Results from the Big Spring basin water quality monitoring and demonstration projects, Iowa, USA

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Abstract Agricultural practices, hydrology, and water quality of the 267-km^2 Big Spring groundwater drainage basin in Clayton County, Iowa, have been monitored since 1981. Land use is agricultural; nitrate-nitrogen (-N) and herbicides are the resulting contaminants in groundwater and surface water. Ordovician Galena Group carbonate rocks comprise the main aquifer in the basin. Recharge to this karstic aquifer is by infiltration, augmented by sinkhole-captured runoff. Groundwater is discharged at Big Spring, where quantity and quality of the discharge are monitored.

Monitoring has shown a threefold increase in groundwater nitrate-N concentrations from the 1960s to the early 1980s. The nitrate-N discharged from the basin typically is equivalent to over one-third of the nitrogen fertilizer applied, with larger losses during wetter years. Atrazine is present in groundwater all year; however, contaminant concentrations in the groundwater respond directly to recharge events, and unique chemical signatures of infiltration versus runoff recharge are detectable in the discharge from Big Spring.

Education and demonstration efforts have reduced nitrogen fertilizer application rates by one-third since 1981. Relating declines in nitrate and pesticide concentrations to inputs of nitrogen fertilizer and pesticides at Big Spring is problematic. Annual recharge has varied five-fold during monitoring, overshadowing any water-quality improvements resulting from incrementally decreased inputs.

Résumé Les pratiques culturales, l'hydrologie et la qualité de l'eau du bassin d'alimentation de la source de Big Spring, étendu de 267 km^2, située dans le comté de Clayton (Iowa, Etats-Unis) ont été suivis depuis 1981. Ce territoire est utilisé par l'agriculture; l'azote des nitrates (N) et les pesticides sont les contaminants des eaux souterraines et des eaux de surface qui en résultent. Les roches carbonatées ordoviciennes du groupe Galena constituent le principal aquifère du bassin. Cet aquifère karstique est rechargé par l'infiltration à laquelle s'ajoute le ruissellement de surface drainé par des pertes. L'eau souterraine ressort à Big Spring, dont le débit et la qualité des eaux sont contrôlés.

Ce contrôle a montré que les concentrations en azote des nitrates des eaux souterraines ont triplé entre les années soixante et les années quatre-vingt. L'azote des nitrates issu du bassin équivaut au tiers de l'azote des engrais appliqués, avec des pertes plus importantes au cours des années plus humides. L'atrazine est présente dans les eaux souterraines tout au long de l'année; cependant, les concentrations en contaminants des eaux souterraines répondent directement aux épisodes de recharge et les signatures chimiques uniques de l'infiltration par rapport à la recharge par le ruissellement sont détectables à l'exutoire de Big Spring.

Les efforts d'éducation et de démonstration ont réduit les taux d'application d'engrais nitratés d'un tiers depuis 1981. La baisse des concentrations en nitrates et en pesticides liée aux entrées d'engrais nitratés et de pesticides à Big Spring est problématique. La recharge annuelle a varié d'un facteur cinq au cours du suivi, ce qui masque toute amélioration de la qualité de l'eau résultant d'entrées diminuées.

Resumen Se han controlado las prácticas agrícolas, hidrología y calidad del agua de la cuenca de Big Spring (267 km^2), en el Condado de Clayton, desde el año 1981. Los usos del suelo son eminentemente agrícolas, hecho que acarrea la presencia de nitratos y herbicidas en las aguas subterráneas y superficiales. El acuífero principal de la cuenca está formado por rocas carbonatadas del Grupo de Galenas del Ordovícico. La recarga a este acuífero kárstico se produce por infiltración, que se ve aumentada por la existencia de dolinas. Las aguas subterráneas descargan al Big Spring, en el que existe una red de control de su cantidad y calidad.

Los registros históricos muestran que las concentraciones de nitratos se han multiplicado por tres entre 1960

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y comienzos de los 80. El nitrato drenado en la cuenca equivale a un tercio del nitrógeno aplicado como fertilizante, si bien se produce más lixiviados en los años húmedos. Se ha detectado atracina de forma regular durante el año en las aguas subterráneas, aunque las concentraciones responden directamente a los episodios de recarga; en la descarga del Big Spring, se aprecia la correlación química existente entre la infiltración y las aguas de escorrentía superficial.

La educación y los esfuerzos de divulgación han reducido en un tercio la carga de fertilizantes nitrogenados desde 1981. Sin embargo, es complicado relacionar las reducciones en el uso de nitratos y pesticidas con las concentraciones de dichos compuestos en el Big Spring. La recarga anual ha variado en un factor de cinco durante el período registrado, difuminando las mejoras de calidad de las aguas obtenidas gracias a la disminución de las dosis de contaminantes.

Keywords agriculture · groundwater monitoring · groundwater quality · groundwater/surface-water relations · karst · rainfall/runoff

Introduction

The agricultural practices, hydrology, and water quality of the Big Spring basin, a 267-km^2 groundwater basin in Clayton County, Iowa, shown in Fig. 1, have been studied by the Iowa Department of Natural Resources–Geological Survey Bureau (GSB) and cooperators since 1981 (Hallberg et al. 1983, 1984, 1985, 1986, 1987, 1989; Libra et al. 1986, 1987, 1991; Rowden et al. 1993, 1995, 1998, 2000; Rowden 1995; Liu et al. 1997). Historic water-quality data have shown regional increases in nitrate-N in the groundwater of the basin paralleling a three-fold increase in nitrogen fertilizer use from the mid-1960s to the early 1980s, as shown in Fig. 2. A network of sites, including tile lines, streams, springs, and wells, was established to monitor water-quality changes accompanying changes in farm management. The network was designed in a nested fashion, monitoring a graduated series of watersheds, from small-scale field plots to the basin groundwater and surface-water outlets (Littke and Hallberg 1991). Water samples from as many as 50 sites have been analyzed for various forms of nitrate, herbicides, and other constituents on a weekly to monthly basis. Key sites were instrumented for continuous or event-related measurement of water discharge and chemistry and for automated sample collection. The development of monitoring sites within the basin has been a cooperative effort among the GSB, the US Geological Survey, Iowa State University, the US Department of Agriculture–Natural Resource Conservation Service, and the US Environmental Protection Agency (USEPA). Water-quality analyses were performed by the University of Iowa Hygienic Laboratory, using standard methods and a USEPA-reviewed quality-assurance/quality-control plan (http://www.uhl.uiowa.edu).

Land use within the basin is 97% agricultural. The basin includes about 200 farms with an average size of 133 ha (330 acres). Small dairy and hog operations are common. Typically, 50% of the basin area is planted to corn, 35–40% to alfalfa, and 10% of the basin is pasture. Fertilizer, manure, and herbicides are applied to corn primarily during the spring planting period. There are no significant urban or industrial point sources of pollution within the basin that impact groundwater quality. These conditions along with the ability to gauge the volume of groundwater passing through the Galena Group carbonate rock aquifer allow unambiguous study of the agricultural ecosystem. By surveying farmers annually for application rates of pesticides and fertilizers, and monitoring the water quality and discharge of surface water and groundwater in the basin, the mass flux of nutrients and chemicals applied within the basin can be quantified, allowing assessment of chemical balances on a basin-wide scale.

Nitrate-N, and the most commonly used corn herbicides, particularly atrazine, are the major agricultural contaminants. Initial investigations in the area (Hallberg et al. 1983, 1984; Libra et al. 1986) showed that atrazine is present (>0.1 μg/L) all year in surface- and groundwater, except during extended dry periods. Detectable concentrations of several other herbicides generally occur following the spring application period, but are also present all year following runoff events. The total mass of nitrate-N leaving the basin annually in groundwater and surface water typically is equivalent to one third of that applied as fertilizer, and during wetter years exceeds one half of that applied. In-stream denitrification and nitrogen uptake also occur before surface waters exit the basin, suggesting that even more nitrogen is lost from agricultural practices (Crumpton and Isenhart 1987). In an effort to reduce these losses, a multi-agency group initiated the Big Spring Basin Demonstration Project, which was funded by the Iowa Groundwater Protection Act and conducted from 1986–1992. The project integrated public education with on-farm research and demonstration projects that stressed and monitored the environmental and economic benefits of efficient chemical management, with a particular focus on nitrogen management. Education and demonstration activities continued from 1992–1999 as part of the Northeast Iowa Demonstration Project, under the direction of the Iowa State University Extension Service.

In 1995 the US General Accounting Office selected the project as one of nine (from a nation-wide field of 618) particularly innovative and successful nonpoint-source pollution prevention efforts. In this article we briefly describe the Big Spring basin's hydrogeologic system, and discuss the response of the system to recharge, and the results of 18 years of hydrologic and nonpoint-source contaminant monitoring in a sensitively responsive hydrogeologic environment.

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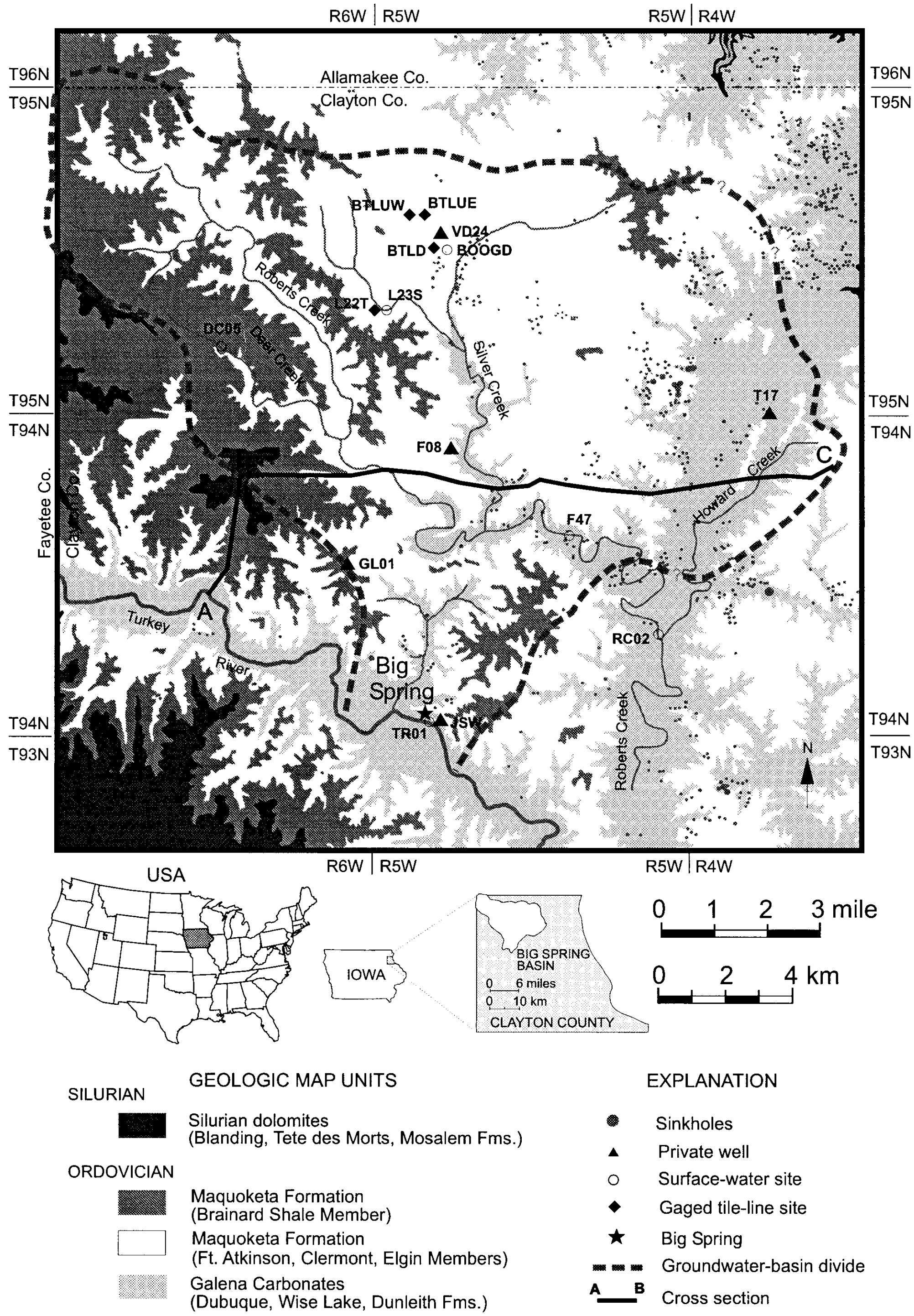

Fig. 1 Bedrock geologic map of the Big Spring study area. (Adapted from Hallberg et al. 1983)

Hydrogeologic Setting

Northeast Iowa is characterized by a mid-continental subhumid climate. Mean annual precipitation (based on the period 1951–1980) is 84 cm, with 70% of the precipitation occurring from April through September. The mean annual temperature is 6.7 °C, with a winter average of –5.6 °C and a summer average of 22.2 °C. The oldest rocks exposed in the Big Spring basin are Ordovician Galena Group carbonates (Fig. 1). These strata have an uneroded thickness of about 76 m, dip to the southwest at about 5 m/km, and form the major aquifer in the area. The Galena crops out low on the landscape in the central and eastern parts of the basin. Big Spring, the largest spring in Iowa, discharges near the base of the aquifer in the Turkey River Valley at a state-owned fish hatchery. The Galena aquifer is underlain by shales and shaley carbonate rocks of the Decorah, Platteville, and Glenwood Formations, which hydrologically isolate it from underlying aquifers. Across most of the basin, the

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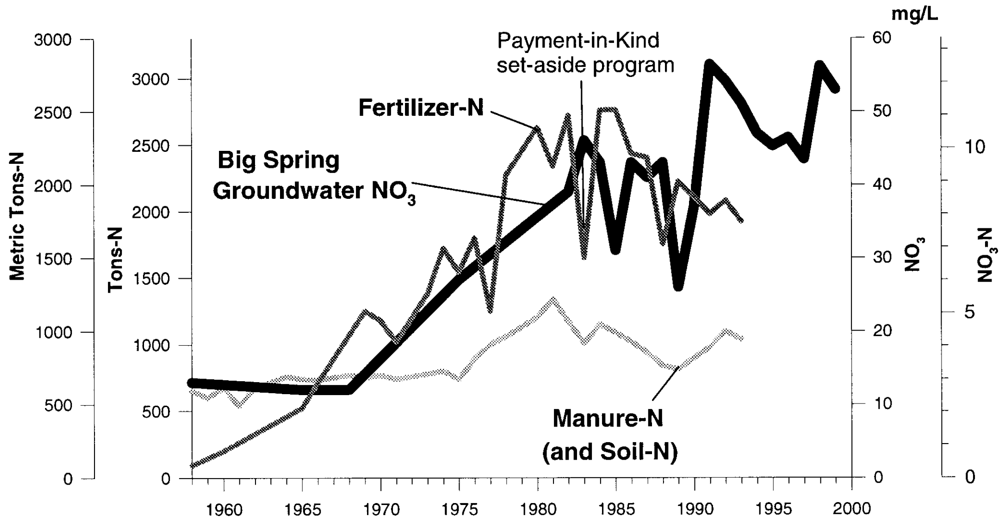

Fig. 2 Annual fertilizer- and manure-N inputs and annual groundwater nitrate-N concentrations from Big Spring basin

Galena Group is overlain by the Maquoketa Formation. The lower Maquoketa consists of silty and shaley carbonate rocks with an uneroded thickness of 23–30 m. These strata are not a barrier to groundwater flow and are hydrologically connected with the Galena aquifer. In the western 20% of the basin, claystones and shales of the upper Maquoketa act as an effective confining bed with a thickness of up to 30 m. Along the western margin of the basin, outliers of Silurian overlie upper Maquoketa strata.

The basin is mantled by thin (typically less than 5 m) Quaternary deposits and the rolling landscape is generally controlled by the bedrock surface. Thin, eroded remnants of Pre-Illinoian glacial till occur on the uppermost drainage divides. The uplands are draped with 2–8 m of Wisconsinian Peoria loess, or loess-derived deposits, and loamy alluvium occurs in stream valleys and drainageways. The Quaternary materials within the basin are not an effective barrier to groundwater flow.

The carbonate rocks of the Galena and lowermost Maquoketa are fractured and exhibit moderate karst development where they form the uppermost bedrock. Figure 1 shows sinkholes generally occurring within the Galena outcrop belt, and near the Galena–Maquoketa contact, where only a limited thickness of the Maquoketa is present. About 10% of the surface area of the basin drains to soil-filled sinkholes. The area of individual sinkhole drainage basins is generally less than 2 km^2. Within the Big Spring basin, the aquifer has both diffused- and conduit-flow systems (Hallberg et al. 1983), using the terminology of White (1969, 1977). The diffused-flow system is recharged by slow infiltration through overlying materials into joints, fractures, and bedding planes with little solutional modification. The diffused-flow parts of the aquifer, along with the overlying shales and Quaternary materials, conceptually form a low transmissivity–high storage part of the groundwater system (Hallberg et al. 1989). Groundwater from this part of the system discharges to the more solutionally modified conduit-flow system, and sustains the discharge from Big Spring during periods of low recharge. The conduit-flow system is directly recharged by diversion of surface water into sinkholes. Hydrograph separation (Singh and Stall 1971; Gustard et al. 1992) of the Big Spring discharge record suggests that infiltration accounts for 75–95% of the annual recharge to the Galena aquifer.

The extent of the groundwater basin was defined by mapping the potentiometric surface of the Galena aquifer, by dye tracing via sinkholes, and by gauging gaining- and losing-stream reaches (Hallberg et al. 1983). A water-distribution system at the hatchery allows the spring's discharge to be monitored and stream-gauging stations allow monitoring of surface-water discharge. Over 85% of the groundwater leaving the basin flows through Big Spring. The Roberts Creek watershed accounts for 65% of the basin's surface area and 75–80% of the surface water leaving the basin. Typical base-flow rates for Big Spring are about 0.8 m^3/s, with peak rates of over 6.0 m^3/s occurring 1–2 d after rainfall or snowmelt. Typically, the base-flow rate for Roberts Creek is about 0.7 m^3/s.

Figure 3 shows an east–west cross section within the southern part of the basin. In the western portions of the basin, the aquifer is confined and the potentiometric surface is above the Galena. Across much of the remainder of the basin, the aquifer is unconfined. There are two north–south-trending troughs in the potentiometric surface of the aquifer which head in sinkhole areas in the north-central and north-eastern portions of the basin and converge at Big Spring. These troughs reflect the presence of highly transmissive conduit zones, where solutional activity has enlarged fractures and bedding planes, increasing the permeability of the rocks (Hallberg et al. 1983). These conduit zones transmit groundwater to Big Spring, and act as drains for the diffused-flow parts of the aquifer.

The basin's main surface drainages head in the northern and western parts of the basin (Fig. 1). These streams gain groundwater in their upper reaches where a relative-

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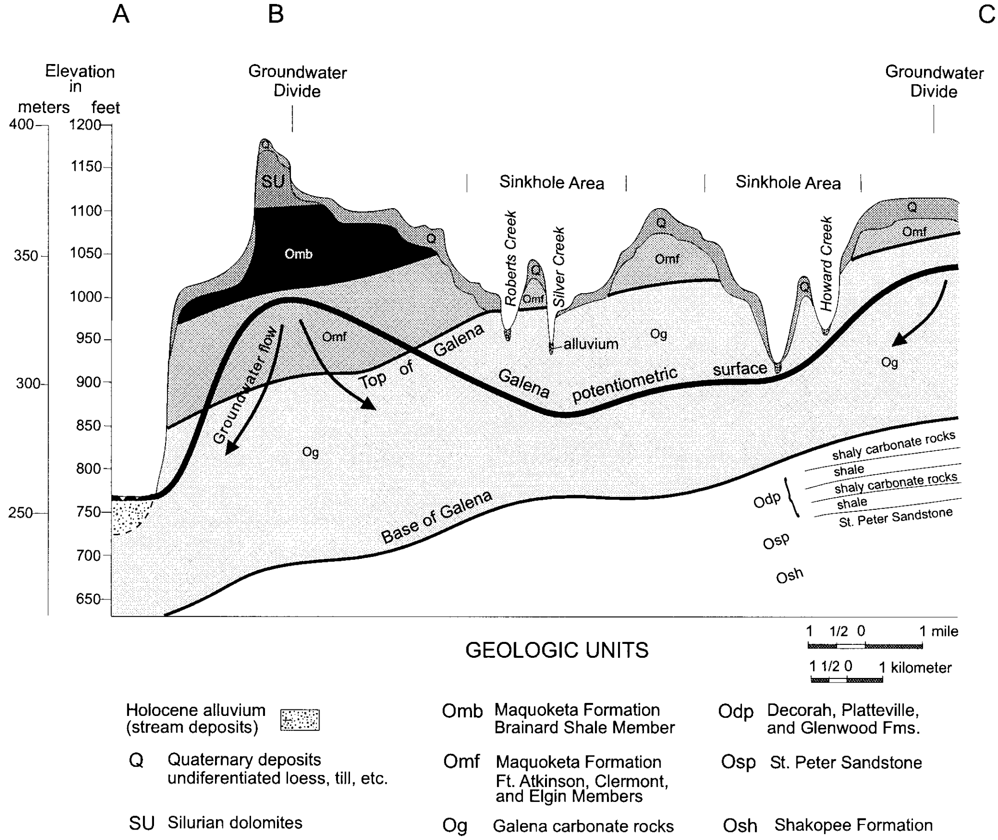

Fig. 3 Hydrologic cross section A–B–C; location shown in Fig. 1. (Adapted from Hallberg et al. 1983)

ly thick sequence of Maquoketa Formation and Quaternary materials is present. Here, these units are saturated, and the water table is above the Galena aquifer and graded to the streams. Downstream, the Maquoketa–Quaternary sequence has been erosionally thinned and the Galena–lowermost Maquoketa strata are more permeable. Here, the water table is located within the aquifer and surface drainages lose water to the aquifer (Hallberg et al. 1983). Although these streams lose water through the central and eastern portions of the basin, they maintain perennial flows except during extended dry periods. This is possible when recharge by shallow groundwater (including tile drainage) in the stream's headwaters is greater than leakage into the groundwater system downstream. Fine-grained materials in the alluvial deposits retard downward leakage through the streambeds (Hallberg et al. 1983; Rowden and Libra 1990).

Hydrologic and Water-Quality Responses to Recharge

The Big Spring groundwater system receives both infiltration and runoff recharge which have unique chemical signatures that can be traced through the monitoring network from the water table beneath individual fields to the basin's surface-water and groundwater outlets (Hallberg et al. 1983, 1984). Similar seasonal trends and pronounced short-term changes in nitrate concentrations are seen at small- to large-scale monitoring sites. The pronounced short-term changes in nitrate concentrations are responses to significant recharge events. Infiltration recharge is enriched in nitrate and other chemicals that are mobile in soil. Runoff recharge has lower concentrations of such compounds, but is enriched in herbicides and other chemicals with low soil mobility. The concentrations of organic- and ammonium-N tend to increase directly with suspended sediment concentration during runoff events. Typically, Big Spring yields groundwater delivered through infiltration, but following significant precipitation or snowmelt, sinkholes within the basin may direct surface runoff into the aquifer, mixing it with the groundwater. As this runoff recharge moves through the groundwater system and discharges from Big Spring, relatively low nitrate and high herbicide concentrations occur during peak discharge periods. This is typically followed by higher nitrate and lower herbicide concentrations as the associated infiltration recharge moves through the hydrologic system.

During a prolonged flow recession, nitrate and atrazine concentrations generally show a slow, steady decline that occurs as an increasing percentage of the discharge is composed of relatively older groundwater from the more diffused-flow parts of the flow system (Hallberg et al. 1984). Figure 4 shows discharge (Q), and nitrate and atrazine concentrations at Big Spring during 5–13 March 1990 (Rowden et al. 1993). On 8 March 1990, precipitation totaling 20 mm and warming temperatures generated a snowmelt event at Big Spring. Three days before

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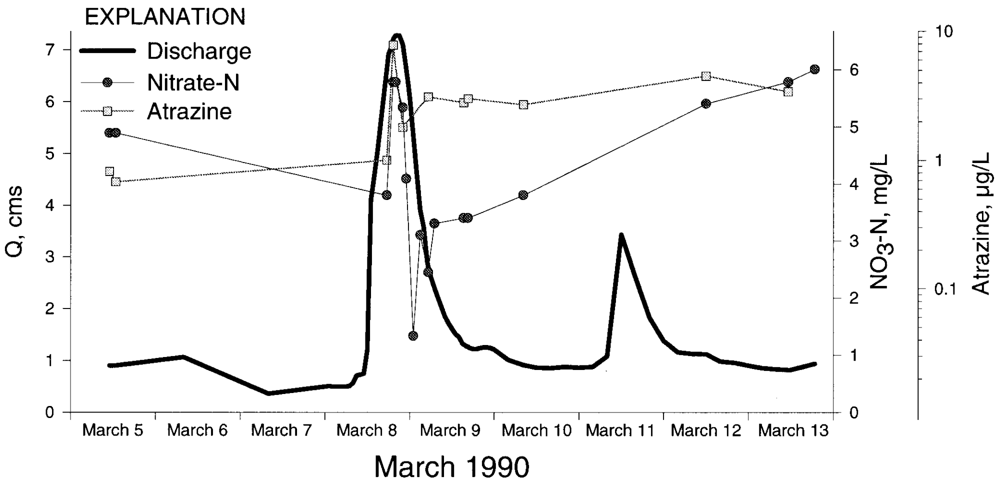

Fig. 4 Groundwater discharge and nitrate-N and atrazine concentrations at Big Spring during a recharge event, March 1990

Table 1 Average basin fertilizer-nitrogen application rates used for corn and continuous corn yields, from surveys and farm census inventories in Big Spring basin

Rotation year	All corn	1st-year corn after alfalfa	2nd-year corn after alfalfa	Continuous corn	Average continuous corn yields (bushels/acre)
	(kg N/acre)				
1981	79	56	73	81	128
1982	79	56	–	81	138
1984	72	52	70	77	130
1986	67	44	–	69	149
1987	68	38	55	71	141
1988	64	38	56	68	79[a]
1989	63	37	57	67	147
1990	56	30	55	66	145
1991	53	27	51	59	138
1992	53	–	–	58	165
1993	52	25	53	56	110[b]

[a] Drought resulted in lowered yields in the basin and across Iowa
[b] Frequent rains resulted in lowered yields in the basin and across Iowa

the event, the groundwater discharge was 0.9 m^3/s, the nitrate-N concentration was 4.9 mg/L, and the atrazine concentration was 0.82 µg/L. On 8 March at 17:30 the discharge was 4.9 m^3/s, the nitrate-N concentration was 3.8 mg/L, and the atrazine concentration was 1.0 µg/L. At this time, little change in chemical concentrations had occurred, indicating that most of the water that discharged during the rising limb of the hydrograph was "pre-event" water. This is typical of large recharge events at Big Spring, where the arrival of "event-water" is nearly coincident with peak discharge (Hallberg et al. 1984). The displacement of large volumes of pre-event water is a common occurrence at many karst springs (Atkinson 1977; Dreiss 1989). Discharge peaked at 7.3 m^3/s at 20:30, 8 March, while the maximum measured atrazine concentration, 7.8 µg/l, occurred earlier at 19:15, and the minimum measured nitrate-N concentration, 1.3 mg/L, occurred at 01:00 the following morning. By 07:00, the discharge had declined to 2.8 m^3/s and the nitrate-N concentration had increased to 3.3 mg/L. On 10 March at 08:15, the groundwater discharge was 0.9 m^3/s, the nitrate-N concentration had increased to 3.8 mg/L, and the atrazine concentration had decreased to 2.7 µg/L. The slowly declining discharge following this and a smaller recharge event on 11 March was derived from infiltration that occurred broadly across the groundwater basin. Note that concentrations of atrazine and nitrate-N in the infiltration-derived recharge following the 11 March event were greater than the concentrations prior to the 8 March recharge event. Infiltration supplies most of the water and chemical discharge from Big Spring (Libra et al. 1986).

Results of Long-Term Monitoring

Based in part on data collected from the Big Spring Basin Demonstration Project, the average fertilizer-N rate on all corn rotations within the basin was reduced from 79 kg/acre in 1981 to 52 kg/acre in 1993, a 34% decrease with no decline in corn yields (Table 1; Rowden 1995). In addition, an estimated 41% of the basin producers reduced herbicide rates, and 34% reduced insecticide rates over a 3-year period without impacting yields (Iowa State University-Cooperative Extension, unpublished data).

During 1983, a payment-in-kind (PIK) set-aside program provided the opportunity to evaluate the results of a 1-year reduction in nitrogen applications of about 40% in the basin (Fig. 2). The program, which provided pay-

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ments to farmers for removing cropland from corn production, resulted in a 35–40% decrease in corn acreage within the basin relative to the prior 3-year period. Comparison of annual discharge and nitrate concentrations at Big Spring suggests that the decline in nitrate concentration during 1985 was related to the reduction in nitrogen inputs during 1983, as well as the declining groundwater flux. Monitoring shows that time lags occur between the implementation of management practices and associated changes in water quality at monitoring sites. While fertilizer use has declined by one-third since 1981, the effects of the incremental reductions have been obscured by year-to-year variations in groundwater discharge resulting from climatic variability. The driest consecutive 2-year period in Iowa's history, water years (WYs; 1 October through 30 September) 1988 and 1989, preceded the wettest consecutive 2-year period since the project's inception. Relating changes in pesticide use to water quality changes has also been difficult. Annual atrazine concentrations and loads appear to have declined significantly, but this has only become apparent during recent years.

Figure 5 shows annual precipitation, groundwater discharge, and flow-weighted mean (mean concentration per unit volume of discharge) nitrate-N and atrazine concentrations and loads for the Big Spring basin for WYs 1982–1999. These data are also summarized in Table 2. Annual precipitation has varied from 58.3–120.1 cm and averaged 90.3 cm for the 18-year period, or 7.5% greater than the 1951–1980 average. The record shows an overall decreasing trend in precipitation during WYs 1982–1989, followed by generally wetter-than-average conditions during WYs 1990–1993. During WYs 1994–1996 annual precipitation was slightly below normal and for WYs 1997–1999 annual precipitation was well above normal.

Annual groundwater discharge varied from 15.6 million m^3 (mcm) in WY 1989 to 71.7 mcm in WY 1993, and averaged 39.2 mcm. Recharge in the basin, and ultimately discharge from Big Spring, is a function of the amount, timing, and intensity of precipitation. On an annual basis, discharge generally follows precipitation, although time lags are evident. The drought in WY 1988 did not cause a decline in annual discharge relative to the preceding year. This indicates there was sufficient groundwater within the less transmissive parts of the groundwater system to sustain the discharge. Other lags are apparent following the drought. While precipitation in WY 1990 was 12.7 cm above average and 34.4 cm greater than that for WY 1989, discharge showed only a modest increase. This suggests that much of the recharge during WY 1990 went towards replenishing soil moisture that was depleted during the drought. While the annual precipitation in WY 1993 was the second greatest for the period of record, WY 1993 had by far the greatest annual groundwater discharge recorded at Big Spring following the wet WYs 1990–1992. Decreases in discharge, as precipitation increased during WYs 1996 and 1997, suggest that some of the recharge during these

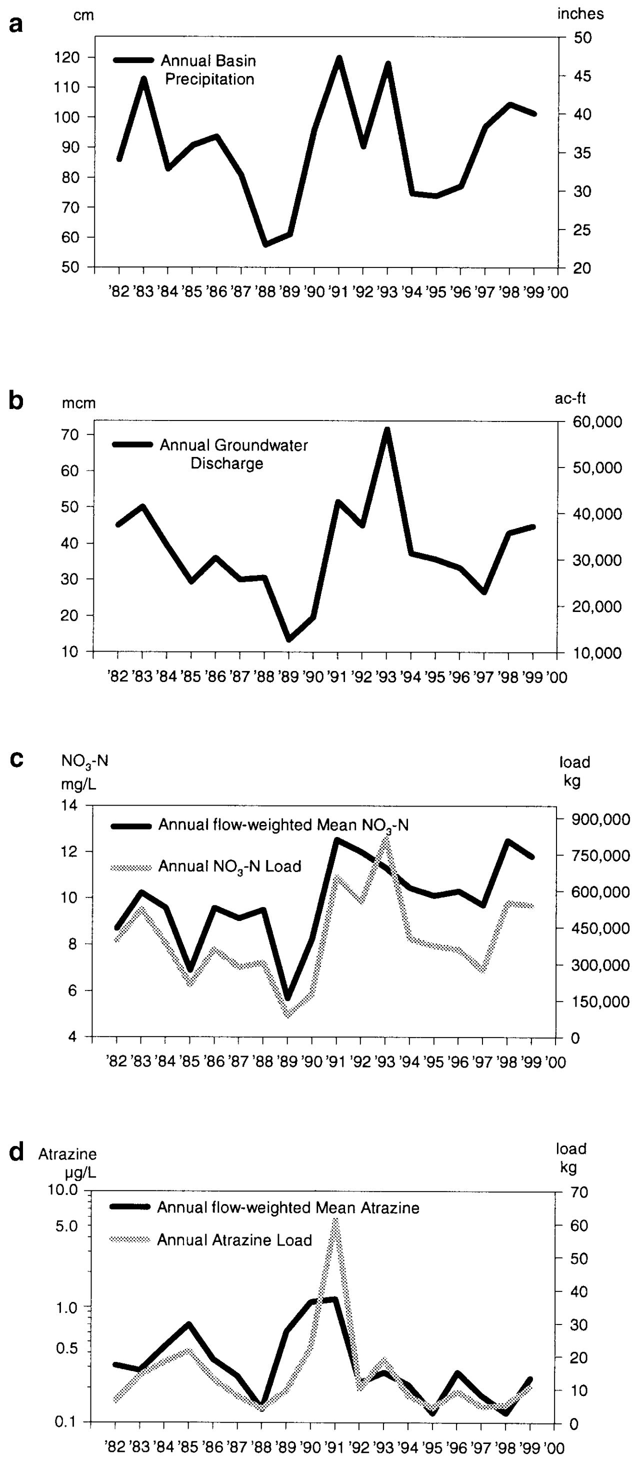

Fig. 5 Summary of annual **a** basin precipitation, **b** groundwater discharge, **c** flow-weighted mean nitrate-N concentrations and nitrogen loads, and **d** flow-weighted mean atrazine concentrations and loads from Big Spring groundwater, water years 1982–1999

years went toward replenishing soil-moisture deficits incurred during WYs 1994–1996. In WY 1999, discharge increased as precipitation decreased, suggesting that groundwater within the less transmissive parts of the groundwater system was being released. During the

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Table 2 Water-year (*WY*) summary data for groundwater, nitrogen, and atrazine discharge from Big Spring basin to Turkey River

	Water Year																	
	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
Precipitation:																		
In cm	86.4	113.0	83.3	91.0	93.9	81.2	58.3	61.8	96.2	120.1	90.8	118.0	77.3	74.4	77.7	97.3	104.7	101.6
In inches	34.0	44.6	32.8	35.8	37.0	32.0	22.9	24.3	37.9	47.3	35.7	46.5	30.4	29.3	30.6	38.3	41.2	40.0
Mean groundwater discharge (Q) to the Turkey River:																		
In m^3/s	1.5	1.6	1.3	1.0	1.2	1.0	1.0	0.5	0.7	1.7	1.5	2.3	1.2	1.2	1.1	0.9	1.4	1.5
In cfs	51.6	56.9	45.3	35.2	42.0	35.4	35.8	17.6	24.1	58.7	51.4	80.4	43.2	41.5	38.8	31.7	49.3	51.3
Total Q																		
In m^3	17.3	19.1	15.0	11.7	14.0	11.7	11.9	5.8	8.1	19.6	17.2	26.9	14.5	13.9	13.0	10.6	16.5	17.2
In million m^3	46.0	50.9	40.2	30.9	37.3	31.4	32.0	15.6	21.5	52.4	46.0	71.7	38.6	37.0	34.7	28.2	44.0	45.8
In inches	6.8	7.5	5.9	4.6	5.5	4.6	4.7	2.3	3.2	7.7	6.8	10.6	5.7	5.5	5.1	4.2	6.5	6.8
In 1,000 acre-feet	37.4	41.4	32.7	25.1	30.3	25.5	26.0	12.7	17.5	42.5	37.3	58.2	31.3	30.0	28.1	22.9	35.7	37.1
Flow-weighted mean concentration (in mg/L) of nitrogen discharged with groundwater:																		
As nitrate ($N0_3$)	39	46	43	31	43	41	43	25	37	56	54	51	47	45	46	44	56	53
As nitrate ($N0_3$-N)	8.8	10.3	9.7	7.0	9.7	9.1	9.5	5.7	8.2	12.5	12.0	11.4	10.4	10.1	10.3	9.7	12.5	11.8
Ammonia-N[a]	[a]	[a]	[a]	[a]	0.1	0.1	0.1	0.6	0.1	0.1	0.1	0.2	0.2	<0.1	<0.1	0.1	<0.1	[c]
Organic-N[a]	[a]	[a]	[a]	[a]	0.5	0.2	0.3	0.8	0.6	0.9	0.3	0.6	0.1	[b]	[b]	[b]	[b]	[b]
Nitrogen load:(nitrate-N+nitrite-N)																		
In 1,000s kg-N	396.0	521.6	382.6	216.3	358.5	285.1	304.8	88.4	176.2	655.6	553.3	814.5	403.0	373.0	358.0	273.3	549.9	539.5
In kg-N/acre	6.0	7.9	5.8	3.3	5.4	4.3	4.6	1.4	2.7	9.9	8.4	12.3	6.1	5.7	5.4	4.1	8.3	8.2
In 1,000 lb-N	873.0	1,150	843.4	476.8	790.5	628.6	672.0	194.9	388.5	1,446	1,220	1,796	888.5	822.6	789.3	602.7	1,212	1.190
In lb-N/acre (for total basin area)	13.2	17.4	12.8	7.2	12.0	9.5	10.2	3.0	5.9	21.9	18.5	27.2	13.5	12.5	12.0	9.1	18.4	18.0
Flow-weighted mean concentration of atrazine discharged with groundwater:																		
In µg/L	0.31	0.28	0.45	0.70	0.35	0.25	0.13	0.61	1.06	1.17	0.22	0.27	0.21	0.12	0.27	0.17	0.12	0.24
Atrazine load																		
In kg	6.4	14.2	18.1	21.6	13.2	8.0	4.2	9.6	22.7	61.2	10.2	19.1	8.1	4.4	9.3	4.8	5.3	10.8
In lb	14.2	31.2	40.0	47.6	29.0	17.6	9.2	21.2	50.0	135.0	22.5	42.0	17.8	9.8	20.5	10.5	11.6	23.8

[a] Prior to WY 1986, ammonia-N and organic-N were not analyzed frequently enough to calculate annual flow-weighted means

[b] Since WY 1995, organic-N has been omitted from analysis list

[c] Since WY 1999, ammonia-N has been omitted from analysis list

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18-year period of record, discharge accounted for 16% of precipitation, and ranged from 8–23% of precipitation for individual years.

On an annual basis, nitrate-N concentrations and loads parallel the overall volume of water moving through the soil and into the groundwater system. From WYs 1982–1989, annual flow-weighted mean nitrate-N concentrations at Big Spring declined from 8.7–5.7 mg/L, and nitrate-N loads decreased from 396,000–88,403 kg, while annual discharge declined from 46.0–15.6 mcm. While some of the decrease in nitrate concentrations may have been due to reductions in application rates, the response cannot be separated from the decrease caused by the decline in groundwater flux. From WYs 1990–1991 annual discharge increased from 21.5–52.4 mcm while the flow-weighted mean nitrate-N concentration increased from 8.2–12.5 mg/L and the nitrate-N load increased from 176,181–655,558 kg. These increases resulted from both the increased groundwater flux and the leaching of unutilized nitrogen left over from the drought years. Any improvements in water quality that may have resulted from the incremental reduction of nitrogen applications were obscured by variations in groundwater flux. From WYs 1992–1993, discharge increased from 46.0–71.7 mcm, and the nitrate-N load increased from 553,333–814,518 kg, while the nitrate-N concentration decreased from 12.0–11.4 mg/L. The decrease in concentration was probably related to having a greater than normal proportion of runoff composing the annual discharge, as well as having less nitrogen available due to increased leaching of nitrogen during the very wet WYs 1991–1992. Groundwater discharge and nitrate-N loads declined from WYs 1993–1997. Annual flow-weighted mean nitrate-N concentrations decreased from 10.4 mg/L in WY 1994 to 10.1 mg/L in WY 1995, then increased to 10.3 mg/L in WY 1996. This increase may be related to limited runoff during the year, which led to an increase in the proportion of infiltration to runoff, constituting the annual discharge. From WYs 1997–1998, discharge increased from 28.2–44.0 mcm, the flow-weighted nitrate-N concentration increased from 9.7–12.5 mg/L, and the nitrate-N load increased from 273,313–549,866 kg. During WY 1999, discharge increased to 45.8 mcm and the annual flow-weighted nitrate-N concentration and load decreased respectively to 11.8 mg/L and 539,478 kg. Some of the decrease in nitrate-N concentration and load in WY 1999 may have been related to increased leaching of nitrogen during the very wet WY 1998.

Atrazine has been detected in 86% of Big Spring samples since WY 1982. The next most frequently detected pesticides during the period include cyanazine at 11%, alachlor at 9%, acetochlor at 6%, and metolachlor at 4%. Unlike nitrate-N, annual flow-weighted mean atrazine concentrations and loads do not vary with groundwater flux (Fig. 5). In WY 1993, groundwater discharge increased to record levels while the annual atrazine concentration and load showed only minor increases.

Annual atrazine concentrations increased from 0.3–0.7 μg/L from WYs 1982–1985, and loads increased from 6.4–21.6 kg, as discharge declined. Increases in atrazine concentrations and loads from WYs 1988–1991, and general decreases from WYs 1991–1995, were probably related to changes in the timing and intensity of rainfall and in values of the proportion of infiltration to runoff, composing Big Spring's discharge. Another factor influencing annual concentrations and loads may be pesticide-degradation rates which vary with environmental factors such as soil moisture (US Environmental Protection Agency 1986). The increases following the drought may be due to the mobilization of atrazine that had not degraded during dry conditions, and the decreases following WY 1991 may reflect the smaller-than-normal mass of herbicide available for mobilization to groundwater, due to enhanced hydrolysis and microbial activity during the wet WYs 1990–1991. The increase in atrazine concentrations and loads in WY 1996 were, in part, due to a large runoff event in late June, not long after most atrazine is applied. June accounted for 19% of the groundwater discharge and 58% of atrazine discharge for WY 1996. In WY 1999, a discharge event on 17 May set a new record for instantaneous discharge from Big Spring. The daily discharge accounted for 2.6% of the annual groundwater total and 13.3% of the annual atrazine load. Twenty percent of the annual groundwater discharge and 44% of the annual atrazine load during WY 1999 occurred in May.

Since atrazine concentrations vary with runoff, the calculation of accurate flow-weighted mean atrazine concentrations and loads requires both routine and event-related sampling. The lack of event-related sampling during WYs 1993–1999, as well as the reduction in sampling frequency from weekly to biweekly during WYs 1998–1999, probably resulted in an apparent reduction of annual concentrations and loads during the last 7 years of monitoring. The declines in concentrations and loads, however, may also be related to changes in application rates. In recent years there has been a tendency to reduce the amount of atrazine applied per acre and to mix it with other pesticides to treat a larger area. The replacement of atrazine by other herbicides may be yet another factor contributing to the declines.

Acetochlor was added to the list of pesticide analyses for the Big Spring Project in August 1994. During August and September of WY 1994, none of the samples from Big Spring contained detectable (>0.10 μg/L) acetochlor. From WYs 1995–1997 the percentage of samples containing detectable acetochlor increased progressively from 2–6%, and in WY 1999, 17% contained acetochlor. It appears, therefore, that the use of acetochlor within the basin is increasing.

In January 1993, two atrazine metabolites, desethylatrazine and desisopropylatrazine, were added to the list of pesticide analyses for the Big Spring Project. Desethylatrazine has been detected (>0.10 μg/L) in 72% of the samples, while desisopropylatrazine has not been detected at Big Spring during WYs 1993–1999. The

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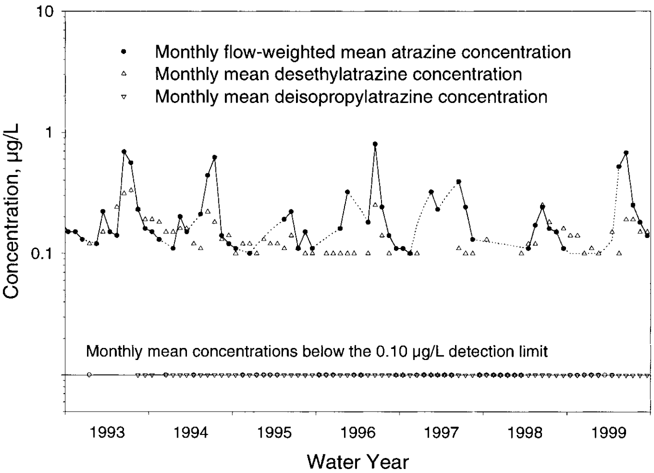

Fig. 6 Monthly flow-weighted mean atrazine concentrations and monthly mean desethylatrazine and desisopropylatrazine concentrations for Big Spring for water years 1993–1999

large number of detections of desethylatrazine, along with the absence of desisopropylatrazine during the monitoring period at Big Spring, as shown in Fig. 6, and other sites, support research that has shown desethylatrazine to be the more stable initial degradation product (Geller 1980; Adams and Thurman 1991). Desethylatrazine has shown trends similar to atrazine at both surface-water and groundwater monitoring sites within the basin (Rowden et al. 1993, 1998, 2000; Liu et al. 1997). In WY 1993, desethylatrazine was detected in 96% of the samples taken at Big Spring during the latter half of the year. Detections of desethylatrazine declined progressively, along with groundwater discharge, from 98% in WY 1994, to 32% in WY 1997. In WY 1998, desethylatrazine was detected in 58% of the samples, and in WY 1999 it was detected in 83% of the samples from Big Spring. The decrease in the number of detections during drier years and the increase during wetter years (Fig. 5a, b) may support the theory that pesticide degradation rates vary with environmental factors such as soil moisture. Desethylatrazine has been detected all year at Big Spring, except in WY 1997 during October, January, February, and April, and in WY 1998 from November through March. At most surface-water sites, concentrations of desethylatrazine were usually greatest during May through July and, at most groundwater sites, concentrations appeared to be more related to groundwater discharge fluctuations than to seasonal variations. These variations may result from differences in biotic degradation processes and/or differences in degradation rates between groundwater and surface water. Since high concentrations of desethylatrazine were detected in both surface- and groundwater in the Big Spring area, it may also be produced by abiotic degradation.

Summary

Annual groundwater data from Big Spring for WYs 1982–1999 indicate that flow-weighted mean nitrate-N concentrations and loads generally parallel groundwater discharge, and flow-weighted mean atrazine concentrations and loads do not. The effects of incremental decreases in nitrogen loading of over 30% within the basin have been overshadowed by changes in groundwater flux. WY 1993 was the first year that the annual nitrate-N concentration decreased as annual groundwater discharge increased, WY 1996 was the first year that the nitrate-N concentration increased as discharge decreased, and WY 1999 was the first year that both the nitrate-N concentration and load decreased as discharge increased. The gradual reduction in nitrogen applications within the basin may be causing changes in the water quality of Big Spring, but the declines in nitrate concentrations during WYs 1993 and 1999 may also be due to increased leaching of nitrogen during preceding years. The general decline in nitrate-N concentrations and loads from WY 1993–1997 cannot be distinguished from decreases caused by declines in groundwater flux.

Infiltration and runoff recharge have unique chemical signatures that can be tracked from the soil zone beneath individual fields to the water outlets of the basin. Pronounced short-term changes in nitrate and atrazine concentrations are responses to significant recharge events. Concentration changes at watershed scales are not as great or immediate as changes at smaller-scale monitoring sites. At watershed scales such as the Big Spring drainage basin, many land-use and management practices are integrated, and water-quality responses are dampened and complicated by climatic variations, storage effects, and biochemical activity.

The mass of nitrate-N leaving the basin annually in groundwater from Big Spring and surface water from Roberts Creek has varied from 96,000 kg in WY 1989, following drought conditions, to 1.4 million kg in WY 1993, following wet conditions. The nitrate-N losses are equivalent to 5 and 79%, respectively, of the chemical nitrogen fertilizer applied during each of those years. The long-term average loss is equivalent to 40% of the chemical fertilizer applied. Additional biochemical losses of nitrate-N occur within streams before they exit the basin, indicating that the actual N losses are greater than those measured. The nitrate-N discharge from the basin enters the Turkey River and becomes part of Iowa's nitrate-N contribution to the Mississippi River and, ultimately, to the Gulf of Mexico. Since 1982, annual losses from the Turkey River basin area have also varied 15-fold, from less than 1 kg/acre during 1989 to around 14 kg/acre during the relatively wet years following the drought.

Large-scale monitoring projects require a long-term commitment. Water quality in groundwater drainage basins and surface watersheds responds slowly to incremental changes in inputs. Time lags caused by antecedent hydrologic conditions also obscure relationships between changes in management practices and water-quality responses. Annual nitrate concentrations generally declined from WYs 1993–1997, but have increased in WYs 1998–1999. Annual atrazine concentrations appear to have declined significantly during the last 8 years of monitoring. This may result from the replacement of atrazine by other pesticides and changes in the way that atrazine is applied. Significant general reductions in pesticide sampling in recent years may also have caused misleading apparent declines in pesticide concentrations.

Significant changes in agricultural management have occurred in the basin, and the environmental benefits of these changes will continue. During recent years, the scope of the monitoring project has been scaled back; starting in WY 2000, Big Spring and Roberts Creek have been sampled on a weekly to biweekly schedule.

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References

Adams CD, Thurman E.M (1991) Formation and transport of desethylatrazine in the soil and vadose zone. J Environ Qual 20(3):540–547

Atkinson TC (1977) Diffuse flow and conduit flow in limestone terrain in the Mendip Hills, Somerset (Great Britain). J Hydrol 35:93–110

Crumpton WG, Isenhart TM (1987) Nitrogen balance in a stream ecosystem: the role of algal assimilation. J Water Pollut Control Fed 50:2043–2046

Dreiss SJ (1989) Regional scale transport in a karst aquifer 1. Component separation of spring flow hydrographs. Water Resour Res 25(1):117–125

Geller A (1980) Studies on the degradation of atrazine by bacterial communities enriched from various biotypes. Arch Environ Contam Toxicol 9(3):289–305

Gustard A, Bullock A, Dixon JM (1992) Low flow estimation in the United Kingdom. Rep 108, Institute of Hydrology, Wallingford

Hallberg GR, Hoyer BE, Bettis EA III, Libra RD (1983) Hydrogeology, water quality, and land management in the Big Spring basin, Clayton County, Iowa. Open-File Rep 83–3, Iowa Geological Survey Bureau, Iowa City

Hallberg GR, Libra RD, Bettis EA III, Hoyer BE (1984) Hydrologic and water-quality investigations in the Big Spring basin, Clayton County, Iowa: 1983 Water-Year. Rep 84–4, Iowa Geological Survey Bureau, Iowa City

Hallberg GR, Libra, RD, Hoyer BE (1985) Nonpoint source contamination of groundwater in karst-carbonate aquifers in Iowa. In: Perspectives on nonpoint source pollution. Rep 440/5 85–001, United States Environmental Protection Agency, Washington, DC, pp 109–114

Hallberg GR, Baker JL, Randall GW (1986) Utility of tile-line effluent studies to evaluate the impact of agricultural practices on groundwater. In: Agricultural impacts on ground water. National Water Well Association, Worthington, Ohio, USA pp 298–326

Hallberg GR, Libra RD, Long KR, Splinter RC (1987) Pesticides, groundwater, and rural drinking water quality in Iowa. In: Pesticides and groundwater: a health concern for the Midwest. The Freshwater Foundation, Navarre, and United States Environmental Protection Agency, Washington, DC, pp 83–104

Hallberg GR, Libra RD, Quade DJ, Littke J, Nations B (1989) Groundwater monitoring in the Big Spring basin 1984–1987: a summary review. Tech Info Ser 16, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Libra RD, Hallberg GR, Hoyer BE, Johnson LG (1986) Agricultural impacts on groundwater quality: the Big Spring Basin study. In: Agricultural impacts on ground water. National Water Well Association, Worthington, Ohio, USA pp 253–273

Libra RD, Hallberg GR, Hoyer BE (1987) Impacts of agricultural chemicals on groundwater quality in Iowa. In: Fairchild DM (ed) Ground water quality and agricultural practices, Michigan, Chelsea, Lewis Publ., Boca Raton, Florida, USA pp 185–217

Libra RD, Hallberg GR, Littke JP, Nations BK, Quade DJ, Rowden RD (1991) Groundwater monitoring in the Big Spring basin 1988–1989: a summary review. Tech Info Ser 21, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Littke JP, Hallberg GR (1991) Big Spring basin water-quality monitoring program; design and implementation. Open-File Rep 91–1, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Liu H, Rowden RD, Libra RD (1997) Groundwater monitoring in the Big Spring basin 1994–1995: a summary review. Tech Info Ser 37, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Rowden RD (1995) Temporal trends in groundwater quality of the Big Spring basin 1982–1994.In: Proc 40th Annu Midwest Ground Water Conf, Abstr of Papers, 16–18 Oct, Columbia, Missouri, USA

Rowden RD, Libra RD (1990) Hydrogeologic observations from bedrock monitoring well nests in the Big Spring basin. Open-File Rep 90–1, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Rowden RD, Libra RD, Hallberg GR, Nations BK (1993) Groundwater monitoring in the Big Spring basin 1990–1991: a summary review. Tech Info Ser 27, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Rowden RD, Libra RD, Hallberg GR (1995) Surface water monitoring in the Big Spring basin 1986–1992: a summary review. Tech Info Ser 33, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Rowden RD, Libra RD, Liu H (1998) Shallow groundwater and surface water monitoring of the Silver Creek sub-basin within the Big Spring basin 1986–1995: a summary review. Tech Info Ser 38, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Rowden RD, Libra RD, Liu H (2000) Groundwater and surface-water monitoring in the Bugenhagen sub-basin 1986–1995: a summary review. Tech Info Ser 41, Iowa Department of Natural Resources, Geological Survey Bureau, Iowa City

Singh KP, Stall JB (1971) Derivation of base flow recession curves and parameters. Water Resour Res 7(2):292–303

US Environmental Protection Agency (1986) Pesticides in groundwater: background document. USEPA, Office of Pesticide Programs, Washington, DC

White WB (1969) Conceptual models for carbonate aquifers. Ground Water 7:15–21

White WB (1977) Conceptual models for carbonate aquifers: revisited. In: Dilamarter R, Csallany SC (eds) Hydrologic problems in karst regions. Western Kentucky University, Bowling Green, Kentucky, USA, pp 176–187

 DOI 10.1007/s100400100150