

## Lithium occurrence in drinking water sources of the United States

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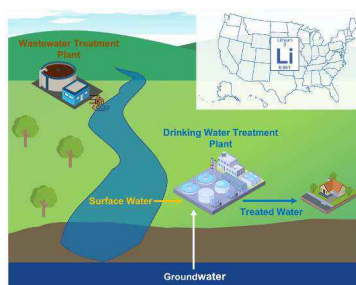
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### HIGHLIGHTS

- 56% of groundwater and 13% of surface samples collected from DWTP source waters had lithium above the HBSL (10 µg/L).
- Sodium can serve as an indicator to identify water sources at higher risk for elevated lithium.
- Lithium was not removed by conventional drinking water treatment processes.
- From a public database, about 60% of potentially suitable drinking water sources had lithium above 10 µg/L.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Lithium (Li) is listed in the fifth Unregulated Contaminant Monitoring Rule (UCMR 5) because insufficient exposure data exists for lithium in drinking water. To help fill this data gap, lithium occurrence in source waters across the United States was assessed in 21 drinking water utilities. From the 369 samples collected from drinking water treatment plants (DWTPs), lithium ranged from 0.9 to 161 µg/L (median = 13.9 µg/L) in groundwater, and from <0.5 to 130 µg/L (median = 3.9 µg/L) in surface water. Lithium in 56% of the groundwater and 13% of the surface water samples were above non-regulatory Health-Based Screening Level (HBSL) of 10 µg/L. Sodium and lithium concentrations were strongly correlated: Kendall's  $\tau > 0.6$  ( $p < 0.001$ ). As sodium is regularly monitored, this result shows that sodium can serve as an indicator to identify water sources at higher risk for elevated lithium. Lithium concentrations in the paired samples collected in source water and treated drinking water were almost identical showing lithium was not removed by conventional drinking water treatment processes. Additional sampling in wastewater effluents detected lithium at 0.8–98.2 µg/L (median = 9.9 µg/L), which suggests more research on impacts of lithium in direct and indirect potable reuse may be warranted, as the median was close to the HBSL. For comparison with the study samples collected from DWTPs, lithium concentrations from the national water quality portal (WQP) database were also investigated. Over 35,000 measurements were collected from waters that could potentially be used as drinking water sources ( $\text{Cl}^- < 250$  mg/L). Data from WQP had comparable median lithium concentrations: 18 and 20 µg/L for surface water and groundwater, respectively. Overall, this study provides a comprehensive occurrence potential for lithium in US drinking water sources and can inform the data collection effort in UCMR 5.

**Abbreviations:** Li, Lithium; DWTP, Drinking water treatment plant; WWTP, Wastewater treatment plant; HBSL, Health-Based Screening Level; MDL, Method detection limit; WQP, Water quality portal.

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## 1. Introduction

The United States Environmental Protection Agency (USEPA) lists lithium (Li) in the fifth Unregulated Contaminant Monitoring Rule (UCMR 5) (USEPA, 2021a) and the 2021 Draft Fifth Contaminant Candidate List (CCL5) (USEPA, 2021b), signifying that lithium occurrence is a data gap for potential future drinking water rule or regulation development. Lithium is the 30th most abundant element with concentrations of 0.002–0.006 wt% in the Earth's crust primarily in rocks and mineral sediments (Aral and Vecchio-Sadus, 2011; Bradley et al., 2017b). Due to its low specific gravity, heat resistance, and electrochemical properties, commercial/industrial interest exists for lithium as a commodity, with a primary end use in batteries (71% of global market) followed by ceramics and glass industry (14%) (USGS, 2021). The growth of renewable energy technologies has increased lithium production. Global lithium demand is projected to increase more than 10-fold from 0.056 million tons (Mt) in 2020 to 0.6–1.5 Mt in 2050 (Greim et al., 2020; USGS, 2021; Xu et al., 2020). This dramatic lithium market growth raises concerns of human exposure to lithium. For example, a recent study by Choi et al. noted a 6-fold lithium increase in a drinking water source in Seoul that received wastewater effluents from municipal, hospitals, and industrial sources (Choi et al., 2019).

Lithium is used as a human therapeutic. For example, it is prescribed to treat bipolar disorder (Cipriani et al., 2013). Studies have shown inverse relationships between consumption of trace lithium in drinking water with suicide (Barjasteh-Askari et al., 2020; Ishii and Terao, 2018), depression, violent crime rates, or incidence of dementia and Alzheimer disease (Kessing et al., 2017). However, human health concerns also exist. Long-term lithium exposure via drinking water was reported to potentially disrupt thyroid function in a study conducted in Puna region in Argentina where local lithium in drinking water ranged from 8 to 1,005 µg/L (Broberg et al., 2011). Lithium in drinking water is not regulated in the United States (US), but the United States Geological Survey (USGS) in collaboration with USEPA provides a non-regulatory Health-Based Screening Level (HBSL) of 10 µg/L, which sets a human health context for lithium in drinking water sources (Norman et al., 2018).

Lithium occurrence data analysis has largely been limited to groundwater. Using data collected in the US from 1984 to 1986, lithium was detected in ~55% of the surveyed public water systems (PWSs), with lithium concentrations ranging from 5 to 7,929 µg/L (USEPA, 2009). A recent USGS publication found lithium in groundwater used for drinking water supplies ranged from <1 to 396 µg/L in public supply wells and <1–1,700 µg/L in domestic supply wells (i.e., private wells) for data collected from 1991 to 2018 (Lindsey et al., 2021). In contrast to groundwater sources, there is limited information about lithium in surface water. The limited occurrence data that are available reported typical background lithium ranges from 0.07 to 40 µg/L in freshwater (Aral and Vecchio-Sadus, 2008).

This paper reports new measurements and statistical analysis of publicly available databases for lithium occurrence in drinking water sources (both surface water and groundwater) in the US. This study aims to complement and inform the lithium data collection effort in UCMR 5 planned for 2023–2025 at PWSs. Field samples from this study were collected from 21 drinking water utilities across the country and analyzed for lithium along with 33 other elements. In addition, because drinking water sources may be impacted by de-facto reuse from upstream wastewater effluents, lithium in tertiary wastewater effluents from 6 municipal wastewater utilities were explored. Finally, lithium data in publicly available databases of surface water ( $n = 74,567$ ) and groundwater ( $n = 57,186$ ) were interpreted for the relevance to drinking water. The paper addresses the following research questions: (i) what is the lithium concentration and geographical distribution in drinking water sources in the US? (ii) Do correlations exist between lithium and frequently measured water quality parameters in drinking water sources? and (iii) is lithium removed by drinking water treatment processes?

## 2. Materials and methods

### 2.1. Source water sampling and analysis

A U.S.-based survey was conducted at 21 public drinking water utilities across 9 states. The utilities were selected based on their geographic location (to cover different regions in the US), types of source water (river, lake, groundwater wells) and their willingness to participate in this program. Detailed information about the utility locations and types of source water, selection criteria, and potential risk factors are summarized in Table S1 in the *Supplementary Information* (SI). Most of these utilities owned more than one drinking water treatment plants (DWTPs) located at different sites, and consequently, multiple source waters were used for drinking water supplies. For these utilities, all the source waters were sampled. In total, 369 water samples were collected from 40 surface water and 42 groundwater sources. These samples are referred to as *study samples from DWTPs* in the following sections. Because limited data is available for lithium in wastewater treatment plants (WWTP) effluents, 33 tertiary wastewater effluent samples were collected from 8 WWTP effluents in 6 municipal WWTP utilities. For privacy reasons, participating utilities agreed to collect samples only if their identity was protected. Therefore, DWTP lithium data are represented in USEPA regions to maintain anonymity of the utility.

Currently, the literature lacks data on seasonal or other temporal trends in lithium concentrations in drinking water sources. Therefore, this study aimed to obtain the first dataset on possible annual variation in lithium concentrations in drinking water sources by sampling across multiple months for one year. Surface water sources were sampled at least 5 times between August 2018 and March 2020 to capture potential seasonal variations. The seasonal variations included capture of flow variations across different precipitation seasons, including low flow conditions during summer and fall periods and generally higher precipitation and streamflow in winter and spring for river-based sources. Although, different watersheds may have dry, average, or wet years, site specific in-stream flow correlations with lithium concentrations were not part of this study. Groundwater sources were sampled at least twice within one year over a period between August 2018 and December 2019. Wastewater effluents were sampled four times within a month (2 weekdays + 2 weekend days) between September 2019 and January 2020. It is to be noted that continuous monitoring of source waters to understand long-term seasonal variation was not the scope of this work, and future studies can expand our understanding of lithium occurrence in various seasons, and precipitation years (wet year, dry year and/or average year) in specific watersheds. Finally, three paired samples of source and treated water at three DWTPs were sampled (once in August 2021) to investigate whether lithium was removed during water treatment processes. These samples were from UD-4 (1 surface water source) and UD-5 (1 surface water + 1 groundwater), where lithium in the source waters was detected above the HBSL.

All the 369 samples were collected by the utility personnel and shipped in ice-packed coolers and received within 48 h of sample collection. Samples were filtered through 0.45 µm nylon syringe filters in the lab. Dissolved lithium and co-existing elements and anions were then analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC), respectively. Detailed analytical methods are summarized in the SI. The method detection limit (MDL) of ICP-MS for lithium was 0.5 µg/L. The concentration of lithium and other constituents that were not detected was set to half the detection limit before doing statistical analysis.

### 2.2. Data collection from publicly available databases

To provide guidance to the expected ranges that will likely be experienced during UCMR sampling, our data from 21 DWTPs provide important data to supplement thousands of groundwater and surface

water samples from the National Water Quality Monitoring Council's (NWQMC) Water Quality Portal. The Water Quality Portal (WQP) is a collection of water quality data collected by the USGS, USEPA, and the NWQMC combined from over 400 state, federal, tribal, and local agencies. In total, 134,446 lithium samples were available from the WQP, including 74,567 surface water and 57,186 groundwater samples across 44,166 locations (8,626 surface water + 35,540 groundwater). The data in these databases had been collected for various reasons and do not necessarily represent drinking water sources. Using a similar approach applied previously in a nationwide assessment of iodide and bromide (Sharma et al., 2019), a cutoff of 250 mg/L of chloride ( $\text{Cl}^-$ ), the secondary MCL set by USEPA, was used to identify as subset of water bodies that may potentially act as drinking water sources. WQP database used a wide variety of analytical techniques for measuring lithium concentrations in water samples. Since 1980, ICP-MS and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) based analytical methods have become the preferred analytical approach for lithium analysis (Houk et al., 1980). Therefore, only data acquired after 1980 were used to achieve recent and higher accuracy data. Paired  $\text{Cl}^-$  and lithium collected after 1980 was available for 49,918 data points, and the subset database (with  $\text{Cl}^- < 250$  mg/L) contained 36,158 data points (7,629 surface water + 28,529 groundwater) across 18,766 monitoring locations (937 surface water + 17,829 groundwater). These samples are referred to as *samples from WQP database*. Details about WQP data handling are presented in the SI.

### 2.3. Statistical analysis

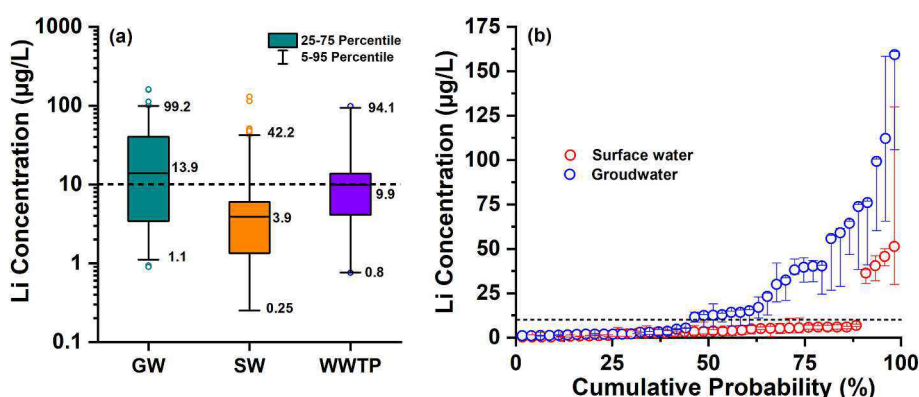
Statistical analyses were conducted using Statistical Package for the Social Sciences (SPSS) version 27. Non-parametric Kendall's tau ( $\tau$ ) rank correlation was used to evaluate the associations between lithium and coexisting elements, anions, and conductivity. Kendall's  $\tau$  measures the strength and direction of association (or monotonic relationship) that exists. Because p-values calculated for large samples tend to be near zero, a certain p-value was not set for the correlation test; meanwhile, 95% confidence intervals were reported. Ten of the 33 elements (*i.e.*, Be, Ge, As, Se, Ag, Cd, Ce, Gd, Tl, and Pb) were measured below MDL in more than 50% of the surveyed samples, therefore, these elements were excluded in the bivariate correlation test.

## 3. Results and discussion

### 3.1. Lithium in 21 public drinking water utilities

#### 3.1.1. Lithium occurrence and distribution

Fig. 1a shows lithium occurrence and distribution in DWTP source waters and WWTP effluents. Table S2 summarizes lithium occurrence statistics, and Fig. S1 plots the cumulative lithium concentration distribution. Lithium in 23 samples was below the detection limit (0.5  $\mu\text{g/L}$



**Fig. 1.** Lithium distribution in 369 study samples collected from drinking water treatment plant (DWTP) source waters and 33 samples collected from tertiary wastewater effluent. (a) Box and whisker plots of lithium occurrence in groundwater (GW) and surface water (SW) used as drinking water source, and in municipal wastewater treatment plant (WWTP) effluents; (b) lithium distribution in the source waters. Since each site was sampled multiple times, the symbols show the median lithium concentration, and the bars denote the range of lithium concentration. Dashed line indicates 10  $\mu\text{g/L}$  non-regulatory Health-Based Screening Level.

L), and all of them were surface water samples. These samples account for 9% of the surface water samples and 6.2% of all samples collected from drinking water sources. In groundwater, lithium ranged from 0.9 to 161.1  $\mu\text{g/L}$  (median = 13.9  $\mu\text{g/L}$ ), and 56% of the samples exceeded the HBSL of 10  $\mu\text{g/L}$ . In surface water samples, lithium ranged from <0.5 to 129.9  $\mu\text{g/L}$  (median = 3.9  $\mu\text{g/L}$ ), and 13% were above the HBSL. Overall, detectable levels of lithium occurred in 80 of the 82 source waters. Fig. 1b shows cumulative frequency distribution plots for surface and groundwater data. The median lithium concentration in 55% of the groundwater sources (23 of 42 source waters) were above the HBSL, with three source waters had median lithium more than 10 times higher than the HBSL. Only 10% of the surface water sources (4 of 40 source waters) had median lithium concentration above the HBSL. The results show that groundwater sources generally had higher lithium than surface water sources. This is likely due to the elevated concentrations of total dissolved solids in groundwater comparing to those in surface water, and groundwater is one primary source of lithium in surface water. The dilution in streams warrants this discussion.

Fig. 2 shows the spatial distribution of lithium in the source waters. Water samples collected in the eastern US along the Ohio River, Cape Fear River, and Alafia Rivers contained <5  $\mu\text{g/L}$  in both surface water and groundwater. The highest lithium concentration (*i.e.*, outliers in Fig. 1a) were observed in the southwest US (Arizona, Nevada, and Texas). Elevated lithium has been attributed to geological deposits of granitic, lithium-cesium-tantalum (LCT) pegmatites (primary mineral source of Li) and lithium brine deposits, which are prominent in southwest US (Bradley et al., 2017a). In addition, all these sites were in the regions with arid and semi-arid climates. Prior work showed a positive correlation between aridity and lithium concentrations in groundwater used for drinking water supply in the US (Lindsey et al., 2021). The authors explain that lithium in groundwater originates through mineral dissolution, cation exchange, and evaporation of rainwater. Soluble lithium containing minerals are more likely to have been depleted by the larger amount of water flow in humid region, while these minerals may persist arid climates. Furthermore,  $\text{Li}^+$  adsorbed on minerals and clays is readily displaced by other cations, as a result, cation exchange generally liberates lithium from solids (Appelo, 1994; Decarreau et al., 2012). Details about cation exchange processes are discussed in the next section. Finally, low precipitation and high evaporation rates concentrate lithium in arid regions through evaporative enrichment (Araoka et al., 2013).

Treated wastewater effluents upstream of drinking water treatment plants can contribute up to 13% (during average flow conditions) to over 80% (during lower streamflow conditions) of treatment plant intake (Nguyen et al., 2018). Limited data exist for lithium occurrence in wastewater effluents. A prior detailed study on Ankeny WWTP, Iowa noted lithium concentrations ranging between 10 and 20  $\mu\text{g/L}$  (Barber et al., 2011; Keefe et al., 2019). Therefore, lithium in 33 samples collected from WWTP effluents were measured to inform its potential

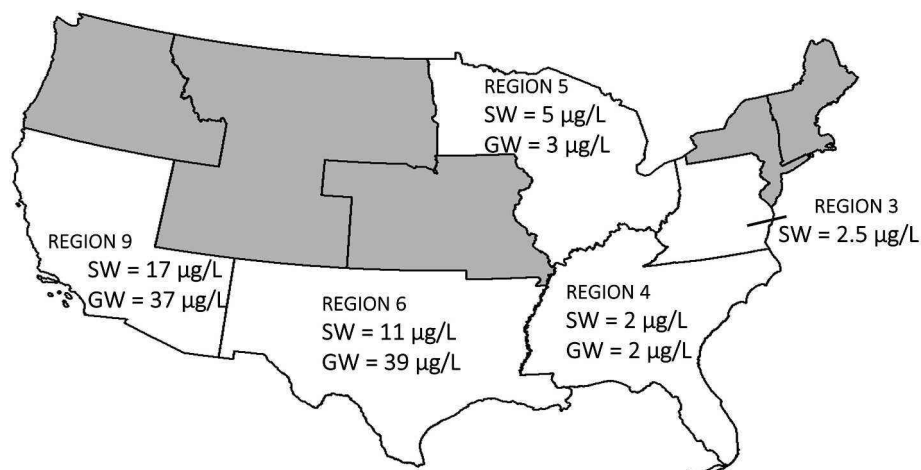


Fig. 2. Lithium distribution in the study samples collected from surface water (SW) and groundwater (GW) that used as drinking water sources in DWTPs. Data were shown based upon USEPA region. The numbers denote median lithium in the region along with concentration range (in µg/L) and number of samples collected (n).

impact on drinking water sources. The results show lithium ranged from 0.8 to 98.2 µg/L (median = 9.9 µg/L). No significant difference was found in lithium concentration between weekdays and weekends during the one-month sampling events, indicating consistent lithium composition in wastewater discharges. Overall, lithium concentrations in WWTP effluents were comparable with that observed in the study samples collected from groundwater ( $p = 0.07$  of z-test); on the other hand, lithium in WWTP effluents was higher than that in surface water samples collected from DWTPs ( $p = 0.02$  of z-test). The results show that WWTP effluents may contribute some additional lithium to surface water sources.

### 3.1.2. Correlations between lithium and other chemical parameters

Kendall's rank correlation was used to test correlations between lithium and common drinking water components (i.e., conductivity, concentrations of co-existing anions and elements). The test results are shown in Fig. 3. Detailed information about correlation coefficients ( $\tau$ ), 95% confidence intervals, and p-values are summarized in Table S3. Strong positive correlations ( $\tau > 0.5$ ) exist between lithium and conductivity,  $\text{Cl}^-$ , fluoride ( $\text{F}^-$ ), sodium (Na), calcium (Ca), magnesium

(Mg), boron (B), barium (Ba), strontium (Sr), and molybdenum (Mo) in surface water. In groundwater, strong positive correlations exist between lithium and Na, potassium (K), and bromide ( $\text{Br}^-$ ), which is consistent with the results from PCA analysis reported in a prior work studying lithium in groundwater in the US (Lindsey et al., 2021). These associations are summarized in Figs. S3 and S4.

Sodium concentrations showed strong positive correlations with lithium concentrations in both surface water ( $\tau = 0.63$ ) and groundwater ( $\tau = 0.64$ ). Sodium commonly coexists with lithium in major lithium sources in the nature (Grew, 2020). For example, lithium brines contain large quantities of NaCl (Bowell et al., 2020; Huang et al., 2021); sodium is also a major component in common lithium-bearing minerals (e.g., elbaite and Neptunite) (Grew, 2020). More importantly, sodium and lithium behave similarly in natural water. Both alkali metals are extremely soluble in water, they tend to stay in solution during weathering of rocks. One study on the leaching of lithium from lacustrine sediment and evaporite deposit reported that both lithium and sodium were leached from the samples in neutral pH water, in contrast, other elements (e.g., magnesium and iron) remained in the solid phase (Araoka et al., 2013). Also, these two elements have similar behavior in

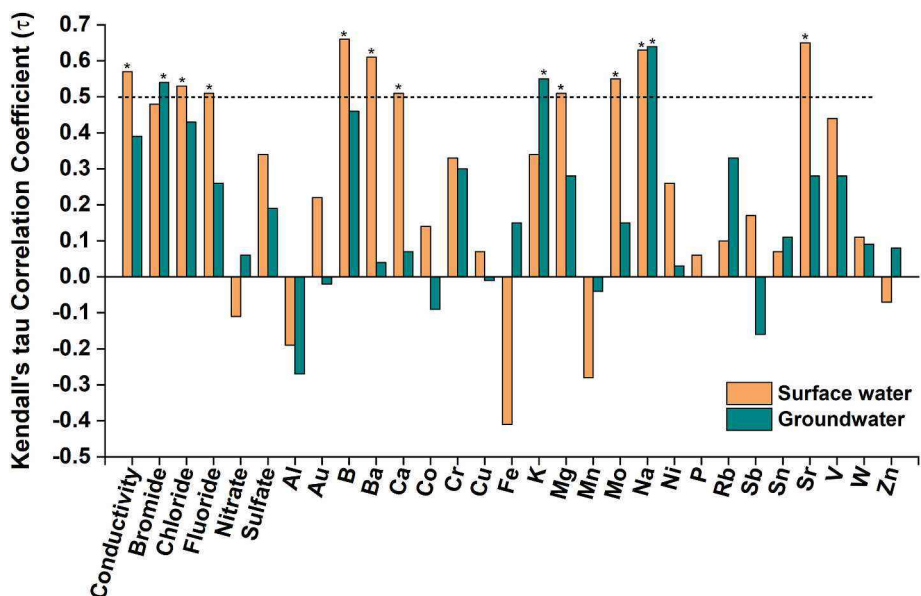


Fig. 3. Kendall's tau rank correlation between lithium and co-existing elements and anions in the study samples from DWTPs. In this work,  $|\tau| > 0.5$  is interpreted as strong correlation as denoted by the symbol “\*”. Only the elements with detection frequency  $>50\%$  in the water samples were considered.

cation exchange. Although both  $\text{Li}^+$  and  $\text{Na}^+$  are monovalent cations,  $\text{Li}^+$  generally does not substitute for  $\text{Na}^+$  in minerals because of ionic size differences (Starkey, 1982). Rather,  $\text{Li}^+$  commonly substitutes for  $\text{Mg}^{2+}$  in the structure of various silicates, leading to a negative charge imbalance (e.g., hectorite) (Decarreau et al., 2012).  $\text{Li}^+$ ,  $\text{Na}^+$ , and other cations are attracted to negatively charged minerals (exchangeable cations) and offset the negative charge. Compared to structural cations, the exchangeable cations are readily displaced to solution, with  $\text{Li}^+$  and  $\text{Na}^+$  being the weakest bound. Therefore, cation exchange processes tend to remove  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from solution, while liberating  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Li}^+$  from solids (Appelo, 1994; Decarreau et al., 2012). The strong correlation between sodium and lithium in the dataset presented herein is consistent with cation exchange as a primary source of those elements (Lindsey et al., 2021).

Lithium in natural water is strongly correlated with sodium. Since sodium is monitored and reported regularly by public water utilities, we propose that sodium can be used as an indicator to predict lithium in source waters. Regression models were built to correlate lithium and sodium concentrations in the study samples collected from DWTPs. As shown in Fig. 4,  $\text{Log}(\text{Li}, \mu\text{g/L}) = 0.74\text{Log}(\text{Na}, \text{mg/L}) + 0.84$ ,  $R^2 = 0.7$  in surface water;  $\text{Log}(\text{Li}, \mu\text{g/L}) = 0.64\text{Log}(\text{Na}, \text{mg/L}) + 0.87$ ,  $R^2 = 0.7$  in groundwater. In addition, mass concentration ratios of lithium to sodium ( $\text{Li}/\text{Na}$ ) were calculated and are summarized in Fig. S5.  $\text{Li}/\text{Na}$  ratio may be a useful parameter for screening whether there is additional source contribute to elevated lithium in source waters.  $\text{Li}/\text{Na}$  ratios ranged from  $2.3 \times 10^{-5}$  to  $8.5 \times 10^{-4}$  with a median of  $2.3 \times 10^{-4}$  in surface water; and  $5.2 \times 10^{-5}$  to  $1.3 \times 10^{-3}$  with a median of  $3.2 \times 10^{-4}$  in groundwater. The median  $\text{Li}/\text{Na}$  ratios in the surveyed source waters were higher than seawater (about  $1.4 \times 10^{-4}$ ) but lower than those reported in processed water from oil & gas production ( $4.9 \times 10^{-4}$ ) and geothermal water ( $5.4 \times 10^{-3}$ ) (Blondes et al., 2018). Due to its similar mobility with sodium, lithium is expected to be carried to the sea by rivers and enriched in the oceans the same way as with sodium (Bolan et al., 2021; Bradley et al., 2017b; Pogge von Strandmann et al., 2016). However, lithium is sequestered from seawater into clay minerals that accumulate in sea-floor oozes (Bradley et al., 2017b; Pogge von Strandmann et al., 2020), leading to its depletion relative to sodium in seawater compared to continental waters.

Besides sodium, lithium was also positively correlated with other elements as shown in Table S3 and Figs. S3 and S4. Elements such as B, Br, Ca, Cl, K, Mg, and Sr are commonly found in lithium brines and geothermal water (Pogge von Strandmann et al., 2016; Tan et al., 2012; Tan et al., 2018). Potassium is also a major component in one most important lithium mineral lepidolite. No correlations were found between lithium and trace metals (e.g., Co, Cu, and Ni), which are indicators of lithium from anthropogenic sources (e.g., Li-based industry

leachate) (Calvert et al., 2019). Gadolinium (Gd), a tracer of urban wastewater (Verplanck et al., 2005), was below the MDL in all the samples, thus it could not be correlated with lithium or used to assess potential contributions of WWTP to downstream DWTP sources. Overall, the results indicated lithium in the source waters was mainly from natural sources, and lithium increased with water-rock interaction.

### 3.1.3. Lithium removal during water treatment

Lithium in the source waters sampled from DWTPs ranged from  $<0.5 \mu\text{g/L}$  to  $>100 \mu\text{g/L}$  (Fig. 1). To screen whether DWTPs removed lithium, three paired samples (source and treated waters) were collected from three DWTPs. Grab samples were not flow-weighted or matched with hydraulic residence time. However, the utility did not note any unusual hydrologic events on the day of sampling which would suggest that lithium concentrations may vary over short (hourly) timescales. Table S4 shows only 8% of the lithium was removed after treatment processes (from 120 to 110  $\mu\text{g/L}$ ) in the samples taken from UD-4. For the samples taken from UD-5, lithium concentrations remained the same (about 47  $\mu\text{g/L}$ ) after treatment. The screening data provide initial evidence that the currently applied drinking water treatment processes at these sampled DWTPs are not effective in removing lithium. This agrees with a nationwide study that compared lithium in source water and treated water from 25 PWSs (Glassmeyer et al., 2017). Because lithium is conserved across DWTPs, residents in regions with elevated lithium in the source waters could be exposed chronically to lithium above the HBSL in their drinking water. Results also suggest that water treatment plant chemicals are unlikely to add any lithium to treated waters. Thus, lithium in source water appears to be a reasonable estimate for human exposures in drinking water.

### 3.2. Lithium in potentially relevant drinking water sources from publicly available database

The WQP database was used to expand the coverage from the nationwide source water survey. Figs. 5a and 5b show the spatial distributions of lithium for surface water and groundwater using all WQP database values, respectively. Additionally, Figs. 5c and 5d plot a subset of the WQP database where the water quality could potentially be suitable as a drinking water source (i.e., sources with  $\text{Cl}^- < 250 \text{mg/L}$  and post 1980; only 27% of the WQP database sources met these criteria). Lithium data in sources potentially-suitable as drinking water was available in 47 states for groundwater sources (Fig. 5d) but only available in 9 states for surface water sources (Fig. 5c). Lithium ranged from  $<1 \mu\text{g/L}$  to 2,500  $\mu\text{g/L}$  in surface water sources and up to 290,000  $\mu\text{g/L}$  in groundwater sources (Fig. S1b). And 58% of the potentially relevant drinking water sources exceeded the recommended HBSL. Although the

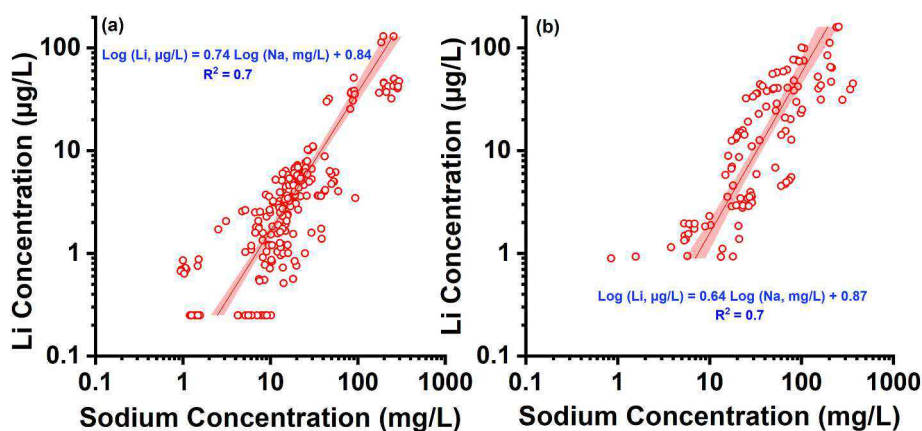
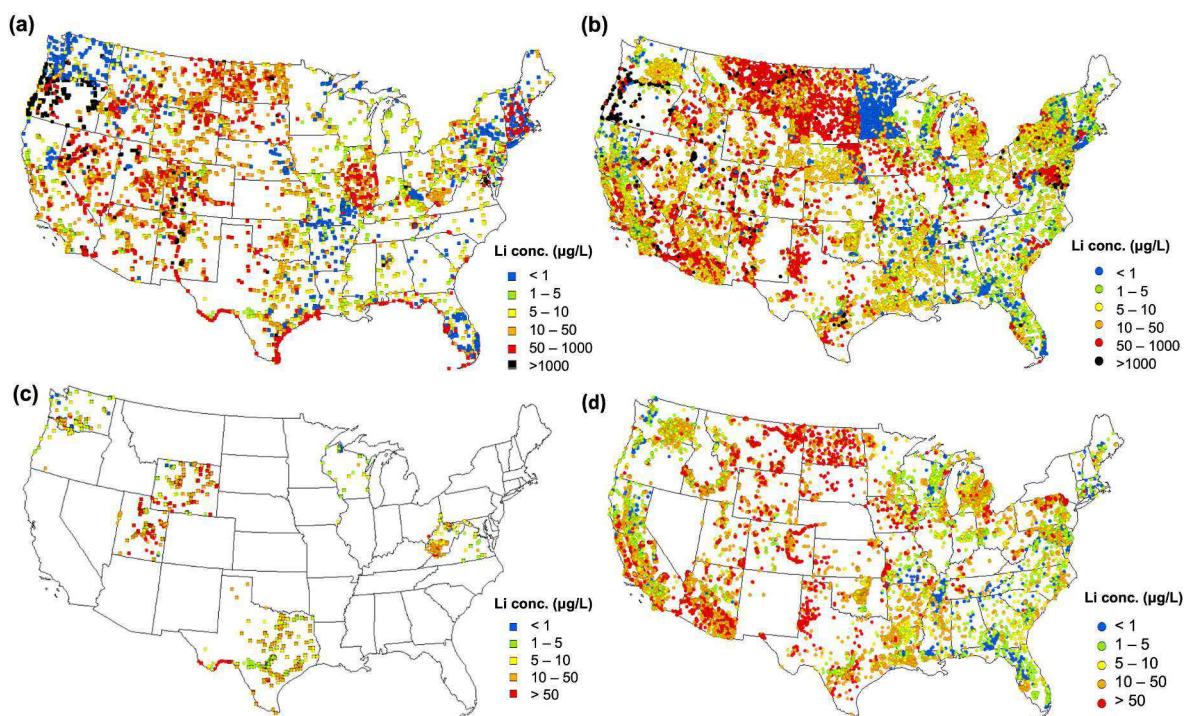


Fig. 4. Correlations between lithium and sodium in the study samples collected from DWTP source waters: (a) surface water; (b) groundwater. Linear regression of lithium concentration with sodium is applied. The fitted formula and correlation coefficient ( $R^2$ ) are provided in the figure. The highlighted area shows 95% confidence interval of the regressions.



**Fig. 5.** Spatial distribution of lithium from the entire WQP database: (a) surface water and (b) groundwater. The subset of WQP database that is potentially-suitable as drinking water sources (with  $\text{Cl}^- < 250$  mg/L, the secondary MCL set by USEPA, and data collected post 1980): (c) surface water and (d) groundwater. Average lithium concentration was used for locations with multiple data point.

maximum and 95th percentile concentrations in the WQP database were 3–20 times greater than those in the drinking water sources surveyed in this study, the median concentrations (13 µg/L in both surface water and groundwater) were in the same order of magnitude (3.3 and 0.9 times higher for surface water and groundwater, respectively) compared to the surveyed source waters. Therefore, the WQP database helps add valuable lithium information where data is sparse. For example, the publicly available databases fill lithium data gaps in USEPA Regions 8 and 10. Median lithium in potentially-relevant drinking water sources were 26.8 µg/L in Region 8 and 5 µg/L in Region 10 (range: 1–2500 µg/L) in surface water; and 43 µg/L in Region 8 and 10 µg/L in Region 10 (range: 1–80,000 µg/L) in groundwater.

#### 4. Conclusions

Lithium in 56% of the groundwater and 13% of the surface water samples from the surveyed DWTP source waters were above the HBSL of 10 µg/L, with a few sites had lithium more than 10 times higher than the HBSL. From the WQP database, approximately 60% of *potentially-suitable drinking water sources* (i.e.,  $\text{Cl}^- < 250$  mg/L) had lithium above the HBSL. Lithium is a conservative element in the natural environment, and more importantly, it is not removed by currently used drinking water treatment processes. Although the pharmacological effects of lithium have been widely studied, limited information is available about the health effects stemming from long-term exposure to trace levels of Li. Our groundwater analysis builds on prior work, and the main contribution herein relates to surface water, which provide roughly 60% of the total drinking water public supply in the US (Dieter et al., 2018). We observed strong positive correlation between Na and Li, indicating that Na can be used to help site selection for lithium surveys.

#### Author contribution

Naushita Sharma: Conceptualization, Methodology, Software, Formal analysis, Investigation, Data curation, and Writing – Original

Draft. Paul Westerhoff: Conceptualization, Resources, Writing – review & editing, Supervision, and Funding acquisition. Chao Zeng: Conceptualization, Software, Formal analysis, Investigation, Data curation, Writing -Original Draft, Writing – review & editing, and Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.135458>.

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