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Lithium in groundwater used for drinking-water supply in the United States

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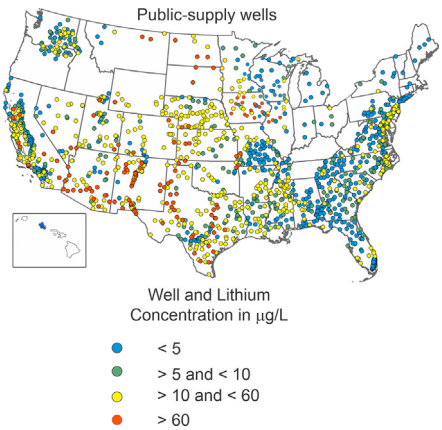
HIGHLIGHTS

- Lithium in groundwater has not been comprehensively evaluated in the US.
- Concentrations in groundwater frequently exceed the human-health benchmark.
- The distribution of lithium concentrations varies widely by lithology and climate.
- Higher lithium concentrations are found in arid regions and older groundwater.
- Cation exchange or mixing with saline water lead to highest concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium concentrations in untreated groundwater from 1464 public-supply wells and 1676 domestic-supply wells distributed across 33 principal aquifers in the United States were evaluated for spatial variations and possible explanatory factors. Concentrations nationwide ranged from <1 to 396 µg/L (median of 8.1) for public supply wells and <1 to 1700 µg/L (median of 6 µg/L) for domestic supply wells. For context, lithium concentrations were compared to a Health Based Screening Level (HBSL, 10 µg/L) and a drinking-water only threshold (60 µg/L). These thresholds were exceeded in 45% and 9% of samples from public-supply wells and in 37% and 6% from domestic-supply wells, respectively. However, exceedances and median concentrations ranged broadly across geographic regions and principal aquifers. Concentrations were highest in arid regions and older groundwater, particularly in unconsolidated clastic aquifers and sandstones, and lowest in carbonate-rock aquifers, consistent with differences in lithium abundance among major lithologies and rock weathering extent. The median concentration for public-supply wells in the unconsolidated clastic High Plains aquifer (central United States) was 24.6 µg/L; 24% of the wells exceeded the drinking-water only threshold and 86% exceeded the HBSL. Other unconsolidated clastic aquifers in the arid West had exceedance rates comparable to the High Plains aquifer, whereas no public supply wells in the Biscayne aquifer (southern Florida) exceeded either threshold, and the highest concentration in that aquifer was 2.6 µg/L. Multiple lines of evidence indicate natural sources for the lithium concentrations; however, anthropogenic sources may be important in the future because of the rapid increase of lithium battery use and subsequent disposal. Geochemical models demonstrate that extensive

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evaporation, mineral dissolution, cation exchange, and mixing with geothermal waters or brines may account for the observed lithium and associated constituent concentrations, with the latter two processes as major contributing factors.

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1. Introduction

Lithium is a potential concern for human health. Previous studies, as discussed in the following sections, have reported potential pharmacological and health effects of lithium in drinking water. Other studies, also discussed in the following sections, have reported the natural and anthropogenic sources of lithium in groundwater. Presently there are no regulatory thresholds for lithium in the United States (U.S.). The purpose of this paper is to: (1) evaluate the concentrations observed in groundwater in the U.S., (2) put those concentrations into a human-health context, and (3) identify environmental factors and potential geochemical processes to help explain the observed lithium concentrations.

1.1. Potential pharmacological effects of lithium in drinking water

The pharmacological effects of lithium are well documented. Lithium is prescribed for the treatment of bipolar disorder (Mitchell and Hadzi-Pavlovic, 2000) with daily therapeutic doses, for a 70 kg individual, ranging from 85 to 170 mg (GlaxoSmithKline, 2003). A meta-analysis of clinical trials concluded that lithium is also an effective treatment for reducing suicide risk in people with mood disorders (Cipriani et al., 2013). However, lithium toxicity occurs at levels close to therapeutic doses (GlaxoSmithKline, 2003; U.S. Environmental Protection Agency, 2008). If a 70-kilogram individual drinks 2 L of water per day, the concentration in water would need to be 42.5 mg/L (42,500 μg/L) in order to ingest 85 mg of lithium.

The potential human-health effects of lithium in drinking water have received considerable study. Several studies of drinking water in Texas have indicated an inverse correlation between suicide rates and lithium (Dawson et al., 1972; Schrauzer and Shrestha, 1990; Hudak, 2016; Fajardo et al., 2018); a maximum concentration of 700 μg/L was observed. Several meta-studies have been published compiling results from studies in nine countries on three continents (Ishii and Terao, 2018; Brown et al., 2018; Barjasteh-Askari et al., 2020). These studies note health effects related to lithium in drinking water that include inverse relations with depression, mortality from Alzheimer's, suicide rates, and violent crime rates; with a maximum concentration of 219 μg/L. In a study of women in four Andean villages in northern Argentina, exposure to lithium via drinking water and other environmental sources was found to potentially affect thyroid function (Broberg et al., 2011). Lithium concentrations in the groundwater in that region ranged from 8 to 1000 μg/L (Concha et al., 2010).

1.2. Natural sources of lithium in groundwater

Lithium is the 30th most abundant element in the upper continental crust, similar to the abundance of lead and copper (Turekian and Wedepohl, 1961; Bradley et al., 2017). Abundance varies by lithology, and average concentrations in shales and granitic rocks are 5 to 10 times those in carbonates (Table SI.1, Turekian and Wedepohl, 1961). Lithium is widely occurring as a trace impurity in micas and clays (phyllosilicate minerals), wherein the monovalent lithium cation commonly substitutes for the higher valence cations magnesium, iron, and aluminum (Starkey, 1982). The structural substitution of lithium for higher valence cations in octahedral sites of phyllosilicates results in a negative structural layer charge; exchangeable cations including lithium and sodium, mainly in the interlayer sites, compensate for the negative structural charge (Decarreau et al., 2012).

Lithium may be concentrated in rarely occurring minerals, such as the lithium micas, lepidolite and petalite, and associated aluminosilicates, including spodumene and eucryptite. These minerals can be recovered commercially from granitic pegmatites (Kesler et al., 2012; Bradley et al., 2017). Other economically important sources of lithium include the hydrothermally altered bentonite clay, hectorite, in areas with volcanic activity and associated ash deposits (Rosen et al., 2020; Bowell et al., 2020). Lithium also can be concentrated in and recovered from evaporites and natural brines (Hem, 1985). Elevated concentrations of lithium are associated with brines produced from oil and gas exploration (Dresel and Rose, 2010; Lester et al., 2015; Blondes et al., 2018). The U.S. currently (2020) has only one active mine for lithium, an igneous deposit in Silver Peak, Nevada (U.S. Geological Survey, 2019); however, several western brine and sedimentary rock deposits have potential for commercial development (Bradley et al., 2017; Bowell et al., 2020).

Lithium, in small amounts, is widespread in soils and sediments of the U.S., especially in the arid southwestern region (Shacklette et al., 1973; Smith et al., 2014). Concentrations are generally greatest in hydrologically closed basins where lithium can be concentrated through evaporation, volcanic areas (Cannon et al., 1975; Munk et al., 2016), and in the Appalachian Basin region in the northeast where clays are abundant (Smith et al., 2014). Although lithium in soils may be present as lithium carbonate, lithium chloride, or lithium oxide (Aral and Vecchio-Sadus, 2008), various clay minerals readily incorporate the lithium cation and are a predominant mode of lithium occurrence (Mehlich, 1981; Appelo and Postma, 2005; Starkey, 1982). Adsorbed lithium tends to be a minor component on exchange sites of clays, because other cations of smaller size or greater charge can easily displace the lithium cation from negatively charged solid surfaces to the aqueous phase (Starkey, 1982; Appelo and Postma, 2005). In general, sorption of cations by clays and humus increases in the order Lithium (Li) < sodium (Na) < potassium (K) < hydrogen (H) < calcium (Ca) (Brady, 1974; Mehlich, 1981).

Naturally occurring lithium in groundwater results from the interactions between water and minerals and, locally, from mixing of meteoric water with saline lithium-bearing waters. Rainwater generally has trace concentrations (0.1 to 1.0 μg/L) of lithium (Poissant et al., 1994). Concentrations in meteoric and saline waters can become elevated from evaporation and water-rock interaction (Dresel and Rose, 2010; Meredith et al., 2013; Rosen et al., 2020). Dissolution of lithium minerals and abundant common minerals containing lithium impurities, especially phyllosilicates, are an important source of lithium in groundwater (Appelo, 1994; Meredith et al., 2013; Pogge von Strandmann et al., 2014). Likewise, cation exchange involving clays and zeolites plays a major role in controlling concentrations of lithium in groundwater (Anghel et al., 2002; Russak et al., 2016). For example, a study in Israel by Russak et al. (2016) demonstrated effects of seawater intrusion on lithium retention and subsequent freshening events on mobilization of adsorbed lithium from the same material.

The importance and compositions of saline lithium-bearing waters that might mix with groundwater vary geographically. Continental brines, particularly in areas underlain by oil and gas deposits, can be sources of high concentrations of lithium (Dresel and Rose, 2010; Pfister et al., 2017; Blondes et al., 2018). Geothermal fluids are another potential source of elevated lithium in areas with past or current volcanic activity (Munk et al., 2016; Blondes et al., 2018; Rosen et al., 2020). Compared to brine or geothermal water, seawater has relatively low concentrations of lithium (Hem, 1985). Nevertheless, studies in

Israel (Russak et al., 2016) and Tunisia (Souid et al., 2018) indicate that seawater intrusion in coastal areas can result in direct contributions of aqueous lithium to fresh groundwater and/or the mobilization of exchangeable lithium from the aquifer. Lithium isotopes have been used with modeling to distinguish sources of lithium and identify active water-rock interaction processes, including the mixing of freshwater and saline waters, in Australia (Meredith et al., 2013), Texas (Pfister et al., 2017), and various global settings (Pogge von Strandmann et al., 2020). Seawater, brines, and geothermal fluids collectively are referred to as saline waters hereinafter; as used in this study, seawater refers to premodern in situ seawater trapped in confining layers rather than intrusion from modern seawater.

1.3. Anthropogenic sources of lithium in groundwater

Lithium is used in batteries, ceramics and glass, lubricants, metallurgy, and medicine, and was historically used in production of tritium for nuclear weapons (Aral and Vecchio-Sadus, 2008; Boyden et al., 2016; Bradley et al., 2017). Leachate from waste disposal is one potential source of lithium in groundwater. The concentration measured in leachate from a waste disposal site was reported at 330 μg/L (Kjølholt et al., 2003) and leachate from a nuclear waste facility was 19,000 μg/L (Kszos and Stewart, 2003). Septic systems and sewage treatment plants have been noted as potential sources of lithium excreted from medicinal users into wastewater (Bexfield et al., 2019; Furlong et al., 2017). Synthetic fertilizers from rock phosphates and naturally occurring brines have been identified as contributing to elevated lithium concentrations in soils (Ebensperger et al., 2005; Senesi et al., 2008). Additionally, produced water from oil and gas wells can have extremely high concentrations of lithium (Dresel and Rose, 2010; Blondes et al., 2018). For example, waters from shale gas wells in the U.S. had reported lithium concentrations ranging from 10 to 634,000 μg/L (median 25,000 μg/L) and those from conventional oil and gas wells had concentrations ranging from <10 to 1,730,000 μg/L (median 5000 μg/L) (Blondes et al., 2018). Lithium and associated components of such brines may be accidentally or intentionally released to the surface or groundwater in certain locations (Tasker et al., 2018; McDevitt et al., 2019).

1.4. Concentrations of lithium in groundwater used for drinking supply

Lithium in groundwater used for drinking supply has been evaluated at regional to national scales. Several of these studies were conducted to evaluate the relationship between lithium in groundwater and health effects, including suicide rates. One example is western Texas, where concentrations were as high as 2790 μg/L (Dawson et al., 1972; Hudak, 2016). Large-scale regional or national studies of lithium in groundwater are uncommon, but include studies in Denmark (Knudsen et al., 2017) and Ireland (Kavanagh et al., 2017) where maximum concentrations in groundwater were 31 μg/L (median 10.5 μg/L) and 97 μg/L, respectively. Lithium has been evaluated in studies of tap water or drinking water in Japan (Ohgami et al., 2009), Italy (Pompili et al., 2015), Austria (Helbich et al., 2012), Greece (Giotakos et al., 2013), England (Kabacs et al., 2011) and others; however, these studies did not specify the source of drinking water and are not directly comparable to the current study.

The U.S. Geological Survey (USGS) has reported lithium concentrations as a part of the National Water-Quality Assessment (NAWQA) Project. Toccalino et al. (2010) assembled data from public-supply wells (PSWs) that had been sampled by NAWQA; lithium analyses were available for 458 samples. The PSWs were not distributed across a broad range of conditions because PSWs were not systematically targeted at that time. Concentrations ranged from 1 to 650 μg/L.

Desimone, (2009) evaluated water quality from domestic supply wells (DSWs) sampled by the NAWQA Project. Lithium analyses were available in 662 samples. With the exception of the High Plains principal aquifer, the domestic networks were targeted to relatively small areas within principal aquifers. However, the DSW networks are broadly distributed across the U.S. Lithium concentrations ranged from <1 to 1200 μg/L in domestic-supply wells.

Ayotte et al. (2011), in a study of the occurrence and factors affecting trace elements in groundwater in the U.S., included lithium. Lithium analyses were available for 936 wells. Ayotte et al. (2011) found higher lithium concentrations to be associated with dry regions compared to humid regions, higher in shallow wells in urban areas than shallow wells in agricultural areas, and the lowest concentrations in carbonate and crystalline lithotype groups.

1.5. Thresholds for lithium in drinking water for protection of human health

A statutory threshold for lithium concentrations in drinking water currently (2020) does not exist in the U.S. The U.S. Environmental Protection Agency (EPA) uses three criteria for regulating a contaminant: "(1) The contaminant may have an adverse effect on the health of persons; (2) the contaminant is known to occur or there is substantial likelihood that the contaminant will occur in public water systems with a frequency and at levels of public health concern; and (3) in the sole judgment of the Administrator, regulation of such contaminant presents a meaningful opportunity for health risk reduction for persons served by public water systems" (U.S. Environmental Protection Agency, 2020). The EPA evaluation of occurrence also considers the number and percentage of concentrations in drinking water greater than the health benchmark, geographic distribution of the contaminant, the production use and trends of the contaminant, the types of systems the contaminant occurs in, and the persistence and mobility of the contaminant in water. The results presented in this study are relevant to the EPA criteria concerning occurrence at levels of health concern.

Although a regulatory value is not available, a nonregulatory Health-Based Screening Level (HBSL) of 10 μg/L has been proposed (U.S. Environmental Protection Agency, 2008; Norman et al., 2018). This paper uses the HBSL to provide context for evaluating concentrations of lithium in groundwater. In addition, a value of 60 μg/L, based upon an assumption that the only source of lithium is from drinking water, is also used for context. The HBSL and drinking-water only thresholds are based upon an EPA provisional reference dose of 0.002 mg/kg-day (U.S. Environmental Protection Agency, 2008). The derivation of the thresholds is described in detail in the supplemental information, section 1.1. The Eurasian Economic Union limit for lithium in drinking water is 30 μg/L (Eurasian Economic Union, 2017), but this value is not used to provide context for this study. The World Health Organization has not published limits on lithium in drinking water (World Health Organization, 2017).

1.6. Scope of study

This study evaluates the distribution of lithium in groundwater in the U.S. at the depth zone used for public supply and the depth zone used for domestic supply. These concentrations are placed into the context of human health based on the HBSL and the drinking-water only threshold. Statistical and geochemical modeling approaches are used to identify potential causes of high lithium concentrations. The results presented in this study provide information that can be used in determining the potential need for establishment of statutory contaminant levels and for other studies of the potential effects of lithium on human health. The large data set provided with this study is available for other scientific studies.

2. Methods

2.1. Data sources and analytical methods

This study relies on three extensive data sets collected by the USGS, one for 1464 PSWs, one for 1676 DSWs and one for 1560 monitoring

wells (MWs). Collectively, the PSWs and DSWs represent 33 principal aquifers. The majority of the data used in this study are from a recently completed national-scale study implemented by the USGS National Water-Quality Program (NWQP). Data for PSWs in the California Coastal Basin and Central Valley were compiled from the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP), a cooperative project between the USGS and the California State Water Resources Control Board (Belitz et al., 2003, 2015). The GAMA-PBP used a similar design and the same field and analytical methods as the NWQP. Some of the data from DSWs and MWs used in this study were summarized in earlier phases of the current study (Desimone, 2009; Toccalino et al., 2010; Ayotte et al., 2011); however, nearly all of the PSW data (98%) and about two thirds of the DSW data evaluated herein were not included in any previous interpretive studies. Data used for this paper are available in a USGS data release (Lindsey et al., 2020) and a GAMA-PBP website (Jurgens et al., 2018).

All of the networks were designed using stratified random sampling (Scott, 1990) but generally targeted different depth zones and geographic areas. The PSW, DSW and MW networks differed with respect to the depth zone and the geographic area targeted by the network. Wells selected for sampling in the PSW networks are representative of the depth zone used for public supply; nearly all are public supply wells (94%) and the remaining wells tap the same depth zone of their respective aquifer. The PSWs are broadly distributed across 24 principal aquifers and consequently, the results can be used to estimate the proportion of each aquifer that has high concentrations with respect to constituent benchmarks (Belitz et al., 2010). These aquifers represent 80% of all groundwater used for public supply in the U.S. (Lovelace et al., 2020) and are a source of drinking water for more than 100 million people. Principal aquifers were grouped by lithotype for some of the analysis (U.S. Geological Survey, 2003) (Table SI.2).

The DSW data set used in this study was obtained from 60 networks that are broadly distributed across the U.S. Wells selected for sampling in the DSW networks are nearly all domestic supply wells (80%) and the remaining wells are at a similar depth zone and representative of the resource used for domestic supply. The DSW networks generally targeted sub-regions of 22 principal aquifers that are intensively used for domestic supply (Gilliom et al., 1995). Although the networks are broadly distributed across the U.S., the wells within a network are not broadly distributed across individual principal aquifers. Therefore, the data from the DSWs are representative at the national scale but are not representative of the principal aquifers in which they are located. Consequently, the DSWs are used to evaluate occurrence at the national scale, but not the principal aquifer scale.

The unused shallow MWs (used in this paper only for evaluating factors affecting lithium concentrations) were targeted to characterize groundwater quality in relatively small areas of urban or agricultural land use (Gilliom et al., 1995). The MWs are not used to evaluate occurrence. All three well types are used to evaluate factors and geochemical processes affecting lithium concentrations in groundwater.

Samples were collected prior to disinfection, softening, and other treatment. Each sample was pumped through a 0.45-micron filter into 250-mL acid-rinsed, clear polyethylene bottle, acidified to pH less than 2 with nitric acid, and analyzed for lithium at the USGS National Water-Quality Laboratory, Lakewood, Colorado, using Inductively Coupled Plasma-Mass Spectrometry (Garbarino, 1999). The lowest long-term method detection limit was 0.15 μg/L, which is also the lowest reporting level. However, the highest reporting level was 1 μg/L, so for statistical summaries, all nondetections and detections less than 1 are referred to as 'less than 1 μg/L.' All 340 lithium blanks for PSWs and DSWs, were nondetections. For 50 replicates of samples with concentrations between the reporting limit and 20 μg/L, the average difference was less than 0.1 μg/L.

2.2. Statistical methods

Statistical tests were used to evaluate factors affecting lithium concentrations. Potential explanatory factors evaluated include aquifer lithotype (U.S. Geological Survey, 2003), well construction (U.S. Geological Survey, 2016), climate (Zomer et al., 2007, 2008), soil chemistry and mineralogy (Smith et al., 2013, 2014), land use (Falcone, 2015), and groundwater age. Groundwater residence time was categorized as modern (recharged in 1953 or later), premodern (recharged prior to 1953), or mixed (having modern and premodern components) based on tritium concentrations. Measured tritium concentrations are used to assign the group based on the date of sampling and the region of the U.S. where the sample was collected and the term 'age category' is used to describe those groups as per Lindsey et al. (2019). Summaries of selected factors are provided in Table SI.3.

Nonparametric statistical methods were used to evaluate differences in groundwater characteristics. Decadal-scale differences in lithium concentrations were evaluated using the Wilcoxon-Pratt signed-rank test (Pratt, 1959; Lindsey and Rupert, 2012). Statistical significance was evaluated using an alpha value of 0.05. Tukey's test (Tukey, 1977; Helsel et al., 2020) was used for categorical comparisons, and Spearman's rank correlation (Helsel et al., 2020) (Table SI.4) was used for continuous variables. Principal components analysis (PCA) used the Spearman's rank correlation coefficients as input to evaluate multivariate correlations among lithium, other solutes, and system variables (pH, specific conductance, temperature). Details of the PCA methods and results are given in supplemental information (Tables SI.7–SI.8; Figs. SI.2–SI.3).

2.3. Conservative-mixing-models

Conservative-mixing-models were developed to evaluate contributions of lithium, and associated ions, observed in groundwater that could result from rainwater, mixing of water from different sources, and water-rock interactions. The case studies selected for modeling included groundwaters with the lowest (Northern Atlantic Coastal Plain-NACP) and highest (High Plains-HPAQ, Basin and Range basin-fill-BNRF) lithium concentrations.

Conservative-mixing-models were used to evaluate solute concentrations resulting from progressive additions of saline, lithium-bearing waters (seawater, brines or geothermal fluids) to dilute meteoric water. The composition of the meteoric water was indicated by evaporation of rainwater having an initial lithium concentration of 0.2 μg/L (Peters and Bonelli, 1982; Poissant et al., 1994). Lithium and other solute concentrations in the unmixed meteoric water were increased respectively by a factor of 2.5, 5.0, or 10 by evaporating (removing) 60% of the volume in the humid east (NACP), 80% in the semi-arid mid-continent (HPAQ), or 90% in the arid west (BNRF).

Representative compositions of saline lithium-bearing waters used in the mixing models and geochemical models are based on literature values (Tables SI.10–SI.12). For the NACP, seawater had a lithium concentration of 170 μg/L (Hem, 1985). For the HPAQ, western brine that had a median lithium concentration of 6000 μg/L (Blondes et al., 2018) was used based on samples located within the outcrop area of the High Plains. For the BNRF, the geothermal water had a lithium concentration of 2830 μg/L (Blondes et al., 2018).

2.4. Geochemical models

Complementary forward-reaction models developed with PHREEQC (Parkhurst and Appelo, 2013) were used to quantify the relative importance and progressive effects of evaporation, mineral dissolution, cation exchange, and mixing with the representative saline waters as potential sources of lithium. The mineralogical assemblages and cation-exchange parameters specified in the geochemical modeling were identified by model calibration. Model results that were consistent with observed

aqueous compositions and element correlations as identified by PCA were retained. Additional details of the geochemical modeling, including methods, selection of specified fluids and mineral assemblages, and results, are given in the supplemental information (Tables SI.9–SI.14; Figs. SI.4–SI.11).

3. Results and discussion

3.1. Distribution of lithium in groundwater used for drinking-water supply in the United States

Concentrations in PSWs ranged from <1 to 396 μg/L with a median of 8.1 μg/L (Table 1). At a national scale, the HBSL was exceeded in 45% of the samples and the drinking-water only threshold was exceeded in 9%.; however, there are systematic and large differences across the U.S. (Table 1, Fig. 1, Fig. 2). There was at least one exceedance of the HBSL in all but two of the principal aquifers, but the High Plains aquifer had a median concentration of 24.6 μg/L and 86% of the wells exceeded the HBSL (Table SI.5a). Other unconsolidated clastic aquifers in the arid West had exceedance rates comparable to the High Plains aquifer (Fig. 2, Fig. 3). In contrast, no public supply wells in the Biscayne aquifer exceeded either threshold and the highest concentration in that aquifer was 2.6 μg/L.

Concentrations in DSWs ranged from <1 to 1700 μg/L with a median of 6.9 μg/L (Table 1). The HBSL was exceeded in 37% of the samples, with the exceedance rate ranging from 0 to 100% in individual DSW networks (Table SI.5b). Also, at a national scale, the drinking-water only threshold was exceeded in 6% of the DSW samples. The exceedance rates for DSWs are comparable to the exceedance rates in PSWs, a result consistent with a naturally occurring contaminant.

3.2. Statistical evaluation of potential explanatory factors

Comparisons of lithium concentrations by lithotype, climate, and groundwater age categories show statistically significant higher lithium concentrations in western unconsolidated clastic aquifers (median 18 μg/L, Fig. 4a), arid regions (median 21 μg/L, Fig. 4b), and premodern groundwater (median 13 μg/L, Fig. 4c). However, a great deal of interaction exists among these variables.

Groundwater lithium concentrations differ among aquifer lithotypes (Fig. 4a) as expected because of differences in lithium abundance among rock types (Table SI.1). Carbonate rocks are low in lithium and these aquifers have the lowest median concentrations in groundwater (1.9 μg/L). Because aridity covaries with lithotype (Fig. 4a), lithium concentrations were compared among PSWs in four pairs of aquifers located in similar climate regions but differing by lithotype (Fig. 5). Median concentrations are higher in unconsolidated clastic, sandstone, and crystalline-rock aquifers, than in carbonate-rock aquifers; the differences are statistically significant in two of the four pairs. Evaluation of lithium concentrations among subcategories of lithotype groups such as general lithology and rock type was confounded by factors such as aridity, groundwater age, and proximity to geothermal features. Analysis within climate regions showed shale (the rock with the highest lithium abundance) having statistically significant higher lithium concentrations in some of the regions (Fig. SI.1a).

Groundwater lithium concentrations are correlated with lithium concentrations in soil horizons A and C (Table SI.4). The concentrations in soils are correlated with percent total clay, which can be derived from weathering of parent bedrock or from transported alluvial or glacial material (Smith et al., 2013, 2014). However, soil lithium concentrations also can be elevated where clay is a minor component, particularly in arid western regions of the U.S., where lithium may be present in secondary carbonate, borate, chloride, and other phases (Smith et al., 2013, 2014).

Lithium concentrations are positively correlated with aridity at a national scale (Table SI.4, Fig. 4b). The national pattern is also observed when controlling for lithotype (Fig. SI.1b). Within the Western unconsolidated clastic group, the Rio Grande (median 27 μg/L) and the Basin and Range (median 24 μg/L) are the most arid and have the highest lithium concentrations (Fig. 2e). Within the carbonates, the semi-arid to arid Basin and Range carbonate aquifer (median 7.3 μg/L) has the highest concentrations and the humid Biscayne aquifer has the lowest (median 1.1 μg/L) (Fig. 2c).

Lithium concentrations increase with groundwater residence time (Fig. 4c) and are positively correlated with well depth, a surrogate for groundwater residence time (Table SI.4). Lithium is also correlated with indicators of groundwater chemical evolution showing a positive association with pH, specific conductance, and concentrations of individual elements (fluoride, sodium, potassium, silica, calcium, chloride, and magnesium), and a negative association with dissolved oxygen. These correlations are consistent with a natural source of lithium acquired along the flow path as mineral dissolution increases with longer residence times. Although pumping rates could affect the observed concentrations, PSWs and DSWs are sampled under ambient pumping conditions and thus reflect the resource as it is utilized.

Lithium concentrations are generally related to the flux of groundwater. In aquifers with high fluxes of freshwater, lithium-bearing minerals are likely to have been flushed (depleted) from shallower parts of the flow system. Although Li^{+} substitutes extensively for Mg^{2+} in silicates because of the similarity of their ionic radii, such lithium impurities in structural positions tend to be less tightly bound than the higher charge cation (Krauskopf and Bird, 1995). Likewise, exchangeable lithium would tend to be removed more efficiently than other cations (Appelo, 1994; Mehlich, 1981). Fluxes tend to be higher in humid regions than in arid regions and at shallower depths than deeper depths. The correlation between lithium and groundwater residence time may be attributed to this flushing effect and not necessarily to the time needed to dissolve the minerals. A study in the Bengal Basin of Bangladesh suggested that flushing was a controlling factor affecting arsenic concentrations (Van Geen et al., 2008). In highly modified hydrologic systems like the Central Valley or California Coastal Basin aquifers, the flux of recharge may be many times greater than the natural rate, making aridity a less reliable predictor of lithium concentrations.

Lithium in some groundwater used for drinking water could result from mixing with small amounts of saline waters. Four of the five sampled wells with lithium concentrations greater than 500 μg/L are less than 1 km from a geothermal spring (Berry et al., 1980); those four wells are in the Basin and Range basin fill (BNRF) principal aquifer. Geothermal waters vary widely in composition with reported lithium concentrations ranging from 20 to 8100 μg/L (median 2590 μg/L) (Blondes et al., 2018). Geothermal springs are mainly found in the western U.S. and in arid to semiarid regions; lithium concentrations are significantly higher in wells within 25 km of a geothermal spring than in more distant wells. Brines produced from oil and gas wells in the U.S. generally have higher lithium and other solute concentrations than geothermal waters (Blondes et al., 2018).

Table 1
Summary of lithium concentrations in public-supply, domestic-supply and monitoring wells.

Characteristic	Network type/depth zone (number of wells)		
	Public supply (1464)	Domestic supply (1676)	Shallow (monitoring) (1560)
	Lithium concentration in μg/L		
Minimum	<1	<1	<1
First quartile	2.6	2.5	<1
Median	8.1	6.9	3
Third quartile	21	19.7	14.5
Maximum	396	1700	474

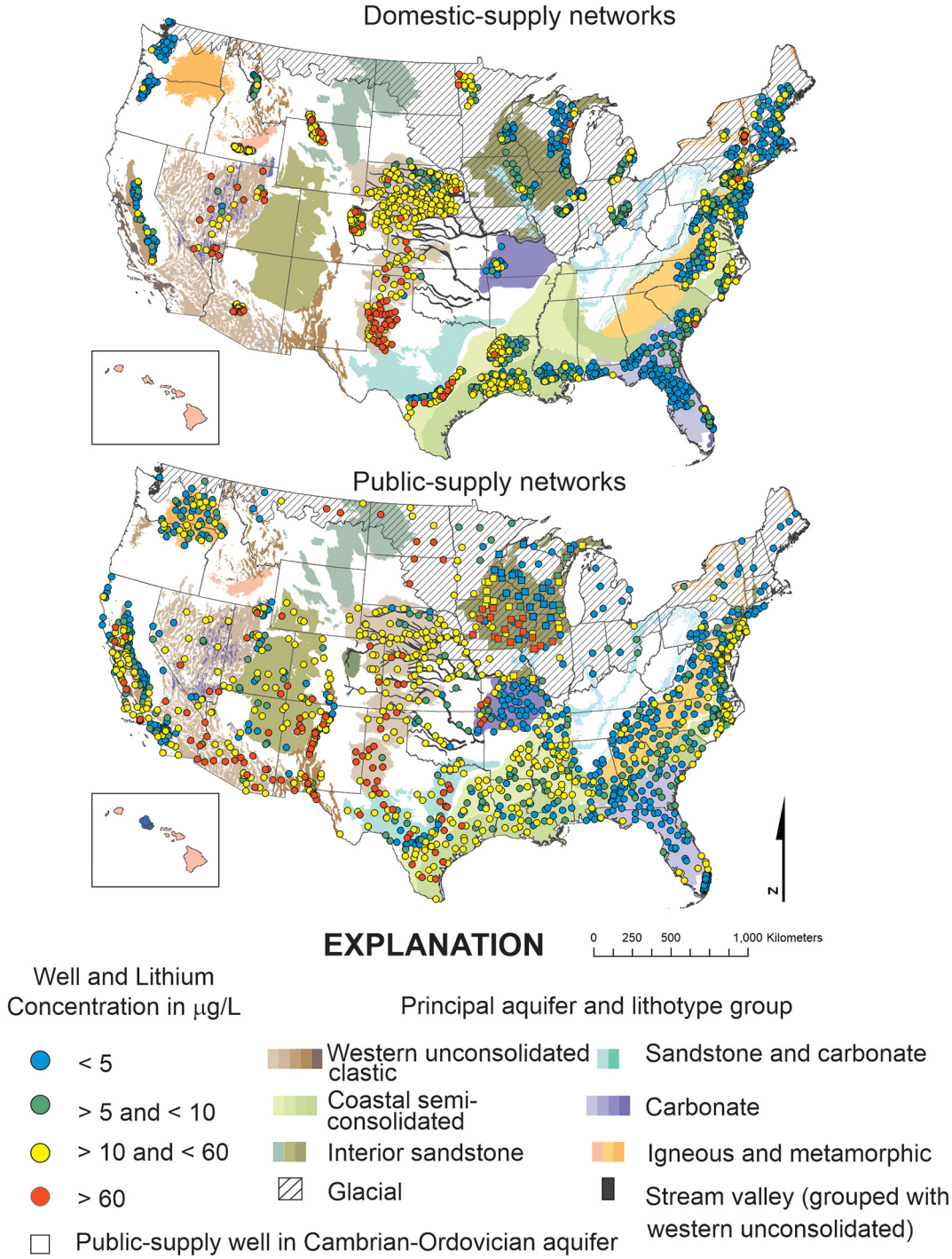

Fig. 1. Locations of wells and concentration ranges of lithium in public- and domestic-supply well networks in the United States by principal aquifer and lithotype group.

PCA was used to evaluate intercorrelations among lithium and associated water-quality variables. Details of the PCA modeling results are given in supplemental information (Tables SI.7–SI.8; Figs. SI.2–SI.3). The model has six principal components (PCs). Lithium is loaded on PC1 and PC2, but is not associated with PC3, PC4, PC5, or PC6. PC1 —"lithium enrichment"—explains 34.2% of the variance in the data, and has lithium as the predominant constituent loading with potassium, fluoride, boron, sodium, sulfate, molybdenum, strontium, bromide, specific conductance (SC), arsenic, silicon, uranium, and pH (Table SI.7). PC1 scores are positively correlated to well depth and negatively correlated to tritium and aridity index values (Table SI.8). PC1 scores by principal aquifer (PA) decrease in the order: western unconsolidated clastic > sandstone > semi-consolidated sand and gravel = crystalline > glacial > carbonate (Fig. SI.2). High positive scores on PC1 may be attributed to: (1) mixing of groundwater with saline waters that are sources of lithium, sodium, chloride, bromide, and other solutes; (2) dissolution of lepidolite; (3) dissolution of Mg-bearing phyllosilicates that contain traces of lithium, such as the hydrothermally altered clay hectorite, or more widely occurring chlorite, montmorillonite (beidellite), or illite; and/or (4) dissolution of major carbonate, sulfate, or silicate minerals that have calcium or magnesium as the principal cation combined with cation-exchange processes involving

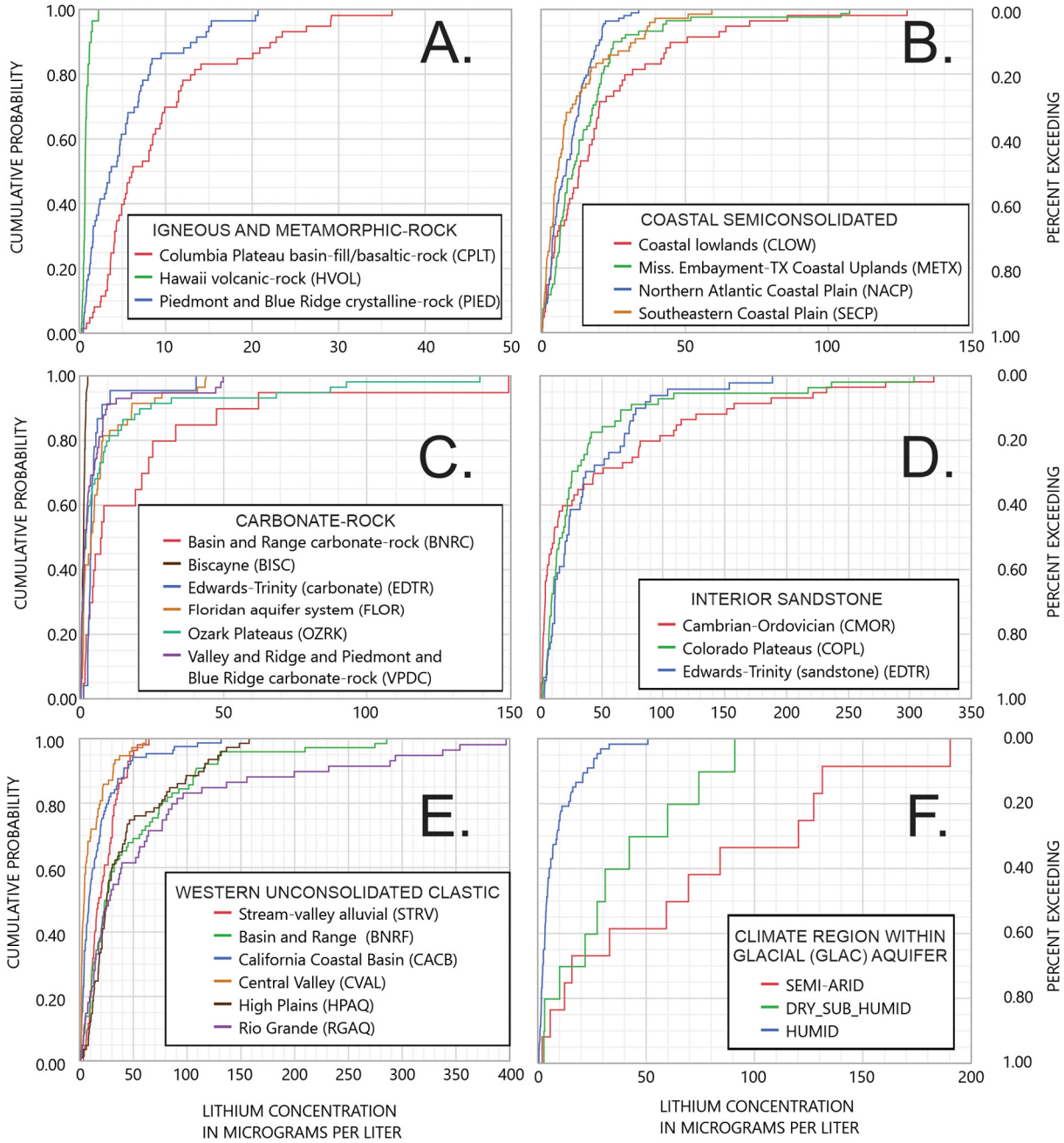

Fig. 2. Cumulative distribution of lithium concentrations among and within aquifers grouped by lithotype and individual aquifers for public-supply wells. Note that the x-axis scale varies by group to accommodate the respective ranges of observed concentrations and, because only public wells are included, some of the highest reported values in this study are not displayed.

the common phyllosilicates. Cation-exchange reactions in freshening systems generally remove calcium and magnesium from solution while liberating sodium, potassium, and lithium from solids (Appelo, 1994; Appelo and Postma, 2005: Chapelle and Knobel, 1983). The groundwaters with higher PC1 scores are in aquifers with lithotypes containing higher lithium and in arid regions with lower groundwater fluxes.

PC2— "hardness"— explains 12.1% of the variance in the data, and has major positive loadings by calcium, magnesium, SC, strontium, alkalinity, sulfate, uranium, chloride, and bromide and minor positive loadings by sodium and lithium (Table SI.7). In contrast with PC1, PC2 scores are negatively correlated to well depth and aridity index and positively correlated to tritium. PC2 scores by major aquifer decrease in the order glacial > carbonate > western unconsolidated = sandstone > crystalline > coastal plain (Fig. SI.2). Higher scores on PC2 are interpreted to indicate weathering of carbonate and sulfate minerals with the associated release of high concentrations of dissolved solids dominated by bicarbonate, sulfate, and base cations without extensive cation exchange. Mixing with saline waters and evaporation could be compounding factors.

3.3. Mixing models and geochemical modeling of lithium in groundwater

Conservative mixing models and geochemical models were developed for three areas: the NACP in the humid East, the HPAQ in the semi-arid midcontinent, and the BNRF in the arid West. For each area, three types of models were developed: (1) conservative mixing model, (2) mixing plus mineral dissolution, and (3) mixing plus mineral

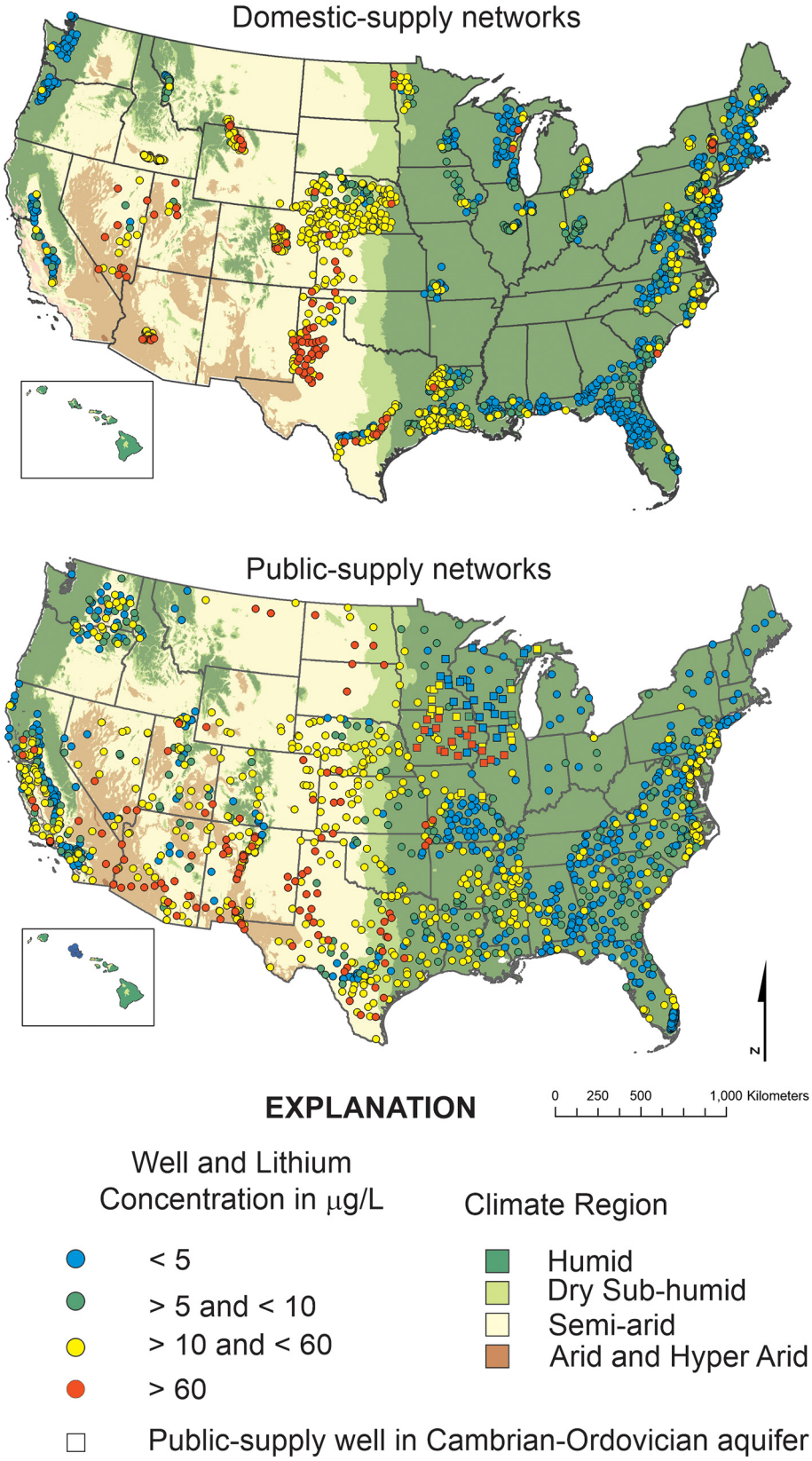

Fig. 3. Locations of wells and concentration ranges of lithium in public- and domestic-supply wells in the United States and climate regions.

dissolution plus cation exchange. A fourth model was applied to the HPAQ: mineral dissolution and cation exchange without mixing. These models were developed to identify plausible explanations for observed concentrations, and the relative importance of the different geochemical processes. For each model, a range of parameters was evaluated and only those that were consistent with aqueous composition and

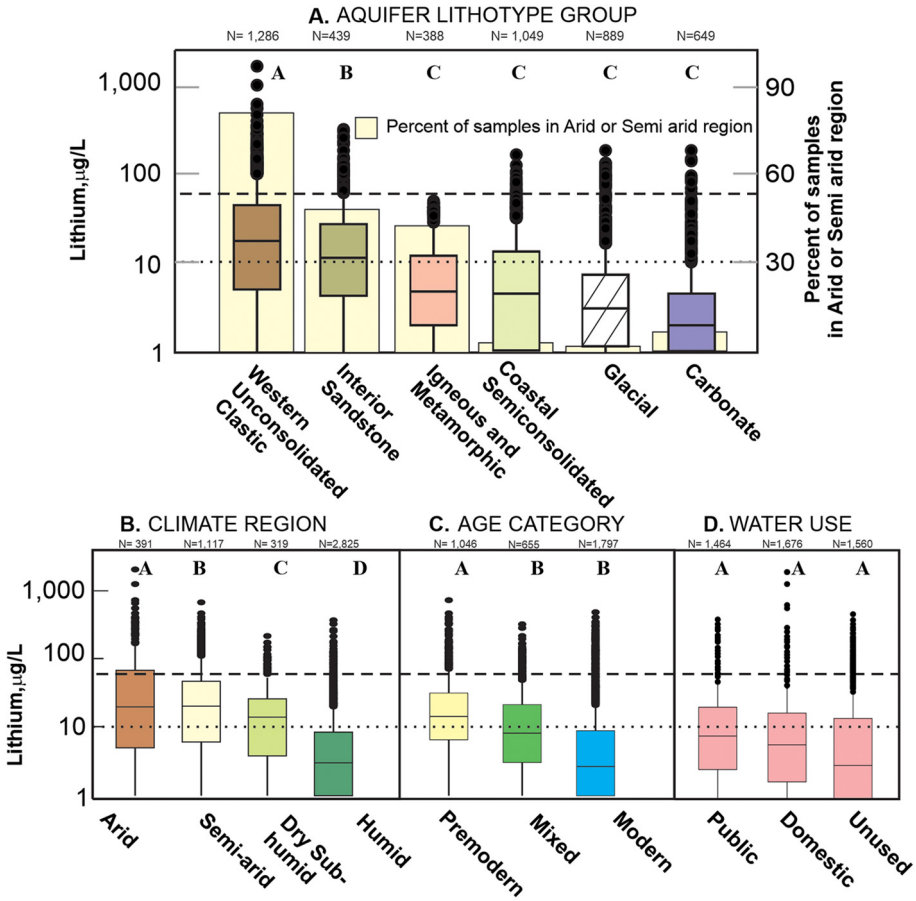

Fig. 4. Box plots illustrating distribution of lithium concentrations among (a) aquifer lithotype groups (including aridity in the shaded bars and on the right y-axis), (b) climate regions (c), groundwater age categories and (d) water use. Dashed line indicates 60 µg/L threshold and dotted line indicates 10 µg/L threshold. Letters above box indicates statistical group from Tukey's test; groups with the same letter are not statistically different (see Table SI.2 and SI.5 for aquifer lithotype groupings).

the PCA analysis were accepted. The modeling is not intended to provide site-specific results. The following sections describe the different types of models for each of the areas.

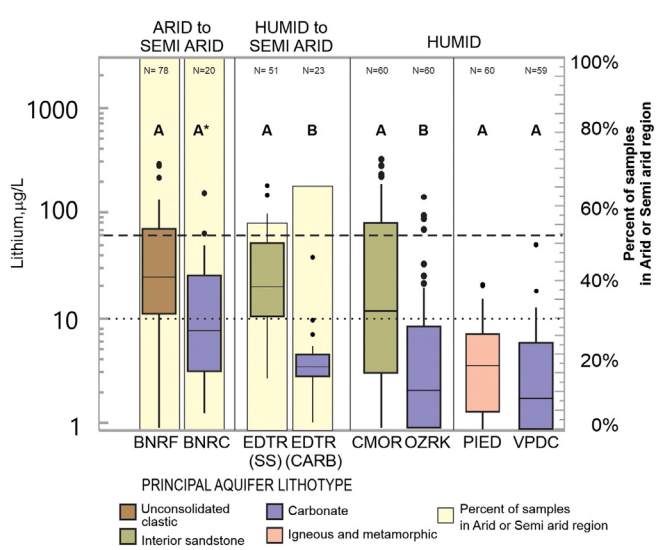

Fig. 5. Box plots illustrating distribution of lithium in noncarbonate (left of each pair) and carbonate (right of each pair) aquifers in similar climate zones. Dashed line indicates 60 µg/L threshold and dotted line indicates 10 µg/L threshold (see Fig. 2 for abbreviations of networks).

3.3.1. Results from mixing models

Conservative-mixing-models demonstrate that observed concentrations of lithium and positive relations among chloride, bromide, sodium, and lithium concentrations that are observed in each of the regional aquifer systems could result from mixing of variable amounts of representative saline waters with dilute meteoric water (Figs. 6 and SI.4–SI.6). The observed and modeled constituent relations with chloride (Figs. 6 and SI.4–SI.6) indicate saline water is a potentially important source of lithium and associated ions in groundwater of HPAQ (brine) and BNRF (geothermal water); however, seawater is indicated as a poor source of lithium in NACP. Elevated lithium in groundwater samples from all three aquifers that have relatively low chloride concentrations plus "excess" sodium ([Na] / [Cl] > 2) compared to simple mixing (Figs. 6 and SI.4–SI.6), suggest additional contributions of lithium and sodium by aquifer mineral dissolution and cation exchange, whereby Ca^{2+} and Mg^{2+} from mineral dissolution displace Na^{+} and Li^{+} from exchanger to groundwater.

3.3.2. Results from geochemical models

The geochemical (forward-reaction) models indicate the potential importance of different processes on lithium concentrations and associated groundwater quality, including: (1) evaporation of rainwater, (2) dissolution of small amounts of lepidolite or hectorite and larger quantities of non-lithium-bearing major minerals and organic matter, (3) cation exchange, and (4) mixing with saline waters. Figs. 7 and 8 show selected results from the forward models; additional results are given in the supplemental information (Figs. SI.8–SI.11). Model 1 (black lines and symbols), which involves rainwater evaporation and

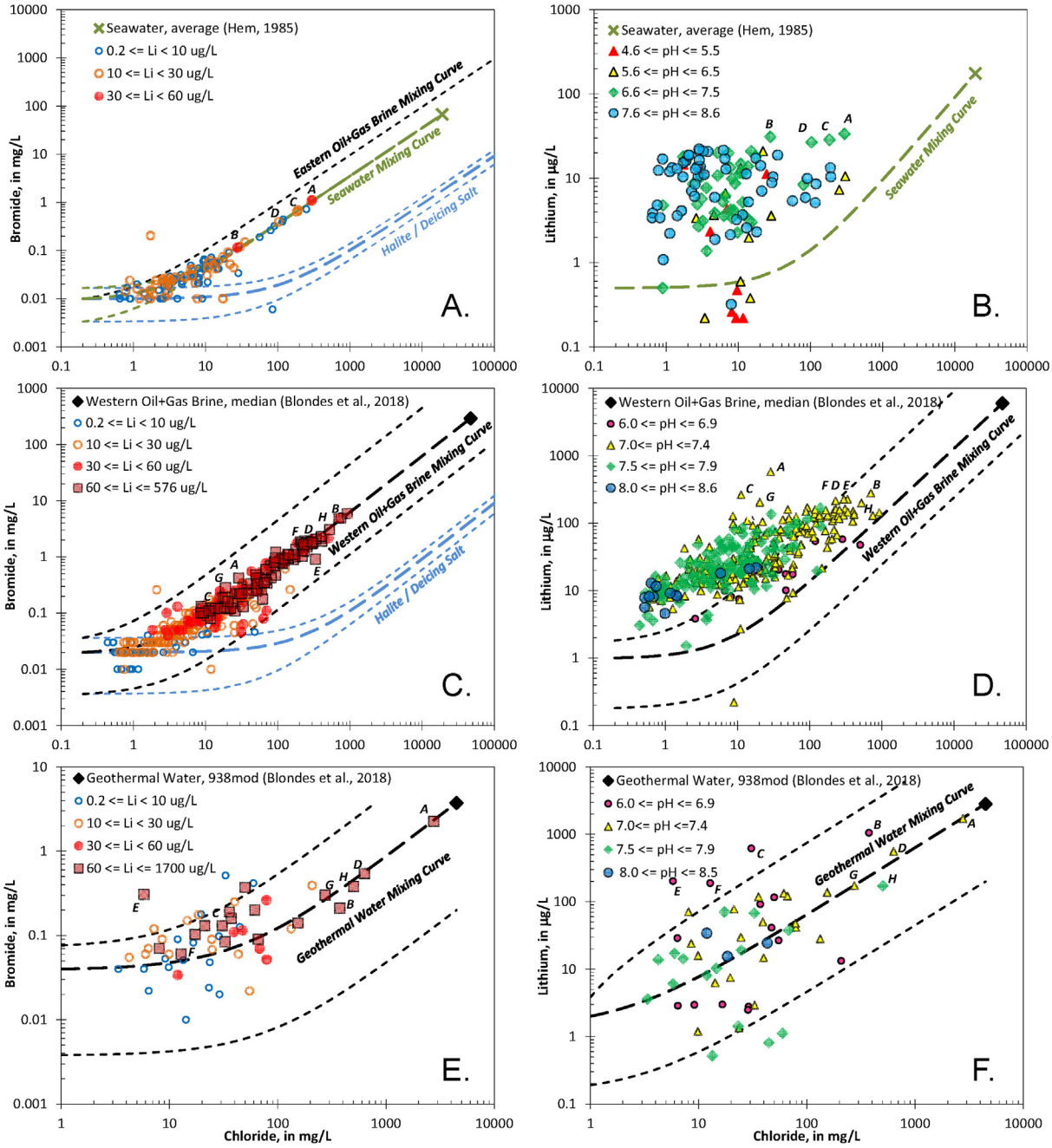

Fig. 6. Plots of chloride-bromide (left) and chloride-lithium (right) for hypothetical mixtures and data from selected aquifers. Dotted and dashed lines show results of conservative mixing models for evaporated rainwater with regionally important saline water sources: seawater (A,B), western brine (C,D), or geothermal water (E,F). Data values for groundwater from NACP (A,B), HPAQ (C,D), and BNRF (E,F) principal aquifers are illustrated with points. Style and color of data points indicate range of lithium concentrations (A,C,E) or pH (B,D,F). Samples with letter labels had relatively high lithium concentrations (Tables SI.10–SI.12). Average seawater composition reported by Hem (1985). Eastern and western oil and gas brine compositions (median and quartiles, indicated by outer dashed curves) and geothermal well water composition and representative low to high lithium samples (indicated by outer dashed curves), excluding samples having charge imbalance ≥20%, from Blondes et al. (2018). Deicing salt, or halite, with trace bromide from Llewellyn (2014).

minor mineral dissolution (to simulate dilute groundwater quality) followed by mixing with saline water, and model 2 (red lines and symbols), which involves 10-times greater mineral dissolution, demonstrate that neither evaporation nor dissolution of lithium-bearing minerals account for many of the observed concentrations of lithium. Without mineral dissolution, rainwater evaporation produces unrealistically low pH values, and although extensive dissolution of lepidolite, hectorite, or other lithium minerals could account for high concentrations of lithium, such minerals generally are not abundant nor widespread. Inclusion of small quantities of lepidolite or hectorite with larger amounts of chlorite, beidellite, and(or) illite in the models (Table SI.13) may be interpreted to represent the dissolution of common phyllosilicate minerals containing minor lithium impurities. Although mixing with saline water can account for elevated chloride, bromide, and some of the observed lithium concentrations, cation exchange may also be involved to achieve the observed high concentrations of lithium.

Model 3 (blue lines and symbols) builds on model 2 but incorporates cation exchange that is sufficient to produce observed, elevated lithium concentrations. A low concentration of exchangeable or adsorbed lithium (<0.1%) on unidentified minerals is considered in these models;

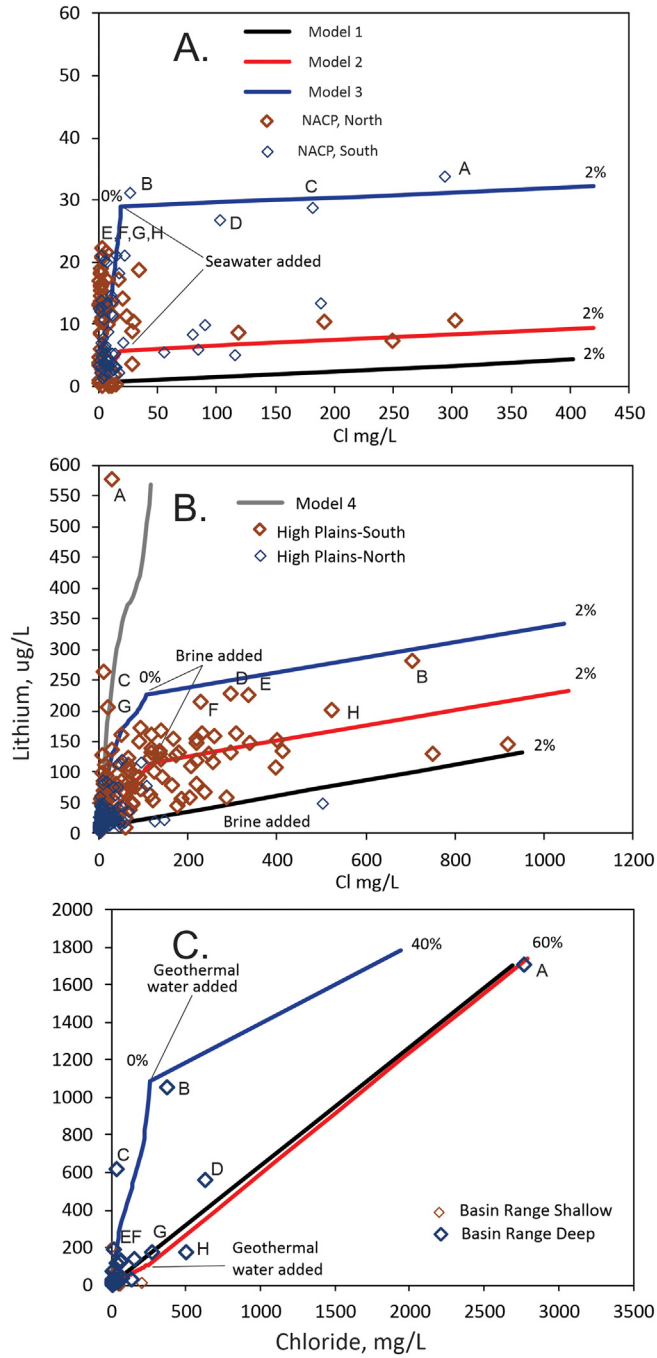

Fig. 7. Selected results from geochemical modeling: A. Northern Atlantic Coastal Plain (NACP), B. High Plains aquifer (HPAQ), and C. Basin and Range basin-fill (BNRF). Black (model 1) represents evaporation and minor mineral dissolution followed by mixing with saline water. Red (model 2) represents model 1 plus factor of 10 increase in mineral dissolution. Blue (model 3) represents model 2 plus cation exchange. Gray (model 4, HPAQ only) represents evaporation, mineral dissolution, and cation exchange without mixing of saline groundwater. Samples with letter labels had relatively high lithium concentrations (Tables SI.10–SI.12). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

calcium, magnesium, sodium, and potassium constitute 99% of the exchangeable cations. This exchanger composition is compatible with the description by Starkey (1982), that "lithium is rarely, if ever, found on the exchange sites of clays, … because it can be replaced by any of the competing cations in water." Model 4 represents a case without mixing of saline water, whereby the high lithium concentration with low chloride may be explained as a result of cation exchange.

In all three study areas, model 2 (evaporation, mineral dissolution, and mixing with saline water) yields lithium concentrations that approach some observed high values; however, calcium, magnesium, sodium, potassium, and other constituent concentrations are not consistent with many observations. As explained above and in greater detail in the supplemental information, many samples with elevated lithium concentrations have "excess" sodium ([Na] / [Cl] > 2) and lower chloride concentrations than can be explained by mixing with saline waters (such points plot above the black or red lines in Fig. 7 and Figs. SI.8–SI.10). Results of model 3 involving cation exchange (blue lines) for lithium and other constituents more closely match the observed water quality.

Piper diagrams, which display sample points for NACP, HPAQ, and BNRF and the reaction paths for the corresponding geochemical models (Fig. 8), help to indicate the lithium concentrations and corresponding hydrochemical evolution patterns resulting from mineral dissolution, cation exchange, and mixing with saline waters. The data points for samples from each of the regions, including those with elevated lithium concentrations, are distributed widely. These sample distributions are generally consistent with the patterns indicated by the geochemical models. Those general patterns across the diamond shaped, upper diagram suggest the following. (1) Rainwater evaporation with minor mineral dissolution can produce sample compositions plotting in the upper section of the diagram that lack bicarbonate. (2) Dissolution of minerals containing base cations can account for groundwater compositions plotting in the upper left side of the diamond; such groundwaters near recharge areas tend to be relatively dilute, beginning with sulfate and chloride as predominant anions but through mineral dissolution can evolve to contain progressively greater concentrations and proportions of bicarbonate, with Ca and Mg as predominant cations. (3) Cation exchange accounts for increased proportions of Na (and Li) in samples plotting from the left corner toward the lower corner. (4) Mixing with saline waters increases the proportions of Na and Cl shifting the points toward saline end-member waters plotting in the right corner.

The geochemical models demonstrate that the range of observed lithium concentrations could feasibly result from (1) evaporation, (2) dissolution of lithium-bearing minerals such as lepidolite or hectorite, (3) dissolution of common minerals that may contain traces of lithium combined with cation exchange, and(or) (4) mixing with saline waters. Although geothermal waters may be the predominant source of the very highest concentrations of lithium, cation exchange is indicated to be an important widespread source of lithium and associated cations in groundwater of the principal aquifers investigated. If one examines the highest modeled concentrations of lithium in the NACP, HPAQ, and BNRF aquifers (Fig. 7), cation exchange accounts for 21 to 76% of the lithium, while saline water contributes 8 to 40% and mineral dissolution 6 to 39%. Mixing with saline water sources, if present, and variations in mineral assemblages and cation-exchange capacities could explain the regional variations within principal aquifers. In humid climates, soluble minerals and associated lithium are more likely to have been depleted by relatively larger amounts of groundwater flow (freshening), whereas in arid climates, these minerals are more likely to be available for interaction with the groundwater.

3.4. Land use and temporal changes in lithium concentrations

Potential anthropogenic effects were evaluated by statistical testing of correlations between lithium and land use, and statistical testing of changes in lithium over time. Correlations were conducted for all wells, and also for the subset of wells characterized as modern groundwater age. For the full data set, correlations with lithium are weak (agricultural and urban land use) or not statistically significant (mining). When considering modern groundwater only, the correlation between lithium and agricultural land use was not statistically significant and the negative correlation with urban land became weaker (Table SI.4). The absence of correlation between land use and lithium within modern

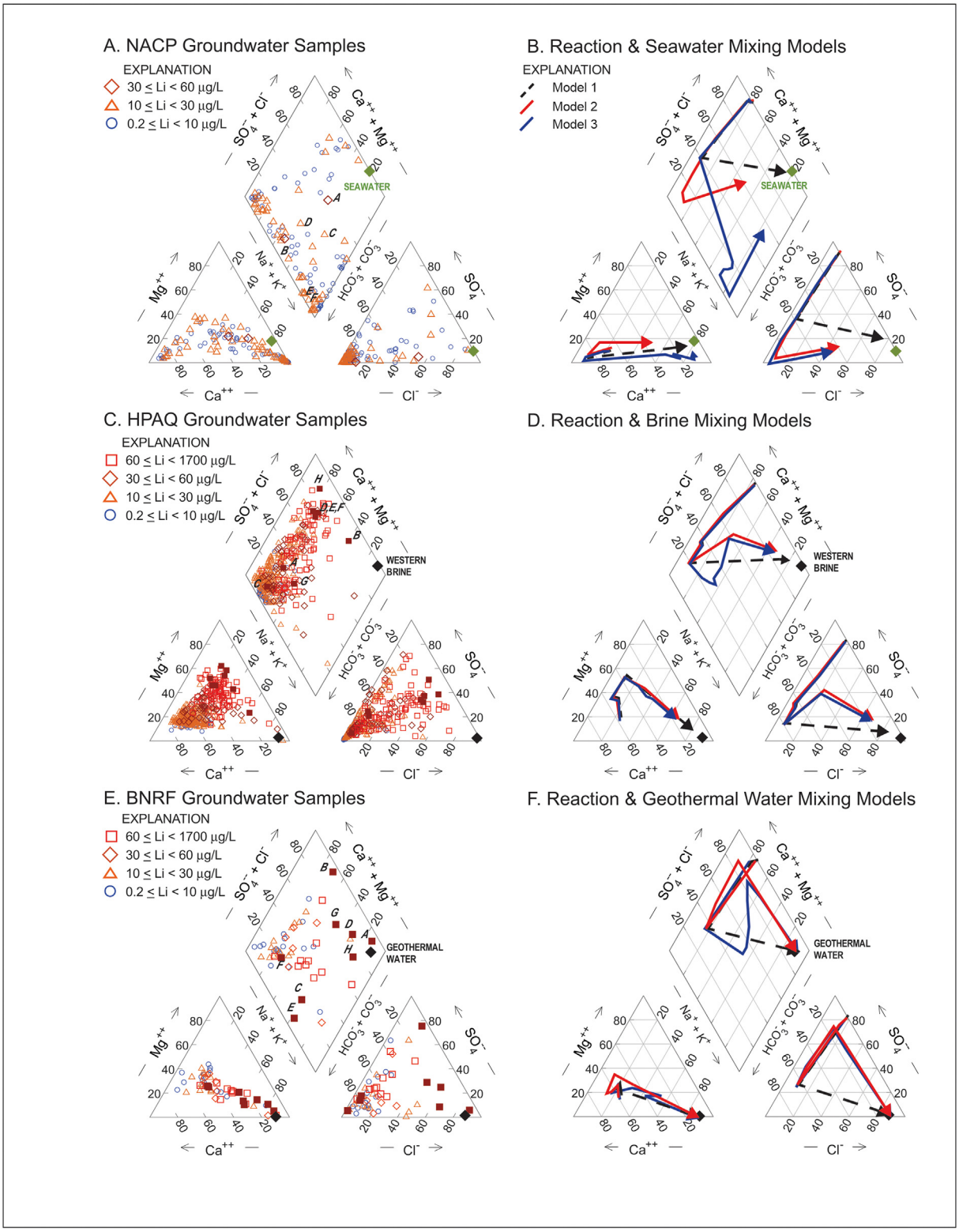

Fig. 8. Piper diagrams showing data for groundwater samples from the NACP, HPAQ, and BNRF principal aquifers (A,C,E) and hypothetical water-quality evolution paths (B,D,F) indicated by corresponding forward reaction models for relatively low-total dissolved solids (TDS), low-lithium samples (NACP), intermediate-TDS, moderate-to-high-lithium samples (HPAQ), and mineralized, high-lithium samples (BNRF) (Figs. SI.8, SI.9, and SI.10, respectively). Models 1,2, and 3 are described on Fig. 7. Samples with letter labels had relatively high lithium concentrations (Tables SI.10–SI.12).

groundwater suggests that anthropogenic sources are not important nationally. Mines and waste disposal sites may be local sources of lithium in groundwater, but those sources are not sufficiently widespread to influence the results at the national scale.

Despite the overall indications that high concentrations of lithium are naturally occurring, more than one third of the concentrations greater than 60 µg/L were detected in modern groundwater, leaving the possibility that some of the high concentrations are from

anthropogenic sources. However, nearly 95% of those samples were in arid or semi-arid regions and about half of those samples were in predominantly undeveloped land use. Only four samples out of 1192 modern samples in humid regions had a concentration greater than 60 μg/L. Although a small percentage of samples with high concentrations of lithium might be from anthropogenic sources, most are likely to be from natural sources.

To explore potential anthropogenic sources of lithium further, 53 networks of 20–30 wells each were evaluated for changes in lithium concentrations over a 10-year time span. Of the networks evaluated, 36 had no statistically significant change, 10 had increasing concentrations and 7 had decreasing concentrations (Table SI.6). Median changes in concentrations were typically less than 1 μg/L per decade. The results from this evaluation of decadal-scale changes do not provide conclusive evidence for or against anthropogenic sources of lithium in groundwater. Given that disposal of lithium batteries in landfills began recently and the quantity disposed will likely continue to increase, these baseline data provide a benchmark for background concentrations that can be used to evaluate future changes in lithium in groundwater.

4. Conclusions

This study is the first comprehensive, national-scale evaluation of lithium in groundwater used for drinking-water supply in the U.S. The median concentration in PSWs was 8.1 μg/L and the median concentration in DSWs was 6.1 μg/L. Forty-five percent of the PSWs and 37% of DSWs have concentrations of lithium greater than the HBSL of 10 μg/L. Nine percent of the PSWs and 6% of the DSWs exceed the drinking-water only threshold of 60 μg/L. The percentage of samples greater than the HBSL is higher than any other contaminant measured in the previous 30 years of sampling by the NWQP (Desimone, 2009; Toccalino et al., 2010).

The study design for the PSW networks provided a set of wells that are broadly distributed across 24 principal aquifers of the U.S., allowing for assessment at a national scale and at the scale of the principal aquifers. The study design for the DSW networks was generally targeted to smaller areas within principal aquifers but does allow for assessment at a national scale. Lithium concentrations were higher in arid regions than in humid regions and in older groundwater than in younger groundwater. For example, 75% of PSWs and 93% of DSWs exceeded the HBSL in older groundwater in arid regions. In contrast, 11% of PSWs and 9% of DSWs exceeded the HBSL in humid regions with modern groundwater. These findings are consistent with a greater flux of freshwater through aquifers in humid settings, resulting in more extensive depletion of lithium from aquifer solids.

Lithium concentrations were also higher in unconsolidated clastic deposits and sandstones than in carbonate, igneous or metamorphic rocks. The highest concentrations were in the High Plains, Rio Grande, Stream-valley aquifers and Basin and Range basin fill aquifers of the West. Nearly 10 million people rely on groundwater for drinking water in these four aquifer systems (Lovelace et al., 2020).

Multiple lines of evidence indicate that high concentrations of lithium are derived from interaction of groundwater with aquifer materials and mixing with saline water sources. Lithium concentrations are not correlated with land use and increase with groundwater age. Geochemical modeling indicates that mineral dissolution, cation exchange, and (or) mixing with saline water are necessary to reach observed concentrations. The relative importance of these sources of lithium cannot be completely resolved given the non-uniqueness of model results. However, modeling suggests that some of the high concentrations are likely to be from mixing with saline waters whereas other high concentrations are more likely to be due to cation exchange. Proximity analysis and modeling strongly suggest that the highest concentrations are related to geothermal fluids.

Studies, by others, using lithium isotopes provide additional insight into the geochemical processes affecting lithium (Meredith et al., 2013; Pfister et al., 2017; Pogge von Strandmann et al., 2020). These studies indicate exchangeable and structurally bound lithium are isotopically distinct, with exchangeable lithium having isotopic values relatively close to the fluid phase, while structurally bound lithium tends to be substantially lighter. Such studies have also indicated that lithium mobility compared to major cations such as calcium, magnesium, and sodium can vary widely because of lithium release during mineral weathering or potential incorporation into secondary silicates. Thus, additional investigation of lithium isotopes in corresponding water and rock could help indicate the relative contributions of lithium in groundwater from mineral sources versus mixing with saline water.

Local anthropogenic sources may be contributing to lithium concentrations in some groundwater samples, but there is no evidence for widespread effects. With the increase in the use of lithium for batteries and other purposes and the subsequent disposal of lithium in landfills, this study provides critical background on natural levels of lithium that can be used as a baseline to evaluate future changes that may be due to anthropogenic sources.

Although studies of lithium in drinking water or tap water are quite common, large-scale studies characterizing lithium in groundwater are rare. The only other national-scale study of lithium in groundwater used for public supply is from Denmark, where the median concentration of 10.5 μg/L is comparable to the study in the U.S., however, the maximum concentration of 31 μg/L was much lower than found in U.S. groundwater. The samples from arid regions, from lithotypes with higher lithium content, near geothermal features, or with longer groundwater residence time likely account for the higher concentrations in the U.S.

This study sampled untreated groundwater with lithium concentrations ranging from <1 to 1700 μg/L and offered explanations for the elevated concentrations. Another study showed lithium passed conservatively through public drinking-water treatment plants (Furlong et al., 2017); however, the maximum concentration in the surface-water sources evaluated for that study was 56 μg/L. Further studies may be warranted to evaluate the potential health effects of naturally elevated lithium in groundwater after treatment by various commercial and emerging water-treatment technologies such as ion exchange, reverse osmosis, and membrane filtration (e.g. Binnie et al., 2002; Zhang et al., 2018).

CRediT authorship contribution statement

Bruce D. Lindsey: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Formal analysis, Visualization, Data curation. **Kenneth Belitz:** Conceptualization, Resources, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Formal analysis. **Charles A. Cravotta:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Software, Formal analysis, Visualization. **Patricia L. Toccalino:** Writing – original draft, Writing – review & editing, Conceptualization, Formal analysis. **Neil M. Dubrovsky:** Conceptualization, Project administration, Writing – review & editing.

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.

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National Water-Quality Assessment Project (NAWQA), a component of the National Water Quality Program; data from the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project funded by the California State Water Resources Control Board were included in the study as well.

Appendix A. Supplementary data

Background information, results of statistical tests, and description and results for geochemical analysis and reaction models. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.144691.

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