Historical and Future Needs for Geospatial Iodide Occurrence and Sources in Surface and Ground Waters of the United States of America

by

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ABSTRACT

Iodide (I^-) in surface and groundwaters is a potential precursor for the formation of iodinated disinfection by-products (I-DBPs) during drinking water treatment. The aim of this thesis is to provide a perspective on the sources and occurrence of I^- in United States (US) source waters based on ~9200 surface water (SW) and groundwater (GW) sampling locations. The median I^- concentrations observed was 16 µg/l and 14 µg/l, respectively in SW and GW. However, these samples were rarely collected at water treatment plant (WTP) intakes, where such iodide occurrence data is needed to understand impacts on DBPs. Most samples were collected in association with geochemical studies. We conclude that I^- occurrence appears to be influenced by geological features, including halite rock/river basin formations, saline aquifers and organic rich shale/oil formations. Halide ratios (Cl^-/I^-, Br^-/I^- and Cl^-/Br^-) were analyzed to determine the I^- origin in source waters. SW and GW had median Cl^-/I^- ratios of ~3600 µg/µg and median Br^-/I^- ratios of ~15 µg/µg. For states with I^- concentration >50 µg/l (e.g., Montana and North Dakota), a single source (i.e., organic rich formations) can be identified. However, for states like California and Texas that have wide-ranging I^- concentration of below detection limit to >250 µg/l, I^- occurrence can be attributed to a mixture of marine and organic signatures. The lack on information of organic iodine, inorganic I^- and IO_3^- in source waters limits our ability to predict I-DBPs formed during drinking water treatment, and new occurrence studies are needed to fill these data gaps. This is first of its kind study to understand the I^- occurrence through historical data; however, we also identify the shortcomings of existing databases used to carry out this study.

DEDICATION

I dedicate this thesis to my parents, Radha Kishan Sharma and Anita Sharma and to my little brother Ashutosh Sharma for their continuous support and motivation to move ahead.

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TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

CHAPTER 1

INTRODUCTION

Disinfection by-products (DBPs) form when oxidants (e.g., chlorine, chloramines and ozone) react with precursors, including natural organic matter and inorganic bromide (Br^-) or iodide (I^-). Br^- and I^- react with oxidants to produce critical intermediates (e.g., $HOBr/OBr^-$ and HOI/OI^-) towards formation of halogenated organic DBPs (e.g., trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs)) and inorganic DBPs (e.g., bromate (BrO_3^-) and iodate (IO_3^-)) (Heeb, Criquet, Zimmermann-Steffens, & von Gunten, 2014; McGuire, et al., 2014; Allard, Nottle, Chan, Joll, & von Gunten, 2013; Jones, Saglam, Song, & Karanfil, 2012; Von Gunten, 2003; Bichsel, 1999; Kim, Amy, & Karanfil, 2013; Hua, Reckhow, & Kim, 2006). Because Br^- and I^- are not currently removed at drinking water treatment plants (DWTPs) by conventional unit processes (Gan, et al., 2018), elevated Br^- and/or I^- in the source waters may pose significant health risks to consumers by enhancing the formation of brominated, iodinated or bromo/iodo- DBPs, which are known to be much more cytotoxic and genotoxic than their chlorinated analogues (Richardson, et al., 2008; Wagner & Plewa, 2017; Yang, et al., 2014; Sawade, Fabris, Humpage, & Drikas, 2016). I-DBPs form when source waters containing I^- are disinfected during drinking water or wastewater treatment (Dong, Masalha, Plewa, & Nguyen, 2017). United States (US) drinking water sources were characterized during the 1996 Environmental Protection Agency (EPA) Information Collection Rule (ICR), and Br^- values ranged from <20 μg/l (i.e., below the detection limit) to 2,230 μg/l (USEPA, 2002). Source water Br^- occurrence has been examined in several occurrence studies along with comparison of source waters in Europe and Australia (Table 1).

Table 1
Representative summary of bromide occurrence in source waters

Source	**# of sources**	**Br^- range (μg/l)**	**Br^- average (μg/l)**	**Cl^-/Br^- (μg/μg)**	**Reference**
European rivers	13	20–1040	150	NA	Legube, 1995
European groundwaters	5	48–209	102		
European lakes	6	12–184	199		
US rivers	35	10–3000	110	NA	Krasner, et al., 1989
US rivers	29	3–426	101	30–2000	Amy, Siddiqui, Zhai, Debroux, & Odem, 1994
US lakes	34	3–322	38	30–5000	
US groundwaters	37	2–429	96	80–2200	
US coastal area	11	50–400	210	145–1310	
US surface waters	211	<20–2230	69	NA	USEPA, 2002
US groundwater	63				
US mix (surface + groundwater)	20				
Southeastern US surface water	12	<10–487	60	NA	Karanfil, Hu, Jones, Addison, & Song, 2011; Uzun, Kim, & Karanfil, 2015
Australian surface water	18	30–4130	505	206–840	Magazinovic, Nicholson, Mulcahy, & Davey, 2004
Australian groundwaters	5	152–2040	1350	310–425	
Chinese surface water	13	10–249	88	NA	Zhang, et al., 2011

NA: Not Available

Due to the less perceived risk of I^- in source and drinking water intakes prior to last decade (Krasner, et al., 2006) coupled with its relatively lower concentration in water bodies limiting analytical detection, much less is known about I^- occurrence in lake, river, ground or other water sources used as drinking water supplies. Geologically, iodine weathered from rocks is the main source of I^- in soils and surface water (SW) (Cohen, 1985). Among natural sources of I^-, rainwater in US has I^- concentration of 1–3 μg/l and seawater contains ~60 μg/l of I^- (Hem, 1992). However, there are numerous potential anthropogenic I^- sources, including discharges related to oil and gas produced waters (Harkness, et al., 2015) and the introduction of iodine additives as alternatives to bromine for controlling mercury emissions from coal-first power plants (Good & VanBriesen, 2017). I^- in municipal sewage has not been reported in the US, although a study done by Gong et al., (2018) reports 6–73 μg/l I^- in wastewater in Hong Kong (Seitz, et al., 2017). For US municipal wastewater, the pharmaceutical industry has been identified as a potential source of total adsorbable organic iodine (TAOI) due to the extensive use of iodinated x-ray contrast media (Drewes, Fox, & Jekel, 2001). Fono and Sedlak, (2007) report 1.7–16 μg/l of TAOI in wastewater treatment influents and effluents in parts of California.

1.1. Chemistry of Iodine and its species in freshwater

Iodine in aqueous form can be found in a variety of species listed in Table 2. However, the typical species is found in natural waters are Iodide (I^-) and Iodate (IO_3^-), with the intermediate species being very short lived in natural environments and cannot be measured directly.

Table 2

Oxidation state of Iodine and its species in aqueous form

Iodine Species	**Oxidation States**
Iodide (I^-), Triiodide (I_3^-)	-1
Iodine (I_2),	0
Hypoiodite (IO^-)	+1
Iodite (IO_2^-)	+3
Iodate (IO_3^-)	+5
Periodate (IO_4^-/IO_6^{5-})	+7

The relation between I^- and IO_3^- and I_2 in water at 25°C and 1 atm is given by the following equation with the standard reduction potential denoted as E° (Vanysek, 2000; Liu & von Gunten, 1988):

$$I_{2\,(aq)} + 2e^- \leftrightarrow 2I^- \qquad E° = 0.54 \qquad (1)$$

$$2IO_3^- + 12H^+ + 10e^- \leftrightarrow I_2 + 6H_2O \qquad E° = 1.195 \qquad (2)$$

$$IO_3^- + 6H^+ + 6e^- \leftrightarrow I^- + 3H_2O \qquad E° = 1.085 \qquad (3)$$

The Pourbaix diagram (or E_h-pH diagram) for these three species in water is shown in Figure 1. The equations and Pourbaix diagram suggest that the occurrence of Iodine species in natural water is dependent on pH, however, under the typical pH range between 6.5-8.5 for drinking water, the most dominant species present in I^-.

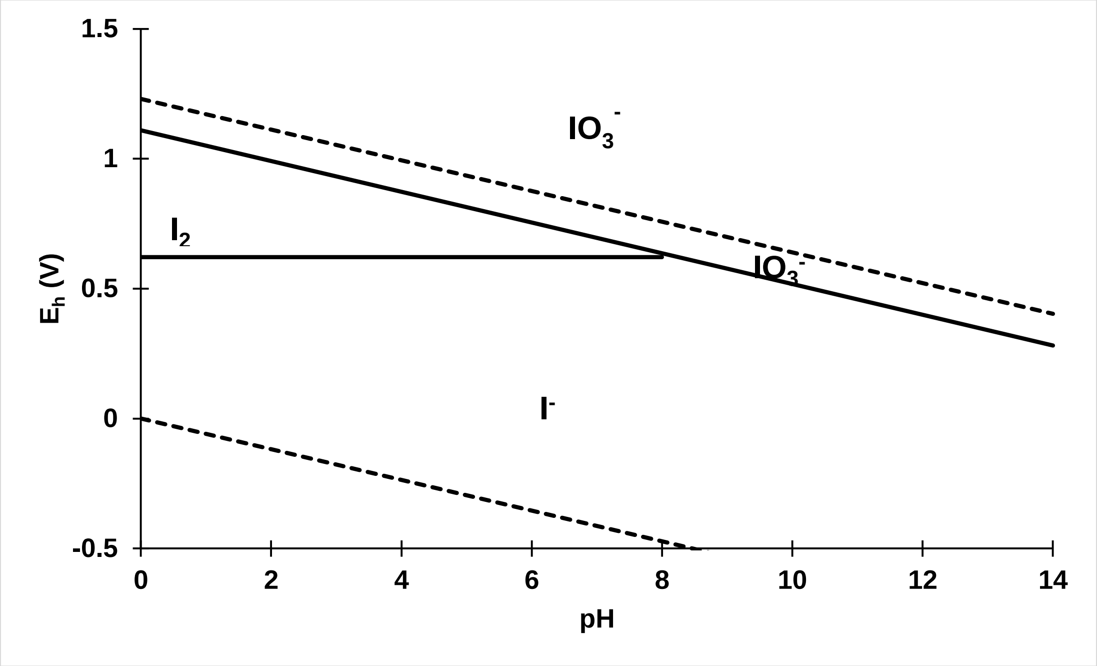


Figure 1: Pourbaix diagram for major Iodine species found in natural waters. The area bounded by dashed lines indicate the domain of stability for water.

The speciation of Iodine species is also dependent on the presence of oxygen – under anoxic conditions, Iodine present will be predominantly in I^- form, whereas under oxic conditions (such as a well-mixed lake or water body or ocean surfaces) – IO_3^- will be the dominant species with typical $IO_3^-/ I^- \sim 10^{15}$ on a mass basis. Another form of Iodine – organic iodine I also present in freshwaters and areas at the interface of anoxic-oxic conditions – this is typically due to reactions with dissolved organic carbon (DOC) for biological uptake of iodine species and subsequent degeneration. Organic Iodine plays an important role in geochemical transport mechanism of Iodine from seawater to atmosphere to freshwater and terrestrial sinks. The cycling of Iodine species in freshwater can also be associated with the mobility and biological/terrestrial absorption capacity of species. For instance, I^- is more mobile in aqueous form and readily used for biological uptake; whereas IO_3^- can be readily absorbed by the soil (Gilfedder, Petri, & Biester, Iodine speciation and cycling in fresh waters: a case study from a humic rich headwater lake (Mummelsee), 2009; Abdel-Moati, 1999; Jones & Truesdale, 1984; Wong & Brewer, 1977). Therefore, in freshwater systems the speciation of Iodine and occurrence of I^- and IO_3^- will be dependent on the depth of water bodies (stratification leading to oxic/anoxic zones), presence of biologically active organisms and regional abundance of forms of iodine from geological/anthropogenic sources. Seasonal variability can impact Iodine speciation as well by indirectly influencing the water flow, stratification effects and causing changes in biological active matter availability. Therefore, only total Iodine in a water body is conservative and the presence of various species can thus be used as geochemical tracers to identify the underlying mechanisms that lead to speciation (Luther III, Ferdelman, Culberson, Kostka, & Wu, 1991).

1.2. Analytical Methods for measuring Iodine Species in water

Various analytical methods have been employed to detect Iodine species in different water matrices. Table 3 summarizes some of the analytical methods used to measure different Iodine species. The analytical methods used for measuring iodine species do not consider the inter-conversion of various species, because typically all the water samples analyzed undergo a filtration process to remove the organic matter that may be capable of reducing iodate to iodide. Although some analytical methods may use acidic or basic environments such as in Inductively coupled Plasma-Mass Spectrometry (ICP-MS) and Ion Chromatography (IC) – no studies have reported a visible interconversion of iodide and iodate during the measurement processes.

Table 3

Analytical methods in use for measuring Iodine species

Method	**Method Detection Limit (MDL in µg/l)**	**Comments**	**Reference**
Iodide (I^-)			
USEPA 300 via Ion Chromatography (IC) with Conductivity Detection	8	Method is applicable to the determination of iodide in ground waters with low sulfate and chloride concentrations	USEPA, 2012
IC with conductivity or UV detection	15	Method used to determine iodide in seawater, synthetic sea salt, and iodized table salt	Hurum & Rohrer, n.d.
IC with fluorescence detection	72	L-ascorbic acid, nitrite, sulfite, oxalate, iodide and thiosulfate measured simultaneously in river and groundwater	Miura, Hatakeyama, Hosino, & Haddad, 2002
Flow injection analyser with UV-VIS spectrophotometer detection	0.1	Spectrophotometric analysis method for determination of Iodide based on catalytic destruction of Iron based quartenery complex	Kamavisdar & Patel, 2002
Colorimetric – Continuous Flow Analyser	1	This method may be used to determine iodide in fresh water and brines containing from 0.001 to 0.060 mg/L of iodide using ceric-	Fishman & Friedman, 1989

		arsenious oxidation reaction in acidic solution	
Iodate (IO_3^-)			
UV Spectrophotometry	1.1	The combination of liquid-phase microextraction and microvolume UV–vis spectrophotometry was applied for measuring iodate in natural water samples. The method is based on the reduction of iodate into vapor iodine and extraction of this volatile onto a single drop of N,N -dimethylformamide	Pena-Pereira, Senra-Ferreiro, Lavilla, & Bendicho, 2010
Liquid Chromatography-Mass Spectrometry	0.1	Method used to analyse oxyhalide ions such as bromate, perchlorate and iodate in bottled waters	Snyder, Vanderford, & Rexing, 2005
Total Iodine			
Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)	0.0013	Method used to determine Bromine and Iodine in seawater and radiactive water samples	Xu, Luo, Ling, Tang, & Wen, 2018; Brix, Hein, Sander, & Kautenburger, 2017
Iodide, Iodate & Organic iodine			
High-performance liquid chromatography (HPLC) coupled with UV	0.2	Method was used to measure the concentrations of iodide species in rain, surface and ground water,	Schwehr & Santschi, 2003

		estuarine and seawater samples after reduction of the sample by $NaHSO_3$	
IC-ICP-MS	0.03	Samples were filtered through cellulose nitrate filters. Iodide and Iodate was directly determined by HPLC-ICP-MS. Dissolved Organic Iodine (DOI) was assessed by the difference between total Iodine (TI) measured by direct ICP-MS and iodide and iodate concentrations.	Gilfedder B. S., Petri, Wessels, & Biester, 2010
Iodoacetic acids (IAAs) – Iodinated DBPs			
IC-ICP-MS	0.33-0.72	Measured 4 IAAs, iodide and iodate in drinking water, groundwater, surface water, and swimming pool water. Samples were filtered through membrane filters. IC separation of ions was conducted using HPLC system followed by continuous injection into ICP-MS system for quantification	Shi & Adams, 2009

1.3. Goals & Objective

This study aims to aggregate and analyze historic I^- data, including geospatial and temporal variability, in surface and groundwaters (GW) in US in order to inform ongoing I^- occurrence studies. Being the first review of the data in the database of I^- concentration in the US, the work delineates the spatial distribution of I^- and identified the I- sources that have the potential to influence I-DBP formation. For a more comprehensive and accurate representation of the I^- occurrence in the US, a geo-statistical approach combined with halide chemistry is presented, to investigate the sources of I^- in water bodies that can eventually impact drinking water. Halide ratios (e.g., Cl^-/I^- and Br^-/I^-) were used to understand potential origins of I^- in water. I^- is rarely monitored in drinking waters. Therefore, databases from the United States Geological Survey (USGS) and other sources developed for reasons separate from drinking water were used to provide a historical perspective and also provide important bounds that impact drinking water directly or indirectly. Given the potential toxicity of I-DBPs, lack of data on iodide in drinking or wastewaters, sources and data gaps of iodide concentration in surface and ground waters were identified. A brief discussion on some of the conclusions derived from existing historical data and deliberations on the need for primary data via field experiments over defined time intervals and priorities for ongoing data collection is presented.

CHAPTER 2

METHODOLOGY

I^- concentrations were obtained from the National Water Quality Monitoring Council's Water Quality Portal (WQP) (Read, et al., 2017) and the Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI)'s HydroDesktop (Ames, et al., 2012). WQP combines field data collected for the United States Geological Survey (USGS), National Water Information System (NWIS), US EPA Storage and Retrieval (STORET) and USGS BioData dataset and US Department of Agriculture Sustaining the Earth's Watersheds - Agricultural Research Database System (STEWARDS). A total of 13797 samples collected at 9197 locations across the US were assembled and reviewed for quality control.

7.78% of the total I^- dataset had values reported as non-detects. As the total reported non-detects was <15%, the non-detect values were replaced with values equal to half of the detection limit (DL/2) following the USEPA 2000 (USEPA, 2000) guidelines. Subsequently, all the detects and revised non-detect values were taken into consideration for the statistical analysis performed thereafter. The collective database was then sorted by decade to understand temporal I^- variation. Once time-based trends were generated, I^- concentrations were organized by state to analyze spatial variation. For locations with I^- data on multiple dates, all samples were included in the analysis. The database also contained locations with multiple samples were taken on same day in the form of duplicates/triplicates. In these cases, the median value of all I^-

concentrations on each particular day was used. Data for Br^-, Cl^- and I^- was simultaneously available for 6041 (234 SW and 6041 GW) locations; while 7611 (1032 SW and 6579 GW) locations had paired Cl^- and I^- concentrations and 7190 (930 SW and 6260 GW) locations had paired Br^- and I^- concentrations on the same date. For Cl^-/Br^- ratios, 28918 (978 SW and 27220 GW) sampling locations were extracted from WQP. These data were used to calculate the Br^-/Cl^-, Br^-/I^- and Cl^-/I^- mass ratios.

A two dimensional geo-spatial analysis was performed using ArcMap 10.5 (ESRI) to explore the geographical I^- variability. A kernel density model was developed for locations having detectable I^-. This provides the advantage of encompassing the variation in number of sample points located in proximity of the estimation point over other density based modules of ArcMap. The mathematical form of kernel density estimator (KDE) is given by equation 1 (Borruso, 2008).

$$C_s = \sum_{i=1}^{n} \frac{1}{\tau^2} k\left(\frac{s-s_i}{\tau}\right) \qquad (4)$$

Where C_s is the density estimate of the spatial iodide concentration measured at location s, s_i is the observed i^th^ event, *k()* represents the kernel weighting function with τ as search radius. The KDE model parameters were chosen after multiple trial and error runs to fit the best representation for the variability of the data. The optimum search radius was calculated using Euclidean distance approach. The density values obtained were scaled down to respective concentration values using linear normalization. The model adjusts itself for search radius and weights depending on the distance from the point within the sphere of influence at which concentration values are estimated.

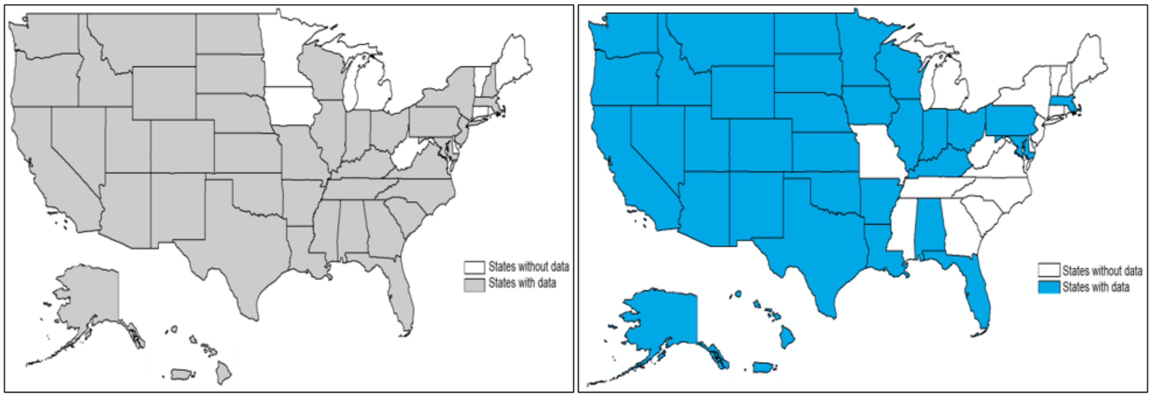
A statistical analysis of the I^- concentration data was done using XLSTAT addin software for Microsoft Excel (XLSTAT, 2017). To verify the statistical significance of GW and SW data sets, we used non-parametric Mann-Whitney-Wilcoxon Test. The Mann-Whitney-Wilcoxon test is a powerful statistic tool to identify differences in population with respect to median and can detect differences in spread even with populations having comparable medians (Hart, 2001; Yue & Wang, 2002). This approach was preferred over standard parametric tests such as t-test and ANOVA due to the increased variability in data points in both the GW and SW data sets. Parametric tests consider mean as the best measure of central tendency of data, assuming a normal distribution. The I^- concentration and various halide ratios for GW and SW were tested for normal distribution by checking against Shapiro-Wilk; Anderson-Darling; Lilliefors and Jarque-Bera Tests provided by the XLSTAT built in modules. All these tests result in $p<0.0001$ indicating that the I^- concentration value do not follow a normal distribution and hence the need for non-parametric statistical significance method. For our dataset, the normality test concludes that the I^- median is the best measure of central tendency due to skewed distribution of data points as a larger spatial variation is taken into consideration (Sheskin, 2006).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Historic data availability and statistical analysis

The combined GW and SW I^- data covered 43 of the 50 US states (Figure 2); no data were available for Michigan, Rhode Island, Delaware, Connecticut, Maine, Vermont or West Virginia. Data was classified as effluent from industrial/wastewater discharges, finished water (water passing through all the stages of a DWTP), atmospheric, soil moisture, interstitial, GW and SW. The last two categories dominate the dataset with GW and SW constituting 80% of the total samples across 41 states and 19.5% of the total samples across 33 states, respectively. More than 55% of the GW data is from California. SW data is primarily from Texas (30%), Utah (~13%) and California (~12%). Consequently, future occurrence studies should aim on collecting data more geospatially relevant to population and location of WTP intakes.



(a) Groundwater (b) Surface water

Figure 2: States with available iodide data. Blank areas indicate no data available.

I^- data was reported between 1930 and 2017. Data availability has increased over the decades, with more data available post 1970 and over one-third of the data collected since 2000. For SW, data availability peaked between 1971 and 1990. For each decade, cumulative I^- concentration probability curves were produced, and then quantile (0, 25th, 50th, 75th and 95th) distribution values were determined. This is represented in Figure 3 and Table 3. The variability in number of data points available for statistical analysis over the decades seem to only have significant effect on the 75th and 95th percentile. This indicates that significant number of $[I^-] > 100$ µg/l date back to pre-1990.

Table 4

I^- percentile distribution for complete dataset and dataset post 1990

Percentile	**All data**		**Post 1990**	
	Surface water (µg/l)	Groundwater (µg/l)	Surface Water (µg/l)	Groundwater (µg/l)
5th	0	1	1	1
25th	3	3	3	3
50th	16	14	9	12
75th	48	70	25	52
95th	323	1230	122.6	603.2

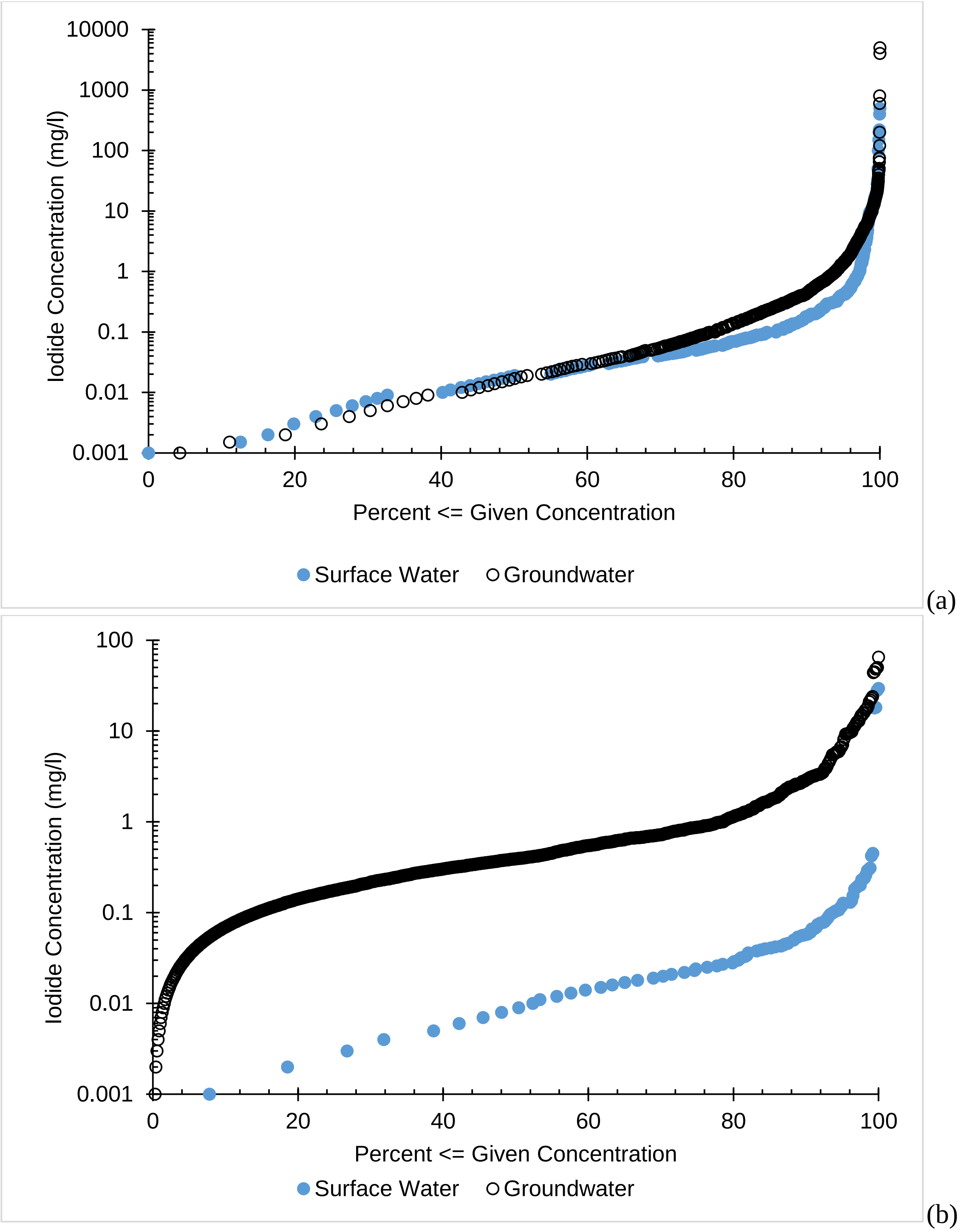


Figure 3: Cumulative probability distribution of I^- concentration in US surface water and groundwater for (a) dataset from 1930 to 2017; (b) dataset from 1990 to 2017.

3.2. Iodide in US waters

The statistical medians for GW and SW data points were 16 µg/l and 14 µg/l, respectively. Most data were collected from non-potable studies (e.g., geochemical or mining studies) and thus does not represent typical drinking water source waters. I^- concentrations range from detection limits to >50 mg/l. High I^- (>50 mg/l) occurs in only ~0.15% of the dataset and 72% of the data points have values <60 µg/l (I^- concentration in seawater, Hem, 1992). After 1990, when the I^- detection limit was 1 µg/l, the median iodide concentration was 12 µg/l in GW (n=7530) and 9 µg/l in SW (n=512). Although the median I^- concentration is comparable for GW and SW for both the timelines, the dataset is statistically significant ($p<0.0001$). The detection limit for I^- decreased over time, from 800 µg/l pre-1990 to ~1 µg/l thereafter. The analytical method used by USGS for measuring I^- as reported in our databases is colorimetry method in conjecture with cerium-arsenious oxidation reaction in filtered water (Fishman & Friedman, 1989). Early field measurements during 1970s, were able to detect as low as 60 µg/l and the method was subsequently improved to attain detection limits ~1 µg/l by the end of 1980s and thereafter. Figure 4 shows I^- concentration by decade in GW and SW. The median I- concentration shows a noticeable decreasing trend.

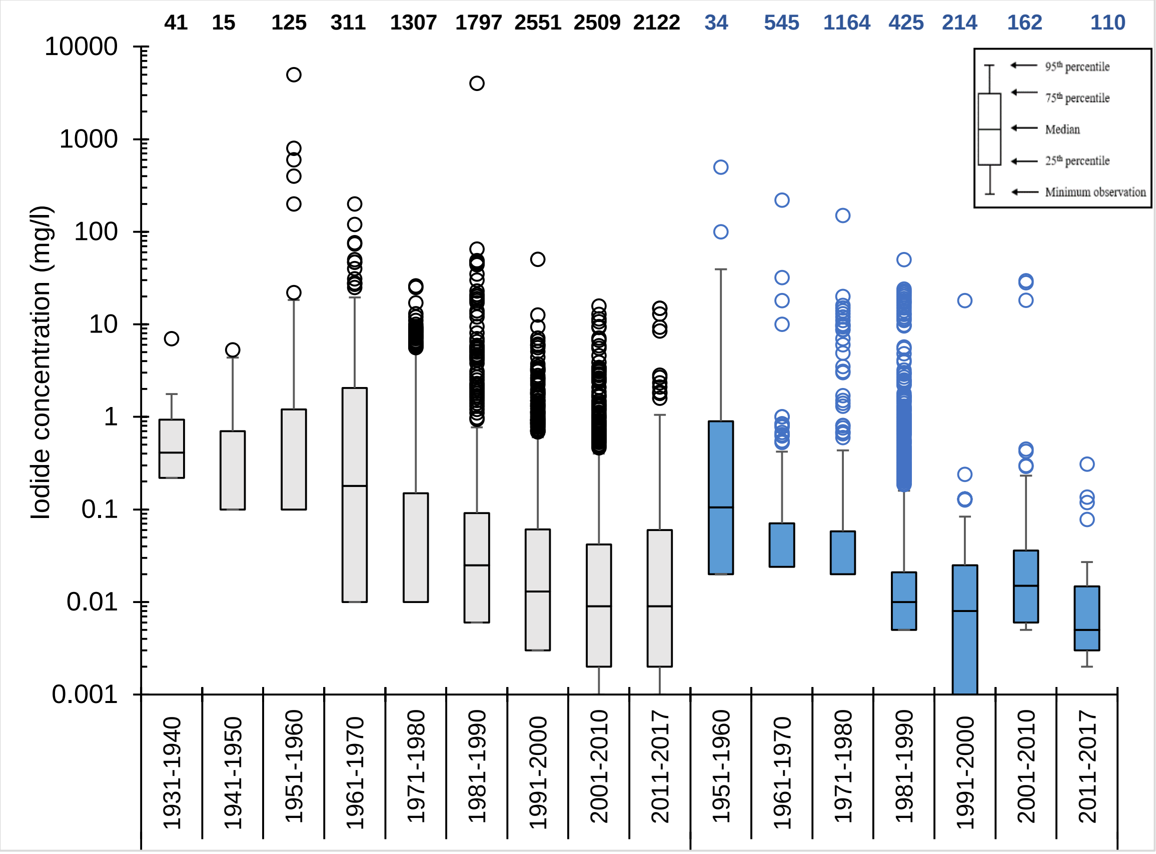
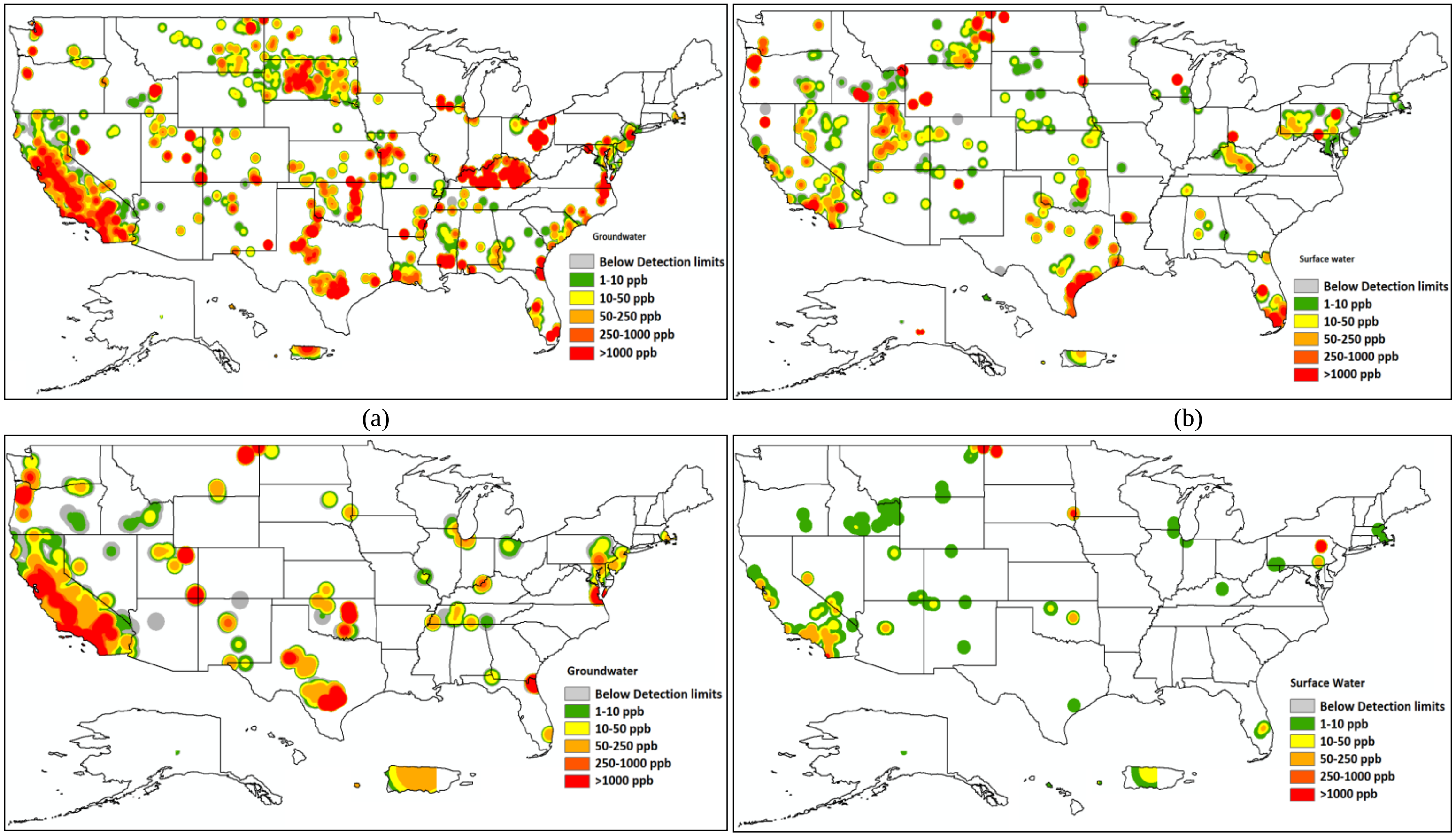


Figure 4: Temporal iodide concentration variation in GW and SW from 1930 to 2017. The number of data points available in each time period is shown at the top of the figure. The legend for the box and whisker plot is depicted in the top right corner.

For GW, it can be noted that the number of samples collected post-1990 is significantly higher than the previous decades and the median and maximum I^- concentration recorded also decreases. Hence, statistically conclusive decreasing trend has been observed for I^- concentration in GW. However, in case of I- concentration in SW, the number of recorded samples is considerably less post 1990. Therefore, the declining median and maximum I^- concentration in SW may be due to absence of sampling at locations that had previously recorded high I- concentration. More interestingly, nearly 46.5% of the total sampling locations were not sampled post 1990.

This indicates that a combination of lower detection limits and reduced number of sampling locations might have also affected the statistical trends.

Figure 5 shows spatial variation of the available I^- data for GW and SW, suggesting that multiple sources of iodide may exist geographically. It was noted that primary natural sources of I^- in source waters were (a) Saline sources that have I^- - saline aquifers and river basin formations and possible seawater intrusions; and (b) diagenesis of organic material and presence of organic rich shale and oil formations. The saline aquifers and water sources have been attributed to seven major brackish groundwater regions across the United States where thorough investigation on the total dissolved solids (TDS) has been carried out (Stanton, et al., 2017). The study estimated that halides can comprise up to 25-30% of brackish groundwater, although specific details of the halide composition is unknown.



(a) (b)

(c) (d)

Figure 5: Spatial variation of $[I^-]$ in GW and SW across the US. (a) GW dataset 1930–2017; (b) SW dataset 1930–2017; (c) GW dataset 1990–2017; and (d) SW dataset 1990–2017. Blank areas indicate regions where data is unavailable. 46.5% of the total sampling locations were not sampled post 1990. The maps are drawn according to NAD 1983 geographic coordinate system.

Figure 6 illustrates the major rock and mineral formations across the US for select formations containing halides (I^- concentration presented in Table 4). Saltwater intrusion is also a possible reason for higher iodide concentrations, where I^- may leach out of the saline aquifers or from seawater into the groundwater (Nowroozi, Horrocks, & Henderson, 1999).

Table 5
Iodine in rock and mineral formations (Maida, 1989)

Formations	**Iodine (ppm)**
Igneous rocks (volcanics)	0.1–0.3
Carbonatite	~2
Sandstone	0.1–6
Limestone	0.4–30
Evaporites	0.005–0.2
Marine phosphate sediments	1–1000
Marine sediments	2–2000

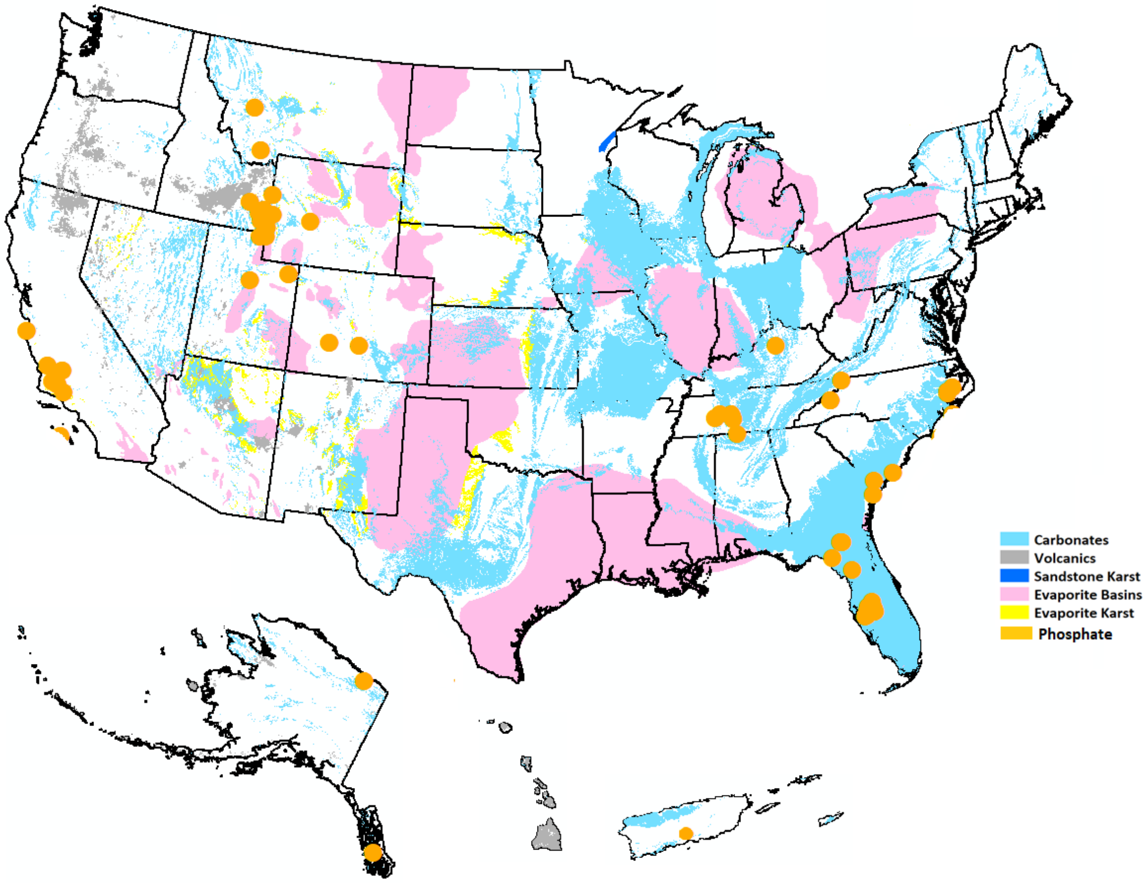


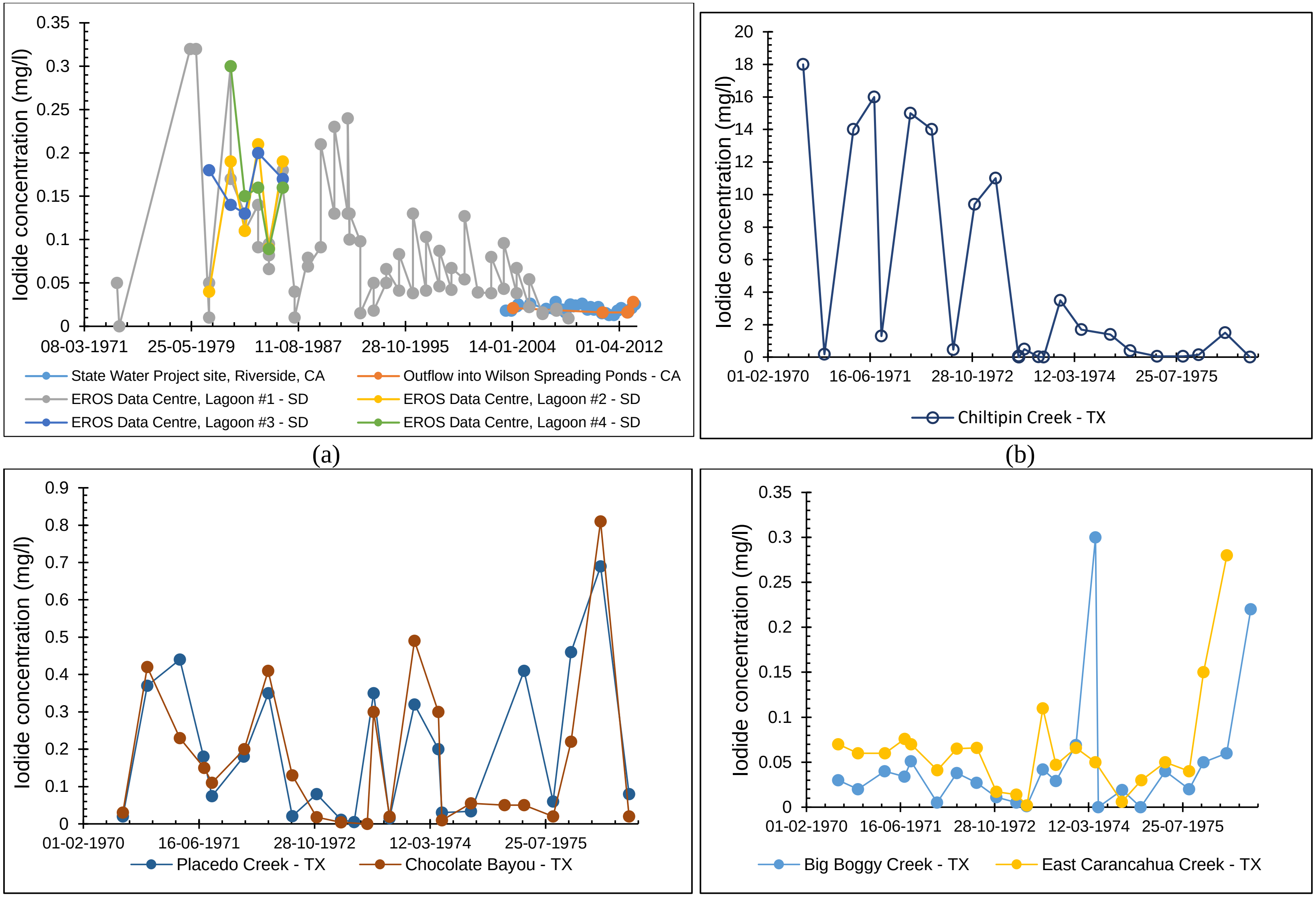
Figure 6: Rock and Mineral Formations in US (Modified from Weary & Doctor, 2014; USGS, 2018). The maps are drawn according to NAD 1983 (Albers) geographic coordinate system.

High I^- (>1 mg/l) occurs in coastal regions of Washington, California, Texas, Florida, Maryland) and Puerto Rico. But inland states of Idaho, Oklahoma, Kentucky, South Dakota and Utah also have relatively high I^-. The majority of sites studied under the collective database with high I^- in source waters are located in saline aquifers and river basin formations. For instance, in inland areas, I^- concentrations >100 mg/l in GW was found in Snake River Group and Yorktown formation in Idaho and North Carolina, respectively (Lindholm, 1996; Wood & Low, 1989). Both of these formations belong to early-middle Pliocene age with typical chloride concentration of ~200–250 mg/l. An example from coastal region would be looking at the halide geochemistry of the Floridan aquifer system (Phelps, 2001). This region also has high I^- concentration however, apart from the influence from aquifer, constant sea water dilution flushing in and out of the aquifer system in northeastern Florida also impacts the halide concentration. Overlaying mineral and saline formations with I^- data suggests that proximity to oceans may not be the sole factor contributing to halide occurrence, because while Florida is dominated by carbonates that contain halides, evaporate basins dominate much of Texas. With exception of California, trends seem to exist between higher iodide and presence of evaporite basin formations across the US (comparing Figures 4, 5 and Table 4).

On the other end, in regions such as Texas, Oklahoma and eastern Montana having I^- concentrations >1 mg/l can be due to the presence of organic rich sedimentary formations, which are known to have higher iodide signatures. This is caused due to the diagenesis or the physical/chemical/biological processes occurring during the conversion of organic matter containing iodine to sediment matter/rocks (Lu, et al., 2015; Collins, 1975; Henrichs, 1992). The higher density of sample locations also contributes to a predominantly higher iodide presence in this state. The Gulf of California is rich in organic sediments having iodide between 20 and 1200 μg/l. The concentration varies with depth, with lower values at greater depths. This might be a possible factor affecting the local iodide concentration, specifically in GW near the west coast. Similarly, the few GW samples in North Dakota and South Dakota originated from the Dakota limestone formation (Bakken formation [USEIA, 2016]) and Inyan Kara formation. These are sedimentary formations where adsorption and deposition of iodine from seawater (sandstone, dolostone, siltstone plays) or diagenesis from skeletal formations stored in the rock matrix (shale plays) may have caused higher iodide signature. For, regions in South Florida, Br^- enrichment over Cl^- has been seen due to diagenesis of organic material the I^- concentration can be correlated with the diagenesis of organic material. This may indicate a potential mechanism for I^- enrichment in South Florida.

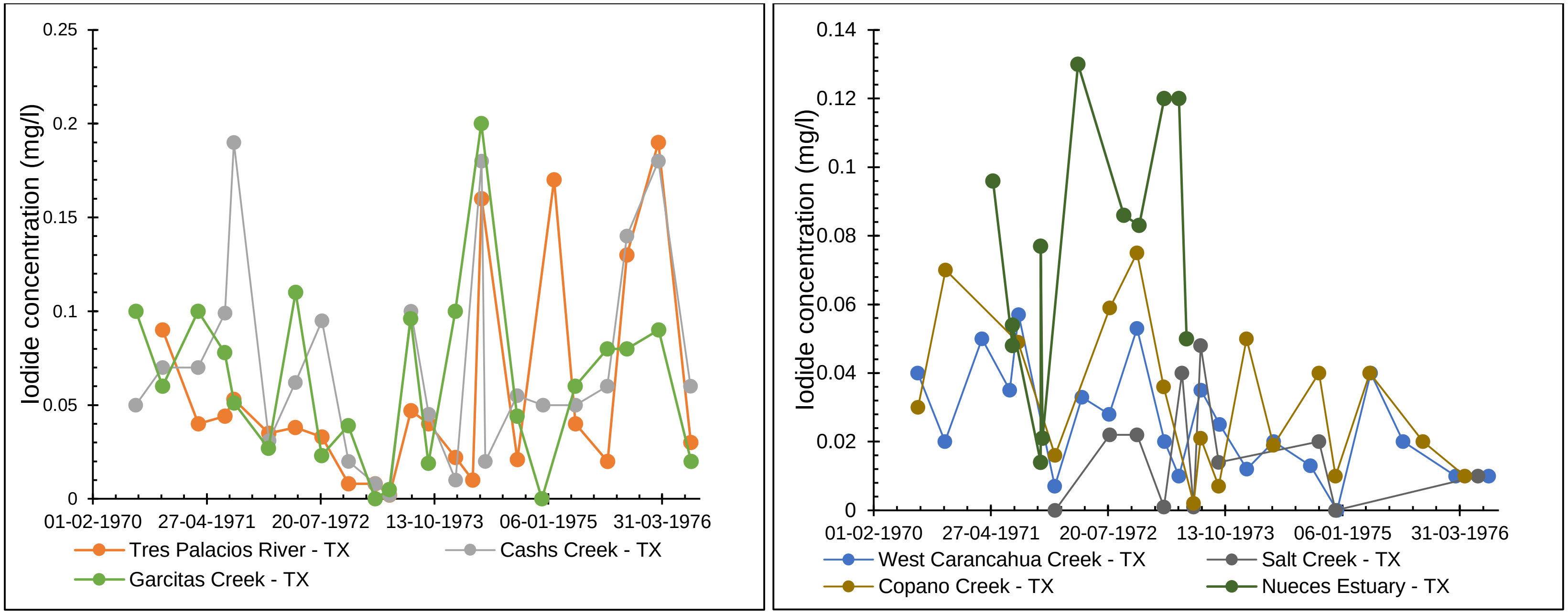
Although, for certain regions, supporting evidence from secondary literature and geological occurrence of I^- can be correlated for identifying sources, in locations such as California and Texas, I^- may be affected by multiple factors such as seawater intrusion, occasional leaching from the oil field formations and presence of saline formations. For other regions, such as Kentucky and Tennessee, we identify that the water samples belong to Knox dolomite and Louisville limestone formations. However, there is sparse literature correlating these formations with I^- occurrence. Some instances of local I^- enrichment, and concentrations ranging from 20 to 1000 μg/l, can be observed in mud volcanoes in Copper River Basin (Alaska) and volcanic waters near Puerto Rico. I^- concentrations are lower (i.e., ≤ 20 μg/l) in arid states of Arizona and New Mexico and central states of Kansas, Nevada and Iowa.

Temporal I- data spanning multiple years was available for 48 (18 SW & 30 GW) of the ~9200 sites have, although not at regular intervals. Figures 7 and 8 plot the varying temporal data grouped by location.


Iodide concentration (mg/l)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
08-03-1971
25-05-1979
11-08-1987
28-10-1995
14-01-2004
01-04-2012
State Water Project site, Riverside, CA
Outflow into Wilson Spreading Ponds - CA
EROS Data Centre, Lagoon #1 - SD
EROS Data Centre, Lagoon #2 - SD
EROS Data Centre, Lagoon #3 - SD
EROS Data Centre, Lagoon #4 - SD
Iodide concentration (mg/l)
20
18
16
14
12
10
8
6
4
2
0
01-02-1970
16-06-1971
28-10-1972
12-03-1974
25-07-1975
Chiltipin Creek - TX
Iodide concentration (mg/l)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01-02-1970
16-06-1971
28-10-1972
12-03-1974
25-07-1975
Placedo Creek - TX
Chocolate Bayou - TX
Iodide concentration (mg/l)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
01-02-1970
16-06-1971
28-10-1972
12-03-1974
25-07-1975
Big Boggy Creek - TX
East Carancahua Creek - TX

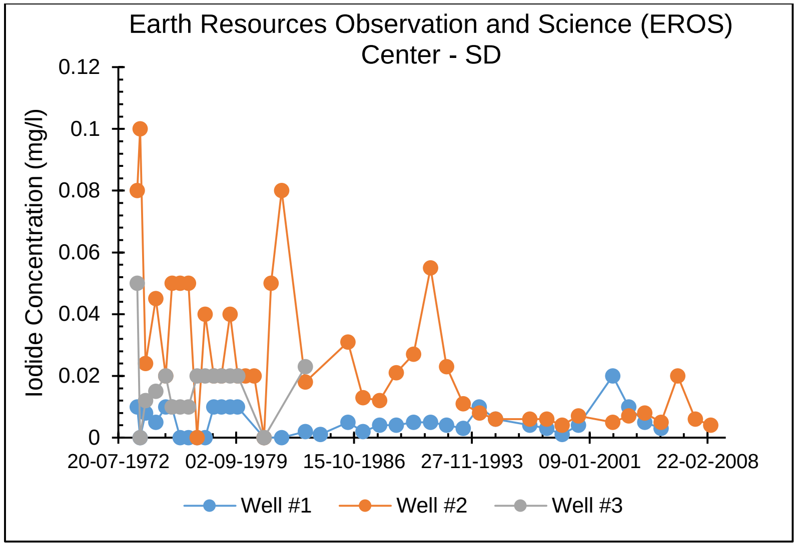
(a) (b)

(c) (d)

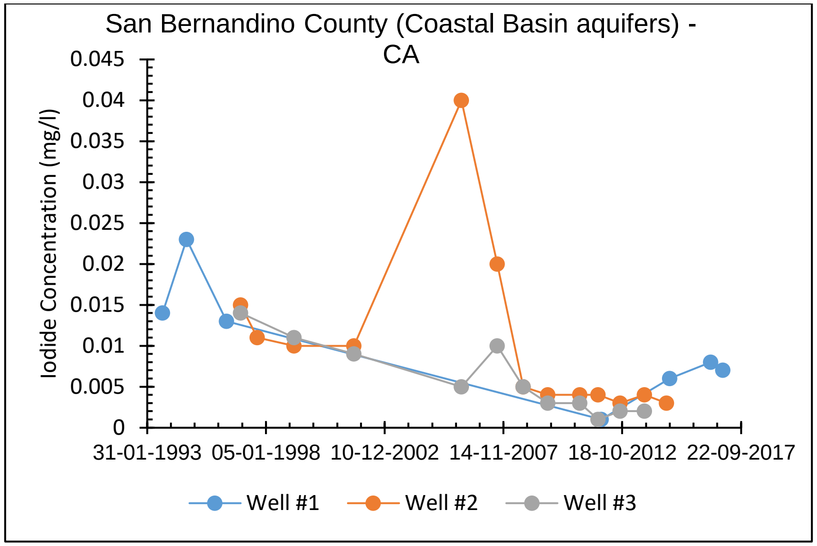


(e) (f)

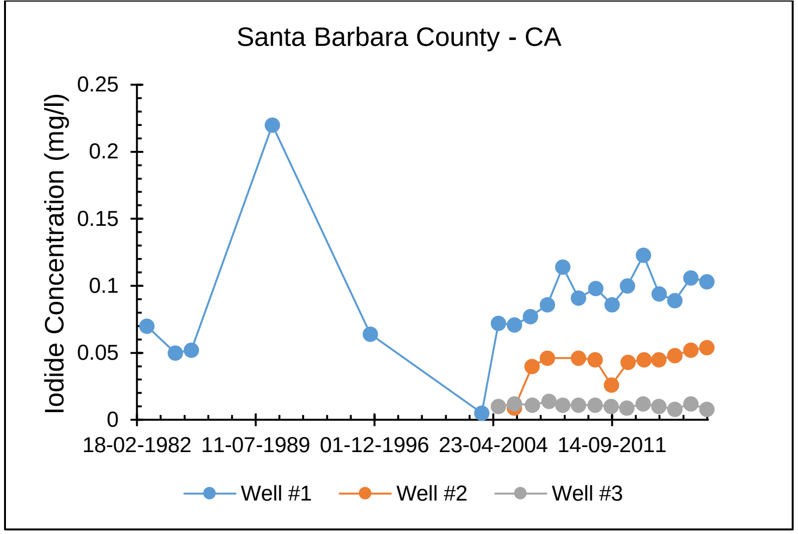
Figure 7: Temporal variation of $[I^-]$ (mg/l) at specific SW locations. The values below detection limits are plotted as 0.001 mg/l. The sites (a)-(f) were identified using USGS monitoring location identifier from Water Quality Portal.


Earth Resources Observation and Science (EROS) Center - SD
Iodide Concentration (mg/l)
0.12
0.1
0.08
0.06
0.04
0.02
0
20-07-1972
02-09-1979
15-10-1986
27-11-1993
09-01-2001
22-02-2008
Well #1
Well #2
Well #3

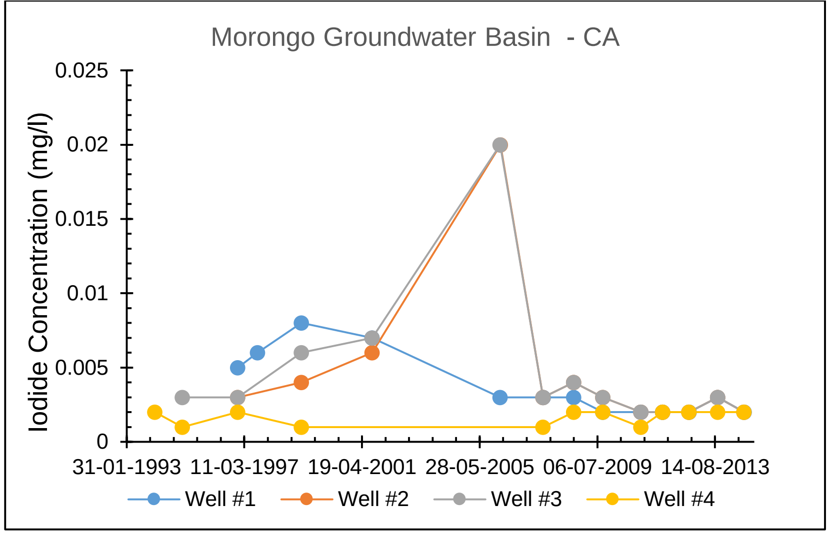
(a)


San Bernandino County (Coastal Basin aquifers) - CA
Iodide Concentration (mg/l)
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
31-01-1993
05-01-1998
10-12-2002
14-11-2007
18-10-2012
22-09-2017
Well #1
Well #2
Well #3

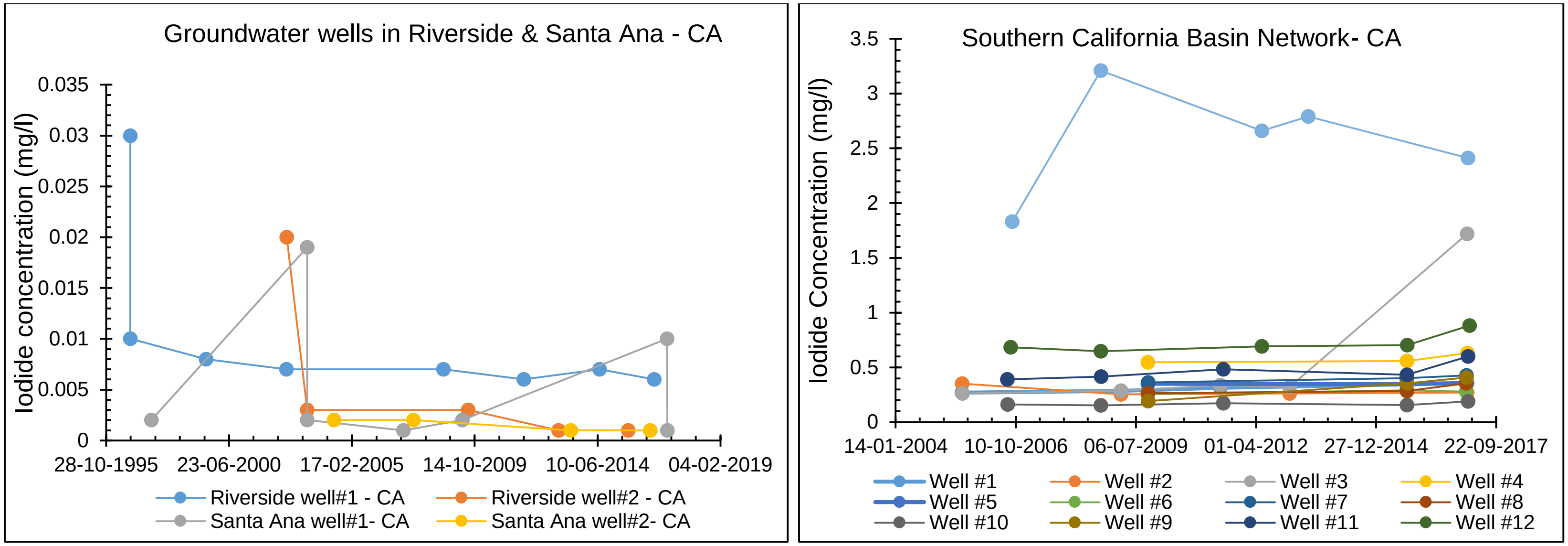
(b)


Santa Barbara County - CA
Iodide Concentration (mg/l)
0.25
0.2
0.15
0.1
0.05
0
18-02-1982
11-07-1989
01-12-1996
23-04-2004
14-09-2011
Well #1
Well #2
Well #3

(c)


Morongo Groundwater Basin - CA
Iodide Concentration (mg/l)
0.025
0.02
0.015
0.01
0.005
0
31-01-1993
11-03-1997
19-04-2001
28-05-2005
06-07-2009
14-08-2013
Well #1
Well #2
Well #3
Well #4

(d)



(e) (f)

Figure 8: Temporal variation of $[I^-]$ (mg/l) in specific GW locations. The values below detection limits are plotted as 0.001 mg/l. The sites (a)-(f) were identified using USGS monitoring location identifier from Water Quality Portal.

The I^- concentration either decreased or remained stable over time for a majority of locations (e.g., California and South Dakota). Data available in Texas was limited to the period of 1970-1980. The recorded I^- concentration in Chiltipin Creek in Texas is one of the highest at ~18 mg/l, but it also shows a declining trend over years. A nearby source water, Oso Creek which has concentrations in the range of 2-4 mg/l - is a saline creek influenced with discharges from wastewater treatment plants, agriculture and industrial power plants. The watershed has been declared impaired due to poor biological and water quality parameters (Nicolau, 2001). SW I^- concentrations in Texas such as Big Boggy and East Carancahua Creek increased over time, although the reasons for these trends are not understood. Thus, understanding of statistical temporal I^- concentration trends across the United States necessitates a continuous and comprehensive sampling to ensure the reliability of analyses conducted in available databases. In other studies, ratios of Br^- and Cl^- concentrations in Monongahela River follows a seasonal flow pattern (Wilson & Van Briesen, 2013), suggesting differing run-off vs GW infiltration sources. Hence, temporal data representative of seasonal and regional variations in WTP source waters is largely absent, and represents an important data need – as sources of halides can vary seasonally.

The analysis noted that 20% of the sampling locations have Cl^- concentration greater than 250 mg/l, i.e., the secondary maximum contamination limit for drinking water (USEPA, 2018). These locations might not be preferably used directly for drinking water supplies. However, many GW and SW sources of water discussed above belonging to brackish sources (TDS ranging from 3000-10,000 mg/l); saline sources (TDS>10,000 mg/l) or brines (GW with salinity>35,000 mg/l) are used for agricultural or industrial uses. Some states like Texas, Florida, Massachusetts among others use desalinated brackish/saline water (TDS<500 mg/l) for drinking supply purposes (Dieter, et al., 2018). Therefore, presence of I^- in such source waters with high Cl^- and/or TDS or wastewater from industrial sector that use brackish/saline water can still enter the drinking water supply chain lying downstream of these sources eventually contributing of DBP formation. This can be prominently seen in case of Br^- (Good & VanBriesen, 2017). Therefore, we have included all the sampling locations with available Cl^- and Br^- concentration of all ranges.

To investigate potential origins of I^- in waters, halide mass ratios were calculated. The median $[Cl^-]/[Br^-]$ for the entire dataset was 275 µg/µg for GW and 237.5 µg/µg for SW. The $[Cl^-]/[I^-]$ ratios for different source waters have overlapping ranges and thus cannot be used for delineating the I- concentration (Figure 9). Cl^- and I^- are not strongly correlated in waters impacted by fossil formations (Figure 10 for $[Cl^-]/[I^-]$ variation for various water types and time periods). The median $[Cl^-]/[I^-]$ for the complete dataset was 3645 µg/µg and 3600 µg/µg for GW and SW, respectively.

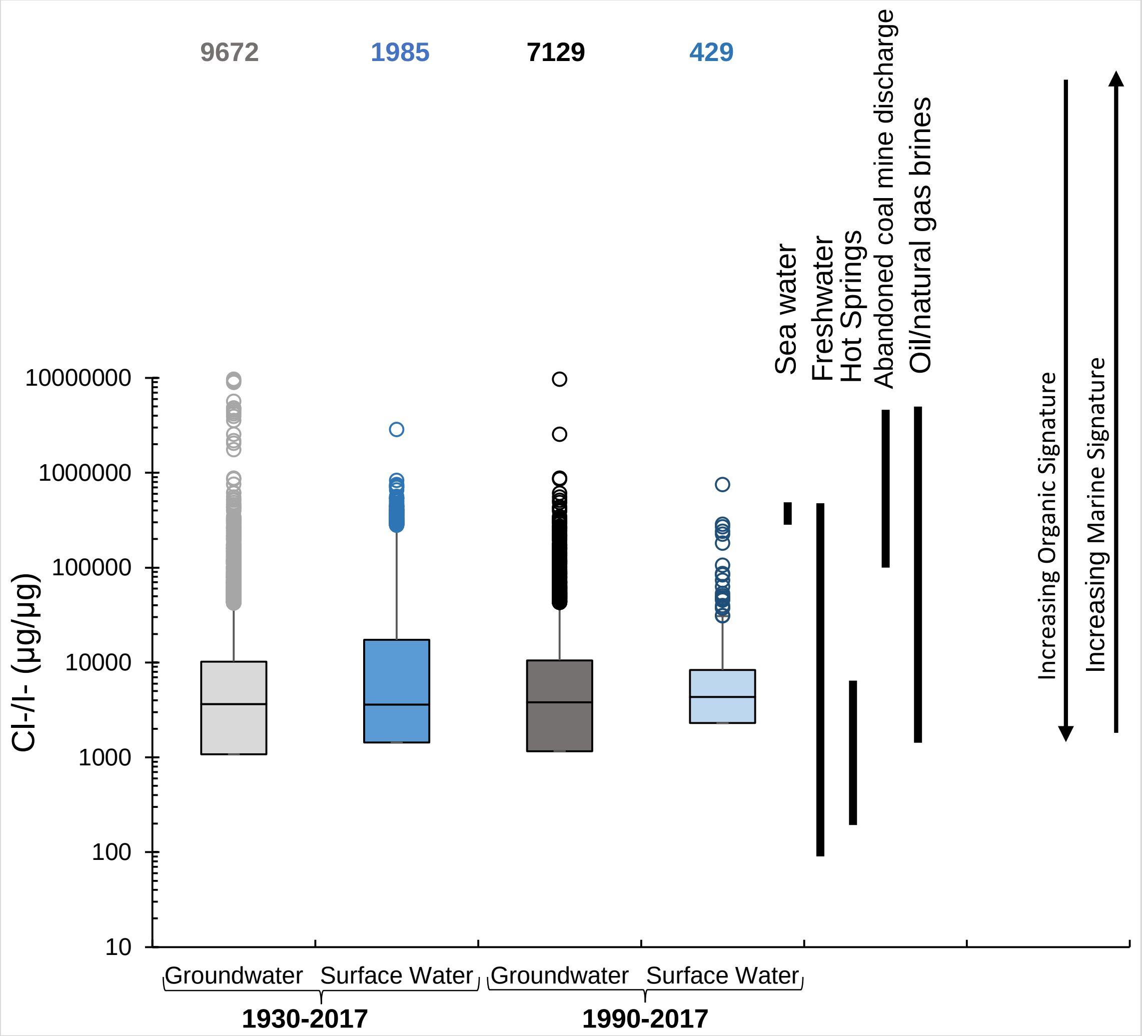
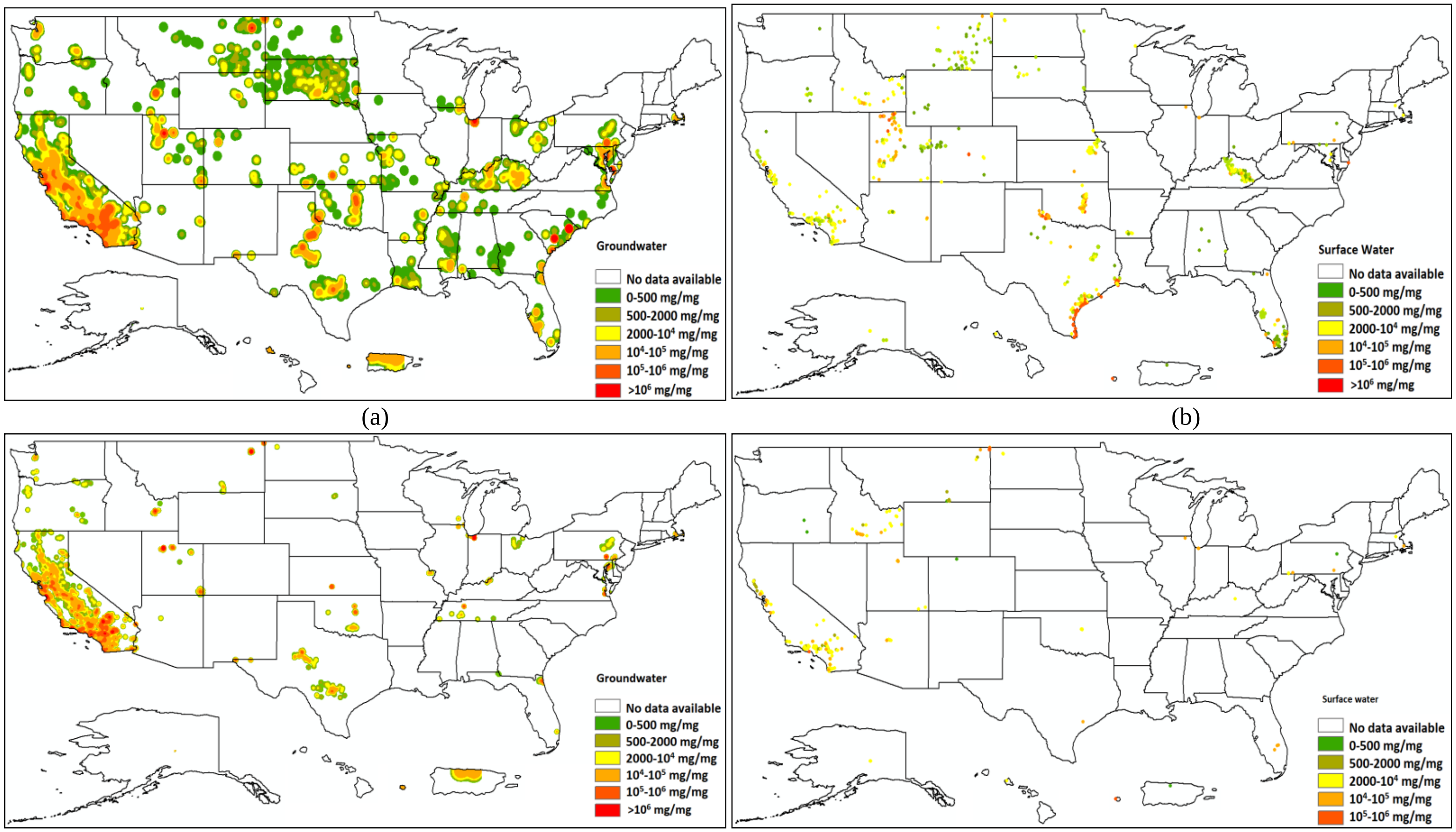


Figure 9: Chloride to Iodide ratios (µg/µg) for surface and groundwater in the US: for 1930–2017 and 1990–2017. The numbers at the top show the available data points for each water type. The ratios for the reference water types (solid lines) were compiled from multiple references (Wilson & Van Briesen, 2013; Davis, Whittemore, & Fabryka-Martin, 1998; Good & VanBriesen, 2017; Wilson, Wang, & Van Briesen, 2013).



(a) (b)

(c) (d)

Figure 10: Spatial variation in [Cl-]/[I-] (μg/μg) ratios across the US. (a) groundwater dataset 1930–2017; (b) surface water dataset 1930–2017; (c) groundwater dataset 1990–2017; and (d) surface water dataset 1990–2017. Blank areas indicate regions where data is unavailable. The maps are drawn according to NAD 1983 geographic coordinate system.

Figure 11 shows [Br^-]/[I^-] ratios for the water types in our databases (Figure 12 for spatial [Br^-]/[I^-] variation). The medians for each water type ranged from 8.5 to 32.5 µg Br^-/µg I^-, which is typical for freshwaters. Although the median Br^-/I^- ratio is comparable for GW and SW, the dataset is statistically significant ($p<0.0001$) and both the GW and SW dataset are derived from different sources as they have different distributions. The [Br^-]/[I^-] ratio for GW is typically higher than that of SW. This indicates that SW has relatively lower Br^- and I^- concentration as compared to GW. Also, various Iodine speciation mechanisms discussed in Section 1.1 (Chapter 1) may have resulted in varying I^- concentrations, however no particular mechanism could be correlated with differences for GW or SW I^- occurrence.

Taking into consideration the halide ratios for the entirety of the US, can cause ambiguity in understanding the regional factors that impact I^- sources. Therefore, the data available was separated by states and we plot the Br^- to I^- concentration for groundwater to compare them with the ratios presented in the reference water types (select states are presented in Figure 13).

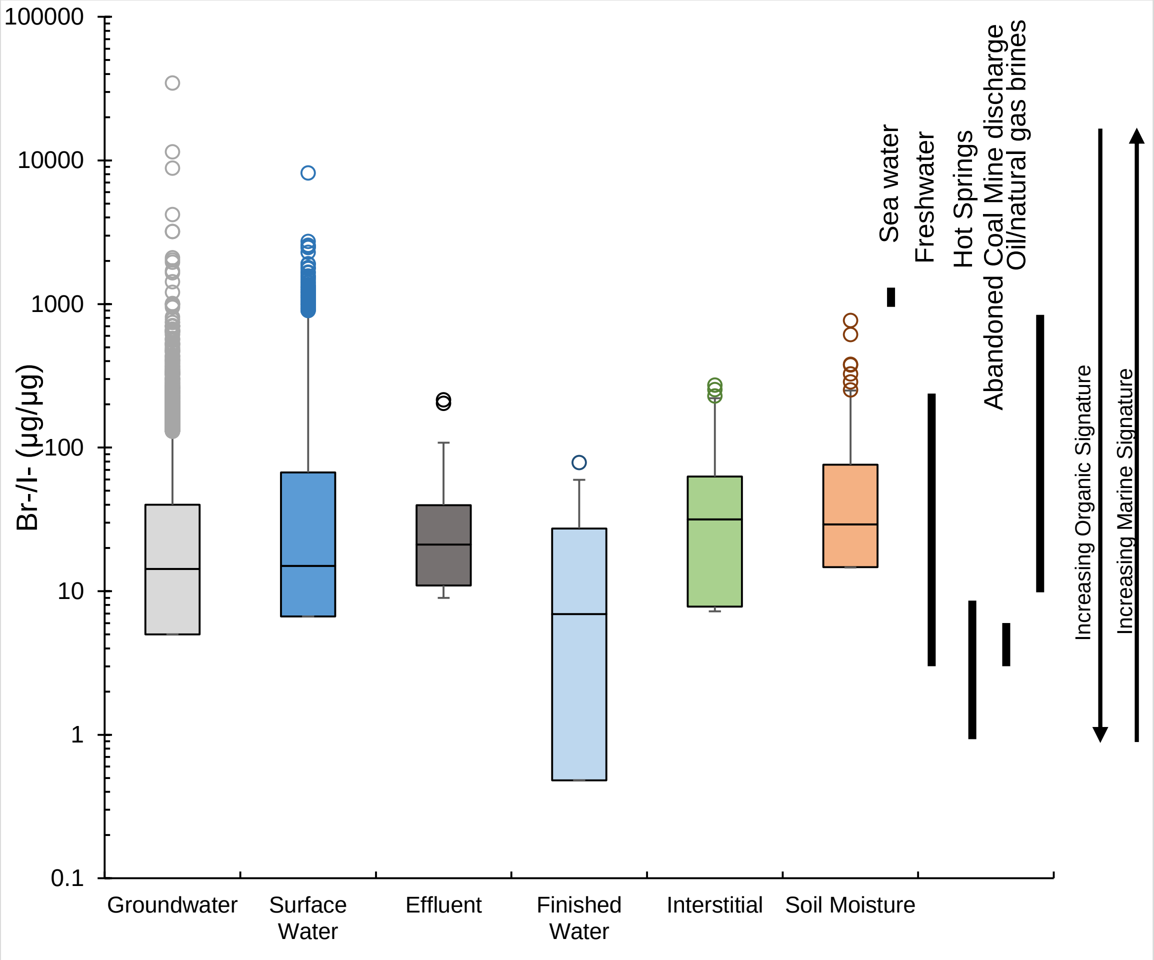
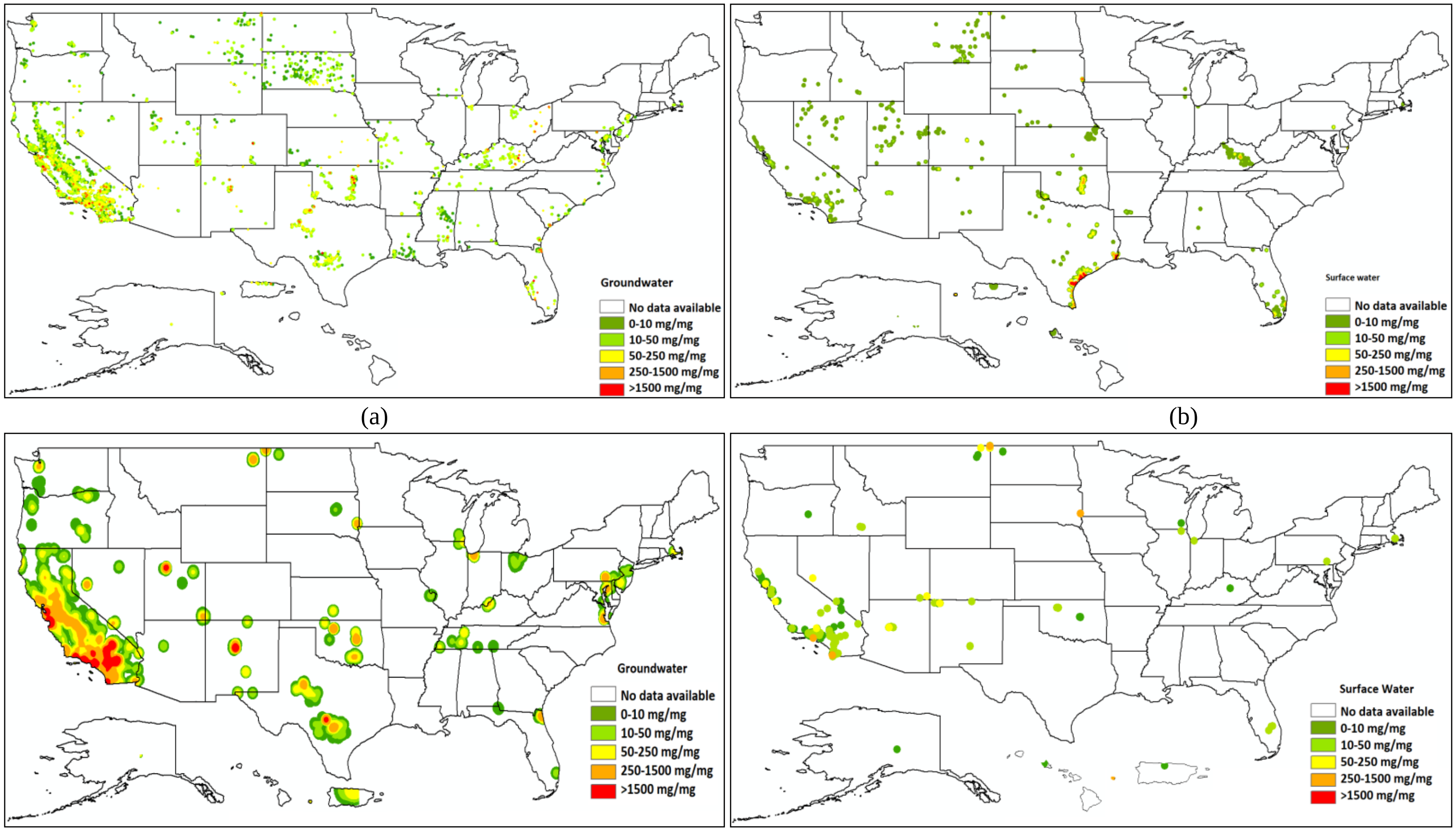


Figure 11: Bromide to iodide ratios for different water types. The numbers at the top show the available data points for each water type. The whiskers indicate minimum and 95th percentile values on the lower and upper side, respectively. The ratios for the reference water types (solid lines) were compiled from multiple references (Jones, 2012; Hem, 1992; Harkness, et al., 2015; Lloyd, Howard, Pacey, & Tellam, 1982; Barnes, 1970; Cravotta III, 2008).



(a) (b)

(c) (d)

Figure 12: Spatial variation in [Br-]/[I-] (µg/µg) ratios across the US. (a) groundwater dataset 1930–2017; (b) surface water dataset 1930–2017; (c) groundwater dataset 1990–2017; and (d) surface water dataset 1990–2017. Blank areas indicate regions where data is unavailable. The maps are drawn according to NAD 1983 geographic coordinate system.

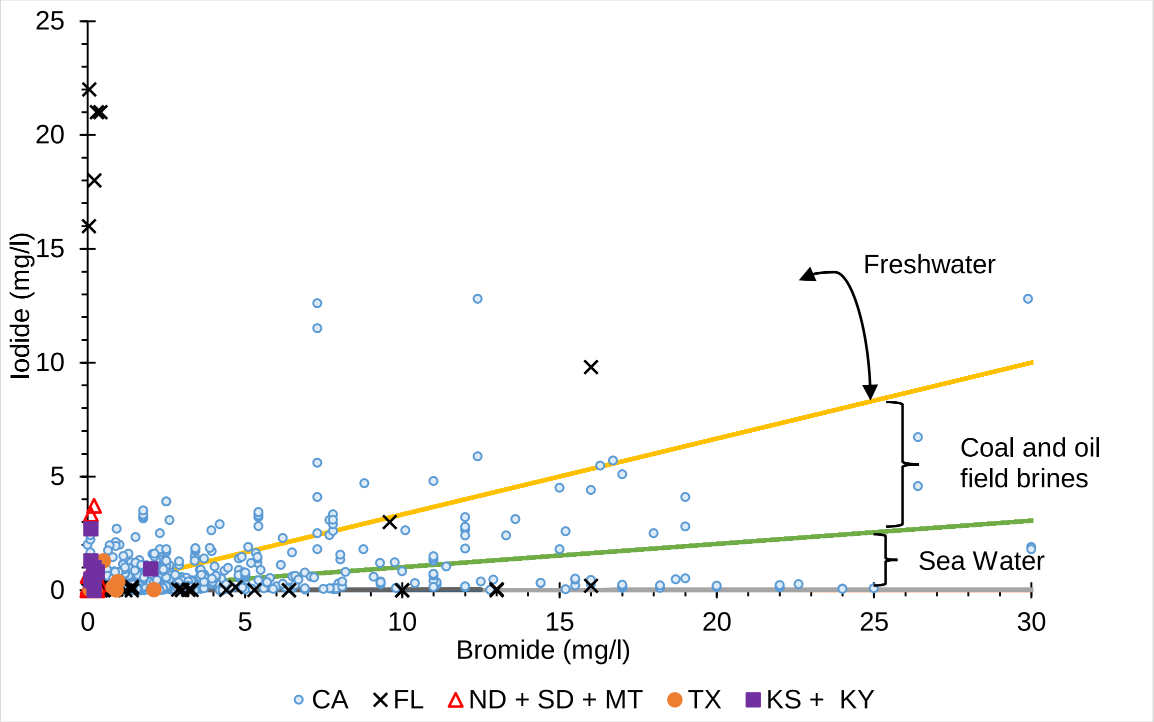


Figure 13: Bromide vs Iodide concentration for specific states across the US.

Nearly 5% of sites located in North Dakota, South Dakota and Montana had no bromide present in GW even though the locations had higher iodide. The median values for SW and GW in these regions ranged from 6-10 µg Br$^-$/µg I$^-$. Low Br$^-$/I$^-$ (µg/µg) ratios indicate plant or fossil rock formations as potential iodide sources, confirming the earlier assertion that I$^-$ in source waters may be due to fossil formations. For example, ratios of ~0.7–10 µg Br$^-$/µg I$^-$ indicate waters impacted by coal or shale formations, while less iodine-enriched materials (>250 µg Br$^-$/µg I$^-$) suggest marine formations. Br$^-$/I$^-$ ratios between 2-1500 µg/µg occurred in GW in central California, Texas, Kentucky and Oklahoma, and thus no singular factor can be correlated with iodide occurrence in GW. In SWs, coastal regions of Florida, east Texas and California had Br$^-$/I$^-$ >250 µg/µg. The ratio in coastal regions decreased as we move inland. This might indicate decreasing influence of seawater spray, tidal impacts and/or salt water intrusion. In this section, we provide a brief state-wise analysis from the available historic halide ratio data. For understanding the origin of water bodies using halide ratios, a more detailed method can involve use of Gibbs diagram (Gibbs, 1970). As noted in previous sections, there is relatively more information on Br^- sources in different waters in the US as compared to I^-. Conversely, in regions where compounding factors affecting I^- in water bodies can be established, the $[Br^-]/[I^-]$ halide ratio (reference water types from Figure 3) can be used to interpolate the range of I^- concentration impacted by same sources. This will necessitate significant knowledge on local geochemistry and underlying anthropogenic factors impacting water bodies. The historic data presented in this study can inform such studies to provide detailed insights on specific locations across the US.

CHAPTER 4

CURRENT WTP DATA LIMITATIONS AND FUTURE NEEDS

Publicly-available databases on iodide occurrence in water sources are limited and tend to focus on locations of geological interests. A few other studies of major US, Canadian and European rivers report iodine and I^{129} sources (Perez & Barcelo, 2007), and they also report [I^-] levels from 0.5 to 9 µg/l in Canadian rivers and US West Coast rivers with a relatively higher value (66 µg/l) in the San Joaquin River. US East Coast rivers and European rivers had lower I^- concentrations (2.12–16.3 µg/l and 0.9–4.2 µg/l, respectively), and US South eastern rivers had higher I^- (5.5–78.9 µg/l). The highest concentration (212 µg/l) was observed in Brownsville, TX on the Rio Grande River. Rivers with high [I^-] have watersheds in arid regions and may be related to intensive irrigation, fertilizers, herbicides, pesticides and certain crops that concentrate iodine. Iodine is incorporated into plant material, and some speculate plant material may be a source of iodide at wastewater treatment plants or agriculture return waters. Furthermore, iodinated x-ray contrast media can be up to 10 µg/l in wastewater effluents (Whitehead, 1979; Moran, Oktay, & Santschi, 2002; Duirk, et al., 2011).

In a study focusing on the formation and toxicity of iodinated DBPs, I^- occurrence in raw source waters of 23 DWTPs (22 cities in US and 1 city in Canada) ranged from <0.13 to 104 µg/l, where 19 of 23 source waters contained 10 µg/l or less (Richardson, et al., 2008). The raw waters with elevated I^- also contained high Br- (up to 699 µg/l). In another study, very low levels of Br^- (11-60 µg/l) and I^- (3-4 µg/l) were reported in

DWTP source waters in South Carolina (Karanfil, Hu, Jones, Addison, & Song, 2011). Recently, Tan et al., (2016) reported 72 µg/l and 87 µg/l of I^- and 754 µg/l and 399 µg/l of Br^- in a SW and a GW, respectively, used as source waters at two Australian DWTPs. Although, there is absence of regulatory monitoring specific to I^-DBPs in DWTPs, a study by Wagner & Plewa, (2017) indicate that iodoacetonitrile concentrations as low as 12.7 µg/L can lead to cytotoxicity in human cells. Post EPA Stage 2 Disinfectant/DBP Rule (USEPA, 2, 2006), water utilities have shifted or are shifting from using free chlorine to chloramines for disinfection. Yang, et al., (2014) conclude that source waters containing Br^- and I^- when treated with chloramines can lead to 1.5 times higher human cell cytoxicity and genotoxicity as compared to treatment with free chlorine. Treatment trains deployed at the DWTPs also play a major role in deciding the fate of various forms of iodine present in the water. For e.g., a DWTP using ozonation prior to disinfection step can avoid I-DBP formation due to the oxidation of I^- to IO_3^-. Therefore, for DWTPs, a combination of I^- in source water, composition in finished water upstream and disinfection method will have to be taken into consideration for evaluating the fate of I^- resulting in DBP formation. Nonetheless, it has been stated that at free chlorine doses of 1-3 mg/l, pH=8 (typical for DWTP disinfection process), only 20% of the iodide present in water gets converted to I-DBPs and the specificity of particular I-DBP formed is unknown (Goslan, 2016). Therefore, it is important to primarily identify and focus on particular I-DBPs that occur at relatively toxic quantities post disinfection process.

Various geochemical reactions can lead to interconversion of I^-, IO_3^- and Iodine in source waters. Therefore, understanding the co-occurrence of such species is also important to simultaneously understand I^- occurrence. There are no widespread iodate occurrence reports for source waters across the US, with some studies reported for bottled water analyses. Iodate is the thermodynamic stable form of iodide in seawater (Luther, Wu, & Cullen, 1995), yet we lack knowledge of iodate occurrence in untreated drinking waters. IO_3^- is generally considered to be an important component of the human diet as it is rapidly reduced to iodide in the body, and iodide is essential for thyroid function. Snyder, Vanderford, & Rosario-Ortiz, (2000) also present an interesting case where the presence of perchlorate and iodate/iodide can have notable impacts on the thyroid function. Therefore, it also becomes imperative to study associated compounds like perchlorate along with iodate occurrence studies. However, in freshwater, iodide and organo-iodine are favored over iodate (Moran, Oktay, & Santschi, 2002). Likewise, presence of organic iodine from natural and anthropogenic origins may provide additional information on iodine in DWTP sources. As such, this is an important area for future monitoring studies where I^-/IO_3^- ratios may help inform possible sources of iodide in drinking water sources. The lack of information of organic iodine, inorganic I^- and IO_3^- in source and finished waters limits our ability to predict I-DBPs formed during drinking water treatment. Standard ion chromatography methods (e.g., USEPA 300 (Pfaff, 1993)) do not have detection limits suitable to quantify I^- and IO_3^- at occurrence levels likely to occur at WTP intakes. Currently, however, the most conservative approach is to measure total iodine in water (e.g., using ICP-MS), which reflects the maximum available iodide for incorporation into I-DBPs Some of the recent methods include a combination of different speciation methods such as gas chromatography, liquid chromatography, ion chromatography with mass spectrometry (Heumann, Gallus, Radlinger, & Vogl, 1998; Snyder, Vanderford, & Rexing, 2005). Additionally, Gong & Zhang, (2013) have suggested various reaction mechanisms to separate the three species of I^-, IO_3^- and organic iodine from water sample and comparing results with total organic iodine measurements. These studies have been able to reach detection limit close to 0.1 μg/l for each species. Future iodine occurrence studies should use applicable methods to differentiate I^- and IO_3^- from organic iodine compounds.

CHAPTER 5

CONCLUSION

Although I^- concentrations are, in general, much lower than Br^- in natural waters, the toxicity of iodinated DBPs is even higher than their brominated or chlorinated analogues. This should necessitate a better understanding of iodide occurrence in sources of drinking water. This study has tried to provide insights on some of the mechanisms responsible for I- presence in different regions of the country. However, it is beyond the scope of this study to identify the share of each mechanism responsible for I^- presence for every location available in the database. The study concludes that there is an overall declining trend in the median concentration of I^- from 1990-2017 mainly due to advancement in analytical methods for I^- detection and also due to variability in data availability. The synthesis presented has tried to connect various geological features, for which literature is available, yet, these formations may also be impacted by anthropogenic sources for which geological data is sparse. Some states lack iodide data, particularly along the eastern portion of the US, and few databases contain temporal iodide sampling, creating difficulties in understanding the sensitivity of iodide occurrence towards time-varying local, tidal influenced, geological and anthropogenic factors. For example, hydraulic fracturing—a process for extracting oil and natural gas that came to prominence in late 2000s—is known to change the geochemistry of local waters. Waters impacted by specific saline geological formations, coastal belts experiencing sea-water intrusion, municipal wastewater effluents and disposal of industrial effluents such as oil/gas produced water and dairy wastewater also contain higher amounts of iodide.

Future I^- occurrence studies should focus on these wastewaters and their impact on natural I^- sources, particularly when they contribute as DWTP sources. A lot of contaminants of emerging concern have been put under scrutiny via Unregulated Contaminant Monitoring Rule 4 (UCMR 4). We recommend that future UCMR studies should also include monitoring Total Iodine, Iodide and Iodate to further understand the I-DBP formation potential in drinking water sources. Also, I-DBPs must be prioritized not only based on their toxicity to human health but also their relative occurrence post-disinfection process. This will be important to focus on drinking water sources that particularly meet the criteria of such I-DBP formation further informing the remediation approaches.

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