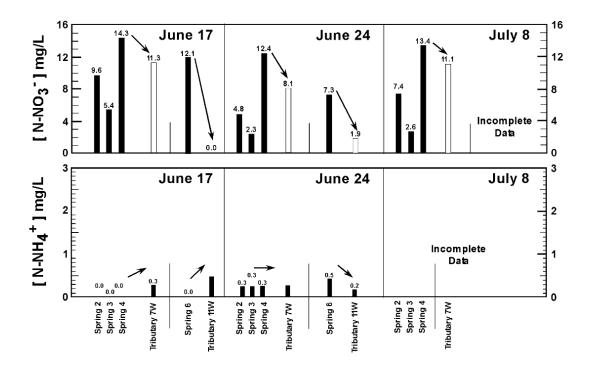


Figure 11. Comparison of connected springs and tributaries to show the decrease in nitrate values down-gradient.

Spring-Tributary Interaction

Springs consistently contain higher dissolved nitrogen concentrations relative to most water sources of the Farm. Most springs on the Farm emanate from the Boyle Dolomite and then flow overland for 10's to 100's of meters within tributaries that but their values decrease moving downgradient within their associated tributaries. This is seen in springs 2, 3, and 4, which are connected to Tributary 7W; and in spring 6 that is connected to Tributary 11W (Fig. 11). The sequential loss of nitrate indicates the presence of a removal mechanism, which may somewhat reduce the amount of nitrate contamination entering Muddy Creek from Farm sources.

Surface and Groundwater Nitrogen Transport

Dissolved nitrogen contamination from Meadowbrook Farm is highest in spring water and runoff water with the predominant contaminant being nitrate. Evans et al. (2017) found that the most prevalent sources for Farm dissolved phosphate contamination were also springs and runoff. Springs generally maintain high levels of dissolved nitrate from the Farm despite weather conditions (Fig. 10). During wetter conditions, surface water dominates contamination on the Farm. Runoff appears to be flushing nutrients accumulated on the fields during drier conditions into the surface water, amplifying nitrogen concentrations and incurring dissolved nitrogen delivery to Muddy Creek.

Comparison of Ammonium and Nitrate to the National Values.

Farm surface water had a large statistical range of measured ammonium values (Fig. 13). National values for dissolved ammonium in agricultural samples are about 0.1 mg/L N-NH₄⁺ with the 75th and 90th percentile values being ~0.15 and ~0.25 mg/L N-NH₄⁺, respectively (Dubrovsky et al. 2010). The median, 75th, and 90th percentiles for the Farm data were approximately 340%, 630%, and 200% higher in N-NH₄⁺ than the national values, respectively (Fig. 13). Although there is a preponderance of zero ammonium values from Farm water samples, sporadic and very high ammonium spikes account for the much higher statistical values. Pristine (undeveloped) ammonium contamination is 0.025 mg/L (Dubrovsky et al. 2010).

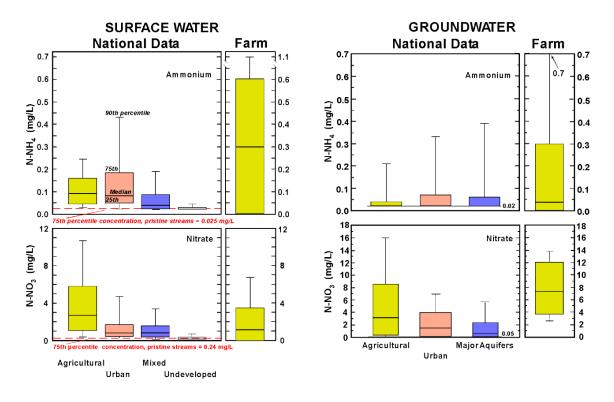


Figure 12. Box-an-whisker plots showing national surface water and groundwater dissolved nitrogen values from Dubrovsky et al. (2010) compared to Farm values. Note the key percentiles are 90%, 75%, median (50%), 25%, and 10% as shown in the first graph.

Nitrate values in Farm surface waters were lower than national percentiles.

National values for dissolved nitrate in agricultural samples have the median, 75th and 90th percentile values being ~3.8 mg/L, ~5.8 mg/L, and 10.8 mg/L N-NO₃-, respectively (Dubrovsky et al. 2010, Fig. 13) The median, 75th, and 90th percentiles for Farm nitrate were approximately 40%, 40%, and 50% lower than the national average.

Farm groundwater (springs) has higher ammonium and nitrate concentrations than national values (Fig. 13). Ammonium exhibits both a much wider ranges of values and significantly larger values within groundwater. The large spread in ammonium values is due in part to sporadic occurrences of very large ammonium values exhibited by most springs on June 24 (Fig. 9). National values for dissolved ammonium in agricultural samples have the 10th, 25th, median, 75th, and 90th percentile values being ~0.02 mg/L, 0.02 mg/L, ~0.04 mg/L, and ~0.22 mg/L N-NH₄⁺, respectively. For farm spring water, the 10th, 25th, and median values were similar to the national values (approaching 0.0 mg/L); however, the 75th and 90th percentile values were approximately 500% and 250% greater than national concentrations, respectively.

Dissolved nitrate values in groundwater at Meadowbrook Farm were usually higher than the national average. National values for dissolved nitrate in agricultural samples are ~2.5 mg/L, ~3.5 mg/L, ~7.2 mg/L, ~12.0 mg/L, and 14.0 mg/L N-NO₃⁻ for the 10th, 25th, median, 75th, and 90th percentiles, respectively. For Farm spring waters, the 10th percentile nitrate concentration was 2.5 mg/L N-NO₃⁻, which is significantly higher than the national 10th percentile. Moreover, the 25th, median, and 75th percentiles were approximately 700%, 110%, and 40% higher than the national values, respectively. These larger nitrate concentrations indicate that groundwater entering the Muddy Creek

watershed is contaminated with nitrate, and may be a significant proportion of overall nitrate export to the Muddy Creek watershed. The exact sources of groundwater nitrate contamination are unknown, but surface infiltration from Farm nutrient sources of manure and fertilizers are likely sources. However, off-Farm sources of nitrate may also be contaminating the groundwater, because the location of spring recharge zones are unknown.

SUMMARY

In conclusion, we found that:

- (1) nitrate was the most significant contaminant in surface and groundwater from Meadowbrook Farm;
- (2) the Big Runoff Channel was the most significant source for dissolved nitrogen in surface runoff;
- (3) springs were also a significant source of dissolved ammonium and nitrate;
- (4) many springs contribute water and hence dissolved nitrogen to tributaries, therefore springs are consistent sources nitrogen to Muddy Creek;
- (5) a nitrate removal mechanism appears to be present within tributaries that likely decreases overall nitrogen contamination in surface waters;
- (6) during normal and drier conditions, nitrate from spring flow is a major source of nitrogen contamination entering Muddy Creek;
- (7) during wetter conditions, surface waters were the primary source of dissolved nitrogen for Muddy Creek;
- (8) ammonium concentrations in surface and groundwater at Meadowbrook Farm were generally lower than national values; and
- (9) nitrate concentrations in surface waters were lower than national statistical values, whereas springs were significantly more contaminated with nitrate relative to national groundwater values.

REFERENCES

- Bartholomew, W.V., Clark, Francis E. Eds. 1965. *SOIL NITROGEN*; American Society of Agronomy Inc: Madison Wisconsin,; no 10, pp 2.
- Borowski, W.S., Aguiar T.A., Jolly E.C., Hunter J., Stockwell R.D., Albright M.S., Godbey S.E., West B.E. 2012 Characteristics and environmental problems of a eutrophic, seasonally-stratified lake, Wilgreen Lake, Madison County, Kentucky. Journal of the Kentucky Academy Sciences, 73(1):41-69.
- Clesceri L.S, Greenberg A.E., Eaton A.D., Franson MAH (Eds.), 1998 (20th ed.) <u>Standard Methods for the Examination of Water and Wastewater</u>, APHA, AWWA, WEF. Baltimore: Port City Press.
- Dubrovsky N.M., Burow K.R., Clark G.M., Gronberg J.O.M., Hamilton P.A., Hitt, K.J., Mueller D.K., Munn M.D., Nolan B.T., Puckett L.J., Rupert M.G., Short T.M., Spahr N.E., Sprague L.A., Wilber W.G. 2010. The quality of our nations's water Nutrients in the nation's streams and groundwater, 1992-2004. USGS Circular 1350, 175pp.
- Evans, H.R., Buskirk, R.E., Borowski, W.S., Malzone, J.M., 2017. Nutrient contamination from non-point sources: Dissolved phosphate in surface and subsurface waters at EKU Meadowbrook Farm, Madison County, Kentucky. *GSA Abstracts with Program*, 49(2), doi: 10.1130/abs/2017NE-290273.
- Freeze, R.A., Cherry, John A. 1979. *Groundwater*. Prentice-Hall, Inc: New Jersey, pp 413-416.
- Gieskes J.M, Gamo T., Brumsack H. 1991. Chemical methods for interstitial water analysis aboard the JOIDES Resolution. *Ocean Drilling Program Technical Note* 15, Ocean Drilling Program, Texas A&M University, 60 pp.
- Greene, R.C., 1968. Geologic map of the Moberly Quadrangle, Madison and Estill Counties, Kentucky. Kentucky Geological Survey.
- Hach. 1986. Nitrate, Instruction Manual, Pocket Colorimeter II. 73 pp.
- Kentucky Mesonet. Western Kentucky University. http://www.kymesonet.org/live_data.html#!ELST (accessed October 11, 2016).
- Method 4500-NH₃ F. Phenate method. *IN* Eaton, A.D., Clesceri L.S., Rice E.W., Greenberg A.E. (Eds.), 2005 (21st ed.). <u>Standard Methods for the Examination of Water and Wastewater</u>. APHA, AWWA, WEF. Baltimore: Port City Press. p. 4-114.

- Method 4500-NO₃ E. Cadmium reduction method. *IN* Eaton, A.D., Clesceri L.S., Rice E.W., Greenberg A.E. (Eds.), 2005 (21st ed.). <u>Standard Methods for the Examination of Water and Wastewater</u>. APHA, AWWA, WEF. Baltimore: Port City Press. pp. 4-123 to 4-125.
- Solorzano L. 1969. Determination of ammonia in natural waters by phenol-hypochlorite method. *Limnology Oceanography*. 14:799-801.

APPENDIX

 Table A1. Sampling stations established at Meadowbrook Farm and Muddy Creek.

Sample	Sampling		Runoff
<u>Code</u>	<u>Site</u>	<u>Description</u>	<u>Туре</u>
	Tile designer 0	O# f	Coordond
t 0	Tile drainage 0	Off-farm	Cropland
MC SB	Steel bridge; upstream farm boundary	Muddy Creek sample	Cropland, pasture
t 1*	Tile drainage 1		Cropland
MR-L	Meadowbrook Rd-upstream, left fork	westerly farm drainage	Cropland, pasture
MR-R	Meadowbrook Rd-upstream, right fork	westerly farm drainage	Cropland, pasture
MR-Con	Meadowbrook Rd-upstream, confluence	westerly farm drainage	Cropland, pasture
MR-Cul	MR culvert	westerly farm drainage	Cropland, pasture
trib 0W*	Tributary 0W	westerly farm drainage	Cropland, pasture
+ 2	Tile drainage 2		Cronland
t 2	Tile drainage 2		Cropland
t 3	Tile drainage 3		Cropland
t 4	Tile drainage 4	Conference for the Conference of the Conference	Cropland
trib 1E*	Tributary 1E	Surface farm/off-farm drainage	Pasture
t 5	Tile drainage 5	Control House Land	Cropland
spr 1	Spring 1	Spring flows overland 10's m	Cattle pasture
trib 2E*	Tributary 2E	Surface farm drainage	Cattle pasture
trib 3E*	Tributary 3E	Surface farm drainage	Cattle pasture
	North branch	Surface farm drainage	Cornfield
	North branch outlet	Surface farm drainage	Cattle pasture
	Central branch	Surface farm drainage	Cattle pasture
	South branch outlet	Surface farm drainage	Cattle pasture
	South branch corn	Surface farm drainage	Cornfield
	Big Runoff	Confluence of surface drainage	Cattle pasture
trib 5W*	Tributary 5W	Big Runoff entry MC	Cattle pasture
trib 6E*		Surface farm/off-farm drainage	Cattle pasture
spr 2	Spring 2	No clear entry into MC	Cattle pasture
spr 3	Spring 3	Spring flows overland 10's m	Cattle pasture
spr 4	Spring 4	Spring flows overland 10's m	Cattle pasture
trib 7W*	Tributary 7W	Spring fed (spr 3, 4)	Cattle pasture
spr 7	Spring 7	Spring flows overland 10's m	Cattle pasture
trib 8W*	Tributary 8W	Spring fed (spr 7)	Cattle pasture
trib 9E*	Tributary 9E	Surface off-farm drainage	Cattle pasture
trib 10E	Tributary 10E	Surface off-farm drainage	Forest
spr 6	Spring 6	Spring flows overland 100+ m	Cattle pasture
trib 11W*	Tributary 11W	Surface farm drainage (spr 6)	Cattle pasture
trib 12W	Tributary 12W	Surface farm drainage (spr 6?)	Cattle pasture
trib 13W*	Tributary 13W	Surface off-farm drainage	Forest
trib 14E	Tributary 14E	Surface off-farm drainage	Cattle pasture
trib 15W*	Tributary 15W	Surface farm drainage	Cattle pasture
trib 16W	Tributary 16W	Surface farm drainage	Cattle pasture
MC XSF	Downstream MC farm boundary	Muddy Creek sample	
	Dia la	Confess	Dia have 100
PL	Pig lagoon	Surface pond Surface pond	Pig barn effluent Cow barn effluent
CL	Cow lagoon		

Table A2. GPS Coordinates for the sampling sites

		NO	ORTH LATITU	DE	WEST LONGITUDE			
Source	Site	Degrees	Minutes	Seconds	Degrees	Minutes	Seconds	
Springs	Spring 1	37	42	59.736	-84	9	13.164	
	Spring 2	37	43	9.126	-84	8	56.429	
	Spring 2B	37	43	7.864	-84	8	55.211	
	Spring 3	37	43	9.349	-84	8	52.255	
	Spring 4	37	43	9.284	-84	8	50.910	
	Spring 5	37	43	10.995	-84	8	38.553	
	Spring 6	37	43	28.487	-84	8	54.910	
	Spring 7	37	43	8.505	-84	8	58.903	
	Spring 8	37	43	9.040	-84	9	7.555	
	Spring 9	37	43	14.747	-84	9	9.281	
	Spring 10	37	43	7.903	-84	9	10.192	
Surface	Stool bridge	37	42	38.355	-84	9	37.900	
burrace	Steel bridge MR C	37	43	23.718	-84	9	46.797	
						_		
	MR culvert	37	42	55.457	-84	9	30.885	
	trib 0 W	37	42	46.349	-84	9	26.313	
	trib 1 E	37	42	47.129	-84	9	13.138	
	trib 2 W	37	42	59.890	-84	9	11.650	
	trib 3 E	37	43	3.554	-84	9	5.603	
	North Branch	37	43	7.888	-84	9	7.999	
	North Branch Outlet	37	43	14.286	-84	9	7.409	
	Central Branch	37	43	11.197	-84	9	9.021	
	South Branch Outlet	37	43	9.517	-84	9	18.608	
	South Branch corn	37	43	9.319	-84	9	19.256	
	Big runoff channel	37	43	6.068	-84	9	7.343	
	trib 5 W	37	43	4.948	-84	9	6.236	
	trib 5W-d	37	43	5.499	-84	9	2.517	
	trib 6 E	37	43	3.994	-84	8	57.405	
	trib 7 W	37	43	7.755	-84	8	52.581	
	trib 8 W	37	43	10.735	-84	8	38.019	
	trib 9E	37	43	12.049	-84	8	36.165	
	trib 10 E	37	43	22.453	-84	8	35.866	
	trib 10d W	37	43	27.181	-84	8	43.314	
	trib 11 W	37	43	27.594	-84	8	45.532	
	trib 12 W	37	43	29.485	-84	8	47.649	
	trib 13 E	37	43	32.537	-84	9	28.761	
	trib 14 E	37	43	46.541	-84	9	30.957	
	trib 15 W	37	43	39.309	-84	8	49.294	
	trib 16 W	37	43	42.711	-84	8	53.661	
	XSF	37	43	43.587	-84	8	54.01	
Tile	Tile 0	37	42	39.618	-84	9	38.661	
drains	Tile 1	37	42	45.661	-84	9	26.486	
	Tile 2	37	42	47.848	-84	9	25.242	
	Tile 3	37	42	48.187	-84	9	24.375	
	Tile 4	37	42	48.724	-84	9	23.937	
	Tile 5	37	42	55.383	-84	9	11.301	

Table A3. Nitrogen concentration data for samples taken at and around Eastern Kentucky University's Meadowbrook Farm in in 2016.

Date	Sample	[NH ₄ ⁺] (mg/L)	[N-NH ₄ ⁺] (mg/L)	[NO ₃ -] (mg/L)	[N-NO ₃ -] (mg/L)	[N-NH ₄ ⁺ + N-NO ₃ ⁻] (mg/L)
24 May 2016	Tile 1	0.0	0.0	14.9	2.9	2.9
24 May	Tile 2	0.0	0.0	3.2	0.6	0.6
24 May	Tile 3	0.0	0.0	4.4	0.9	0.9
24 May	Tile 4	0.0	0.0	2.0	0.4	0.4
24 May	Tile 5	0.0	0.0	10.5	2.0	2.0
24 May	Spring 1	0.0	0.0	-	_	0.0
24 May	Spring 2	0.0	0.0	-	-	0.0
24 May	Spring 3	0.0	0.0	-	-	0.0
24 May	Spring 4	0.0	0.0	-	-	0.0
24 May	Spring 6 (C)	0.0	0.0	-	-	0.0
24 May	trib at tile 1	-	_	3.2	0.6	0.6
24 May	Trib 1E	0.0	0.0	6.4	1.2	1.2
24 May	Trib 3E	0.0	0.0	0.4	0.1	0.1
24 May	Trib 6E	0.0	0.0	10.5	2.0	2.0
24 May	Trib 9E	0.0	0.0	4.8	0.9	0.9
24 May	Trib 13E	0.0	0.0	4.8	0.9	0.9
24 May	Trib 14E	0.0	0.0	2.8	0.5	0.5
24 May	Trib 2W	0.0	0.0	12.5	2.4	2.4
24 May	Big runoff	0.0	0.0	-	-	0.0
24 May	Trib 5W	0.0	0.0	4.0	0.8	0.8
24 May	Trib 7W	0.0	0.0	26.6	5.1	5.1
24 May	Trib 8W	0.0	0.0	1.2	0.2	0.2
24 May	Trib 11W	0.0	0.0	4.8	0.9	0.9
24 May	Trib 12W	0.0	0.0	23.0	4.4	4.4
24 May	Trib 15W	0.0	0.0	4.4	0.9	0.9
24 May	Steel bridge	0.0	0.0	3.2	0.6	0.6
24 May	MC 2E	0.0	0.0	2.8	0.5	0.5
24 May	MC 6E	0.0	0.0	2.8	0.5	0.5
24 May	MC tile 1	0.0	0.0	-	-	0.0
24 May	MC trib 11W	0.0	0.0	2.8	0.5	0.5
17 June 2016	Spring 1	0.2	0.1	16.4	3.7	3.8
17 June	Spring 7	0.0	0.0	-	-	0.0
17 June	Spring 2	0.1	0.0	42.5	9.6	9.6
17 June	Spring 3	0.1	0.0	24.1	5.4	5.5
17 June	Spring 4	0.0	0.0	63.5	14.3	14.3
17 June	Spring 6 (C)	0.0	0.0	53.3	12.0	12.1
17 June	trib at tile 1	0.0	0.0	0.0	0.0	0.0
17 June	Trib 6E	0.7	0.6	0.0	0.0	0.6
17 June	Trib 9E	0.0	0.0	0.0	0.0	0.0
17 June	Trib 2W	1.5	1.1	14.9	3.4	4.5

Table A3, continued.

Date	Sample	[NH ₄ ⁺] (mg/L)	[N-NH ₄ ⁺] (mg/L)	[NO ₃ ·] (mg/L)	[N-NO ₃ -] (mg/L)	[N-NH ₄ ++ N-NO ₃ -] (mg/L)
17 June 2016	N. Branch out	-	-	4.6	1.0	1.0
17 June	N. branch	0.0	0.0	-	-	0.0
17 June	C. branch	0.0	0.0	3.6	0.8	0.8
17 June	S. branch out	3.4	2.7	0.0	0.0	2.7
17 June	Big runoff	0.0	0.0	29.7	6.7	6.7
17 June	Trib 7W	0.4	0.3	50.2	11.3	11.6
17 June	Trib 11W	0.7	0.6	0.0	0.0	0.6
17 June	Trib 12W	0.4	0.3	0.0	0.0	0.3
17 June	Trib 15W	1.0	0.7	2.6	0.6	1.3
17 June	MC 15W	0.0	0.0	0.0	0.0	0.0
17 June	MC tile 1	0.0	0.0	0.0	0.0	0.0
24 June 2016	Tile 0	0.0	0.0	8.4	1.9	1.9
24 June	Tile 1	0.6	0.5	16.1	3.6	4.1
24 June	Spring 1	0.8	0.6	19.5	4.4	5.0
24 June	Spring 7	1.0	0.7	34.0	7.7	8.4
24 June	Spring 2	0.3	0.3	21.4	4.8	5.1
24 June	Spring 3	0.4	0.3	10.0	2.3	2.6
24 June	Spring 4	0.4	0.3	55.1	12.4	12.8
24 June	Spring 8	0.6	0.5	12.7	2.9	3.3
24 June	Spring 6 (C)	0.7	0.5	32.2	7.3	7.8
24 June	Trib 3E	0.9	0.7	8.4	1.9	2.6
24 June	Trib 6E	0.1	0.1	23.7	5.4	5.5
24 June	Trib 9E	0.2	0.2	11.6	2.6	2.8
24 June	Trib 10E	0.5	0.4	8.4	1.9	2.3
24 June	MR-up L	4.5	3.5	4.7	1.1	4.5
24 June	MR-up R	0.3	0.2	19.0	4.3	4.5
24 June	MR-Con	0.3	0.3	3.4	0.8	1.0
24 June	MR Cul	0.7	0.5	3.4	0.8	1.3
24 June	Trib 0W	0.1	0.1	6.3	1.4	1.5
24 June	N. branch out	0.8	0.6	10.5	2.4	3.0
24 June	N. branch	1.3	1.0	31.4	7.1	8.1
24 June	C. branch	0.5	0.4	24.0	5.4	5.8
24 June	S. branch corn	0.8	0.6	9.0	2.0	2.7
24 June	S. branch out	0.4	0.3	18.7	4.2	4.5
24 June	Big runoff	0.7	0.5	16.6	3.8	4.3
24 June	Trib 5W	1.0	0.7	9.8	2.2	2.9
24 June	Trib 7W	0.3	0.3	35.9	8.1	8.4
24 June	Trib 8W	0.0	0.0	4.7	1.1	1.1

Table A3, continued.

Date	Sample	[NH ₄ ⁺] (mg/L)	[N-NH ₄ ⁺] (mg/L)	[NO ₃ -] (mg/L)	[N-NO ₃ -] (mg/L)	[N-NH ₄ ⁺ + N-NO ₃ ⁻] (mg/L)
24 June 2016	Trib 10d (W)	0.6	0.5	-	-	0.5
24 June	Trib 11W	0.3	0.2	8.4	1.9	2.1
24 June	Trib 12W	0.7	0.5	8.4	1.9	2.4
24 June	Trib 15W	0.0	0.0	7.6	1.7	1.7
24 June	Trib 16W	1.3	1.0	-	-	1.0
24 June	Steel bridge	0.7	0.6	12.9	2.9	3.5
24 June	MC 5W	0.1	0.1	1	-	0.1
24 June	MC 6E	0.5	0.4	5.3	1.2	1.6
24 June	MC 9E	-	-	6.3	1.4	1.4
24 June	MC trib 11W	2.5	2.0	8.4	1.9	3.9
24 June	MC 13E	-	-	8.4	1.9	1.9
24 June	XSF	-	-	12.9	2.9	2.9
8 July 2016	Spring 2	0.1	0.0	32.7	7.4	7.4
8 July	Spring 3	0.3	0.2	11.7	2.6	2.9
8 July	Spring 4	0.0	0.0	59.4	13.4	13.4
8 July	Trib 3E	0.8	0.6	0.0	0.0	0.6
8 July	Trib 6E	0.1	0.1	0.8	0.2	0.3
8 July	Trib 9E	0.0	0.0	0.0	0.0	0.0
8 July	Trib 13E	0.0	0.0	0.0	0.0	0.0
8 July	N. branch out	0.3	0.3	10.1	2.3	2.5
8 July	C. branch	0.4	0.3	0.0	0.0	0.3
8 July	S. branch corn	0.1	0.1	15.4	3.5	3.6
8 July	S. branch out	0.0	0.0	0.8	0.2	0.2
8 July	Big runoff	0.3	0.2	4.0	0.9	1.1
8 July	Trib 5W	0.0	0.0	3.2	0.7	0.7
8 July	Trib 7W	0.0	0.0	49.3	11.1	11.1
8 July	Trib 8W	0.0	0.0	0.0	0.0	0.0
8 July	Trib 10d (W)	0.0	0.0	17.8	4.0	4.0
8 July	Trib 11W	0.0	0.0	20.2	4.6	4.6
8 July	Trib 12W	0.0	0.0	20.2	4.6	4.6
8 July	Trib 15W	0.0	0.0	0.0	0.0	0.0
8 July	MC 9E	0.0	0.0	2.4	0.5	0.5
8 July	MC trib 11W	0.0	0.0	2.4	0.5	0.5
8 July	MC 13E	0.0	0.0	1.6	0.4	0.4
8 July	MC XSF	0.0	0.0	1.6	0.4	0.4

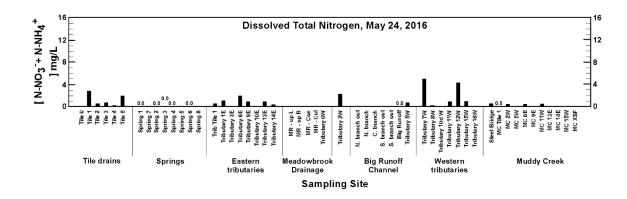
Table A3, continued.

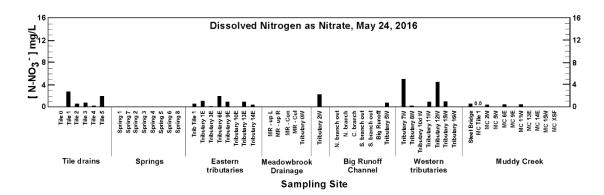
Date	Sample	[NH ₄ ⁺] (mg/L)	[N-NH ₄ ⁺] (mg/L)	[NO ₃ ⁻] (mg/L)	[N-NO ₃ -] (mg/L)	[N-NH ₄ ++ N-NO ₃ -] (mg/L)
27 July 2016	Trib 3E	1.4	1.1	0.0	0.0	1.1
27 July	Trib 6E	1.2	1.0	3.7	0.8	1.8
27 July	Trib 9E	1.1	0.8	0.0	0.0	0.8
27 July	Trib 13E	1.5	1.1	17.8	4.0	5.1
27 July	Trib 14E	1.2	1.0	2.6	0.6	1.5
27 July	MR-Con	0.8	0.6	0.7	0.2	0.8
27 July	MR Cul	0.9	0.7	0.0	0.0	0.7
27 July	Trib 0W	2.7	2.1	24.0	5.4	7.5
27 July	Trib 5W	-	-	8.1	1.8	1.8
27 July	Trib 11W	0.9	0.7	7.0	1.6	2.2
27 July	Trib 12W	1.4	1.1	10.7	2.4	3.5
27 July	Trib 15W	-	-	30.0	6.8	6.8
27 July	Steel bridge	0.4	0.3	0.0	0.0	0.3
27 July	MC 5W	0.8	0.6	-	-	0.6
27 July	MC 6E	0.9	0.7	14.1	3.2	3.9
27 July	MC 9E	1.2	0.9	12.2	2.8	3.7
27 July	MC trib 11W	1.1	0.8	7.8	1.8	2.6
27 July	MC 13E	1.2	1.0	5.9	1.3	2.3
27 July	MC 15W	0.5	0.4	-	-	0.4
27 July	MC XSF	0.9	0.7	12.2	2.8	3.5
18 August 2016	Tile 0	0.6	0.4	-	_	0.4
18 August	Spring 1	0.1	0.1	-	-	0.1
18 August	Spring 5	3.0	2.3	-	-	2.3
18 August	Spring 6 (C)	0.0	0.0	-	-	0.0
18 August	trib at tile 1	0.0	0.0	-	-	0.0
18 August	Trib 3E	0.9	0.7	-	-	0.7
18 August	Trib 6E	0.2	0.2	-	-	0.2
18 August	Trib 9E	0.0	0.0	-	-	0.0
18 August	Trib 13E	0.2	0.2	-	-	0.2
18 August	MR-up L	0.7	0.5	-	-	0.5
18 August	MR-up R	0.2	0.2	-	-	0.2
18 August	MR-Con	0.2	0.1	-	-	0.1
18 August	MR Cul	0.5	0.4	-	-	0.4
18 August	Trib 0W	0.4	0.3	-	-	0.3
18 August	N. branch	0.7	0.5	-	-	0.5
18 August	C. branch	0.0	0.0	-	-	0.0
18 August	S. branch corn	0.0	0.0	-	-	0.0
18 August	Trib 5W	0.1	0.0	-	-	0.0
18 August	Trib 7W	0.0	0.0	-	-	0.0
18 August	Trib 8W	0.0	0.0	-	-	0.0
18 August	Trib 11W	5.5	4.3	-	-	4.3

Table A3, continued.

Date	Sample	[NH ₄ ⁺] (mg/L)	[N-NH ₄ ⁺] (mg/L)	[NO ₃ ·] (mg/L)	[N-NO ₃ -] (mg/L)	[N-NH ₄ ++ N-NO ₃ -] (mg/L)
18 August 2016	Trib 12W	0.1	0.0	-	-	0.0
18 August	Steel bridge	0.6	0.5	-	1	0.5
18 August	MC 2W	0.0	0.0	-	ı	0.0
18 August	MC 5W	0.4	0.3	-	-	0.3
18 August	MC 6E	1.2	0.9	-	1	0.9
18 August	MC 9E	0.2	0.2	-	-	0.2
18 August	MC trib 11W	0.0	0.0	-	-	0.0
18 August	MC 13E	0.0	0.0	-	-	0.0
18 August	MC 14E	0.0	0.0	-	-	0.0
18 August	MC XSF	0.0	0.0	-	-	0.0

Figure A1. Graphs presenting dissolved nitrogen concentrations at and around Eastern Kentucky University Meadowbrook Farm, 24 May, 2016.





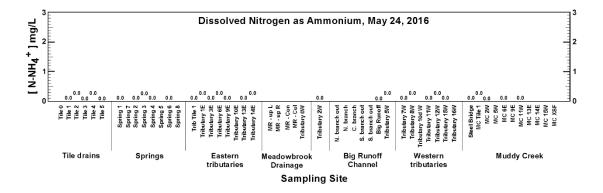
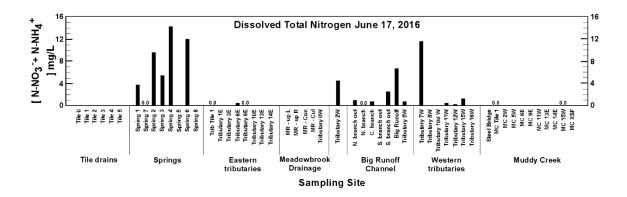
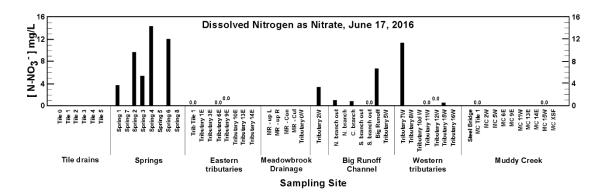


Figure A1, continued, June 17, 2017





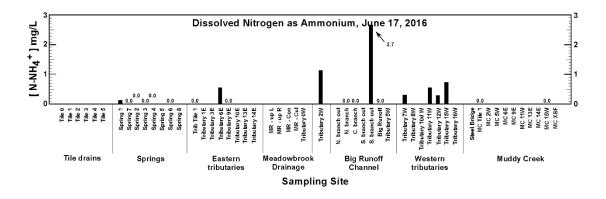
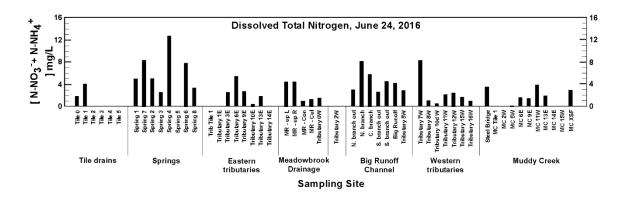
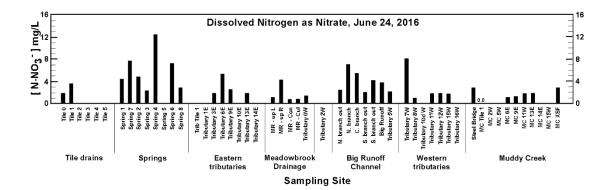


Figure A1, continued, 24 June, 2016.





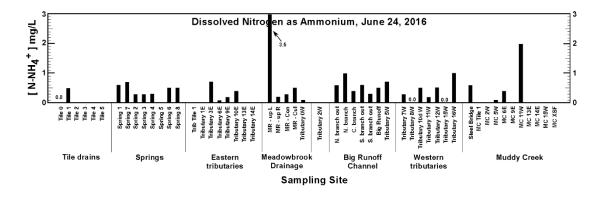
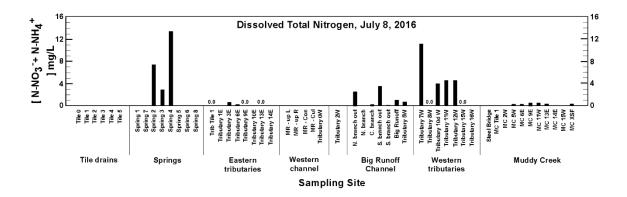
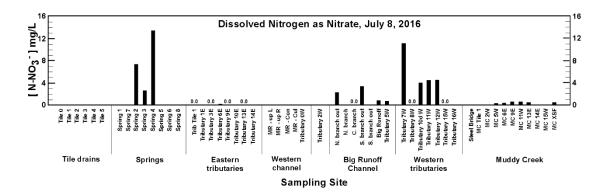


Figure A1, continued, 8 July, 2016.





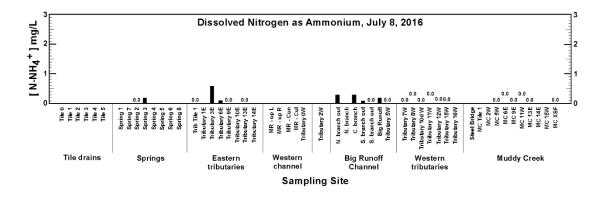
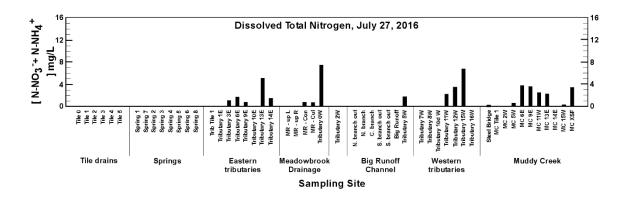
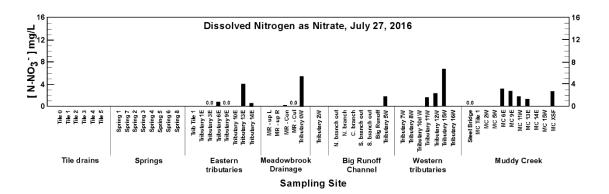


Figure A1, continued, 27 July, 2017.





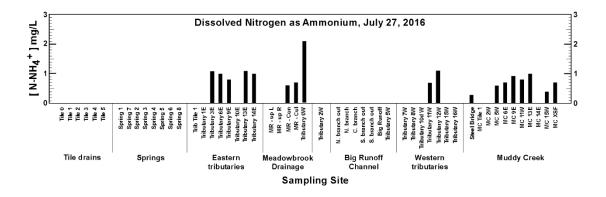


Figure A1, continued, 18 August, 2016.

