# Database for the Chemical and Isotopic Composition of the Illinois River Basin, Illinois (2003-2005)

Samuel V. Panno, Walton R. Kelly, Keith C. Hackley, and Hue-Hwa Hwang

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### **INTRODUCTION**

Since pre-settlement times, human activities have led to increased concentrations of dissolved and suspended compounds in streams and rivers, in many cases adversely affecting the health of aquatic ecosystems (e.g., Hart 1991). Two of the most important water quality concerns in surface water bodies are excess nutrients (nitrogen (N) and phosphorus) and salinity (Perry, 1998; Kaushal et al. 2005). One of the primary reasons for stream impairment in Midwestern U.S. states is high nutrient levels, caused by agricultural activities such as erosion of soils and leaching of excess fertilizer and livestock manure, as well as direct discharge of treated wastewater (TWW) at some localities (David and Gentry 2000). Elevated salinity is an issue in northern U.S. and Canadian metropolitan areas due to road salt runoff (Howard and Haynes 1993; Kaushal et al. 2005), and TWW discharge may also contribute to increased salinity.

Excess concentrations of nutrients in surface water bodies have been linked to conditions harmful to aquatic biota, including toxic algal blooms, excessive macrophyte growth, fish kills, and reduction in species richness (Carpenter et al., 1998). Most of the N in surface water bodies in the Midwestern U.S. is from agricultural sources, primarily soil organic matter (SOM) and synthetic fertilizers. For example, Goolsby et al. (1999) estimated that, as of the mid-1990s, about 60% of the N input into the Mississippi River Basin was from synthetic fertilizer and mineralized soil N. The remaining 40% comes from legumes (N<sub>2</sub> fixation), manure, atmospheric deposition, and point sources such as effluent from wastewater treatment plants (WWTPs). Howarth et al. (1996) estimated that about 9% of the total N load in the Mississippi River basin was derived from sewage. Policy makers are using estimated contributions of these N sources, typically calculated by mass balance approaches, to develop strategies to reduce N inputs to the Mississippi River in hopes of decreasing the hypoxic zone in the Gulf of Mexico. However, there is a great deal of uncertainty in these estimates, and there has actually been a significant decrease in the N load in the Mississippi-Atchafalaya River Basin in recent years without a concomitant decrease in the size of the hypoxic zone (USGS, 2007). When comparing the input and outputs of the N mass balance calculations for various river systems, there is typically a significant deficit in the output portion, most of which is generally attributed to denitrification (David and Gentry, 2000).

Road salt has been linked to groundwater degradation in many urban and roadside areas in snowy climes (Huling and Hollocher 1972; Pilon and Howard 1987; Amrhein et al. 1992; Williams et al. 2000; Bester et al. 2006). Road salt runoff reaches streams via direct runoff during snowmelts and also from groundwater discharge, and can cause large spikes in sodium (Na) and chloride ( $CI^-$ ) concentrations in the winter and early spring (Howard and Haynes 1993). Significant application of road salt began after World War II, and accelerated rapidly from the 1960s (Salt Institute 2006). Salinity levels have been increasing in surface waters in the northeastern U.S. since the 1960s, causing an adverse effect on aquatic life (Kaushal et al. 2005).

The Illinois River watershed drains approximately 78,000 km<sup>2</sup> or 44% of the land area of Illinois (plus small areas of Wisconsin and Indiana) (Figure 1). The headwaters are in the Chicago region, where the hydrology has been highly modified, including the building of canals and reversing the flow of the Chicago River. The primary streams in Chicago are the Des Plaines River, the Chicago Sanitary & Ship Canal (SSC), and the Calumet Sag Channel. Downstream of Channahon, the Kankakee River flows into the Des Plaines River, forming the Illinois River. Downstream of the Chicago region, land use is dominated by row crop agriculture; slightly more than 70% of the land in the lower Illinois River basin was in agricultural production in 2004, predominantly corn and soybeans (Illinois Agricultural Statistics Service, 2006).

Surface runoff and diffuse groundwater discharge are the primary sources of water to most rivers and streams. The Illinois River, however, has additional sources. The headwaters receive substantial volumes of TWW, over 5 billion L per day, and industrial discharge. Approximately 40% of the flow in the Des Plaines River at the Brandon Lock & Dam in Joliet is from TWW or industrial discharge (Singh and Ramamurthy 1991; Illinois State Water Survey 2006). At low flow, TWW can account for almost 100% of the flow in these tributaries. Treated wastewater can contribute significantly to the flux of some constituents; for example, David and Gentry (2000) estimated 21% of total N in the Illinois River comes from TWW. The SSC and Calumet Sag Channel also receive a small amount of water from Lake Michigan (< 5%). Downstream of Chicago, tile drains are common in agricultural areas and provide the bulk of water to tributaries discharging into the Illinois River. While tile drainage is shallow groundwater, it passes through the subsurface at much greater rates than typical for groundwater so there is less time for chemical, physical, and biological reactions to modify the chemical composition of the discharging water.

This report presents the data obtained during a two-year investigation of dissolved constituents in the Illinois River. The objective of that two-year investigation was to indentify the major sources of nitrate  $(NO_3^-)$ , chloride  $(Cl^-)$ , and other inorganic constituents present in the Illinois River Watershed from the Chicago area to its confluence with the Mississippi River. The results of that investigation yielded valuable information about the major sources of these nutrients that are exported from the state and transported down the Mississippi River to the Gulf of Mexico. We also gained an understanding of the seasonal variability of  $NO_3^-$  and  $Cl^-$  concentrations and sources, the likely role of denitrification within the subsurface and the river, and the contributions of road salt and sewage to the nutrient load of the Illinois River and its tributaries (Panno et al. 2008; Kelly et al. submitted).

### **METHODS**

A total of 131 water samples were collected during this investigation, 93 river samples and 38 from potential  $NO_3^-$  and  $Cl^-$  sources. River samples were collected seasonally from 14 locations in the Illinois River basin: three in the upper Illinois River and four in tributaries (one each in the Fox River and SSC, and two in the Des Plaines River) in 2003/2004, and six in the lower Illinois River and one in the Sangamon River in 2004/2005 (Figure 1). For this investigation, the upper Illinois River is defined as the stretch from the Chicago area to Peoria, and the lower Illinois River from Peoria to its confluence with the Mississippi River. The main stem of the Illinois River is also defined here to include the the SSC at Willow Springs and the Des Plaines River at Brandon Road Lock & Dam near Joliet (Figures 1–4). Samples were collected approximately quarterly, in August, October, February, and May, and additionally in April and late November/early December fol-

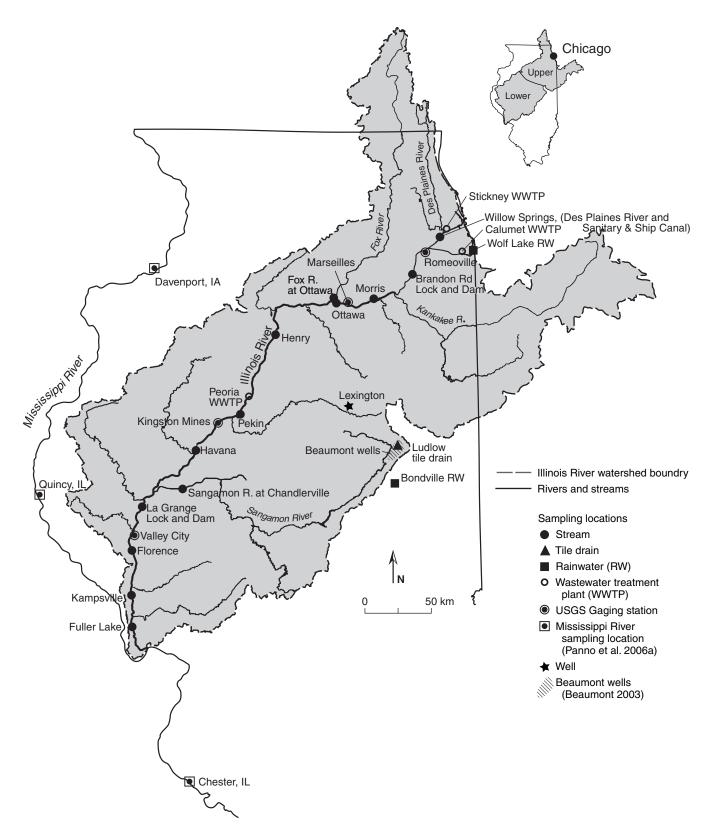


Figure 1. Map of the Illinois River Basin, including major tributaries and sampling locations. Mississippi River locations sampled by Panno et al. (2006a).



**Figure 2.** View of the Des Plaines River near Western Springs, showing ISGS and ISWS scientists sampling the centroid of the river from an abandoned bridge.

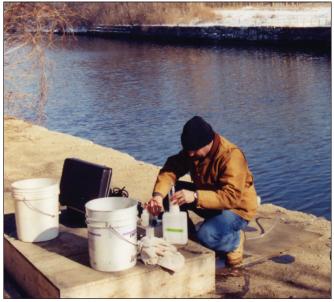


Figure 3. ISWS scientist collecting water samples from the west bank of the Sanitary & Ship Canal.

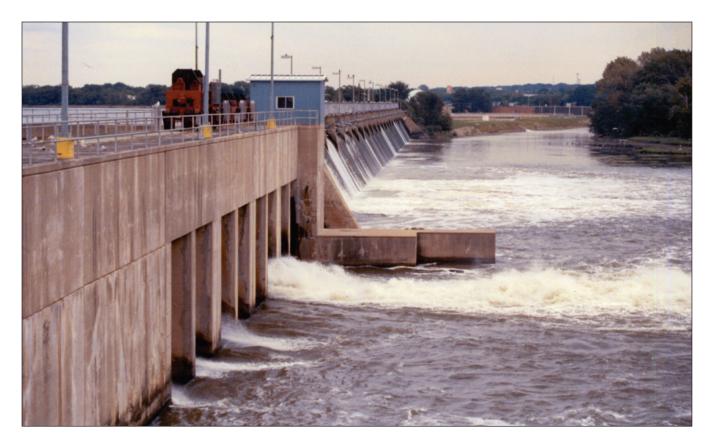


Figure 4. River water samples were collected from the upstream side of the Brandon Road Lock and Dam near Joliet.

lowing the main periods of synthetic fertilizer application. Samples were collected from all 14 sampling locations during one sampling trip during a drought in August 2005; river stage was below its 5th percentile value at that time. Due to access problems, Fuller Lake was only sampled three times, August and October 2004, and August 2005. The Fox River was not sampled in August 2003.

Potential  $NO_3^-$  and  $Cl^-$  sources in the watershed that were sampled included TWW, an agricultural drain tile, and precipitation. Treated wastewater samples were collected on three separate occasions from the outfalls of three municipal sewage treatment plants, two in the Chicago area (Stickney and Calumet) and Peoria (Figures 1, 5, and 6). On two occasions wastewater samples were collected from 3 different points along the aeration batteries at Stickney. A continuously flowing field tile draining 1.82 km<sup>2</sup> (450 acres) of land planted in row crops (corn and soybeans) near Ludlow in central Illinois was sampled seven times between September 2003 and September 2004 (Figures 1 and 7). Because most tiles do not flow continuously, it is likely that this tile also has a component from a shallow sand aquifer. Composite precipitation samples were collected approximately monthly for one year periods from two locations, one in an industrial area in south Chicago (Wolf Lake) and the other in a rural cropland area near Bondville in east central Illinois (Figures 1 and 8). Some months there was insufficient sample for analysis, and samples from Wolf Lake were not collected between December 2003 and March 2004 due to logistical problems.

Data collected in other studies were also considered in this study to help interpret our data. Additional source samples included livestock manure (Panno et al. 2005), shallow groundwater in central Illinois collected from monitoring wells located in untiled fields (Beaumont, 2003; Kelly, unpublished data), drain tiles that flowed only during wet periods (Beaumont, 2003), and soil water samples from a tilled, unfertilized plot in a row crop area (Kelly, unpublished data). Soil water samples from a seep in Mammoth Cave, KY, beneath an uninhabited

wooded area (Panno et al. 2005), and from an undisturbed area in the Carter Cave region of Kentucky (collected by J. Angel, Illinois State University, and analyzed as part of this investigation) were assumed to be representative of pristine soil water in the Midwest.



Figure 5. Discharge of TWW entered the Sanitary & Ship Canal (looking south) from the Stickney WWTP.



Figure 6. Discharge of TWW entered the Illinois River (looking north) from the Peoria WWTP.



Figure 7. Tile drain near Ludlow. The tile drained an area that was exclusively row crop agriculture.



Figure 8. Month-long composite rainwater and snow melt samples were collected in clean plastic buckets with automatic lids at the NADP site at Bondville, IL.

Samples from the Mississippi River that were collected quarterly for one year from three locations adjacent to Illinois (Panno et al., 2006a) were also considered. The additional well, tile, and Mississippi River locations are included in Figure 1.

In sampling the rivers, our aim was to collect representative samples from the main channel. Samples from the Illinois and Fox Rivers were collected from a boat, except at the two lock and dam sites, near the centroid of the river flow using a peristaltic pump and a weighted sampling tube (Figure 9). This method has been shown to yield water samples whose dissolved chemical and isotopic compositions are representative of the bulk of the water in the river (Antweiler et al., 1995; Panno et al., 2006a). Samples at the lock and dam sites (Brandon Road and La Grange) were collected from walkways located just upstream of the dam spillways (Figure 4). The Des Plaines River at Willow Springs was sampled at the centroid of the river from a bridge (Figure 2). The SSC and Sangamon River were sampled by placing tubing at approximately one half the depth of the channel from the bank (Figure 3). Field parameters, including temperature, specific conductance, pH, Eh, and dissolved oxygen (DO), were measured in situ using temperature compensated meters. Samples for cation, anion, and isotope analysis were passed through 0.45- µm membrane filters and stored in polyethylene bottles. Unfiltered samples were collected in amber glass bottles for the determination of total Kjeldahl nitrogen (TKN). Because the majority of TKN is typically associated with particulate matter, grab samples in rivers do not give accurate TKN results (Meade et al. 1995). Samples collected from the centroid of the river where

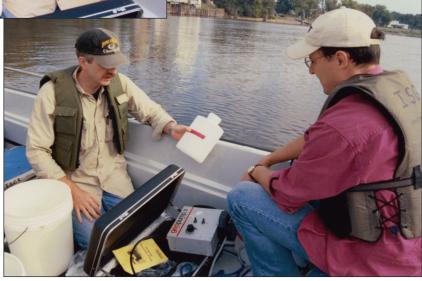


flow is at a maximum probably yield overly large TKN concentrations. Cation samples were acidified in the field with ultra-pure nitric acid to a pH of < 2. Samples were transported in icefilled coolers, and kept refrigerated at approximately 4° C until analysis.

Major anions were determined by ion chromatography, following U.S. EPA Method 300.0 (Pfaff, 1993). TKN was determined by converting organic N to ammonium ( $NH_4^+$ ) by digestion with  $H_2SO_4$ ; the resultant solution was analyzed for  $NH_4$ -N using a titrimetric procedure (Bremner and Mulvaney, 1982). Ammonium-N was determined using semi-automated colorimetry (USEPA, 1993). Seventy-one of the samples were analyzed with neutron activation in order to determine concentrations of Na, Cl<sup>-</sup>, bromide

Figure 9. ISGS and ISWS scientists collecting water samples from the Illinois River.

(Br<sup>¬</sup>), and iodide (I<sup>¬</sup>) at low detection limits (Strellis et al., 1996; Landsberger et al., 2006). Appropriate QA/QC procedures were followed in the field and analytical laboratories, including analysis of blanks, duplicates, calibration check standards, and reference standards. Approximately seven samples per trip were collected in addition to one blank and one duplicate sample. All instruments were calibrated at the beginning of the day and rechecked at the end of the day. All laboratory instruments were calibrated before analizing each set of samples and blank and duplicate samples were included in each run (approximately nine samples).



Nitrogen and oxygen isotopic analyses of  $NO_3^-$  were conducted following the methods of Silva et al. (1994; 2000), Wassenaar (1995), and Hwang et al. (1999). Briefly, hydrochloric acid was added to samples to reach a pH of 4, then the samples were boiled to remove bicarbonate (HCO<sub>3</sub><sup>-</sup>) and dissolved CO<sub>2</sub>. Sulfate (SO<sub>4</sub><sup>2-</sup>) was removed by precipitation of BaSO<sub>4</sub>. Dissolved organic carbon (DOC) was removed by a cation exchange column packed with Bio-Rad AG 50W-X8 resin. Nitrate was extracted using a pre-packed BioRad AG 1-X8 anionexchange column, eluted with HBr solution, converted to AgNO<sub>3</sub> by adding silver oxide, and precipitated by freeze-drying in a vacuum system. The dried AgNO<sub>3</sub> was converted to N<sub>2</sub> gas by quartz tube combustion. The N<sub>2</sub> gas was analyzed for  $\delta^{15}N$  on a Finnigan Mat Delta-E Isotope Ratio Mass Spectrometer. The  $\delta^{18}O$  of NO<sub>3</sub><sup>-</sup> was determined by a Finnigan thermal conversion elemental analyzer (TC/EA). International isotope standards IAEA-N1, IAEA-N2, IAEA-N3, USGS 25, and USGS 26 were used for  $\delta^{15}$ N calibration; standards IAEA-N3, USGS 34 and USGS 35 were used for  $\delta^{18}$ O calibration. Reproducibility of duplicate analyses were equal to or better than 0.5 ‰ for  $\delta^{15}$ N and 1.0 ‰ for  $\delta^{18}$ O.

## RESULTS

#### Characterization of Major Nutrient and Ion Sources

The chemical composition of potential sources of  $NO_3^-$  and  $CI^-$  in the Illinois River are found in Tables 1 and 2. Rainwater and snow melt samples collected from the Chicago area (Wolf Lake) and Bondville were dilute calcium (Ca)  $-HCO_3^-$  type waters with a pH that typically ranged from 6.0 to 6.9 and a total dissolved solids (TDS) concentration of between 4.7 and 25 mg/L. Kim et al. (2005) showed that fine particles containing  $NO_3^-$  aerosols at the Bondville site are responsible for most of the  $NO_3^-$  concentrations in the rainfall and snow melt samples. Sodium concentrations in rainwater and snow melt samples ranged from <0.1 to 1.3 mg/L at Wolf Lake and 0.08 to 0.19 mg/L in Bondville, suggesting an industrial component in the Chicago area could have been added to the original marine aerosol component. Exceptionally high Na concentrations were found in spring-time runoff of road salt from a bridge (Figure 10) with Na and Cl<sup>-</sup> concentrations of 6,270 and 8,930 mg/L, respectively.

Soil water samples from Mammoth Cave (Panno et al. 2005) and an area in the Carter Cave region of Kentucky were assumed to approximate the composition of pristine soil water in the Midwestern U.S. These soil water samples were dilute Ca-HCO<sub>3</sub><sup>-</sup> type waters similar to rainwater (Tables 1 and 2 in Panno et al. 2005). Nitrate-N and Cl<sup>-</sup> concentrations were very low, < 0.5 and < 2 mg/L, respectively. Analyses of soil water from an agricultural field near Lexington, IL had significantly higher NO<sub>3</sub>-N concentrations, between 15 and 21 mg/L, and Cl<sup>-</sup> concentrations between 16 and 21 mg/L (W.R. Kelly, unpublished data).

Tile drain samples were Ca-Mg HCO<sub>3</sub><sup>-</sup>-type waters that contained relatively high concentrations of agriculture-related nutrients potassium (K) (1–11 mg/L), NO<sub>3</sub>-N (9.52–15.3 mg/L) and TKN (1.18–4.31 mg/L). However, these tiles flowed year round indicating that the tile was in or above a sand deposit which provided water from much larger distances than normal. Tile drain data from tiles that flowed only during wet periods (Beaumont 2003) had elevated spring-time concentrations of NO<sub>3</sub>-N that ranged from 11.9 to 33.1 mg/L, with a median of 17.1 mg/L. The tile drain samples from Ludlow, IL had low Cl<sup>-</sup> (10 to 18 mg/L) and Na concentrations (6.8 to 9.4 mg/L) but elevated Cl<sup>-</sup>/Na ratios, relative to all other samples (Figure 11), suggesting either significant ion exchange within the soil zone and/or contributions from fertilizer (KCl). Potassium chloride is applied to crop lands in Illinois at a rate of about 90 kg/acre every 2 years (Panno et al. 2006b), and some of this could leach to tile drains.

Ammonium-N (< 0.01 to 0.03 mg/L), phosphate-P (PO<sub>4</sub>-P) (< 1 mg/L), fluoride ( $F^-$ ) (0.1 to 0.2 mg/L) and boron (B) (median = < 0.02 mg/L) concentrations were relatively low in our tile drain samples. Tile drain samples sometimes had relatively elevated TKN values (as high as 4.3 mg/L).

Nitrate isotopes of tile water fall along a denitrification vector that project back to the synthetic fertilizer/soil organic matter domains. Those samples falling closest to the synthetic fertilizer/soil organic matter domains (the least denitrified) were collected primarily in the spring; those samples falling farthest from the fertilizer/soil organic matter domain (the most denitrified) were collected primarily in the summer and early fall (Figure 12).

Treated wastewater from the outfalls of municipal WWTPs in the Chicago area and Peoria were mixed cation-HCO<sub>3</sub><sup>-</sup>-type waters with high TDS contents and enriched in many ions, including Na, K, B, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub>N, NH<sub>4</sub>N, TKN, PO<sub>4</sub>-P and DOC (Table 1). Sodium ranged from 83 to 294 mg/L, Cl<sup>-</sup> from 150 to 300 mg/L, and F<sup>-</sup> from 0.6 to 1.3 mg/L. Boron concentrations were higher in TWW than any other sources, ranging from 0.06 to 0.56 mg/L. All nutrients except NH<sub>4</sub>N were elevated in TWW, with NO<sub>3</sub>N between 3.3 and 11.5 mg/L, TKN ranging from 0.16 to 6.2 mg/L, and PO<sub>4</sub>-P concentrations between < 0.01 and 12.1 mg/L. Ammonium-N concentrations ranged from 0.1 to 0.3 mg/L. Potassium ranged from 9 to 11 mg/L and DOC from 4.4 to 12 mg/L. The pH of TWW was near neutral, while the alkalinity was typically less than 200 mg/L. All of the headwaters and many tributaries had TWW components. The Stickney WWT facility discharges to the SSC and the Calumet WWT facility to the Calumet-Sag Channel. Flow in the Fox River was on average about 8% TWW (Knapp and Myers 1999; Illinois State Water Survey 2006). The Springfield WWT facility discharges its wastewater to the Sangamon River. The PeoriaWWT facility outfall discharges directly to the Illinois River.

#### Composition of Illinois River Water

The chemical composition of river water samples is shown in Table 1. In general, samples of Illinois River water can be characterized as a well-oxygenated, mixed cation- $HCO_3^-$  type water with concentrations of Cl<sup>-</sup>, NO<sub>3</sub>-N, and SO<sub>4</sub><sup>2-</sup> and associated cations elevated above natural background. The specific conductance decreased from a high of about 2100  $\mu$ S/cm in the Chicago area to between 600 and 900  $\mu$ S/cm near the confluence with the Mississippi River (similar to that of the local shallow groundwater). Many of the dissolved solids of the Illinois River are due to both urban and rural sources of contamination. Water samples from the tributaries of the Chicago area (i.e., the Des Plaines River and the SSC) had elevated concentrations of a number of analytes, including Na, K, B, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub>-N, NH<sub>4</sub>-N, TKN, PO<sub>4</sub>-P, and DOC relative to the lower Illinois River and its tributaries, and low levels of DO (Table 2). Because these tributaries receive TWW along their reaches, the analyte concentrations of these parameters and their ranges generally decreased with distance from the Chicago area.

Dissolved oxygen was lowest in the waterways of the Chicago area and greater downstream of Joliet (Figure 13). The low DO in the headwaters was likely due to TWW, which was generally depleted in DO (as low as 3.1 mg/L) and discharged high levels of nutrients that

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Sample Location	Date	River Mile	⊢°	Нd	ORP V	S – DO	Sp Cond μS/cm	Alkalinity (CaCO <sub>3</sub> )	L	C'	Ē	PO.⁴	SO <sub>4</sub> <sup>2-</sup>	NO <sup>"-</sup> N	NH <sup>3-</sup> N	TKN	ш	Ba
Henry	09/02/2003	195.5	24.4	7.94	494	4.7	742	169	0.7	92.6	0.2	0.9	81.7	2.49	0.27	2.13	0.20	0.042
Ottawa	09/02/2003	240	25.4	7.65	520	7.3	704	151	0.6	86.9	0.2	1.9	77.6	3.60	0.16	8.52	0.20	0.030
Morris	09/02/2003	263.5	26.8	7.55	534	7.7	669	148	0.7	86.3	0.2	1.9	78.3	3.58	0.17	1.96	0.20	0.026
Joliet	09/02/2003	286	25.5	7.11	556	4.3	692	129	0.8	96.2	0.1	2.3	68.8	4.30	0.29	2.17	0.18	0.018
Willow Spr-Des Plaines	09/02/2003	308	22.4	7.33	529	5.4	749	110	0.7	125	<0.1	3.2	62.9	5.58	0.19	2.29	0.21	0.022
Willow Spr- SSC	09/02/2003	308	24.7	6.88	556	4.1	487	96	0.8	65.8	<0.1	1.6	32.8	4.25	0.28	3.73	0.08	0.011
Henry	10/30/2003	195.5	12.5	8.43	474	9.0	834	179	0.7	96.6	<0.1	1.1	97.9	3.61	0.28	2.50	0.14	0.033
Ottawa-Fox R.	10/30/2003	239	9.0	9.05	436	11.2	1,008	239	0.6	156	<0.1	0.2	64.6	0.99	0.25	2.58	0.10	0.103
Ottawa-Illinois R.	10/30/2003	240	13.2	7.83	469	9.0	814	167	1.0	91.0	<0.1	1.5	96.2	5.28	0.12	1.11	0.13	0.028
Morris	10/30/2003	263.5	12.7	7.95	477	9.3	798	179	0.6	79.4	<0.1	1.5	97.1	4.88	0.17	1.29	0.19	0.031
Joliet	10/30/2003	286	16.6	7.19	473	5.0	826	135	0.8	120	<0.1	1.4	84.8	6.78	0.27	2.02	0.18	0.015
Willow Spr-Des Plaines	10/30/2003	308	12.9	7.69	494	5.2	1,054	153	0.8	161	<0.1	3.3	94.8	8.56	0.10	1.51	0.25	0.023
Willow Spr- SSC	10/30/2003	308	19.3	6.95	497	3.6	751	118	1.0	103	<0.1	4.0	63.6	8.75	0.96	2.91	0.17	0.012
Henry	11/20/2003	195.5	12.0	7.86	489	8.5	846	179	0.7	101	<0.1	1.0	86.4	5.16	0.08	3.49	0.08	0.040
Ottawa-Fox R.	11/20/2003	239	8.6	8.08	483	8.6	804	202	0.6	101	<0.1	<0.1	57.6	2.90	0.10	2.59	<0.01	0.076
Ottawa-Illinois R.	11/20/2003	240	12.1	7.60	490	8.9	606	141	0.5	58.5	<0.1	1.2	58.9	5.12	0.29	3.03	0.05	0.026
Morris	11/20/2003	263.5	11.9	7.56	494	10.0	588	140	0.5	55.6	<0.1	1.2	55.6	4.61	0.23	2.46	0.05	0.027
Joliet	11/20/2003	286	13.2	7.27	489	7.0	572	107	0.4	74.3	<0.1	<0.1	53.1	2.66	0.35	2.07	0.05	0.015
Willow Spr-Des Plaines	11/20/2003	308	12.3	7.63	292	7.7	766	137	0.3	120	<0.1	1.1	60.0	2.54	0.21	1.84	0.07	0.021
Willow Spr- SSC	11/20/2003	308	16.0	7.16	503	6.2	767	137	0.5	104	<0.1	<0.1	67.6	7.18	0.27	1.94	0.07	0.016
Henry	02/17/2004	195.5	0.2	8.02	477	14.0	1,172	254	0.4	174	<0.2	0.5	90.4	5.10	0.15	3.71	0.15	0.062
Ottawa-Fox R.	02/17/2004	239	0.1	8.64	491	15.9	1,223	295	0.3	179	<0.2	0.6	81.3	4.07	0.08	2.47	0.08	0.120
Ottawa-Illinois R.	02/17/2004	240	4.0	8.08	483	10.2	1,636	200	0.5	347	0.2	1.5	105	5.55	0.42	2.39	0.20	0.033
Morris	02/17/2004	263.5	3.0	8.01	513	13.4	1,412	204	0.4	255	<0.2	1.0	100	4.83	0.30	2.12	0.16	0.034
Joliet	02/17/2004	286	9.6	7.39	517	6.1	2,116	150	0.9	488	<0.5	2.1	101	7.93	0.83	5.06	0.22	0.018
Willow Spr-Des Plaines	02/17/2004	308	0.3	8.39	468	4.8	1,924	197	0.7	446	<0.2	3.3	103	7.56	0.31	2.75	0.25	0.031
Willow Spr- SSC	02/17/2004	308	11.0	7.01	511	-2.6	1,943	130	1.2	424	<0.2	<0.2	117	9.36	1.19	4.57	0.55	0.015

Table 1. Chemical data for surface water samples from the Illinois River and tributaries. Results in mg/L unless otherwise stated. ND = Not Determined.

ND = NOI DEFINITIED.																	
Sample Location	Date	Ca <sup>2+</sup>	Ъө	¥	$Mg^{2+}$	ЧМ	Na⁺	Si	t S	DOC	δ <sup>15</sup> N <sub>NO3</sub> - (‰)	δ <sup>18</sup> O <sub>NO3</sub> - (‰)	δ <sup>18</sup> Ο (‰)	δD (‰)	$\delta^{13}C_{\text{DIC}}$	Br (INAA)	I <sup>-</sup> (INAA)
Henry	09/02/2003	66.8	<0.01	ω	28.3	<0.01	70.6	1.65	0.26		10.1	4.9	-5.64	-43.2	-7.25	0.181	0.0052
Ottawa	09/02/2003	62.2	<0.01	6	25.7	<0.01	69.3	2.00	0.25	4.7	10.6	4.4	-5.45	-42.8	-6.91	QN	QN
Morris	09/02/2003	60.3	<0.01	6	23.1	<0.01	72.0	2.13	0.24	4.3	10.4	6.7	-5.60	-43.7	-7.13	0.134	0.0059
Joliet	09/02/2003	53.8	<0.01	8.5	19.6	0.02	79.0	1.98	0.22	7.6	8.7	4.8	-5.60	-43.7	-7.96	QN	QN
Willow Spr-Des Plaines	09/02/2003	46.5	0.01	12	18.4	0.03	96.7	2.05	0.26	6.2	13.4	6.8	-7.81	-58.1	-10.8	0.084	0.0068
Willow Spr- SSC	09/02/2003	40.8	0.02	Ŋ	13.2	0.02	48.1	1.63	0.16	5.3	6.8	9.6	-7.10		-7.66	0.056	BDL
Henry	10/30/2003	70.6	<0.01	7	27.9	<0.01	69.3	0.83	0.26	4.8	9.6	9.7	-6.36	-48.9	-6.96	0.195	0.0048
Ottawa-Fox R.	10/30/2003	65.9	0.03	10	42.0	<0.01	99.8	0.03	0.47	6.5	12.5	11.4	-5.82	-45.8	-4.58	0.091	0.0059
Ottawa-Illinois R.	10/30/2003	71.5	<0.01	7.5	25.7	<0.01	68.2	1.69	0.25	4.7	9.0	5.8	-6.85	-52.2	-7.94	QN	QN
Morris	10/30/2003	78.2	0.01	œ	27.4	<0.01	57.3	2.19	0.24	4.5	9.1	6.5	-6.84	-50.7	-7.91	0.204	0.0047
Joliet	10/30/2003	57.7	<0.01	8	20.6	0.02	90.4	2.02	0.25	4.7	8.1	5.4	-6.28	-48.1	-7.94	QN	QN
Willow Spr-Des Plaines	10/30/2003	66.1	0.12	15	26.3	<0.01	117	2.27	0.39	6.2	10.3	10.9	-6.25	-49.5	-9.97	0.091	0.0110
Willow Spr- SSC	10/30/2003	53.2	0.03	11	18.4	0.02	71.4	1.78	0.21	5.2	8.2	3.6	-5.86	-46.5	-7.17	0.083	0.0069
Henry	11/20/2003	77.0	0.01	10	30.5	0.011	73.5	3.05	0.31	6.1	7.6	6.4	-6.14	-43.2	-8.99	QN	QN
Ottawa-Fox R.	11/20/2003	66.7	0.03	9	37.3	0.114	62.1	1.69	0.54	5.9	6.2	6.6	-6.84	-48.0	-8.05	QN	QN
Ottawa-Illinois R.	11/20/2003	58.1	0.03	12	21.5	0.008	37.9	3.30	0.15	6.3	7.2	7.7	-7.32	-52.6	-9.34	QN	DN
Morris	11/20/2003	57.5	0.03	10	20.7	0.008	35.3	3.34	0.15	6.0	7.2	7.8	-7.24	-49.0	-9.69	QN	QN
Joliet	11/20/2003	42.5	0.05	10	14.6	0.024	54.1	2.18	0.15	7.6	6.7	7.5	-7.60	-51.8	-11.8	QN	QN
Willow Spr-Des Plaines	11/20/2003	52.7	0.03	7	19.6	0.015	77.0	2.26	0.23	5.4	8.2	6.8	-7.12	-49.8	-11.8	QN	QN
Willow Spr- SSC	11/20/2003	58.1	0.03	12	21.1	0.012	70.9	2.55	0.21	4.4	3.9	5.1	-7.83	-56.6	-9.57	QN	QN
Henry	02/17/2004	93.0	0.03	12	38.9	<0.01	109	2.42	0.31	5.1	9.4	6.9	-7.60	-48.0	-7.60	0.102	0.0039
Ottawa-Fox R.	02/17/2004	94.8	0.08	15	50.7	0.013	106	0.54	0.75	7.8	10.1	7.3	-7.66	-52.1	-7.63	0.074	0.0048
Ottawa-Illinois R.	02/17/2004	84.3	0.02	16	29.4	0.018	230	2.25	0.26	5.7	9.3	7.2	-7.50	-49.0	-7.43	QN	DN
Morris	02/17/2004	84.1	0.02	15	29.2	0.029	165	2.45	0.24	5.0	8.7	7.2	-7.50	-46.3	-7.80	0.117	0.0064
Joliet	02/17/2004	71.9	0.02	17	24.5	0.03	335	2.20	0.31	7.6	7.4	6.1	-6.44	-47.8	-7.55	QN	QN
Willow Spr-Des Plaines	02/17/2004	87.5	0.03	20	34.8	<0.03	290	0.93	0.44	8.1	11.8	6.5	-8.37	-47.8	-8.91	0.127	0.0114
Willow Spr-SSC	02/17/2004	61.1	0.04	18	20.4	<0.015	303	3.16	0.26	8.1	4.1	4.6	-6.42	-49.6	-7.03	0.121	0.0091

**Table 1.** Continued. Chemical data for surface water samples from the Illinois River and tributaries. Results in mg/L unless otherwise stated. ND = Not Determined.

Sample Location	Date	River Mile	⊢°	Hd	ORP √	DO	Sp Cond µS/cm	Alkalinity (CaCO <sub>3</sub> )	<u>ل</u> د	- O	Br	PO₄-P	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> -N	NH <sub>3</sub> -N	TKN	В	Ва
Henry	04/22/2004	195.5	16.9	8.30	473	9.5	890	201	0.4	117	<0.1	0.21	101	5.38	<0.01	3.27	0.05	0.042
Ottawa-Fox R.	04/22/2004	239	14.8	8.20	489	11.1	844	215	0.3	114	<0.1	<0.01	70.7	4.24	<0.01	3.12	0.03	0.089
Ottawa-Illinois R.	04/22/2004	240	18.0	8.20	487	11.5	976	199	0.5	133	<0.1	0.46	117	5.96	<0.01	3.01	0.18	0.037
Morris	04/22/2004	263.5	18.3	8.00	466	11.7	960	198	0.5	131	0.1	0.6	114	6.17	<0.01	4.06	0.07	0.032
Joliet	04/22/2004	286	17.2	7.50	481	7.7	1203	186	0.7	201	0.2	0.91	114	6.10	<0.01	4.90	0.18	0.025
Willow Spr-Des Plaines	04/22/2004	308	14.8	7.50	495	8.7	1168	166	0.4	215	0.3	0.51	84.6	3.44	<0.01	2.49	0.06	0.030
Willow Spr-SSC	04/22/2004	308	17.4	6.90	505	4.6	929	156	0.9	156	0.1	2.13	76.0	3.68	0.76	2.66	0.15	0.013
Henry	05/26/2004	195.5	20.5	7.71	DN	7.6	759	194	0.5	90.5	<0.1	<0.01	64.7	7.08	0.04	2.61	<0.02	0.048
Ottawa-Fox R.	05/26/2004	239	19.0	7.74	QN	7.2	644	195	<0.3	67.1	<0.1	<0.01	45.6	4.69	0.02	2.32	<0.02	0.061
Ottawa-Illinois R.	05/26/2004	240	21.1	7.54	DN	7.3	765	184	<0.3	95.9	<0.1	<0.01	70.3	6.05	<0.01	2.05	<0.02	0.033
Morris	05/26/2004	263.5	21.2	7.47	QN	6.9	732	182	<0.3	89.8	<0.1	<0.01	67.0	6.49	0.03	1.99	<0.02	0.033
Joliet	05/26/2004	286	19.1	7.26	QN	3.9	755	157	<0.3	118	<0.1	0.29	57.8	3.10	0.10	2.42	0.02	0.023
Willow Spr-Des Plaines	05/26/2004	308	17.7	7.41	DN	4.6	577	142	<0.3	81.3	<0.1	<0.01	36.6	2.31	0.04	1.59	<0.02	0.025
Willow Spr-SSC	05/26/2004	308	21.4	7.04	ND	4.0	887	149	0.6	148	<0.1	0.46	75.5	5.62	0.32	2.63	0.06	0.016
Fuller Lake Mgmt Area	08/04/2004	14	27.2	7.60	478	4.9	718	208	0.3	69.8	<0.1	0.19	64.7	1.64	0.06	0.70	0.04	0.062
Kampsville	08/04/2004	32	27.2	7.65	480	4.6	740	210	0.3	73.9	<0.1	0.23	66.5	1.68	0.10	0.76	<0.03	0.062
Florence	08/04/2004	56	27.7	7.45	500	5.0	730	207	0.3	75.0	<0.1	0.24	65.6	1.47	0.13	1.22	0.06	0.059
La Grange	08/04/2004	80	28.0	7.65	497	5.3	727	201	0.4	77.6	<0.1	0.17	67.4	1.50	0.09	1.27	0.06	0.057
Chandlerville-Sang. R.	08/04/2004	101	27.5	8.19	480	14.8	640	207	0.2	51.6	<0.1	0.04	55.3	0.44	0.05	1.01	0.12	0.058
Havana	08/04/2004	121	28.1	7.76	490	4.6	760	199	0.4	85.5	0.1	0.29	72.8	1.60	0.22	1.20	0.04	0.048
Pekin	08/04/2004	152.5	28.8	8.07	483	6.4	762	192	0.3	91.1	0.2	0.28	76.6	1.36	0.15	1.27	0.10	0.043
Fuller Lake Mgmt Area	10/21/2004	14	13.7	7.77	480	7.4	711	203	0.4	72.9	0.1	QN	76.6	1.79	0.04	1.17	0.14	0.057
Kampsville	10/21/2004	32	13.3	7.83	479	8.4	732	213	0.3	73.7	0.1	QN	80.4	1.86	0.04	1.40	0.14	0.060
Florence	10/21/2004	56	13.0	7.82	500	8.8	732	208	0.3	74.0	0.1	QN	81.8	1.93	0.03	1.38	0.14	0.057
La Grange	10/21/2004	80	12.6	7.87	472	8.6	756	211	0.3	78.0	0.2	QN	84.7	2.30	0.03	1.31	0.18	0.059
Chandlerville-Sang. R.	10/21/2004	101	14.0	7.20		6.5	509	168	0.2	40.3	<0.05	QN	38.2	3.18	0.04	1.24	0.07	0.049
Havana	10/21/2004	121	12.6	7.90	510	8.4	796	200	0.4	92.5	0.6	ND	93.9	2.13	0.04	1.23	0.20	0.046

Table 1. Continued.

ND = Not Determined.																	
Sample Location	Date	Ca⁺	Fe	¥+	$Mg^{2+}$	NN	Na⁺	Si	$\mathrm{Sr}^{2+}$	DOC	δ <sup>15</sup> N <sub>NO3</sub> δ <sup>15</sup> (%)	δ <sup>18</sup> O <sub>NO3</sub> - (‰)	δ <sup>18</sup> Ο (‰)	δD (‰)	δ <sup>13</sup> C <sub>DIC</sub> (‰)	Br <sup>–</sup> (INAA)	I <sup>–</sup> (INAA)
Henry	04/22/2004	77.0	<0.01	12	35.2	<0.01	60.1	0.29	0.26		9.6	8.6	-6.22	-44.5	-6.73	QN	QN
Ottawa-Fox R.	04/22/2004	69.1	0.03	11	39.6	0.19	53.5	1.43	0.42	9.9	8.3	8.7	-6.31	-44.0	-7.86	QN	DN
Ottawa-Illinois R.	04/22/2004	85.6	<0.01	<10	35.1	<0.01	78.8	0.74	0.27	7	8.8	7.6	-6.06	-43.9	-7.06	QN	DN
Morris	04/22/2004	78.0	<0.01	1	31.1	<0.01	70.8	0.99	0.25	6.3	8.3	8.1	-6.11	-45.8	-7.53	QN	QN
Joliet	04/22/2004	74.2	0.02	20	30.8	<0.01	116	1.36	0.29	8.2	8.9	6.5	-5.83	-44.4	-9.03	QN	DN
Willow Spr-Des Plaines	04/22/2004	64.0	0.02	16	27.4	0.02	118	1.14	0.29	9.2	10.3	9.2	-5.80	-42.3	-10.72	QN	DN
Willow Spr-SSC	04/22/2004	53.1	0.04	17	18.4	0.03	90.5	1.81	0.21	10.5	7.2	7.3	-5.90	-46.1	-9.16	QN	DN
Henry	05/26/2004	72.8	0.01	<10	31.3	<0.003	47.8	3.18	0.23	7.3	7.1	7.3	-5.46	-39.5	-9.37	0.121	0.0040
Ottawa-Fox R.	05/26/2004	64.3	0.02	<10	30.2	0.004	32.4	3.74	0.29	12.4	7.1	7.9	-5.29	-39.4	-10.54	0.055	0.0049
Ottawa-Illinois R.	05/26/2004	70.2	<0.01	<10	28.0	0.007	51.9	3.31	0.19	5.6	7.1	7.5	-5.33	-39.8	-9.92	0.120	0.0070
Morris	05/26/2004	69.2	<0.01	<10	27.3	0.01	47.4	3.56	0.19	6.2	7.1	7.8	-5.43	-37.5	-9.99	0.107	0.0054
Joliet	05/26/2004	55.5	0.02	<10	22.3	0.021	67.8	3.14	0.19	7.9	9.2	7.9	-4.73	-34.0	-12.24	0.101	0.0098
Willow Spr-Des Plaines	05/26/2004	45.0	0.03	<10	19.4	0.011	42.1	3.35	0.14	8.4	7.9	8.4	-4.66	-32.8	-13.02	0.059	0.0073
Willow Spr-SSC	05/26/2004	56.3	0.03	<10	20.3	0.016	88.7	2.67	0.23	7.0	8.7	6.1	-4.97	-36.7	-9.66	0.130	0.0135
Fuller Lake Mgmt Area	08/04/2004	66.6	<0.01	4	31.4	0.011	43.3	2.03	0.20	4.4	10.8	8.5	-5.17	-40.1	-7.90	0.136	0.0098
Kampsville	08/04/2004	67.7	<0.01	9	31.6	0.04	45.9	2.07	0.21	4.6	11.2	8.4	-5.16	-38.5	-7.88	0.126	0.0100
Florence	08/04/2004	66.5	<0.01	ß	31.4	<0.001	46.9	2.10	0.21	4.8	11.7	6.8	-5.09	-40.2	-7.87	0.122	0.0097
La Grange	08/04/2004	66.2	<0.01	Ŋ	30.9	0.003	48.2	1.95	0.22	5.5	11.6	7.8	-5.12	-41.8	-8.23	0.129	0.0079
Chandlerville-Sang. R.	08/04/2004	56.0	<0.01	Ð	36.8	0.004	33.0	1.44	0.12	2.9	22.5	18.5	-5.76	-42.6	-5.61	060.0	0.0103
Havana	08/04/2004	65.7	<0.01	9	28.8	0.005	52.9	1.91	0.22	5.1	12.8	8.8	-5.03	-41.1	-7.45	0.148	0.0072
Pekin	08/04/2004	65.1	<0.01	7	28.6	<0.001	57.3	1.26	0.23	5.3	14.4	9.5	-5.11	-42.3	-6.93	0.156	0.0096
Fuller Lake Mgmt Area	10/21/2004	72.5	<0.01	ß	29.7	0.005	51.5	2.82	0.21	QN	11.0	7.3	-5.91	-40.5	-8.32	QN	DN
Kampsville	10/21/2004	75.5	<0.01	7	30.6	0.003	52.1	2.94	0.21	QN	11.0	7.2	-5.51	-39.6	-8.17	QN	QN
Florence	10/21/2004	74.2	<0.01	4	30.5	0.001	53.4	3.03	0.22	QN	11.0	7.7	-5.56	-38.5	-8.37	QN	QN
La Grange	10/21/2004	77.1	<0.01	9	31.9	0.004	57.7	3.23	0.21	QN	10.2	7.1	-5.73	-40.2	-8.38	QN	QN
Chandlerville-Sang. R.	10/21/2004	55.0	0.02	9	23.1	0.012	29.0	3.9	0.10	QN	9.7	9.5	-7.29	-45.1	-8.85	QN	DN
Havana	10/21/2004	76.7	<0.01	4	31.8	0.004	66.3	2.45	0.25	DN	11.6	6.3	-5.28	-39.7	-7.85	QN	ND

**Table 1.** Continued. Chemical data for surface water samples from the Illinois River and tributaries. Results in mg/L unless otherwise stated. ND = Not Determined.

Sample Location	Date	River Mile	⊢°	Hd	ORP mV	DO	Sp Cond µS/cm	Alkalinity (CaCO <sub>3</sub> )	Ĺ	CI-	Br	PO₄-P	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> -N	NH <sub>3</sub> -N	TKN	в	Ba
Kampsville	12/09/2004	32	8.1	8.07	DN	6.5	555	191	0.29	40.5	<0.01	<0.01	41.0	4.75	0.15	1.31	<0.01	0.05
Florence	12/09/2004	56	8.3	8.03	DN	6.4	556	193	0.23	40.3	<0.01	<0.01	41.7	4.74	0.14	1.27	<0.01	0.05
La Grange	12/09/2004	80	6.9	8.04	DN	8.6	578	201	0.29	41.8	<0.01	<0.01	42.3	4.89	0.10	1.17	<0.01	0.05
Chandlerville-Sang. R.	12/09/2004	101	8.7	7.88	DN	6.1	498	185	0.27	27.5	<0.01	<0.01	27.3	4.88	0.08	1.14	<0.01	0.06
Havana	12/09/2004	121	7.0	8.13	DN	9.5	639	201	0.24	53.7	<0.01	<0.01	51.4	5.86	0.12	1.31	0.04	0.05
Pekin	12/09/2004	152.5	6.8	7.98	DN	9.9	681	208	0.26	61.8	<0.01	<0.01	58.0	5.60	0.16	2.43	0.05	0.04
Pekin	02/09/2005	152.5	3.6	8.00	DN	10.0	873	223	0.25	118	<0.01	0.18	78.6	4.23	0.21	1.08	0.10	0.03
Havana	02/09/2005	121	4.1	7.86	QN	10.2	784	209	0.23	98.4	<0.01	0.18	69.6	4.51	0.17	1.13	0.12	0.07
Kampsville	02/10/2005	32	з.1	8.11	DN	QN	711	212	0.23	78.1	<0.01	0.17	64.0	4.69	0.12	0.96	0.10	0.02
Florence	02/10/2005	56	3.2	8.04	QN	QN	722	217	0.22	80.0	<0.01	0.10	65.2	4.77	0.13	1.10	0.10	0.08
La Grange	02/10/2005	80	3.5	7.97	DN	11.6	747	218	0.23	87.8	<0.01	<0.01	69.6	4.46	0.15	1.03	0.12	0.08
Chandlerville-Sang. R.	02/10/2005	101	4.3	7.80	QN	QN	590	221	0.20	41.2	<0.01	0.23	37.9	9.91	0.07	0.93	0.20	0.08
Kampsville	04/25/2005	32	15.6	7.80	DN	8.9	674	198	0.20	72.1	<0.01	<0.01	65.0	3.34	0.10	1.47	0.10	QN
Florence	04/25/2005	56	14.8	8.10	QN	QN	668	198	0.22	69.6	<0.01	<0.01	64.5	3.71	0.07	0.98	0.10	QN
LaGrange	04/25/2005	80	13.7	7.70	DN	9.6	579	167	0.22	56.2	<0.01	<0.01	54.3	4.78	0.09	1.33	<0.01	QN
Chandlerville-Sang. R.	04/25/2005	101	13.5	8.04	QN	13.5	756	265	0.21	68.1	<0.01	0.76	59.6	4.82	<0.01	2.04	0.10	QN
Havana	04/25/2005	121	12.8	8.26	QN	8.9	776	209	0.25	91.3	<0.01	0.27	75.9	3.78	0.08	2.11	0.10	QN
Pekin	04/25/2005	152.5	11.9	8.38	DN	9.7	818	219	0.29	99.9	<0.01	0.37	80.9	3.68	0.06	1.23	0.12	QN
Kampsville	05/26/2005	32	22.8	8.20	DN	9.4	779	210	0.12	87.3	<0.01	<0.01	80.3	3.07	<0.01	0.81	0.15	0.02
Florence	05/26/2005	56	22.4	8.30	QN	8.4	801	225	0.35	92.0	<0.01	<0.01	82.3	3.19	<0.01	0.41	0.09	QN
LaGrange	05/26/2005	80	22.2	8.20	DN	8.0	804	214	0.32	94.0	<0.01	<0.01	82.9	3.05	<0.01	0.33	QN	QN
Chandlerville-Sang. R.	05/26/2005	101	21.1	8.20	ΔN	8.6	646	243	0.25	45.3	<0.01	<0.01	49.1	3.88	<0.01	1.23	0.08	QN
Havana	05/26/2005	121	21.8	8.40	QN	QN	864	223	0.37	107	<0.01	<0.01	91.8	2.69	0.02	1.58	<0.01	0.05
Pekin	05/26/2005	152.5	22.0	8.00	DN	QN	861	225	0.35	108	<0.01	<0.01	94.4	2.33	0.06	0.97	0.47	0.04

Table 1. Continued.

Comple Location	Dato	C.2+	с Ц	÷ Ł	NA~2+	A Lo		ü	O*2+			A180	1	ŪŸ	A130	ļ	<u>-</u>
	רמופ	Ď	D -	<	л М			5	5	222	(%)	(%) (%)	ء (%)	(%)	(%)	(INAA)	(INAA)
Kampsville	12/09/2004	56.4	0.041	7.7	26.3	0.005	21.0	4.36	0.14	4.3	5.9	7.7	-7.09	-53.0	-8.42	0.068	0.0043
Florence	12/09/2004	57.8	0.039	5.0	26.5	0.057	23.4	4.34	0.21	4.4	5.9	7.0	-6.93	-54.0	-8.36	0.057	0.0042
La Grange	12/09/2004	59.8	<0.01	5.9	28.2	0.003	22.7	4.33	0.15	4.2	6.1	7.4	-6.98	-52.2	-8.33	0.061	0.0031
Chandlerville-Sang. R.	12/09/2004	52.6	<0.01	6.8	25.7	<0.001	12.1	4.9	0.11	4.3	5.0	7.4		-53.4	-8.31	0.041	0.0034
Havana	12/09/2004	62.4	0.057	5.3	28.4	0.062	31.3	3.87	0.23	4.5	6.4	7.4	-6.84	-50.4	-8.30	0.080	0.0037
Pekin	12/09/2004	65.7	<0.01	6.8	29.9	<0.001	37.9	3.82	0.19	5.0	7.0	8.6	-6.68	-51.9	-8.22	0.087	0.0046
Pekin	02/09/2005	71.1	<0.01	5.1	30.3	0.044	59.6	2.18	0.23	4.4	6.8	6.9	-7.51	-53.3	-8.72	QN	QN
Havana	02/09/2005	70.2	<0.01	5.5	29.7	0.008	63.5	1.83	0.25	4.5	7.6	7.2	-7.41	-46.6	-9.02	QN	QN
Kampsville	02/10/2005	70.3	<0.01	9.5	31.2	0.024	47.9	2.36	0.37	4.0	7.2	7.6	-7.49	-53.2	-9.02	QN	QN
Florence	02/10/2005	70.4	<0.01	4.5	31.0	0.010	50.2	2.57	0.05	3.9	7.2	7.1	-7.37	-52.6	-8.72	QN	QN
La Grange	02/10/2005	71.7	<0.01	5.4	31.4	0.033	53.0	2.59	0.05	4.0	7.4	7.1	-7.50	-53.0	-8.74	QN	DN
Chandlerville-Sang. R.	02/10/2005	56.3	<0.01	5.1	30.2	0.030	31.2	2.67	0.07	2.5	6.1	6.0	-7.25	-43.7	-7.96	QN	QN
Kampsville	04/25/2005	70.4	<0.01	4.5	31.0	0.010	50.2	2.57	0.05	QN	7.4	7.3	-6.23	-43.4	-8.20	0.065	0.0093
Florence	04/25/2005	70.2	<0.01	5.5	29.7	0.008	63.5	1.83	0.25	QN	6.7	6.9	-6.25	-43.8	-8.23	0.068	0.0111
LaGrange	04/25/2005	71.4	<0.01	7.1	33.1	<0.001	61.4	2.03	0.19	QN	5.0	6.3	-6.29	-41.4	-8.70	0.051	0.0077
Chandlerville-Sang. R.	04/25/2005	70.3	<0.01	9.5	30.3	0.044	59.6	1.97	0.23	QN	8.0	7.4	-6.1	-41.8	-7.56	0.061	0.0089
Havana	04/25/2005	70.2	<0.01	5.5	29.7	0.008	63.5	2.31	0.25	QN	8.3	7.4	-6.55	-44.6	-7.73	0.085	0.0084
Pekin	04/25/2005	71.7	<0.01	5.4	31.2	0.024	47.9	2.55	0.37	QN	9.0	7.7	-6.39	-46.5	-7.56	0.087	0.0101
Kampsville	05/26/2005	68.1	0.058	5.0	28.2	0.050	21.0	2.22	0.09	5.7	10.7	7.5	-5.61	-42.7	-7.16	QN	QN
Florence	05/26/2005	68.1	<0.01	6.0	30.3	0.040	48.0	2.16	0.07	5.4	10.9	8.5	-5.84	-42.2	-7.27	QN	QN
LaGrange	05/26/2005	72.5	<0.01	6.0	32.7	0.020	52.0	3.88	0.05	5.2	11.4	7.7	-5.69	-43.1	-7.40	QN	QN
Chandlerville-Sang. R.	05/26/2005	68.5	<0.01	5.0	30.8	0.010	46.0	4.15	0.04	2.6	9.5	8.0	-5.92	-41.2	-7.62	QN	QN
Havana	05/26/2005	59.8	<0.01	6.0	28.2	0.003	23.0	4.34	0.15	5.6	12.6	7.5	-5.47	-42.8	-7.40	QN	QN
Pekin	05/26/2005	65.7	<0.01	7.0	29.9	<0.001	38.0	3.82	0.19	6.0	13.1	8.3 0	-5.86	-42.5	-7.38	QN	DN

**Table 1.** Continued. Chemical data for surface water samples from the Illinois River and tributaries. Results in mg/L unless otherwise stated. ND = Not Determined.

Table 1. Chemical data for surface water samples from the Illinois River and tributaries. Results in mg/L unless otherwise stated. ND = Not Determined.	ta for surface w	/ater sa	mples t	rom th	e Illino	is Rive	r and tri	butarie:	s. Rest	ults in r	ng/L ur	less ot	herwis	e state	d. ND =	Not De	termine	.p	
Sample Location	Date	River Mile	гô	Hd	ORP MV	DO	Sp Cond μS/cm	Alkalinity (CaCO <sub>3</sub> )	D <sub>3</sub> ) F	- -		Br	PO₄-P	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> -N	NH <sub>3</sub> -N	TKN	В	Ba
Joliet	08/08/2005	286	32.1	7.48	DN	6.2	704	129	0.6				3.9	66.2	4.37	0.36	1.00	0.10	0.03
Willow Spr-Des Plaines	08/08/2005	308	26.6	7.56	QN	5.2	1,103	135	0.73	73 185		0.15	4.3	112	7.41	0.10	0.92	0.32	0.04
Willow Spr-SSC	08/08/2005	308	30.1	7.20	QN	5.4	604	117	0.6				3.0	54.6	5.44	0.24	1.80	0.10	0.02
Chandlerville-Sang. R.	08/09/2005	101	30.6	8.79	QN	DN	791	169	0.5		•	-	0.01	99.3	<0.01	<0.01	0.83	0.01	0.05
Havana	08/09/2005	121		8.53	QN	9.1	810	184	0.5				1.7	93.2	1.09	0.05	0.70	<0.01	0.02
Pekin	08/09/2005	152.5	33.0	8.60	QN	11.7	800	184	0.5				1.9	93.7	0.83	0.23	1.12	0.01	0.05
Henry	08/09/2005	195.5		8.79	QN	8.6	745	135	0.5			-	0.01	94.8	1.69	0.27	4.86	0.01	0.03
Ottawa-Fox R.	08/09/2005	239		9.12	QN	14.0	950	169	0.5		•	-	0.01	62.3	<0.01	0.01	1.71	0.01	0.01
Ottawa-Illinois R.	08/09/2005	240		8.35	DN	10.2	681	137	0.5				1.9	87.9	2.21	0.08	0.62	<0.01	0.04
Morris	08/09/2005	263.5	31.4	7.80	QN	8.0	698	126	0.5				2.2	78.9	3.18	0.06	3.02	0.01	0.08
Wilmington-Kank. R.	08/09/2005	273		7.85	DN	7.5	537	120	0.1				0.01	107	0.31	0.12	2.06	0.01	0.03
Fuller Lake Mgmt Area	08/10/2005	14		8.46	QN	7.6	809	213	0.5				1.2	89.3	0.53	0.06	0.91	0.01	0.04
Kampsville	08/10/2005	32	29.9	8.49	DN	10.1	788	194	0.4				1.2	87.5	0.58	0.09	0.92	<0.01	0.05
Florence	08/10/2005	56		8.71	QN	10.2	792	181	0.5				1.3	91.0	0.87	0.05	0.75	0.05	0.06
LaGrange	08/10/2005	80	30.1	8.70	DN	7.6	802	175	0.5				1.3	92.4	1.00	0.08	0.72	<0.01	0.06
Sample Location	Date	Ca <sup>2+</sup>	Fe	¥	Mg²₁		Mn N	Na⁺ 3	SiS	Sr <sup>2+</sup> D	DOC 01	δ <sup>15</sup> Ν <sub>NO3</sub> δ <sup>18</sup>	<sup>8-</sup> δ <sup>18</sup> Ο <sub>NO3</sub> -	δ <sup>18</sup> Ο	δD	δ <sup>13</sup> C <sub>DIC</sub>	Br	-	
												(00)	(00)	(%)		~	INAA)	(INAA)	
Joliet	08/08/2005	70.2	<0.01		5 29.	<ol> <li>0.</li> </ol>											0.158	0.0211	
Willow Spr-Des Plaines	08/08/2005	55.5	<0.03	·											1		0.198	0.0319	
Willow Spr-SSC	08/08/2005	70.3	<0.01	9.5	5 31.2				2.36 0	0.37	5.3	6.9	3.7 -	-5.16 -	-44.8	-6.17	0.152	0.0174	
Chandlerville-Sang. R.	08/09/2005	59.8	<0.01														0.088	0.0179	
Havana	08/09/2005	65.7	<0.01														0.150	DN	
Pekin	08/09/2005	71.1													-34.0		0.218	0.0276	
Henry	08/09/2005	70.2													-36.8		0.150	DN	
Ottawa-Fox R.	08/09/2005	70.3													-35.8		0.139	0.0270	
Ottawa-Illinois R.	08/09/2005	71.4													-36.5		0.280	0.0178	
Morris	08/09/2005	70.2	<0.01		3 29.7		<0.007 5	53.8 2.							-39.3	-6.92	0.140	DN	
Wilmington-Kank. R.	08/09/2005	71.7	<0.01												-40.8		0.145	0.0099	
Fuller Lake Mgmt Area	08/10/2005	68.5	<0.01			-									-33.1		0.130	DN	
Kampsville	08/10/2005	71.3	<0.01		2 38.2	-	<0.007 5				-				-33.0	-7.03	0.178	0.2730	
Florence	08/10/2005	72.5	<0.01	7.7		-	007 6	3.9 4		.11	5.1				-35.5		0.174	0.0250	
LaGrange	08/10/2005	68.1	<0.01				007 6	i6.5 3		.12	5.2				-34.9		0.140	ND	

		Iable 2. Otheritical data for various source waters to tite		כם יימור	2010			יטווס ייי יייארי			אוסס סומוי	1						
Sample	Sample	Date	⊢	Hd	ORP	DO	Sp Cond	Alkalinity	۱Ŀ	- U	Br	PO,-P	SO <sup>2-</sup>	NO <sup>-</sup> ON	NH <sub>-</sub> -N	TKN	В	Ba
Location	Type		ů		л Ч		μS/cm	(CaCO <sub>3</sub> )				t	t	D.	2			
Big Ditch	tile	10/30/2003	14.2	7.55	493	6.2	763	281	<0.5	17.8	<0.1	<0.1	75.3	12.2	<0.01	1.18	<0.01	0.054
Big Ditch	tile	11/20/2003	12.4	7.02	504	7.4	696	241	0.2	15.1	<0.1	0.2	74.4	12.1	0.03	3.04	<0.01	0.050
<b>Big Ditch</b>	tile	02/17/2004	4.7	7.33	527	13.8	706	250	0.1	14.2	<0.1	<0.1	81.1	11.4	0.02	3.36	0.03	0.041
Big Ditch	tile	04/22/2004	9.3	7.20	498	12.7	687	247	0.2	15.4	<0.1	<0.01	82.3	13.2	0.03	4.31	<0.02	0.043
<b>Big Ditch</b>	tile	05/26/2004	13.5	6.83	QN	6.8	711	250	<0.3	14.5	<0.1	<0.01	81.8	15.3	<0.01	4.10	<0.02	0.047
Big Ditch	tile	09/09/2004	QN	QN	QN	ND	ND	276	0.2	13.2	<0.1	<0.1	86.4	12.1	<0.01	1.89	0.04	0.058
Wolf Lake	ppt	Aug/2003	ND	6.38	QN	ND	23	4	0.2	0.3	<0.1	QN	2.50	0.69	0.66	1.04	<0.01	<0.001
Wolf Lake	ppt	Sep/2003	QN	6.53	QN	ND	13	ND	0.3	0.3	<0.1	QN	2.47	0.21	0.30	0.35	<0.01	<0.001
Wolf Lake	ppt	Oct/2003	DN	6.24	QN	ND	32	ND	<0.5	0.5	<0.1	<0.01	3.90	0.44	0.42	0.72	DN	QN
Wolf Lake	ppt	Nov/2003	QN	6.77	QN	ND	15	4	<0.1	0.3	<0.1	QN	2.60	0.21	0.24	0.24	<0.01	<0.001
Wolf Lake	ppt	Apr/2004	QN	QN	QN	ND	ND	14	<0.3	1.8	<0.1	<0.01	4.40	0.12	0.04	0.67	<0.02	0.008
Wolf Lake	ppt	05/04/2004	QN	QN	QN	ND	ND	8	<0.3	1.2	<0.1	<0.01	11.3	0.05	BDL	1.86	<0.02	0.010
Wolf Lake	ppt	05/31/2004	Q	QN	QN	DN	ND	8	<0.1	0.3	1.1	<0.01	2.10	<0.02	1.14	2.03	<0.02	0.015
Wolf Lake	ppt	06/11/2004	QN	QN	QN	ND	ND	10	<0.1	0.2	1.2	<0.01	2.90	<0.02	0.42	0.58	<0.02	0.009
Wolf Lake	ppt	06/16/2004	QN	QN	DN	ND	DN	9	<0.1	0.1	<0.1	<0.01	1.80	<0.02	0.02	0.21	<0.02	0.003
Wolf Lake	ppt	07/07/2004	QN	QN	QN	ND	DN	11	<0.1	0.2	<0.1	<0.01	2.40	<0.02	0.10	0.14	<0.02	0.009
Wolf Lake	ppt	Aug/2004	ND	6.74	QN	ND	21	0	<0.1	0.3	<0.05	QN	2.80	0.20	0.11	0.11	<0.01	0.008
Wolf Lake	ppt	Sep/2004	QN	6.89	QN	ND	24	11	<0.1	0.2	<0.05	DN	2.50	<0.01	0.03	0.34	<0.01	0.006
Bondville	ppt	Oct/2004	QN	QN	QN	ND	ND	ო	<0.1	0.2	<0.1	QN	1.60	0.17	0.12	0.20	<0.01	<0.001
Bondville	ppt	Nov/2004	QN	QN	QN	ND	ND	7	0.01	0.01	<0.01	<0.01	1.36	0.16	0.34	0.34	<0.01	<0.001
Bondville	ppt	Dec/2004	QN	QN	QN	ND	ND	-	0.24	0.04	<0.01	QN	0.86	0.09	0.15	0.15	<0.01	0.021
Bondville	ppt	Jan/2005	QN	ND	ND	ND	DN	N	<0.01	0.19	<0.01	ND	1.26	0.20	0.21	0.39	<0.01	0.006
Bondville	ppt	Feb/2005	QN	ΟN	DN	ND	ND	-	<0.01	0.09	<0.01	DN	<0.01	0.02	0.16	0.78	<0.01	0.014
Bondville	ppt	Mar/2005	ND	ΠD	ND	ND	DN	0	<0.01	0.14	<0.01	ND	<0.01	<0.01	0.38	0.55	<0.01	0.019
Bondville	ppt	Apr/2005	DN	ND	DN	ND	DN	-	<0.01	0.23	<0.01	<0.01	2.14	0.31	0.50	0.55	<0.01	<0.001
Bondville	ppt	Jun/2005	QN	QN	DN	ND	ND	0	<0.01	0.15	<0.01	QN	12.0	0.65	0.75	1.24	<0.034	<0.004
Bondville	ppt	Jul/2005	ΩN	6.42	ND	ND	23	0	0.01	0.09	<0.01	ND	2.85	0.36	0.36	0.36	<0.034	<0.004
Bondville	ppt	Aug/2005	DN	ND	ΠD	ND	ND	0	<0.01	0.06	<0.01	ND	1.65	0.21	ND	ND	<0.034	<0.004

Table 2. Chemical data for various source waters to the Illinois River. Results in mg/L unless otherwise stated. ND = Not Determined.

Sample	Sample	Date	Ca <sup>2+</sup>	Ъе	¥	$Mg^{2+}$	Mn	Na <sup>2+</sup>	Si	$Sr^{2+}$	DOC	$\delta^{15}N_{NO3^{-}}$	δ <sup>18</sup> Ο <sub>NO3</sub> -	Q <sup>18</sup> Ο	δD	$\delta^{13}C$	Br	<u> </u>
Location	Type											(%)	(00)	(%)	(%)	(%)	(INAA)	(INAA)
Big Ditch	tile	10/30/2003	104		сч ~	43.8	<0.01	7.5	5.81	0.14	1.1	11.2		-6.49	-41.9	-7.44	0.0178	BDL
Big Ditch	tile	11/20/2003	93.9		-	40.2	<0.001	7.4	5.05	0.13	2.3	9.2		-6.34	-40.0	-8.20	<0.1	QN
Big Ditch	tile	02/17/2004	91.5		÷	38.8	<0.02	6.8	4.1	0.12	1.6	10.0		-6.85	-38.8	-7.96	0.151	BDL
Big Ditch	tile	04/22/2004	88.9		80	37.4	<0.01	6.8	4.26	0.12	1.5	9		-6.56	-42.9	-7.66	<0.1	QN
Big Ditch	tile	05/26/2004	91.6		<10	38.8	<0.003	7.0	4.8	0.13	1.9	7.7		-6.51	-42.2	-7.31	<0.1	DN
Big Ditch	tile	09/09/2004	98.6		ī	42.9	<0.001	9.4	9	0.14	QN	12.4		-6.29	-41.4	-8.54	ΟN	QN
Wolf Lake	ppt	Aug/2003	1.84	<0.01	4>	0.45	0.03	0.2	<0.01	<0.01	2.3	-1.4		QN	DN	QN	0.009	0.0026
Wolf Lake	ppt	Sep/2003	0.91		4>	0.24	0.01	0.3	0.19	0.01	0.8	-4.1		QN	-57.2	QN	<0.1	QN
Wolf Lake	ppt	Oct/2003	2.44		4	0.64	0.02	0.2	QN	QN	1.5	-1.6		-7.93	-84.0	QN	<0.1	QN
Wolf Lake	ppt	Nov/2003	1.46		<5	0.37	0.01	0.2	0.05	<0.01	1.5	1.2	•	-12.0	-49.8	QN	<0.1	QN
Wolf Lake	ppt	Apr/2004	3.82		<10	0.85	0.008	1.3	0.39	0.01	4.8	-1.5		-2.88	-21.6	QN	0.0062	0.0037
Wolf Lake	ppt	5/4/2004	5.16		<10	0.59	0.006	0.9	0.29	0.01	4.6	-1.5		-3.54	-21.7	QN	0.0057	0.0032
Wolf Lake	ppt	05/31/2004	1.74		ო	0.36	0.025	0.5	0.2	<0.01	QN	0.4		-4.41	-19.4	QN	<0.1	QN
Wolf Lake	ppt	06/11/2004	2.14		ო	0.835	0.015	<0.1	0.33	<0.01	QN	0.4		-6.70	-44.6	QN	<0.1	QN
Wolf Lake	ppt	06/16/2004	1.26		4	0.47	<0.001	<0.1	0.22	<0.01	QN	ND		-5.38	-33.3	QN	<0.1	QN
Wolf Lake	_	07/7/2004	2.93		ო	0.97	<0.001	<0.1	0.65	0.01	QN	ND		-5.50	-28.3	QN	<0.1	QN
Wolf Lake		Aug/2004	2.44		8	0.67	0.01	0.16	0.34	<0.01	QN	3.0		QN	-26.5	QN	DN	QN
Wolf Lake		Sep/2004	3.05		8	0.83	0.003	0.11	0.47	0.01	QN	ND		QN	-39.8	QN	DN	QN
Bondville	ppt	Oct/2004	0.18		8	0.04	<0.001	0.18	<.02	<0.001	1.4	1.2		QN	-54.2	QN	0.0023	0.0014
Bondville	ppt	Nov/2004	0.41		3.8	0.1215	<0.001	0.35	0.03	<0.001	1.9	0.4		QN	-71.6	QN	0.0032	0.0011
Bondville	ppt	Dec/2004	3.36		2.4	0.96	0.004	0.09	0.38	<0.005	0.7	DN		-10.3	-80.1	QN	<0.002	<0.0010
Bondville	ppt	Jan/2005	3.05		2.0	0.83	<0.001	0.11	0.47	<0.005	1.4	QN		-10.1	DN	QN	0.0025	0.0014
Bondville	ppt	Feb/2005	2.27		1.9	0.77	<0.001	0.09	0.02	<0.005	6.0	QN		QN	-60.7	QN	0.0027	0.0011
Bondville	ppt	Mar/2005	2.89		2.2	1.14	0.004	0.11	0.04	<0.005	1.9	DN		QN	-67.5	QN	0.0032	0.0015
Bondville	ppt	Apr/2005	0.41		3.8	0.122	<0.001	0.17	0.03	<0.005	1 2	-4.2		QN	-28.6	QN	0.0062	0.0026
Bondville	ppt	Jun/2005	0.39		<8.24	<0.050	<0.007	<0.496	<0.104	<0.005	4.7	DN		QN	-39.6	QN	0.0048	0.0019
Bondville	ppt	Jul/2005	0.43		<8.24	0.0696	<0.007	<0.496	<0.104	<0.005	1.4	QN		QN	-6.8	QN	0.0032	0.0012
Bondville	ppt	Aug/2005	1.74		<8.24	0.0546	<0.007	<0.496	<0.104	<0.005	1.9	-6.8		QN	-42.6	QN	0.0032	0.0017

Table 2. Continued.

Table 2. Continued. Chemical data for various source waters to the Illinois River. Results in mg/L unless otherwise stated. ND = Not Determined.	led. Chen	nical data for	various	s sourc	e wate	rs to th	e Illinois F	liver. Re	sults in	mg/L	unless	otherwis	e stated	. ND = I	Not Det	erminec		
Sample Location	Sample Type	Date	⊢°	Hd	ORP MV	8	Sp Cond µS/cm	Alkalinity (CaCO <sub>3</sub> )	۱L	Ģ	Br	PO₄-	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> -N	NH <sub>3</sub> -N	TKN	B Ba	I
Calumet WWTP	WWT WWT	01/13/2005 08/08/2005	UN 1 92	ND 7 26	Q Q	Q Q	950 840	119 152	0.57 0.8	222 120	<0.01	2.01 12 1	76.1 89.5	6.54 7 10	0.12 0.02	0.16 0 6.90 0	0.06 0.018	8 -
Calumet WWTP	TWW	09/02/2004	QN	ND	QN	ND	1,056	180	0.8	145	0.4	ND	107	7.48	0.14		-	. v
Stickney WWTP	TWW	09/30/2004	22.4	6.66	505	7.4	1,075	128	1.3	137	0.2	QN	158	11.5	0.31		-	3
Stickney WWTP	TWW	01/13/2005	QN	QN	QN	DN	929	103	0.6	209	<0.01	<0.01	59.5	3.77	0.03		-	5
Stickney WWTP	TWW	08/08/2005	26.6	7.18	QN	DN	758	134	0.9	114	0.09	6.7	69.7	7.95	0.10		-	0
Peoria WWTP	TWW	02/10/2005	12.0	7.67	QN	DN	1,681	395	0.63	291	<0.01	1.50	108	3.32	2.23		-	с С
Peoria WWTP	TWW	06/28/2005	26.9	7.61	QN	ND	1,853	287	0.73	176	<0.01	<0.01	104	4.92	0.62			
Peoria WWTP	TWW	08/09/2005	29.6	7.96	DN	9.9	1,955	438	0.92	239	0.29	4.7	163	2.39	0.49	-	0.36 0.11	0
Sample	Sample	Date	Ca <sup>2+</sup>	Ге	¥	Mg²⁺	™	Na⁺	Si	$Sr^{2+}$	DOC	δ <sup>15</sup> Ν <sub>NO3</sub> -		δ <sup>18</sup> Ο	δD	δ <sup>13</sup> C <sub>D1</sub>		
Location	Type											(%)	(0%)	(%)	(%)	(00)	(INAA)	(INAA)
Calumet WWTP	TWW	01/13/2005	51.3	<0.01				118.3	2.83	0.19	7.3	15.0	4.2	-8.90	-64.7	-	0.385	0.0142
Calumet WWTP	TWW	08/08/2005	61.8	0.04	•			99.1	3.09	0.22	ND	9.6	2.7	QN	·			-
Calumet WWTP	TWW	09/02/2004	70.3	0.03				126.0	3.72	0.24	DN	8.2	8.1	-5.82	Ċ			-
Stickney WWTP	TWW	09/30/2004	60.0	0.04				154.0	4.86	0.23	DN	7.8	3.7	QN	·			-
Stickney WWTP	TWW	01/13/2005	40.9	<0.01	10.2	16.2	<0.001	123.8	2.02	0.18	4.4	3.6	3.4	-9.66	·	) -9.94		-
Stickney WWTP	TWW	08/08/2005	56.3	0.03	•			83.2	2.69	0.24	ND	6.5	1.9	QN	·			
Peoria WWTP	TWW	02/10/2005	70.3	0.05				126.4	3.72	0.24	10.3	8.6	3.2	QN	·			-
Peoria WWTP	TWW	06/28/2005	61.3	<0.01				44.6	2.68	0.05	12.0	15.1	7.5	Q	Ċ			-
Peoria WWTP	TWW	08/09/2005	99.2	0.05				294.5	6.28	0.24	ΩN	15.5	0.6	QN	·			



Figure 10. Saline water runoff from a bridge crossing the Des Plaines River in Western Springs, February 2005.

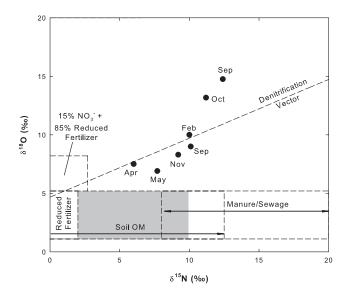


Figure 12. Nitrate isotope values for tile drain samples showing relative to denitrification vectors. Samples identified by sample date.

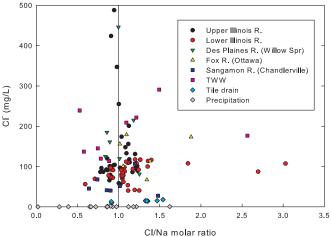


Figure 11. Chloride vs. Cl/Na molar ratio showing that most river water samples cluster around a vertical line defined by halite. Tile drain samples tend to have greater Cl/Na ratios and fall to the right of the halite line.

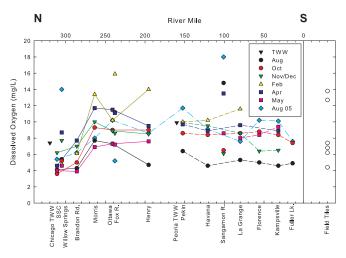
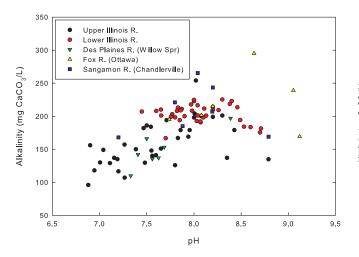


Figure 13. Dissolved oxygen in river water, TWW, and tile samples.

promote algal blooms that consume DO (Table 1). Degradation of organic matter from TWW would also consume DO. Continual or periodic low DO concentrations are known to be deleterious to aquatic organisms; concentrations less than 3 mg/L are stressful and less than 2 mg/L are defined as hypoxic (SCDNR 2004), potentially killing all aquatic vertebrates and invertebrates. The sampling site at the Brandon Road Lock and Dam in Joliet was located just above the spillway; the spillway itself is probably responsible for significant aeration of the river. Substantially higher DO concentrations were measured downstream at Morris. The highest DO concentrations measured in this study were in the Sangamon River during the summer, when benthic algae production of oxygen can exceed respiration resulting in the water being supersaturated with DO.

Alkalinity and pH tend to covary (as would be expected) in the Illinois River samples (Figure 14), and both increased with distance from the Chicago area to Pekin after which the values seems to level off to the confluence with the Mississippi River (Figure 15). The lowest pH and alkalinity values were in Lake Michigan water and, especially, rainwater/snow melt. Most of the TWW originates as Lake Michigan water, thus accounting for the relatively low values in the SSC. The addition of groundwater from tributaries and from groundwater discharge into the main stem of the Illinois River is probably responsible for the increases in pH and alkalinity in the river water with distance from the Chicago area.

Chloride concentrations in the Illinois River ranged from 70 to 488 mg/L and generally decreased with distance from the Chicago area (Figure 16); Cl<sup>-</sup> concentrations were greatest in February 2004. Just prior to our February sampling, there had been a warming trend following a



**Figure 14.** Alkalinity vs. pH graph showing a distinct separation of the chemical composition of the Upper Illinois River Basin from the Lower Illinois River Basin.

very cold and snowy winter in northeastern Illinois; Cl<sup>-</sup> concentrations were as high as 488 mg/L, and the dominant source of Clduring that time was road salt (Kelly et al. submitted). During August 2005, when drought conditions dominated, Cl<sup>-</sup> concentrations for the Illinois River were typically over 100 mg/L, including in the lower Illinois. This was in part due to the lack of dilution by low-Cl<sup>-</sup> water downstream of Chicago and in part due to in-stream evaporation (Kelly et al. submitted). Chloride concentrations in the Mississippi River were much lower than the Illinois River, ranging from 9.3 to 34 mg/L (similar to that of tile drains). Halide ratios were used to help evaluate the Cl- data. Panno et al. (2006b) found that different Cl<sup>-</sup> sources tended to plot in distinct domains for several different ratio plots, including Cl<sup>-</sup> vs. Cl<sup>-</sup>/Br- and Br<sup>-</sup> vs. I<sup>-</sup>/Na. Consequently, with these plots, it was possible to identify each of the multiple sources of Cl<sup>-</sup> that entered the watershed, and isolate those sources that dominated seasonally (Kelly et al. submitted).

Sodium concentrations in the Illinois River ranged from 20 to 335 mg/L, and Na concentrations were greatest in February 2004, with a high of 335 mg/L, due to road salt runoff (Kelly et al. submitted). During the summer of 2005, when drought conditions dominated, Na concentrations for the Illinois River were typically around 80 mg/L. As with Cl<sup>-</sup>, the dominant sources of Na in the Illinois River were TWW and road salt. Sodium was lower in the Sangama Bing accompany (12 to 100 mg/L) then the Illinois River

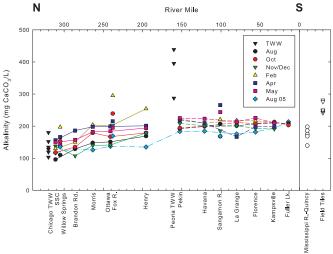
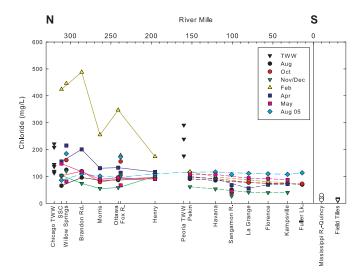


Figure 15. Alkalinity concentrations in river water, TWW, and tile samples.



**Figure 16.** Chloride concentrations in river water, TWW, and tile samples. Concentrations from the Mississippi River at Quincy (Panno et al., 2006a) also shown.

Sangamon River samples (12 to 100 mg/L) than the Illinois River, and much lower in the Mississippi River (8.3 to 31 mg/L) (Panno et al. 2006a), similar to that of tile drains.

The relationship between Na and Cl<sup>-</sup> was stoichiometrically 1:1, suggesting halite (NaCl) as the dominant source of the ions. A plot of Cl<sup>-</sup> vs. Cl<sup>-</sup>/Na ratios suggests that the source of most of the Illinois River water and TWW was road salt (Figure 11).

Potassium in the Illinois River ranged from 4 to 15 mg/L and decreased with distance from the Chicago area (Figure 17). Possible sources of K include soil amendments, TWW, and industrial wastes. There was a clear enrichment of K in the Chicago area (up to 20 mg/L in the Des Plaines River, Table 1). The source of the additional K is unclear. Because none of our TWW samples had K concentrations as high as those of the Des Plaines River and SSC, there must be other sources (e.g., industrial outfalls).

Because the greatest concentrations of K coincided with the influx of Na and Cl<sup>-</sup> during melting near the end of winter of 2004, and because there is some correlation between K and Cl<sup>-</sup> (Figure 18), it is possible that the elevated K concentrations in the winter of 2004 (as high as 20 mg/L) are due, at least indirectly (e.g., ion exchange), to road deicers. The K concentration in a deicing brine running off a bridge in Pekin was 225 mg/L (Table 1). Concentrations of K in the Mississippi River were typically lower that those of the Illinois River,

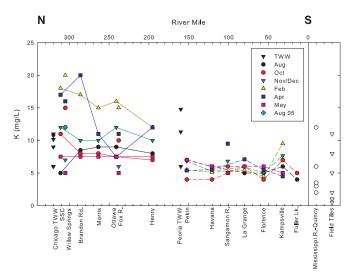


Figure 17. Potassium concentrations in river water, TWW, and tile samples.

usually ranging from 2 to 6 mg/L and, during flooding, as high as 13 mg/L. The Sangamon and Fox Rivers had slightly higher concentrations of K ranging from 5 to 10 mg/L and 6 to 15 mg/L, respectively.

Fluoride was typically enriched in river water samples from the Chicago tributaries to Henry, decreasing with distance from the Chicago area (Figure 19). The greatest concentrations in the Illinois River were found in the SSC at levels as high as 1.2 mg/L. There is little doubt that the source of the F<sup>-</sup> is TWW (0.6 to 1.3 mg/L), most likely from fluoridated tooth paste and the adjusted levels of F<sup>-</sup> in municipal water in the Chicago area (0.90 to 1.2 mg/L, by law). Fluoride concentrations in our Mississippi River samples ranged from < 0.1 to 0.5 mg/L. Because F<sup>-</sup> was so low in tile drains (0.1 to 0.4 mg/L), enriched in TWW, and because it probably does not undergo ion exchange or uptake along the river, it may be a useful proxy for estimating the amount of dilution of TWW as it flows down the river. Fluoride was compared to discharge measurements (Kelly et al. submitted) and was found to be reduced in concentration by dilution from tributaries and groundwater along the Illinois River (Figure 19). Also, there appears to be a relationship between F<sup>-</sup> and NO<sub>2</sub>-N, being positively correlated when F<sup>-</sup> concentrations were greater than 0.5 mg/L (Figure 20) suggesting a common source (i.e., TWW).

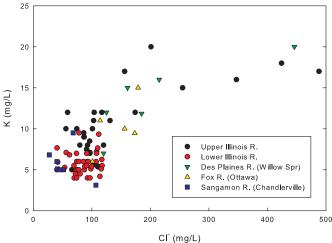


Figure 18. Potassium vs. chloride concentrations.

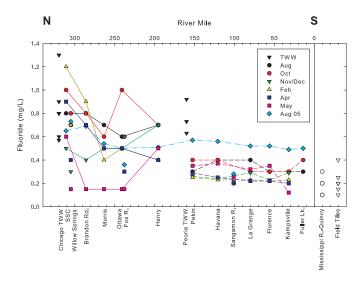


Figure 19. Fluoride concentrations in river water, TWW, and tile samples.

Boron concentrations were greatest in the Des Plaines and SSC (median = 0.16 mg/L). Boron is present in detergents; however, there is little change in B with distance from the Chicago area. The lowest B concentrations were found in the Fox and Sangamon Rivers (median = 0.08 mg/L) and tile drain samples (median = < 0.02 mg/L).

Nitrate-N concentrations in river water samples varied seasonally and ranged from <0.01 to 9.36 mg/L with a median concentration of 3.51 mg/L. This is consistent with Moody and Battaglin (1995) who found that the median  $NO_3$ -N concentration for the Illinois River from 1970 to 1991 was 3.5 mg/L. The greatest concentrations of  $NO_3$ -N in the Illinois River Basin were in the Des Plaines River and SSC; concentrations ranged between 4 and 10 mg/L in the SSC, Des Plaines River, and Illinois River at Joliet. In general, concentrations of  $NO_3$ -N decreased with distance from the Chicago area (Figures 21). Sources of  $NO_3$ -N near Chicago are primarily TWW discharged into the SSC and Des Plaines River.

Farther down river, the primary source of  $NO_3$ -N entering the Illinois River (based on land use) is row-crop agriculture (Panno et al. 2008). The tile drain samples from near Rantoul had the highest  $NO_3$ -N concentrations (as high as 15 mg/L); Beaumont (2003) found (in other tile drains in the same area) concentrations as high as 33 mg/L. The source of  $NO_3$ -N in the Sangamon River should also be predominantly agricultural;  $NO_3$ -N concentrations in the Sangamon River ranged from <0.01 to 10.5 mg/L. In comparison,  $NO_3$ -N levels in Mississippi River samples at Quincy were relatively low, ranging from 0.4 to 4.1 mg/L (Panno et al. 2006a).

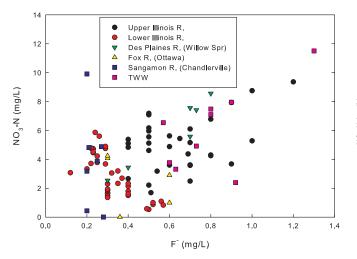


Figure 20. Nitrate vs. fluoride concentrations. The correlation between the two ions in the upper reaches of the Illinois River Basin is due to outfall from the WWTPs.

Ammonium-N concentrations were greatest in the Des Plaines River and SSC, ranging from 0.24 to 1.19 mg/L. These concentrations dropped dramatically downstream to typically less than 0.1 mg/L (similar to what was found in the Mississippi River by Panno et al. 2006a) (Figure 22). The  $NH_4$ -N concentrations of the TWW were relatively low (0.1 to 0.3 mg/L), consequently, there appeared to be another source entering the SSC (e.g., industrial-waste discharge).

Total Kjeldahl Nitrogen (TKN) concentrations steadily decreased with distance from Chicago from a high of 5.1 mg/L to a low of 0.41 mg/L near the Mississippi River. The TKN concentrations remained low in the lower part of the Illinois River in spite of the fact that tile drain samples can be relatively enriched (observed in this study as high as 4.3 mg/L). Mississippi River samples ranged from 0.2 to 2.0 mg/L (Panno et al. 2006a). However, because we did not collect an integrated water sample that spanned the width and depth of the river, the TKN data are not completely reliable.

Phosphate-P concentrations ranged from 1 to 7 mg/L in the SSC and decreased in range and concentration with distance down river to levels ranging from 0.01 to 1.0 mg/L (Figure 23). The tile drains and Fox River had the lowest  $PO_4$ -P concentrations of less than 1 mg/L. Concentrations of  $PO_4$ -P as high as 7 mg/L were observed in water samples from the SSC, presumably due to TWW. The decrease in P-concentrations down river for most sampling events (the exception was August 2005) was maybe due to dilution (Kelly

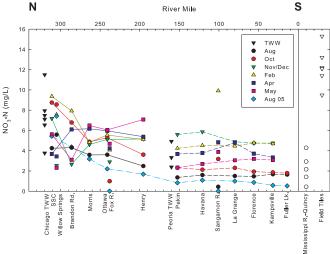
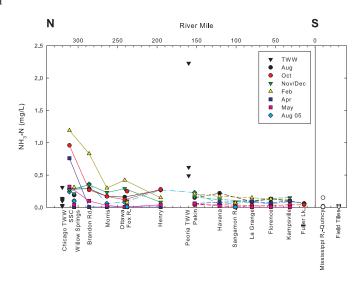


Figure 21. Nitrate concentrations in river water, TWW, and tile samples. Concentrations from the Mississippi River at Quincy (Panno et al. 2006a) also shown.



**Figure 22.** Ammonium concentrations in river water, TWW, and tile samples. Concentrations from the Mississippi River at Quincy (Panno et al. 2006a) also shown.

et al. submitted). This statement is based on  $PO_4$ -P concentrations in August 2005 when concentrations decreased dramatically from the Chicago area, but were consistently above 1 mg/L from the Chicago area to the Illinois River's confluence with the Mississippi River (Figure 23). Concentrations of  $PO_4$ -P in the Mississippi River were all less than 0.1 mg/L, the same as tile drain samples.

Dissolved organic carbon concentrations in the Illinois River ranged from 3.9 to 11 mg/L. In general, the greatest concentrations of DOC were found in the Chicago area, particularly during the spring, and they decreased to between 4 and 7 mg/L down river (Figure 24). A possible source of DOC in this area is TWW (4.4 to 12 mg/L). The greatest concentrations of DOC within the Illinois River Basin were found in the Fox River (6.5 to 12.4 mg/L), and the lowest were found in the Sangamon River (2.6 to 5.5 mg/L). Land use in the Sangamon River watershed is dominated by row-crop agriculture and DOC in tiles were very low and ranged from 1.1 to 2.9 mg/L. Water samples from the Mississippi River had DOC concentrations that were similar, ranging from 2.2 to 8.6 mg/L (Panno et al. 2006a).

 $\delta D$  and  $\delta^{18}O$  plotted along the meteoric water line (Figure 25) with linear excursions along the lower side of the line indicating the isotopic fractionation effects of evaporation within the river.

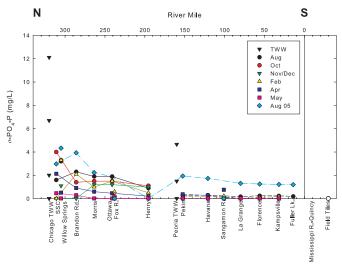
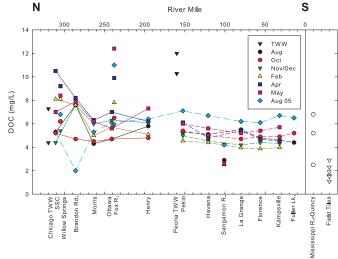


Figure 23. Phosphate concentrations in river water, TWW, and tile samples.



**Figure 24.** Dissolved organic carbon concentrations in river water, TWW, and tile samples. Concentrations from the Mississippi River at Quincy (Panno et al. 2006a) also shown.

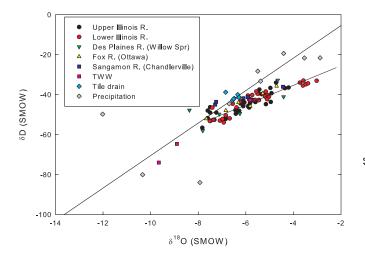


Figure 25.  $\delta D$  vs.  $\delta^{18}O$  for water. Mean water line (MWL) also shown. Deviations from MWL indicate evaporation.

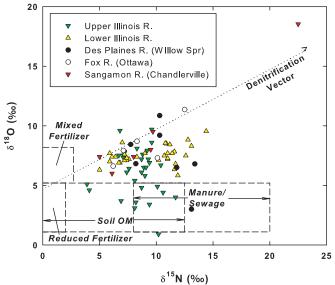


Figure 26.  $\delta^{15}$ N vs.  $\delta^{18}$ O for all samples.

 $\delta^{15}$ N and  $\delta^{18}$ O of NO<sub>3</sub><sup>-</sup> are plotted in Figure 26. Those data for tile water samples plotted in and around the domains of N-fertilizer and/or SOM (6.0–12.4 (median = 10.0) and 6.9–4.8 (median = 9.0), respectively). The isotopic composition of NO<sub>3</sub><sup>-</sup> in TWW typically had light  $\delta^{18}$ O values (0.6–8.1, median = 3.4) and a relatively broad range of  $\delta^{15}$ N values (3.6–15.5, median = 8.6). Most of the data fell outside the expected sewage/manure domain; this is discussed in detail in Panno et al. (2008).

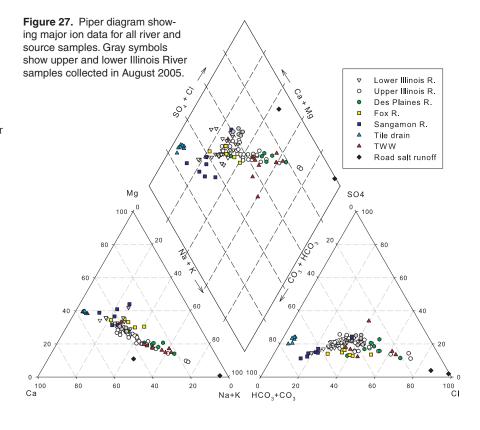
 $\delta^{15}$ N and  $\delta^{18}$ O of NO<sub>3</sub><sup>-</sup> in the SSC samples ranged from 3.9–8.7 (median = 6.9) and 3.6–9.6 (median = 5.1), respectively, and generally had light  $\delta^{15}$ N and  $\delta^{18}$ O values relative to downstream samples, except in the springtime and September 2003. Samples from the Des Plaines River at Willow Springs (8.2–13.4 (median = 10.3) and 3.0–10.9 (median = 6.8), respectively), which drains urban and suburban areas and whose flow is on average about 30% TWW, often had isotopic signatures different from those of TWW.

 $\delta^{15}$ N and  $\delta^{18}$ O values were significantly higher in the lower Illinois compared to the upper Illinois (Panno et al. 2008). Downstream of Chicago, the NO<sub>3</sub><sup>-</sup> isotopic values of samples from the main tributary of the Illinois River tended to cluster in fairly tight groups, especially between late fall and April when NO<sub>3</sub>-N concentrations were often near their highest (Figure 21). For the tributaries, the only significant difference in  $\delta^{15}$ N values was for the Des Plaines at Willow Springs, which was higher than the upper Illinois. For  $\delta^{18}$ O, values were substantially higher in the Sangamon (6.4–18.5 (median = 7.7), respectively) than both reaches of the Illinois and the Des Plaines, and higher

in the Fox  $(6.6-11.5 \pmod{7.9})$  than the upper Illinois.

There were significant seasonal and stage effects on the isotope values for all the rivers and reaches (Panno et al. 2008), although the effects were opposite for  $\delta^{15}N$ vs.  $\delta^{18}$ O.  $\delta^{15}$ N values were significantly greater in the summer compared to the other seasons, while  $\delta^{18}$ O values were significantly lower in the summer. The  $\delta^{18}O$  seasonal differences were greater in the upper Illinois than the lower Illinois.  $\delta^{15}N$  values decreased as the river stage increased from low to intermediate to high. For the Illinois River,  $\delta^{18}$ O values were significantly lower when the river stage was low; this relationship was not significant for the other rivers (Table 1).

Major ion data plotted on a piper diagram show significant differences among the different sources, river reaches, and tributaries (Figure 27). In general, the Sangamon River samples are most similar to the tile drain samples, while upper Illinois and Des Plaines River samples are most similar to road salt runoff and TWW. Fox River samples, which have a mixed urban-rural watershed, are intermediate between the



Des Plaines (mainly urban) and Sangamon (mainly rural) river samples.

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