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Water Quality Monitoring and Constituent Load Estimation in the Kings River near Berryville, Arkansas, 2009

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Water Quality Monitoring and Constituent Load Estimation in the Kings River near Berryville, Arkansas, 2009

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The Arkansas Water Resources Center monitored water quality at the Kings River near Berryville, Arkansas, during base flow conditions and storm events from July 1, 2009 through June 30, 2010. Water samples were collected manually with an alpha or Kemmerer style sampler and analyzed for nitrate-nitrogen (NO_3-N), sulfate (SO_4), chloride (Cl), soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved ammonia (NH_3-N), total N (TN), total suspended solids (TSS), and turbidity. Physico-chemical parameters were measured in field including pH, conductivity, water temperature, and dissolved oxygen concentration. The selected site was at an established discharge monitoring station maintained by the US Geological Survey, and total annual discharge was 825,848,000 m^3. Constituent loads were determined using regression models between constituent concentrations, discharge, and seasonal factors to estimate daily loads, which were then summed to produce monthly and annual load estimates. The constituent loads and annual flow-weighted concentrations for the 2009 calendar year are summarized in the table below, using the data collected in this study. Semi-annual loads from 1 January to 30 June 2010 are also summarized.

Summary of calculated total loads (kg) for each parameter at the Kings River near Berryville, Arkansas for the period, January through December 2009.

Site	Cl^-	SO_4	NH_3-N	NO_3-N	SRP	TN	TP	TSS
Kings River near Berryville, AR	2,516,000	4,170,000	47,000	663,000	51,000	920,000	250,000	169,710,000

Summary of calculated flow weighted concentrations (FWC, mg L^{-1}) for each parameter at the Kings River near Berryville, Arkansas for the period, January through December 2009.

Site	Cl^-	SO_4	NH_3-N	NO_3-N	SRP	TN	TP	TSS
Kings River near Berryville, AR	3.05	5.05	0.06	0.80	0.06	1.11	0.30	206

ABBREVIATIONS: Chloride (Cl^-), Sulfate (SO_4), Ammonia-Nitrogen (NH_3-N), Nitrate-Nitrogen (NO_3-N), Soluble Reactive Phosphorus (SRP), Total Nitrogen (TN), Total Phosphorus (TP), Total Suspended Solids (TSS), Kings River Watershed Partnership (KRWP), Arkansas Water Resources Center (AWRC), Arkansas Natural Resources Commission (ANRC), Arkansas Department of Environmental Quality (ADEQ)

INTRODUCTION

The Kings River Watershed (HUC 11010001) is located in northwest Arkansas within the Upper White River Basin. The Kings River flows northward from the Boston Mountains in Arkansas to the White River arm of Table Rock Lake on the Arkansas-Missouri border. The largest tributary of the Kings River is Osage Creek, which is the receiving body for treated effluent from the City of Berryville, Arkansas, wastewater treatment plant. Other smaller tributaries include Piney Creek, Keels Creek, Dry Fork Creek, Warmfork Creek, Pine Creek, Felkins Creek, and Sweden Creek. The Kings River Watershed drains 1530 km^2 of which 96% lies in Arkansas and 4% lies in Missouri. The catchment is primarily forest (75%) and agricultural lands (i.e., pasture and forages; 23%). Only 2% of the watershed is urban area, and the only incorporated city located entirely within the watershed boundary is Berryville, Arkansas. The designated uses for the Arkansas portion of the Kings River Watershed are primary contact recreation, secondary contact recreation, domestic, industrial and agricultural water supply, and perennial fishery (for streams with drainage areas of at least 10 mi^2). The Kings River is also an extraordinary resource waters, and natural and scenic waterway (Madison County portion) within Arkansas.

The Kings River has been identified as a potential source of nutrients to Table Rock Lake, and reaches within the Kings River and its tributaries (including Dry Fork and Osage Creek) were included on Arkansas Department of Environmental Quality's (ADEQ) 2008 303d list. The Arkansas Natural Resources Commission (ANRC) has also listed Upper White River Basin as a priority 319 watershed; therefore, monitoring water quality at the Kings River near Berryville is important. The Kings River Watershed Partnership (KRWP) has managed several 319 projects addressing nutrient and sediment sources within the catchment, including stream bank restoration project in recent years. The selected site on the Kings River has been historically monitored by the U.S. Geological Survey (USGS), ADEQ and Arkansas Water Resources Center (AWRC). Constituent loads and flow-weighted concentrations in the Kings River near Berryville, Arkansas have been documented since 2001, and this report presents the annual load and flow-weighted concentrations (FWC) of select constituents at this site for the 2009 calendar year.

METHODS

Sample Collection

Storm and base flow events were sampled at the Kings River near Berryville, Arkansas at the Highway 143 Bridge from July 1, 2009 through June 30, 2010 (Appendix 1 and 2). Water samples were collected using an alpha style horizontal sampler or a Kemmerer type vertical sampler near the vertical centroid of flow (i.e., middle of the channel where water is actively moving). Water samples were collected every 168 hours, on average, at each site where up to 25% of the collected samples represented storm events or surface runoff conditions following episodic rainfall events, including small and large storm events.

Physico-chemical parameters including pH, conductivity, temperature, and dissolved oxygen concentration were measured on site. All water samples were delivered to the AWRC Water Quality Laboratory (WQL) and analyzed for nitrate-nitrogen (NO_3-N), sulfate (SO_4), chloride (Cl), soluble reactive phosphate (SRP), total phosphorus (TP), dissolved ammonia (NH_3-N), total nitrogen (TN), total suspended solids (TSS), and turbidity. Duplicate samples were collected at a frequency of 10% throughout the duration of the project for quality assurance quality control purposes. All water samples were analyzed following analytical procedures outlined in the quality assurance project plan.

Load Determination and Mean Concentrations

Constituent loads (L) were calculated at this site using the constituent concentration data from the collected samples and average daily discharge data (Q_d) from the USGS for the study periods. Daily measured loads were calculated by multiplying Q_d by a corresponding constituent concentration. The calculated loads were plotted as a function of Q_d then linear regression was used to develop an equation that described daily constituent loads (L_d) at the site as a function of measured discharge. The basic log-log linear regression model for L_d can be expressed solely as a function of discharge:

$$\ln(L_d) = \beta_0 + \beta_1 \ln(Q_d) \quad (1)$$

where ln represents the natural logarithm function, β_o is a constant, β_1 is the coefficient for discharge and Q_d is the daily mean discharge (cfs). Regression models were also developed to consider seasonal influences using the Fourier's sine and cosine functions:

$$\ln(L_d) = \beta_0 + \beta_1 \ln(Q_d) + \beta_2 \sin(2\pi T) + \beta_3 \sin(2\pi T) \quad (2)$$

where β_2 and β_3 are the coefficients for seasonal variation, and T is decimal time.

Log-log regression often results in bias when transforming the log values, where the retransformed values often underestimate the actual mean. Therefore, a nonparametric bias correction factor (BCF; Helsel and Hirsh, 2002) was calculated and used when transforming the logarithmic results back to actual loads. BCF for natural logarithmic transformation is:

$$BCF = \frac{\sum e^{e}{}_{i}}{n} \quad (3)$$

where n is the number of samples and e_i is the residual or difference between measured and estimated loads in natural log units. This factor was multiplied by the retransformed value to account for any bias.

Daily loads often show two distinct relations with Q_d representing different flow regimes (e.g., base flow conditions and storm events). Thus, load estimation using regression models can be complex requiring the model developer to really get to know the data. This project evaluated whether all the data could be used to develop regression models, or whether the data needed to be split at some breakpoint separating the data into flow regimes. Then, separate regression models would be developed based on the breakpoint. The appropriate regression model (i.e., Equation 1 or 2) was selected based upon the coefficient of determination (R^2), calculated BCFs, and visual observation of any breakpoints in the relations between L_d and Q_d. Season factors were included in the regression models (i.e., Equation 2) for all data or data representing the low flow regimes, when the regression coefficients were both significant and or when the regression model with seasonal factors explained an additional ~5% of the variation in L_d. Whereas, only equation 1 was used with the data to represent the high flow regime or storm event conditions.

The selected regression was applied and then used to estimate L_d. The retransformed, estimated loads were multiplied by the calculated BCF and summed into annual loads during the calendar year. The annual flow-weighted concentration (mg L^{-1}) was determined by dividing the total load (kg) by the annual discharge volume (m^3).

RESULTS

Physico-chemical parameters were measured on-site during this project period (i.e., from 1 July 2009 to 30 June 2010). Physico-chemical parameters varied seasonally and with episodic rainfall events; a summary of the parameters measured at Kings River are provided in Table 1. The pH was within the expected range (7.8-8.4)

Table 1. Minimum, Maximum and geometric mean of physico-chemical parameters at the Kings River at Highway 143 Bridge from 1 July 2009 to 30 June 2010.

Parameter	Minimum	Maximum	Geometric Mean
pH	7.8	8.4	8.1
Conductivity (µS cm^{-1})	116	278	214
Dissolved Oxygen (mg L^{-1})	5.6	14.6	9.5
Temperature (^oC)	0.7	29.1	10.3

for streams with groundwater inflows from limestone geology. The conductivity ranged from 116 to 278 µS cm^{-1}, and it was representative of stream with an effluent discharge and a mixed land use catchment. Dissolved oxygen concentrations were variable likely dependent on upon the time of sampling, as well as the flow conditions sampled. The water temperature was variable, reflecting the seasonal influence of the local climate.

Discharge and constituent concentrations were variable throughout the year showing the effects of episodic rainfall events and seasonal influences (see Appendix 3). Average daily flow during 2009 at the Kings River near Berryville, Arkansas, was 2,240,000 m^3, but was as great as 59,270,000 m^3 during storm events. Total annual discharge was 825,848,000 m^3 which is approximately 4% greater than that observed during 2008. A total of 58 samples collected during the study period at Kings River near Berryville, Arkansas were used in linear regression with flow to estimate annual loads for 2009. Three parameters (i.e., SO_4, Cl, and NH_3-N) were adequately described by one equation for all flow regimes, while the other five parameters (i.e., NO_3-N, TN, SRP, TP, and TSS) required separate equations for low flow and high flow regimes. Phosphorus, NH_3-N and TSS had a significant seasonal influence, while the other parameters did not. The amount of variation in the dependent variable explained by the selected linear regression equations ranged from 42% during the low flow regime for SRP to 99% for all flow conditions for SO_4 (P ≤0.004). A summary of the regressions equation used and statistical significance of the selected model is provided in Table 2.

Table 2. Regression equations and statistics of linear regression models used to estimate constituent loads at the Kings River near Berryville, Arkansas during calendar year 2009.

Parameter	Regression Equation	Flow Regime	R^2	P
NO_3-N	$\ln(L_d) = -4.98 + 1.90 \ln(Q_d)$	Low	0.96	<0.001
	$\ln(L_d) = 1.44 + 0.90 \ln(Q_d)$	High	0.88	<0.001
SO_4	$\ln(L_d) = 3.29 + 0.90 \ln(Q_d)$	All	0.99	<0.001
Cl	$\ln(L_d) = 4.17 + 0.71 \ln(Q_d)$	All	0.97	<0.001
SRP	$\ln(L_d) = -1.77 + 0.89 \ln(Q_d) - 0.52\sin(2\pi T) - 0.99\cos(2\pi T)$	Low	0.42	<0.001
	$\ln(L_d) = -5.37 + 1.39 \ln(Q_d)$	High	0.73	0.004
TP	$\ln(L_d) = -0.80 + 0.79 \ln(Q_d) - 0.29\sin(2\pi T) - 0.83\cos(2\pi T)$	Low	0.60	<0.001
	$\ln(L_d) = -8.08 + 1.91 \ln(Q_d)$	High	0.84	<0.001
TN	$\ln(L_d) = -2.46 + 1.51 \ln(Q_d)$	Low	0.98	<0.001
	$\ln(L_d) = -5.37 + 1.39 \ln(Q_d)$	High	0.95	<0.001
NH_3-N	$\ln(L_d) = -4.98 + 1.34 \ln(Q_d) - 0.28\sin(2\pi T) - 0.79\cos(2\pi T)$	All	0.87	<0.001
TSS	$\ln(L_d) = 0.54 + 1.24 \ln(Q_d) - 0.32\sin(2\pi T) - 0.98\cos(2\pi T)$	Low	0.78	<0.001
	$\ln(L_d) = -6.92 + 2.49 \ln(Q_d)$	High	0.79	0.001

Table 3. Bias correction factors (BCF), annual loads (kg) and flow-weighted concentrations (FWC) for each constituent at the Kings River near Berryville, Arkansas during 2009.

Parameter	BCF			Total Load	FWC
	All Flows	Low Flow	High Flow	(kg)	(mg L^{-1})
Cl	1.01	-	-	2,516,000	3.05
SO_4	1.01	-	-	4,170,000	5.05
NH_3-N	0.87	-	-	47,000	0.06
NO_3-N	-	1.07	1.04	663,000	0.80
SRP	-	1.30	1.35	51,000	0.06
TN	-	1.02	1.02	920,000	1.11
TP	-	1.13	1.33	250,000	0.30
TSS	-	1.12	1.87	169,710,000	206

Daily loads are presented in Figure 1, and this figure shows the order of magnitude difference between daily constituent loads and flow regimes at the Kings River near Berryville, Arkansas. The daily constituent loads clearly show the influence of episodic storm events which re-suspend materials from within the fluvial channel and transport these materials from the landscape. Daily loads were summed to produce monthly loads, which were also dependent upon the frequency and intensity of storm events. Higher loads were observed during the rainy seasons of spring and fall, and the highest loads observed during May an October. Loads were least during the dry, summer months of July and August. A summary of the monthly loads from CY 2009 are presented in Table 4. Monthly loads and semi-annual loads were also summed through June 2010 and are presented in Appendix 4 and 5.

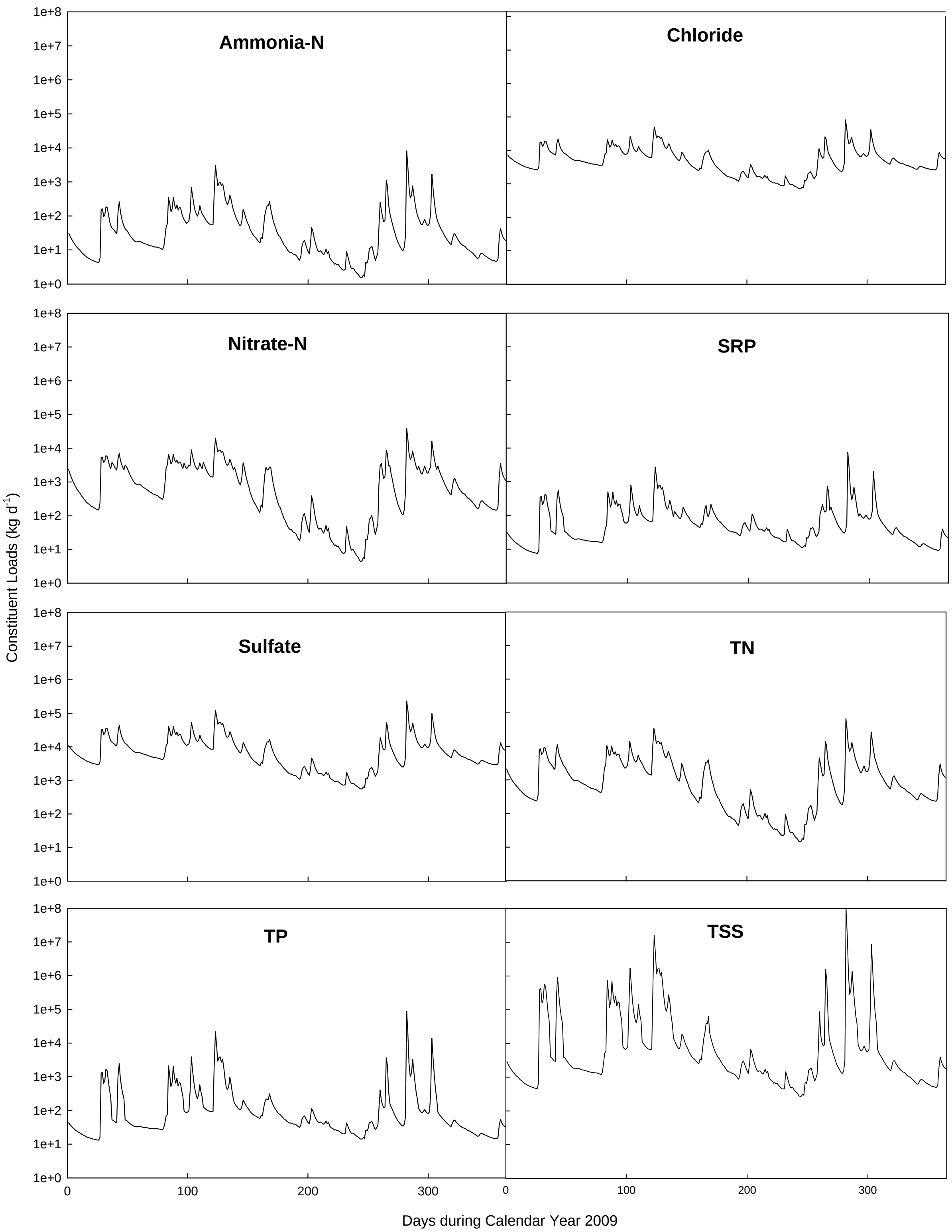
DISCUSSION

This project successfully estimated constituent loads in calendar year 2009 using water samples collected during this project. Load observed during 2009 were similar to those observed during 2008 for all parameters except SRP; the difference in SRP loads between CY 2008 and CY 2009 requires additional investigation, evaluating whether historical load estimation methods precisely characterized dissolved P loadings or whether the change in load estimation technique has introduced some bias into dissolved P loadings. It is also possible that some change within the catchment has resulted in differences that were observed. Overall, constituent loads have been variable from 1999 through 2009 following the general trend in annual discharge (Figure 2). Loads estimated during both 2008 and 2009 were typically

Table 4. Summary of estimated monthly loads (kg) for each constituent at the Kings River near Berryville, Arkansas for Calendar Year 2009.

Month	Cl	SO_4	NH_3-N	NO_3-N	SRP	TN	TP	TSS
January	169,000	248,000	800	34,000	1,500	46,400	4,700	1,310,000
February	272,000	446,000	1,800	82,000	3,300	103,400	10,900	3,370,000
March	222,000	348,000	2,000	53,000	2,700	72,900	9,000	2,810,000
April	317,000	525,000	4,200	98,000	4,500	126,000	14,000	4,280,000
May	435,000	820,000	13,500	141,000	11,500	207,000	58,000	32,400,000
June	130,000	172,000	1,900	23,000	2,600	28,000	3,400	332,600
July	58,000	59,000	390	2,000	1,400	3,900	1,600	67,100
August	35,000	31,000	140	560	730	1,300	870	25,300
September	157,000	244,000	3,200	39,600	3,300	51,400	8,500	2,820,000
October	435,000	893,000	17,300	152,700	16,900	233,500	140,000	136,000,000
November	169,000	238,000	1,100	35,000	1,600	41,800	2,900	549,000
December	116,000	146,000	330	18,000	490	19,200	720	36,100

Figure 1. Estimated daily constituent loads estimated using the regression models as a function of time at the Kings River near Berryville, Arkansas, during 2009.



greater than previous years, but annual discharge in 2008 and 2009 was greater than previous years when loads have been estimated at the Kings River. Since constituent loading is so closely tied to hydrology, loads should be evaluated over time using a statistical technique to remove the influence of discharge to accurately determine trends in water quality.

Historically, annual constituent loads have been estimated at the Kings River using an autosampler. However, 2009 annual loads were estimated using regression models that were developed from a weekly monitoring program that specifically targeted storm events. This method of load estimation was cheaper, evaluated more sites, and easily estimated loads backwards or forwards [in time] during data gaps. Using the autosampler method i.e., the historical method, required that concentrations be applied to the annual hydrograph during data gaps, i.e., the time in between sample collection. So, using the regression model method takes the bias out of applying observed concentrations to time periods when data was not available. The autosampler method did, however, provide event based information that the current monitoring program does not, because autosamplers collect flow composite samples which represent the rising and falling limb of individual storm events. Therefore, it is important to target storm events in weekly monitoring programs so that loads are accurately estimated when using regression models. While both load estimation methods have their advantages, ANRC should have confidence that switching monitoring programs provided data that is comparable to that collected with autosamplers.

When estimating constituent loads using statistical models, multiple factors including flow regimes and seasonal variations need to be considered so that the selected model best describes the relationship between load and discharge at a site. To estimate loads at the Kings River during 2009, some constituents required different models for low and high flow (i.e., NO_3, SRP, TN, TP and TSS), and some constituents required a seasonal component be included in the model (i.e., SRP low flow, TP low flow, NH_3 and TSS low flow). Most often, the model with the best statistics (e.g., lowest BCF and highest R^2 value) was chosen to predict loads; however, this model might not always be the best descriptor of the true relation between L_d and Q_d. For example, two models were developed to estimate annual TP loads at Kings River. One model considered all flow regimes (BCF: 1.28; R^2: 0.87), and the other model considered both low flow (BCF: 1.13 R^2: 0.60) and high flow (BCF: 1.33; R^2: 0.84) regimes. While the all flows model exhibited higher R^2, a pattern in the residuals was observed when comparing predicted and observed daily loads that influenced load estimations for the all flows model. Therefore, the split hydrograph model was selected to estimate loads for TP, and this example highlights the need to closely examine predicted versus observed data. In other cases, the annual loads predicted with certain regression models were not comparable to that previously measured. For example, the regression model with TSS using all data had the highest R^2 whereas the split hydrograph method predicted loads that were more comparable to that historically measured. The statistic R^2 varies in significance with the number of observations used in the regression model development. The regression model with lower BCF and or higher R^2 may or may not represent daily loads in the selected stream, and it is critical that the data be closely investigated to determine the most appropriate regression model.

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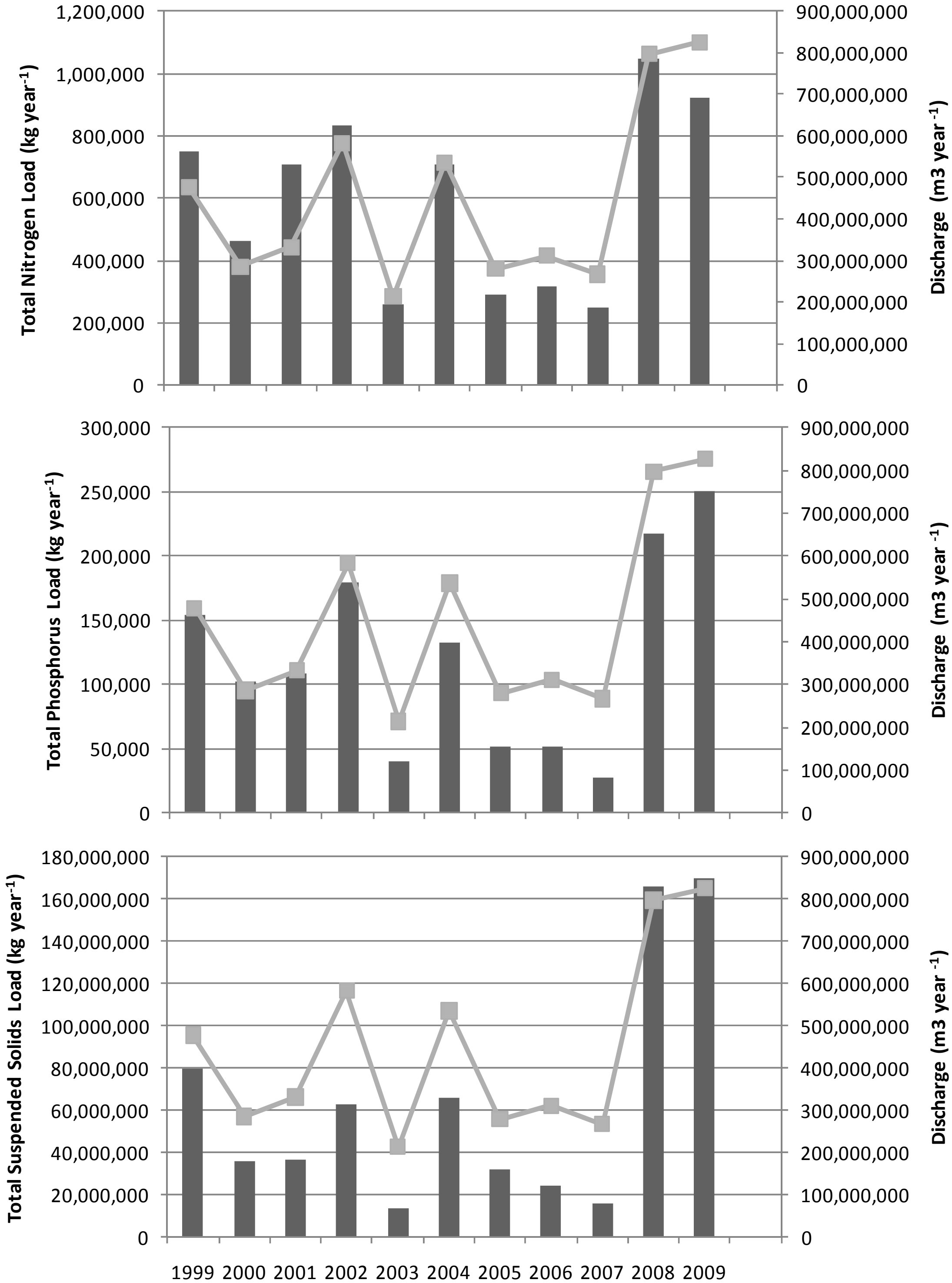

Figure 2. Total nitrogen (TN), total phosphorus (TP), total suspended solids (TSS) and discharge at the Kings River near Berryville, Arkansas, 1999-2009.

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APPENDIX 1. Location of the sampling station on the Kings River at Highway 143 Bridge near Berryville, Arkansas.

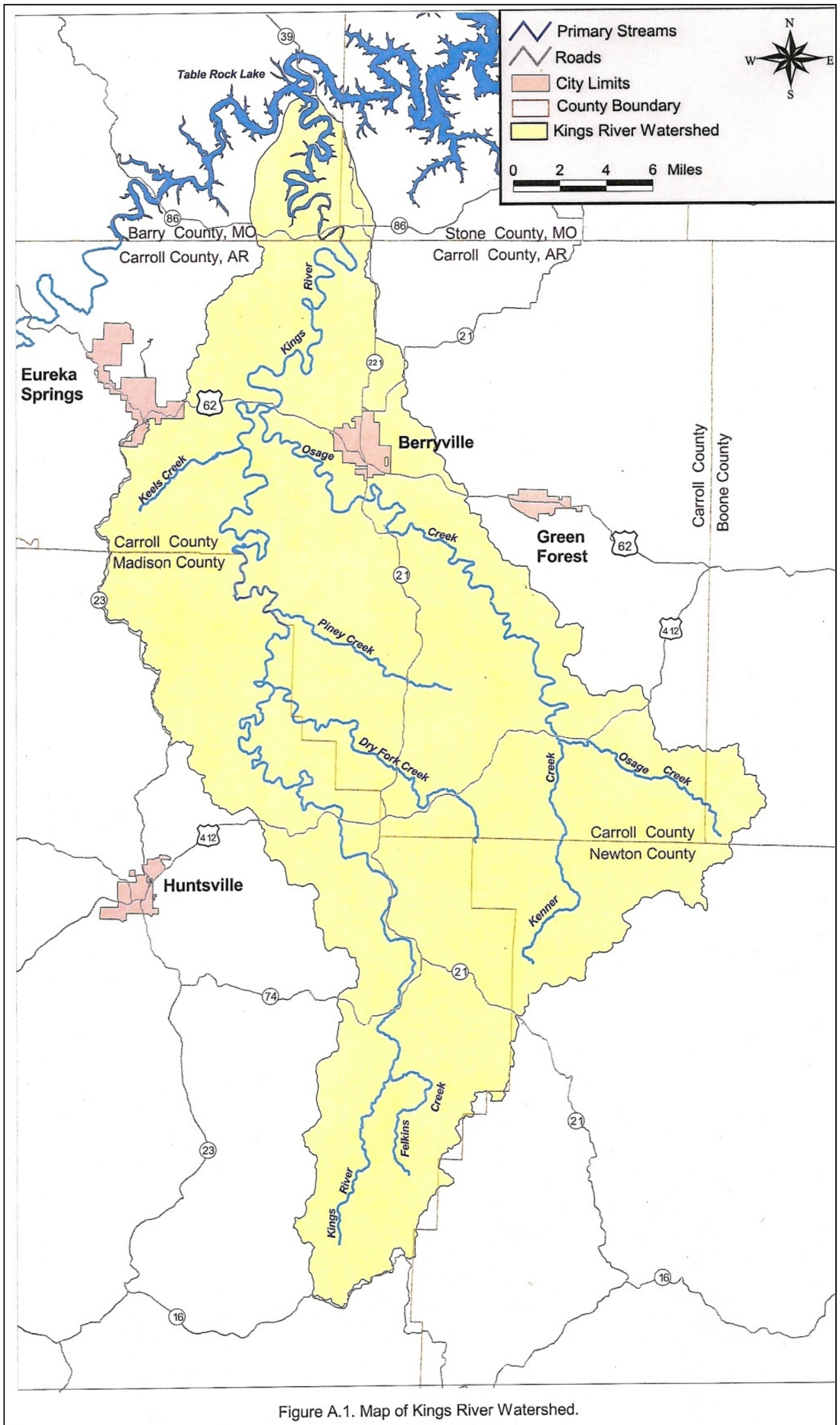
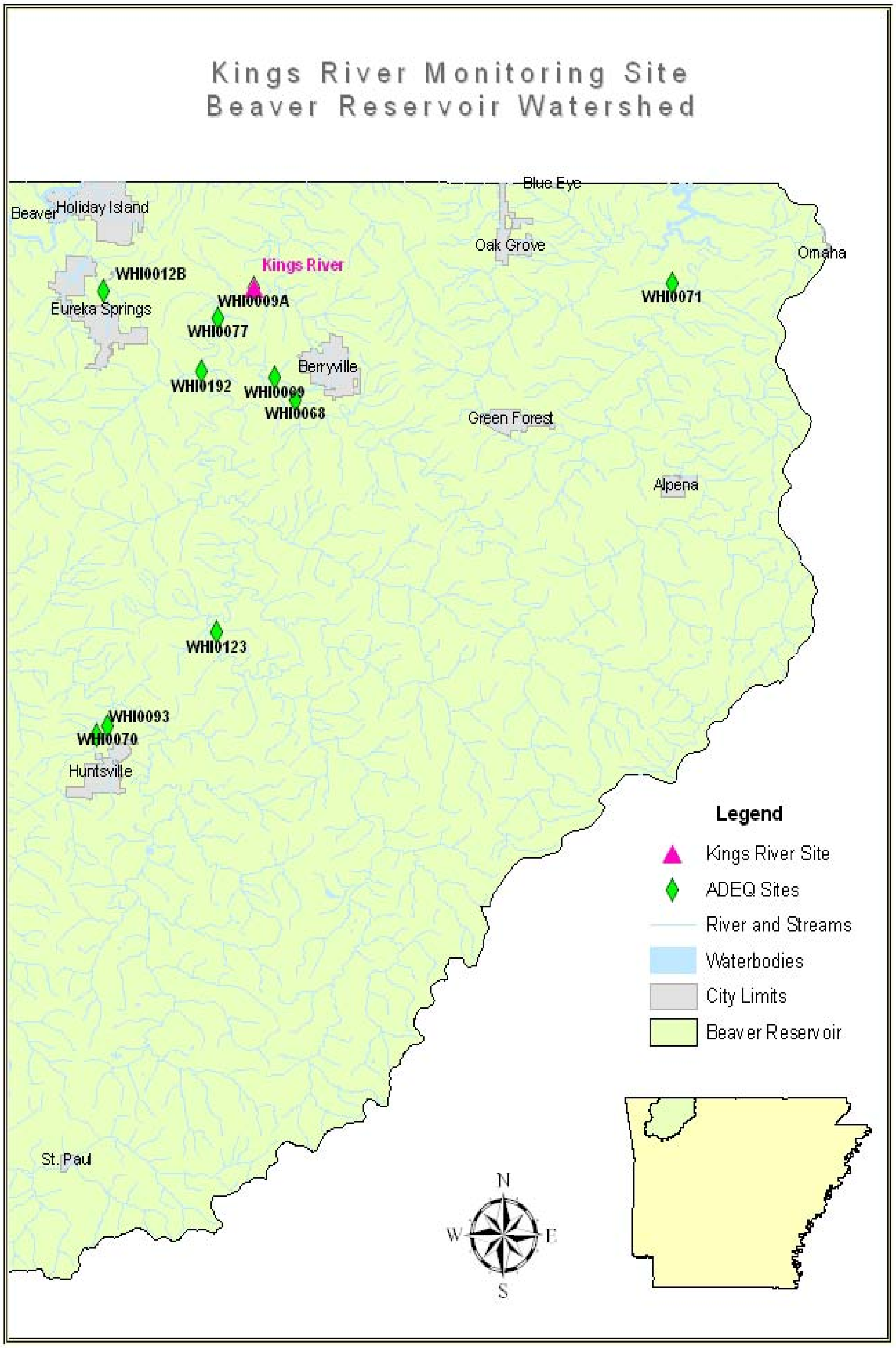


Figure A.1. Map of Kings River Watershed.

APPENDIX 2. Location of Monitored Site on the Kings River near Berryville, Arkansas and ADEQ Monitoring Sites in the Kings River Watershed.



Appendix 3. Sample collection record and constituent concentrations[A] measured at the Kings River near Berryville, Arkansas from 1 July 2009 to 30 June 2010.

Date	Time	Collector	NH_3-N (mg L^{-1})	Cl (mg L^{-1})	NO_3-N (mg L^{-1})	SRP (mg L^{-1})	SO4 (mg L^{-1})	TN (mg L^{-1})	TP (mg L^{-1})	TSS (mg L^{-1})	Turbidity (NTU)
09-Jul-09	8:00	AWRC, Wade Cash	0.03	6.935	0.197	0.068	6.216	0.38	0.092	5	5.8
15-Jul-09	6:45	AWRC, Wade Cash	0.04	10.286	0.343	0.115	8.204	0.57	0.150	8	7.8
22-Jul-09	7:15	AWRC, Wade Cash	0.01	6.206	0.347	0.116	6.043	0.53	0.144	10	5.4
29-Jul-09	7:00	AWRC, Wade Cash	0.11	5.634	0.200	0.039	5.884	0.34	0.060	5	5.3
05-Aug-09	10:00	AWRC, Wade Cash	0.02	5.890	0.132	0.093	5.540	0.21	0.120	5	4.3
12-Aug-09	10:15	AWRC, Wade Cash	0.02	9.435	0.148	0.206	5.806	0.26	0.254	8	6.0
19-Aug-09	10:45	AWRC, Wade Cash	0.03	10.700	0.065	0.166	6.380	0.24	0.316	6	6.3
26-Aug-09	7:30	AWRC, Wade Cash	0.02	9.026	0.081	0.216	6.792	0.27	0.238	5	4.8
02-Sep-09	8:15	AWRC, Wade Cash	0.08	12.740	0.025	0.283	7.784	0.19	0.310	4	4.5
02-Sep-09	8:15	AWRC, Wade Cash	0.02	13.130	0.025	0.273	7.851	0.19	0.308	5	4.6
09-Sep-09	6:45	AWRC, Wade Cash	0.03	6.271	0.156	0.098	6.258	0.33	0.112	9	8.5
16-Sep-09	6:45	AWRC, Wade Cash	0.02	5.623	0.393	0.166	6.615	0.67	0.206	17	15
17-Sep-09	9:00	AWRC, Wade Cash	0.07	2.981	0.571	0.094	6.200	1.70	0.292	131	128
23-Sep-09	9:15	AWRC, Wade Cash	0.12	2.346	0.862	0.024	4.538	1.12	0.134	43	62
30-Sep-09	8:15	AWRC, Wade Cash	0.02	4.483	0.997	0.064	6.340	1.35	0.092	2	2.4
07-Oct-09	7:15	AWRC, Wade Cash	0.01	5.568	0.659	0.060	6.898	0.81	0.072	2	2.8
09-Oct-09	12:30	AWRC, Wade Cash	0.18	1.507	0.754	0.103	2.840	1.05	1.325	783	776
14-Oct-09	7:30	AWRC, Wade Cash	0.12	2.983	1.116	0.035	4.925	1.33	0.120	52	54
21-Oct-09	7:15	AWRC, Wade Cash	0.01	4.033	1.344	0.022	6.029	1.47	0.028	5	5.2
28-Oct-09	8:00	AWRC, Wade Cash	0.01	3.866	0.886	0.039	5.887	1.00	0.038	2	2.5
30-Oct-09	9:45	AWRC, Wade Cash	0.05	2.046	0.484	0.049	3.506	1.04	0.680	462	400
04-Nov-09	8:15	AWRC, Wade Cash	0.03	3.379	1.091	0.026	5.429	1.16	0.030	3	7.2
11-Nov-09	8:15	AWRC, Wade Cash	0.01	4.134	0.910	0.036	5.795	0.96	0.048	1	2.4
18-Nov-09	8:00	AWRC, Wade Cash	0.01	3.738	0.784	0.026	5.756	0.92	0.040	2	1.9
24-Nov-09	7:45	AWRC, Wade Cash	0.01	3.759	0.551	0.029	6.131	0.67	0.042	1	1.2
02-Dec-09	7:15	AWRC, Wade Cash	0.01	3.958	0.547	0.023	6.226	0.59	0.036	1	0.7
09-Dec-09	8:00	AWRC, Wade Cash	0.01	4.936	0.561	0.023	6.598	0.66	0.024	1	1.2
16-Dec-09	6:30	AWRC, Wade Cash	0.01	5.831	0.462	0.008	7.065	0.52	0.006	1	2.7
22-Dec-09	7:15	AWRC, Wade Cash	0.01	5.836	0.428	0.001	6.947	0.48	0.012	2	1.2
31-Dec-09	7:15	AWRC, Wade Cash	0.01	3.643	0.704	0.022	6.058	0.78	0.032	1	3.1
06-Jan-10	7:15	AWRC, Wade Cash	0.01	3.912	0.674	0.019	6.401	0.73	0.020	1	4.8
13-Jan-10	8:00	AWRC, Wade Cash	0.01	4.821	0.639	0.043	6.820	0.70	0.038	1	1.2
20-Jan-10	7:30	AWRC, Wade Cash	0.01	5.153	0.495	0.001	7.543	0.60	0.016	1	1.4
27-Jan-10	7:45	AWRC, Wade Cash	0.05	3.625	1.131	0.007	6.348	1.22	0.012	4	9.1
04-Feb-10	7:30	AWRC, Wade Cash	0.01	4.418	1.000	0.013	7.047	1.11	0.034	2	5.0
11-Feb-10	7:15	AWRC, Wade Cash	0.02	4.154	1.225	0.023	6.008	1.30	0.032	3	7.2
17-Feb-10	7:15	AWRC, Wade Cash	0.01	4.128	1.122	0.028	6.371	1.11	0.034	2	5.0
25-Feb-10	7:30	AWRC, Wade Cash	0.03	3.658	0.942	0.036	5.771	1.04	0.056	2	9.7
03-Mar-10	7:30	AWRC, Wade Cash	0.01	4.204	0.897	0.019	6.477	0.97	0.016	2	3.9
10-Mar-10	7:30	AWRC, Wade Cash	0.01	4.738	0.698	0.041	6.539	0.86	0.048	2	2.0
17-Mar-10	7:45	AWRC, Wade Cash	0.02	4.773	0.689	0.060	6.762	0.83	0.080	3	4.0
23-Mar-10	10:15	AWRC, Wade Cash	0.08	3.045	0.997	0.037	5.825	1.37	0.194	125	94
31-Mar-10	7:45	AWRC, Wade Cash	0.01	3.501	1.074	0.019	5.544	1.26	0.056	6	8.7
07-Apr-10	8:00	AWRC, Wade Cash	0.02	3.398	0.803	0.022	5.482	0.90	0.044	6	8.0
14-Apr-10	7:30	AWRC, Wade Cash	0.01	4.088	0.526	0.005	5.776	0.65	0.034	3	3.0
21-Apr-10	7:30	AWRC, Wade Cash	0.01	3.905	0.469	0.031	5.582	0.59	0.044	2	2.9
28-Apr-10	7:30	AWRC, Wade Cash	0.01	3.645	0.501	0.043	5.758	0.60	0.042	2	2.7
05-May-10	7:30	AWRC, Wade Cash	0.06	3.785	0.394	0.050	5.528	0.53	0.075	3	3.1

Appendix 3 Continued. Sample collection record and constituent concentrations[A] measured at the Kings River near Berryville, Arkansas from 1 July 2009 to 30 June 2010.

Date	Time	Collector	NH_3-N (mg L^{-1})	Cl (mg L^{-1})	NO_3-N (mg L^{-1})	SRP (mg L^{-1})	SO4 (mg L^{-1})	TN (mg L^{-1})	TP (mg L^{-1})	TSS (mg L^{-1})	Turbidity (NTU)
12-May-10	7:30	AWRC, Wade Cash	0.09	2.953	0.673	0.048	4.829	0.87	0.086	9	14
14-May-10	21:15	AWRC, Wade Cash	0.09	2.582	0.609	0.125	4.156	1.09	0.428	169	154
15-May-10	14:30	AWRC, Wade Cash	0.04	2.475	0.630	0.057	4.755	1.01	0.282	165	103
17-May-10	7:30	AWRC, Wade Cash	0.01	2.309	0.625	0.018	4.306	0.85	0.086	26	23
20-May-10	16:30	AWRC, Wade Cash	0.38	1.715	0.458	0.187	3.247	1.69	0.964	745	570
26-May-10	7:15	AWRC, Wade Cash	0.07	3.211	0.972	0.044	4.930	1.13	0.066	5	6.0
02-Jun-10	7:30	AWRC, Wade Cash	0.01	3.727	0.452	0.019	5.088	0.57	0.040	3	1.9
09-Jun-10	7:30	AWRC, Wade Cash	0.04	4.833	0.518	0.082	5.454	0.66	0.102	4	2.7
16-Jun-10	7:30	AWRC, Wade Cash	0.04	5.327	0.427	0.092	5.730	0.53	0.110	5	3.9
24-Jun-10	9:30	AWRC, Wade Cash	0.07	5.717	0.393	0.103	5.495	0.52	0.152	2	2.9

[A]All concentrations are reported to three decimal places to provide raw data, except for TSS which is reported as a whole number; the PQLs of thes constituents are 0.90 mg L^{-1} NH_3-N, 0.16 mg L^{-1} Cl, 0.003 mg L^{-1} NO_3-N, 0.01 mg L^{-1} SRP, 0.02 mg L^{-1} SO_4, 0.05 mg L^{-1} TN, 0.02 mg L^{-1} TP, and 7 mg L^{-1} TSS.

Appendix 4. Summary of estimated semi-annual loads and flow-weighted concentrations for each constituent at the Kings River near Berryville, Arkansas from 1 January through 30 June 2010; the data are provisional as the US Geological Survey has not finalized its discharge record for this period.

4A. Summary of calculated total loads (kg) for each parameter at the sampled sites in the Kings River near Berryville, Arkansas for the period, 1 January through 30 June 2010.

Site	Cl^-	SO_4	NH_3-N	NO_3-N	SRP	TN	TP	TSS
Kings River near Berryville, AR	1,319,000	2,083,000	17,000	332,000	19,000	435,000	64,000	22,611,000

4B. Summary of calculated flow weighted concentrations (FWC, mg L^{-1}) for each parameter at the sampled sites in the Kings River near Berryville, Arkansas for the period, 1 January through 30 June 2010.

Site	Cl^-	SO_4	NH_3-N	NO_3-N	SRP	TN	TP	TSS
Kings River near Berryville, AR	3.32	5.24	0.04	0.84	0.05	1.09	0.16	57

Appendix 5. Summary of estimated monthly loads (kg) for each constituent at the Kings River near Berryville, Arkansas from 1 January 2010 to 30 June 2010s; the data are provisional as the US Geological Survey has not finalized its discharge record for this period.

Month	Cl	SO_4	NH_3-N	NO_3-N	SRP	TN	TP	TSS
January	680	176,000	38,200	1,050	248,000	44,400	91,100	2,480
February	1,370	242,000	70,900	2,240	379,000	83,800	171,000	6,330
March	3,350	292,000	79,500	4,660	493,000	112,000	339,000	18,900
April	1,600	194,000	47,400	1,920	281,000	53,800	134,000	3,900
May	9,600	324,000	96,000	7,400	574,000	137,000	727,000	31,200
June	800	91,600	7,900	1,850	107,000	10,800	48,700	2,300