Arkansas Water
Resources Center

Determination of the Pollutant Loads in the Kings River Near Berryville

Submitted to the
Arkansas Soil and Water Conservation Commission

By

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INTRODUCTION

An automatic sampler and a U.S. Geological Survey (USGS) gauging station were established in 1998 and water quality sampling was begun in 1999 on the Kings River near Berryville, Arkansas. Continuous stage and discharge measurements and frequent water quality sampling have been used to determine pollutant concentrations and loads in the river. In addition, ten samples were taken by Arkansas Water Resources Center (AWRC) concurrently with USGS samples in order to assess whether AWRC and USGS samples can be compared. This report presents the results from the sampling and analysis for January 1, 1999 to December 31, 1999.

The objectives of this project were to 1) determine pollutant loads in the Kings River, and 2) to compare USGS cross-sectionally averaged samples to AWRC automatic sampler samples.

BACKGROUND

In 1999, water quality sampling was begun at a new site established on the Kings River in the White River basin. The Kings River flows into Table Rock Lake at the Missouri border and the river basin contains forested and agricultural land and the wastewater from Berryville, Arkansas. The USGS installed a stage guage and developed a stage-discharge relationship for the site. The site is at "Lat 3625'36", long 9337'15", in SE1/4NE1/4 sec.3, T.20 N., R.25 W., Carroll County, Hydrologic Unit 11010001, on right bank at downstream side of bridge on State Highway 143, 1.5 mi downstream from Bee Creek, 2.5 mi upstream from Clabber Creek, 5.3 mi northwest of Berryville, and at mile 35.1" (from USGS web site). Figure 1 shows a map of the site.

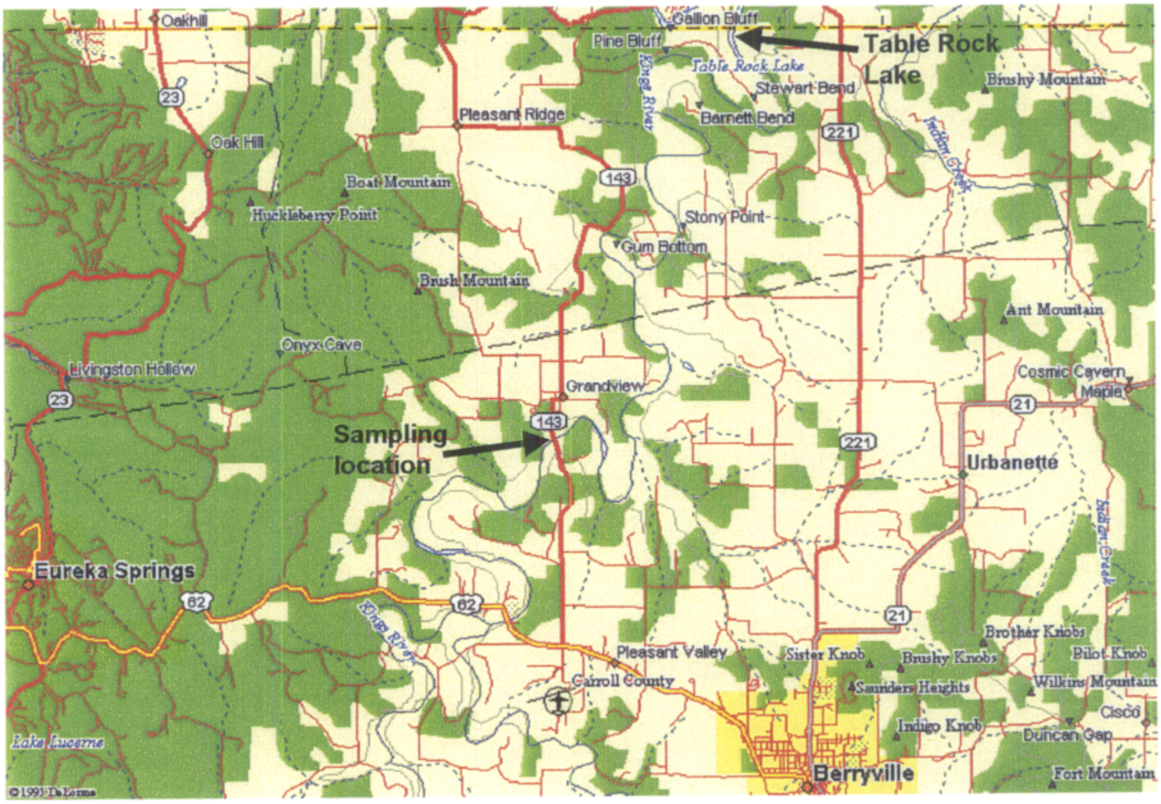


Figure 1. Map of Kings River Sampling Site

METHODS

This site was intensively sampled during five storms in 1999 using a methodology developed by AWRC at Illinois River sites. AWRC installed an automatic sampler programmed to take samples every thirty minutes during the rising limb of a storm hydrograph and every hour during the falling limb. In addition, grab samples were taken weekly between storms or more frequently on the tail end of storms. One of the objectives of the Kings River study was to compare samples taken by the AWRC automatic sampler with those taken by USGS using a manual cross-sectional sampling technique. Ten USGS cross-sectionally averaged samples were taken concurrently with AWRC automatic samples and analyzed at the Arkansas Water Quality Lab. Figure 2 shows the discharge during 1999 along with the samples taken.

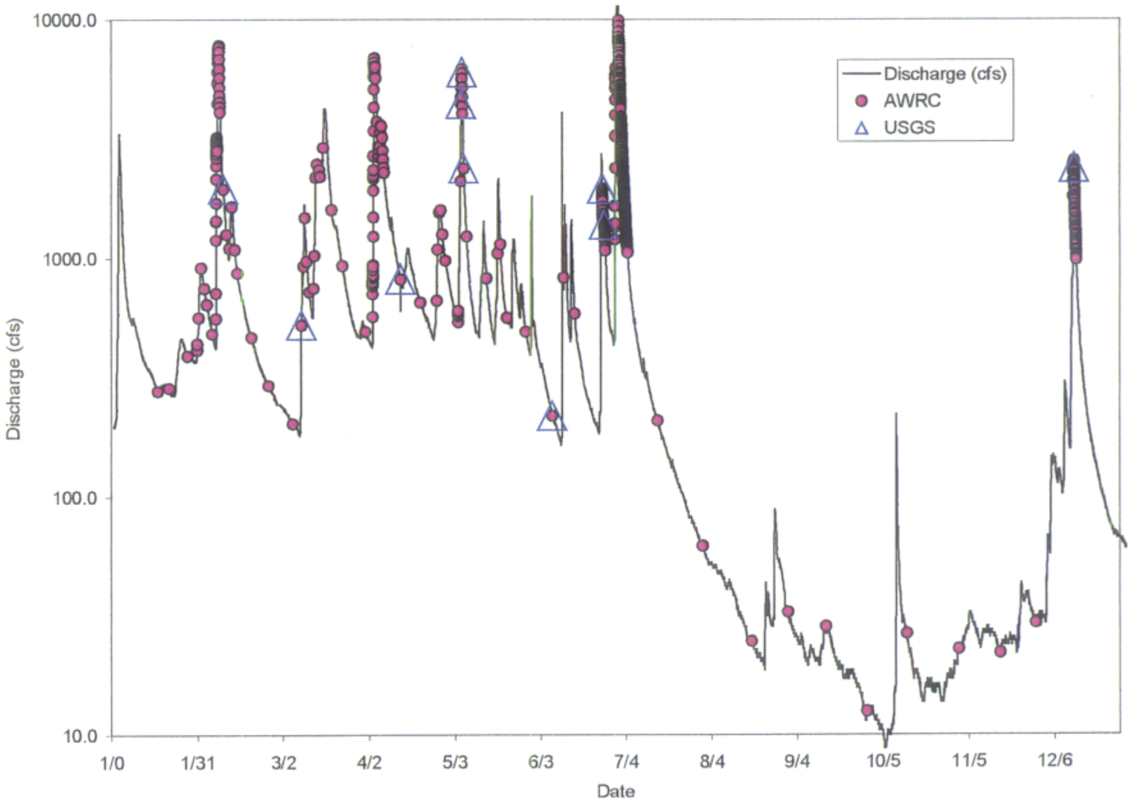


Figure 2. 1999 Discharge and Water Quality Samples at the Kings River Site by AWRC and USGS

All samples were collected from the sites within 24 hours and analyzed at the Arkansas Water Resources Center Water Quality Lab using U.S. EPA approved analysis and QA/QC procedures. The samples were analyzed for nitrate-N, ammonium-N, TKN, Ortho-P, Total-P, TSS, sulfate, and chloride.

Pollutant loads and mean concentrations were calculated by multiplying the concentration for each 30 minute time period times the discharge during that time period. Pollutant concentrations were assigned to each time period by taking the measured concentration and applying it from half way to the previous sample to half way to the subsequent sample. The yearly load is the sum of all the loads for all the time periods. The yearly mean concentrations were calculated by dividing the yearly load by the yearly discharge.

RESULTS

The calculated loads and flow-weighted mean concentrations are shown in Table 1.

Table 1. Kings River near Berryville 1999 Loads and Mean Concentrations

Parameter	Total Load (kg/yr)	mean concentration (mg/L)
Discharge	4.35×10^8 (m^3/yr)	488 cfs
NO_3-N	3.65×10^5	0.84
TP	1.34×10^5	0.31
NH_4-N	1.10×10^4	0.025
TKN	3.24×10^5	0.75
PO_4-P	3.25×10^4	0.075
TSS	7.80×10^7	179

Table 2 shows the load per drainage area for the Kings River site compared to the Illinois River Highway 59 site.

Table 2. Loads per Drainage Area for Kings River and Illinois River

Parameter	Kings River load / drainage area (kg/hectare)	Illinois River load / drainage area (kg/hectare)
Drainage area	527 mi^2	575 mi^2
Runoff*	31.9 cm	42.4 cm
NO_3-N	2.67	10.4
TP	0.982	1.78
NH_4-N	0.0806	
TKN	2.37	3.43
PO_4-P	0.238	
TSS	571	513

*Runoff = annual discharge / drainage area

Table 3 shows the flow-weighted mean concentrations at the Kings River site compared to the Illinois River Hwy 59 site and two groups of USGS undeveloped benchmark sites: 1) 43 basins from the Hydrologic Benchmark Network, and 2) 22 basins from the National Water-Quality Assessment (NAWQA) as reported by Clark et al. (2000).

Table 3. Kings River Mean Concentrations Compared to the Illinois River and to Benchmark Sites

Parameter	Kings River mean conc (mg/L)	Illinois River	Hydrologic Benchmark Network	NAWQA undeveloped
Discharge	488 cfs	706 cfs		
NO_3-N	0.84	2.45	0.075	0.080
TP	0.31	0.42	0.020	0.037
NH_4^+-N	0.025		0.019	0.020
TKN	0.75	0.81	0.17	0.24
PO_4^{2-}-P	0.075		<0.01	0.010
TSS	179	121		

Table 4 shows the median of the errors between each AWRC and USGS sample pair for the eight measured parameters and the median of the absolute errors. The errors are defined as :

error = (AWRC-USGS)/(USGS)

The median of the errors gives a measure of the overall direction of the error – e.g., if the median of the errors is negative, then AWRC tends to be less than USGS. The median of the absolute errors gives a measure of the precision between the individual measurements. Also shown in Table 4 are the correlation coefficient between the measurements and the slope of the regression of AWRC samples on USGS samples. A correlation coefficient near one indicates a strong positive correlation. A regression slope greater than one indicates that AWRC samples tend to be higher than USGS samples. One sample pair (#3 in Table 5) was identified as an outlier; it is graphed in Figures 5 and 6, but was not used in the analysis, as explained in the Discussion section.

Table 4. Comparison Between AWRC and USGS Samples – Medians and Correlation.

	Median of errors	Median of absolute errors	Correlation Coefficient r	Slope of Regression
SO4	0.81%	3.60%	0.89	1.02
Cl-	1.39%	1.61%	0.82	1.03
NO3-N	-2.58%	4.20%	0.97	0.94
T-P	0.00%	17.65%	0.83	0.93
NH4	19.91%	53.28%	0.82	1.02
TKN	26.92%	26.92%	0.93	1.17
PO4	9.09%	14.29%	0.98	0.88
TSS	37.71%	44.32%	0.95 log(TSS)	1.03 log(TSS)

Table 5 shows the AWRC sample and USGS sample values for the eight measured parameters for the ten concurrent samples.

Table 5. AWRC and USGS Concurrent Samples

	SO_4		Cl^-		NO_3-N		T-P		NH_4-N		TKN		PO_4-P		TSS		
	AWRC	USGS	AWRC	USGS	AWRC	USGS	AWRC	USGS	AWRC	USGS	AWRC	USGS	AWRC	USGS	AWRC	USGS	
1	2.76	2.75	5.37	5.39	1.482	1.485	0.085	0.085	<0.009	<0.009	0.27	0.18	0.036	0.03	33.5	19.2	
2	3.33	m	m	m	0.729	0.876	0.220	0.205	0.054	0.056	0.53	0.51	0.147	0.181	33.1	27.3	
3	3.19	2.94	5.31	5.38	0.838	0.915	0.390	0.070	<0.009	<0.009	1.00	0.12	0.055	0.059	327.2	1.5	**
4	1.84	3.22	5.05	8.36	0.427	0.740	0.625	0.645	<0.009	<0.009	1.47	1.65	0.080	0.070	275.6	301.2	
5	1.73	1.51	3.86	3.64	0.120	0.371	0.306	0.450	<0.009	<0.009	1.90	1.38	0.024	0.021	118.8	279.5	
6	1.85	1.77	4.49	4.42	0.531	0.504	0.070	0.085	0.076	0.053	0.27	0.31	0.027	0.024	37.9	27.5	
7	5.76	3.68	5.50	5.49	0.479	0.491	0.145	0.145	0.069	0.078	0.26	0.25	0.116	0.124	4.4	2.7	
8	3.97	3.92	2.28	2.24	0.726	0.738	0.470	0.640	0.031	0.019	1.41	1.05	0.067	0.080	248.3	180.4	
9	4.06	4.06	2.18	2.15	0.731	0.763	0.285	0.165	0.010	0.033	0.89	0.55	0.066	0.085	144.0	58.1	
10	7.29	7.47	4.65	4.56	1.756	1.749	0.585	0.335	0.045	0.012	0.91	0.72	0.053	0.046	118.2	81.9	

** sample pair 3 is an outlier and was omitted from the analysis. m = missing data.

Figures 5a - c show the results of comparison between the USGS samples and the AWRC samples for TSS, total Phosphorus, and PO_4-P.

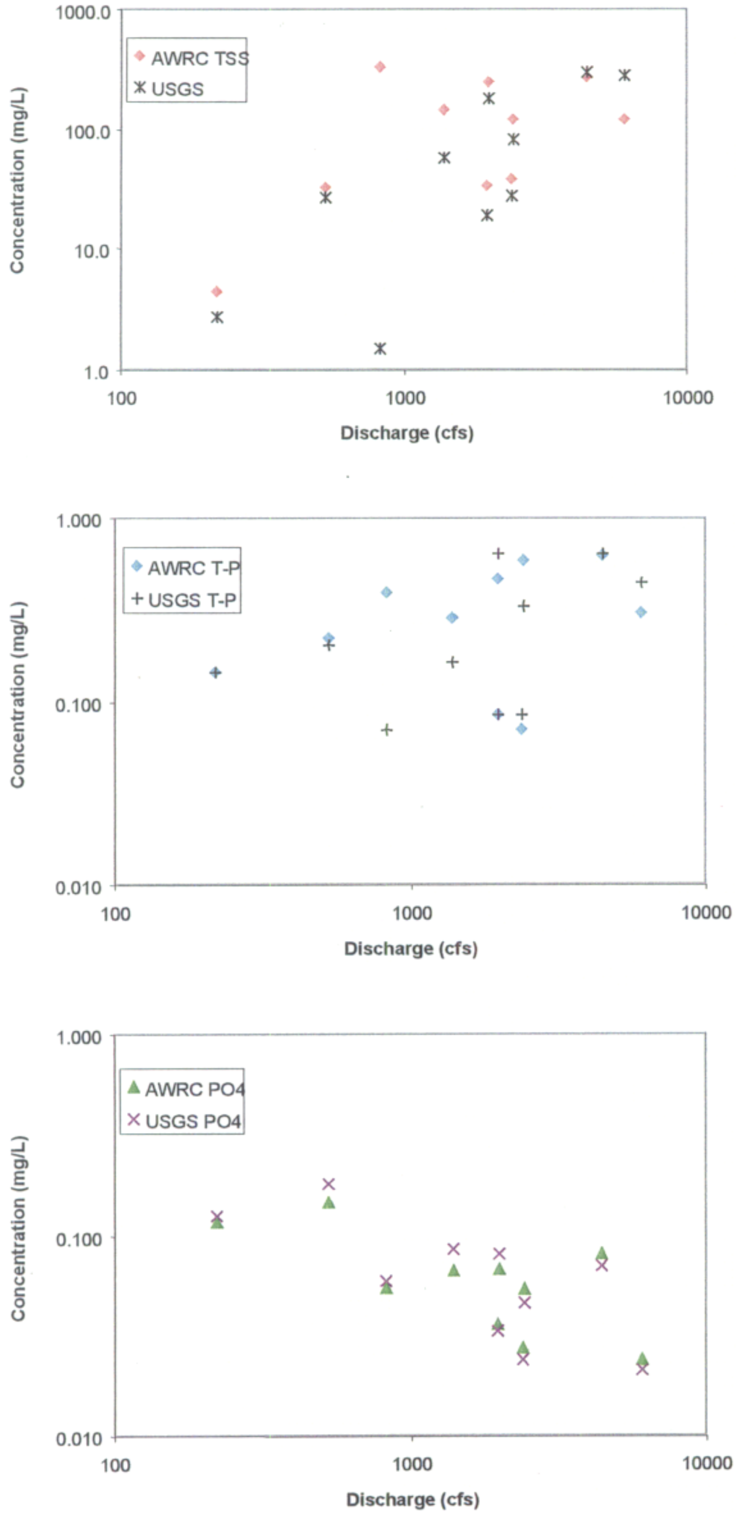
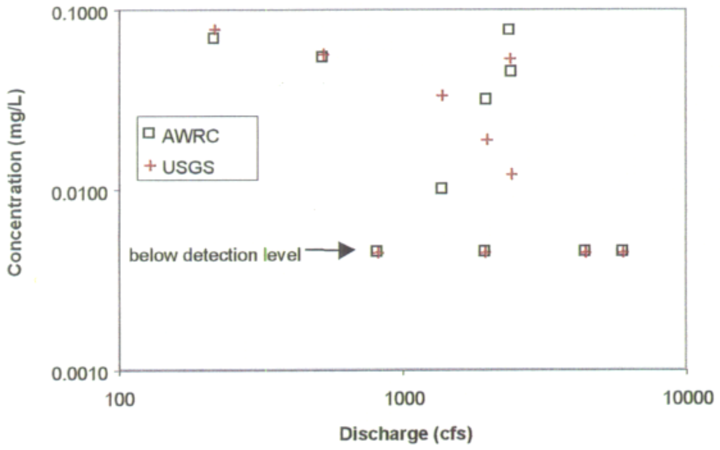
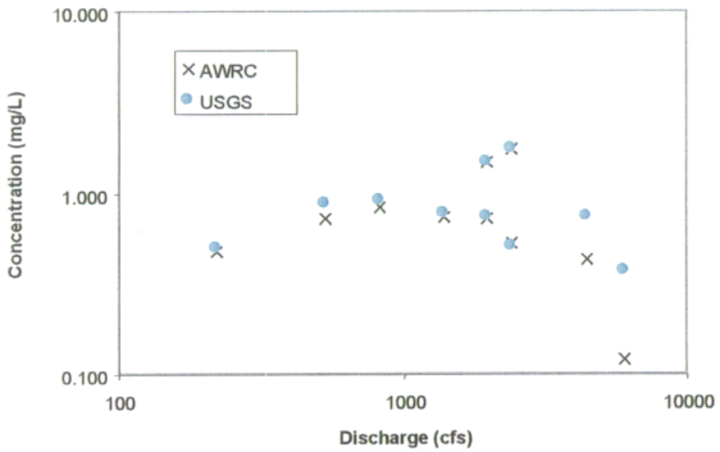


Figure 5 Comparison Between ARWR and USGS Samples – a. TSS, b. Total P, c. PO_4-P

Figures 6a - c show the results of a comparison between the USGS samples and the AWRC samples for NH_4-N, NO_3-N, and TKN.





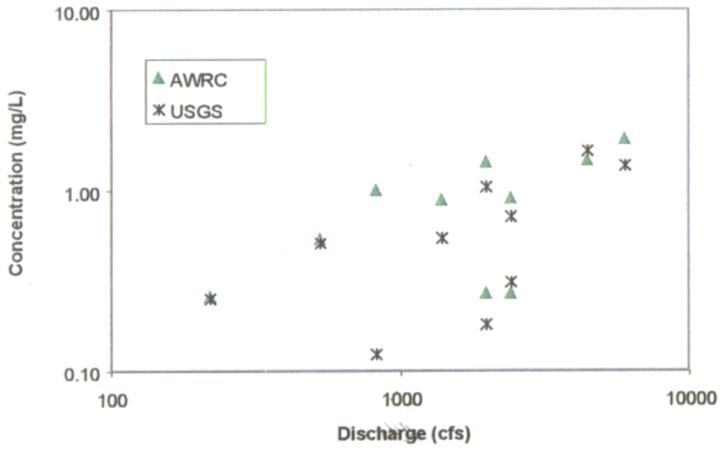
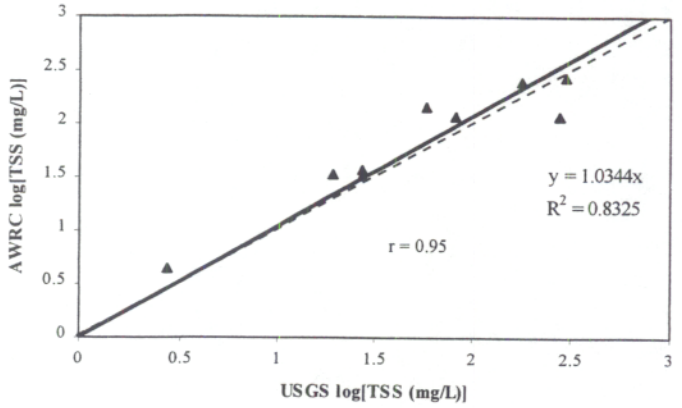
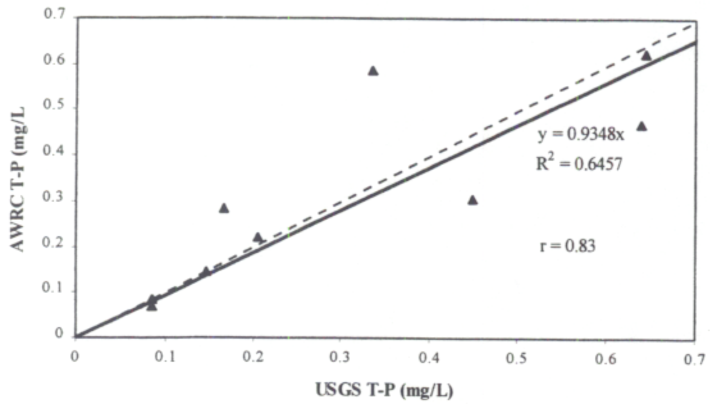


Figure 6 Comparison Between ARWR and USGS Samples – a. NH_4-N, b. NO_3-N, c. TKN

Figure 7 a.-c. show the AWRC samples plotted against the USGS samples for log(TSS), total Phosphorus, and PO_4-P. The regression line between the samples is shown as a thicker line and the regression equation and R^2 for the regression (forced through zero) are shown on the graph. A dashed line shows a 1:1 correlation. Also shown is the correlation coefficient, r.





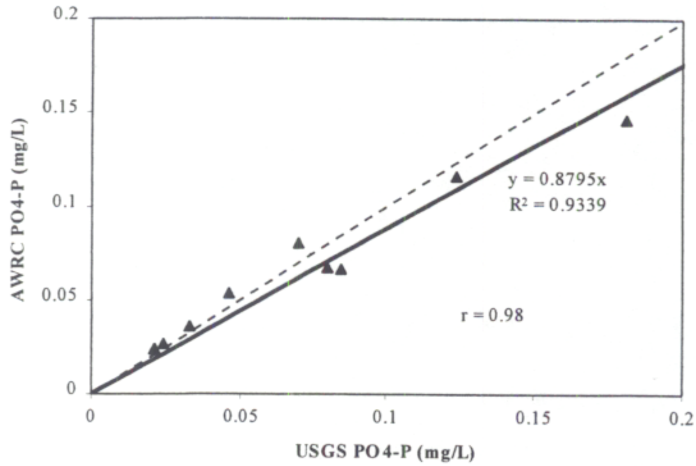
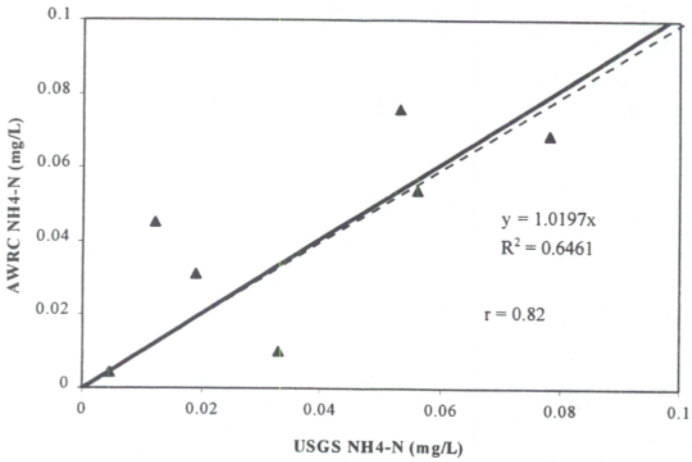
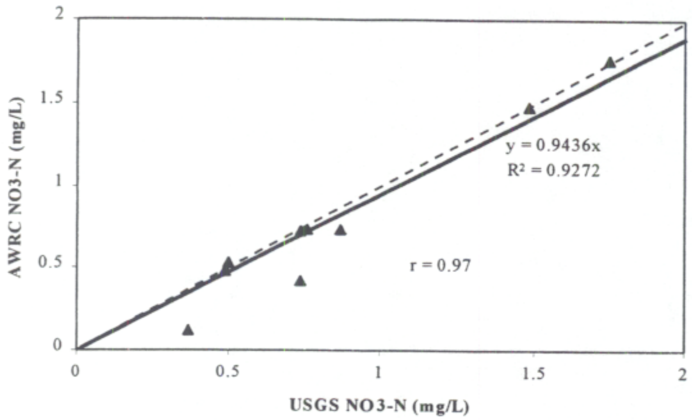


Figure 7. AWRC versus USGS Samples a. log(TSS), b. Total Phosphorus, c. PO_4-P.

Figure 8 a.-c. shows AWRC versus USGS samples for NH_4-N, NO_3-N, and TKN.





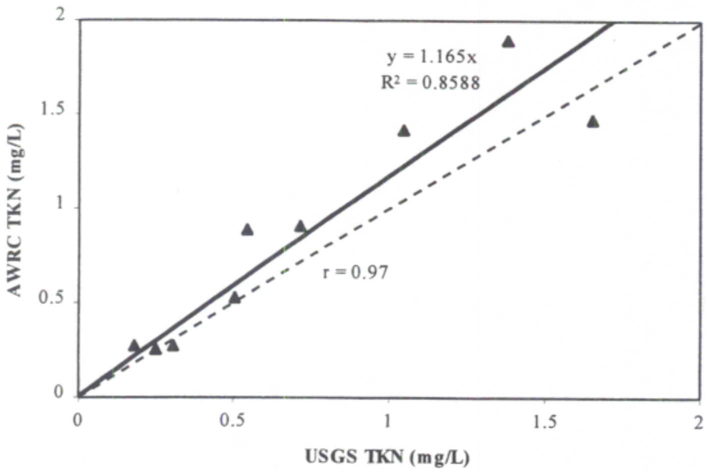


Figure 8. AWRC versus USGS Samples a. NH_4-N, b. NO_3-N, c. TKN.

DISCUSSION

The loads per drainage area and mean concentrations in the Kings River are lower than that for the Illinois River, except for TSS, which is slightly higher. Most notably, nitrate in the Kings River is significantly lower. This is probably due to more point sources, namely wastewater discharges, in the Illinois River. The mean concentrations in the Kings River are higher than USGS pristine benchmark sites.

In comparing the AWRC samples to the USGS samples, we observe in Figures 5-8 that the samples are correlated, but there are discrepancies for several samples. The observation that TSS and TKN are higher in the AWRC samples in most cases may be the result of the AWRC automatic sampler taking samples closer to the stream bed, which results in more solids than the USGS cross-sectional averaged samples. This difference, however, is not seen in the total P measurements, which are quite close to eachother.

The median of errors for NH_4-N is higher than for the other parameters; however, as seen in the data and in Figure 6a., four of the data points were samples that were below detection level in both samples, and were not included in calculating the median errors. If the errors for these sample pairs were taken to be zero, the median of errors would be 0% and the median of absolute errors would be 11.5%.

The largest difference in the sediment related parameters (TSS, TKN, and total-P) is at the one outlier point (TSS: AWRC=327, USGS=1.5, @Q=821 cfs), which was not used in the analysis. At this point, the TSS in the AWRC sample is much higher than that expected for that flow, while the USGS sample is much lower than that expected for that flow, as seen in Figure 9. This is possibly due to incomplete purging of the autosampler before collecting the sample.

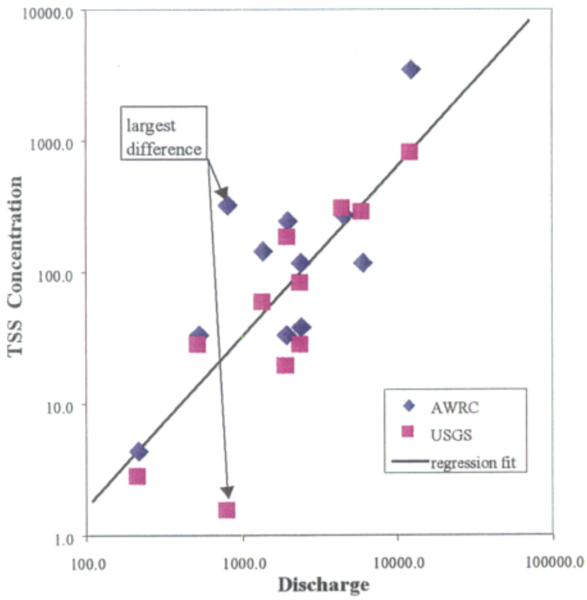


Figure 9. AWRC and USGS TSS values versus Discharge with Regression Line

We will continue to investigate the differences between sampling methods and to ensure quality control for sampling, sampling analysis, and load calculation. The fact that differences in total-P and in NO_3-N are small supports the assertion that automatic sampler data can be used to accurately estimate phosphorus and nitrogen loads.

REFERENCES

Clark, G.M., D.K. Mueller, and M.A. Mast, "Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States", Journal of the American Water Resources Association, Vol.36, No.4, August 2000.