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Kings River Quality Assurance Project Final Report

Marc Nelson
University of Arkansas, Fayetteville

Sam Davis

Arkansas Water Resources Center

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Marc Nelson, Ph.D.
Arkansas Water Resources Center
Water Quality Lab
University of Arkansas
Fayetteville

Sam Davis
Kings River Watershed Partnership
Chairman of the Monitoring Committee

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ARKANSAS WATER RESOURCES CENTER
UNIVERSITY OF ARKANSAS
112 OZARK HALL
FAYETTEVILLE, ARKANSAS 72701

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Marc Nelson Ph.D.
Arkansas Water Resources Center – Water Quality Lab
University of Arkansas

Sam Davis
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INTRODUCTION

The Kings River Watershed Partnership non-profit citizens group formed to take local control over water quality issues in the Kings River watershed in Arkansas. One of the first items the group addressed was water quality monitoring of the Kings River and Osage Creek. To this end they formed a water quality monitoring committee that was charged with the development of a water quality monitoring plan. The objectives of the plan they developed are: 1) to characterize both spatial and temporal variability in water quality parameters throughout the watershed during each year, 2) to utilize volunteers to monitor the water quality, and 3) to institute QA/QC procedures that will insure the quality of the data collected and allow its use in development of a Watershed Management plan.

This project was initiated to assist the KRWP in developing QA/QC procedures and analytical methods that would provide high quality data. The method chosen to provide this assistance was to analyze duplicate samples. One sample collected and analyzed by the KRWP volunteers and one sample analyzed by the Arkansas Water Resources Center – Water Quality Lab (AWRC-WQL). The QA plan called for the collection of water samples and measurement of water quality parameters at one of 11 sites once per quarter. In addition, once or twice per year volunteers were to collect samples and measure water quality at the eleven sites distributed throughout the watershed at the same time. The decision as to where to sample was made at the sampling time. It was determined by the chairman of the monitoring committee based upon the number of volunteers present, access to sites and the logistics involved. All sites had the same test parameters measured either on-site or transported immediately to a central location for analysis. All volunteer monitors were trained to perform the analyses and are certified as capable of performing water testing according to the KRWP training manual. The parameters measured in-situ were: air temperature, water temperature, pH and TDS. The parameters measured after sample collection using Hach test kits were dissolved oxygen, turbidity, nitrate-N, phosphate-P, hardness and alkalinity. In addition, field logs included the following information: date, time, sampling person, and depth of water. Duplicate water samples were collected three times at one of the sampling sites and twice at all of the available sampling sites and transported to the Arkansas Water Resources Center – Water Quality Lab (WQL) for analysis. The WQL is a certified lab located on the campus of the University of Arkansas that specializes in analyzing water samples. The lab is certified by the Arkansas Department of Environmental Quality for analysis of surface water samples, by the Louisiana Department of Health for analysis of drinking water samples under the NELAP standards and by the USGS for analysis of major nutrients.

A Quality Assurance Project Plan was developed for this project and submitted to EPA Region 7 for approval on December 10, 2004. The QAPP was approved on June 2, 2006. Data collection began shortly thereafter.

Figure 1. Map of the Kings River Watershed sampling sites.

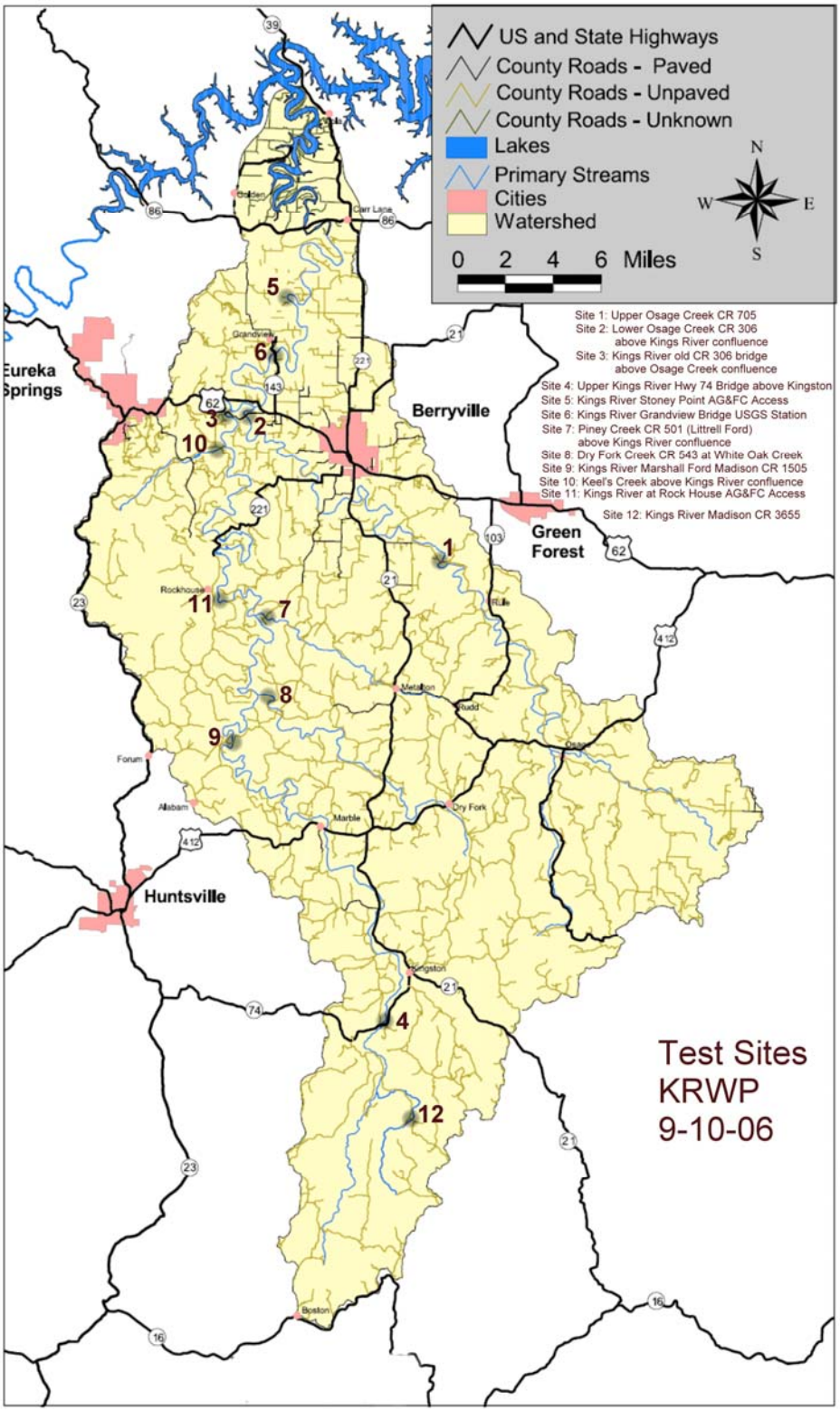

Table 1 List of the Monitoring sites

Site 1 = Upper Osage Creek @ CR 705 above Berryville "Clearwater bridge"
Site 2 = Lower Osage Creek @ CR 306 bridge below Berryville, just above Kings River confluence
Site 3 = Kings River,just above Osage Creek confluence (Old CR 306 bridge site)
Site 4 = Upper Kings River HWY 74 bridge south of Kingston
Site 5 = Stoney Point - Kings River AG&FC Access below Grandview
Site 6 = Kings River at Grandview Bridge - USGS station
Site 7 = Piney Creek @ CR 501 Low water bridge upstream from Kings River (Littrell Ford)
Site 8 = Dry Fork Creek @ CR 543 at confluence of White Oak Creek, near White Oak Church
Site 9 = Kings River @ Marshall Ford Madison County CR 1505
Site 10 = Keel's Creek above Kings River confluence
Site 11 = Kings River at Rock House Access
Site 12 = Kings River Madison County CR 3655 bridge above Site 4

RESULTS

AWRC- Water Quality Lab analyzed 22 duplicate samples collected by the KRWP over the period from June, 2005 to September 2006. These results are summarized in table 2.

Table 2 Summary of duplicate sample analyses

Agency	Date Received	Sample ID	Sample No.	Alkalinity	Hardness	Nitrate	Ortho Phosphate	TDS	Turbidity
KRWP	6/19/2005	Kings Site 4	Site 4	60	60	0.7	0.2	52	0
AWRC	6/19/2005	Kings Site 4	50547-01	40	42	0.13	0.005	61	1
KRWP	9/28/2005	Kings Rockhouse	Site 11	120	120	0.5	0.31	116	1
AWRC	9/29/2005	Kings Rockhouse	60127-01	108	110	0.041	0.003	139.3	1.4
KRWP			60127-01	108	110	0.5	0.31	139.25	1.4
AWRC	4/16/2006 11:00	Site #3 KRWP	60366-01	90	86	0.11	0.002	106.3	1
KRWP	4/16/2006 11:00	Kings Site 3		120	100	0.7	0.08	87	2
AWRC		Blank	60366-02	2	2	0.01	0	1.75	0.1
AWRC	7/17/2006	Kings 74	70018-01			0.544	0.03		
KRWP	7/17/2006	Kings 74	Site 4			0.47	0.20		
AWRC	7/17/2006	Osage CR 705	70018-02			0.057	0.012		
KRWP	7/17/2006	Osage CR 705	Site 1			0.03	0.28		
AWRC	7/17/2006	Std NO3 0.20	70018-03			0.213	0.003		

KRWP	7/17/2006	Std NO3 0.20				0.20			
AWRC	8/3/2006	Osage Site 2	70053-01	220	116	0.021	0.51	432.5	1.8
KRWP	8/2/2006	Osage Site 2	Site 2	240	140	0.00	1.51	373	3
AWRC	8/3/2006	Kings Site 3	70053-02	124	116	0.049	0.005	151	1.4
KRWP	8/2/2006	Kings Site 3	Site 3	140	120	0.01	0.19	123	1
AWRC	8/3/2006	Kings Rockhouse	70053-03	104	104	0.081	0.008	133.3	1.3
KRWP	8/2/2006	Kings Rockhouse	Site 11	120	120	0.03	0.20	108	1
AWRC	8/3/2006	DI water	70053-04			0	0.004		
KRWP	8/31/2006	blank							
AWRC	8/31/2006	King	70110-01	82*	76	0.216	0.029	119.2*	14*
KRWP	8/31/2006	Kings Site 4		100	100	0.04	0.18	95	23
AWRC	8/31/2006	Kings	70112-01	88*	84	0.106	0.023	118.5*	12*
KRWP	9/17/2006	Piney Creek	Site 7						
AWRC	9/17/2006	Piney Creek	70139-01	166	172	5.302	0.058	248.8	0.4
KRWP	9/17/2006	Piney Creek at Hwy 21 S bridge		n/a	n/a	exceeded limit	0.32	n/a	n/a
AWRC	9/17/2006	Keels Creek	70139-02	116	112	0.112	0.005	137.3	1.3
KRWP	9/17/2006	Kings Site 10 -Keels Creek		116	112	0.112	0.005	137.3	1.3
AWRC	9/17/2006	Kings 74 Bridge	70139-03	90	94	0.093	0.01	120	5.4
KRWP	9/17/2006	Kings Site 4 Hwy74 Bridge		n/a	n/a	0.07	0.11	n/a	n/a
AWRC	9/17/2006	Dry Fork Creek	70139-04	130	136	0.714	0.007	173.8	0.5
KRWP	9/17/2006	Dry Fork Creek - Site 8		n/a	n/a	0.51	0.26	n/a	n/a
AWRC	9/17/2006	Site #3 Kings	70139-05	122	120	0.017	0	151	0.7
KRWP	9/17/2006	Kings - Site 3		140	140	0.01	0.20	141	3
AWRC	9/17/2006	Site #5 Stoney Pt.	70139-06	140	122	0.005	0.088	218.8	2.1
KRWP	9/17/2006	Kings- Site 5 Stoney Pt.		n/a	n/a	0.00	0.28	n/a	n/a
AWRC	9/17/2006	Upper Osage	70139-07	112	116	0.21	0.007	147	2.5
KRWP	9/17/2006	Upper Osage Site 1		n/a	n/a	0.12	0.11	n/a	n/a
AWRC	9/17/2006	Rockhouse Kings R.	70139-08	228	176	0.964	0.003	266.8	1
KRWP	9/17/2006	Kings Rockhouse-Site 11		n/a	n/a	0.17	0.21	n/a	n/a
AWRC	9/17/2006	Osage Creek #2	70139-09	188	132	0.031	1.026	302.3	2.2
KRWP	9/17/2006	Osage Creek Site 2		180	160	0.06	2.96	260	3

Comparison between KRWP and AWRC analyzed samples from the first two sampling events showed a significant discrepancy between the results for nitrates and phosphates. Table 3 and 4 list the method and results for the duplicates.

Table 3 Nitrate results from the first two sampling events (mg/l NO3-N).

Analysis	Method	Date	Result
KRWP	HACH 8039	June 19, 2005	0.7
AWRC	EPA 300.0	June 19, 2005	0.130
KRWP	HACH 8039	September 29, 2005	0.5
AWRC	EPA 300.0	September 29, 2005	0.041

Table 4 Phosphate results from the first two sampling events (mg/l PO4-P)

Analysis	Method	Date	Result
KRWP	HACH 8048	June 19, 2005	0.20
AWRC	EPA 365.2	June 19, 2005	0.005
KRWP	HACH 8048	September 29, 2005	0.31
AWRC	EPA 365.2	September 29, 2005	0.003

These results did not meet the QA target of +/- 20% difference. The KRWP nitrates were from 5 to 10 times higher than AWRC's results and the phosphates were from 40 to 100 times higher. Marc Nelson of AWRC met with Sam Davis, the chairman of the monitoring committee to be certain that all procedures were being followed and to try to find out where the problem was occurring. This discussion led to the following corrective actions:

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1. Use a reagent blank correction for both nitrate and phosphate.
2. Use the low range (0-0.5mg/l) nitrate test in place of the high range test (0-30 mg/l)
3. Take duplicates below the Berryville WWTP discharge

Using reagent blanks in the procedures for nitrate and phosphate removes interference from the reagents especially at low sample concentrations. This is an important step in the analytical process that was not being done. The values for nitrate and especially phosphate measured in their samples were typically very low. The nitrate ranged below 1 mg/l, so using the high range test of 0 to 30 mg/l was not providing enough sensitivity. HACH's mid range test 0 to 10 mg/l would have been better. However, it could not be done with the equipment the KRWP was using. The low range was chosen to give greater sensitivity at the low levels that were being measured. The phosphate values measured by AWRC (0.003 and 0.005 mg/l) were at the threshold of being non-detectable even by the very sensitive methods used by AWRC. The HACH kits could not be expected to quantify the phosphates at these low levels. The third corrective action recommendation was to take samples below the Berryville WWTP where phosphate levels would be high enough to quantify.

These corrective actions were implemented by the KRWP in May of 2006. The results, shown in table 5, show a much closer agreement between the KRWP and AWRC analyses.

Table 5 Duplicate results for N and P after corrective actions

Agency	Date Received	Sample ID	Sample No.	Nitrate-N (mg/l)	Ortho Phosphate-P (mg/l)
AWRC	7/17/2006	Kings 74	70018-01	0.544	0.03
KRWP	7/17/2006	Kings 74	Site 4	0.47	0.20
AWRC	7/17/2006	Osage CR 705	70018-02	0.057	0.012
KRWP	7/17/2006	Osage CR 705	Site 1	0.03	0.28
AWRC	7/17/2006	Std NO3 0.20	70018-03	0.213	0.003

The results for these two parameters still did not meet the QA criteria of +/- 20% difference. Subsequent analyses by the KRWP emphasized careful adherence to the method and procedures. The last duplicate sampling during the project was during a watershed wide testing event at 8 sites (shown in figure 2 and 3). These results show a much better agreement between AWRC and KRWP results. Most results still did not meet the QA target of +/- 20%. However, in most cases, the absolute difference was small. The phosphate results still show a high bias from the KRWP results. The source of this bias is unknown. The nitrate results show good agreement between most results and no consistent bias. One sample showed considerable difference and probably points out inconsistency in procedures or sampling.

Figure 2

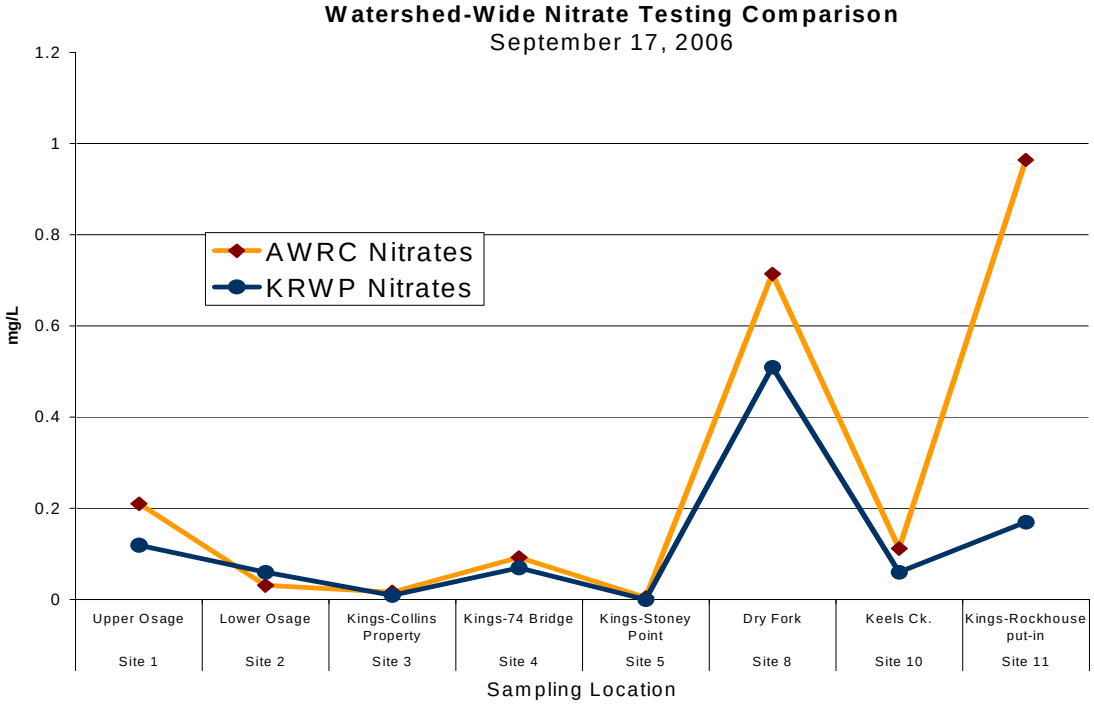
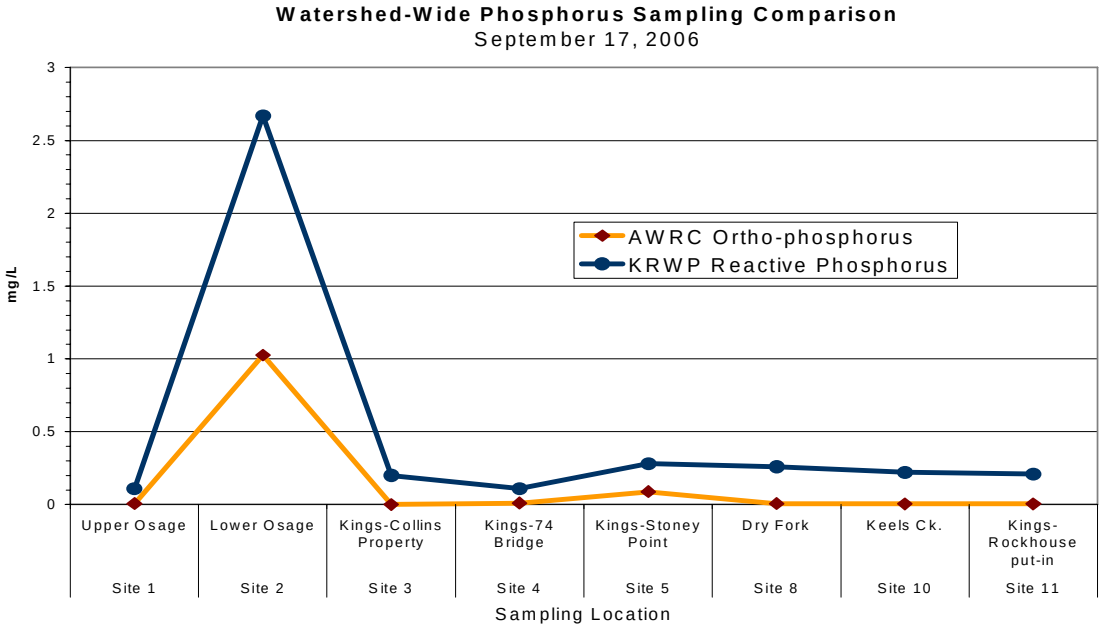


Figure 3



CONCLUSIONS

The use of volunteer monitors and HACH testing kits is an accurate method for evaluating water quality. Careful attention must be paid to following testing procedures, training, and using appropriate test methods. Duplicate testing using a certified lab is a viable way to assure volunteer monitoring programs are collecting accurate data.