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REPORT

Long-term (1970s–2016) changes in groundwater geochemistry in the High Plains aquifer in south-central Kansas, USA

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Abstract

Changes in groundwater chemistry in the Great Bend Prairie aquifer, a portion of the High Plains aquifer in south-central Kansas (USA), were studied in order to better understand factors influencing groundwater quality and aquifer sustainability. To assess changes, groundwater samples from 22 monitoring wells were analyzed during 2016. Results were then compared to data obtained previously from the same wells in the 1970s and 1980s. Of the wells sampled, 13 wells were screened near the water table (average depth 22 m) and 9 wells were screened near the aquifer base (average depth 41 m). Nitrate levels in 2016 were higher for 20 of 21 wells with data available for comparison. The average increase for shallow-aquifer and aquifer-base samples was 9.5 (standard deviation, SD, 12.9) and 3.4 (SD 3.1) mg/L as N, respectively. Nitrate isotope ratios (δ^{15}N-NO_3 and δ^{18}O-NO_3) of the 2016 samples are consistent with nitrification of ammonium-based fertilizers as the nitrate source with potential contributions from animal waste. Total dissolved solute levels were also higher in samples from nine of 12 shallow-aquifer wells and four of eight aquifer-base wells, with average increases of 191 (SD 238) and 194 (SD 133) mg/L, respectively. Taken together, the results demonstrate that water quality has decreased considerably over the past 40 years primarily because of fertilizer use, but that groundwater mixing, evapotranspiration, and potentially animal waste inputs also affected groundwater chemistry. These findings help identify the scale of water-quality degradation in the High Plains aquifer.

Keywords Groundwater quality · Nitrate · Contamination · Agriculture · USA

Introduction

The High Plains aquifer is a vital source of water for food production and human populations in the Great Plains of the United States. The aquifer underlies an area of about 450,000 km^2 in parts of eight states (Fig. 1) and supplies about 23% of the groundwater used in the US (Maupin and Barber 2005). Most (97%) of the groundwater pumped from the aquifer is used for irrigation although nearly 2 million people use it as a source of drinking water (Gurdak et al. 2009). As a result of these withdrawals, groundwater storage has declined significantly in many portions of the aquijfer, limiting the supply available for future use (Butler et al. 2013; Scanlon et al. 2012). Aquifer sustainability is also threatened by changes in water quality (McMahon et al. 2007; Scanlon et al. 2010), which is the focus of this study.

Potential threats to groundwater quality include agricultural activities and hydrocarbon production, which both occur over a large area of the aquifer (Guerra et al. 2011, Whittemore 1993). Agricultural activities that can impact water quality include

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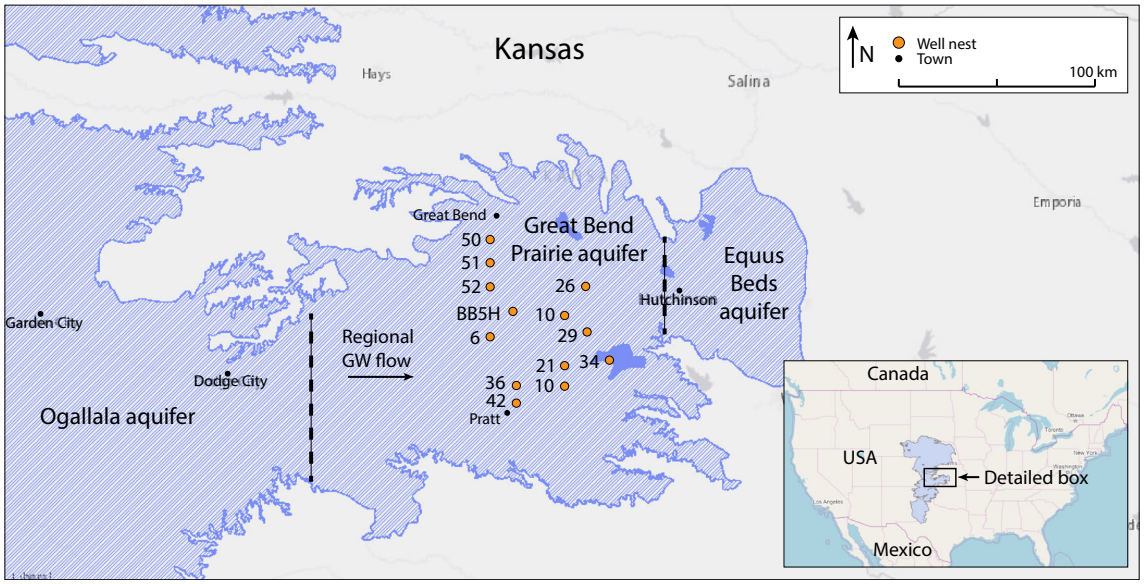

Fig. 1 Location of well nests. Shaded areas in the regional and detailed maps depict portions of the High Plains aquifer. Dashed vertical lines approximate boundaries between the Ogallala, Great Bend Prairie, and Equus Beds aquifers, portions of the High Plains aquifer in Kansas, USA

irrigation and application of fertilizers and pesticides to soils and plants. These activities can ultimately change groundwater pH and increase salinity and concentrations of nitrate, pesticides, and hazardous trace elements (Bailey et al. 2014; Böhlke 2002; Mas-Pla et al. 2016; Mencio et al. 2016; Nolan and Weber 2015; Rice and Herman 2012). Oil and gas wells often produce large volumes of deep groundwater, referred to as produced water, that usually contain high concentrations of dissolved salts, trace metals, and radionuclides (Guerra et al. 2011). Where produced water has been discharged or spilled at the surface, it can ultimately increase salinity and concentrations of organic contaminants in groundwater (Kharaka et al. 2007; Shores et al. 2017; Whittemore 2007).

Indeed, studies that have examined long-term trends in groundwater composition across the High Plains aquifer have concluded that human activities are causing water quality to decrease, particularly in shallow portions of the aquifer. Litke (2001) compiled groundwater geochemistry data collected from 1930 to 1998. Their analysis shows that nitrate levels measured between 1980 and 1998 were significantly higher than those measured from 1930 to 1969 in about 70% of the counties within the High Plains study area. Moreover, 16% of all measured nitrate concentrations were greater than the US Environmental Protection Agency (EPA) standard for public drinking water supplies (10 mg/L as N) and the pesticide atrazine was detected in 25% of the samples. Gurdak et al. (2009) evaluated long-term trends in groundwater geochemistry using age-dating techniques. Their results indicate that nitrate levels in recharge during the past ~12,000 years ranged from 0.8 to 4.2 mg/L as N but, within the past 60 years, nitrate levels have substantially increased.

Although these studies have greatly advanced the understanding of long-term changes in groundwater quality, data available to directly assess changes in groundwater quality are sparse in many portions of the High Plains aquifer (Chaudhuri and Ale 2014). Adding more detail to the understanding of factors that control groundwater quality is important because of the implications to human health, the sustainability of rural agriculture, and the costs associated with land and water management (Gurdak et al. 2009).

This study considers variation in groundwater quality in the Great Bend Prairie aquifer, a portion of the High Plains aquifer in south-central Kansas (Fig. 1). Goals are to quantify how groundwater quality has changed and assess reasons for those changes. The aquifer is vulnerable to contamination from human activities. Long travel times through the vadose zone delay impacts of land use on groundwater quality (Ascott et al. 2017; Scanlon et al. 2007). However, the Great Bend Prairie aquifer has a relatively shallow water table (generally <15 m) and sediment overlying the aquifer has high hydraulic conductivity (up to 1×10^{-3} m/s when saturated; Young 1992), favoring rapid transport. Moreover, agricultural activities and hydrocarbon production both occur throughout the study area (Whittemore 1993). Therefore, the results of this study can help identify the extent of potential water-quality degradation in the High Plains aquifer.

Materials and methods

Study area

The Great Bend Prairie aquifer and overlying sediment consist of unconsolidated sand and gravel with interbedded silt and clay deposited by wind and the ancestral Arkansas River during the Quaternary period (Fader and Stullken 1978; Gutentag et al.

1984; Latta 1950). The Quaternary sediments have a maximum thickness of 110 m. The sediments are capped by loamy and sandy mollisols and alfisols (Dodge et al. 1978) and underlain by Permian bedrock in the eastern half of the aquifer, where samples were collected for this study, and Cretaceous bedrock in the western half. The Permian bedrock includes interbedded sandstones, siltstones, and mudstones. Halite exists as cement, discrete crystals, and as bedded units in portions of the Permian strata in Kansas and dissolution of that halite causes groundwater in the bedrock to have high salinity (Whittemore 1993; Young 1992). The Cretaceous bedrock consists of interbedded sandstones and shales and is considered a confining or leaky confining layer between the Quaternary sediments and the Permian bedrock (Young 1992).

Regional groundwater flow in the Great Bend Prairie aquifer is to the east along a gradient ranging between 0.0013 and 0.0017, based on data reported by Young (1992). High temporal-resolution monitoring of water levels in index wells by the Kansas Geological Survey shows small amplitude fluctuations in response to precipitation events and larger-scale seasonal fluctuations (0.15–0.4 m) caused by irrigation pumping (Butler et al. 2019). On a longer timescale, groundwater levels are relatively stable in the Great Bend Prairie aquifer compared to portions of the High Plains aquifer in western Kansas, where the climate is drier (Whittemore et al. 2018). Water levels measured annually during the non-pumping season indicate an average decline of 2.5 m in the Great Bend Prairie aquifer since the onset of substantial irrigation development (1940s–1950s; Whittemore et al. 2018). In contrast, the average water level decline in the Ogallala aquifer in southwest Kansas is 31.4 m (Whittemore et al. 2018).

Spatial variation in groundwater composition is described in detail by Whittemore (1993). Groundwater salinity in the upper portion of the Great Bend Prairie aquifer is relatively low (chloride concentration <100 mg/L), except in the northeast portion of the aquifer, where groundwater discharges at the surface. In the aquifer base, chloride levels are generally <250 mg/L, except in the northern and central portion of the aquifer. Along the northern margin of the aquifer, chloride concentration ranging to over 20,000 mg/L has been measured in groundwater from the aquifer base.

The main cause of high salinity groundwater in portions of the Great Bend Prairie aquifer is the natural discharge of Permian saltwater (Whittemore 1993). This conclusion is supported by variation in groundwater chemistry as well as density-corrected head data, which indicate upward leakage from the Permian bedrock into the aquifer in some locations (Buddemeier 1994; Young 1992). Salinity has also increased in a few locations as a result of brine contamination from oil and gas wells and increased leakage of Permian saltwater driven by irrigation pumping (Whittemore 1993).

Study design

Groundwater samples were collected during summer 2016 from monitoring wells constructed during the late 1970s and early 1980s. Results were then compared to data collected previously from the same wells soon after construction by the Kansas Geology Survey (Whittemore 1993). The sites are nests of two to four wells completed at different depths in the Great Bend Prairie aquifer as well as the underlying Permian bedrock at many sites.

Overall, 22 wells were sampled in 13 well nests (Fig. 1). At nine of the nests, two wells were sampled, one completed near the upper part of the aquifer (22.4 m avg. depth, standard deviation (SD) 6.8) and one at greater depth and typically near the aquifer base (40.8 m avg. depth, SD 5.6). Throughout this article, these wells are referred to as shallow wells and aquifer base wells, respectively. At four well nests (34, 36, 51, 52), only groundwater from the shallow well was sampled. More details about the wells and the data reported by Whittemore (1993) are available in Tables S1 and S2 of the electronic supplementary material (ESM).

In addition to Whittemore (1993), other research on water quality in the Great Bend Prairie aquifer include Townsend and Young (1992) and Pope et al. (2001). The findings of those studies are consistent with Whittemore (1993). This analysis focuses on results reported by Whittemore (1993) because those results were collected from the same wells as this study.

Field methods

Prior to sampling, depth to water (DTW) was measured using a water-level meter (Solinst). Next, stagnant water was pumped out of the wells at a flow rate of up to 6 L/min using a submersible pump (Geotech SS Geosub Pump). After at least one well volume had been removed, the pump was then lowered to the middle of the well screen, pumping rate was decreased to about 2 L/min, and temperature, pH, and electrical conductivity were monitored using an Oakton PC-300 m. Samples were collected after each parameter had stabilized for three consecutive measurements (<5% variation) taken at least 5 min apart.

Dissolved oxygen (DO) levels were measured in the field using a field test kit (LaMotte). Filtered (0.45 μm) groundwater samples were collected for major cations and anions and trace elements and unfiltered samples were collected for nitrate isotope analysis. Samples were stored in high-density polyethylene bottles. Prior to sampling, bottles for trace element samples were cleaned by soaking them in dilute hydrochloric acid (2%) and rinsing them with 18 MΩ deionized water. Cation and trace element samples were preserved by acidifying them to pH <2 with trace metal grade nitric acid. For dissolved organic carbon (DOC) analysis, groundwater

was filtered using prewashed glass-fiber membrane filters (0.7 μm) and stored in precombusted amber glass bottles. DOC samples were preserved by acidifying them to pH < 2 with hydrochloric acid. All samples were stored on ice in the field and, except for nitrate isotope samples, at 4 °C refrigerator in the lab. Samples for nitrate isotope analysis were stored frozen (−40 °C) in the lab to limit potential biological reactions.

Laboratory analysis

Alkalinity was measured using Gran alkalinity titrations with 0.02 N sulfuric acid titrant. Concentrations of cations (sodium, ammonium, potassium, magnesium, calcium) and anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate) were measured using a Dionex ICS-1100 ion chromatograph (IC). Select trace elements (lithium, boron, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, rubidium, molybdenum, cadmium, barium, lead, uranium) were analyzed on an Agilent 7500cx inductively coupled plasma mass spectrometer (ICP-MS) at the Redox Biology Center in the Department of Biochemistry at the University of Nebraska-Lincoln. Detection limits for IC and ICP-MS data are available in Table S3 of the ESM.

Stable hydrogen ($^{2}H/^{1}H$) and oxygen ($^{18}O/^{16}O$) isotope ratios of water were analyzed on a Thermo Finnigan MAT 253 at the Keck-NSF Paleoenvironmental and Environmental Laboratory at the University of Kansas. Results are expressed in delta notation relative to Vienna standard mean ocean water (VSMOW) for hydrogen ($\delta D\text{-}H_2O$) and oxygen ($\delta^{18}O\text{-}H_2O$). Stable nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) isotope ratios of nitrate were analyzed on a Trace Gas-GVI IsoPrime isotope ratio mass spectrometer (TG-IRMS) by the Environmental Isotope Laboratory in the Department of Earth and Environmental Sciences at the University of Waterloo. Results are expressed in delta notation relative to atmospheric air for nitrogen ($\delta^{15}N\text{-}NO_3$) and VSMOW for oxygen ($\delta^{18}O\text{-}NO_3$) with precisions of ± 0.3 and ± 0.8‰, respectively.

Calculations

Charge imbalance and total dissolved solids (TDS) were calculated using The Geochemist's Workbench software (Aqueous Solutions). To create a uniform basis of comparison between studies, TDS was calculated for the 2016 samples and samples collected by Whittemore (1993) using only parameters that were measured in both sets of samples: fluoride, chloride, bromide, sulfate, sodium, magnesium, calcium, strontium, bicarbonate, nitrate, nitrite, ammonium, and phosphate.

Vertical hydraulic gradients were calculated for each well nest with DTW data from multiple wells as described by Gurdak et al. (2009). Those calculations used DTW measurements collected just before sampling and well depth and screen length information from well logs (Table S1 of the ESM). Vertical distance between head values was evaluated as the difference between well screen midpoints. Positive gradients indicate potential for downward flow. The horizontal hydraulic gradient for the study area was estimated using a three-point approach. The analysis used head values from shallow wells in nests 50, 42, and 34, which are located at the margins of the study area (Fig. 1).

The statistical significance of relationships among geochemical parameters was tested using GraphPad Prism, version 6 (GraphPad Software). Unpaired two-tailed t-tests with Welch's correction were used to test the significance of differences between groups of data. For ungrouped data, the significance of the relationship between parameters was tested using two-tailed Spearman's rho rank correlation. For both approaches, probability (P) values less than 0.05 were considered to be significant.

Results

Vertical and horizontal hydraulic head gradients were largely consistent with downward and eastward flow, respectively. Vertical gradients were positive, indicating downward flow, for nine of the 12 well nests where the data required for the calculation were obtained (avg. 0.05, standard deviation (SD) 0.03) (Table S1 of the ESM). Well nests 6 (−0.06), 29 (−0.01), and 36 (−0.02) had negative vertical head gradients, consistent with upward flow. The horizontal gradient estimated from shallow wells at nests 34, 42, and 50 is consistent with eastward flow along a gradient of 0.0014, a value within the range reported by Young (1992).

Samples from shallow wells tended to have lower temperature and pH and higher dissolved oxygen (DO) levels compared to groundwater samples from aquifer base wells (Fig. 2; Table S3 of the ESM). Temperature and pH averaged 16.4 °C (SD 0.7) and 7.30 (SD 0.2), respectively, for shallow groundwater samples and 17.1 °C (SD 0.7) and 7.42 (SD 0.2) for aquifer base samples. Dissolved oxygen (DO) levels averaged 4.5 mg/L (SD 2.6) in shallow samples and 2.0 mg/L (SD 2.2) in aquifer base samples.

Similarly, the abundance and proportions of major ions in the groundwater samples and the isotopic composition of the groundwater itself also varied with depth. Shallow groundwater samples tended to have lower concentrations of chloride, sulfate, sodium, potassium, magnesium and calcium than aquifer base samples (Fig. 2, and Fig. S1 and Table S3 of the ESM). Reflecting this variation, calculated TDS content of shallow samples and aquifer base samples averaged 603 (SD 325) and 4,662 mg/L (SD 7,438), respectively, consistent with previous research documenting the discharge of saltwater

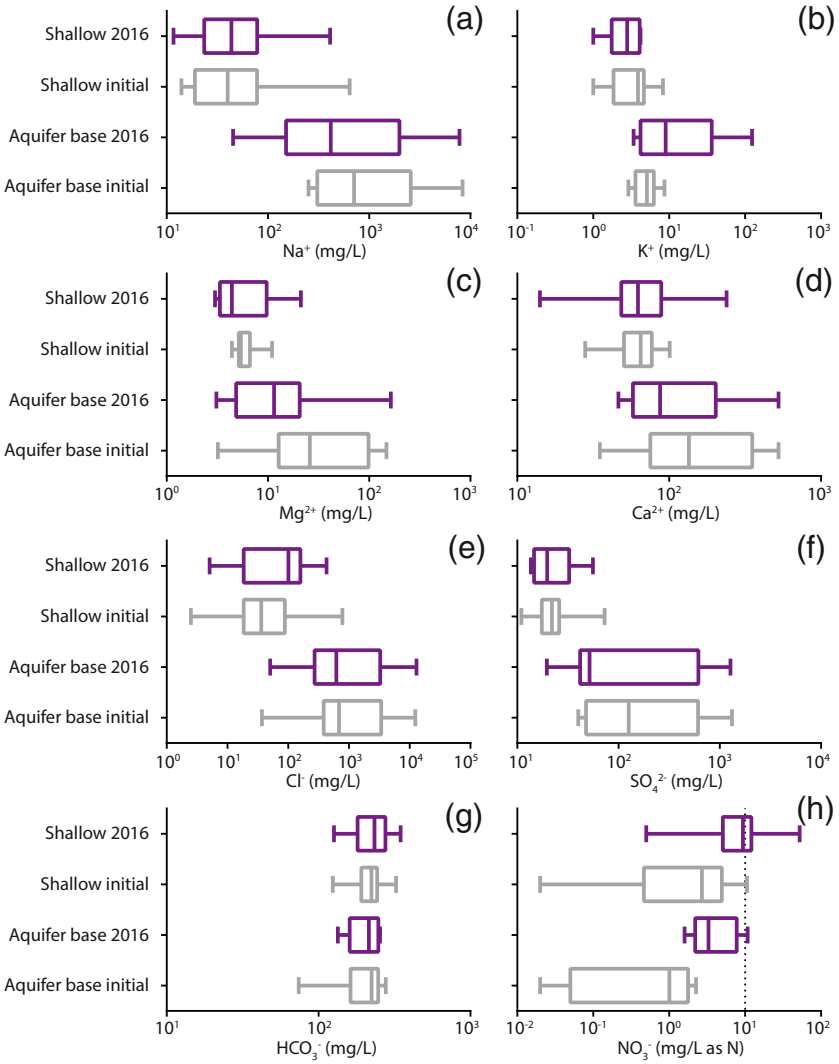

Fig. 2 Variation in concentrations of (**a**) sodium, (**b**) potassium, (**c**) magnesium, (**d**) calcium, (**e**) chloride, (**f**) sulfate, (**g**) bicarbonate, and (**h**) nitrate. The 2016 samples were collected for this study. Initial samples are those collected by Whittemore (1993). The dashed vertical line on (**h**) depicts the US EPA maximum contaminant level for nitrate. Complete data are available in Tables S1, S2, and S3 of the ESM

into the aquifer from the underlying Permian bedrock. Most of the shallow groundwater samples were Ca-HCO_3 type water whereas most of the aquifer base samples were Na-Cl type (Table S3 of the ESM). Isotope ratios of groundwater (δD-H_2O and δ^{18}O-H_2O) were higher on average in shallow samples compared to samples from the aquifer base (Fig. 3). Water δD values averaged −44 (SD 3) and − 47‰ (SD 4) in shallow and aquifer base samples, respectively, and water δ^{18}O values averaged −6.54 (SD 0.39) and − 6.90‰ (SD 0.33).

In contrast to most of the other solutes, nitrate concentrations ranged to considerably higher levels in shallow groundwater samples (Fig. 2; Table S3 of the ESM). Values ranged from 0.5 to 52.3 mg/L as N in shallow samples and 1.6 to 10.8 mg/L as N in aquifer base samples. Although concentration varied widely, nitrate δ^{15}N values in shallow and aquifer base samples were virtually identical on average. Nitrate δ^{15}N values for shallow samples and aquifer base samples averaged 4.04 (SD 1.94) and 4.05‰ (SD 1.42), respectively. By comparison, nitrate δ^{18}O values were more variable and averaged 5.87 (SD 2.48) and 1.94‰ (SD 4.40), respectively (Fig. 4; Table S3 of the ESM).

Concentrations of nitrite, ammonium, phosphate, and dissolved organic carbon (DOC) were generally near or below detection. Nitrite and ammonium concentrations were below the detection limit of our analysis in all samples (<0.04 mg/L as N and < 0.1 mg/L as N, respectively). Phosphate was above the detection limit (0.16 mg/L as P) in three shallow samples, with concentration averaging 0.2 mg/L as P (SD 0.1), while DOC was above detection (0.5 mg/L) in seven samples, with concentration averaging 0.8 mg/L (SD 0.2).

Trace element concentrations were generally below the US EPA drinking water standards, with a few exceptions (Table S3 of the ESM). The sample collected from well 10D had a uranium concentration of 61.2 μg/L, exceeding the US EPA Maximum Contaminate Level (MCL) of 30 μg/L. The sample from 21C had a barium concentration of 2.5 mg/L,

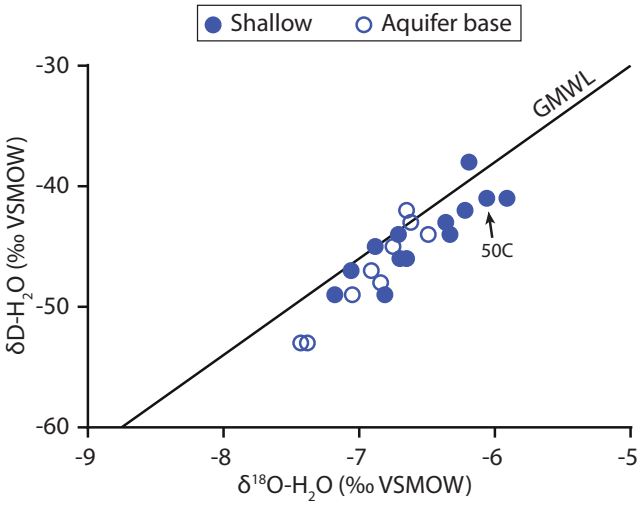

Fig. 3 Variation in the oxygen ($\delta^{18}O$-H_2O) and hydrogen (δD-H_2O) isotope ratios of groundwater in the 2016 samples. Data are shown relative to the global meteoric water line (GMWL; Craig 1961). The result for well 50C is identified for discussion purposes

exceeding the MCL of 2 mg/L. Lead concentrations exceeded the US EPA Action Level of 15 µg/L in 19 out of 22 samples. For those samples, lead concentration averaged 33 µg/L (SD 18). Samples collected from 10C, 26B, 42B, 50B, and BB5HA had manganese concentrations above the US EPA Secondary MCL (SMCL) of 50 µg/L, with concentration averaging 148 µg/L (SD 19). Lastly, the sample from 42B had an iron concentration of 0.62 mg/L, above the SMCL of 0.3 mg/L. Note that the observation wells sampled for this study are not used to supply drinking water; however, the Great Bend Prairie aquifer is the main drinking water source for the study area.

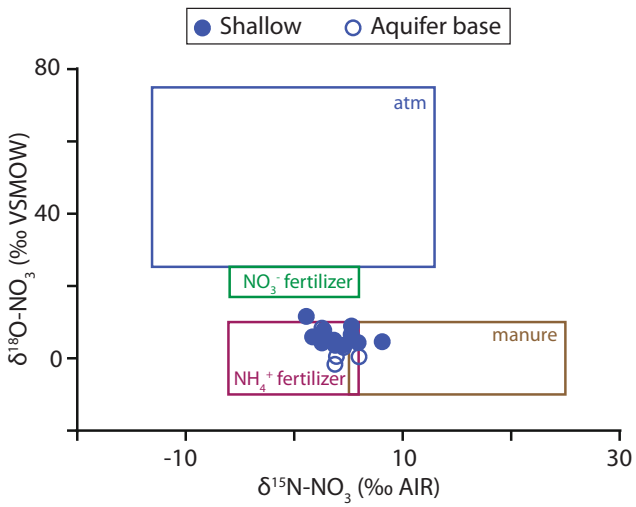

Fig. 4 Nitrate nitrogen ($\delta^{15}N$-NO_3) and oxygen ($\delta^{18}O$-NO_3) isotope ratios of the 2016 groundwater samples. Boxes depict typical ranges in nitrate sources as described by Xue et al. (2009)

Discussion

Changes in groundwater geochemistry

Results from analysis of the 2016 samples, when combined with data collected from the same wells by Whittemore (1993) between 1979 and 1987, allow this study to directly assess how groundwater quality has changed during the past 40 years. Some wells were sampled multiple times by Whittemore (1993; Table S2 of the ESM). For those wells, results between samplings were generally very similar and change relative to 2016 results was assessed using results from the initial sample collected.

The analysis shows that solute concentrations have increased for most but not all of the wells. TDS values were higher than those from Whittemore (1993) in nine of 13 shallow groundwater samples and four of eight samples from the aquifer base. For those samples, the average increase in TDS content was 191 (SD 238) and 194 mg/L (SD 133) in groundwater from shallow and aquifer base wells, respectively. Of the samples with lower TDS levels, samples from two aquifer base wells, 21B and 6B, had by far the largest decreases in TDS content. For those samples, TDS levels were 1,014 and 2,645 mg/L lower, respectively, than corresponding samples measured by Whittemore (1993).

The analysis also shows that nitrate concentrations have increased considerably. Nitrate levels in the 2016 samples were higher than levels measured by Whittemore (1993) in every sample collected from shallow aquifer wells and seven of eight samples from aquifer base wells. The one sample that did not have an increased concentration of nitrate had a concentration that was nearly identical to that measured in 1978. These changes in nitrate concentration are significant. When taken as a whole, nitrate levels in the 2016 samples were significantly higher than those in samples collected by Whittemore (1993) for shallow wells ($P = 0.031$) and aquifer base wells ($P = 0.0086$). For samples that had higher concentrations, the average increase in nitrate concentration was 9.5 (SD 12.9) and 3.4 mg/L as N (SD 3.1) for shallow and aquifer base wells, respectively. Thus, nitrate levels have increased more in the shallow aquifer than the aquifer base, consistent with depth variation observed in other aquifers in agricultural areas (e.g., Burow et al. 2007, 2008; Gurdak et al. 2009; Juntakut et al. 2019).

These increases in nitrate levels are large relative to increases observed in other agricultural landscapes. For example, the US Geological Survey National Water-Quality Assessment (NAWQA) project monitored the chemistry of shallow groundwater from about 241 wells in 12 well networks across the US during 1988–2016 (NAWQA project cycles 1, 2, and 3). Among those networks, the San Joaquin Valley agricultural land-use network (23 wells; avg. depth 49 m) had the largest median change in nitrate concentration

at 3.8 mg/L as N (Lindsey and Johnson 2018). The median change in nitrate concentration observed in wells sampled for this study was 4 mg/L as N. The length of time between samplings for this study (avg. 33.6 years, SD 2.9) is longer than the time between sampling for NAWQA cycles 1 and 3 at the network (avg. 19 years, SD 0.1). However, the median change in nitrate concentration in the Great Bend Prairie aquifer is comparable to the most extreme change observed in NAWQA networks between cycles 1 and 3.

Moreover, these increases in nitrate levels represent a significant decrease in water quality. Nitrate concentrations measured during this study exceed the US standard for public supplies of drinking water (10 mg/L as N) in seven of the samples. Six out of those seven samples were collected from shallow aquifer wells. Thus, 46% of the shallow groundwater samples had nitrate concentration above the drinking water standard. By comparison, only one of the samples collected by Whittemore (1993) had a nitrate concentration above 10 mg/L as N.

Nitrate source

Potential sources of nitrate to the aquifer include direct application of nitrogen-based chemical fertilizers, spreading of sewage and manure, discharge from septic tanks and leaking sewers, and atmospheric deposition (Wakida and Lerner 2005). Based on nitrate isotope ranges summarized by Xue et al. (2009), the nitrogen (δ^{15}N-NO_3) and oxygen (δ^{18}O-NO_3) isotope ratios in the 2016 samples are largely consistent with nitrification of ammonium-based fertilizer. Thus, application of ammonium-based fertilizer, followed by nitrification in the soil and subsurface, appears to be the main cause of the increase in nitrate levels. In addition, nitrate from animal waste likely also contributed. Indeed, the sample from shallow well 26C plots within ranges associated with manure (Fig. 4), consistent with the location of the well within a pasture.

These results imply that land use is a major factor influencing changes in nitrate concentration over time. Wells sampled in 2016 are located in two land-use categories: crop and pasture (Table S1 of the ESM). In the shallow portion of the aquifer, nitrate concentration was significantly higher in groundwater from wells in areas with crops than pasture ($P = 0.035$; Fig. S2 of the ESM). This result is consistent with the interpretation of nitrate isotope data. Ammonium-based fertilizer is applied to crop soil but not to pastures; therefore, if ammonium-based fertilizer is the primary source of nitrate to the aquifer, it is not surprising to find higher nitrate concentrations in crop areas. In the aquifer base, nitrate levels did not vary significantly with land use in our dataset; thus, the results suggest that land use will be a better predictor of nitrate levels in the shallow aquifer than the aquifer base.

Greater nitrate accumulation in the shallow aquifer than the aquifer base in areas with crops likely reflects proximity to the nitrate source (i.e., fertilization at the surface). Increased nitrate concentrations in groundwater from the aquifer base, together with isotopic results consistent with fertilizer, indicates that nitrate entering the aquifer from the surface has been transported by groundwater flow to the aquifer base during the past 40 years.

Along flow, aquifer heterogeneity and denitrification have the potential to affect nitrate distribution. Clay lenses may limit nitrate transport to some portions of the aquifer. Indeed, Townsend and Young (1992) found that the thickness of clay above the well screen negatively correlated with nitrate concentration in domestic and stock wells in a portion of the Great Bend Prairie aquifer. Relatively high DO and low DOC concentrations measured in the 2016 samples suggest that the capacity for denitrification in the aquifer is limited and not the primary control on nitrate concentrations and isotopes. Lower DO levels in the aquifer base compared with the shallow aquifer, however, suggest that the deeper portions of the aquifer may contain more anoxic zones, where denitrification and other forms of anaerobic respiration would be possible.

Interestingly, the pattern of nitrate changes over time was different at well nests in pastures compared to those in areas used for crops (Fig. S2 of the ESM). At crop sites, the increase in nitrate concentration was greater for shallow wells than aquifer base wells on average, but at pasture sites the opposite was true; nitrate concentration increased more for aquifer base wells than shallow wells. At pasture sites, greater nitrate increases in the aquifer base than the shallow aquifer may reflect horizontal transport of nitrate from adjacent locations where crops are grown. At crop sites, changes in nitrate concentration in the aquifer base may have been impacted by irrigation pumping. The 2016 samples were collected during irrigation season. Pumping of irrigation wells has the potential to induce flow from below the well screen. If that upward flowing groundwater has low nitrate content, it could lower nitrate concentration by dilution. Consistent with this hypothesis, Whittemore (1993) found that induced upward flow of deep saline groundwater below an irrigation well in the Great Bend Prairie aquifer can increase the salinity of irrigation water during the pumping season. Additional sampling to assess seasonal variation in groundwater chemistry is necessary to fully test this hypothesis.

Contribution of groundwater mixing

Following Whittemore (1995, 1993), this study used chloride and bromide concentrations to examine the contribution of groundwater mixing to variation in groundwater geochemistry. Mixing end-members in the study area include dilute recharge water, brine produced from oil and gas wells and discharged at the surface or within the aquifer, and saltwater formed by dissolution of evaporite minerals in Permian bedrock beneath the aquifer.

These end-members have different ranges in chloride concentrations and chloride/bromide ratios (Cl/Br). Chloride concentration is lower in the recharge water (0.1–10 mg/L) compared to brines (up to 240,000 mg/L in Kansas). Chloride/bromide mass ratios are generally below 150 for fresh recharge, between 200 and 400 for brine produced from oil and gas wells in the region, and between 5,000 and 17,000 for Permian saltwater in Kansas (Davis et al. 1998; Whittemore 1995, 1993). Therefore, mixing among these waters causes variation in chloride concentration as well as Cl/Br, providing a basis for mixing analysis. Processes that can cause deviation from a mixing trend include evapotranspiration and flushing of salts from soils and the unsaturated zone.

Whittemore (1993) concluded that the major ion chemistry of Great Bend Prairie aquifer water primarily reflects mixing between fresh recharge water and saltwater from the Permian bedrock. Results of the analysis are consistent with that conclusion (Fig. 5). Among the 2016 samples, only six fell outside of the zone of mixing between freshwater and Permian saltwater (6C, 10C, 10D, 26C, 36D, 50C). However, some to most of the chloride source for these six samples is still interpreted to be Permian saltwater. Thus, the results suggest that variation in TDS in the aquifer is primarily driven by groundwater mixing.

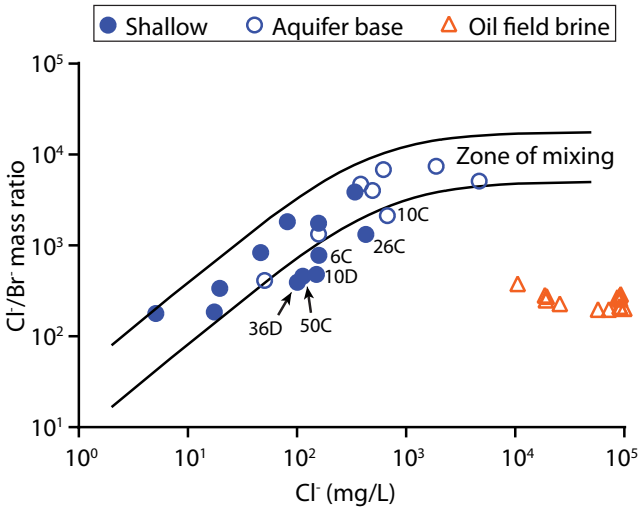

Fig. 5 Variation in chloride-bromide mass ratio (Cl/Br) with chloride concentration in the 2016 groundwater samples and oil field brines. Oil field brine data are taken from Whittemore (1993). The zone of mixing depicts the natural mixing relationships defined by Whittemore (1993) between freshwater and Permian bedrock saltwater. The saline ends of the two mixing lines represent the range in Cl/Br for nine samples of Permian saltwater (avg. 7,100) with chloride concentration >30,000 mg/L (avg. 36,000 mg/L). Samples plotting outside of the zone of mixing are identified. For reference, the sample with the highest chloride concentration is estimated to be a mixture of 4% freshwater with 96% Permian saltwater, based on chloride concentrations of 10 and 13,470 mg/L for the freshwater and Permian saltwater end-members, respectively. The saltwater concentration used for the estimate was measured by Whittemore (1993) in a groundwater sample from the Permian bedrock at that well site (site 26)

This conclusion seems to contradict the downward vertical gradient observed at most of the well nests; however, the downward vertical gradient within the aquifer likely reflects irrigation pumping. As noted previously in the study area section, head gradients favoring upward flow of groundwater from the Permian bedrock into the Great Bend Prairie aquifer have been measured in the past (Buddemeier 1994; Young 1992). This gradient and geochemical relationships indicate that Permian saltwater discharged into the aquifer at least historically.

Groundwater from wells 6C, 10C, 10D, and 26C also plotted outside of the mixing trend when samples were collected by Whittemore (1993). According to their interpretation, the deviation occurred as a result of contamination by oil-well brine. Compared to data reported by Whittemore (1993), the 2016 sample from 10D differed little in chloride concentration and Cl/Br, suggesting little change in brine proportion. Results for 26C (lower chloride concentration and Cl/Br in 2016) and 10C (higher chloride concentration and Cl/Br in 2016) suggest flushing of oil brine contamination with dilute recharge and an increase in brine proportions, respectively. Results for 6C show a mixed result (lower chloride content and higher Cl/Br in 2016), a result that may reflect a decrease in the proportion of oil brine contamination and an increase in the proportion of Permian saltwater.

In contrast to the 2016 samples, groundwater from 36D and 50C plotted within the mixing trend when sampled by Whittemore (1993). Compared to the initial study, the 2016 samples from those wells had higher chloride concentration (72 mg/L for both) but nearly identical Cl/Br. Both wells are completed in the shallow portion of the aquifer and produce water that does not contain a large component of Permian saltwater (e.g., chloride concentrations <120 mg/L). The result for 50C likely reflects evapotranspiration. The well site is in a crop field. In addition to chloride, the concentration of sulfate and other dissolved constituents also increased. Moreover, the $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ of the 2016 sample were higher than all but one other sample, potentially as a result of enrichment of heavy isotopes during evapotranspiration (Chen et al. 2006). Results for 36D may reflect inputs of animal waste. Evidence for this interpretation includes the location of the well in a pasture, nitrate isotope values of the 2016 groundwater sample consistent with manure, and little change in sulfate concentration over time. Consistent with both of these interpretations, nitrate levels increased 4.6 and 18.2 mg/L as N in wells 36D and 50C, respectively, implying inputs of agriculturally-impacted water.

Some of the other samples plotting within the chloride-bromide mixing trend may have been impacted by evapotranspiration and/or flushing of salts from soil or the unsaturated zone. However, these impacts would have been obscured where the influence of Permian saltwater is high enough to be the dominant driver of variation in major ion chemistry overall.

Controls on trace element mobility

Increasing nitrate concentrations in groundwater have been linked to increases in concentrations of hazardous trace elements, including uranium, selenium, and chromium (Gates et al. 2009; Hausladen et al. 2018; Manning et al. 2015; Nolan and Weber 2015; van Berk and Fu 2017). Nitrate has the potential to mobilize these elements by oxidizing them to more soluble states and/or oxidatively dissolving minerals that house them (Langmuir 1978; Mills and Goldhaber 2012; Postma et al. 1991).

To evaluate whether similar effects may be occurring in the study area, relationships between concentrations of trace elements and nitrate were tested using Spearman's rho rank order correlation tests. Trace elements were not analyzed in the initial study by Whittemore (1993). In the 2016 samples, however, concentrations of nitrate do not significantly correlate with those of uranium, selenium, or chromium. Thus, the data suggest that nitrate accumulation is not a major cause of the release of those elements from aquifer sediment in the study area.

In contrast, nitrate concentration does share a significant negative correlation with iron ($\rho = -0.54$, $P = 0.0114$), rubidium ($\rho = -0.42$, $P = 0.0479$), and molybdenum ($\rho = -0.44$, $P = 0.0362$). Whether the relationships of nitrate with rubidium and molybdenum are meaningful is unclear. The relationship between iron and nitrate, however, likely reflects aquifer microbiology. The near neutral pH of the groundwater samples implies that the iron they contained was primarily ferrous iron [Fe(II)], the main product of microbial iron reduction (Kirk et al. 2016). Where nitrate is available, the microbial community is likely to use nitrate as its electron acceptor before respiring ferric iron [Fe(III)] minerals, limiting production of ferrous iron (Bethke et al. 2011). Alternatively, where nitrate is added to groundwater that contains ferrous iron, that ferrous iron can then serve as the electron donor in microbial nitrate respiration (Straub et al. 1996). In either scenario, nitrate addition can lead to lower ferrous iron concentration, consistent with the data from this study.

Sources of uncertainty

Seasonal variation in groundwater chemistry has the potential to impact the magnitude of changes in groundwater composition identified by this study. The 2016 samples were collected during the summer, whereas most of the samples for Whittemore (1993) were collected in the fall and winter. Irrigation pumping during the summer can cause changes in groundwater composition, as noted earlier. Moreover, the composition of groundwater recharge can vary in response to seasonal differences in land management and soil biogeochemistry (Ostrom et al. 1998). Groundwater sampled during different seasons by Whittemore (1993) does not show strong seasonal variation in composition (Table S2 of the ESM; wells 21C, 29C, 34B, 35C, 42C). Nonetheless, additional sampling is necessary to evaluate the current extent of seasonal variation.

Secondly, this analysis is limited in its ability to describe changes across the expanse of the aquifer as well as temporal trends in groundwater chemistry. The aquifer spans an area of about 14,000 km^2 (Fader and Stullken 1978), a relatively large area compared to the number of wells that were sampled. Changes identified, therefore, may not be representative of the entire aquifer Moreover, because this analysis evaluates change with only two time points (i.e., 2016 data and the data reported by Whittemore (1993)), it does not constrain current rates of change in groundwater chemistry. Nitrate concentrations, for example, may be stabilizing or increasing exponentially. Additional time points are needed to evaluate current trends.

Lastly, plots containing a common variable such as chloride in Fig. 5, have the potential to induce correlation (Lenahan et al. 2011). However, concentrations of chloride and bromide share a significant positive correlation ($\rho = 0.63$, $P = 0.002$) in this study's dataset. This correlation implies that the relationship observed in the mixing plot is not induced.

Conclusions

Changes in groundwater quality over time can occur in response to a variety of natural processes and human activities. This study identifies and evaluates reasons for changes in groundwater quality during the past 40 years in the Great Bend Prairie aquifer using changes in groundwater chemistry, nitrogen and water isotope data, and Cl/Br mixing analysis.

Study findings demonstrate that some changes in groundwater chemistry have occurred during the past 40 years in response to flushing of oil-well brine, evapotranspiration, and potentially animal-waste inputs. However, groundwater quality has primarily changed because fertilizer use is causing nitrate to accumulate. Nitrate concentrations were significantly greater in groundwater samples from the shallow portion of the aquifer where the land is used for crops compared to areas with pasture. The amount of change in nitrate concentration appears to be large relative to nitrate increases observed in aquifers in other agricultural areas. Nitrate levels exceeded the US EPA standard for drinking water (10 mg/L as N) in groundwater from seven of the 22 wells sampled for this study. When the wells were sampled by Whittemore (1993) between 30 and 40 years ago, only one of the 22 wells produced water with nitrate concentration above the drinking water standard.

The findings of this study have important implications for the future use of the Great Bend Prairie aquifer for drinking

water. Municipalities may need to implement additional treatment measures to continue using the aquifer as a source of drinking water. Moreover, monitoring of groundwater quality from rural domestic water wells may be needed to avoid potential negative health impacts of nitrate contamination. Long travel times through the vadose zone can delay potential impacts of land use on groundwater quality (Ascott et al. 2017; Scanlon et al. 2007). However, the Great Bend Prairie aquifer is vulnerable to impacts of land use because the water table is relatively shallow and the sediment making up the vadose zone has a high hydraulic conductivity. Therefore, the findings of this study may provide an early warning for other portions of the High Plains aquifer and other aquifers in agriculturally dominated landscapes, where travel times through the vadose zone are longer.

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