



WATER QUALITY SAMPLING, ANALYSIS AND ANNUAL LOAD
DETERMINATIONS FOR NUTRIENTS AND SOLIDS ON THE
BALLARD CREEK, 2008

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Water Quality Sampling, Analysis and Annual Load Determinations for Nutrients and Solids at the Washington County Road 76 Bridge on Ballard Creek, 2008

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The Arkansas Water Resources Center monitored water quality at Ballard Creek at the Washington County Road 76 Bridge in northwest Arkansas 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. Instantaneous stage and discharge were recorded at the site; total annual discharge was 55,800,000 m³, with 27% attributed to base flow and 73% attributed to storm flow. Loads were estimated using the mid-interval integration approach using continuous discharge (i.e., 30 min intervals) and measured concentrations 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 are summarized in the table below, using data collected through this study (July through December 2008) plus data from the prior study (January through June 2008).

Summary of calculated loads (kg) for each parameter at the Illinois River at Washington County Road 76 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)	191,000	324,000	515,000
Sulfate (SO ₄)	238,000	455,000	693,000
Ammonia (NH ₃ -N)	288	5,700	5,990
Nitrate (NO ₃ -N)	63,000	88,600	151,000
Soluble Reactive Phosphorus (SRP; PO ₄ -P)	1170	13,200	14,400
Total Nitrogen (TN)	66,200	118,000	184,000
Total Phosphorus (TP)	1,410	25,600	27,000
Total Suspended Solids (TSS)	50,600	5,180,000	5,230,000

Summary of average flow weighted concentration (FWC, mg L⁻¹) for each parameter at the Washington County Road 76 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)	12.83	7.93	11.49
Sulfate (SO ₄)	15.96	11.14	12.42
Ammonia (NH ₃ -N)	0.02	0.14	0.11
Nitrate (NO ₃ -N)	4.22	2.17	2.70
Soluble Reactive Phosphorus (SRP; PO ₄ -P)	0.08	0.32	0.26
Total Nitrogen (TN)	4.43	2.88	3.30
Total Phosphorus (TP)	0.09	0.63	0.48
Total Suspended Solids (TSS)	3.4	127	94

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INTRODUCTION

The Upper Illinois River Watershed (UIRW) drains 757 mi² in northwest Arkansas; the watershed has expanding urban areas (urban land use has increased to 13%) but is characterized primarily by forest (41%) and agricultural lands (46%). The Illinois River is used for recreation, aquatic life and refuge, and agricultural, industrial and residential water supply to some communities in northwest Arkansas and northeast Oklahoma. The dominant agriculture in the watershed is integrated poultry broiler and beef grazing production, and water quality concerns associated with agricultural land in pasture and forage production include loss of nitrogen, phosphorus and sediment in surface runoff and nitrate in groundwater. Several stream reaches within the Illinois River and its tributaries were either listed as impaired due to nutrients, sediment and or pathogens on ADEQ's 303d list or added to the list by the USEPA; the ANRC has also listed the Illinois River drainage areas as a priority 319 watershed.

In 1996, the University of Arkansas (see Parker et al., 1996) completed a project to prioritize subwatersheds within the Illinois River drainage area. The Upper Ballard Creek Watershed met all the criteria for a high priority within the Illinois River, and Ballard Creek drains a subwatershed with an area of 23 mi² that is predominately pasture (i.e., 60%) without any wastewater treatment plant discharges. Thus, this subwatershed became the focus of the implementation of voluntary best management practices. A water quality sampling station was installed in 2001 at the Washington County Road 76 Bridge over Ballard Creek (see Figure 1) to monitor water quality. Since July 2002, continuous stage and discharge measurements and water quality samples have been used to determine flow-weighted constituent concentrations and loads from Ballard Creek. This report details 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 were sampled in Ballard Creek from July 1, 2008 through June 30, 2009 at the water quality sampling station at Washington County Road 76 Bridge in northwest Arkansas (Appendix 1); 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 discharge remained above the defined trigger level of 20 cfs, and discharge below the trigger level of 20 cfs 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 Arkansas Water Resources Center.

Storm events were sampled using an ISCO or Sigma type auto-sampler configured to take flow-weighted composite samples. The sampler began sampling when the trigger level of 20 cfs had been exceeded and a discrete sample was collected after every 10 thousand 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 discharge remained above the trigger level (i.e., 20 cfs). 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 ($\text{NO}_3\text{-N}$), ammonia-nitrogen ($\text{NH}_3\text{-N}$), 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, 19 composite storm samples, 2 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 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 discharge remained in storm even conditions (i.e., approximately 20 cfs or greater). Loads (kg) were calculated by summing the thirty-minute loads into monthly loads and then into annual loads during the

2008 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 all the measured constituents (i.e., Cl, SO_4 , NH_3 , $\text{NO}_3\text{-N}$, SRP, TN, TP and TSS). Total discharge during the sampling period was approximately 58,800,000 m^3 with 27% attributed to base flow and 73% 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. The greatest percentage of the constituent load was transported during storm events for all measured parameters. Thus, it is important to collect water samples across the discharge regime in smaller basins like the Upper Ballard Creek Watershed because more than 59% of the load for all parameters was transported during high flow events. It is extremely critical to sample storm events when estimating loads of $\text{NH}_3\text{-N}$, SRP, TP and TSS as 95%, 92%, 95%, and 99%, respectively of these constituents is transported during storm flow regime at Ballard Creek.

The constituent loads calculated at Ballard Creek also varied by orders of magnitude between months, and a summary of the

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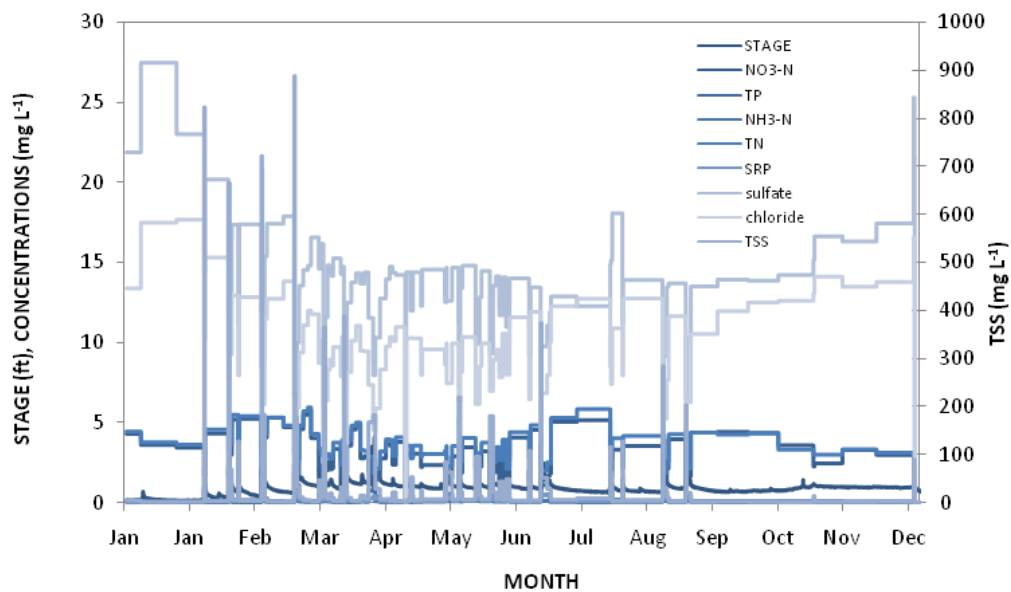


Figure 1. Continuous discharge with constituent concentrations extended to midpoint to determine annual loads for 2008 at Ballard Creek at Washington County Road 76, northwest Arkansas.

Table 1. Calculated annual loads (kg) for each constituent at Ballard Creek at Washington County Road 76 during base, storm and combined flows.

Parameter	Base Load (kg)	Storm Load (kg)	Total Load (kg)
Chloride (Cl)	191,000	324,000	515,000
Sulfate (SO ₄)	238,000	455,000	693,000
Ammonia (NH ₃ -N)	290	5,700	5,990
Nitrate (NO ₃ -N)	63,000	88,600	151,000
Soluble Reactive Phosphorus (SRP; PO ₄ -P)	1170	13,200	14,400
Total Nitrogen (TN)	66,200	118,000	184,000
Total Phosphorus (TP)	1,410	25,600	27,000
Total Suspended Solids (TSS)	50,600	5,180,000	5,230,000

Table 2. Average Flow Weighted Concentration (FWC, mg L⁻¹) for each constituent at the Illinois River at Ballard Creek at Washington County Road 76 during base, storm and combined flow.

Parameter	Base FWC (mg L ⁻¹)	Storm FWC (mg L ⁻¹)	Total FWC (mg L ⁻¹)
Chloride (Cl)	12.83	7.93	11.49
Sulfate (SO ₄)	15.96	11.14	12.42
Ammonia (NH ₃ -N)	0.02	0.14	0.11
Nitrate (NO ₃ -N)	4.22	2.17	2.70
Soluble Reactive Phosphorus (SRP; PO ₄ -P)	0.08	0.32	0.26
Total Nitrogen (TN)	4.43	2.88	3.30
Total Phosphorus (TP)	0.09	0.63	0.48
Total Suspended Solids (TSS)	3.39	126.80	93.73

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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 number and frequency of storm events during the month, and this is an artifact of the method that was used to determine storm flows (i.e., discharge greater than 20 cfs). 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 late summer, fall and winter, where January and October did not have discharge exceeding 20 cfs. Thus, no storm event loads are reported for Ballard Creek during these two months. During 2008, the total loads were least during late fall and the winter months, January, November and December.

The potential sources of nutrients and other chemicals within the Upper Ballard Creek Watershed are diffuse in nature, because this catchment does not contain any known effluent discharges. Thus, nonpoint sources would be primarily from pastures and its agricultural management as more than 60% of this catchment was in pasture during 2006. The storm events transport nutrients and other chemicals from the landscape through Ballard Creek, and total constituent loading is dependent on annual discharge volume which is closely tied to the frequency and duration of storm events. The concentration and loads of the various constituent during base flow may be attributed to season and annual variations in groundwater inflows. The constituent concentrations observed during base flow are also reflective of the catchment land use, as several studies in this region have shown that nutrient concentrations increase with the amount of pasture within a stream's catchment (e.g., see Haggard et al., 2007).

Table 4 provides various constituent loads from 2008 and the historical studies (see Nelson et

al., 2007); the loads from 2007 were from unpublished data. Constituent loads have been variable from 2003 through 2008 following the pattern in annual discharge volume (Figure 2, Table 4). Constituent loads estimated in 2008 were greater than the previous year because annual discharge was 2.4 times greater in 2008 than that observed in 2007; the increase in annual discharge was reflective of the increase in precipitation between years. The loads estimated in 2008 were the greatest of the period of record (i.e., 2003 through 2008), as was the annual discharge volume.

The monitoring continued from January 1, 2009 through June 30, 2009. During that time, total discharge (six months) was 25,200,000 m³ with 42% attributed to base flow and 58% 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.

CONCLUSIONS

This project successfully estimated constituent loads at Ballard Creek in calendar year 2008 using data collected in this study combined with data from the previous year. The constituent loads in 2008 were greater than those reported historically (i.e., from 2003 to 2009), likely because annual discharge was also greatest. Overall, historical constituent loads follow a pattern that reflects the influence of annual discharge volume on constituent transport at Ballard Creek.

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Table 3. Calculated monthly loads (kg) for each constituent at the Illinois River at Ballard Creek at Washington Country Road 76 Bridge during base, storm and combined flows for calendar year 2008.

Base Flow 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	21,300	32,500	20	4,750	57	4,960	90	2,470
February	26,200	35,000	31	8,570	178	8,940	226	4,940
March	15,700	21,700	23	6,080	72	6,150	109	7,730
April	1,420	2,240	0	491	10	550	16	272
May	4,800	7,320	25	1,180	43	1,520	71	2,790
June	2,050	2,720	14	702	17	788	25	426
July	23,800	25,100	67	9,490	180	10,200	163	11,100
August	32,900	36,700	86	10,600	277	12,300	294	14,200
September	19,100	23,200	27	7,140	134	7,300	155	3,180
October	36,700	41,600	0	12,700	182	12,240	235	2,720
November	4,520	5,110	0	1,290	19	1,180	24	0
December	5,040	8,240	6	688	20	740	26	162
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	12,300	17,800	461	3,420	913	4,910	2,320	596,000
March	58,600	87,400	2,640	18,300	5,820	27,400	12,000	2,620,000
April	50,500	81,100	1,030	15,900	2,190	21,500	4,770	936,000
May	33,000	47,600	137	9,230	387	11,100	722	67,800
June	39,200	55,600	459	10,600	918	14,100	1,750	239,000
July	20,100	24,800	314	5,670	1,160	8,450	1,060	342,000
August	4,600	7,170	63	1,260	119	1,660	216	14,200
September	19,100	23,200	27	7,140	134	7,300	155	3,180
October	0	0	0	0	0	0	0	0
November	42,160	49,500	33	9,250	142	9,840	210	3,273
December	42,700	54,100	55	9,350	106	9,720	186	11,300
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	21,300	32,500	20	4,750	57	4,960	90	2,470
February	38,400	52,600	491	11,900	1,090	13,800	2,550	601,000
March	74,000	108,000	2,660	24,300	5,890	33,500	12,100	2,630,000
April	51,600	82,900	1,030	16,300	2,200	21,900	4,780	936,000
May	37,200	54,100	159	10,300	425	12,500	784	65,500
June	40,000	56,800	465	10,900	925	14,400	1,760	239,000
July	42,900	48,800	377	14,700	1,330	18,300	1,210	353,000
August	37,400	43,700	149	11,900	395	13,900	508	35,500
September	42,000	56,000	537	13,500	1,620	17,000	2,510	353,000
October	36,700	41,600	0	12,700	182	12,240	235	2,720
November	45,800	53,600	33	10,300	157	10,800	229	3,270
December	47,600	62,200	61	10,030	126	10,500	211	11,450

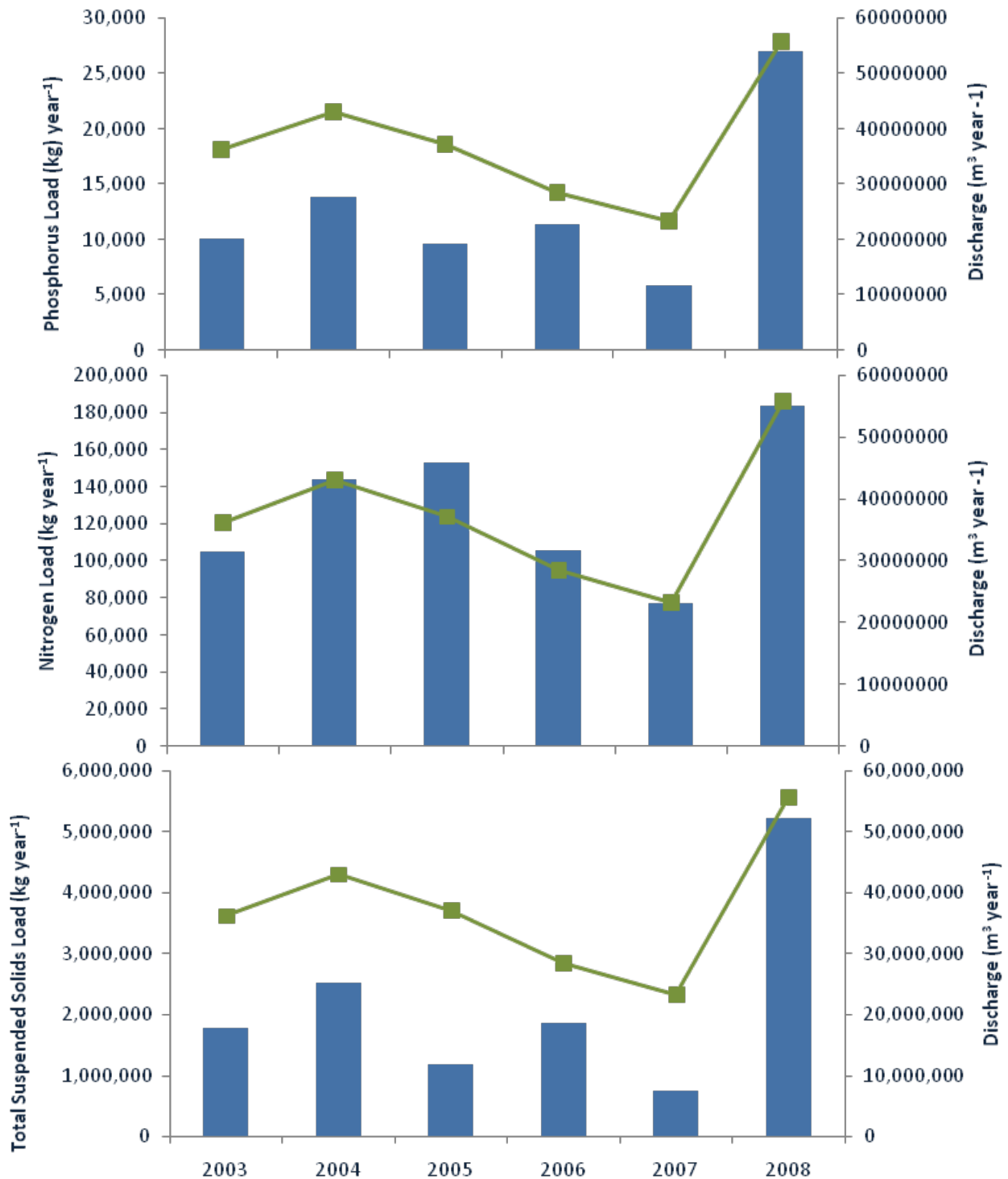


Figure 2. Total P (TP), Total N (TN) and Total Suspended Solids (TSS) loads and discharges at Ballard Creek at Washington County Road 76 Bridge, northwest Arkansas, from 2003-2008; the bars represent the total load during these calendar years (data from Nelson et al., 2007).

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Table 4. Calculated total annual loads (kg) for each constituent at the Ballard Creek at Washington County Road 76 Bridge from 2003-2008.

Constituent	2003	2004	2005	2006	2007	2008
NO ₃ -N (kg yr ⁻¹)	75,200	110,203	68,000	46,901	68,118	151,000
TP (kg yr ⁻¹)	10,100	13,900	9,700	11,400	5,870	27,000
NH ₃ -N (kg yr ⁻¹)	2,600	2,540	5,490	4,400	1,640	5,990
TN (kg yr ⁻¹)	105,500	144,000	153,000	106,000	77,500	184,000
PO ₄ -P (kg yr ⁻¹)	4,100	6,390	5,500	5,300	3,340	14,400
TSS (kg yr ⁻¹)	1,787,000	2,524,000	1,170,000	1,860,000	738,000	5,230,000
Cl (kg yr ⁻¹)	--	--	--	--	288,200	515,000
SO ₄ (kg yr ⁻¹)	--	--	--	--	361,400	93,000

Table 5. Summary of calculated annual loads (kg) for each constituent at Ballard Creek at Washington County Road 76 Bridge during base, storm and combined flows from January 1, 2009 to June 30, 2009.

Parameter	Base Flow (kg)	Storm Flow (kg)	Total (kg)
Chloride (Cl)	131,000	111,000	242,000
Sulfite (SO ₄)	199,000	189,000	388,000
Ammonia (NH ₃ -N)	411	2,720	3,130
Nitrate (NO ₃ -N)	30,100	21,300	51,400
Soluble Reactive Phosphorus (SRP; PO ₄ -P)	573	5,100	5,670
Total Nitrogen (TN)	32,300	32,000	64,300
Total Phosphorus (TP)	852	8,540	9,390
Total Suspended Solids (TSS)	33,900	1,070,000	1,100,000

Table 6. Summary of average Flow Weighted Concentration (mg L⁻¹) for each constituent at the Ballard Creek at Washington County Road 76 Bridge during base, storm and combined flows.

Parameter	Base Flow (mg L ⁻¹)	Storm Flow (mg L ⁻¹)	Total (mg L ⁻¹)
Chloride (Cl)	12.33	7.66	9.61
Sulfite (SO ₄)	18.71	13.02	15.41
Ammonia (NH ₃ -N)	0.04	0.19	0.12
Nitrate (NO ₃ -N)	2.82	1.47	2.04
Soluble Reactive Phosphorus (SRP; PO ₄ -P)	0.05	0.35	0.23
Total Nitrogen (TN)	3.04	2.20	2.55
Total Phosphorus (TP)	0.08	0.59	0.37
Total Suspended Solids (TSS)	3.18	73.72	43.84

REFERENCES

Haggard, B.E., Smith, D.R., and Brye, K.R. 2007. Variations in stream water and sediment phosphorus among select Ozark catchments. *Journal of Environmental Quality* 36: 1723-1734.

Nelson, M.A., Cash, W., Trost, G.K., and Purtle, J.M. 2007. Water quality sampling, analysis and annual load determinations for TSS, nitrogen and phosphorus at the Ballard Creek near Arkansas/Oklahoma Line. Arkansas Water Resources Center, Fayetteville, AR, publication number MSC-304.

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APPENDIX 1. Location of the sampling station at Ballard Creek at the Washington County Road 76 Bridge, northwest Arkansas.

