Arkansas Water Resources Center

WATER QUALITY SAMPLING, ANALYSIS AND ANNUAL LOAD DETERMINATIONS FOR TSS, NITROGEN AND PHOSPHORUS AT THE WYMAN BRIDGE ON THE WHITE RIVER

Submitted to the
Arkansas Soil and Water Conservation Commission

By
Marc Nelson
And
L. Wade Cash
Arkansas Water Resources Center
Water Quality Lab
University of Arkansas
Fayetteville, Arkansas 72701

July 2004

Publication No. MSC-321

**WATER QUALITY SAMPLING, ANALYSIS AND ANNUAL LOAD
DETERMINATIONS FOR TSS, NITROGEN AND PHOSPHORUS AT THE
WYMAN BRIDGE ON THE WHITE RIVER**

FINAL REPORT

Presented to the Arkansas Soil and Water Conservation Commission
By
Marc Nelson
And
Wade Cash
University of Arkansas
AWRC- Water Quality Lab

July 2004

INTRODUCTION

An automatic water sampler was established in 2000 on the main stem of the White River at the Wyman Road Bridge. The Quality Assurance Project Plan (QAPP) was approved by EPA Region six on April 2000 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 White River. 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. The Wyman Bridge was torn down for reconstruction in early 2002. For this reason, sampling was discontinued at the end of 2001 after 21 months of sample collection. This report details the sampling and results for that period of time.

SCOPE

This project was a component of a larger multi-cooperator effort to address BMP implementation on the Beaver Watershed. The parameters measured from collected samples were nitrate-nitrogen, ammonia-nitrogen, total Kjeldahl nitrogen, total phosphorus, dissolved reactive phosphorus and total suspended solids. Also, the AWRC in conjunction with the USGS conducted cross-section sampling to determine the relationship between autosampler concentrations and cross-section concentrations.

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 8 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. Five paired samples were taken and compared during 2000 and nine paired

samples were taken and compared during 2001. 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 it's Quality Management Plan and submitted the QAPP to EPA, Dallas for review and approval.

RESULTS

Sampling began with the approval of the QAPP in April 2000. During the first year, 230 individual samples were collected and analyzed. They include 17 base-flow grab samples, 202 discrete storm samples, 3 duplicate samples, 3 field blanks and 5 USGS cross-section samples. The stage for 2000 as well as the concentration results from the samples is summarized in Figure 1 and Table 1.

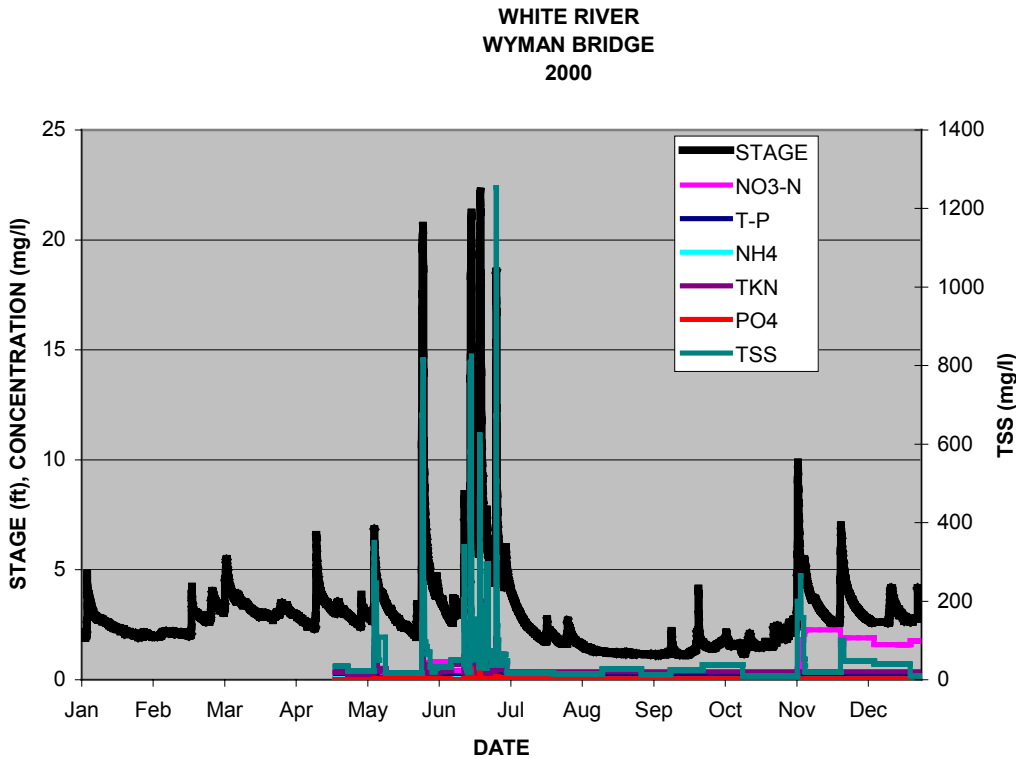Figure 1. 2000 Stage and Concentrations

WHITE RIVER
WYMAN BRIDGE
2000

Table 1. 2000 loads and mean concentrations.

parameter	Partial Year Loads (kg)	Flow-weighted Mean Concentrations (mg/l)
Nitrate-N	215,937	0.63
Total Phosphorus	174,636	0.51
Ammonia-N	12,437	0.04
TKN	372,651	1.09
Phosphate-P	18,806	0.05
TSS	85,914,146	250.51

Discrete storm samples were collected on 5 storms in 2000 using 200 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 2. 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.

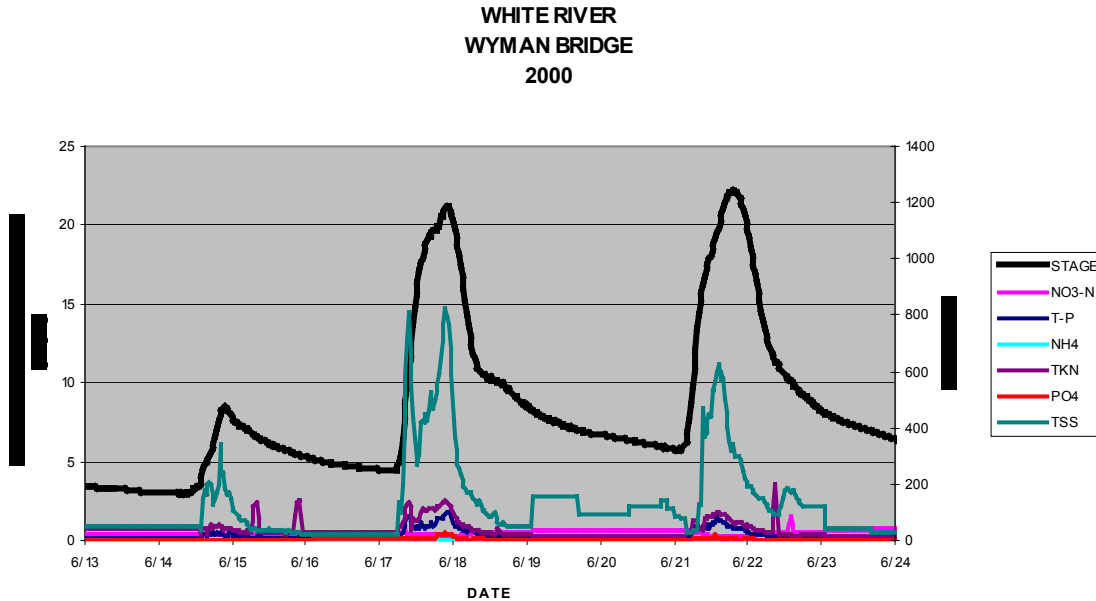Figure 2. Discretely sampled storm events.

Table 2. Regression equations determined from discrete storm samples 2000.

parameter	Regression equation	Regression coefficient
Nitrate-N	y = -0.0122x + 0.5391	$R^2 = 0.1892$
Total Phosphorus	y = 0.0524x – 0.05	$R^2 = 0.5886$
Ammonia-N	y = -0.0002x + 0.0281	$R^2 = 0.006$
TKN	y = 0.0648x + 0.3034	$R^2 = 0.3052$
Phosphate-P	y = 0.0076x -.0203	$R^2 = 0.3903$
TSS	y =23.385x –15.124	$R^2 = 0.4458$

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 5 feet, the segregated loads and mean concentrations for 2000 are shown in Table 3.

Table 3. Storm flow and Base flow Loads and Mean Concentrations Partial Year 2000.

	Storm Loads (kg)	Base Loads (kg)	Storm Concentrations (mg/l)	Base Concentrations (mg/l)
VOLUME (M3)	230,262,492	112,697,891		
NO3-N	99,358	118,618	0.43	1.05
T-P	163,984	10,721	0.71	0.10
NH4	7,195	5,265	0.03	0.05
TKN	330,983	42,000	1.44	0.37

4

| PO4 | 17,351 | 1,498 | 0.08 | 0.01 |
| TSS | 81,757,471 | 4,169,270 | 355.06 | 37.00 |

In 2001 there were 21 composite storm samples, 32 base flow grab samples, 4 blank samples, 4 duplicate samples and 9 USGS / AWRC paired samples collected and analyzed. There were no significant storm events that were not adequately sampled. The stage for 2001 as well as the measured concentration results from the samples is summarized in Figure 3.

Figure 3 2001 Stage and measured concentrations.
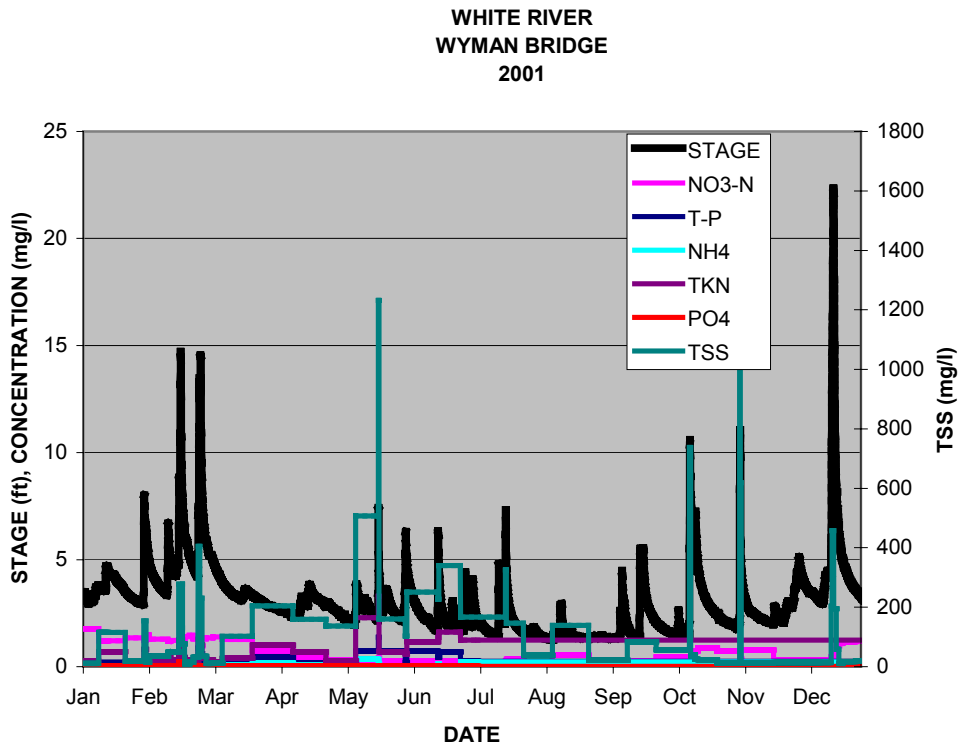
In 2001 it was determined that the sampler intake line had broken loose from it's mooring at one foot above the bottom of the river. The intake line had fallen into the sediments on the river bottom. This lead to samples with elevated levels of particulates relative to in-stream concentrations. The evidence for this conclusion came from the USGS / AWRC paired samples. The regression of the paired samples for 2000 showed a deviation of 4 % for TSS as shown if figure 4. The regression for the 2001 paired samples showed a deviation of 124% for TSS as shown in figure 5. This conclusion was confirmed when the sampling line was removed at the end of 2001. The nine-paired samples taken during 2001 were used to develop regression equations to correct the storm-flow concentrations measured during 2001.
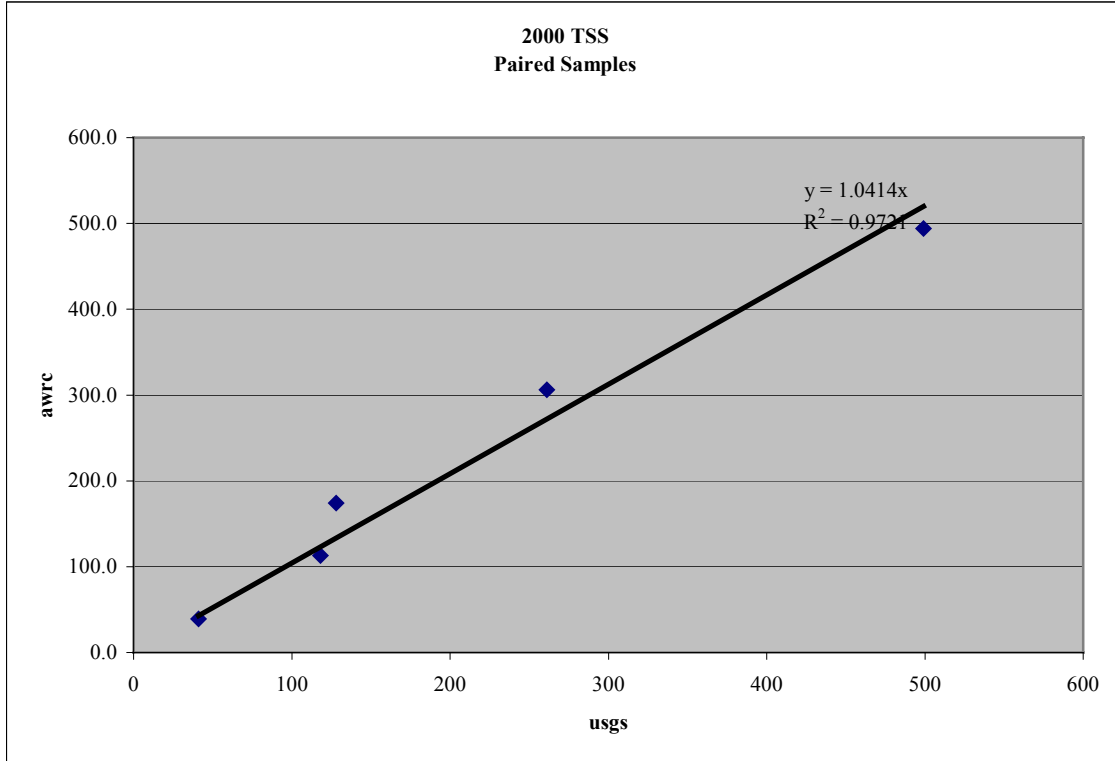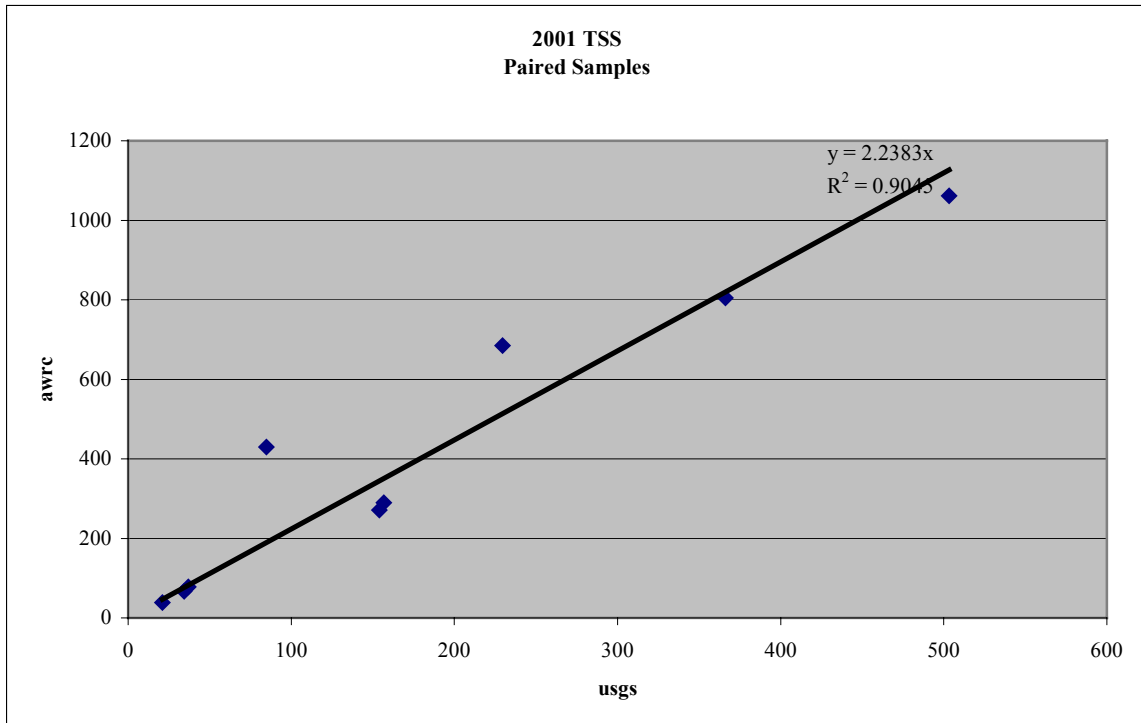
Figure 4 2000 paired USGS / AWRC TSS samples

2000 TSS
Paired Samples

$y = 1.0414x$
$R^2 = 0.9731$

Figure 5 2001 paired TSS samples

2001 TSS
Paired Samples

$y = 2.2383x$
$R^2 = 0.9045$

The concentrations measured in this project were corrected using the nine USGS /AWRC paired grab samples taken in 2001 for storm-flows only. Storm-flows are here defined as all discharges when the stage was above the 5-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 2001 were corrected. Table 4 lists the equations used for correction.

Table 4. Regression equations determined from USGS /AWRC paired samples

Parameter	Regression equation	Regression coefficient
Nitrate-N	$y = 0.981x$	$R^2 = 0.9923$
Total Phosphorus	$y = 0.829x$	$R^2 = 0.9003$
Ammonia-N	$y = 1.72x$	$R^2 = 0.8682$
TKN	$y = 0.820x$	$R^2 = 0.9582$
Phosphate-P	$y = 0.985x$	$R^2 = 0.8071$
TSS	$y = 0.446x$	$R^2 = 0.9045$

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 nine paired storm samples taken at this site in 2001 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) $TSS = 0.70\ SSC$

This relationship was used to convert USGS SSC concentrations measured during storm-flows to TSS before the above regression relationship was determined.

Base-flow concentrations were corrected using twenty-six USGS routine grab samples collected during base-flow conditions. The average value for SSC measured by the USGS during base-flow conditions in 2001 was 41.6 mg/l. This value was used as equivalent to TSS for base-flows, since at the low base-flow velocities they should have none of the heavier particles that create the difference during storm-flows. This value was applied as the TSS concentration for all base-flows for 2001. 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 6 summarizes the concentrations that were applied.

Table 6 Applied Base-flow Concentrations

Parameter	Concentration (mg/l)
Nitrate-N	0.04
Total Phosphorus	0.38
Ammonia-N	0.48
TKN	0.03
Phosphate-P	0.01
TSS	41.62

Table 7 summarizes the resulting corrected annual loads and mean concentrations.

Table 7. Corrected 2001 loads and mean concentrations.

parameter	Annual Loads (kg)	Flow-weighted Mean Concentrations (mg/l)
Nitrate-N	182,009	0.43
Total Phosphorus	176,522	0.42
Ammonia-N	109,346	0.26
TKN	187,650	0.45
Phosphate-P	12,363	0.03
TSS	33,371,462	79.63

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 5 feet, the corrected segregated loads and mean concentrations for 2001 are shown in Table 8.

Table 8. Corrected Storm-flow and Base-flow Loads and Flow-weighted Mean Concentrations 2001.

	Storm Loads (kg)	Base Loads (kg)	Storm Concentrations (mg/l)	Base Concentrations (mg/l)
VOLUME (M3)	210,542,386	208,549,795		
NO3-N	173,226	8,783	0.82	0.04
T-P	96,471	80,051	0.46	0.38
NH4	8,360	100,986	0.04	0.48
TKN	181,313	6,337	0.86	0.03
PO4	10,719	1,644	0.05	0.01
TSS	24,692,583	8,678,880	117.28	41.62

DISCUSSION

The White River at Wyman Bridge during 2000 and 2001 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 9 and Figure 6. The results shown for the White River at Wyman Bridge are pro-rated annual values for 2000 and corrected annual values for 2001. The table and figure show TSS and phosphorus as total annual loads per watershed acre, as annual 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 annually. Storm loads per acre may be used to represent relative impacts from non-point sources. In Figure 6, a red line represents the total loads and blue diamonds represents the storm loads. The White River at Wyman Bridge watershed has the highest levels of total TSS measured compared to the others and while most of the TSS is transported during storm events, a significant percentage is transported during base-flow conditions.

The P load for the White River at Wyman Bridge is similar to the other watersheds with the primary transport occurring during storm events. Base Flow P concentrations are higher than the other watersheds studied. This may be evidence of organic phosphorus bound to TSS measured particles. Phosphate concentrations were low with the storm and base flow mean concentrations of 0.05 and 0.01 mg/l respectively.
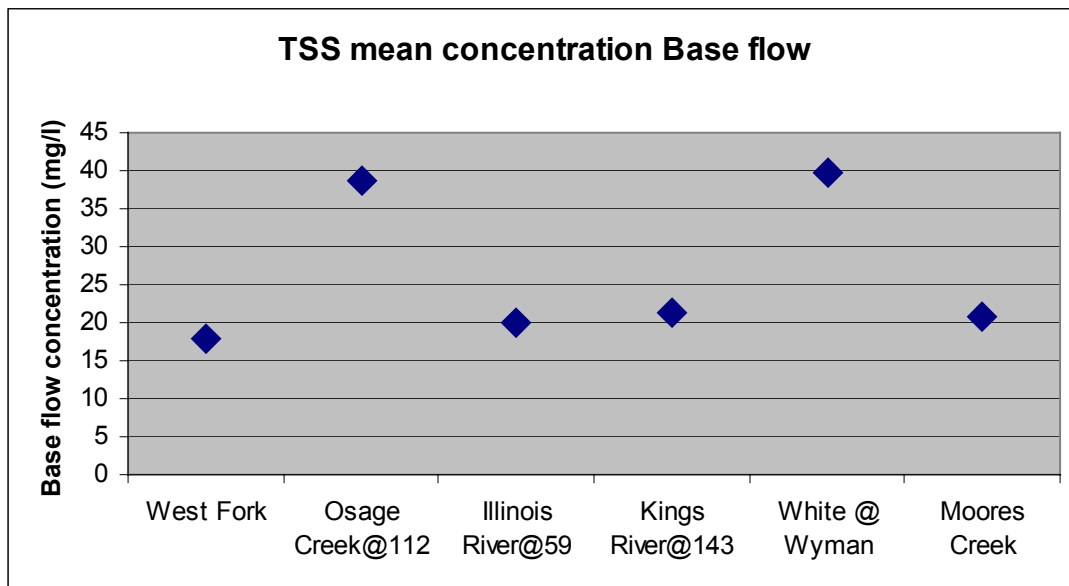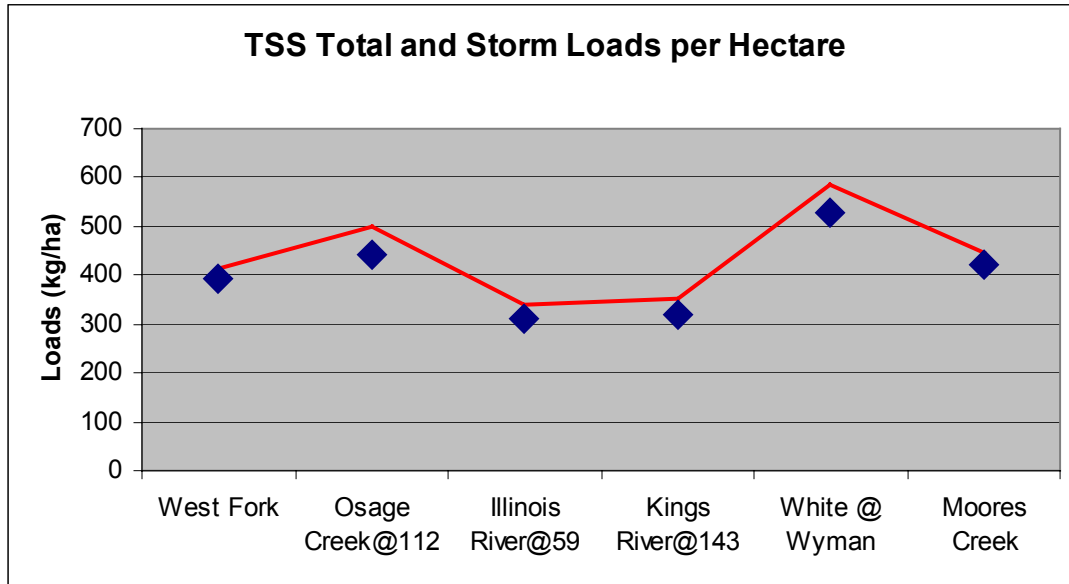
The base-flow concentrations show relative levels of TSS and P that are impacting in-stream biological activity during most of the year. These are the values that are of greatest interest for determining impacts to in-stream macro invertebrate habitat and nuisance algae production. The base-flow TSS is higher than the other watersheds. The base-flow concentration of T-P is high. The source of this base-flow phosphorus may be Lake Sequoyah, which collects the Main and Middle forks of the White before they combine with the West Fork. The West Fork has significantly lower values of T-P indicating the T-P source is in the other branches of the river.
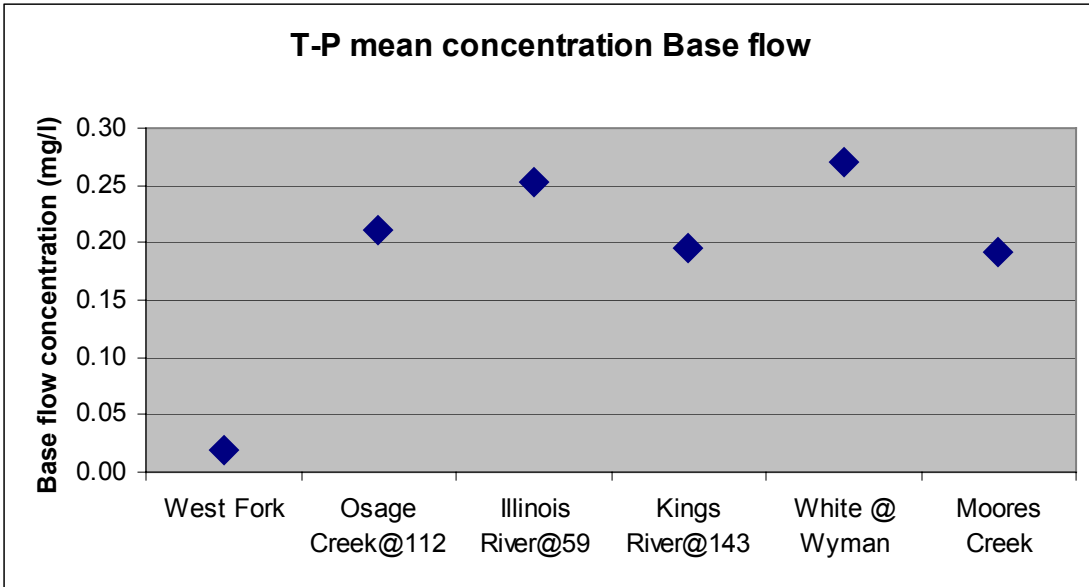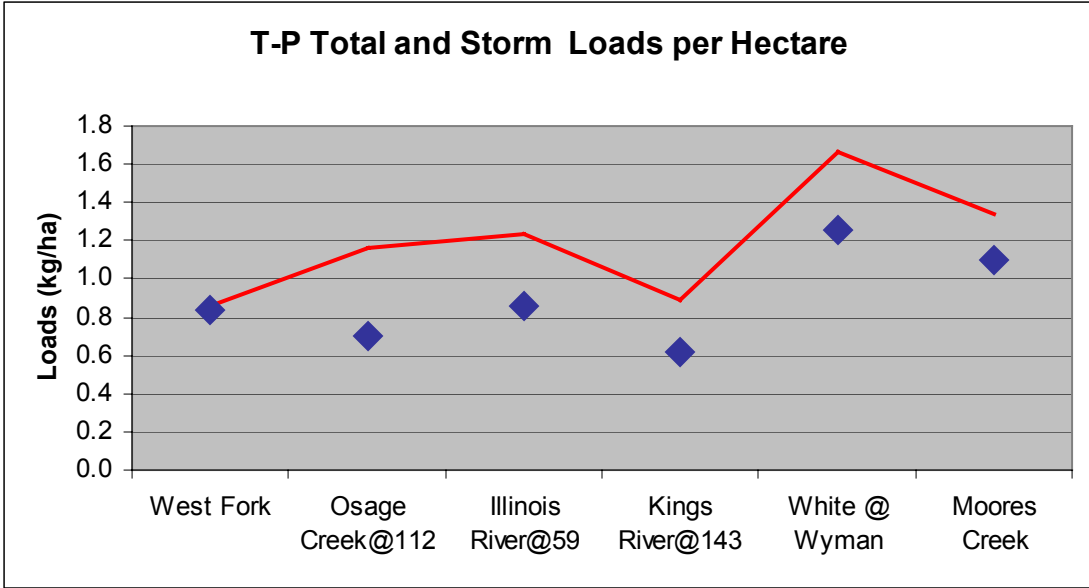
Table 9. Comparison of results to other Northwest Arkansas Watersheds.

	West Fork	Osage Creek@112	Illinois River@59	Kings River@143	White @ Wyman	Moores Creek
Hectares	29,964	10,095	167,273	153,309	116,364	1,000
YEARS of data	2	2	6	4	2	3
tss load (kg/ha)	414	501	340	351	586	445
tss load storm (kg/ha)	394	442	312	320	528	420
tss conc. base (mg/l)	18	39	20	21	40	21
p load (kg/ha)	0.86	1.16	1.24	0.89	1.66	1.34
p storm load (kg/ha)	0.84	0.70	0.86	0.62	1.26	1.10
p base conc. (mg/l)	0.02	0.21	0.25	0.19	0.27	0.19
DISCHARGE (m^3)	99,226,522	38,827,312	545,516,682	419,567,171	413,400,011	2,457,683
DISCHARGE/AC (m^3/ha)	3,312	3,846	3,261	2,737	3,553	2,458

The correction factors that are detailed in this report and were applied to the data for the last year of data 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 6. Comparisons between 6 watersheds.

T-P Total and Storm Loads per Hectare

Loads (kg/ha) vs stations: West Fork, Osage Creek@112, Illinois River@59, Kings River@143, White @ Wyman, Moores Creek

T-P mean concentration Base flow

Base flow concentration (mg/l) vs stations: West Fork, Osage Creek@112, Illinois River@59, Kings River@143, White @ Wyman, Moores Creek

REFERENCES

Glysson, D.G, J.R. Gray and L.M. Conge Adjustment of Total Suspended Sediment Data for use in Sediment Studies. U.S. Geological Survey, 2001

Nelson, M.A., T.S. Soerens, J. Spooner "Results of Investigation of Optimum Sample Interval for Determining Storm Water Pollutant Loads", Proceedings of the Water Environment Federation WEFTEK Conference, New Orleans, LA, 1999
.
Nelson, M.A., T.S. Soerens "1997 Pollutant Loads At. Arkansas Highway 59 Bridge" Presented at Arkansas-Oklahoma Arkansas River Compact Commission Meeting, September 1998.

Nelson, M.A., T.S. Soerens "1998 Pollutant Loads At. Arkansas Highway 59 Bridge" Arkansas Water resources Center Publication, 1999.

Nelson, M.A., T.S. Soerens "1999 Pollutant Loads At. Arkansas Highway 59 Bridge" Arkansas Water resources Center Publication, 2000.

Nelson, M.A., T.S. Soerens "2000 Pollutant Loads At. Arkansas Highway 59 Bridge" Arkansas Water resources Center Publication, 2001.

Nelson, M.A., T.S. Soerens "2001 Pollutant Loads At. Arkansas Highway 59 Bridge" Arkansas Water resources Center Publication, 2002.

Nelson, M.A., T.S. Soerens, J. Spooner " Preliminary Results of Investigation of Optimum Sample Interval for Determining Storm Water Pollutant Loads", Presented at ASCE Watershed Management Conference, Memphis, TN, 1998.

Nelson, M.A., T.S. Soerens and D.G. Parker "Phosphorus Transport in the Illinois River: Preliminary Results of Intensive Sampling" Proceedings of the Arkansas Water Resource Center Annual Conference, 1998.

Parker, D.G., R. Williams and E. Teague "Illinois River Water Quality Automatic Sampler Installation" Arkansas Water Resource Center Miscellaneous Publication 0227, 1997.

Nelson, M.A., T.S. Soerens, J. Spooner "Investigation of Optimum Sample Number and Timing for Determining Storm Water Pollutant Loads Year [1998 and 1999}", Arkansas Water Resources Center Annual Report 1999-2000, August 2001.

Nelson, M.A., L.W. Cash "Water Quality Sampling, Analysis And Annual Load Determinations For TSS, Nitrogen And Phosphorus At The Wyman Road Bridge On The White River, Final Report" Arkansas Water Resources Center Publication, 2003.

Nelson, M.A., L.W. Cash "Illinois River 2002 Pollutant Loads at the Arkansas Highway 59 Bridge" Arkansas Water Resources Center Publication, 2003.

Nelson, M.A., L.W. Cash "Water Quality Sampling, Analysis And Annual Load Determinations For TSS, Nitrogen And Phosphorus At The 143 Bridge On The Kings River, 2002 Annual Report" Arkansas Water Resources Center Publication, 2003.

Nelson, M.A., S. L. Diffin "Water Quality Sampling, Analysis And Annual Load Determinations For TSS, Nitrogen And Phosphorus At The 112 Bridge On The Osage Creek, Final Report" Arkansas Water Resources Center Publication, 2003.

Nelson, M.A., L.W. Cash "Water Quality Sampling, Analysis And Annual Load Determinations For TSS, Nitrogen And Phosphorus On Moores Creek, 2002 Annual Report" Arkansas Water Resources Center Publication, 2003.