The hydrogeochemistry of the Lake Waco drainage basin, Texas

S.I. Dworkin

Abstract The origin of surface water chemistry in highly impacted drainage basins must be investigated on a drainage-basin scale if the causes of the pollution are to be elucidated. This study characterizes and deciphers the surface water chemistry of a nutrient polluted river system in central Texas. Four tributaries of the Lake Waco reservoir were chemically characterized temporally and spatially in order to gain a complete understanding of the nature and origin of dissolved solids being transported into the lake. Temporal chemical variations measured at the base of each of the drainage basins are repetitive and seasonal. The most periodic and well-defined variation is exhibited by nitrate concentrations although many of the other solutes show seasonal changes as well. These temporal chemical changes are controlled by seasonal precipitation. During rainy seasons, the shallow aquifer is recharged resulting in stream discharge that is high in nitrate, calcium, and bicarbonate. When the shallow flow system is depleted in the summer, stream waters are dominated by deeper groundwater and become rich in sodium. Spatial variations in the chemistry of South Bosque surface waters were characterized using the snapshot technique. The spatial distribution of nitrate in surface waters is controlled by fertilizer application to row crops and the location of a munitions factory. The concentrations of naturally derived solutes such as Ca^+, Na^+, Cl^-, and $SO_4^{-2}$are controlled by underlying lithologies.

Keywords Nutrients · Hydrogeochemistry · Nitrogen · Snapshot · Lake Waco · Waco · Texas

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S.I. Dworkin
Department of Geology, Baylor University,
Waco, TX 76798, USA
E-mail: Steve_Dworkin@Baylor.edu
Tel.: +1-254-7102361
Fax: +1-254-7102673

Introduction

The chemical characterization of surface water on a drainage basin scale lends insight into processes that are responsible for the origin of the water chemistry. This is particularly important in watersheds that drain into lakes or reservoirs that are used for municipal purposes. In many cases, undesirable water chemistry, whether the result of natural or anthropogenic causes, can be modified at the source to fit man's use if the origin of the water chemistry is understood (James and others 1995; McFarland and Hauck 2001).

The two methods most commonly used to gain an understanding of the origin of surface-water chemistry are temporal and spatial chemical characterizations. Temporal chemical characterization is accomplished by repeatedly sampling a stream at one location over a long period of time. Changes in stream-water chemistry over time have been attributed to storm events, seasonal effects (driven primarily by precipitation patterns), mixing of waters derived from different parts of the water shed, and increasing or repetitive activity by man (Pinault and others 2001; Land and others 2000; Arheimer and Liden 2000; Robson and others 1991; Christophersen and others 1982). Spatial differences in stream-water chemistry are caused by the spatial distribution of different lithologic units throughout a watershed and the spatial distribution of man's activities (Douglas and others 2002; Sullivan and Drever 2001; Semhi and others 2000; Hercod and others 1998).

This study characterizes the spatial and temporal chemical variations in surface water of the Lake Waco drainage basin. This highly impacted water shed (TWC & TSSWCB 1991; TNRCC 1996) is utilized by the city of Waco, Texas, for its municipal water supply. The drainage basin is occupied by many nutrient sources and a wide range of rock types. Remediation of this drainage basin will only be accomplished if the hydrogeochemistry of the watershed is understood on a drainage basin scale. The goals of this study are to characterize the spatial and temporal changes in surface water chemistry of the four major tributaries that drain into lake Waco. Although another one of the goals of this study is to discern the origin of anthropogenic contributions to surface waters, the more encompassing objective is to understand the overall hydrogeochemistry of the drainage basin.

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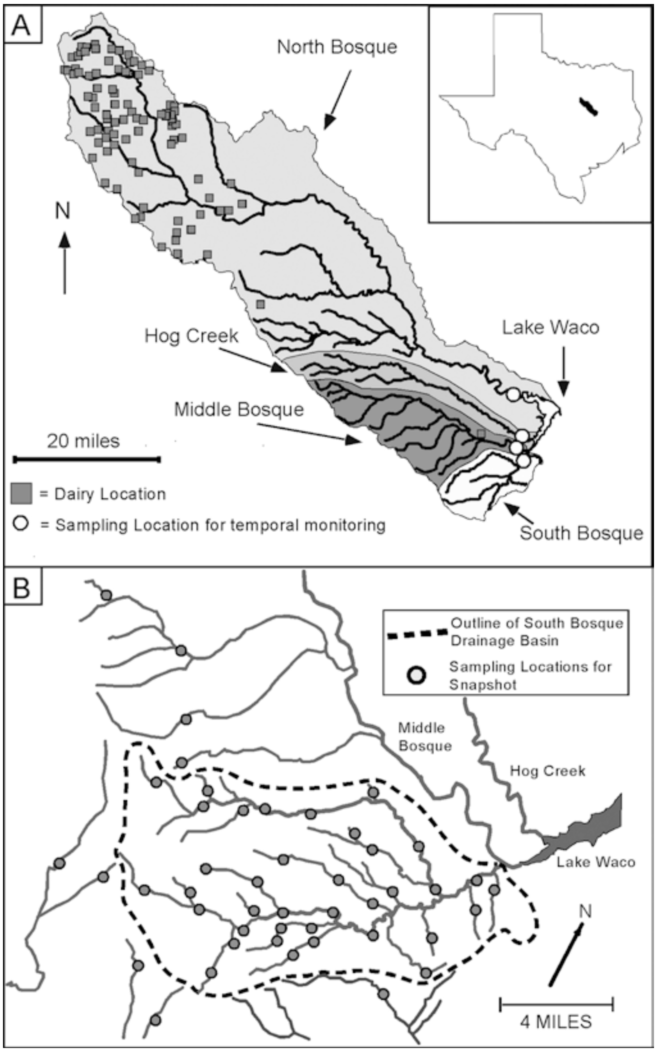

Fig. 1
A The four sub-basins of the Lake Waco drainage basin. Sampling locations for the temporal chemical characterization are show near the base of each watershed. **B** Sampling locations for the South Bosque Basin snapshot chemical characterization

Study area

Physiography

The Lake Waco drainage basin is composed of four large sub-basins that drain into the lake from the west (Fig. 1A) and a small sub-drainage basin that drains into the lake from the east. The four large tributaries carry a substantial load of dissolved species and are primarily responsible for the water quality of the reservoir. From south to north the streams studied in this investigation are the South Bosque, Middle Bosque, Hog Creek, and North Bosque.

Geology

The Lake Waco drainage basin is underlain by Cretaceous sedimentary rocks. Abraham (1998) characterized the lithologies of the rocks in the drainage basin. Rocks in the north part of the basin are composed of limestone, marl, and sandstone. The southern part of the basin is underlain by limestones, marls, calcareous shales, and shales. The main lithologic difference between the two areas is the abundance of fine-grained terrigeneous sediment in the South Basin particularly in the South Bosque watershed. The South Bosque basin has abundant mud rocks containing higher concentrations of pyrite than the carbonates and coarser clastics that dominate the North basin.

Land use

In a similar fashion to the varying geology of the study area, the land use also varies over the Lake Waco drainage basin. The North Bosque watershed is dominated by woods and rangeland, whereas the other three watersheds are utilized primarily for row crops and range land. The North Bosque river watershed is also utilized extensively by the dairy industry with about 100 dairies occupying the northern half of the drainage basin (Fig. 1A). Other land uses that impact nutrient loading include several large wastewater treatment plants (located primarily along the North Bosque river), a large munitions factory (now closed) located in the South Bosque watershed, and scattered rural communities which utilize septic systems as their means for waste water disposal.

Hydrogeology

Because this study investigates the surface water chemistry of the Lake Waco drainage basin only during times of base flow, the hydrogeology of the watershed is critical to the understanding of the origin of the water chemistry. Shallow groundwater in the Lake Waco drainage basin can be divided into two systems with distinct chemical and flow characters. A fracture flow system dominates the upper part of the aquifer. This aquifer is perennial and goes dry in the summer. Water moves relatively quickly through the fractures and discharges into streams. The deeper part of the aquifer is dominated by groundwater flow through interparticle pores and along bedding planes and has a low hydraulic conductivity (Hercod and others 1998).

Material and methods

One of the standard techniques used to monitor temporal variation in stream-water chemistry is to sample water at the bottom of a drainage basin periodically over a long period of time. This method was utilized in this study by sampling water at the base of the four major subdrainage basins (Fig. 1A) approximately monthly for 3 years. Water samples were collected only under base-flow conditions. In addition to documenting temporal variations, spatial variation in surface water chemistry was investigated using the snapshot method (Grayson and others 1997). This method is labor intensive, but yields information that is invaluable in understanding the source of dissolved solids. The snapshot yields high-resolution spatial information and involves collecting many samples over a short period of time over the entire drainage basin. Other studies that have utilized the snapshot method for surface-water studies include Salvia and others (1999), Hutchins and

others (1999), Grayson and others (1997) and Lahermo and others (1995), and a snapshot of ground-water chemistry was carried out by Antonakos and Lambrakis (2000). Because the water of the South Bosque watershed consistently has the highest total dissolved solids (TDS) and the highest nitrate concentrations, the water chemistry of this basin was investigated using the snapshot method. This involved sampling 46 surface water locations (Fig. 1B) within or close to the South Bosque basin over a period of 48 h.
The pH, conductivity, and temperature of surface-water samples were measured in the field. Solute concentrations were determined by capillary electrophoresis (Water, Quanta 4000) within 24 h of collection. Analysis of standards and duplicate unknowns indicates that the analytical uncertainty for all species is no greater than 4%. Bicarbonate concentrations were calculated by charge balance. Speciation and saturation indices calculations were carried out using PHREEQC (Parkhurst 1995). Sulfur and nitrogen isotopic compositions were measured by Coastal Science Laboratories in Austin, Texas. Reported precision on these isotope ratios are ±0.5 and 1.0‰, respectively.

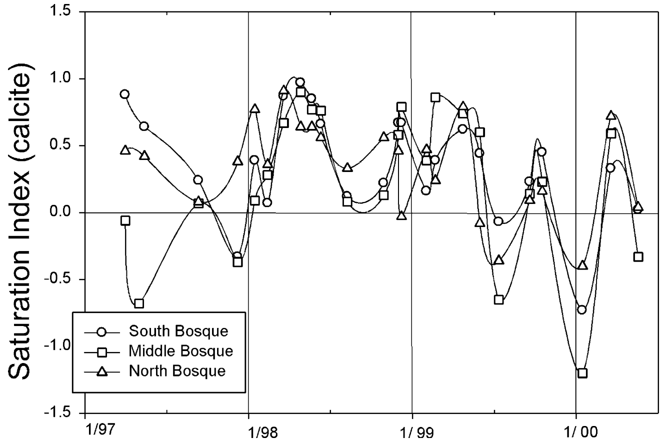

Fig. 2
Calcite saturation indices at the base of Lake Waco sub-basins over the course of the study. Hog Creek is not shown because it mimics the magnitude and pattern of the Middle Bosque

Results

General water chemistry of the Lake Waco drainage basin

The TDS of baseflow at the bottom of the four drainage basins ranges between 200–500 mg/L. The concentration of dissolved species in base flow exhibits considerable variation over time. The range and average concentration of the measured chemical components in the four drainage basins is shown in Table 1. Water in all four basins is usually saturated with respect to calcite although considerable variation in the saturation index for calcite was observed over the study period (Fig. 2) and corresponds to seasonal and co-varying changes in calcium and carbonate concentrations.
The water sampled at the bottom of all four drainage basins is dominated by calcium and bicarbonate. Although the stream waters plot in similar areas of a piper diagram (Fig. 3), there are distinct chemical differences between the basins. The North Bosque consistently has the highest magnesium and lowest nitrate concentrations and can be differentiated from the other basins on the cation triangle of a Piper plot (Fig. 3). The South Bosque has higher concentrations of most dissolved species, particularly sulfate and nitrate. The Middle Bosque and Hog Creek have fairly similar chemistries, and the concentration of most of their dissolved species are lower than the South and North Bosque.

Temporal variations in water chemistry

Many of the chemical species show repetitive changes in their concentration over the course of the study and for the most part, these temporal trends occur simultaneously in all four subbasins. The concentration of nitrate exhibits the most periodic and well-defined behavior of all the measured species (Fig. 4A). Nitrate concentrations are highest in the winter or early spring and are lowest in the summer and fall, a trend that has been observed in many other watersheds that are polluted with nutrients (Khadija and others 2000; Elder 1985). Other anionic species (Cl^-, SO_4^{-2}, and F^-) exhibit much less variation and temporal trends are not readily apparent. The exception to this is sulfate concentrations in the South Bosque which are inversely related to nitrate concentrations. The cation concentrations also demonstrate repeated concentration

Table 1
Range and average (in parentheses) of solute concentrations at the base of streams in the Lake Waco drainage basin. Solute concentrations are ppm

	pH	Conductivity (uS)	Ca^{+2}	Na^{+}	Mg^{+2}	HCO_3	Cl^-	SO_4^{-2}	NO_3^-	F^-
South	7.1–8.2	418–627	33–108	12–57	2–8	117–276	9–58	30–122	0–64	0.22–0.42
Bosque	(7.7)	(525)	(77)	(29)	(4)	(201)	(25)	(56)	(27)	(0.29)
Middle	7–8.5	280–562	25–121	7–28	1–5	85–279	7–41	13–102	0–33	0.18–0.43
Bosque	(7.8)	(371)	(65)	(14)	(2.5)	(179)	(16)	(29)	(9)	(0.3)
Hog Creek	7.1–9.0	259–474	31–91	7–31	1–4	106–267	6–50	4–83	0–21	0.17–0.38
	(7.8)	(381)	(61)	(14)	(2)	(188)	(14)	(21)	(5.3)	(0.20)
North	7.2–8.7	328–652	28–93	11–39	3–11	101–307	10–55	15–39	0–6	0.10–0.30
Bosque	(7.8)	(457)	(61)	(23)	(7)	(215)	(23)	(31)	(2)	(0.20)

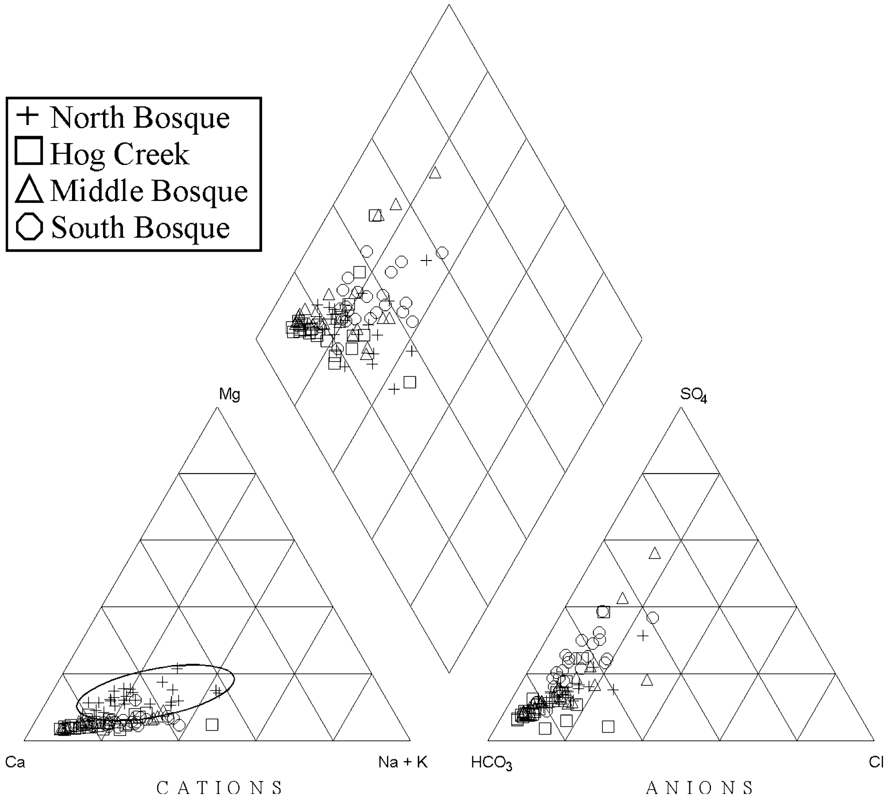

Fig. 3
Piper diagram of the surface water chemistry of the four drainage basins over the course of the study. High-magnesium North Bosque waters are circled on the cation triangle

changes over the study period (for example, calcium variations are shown in Fig. 4B).

The concentration of many of the dissolved species co-vary. Nitrate, bicarbonate, and calcium concentrations are positively correlated (Fig. 4A, B) whereas sodium concentrations are negatively correlated with nitrate (Fig. 5) and calcium. Correlations between the concentrations of dissolved species are the strongest in the South Bosque drainage basin.

Spatial variations in water chemistry

The spatial distribution of surface water chemistry in the South Bosque drainage basin was investigated using the snapshot method. There are two spatial trends identified for the surface water chemistry; one defined by nitrate concentrations (Fig. 6A) and a trend defined by the concentrations of all the other dissolved species (for example, sodium, calcium, and sulfate are illustrated in Fig. 6B–D).

The snapshot reveals that nitrate concentrations are uniformly low along the entire southern part of the South Bosque drainage basin. Nitrate concentrations rapidly rise to the north and reach levels between 50–70 ppm for most of the basin. Two areas have particularly high nitrate concentrations: the west-central region and the north-west region. These locations have surface waters with nitrate concentrations over 100 ppm (Fig. 6A).

The second spatial distribution pattern is followed by all other solutes. These elements have high concentrations in streams in the south-central part of the South Bosque basin, which then decrease to the north becoming uniform over the north half of the basin (Fig. 6B–D).

Isotope ratios

A cursory analysis of sulfur and nitrogen isotopic compositions was undertaken to help elucidate the origin of dissolved solids (Table 2). Nitrogen isotopic compositions of surface water within the Lake Waco drainage basin vary between $\delta\ ^{15}N$ values of 3.5 to 10.2‰ (AIR). There is no apparent relationship between nitrate concentration and nitrogen isotopic composition. The sulfur isotopic composition of aqueous sulfate varies between $\delta\ ^{34}S$ values of −8.3 to 6.6‰ (CDT). The more dissolved sulfate in the water, the lighter the isotopic composition of the sulfur.

Discussion

Anthropogenic solutes

The majority of the load of nitrogen discharged to Lake Waco comes from the Middle and South Bosque rivers (Fig. 7). The correlation of nitrate concentration with the percent of land covered by row crops (Table 3) indicates that one of the major controls on nitrate concentration is the amount of fertilizer applied to fields. However, the disproportionally high concentration of nitrate at the base of the South Bosque drainage basin cannot be accounted for solely by the amount of fertilized land because this watershed has almost the same proportion of row crops as the Middle Bosque and yet has three times the average concentration of nitrate. Other factors that control the nutrient concentrations in base flow are depth of stream incisement, speed of groundwater flow to the streams, groundwater residence time, the water storage capacity of

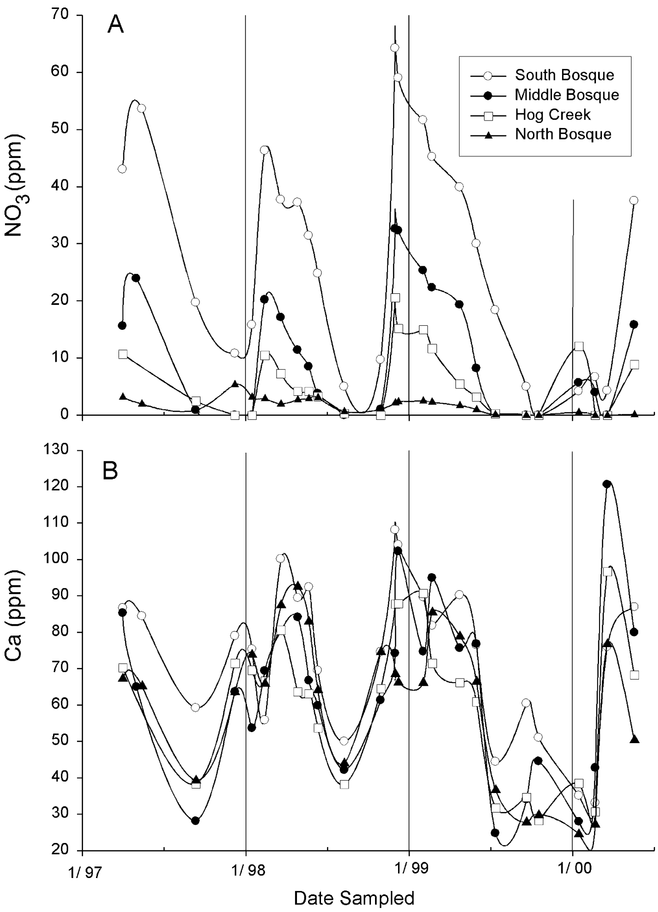

Fig. 4
Repetitive and seasonal stream water chemistry shown by **A** nitrate and **B** calcium concentrations

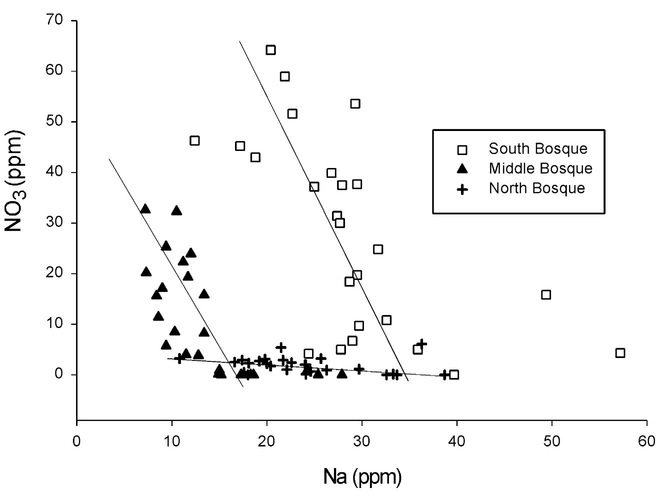

Fig. 5
Negative correlation between nitrate and sodium concentrations over the study period

the rocks in each basin, and other sources of anthropogenic nitrogen.

The deeply incised stream channels of the Middle Bosque have lower concentrations of nitrate under base-flow conditions than the South Bosque because the discharging deeper groundwaters have low nitrate concentrations. Additionally, the dominance of mudrocks in the South Bosque basin causes deep surface cracks that facilitate the rapid passage of shallow groundwater to the streams resulting in short groundwater residence times. This promotes the efficient transfer of nitrogen that has been applied to row crops into shallow groundwater and its subsequent discharge to the streams. Another possible reason for the distinct difference in nitrate concentration between the South and Middle Bosque is the relationship between aquifer storage capacity and lithology (documented for central Texas units by Knisel 1963). The high storage capacity of limestones in the Middle Bosque accommodates more recharge into the aquifer than the mudrocks of the South Bosque resulting in dilution of nitrogen in shallow groundwater of the Middle Bosque basin.

The fertilizer origin of nitrogen is also supported by comparing the snapshot of nitrate concentrations in the South Bosque basin with land use (Fig. 8). The lack of row crops in the southern part of the South Bosque basin corresponds with low concentrations of nitrate in surface waters, whereas the highest nitrate concentrations are in the central and western parts of the basin where row crops cover almost all of the land surface. The snapshot also reveals that a second important source of nitrogen contributes to high nutrient concentrations in the South Bosque drainage basin. Streams draining the southern part of the (now closed) Hercules munitions factory in the west central portion of the drainage basin have some of the highest nitrate concentrations in the basin (Fig. 8). Based on the spatial relationship between nitrate concentrations and the munitions factory it appears that the southeast corner of the factory is a second major source of nitrogen in the South Bosque basin.

Nitrogen isotope ratios measured at the bottom of all the basins fall within the range of natural soil nitrogen (Table 2) and are not of much use for discriminating between nutrient sources. Nitrogen isotope ratios measured at two locations within the South Bosque basin with nitrate concentrations over 100 ppm reveal soil nitrogen (+6.4‰) and fertilizer (+3.5‰) isotopic signatures. Soil nitrogen isotopic signatures may indicate that much of the fertilizer applied to fields is cycled through plants or undergoes redox reactions before being transported to shallow groundwater and then subsequently discharged to the streams. Lastly, nitrogen isotopic ratios sampled within the North Bosque river drainage basin vary from heavy values indicative of mammal excrement in the upper part of the basin (Stephenville sampling location) to lighter ratios in the middle part of the basin (Hico and Clifton sampling locations) and then back to heavy ratios even lower in the basin (Del Mar Ranch location). These nitrogen isotope ratios probably reflect a dairy cattle source up basin, a soil nitrogen source in the middle of the basin, and contributions from waste water treatment plants in the lower parts of the basin. Systematic and long-term monitoring of nitrogen isotopes would be necessary to support these conclusions.

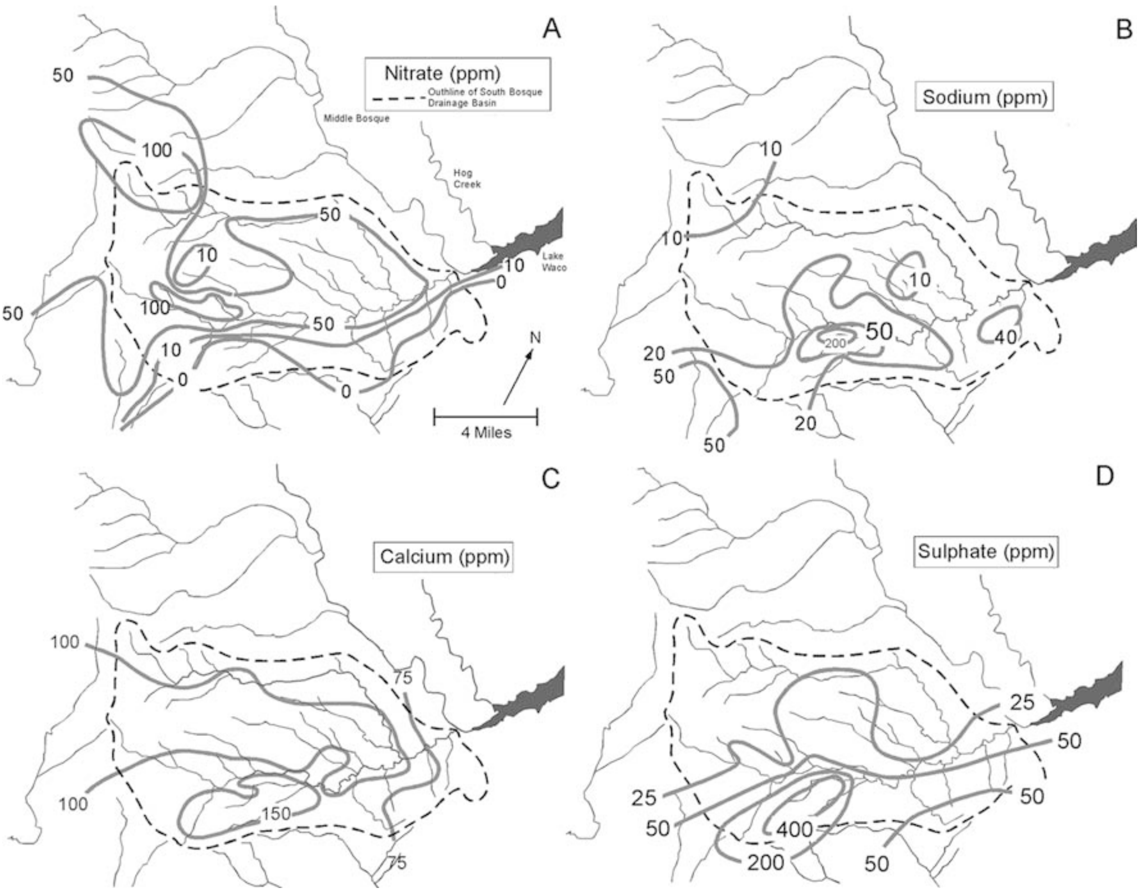

Fig. 6A–D
Spatial distribution of solutes in surface waters of the South Bosque basin. **A** Nitrate, **B** sodium, **C** calcium, **D** sulfate

The periodic change in nitrate concentrations exhibited by all four basins (Fig. 4A) reflects the seasonally changing source of baseflow. During rainy seasons, base-flow discharge volumes are high and the shallow parts of the aquifer are the dominant source of the stream water. Shallow groundwater receives nitrogen from surface applications of fertilizer that is rapidly mobilized downward during periods of abundant rainfall. During time periods with little precipitation, the shallow aquifer is depleted and deeper waters that have little or no nitrate dominate baseflow. Mixing of different water reservoirs (soil waters, regolith waters, shallow groundwater, or deep groundwater) caused by seasonal precipitation differences has been observed in many studies to cause periodic stream water chemistry variations (Holloway and Dahlgren 2001; Rice and Bricker 1995)

Table 2
Isotope chemistry of surface water in the Lake Waco drainage basin

Location	Date	δ ^{15}N ‰(AIR)	NO_3^- (ppm)	δ^{34}S ‰ (CDT)	SO_4^{-2} (ppm)
South Bosque[a]	2/17/98	6.0	46.3	−3.8	46.7
Middle Bosque[a]	2/17/98	7.2	20.2	4.7	18.0
Hog Creek[a]	2/17/98	6.9	10.5	4.3	18.2
North Bosque[a]	2/17/98	5.8	2.9	−1.1	38.2
SB-11[b]	3/26/98	3.5	100.6	6.6	16.1
SB-29[b]	2/3/98	6.4	106.6		
SB-36[b]	3/26/98			−8.3	751.1
Stephenville[c]	10/30/98	10.2	0.4		
Hico[c]	10/30/98	7.2	0.5		
Clifton[c]	10/30/98	4.9	1.4		
Del Mar Ranch[c]	10/30/98	9.7	2.1		

[a]Sampling locations at the bottom of the drainage basins
[b]Snapshot location within the South Bosque drainage basin
[c]Locations within the North Bosque drainage basin

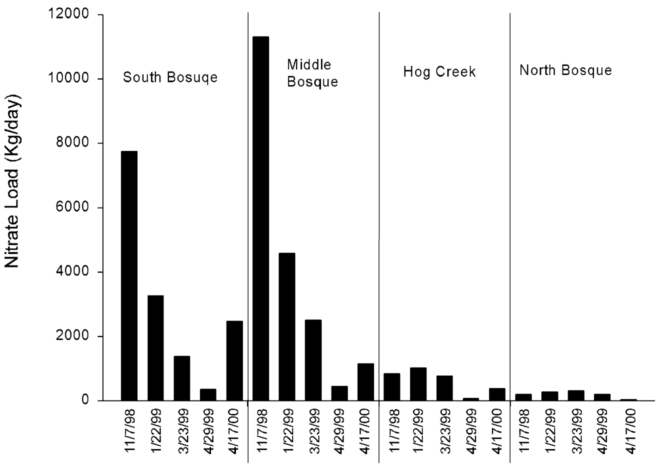

Fig. 7
Flux of nitrate from each tributary of the Lake Waco drainage basin

Table 3
Average nitrogen concentration and percent of land area occupied by row crops in each drainage basin

Basin	Average NO_3^- (ppm)	Land area covered by row crops (%)	Drainage area (mi^2)
South Bosque	27	51	91
Middle Bosque	9	48	182
Hog Creek	5	41	78
North Bosque	2	12	1,146

Naturally derived solutes

Solutes derived from water-rock interaction dominate the water chemistry of the Lake Waco drainage basin. The water chemistry of each drainage basin reflects the lithologies within the basin. Good examples of this relationship are demonstrated by: (1) elevated magnesium concentrations in the North Bosque River, and (2) elevated sulfate concentrations in the South Bosque. The relatively high magnesium concentrations in the North Bosque are the result of dissolution of dolomitized limestones in the upper part of the basin (Glenn Rose Formation). Similarly, the high sulfate concentrations in the South Bosque Basin can be attributed to the numerous pyrite-bearing mudrocks which crop out in the southern half of the basin. The relatively high TDS of the South Bosque water is undoubtedly related to the generation of acid during the oxidation of this pyrite resulting in the dissolution of calcite and leaching of metals from clay surfaces.

The isotopic composition of sulfur in aqueous sulfate also supports the natural source for this solute. The higher the concentration of sulfate in surface waters of the Lake Waco drainage basin, the lighter the sulfur isotopic composition (Table 2). This relationship indicates that the oxidation of pyrite, which typically has a light sulfur isotopic composition (Krouse 1980), is the source of sulfur in sulfate-rich waters. In contrast, the waters with sulfate concentrations less than 20 ppm all have sulfur isotopic compositions that average around +5‰ which is a common sulfur isotopic composition for rain water.

Covariation of solute concentrations also lends insight into the origin of naturally derived species. Perhaps the best example of this is the negative correlation between nitrate and sodium concentrations. As discussed above, aqueous nitrate is a pollutant and discharges into streams from shallow groundwater. The inverse relationship between the concentration of these two species indicates that discharging deeper waters are the source of abundant sodium. High sodium concentrations occur during summer months and at times when discharge is low. It is at these

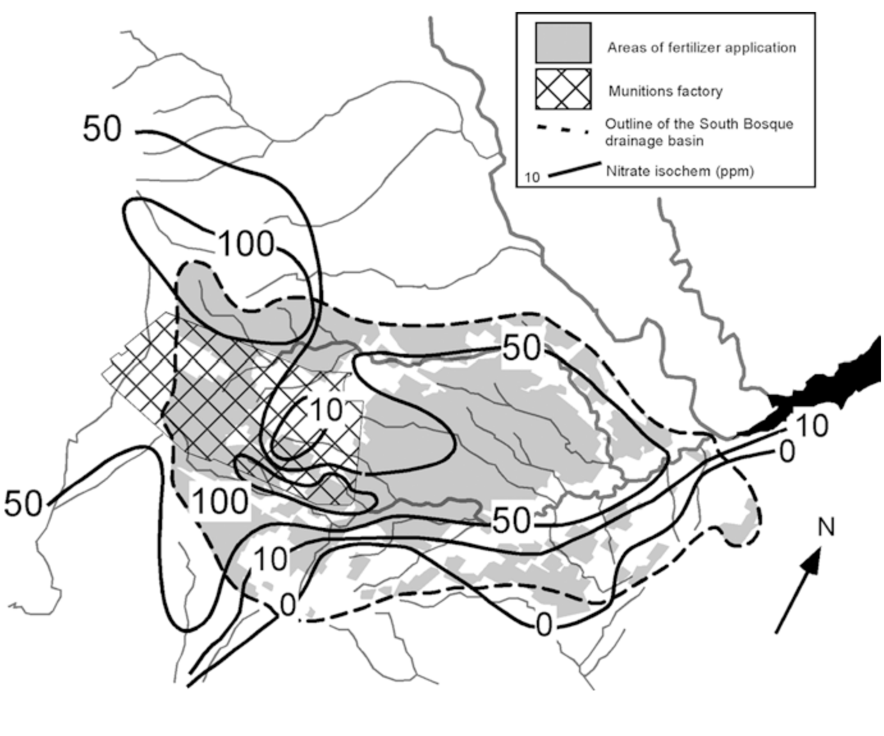

Fig. 8
Nitrate isochems plotted over selected land use areas in the South Bosque drainage basin

times that shallow groundwater contributes little to base flow. Sodium probably originates from clays in shales and marls and as a trace constituent in limestones. In contrast to sodium, calcium and bicarbonate concentrations are positively correlated with nitrate. Most of the calcium and dissolved carbon are naturally derived from calcite dissolution resulting from high CO_2 pressures generated during the decomposition of soil organic material. Calcium and bicarbonate have elevated concentrations when shallow groundwater dominates baseflow during times of seasonally high precipitation.

Lastly, the spatial distribution of most solutes in the South Bosque basin is strongly correlated to underlying rock types. The SW-NE trend of high solute concentrations in the southern part of the basin (Fig. 7B–D) parallels the strike and the outcrop areas of the shales and marls that crop out in the basin (Del Rio, Pepper, Lake Waco, and the South Bosque Formations). The oxidation of the abundant pyrite in these rocks results in high sulfate concentrations and acid that subsequently dissolves calcite and leaches metals from clays. The particularly high concentrations of naturally derived solutes in the south-central South Bosque watershed appears to be caused by discharge from an escarpment that forms a prominent outcrop of these mudrocks. The waters in the southern part of this basin also have elevated fluoride concentrations (up to 0.7 ppm) that is probably derived from collophane which is concentrated in these fine-grained sedimentary rocks.

Conclusions

The temporal and spatial chemical characterization of surface waters in the Lake Waco drainage basin reveals that the controls on the surface water chemistry are land use, geology, and groundwater flow dynamics. The chemistry of the four tributaries that drain into Lake Waco is dominated by calcium and bicarbonate and the water in three of the tributaries (South Bosque, Middle Bosque, and Hog Creek) exhibit elevated nitrate concentrations. These surface waters also exhibit repetitive changes in composition that occur seasonally.

Variations in the contribution of shallow and deeper groundwaters to base flow is due to seasonal precipitation patterns that result in the repetitive temporal variations of many of the solutes. When the shallowest parts of the aquifer are filled with water in the winter and early spring, these shallow groundwaters become highly charged with dissolved carbon dioxide due to microbial degradation of organic material and thus become calcium and bicarbonate rich. When this water discharges to streams in the rainy seasons, the stream water becomes oversaturated with respect to calcite thus resulting in a cyclical pattern of the calcite saturation index.

Additionally, nitrogen from fertilizer applied to row crops is readily transported into shallow groundwater and discharges to the streams during seasons with high rainfall. When the shallow aquifers are depleted in seasons with little rainfall, deeper groundwaters become the main source of baseflow and generate stream flow that has low nitrate and higher sodium concentrations.

The spatial distribution of surface-water solutes in the South Bosque basin was investigated using the snapshot technique. The resulting high-resolution spatial chemistry data shows the control of different lithologic units and land use on stream water chemistry. High nitrogen concentrations in streams correlate with land areas that are utilized for row crops. A portion of a munitions factory also apparently contributes nitrogen to the surface waters of the South Bosque basin. High concentrations of most other solutes correspond to land areas underlain by mudrocks. These pyrite-rich rocks generate acid during pyrite oxidation resulting in high concentrations of the naturally derived solutes.

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