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Chemical Ratios and Groundwater Contamination in East Texas

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Multiple sources of contamination often impact groundwater quality. These sources may be anthropogenic, natural, or a combination of both. Chemical ratios can be useful for identifying probable sources of groundwater contamination (Richter and Kreitler, 1993). The purpose of this study was to map and interpret chemical ratios in groundwater of east Texas.

Previous studies (conducted in various regions) showed that certain chemical ratios may be useful for identifying salt domes, lignite deposits, or oilfield brine as sources of groundwater contamination. All of these sources are present in the study area. For these sources, useful chemical ratios include Br/Cl, (Ca+Mg)/(Na+K), (Na+Cl)/(TDS), and (moles SO_4)/(moles Ca) (Rittenhouse 1967; Morton 1986; Whittemore 1995). Waters associated with petroleum production are commonly enriched in bromine relative to chlorine (Rittenhouse 1967). Gypsum and anhydrite, commonly found in cap rocks of salt domes, release SO_4 and Ca in a molar ratio of one-to-one. Higher molar ratios indicate additional sulfate sources, such as oilfield brine or lignite, whereas lower ratios indicate additional calcium sources, such as calcite cement in sedimentary rocks. Values of (Ca+Mg)/(Na+K) generally decrease, whereas values of (Na+Cl)/(TDS) generally increase with cation exchange along regional groundwater flow paths (Whittemore 1995). Anomalies to these trends can signal water quality impacts from such sources as those mentioned above. Values of $\log_{10}((Na+Cl)/TDS)$ equal to or greater than -0.2 indicate possible impacts from oilfield brine (Morton 1986).

The study area includes six counties in rural, northeast Texas (Figure 1). Throughout this area, the Eocene Sparta-Queen City Aquifer (SQ) and underlying Carrizo-Wilcox Aquifer (CW) provide water for irrigation, industry, and public uses. Underlying formations produce oil and gas in each county of the study area, with heaviest production from Upshur, Gregg, and southeastern Wood Counties. Oilfield brine from past (surface pits) and present (injection wells) disposal practices is a potential source of groundwater contamination in the study area.

Sediments in the aquifers were deposited in fluvial-deltaic and shallow marine environments (Fogg and Kreitler 1982). SQ consists of interbeds of sand, sandy

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clay, and loosely cemented, ferruginous sandstone (BEG 1965). Interbedded ferruginous sand with clay, sandstone, lignite, and gravel make up CW. The Recklaw and Midway Aquitards underlie SQ and CW, respectively. At the southern tip of the study area, the Cook Mountain Aquitard underlies SQ.

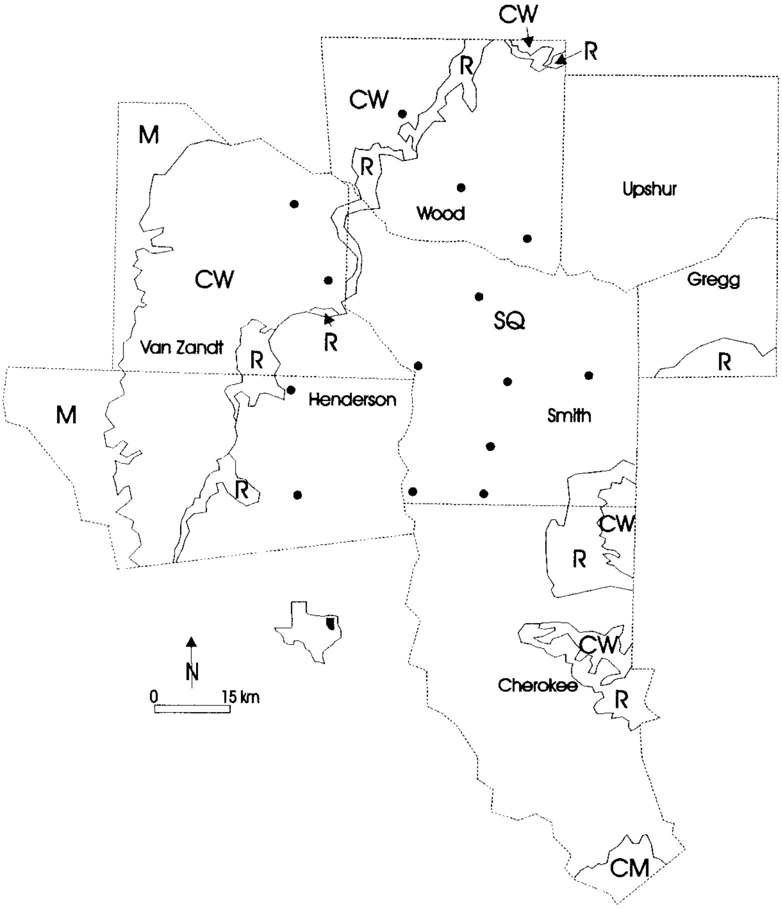

Figure 1. Map of study area showing county boundaries (dashed lines), surface formations, excluding recent alluvium (solid lines: SQ-Sparta-Queen City, CW-Carrizo-Wilcox, M-Midway, R-Recklaw, CM-Cook Mountain), and salt domes (dots) (modified from Fogg and Kreitler 1982).

Aquifer sediments dip underground, toward Smith County, from the northwest side and southeast of the study area, where they outcrop at the land surface. Groundwater flow generally follows the slopes of the aquifers, which have average thicknesses of approximately 100 m (SQ) and 300 m (CW). Precipitation on outcrop zones recharges both aquifers, which discharge to pumping wells, seeps, and streams (Preston and Moore 1991).

Extensive salt activity has occurred beneath the study area. Figure 1 shows several shallow salt domes, some within 30 m of the land surface, which could potentially impact groundwater in the study area (Fogg and Kreitler 1982).

Previous studies inventoried groundwater quality in selected counties of the study area (Broadhurst 1950; Broom 1968). Others compiled maps of solute concentrations, salinity, and total dissolved solids in CW using groundwater samples and/or geophysical logs (Henry et al. 1980; Kaiser et al. 1980; Fogg and Kreitler 1982). The present study employed chemical ratios and geostatistics to identify potential sources of groundwater contamination.

MATERIALS AND METHODS

Various data were compiled from the Texas Water Development Board's Groundwater Database, including well locations, producing aquifers, depths of completion intervals, and chemical concentrations. The study area was divided into a grid of 0.05 by 0.05 degree cells, and the aquifers were divided into three depth zones: 0-150 ft (0-46 m) for SQ, 300-600 ft (92-183 m) for CW (CW1), and 600-900 ft (183-274 m) for CW (CW2). Of the resulting 470 cells (in three dimensions), 426 had at least one well. The number of wells in each cell ranged from one (290 cells) to eight (one cell). Chemical ratios in each cell were averaged, and kriging (Kaluzny et al. 1996) was used to estimate ratios for cells containing no wells.

Three ratios were mapped based on available data and potential to discern potential sources of groundwater contamination in the study area: $\log_{10}((Ca+Mg)/(Na+K))$, $\log_{10}((Na+Cl)/TDS)$, and $\log_{10}(\text{moles } SO_4/\text{moles } Ca)$. Logarithmically-transformed ratios were normally distributed.

RESULTS AND DISCUSSION

Overall, $\log_{10}((Ca+Mg)/(Na+K))$ decreased southeastward with regional groundwater flow in CW1 and CW2 (Figure 2). However, there were localized increases in this ratio near salt domes. Higher ratios in CW1 at the southeastern edge of the study area reflect recharge in outcrop zones located there (and further southeast).

In contrast, no overall trend in $\log_{10}((Ca+Mg)/(Na+K))$ was apparent in SQ, where the ratio took on a smaller range of values. These results reflect the relatively shallow, unconfined nature of SQ. Such conditions develop more localized groundwater flow paths and, consequently, less opportunity for regional geochemical trends induced by cation exchange.

Ratios of $\log_{10}((Na+Cl)/TDS)$ generally increased southeastward in CW1 and CW2 (Figure 3). Similar to the preceding ratio, there was no overall trend in SQ. There were no cells with $\log_{10}((Na+Cl)/TDS)$ greater than -0.2 in any of the three depth zones, although values approached -0.2 in the northeast corners of CW2 and

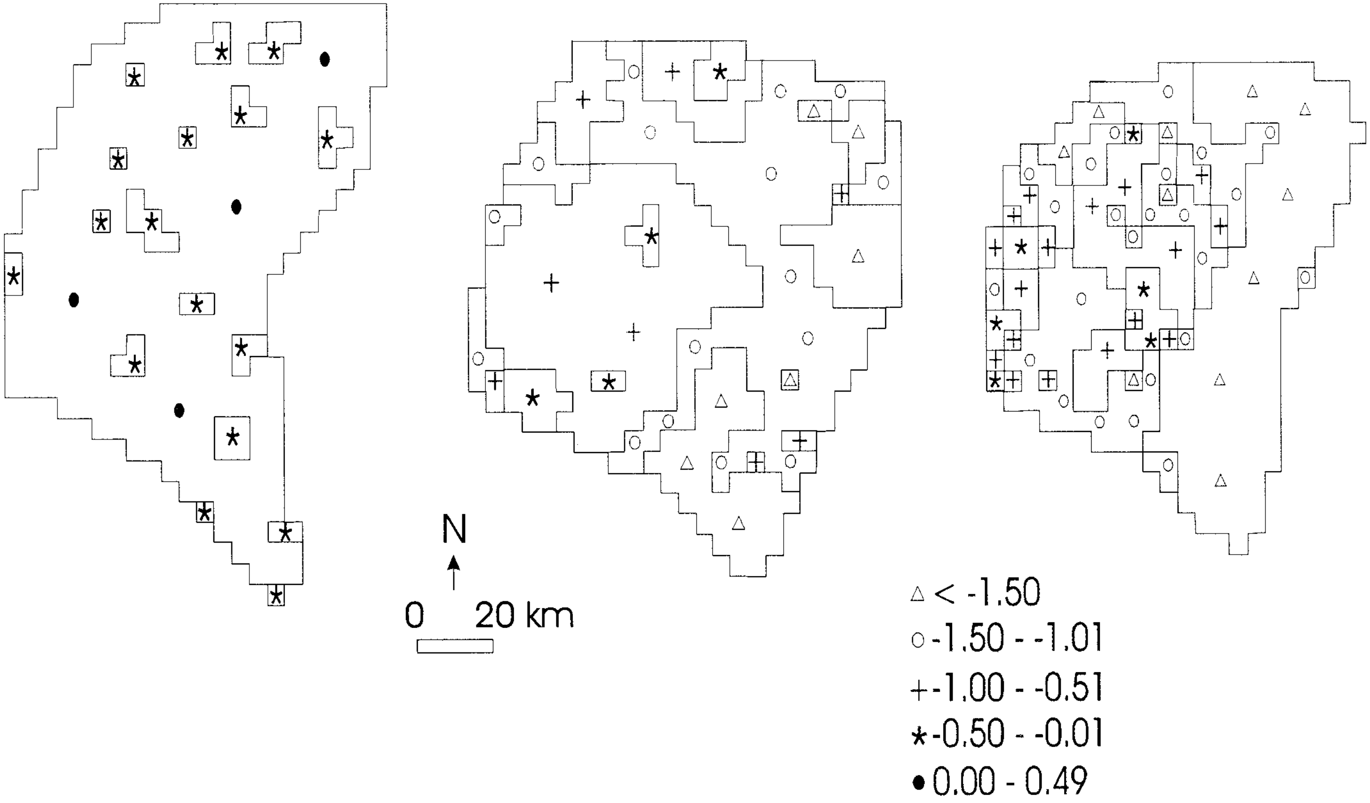

Figure 2. Maps of $\log_{10}((Ca+Mg)/(Na+K))$ in SQ (left), CW1 (middle), and CW2 (right).

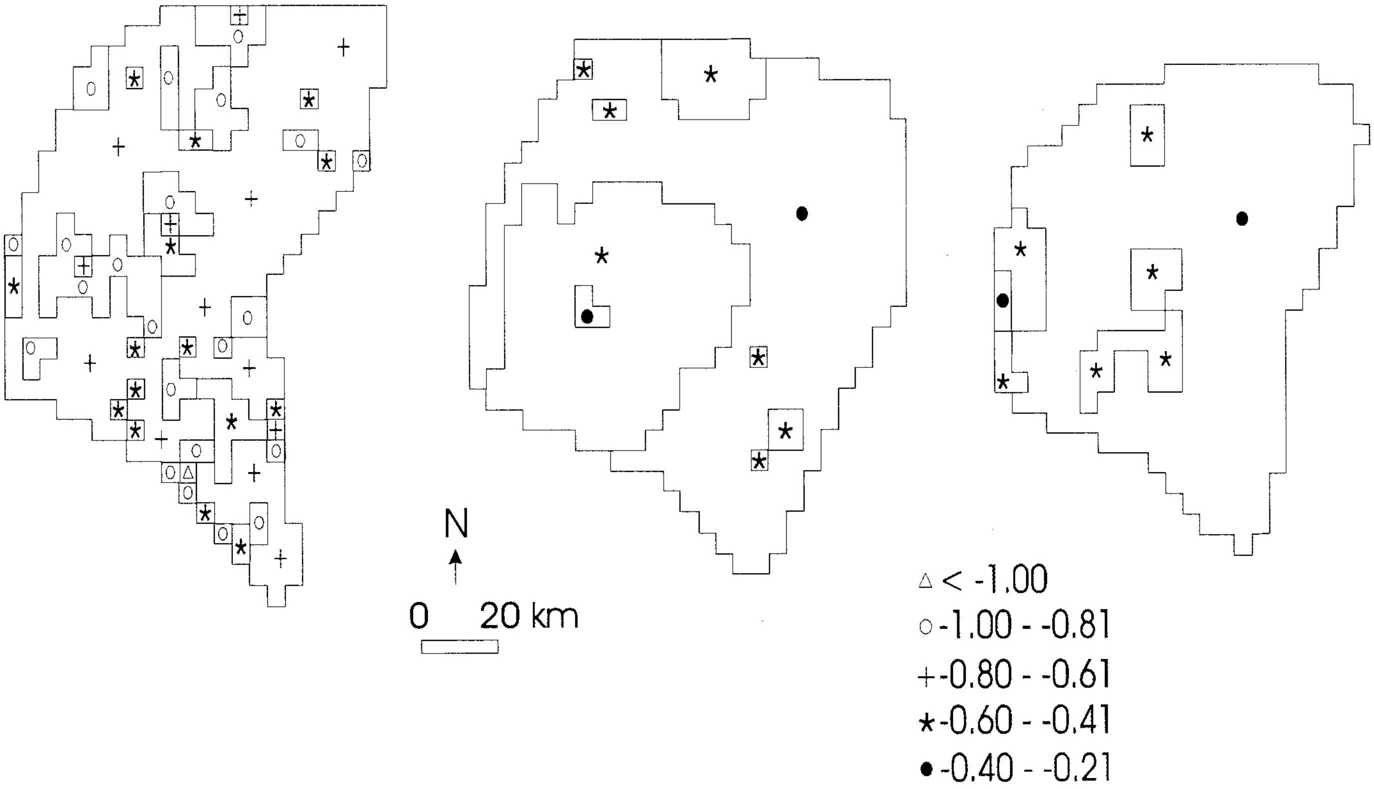

Figure 3. Maps of $\log_{10}((Na+Cl)/TDS)$ in SQ (left), CW1 (middle), and CW2 (right).

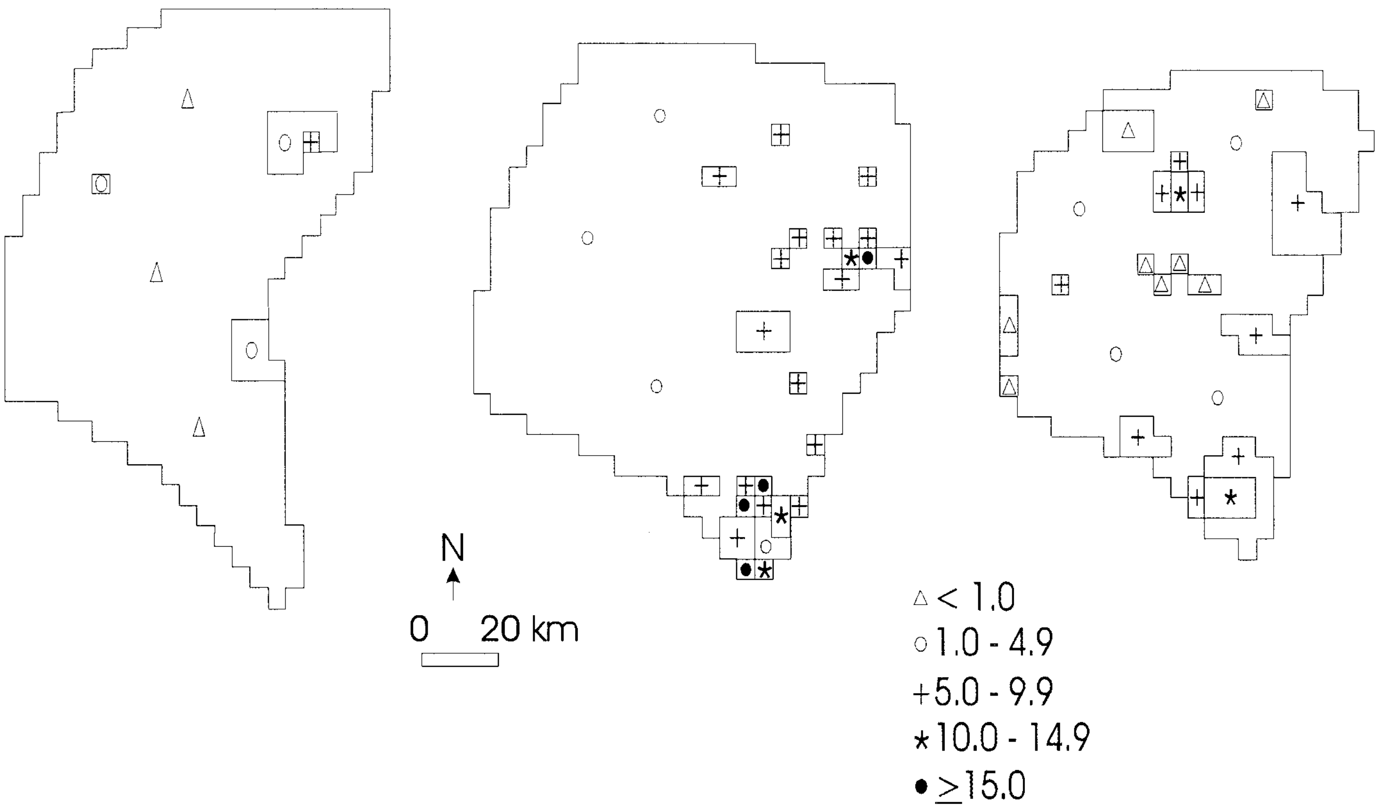

Figure 4. Maps of $\log_{10}$(moles SO_4/moles Ca) in SQ (left), CW1 (middle), and CW2 (right).

CW1, an area of heavy oil and gas production.

Values of $\log_{10}$(moles SO_4/moles Ca) in SQ were less than 1.0 over most of the study area (Figure 4). Higher values in the northeastern area of SQ suggest possible impacts from oilfield brine. Higher molar ratios were also observed throughout CW1 and CW2, reflecting abundant lignite seams in those zones.

Results outlined above suggest that chemical ratios can be useful for identifying probable sources of groundwater contamination over regional scales. Chemical ratio maps compiled in this study reflect natural processes (cation exchange) along regional groundwater flow paths, with local anomalies related to lignite, salt domes, and oilfield activity. Regional studies employing chemical ratios can prioritize future, localized studies to identify specific sources of contamination and implement appropriate remedial measures.

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