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Evaluation of Long-Term (1960–2010) Groundwater Fluoride Contamination in Texas

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Abstract

Groundwater quality degradation is a major threat to sustainable development in Texas. The aim of this study was to elucidate spatiotemporal patterns of groundwater fluoride (F^-) contamination in different water use classes in 16 groundwater management areas in Texas between 1960 and 2010. Groundwater F^- concentration data were obtained from the Texas Water Development Board and aggregated over a decadal scale. Our results indicate that observations exceeding the drinking water quality threshold of World Health Organization (1.5 mg F L^{-1}) and secondary maximum contaminant level (SMCL) (2 mg F L^{-1}) of the USEPA increased from 26 and 19% in the 1960s to 37 and 23%, respectively, in the 2000s. In the 2000s, F^- observations > SMCL among different water use classes followed the order: irrigation (39%) > domestic (20%) > public supply (17%). Extent and mode of interaction between F^- and other water quality parameters varied regionally. In western Texas, high F^- concentrations were prevalent at shallower depths (<50 m) and were positively correlated with bicarbonate (HCO_3^-) and sulfate anions. In contrast, in southern and southeastern Texas, higher F^- concentrations occurred at greater depths (>50 m) and were correlated with HCO_3^- and chloride anions. A spatial pattern has become apparent marked by "excess" F^- in western Texas groundwaters as compared with "inadequate" F^- contents in rest of the state. Groundwater F^- contamination in western Texas was largely influenced by groundwater mixing and evaporative enrichment as compared with water–rock interaction and mineral dissolution in the rest of the state.

Fluoride (F^-) is an anionic constituent of the majority of natural surface and ground waters, with both beneficial and harmful effects on human and animal physiology (Biswas et al., 2007; Fawell et al., 2006). Although F^- can improve dental health (Chouhan and Flora, 2010), prolonged exposure to high F^- levels can lead to dental and skeletal fluorosis (Gbadebo, 2012). Other potential concerns of high F^- intake include damage to kidney, liver, and brain; growth retardation; changes in DNA structure; and reduced intelligence (Guan et al., 1999; Fawell et al., 2006; Tang et al., 2008; Reddy et al., 2010; Salifu et al., 2012). The United States Department of Health and Human Services (HHS) recommends a threshold concentration of 0.7 mg F L^{-1} in drinking water to optimize the prevention of tooth decay while limiting unwanted health effects (HHS, 2011). The World Health Organization (WHO) recommends a threshold of 1.5 mg F L^{-1} in drinking water, beyond which F^- can cause detrimental effects (WHO, 2004). The USEPA established a maximum contaminant level (MCL) of 4 mg F L^{-1} to protect against crippling skeletal fluorosis and a secondary maximum contaminant level (SMCL) of 2 mg F L^{-1} to prevent against enamel fluorosis. The MCL is an enforceable water quality threshold, whereas the SMCL is a non-enforceable guideline related to undesirable cosmetic or aesthetic effects.

Drinking water is a major pathway of F^- intake by humans (Tekle-Haimanot et al., 2006). Over 200 million people worldwide rely on drinking water with F^- levels exceeding the WHO threshold (WHO, 2004). A recent study in the United States found that the number of children between 12 and 15 yr of age with dental fluorosis has increased from 23% in 1986–1987 to about 41% in 1999–2004 (Beltran, 2010). In the United States, high groundwater F^- levels have been reported from Wisconsin (Ozsvath, 2006), Ohio (Deering et al., 1983), Utah (Mayo and Loucks, 1995), South Carolina (Childress, 2003), and Texas (Hudak and Sanmanee, 2003). Texas is among the top states with the largest population (36,863 persons) receiving water supplies with F^- levels greater than MCL (up to 8.8 mg F L^{-1}) (BEST, 2006). A previous assessment by Hudak (1999) revealed that median groundwater F^- levels in Texas exceeded the SMCL and MCL in 25 and 5 counties, respectively, in the 1990s.

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Abbreviations: GMA, groundwater management area; HHS, Department of Health and Human Services; LISA, Local Indicators of Spatial Association; MCL, maximum contamination level; SMCL, secondary maximum contaminant level; TDS, total dissolved solids; TWDB, Texas Water Development Board.

High levels of F^- in groundwater in different parts of Texas pose a serious threat to groundwater quality and pose a potential hazard to public health. Earlier hydrochemical investigations into F^- levels were either site specific (Hudak, 2009; Hudak and Sanmanee, 2003) or constrained by shorter time periods (Hudak, 1999) and lacked rigorous spatial statistical analysis. Long-term, regional-scale assessment to evaluate groundwater F^- contamination in Texas is lacking, especially in relation to human health impacts (direct and/or indirect). Although groundwater is a major resource in Texas, it is challenged by issues of contamination and depletion. For example, our studies have revealed substantial groundwater quality degradation due to the rise of salinity (Chaudhuri and Ale, 2013a, 2013b; 2014b, 2014c) and nitrate (Chaudhuri et al., 2012). Coupled to this, our recent study has shown declining water levels, leading to concerns over the future availability of "healthy" potable groundwater resources across the state, thus underscoring a need for conducting more rigorous spatial assessment of groundwater quality to ensure sustainable development (Chaudhuri and Ale, 2014a). The main objective of this study was to elucidate regional patterns of groundwater F^- contamination in Texas with reference to existing groundwater management areas (GMAs). Specific objectives of this study were (i) to characterize temporal evolution of the spatial structure of groundwater F^- contamination between 1960 and 2010, (ii) to evaluate F^- contamination within different water use classes and GMAs, (iii) to assess the relative impacts of different water quality parameters on regional groundwater F^- contamination, and (iv) to assess the availability of adequate water quality data to ascertain future needs. The GMAs were chosen as the units of assessment to facilitate implementation of necessary management actions across the state.

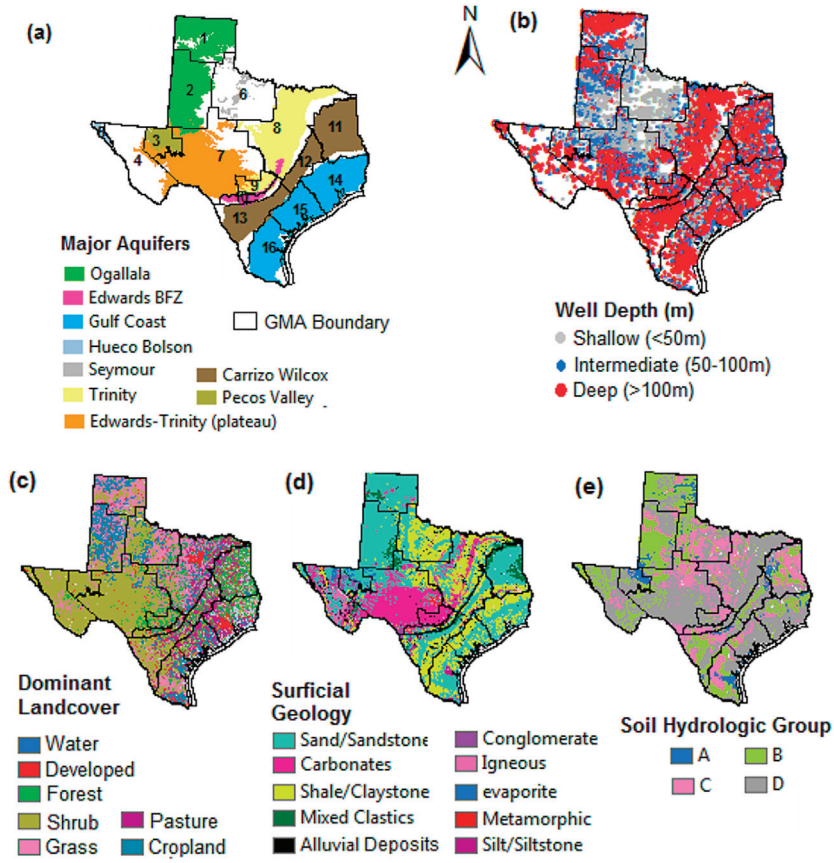

Fig. 1. (a) Groundwater management areas (GMA) and major aquifers (data source: Texas Water Development Board), (b) distribution of wells according to borehole depth, (c) dominant land cover following Land Cover Dataset of 2006 (Fry et al., 2011), (d) surficial geology (USGS, 2005), and (e) soil hydrologic groups (State Soil Geographic Database; STATSGO, 2006) across Texas.

Materials and Methods

Study Area

Texas ranks among the top three states in the United States that rely on groundwater resources (Kenny et al., 2009). Groundwater accounts for about 59% of the total and 36% of municipal (domestic and public) water supplies in the state (George et al., 2011). Texas is divided into 16 GMAs that have spatial resolutions varying over several hundreds of km^2 (Fig. 1a). The GMAs were originally created to provide for conservation, preservation, protection, recharging, and prevention of groundwater contamination and to control subsidence caused by groundwater withdrawal (TWDB, 2007). The GMA boundaries, in general, follow the nine major aquifer boundaries of the state (Fig. 1a). For example, GMAs 1 and 2 cover aerial extent of the Ogallala aquifer in western Texas.

The majority of the shallow (borehole depth <50 m) and intermediate (50–100 m) wells are in GMAs 1 through 4, 6, and 7, and deeper wells (>100 m) are in the remaining GMAs (Fig. 1b). About 79% of total groundwater withdrawals of the state—the majority of them from the Ogallala aquifer—are used for irrigation (Kenny et al., 2009). About 99% of the rural households in the state rely on groundwater (TWDB, 2007).

The geology of Texas is comprised mostly of sedimentary formations (Fig. 1d). The state's economy is heavily dependent on agricultural production, and it ranks first in the United States in cotton and forage, second in grain sorghum, and fourth in wheat production. The major agricultural regions include GMAs 1, 2, and 6 (Fig. 1c). Rangelands are dominant across vast regions of western Texas, covering GMAs 3, 4, and 7. Regions under the "developed" landcover class consisted of some of the nation's largest metropolitan areas, such as Dallas-Fort Worth (GMA 8), San Antonio (GMA 10), and Houston (GMA 14). The majority of the soils in the western Texas (GMAs 1–4) and parts of eastern and south-eastern Texas (parts of GMAs 14 and 16) have high to moderately high infiltration potential (soil hydrologic groups A and B), and the remaining areas have low to moderately low infiltration potential (soil hydrologic groups C and D) (Fig. 1e).

Groundwater Database

The Texas Water Development Board (TWDB) database contains groundwater quality data related to 33 water quality parameters collected from over 120,000 locations in Texas

since 1896 as a part of the Water Information Integration and Dissemination system. Water quality samples are collected after temperature, specific conductivity, and pH has stabilized (Boghici, 2003). Water samples are filtered using a pressure tank system before analysis and are preserved with acid for analysis of cationic species (Hudak, 2000). Geochemical data include concentrations of different major and minor ionic species and general water quality parameters (e.g., pH, conductivity, hardness, and well depth) along with designated water use class for each well. There are 20 water use classes in the database, including Domestic, Irrigation, Mining, Industrial, Public Supply, and Stock classes. Available water quality observations had decreased substantially with time (Table 1). For example, 5295 and 3049 wells were found to have F^- concentration data for the domestic and irrigation water use classes, respectively, in the 1960s, as compared with 1833 and 2098 wells in the 2000s.

Data Analysis

Data Preprocessing

The groundwater F^- concentration dataset between 1960 and 2010 was obtained from the TWDB database (Table 1). Decadal statewide assessment of F^- contamination was performed by considering all wells that had F^- concentration data in each decade instead of limiting the analysis to a smaller subset of wells that had data in all decades (only about 4% of total number of wells sampled in the 2000s had data in all preceding decades), which would have provided only a fractional glimpse of water quality. Due to the unavailability of continuous annual information for each well, data were aggregated at the decadal scale (1960s [1960–1969], 1970s [1970–1979], until the 2000s [2000–2010]) and analyzed at two spatial scales: (i) state and (ii) GMA. Data related to borehole depths (referred to as "well depth" hereafter) and additional water quality parameters, such as concentrations (mg L^{-1}) of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), bicarbonate (HCO_3^-), and total dissolved solids (TDS), were also obtained from the TWDB database to evaluate their influences on F^- distribution.

Several transformation techniques were applied to obtain normal distribution of the decadal F^- concentration data, which was assessed by using the Shapiro-Wilks test (Shapiro and Wilk, 1965). Because none of the transformations yielded the desired results, nonparametric methods were used for statistical analyses (USEPA, 2009; USGS, 2002). Temporal changes in groundwater F^- concentrations were evaluated by the Wilcoxon rank sum test, a nonparametric equivalent to the two-sampled *t* test, using Tukey's least significant difference at $\alpha = 0.05$. The test was performed for (i) statewide (for all decades) and (ii) GMA-wise (for the 1960s and 2000s) median F^- concentrations. The null hypothesis (H_o) indicated a lack of significant ($p < 0.05$) differences between median F^- concentrations between decades. The main statistical assumptions included (i) independence between water quality observations, which was justified by the presence of only 4% of the wells that were commonly sampled in all the five decades, and (ii) equality of variance, which was verified by Ansari-Bradley test. To compensate for potential undesirable effects of disproportionate sample sizes in the studied decades, inferences on water quality were supported by computing statewide (Table 2) and GMA-wise (Tables 3 and 4) percentages of observations exceeding different drinking water quality standards, which essentially "normalized" the decadal differences in sample sizes.

Assessment of F^- Contamination by Water Use Classes: Human Health Impacts

Human health risk potential of F^- contamination was evaluated by F^- contents exceeding drinking water quality thresholds established by the WHO and the USEPA. The percentage of observations below the HHS "optimal" F^- concentration threshold was also evaluated. Four water use classes—domestic, public supply, irrigation, and "other" (i.e., bottling, livestock, commercial, power generation, fire, industrial, recreation, desalination, mining, institutional, and other purposes)—were considered for this analysis (Table 1). Water use classes were selected on the basis of their expected impacts (direct and indirect) on human and livestock health. The "domestic" and "public supply" water use classes have "direct" impact on human health and are critical to ensure safe drinking water quality because municipal use of groundwater is expected to rise in Texas over the coming years (TWDB, 2012). The "irrigation" water use class was selected for its anticipated "indirect" impact on human health because long-term consumption of agronomic products contaminated by F^- uptake from irrigation water might lead to bioaccumulation of F^- and adversely affect humans. The "other" water use class was included to elucidate the potential F^- contamination threat to livestock resulting from direct consumption of groundwater or due to feeding on grass or hay irrigated with F^-–contaminated groundwater.

Spatial Assessment of F^- Contamination

Spatial patterns in groundwater F^- concentrations were evaluated by computing Moran's I and Local Indicators of Spatial Association (LISA) at $\alpha = 0.05$ (Chaudhuri et al., 2012). Moran's I was computed using the following equation (Moran, 1950):

$$\mathrm{I} = \frac{n}{\sum_{i=1}^{n}\sum_{j=1}^{n}\mathbf{W}_{ij}} \frac{\sum_{i=1}^{n}\sum_{j=0}^{n} w_{ij}(x_i - X)(x_j - X)}{\sum_{i=1}^{n}(x_i - X)^2} \quad [1]$$

Table 1. Number of groundwater F^- observations included in the study.

Decade	Water use class				Total
	Domestic	Public supply	Irrigation	Other	
1960s	5295	1617	3049	6868	16,829
1970s	4150	2409	2912	4962	14,433
1980s	2478	2461	1585	2976	9,500
1990s	2177	2510	1140	2212	8,039
2000s	1833	862	2098	1296	6,089

where n is total number of observations, i and j represent locations of groundwater wells, $\mathbf{W}_{ij}$ is the spatial weight matrix, x_i and x_j are the F^- concentrations at locations i and j, and X represents the average value of x. Moran's I varies from −1 (perfect negative spatial autocorrelation) to +1 (perfect positive spatial autocorrelation), with 0 indicating a random pattern.

Moran's I is a global indicator of spatial autocorrelation that smooths out local variations (Anselin, 1995). In contrast, the LISA provides a more localized view of the spatial association by deconstructing the Global Moran's I into contributions of individual data points within numerous smaller spatial regions (i.e., neighborhoods defined by spatial geometry of groundwater wells) and computes spatial statistics for each neighborhood so that the sum of local statistics is proportional to the Global Moran's I (Dale and Fortin, 2002; Anselin, 1995).

Computation of Moran's I and LISA was based on derivation of a spatial weight matrix to conceptualize the "neighborhood" structure. The inverse distance squared method was used coupled with first-order queen contiguity (each data point [e.g., groundwater wells] is influenced by eight neighboring groundwater wells, like following the queen's move on a chess board) at variable spatial resolution. The spatial weight matrix was computed individually for each decade. The ratio of n and $\mathbf{W}_{ij}$ (Eq. [1]) normalized the differences in sample sizes between decades, thus providing unbiased estimates of spatial association. The weight matrix was "row standardized" (by dividing each weight by the sum of the weights of all neighboring observations) to obtain a relative, rather than absolute, weighting scheme.

Identifying Groundwater Management Area–Wise F^- Contamination Zones in Texas

Hierarchical cluster analysis was performed using GMA-wise median groundwater F^- concentrations for the 1960s and 2000s to delineate the statewide spatial zones by aggregating homogeneous GMAs in terms of groundwater F^- contamination (Chaudhuri and Ale, 2013a). Ward's Minimum Variance algorithm, which has the ability to identify outliers and to account for up to 50% variability in the data (Blackwood et al., 2003), was used in conjunction with squared Euclidean distance to determine the total sum of squared deviations from the mean of each cluster (Lin et al., 2012). The rationale behind this approach was to produce the smallest possible increases in error sum of squares to minimize total within-cluster variance (e.g., F^- concentration variability within each GMA). At each step, a pair of clusters with minimum between-cluster distance is merged by detecting a pair of clusters that leads to a minimum increase in total within-cluster variance. This increase is a weighted squared distance between the cluster centers (e.g., spatial variability in F^- concentrations between the clusters). The squared Euclidean distance was used, instead of Euclidean distance, to progressively

Table 2. Statewide decadal groundwater F^- median concentrations and percentage of F^- observations above or below the drinking water quality thresholds of World Health Organization (WHO), USEPA, and U.S. Department of Health and Human Services (HHS).

Decade	Median	% Obs. > WHO threshold	USEPA		% Obs. < HHS threshold
			% Obs. > SMCL†	% Obs. > MCL‡	
	mg F L^{-1}				
			Domestic		
1960s	0.63c§	21.1	15.3	2.6	48.38
1970s	0.60c	21.2	15.2	3.1	54.74
1980s	0.61c	25.5	16. 6	5.2	52.21
1990s	0.74b	28.1	18.7	5.3	48.55
2000s	0.84a	31.7	20.4	5.9	50.24
			Public supply		
1960s	0.70a	21.1	15.2	2.7	51.63
1970s	0.60b	22.2	14.4	1.6	53.09
1980s	0.60b	22.9	16.3	3.1	49.85
1990s	0.58b	21.4	16.1	2.9	57.21
2000s	0.59b	22.6	17.2	3.2	58.15
			Irrigation		
1960s	1.20c	46.9	35.2	9.9	35.51
1970s	1.00d	37.9	25.9	5.3	33.96
1980s	1.40b	55.5	38.6	8.5	21.19
1990s	1.38b	45.4	28.9	7.3	25.08
2000s	1.62a	53.1	38.8	7.8	23.54
			Other		
1960s	0.80b	30.7	21.1	3.8	39.48
1970s	0.70c	34.7	20.7	4.3	40.52
1980s	0.81b	31.6	21.9	5.2	41.71
1990s	0.81b	28.8	18.9	4.3	43.03
2000s	0.94a	31.5	21.1	3.1	42.51

† Secondary maximum contaminant level.

‡ Maximum contaminant level.

§ Decadal median F^- concentrations for any particular water use class followed by the same letter indicates no significant difference between the decades at $\alpha = 0.05$.

increase the weights on objects (e.g., groundwater wells with F^- concentration data) that are further apart.

Evaluating Impacts of Common Water Quality Parameters on F^- Contamination

Spearman rank correlation coefficients (ρ) were computed between groundwater F^- concentrations and a variety of other routinely monitored water quality parameters to evaluate their relative influences on groundwater F^- contamination. Whereas the statewide correlation analysis was conducted for each decade, the GMA-wise analysis was conducted for the 2000s only. Water quality parameters used for the correlation analysis included (i) molar ratios of $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$, $HCO_3^-/(SO_4^{2-} + Cl^-)$, and SO_4^{2-}/Cl^-; (ii) concentrations of nitrate (NO_3^-) and TDS; and (iii) well depth. The $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ molar ratio was used to identify dominant cationic species and to understand their potential roles in groundwater F^- mobilization (Alderman et al., 2002; Chaudhuri and Ale, 2014b). The $HCO_3^-/(SO_4^{2-} + Cl^-)$ molar ratio was used to assess the relative abundance of major anionic species and overall ionic identity of groundwater (Richter and Kreitler, 1987; Chaudhuri and Ale, 2013a, b; Chaudhuri and Ale, 2014b)

Table 3. Comparative assessment of groundwater management area–wise groundwater median F^- concentrations between the 1960s and the 2000s.

Groundwater management area	Domestic		Irrigation		Public supply		Other	
	1960s	2000s	1960s	2000s	1960s	2000s	1960s	2000s
	mg F L^{-1}							
GMA 1	1.06	1.16†	1.22	1.30	1.44	1.50	1.22	1.20
GMA 2	**2.39‡**	**2.79**	**2.18**	**2.37**	**2.17**	**2.40**	**1.94**	**2.00**
GMA 3	1.44	1.63	1.23	1.48	0.97	1.00	1.36	1.49
GMA 4	1.18	1.16	1.20	1.27	1.51	1.67	1.38	1.40
GMA 5	NA§	NA	0.75	0.77	0.58	0.60	0.54	0.56
GMA 6	0.58	0.60	0.65	0.70	0.54	0.55	0.69	0.70
GMA 7	0.70	0.71	1.42	1.53	0.65	0.70	0.79	1.00
GMA 8	0.46	0.40	0.47	0.48	0.78	0.93	0.50	0.50
GMA 9	0.82	0.86	1.68	1.70	0.84	0.90	0.43	0.54
GMA 10	0.18	0.18	0.21	0.20	0.16	0.18	0.24	0.26
GMA 11	0.12	0.11	0.09	0.10	0.20	0.20	0.10	0.09
GMA 12	0.08	0.11	0.22	0.22	0.18	0.20	0.23	0.30
GMA 13	0.40	0.40	0.31	0.34	0.32	0.35	0.38	0.41
GMA 14	0.18	0.20	0.16	0.21	0.22	0.29	0.35	0.38
GMA 15	0.36	0.40	0.23	0.25	0.40	0.44	0.45	0.45
GMA 16	0.81	0.87	0.69	0.87	0.79	0.89	0.94	1.00

† Underlined numbers indicate statistically significant ($p < 0.05$) changes over time for corresponding water use classes in respective groundwater management areas.

‡ In each water use class, the highest median F^- concentration is marked in bold.

§ Observations not available.

Table 4. The groundwater management area–wise percentage of groundwater quality observations exceeding the drinking water quality threshold of the World Health Organization (WHO) and secondary maximum contaminant level (SMCL) for F^- for the 2000s.

Groundwater management area	% Observations > WHO threshold				% Observations > SMCL			
	Domestic	Irrigation	Public supply	Other	Domestic	Irrigation	Public supply	Other
GMA 1	31.9	38.8	50.9	37.3	17.3	22.4	35.7	26.3
GMA 2	**81.1†**	**84.6**	**81.4**	**64.2**	**71.2**	**63.4**	**66.0**	**52.0**
GMA 3	65.4	51.2	27.5	50.7	42.3	22.0	12.5	34.7
GMA 4	46.0	33.3	66.7	44.7	38.0	22.2	45.8	26.3
GMA 5	0.0	0.0	6.3	0.0	0.0	0.0	0.0	0.0
GMA 6	14.3	2.8	14.3	17.6	7.1	0.0	0.0	7.8
GMA 7	27.3	53.3	20.4	34.4	16.2	27.6	9.3	22.5
GMA 8	17.7	20.0	28.7	27.9	15.6	11.4	16.3	13.1
GMA 9	32.0	58.8	35.4	29.4	25.2	47.1	17.8	19.6
GMA 10	15.1	0.0	7.2	29.8	13.2	11.1	5.9	25.0
GMA 11	4.0	0.0	0.8	0.0	3.0	0.0	0.4	0.0
GMA 12	0.0	0.0	1.8	3.3	1.5	0.0	0.0	0.0
GMA 13	10.0	2.3	4.0	18.7	6.0	0.0	0.0	13.2
GMA 14	4.4	0.0	5.2	2.7	3.3	6.7	3.2	2.7
GMA 15	0.0	0.0	1.0	6.1	1.7	0.0	2.1	0.0
GMA 16	19.2	21.4	0.0	23.5	10.1	17.9	2.6	14.7

† In each water use class, the highest % of exceedance is marked in bold.

and the influence of agricultural activities (Hudak, 2000). The presence of higher HCO_3^- than (SO_4^{2-} + Cl^-) generally indicates alkaline conditions, higher salinization, and less freshwater recharge (Hudak, 2000; Chaudhuri and Ale, 2013a, b). To evaluate the relative influences of different natural processes (e.g., evaporation, rock–water interaction, and precipitation on hydrochemistry), $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ ratios were calculated because Na^+ and Cl^- are the most common species that impart high salinity to water bodies around the world (Gibbs, 1970).

Results and Discussion

Spatio-Temporal Assessment of Groundwater F^- Concentrations

Three striking geographic assemblages of high groundwater F^- concentrations (exceeding different drinking water quality thresholds) were apparent in western Texas encompassing GMAs 1 to 4 in the northwestern parts of GMA 7, GMA 8 in north-central Texas, and GMA 16 in southern Texas (Fig. 2a), and this observation was in agreement with earlier studies (Hudak, 1999, 2009; Hudak and Sanmanee, 2003). A significant ($p < 0.05$) and progressive rise in the statewide median groundwater F^- concentrations was observed between the 1960s (0.59 mg F L^{-1}) and the 2000s (0.88 mg F L^{-1}) (Fig. 2b). Observations exceeding the WHO threshold increased from 26 to about 38% between the 1960s and 2000s (Fig. 2b), accompanied by a corresponding rise in observations > SMCL from 19 to 23% (Fig. 2b). In all decades, over 4% observations exceeded the MCL (Fig. 2b). A vast region across GMA 6 and GMAs 11 to 15 had F^- concentrations below the HHS threshold in all decades (Fig. 2a). Observations below the HHS threshold in the state increased from 36 to 48% between the 1960s and the 2000s, indicating a potential risk of inadequate F^- in drinking water. Overall, our results showed evidence of either high or low F^- levels in groundwater that need to be addressed in the future.

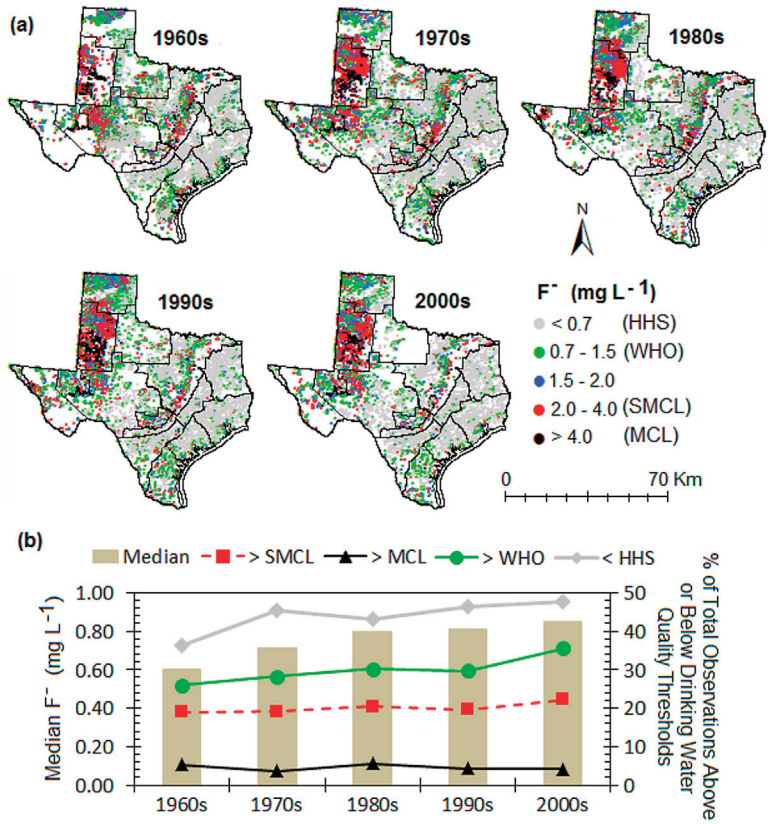

Fig. 2. (a) Spatio-temporal distribution of groundwater F^- concentrations in Texas by decades. (b) Temporal trends in statewide decadal median groundwater F^- concentration and percentage of total observations (all water use classes combined) above or below different drinking water quality thresholds. HHS, Health and Human Services; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; WHO, World Health Organization.

The spatial structure of groundwater F^- contamination became apparent with time as indicated by Moran's I and LISA (Fig. 3). Moran's I increased from 0.19 to 0.51 from the 1960s to the 2000s (Fig. 3a), which indicated an increasing statewide spatial autocorrelation between "similar" groundwater F^- observations. However, localized patterns of groundwater F^- contamination, which are critical for the groundwater and natural resources managers to implement strategies to protect and restore groundwater quality, could not be envisaged through Moran's I. LISA maps provided a more in-depth visual summary of spatial autocorrelation patterns in groundwater F^- contamination (Fig. 3a). Five scenarios emerged under LISA: (i) high-high: clusters of high groundwater F^- concentrations or hotspots; (ii) low-low: clusters of low groundwater F^- concentrations or coldspots; (iii and iv) high-low and low-high: spatial outliers with clusters of dissimilar groundwater F^- concentrations; and (v) random: no significant ($p < 0.05$) clustering (Fig. 3a). Hotspots increased from 21 to about 39% from the 1960s to the 2000s (Fig. 3b), accompanied by a corresponding drop in the random scenarios from 43 to about 32%. These features clearly indicated a gradual emergence of an identifiable spatial structure of F^- contamination across the state over time (Fig. 3a). The most prominent and consistent hotspot, apparent since the 1960s, was identified in western Texas (parts of GMAs 1–4 and northwestern parts of GMA 7). Consistently high F^- concentrations in this region indicated that the underlying hydrogeologic processes that led to high F^- loading to groundwater were more stable and, as such, might present more difficulties to designing ameliorative strategies. The main hydrogeologic processes in this region included groundwater depletion, source-water contamination from irrigation return flows, low precipitation accompanied by high evapotranspiration, and groundwater seepage and mixing. Several of these hydrologic processes were triggered by anthropogenic activities. For example, groundwater seepage and mixing in this region are largely caused by the lowering of hydraulic heads due to prolonged irrigational extraction, which facilitated mixing of highly saline and mineralized groundwater from playa lakes and the underlying hydrogeologic formations (e.g., Edwards-Trinity High Plains aquifer and Rustler) (Ale and Chaudhuri, 2013), with relatively better quality groundwater in the Ogallala aquifer. Regarding natural hydrologic processes, evapotranspiration, which was spatially and temporally stable, appeared to be a main driver of groundwater chemistry at shallower depths in this region.

The LISA illustrations enable groundwater managers to identify regions of future water quality impairment and thus help

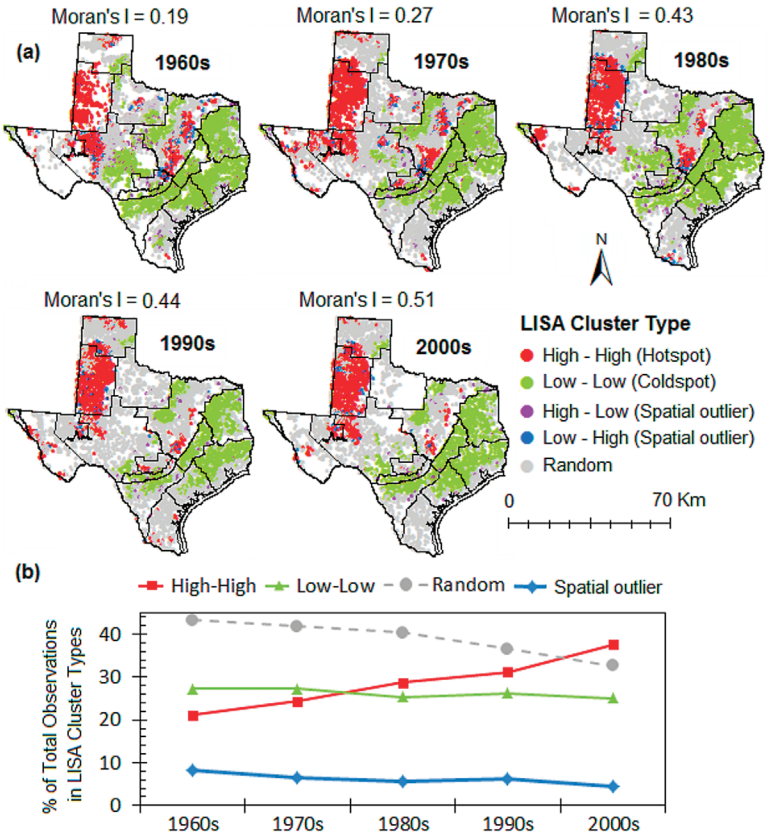

Fig. 3. (a) Distribution of Moran's I and Local Indicator of Spatial Association (LISA) clusters of groundwater F^- concentrations. (b) Temporal variation in the percentage of total observations within each LISA cluster class.

prioritize much-needed detailed hydrochemical investigation. These visually dynamic maps can also build awareness about existing water quality conditions and encourage the general public to have their groundwater wells tested following appropriate instructions from proper authorities. However, the need for in situ monitoring to establish site-specific water quality management protocols cannot be substituted by LISA, which can only be used as a reconnaissance tool by the groundwater and natural resources managers. In addition, due to diminishing sample sizes with time and variability in spatial resolution associated with LISA, caution should be exercised while making management decisions based on LISA illustrations.

Groundwater F^- Contamination by Water Use Classes

Statewide Assessment

The extent of groundwater F^- contamination was the highest in the irrigation water use class in all decades, as marked by the highest median F^- concentrations and the highest percentage of observations exceeding the WHO threshold (38–53%), SMCL (26–39%), and MCL (5–8%) (Table 2). High F^- levels in irrigational groundwater indicated high potential for source water contamination via F^- recycling and an indirect pathway for human exposure through consumption of potentially F-contaminated agricultural products. Fluoride uptake by plants from high F^- contents of irrigation water (Singh et al., 1995; Arnesen, 1997; Ruan et al., 2003) causes phytotoxicity and adverse effects on plant metabolism (Miller, 1993). High F^- accumulation in plants has been related to necrosis, needle scratch, and tip burn diseases (Ramanaiah et al., 2006). Singh et al. (1995) found a high probability of human ingestion of fluorides due to consumption of F^-–contaminated vegetables. Ingesting water with high F^- contents on a regular basis over long periods of time could lead to high bioaccumulation of F^- in human tissues (Paul et al., 2011).

Among the municipal uses, groundwater F^- contamination in the domestic water use class in all decades indicates a substantial health risk potential (Table 2). In the 2000s, 32 and 20% of observations exceeded the WHO threshold and SMCL, respectively, in the domestic water use class as compared with about 23 and 17% of such observations in the public supply water use class. Higher F^- contamination in the domestic water use class was probably due to a lack of appropriate well-head protection measures and/or regular monitoring and thus a lack of awareness or management plan to protect groundwater quality from degradation. Because over 56% of municipal water demand in Texas is supplied from groundwater resources and about 99% of rural households depend on domestic wells, a large fraction of the Texas population might be at risk due to "direct" exposure to high F^- levels in groundwater. About 50% of observations in the domestic and public supply water use classes were below the HHS threshold in all decades, indicating potential risk of dental caries due to lack of adequate F^- in drinking water. A major revelation over the course of the study was a clear spatial segregation of "inadequate" (F^- levels < HHS) and "excess" F^- levels (> WHO and/or SMCL) across the state. For example, the majority of the eastern, central, and southern parts of the state (GMA 6, most of GMA 7, and GMAs 9–16) were characterized by "inadequate" F^- values, whereas the western parts of the state (GMAs 1–5) had "excess" F^- levels. The above observations indicated inherent differences in hydrologic processes, climate, and human dimensions that warrant further investigation to ascertain sources and differential behavior of F^- across the state.

In the face of rapidly emerging concerns over groundwater quality in different parts of the state (Chaudhuri et al., 2012; Chaudhuri and Ale, 2013a, b) and the expected reductions in fresh groundwater availability, implementation of appropriate well-head protection strategies (especially in rural settings) will be of utmost importance to ensure sustained availability of "safe" potable groundwater.

Groundwater Management Area–wise Assessment

Contrasting patterns of groundwater F^- contamination were apparent across the state (Tables 3 and 4). In GMA 2, median F^- concentrations were the highest and exceeded the WHO threshold and SMCL significantly ($p < 0.05$) for the domestic, public supply, and irrigation water use classes in the 1960s and 2000s (Table 3). In addition, >80% of observations in GMA 2 in the 2000s exceeded the WHO threshold among all water use classes, except the "other" water use class, and about 52 to 72% of observations in all water use classes exceeded the SMCL (Table 4). In western Texas, the median F^- concentrations have significantly ($p < 0.05$) increased in the domestic (GMAs 1 and 2), public supply (GMAs 1, 2, and 4), and irrigation water use

classes (GMAs 1–4) between the 1960s and 2000s. In GMAs 1, 3, and 4, median F^- concentrations significantly ($p < 0.05$) exceeded or were close to the WHO threshold for the public supply water use class in the 1960s and 2000s. Furthermore, >25% of observations in GMAs 3 and 4 exceeded water quality thresholds for domestic and public supply water use classes. In contrast, median F^- concentrations in eastern and southern Texas (GMAs 8–15) were significantly ($p < 0.05$) lower for all water use classes since the 1960s, with the majority of the GMAs registering below the HHS. Less than 25% of observations exceeded water quality thresholds (WHO and SMCL) in these GMAs (Table 3).

Fluoride contamination has consistently been higher in western Texas (GMAs 1–4) since the 1960s as marked by median F^- levels that are (i) substantially higher than the rest of the state and (ii) exceed different water quality thresholds (Fig. 4a). The hierarchical cluster analysis grouped the GMAs into three statistically significant ($p < 0.05$) clusters in the 1960s (Fig. 4b), compared with four in the 2000s (Fig. 4c). Over time, GMA 2 has emerged as an independent cluster, indicating its increasing dissimilarity (in the relative intensity of F^- contamination) from the rest of the GMAs. This was due to the highest median F^- levels and the percentage of exceedance of different water quality thresholds in GMA 2 (Tables 3–4). Interestingly, GMA 16 was not grouped under Cluster 3, which contains all of its adjacent GMAs in both decades; this finding warrants further monitoring and geochemical assessment.

Influence of Major Ion Chemistry and other Water Quality Parameters on Groundwater F^- Concentration

Distinct spatial patterns were apparent in the GMA-wise distribution of Spearman correlation coefficients (ρ) between F^- and different water quality parameters (Fig. 5). Strong (ρ: > −0.50; $p < 0.05$) to moderately (−0.25 < ρ < −0.49; $p < 0.05$) negative correlations between F^- and $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ ratio were observed in all the GMAs (Fig. 5a), which indicated direct association of high groundwater F^- contents with high Na^+ and K^+ and lower Ca^{2+} and Mg^{2+} levels. This trend is in agreement with earlier studies that found a common occurrence of F^- with Na^+ and an inverse correlation with Ca^{2+} (Karro and Rosentau, 2005; Subramani et al., 2005; Rafique et al., 2009; Rango et al., 2009, 2012; Borgnino et al., 2013). Negative correlation between F^- and Ca^{2+} and/or Mg^{2+} results from low solubility of fluorides in these ions (Handa, 1975; Sujatha, 2003; Chae et al., 2007). Strong positive (ρ: > 0.50; $p < 0.05$) correlations between F^- and $HCO_3^-/(SO_4^{2-} + Cl^-)$ ratio were found in GMAs 2, 3, 11 to 13, and 15, which indicated preferential association between F^- and HCO_3^- across most parts of the state (Fig. 5b). A high abundance of HCO_3^- ion generally signifies alkaline conditions, which enhance F^- leaching from natural sources such as fluorite and CaF_2 (Amini et al., 2008; Rao, 2009; Brindha et al., 2011; Arveti et al., 2011) by the following mechanisms:

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \quad [2]$$

$$CaF_2 + Na_2CO_3 \rightarrow CaCO_3 + 2F^- + 2Na^+ \quad [3]$$

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \quad [4]$$

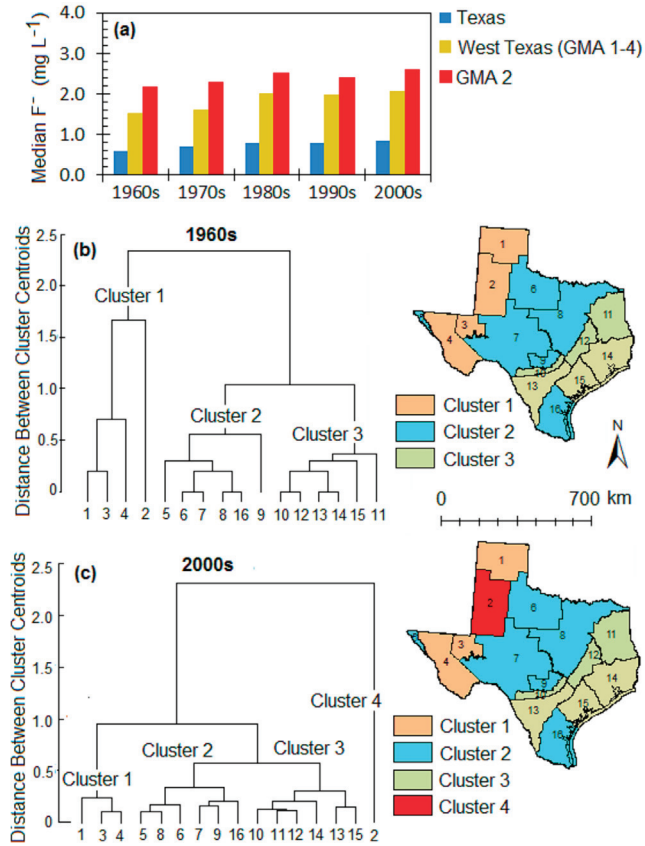

Fig. 4. (a) Decadal median groundwater F^- concentrations (all water use classes combined). Groundwater management area (GMA) clusters obtained by hierarchical cluster analysis for the (b) 1960s and (c) 2000s.

Equations [2], [3], and [4] also account for the inverse relationship between F^- and Ca^{2+} and the direct relationship between F^- and Na^+. There is a vast abundance of sedimentary deposits across the state because all major aquifers are of sedimentary origin (Fig. 1). The Ogallala aquifer in GMAs 1 and 2 (where some of the highest F^- levels in the state have been reported) is mainly composed of unconsolidated sandy sediments with alumino-silicate minerals, which release HCO_3^- ion to facilitate fluorite dissolution. Fluorite can form due to interactions between F-rich groundwater and calcite ($CaCO_3$) by the following reaction:

$$CaCO_3 + H^+ + 2F^- \rightarrow CaF_2 + HCO_3^- \quad [5]$$

The occurrence of caliche (also known as "caprock") has been reported from western Texas (GMA 1 and 2) (Knowels et al., 1984), where calcite cements are abundant. The Edwards-Trinity (plateau) (GMA 7) and Edwards-BFZ aquifers (GMA 10) are mostly composed of carbonates, which offer suitable substrate for fluorite formation. In addition, high hydroxyl (OH^-) concentrations, commonly found in alkaline conditions, can replace F^- from phyllosilicate species such as muscovite ($KAl_2[AlSi_3O_{10}]F_2$) and biotite ($KMg_3[AlSi_3O_{10}]F_2$) by isomorphic substitution mechanism as follows:

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \rightarrow KAl_2[AlSi_3O_{10}][OH]_2 + 2F^- \quad [6]$$

$$KMg_3[AlSi_3O_{10}]F_2 + 2OH^- \rightarrow KAl_2[AlSi_3O_{10}][OH]_2 + 2F^- \quad [7]$$

Similar ionic charges (-ve) and ionic sizes of F^- (0.13 nm) and OH^- (0.11 nm) facilitates substitution. Madhavan and

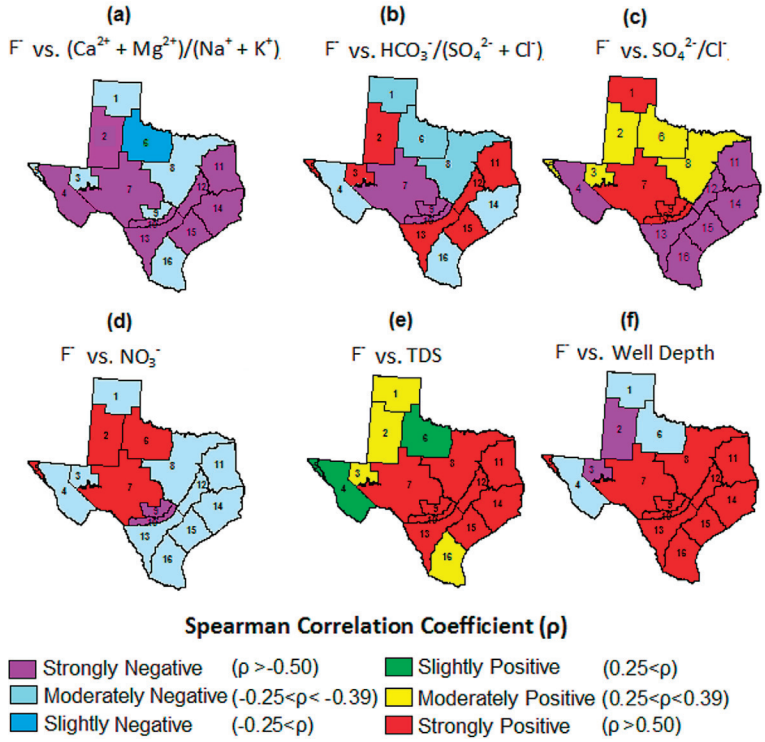

Fig. 5. Spatial assessment of groundwater management area–wise Spearman correlation coefficient (ρ) for the 2000s to assess interrelationships between F^- vs. (a) $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$, (b) $HCO_3^-/(SO_4^{2-} + Cl^-)$, (c) SO_4^{2-}/Cl^-, (d) NO_3^-, (e) total dissolved solids (TDS), and (f) well depth.

Subramanian (2002) found that F^- contents of the clay minerals exceeded that of sand and silt fractions.

Statewide assessment revealed significant ($p < 0.05$) negative correlation between F^- and $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ since the 1980s and significant ($p < 0.05$) positive correlation coefficients between F^- and $HCO_3^-/(SO_4^{2-} + Cl^-)$ ratio since the 1960s (Table 5). The above observations indicated the high likelihood of finding F^- contamination in association with alkaline earth metals in the state with prevalence of HCO_3^- ions. However, regional differences were noted across the state. For example, strong (ρ: > 0.50; $p < 0.05$) to moderately ($0.25 < \rho < 0.49$; $p < 0.05$) positive correlations between F^- and SO_4^{2-} were found in most of western and central Texas (Deboradaran et al., 2009), whereas a relatively greater influence of Cl^- was observed in GMAs 11 to 16 (Fig. 5c). Overall, the above observations indicated the likelihood of high F^- occurrence in Na-HCO_3–SO_4–type hydrochemical assemblage in western Texas as compared with Na-HCO_3–Cl type in the rest of the state, which was consistent with similar studies (Rango et al., 2009; Chae et al., 2007; Amini et al., 2008; Reddy et al., 2010; Saikia and Sarma, 2011; Salifu et al., 2012)

Significant ($p < 0.05$) positive correlations were found between F^- and NO_3^-, which increased with time, indicating a stronger association between these two species (Table 5). The presence of strong positive (ρ: > 0.50; $p < 0.05$) correlations between NO_3^- and F^- in GMAs 2, 6, and 7 in western Texas (Fig. 5d) suggested common sources. Western Texas is among the major agro-ecologic regions of the state where fertilizer application coupled with irrigation with groundwater resources is a common practice. A major anthropogenic source to F^- in this region could be the phosphate fertilizers applied to agricultural croplands (Mirlean and Roisenberg, 2007; Mourad et al., 2009). High NO_3^- contamination in western Texas, resulting from the application of different agrochemicals, has also been reported (Hudak, 2000; Chaudhuri et al., 2012). Although F^- is not a constituent of NO_3 fertilizers, coexistence of F^- and NO_3^- at high levels can be attributed to common sources, such as agrochemicals used in crop production (Kundu et al., 2009; Datta et al., 1999). Nitrate and F^- released from different agrochemicals can leach simultaneously to groundwater systems by the infiltrating rain and irrigation water, leading to a high abundance of both species (Kundu and Mandal, 2009). In addition, prolonged irrigational pumping in western Texas has led to alteration of hydraulic heads in the aquifers and has resulted in intense groundwater mixing and solute exchange between different hydrostratigraphic formations, which partially accounts for the high F^- contamination (Currell et al., 2011).

The GMA-wise correlations showed strong (ρ: > 0.50; $p < 0.05$) to moderately ($0.25 < \rho < 0.49$; $p < 0.05$) positive correlations between F^- and TDS in the majority of the GMAs in the 2000s, which suggested that high F^- levels contributed to groundwater salinization processes throughout the state (Fig. 5e) (Ramanaiah et al., 2006; Rafique et al., 2009; Rahmani et al., 2010; Gbadebo, 2012). In addition, statewide assessment revealed significant ($p < 0.05$) positive correlations between statewide decadal F^- and TDS concentrations since the 1960s (Table 5), which indicate a persistent effect of high F^- contents on overall groundwater salinization in Texas. As a collective measure of salinity, TDS is also an indicator of ionic strength of groundwater. High ionic strength favors fluorite (CaF_2) dissolution (Sujatha, 2003) and F^- desorption from colloidal surfaces (Rafique et al., 2009), leading to F^- release to groundwater. The highest correlation coefficient found between F^- and TDS in the 2000s (ρ = 0.52;

Table 5. Spearman correlation coefficients between statewide decadal groundwater F^- concentrations and corresponding water quality parameters.

Parameter	1960s	1970s	1980s	1990s	2000s
$(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$	−0.23	−0.17	−0.39*	−0.38*	−0.41*
$HCO_3^-/(SO_4^{2-} + Cl^-)$	0.44*	0.41*	0.46*	0.45*	0.47*
SO_4^{2-}/Cl^-	0.14	0.09	0.2	0.14	0.15
NO_3^-	0.18	0.19	0.42*	0.47*	0.48*
Total dissolved solids	0.39*	0.39*	0.36*	0.47*	0.52**
Well depth	−0.18	−0.28	−0.32	−0.45*	−0.46*

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

$p < 0.01$) revealed that the effect of the chemical environment on F^- contamination has increased over time as groundwater salinization has increased in the state, raising concerns about sustainable water quality (Chaudhuri and Ale, 2014b).

A contrasting depth stratification pattern was apparent in F^- contamination across the state as illustrated by significant ($p < 0.05$) negative correlation between well depth and F^- concentrations in western Texas and a significant positive correlation in central and eastern Texas (Table 5; Fig. 5f) and in agreement with Hudak (2009). Significant ($p < 0.05$) negative correlations between F^- and well depth in GMA 2 (ρ: −0.47) and GMA 3 (ρ: −0.39) indicated shallower F^- sources in western Texas. In addition to natural sources (e.g., fluorite), potential anthropogenic sources of F^- in western Texas included agrochemicals and evaporative enrichment (Hudak, 2009). Shallow groundwater wells in western Texas (Fig. 1) suggested the presence of shallow water levels, which allowed for rapid contaminant transport from surficial sources to groundwater systems. In addition, shallow water levels coupled with high temperature and "porous" surficial materials (the prevalence of soil hydrologic groups B and/or A and sand/sandstone type geology) in this region facilitated faster evaporation of groundwater, which led to evaporative enrichment of F^-. Significant ($p < 0.05$) positive correlations in GMAs 8 to 14 indicated deeper origin of F^- in eastern, north-central, and southern Texas (Fig. 5f), such as mineral dissolution and/or ion exchange processes during deep regional groundwater circulation (Hudak and Sanmanee, 2003).

Assessment of well depth in conjunction with geology and soil properties across the state provided additional insights into F^- contamination. General abundance of shallow wells (Fig. 1b) in western Texas (GMAs 1–4 and northwestern GMA 7) coupled with the predominance of soil hydrologic groups A and B suggested better drainage conditions and faster infiltration and thus a higher probability for contaminant transport from surficial sources (e.g., agrochemicals from agricultural lands) to groundwater systems. The predominance of sandy/sandstone type geology (unconsolidated sediments of the Ogallala aquifer) across much of western Texas (Fig. 1d) affected by high F^- contamination also facilitated infiltration processes, thus increasing the potential for surficial contamination of groundwater. On the other hand, deeper wells (Fig. 1b) coupled with poor soil drainage conditions (hydrologic groups C and D) and dominance of clay/shale type geology in the eastern, north-central, and southern parts of the state indicated "natural" causes of F^- contamination due to prolonged water–rock interaction at deeper levels.

Mechanistic differences in groundwater F^- contamination across the state were assessed by plotting water quality observations from western (GMAs 1–4) and north-central (GMA 8) Texas for the 2000s on the Gibbs diagram (Gibbs, 1970) (Fig. 6a). Although a combination of evaporation and rock-weathering processes became apparent, the high F^- observations in GMAs 1 to 4 were shifted more toward the evaporation domain, indicating evaporative enrichment of F^- (Vasak et al., 2003; Rafique et al., 2009; Rao, 2009). On the other hand, observations from GMA 8 were more clustered in the rock-weathering domain, indicating the dominant role of mineral dissolution and ion-exchange processes as supported by the occurrence of deeper groundwater wells in this region (Fig. 1b). Shallow wells with substantially lower precipitation (Fig. 6b) in western Texas also influenced direct evapotranspiration from the groundwater table, leading to salt enrichment with high F^- concentrations. The presence of numerous playa lakes throughout western Texas (Fig. 6c) further underscored the importance of evaporative processes on local/regional hydrology (Nativ and Smith, 1987; Ashworth et al., 1991).

Availability of Water Quality Data: Existing Data Gaps

A major revelation of this study was the reduction in the availability of hydrochemical data over time (Table 1), which was presumably due to the lack of a water quality monitoring program where monitoring locations were not selected based on prior knowledge of historic water quality conditions and extent of contamination. For example, among the total number of wells having F^- concentration data in the 1960s, only about 21, 19, 14, and 11% of the wells were revisited in the 1970s, 1980s, 1990s, and 2000s, respectively. Only about 4% of the wells sampled in the 2000s had been mentioned in the earlier decades. In addition, several of the groundwater wells with high levels of F^- in in one decade had no records from other decades. The reduction in number of observations with time hindered a detailed well-by-well temporal evaluation of F^- contamination.

The lack of sufficient data could pose serious implications on human health and sustainable development because F^- contamination can go undetected. The available number of F^-

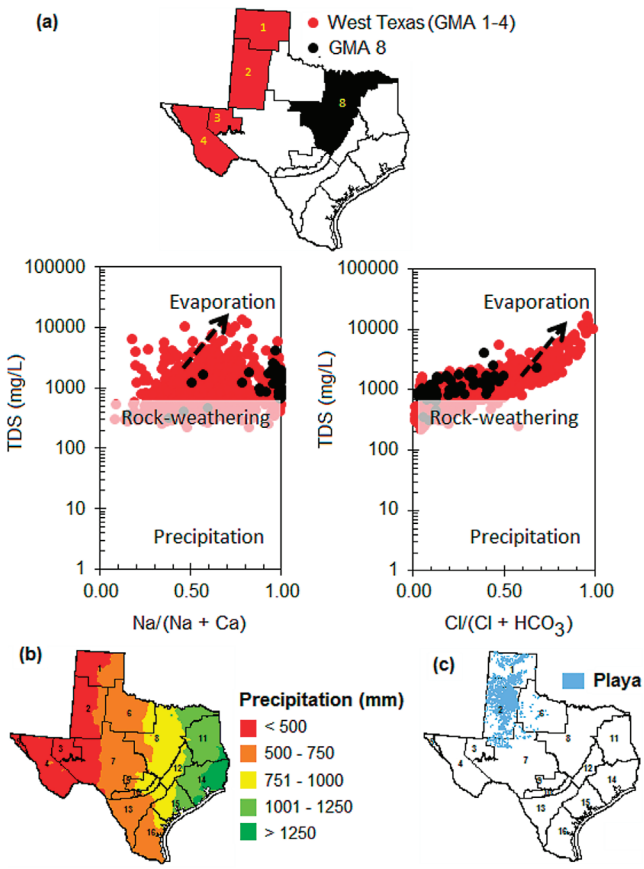

Fig. 6. Distribution of (a) high F^- observations (>SMCL) in the 2000s on Gibbs (1970) diagram, (b) average (1960–1990) annual precipitation across Texas, and (c) locations of playa lakes in Texas. GMA, groundwater management area; TDS, total dissolved solids.

observations decreased by about 65 and 47%, respectively, for the domestic and public supply wells between the 1960s and 2000s. Because water from both of these well types is used for human consumption, a lack of adequate information might result in consumption of contaminated water. A lack of adequate resampling activities is also indicated by the fact that only about 4 and 3.5% of total observations that exceeded the WHO threshold and SMCL, respectively, in the 1960s were resampled in the 2000s (Fig. 7a). Since the 1960s, 34 groundwater wells showed F^- concentrations above 10 mg F L^{-1} (Fig. 7c), a threshold for crippling fluorosis in humans (Tekle-Haimanot et al., 2006). Even though several of these wells represented domestic and public supply water use classes, none of them has been revisited in the later decades, leading to the lack of adequate knowledge about water quality and the extent of F^- contamination in these high-risk wells.

The greatest reductions in F^- concentration data over time were observed in GMAs 6, 7, and 8 (Fig. 2a and 7b). No F^- concentration data were available for seven counties (Archer, Palo Pinto, Rockwall, Shackelford, Stephens, Throckmorton, and Young) in the 2000s. Decreasing temporal data have also translated into a general lack of spatial representation of groundwater quality, which is undesirable for Texas, a state known for its heavy reliance on groundwater resources for sustainable development (Chaudhuri et al., 2012; Chaudhuri and Ale, 2013a, 2013b, 2014b).

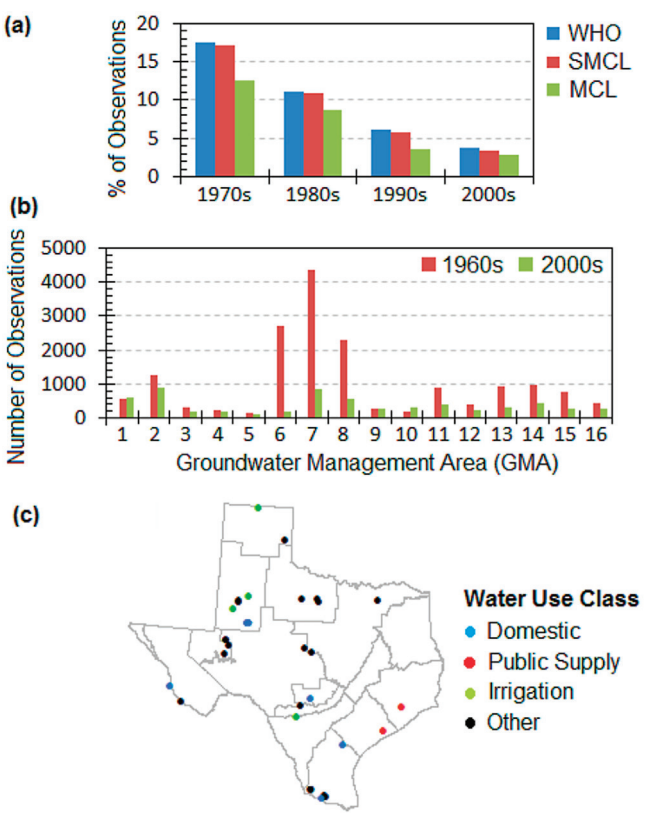

Fig. 7. (a) Groundwater wells resampled between 1970s and 2000s, expressed as percentages of wells that exceeded the drinking water quality thresholds for World Health Organization (WHO), secondary maximum contamination level (SMCL), and maximum contamination level (MCL) (USEPA) in the 1960s. (b) Groundwater management area (GMA)-wise total F^- observations for the 1960s and 2000s. (c) Groundwater wells registering over 10 mg L^{-1} of F^- in different water use classes since the 1960s.

Limitations, Recommendations, and Future Research Directions

A major constraint in performing rigorous well-by-well assessment of groundwater F^- contamination across the state was the diminishing sample size over time and a lack of resampling frequency, which led us to resort to decadal estimates of F^- contamination. To evaluate changes in groundwater F^- concentrations over time accurately, we recommend a spatially intensive and more frequent monitoring scheme based on a priori knowledge of the extent of contamination. Increased resampling frequency, at least for the municipal wells that have F^- levels above the drinking water quality thresholds, is highly desirable for accurate assessment of F^- contamination.

Groundwater F^- distribution was largely governed by major ion chemistry. Additional research into the sources and spatial distribution of these dissolved constituents in the underlying aquifers could provide critical insight into the hydrogeochemical processes that led to F^- contamination, especially in the hotspots. Because the GMAs closely followed major aquifer boundaries (Fig. 1), our results have provided some interesting clues about the F^- contamination patterns in the aquifers. For example, high F^- levels in western Texas (GMAs 1–4) indicated high F^- levels in the Ogallala, Pecos Valley, and Edwards-Trinity (plateau) aquifers. In addition, sources of localized anthropogenic contamination, such as agrochemicals (phosphate fertilizers) and industrial (aluminum) effluents, warrant investigation.

High groundwater F^- contamination in the domestic water use class needs to be re-evaluated, and home owners (especially in rural areas) should be informed about the amount of F^- intake in their daily diet due to consumption of groundwater, potential risks of consuming high F^- groundwater, and available defluoridation technologies. Efforts should be made to assess the suitability of high F^-–laden groundwater for irrigational purposes and consequent influences on agricultural products. In addition, the rates of fluorosis and related health issues in F^-–affected regions should be monitored on a regular basis, and health officials should be consulted as needed.

Conclusions

Groundwater F^- levels in Texas have been rising since the 1960s. In domestic, public supply, and irrigation wells, observations exceeding the WHO threshold increased, respectively, from about 21, 21, and 47% in the 1960s to about 32, 22, and 53% in the 2000s. Over time, hotspots of F^- contamination became increasingly apparent in western Texas (GMA 1–4) and in parts of north-central Texas (GMA 8). In GMAs 1 through 4, between 32 and 81% of observations exceeded the WHO threshold in the 2000s. Median F^- concentrations in GMA 2 exceeded the SMCL for all water uses in the 2000s. In western Texas, shallower wells were more contaminated due largely to agricultural activities and evaporative enrichment. In contrast, high F^- levels in rest of Texas were detected in deep wells and were mostly attributable to natural processes, such as rock–water interaction. A key recommendation to assess F^- contamination accurately is to improve existing water quality monitoring plans.

Acknowledgments

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References

Alderman, J.H., P.F. Hudak, and M. Acevedo. 2002. Chemical ratios and groundwater contamination in east Texas. Bull. Environ. Contam. Toxicol. 69:793–799. doi:10.1007/s00128-002-0130-6

Ale, S., and S. Chaudhuri. 2013. Groundwater resources and associated environmental issues in Texas: A changing scenario. American Society of Agricultural and Biological Engineers (ASABE) Annual International Meeting, 21–24 July 2013, Kansas City, MO.

Amini, M., K. Mueller, K.C. Abbaspour, T. Rosenberg, M. Afyni, K.N. Moller, M. Sarr, and C.A. Johnson. 2008. Statistical modeling of global geogenic fluoride contamination in groundwaters. Environ. Sci. Technol. 42:3662–3668. doi:10.1021/es071958y

Anselin, L. 1995. Local indicators of association-LISA. Geogr. Anal. 27:93–115. doi:10.1111/j.1538-4632.1995.tb00338.x

Arnesen, A.K.M. 1997. Availability of fluoride to plants grown in contaminated soils. Plant Soil 191:13–25. doi:10.1023/A:1004210713596

Arveti, N., N.R.S. Sharma, J.A. Aikenhead, and K. Sunil. 2011. Fluoride incidence in groundwater: A case study from Talpura, Andhra Pradesh, India. Environ. Monit. Assess. 172:427–443. doi:10.1007/s10661-010-1345-3

Ashworth, J.B., P. Christian, and T.C. Waterreus. 1991. Evaluation of groundwater resources in the Southern High Plains, Texas. Report 330. Texas Water Development Board, Austin, TX.

Beltran, E.D. 2010. Prevalence and severity of dental fluorosis in the United States, 1999–2004. NCHS data brief no. 53. National Center for Health Statistics, Centers for Disease Control and Prevention, Atlanta, GA.

BEST (Board on Environmental Studies and Toxicology). 2006. Fluoride in drinking water: A scientific review of EPA's standards. http://www.actionpa.org/fluoride/nrc/NRC-2006.pdf (accessed 18 Feb. 2013).

Biswas, K., D. Bandhoyapadhyay, and U.C. Ghosh. 2007. Adsorption kinetics of fluoride on iron (III)–zirconium hybrid oxide. Adsorption 13:83–94. doi:10.1007/s10450-007-9000-1

Blackwood, C.B., T. Marsh, S.-H. Kim, and E.A. Paul. 2003. Terminal restriction fragment length polymorphism data analysis for quantitative comparison of microbial communities. Appl. Environ. Microbiol. 69:926–932. doi:10.1128/AEM.69.2.926-932.2003

Boghici, R. 2003. A field manual for ground-water sampling. Texas Water Development Board, Austin, TX.

Borgnino, L., M.G. Garcia, G. Bia, Y.V. Stupar, P.L. Costumer, and P.J. Depertis. 2013. Mechanisms of fluoride release in sediments of Argentina's central region. Sci. Total Environ. 443:245–255. doi:10.1016/j.scitotenv.2012.10.093

Brindha, K., R. Rajesh, R. Murugan, and L. Elango. 2011. Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. Environ. Monit. Assess. 172:481–492. doi:10.1007/s10661-010-1348-0

Chae, G.T., S.T. Yun, B. Mayer, K.H. Kim, S.Y. Kim, J.S. Kwon, K. Kim, and Y.K. Koh. 2007. Fluorine geochemistry in bedrock groundwater of South Korea. Sci. Total Environ. 385:272–283. doi:10.1016/j.scitotenv.2007.06.038

Chaudhuri, S., and S. Ale. 2014a. Long-term (1930–2010) Trends in groundwater levels in Texas: Influence of soils, landcover and water use. Sci. Total Environ. 10.1016/j.scitotenv.2014.05.013.

Chaudhuri, S., and S. Ale. 2014b. Development of groundwater salinity in municipal wells in major aquifers in Texas. Sci. Total Environ. 472:370–380. doi:10.1016/j.scitotenv.2013.10.120

Chaudhuri, S., and S. Ale. 2014c. An appraisal of groundwater quality in the Seymour and Blaine aquifers in a major agro-ecological region in Texas, USA. Environ. Earth Sci. 71:2765–2777. doi:10.1007/s12665-013-2655-x

Chaudhuri, S., and S. Ale. 2013a. Characterization of groundwater resources in the Trinity and Woodbine aquifers in Texas. Sci. Total Environ. 452–453:333–348. doi:10.1016/j.scitotenv.2013.02.081

Chaudhuri, S., and S. Ale. 2013b. Regional trends in groundwater depletion and quality as affected by irrigational use in the Southern High Plains of Texas. American Society of Agricultural and Biological Engineers (ASABE) Annual International Meeting, 21–24 July 2013, Kansas City, MO.

Chaudhuri, S., S. Ale, P. Delaune, and N. Rajan. 2012. Spatio-temporal variability in groundwater nitrate concentration in Texas: 1960–2010. J. Environ. Qual. 41:1806–1817. doi:10.2134/jeq2012.0022

Childress, J.M. 2003. South Carolina ambient groundwater quality report. Summary: Pee Dee Basin. Bureau of Water, South Carolina Department of Health and Environmental Control, Columbia, SC.

Chouhan, S., and S.J.S. Flora. 2010. Arsenic and fluoride: Two major groundwater pollutants. Indian J. Exp. Biol. 48:666–678.

Currell, M., I. Cartwright, M. Raveggi, and D. Han. 2011. Controls on elevated fluoride and arsenic concentrations in groundwater from the Yuncheng Basin, China. Appl. Geochem. 26:540–552. doi:10.1016/j.apgeochem.2011.01.012

Dale, M.R., and M.J. Fortin. 2002. Spatial autocorrelation and statistical tests in ecology. Ecoscience 9:162–167.

Datta, P.S., S.K. Tyagi, P. Miikherjee, S.K. Bhattacharya, N. Gupta, and P.D. Bhatnagar. 1999. Groundwater NO_3 and F contamination processes in Pushkar Valley, Rajasthan as reflected from ^{18}O isotopic signature and ^{3}H recharge studies. Environ. Monit. Assess. 56:209–219. doi:10.1023/A:1005903619718

Deboradaran, S., A.H. Mahvi, S. Dehdasti, S. Deboradaran, and R. Shoara. 2009. Correlation of fluoride with some inorganic constituents in groundwater of Dashtestan, Iran. Fluoride 42:50–53.

Deering, M.F., E.T. Mohr, B.F. Sypniewski, and E.H. Carlson. 1983. Regional hydrogeochemical patterns in ground water of northwestern Ohio and their relation to Mississippi Valley-type mineral occurrences. J. Geochem. Explor. 19:225–241.

Fawell, J., K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, and Y. Magara. 2006. Fluoride in drinking water. IWA Publishing, London.

Fry, J., G. Xian, S. Jin, J. Dewitz, C. Homer, L. Yang, C. Barnes, N. Herold, and J. Wickham. 2011. Completion of the 2006 National Land Cover Database for the conterminous United States. Photogramm. Eng. Remote Sens. 77:858–864.

Gbadebo, A.M. 2012. Groundwater fluoride and dental fluorosis in southwestern Nigeria. Environ. Geochem. Health 34:597–604. doi:10.1007/s10653-012-9455-1

George, P.G., R.E. Mace, and R. Petrossian. 2011. Aquifers of Texas. Report 380. Texas Water Development Board, Austin, TX.

Gibbs, R.J. 1970. Mechanisms controlling world water chemistry. Science. 170:188-190.

Guan, Z.Z., Y.N. Wang, K.Q. Xiao, D.Y. Dai, Y.H. Chen, J.L. Liu, P. Sindelar, and G. Dallner. 1999. Influence of chronic fluorosis on membrane lipids in rat brain. Neurotoxicol. Teratol. 20:537–542. doi:10.1016/S0892-0362(97)00136-0

Handa, B.K. 1975. Geochemistry and genesis of fluoride-containing groundwaters in India. Ground Water 13:275–281. doi:10.1111/j.1745-6584.1975.tb03086.x

HHS. 2011. HHS and EPA announce new scientific assessment and actions on fluoride. https://www.federalregister.gov/articles/2011/01/13/2011-637/proposed-hhs-recommendation-for-fluoride-concentration-in-drinking-water-for-prevention-of-dental (accessed 9 June 2014).

Hudak, P.F. 2009. Elevated fluoride and selenium in west Texas groundwater. Bull. Environ. Contam. Toxicol. 82:39–42. doi:10.1007/s00128-008-9583-6

Hudak, P.F., and S. Sanmanee. 2003. Spatial patterns of nitrate, chloride, sulfate, and fluoride concentrations in the woodbine aquifer of north-central Texas. Environ. Monit. Assess. 82:311–320. doi:10.1023/A:1021946402095

Hudak, P.F. 2000. Regional trends in nitrate content of Texas groundwater. J. Hydrol. 228:37–47. doi:10.1016/S0022-1694(99)00206-1

Hudak, P.F. 1999. Fluoride levels in Texas groundwater. J. Environ. Sci. Health A 34:1659–1676. doi:10.1080/10934529909376919

Karro, E., and A. Rosentau. 2005. Fluoride levels in the Silurian-Ordovician aquifer system of western Estonia. Fluoride 38:307–311.

Kenny, J.F., N.L. Barber, S.S. Hutson, K.S. Linsey, J.K. Lovelace, and M.A. Maupin. 2009. Estimated use of water in the United States in 2005. USGS Circ. 1344. USGS, Reston, VA.

Knowels, T., P.L. Nordstrom, and W.B. Klemr. 1984. Evaluating the groundwater resources of the high plains of Texas. Report 288. Texas Department of Water Resources, Austin, TX.

Kundu, M.C., and B. Mandal. 2009. Assessment of potential hazards of fluoride contamination in drinking groundwater of an intensively cultivated district in West Bengal, India. Environ. Monit. Assess. 152:97–103. doi:10.1007/s10661-008-0299-1

Kundu, M.C., B. Mandal, and G.C. Hazra. 2009. Nitrate and fluoride contamination in groundwater of an intensively managed agroecosystems: A functional relationship. Sci. Total Environ. 407:2771–2782. doi:10.1016/j.scitotenv.2008.12.048

Lin, C.Y., M.H. Abdullah, S.M. Praveena, A.H.B. Yahaya, and B. Musta. 2012. Delineation of temporal variability and governing factors influencing the spatial variability of shallow groundwater chemistry in a tropical sedimentary island. J. Hydrol. 432–433:26–42. doi:10.1016/j.jhydrol.2012.02.015

Madhavan, N., and V. Subramanian. 2002. The natural abundance of fluoride in soils of the Ajmer district, Rajasthan. J. Environ. Monit. 4:821–822. doi:10.1039/b208151b

Mayo, A.L., and M.D. Loucks. 1995. Solute and isotopic geochemistry and ground water flow in the central Wasatch Range, Utah. J. Hydrol. 172:31–59. doi:10.1016/0022-1694(95)02748-E

Miller, G.W. 1993. The effect of fluoride on high plants: With special emphasis on early physiological and biochemical disorders. Fluoride 26:3–22.

Mirlean, N., and A. Roisenberg. 2007. Fluoride distribution in the environment along the gradient of a phosphate-fertiliser production emission (southern Brazil). Environ. Geochem. Health 29:179–187. doi:10.1007/s10653-006-9061-1

Moran, P.A.P. 1950. Notes on continuous stochastic phenomena. Biometrika 37:17–23. doi:10.1093/biomet/37.1-2.17

Mourad, N.M., T. Sharshar, T. Elminr, and M.A. Mousa. 2009. Radioactivity and fluoride contamination derived from phosphate fertilizer plant in Egypt. Appl. Radiat. Isot. 67:1259–1268. doi:10.1016/j.apradiso.2009.02.025

Nativ, R., and D.A. Smith. 1987. Hydrogeology and geochemistry of the Ogallala aquifer, southern high plains. J. Hydrol. 91:217–253. doi:10.1016/0022-1694(87)90206-X

Ozsvath, D.L. 2006. Fluoride concentrations in a crystalline bedrock aquifer, Marathon County, Wisconsin. Environ. Geol. 50:132–138. doi:10.1007/s00254-006-0192-6

Paul, E.D., C.E. Gimba, J.A. Kagbu, G.I. Ndukwe, and F.G. Okibe. 2011. Spectrometric determination of fluoride in water, soil and vegetables from the precinct of Rive Basawa, Zaria, Nigeria. J. Basic. Appl. Chem. 1:33–38.

Rahmani, A., K. Rahmani, S. Debodaran, A.H. Mahvi, R. Mohamadjani, and H. Rahmani. 2010. Child dental carries in relation fluoride and some inorganic constituents in drinking water in Arsanjan, Iran. Fluoride 43:179–186.

Rafique, T., S. Naseem, T.H. Usmani, E. Bashir, F.A. Khan, and M.I. Bhanger. 2009. Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parker, Sindh, Pakistan. J. Hazard. Mater. 171:424–430. doi:10.1016/j.jhazmat.2009.06.018

Ramanaiah, S.V., S.V. Mohan, B. Rajkumar, and P.N. Sarma. 2006. Monitoring of fluoride concentrations in ground water of Prakasham District in India: Correlation with physico-chemical parameters. J. Environ. Sci. Eng. 48:129–134.

Rango, T., G. Bianchini, L. Beccaluva, T. Ayenew, and N. Colombani. 2009. Hydrogeochemical study in the main Ethiopian rift: New insights to source and enrichment mechanism of fluoride. Environ. Geol. 58:109–118. doi:10.1007/s00254-008-1498-3

Rango, T., J. Kravchenko, B. Atlaw, P.G. Mccornick, M. Jeuland, B. Merola, and A. Vengosh. 2012. Groundwater quality and its health impact: An assessment of dental fluorosis in rural inhabitants of the main Ethiopian Rift. Environ. Int. 43:37–47. doi:10.1016/j.envint.2012.03.002

Rao, N.S. 2009. Fluoride in groundwater, Vahara River Basin, Visakhapatnam District, Andhra Prades, India. Environ. Monit. Assess. 152:47–60. doi:10.1007/s10661-008-0295-5

Reddy, D.V., P. Nagabhushanam, B.S. Sukhija, A.G.S. Reddy, and P.L. Smedley. 2010. Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda district, India. Chem. Geol. 269:278–289. doi:10.1016/j.chemgeo.2009.10.003

Richter, B.C., and C.W. Kreitler. 1987. Sources of groundwater salinization in parts of West Texas. Ground Water Monit. Rev. 7:75–84. doi:10.1111/j.1745-6592.1987.tb00966.x

Ruan, J., L. Ma, Y. Shi, and W. Han. 2003. Uptake of fluoride be tea plant (Camellia *sinessis*). J. Sci. Food Agric. 83:1342–1348. doi:10.1002/jsfa.1546

Saikia, M.M., and H.P. Sarma. 2011. Fluoride geochemistry of Kollong river basin, Assam, India. Appl. Sci. Res. 3:367–372.

Salifu, A., B. Petruvski, K. Ghebremichael, R. Buamah, and G. Amy. 2012. Multivariate statistical analysis for fluoride occurrence in groundwater in the northern region of Ghana. J. Contam. Hydrol. 140–141:34–44. doi:10.1016/j.jconhyd.2012.08.002

Shapiro, S.S., and B.B. Wilk. 1965. An analysis of variance test for normality (complete samples). Biometrika 52:591–611. doi:10.1093/biomet/52.3-4.591

Singh, V., M.K. Gupta, P. Rajwansi, S. Misra, S. Srivastava, R. Srivastava, M.R. Srivastava, S. Prakash, and S. Dass. 1995. Plant uptake of fluoride in irrigation water by ladyfinger (Abelmorchus *esculentus*). Food Chem. Toxicol. 33:399–402. doi:10.1016/0278-6915(95)00005-M

STATSGO. 2006. State Soil Geographic Database. http://datagateway.nrcs.usda.gov/ (accessed 10 Jan. 2013).

Subramani, T., L. Elango, and S.R. Damodarasamy. 2005. Groundwater quality and its suitability for drinking and agricultural use in Chitihar Basin, Tamil Nadu, India. Environ. Geol. 47:1099–1110. doi:10.1007/s00254-005-1243-0

Sujatha, D. 2003. Fluoride levels in the groundwater of the south-eastern part of Ranga Reddy district, Andhra Pradesh, India. Environ. Geol. 44:587–591. doi:10.1007/s00254-003-0795-0

Tang, Q., J. Du, H. Ma, S. Jiang, and X. Zhou. 2008. Fluoride and children's intelligence: A meta-analysis. Biol. Trace Elem. Res. 126:115–120. doi:10.1007/s12011-008-8204-x

Tekle-Haimanot, R., Z. Melaku, H. Kloos, C. Reimann, W. Fantaye, L. Zerihun, and K. Bjorvatn. 2006. The geographic distribution of fluoride in surface and groundwater in Ethiopia with an emphasis on the Rift Valley. Sci. Total Environ. 367:182–190. doi:10.1016/j.scitotenv.2005.11.003

TWDB. 2007. Water for Texas. Texas Water Development Board. Austin, TX.

TWDB. 2012. Water for Texas. Texas Water Development Board, Austin, TX.

USEPA. 2009. Statistical analysis of groundwater monitoring data at RCRA facilities. EPA 530/R-09–007. USEPA, Washington, DC.

USGS. 2002. Techniques of water resources investigations of the United States Geological Survey. USGS, Reston, VA.

USGS. 2005. Preliminary integrated geologic map databases for the United States: Central states: Montana, Wyoming, Colorado, New Mexico, North Dakota, South Dakota, Nebraska, Kansas, Oklahoma, Texas, Iowa, Missouri, Arkansas, and Louisiana. USGS Open-File Report 2005-1351. USGS, Reston, VA.

Vasak, S., R. Brunt, and J. Griffioen. 2003. Mapping of hazardous substances in groundwater on a global scale. In: T. Appelo, editor, Arsenic in groundwater: A world problem. Proc. Seminar, Utrecht, 29 November. Chapter 6. Netherlands National Committee of the IAH Secretariat, Utrecht, the Netherlands. p. 82–91.

WHO. 2004. Guidelines for drinking-water quality. 3rd ed. World Health Organization, Geneva.