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Nitrate and Chloride Concentrations in Groundwater beneath a Portion of the Trinity Group Outcrop Zone, Texas

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ABSTRACT: Using a geographic information system and statistics, we evaluated spatial distributions of nitrate and chloride concentrations in groundwater in an area of north-central Texas with agricultural activity, in addition to oil and natural gas exploration and production. Data were compiled from 40 water wells sampled in 2007. Nitrate concentrations in three wells exceeded the maximum contaminant level (44 mg/L) for drinking water. The highest nitrate concentration was 149 mg/L, and concentrations were generally higher in shallower wells. Chloride concentrations exceeded the 250 mg/L secondary drinking water standard in two wells, with no significant association between chloride concentration and well depth. Results of this study suggest localized human impacts, especially for nitrate, and identify areas warranting future monitoring.

Key words: Nitrate,Chloride, Groundwater,Trinity Aquifer,Texas

INTRODUCTION

A highly soluble complex ion, nitrate is a common contaminant in groundwater worldwide (Spalding and Exner, 1993). Exposure to high nitrate concentrations in drinking water over long time periods may cause colon and rectum cancers, methemoglobinemia in infants, and non-Hodgkin's lymphoma (Ward *et al.*, 1996; Knobeloch *et al.*, 2000; De Roos *et al.*, 2003; Coetzee *et al.*, 2011). The standard, or maximum contaminant level (MCL), for nitrate in drinking water is 44 mg/L (EPA 2009). Lots of studies are run regarding the groundwater quality degradation through discharge of different pollutants (Eneke *et al.*, 2011; Belkhiri *et al.*, 2011; Hudak, 2011;, Martinez-Paz and Perni, 2011; Romanelli *et al.*, 2011). There are many potential sources of nitrate in groundwater, including fertilizers, septic tank effluent, municipal sewage, animal feedlots, decaying vegetation, and atmospheric deposition (Wilhelm *et al.*, 1996). In aerated soils, oxygen transforms nitrogen to nitrate, which may percolate to groundwater. Annually, U.S. farmers apply nearly 11 million metric tons of nitrogen-bearing fertilizer to cropland and pastures (Nolan *et al.*, 1997); harvested crops remove only 40% of that amount, leaving an excess in the environment (Power, 1987). Animal manure contains another 6 million metric tons of nitrogen, some of which is lost by volatilization during storage and handling (Puckett, 1994). Other potential agricultural sources of nitrate include organic nitrogen in plant detritus, bacterial biomass, and soil constituents. For example, plowing native vegetation releases nitrogen-bearing plant detritus and aerates the soil, thus promoting nitrate formation. Nonagricultural sources of nitrate include septic systems, yard fertilizer, discharges containing nitrogen-bearing effluent, and atmospheric deposition. Upon reaching the saturated zone, nitrate tends to stay in solution, rather than adsorb or precipitate onto aquifer solids (Hem, 1985). Most public and private water treatment systems do not remove nitrate from well water. Determining sources of nitrate in groundwater can be difficult; sometimes, associations between nitrate concentrations and other parameters, such as well depth and chloride concentrations, may be useful for this purpose. Inverse associations between nitrate concentration and well depth suggest a shallow source, and direct associations between nitrate and chloride concentrations may indicate a common source. A soluble constituent of various minerals, chloride resides in virtually all freshwater, usually at low concentrations (Hem, 1985). Chloride compounds may accumulate in cropland from evaporated irrigation water and fertilizer. In areas with oil and gas production, brine may also be a source of

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chloride in surface soils or groundwater. Texas oilfield brine averages 50,000 mg/L chloride (TWC, 1989). Historically, oilfield brine produced in the U.S. was discharged to surface excavations, natural depressions, or gullies, and sprayed onto dirt roads. Presently, most oilfield brine is injected into deep disposal wells; however, both present and historical brine disposal practices may contaminate groundwater (TDA, 1985). High chloride concentrations may adversely impact drinking water or irrigation water. The U.S. secondary drinking water standard for chloride is 250 mg/L (EPA, 2009). In irrigation water, chloride concentrations above 140 mg/L may damage sensitive crops; values exceeding 360 mg/L may cause severe problems (Bower, 1978). Previous investigations suggested regions within Texas susceptible to high nitrate concentrations in groundwater (TWC, 1989; Hudak, 2000). This article documents the occurrence and possible sources of nitrate and chloride concentrations in groundwater beneath agricultural land overlying a shallow aquifer and deeper oil and gas reservoirs in north-central Texas, USA (Fig. 1).

MATERIALS & METHODS

The study area comprises five counties—Brown, Comanche, Eastland, Erath, and Mills—in a rural part of north-central Texas (Fig. 1, Table 1). Throughout this area, the Cretaceous Trinity Group provides groundwater for several purposes. The aquifer is unconfined in this area and vulnerable to contamination from sources originating at or near the land surface.

Rainfall, irrigation, and influent surface water recharge the Trinity Aquifer. On average, the study area receives approximately 76 cm of precipitation per year; approximately 2.5 cm recharges the aquifer (Baker, 1990). Average depth to groundwater in the study area is about 15 m, and groundwater flows generally southeastward. Water-bearing sand formations of the Trinity Group outcrop within the study area and dip underground to the east, where the aquifer becomes confined (Baker, 1990). From bottom to top, the Trinity Group includes the Twin Mountains, Glen Rose, and Paluxy Formations. The Twin Mountains Formation consists of sand, shale, clay, and a basal gravel and conglomerate (Peckham *et al.*, 1963). A confining unit, the Glen Rose Formation includes limestone, marl, shale, and anhydrite. The Paluxy Formation consists mainly of sand and shale. Thickness of water-bearing sand zones within the Trinity Group ranges up to approximately 15 m (Ulery and Brown, 1995). Farms account for over 90% of the study area, with pasture and cropland the predominant land cover (Table 1). Forage (hay), pecans, wheat, and sorghum are major crops grown in the study area. Farmers also raise various livestock, including cattle, goats, quail, and sheep. Patches of remnant oak forest, suited to well-drained soils, also occupy portions of the study area. Currently, there are more than 5,000 oil and gas wells (active, inactive, and injection) tapping Paleozoic reservoirs beneath the study area (Table 1); mainly these wells occupy the northwest half of the area. Well depth, nitrate, and chloride concentrations were compiled for 40 water wells in the Groundwater Database of the Texas Water Development Board. Water samples were collected in 2007. Sampled wells served various uses, but primarily domestic (27 wells) and public (7 wells) water supply. Other wells in the dataset were used for irrigation (3 wells) and stock (2 wells), and one well was unused.

Depths of sampled wells ranged from 44 ft (13 m) to 460 ft (140 m), with a median depth of 160 ft (49 m) (Table 2, Fig. 2). Sampling and analysis followed standard procedures described in TWDB (2003). After measuring water depth, wells were pumped until temperature, conductivity, and pH stabilized. Samples were taken directly from each well, filtered, preserved, and delivered to an analytical laboratory. Analyses were completed using automated colorimetry or ion chromatography.

MINITAB (Minitab, State College, Pennsylvania) was used to compute descriptive statistics and rank correlations among well depth and solute concentrations. Rank correlations were computed

Table 1. Population and Land Use

County	Total Oil Well Counts	Total Gas Well Counts	Population	Percent Land in Farms
Brown	1,237	701	38,088	93
Comanche	121	244	13,559	97
Eastland	1,418	1,177	18,167	88
Erath	28	515	36,184	90
Mills	1	3	4,994	99

Sources: Railroad Commission of Texas; U.S. Census Bureau

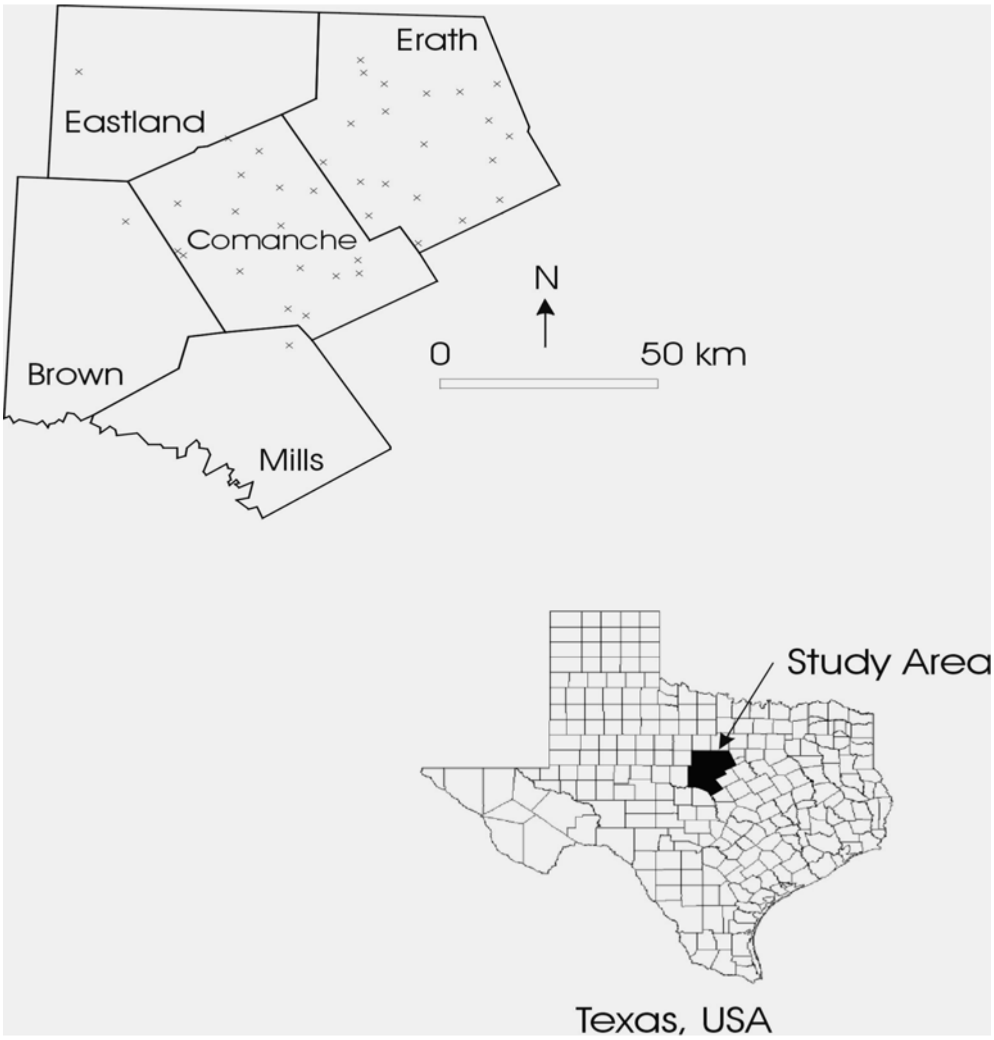

Fig. 1. Five-county study area and sampled wells (x)

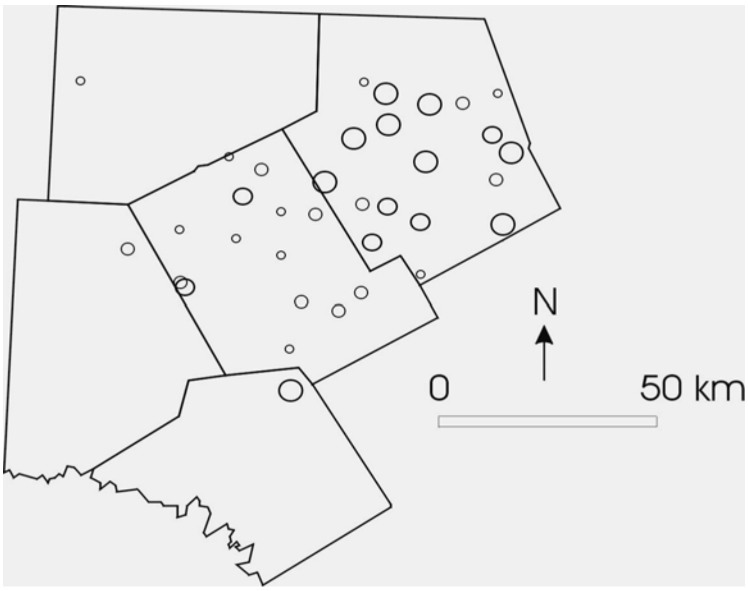

Fig. 2. Well depths; from smallest to largest, circles represent 44-100, 101-200, 201-300, and 301-460 ft; 1 ft = 0.31 m

because the data were non-normally distributed. Solute concentration and well depth categories were mapped with the ArcView (Environmental Systems Research Institute, Redlands, California) geographic information system.

RESULTS & DISCUSSION

`Observed nitrate concentrations ranged from non-detected to 149 mg/L (Table 2, Fig. 3). Twenty-six of 40 samples had detectable nitrate levels; however, the median concentration was only 2 mg/L (Table 2). Eleven of 40 nitrate observations exceeded 10 mg/L, but only three of those observations also exceeded the MCL of 44 mg/L.

A statistically significant, inverse association between nitrate concentration and well depth (Table 3) is consistent with nitrate originating from agricultural sources at or near the land surface. From a planning perspective, an inverse association between nitrate concentration and well depth suggests that deeper wells may reduce the threat of pollution in vulnerable parts of the study area. Agricultural practices, especially fertilizer applications, probably account for nitrate observations in the highest mapped categories.

Only two chloride observations surpassed the secondary MCL of 250 mg/L. The highest chloride

Table 2. Summary of Solute Concentrations and Well Depths*

Parameter	Minimum	Median	Maximum
Nitrate (mg/L)	<0.44	2	149
Chloride (mg/L)	2	36	595
Well depth (ft)	44	160	460

*1 ft = 0.31 m

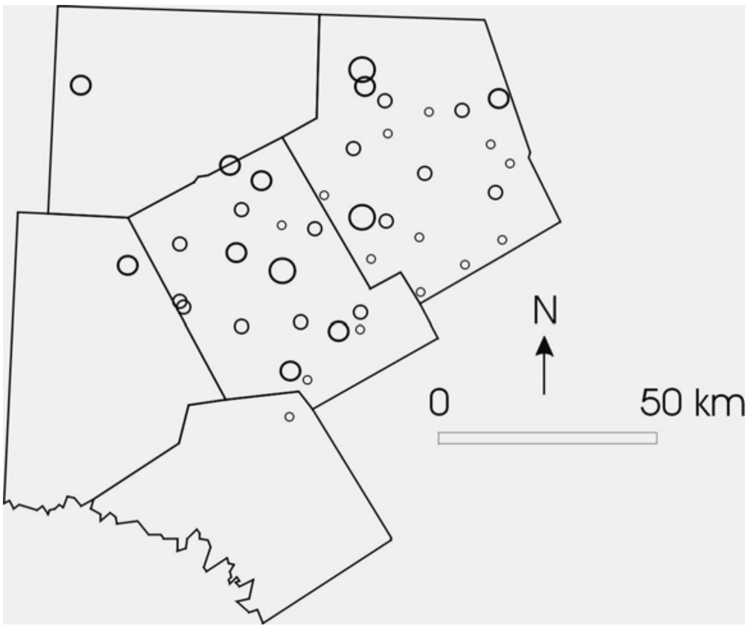

Fig. 3. Nitrate concentrations; from smallest to largest, circles represent <0.44, 0.44-10, 11-44, and 45-149 mg/L

Table 3. Rank Correlations

	Depth	Chloride
Chloride	-0.159	
Nitrate	-0.626*	0.265

*Statistically significant at significance level of 0.01

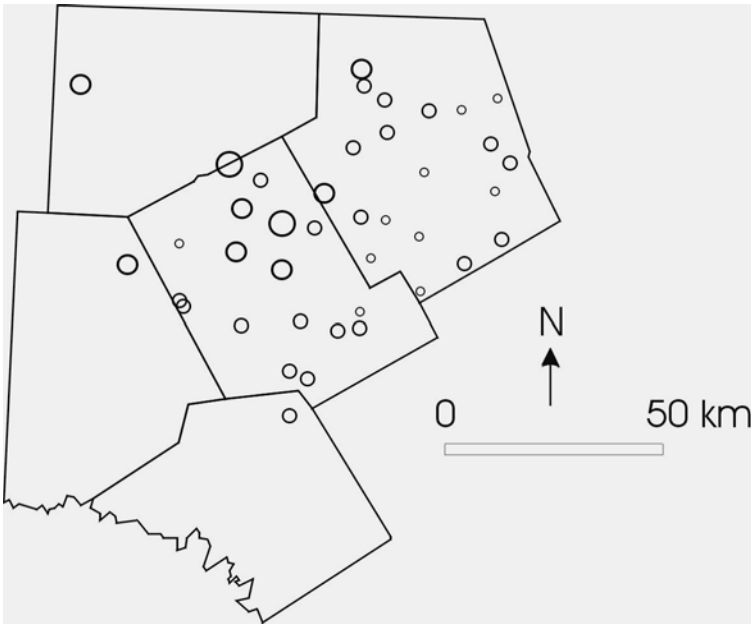

Fig. 4. Chloride concentrations; from smallest to largest, circles represent 2-20, 21-100, 101-250, and 251-595 mg/L

concentrations were in relatively shallow wells, less than 100 ft (31 m) deep; these wells may have been impacted by a contaminant source near the land surface, for example, oil and gas activity or irrigation return flow. However, over the entire study area, there was no significant association between chloride concentration and well depth. While natural constituents of the Trinity Group likely exert a major control on observed chloride concentrations, anomalous concentrations (above 250 mg/L), and a tendency for higher chloride concentrations in the northwestern part of the study area (with much heavier oil and gas activity), suggest possible human impacts. Figs 3 and 4 show locations within the study area with relatively high nitrate and chloride concentrations, which have the potential to produce high concentrations in present and future water wells. Groundwater in these areas especially should be periodically monitored to determine whether nitrate, chloride, and other solute concentrations are suitable for drinking, irrigation, or other intended uses. Both concentration levels and water use dictate appropriate filtration measures; for example, reverse osmosis could remove nitrate, chloride, and other solutes from drinking water, though this process is relatively expensive. Less costly options may include treating only drinking water, or consuming bottled water.

Nitrate observations in this study are well within the range reported in other parts of the world. For example, Kolpin et al. (1994) reported nitrate concentrations above 45 mg/L in six percent of 303 wells tapping shallow aquifers (less than 15 m deep) in corn- and soybean-producing areas of the midwestern United States. Moreover, Strebel et al. (1989) and Fried (1991) reviewed nitrate pollution of groundwater in Europe; highest nitrate concentrations, above 50 mg/L, occurred in sandy soils beneath intensely managed crops and grazed grassland. Furthermore, Zhang et al. (1996) reported that more than 50% of sampled water wells in a fertilized region of northern China had nitrate levels above 50 mg/L. Very high concentrations, up to 300 mg/L, were found in groundwater beneath vegetable-producing areas, small cities and towns, and farmers' yards. Chloride concentrations observed in this study are low relative to those observed in some areas with intensive agriculture and oil and gas production. For example, Hudak (2003) compiled samples from 198 water wells in the Edwards-Trinity Plateau Aquifer of west-central Texas; 49 samples had chloride concentrations above 250 mg/L, 22 samples had greater than 500 mg/L chloride, and nine samples exceeded 1,000 mg/L chloride.

CONCLUSION

In conclusion, out of 40 samples, only three nitrate observations and two chloride observations exceeded the respective drinking water standards. Shallower wells within the study area tend to be more vulnerable to nitrate contamination. A few (relatively shallow) wells produced samples with high chloride concentrations; however, there was no significant association between chloride concentration and well depth across the study area. Continued monitoring of locations experiencing elevated nitrate and chloride concentrations within the study area would help identify contaminant sources, assess impacts to groundwater, and facilitate appropriate source control measures.

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