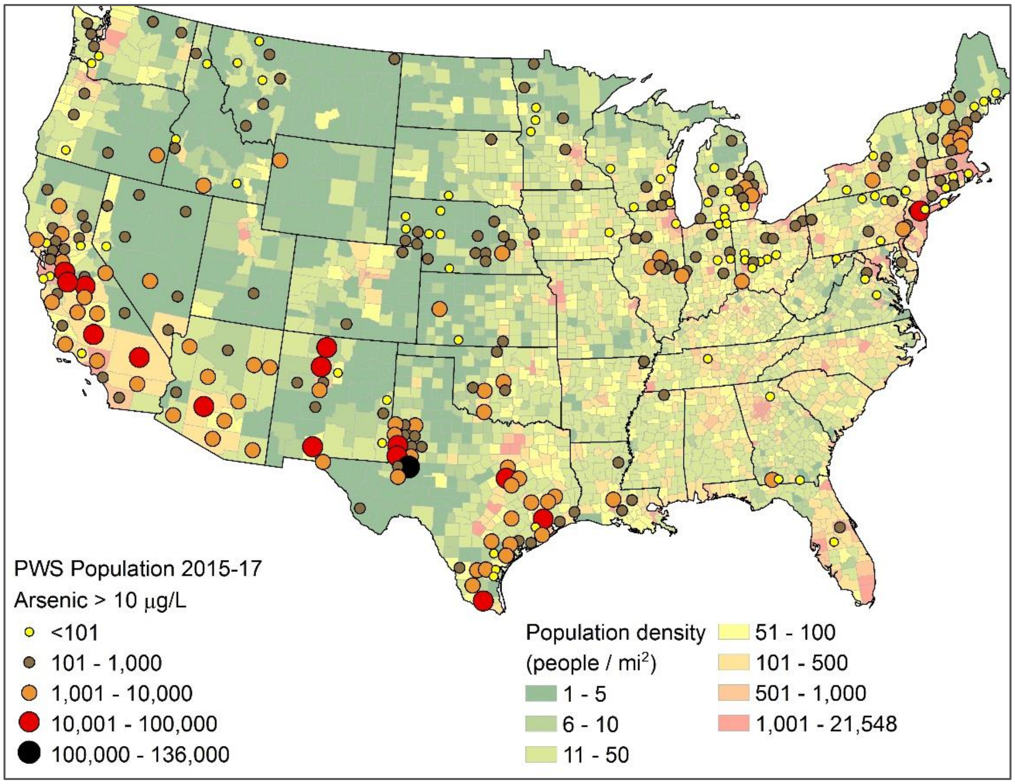
Update on Groundwater Arsenic Levels in Major and Minor Aquifers in Texas



by
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Executive Summary

Assessing the safety of public water systems for communities is a critical issue with strong implications for human health. In this study we update the analysis of arsenic contamination in Texas that was conducted in 2018 by evaluating groundwater arsenic contamination in domestic and Public Water Systems (PWSs) in the state and comparing arsenic contamination in Texas with that in other states and assessing treatment options for arsenic and related inorganic contaminants.

Results show that there are ~6,800 active PWSs in Texas, mostly (56%) privately owned. Community water systems (account for 67% of the total number of PWSs in the state. Although most community water systems, in terms of number of systems, are based on groundwater (72%), the population served by PWSs is dominated by surface water sources, with 80% of the population served by surface water PWSs.

In Texas, ~43% of Community Water Systems had at least one health-based violation of the EPA Safe Drinking Water Act (SDWA) rules during the study period (1980 – 2018). Health based violations include exceedances of maximum contaminant levels (MCLs), exceedances of maximum residual disinfectant levels (MRDLs), and treatment technique requirements. The percentage of systems with violations is higher for privately owned systems (49%) than for those owned by local governments (33%). Community Water Systems based on surface water sources have a higher percentage of violations (62%) than those based on groundwater sources (36%). The population exposed to violations totals 16 million, 14 million for surface water based Community Water Systems relative to 2 million for groundwater based Community Water Systems. The corresponding population percentages range from 63% for surface water to 43% for groundwater.

PWS violations in 2018 were dominated by those related to inorganics (~480 violations), followed by radionuclides (~230), and disinfection byproducts (~160). The time series shows that inorganic violations were highest throughout most of the period of record, increasing to ~740 in 2006, reflecting the Arsenic Rule (2006). Radionuclide violations were also high throughout much of the record, peaking in 2004 at ~390 and decreasing to ~230 in 2018. Groundwater accounts for the majority of violations in inorganics (mean 88%) and radionuclides (mean 88%).

Populations impacted by PWS violations in Texas are shown within the context of those in the U.S. for arsenic and related inorganics and radionuclides violations. The maps of impacted populations by arsenic violations peaked in 2006 – 2008 in response to implementation of the Arsenic Rule, showing widespread impacts in parts of Texas, California, Arizona, Oklahoma, northeastern U.S., and the region surrounding the Great Lakes. The arsenic map based on 2016 – mid 2019 data shows similar distributions in many regions with reductions in populations impacted by arsenic violations in the Northeast, Arkansas, and Arizona. Maps of populations impacted by fluoride violations show the largest impact in the High Plains of Texas and central regions of Oklahoma with isolated regions along the east coast based on 2000 – 2002 data. The

2016 – mid 2019 map shows that the fluoride violations in systems along the east coast have been resolved but fluoride concentrations remain high in the Texas High Plains and also some isolated regions in S California and Arizona. Populations impacted by radionuclides are dominated by combined radium in the Great Lakes region and along the East Coast with lower levels throughout the central region, including Texas and surrounding states whereas populations affected by uranium are located primarily in the southwest, ranging from California to Texas and populations affected by gross alpha are highest in Texas and also in the northeast. The distribution of populations impacted by inorganics and radionuclides likely reflect geologic controls.

We examined various techniques that could be used to achieve compliance with EPA regulations. Two primary approaches for noncompliant systems include: (1) Non Treatment Options, such as blending or alternative water sources or (2) Treatment Options. Water treatment was examined for arsenic and fluoride violations. Several Best Available Techniques for treating non-compliant water were considered, primarily RO – Reverse osmosis; ED – Electrodialysis; AA – Activated alumina; IX – Ion exchange; and IBS – Iron based sorbents for inorganic contaminants. Limitations of treatment were also considered, particularly water chemistry effects and competing ions. Chemical reactions can degrade membranes through scaling and corrosiveness. Competing ions can negatively affect treatment efficiency, particularly levels of Si which are moderately high in many regions in Texas and can reduce the ability to sorb inorganic contaminants.

1.0 Introduction

There is increasing concern about exposure to contaminated water through drinking water sources. The Texas population was ~27.5 million in 2015 (Dieter et al., 2017) and increased to 28.3 million in 2018. Approximately 26.2 million people relied on Public Water Systems (PWSs) in 2015 and an estimated 1.3 million people relied on non-PWSs (Dieter et al., 2017).

1.1 EPA Regulations

EPA regulates water quality of PWSs under the Safe Drinking Water Act (SDWA) that was passed by Congress in 1974 and amended in 1986 and 1996. EPA granted primacy to the Texas Commission on Environmental Quality (TCEQ). Data on PWS violations of EPA drinking water regulations are compiled by EPA in the EPA Safe Drinking Water Information System (SDWIS) database. Violations of the SDWA are categorized as follows:

(1) health based violations,
(2) acute health based violations,
(3) monitoring and reporting violations, and
(4) public notification and other violations.

Health-based violations include those related to exceedances of maximum contaminant levels (MCLs) referring to the highest permitted concentration of contaminants allowed in drinking water (Table 1), or exceedances of maximum residual disinfectant levels (MRDLs), or violations of treatment technique (TT) rules, referring to required processes to decrease contaminant levels in drinking water.

Table 1. EPA rules and the time they were implemented.

	Rules
Total Coliform Rule (TCR)	NIPDWR (1977), TCR (1990)
Revised Total Coliform	Revised Total Coliform Rule (2016)
Arsenic	NPPDWR, Arsenic Rule (2006)
DBPs	Disinfectants and Disinfection Byproducts, Total trihalomethanes (1981 -1983)
	Stage 1 DBPs (2002 - 2004)
	Stage 2 DBPs (2012 - 2013
LCR	Lead and Copper Rule (1992)
RLCR	Revised Lead and Copper Rule (2007)
Radionculides	NIPDWR, Radionuclides Rule (2003)
Inorganic chemicals	NIPDWR, Phase 1 Rule (198), Phase II Rule (1992), Phase V Rule (1994)
Organic chemicals	NIPDWR, Phase 1, Phase II, Phase V
Groundwater Rule	2009
SWTR	Surface Water Treatment Rule (1993)
IESW	Interim Enhanced SWTR (2002)
LTIESW	Long-term 1 Enhanced SWTR (2005)

NIPDWR: National Interim Primary Drinking Water Rule (https://www.epa.gov/dwreginfo).

1.2 Categories of Public Water Systems

There are a variety of PWSs that are regulated by TCEQ. PWSs provide piped water for human consumption, with a minimum of 15 service connections or regularly serving an average of 25 people for at least 60 days during the year (https://www.epa.gov/dwreginfo).

1. Community water systems (CWSs) provide water to at least 15 service connections used by residents throughout the year or regularly serve ≥25 residents year round.
2. Non-community water system include transient and non-transient systems.
    2a. Transient non-community water systems - do not regularly serve a minimum of 25 of the same people over 6 months in a year. Examples of these systems include campgrounds or highway rest stops with its own water source.
    2b. Non-transient non-community water system refer to PWSs that serve a minimum of 25 of the same people over 6 months in a year, such as schools, office buildings with their own water sources (e.g. wells).

The compliance status of a PWS is categorized as follows:

Serious Violator: A PWS with unresolved serious, multiple, and/or continuing violations in a system that is designated as a priority candidate for formal enforcement (https://www.epa.gov/dwreginfo).

Health-Based Violations of MCLs, specifying the highest contaminant concentrations permitted in drinking water (Table 2); or of treatment technique (TT) rules, which indicate the required processes to reduce drinking water contaminant amounts. Health-based drinking water standards include MCLs and treatment technique rules.

1.3 Results of Previous Study

In 2018, we evaluated the probability of groundwater arsenic concentrations exceeding threshold levels of 5 µg/L, considered above background, and those exceeding 10 µg/L (the EPA MCL) based on 10,495 analyses (data from 1992 – 2017) (Reedy et al., 2018). Results of the study underscore hotspots of groundwater arsenic contamination with probabilities of contamination exceeding 50% in the southern Ogallala aquifer, southern Gulf Coast aquifer, the Hueco-Mesilla Bolson and West Texas Bolson aquifers, and the Trinity aquifer. The number of water samples that exceeded the MCL totaled 733 (7% of all analyses). This study shows that 78 PWSs were non-compliant in terms of arsenic contamination with water sourced from one of the major or minor aquifers providing water to a total of ~100,000 people. The results show that the PWS locations are generally consistent with the hotspots of groundwater arsenic contamination, with 25 PWSs in the southern Gulf Coast, 37 in the southern High Plains, and 12 in the Trinity Aquifer, east of the city of Waco. The number of PWSs does not reflect the populations being served with 12 systems in the Gulf Coast serving 43,141 people and 12 systems east of Waco serving 40,226 people. Texas ranked second in the U.S. for both the total state population at-risk of PWS arsenic violations (99,653 people) and the total number at risk of serious PWS violations (21,761). A county level analysis revealed that an additional 81,500 people use groundwater that exceeds the arsenic MCL outside the PWSs in Texas.

1.4 Management of Non-Compliant Public Water Systems

Various approaches can be used by PWSs to achieve compliance with EPA regulations. Non Treatment Options or Treatment Options are the two primary methods for dealing with non-compliant PWSs. The following description relies on published papers and information presented in the EPA web site: **https://www.epa.gov/ground-water-and-drinking-water**.

Table 2: Maximum Contaminant Level Goals (MCLGs), Maximum Contaminant Levels (MCL), and Secondary Maximum Contaminant Levels (SMCL) for different contaminants.

Contaminant	MCLGs	MCLs	SMCLs
As	0	10 ppb	
F	4 ppm	4 ppm	2 ppm
Se	50 ppb	50 ppb	
N	10 ppm	10 ppm	
U	0	30 ppb	
Ra	0	5 pCi/L	
Gross alpha	0	15 pCi/L	

1.4a Non-Treatment Options

EPA recommends that non-treatment options be considered first because of lower costs and to avoid creation of residuals (waste products). Non-treatment options include:
(1) using alternative sources that meet the MCL;

(2) seasonal use of high pollution sources while maintaining a running annual pollutant concentration that meets the MCLs at each entry point to the distribution system; and
(3) blending high and low-pollutant sources to meet the MCLs.

The simplest non-treatment option is considered to be abandoning the contaminated water source or developing a new water source with concentrations less than the MCL. This option may work for PWS utilities that have multiple water sources with at least one source that produces water that is compliant with the EPA regulations. However, abandoning one of a multiple number of sources may not be feasible if the resultant capacity is inadequate or because of water rights considerations. Many small PWSs rely on a single water source, limiting their flexibility for switching to an alternate source. In this situation, the PWS could develop a new compliant source, or purchase water from another compliant source or consolidate with a nearby PWS. However, installing a new source may be more expensive than treating the water. Another non treatment option would be to limit production from sources that exceed the MCL from full-time to peak times or specific seasons. Systems with only one source will need to find another primary source of supply while systems with one or more sources can switch the problematic source to a back-up or seasonal source. When this option is used, systems must conduct monitoring (in accordance with the primary agency's requirements) at the entry point to ensure the running annual average is at or below the MCLs. Blending is also an option if the PWS is large and includes compliant sources which can be produced in addition to non-compliant sources. Groundwater from the compliant wells should be less than the MCL all of the time. The target concentration of the blended stream should be less than the MCL by about 10-20%.

1.4b Treatment Options Best Available Techniques (BATs)

The EPA lists several techniques as BATs for different contaminants. Not all of the techniques that are listed are suitable for each contaminant (Table 3). The most suitable technique for a contaminant is generally considered the BAT.

Table 3. EPA list of Best Available Technologies for selected contaminants.

	Coag/ Filt[1,2]	Lime softening[2]	RO[3]	ED	AA	IX cation	IX anion	IBS	Greensand filtration	Other
As	BAT	BAT[3,4]	BAT	no	BAT[4]	no	Yes[4,5,6]	yes	yes	Oxidation/ filtration[7]
F	no	yes	BAT		BAT	no	yes	no	no	
Ra	no	BAT	BAT	no	no	Yes[5,6]	no	yes	BAT	
U	BAT	BAT	BAT	no	BAT	no	BAT[6]	yes	no	

RO – Reverse osmosis; ED – Electrodialysis; AA – Activated alumina; IX – Ion exchange; IBS – Iron based sorbents.

[1] low capital costs

[2] operator care required with chemical usage

[3] for waters with pH ≥10.5;

[4] requires oxidation to As(V)

[5] significantly impacted by high TDS

[6] significantly impacted by high sulfate

Limitations of Treatments:

Limitations of different BATs include:

- Complexity of treatment technology, ranging from simple to operate (such as point of use (POU) under the sink systems) to those requiring trained personnel (e.g. a reverse osmosis plant).
- Cost. Water treatment cost may vary according to the severity of the water contamination, types of contaminants, and size of community served by the water system. It is very important to know the chemical composition of the influent.
- Competing ions and various chemical reactions may affect the ability to treat water.

Competing ions:

Many treatments are based on a contaminant's ability to sorb/exchange. Competing ions in the effluent may reduce the ability to remove contaminants (Table 4). For example, the presence of 10 mg/L Si could decrease arsenic sorption on $FeCl_3$ by up to 70% [*Meng et al.*, 2000]. Ion hierarchy, in the order of competing ion selectivity, varies according to treatment method and related chemical reaction. Sorption methods, such as activated alumina, have the following hierarchy of competing ions [*USEPA*, 2000]:

$OH^- > H_2AsO^{4-} > Si(OH)_3O^- > F^- > HSeO_3^- > TOC > SO_4^{2-} > H_3AsO_3$

An ion hierarchy in relation to affinity for resin exchange of a Strong Base Anion (SBA) selectivity (ion exchange resin) causes ions higher in the hierarchy to flush out other ions from the resin. The hierarchy of competing ions in relation to arsenic and fluoride is [*MWH*, 2005; *USEPA*, 2000]:

$HCrO^{4-} > CrO_4^{2-} > ClO_4^- > SeO_4^{2-} > SO_4^{2-} > NO_3^- > Br^- > (HPO_4^{2-}, HAsO_4^{2-}, SeO_3^{2-}, CO_3^{2-}) > CN^- > NO_2^- > Cl^- > (H_2PO_4^-, H_2AsO_4^-, HCO_3^-) > OH^- > CH_3COO^- > F^- > (Si(OH)_4, H_3AsO_4)$

Chemical reactions:

Other problems that may occur include fouling of membranes. Potential fouling can be caused by scaling and by corrosive damage. Scaling occurs when certain ions react in the water and precipitate. These scales clog the membranes and decrease efficiency. SiO_2 and SO_4^{2-} are the main ions that might precipitate. High TDS may also decrease efficiency of different treatments. High chloride concentrations possess a different risk in membrane processes. The corrosive nature of chloride may damage the membranes. Therefore, it is important to decrease chloride concentrations before running the water through a reverse osmosis plant.

Table 4: List of critical concentrations of competing ions relative to impacts on different treatments.

Treatment	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	PO_4^{3-} (mg/L)	SiO_2 (mg/L)	Fe^{3+} (mg/L)	TDS (mg/L)	TOC (mg/L)	Turbidity (NTU)
AA	250		360		30	0.5	1000	4	0.3
IX		5	50				500		0.3
IBS			50	1	10				0.3
RO	300		100	5	20		1800		5

AA – activated alumina; IX – ion exchange; IBS – iron based sorbents; RO – reverse osmosis. The operation of reverse osmosis on water with substantial amounts of silica is only feasible if there is chemical pretreatment to prevent excessive fouling by this refractory deposit. Precipitation, coagulation, and flocculation should be used to remove silica (Table 4) [*Sheikholeslami and Bright*, 2002].

The operation of reverse osmosis on water with substantial amounts of silica is only feasible if there is chemical pretreatment to prevent excessive fouling by this refractory deposit. Precipitation, coagulation, and flocculation should be used to remove silica (Table 5) [*Sheikholeslami and Bright*, 2002].

Table 5. Silica removal pretreatments.

Method	**Chemicals**
Precipitation	Lime ($Ca(OH)_2$ and soda ash (Na_2CO_3)
Coagulation	Alum ($Al_2(SO_4)_3$, IBS ($FeCl_3$, $Fe_2(SO_4)_3$
Flocculation	Polyelectrolytes

The objective of this study was to assess water quality violations in Texas, primarily arsenic and related ions, including fluoride and radionuclides, using data from the EPA SDWIS database as a resource. Clean water is an essential prerequisite for healthy communities underscoring the need to understand spatiotemporal variability in the quality of water supplies.

2.0 Materials and Methods

Data on PWS drinking water quality violations were obtained from the SDWIS database [*SDWIS*, 2019]. The analysis focused primarily on inorganics, including arsenic, fluoride, and radionuclides; however, violations for these ions were considered in a broad context of all violations.

2.1 Data Analysis

This study focuses on health violations in the SDWIS database, excluding monitoring and reporting violations. Various types of data analyses were conducted, including the type of system, focusing primarily on community water systems, ownership (e.g. private, local government), and water source (surface water, groundwater). The spatial and temporal variations in violations were characterized, focusing in 1980 – mid 2019. The number of system violations may be underestimated because of monitoring and reporting violations. The populations served by noncompliant systems may be overestimated because SDWIS includes the total population served by a system but in some cases only one component of a distribution system may be affected.

3.0 Results

3.1 Description of Water Systems

The following analysis is based on data from SDWIS from 1980 through mid-2019. There is a total of ~6,800 active PWSs in Texas. Community water systems (4,600) account for 67% of the total number of PWSs (~6,800), with 72% of CWSs by number based on groundwater (~3,300) and 28% based on surface water (~1,300) (Figure 1a). The population served by groundwater and surface water systems is also inversely related to the number of systems, 19% served by groundwater (~5 million people) and ~80% served by surface water (~22 million people) (Figure 1b). In Texas, ~43% of CWSs had at least one violation during the study period (1980 – mid 2019), less than the 60% in the U.S. (Figure 2a). The percentage of systems with violations is higher for privately owned systems (49%) than for those owned by local government (33%). CWSs based on surface water have a higher percentage of violations (62%) than those based on groundwater (36%). The population exposed to violations totals 16 million, 14 million for surface water based CWSs relative to 2 million for groundwater based CWSs (Figure 2b). The corresponding population percentages range from 63% for surface water to 43% for groundwater.

3.2 Temporal Variability in Drinking Water Quality Violations

The following analysis focuses on health based violations for CWSs and excludes violations related to monitoring and reporting. In Texas the dominant violation in 2018 is related to inorganics (~480 violations), followed by radionuclides (~230), and DBPs (~160) (Figure 3a). Other violations are much lower, ranging from 20 – 32 (Total Coliform, SWR, and lead and copper rule). There were no GWR violations in 2018. The time series shows that inorganic violations were highest throughout most of the record, increasing to ~470 in 2005 and increasing sharply to 740 in 2006, reflecting the Arsenic Rule. Inorganics remain high for several years, decreasing gradually from 2012 to the current level of ~480 violations. Radionuclide violations are also high through much of the record, peaking in 2004 at ~390 and decreasing to ~230 currently. DBPs also show double peaks in 2005 (260) and 2015 (250). Total Coliform violations are generally low at ~100 until 2015 and declined sharply in response to Revised Total Coliform Rule. All other violations are low. Groundwater accounts for the majority of violations in inorganics (mean 88%), and radionuclides (mean 88%) (Figure 5a).

In Texas, inorganic violations had a large impact on populations, peaking at ~ 0.2 million in 2006 in response to the Arsenic Rule and declining to ~0.1 million people in 2018. The largest number of people are affected by total coliform, peaking in 1993 at 0.26 million with spikes in mid 2000s (~0.15 million people) and 2015 (0.2 million) followed by a sharp decline after this time in response to the Revised Total Coliform Rule (Figure 3b). DBP violations impact peak populations of 0.1 million people (2005) to 0.12 million people (2015). The Lead Copper Rule violations impacted 0.06 million people in 2015. Surface water is the primary source of DBP violations (mean 93%) and total coliform violations (mean 64%) whereas groundwater is the primary source of radionuclide (82%) and inorganic (60%) violations in terms of impacted population (Figs. 4b and 5b).

3.3 Spatial Variability in Drinking Water Quality Violations

Previous analysis of groundwater arsenic concentrations in Texas show that out of 10,489 groundwater wells in the state, 6,667 samples had arsenic concentrations less than the method detection limits (64% of samples) (Figure 6). Most of the non-detect samples (6,026, 57% of all samples) have a detection limit of 2 µg/L. The remaining 3,823 samples had arsenic concentrations above the method detection limits (36% of samples) (Figure 6). The median concentration of these samples is 4.3 µg/L. Approximately 19% of samples with detected concentrations exceeded the arsenic MCL (733 samples) and 7% of all arsenic data exceeded the MCL. The PWSs that are noncompliant relative to arsenic are mapped on top of the arsenic concentration map. Based on the EPA database, a total of 99,190 people are served by 78 PWS systems that have been non-compliant with respect to drinking water arsenic concentrations in at least one of the last 10 quarters (Jan 2016 – mid-2019) representing 0.35% of the 2018 total population (Figure 6). Most (99.7%, 98,923 people) are associated with PWS systems that source their water from one of the major aquifers while the remaining (0.3%, 267 people) are associated with minor aquifer PWS systems. These noncompliant PWSs are generally collocated with hotspots of groundwater arsenic contamination, primarily in the southern High Plains, southern Gulf Coast, and in the Waco metropolitan area.

Spatial variability in health based violations focus on U.S. maps of impacted populations related to inorganic and radionuclide system violations (Figs 7 – 16). The maps of populations impacted by arsenic violations peaked in 2006 – 2008, showing widespread impacts in parts of Texas, California, Arizona, northeastern U.S. and in glacial aquifers surrounding the Great Lakes (Figure 7). The largest changes between 2006 – 2008 and 2009 – 2011 are reductions in impacted populations in the region around the Great Lakes and northeastern U.S. (Figures. 7 and 8). The 2012 – 2014 maps show continued declines in these regions; however, impacted populations remain high in parts of Texas, California, Arizona, and Oklahoma (Figure 9). The 2016 – mid 2019 arsenic map shows similar distributions in many regions with further reductions in the northeast, Arkansas, and Arizona (Figure 10).

Maps of populations impacted by fluoride violations show the largest impact in the High Plains of Texas and middle regions of Oklahoma with isolated regions along the East Coast based on 2000 – 2002 data (Figure 11). The 2016 – mid 2019 map shows that the systems along the east coast have been resolved but concentrations remain high in the Texas High Plains and also some isolated regions in S California and Arizona (Figure 12). Populations impacted by combined radium are high in the Great Lakes region and moderate along the East Coast with lower levels throughout the central region, including Texas and surrounding states (Figure 13). Populations affected by uranium are located primarily in the southwest, ranging from California to Texas with isolated regions in the east (Figure 14). Populations affected by gross alpha are highest in Texas and also in the northeast (Figure 15). The distribution of populations impacted by inorganics and radionuclides likely reflect geologic controls on these contaminants.

3.4 Limitations for Treating Groundwater for Arsenic and Related Contaminants

Using the TWDB database (1992 – 2019), maps were created to show the spatial distribution of competing ions and potential threats to treatment facilities in Texas and the main aquifers (Figures 16 – 20). Silica is a problem in most aquifers (Figure 16). High to very high silica concentrations would interfere with some of the potential treatments. Levels of pH are not a problem for treatment in most aquifers (Figure 17). TDS values are variable and could cause issues with some treatments (Figure 18).

Silica (SiO_2) concentrations above 20 mg/L are prevalent and wide spread in the Ogallala, Pecos Valley Alluvium, West Texas Bolson, Igneous, and Gulf Coast aquifers and less prevalent in the Carrizo-Wilcox aquifer (Figure 16). Concentrations range from <1 to 256 mg/L. Concentrations above 100 mg/L are found exclusively in the Ogallala and Gulf Coast aquifers.

Total dissolved solids (TDS) concentrations range widely between 16 to 55,000 mg/L with highest concentrations found in the southern Ogallala, Pecos Valley Alluvium, southern Gulf Coast, Blaine, Lipan and Trinity aquifers (Figure 18). Chloride (Cl) concentrations also range widely from <1 to 30,000 mg/L (Figure 19). Elevated chloride concentrations tend to follow those of TDS in the more arid regions of West Texas and the Southern Gulf Coast where chloride tends to be the dominant anion present. Sulfate (SO_4) concentrations range from <1 to 6,900 mg/L with highest concentrations found primarily in high TDS regions of the Ogallala, Pecos Valley Alluvium, the southern Gulf Coast and Trinity aquifers, and in the Blain, Dockum, and Lipan aquifers (Figure 20).

4.0 Summary

Evaluating the reliability of water provided by public water systems for communities is an important issue with human health implications. This study updated an analysis of groundwater arsenic contamination in Texas that was completed in 2018 by focusing on arsenic levels and related inorganic contaminants in Public Water Systems (PWSs) throughout the State and comparing health based violations in PWSs in Texas with those in other states. Treatment options were also considered for inorganic contaminants.

A total of 6,800 active public water systems are found in Texas. Community water systems (CWSs) account for 67% of the total number of PWSs in Texas. The primary water source for these PWS systems is groundwater (72%). However, the population served by PWSs is dominated by surface water sources (80% of PWSs).

Health based violations were widespread in PWSs in Texas, with ~43% of Community Water Systems (CWSs) having at least one health-based violation of the EPA Safe Drinking Water Act (SDWA) rules during the study period (1980 – 2018). Privately owned systems had a larger percentage of violations (49%) than those owned by local governments (33%). Community water systems based on surface water sources have a higher percentage of health based violations (62%) than those based on groundwater sources (36%). The population exposed to violations totaled 16 million, 14 million for surface water based CWSs relative to 2 million for groundwater based CWSs. The corresponding impacted population percentages range from 63% for surface water to 43% for groundwater. Health based violations in 2018 were dominated by those related to inorganics (~480 violations), followed by radionuclides (~230), and disinfection byproducts (~160). Inorganic violations were highest throughout most of the period of record, increasing to 740 in 2006 in response to implementation of the Arsenic Rule (2006). Radionuclide violations were also high through much of the record. Inorganic and radionuclide violations are found primarily in groundwater PWSs (mean 88% for both inorganics and radionuclides).

Populations impacted by PWS health based violations in Texas were compared with those in other states throughout the U.S. for arsenic and related inorganics and radionuclides violations. Populations affected by arsenic violations peaked in 2006 – 2008 in response to implementation of the Arsenic Rule, with large impacts in Texas, California, Arizona, Oklahoma, northeastern U.S., and the region surrounding the Great Lakes. Over time the populations affected by arsenic were reduced, particularly in the Northeast, Arkansas, and Arizona. Populations affected by fluoride violations were highest in the High Plains of Texas and central regions of Oklahoma based on 2000 – 2002 data. The 2016 – mid 2019 map shows that fluoride concentrations remain high in the Texas High Plains and also some isolated regions in S California and Arizona. The distribution of populations affected by inorganics and radionuclides likely reflect geologic controls.

Various approaches for bringing PWSs into compliance with EPA regulations were considered. (1) Non-treatment Options and treatment options were considered. Water treatment was examined for arsenic and fluoride violations. Several Best Available Techniques for treating non-compliant water were considered, primarily RO – Reverse osmosis; ED – Electrodialysis; AA – Activated alumina; IX – Ion exchange; and IBS – Iron based sorbents for inorganic contaminants. Limitations of treatment were also considered, particularly water chemistry effects and competing ions. Chemical reactions can degrade membranes through scaling and corrosiveness. Competing ions, such as silica, are moderately high in many regions in Texas and can reduce the ability to sorb inorganic contaminants.

5.0 Figures

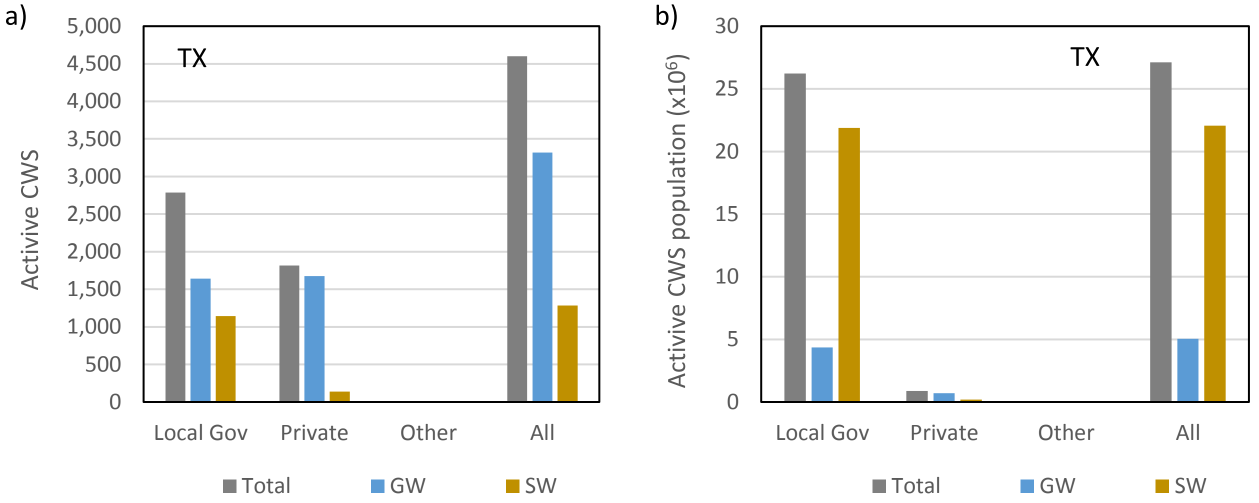

Figure 1. Active Community Water Systems (CWSs) shown by ownership category and by primary water source type (GW: groundwater, SW: surface water) in the SDWIS database for a) Texas and b) the populations served by those systems in Texas. The “Other” ownership category includes the sum of federal government, state government, public/private partnerships, Native American, and unknown ownerships.

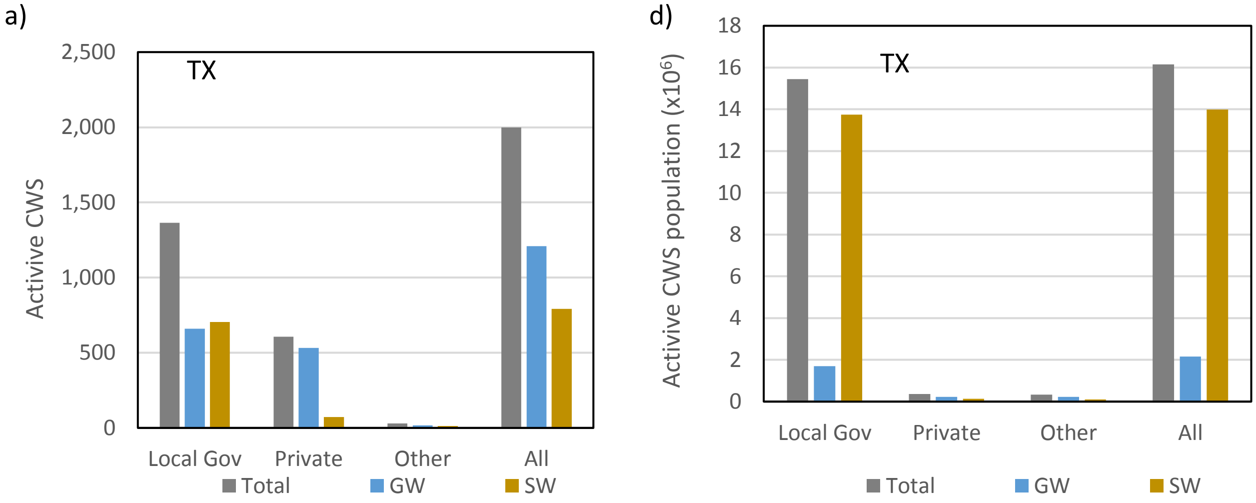

Figure 2. Active Community Water Supply (CWS) systems that have health-based violations. Values are shown by ownership category and by primary water source type (GW: groundwater, SW: surface water) in the SDWIS database for a) Texas and the populations served by those systems in b) Texas. The “Other” ownership category includes the sum of federal government, state government, public/private partnerships, Native American, and unknown ownerships.

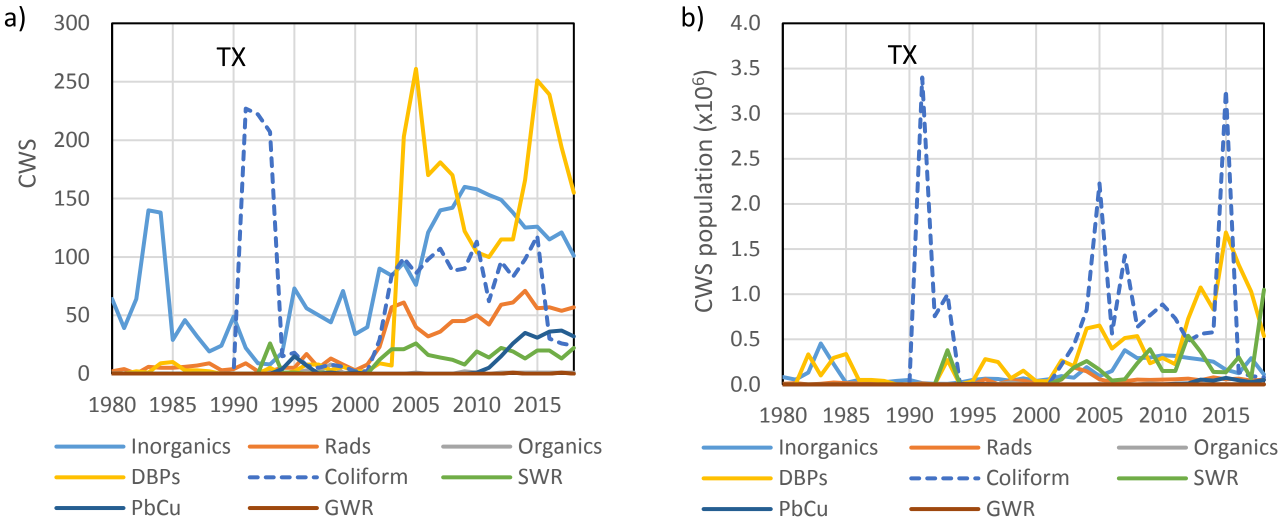

Figure 3. Time series of numbers of active Community Water Supply (CWS) systems with health-based violations. Values are shown by a) contaminant type/rule category and b) time series of the total populations served by those active CWS systems. Inorganics considered include arsenic, fluoride, and nitrate-N. Radionuclides include combined radium 226 and 228, alpha radiation, and uranium. Organics include volatile and synthetic organics. DPBs: disinfection byproducts; total coliform and revised total coliform; SWR: surface water rule; PbCu: lead copper rule; and GWR, groundwater rule.

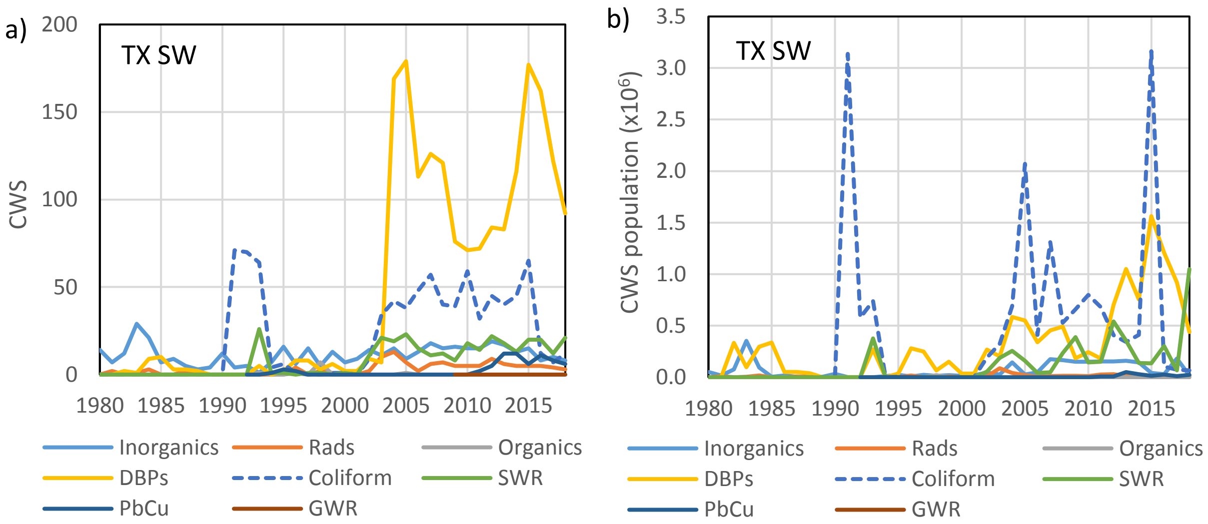

Figure 4. Time series of numbers of active Community Water Supply (CWS) systems with health-based violations that use surface water (SW) as their primary source. Values are shown by contaminant type/rule category for the a) Texas and time series of the total populations served by those active CWS systems for b) Texas.

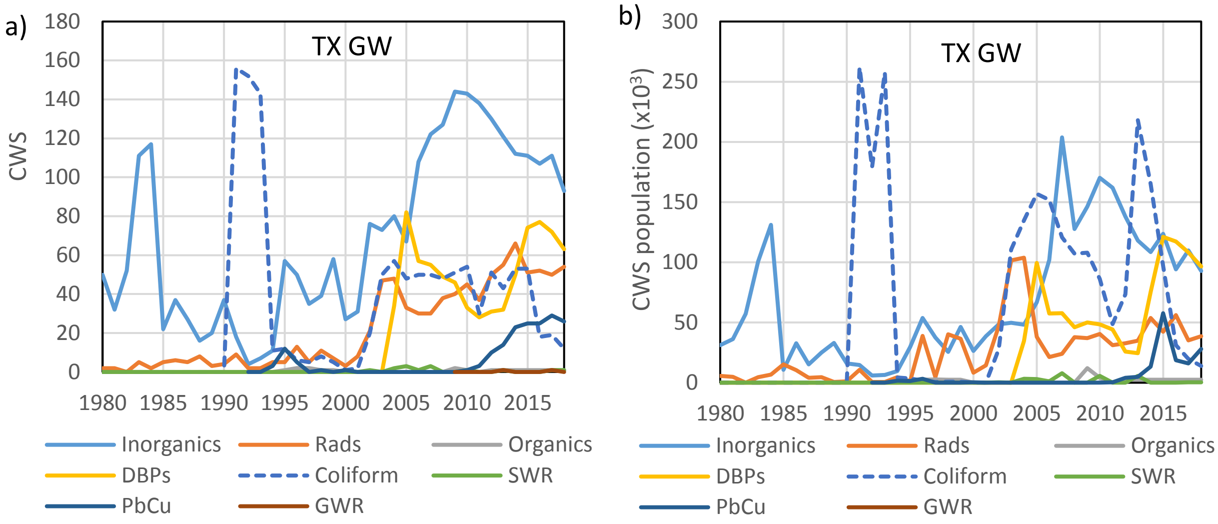

Figure 5. Time series of numbers of active Community Water Supply (CWS) systems with health-based violations that use groundwater (GW) as their primary source. Values are shown by contaminant type/rule category for a) Texas and time series of the total populations served by those active CWS systems for b) Texas.

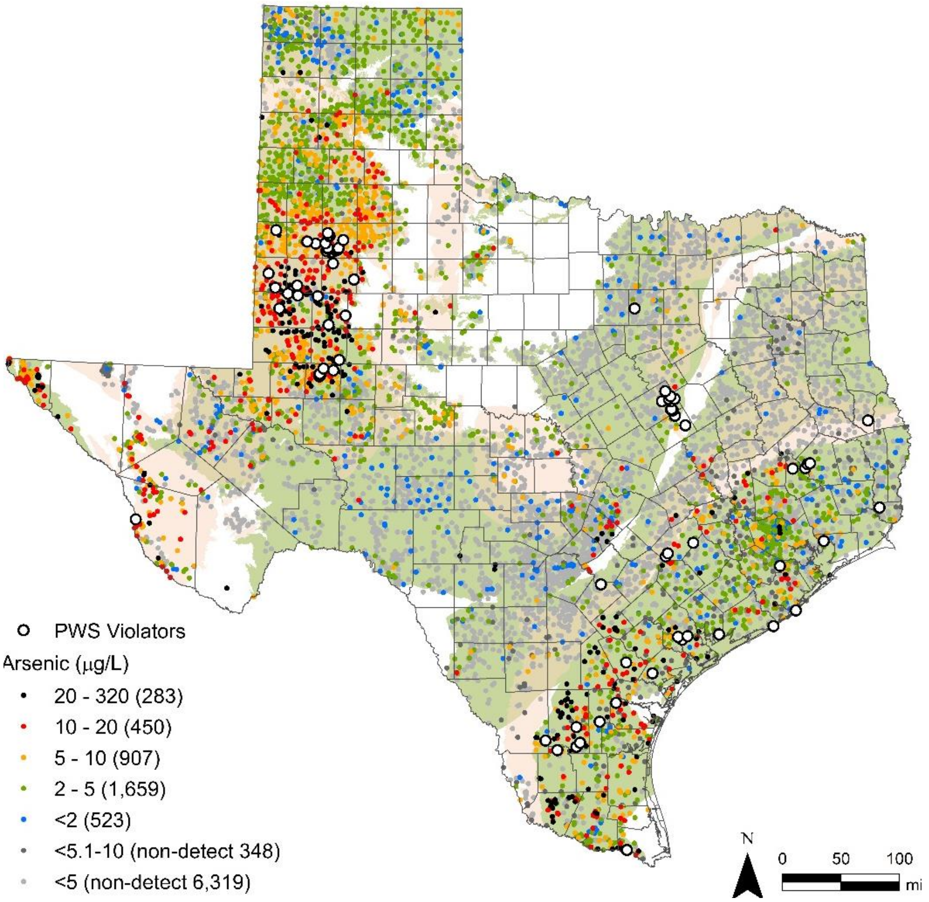

Figure 6. Spatial distribution of groundwater arsenic concentrations in Texas groundwater, including samples collected from 1992 – 2017 with detected concentrations (<2 – 320 µg/L) and non-detected concentrations (<5 and <10 µg/L). This map is based on groundwater arsenic concentrations from all sampled wells in Texas based on the Texas Water Development Board database. The numbers of samples within the stated concentration ranges are shown in parenthesis and include some samples that are not in a named major or minor aquifer and not used in this study. Overlain on the groundwater arsenic concentrations are the locations of 78 PWS systems that have health-related non-compliance violations for arsenic concentration in distributed water based on the EPA database. The violating systems are located primarily in the southern High Plains, the Gulf Coast, and the Waco metropolitan area.

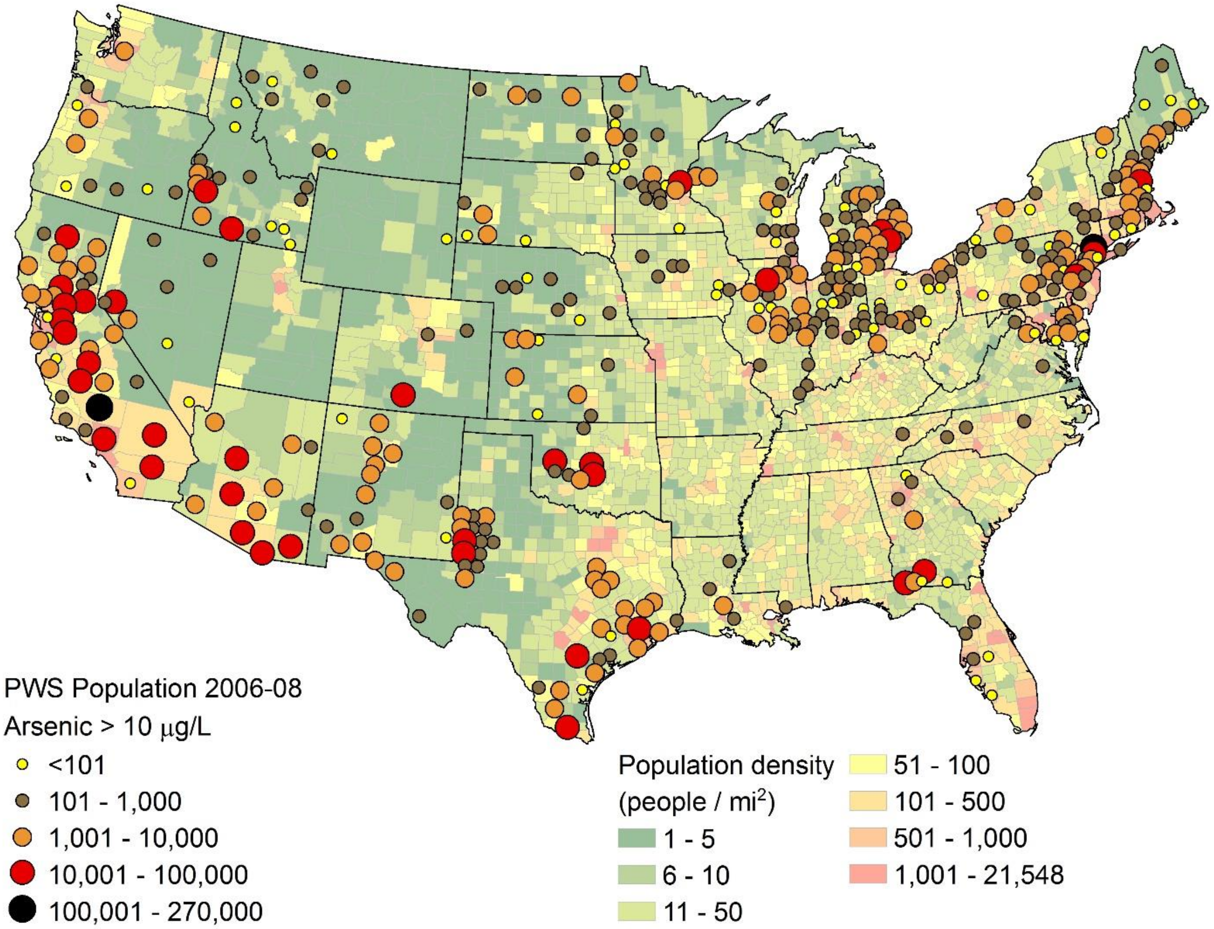

Figure 7. Spatial distribution of arsenic violations based on data from CWSs in 2006 – 2008, immediately after the Arsenic Rule. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

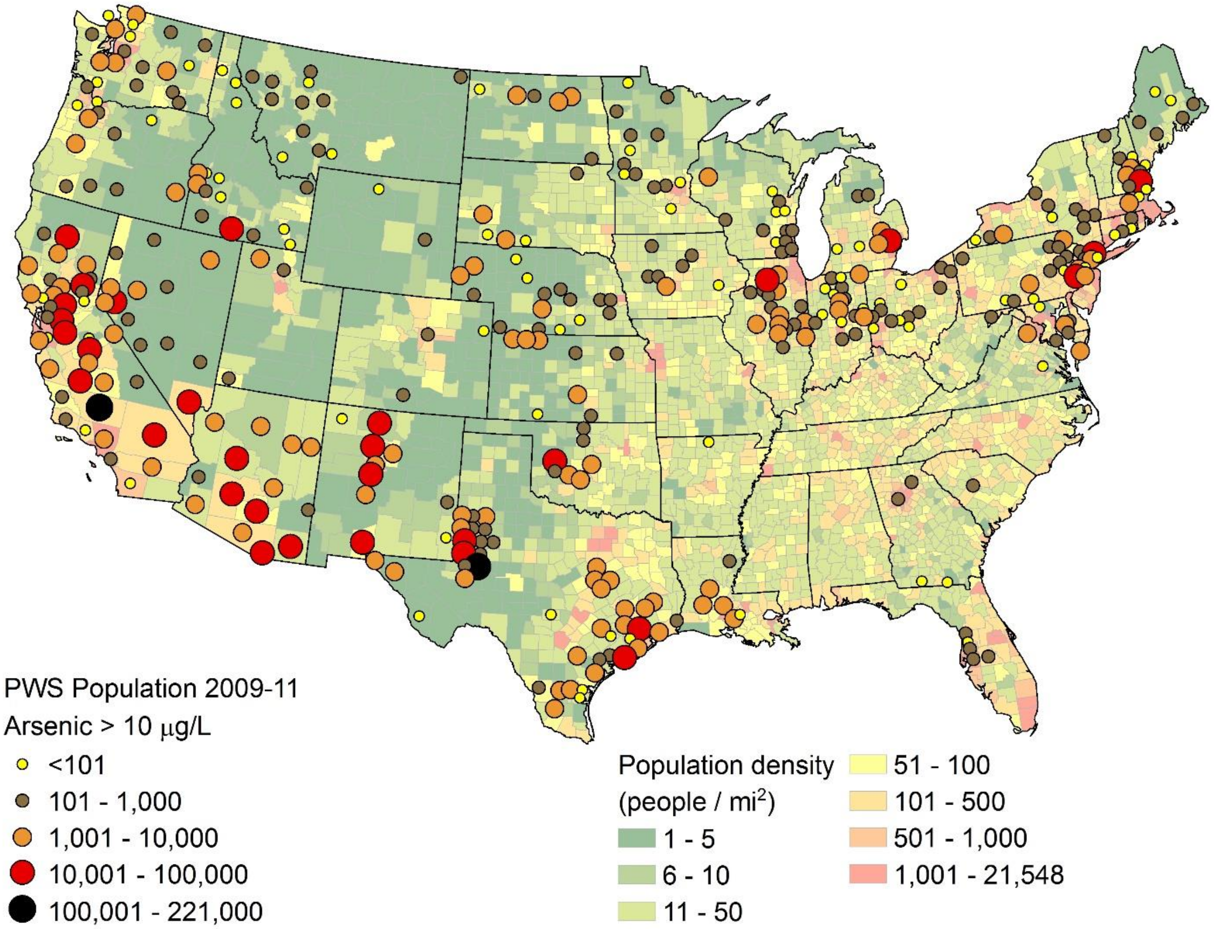

Figure 8. Spatial distribution of arsenic violations based on data from CWSs in 2009 – 2011. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

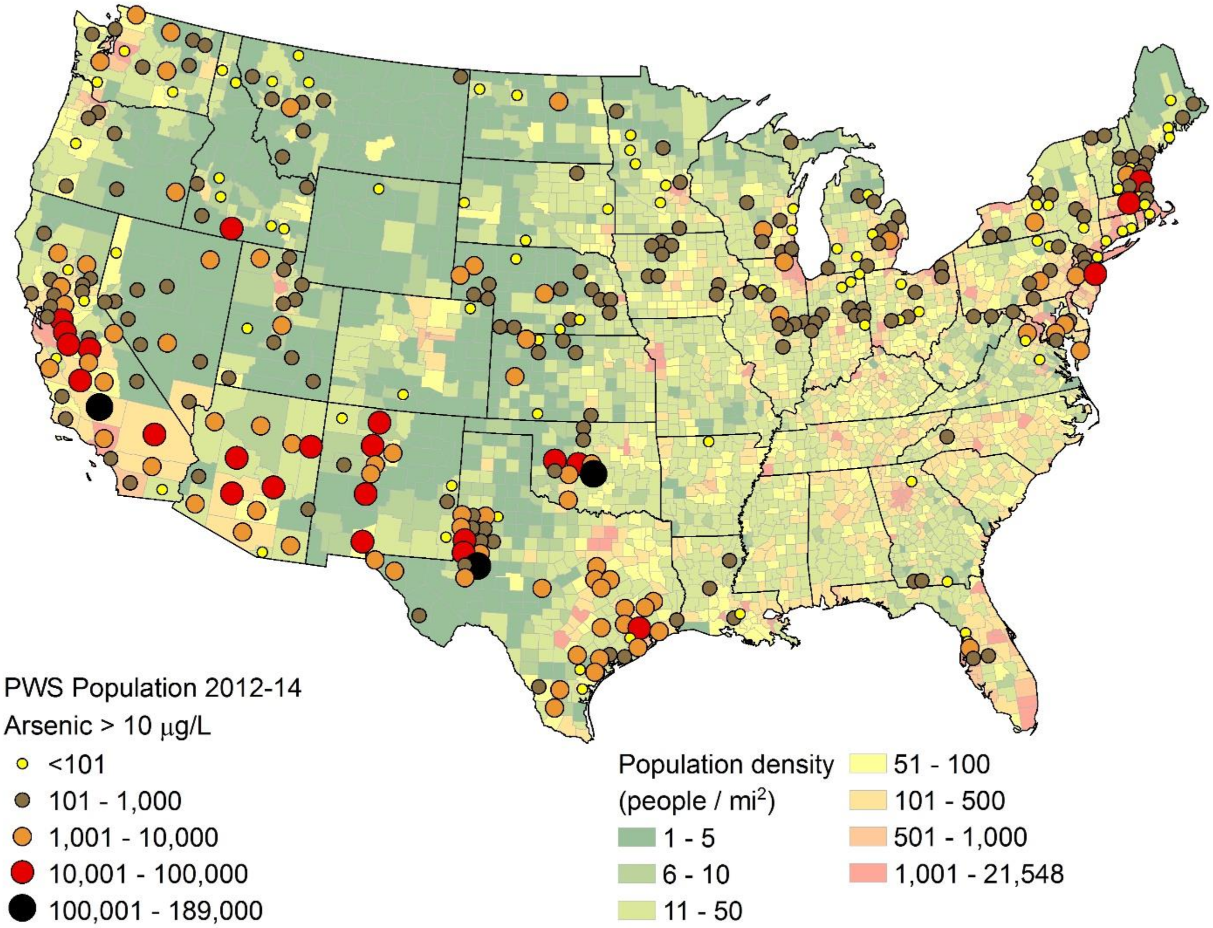

Figure 9. Spatial distribution of arsenic violations based on data from CWSs in 2012 – 2014. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

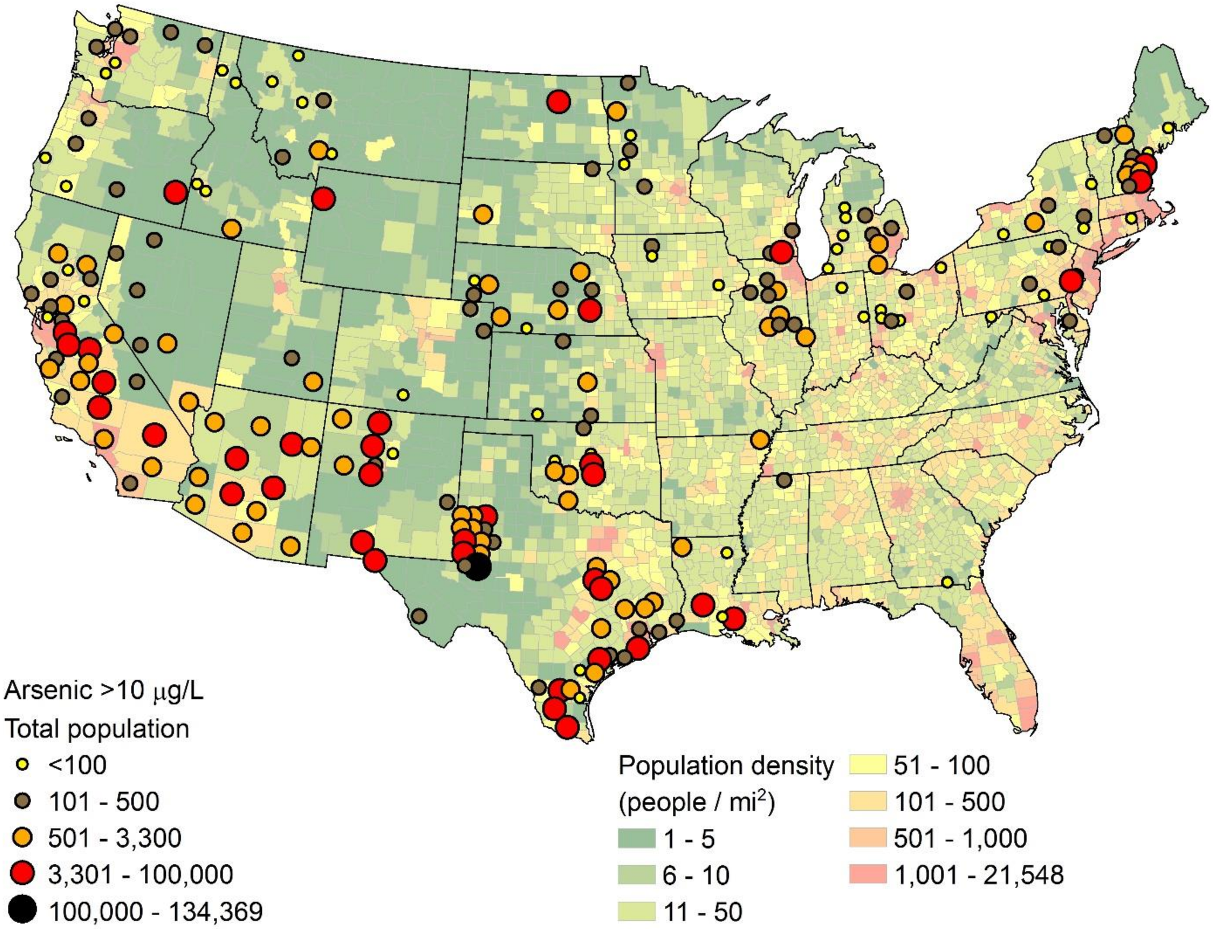

Figure 10. Spatial distribution of arsenic violations based on data from CWSs in 2016 – mid-2019. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

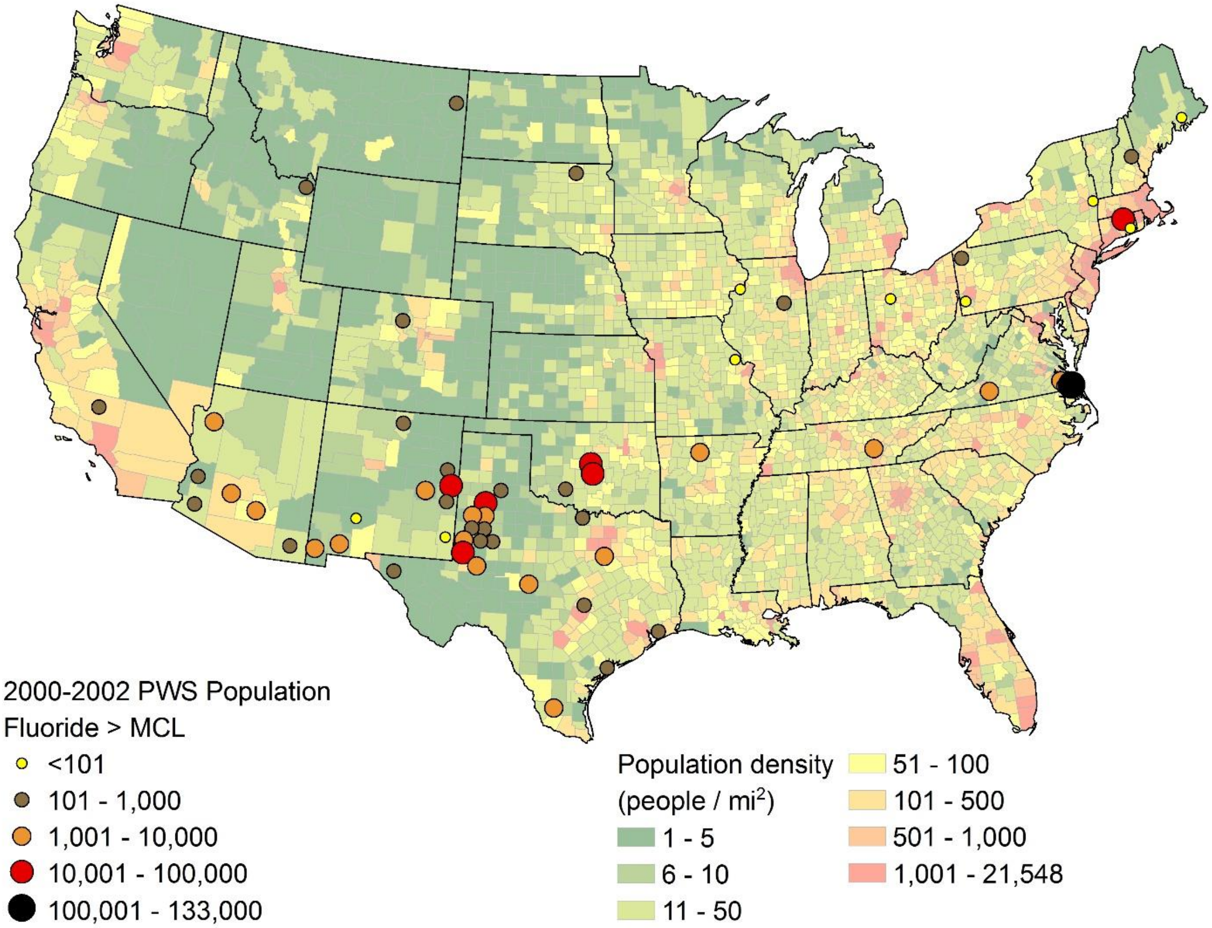

Figure 11. Spatial distribution of fluoride violations based on data from CWSs in 2000 – 2002, immediately after the arsenic rule. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

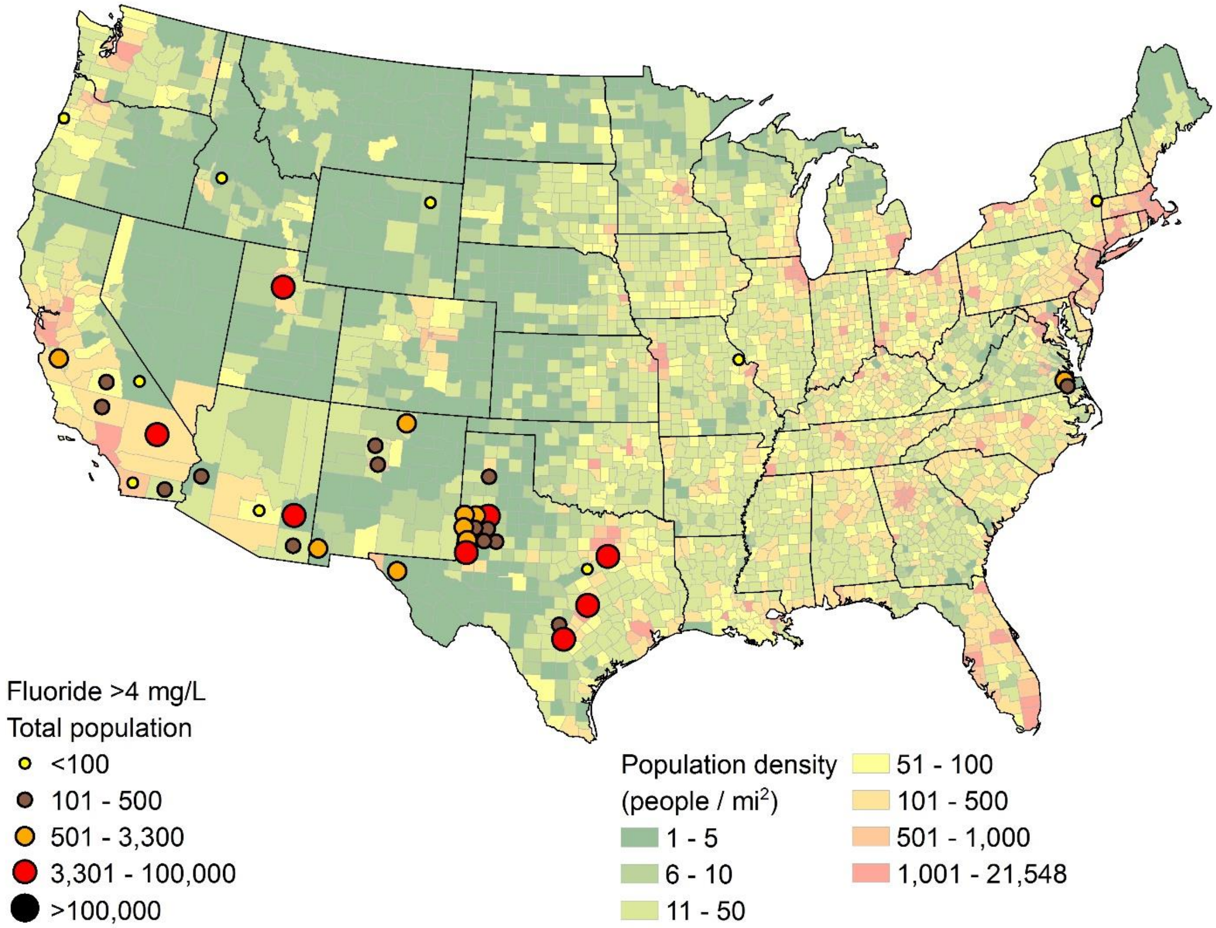

Figure 12. Spatial distribution of fluoride violations based on data from CWSs in 2016 – mid 2019. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

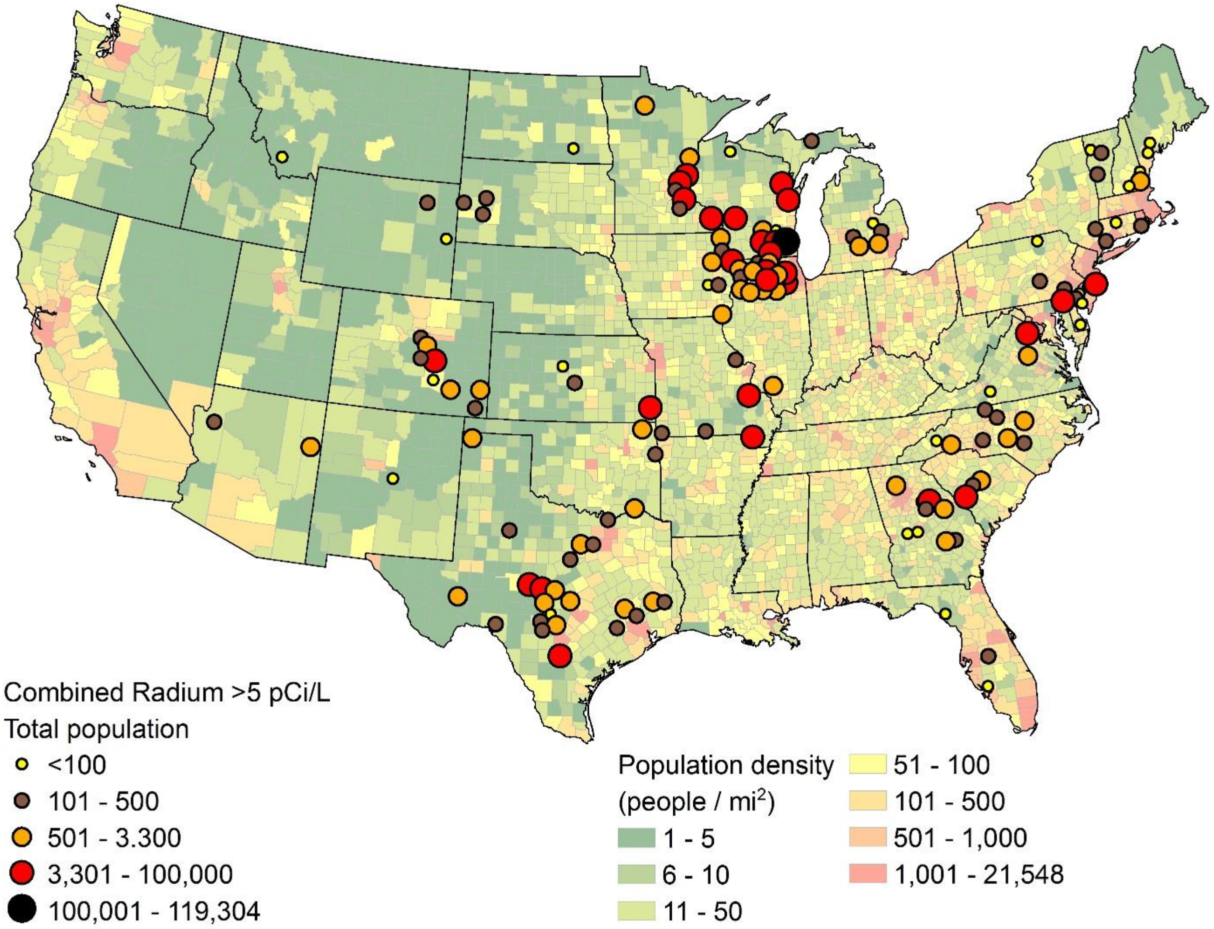

Figure 13. Spatial distribution of combined radium violations based on data from CWSs in 2016 – mid 2019. The populations impacted by the radium violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

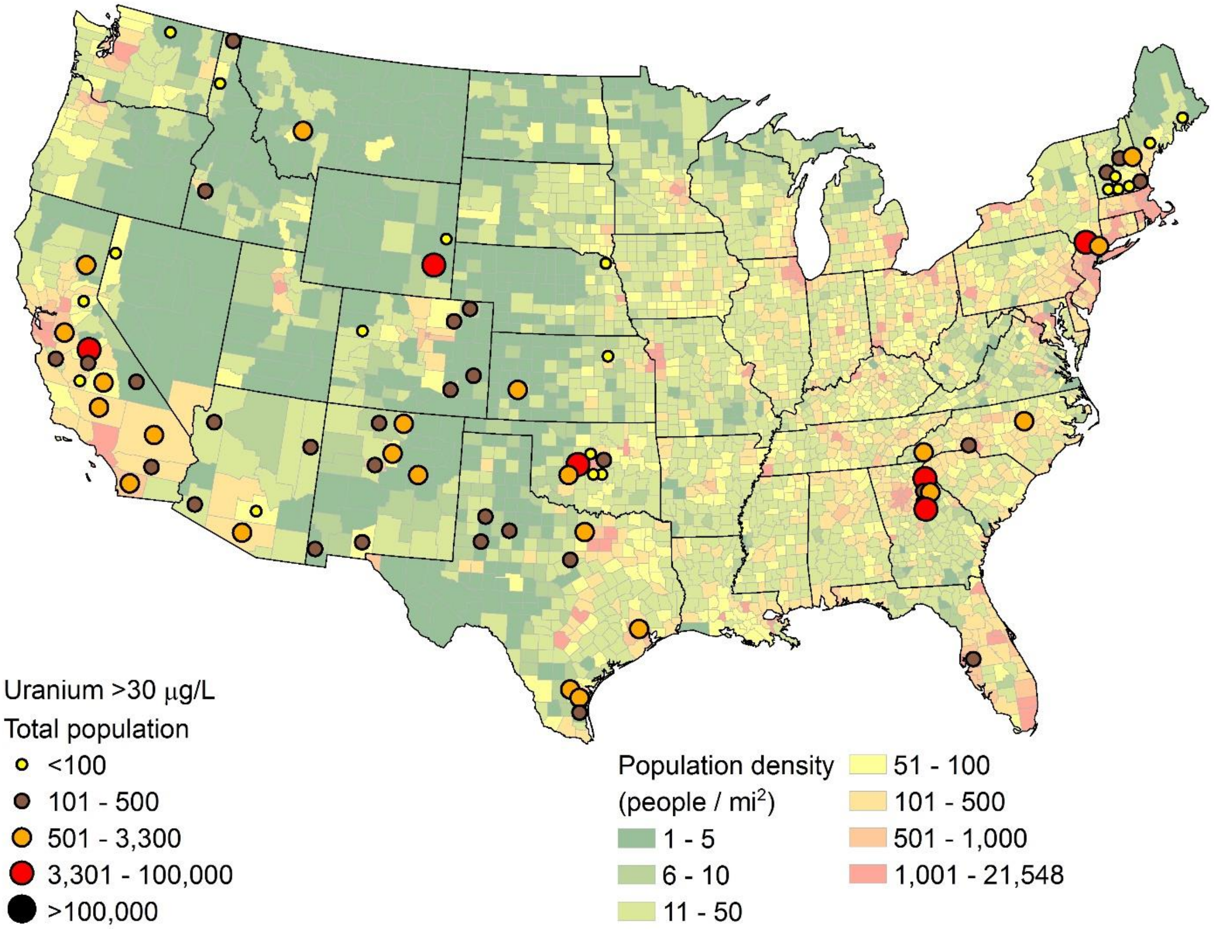

Figure 14. Spatial distribution of uranium violations based on data from CWSs in 2016 – mid 2019. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

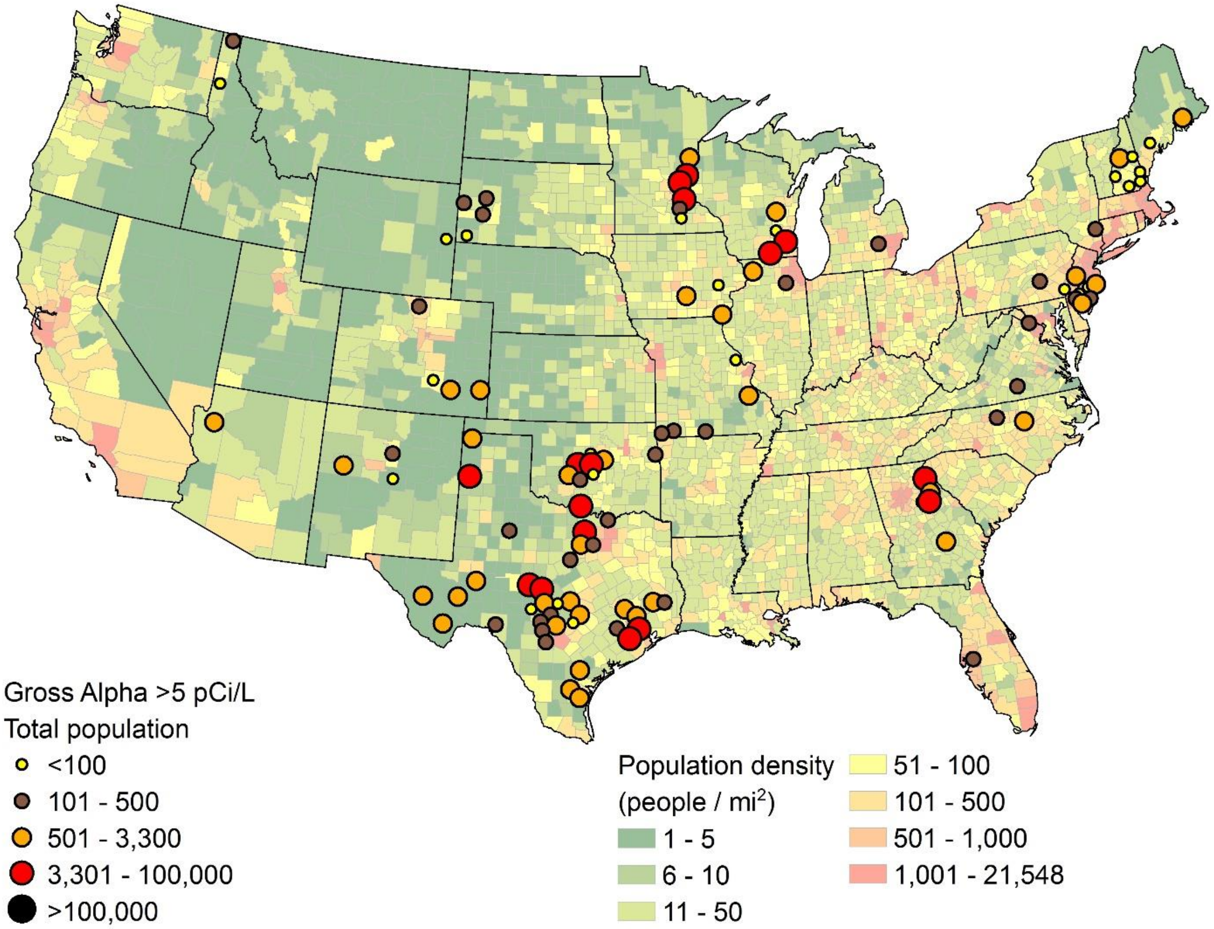

Figure 15. Spatial distribution of gross alpha violations based on data from CWSs in 2016 – mid 2019. The populations impacted by the arsenic violations are shown, with the centroid of each point representing the impacted county. The background map reflects the population density in no. of people/ square mile.

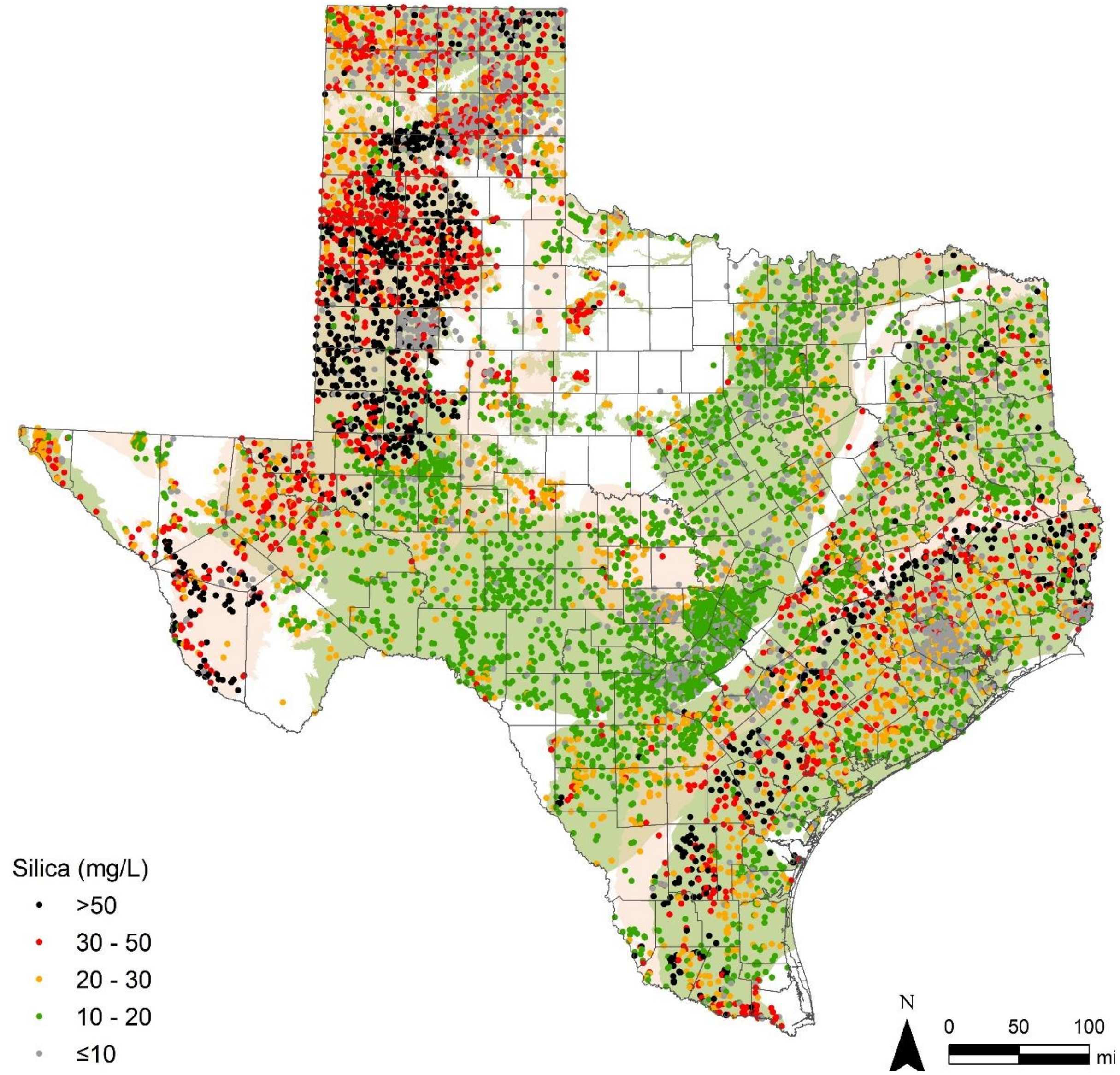

Figure 16. Distribution of silica concentrations as SiO_2 based on data from 1992 – 2019 from the Texas Water Development Board data.

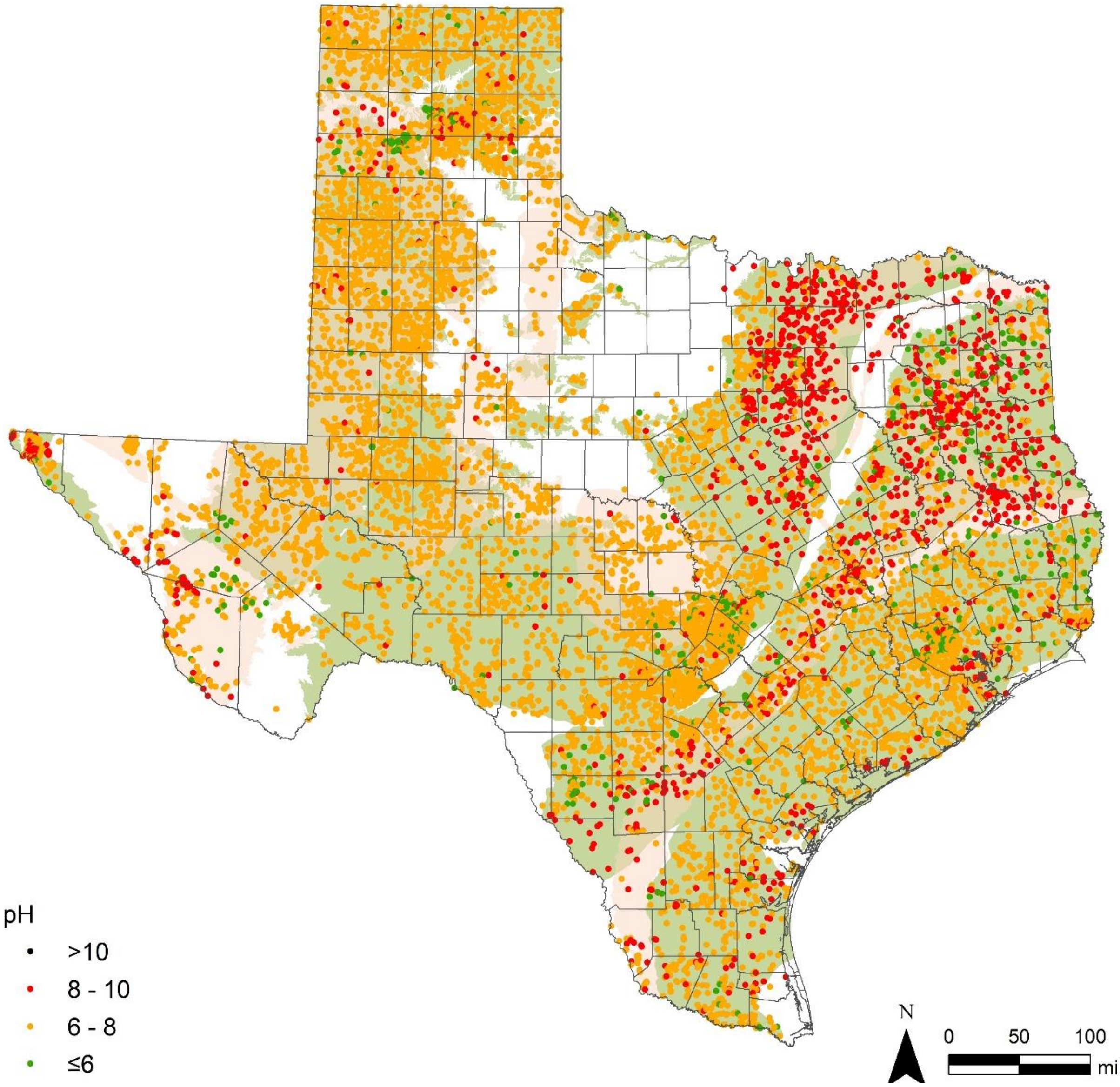

Figure 17. Distribution of pH based on data from 1992 – 2019 from the Texas Water Development Board data.

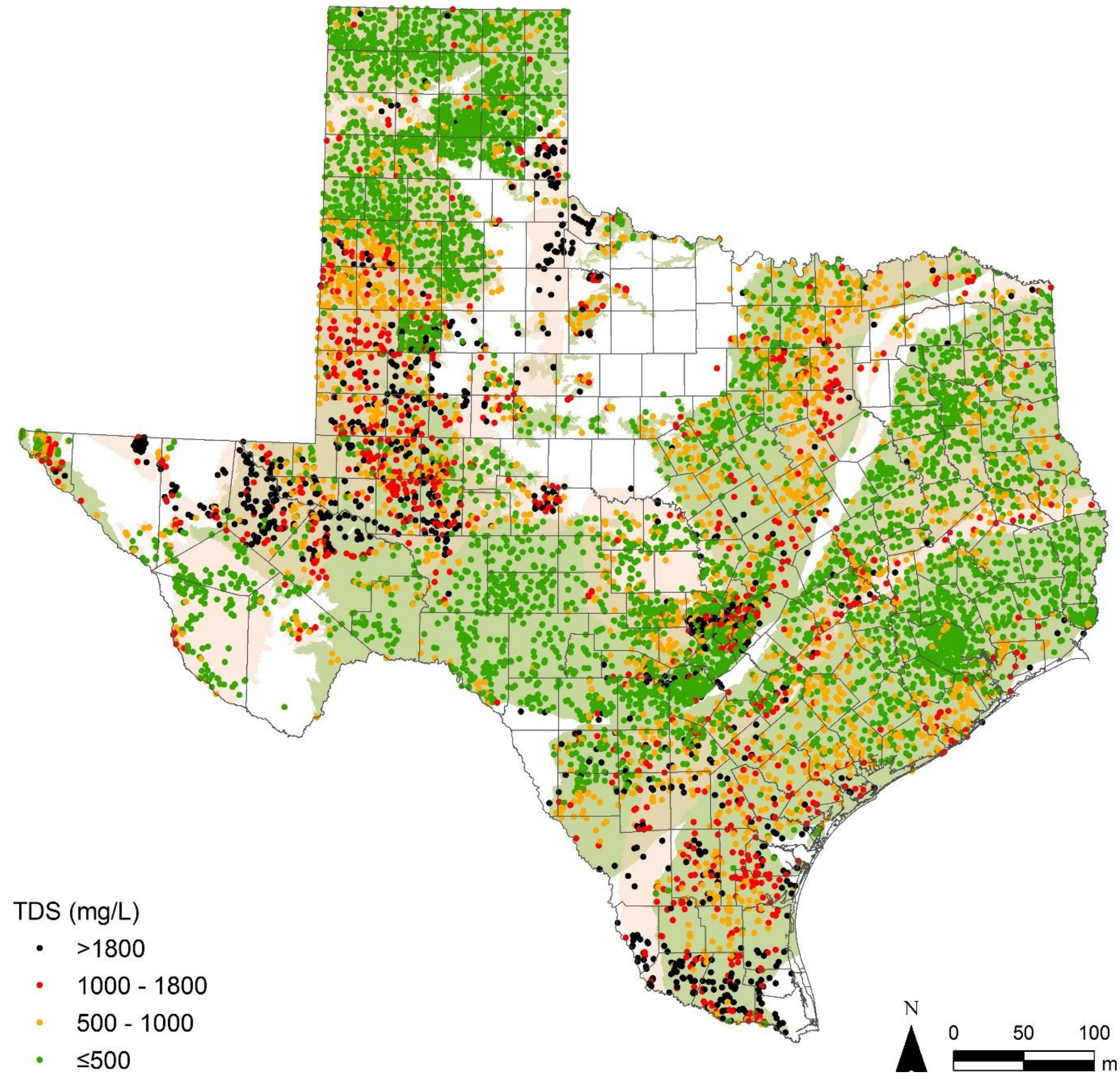

Figure 18. Distribution of Total Dissolved Solids (TDS) based on data from 1992 – 2019 from the Texas Water Development Board data.

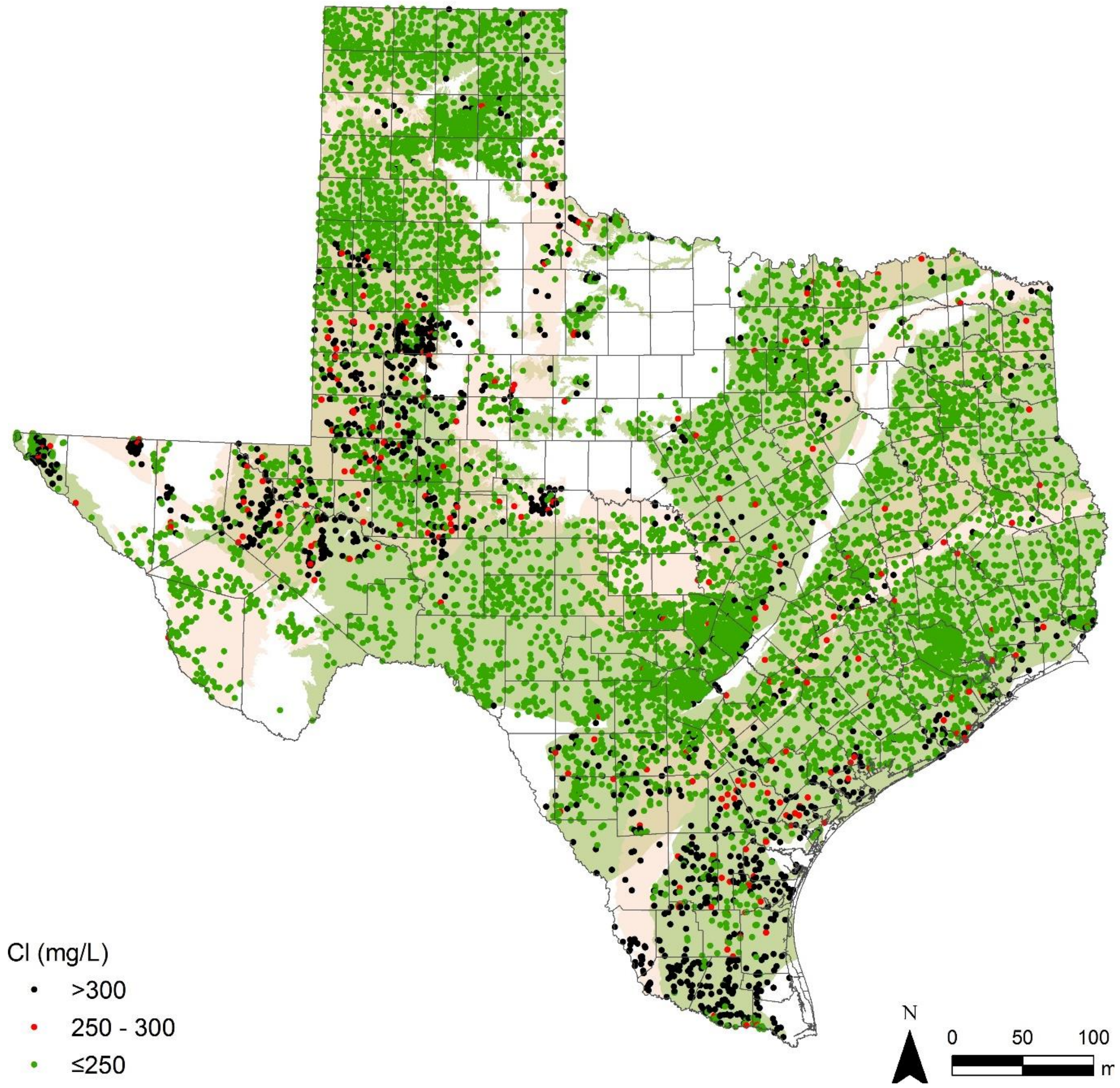

Figure 19. Distribution of Chloride (Cl) concentrations in groundwater based on data from 1992 – 2018 from the Texas Water Development Board data.

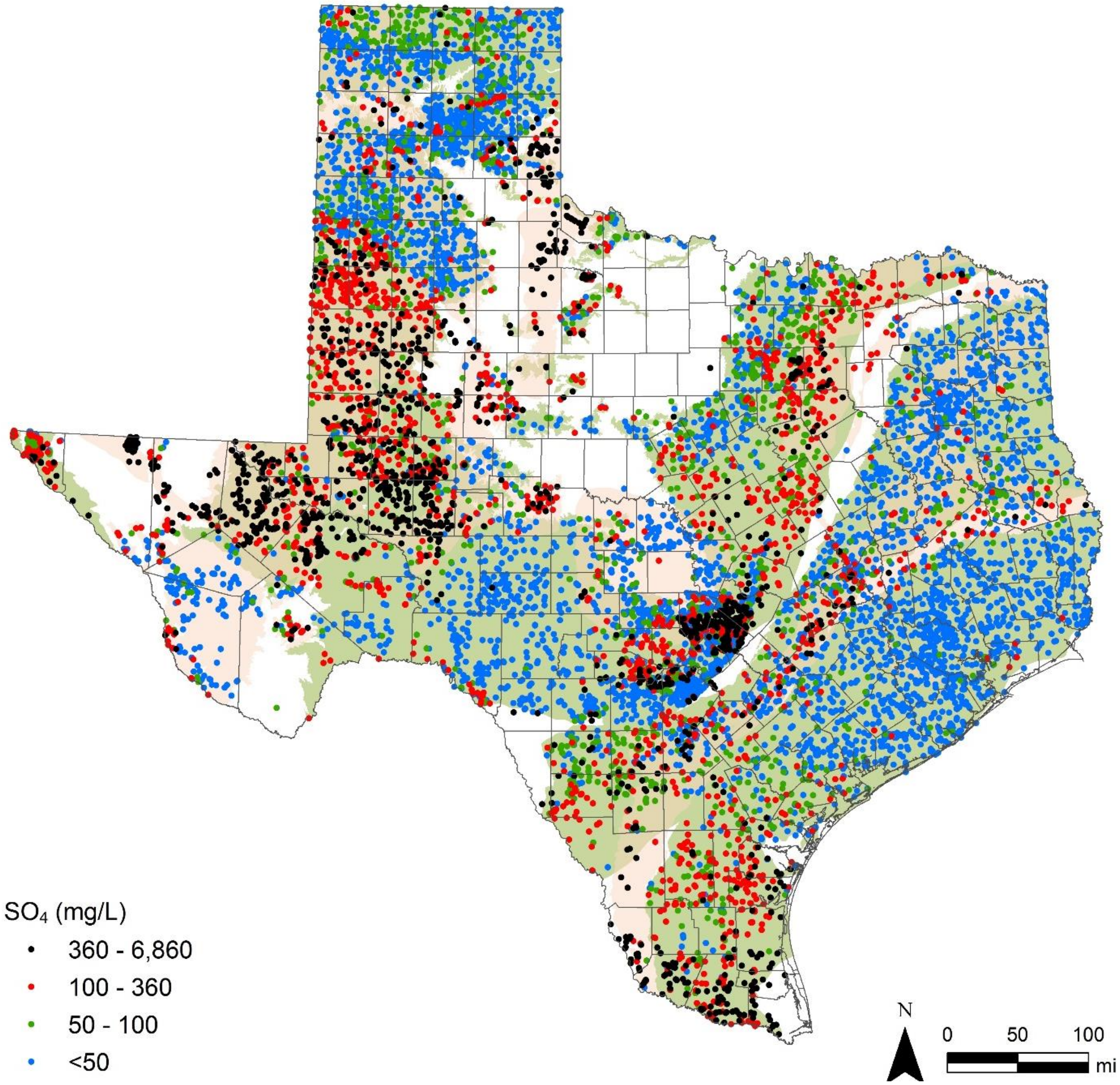

Figure 20. Distribution of Sulfate (SO_4) concentrations in groundwater based on data from 1992 – 2018 from the Texas Water Development Board data.

Appendix A – Treatment Techniques

Membrane Processes

Membrane processes involve separating contaminants from water by passing water through a semi-permeable barrier or membrane. The driving force for separation is the pressure difference. Removal efficiency depends on membrane pore size and particle size of the contaminant. Four types of pressure membranes include: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis [*Shih*, 2005; *Van der Bruggen et al.*, 2003]. Groundwater contamination generally consists of dissolved matter; therefore, only reverse osmosis will be discussed further.

Table 6: Overview of pressure-driven membrane processes and their characteristics

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Pressure (bar)	0.1 - 2.0	0.1 - 5.0	3.0 - 20	5.0 - 120
Pore size (nm)	100 - 1000	2 - 100	0.5 - 2.0	< 0.5
Rejection				
Monovalent ions	−	−	−	+
Multivalent ions	−	−	+	+
Small organic compounds	−	−	+	+
Macromolecules	−	+	+	+
Particles	+	+	+	+
Separation mechanism				
	Sieving	Sieving	Sieving charge effect	Diffusion

Reverse Osmosis (RO)

Reverse osmosis uses a pressure-driven membrane separation process to remove dissolved solutes from water by means of particle size, dielectric characteristics, and hydrophilicity/hydrophobicity. Reverse osmosis is an effective process for removing constituents from water, including organic carbon, salts, dissolved minerals, and color. RO is also relatively insensitive to pH. In the RO process, water is forced through a membrane using a high-pressure force (100-150 psi) and the treated water is collected on the other side of the membrane. Contaminants and rejected water (up to 70% of influent water) cannot pass through the filter. Membranes used in RO can remove salts and low molecular weight organic molecules. Fouling in RO may be caused by adsorption of organic material on the surface of the membrane and/or pore blocking, and by scaling due to precipitation of $CaC0_3$ or $CaS0_4$. Biofouling may occur if pretreatment is insufficient. One possible solution is to dose with chlorine before the membrane step. Most membranes are sensitive to high chlorine concentrations; therefore, a chlorine scavenger ($NaHS0_3$) should be used [*Van der Bruggen et al.*, 2003].

Adsorption Media

The chemical process of adsorption involves removal of contaminants by passing untreated water though adsorptive granular media in a pressure vessel. As the water passes through the media, negatively charged ions are adsorbed onto the surfaces of the positively charged media particles. Many different types of adsorption media available, including: activated alumina (AA), and iron, titanium, and zirconiam-based sorbents. The most common media include AA and iron based sorbents (IBS). There are several advantages to using adsorptive media for treatment in systems installing treatment for the first time, including (1) low-cost and simplicity of operation; (2) minimal operator attention (part time) required during treatment runs; and (3) options for manual or automated operation. The recommended empty bed contact time (EBCT) for adsorptive media systems ranges from 3 to 10 minutes (median ~ 5 min). Bed depth is mostly 3 to 6 ft, depending on vessel size, allowing space for bed expansion of 15 to 50% during backwash. Most adsorptive media systems require backwash to remove particulates and redistribute the bed material. For all adsorption media, liquid residuals from the filter backwashing step contain different concentrations of contaminants. Spent media need to be disposed of as either a solid or hazardous waste.

Ion Exchange (IX)

Ion exchange is a physical-chemical process in which ions (anions, cations, or both) are swapped between a solution phase and solid resin phase. The solid resin is typically an elastic three-dimensional hydrocarbon network containing a large number of ionizable groups electrostatically bound to the resin. These groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity (i.e. selectivity) for the resin. The hierarchy of water constituents according to strong-base anion (SBA) selectivity is [*MWH*, 2005]:

$SO_4^{2-} > NO_3^- > HAsO_4^{2-} > NO_2^- > Cl- > H_2AsO_4^- > HCO_3^- >> Si(OH)_4 > H_3AsO_4$

High levels of total dissolved solids (TDS) can adversely affect ion exchange system performance. Ion exchange is generally not an economically viable treatment technology if source water contains more than 500 mg/L of TDS or over 50 mg/L of sulfate ($SO_4{}^{2-}$). Hydraulic considerations associated with ion exchange include empty bed contact time (EBCT) and head-loss. The recommended EBCT ranges from 1.5 to 3 min. Presence of suspended solids in feed water can gradually plug the media; thereby increasing head-loss and necessitating more frequent backwashing. Therefore, pre-filtration is recommended if the source water turbidity exceeds 0.3 NTU. The resin needs to be regenerated periodically. Resin regeneration can be conducted on-site using the following steps: (1) backwash; (2) regeneration with brine; (3) slow water rinse, and (4) fast water rinse. Ion exchange produces liquid residuals consisting of backwash water, brine solution, and rinse water. The spent regenerant may contain high levels of arsenic and may need to be treated before disposal. In accordance with the Resource Conservation and Recovery Act (RCRA), systems are required to determine whether the waste is hazardous using knowledge of the waste generation process, analytical testing, or a combination of both. One analytical method, the Toxicity Characteristic Leaching Procedure (TCLP) (EPA Method 1311), is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. The TCLP predicts if hazardous components of a waste are likely to leach out and become a threat to public health or the environment.

Electrodialysis (ED) and Electrodialysis Reversal (EDR)

Electrodialysis involves the use of an applied electric potential difference to transport ions from one solution through ion-exchange membranes to another solution within a configuration called an ED cell. The cell consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. Multiple ED cells are generally arranged into an ED stack, with alternating anion and cation exchange membranes forming the multiple ED cells. The EDR process is similar to the ED process, but using periodic reversal of polarity, to prevent membrane scaling and fouling by removing ions that attach to membranes at the time of polarity change. Electrodialysis processes are unique compared with distillation techniques and other membrane based processes (such as RO) in that dissolved species are moved away from the feed stream rather than the reverse. Because the quantity of dissolved species in the feed stream is far less than that of the fluid, ED results in much higher feed recovery in many applications. . Standard ED has the ability to treat feed water TDS up to 15,000 mg/L, while emerging ED technologies are reported to be able to treat ~35,000 mg/L TDS at flow rates of 10,000 bbl/day, with 75% water recovery (USBR 2010).

Coagulation Filtration

Coagulation/filtration is an adsorptive/precipitative process. Aluminum ($Al_2(SO_4)_3$) and ferric ($FeCl_3$) salts are among the most widely used coagulations and hydrolyze to form aluminum and iron hydroxide particulates, respectively:

$FeCl_3 + 3H_2O = Fe(OH)_{3(s)} + 3H^+ + 3Cl^-$

$Al_2(SO_4)_3 + 3H_2O = 2Al(OH)_{3(s)} + 3H^+ + 3SO_4^{2-}$

The efficiency and economics of the system are contingent upon several factors including type and dosage of coagulant, mixing intensity, and pH. Coagulation filtration involves adsorption of contaminants to an aluminum or ferric hydroxide precipitate and removal by either sedimentation or filtration. The filtration step can be accomplished using either media filters or micro-filters. The iron/aluminum hydroxides adsorb the contaminants and the resultant solids are filtered out in the pressure filter vessel. Removing these chemical solids is easier than removing turbidity solids from surface water; therefore, higher filtration rates can be used. This allows use of smaller filters reducing treatment plant size and treatment capital costs. The coagulation/filtration process produces spent filter backwash water as a liquid waste. When this waste is treated in a sludge thickener, iron or aluminum sludge will be produced. Liquid residuals may be disposed using indirect discharge, if all Technically Based Local Limits (TBLLs) are met.

Dewatering of sludge can be accomplished by gravity thickening, followed by other mechanical or nonmechanical techniques. The resultant sludge can be disposed of in a municipal solid waste landfill if it meets the criteria of the paint filter liquids test (no free liquid) and the TCLP. Previous studies have indicated that typical coagulation/filtration sludge will not exceed RCRA toxicity characteristic limits.

Lime Softening

Lime softening is commonly used to reduce hardness in source waters. Hardness results primarily from the presence of calcium and magnesium ions. Lime provides hydroxide ions that increase pH, which removes calcium and magnesium due to formation of $CaCO_3$ and $Mg(OH)_2$ precipitates. Also, lime softening has been used for removal of heavy metals, radionuclides, dissolved organics, and viruses (Benefield and Morgan, 1990) through adsorption and occlusion with calcium carbonate and magnesium hydroxide. The typical lime softening treatment process train includes rapid mixing of lime, flocculation of solids, and sedimentation. These three processes are often combined into a single unit referred to as a solids-contact softener (Benefield and Morgan, 1990). Filtration usually follows these three processes. Lime and lime-soda typically are used for softening, and selection is dependent on type of hardness of source water. Lime alone is used for source waters that contain little or no noncarbonate hardness, while high noncarbonate hardness may require both lime and lime soda. Caustic soda is sometimes used instead of lime and lime-soda to decrease sludge production 25 (increases dissolved solids, but produces less sludge) [*Kartinen and Martin*, 1995; *Leist et al.*, 2000; *Mondal et al.*, 2006].

Greensand Filtration

Greensand is a zeolite mineral called glauconite processed with manganese sulfide or manganese sulfate, (Ellis, 1996) and potassium permanganate in alternating steps to produce a black precipitate of manganese dioxide on the granules (Knocke, et al, 1990). It is used as a filter media, operated the same as a rapid sand filter except for a regeneration step.

In Situ Treatment

A thorough report on in-situ treatment [*CH2MHILL*, 2005] discusses pros and cons of these methods. These include: zero valent iron (ZVI) permeable reactive barriers (PRB); injectable nano-scale ZVI (FeroxTM process); phosphate PRB; in situ chemical reduction using dithionite and calcium polysulfide; and in situ biological treatment. The methods were assessed for water contaminated by arsenic, fluoride, nitrate, selenium, uranium, and radium. ZVI in PRB was found to have the greatest potential for groundwater treatment.

Point of Use / Point of Entry

Point of use treatment devices are placed on a single tap and used when treated water is used only for drinking and cooking purposes. Point of use devices are appropriate for removing contaminants that pose an ingestion risk only, as is the case with arsenic and fluoride. Because only a small fraction of the total water supplied to a given household is ultimately treated and consumed, only that small fraction needs to be treated to reduce exposure risk. In most cases, the point of use unit is plumbed in at the kitchen sink (the device has its own faucet) and treats only the water intended solely for consumption (i.e., one tap and the refrigerator ice maker and ice water dispenser). The primary advantage of using point of use treatment in a small system is reduction in capital and treatment costs, relative to installing centralized treatment. On the downside, however, point of use installations generally incur higher administrative and monitoring costs to ensure that all units are functioning properly. Point of entry treatment devices are used when a whole building is served with treated water, and are similar to centralized treatment systems. Treatment techniques used for POE could include ion exchange, adsorptive media, and reverse osmosis. Point of use and point of entry systems must be owned, controlled and maintained by the utility or by an agency under contract with the utility. These systems reduce capital cost but increase administrative and monitoring costs. Studies have suggested that POU and POE programs are an economically viable alternative to centralized treatment for systems serving roughly 50-500 people.

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Appendix B – Contaminant Treatments

The data discussed in this section focuses on different contaminants (as opposed to different treatment technologies discussed in the previous section).

Arsenic Removal

A variety of techniques can be used to remove arsenic, including precipitation, adsorption, and filtration. Removal techniques can be conducted at a variety of scales ranging from small to large and in different locations, such as in-situ, centralized treatment, POE, and POU. Considering regional water quality parameters in Texas, the presence of iron (Fe) will likely play a prominent role in selecting an appropriate technology and ability to treat a given water source. Because of the unique role that iron can play in facilitating arsenic removal, the level of iron in the source water is a primary consideration in selection of an optimal treatment technology. Below is a more detailed description of the range of iron concentrations relative to arsenic concentrations and how the Fe:As ratio can influence the treatment technology selected (Figure 20).

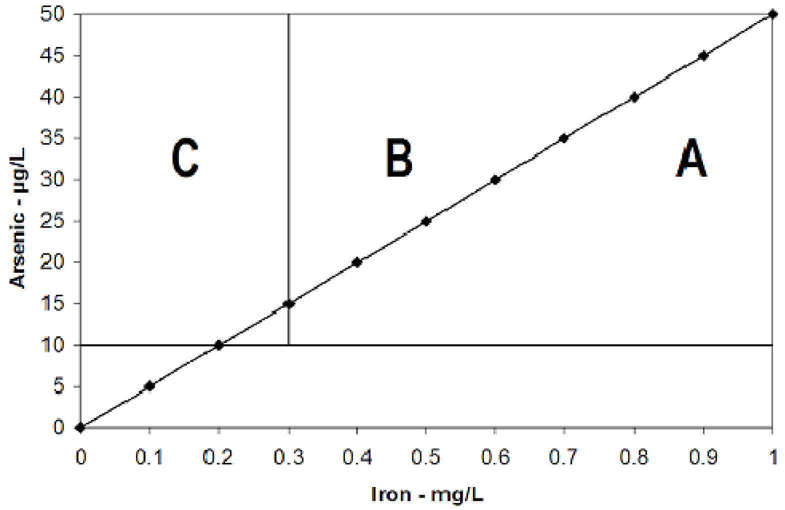

Figure 21. Arsenic treatment selection as a function of initial arsenic and iron in water (Sorg, 2002). A: iron removal process (optimized for maximum arsenic removal); B: modified iron removal process; C: media adsorption iron coagulation/filtration/Ion exchange iron removal, RO/NF. MCL for arsenic: 10 ug/L, secondary MCL for Fe is 0.3 mg/L.

- High iron levels (≥0.3 mg/L) and high iron to arsenic ratio (20:1). Iron removal processes can be used to promote arsenic removal from drinking water via adsorption and co-precipitation. Source waters with this iron/arsenic ratio are potential candidates for arsenic removal by iron removal.
- High iron levels (≥0.3 mg/L) and low iron to arsenic ratio (<20:1). If the iron to arsenic ratio in the source water is less than 20:1, then a modified treatment process such as coagulation/filtration with the addition of iron salts should be selected.

- Low iron levels (<0.3 mg/L). Technologies such as adsorptive media and ion exchange are best suited to sites with relatively low iron levels in their source waters (less than 0.3 mg/L, the secondary MCL for iron). Above this level, taste, odor, and color problems can occur in the treated water, along with increased potential for fouling of system components with iron particulates.

In-situ treatment requires having high oxygen and iron values [*Rott and Kauffmann*, 2008; *Stollenwerk et al.*, 2008]. High oxygen values can be achieved using aeration of low DO water and addition of iron to low iron aquifers. A high iron to arsenic ratio (≥10:1) is required. Precipitation and/or sorption occur in the aquifer prior to pumping water. The high DO levels in groundwater oxidize arsenite to less-mobile arsenate and ferrous iron to ferric iron in the aquifer, decreasing the arsenic content in groundwater [World-Bank, 2005]. Rott and Kauffmann [2008] were able to decrease arsenic levels from 50 ppb to <10 ppb (and in some cases as low as 1 ppb), within 16-19 months by alternating pumping in and out water from a single well throughout the 19 months. Aerated groundwater can be spiked with ferric chloride ($FeCl_2$) salt which would sorb the oxidized arsenate.

Centralized treatments include precipitation/sorbent/coagulation technologies, filtration, and ion exchange. Metal coagulants facilitate precipitation and adsorption of arsenic. Coagulants include iron oxides, activated alumina, and alum. Arsenic removal by adsorption has to be conducted under high dissolved oxygen conditions [*Bang et al.*, 2005].

Coagulation and filtration can be optimized to remove dissolved inorganic arsenate (As(V)) from water. Arsenate is removed by adsorption to an aluminum or ferric hydroxide precipitate followed by filtration. The neutral charge of arsenite (As(III)) under near neutral pH precludes effective removal. Arsenic is often treated by initially oxidizing it to arsenate in an initial step. Up to 90% of arsenate can be removed in optimized coagulation/filtration systems. Several batch studies have shown that arsenate removal is directly related to coagulant dosage. However, the source water quality and pH impacts the specific dose requirements needed to meet arsenate removal objectives. Effective coagulant dosages range from 5 to 25 mg/L of ferric chloride and up to 40 mg/L of alum.

Oxidation and filtration are used in groundwater containing iron and arsenic in reduced form (i.e., Fe(II) and As(III)). The iron and arsenic should both be oxidized at the same time for optimal arsenic removal. A chemical oxidant is required because air oxidation will only oxidize Fe(II) and not As(III). Arsenic can be removed by adsorption or co-precipitation. First, soluble iron Fe(II) and As(III) are oxidized. The As(V) then adsorbs onto the iron hydroxide precipitates that are ultimately filtered out of the solution. Removal efficiency of arsenic is dependent on the initial iron and arsenic concentrations. The Fe:As mass ratio should be at least 20:1, which assumes 1 mg Fe removes 50 µg As. These conditions generally result in an arsenic removal efficiency of 80-90%. Arsenic removal decreases with increasing pH. In addition, high levels of natural organic matter (NOM), orthophosophates, and silicates weaken arsenic removal efficiency by competing for sorption sites on iron hydroxide precipitates. Oxidation/filtration can be used as a special case of pressurized granular-media filtration where the granular media catalyzes the oxidation and precipitation of iron and manganese. Manganese-oxide (MnOx) media, which include manganese greensand and pyrolucite, are commonly used in oxidation/filtration processes because of their unique adsorptive and catalytic capabilities. Greensand is manufactured by coating glauconite with manganese dioxide, while pyrolucite is a naturally mined ore composed of solid manganese dioxide. Greensand media has been shown to be capable of removing up to 80% of arsenic by oxidation/adsorption. In oxidation/filtration processes, water is passed through a column of MnOx media which adsorbs and catalyzes the oxidation of the iron and manganese. The filtering capacity of granular MnOx media then retains the precipitated iron, manganese, and arsenic until it is backwashed out of the column. Waste water and sludge are created from backwashing, which must be properly disposed by the water system. Arsenic appears to be removed mostly by the iron precipitates as opposed to manganese precipitates. Water systems with low levels of influent iron (<1.5 mg/L or < 20:1 ratio with arsenic) may want to consider adding ferric chloride prior to oxidation. It is generally recommended that green sand be preceded by a 12 inch anthracite cap to filter any precipitated iron particulates before the green sand. In order for greensand to retain its adsorption and catalytic oxidation capabilities for iron and manganese removal, the media must be regenerated with permanganate or chlorine. Typically these oxidants are added ahead of the filter where they provide continuous oxidation of the contaminants as well as regeneration of the MnOx media. Arsenic adsorbs to the iron floc formed in this chemical oxidation step and is physically filtered from solution by the greensand. Any arsenic that is not oxidized is adsorbed onto the MnO2 surface of the greensand particles.

Ion exchange is often used for softening and nitrate removal. This technology removes only charged arsenic ($HAsO_4^{2-}$ and $H_2AsO_4^-$). All SO_4^{2-}, NO_3^-, and VO_4^{3-} (if present) must be removed to avoid elution of $HAsO_4^{2-}$ from resin. If As(III) is present, it must be oxidized to As(V) for effective ion exchange. This is a high cost operation, and resin regeneration creates a sludge disposal problem. Liquid waste streams with ≥5 mg/L of arsenic are hazardous waste based on toxicity characteristics listed in RCRA. In drinking water treatment, arsenic removal is accomplished by continuously passing water under pressure through one or more columns packed with SBA exchange resin. These resins are insensitive to pH in the range 6.5 to 9.0.

Reverse osmosis removes arsenic with a net ionic charge (arsenic oxide, As2O3, is a form of arsenic that is soluble, but has no net charge). Scaling can occur when certain ions react in the water. To protect RO systems water should be pretreated to achieve the following values:

≤20 mg/L Si; ≤100 mg/L SO_4^{2-}; ≤5 mg/L PO_4^{3-}; ≤300 mg/L Cl-; ≤5 NTU turbidity; ≤1800 mg/L TDS; ≤0.01 mg/L Ba^{2+} + Sr^{2+}; ≤200 mg/L Ca+.

Studies indicate RO can treat water to below the MCL provided the arsenic exists as (or is converted to) arsenate (As(V)). Increasing pH increases As(III) removal but also scaling from calcium or silica precipitation may increase above pH 7.

Point of use systems listed in the Arsenic Rule include activated alumina and reverse osmosis POU for systems serving between 25 and 10,000 people. Most POU devices do not address the issue of pre-oxidation. While RO may remove As(III) to acceptable standards, sorptive processes such as AA or Iron Based Sorbents will probably not. In this case, water systems may need to conduct centralized chlorine treatment to convert As(III) to As(V). There is also a concern that even with centralized pre-oxidation, anoxic conditions could exist in the distribution system that allow As(V) to reduce back to As(III). Depending on the extent of reduction, this could be detrimental to a POU program.

Fluoride Removal

Fluoride removal can be achieved through the following methods: precipitation, adsorption, and filtration. Removal techniques can be applied at small and large scales and in different locations, such as in-situ, centralized treatment, POE, and POU. Precipitation and adsorption of fluoride with calcium and aluminium salts has been used to remove fluoride [e.g. *Hichour et al.*, 2000; *Saha*, 1993]. Different methods with a variety of adsorbents can be used. Typically, lime is used as a calcium source, and firstly reduces the fluoride concentration down to 10–20 mg/l. The Ca^{2+} ions released from calcium salts interact with fluoride and form fluorite (CaF_2) precipitate. Then, aluminum salts are used to reduce the fluoride concentration further to about 2 mg/l [*Yang and Dluhy*, 2002]. The aluminum salts interact with fluoride in water and form AlF_n^{3-n} and $Al(OH)_{3-m}F_m$, etc. The final concentration of fluoride in the treated water based on this method depends on the solubility of precipitated fluorite, as well as calcium and aluminum salts. The solubility of CaF_2 is 8 mg/l fluoride; therefore, even when a large dosage of calcium is used, the concentration of fluoride in water is still greater than 2 mg/l [*Wang and Reardon*, 2001], and the pH of treated water is relatively high, resulting in additional difficulties of eliminating excess chemicals [*Castel et al.*, 2000].

Radionuclides

Uranium can be removed through various methods: precipitation, adsorption, ion exchange, and filtration. Uranium removal can be conducted in-situ, in centralized treatment systems, or POE and POU. Radium can be removed mainly by ion exchange and reverse osmosis. Sorption of radium by a mixed iron-manganese oxide solid phase shows promise for treating radium-contaminated water based on batch experiments. The capacities of these mixed oxides for sorption of radium depend on the solid phase composition, aqueous solution pH, and presence of competing cations. Removal of the oxide-radium complexes from aqueous suspension by manganese greensand filtration reduces influent radium concentrations of 100 pCi/L to 2-9 pCi/L [*Mott et al.*, 1993] Membrane methods are preferable when dealing with radionuclide contamination (both uranium and radium). These methods were found more efficient than lime softening, coagulation, and ion exchange methods [*Khedr*, 2009]. Wastewater resulting from radionuclide removal is radioactive waste, and cannot be disposed of in sewage systems. The waste can be disposed of according to Chapter 336 of the Texas Administrative Code (TCEQ

Radioactive Substance Rule), only by a person or company licensed for commercial disposal of naturally occurring radioactive material (NORM), and only into Class I injection wells.

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