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Marc Nelson

University of Arkansas, Fayetteville


L. Wade Cash

University of Arkansas, Fayetteville, Fayetteville

Sandi Formica

Arkansas Department of Environmental Quality

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Arkansas Water Resources Center

**WATER QUALITY SAMPLING, ANALYSIS AND
ANNUAL LOAD DETERMINATIONS FOR TSS, NITROGEN AND
PHOSPHORUS AT THE WASHINGTON COUNTY ROAD 195 BRIDGE ON
THE WEST FORK OF THE WHITE RIVER
2003 ANNUAL REPORT**

Submitted to the
Arkansas Soil and Water Conservation Commission

By

Marc A. Nelson, Ph.D., P.E.

and

L. Wade Cash, Research Specialist

Arkansas Water Resource Center

Water Quality Lab

University of Arkansas

Fayetteville, Arkansas

And

Sandi Formica

Arkansas Department of Environmental Quality

Little Rock, Arkansas

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112 Ozark Hall

University of Arkansas

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INTRODUCTION

A water quality sampling station was installed at the Washington County road 195 bridge on the West Fork of the White River just above the confluence of the three main forks of the Upper White River in December 2001. The Quality Assurance Project Plan (QAPP) was approved by EPA Region six on March 2002 and sampling was begun at that time. This station is coordinated with a USGS gauging station at the same location. This station was instrumented to collect samples at sufficient intervals across the hydrograph to accurately estimate the flux of total suspended solids, nitrogen and phosphorus into the upper end of Beaver Lake from the West Fork of the White River. The West Fork is listed on Arkansas' 1998 303d list as impaired from sediment. The Upper White was designated as the states highest priority watershed in the 1999 Unified Watershed Assessment. 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 project is a cooperative effort between AWRC and the ADEQ Environmental Preservation and Planning divisions. All aspects of the project are coordinated with and subject to technical review and comments from ADEQ. This report is for 2003 water quality sampling, water sample analysis and annual pollutant load calculations at the Washington County road 195 bridge on the West Fork of the White River. The parameters measured from collected samples were nitrate-nitrogen, ammonia-nitrogen, total Kjeldahl nitrogen, total phosphorus, dissolved reactive phosphorus and total suspended solids. In addition turbidity, conductivity and pH were measured in-situ and recorded in thirty-minute intervals. Also, the AWRC in conjunction with the USGS conducted cross-section sampling to determine the relationship between autosampler concentrations and cross-section concentrations.

In October 2003 it was determined that the sampling intake was being contaminated from sediment collected in the outer line. This report will detail the methods used to correct the data for this contamination and provide corrected data and results for 2002 and 2003.

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. 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 three samples between each storm. 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.

After the initial phase, the sampler was reconfigured to take flow-weighted composite samples. The sampler began sampling after the stage exceeded a set trigger level of four feet. It took a discrete sample after a fixed volume of water had passed. The volume of water used for the flow weighted composite samples, i.e. sampling frequency, was 4 million cubic feet, as determined from the initial sampling phase. 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 above the trigger level. Grab samples were taken every two weeks after the initial sampling phase. All samples were collected by AWRC Field Services personnel and transported to the AWRC Water quality Laboratory for analysis. All samples were analyzed for nitrate-nitrogen, ammonia-nitrogen, total Kjeldahl nitrogen, total phosphorus, dissolved reactive phosphorus and total suspended solids.

In addition to the above sampling for load determination, the AWRC in conjunction with the USGS conducted cross-section sampling to determine the relationship between auto sampler concentrations and cross-section concentrations. The USGS collected evenly weighted integrated (EWI) cross section samples at the same time AWRC collected discrete auto samples. All samples were transported and analyzed by the AWRC Water Quality Lab and the results used to determine correction factors for the auto sample concentrations. Seven samples were taken and compared during both years. All samples taken and used for analysis were done in accordance with an approved quality assurance project plan. This QAPP was prepared by the AWRC and submitted to the ASWCC for approval. The ASWCC reviewed the plan for conformance to its Quality Management Plan and submitted the QAPP to EPA, Dallas for review and approval. The plan was approved on March 19, 2002.

In October 2003 it was determined that the sampler intake was being contaminated by sediment trapped in the 2-inch outer pipe. The intake line that is located inside the outer pipe was initially secured with the intake strainer outside the end of the outer pipe. This intake line at some point was pulled up into the outer line. In that position, sediments inside the outer line were disturbed during purging prior to taking a sample. This led to samples with elevated levels of particulates relative to in-stream concentrations. The results for 2002 were reported as measured in the 2002 annual report. This report will provide the corrected results for 2002 and 2003.

The concentrations measured in this project were corrected using the seven USGS /AWRC paired grab samples taken in 2002 and 2003 for storm flows only. Storm flows are here defined as all discharges when the stage was above the 4-foot trigger level. This definition is an arbitrary distinction based upon sampling technique and does not represent the distinction between true storm and base flows. A linear regression analysis was performed on each of the parameters measured. The coefficients determined from the

regression were used to correct measured storm flow concentrations. All storm flow concentrations from the beginning of the project until October 15, 2003 were corrected. Table 1 lists the equations used for correction.

Table 1. Regression equations determined from USGS /AWRC paired samples

| Parameter | Regression equation | Regression coefficient |
|------------------|---------------------|------------------------|
| Nitrate-N | $y = 0.874x$ | $R^2 = 0.0682$ |
| Total Phosphorus | $y = 0.7065x$ | $R^2 = 0.4002$ |
| Ammonia-N | $y = 1.0848x$ | $R^2 = 0.1666$ |
| TKN | $y = 0.7025x$ | $R^2 = 0.2201$ |
| Phosphate-P | $y = 0.436x$ | $R^2 = 0.1339$ |
| TSS | $y = 0.5167x$ | $R^2 = 0.4742$ |
| | | |

Base flow concentrations were corrected using twenty USGS routine grab samples collected approximately monthly during base flow conditions. The parameter measured by USGS was suspended sediment concentration (SSC). SSC and TSS are not equivalent and the relationship is not consistent between sites (Glysson, et al., 2001). However, paired samples can be used to develop a site-specific relation between the two. There were seven paired samples taken at this site in 2002 and 2003 where both TSS and SSC were measured. The average relation between paired TSS and SSC determined from these paired samples can be described by the following relationship:

$$(1) \text{ TSS} = 0.685 \text{ SSC}$$

The average value for SSC measured by the USGS during base-flow conditions in 2002 and 2003 was 27.2 mg/l. Using the relationship in formula 1, the average value for TSS during the time period was 18.5 mg/l. This value was applied as the TSS concentration for all base flows from the beginning of the project until October 15, 2003. Similarly, the other concentrations measured by USGS in their base flow grab samples during this time period were applied as the concentrations for the base flows. Table 2 summarizes the concentrations that were applied.

Table 2 Applied Base-flow Concentrations

| Parameter | Concentration (mg/l) |
|------------------|----------------------|
| Nitrate-N | 0.33 |
| Total Phosphorus | 0.0125 |
| Ammonia-N | 0.027 |
| TKN | 0.25 |
| Phosphate-P | 0.005 |
| TSS | 18.5 |

RESULTS

Sampling began with the approval of the QAPP on March 11, 2002 and continued through the end of the year. During the first year, 220 individual samples were collected and analyzed. They include 20 base-flow grab samples, 143 discrete storm samples, and 4 USGS cross-section samples. The stage for 2002 as well as the corrected concentration results from the samples are summarized in Figure 1 and Table 2. Prorated loads listed in Table 2 were determined from partial year loads by multiplying by total annual discharge and dividing by the discharge from March 12 to the end of the year. That factor was 1.398

Figure 1. Corrected 2002 Stage and Concentrations

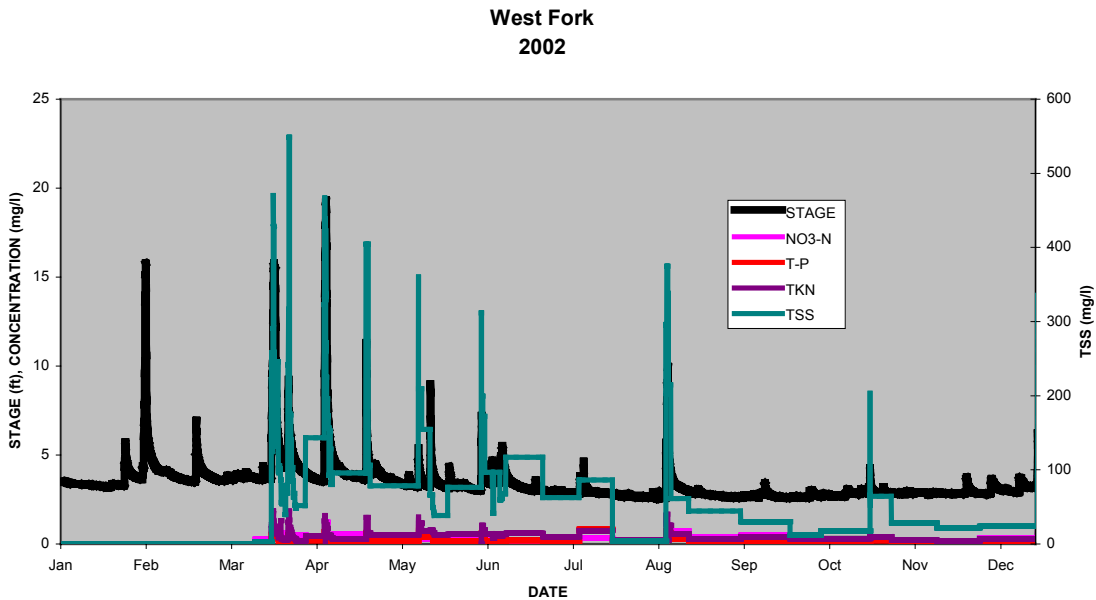


Table 2. Corrected 2002 loads and mean concentrations.

| parameter | Partial Year Loads (kg) | Pro-rated Annual Load (kg) | Flow-weighted Mean Concentrations (mg/l) |
|------------------|-------------------------|----------------------------|--|
| Nitrate-N | 37,366 | 52,245 | 0.43 |
| Total Phosphorus | 29,656 | 41,465 | 0.34 |
| Ammonia-N | 4,270 | 5,971 | 0.05 |
| TKN | 60,721 | 84,901 | 0.70 |
| Phosphate-P | 2,707 | 3,784 | 0.03 |
| TSS | 13,829,552 | 19,336,621 | 158 |

Discrete storm samples were collected on 5 storms in 2002 using 190 individual samples. The results from three of these storms are illustrated in Figure 2. These results were modeled using least-squares linear regressions to determine a relationship between concentrations and stage. These relationships can be used to predict concentrations of the different constituents as a function of stage during storm events if actual measured values

are unavailable due to equipment failure. The relationships determined are summarized in Table 3. Although these relationships were determined, they were not used to model any of the storm events during the project since all storms were sampled adequately.

Figure 2.

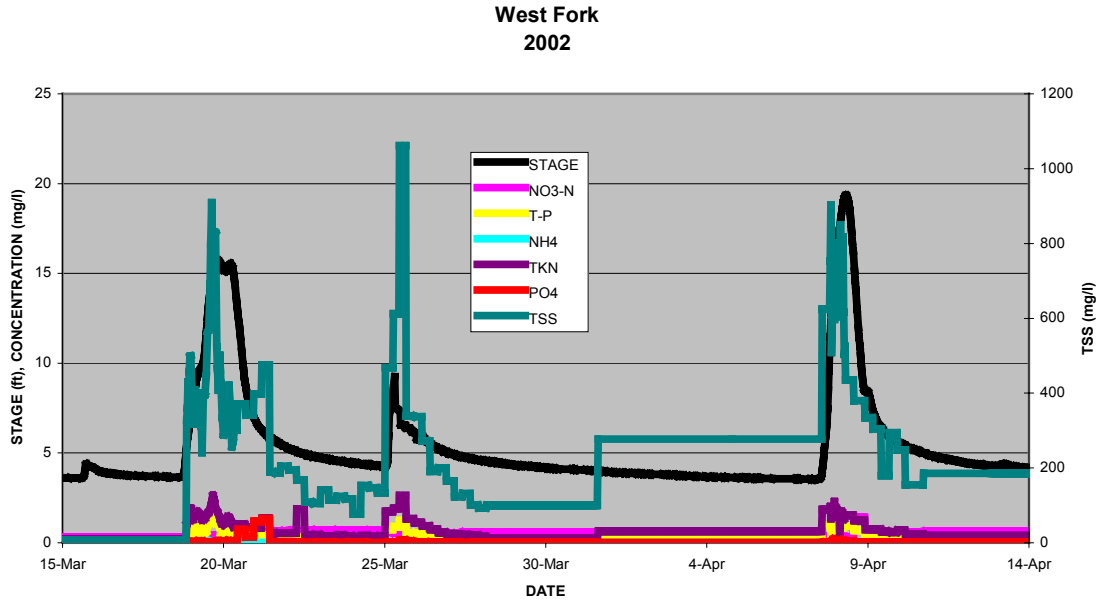


Table 3. Corrected Regression equations determined from discrete storm samples 2002

| parameter | Regression equation | Regression coefficient |
|------------------|------------------------|------------------------|
| Nitrate-N | $y = -0.054x + 0.416$ | $R^2 = 0.0379$ |
| Total Phosphorus | $y = 0.0299x + 0.1626$ | $R^2 = 0.377$ |
| Ammonia-N | $y = 0.003x + 0.0361$ | $R^2 = 0.1248$ |
| TKN | $y = 0.0424x + 0.4855$ | $R^2 = 0.224$ |
| Phosphate-P | $y = 0.002x + 0.0035$ | $R^2 = 0.2611$ |
| TSS | $y = 16.008x + 53.214$ | $R^2 = 0.443$ |

The loads and mean concentrations can be segregated into storm-flow and base-flow using the trigger level as an arbitrary distinction between flow regimes. Using the trigger level value of 4 feet, the segregated loads and mean concentrations for 2002 are shown in Table 4.

Table 4. Corrected Storm flow and Base flow Loads and Mean Concentrations Partial Year 2002.

| | Storm Loads (kg) | Base Loads (kg) | Storm Concentrations (mg/l) | Base Concentrations (mg/l) |
|----------------|---------------------|--------------------|-----------------------------------|----------------------------------|
| VOLUME (M3) | 68,348,038 | 19,347,203 | | |
| NO3-N | 30,981 | 6,385 | 0.45 | 0.33 |
| T-P | 29,414 | 242 | 0.43 | 0.01 |
| NH4 | 3,748 | 522 | 0.05 | 0.03 |
| TKN | 55,884 | 4,837 | 0.82 | 0.25 |
| PO4 | 2,610 | 97 | 0.04 | 0.01 |
| TSS | 13,471,628 | 357,923 | 197.10 | 18.50 |

In 2003 there were 54 discrete storm samples, 22 composite storm samples, 26 base flow grab samples, 4 blank samples, 4 duplicate samples and 3 USGS / AWRC paired samples collected and analyzed. There were no significant storm events that were not sampled. The stage for 2002 as well as the corrected concentration results from the samples is summarized in Figure 3 and Table 5.

Figure 3 2003 Stage and Corrected concentrations.

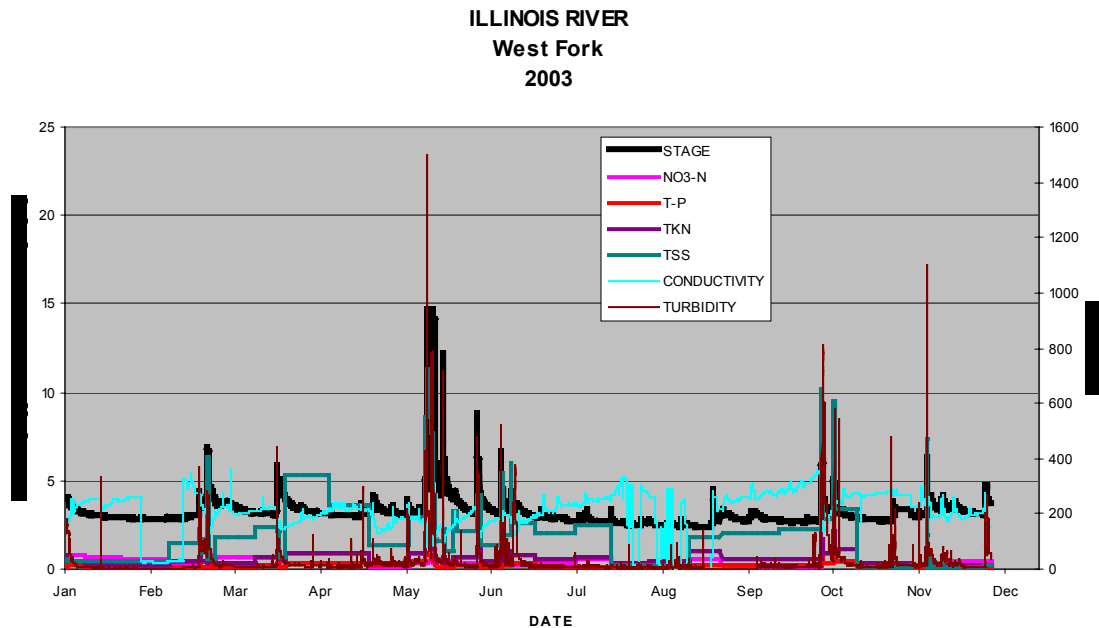


Table 5. Corrected 2003 loads and mean concentrations.

| parameter | Annual Loads (kg) | Flow-weighted Mean Concentrations |
|-----------|----------------------|--------------------------------------|
| | | |

| | | |
|------------------|-----------|--------|
| | | (mg/l) |
| Nitrate-N | 33,377 | 0.37 |
| Total Phosphorus | 14,712 | 0.16 |
| Ammonia-N | 2,718 | 0.03 |
| TKN | 49,587 | 0.55 |
| Phosphate-P | 1,084 | 0.01 |
| TSS | 7,622,866 | 84.59 |

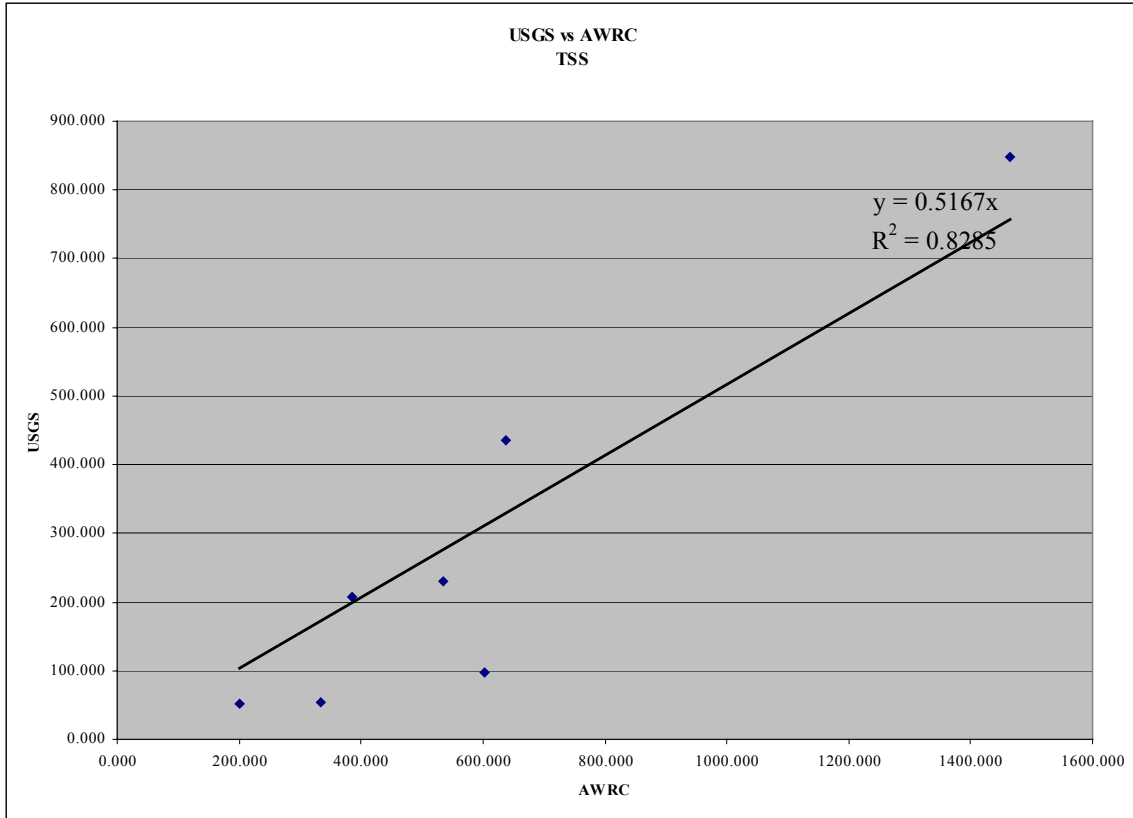
The loads and mean concentrations can be segregated into storm-flow and base-flow using the trigger level as an arbitrary distinction between flow regimes. Using the trigger level value of 4 feet, the segregated loads and mean concentrations for 2003 are shown in Table 6.

Table 6. Corrected Storm-flow and Base-flow Loads and Flow-weighted Mean Concentrations 2003.

| | Storm Loads (kg) | Base Loads (kg) | Storm Concentrations (mg/l) | Base Concentrations (mg/l) |
|-------------|------------------|-----------------|-----------------------------|----------------------------|
| VOLUME (M3) | 49,021,281 | 41,092,002 | | |
| NO3-N | 18,789 | 14,588 | 0.38 | 0.36 |
| T-P | 13,716 | 996 | 0.28 | 0.02 |
| NH4 | 1,744 | 975 | 0.04 | 0.02 |
| TKN | 39,483 | 10,103 | 0.81 | 0.25 |
| PO4 | 855 | 229 | 0.02 | 0.01 |
| TSS | 6,919,208 | 703,658 | 141.15 | 17.12 |

The storm-flow concentrations measured in this project were corrected using the seven USGS /AWRC paired grab samples taken in 2002 and 2003. A linear regression analysis was performed on each of the parameters measured. The coefficients determined from the regression were used to correct initial storm flow concentrations. All concentrations from the beginning of the project until October 15, 2003 were corrected. Table 1 lists the equations used for correction. Figure 4 shows the regressed TSS concentrations and correction equation.

Figure 4. USGS / AWRC TSS Regression



In addition to measuring TSS, turbidity was measured and recorded every fifteen minutes during the project. Figure 5 shows the stage TSS and turbidity measured during the year. The Maximum value recorded during 2003 was 1500 NTUs. This value was above the calibration range for the meter (1 to 1000 NTUs) and was probably just an over maximum value reported by USGS. The average turbidity value for 2003 was 27 NTUs.

A linear regression was calculated for discrete samples with turbidity measurements. These results are shown in figure 6. Turbidity measurements appear to correlate well with storm TSS on the rising limb but tend to peak earlier and fall slower than TSS on the falling limb as exemplified in figure 7. This may be due to the effect of different particle sizes.

Figure 5 2003 Stage, TSS and Turbidity measurements

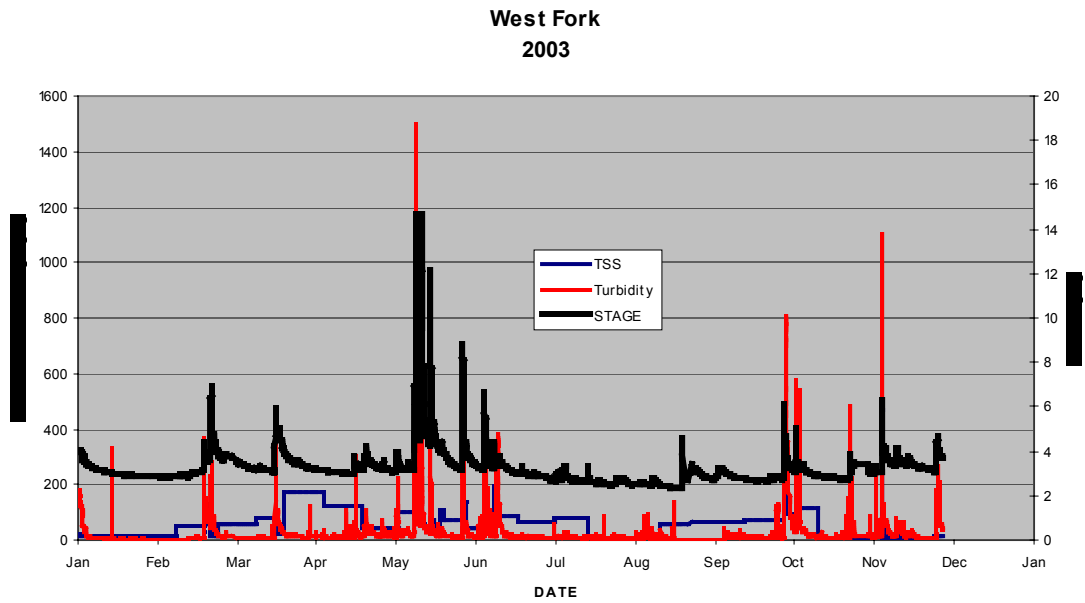


Figure 6 2003 measured TSS and Turbidity Regression.

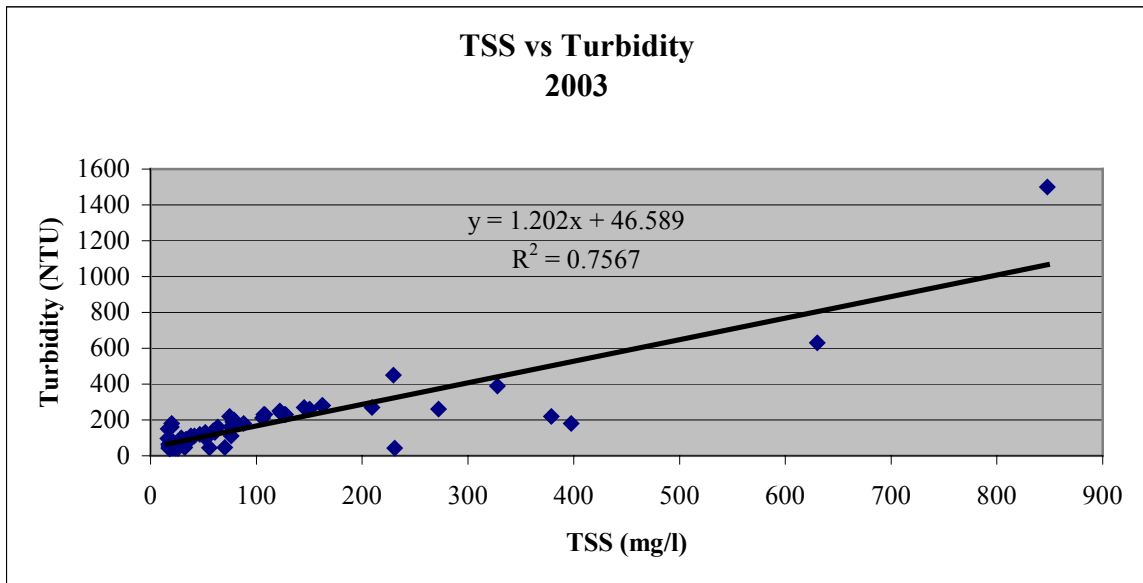
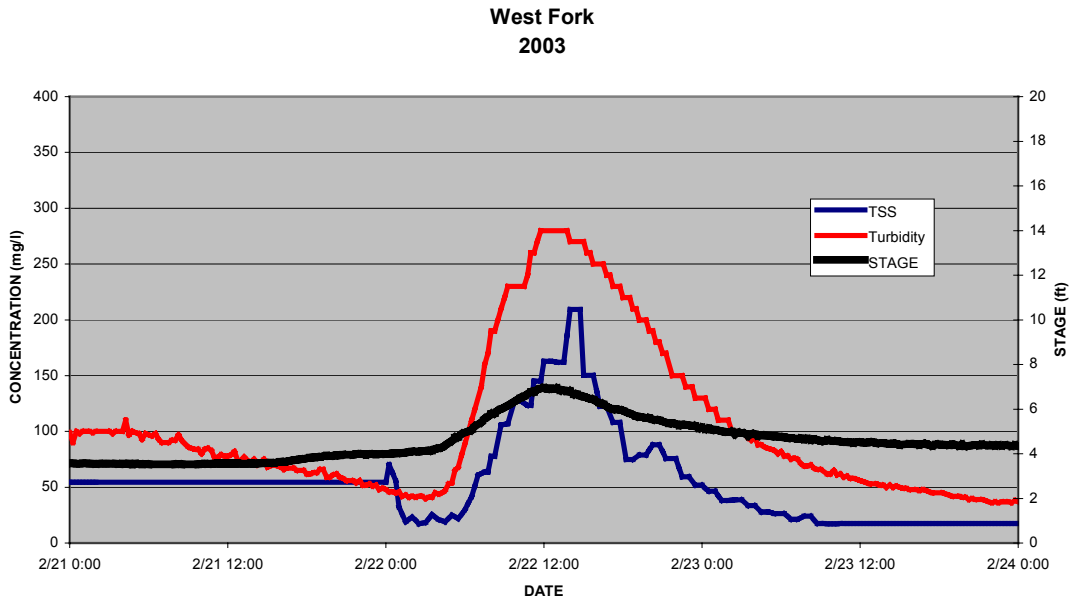


Figure 7. Storm event TSS and turbidity.



DISCUSSION

West Fork @ 195 Bridge site during 2002 and 2003 can be compared to loads and concentrations developed in other watersheds in Northwest Arkansas. Five other watersheds have been monitored using the same monitoring and load calculation protocols. The only differences between the protocols are that trigger levels and storm composite sample volumes are different for each site. This means that the distinction between storm and base flows (defined here as the trigger level) may be relatively different at each site.

The results for the six watersheds are summarized in Table 7 and Figure 8. The results shown for the West Fork are corrected pro-rated annual values for 2002 and corrected annual values for 2003. The table and figure show TSS and phosphorus as total annual loads per watershed acre, as storm loads per watershed acre and as base-flow concentrations. Normalizing total and storm loads to a per acre basis allows comparison between watersheds of differing sizes. The total loads indicate the mass of TSS or P that are being transported to a receiving water body. Storm loads per acre may be used to represent relative impacts from non-point sources. In Figure 8, a red line represents the total loads and blue diamonds represents the storm loads. The West Fork watershed has high levels of total TSS compared to the others and most of the TSS is transported during storm events.

The P load for the West Fork is similar to the other watersheds with the primary transport occurring during storm events. Base Flow P concentrations are lower than the other watersheds studied.

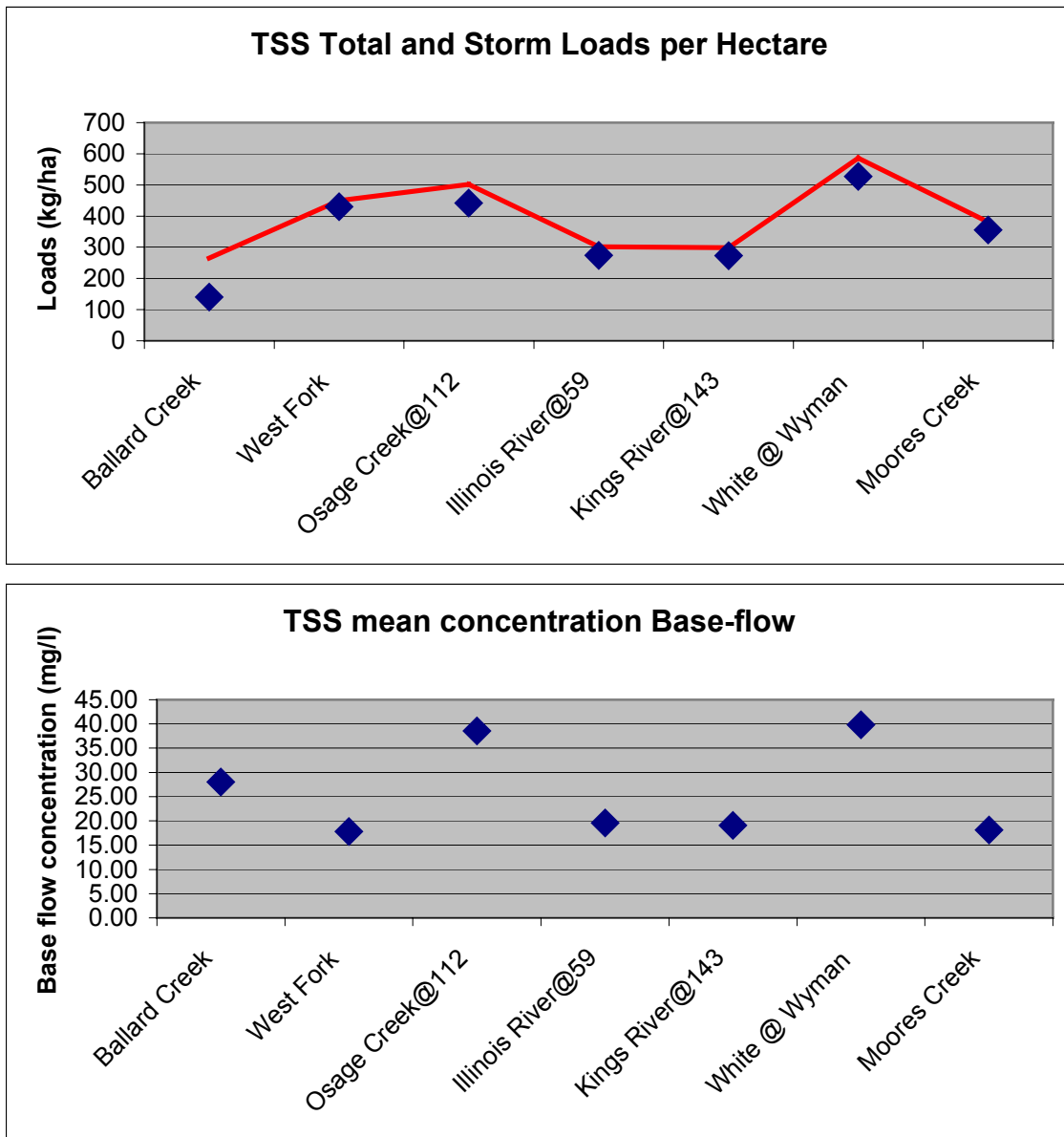
The base-flow concentrations show relative levels of TSS and P that are impacting in-stream biological activity during most of the year. These are the values that are of greatest interest for determining impacts to in-stream macro invertebrate habitat and nuisance algae production. The base-flow TSS is low compared to the other watersheds. The base-flow concentration of T-P is very low compared to the other watersheds

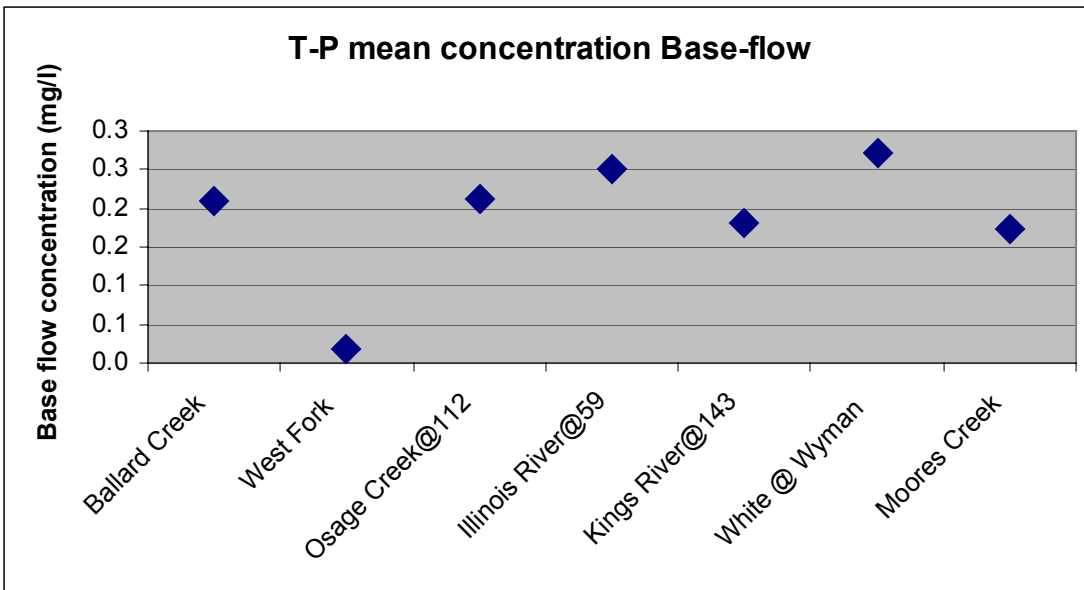
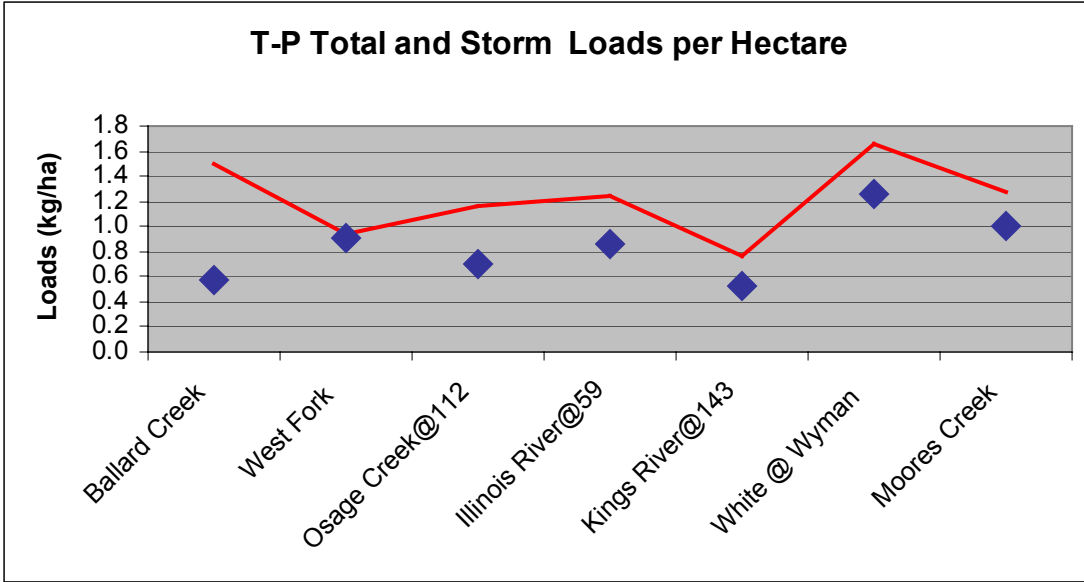
Table 7. Comparison of results to other Northwest Arkansas Watersheds.

| | Ballard Creek | West Fork | Osage Creek@ 112 | Illinois River@59 | Kings River@ 143 | White @ Wyman | Moore's Creek |
|--|------------------|-----------------|------------------------|----------------------|------------------------|------------------|---------------|
| Hectares | 6,742 | 29,964 | 10,095 | 167,273 | 153,309 | 116,364 | 1,000 |
| YEARS of data | 1 | 2 | 2 | 7 | 5 | 2 | 4 |
| tss load (kg/ha) | 265 | 450 | 501 | 302 | 299 | 586 | 381 |
| tss load storm (kg/ha) | 141 | 430 | 442 | 274 | 273 | 528 | 355 |
| tss conc. base (mg/l) | 28.03 | 18 | 39 | 20 | 19 | 40 | 18 |
| p load (kg/ha) | 1.50 | 0.94 | 1.16 | 1.24 | 0.76 | 1.66 | 1.27 |
| p storm load (kg/ha) | 0.58 | 0.92 | 0.70 | 0.86 | 0.53 | 1.26 | 1.01 |
| p base conc. (mg/l) | 0.21 | 0.02 | 0.21 | 0.25 | 0.18 | 0.27 | 0.17 |
| DISCHAR GE (m ³) | 36,251, 012 | 106,081, 072 | 38,827,31 2 | 545,516,68 2 | 378,398,6 02 | 243,428,68 8 | 3,011,285 |
| DISCHAR GE/AC (m ³ /ha) | 5,377 | 3,540 | 3,846 | 3,261 | 2,468 | 3,540 | 3,011 |

The correction factors that are detailed in this report and were applied to the data for the first 18 months of this project can be expected to add considerable uncertainty to the results. While the corrected results are certainly more accurate than the uncorrected results would have been, they should be used with caution. The correction factors were calculated from just seven paired samples. Those samples do not adequately characterize the variation during different flow regimes, which may be significant.

Figure 8. Comparisons between 6 watersheds.





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