UNIVERSITY OF ARKANSAS
DIVISION OF AGRICULTURE

July 2009

AWRC

Water Quality Sampling, Analysis and Annual Load Determinations for the Illinois River at Arkansas Highway 59 Bridge, 2008

Funded by Arkansas Natural Resources Commission
MSC Publication 352 | Arkansas Water Resources Center

Water Quality Sampling, Analysis and Annual Load Determinations for the Illinois River at Arkansas Highway 59 Bridge, 2008

L.B. Massey[1], L.W. Cash[2], and B.E. Haggard[3]

[1]Project Manager, Arkansas Water Resources Center, UA Division of Agriculture
[2]Field Services Technician, Arkansas Water Resources Center, UA Division of Agriculture
[3]Director and Associate Professor, Arkansas Water Resources Center, UA Division of Agriculture, 203 Engineering Hall, Fayetteville, AR 72701. Corresponding author: haggard@uark.edu

The Arkansas Water Resources Center monitored water quality at the Illinois River at the Arkansas Highway 59 Bridge, just upstream from the Arkansas-Oklahoma state border during base flow and storm events from July 1, 2008 through June 30, 2009. Water samples were collected manually or with an auto-sampler and analyzed for nitrate-nitrogen, ammonia-nitrogen, total nitrogen, total phosphorus, soluble reactive phosphorus, sulfate, chloride and total suspended solids. The U.S. Geological Survey recorded instantaneous stage and discharge at the site, total annual discharge was 1,010,000,000 m^3, with 37% attributed to base flow and 63% attributed to storm flow. Loads were estimated using the mid-interval integration approach using continuous discharge (i.e., 30 min intervals) and measured concentration as applied to sampling intervals; the incremental loads were then summed to get annual loads for the 2008 calendar year. The constituent loads and annual flow-weighted concentrations for the 2008 calendar year are summarized in the table below, using data collected through this study (July through December 2008) plus data from the prior study year (January through June 2008).

Summary of calculated loads (kg) for each parameter at the Illinois River at Highway 59 Bridge separated into base flow and storm events for the period, January through December 2008.

Parameter	Base Load (kg)	Storm Load (kg)	Total Load (kg)
Chloride (Cl)	5,100,000	3,610,000	8,710,000
Sulfate (SO_4)	5,210,000	5,570,000	10,800,000
Ammonia (NH_3-N)	4,770	106,000	111,000
Nitrate (NO_3-N)	1,150,000	1,360,000	2,510,000
Soluble Reactive Phosphorus (SRP; PO_4-P)	25,800	108,000	134,000
Total Nitrogen (TN)	1,180,000	1,740,000	2,920,000
Total Phosphorus (TP)	34,700	391,000	426,000
Total Suspended Solids (TSS)	2,410,000	165,000,0000	167,000,000

Summary of average flow weighted concentration (FWC, mg L^{-1}) for each parameter at the Illinois River at Highway 59 Bridge separated into flow regimes representing January through December 2008.

Parameter	Base FWC (mg L^{-1})	Storm FWC (mg L^{-1})	Overall FWC (mg L^{-1})
Chloride (Cl)	13.71	5.65	8.61
Sulfate (SO_4)	14.02	8.71	10.66
Ammonia (NH_3-N)	0.01	0.17	0.11
Nitrate (NO_3-N)	3.09	2.12	2.48
Soluble Reactive Phosphorus (SRP; PO_4-P)	0.01	0.17	0.13
Total Nitrogen (TN)	3.18	2.71	2.89
Total Phosphorus (TP)	0.09	0.61	0.42
Total Suspended Solids (TSS)	6.5	257	165

INTRODUCTION

The headwaters of the Illinois River originate near Hogeye in northwest Arkansas, and the river flows northwesterly through the Ozarks, into Oklahoma and eventually into Lake Tenkiller Ferry. The main tributaries to the Illinois River in northwest Arkansas include Osage Creek, Clear Creek, and Muddy Fork. The Illinois River and its tributaries drain 757 mi2 that are primarily forest (41%) and agricultural lands (i.e., pasture and forages; 46%); however, over the past decade increases in residential, commercial and industrial development have been observed (i.e., urban landuse has increased to 13%). The Illinois River is used for recreation, aquatic life and refuge, and agricultural, industrial and residential water supply by some communities in northwest Arkansas and northeast Oklahoma. The Illinois River and its tributaries also provide the ecological service of wastewater treatments as several tributaries receive treated effluent from wastewater treatment plants.

Because of the Illinois River's varying designated uses in Arkansas and Oklahoma, the river is center to many political, scientific and legal debates. Several stream reaches within the Illinois River and its tributaries (including Muddy Fork, Clear Creek, Osage Creek, Spring Creek and Little Osage Creek) were either included on Arkansas Department of Environmental Quality's (ADEQ) 303d list or added to the list by the U.S. Environmental Protection Agency (USEPA); the Arkansas Natural Resources Commission (ANRC) has also listed the Illinois River drainage area as a priority 319 watershed. Therefore, monitoring water quality of the Illinois River at the Arkansas Highway 59 Bridge just upstream of the Oklahoma border is important, and this site has been historically monitored by multiple agencies including the U.S. Geological Survey (USGS), ADEQ and Arkansas Water Resources Center (AWRC). An automatic water sampler was established at the Illinois River on the Arkansas Highway 59 Bridge in 1995 by the AWRC. Since that time, water quality samples from the AWRC and continuous stage and discharge measurements by the USGS have been used to determine constituent loads and flow-weighted concentrations in the Arkansas portion of the Illinois River. This report presents the annual loads and mean flow-weighted concentrations of select constituents at this site for the 2008 calendar year.

METHODS

Sample Collection

Storm and base flow events in the Illinois River were sampled from July 1, 2008 through June 30, 2009 at the water sampling station at the Arkansas Highway 59 Bridge (Appendix 1) just upstream of the Arkansas-Oklahoma border; data from the previous monitoring was available from January 1, 2008 through June 30, 2008 to estimate constituent loads for calendar year 2008. Storm flow was defined as any event where stage remained above the defined trigger level of 5 feet, and stage below the trigger level of 5 feet was considered base flow for the purpose of this study. The definitions of base flow and storm conditions defined here were based on previous studies (e.g., Nelson et al. 2007) to be consistent with historical data and reporting. Stage and discharge were measured at this site in thirty-minute intervals by the USGS (USGS Station Number 07195430), and these data were provided by the USGS Fayetteville Field Office when requested or these data are available on-line at http://ar.water.usgs.gov/.

Storm events were sampled using an ISCO or Sigma type auto-sampler configured to take samples based on the amount of flow passing the sampling site. The sampler began sampling when the trigger level of 5 feet had been exceeded and a discrete sample was collected after every 8 million cubic feet had passed the sampling station. The discrete samples were composited by combining equal volumes of each sample into a single composite sample for analysis. The discrete samples were composited when all 24 sample bottles in the auto-sampler were filled or within 48 hours after the collection of the first sample. Storm events were sampled in this manner as long as the stage remained above the trigger level (i.e., 5 feet).

Manual grab samples were collected by AWRC field personnel every two weeks (on approximately the first and fifteenth of every month) during base flow conditions using a Kemmerer type vertical sampler. All grab and composite samples were analyzed for nitrate-nitrogen (NO_3-N), ammonia-nitrogen (NH_3-N), total nitrogen (TN), total phosphorus (TP), soluble reactive phosphorus (SRP), total suspended solids (TSS), sulfate (SO_4) and chloride (Cl) by the Arkansas Water Resources Center Water Quality Laboratory. Once per quarter, field blanks, sampler duplicate and bridge replicate samples were collected for quality assurance/ quality control (QA/QC) purposes. During the 2008 calendar year, 26 base flow grab samples, 26 composite storm samples, four field blanks, four duplicates, and four replicates were collected and analyzed. From January through June 2009, 13 base flow grab samples, 22 composite storm samples, two field blanks, two duplicates and two replicates were collected and analyzed. All water samples were analyzed following standard analytical procedures as approved by the USEPA.

Load Determination and Mean Concentrations

Annual constituent loads were calculated using the data from the collected samples and USGS stage and discharge data in thirty minute intervals for base and storm flow conditions. Loads were calculated by multiplying the thirty-minute volume by a corresponding constituent concentration using the mid-interval approach. Corresponding constituent concentrations were determined from grab samples collected between storm events and samples collected by the auto-sampler during storm events, and these concentrations were applied to the mid-point between measured concentrations. However, constituent concentrations from grab samples were applied forward or backward to where the stage remained even in storm conditions (i.e., approximately 5 ft). Loads (kg) were calculated by summing the thirty-minute loads into monthly loads and then 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 AND DISCUSSION

Discharge and constituent concentrations were variable throughout the year (Figure 1) showing the effects of episodic rainfall events on stage and the chemograph of the various constituents. The increased discharge following rainfall-runoff events increased the concentrations of many constituents including SO_4, NH_3-N, NO_3-N, SRP, TP, and TSS. Total discharge during the sampling period was approximately 1,010,000,000 m^3 with 37% attributed to base flow and 63% attributed to storm events.

Constituent loading and average flow-weighted concentrations varied between base flow and storm flow conditions reflecting the influence of discharge on constituent concentrations, as well as the increased water volume transported during storms. The total calculated loads and flow-weighted concentrations for each parameter and the loads and concentrations attributed to base and storm flows are provided in Tables 1 and 2. Overall, the greatest percentage of the constituent load was transported

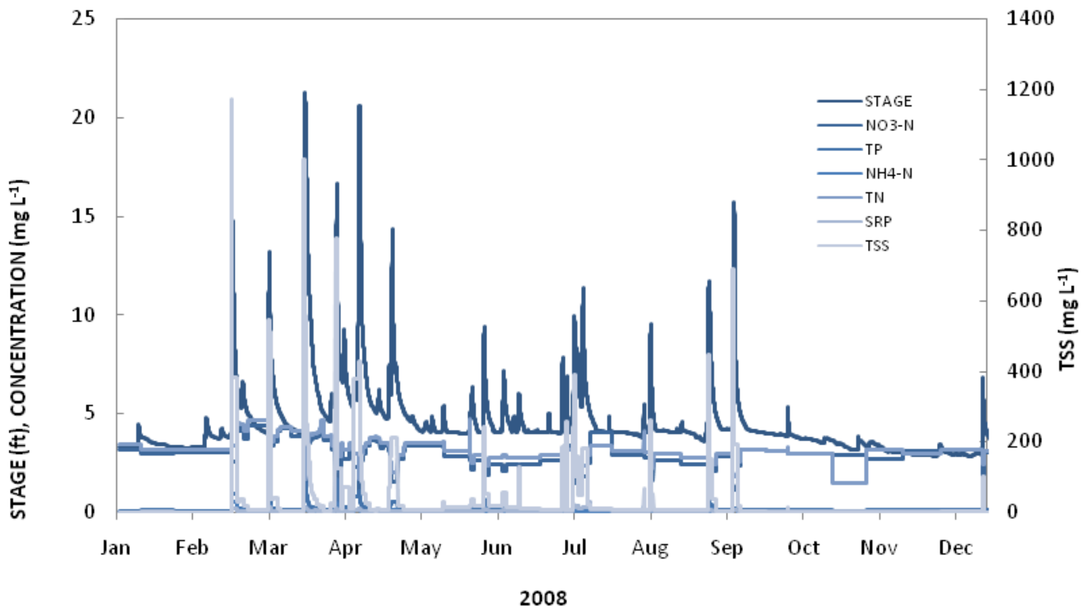

Figure 1. Continuous discharge with constituent concentrations extended to midpoint to determine annual loads for 2008 at the Illinois River at AR Highway 59 Bridge, northwest Arkansas.

Table 1. Calculated annual loads (kg) for each constituent at the Illinois River at Highway 59 Bridge during base, storm and combined flows during 2008.

Parameter	Base Load (kg)	Storm Load (kg)	Total Load (kg)
Chloride (Cl)	5,100,000	3,610,000	8,710,000
Sulfate (SO_4)	5,210,000	5,570,000	10,800,000
Ammonia (NH_3-N)	4,770	106,000	111,000
Nitrate (NO_3-N)	1,150,000	1,360,000	2,510,000
Soluble Reactive Phosphorus (SRP; PO_4-P)	25,750	108,000	134,000
Total Nitrogen (TN)	1,180,000	1,740,000	2,920,000
Total Phosphorus (TP)	34,700	391,000	426,000
Total Suspended Solids (TSS)	2,410,000	165,000,0000	167,000,000

Table 2. Average Flow Weighted Concentration (FWC, mg L^{-1}) for each constituent at the Illinois River at Highway 59 Bridge during base, storm and combined flows during 2008.

Parameter	Base FWC (mg L^{-1})	Storm FWC (mg L^{-1})	Total FWC (mg L^{-1})
Chloride (Cl)	13.71	5.65	8.61
Sulfate (SO_4)	14.02	8.71	10.66
Ammonia (NH_3-N)	0.01	0.17	0.11
Nitrate (NO_3-N)	3.09	2.12	2.48
Soluble Reactive Phosphorus (SRP; PO_4-P)	0.07	0.17	0.13
Total Nitrogen (TN)	3.18	2.71	2.89
Total Phosphorus (TP)	0.09	0.61	0.42
Total Suspended Solids (TSS)	6.5	257	165

during storm events at the Illinois River, except for Cl. Approximately 41% of the annual Cl load was transported during storms at the Illinois River. The other constituents were mainly transported during storms, showing the importance of collecting water samples during high flow events regardless of what type of monitoring program is used to estimate annual loads. It is extremely critical to sample storm events when estimating loads of NH_3-N, SRP, TP and TSS as 95%, 81%, 92% and 99%, respectively of these constituents is transported during this flow regime.

The constituent loads calculated at the Illinois River Highway 59 Bridge also varied between months. A summary of the monthly loads during base flow, storm flow and combined (total) flow is provided in Table 3. Monthly base flow loads were variable dependent upon the frequency and intensity of storm events during the month, and this is also an artifact of the method that was used to determine storm flows (i.e., stage greater than 5 feet). Storm events were variable following typical precipitation patterns, where loads were generally greater during the spring season (especially March and April). The lowest storm loads occurred during fall through winter, where January and November did not have stage exceeding 5 feet in 2008. Thus, no storm event loads are reported for the Illinois River during those two months. During 2008, the total loads were least during late fall and the winter months, January, November and December.

Overall, constituent loads have been variable from 1997 through 2008 following the general trend in annual discharge (Figure 2, Table 4). Constituent loads estimated in 2008 were greater than the previous year (i.e., 2007) because annual discharge was 2.6 times greater in 2008 than that observed in 2007; the increase in annual discharge was reflective of the change in precipitation between years. In 2008, the nitrogen, phosphorus and sediment loads were the greatest observed since monitoring started in 1997 at the Illinois River on Arkansas Highway 59.

Related to phosphorus loads, there are three major permitted wastewater treatment plants (WWTPs) that discharge treated effluent into tributaries of the Illinois River upstream from this monitoring station (i.e, Fayetteville, Springdale and Rogers). These major facilities discharge into Goose Creek, Osage Creek, and Spring Creek, and after 2003 the Springdale facility has substantially reduced its effluent concentrations. The average phosphorus loads from the major WWTPs was an average of 91,000 kg $year^{-1}$ from 1997 to 2000, 73,000 kg $year^{-1}$ from 2001 to 2003, and 22,000 kg $year^{-1}$ from 2004 to 2006 (data from municipalities), reflecting the decrease in effluent P concentrations at Springdale's facility. The P load transported during base flow conditions reflects variations in the amount of time that stage is greater than 5 feet (i.e., storm flows), as well as seasonal and annual variations in the discharge when stage is below 5 feet. The decreases in base flow loads over time at the Illinois River also reflect the reductions in effluent P concentrations at the Springdale facility.

The reductions in P load from the WWTPs have also likely resulted in some reductions in the total P loads over the last decade at the Illinois River. However, the total P loads are more dependent upon the annual discharge volume that is directly related to the amount of storm

Table 3. Calculated monthly loads (kg) for each constituent at the Illinois River at Highway 59 Bridge during base, storm and combined flows for calendar year 2008.

Month	Chloride (Cl, kg)	Sulfate (SO_4, kg)	Ammonia (NH_3-N, kg)	Nitrate (NO_3-N, kg)	Soluble Reactive Phosphorus (SRP, kg)	Total Nitrogen (TN, kg)	Total Phosphorus (TP, kg)	Total Suspended Solids (TSS, kg)
Base Flow Load								
January	389,000	401,000	335	58,500	778	62,400	1,030	21,000
February	511,000	530,000	127	96,700	1,240	102,000	1,770	138,000
March	323,000	399,000	162	108,000	1,580	113,000	2,330	143,000
April	79,500	104,000	57	30,000	523	31,400	746	60,700
May	460,000	555,000	443	148,000	3,230	159,000	5,400	528,000
June	394,000	450,000	1,820	100,000	3,460	115,000	5,023	569,000
July	545,900	406,000	1,020	119,000	3,500	111,000	3,240	346,000
August	452,000	445,000	605	95,356	2,880	107,000	3,740	318,000
September	465,000	507,000	71	119,000	2,870	123,000	3,480	175,000
October	703,000	676,000	0	135,000	2,970	126,000	4,390	50,900
November	410,000	393,000	137	70,900	1,580	65,700	2,000	20,500
December	368,000	350,000	0	67,800	1,130	67,800	1,590	42,400
Storm Event Load								
Month	Chloride (Cl, kg)	Sulfate (SO_4, kg)	Ammonia (NH_3-N, kg)	Nitrate (NO_3-N, kg)	Soluble Reactive Phosphorus (SRP, kg)	Total Nitrogen (TN, kg)	Total Phosphorus (TP, kg)	Total Suspended Solids (TSS, kg)
January	0	0	0	0	0	0	0	0
February	398,000	570,000	19,000	150,000	7,860	182,000	35,600	14,500,000
March	1,100,000	1,740,000	35,200	464,000	41,600	586,000	176,000	66,800,000
April	1,440,000	29,800	33,100	480,000	29,800	609,000	135,700	54,700,000
May	48,000	62,200	407	12,600	488	15,300	997	190,000
June	160,000	211,000	2,470	42,400	3,150	56,500	8,720	2,550,000
July	368,000	437,000	5,040	95,500	14,500	128,000	11,000	8,120,000
August	75,300	92,000	962	16,300	1,290	22,800	4,800	1,990,000
September	282,000	538,000	9,630	88,100	8,990	127,000	16,600	15,500,000
October	8,870	8,900	43	2,150	40	2,410	84	12,000
November	0	0	0	0	0	0	0	0
December	29,500	37,700	316	5,470	642	7,750	1,580	323,000
Total Load								
Month	Chloride (Cl, kg)	Sulfate (SO_4, kg)	Ammonia (NH_3-N, kg)	Nitrate (NO_3-N, kg)	Soluble Reactive Phosphorus (SRP, kg)	Total Nitrogen (TN, kg)	Total Phosphorus (TP, kg)	Total Suspended Solids (TSS, kg)
January	389,000	401,000	335	58,500	778	62,400	1,030	21,000
February	909,000	1,010,000	19,300	246,000	9,100	284,000	37,400	14,700,000
March	1,420,000	2,140,000	35,400	572,000	43,200	699,000	179,000	67,000,000
April	1,220,000	1,980,000	33,200	510,000	30,400	640,000	136,000	54,700,000
May	508,000	618,000	851	161,000	3,730	174,000	6,390	717,000
June	554,000	660,000	4,290	143,000	6,620	171,000	13,700	3,120,000
July	914,000	843,000	6,060	215,000	18,000	239,000	14,320	8,460,000
August	528,000	537,000	1,570	112,000	4,160	129,000	8,540	2,310,000
September	747,000	1,050,000	9,700	207,000	11,900	250,000	20,100	15,600,000
October	712,000	685,000	43	137,000	3,000	129,000	4,470	62,800
November	410,000	393,000	134	70,900	1,580	65,700	2,000	20,500
December	397,000	387,000	316	73,300	1,770	75,500	3,160	366,000

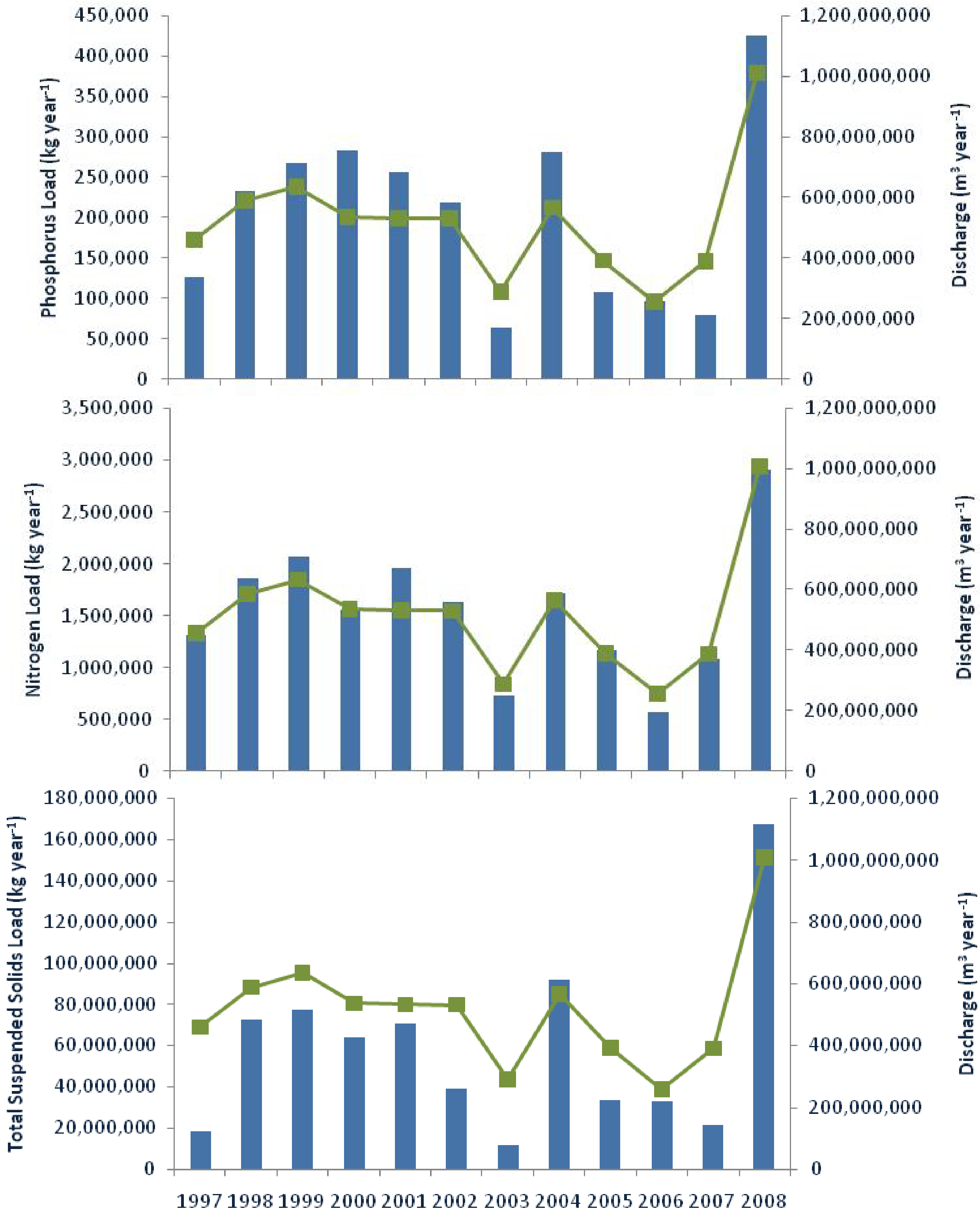

Figure 2. Total P (TP), Total N (TN) and Total Suspended Solids (TSS) loads (bars) and discharges (symbols) at the Illinois River at Arkansas Highway 59 Bridge, northwest Arkansas, from 1997-2008; the bars represent the total load during these calendar years (data from Nelson et al., 2007).

Table 4. Calculated total annual loads (10^3 kg) for each constituent at the Illinois River at Highway 59 Bridge during base flow from 1997-2008.

Total (Base and Storm Flow) Load (10^3 kg)						
Parameter	1997	1998	1999	2000	2001	2002
NO_3-N	1,020	1,390	1,560	1,100	1,520	1,340
TN	1,320	1,870	2,070	1,560	1,970	1,630
SRP	--	--	--	--	--	--
TP	127	232	267	283	256	218
TSS	18,400	72,600	77,100	63,600	70,800	39,000
SO_4	--	--	--	--	--	--
Cl	--	--	--	--	--	--
Parameter	2003	2004	2005	2006	2007	2008
NO_3-N	591	1,200	1,020	514	962	2,510
TN	735	1,720	1,170	575	1,080	2,920
SRP	--	--	44	34	35	134
TP	64	281	107	97	79	194
TSS	11,845	92,080	33,560	33,054	21,600	167,000
SO_4	--	--	--	--	5,940	10,800
Cl	--	--	--	--	5,480	8,710

flow (Figure 2). Storm events transport P form the landscape (e.g., pasture and urban nonpoint sources), and the increased discharge can resuspend P that was stored within the fluvial channel and transport it downstream. So, the P load transported during storm events represents contribution from nonpoint and point sources in the Illinois River drainage area. Overall, total P loads at the Illinois River have closely followed the annual discharge volume over the past decade or more.

The monitoring continued from January 1, 2009-June 30, 2009. During that time, total discharge (six months) was 469,000,000 m^3, with 40% attributed to base flow and 60% attributed to storm flow. Constituent loads and average flow weighted concentrations over the six month period are provided in Tables 5 and 6, and these will be combined with future monitoring to estimate loads in calendar year 2009; this will be detailed in future reports.

Table 5. Summary of calculated annual loads (kg) for each constituent at the Illinois River at Highway 59 Bridge during base, storm and combined flows from January 1, 2009 to June 30, 2009.

Parameter	Base Load (kg)	Storm Load (kg)	Total Load (kg)
Chloride (Cl)	2,280,000	1,900,000	4,180,000
Sulfate (SO_4)	2,530,000	2,850,000	5,380,000
Ammonia (NH_3-N)	3,260	22,300	25,600
Nitrate (NO_3-N)	548,000	570,000	1,120,000
Soluble Reactive Phosphorus (SRP; PO_4-P)	8,550	36,000	44,500
Total Nitrogen (TN)	570,00	669,000	1,239,000
Total Phosphorus (TP)	13,600	80,800	94,300
Total Suspended Solids (TSS)	1,250,00	19,700,000	20,990,000

Table 6. Summary of average Flow Weighted Concentration (mg L^{-1}) for each constituent at the Illinois River at Highway 59 Bridge during base, storm and combined flows.

Parameter	Base FWC (mg L^{-1})	Storm FWC (mg L^{-1})	Overall FWC (mg L^{-1})
Chloride (Cl)	12.12	6.78	8.92
Sulfate (SO_4)	13.45	10.15	11.48
Ammonia (NH_3-N)	0.02	0.08	0.05
Nitrate (NO_3-N)	2.91	2.03	2.38
Soluble Reactive Phosphorus (SRP; PO_4-P)	0.05	0.13	0.09
Total Nitrogen (TN)	3.03	2.38	2.64
Total Phosphorus (TP)	0.07	0.29	0.20
Total Suspended Solids (TSS)	6.65	70.24	44.73

CONCLUSIONS

This project successfully estimated constituent loads in calendar year 2008 using water samples collected in this project, as well as those collected in a previous study. Historical constituent loads at the Illinois River generally follow the same pattern as annual discharge, and loads in 2008 were greater than the previous year because annual discharge was more than double that observed in 2007. In 2008, nitrogen, phosphorus and sediment loads were the greatest observed throughout the period of record.

REFERENCES

Nelson, M.A., W. Cash, K. Trost, and J. Purtle. 2007. Illinois River 2006 Water Quality Assessment at the Arkansas Highway 59 Bridge. Arkansas Water Resources Center, Fayetteville, AR, publication number MSC-341.

APPENDIX 1. Location of the sampling station on the Illinois River at Arkansas Highway 59, south of Siloam Springs, northwest Arkansas.