WATER SAMPLING, ANALYSIS AND ANNUAL LOAD DETERMINATIONS FOR TSS, NITROGEN AND PHOSPHORUS AT THE L’ANGUILLE RIVER NEAR PALESTINE

Submitted to the
Arkansas Soil and Water Conservation Commission

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WATER QUALITY SAMPLING, ANALYSIS AND ANNUAL LOAD DETERMINATIONS FOR TSS, NITROGEN AND PHOSPHORUS AT THE L’ANGUILLE RIVER NEAR PALESTINE
2004 Annual Report

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INTRODUCTION

A water quality sampling station was installed at the L’Anguille River near Palestine in 2003. This station is coordinated with a USGS gauging station at the same location. This station is instrumented to collect samples at sufficient intervals across the hydrograph to accurately estimate the flux of total suspended solids, nitrogen and phosphorus in the River. The L’Anguille River was listed on Arkansas’ 1998 303d list as impaired from sediment (turbidity). The L’Anguille River was the second TMDL determined in Arkansas. Accurate determination of stream nutrients and sediment is critical for future determinations of TMDLs, effectiveness of best management practices and trends in water quality.

SCOPE

This report is for water quality sampling, water sample analysis and annual pollutant load calculations at the L’Anguille River near Palestine for the period of January 1, 2004 to December 31, 2004. This project is a cooperative effort between AWRC and the ASU Department of Biological Science. The parameters measured from collected samples will be nitrate-nitrogen, ammonia-nitrogen, total nitrogen, total phosphorus, dissolved reactive phosphorus and total suspended solids. In addition turbidity, conductivity and pH will be measured in-situ and recorded in thirty-minute intervals. Also, the AWRC in conjunction with the USGS will conduct cross-section sampling to determine the relationship between autosampler concentrations and cross-section concentrations. The AWRC will collect samples and analyze the data from the water quality sampling station, compute the annual load for all parameters and report annually to the ASWCC. In addition ASU will conduct biological monitoring at the same site. This data will be incorporated into ASWCC’s Annual Report on the NPS Management Program.

METHODS

Initially the sampler was operated in a discrete mode taking samples at thirty-minute intervals for the first twenty-four samples and sixty-minute intervals for the next twenty-four samples of each storm event. The sampler was set to begin taking samples when the stage rose to ten percent over the prior base flow. Discrete samples were collected when all twenty-four bottles were filled or within forty-eight hours after the first sample. Grab samples were taken often enough to have a minimum of one sample between each storm event. The sampler was operated using this protocol until three storms were adequately sampled. The results from this initial sampling phase were used to determine the sampling start (trigger) and frequency for flow-weighted composite sampling. In addition, the results were used to develop rating curves to predict pollutant concentrations as a function of discharge in order to calculate loads for inadequately sampled storm events.

The trigger level for the storm sampling was not set to a fixed value. It was determined that there was no consistent base-flow, just rising and falling stages. Therefore, a variable storm trigger was used and the value was set at each grab sample to just above the stage.

After the initial phase, the sampler was reconfigured to take flow-weighted composite samples. The sampler began sampling after the stage exceeded the set trigger level. It took a discrete sample after a fixed volume of water had passed. The volume used in the flow-weighted composite sampling was set to 4 million gallons. The discrete samples were composited by combining equal volumes of each into a single sample for analysis. Discrete samples were collected for compositing when all twenty-four bottles were filled or within forty-eight hours after the first sample. Storms were sampled in this manner for the period when the river stage was rising or falling quickly. Grab samples were taken approximately every two weeks, but a minimum of once between each storm event after the initial sampling phase. All samples were collected by ASU Personnel and transported to the AWRC Water quality Laboratory for analysis. All samples were analyzed for nitrate-nitrogen, ammonia-nitrogen, total nitrogen, total phosphorus, dissolved reactive phosphorus and total suspended solids.
RESULTS

This report details the sampling results for the period from January 1, 2004 to December 31, 2004. From that time until the end of December, 216 individual samples were collected and analyzed. There were 26 grab samples, 88 duplicate samples, 1 blank sample and 101 storm samples. These results are illustrated in figure 1.

Figure 1. Sampling results for 2004

Two storm events were sampled in 2003 using discrete samples every two hours. The results from this sampling are illustrated in figure 2. One additional storm was sampled using discrete samples in 2004. These storms were used to develop regression relationships between concentration and discharge. However, the regressions showed that there was no consistent relationship between concentrations and discharge for any of the parameters measured. Table 1 lists the equations and their regression coefficients.
Figure 2 Discretely measured storm events

Table 1. Regression equations and coefficients for various parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regression equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate-N</td>
<td>y = -0.00005x + 2.483</td>
<td>0.0413</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>y = 0.000006x + 0.4814</td>
<td>0.0007</td>
</tr>
<tr>
<td>Ammonia-N</td>
<td>y = 0.0005x + 0.0796</td>
<td>0.0469</td>
</tr>
<tr>
<td>TN</td>
<td>y = -0.00002x + 1.1448</td>
<td>0.0045</td>
</tr>
<tr>
<td>Phosphate-P</td>
<td>y = -0.00001x + 0.1398</td>
<td>0.0217</td>
</tr>
<tr>
<td>TSS</td>
<td>y = 0.0146x + 148.97</td>
<td>0.0150</td>
</tr>
</tbody>
</table>

In July, it was noticed that there was potential intake line contamination at the site. Twenty paired samples were taken from the bridge with a Kemmerer type sampler and from the autosampler over the next 5 months. The results showed the autosampler samples had 64% higher TSS values than the bridge samples. In December it was determined that the intake line and transducer had broken loose and fallen into the mud. It was decided to stop sampling with the autosampler until the intakes could be repaired. Instead, one grab sample per week would be collected and used to estimate loads. The results for loads and concentrations detailed in this report used the grab samples from the bridge and not the autosampler samples. Table 2 lists the annual loads and mean concentrations determined in 2004 for this site.

Table 2. 2004 results L’Anguille near Palestine.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Total Discharge (m³/yr)</th>
<th>Total Load (kg/yr)</th>
<th>Average Discharge (m³/s)</th>
<th>Mean Concentrations (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N03-N</td>
<td>508,360,564</td>
<td>77,845</td>
<td>16.1</td>
<td>0.153</td>
</tr>
<tr>
<td>TP</td>
<td>232,872</td>
<td></td>
<td></td>
<td>0.46</td>
</tr>
<tr>
<td>NH4</td>
<td>45,764</td>
<td></td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>TKN</td>
<td>576,511</td>
<td></td>
<td></td>
<td>1.134</td>
</tr>
<tr>
<td>PO4</td>
<td>39,284</td>
<td></td>
<td></td>
<td>0.077</td>
</tr>
<tr>
<td>TSS</td>
<td>90,599,070</td>
<td></td>
<td></td>
<td>178</td>
</tr>
</tbody>
</table>
DISCUSSION

The 2004 monitoring results from the L’Anguille River should be considered a moderately accurate estimate of sediment and nutrient loads and concentrations. Problems with intake line contamination mean that sediment, TP and TKN are probably overestimated somewhat. Inadequate sampling during storm events in the last three months means these parameters were probably underestimated during that time. These two sources of potential error tend to cancel each other but the extent is unknown.

Results for specific conductance (conductivity) shown in figure 1 are somewhat unusual. Conductivity is a measure of the dissolved ions in the water. These ions may be nutrients such as nitrates or non-nutrient salts such as chloride. The results show the conductivity values peaking in the summer at near 730 us. This represents a significant concentration of ions that does not seem to correlate to nutrients. Often conductivity has an inverse relationship with discharge in that constant sources are diluted with runoff. However, the summertime peaks seem directly related to discharge indicating NPS runoff impacts or direct discharges that are seasonal in nature.

The L’Anguille river results can be compared to monitoring results from 7 Northwest Arkansas (NWA) watersheds. The watersheds in NWA are not directly comparable to those in the Delta because of numerous differences such as ecoregion, land use, morphology and watershed size. However, if all are results are normalized by dividing by watershed size, the results can be compared with caution. The comparison values are listed in table 3.

<table>
<thead>
<tr>
<th></th>
<th>Average of 7 NWA watersheds</th>
<th>L’Anguille</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hectares</td>
<td>67,925</td>
<td>203,580</td>
</tr>
<tr>
<td>years of data</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>tss load (kg/ha)</td>
<td>618</td>
<td>445</td>
</tr>
<tr>
<td>p load (kg/ha)</td>
<td>1.83</td>
<td>1.14</td>
</tr>
<tr>
<td>total nitrogen load (kg/ha)</td>
<td>9.84</td>
<td>3.21</td>
</tr>
<tr>
<td>discharge/area (m³/ha)</td>
<td>4,409</td>
<td>2,497</td>
</tr>
</tbody>
</table>
REFERENCES


