Nitrate, Arsenic and Selenium Concentrations in The Pecos Valley Aquifer, West Texas,USA

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ABSTRACT: Nitrate, arsenic, and selenium concentrations in the Pecos Valley Aquifer of west Texas were compiled, mapped, and analyzed in the context of local geology and land use. Alluvial deposits of sand, silt, clay, and gravel compose the unconfined aquifer. Ranching and farming are predominant land uses in the rural study area. Data were tabulated from 79 water wells with a median depth of 75 m and mapped with a geographic information system (GIS). The wells were sampled between the years 2003 and 2008. Total dissolved solids (TDS) concentrations in the aquifer were very high, with a median value of 2,687 mg/L. Approximately 18% of observations exceeded the 44.27 mg/L drinking water standard for nitrate, whereas 6% exceeded the 10 µg/L standard for arsenic, and only 4% surpassed the 50 µg/L standard for selenium. There was a statistically significant, direct correlation between arsenic and selenium, as well as between nitrate and selenium concentrations. Moreover, arsenic and selenium concentrations were significantly higher in shallower wells. Probable sources of groundwater contamination in the study area include natural (geological) sources and agricultural activity.

Key words: Nitrate, Arsenic, Selenium, Groundwater, Texas

INTRODUCTION

The objective of this study was to compile, map, and evaluate nitrate, arsenic, and selenium levels in groundwater within the Pecos Valley Aquifer beneath a six-county area of west Texas (Fig. 1). Agricultural and oilfield activity, as well as natural sources, are potential sources of groundwater pollution in the study area.

Nitrate, arsenic, and selenium in drinking water pose health risks. Worldwide, nitrate is one of the most common contaminants in groundwater (Strebel *et al.,* 1989; Spalding and Exner, 1993; Lagerstedt *et al.,* 1994; Zhang *et al.,* 1996; Kacaroglu and Gunay, 1997; Nolan *et al.,* 1997; Pacheco and Cabrera, 1997). Nitrate can cause methemoglobinemia and non-Hodgkin's lymphoma (Johnson *et al.,* 1987; Ward *et al.,* 1994). Potential sources of nitrate in soil and groundwater include: fertilizer, animal waste, septic systems, crop residue, soil organic nitrogen (in native plant detri-

tus, bacterial biomass, and soil constituents), and municipal/industrial discharges. In aerated soils, nitrogen compounds oxidize to soluble nitrate, which may percolate to the saturated zone.Nitrate in groundwater has a low tendency to adsorb to aquifer solids. The U.S. maximum contaminant level (MCL) for nitrate in drinking water is 44.27 mg/L (EPA, 2006).

The MCL for arsenic, a highly toxic substance, in drinking water is only 10 µg/L (EPA, 2006). Arsenic uptake can cause numerous diseases, including cancer, nervous system disorders, cardiovascular problems, kidney and liver disease, diabetes, and respiratory problems (EPA, 2002). Arsenic has been documented in drinking water in several countries, including Argentina, Bangladesh, China, Chile, Ghana, Hungary, India, Mexico, Thailand, and the U.S. (Nicolli *et al.,* 1989; Bagla and Kaiser, 1996; Williams *et al.,* 1996; Nickson *et al.,* 1998; Nimick, 1998;

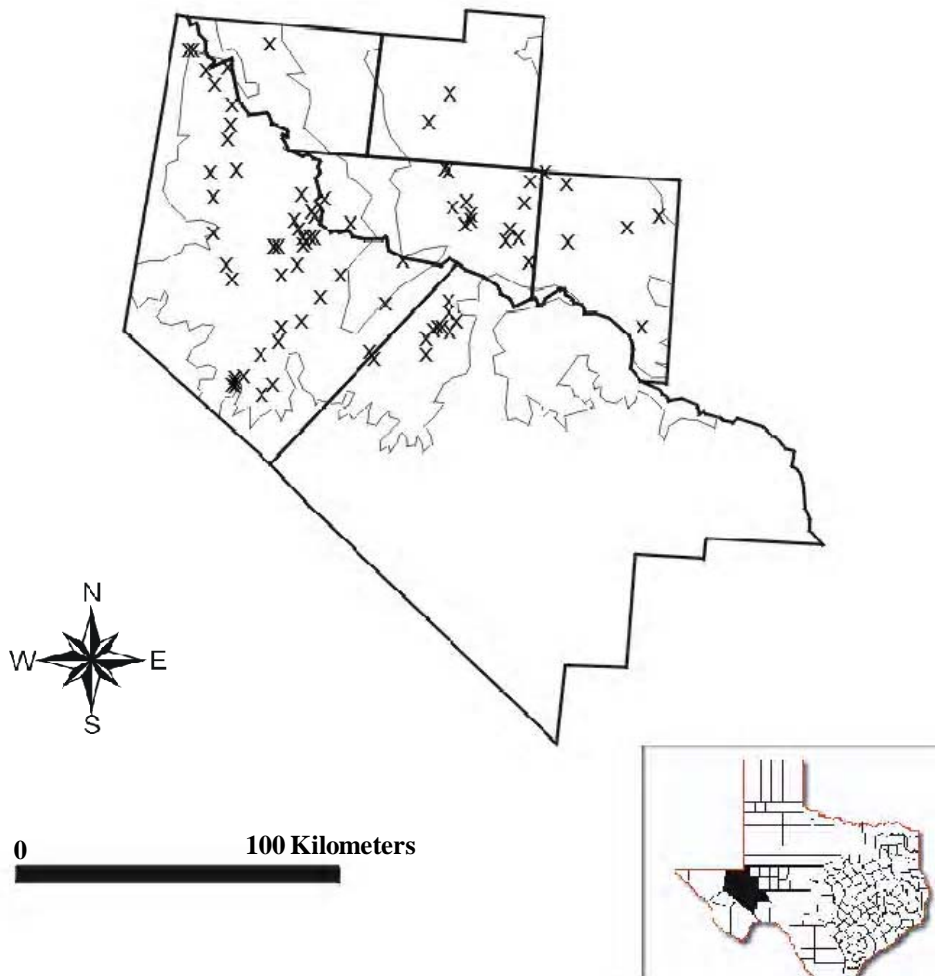*Corresponding author E-mail: hudak@unt.edu

Fig. 1. Location of study area; x – sampled water well; dark lines – county boundaries; irregular dark line – Pecos River (flowing southeastward); irregular thin line – aquifer boundary

Burkel and Stoll, 1999; WHO, 1999; Welch *et al.,* 2000). Historically, wood preservation (current) and agriculture (pre-1980) are the largest uses of arsenic in the U.S. (Weast, 1992; Welch *et al.,* 2000). Arsenic has been applied extensively to cropland, especially cotton fields, as a pesticide and defoliant (Piltz, 1987). Arsenic also occurs naturally in rock, especially in association with metal sulfide and oxide deposits (Korte and Fernando, 1991).

Selenium, another potential toxin, is a natural constituent of groundwater that may become concentrated by irrigation practices. For example, selenium in water drained from irrigated fields of the San Joaquin Valley, California has caused congenital deformities and mortality of birds (Kehew, 2001). Especially in dry regions, evaporation and transpiration of irrigation water builds up salts containing these elements and others, which may leach to groundwater during periods of excess irrigation or heavy rainfall.

Excess selenium in irrigation drainage has been documented at several locations in the western U.S. At many of these locations, the selenium originated from Upper Cretaceous or Tertiary marine sedimentary rocks (USGS, 1997). The average concentration of selenium in seawater is only 0.45 µg/L, and it rarely exceeds 1 µg/L in groundwater (Hem, 1985). Small amounts of selenium are essential for animals, but excess intake can be toxic. The maximum contaminant level (MCL) for selenium in drinking water is 50 µg/L (EPA, 2006). However, in irrigation water, selenium concentrations exceeding 20 µg/L may be harmful to plants (Fipps, 1996).

The study area occupies alluvial plains of the upper Pecos River valley in west Texas (Fig. 1). Arid conditions characterize this subtropical region; over the entire study area, annual precipitation and gross lake evaporation average approximately 30 cm and 175 cm, respectively (Lu, 2007). Desert shrubs and grasses are common native flora of the region. Salt cedar and common reed have invaded riparian areas (Griffith *et al.,* 2004). Farming, ranching, and oil/gas production dominate the sparsely populated region's economy. Primary crops grown in the region are forage/hay, cotton, and wheat (USDA, 2007). Several of these croplands are irrigated. Though sporadic throughout the region, many of the irrigated fields occupy the west-central part of the study area and locations southeastward near the Pecos River. Oilfields occupy all counties in the study area, but are more concentrated in the four smaller, northeastern counties.

Aquifers supply most of the water consumed in the study area. The Pecos Valley Aquifer furnishes water to each county in the study area. This aquifer is the main source of irrigation water in the two largest counties (Fig.1). elsewhere, it supplies industrial, power generation, and public water organizations (Ashworth and Hopkins, 1995). Irrigation consumes most of the water pumped from the aquifer. Heavy pumping has lowered the water table by over 60 m at some locations, thereby intercepting groundwater that naturally flowed toward the Pecos River (Ashworth and Hopkins, 1995). At some locations, groundwater pumping has induced seepage of saline water in the Pecos River to the underlying aquifer (Scalf *et al.,* 1973).Precipitation and infiltration from ephemeral drainages recharge the Pecos Valley Aquifer (Muller and Price, 1979). Inter-aquifer flow (mainly from bedrock to the south and west) and irrigation return flow also contribute water to the aquifer (Ashworth, 1990). Pumping and evapo-transpiration, along with base flow to portions of the Pecos River, are the principal forms of groundwater discharge (TWC, 1989; Jones, 2001). Depth to groundwater may be less than 6 m at some locations in the Pecos River valley, but increase significantly away from the river (Boghici, 1999). Depths to groundwater are much greater in cones of depression adjacent to production wells.

Quaternary-age alluvial (fill) deposits composing the aquifer range up to 460 m thick (Muller and Price, 1979), thinning laterally toward bedrock uplands bounding the formation (Fig.1). Sedimentary bedrock of Permian, Triassic, and Cretaceous age bound, both laterally and beneath, most of the aquifer (Renfro *et al.,* 1973). Alluvial fill composing the aquifer occupies two main basins (Figure 1), formed by dissolution of Permian-age evaporates and subsidence of overlying rocks (Ashworth, 1990). Groundwater in the aquifer occurs primarily under unconfined conditions, but is locally confined by clay beds. Groundwater quality varies naturally, with total dissolved solids (TDS) concentrations locally exceeding 5,000 mg/L (Ashworth and Hopkins, 1995).

MATERIALS & METHODS

Water quality and well data were obtained from the Texas Water Development Board (TWDB) (TWDB, 2008). Samples were collected and analyzed using standard methods, in accordance with the TWDB field manual for groundwater sampling (TWDB, 2003). Field samples were collected when temperature, conductivity and pH stabilized. Samples were filtered and field tested for alkalinity, preserved as applicable, chilled, and delivered within prescribed holding times to certified analytical laboratories. Inductively coupled plasma mass spectrometry (ICP-MS) (arsenic, selenium), and automated colorimetry or ion chromatography (nitrate), were used to measured dissolved analyte concentrations. Data compiled in this study were collected from 2003-2008, using the most recent measurement at wells sampled more than once during this time interval.

Concentrations of nitrate, arsenic, and selenium were compiled for 79 wells (Fig. 1). These wells were used for public (12 wells), stock (26 wells), domestic (13 wells), irrigation (20 wells), and industrial (5 wells) purposes. The remaining three wells were used only for monitoring purposes. Minitab (Minitab Incorporated, State College, Pennsylvania) was used to compute summary statistics for each solute, correlations between solutes and well depth, and variations in solute concentrations between well-use categories. ArcView (Environmental Systems Research

Institute, Redlands, California) was used to map well locations and solute concentration categories.

RESULTS & DISCUSSION

Typical of water-quality data, solute concentrations were non-normally distributed; median concentrations were closer to minimum than maximum values (Table 1). Distribution of well depths showed a similar pattern. Based upon observed, non-normal solute-concentration and well-depth distributions, non-parametric tests (Spearman and Kruskal-Wallis) were used to compare and evaluate associations between study variables.

Total dissolved solids (TDS) concentrations varied widely, ranging from low concentrations typically found in groundwater to extremely high concentrations (Table 1). Most TDS observations were high relative to typical (potable) groundwater; the median value was 2,687 mg/L (Table 1). Approximately 92% of observations exceeded the secondary drinking water standard of 500 mg/L, and 74% of observations exceeded 1,000 mg/L, or double the standard for TDS. Most observations exceeded 1,920 mg/L TDS – concentrations above this amount frequently cause severe problems for crops (Bouwer, 1978).

Table 1. Summary of Well Depth and Solute Concentrations

	N	Minimum	Median	Maximum
Depth (m)	72	6	75	354
TDS (mg/L)	62	216	2,687	10,508
Nitrate (mg/L)	62	<0.44	8.97	266
Arsenic (µg/L)	79	<1	1	26
Selenium (µg/L)	79	<1	4	117

TDS concentrations were high in several parts of the study area, with multiple clusters near the Pecos River (Fig. 2). One well, in the northwestern corner of the study area, registered an extremely high TDS of 10,508 mg/L. Along the Pecos River and in other irrigated parts of the study area, high evapo-transpiration rates create potential for salt accumulation in the soil. Subsequently, these salts may leach to groundwater with irrigation return flow. Potentially, oilfield brine is an additional source of dissolved solids in the study area. Both past and presently producing oil wells are scattered over the study area.
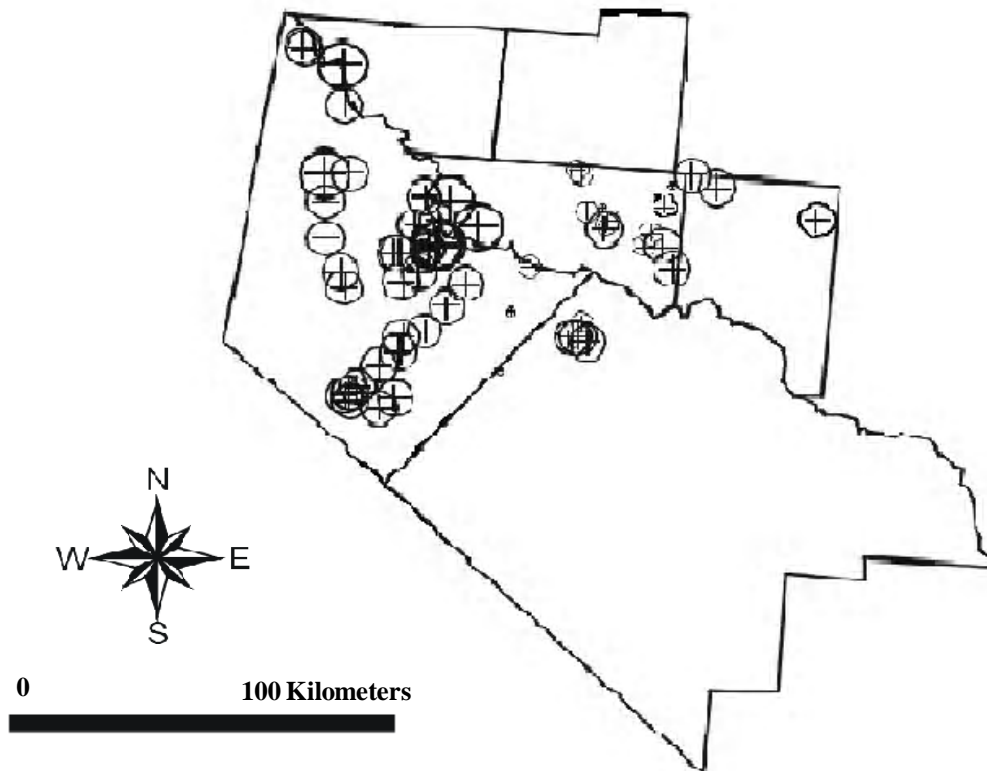

Fig. 2. Total dissolved solids (TDS) concentrations; from smallest to largest, circles indicate 216-500, 501-1,000, 1,001-5,000, and 5,001-10,500 mg/L

There was a slight tendency for higher TDS concentrations in shallower wells. While the median well depth was 81 m, some wells were as shallow as 6 m. Generally, depth to water (and well depth) decrease toward the Pecos River. A trend for increased TDS near the river may reflect mineralization along regional flow paths terminating along the river, as well as return flow beneath irrigated fields and seepage of saline surface water. Evaporates beneath the aquifer, especially in western/northwestern parts of the study area, are a potential source of sulfate in groundwater (Ashworth, 1990). Pumping could draw saline water from underlying formations upward into the Pecos Valley Aquifer.

Clusters of elevated nitrate concentrations occupy several parts of the study area, reaching a maximum concentration of 266 mg/L (Table 1, Fig. 3). Approximately 18% of nitrate observations exceeded the MCL, and the median concentration was 8.97 mg/L. While nitrate concentrations inversely correlated with well depth, this association was statistically insignificant (Table 2). Such inverse correlation is consistent with nitrogen sources at or the land surface, though mixing of

Table 2. Rank Correlation Matrix

	Depth	Nitrate	Arsenic	Selenium
Nitrate	-0.207			
Arsenic	-0.447*	0.213		
Selenium	-0.503*	0.460*	0.508*	
TDS	-0.270*	0.317*	0.018	0.292*

** **Statistically significant, α=0.05***

nitrate over varying depths within the aquifer would weaken this association.

Arsenic concentrations were generally highest in the eastern part of the study area (Fig. 4). Significantly higher arsenic concentrations in shallower wells (Table 2) suggest an origin at or near the land surface. However, only 6% of arsenic observations exceeded the MCL, and the median concentration was only 1 µg/L (Table 1). Arsenic did not correlate with TDS; that is, there was no tendency for arsenic concentrations to increase along with overall salinity. Progressive dissolution along regional flow paths does not account for arsenic patterns observed in this study. The pattern of selenium concentrations generally resembled that of nitrate, with elevated clusters in several parts of the study area (Fig. 5). Indeed,
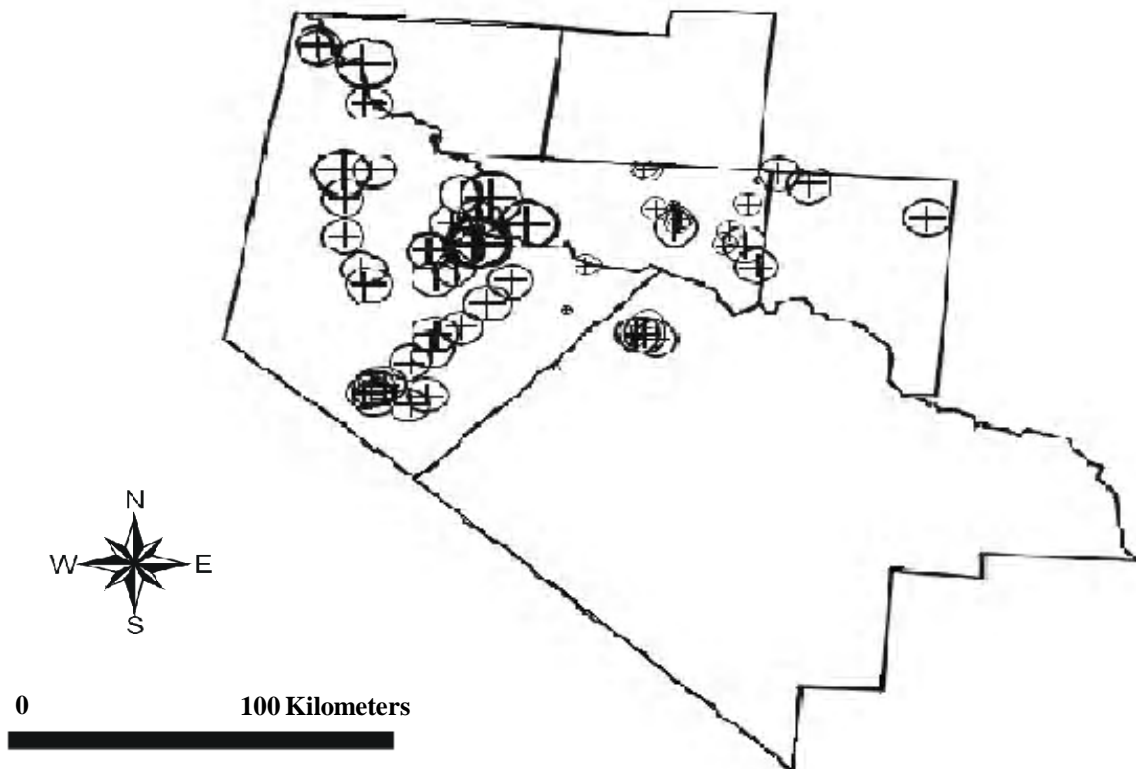

Fig. 3. Nitrate concentrations; from smallest to largest, circles indicate <0.44, 0.44-10, 10.01-44.27, and >44.27 mg/L
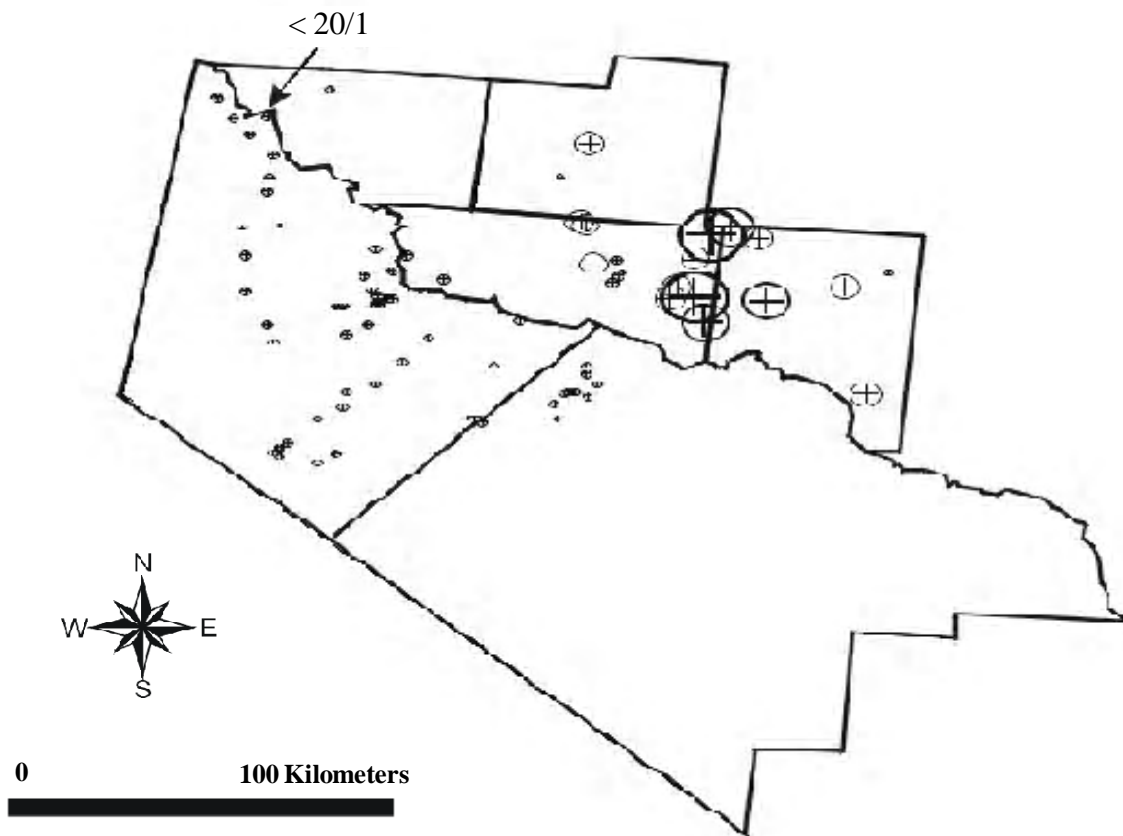
< 20/1

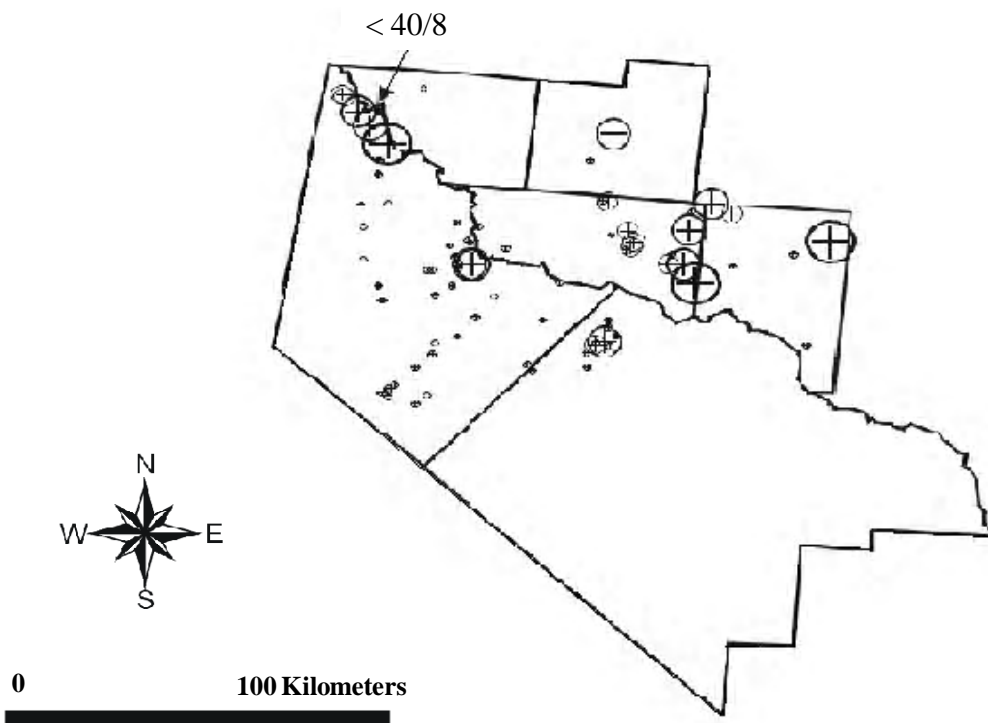**Fig. 4. Arsenic concentrations; from smallest to largest, circles indicate <4, 4-10, 11-20, and 21-26 μg/L**

< 40/8

Fig. 5. Selenium concentrations; from smallest to largest, circles indicate <8, 8-10, 11-50, and 51-117 μg/L

there was a statistically significant correlation between selenium and nitrate concentrations (Table 2). Selenium concentrations also correlated with arsenic concentrations. Moreover, selenium concentrations were significantly higher in shallower wells. These observations are consistent with localized impacts from sources at or near the land surface. Selenium only weakly correlated to TDS; increased dissolution (of natural sources) along regional groundwater flow paths is probably not the main control on observed selenium concentration patterns. Over the study area, only four selenium observations exceeded the recommended 20 μg/L limit for irrigation water, and only three observations (4% of the total) exceeded the 50 μg/L MCL for drinking water. The median selenium concentration was 4 μg/L; however, the maximum concentration was 117 μg/L, more than double the MCL (Table 1). This latter well, at the northeastern corner of the study area, also had high nitrate (105 mg/L) and TDS (4,279 mg/L) concentrations, suggesting a possible impact from irrigation return flow. Oilfields also occupy the northeastern corner of the study area; however, brine would not account for the high nitrate observation. Kruskal-Wallis tests comparing chemical concentrations between well-use categories (with at least five observations) were statistically significant only for TDS (p=0.002). Public wells had a significantly lower median TDS concentration (587 mg/L) than other wells (ranging from 2,682 mg/L for industrial wells to 2,842 mg/L for irrigation wells), suggesting some tendency to locate and/or continue operating public wells in areas of relatively good-quality groundwater.

CONCLUSION

Recent groundwater monitoring data indicate elevated nitrate, arsenic, and selenium concentrations at several locations in the Pecos Valley Aquifer. Natural (geological) and agricultural sources likely influence observed concentration patterns. Inter-aquifer flow and possibly oilfield brine also influence groundwater quality within the study area. Additional studies, prioritized to areas of elevated solute concentration, would further characterize the magnitude and extent of contamination in the study area. Though locally elevated in different parts of the study area, only five arsenic observations and three selenium observations sur-

passed their respective drinking water standards. However, 18% of nitrate observations exceeded the MCL for that solute. Low recharge rates and deep wells away from the river valley mitigate potential pollution from sources near the land surface. While public water providers must filter water (if necessary) to adhere to MCLs, the above contaminants are not routinely removed from other types of water wells. This study documents possible areas of vulnerability to nitrate, arsenic, and selenium contamination in the Pecos Valley Aquifer.

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