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Nutrient Sources and Transport from the Goodwater Creek Experimental Watershed

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Abstract. *The Goodwater Creek watershed has been monitored for flow since 1971 and for dissolved nutrients since 1991 for 3 nested watersheds (12.1, 31.5 and 73.0 km^2 drainage area). This watershed includes row crop land (76%), grassland (14%), woodland (6%) and a small town at the upper end (4%). The objectives of this paper are to analyze nutrient loadings at the 3 gauging stations from 1991 to 2004. Daily, monthly and annual loadings and flow-weighted concentrations of ammonium-nitrogen, nitrate-nitrogen, dissolved phosphorus and atrazine were calculated and analyzed using the non parametric tests for differences, homogeneity, and trends. Atrazine was included in the analysis as one compound not implicated with point source discharges in the watershed. Dissolved phosphorus and ammonium-nitrogen concentrations and loads at the upstream weir were significantly greater than those at the two downstream weirs, which suggest wastewater was a potential source of these nutrients. Possible explanations for these differences were drawn from our knowledge of the watershed and tested with a SWAT model of the watershed. These findings provide insight to what should be included in a complete analysis of the nutrient sources in the watershed and how stream processes affect nutrient loadings.*

Keywords: nutrient, monitoring, Goodwater Creek, claypan, Watershed modeling.

Introduction

Taste and odor problems in 2006 and 2007 at the drinking water treatment plant in Mark Twain Lake have implicated nutrient loadings in the lake and its tributaries. The Goodwater Creek Experimental Watershed (GCEW), a 73 km^2 watershed within the lake drainage area, has been monitored for flow since 1971 and for dissolved nutrients since 1991 for 3 nested watersheds (10.4, 30.6 and 73.0 km^2 drainage area). It is representative of the land use and soils in the area. This watershed includes row crop land (76%), pasture and other grassland (14%), woodland (6%) and a small town in the upper end of the watershed (4%) (fig.1). Major crops during that period included corn, soybeans, grain sorghum, and winter wheat.

The objectives of this paper are to analyze nutrient loadings at the 3 gauging stations in GCEW over 14 years, from 1991 to 2004 using monitoring data. While the study of atrazine transport from the GCEW was beyond the focus of this writing, some results were included in this study as one compound not implicated in the discharge of domestic wastewater. Atrazine is an herbicide regularly applied on corn and grain sorghum.

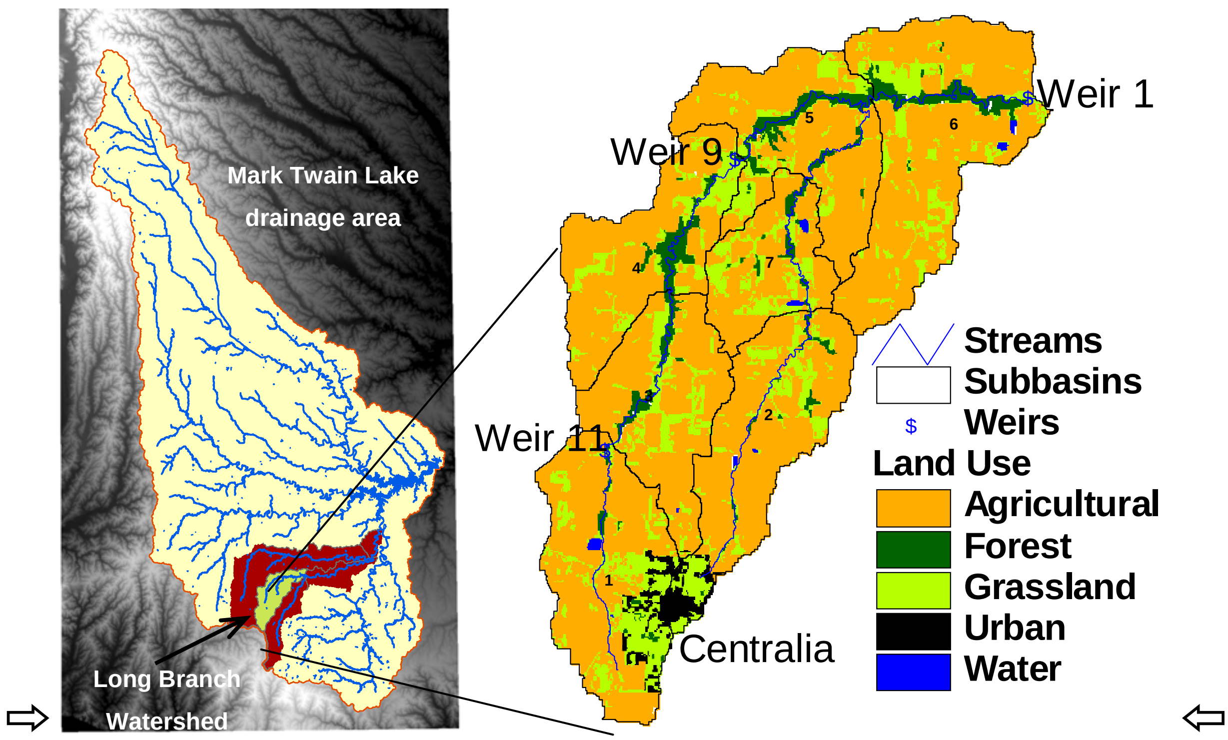

Figure 1. Location and land use of the Goodwater Creek watershed.

Methods

The 3 nested weirs of the Goodwater Creek watershed (drainage areas of 1044, 3066, and 7299 ha) were installed in 1970. Flow has been monitored since 1971, on a 15-minute basis until 1993 and on a 5 minute basis thereafter. Five and fifteen minute flow volumes were aggregated to calculate daily flow values. Flow monitoring stopped at weirs 9 and 11 in April 1997.

From 1992 to April 1997 at weirs 9 and 11 and from 1992 to present at weir 1, water samples were collected to characterize storm and base flow. Auto-samplers were programmed to collect one or more composite samples during storm events, based on stream flow. The samplers were triggered by flows greater than 317 L s^{-1} at weir 1 and 35 L s^{-1} at weir 9 and 11. In 2003, the trigger level of weir 1 autosampler was adjusted to a flow of 60 L s^{-1}. During the same periods, base flow grab samples were collected weekly.

Samples were refrigerated until processing. All samples were filtered through 0.45-µm nylon filters within 48 hours of sampling and analyzed for atrazine, ammonium nitrogen, nitrate nitrogen and dissolved phosphorus within five days. If samples could not be analyzed within five days, they were frozen and analysis was done within 30 days of collection. Dissolved N and P were determined by a Lachat flow injection system (Lachat Instruments, Milwaukee, WI). From 1992 to 1997, atrazine concentrations were determined by gas chromatography (Lerch and Blanchard, 2003). From 1998 to 2006, atrazine concentrations were determined by GC-mass spectrometry (GC/MS) using a Saturn 2000 ion-trap MS detector (Varian Inc., Harbor City, CA). Specific GC/MS conditions were detailed by Lerch and Blanchard (2003). The limits of detection were 0.003 mg L^{-1} for atrazine, 0.1 mg L^{-1} for NO_3-N, 0.02 mg L^{-1} for NH_3-N, and 0.005 mg L^{-1} for dissolved P.

For each event, individual sample concentrations were multiplied by 5-minute runoff volumes to calculate 5-minute compound loads, which were then aggregated to calculate daily loads. The area unit load was calculated by dividing the compound load by the drainage area at the weir. A daily flow weighted concentration was then calculated by dividing the daily load by the daily flow volume. A monthly flow weighted concentration was calculated by dividing the monthly load by the monthly flow volume.

Flow conditions, base flow or storm flow, were determined for each day based on the trigger level of 60 L s^{-1} at weir 1, and 35 L s^{-1} at weirs 9 and 11. These thresholds were considered to capture all events that would be affected by storm runoff.

The Hydrologic Frequency Analysis (Hyfran) (Bobée and Ashkar 1991) software was utilized to perform independence, stationarity, and homogeneity tests on the dissolved P, nitrate-N, ammonium-N, and atrazine data series. Independence of the elements of each data series at weir 1 was tested with the Wald-Wolfowitz test; annual and seasonal homogeneity were tested with the Mann-Whitney test; existence of trends was tested using the Kendall test.

Hypotheses were developed regarding the possible source of nutrients in the watershed: runoff from crop fields, rain, and discharges from wastewater lagoons. A model of the watershed that incorporates these hypotheses was developed using the Soil and Water Assessment Tool. It was calibrated (1992-1997) and validated (1998-2004) for Goodwater Creek flow, as well as atrazine and nutrient concentrations and loads. Land use was derived from Landsat images taken in the early 1990's and early 2000's. Land management information was derived from surveys of land managers in the watershed. Soil information included the SSURGO map and its associated soil characteristics. In order to better characterize the claypan, the hydraulic conductivities were adjusted to reflect values measured in soil cores and in-situ (unpublished), in a field of the watershed. The discharges from wastewater lagoons were specified in the model on a monthly basis. Concentrations of 2 mg L^{-1}, 5 mg L^{-1} were assumed for dissolved phosphorus and nitrate nitrogen, 30 mg L^{-1} for suspended solids and $CBOD_5$, and 2.9 and 1.6 mg L^{-1} for ammonium-N in winter (November-March) and summer (April to October), respectively. These concentrations were determined using professional knowledge and information included in the discharge permit (MDNR 2008).

Results

Independence of the data series

As expected, daily concentrations or loads were not independent from each other, possibly because of the strong dependence between successive daily flow values. Statistical tests indicated that monthly dissolved phosphorus loads could be assumed to be independent at the 1% level, meaning that no correlation could be detected between successive monthly dissolved phosphorus loads. On the other hand, nitrate and ammonium nitrogen monthly loads could not be assumed to be independent. There seemed to be significant correlation between the successive monthly loads of nitrogen.

Homogeneity of the data series

Annual stationarity of the water quality data series was only investigated at weir 1 since sampling stopped at weirs 9 and 11 and the data series were too short to consider detecting possible changes. At weir 1 and for all compounds, monthly area unit loads were homogeneous over the study period, at the 5% confidence level. No shift or trend was detected for any of the pollutant monthly loads from 1992 to 2004.

On the other hand, seasonal effects could be detected for all compounds. The existence of seasonal differences is shown on figure 2 using the average monthly loads over the 12 years. Only weir 1 data were considered because 12 complete years of data were available (1993-2004) while only 4 complete years were available at weirs 9 and 11. Similarly, atrazine loads showed very strong seasonal differences, which was expected because of the seasonal application of atrazine and the bio-physical degradation of this compound. The pie charts for the dissolved nutrients highlight the importance of January through June for ammonium and nitrate nitrogen. These apparent seasonal differences for nitrogen loads were verified by the Wilcoxon test at the 1% significance level. For dissolved phosphorus, the loads appear to have been more evenly distributed throughout the year although the loads that correspond to the last quarter were lower. The Wilcoxon test confirmed that winter, spring and early summer dissolved phosphorus loads were different from later summer and fall loads.

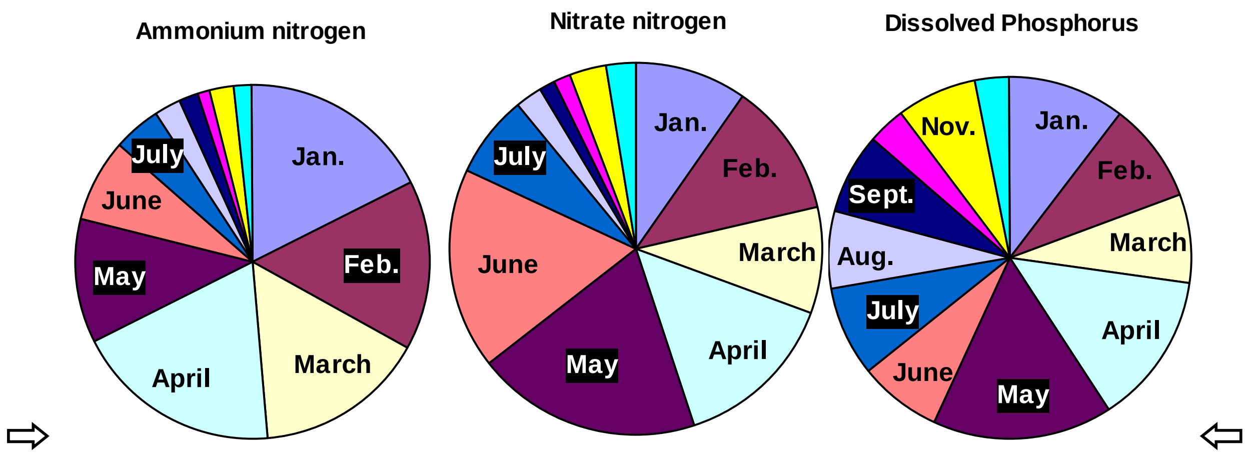

Figure 2. Monthly distribution of dissolved nutrient loads from 1993 to 2004 at weir 1 of Goodwater Creek watershed.

Daily area unit loads

Characteristics of daily area unit loads for each compound are given in tables 1 through 4. Daily flow weighted concentrations of dissolved phosphorus and ammonium nitrogen show distinct differences for each weir while atrazine and nitrate concentrations were similar at all weirs. These tables present the general statistics for area unit loads and concentrations. They also indicate the percent of average daily load that is transported during storm flow events or base flow conditions. Similarly, they specify the average concentrations of storm flow events and base flow, expressed as a percentage of the average daily concentration. Overall, the larger part of the annual load was transported by storm events and compound concentrations during these events were higher than during base flow.

Table 1. Characteristics of daily transport of ammonium N at the 3 weirs of GCEW.

	Area unit load (kg ha^{-1})			Flow weighted concentrations (mg L^{-1})		
	Weir 11	Weir 9	Weir 1	Weir 11	Weir 9	Weir 1
average	0.0054	0.0016	0.0017	0.57	0.17	0.12
median	0.0002	0.0001	0.00004	0.21	0.09	0.06
Standard deviation	0.0264	0.0086	0.0094	1.03	0.26	0.17
CV	4.9	5.4	5.5	1.8	1.5	1.5
Skewness	10.2	15.3	10.4	5.0	3.3	2.9
Maximum value	0.46	0.23	0.15	13.03	2.36	1.34
Storm %*	92%	98%	99%	116%	141%	130%
Base %*	8%	2%	1%	96%	74%	60%

* For area unit loads, Storm % and Base % are the amounts of ammonium-N transported during storm events and base flow, respectively. For concentrations, they represent the average concentrations of storm events and base flow relative to the total average daily concentration.

Table 2. Characteristics of daily transport of nitrate N at the 3 weirs of GCEW

	Area unit load (kg ha^{-1})			Flow weighted concentrations (mg L^{-1})		
	Weir 11	Weir 9	Weir 1	Weir 11	Weir 9	Weir 1
average	0.026	0.013	0.018	1.5	1.2	1.2
median	0.001	0.001	0.001	1.3	1.0	1.0
Standard deviation	0.121	0.064	0.084	1.6	1.1	1.1
CV	4.7	4.8	4.8	1.1	0.9	0.9
Skewness	9.0	12.1	9.8	2.6	1.4	1.4
Maximum value	2.098	1.544	1.524	12.9	7.4	6.6
Storm %*	96%	98%	99%	145%	147%	141%
Base %*	4%	2%	1%	85%	66%	49%

* For area unit loads, Storm % and Base % are the amounts of ammonium-N transported during storm events and base flow, respectively. For concentrations, they represent the average concentrations of storm events and base flow relative to the total average daily concentration.

Table 3. Characteristics of daily transport of dissolved P at the 3 weirs of GCEW.

	Area unit load (kg ha^{-1})			Flow weighted concentrations (mg L^{-1})		
	Weir 11	Weir 9	Weir 1	Weir 11	Weir 9	Weir 1
average	0.0057	0.0022	0.0021	0.30	0.13	0.12
median	0.0002	0.0001	0.0001	0.21	0.09	0.09
Standard deviation	0.027	0.014	0.011	0.35	0.14	0.12
CV	4.8	6.6	5.2	1.2	1.0	1.0
Skewness	9.5	18.9	10.6	2.0	2.2	5.3
Maximum value	0.4576	0.4332	0.2186	2.65	1.32	1.79
Storm %*	96%	99%	100%	135%	147%	119%
Base %*	4%	1%	0%	94%	68%	76%

* For area unit loads, Storm % and Base % are the amounts of ammonium-N transported during storm events and base flow, respectively. For concentrations, they represent the average concentrations of storm events and base flow relative to the total average daily concentration.

Table 4. Characteristics of daily area unit loads of atrazine at weirs 11, 9, and 1 of GCEW.

	Area unit load (kg ha^{-1})			Flow weighted concentrations (µg/l)		
	Weir 11	Weir 9	Weir 1	Weir 11	Weir 9	Weir 1
average	0.0001101	0.0000465	0.0000565	3.0	3.4	5.2
median	0.0000004	0.0000003	0.0000007	0.3	0.4	0.6
Standard deviation	0.0010994	0.0004515	0.0004538	9.5	16.5	13.3
CV	10.0	9.7	8.0	3.2	4.8	2.6
Skewness	15.4	20.8	14.0	5.5	14.9	4.8
Maximum value	0.0001101	0.0000465	0.0000565	103.2	356.6	146.0
Storm %*	99%	99%	99%	225%	156%	81%
Base %*	1%	1%	1%	63%	62%	119%

* For area unit loads, Storm % and Base % are the amounts of ammonium-N transported during storm events and base flow, respectively. For concentrations, they represent the average concentrations of storm events and base flow relative to the total average daily concentration.

The statistical comparison of nutrient loads between weirs was performed with the Mann-Whitney test based on monthly area unit loads and monthly flow weighted concentrations between May 1992 and April 1997, the period of common data among all the weirs and all compounds. The presence or absence of significant differences between series of each weir is summarized in table 5 for all compounds under study by indicating the value of the Mann-Whitney statistics. This statistic is approximately normally distributed under the null hypothesis that two samples come from the same population. Thus, at a 5% significance level, values greater than 1.96 indicate that the two samples did not come from the same population. The threshold is 2.57 for the hypothesis to be rejected at a 1% significance level.

Table 5. Values of the Mann-Whitney statistic to compare data series at weirs 1, 9 and 11 of GCEW.

	Monthly Area unit load			Monthly Flow weighted concentrations		
Weirs	11 & 9	11 & 1	9 & 1	11 & 9	11 & 1	9 & 1
Dissolved P	**2.13**	**1.97**	0.15	**4.86**	**5.65**	**2.88**
Ammonium-N	**3.37**	**3.25**	0.25	**4.06**	**4.47**	0.68
Nitrate-N	1.71	1.02	0.73	**2.15**	1.31	0.86
Atrazine	1.56	0.38	0.99	1.13	1.07	**3.04**

Discussion

Nutrient concentrations for the Goodwater Creek were average in comparison to streams of the US Environmental Protection Agency (EPA) nutrient ecoregion IX, to which it belongs. Base flow and storm flow average values obtained at weir 1 of Goodwater Creek were 0.57 and 1.65 mg L^{-1} for nitrate-N, 0.07 and 0.16 mg L^{-1} for ammonium-N, and 0.09 and 0.14 mg L^{-1} for dissolved phosphorus, respectively. These base flow values fall within the ranges of median values reported by the US EPA (2000) for the Central Irregular Plains (Table 6), which includes GCEW. Since regional studies are based on available data, mostly obtained from monthly or bi-monthly grab samples collected with higher frequency during base flow, it is reasonable to say that Goodwater Creek was characterized by average nutrient concentrations compared to streams in this region.

Table 6. Median and 75th values for dissolved nutrients in streams of the Central Irregular Plains (USEPA, 2000).

Compound	Median values	75th percentile values
NO_3/NO_2-N	0.34 to 0.67	0.76 to 1.24
TKN	0.60 to 1.00	0.89 to 1.35
Orthophosphate-P	0.065 to 0.095	0.118 to 0.170

Nutrient concentrations and unit area loads increased toward the upstream end of the watershed. Area unit loads and average concentrations were all higher for weir 11 than 9 and 1; for ammonium-N and dissolved phosphorus, the differences between loads and concentrations at weir 11 and either 9 or 1 were significant at the 5% level of significance. Ammonium N and dissolved P concentrations were particularly elevated at weir 11; average daily concentrations were 0.57 and 0.30 mg L^{-1}. Average base flow concentrations were close to these values: 0.54 and 0.28 mg L^{-1} for ammonium-N and dissolved P, respectively, or close to 8 and 3 times what they were at weir 1. Average nitrate-N base flow concentrations at weir 11 were twice what they were at weir 1, 1.29 and 0.57 mg L^{-1}, respectively. In comparison, atrazine average and median as well as base flow daily concentrations were lower (40% less) at weir 11 than at weir 1. These unexpected high nutrient concentrations put the headwaters of Goodwater Creek in the 95th percentile of streams of the Central Irregular Plains for dissolved phosphorus and in the 75th percentile for nitrate-N. GCEW ammonium concentrations were not directly comparable to regional values because organic nitrogen was not measured.

These high concentrations and unit area loads were unexpected because land in the headwaters includes the town of Centralia. While urbanized land covers less than 2% of the total watershed area, it represents close to 5% of the drainage area of weir 11. In addition, Centralia city limits covered 20% of that drainage area in 2000. This land was not cropped and should not contribute herbicides or nutrients to the stream load. Thus we expected lower loads per unit area and lower concentrations of nutrients as well as herbicides.

Nitrate N, ammonium-N, and dissolved P were transported mostly during storm events, as indicated by the high storm event percentage of the load, from around 92 to 95% at weir 11 to 99% or 100% at weir 1. The high storm loads in comparison to total annual loads were certainly due to the flashy hydrology of this watershed. The presence of the claypan and the high potential for runoff lead to short and intense storm events followed by little base flow. These percentages were slightly lower than they were for atrazine for which the storm load was 99% of the total load everywhere in the watershed. Thus, a small fraction of the nutrient loads was transported during base flow. Potential sources include groundwater contributions, benthic sources, or point source discharges.

Possible sources of nutrients linked to the presence of the city include failing septic systems, illicit discharges, or discharges from the lagoons owned by the city. Monthly discharges from the lagoon were provided by the City of Centralia. Significant discharges occurred from 1992 to 1995, in connection but not necessarily at the time of wet weather. Those occurred during 1993 and the springs of 1994 and 1995. By multiplying these discharges by the maximum allowed ammonium-N concentration specified in the discharge permit (MDNR 2008), we estimated average monthly discharges of ammonium-N from May 92 to April 97. Permit limitations on monthly average ammonium-N concentrations were 1.6 mg L^{-1} and 2.9 mg L^{-1} from May to October and November to March, respectively. These values resulted in average daily discharges of 0.00037 kg ha^{-1}. In comparison, the average storm flow and base flow area unit stream load of ammonium-N at weir 11 were 0.005 kg ha^{-1} and 0.00042 kg ha^{-1}, respectively. Thus, these discharges could explain 88% of the base flow ammonium-N load in the stream and 7% of the storm flow load. While we do not yet have any data on phosphorus concentration of the releases, we sense they could explain the high phosphorus stream loads, especially because there was no limitation on effluent phosphorus concentrations.

Nitrate concentration of groundwater throughout the watershed and in specific fields was investigated by Kitchen et al. (1997). Groundwater concentrations in nitrate-N were very variable, ranging from 0 to 20 mg L^{-1}. Average groundwater nitrate-N concentration was 7 mg L^{-1} for samples collected from 1991 to 1995, a much higher number than the average daily concentration measured in the creek during that period (1.2 to 1.5 mg L^{-1}). Annual groundwater flow in Goodwater Creek represented on average 15% of the total flow, which would therefore lead to around 1 mg L^{-1} of nitrate-N concentration being caused to groundwater contributions. Thus it appears that storm flow diluted groundwater flow. In agreement with this hypothesis, highest nitrate-N concentrations occurred for flows ranging from 1 to 35 L s^{-1} at weir 11, and from 1 to 60 L s^{-1} at weir 1. These flows were all classified as base flow conditions according to our criteria.

Attempts to calibrate the model for dissolved nutrients were conducted with limited success. While calibration of dissolved phosphorus was acceptable at weir 11, calibration of ammonium-N and nitrate was not. Results were not satisfactory at weir 9 and 1. Ammonium and nitrate nitrogen were largely underpredicted in the headwaters, indicating additional sources of nitrogen than those associated with a discharge of the lagoon, runoff from crop fields, and rain water. Possibilities include fields irrigated with wastewater effluent, discharges from animal operations that existed in the early 1990's and don't exist anymore, or discharges from failing septic systems and individual lagoons. Simulated dissolved phosphorus daily loadings were closest to measured ones at weir 11 and calibration criteria were in the range of values found in the literature on water quality modeling (Nash-Sutcliffe efficiency of 0.3, r^2 of 0.4, and a percent bias of 11%). However, they were over-predicted at the two downstream stations. Potential reasons include errors in the simulation of stream processes or the lack of representation of significant forested stream buffers on either side of the creek in the lower part of the watershed.

Conclusion

Flow and dissolved nutrient concentrations were measured in GCEW from 1992 to 1997 at the outlet of three nested watersheds of drainage areas 1044, 3066, and 7299 ha. While average concentrations at the outlet of the larger watershed were within the median values that characterize streams of the Central Irregular Plains nutrient ecoregion, concentrations of dissolved phosphorus and ammonium-N were significantly higher in the headwaters of the watershed, both at base flow and during storm flow conditions. Nitrate-N and atrazine concentrations were not higher in that area.

Possible sources of dissolved phosphorus and ammonium-N could be discharges from the wastewater treatment lagoons. Significant discharges occurred from 1992 to 1995, in connection but not necessarily at the time of wet weather. By comparing the average potential ammonium–N load associated with these discharges to the average stream load, we showed that it could explain practically all the base flow load, and around 10% of the storm load. Similar calculations for phosphorus could be conducted once we determine the phosphorus effluent concentrations. This will require consultation of monitoring records since effluent phosphorus concentrations were monitored but not limited by the permit.

In the absence of additional data about the discharge of wastewater affluent, we used the SWAT model to simulate flow and nutrient loads, assuming specific effluent concentrations for the discharge. The model results show that additional nitrogen sources were present in the headwaters of the watershed. On the other hand, stream processes represented in the model did not correctly simulate the transport and fate of the phosphorus loadings in the stream.

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