Minimum energy requirements for desalination of brackish groundwater in the United States with comparison to international datasets

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Minimum energy requirements for desalination of brackish groundwater in the United States with comparison to international datasets

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Citation

Abstract
This paper uses chemical and physical data from a large 2017 U.S. Geological Survey groundwater dataset with wells in the U.S. and three smaller international groundwater datasets with wells primarily in Australia and Spain to carry out a comprehensive investigation of brackish groundwater composition in relation to minimum desalination energy costs. First, we compute the site-specific least work required for groundwater desalination. Least work of separation represents a baseline for specific energy consumption of desalination systems. We develop simplified equations based on the U.S. data for least work as a function of water recovery ratio and a proxy variable for composition, either total dissolved solids, specific conductance, molality or ionic strength. We show that the U.S. correlations for total dissolved solids and molality may be applied to the international datasets. We find that total measured molality can be used to calculate the least work of dilute solutions with very high accuracy. Then, we examine the effects of groundwater solute composition on minimum energy requirements, showing that separation requirements increase from calcium to sodium for cations and from sulfate to bicarbonate to chloride for anions, for any given TDS concentration. We study the geographic distribution of least work, total dissolved solids, and major ions concentration across the U.S. We determine areas with both low least work and high water stress in order to highlight regions holding potential for desalination to decrease the disparity between high water demand and low water supply. Finally, we discuss the implications of the USGS results on water resource planning, by comparing least work to the specific energy consumption of brackish water reverse osmosis plants and showing the scaling propensity of major electrolytes and silica in the U.S. groundwater samples.

Keywords: desalination, brackish groundwater composition, least work of separation, energy requirements, saturation index
Nomenclature

Roman Symbols

\[ \text{Activity} \]
\[ \text{Molality, \ mol/kg}_{\text{solvent}} \]
\[ \text{Polynomial fit for recovery ratio, \ kg/kg} \]
\[ \text{Gibbs free energy, \ J} \]
\[ \text{Gibbs free energy flow rate, \ J/s} \]
\[ \text{Specific Gibbs free energy, \ J/kg} \]
\[ \text{Molal ionic strength, \ mol/kg} \]
\[ \text{Solubility product} \]
\[ \text{Molecular weight, \ kg/mol} \]
\[ \text{Mass fraction, \ kg/kg} \]
\[ \text{Mass flow rate, \ kg/s} \]
\[ \text{Mole flow rate, \ mol/s} \]
\[ \text{Groundwater property} \]
\[ \text{Activity product} \]
\[ \text{Heat rate, \ kJ/s} \]
\[ \text{Correlation coefficient} \]
\[ \text{Coefficient of determination} \]
\[ \text{Universal gas constant, \ J/mol-K} \]
\[ \text{Recovery ratio, mass basis, \ kg/kg} \]
\[ \text{Recovery ratio, mole basis, \ mol/mol} \]
\[ \text{Salinity, \ kg}_{\text{solute}}/\text{kg}_{\text{solution}} \]
SI Saturation Index, $\log_{K_{s,p}}$

$\dot{S}_{gen}$ Entropy generation flow rate, J/s-K

$T$ Temperature, K

$\dot{W}$ Work rate (power), J/s

$x$ Mole fraction, mol/mol

$Y$ Dimensional constant

$z$ Valence of ion

Greek Symbols

$\nu$ Stoichiometric coefficient

Subscripts

$a, A$ Anion

$b$ Brine

$c, C$ Cation

$e$ Environment

$f$ Feed

$i$ Species

$least$ Reversible operation

$p$ Product

$s$ Binary salt species

$sep$ Separation

$H_2O, w$ Water
<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>BGW</td>
<td>Brackish groundwater</td>
</tr>
<tr>
<td>BWRO</td>
<td>Brackish water reverse osmosis</td>
</tr>
<tr>
<td>CCRO</td>
<td>Closed circuit reverse osmosis</td>
</tr>
<tr>
<td>EDR</td>
<td>Electrodialysis reversal</td>
</tr>
<tr>
<td>LWS</td>
<td>Least work of separation, J/s</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SEC</td>
<td>Specific energy consumption, kWh/m³</td>
</tr>
<tr>
<td>SC</td>
<td>Specific conductance, µS/cm</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids, mg/L</td>
</tr>
</tbody>
</table>
1 Introduction

Water scarcity around the world (Fig. 1) is motivating rising interest in the use of groundwater to meet fresh water demand. The majority of Earth’s groundwater resources are brackish, requiring desalination before use to provide an alternative fresh water source. In the United States, brackish groundwater (BGW) is a widely available but minimally used resource. In 2010, 21% of the U.S. water supply came from fresh groundwater (TDS < 1,000 mg/L), while less than 1% came from saline groundwater (TDS ≥ 1,000 mg/L) (Maupin et al., 2014). A recent national study by U.S. Geological Survey (USGS) indicates that the volume of BGW (1,000 mg/L ≤ TDS ≤ 10,000 mg/L) is over 800 times the amount of saline groundwater used each year and over 35 times the amount of fresh groundwater used (Stanton et al., 2017). Thus, increased exploitation of BGW might relieve some of the growing pressure on freshwater supplies around the world, particularly in drier landlocked regions (Fig. 1).

![Map of water-supply-sustainability risk index for 2050 across the U.S. (left). The index relates water demand to population growth, increases in power generation, and climate change for the year 2050 (McMahon et al., 2016; Roy et al., 2012). Global annual average monthly blue water scarcity from 1996-2005 (right). Blue water includes fresh surface water and groundwater (Mekonnen and Hoekstra, 2017).](image)

Despite BGW’s potential to relieve the mounting pressure on freshwater supplies, the resource has been studied far less as a water source than seawater or freshwater. A 1965 USGS report (Feth, 1965) served as the primary source of information on the U.S. distribution of BGW until USGS published an updated assessment in 2017 (Stanton et al., 2017). Moreover, comprehensive assessments of BGW desalination energy requirements are absent in the literature. Because groundwater ionic composition varies greatly
from location to location, unlike seawater (Stewart, 2008; World Health Organization, 2007), a large-scale analysis of the resource’s energy costs in the U.S. and several other countries was undertaken in the current study. Because water stress occurs worldwide, this assessment has implications beyond the countries studied. Water shortages experienced by an individual country are a function of physical water scarcity, technology and policy, and water distribution and consumption not just within its borders, but also in other nations that are its trading partners. For example, the U.S. is currently the largest importer and largest exporter of water, so changes to the U.S. water supply, such as increased exploitation of an underused resource like BGW, may have significant impacts on water use elsewhere (Hoekstra and Mekonnen, 2012).

This paper summarizes an investigation of BGW characteristics and minimum desalination energy requirements in the continental United States (Qi and Harris, 2017; Stanton et al., 2017), South Australia (Gray and Bardwell, 2016), Spain (Hidalgo and Cruz-Sanjulian, 2001; Hidalgo, 1993), and numerous other countries (United Nations Environment Programme, 2017). In the present analysis, we define BGW as containing 500 - 10,000 mg/L of TDS. The lower bound on TDS is extended to 500 mg/L based on the lower TDS recommendation for drinking water and irrigation (Office of Water of the U.S. Environmental Protection Agency, 2018). First, the site-specific least work of separation (LWS) is calculated for approximately 28,000 BGW samples across the U.S. LWS represents an absolute minimum for specific energy consumption (SEC) of desalination systems. By focusing on LWS, we use a metric that is independent of desalination technology and which will not change as technologies are improved. LWS calculations are used to develop simplified equations between LWS and TDS, specific conductance, ionic strength, and molality, as well as to explore the impact of groundwater composition on LWS. Second, we show the geographic distribution of TDS for 45,000 BGW samples and of major ions and LWS for 28,000 BGW samples. Areas with high water stress and low LWS requirements are mapped to highlight regions with high potential for effective desalination and use of BGW. Third, we show that the TDS and molality simplified equations, as well as the groundwater composition trends, can be extended to BGW samples elsewhere in the world, by comparing USGS groundwater samples to 5,650 BGW samples from three international groundwater datasets with wells in twenty-three countries. Lastly, we discuss the implications of our results on water resource planning. We compare LWS to SEC of brackish water reverse osmosis (BWRO) plants, and we show the scaling propensity of major electrolytes and silica in USGS groundwater samples.
2 Groundwater datasets

This paper performs a BGW analysis, using one U.S. dataset and three international datasets: the U.S. Geological Survey (USGS) major-ions groundwater dataset and the Continental Scale Hydrogeochemistry South Australia database (CSHSA), Global Water Quality database and information system (GEMStat), and the University of Grenada (UGR) hydrochemical study of the Baza-Caniles aquifer in Spain.

2.1 USGS major-ions dataset

USGS recently compiled a database of the major ions in groundwater to provide an updated summary of the occurrence of BGW and a more complete characterization of BGW resources (Stanton et al., 2017; Qi and Harris, 2017). The major ions database contains chemical, physical, and geographic properties of groundwater compiled from 16 data sources for approximately 124,000 groundwater samples across the continental U.S., Alaska, Hawaii, Puerto Rico, the U.S. Virgin Islands, Guam, and American Samoa. This paper uses BGW data from the continental U.S. only.

2.1.1 Coverage

The geochemical sources used to compile the major-ions dataset range from single publications to large datasets and from state studies to national assessments (Stanton et al., 2017; Qi and Harris, 2017). Groundwater properties in the dataset include the concentrations of TDS, major ions, trace elements and radionuclides, pH, temperature, specific conductance, saturation indexes, and density. Many of these properties are necessary to evaluate LWS. Some samples in the database have missing density or bicarbonate and/or carbonate concentration data. In these cases, density was calculated using a well-established correlation for density, temperature and TDS (Millero and Poisson, 1981). Alkalinity was converted to bicarbonate and carbonate concentrations according to methods outlined by Stumm and Morgan (Stumm and Morgan, 1996), using the Debye-Hückel limiting law (Debye and Hückel, 1923). The dataset also contains latitude and longitude for each sample, enabling geographic distribution analyses of groundwater characteristics. Approximately 66,500 samples are freshwater (TDS < 500 mg/L) and 45,200 samples are brackish water. Of the brackish samples, approximately 28,000
have complete composition data, not diverging from electroneutrality by more than 5%\textsuperscript{1}. Groundwater samples are drawn from all 50 states.

2.1.2 Limitations

Although the major ions dataset covers large areas across the United States, it has some limitations. USGS was unable to compile all available groundwater data for the nation, particularly from local sources. The agency relied on larger datasets available in a digital format from national and state-level organizations. Well selection biases also influence the type of groundwater data that are available. Well sites are not methodologically selected to characterize entire aquifers. Rather, they tend to be drilled in areas that have freshwater and/or a lower depth requirement to tap into the resource. This preference for freshwater and shallow wells results in a lack of comprehensive and consistent data. Consequently, the dataset does not represent a complete characterization of BGW resources in the U.S.

The majority of samples have a TDS less than 500 mg/L, and there is an uneven distribution of wells across the 50 states, resulting in data gaps for many parts of the nation. This non-uniform well distribution may result partly from population density and total groundwater withdrawals in a given area, where total groundwater withdrawals includes fresh, brackish, and saline water. Correlation coefficients of number of wells per state, with state population and with total state groundwater withdrawals, are 0.53 and 0.60, respectively; these values indicate that number of wells in a state is related to these two parameters. Figure 2 shows the total groundwater withdrawals per state in 2010 versus the number of groundwater samples per state in the major-ions dataset. Texas and California have both the highest number of samples and the highest total groundwater withdrawals, while Rhode Island and Vermont have the smallest number of samples and the smallest total groundwater withdrawals.

\textsuperscript{1}The percent deviation from electroneutrality is calculated by summing over all of the molalities of cation species $c$ and anion species $a$ in the distributed solution, using the charge $z$ of each species:

$$\text{percent error} = 100 \frac{\sum_{c} (z_{c} \cdot b_{c}) - \sum_{a} (z_{a} \cdot b_{a})}{\sum_{c} (z_{c} \cdot b_{c}) + \sum_{a} (z_{a} \cdot b_{a})}.$$
Figure 2: Total annual groundwater withdrawals per state in 2010 (Maupin et al., 2014) versus number of samples per state in USGS major-ions dataset. Each dot corresponds to a state. Red labels are used to specify 16 of the 48 states in the contiguous U.S. by their postal abbreviations.

2.2 Datasets for Twenty-three Additional Countries

CSHSA (Gray and Bardwell, 2016), GEMStat (United Nations Environment Programme, 2017), and the UGR dataset (Hidalgo and Cruz-Sanjulian, 2001; Hidalgo, 1993) include the concentrations of TDS, major ions, pH, and temperature, necessary for evaluating LWS, as well as latitude and longitude for each sample. CSHSA contains approximately 5,200 BGW samples with complete composition data in South Australia. The UGR dataset contains approximately 260 BGW samples with complete composition data in the Baza-Caniles detrital aquifer system in Granada, Spain. GEMStat contains 100 BGW samples with complete composition data in Afghanistan, Argentina, Canada, Chile, Hungary, Indonesia, India, Iran, Gambia, Japan, Kenya, Morocco, Mexico, Mali, Norway, New Zealand, Pakistan, Senegal, Sweden, Turkey, Tanzania, and Uruguay. Figure 3 shows the location of BGW samples from the three international datasets and the USGS dataset. Data limitations have prevented broader global coverage of groundwater in this paper. Groundwater data often includes TDS, but not the ionic content necessary for evaluating LWS, so certain other datasets from around the world could not be used.
3 Evaluation of LWS

LWS is the benchmark energy consumption for any desalination system. It represents the minimum amount of work required to separate the supplied water into pure H$_2$O and brine streams leaving the desalination process, as determined for a thermodynamically ideal (reversible) process. The USGS data in combination with the Pitzer mixed electrolyte model (Pitzer, 1987; Pitzer, 1973) are used to compute the difference in chemical potential (Mistry et al., 2011) of these streams, which determines LWS for each groundwater sample. In this study, LWS is calculated per unit mass of pure H$_2$O produced ($\dot{m}_p$, 1 kg/s) and written as $\dot{W}_{	ext{least}}/\dot{m}_p$, with results presented in the more convenient units kWh/m$^3$. 

Figure 3: Map of groundwater samples analyzed in this paper from USGS, CSHSA, GEMS and UGR datasets.
3.1 Derivation

LWS on a mass basis is derived from a control volume surrounding a black-box separator. The desalination system is modeled as a black-box separator with an inlet stream, the feed ($f$), and two outlet streams, the brine ($b$) and the product ($p$), as shown in Fig. 4. All streams have different salinities $S$. A control volume is chosen far enough away from the separator that the inlet and outlet streams are at ambient pressure and temperature, $T_e$. The heat entering the system at environmental temperature is $\dot{Q}$, and the rate of work done on the system to cause separation is $\dot{W}_{sep}$. Mistry et al. (Mistry, A.Hunter and Lienhard, 2013) provide a detailed discussion regarding this choice of control volume.

![Figure 4: A control volume of a desalination system modeled as a black-box separator for deriving LWS. $S$ is salinity of the indicated stream in kg solute/kg solution.](image)

Combining the first and second laws of thermodynamics on this control volume gives the rate of work for separation:

$$\dot{W}_{sep} = \dot{m}_p g_p + \dot{m}_b g_b - \dot{m}_f g_f + T_e \dot{S}_{gen}$$  (1)

where $g_j$ is the specific Gibbs free energy per kilogram of solution $j$, $\dot{m}_j$ is the mass flow rate of stream $j$, and $\dot{S}_{gen}$ is the total entropy generated by the separation process within the control volume. LWS represents the minimum amount of work required for separation, which occurs when the entropy generation is zero, i.e., for thermodynamically reversible operation (Mistry et al., 2011):

$$\dot{W}_{least} = \dot{m}_p g_p + \dot{m}_b g_b - \dot{m}_f g_f$$  (2)

Therefore, the difference between LWS and actual specific energy consumption results
from irreversibilities generated in desalination systems. Entropy generation for thermal desalination systems primarily results from heat transfer across a finite temperature difference, while entropy generation for membrane desalination systems (e.g., reverse osmosis) mainly results from water transport through the high pressure drop across the membrane (Mistry, A.Hunter and Lienhard, 2013). Consequently, compositional effects do not substantially impact entropy generation in many systems (Mistry, A.Hunter and Lienhard, 2013). Conservation of mass for the water and the salts yields LWS per mass flow rate of product in terms of mass recovery ratio:

\[
\frac{W_{\text{least}}}{\dot{m}_p} = (g_p - g_b) - \frac{1}{r}(g_f - g_b)
\]  

where the mass recovery ratio is defined as the ratio of the mass flow rate of product stream to the mass flow rate of feed stream:

\[
r = \frac{\dot{m}_p}{\dot{m}_f}
\]

We can gain more insight into the effect of physical properties on LWS by rewriting Eq. (1) on a molar basis (Mistry et al., 2011; Mistry, A.Hunter and Lienhard, 2013):

\[
\frac{\bar{W}_{\text{least}}}{\bar{n}_{\text{H}_2\text{O},p}}R_gT = \left( \ln \frac{a_{\text{H}_2\text{O},p}}{a_{\text{H}_2\text{O},b}} + \sum_s b_{s,p}M_{\text{H}_2\text{O}} \ln \frac{a_{s,p}}{a_{s,b}} \right) - \frac{1}{\bar{r}} \left( \ln \frac{a_{\text{H}_2\text{O},f}}{a_{\text{H}_2\text{O},b}} + \sum_s b_{s,f}M_{\text{H}_2\text{O}} \ln \frac{a_{s,f}}{a_{s,b}} \right)
\]

where \( M \) is molar mass, \( R_g \) is the universal gas constant, \( T \) is the ambient temperature, subscript \( s \) represents all binary salt species formed from ion species \( i \) in the mixture, \( a \) represents the activities of solutes and solvent in each stream, the molar recovery ratio \( \bar{r} \) is defined as the ratio of molar flow rate of water in product stream to molar flow rate of water in feed stream:

\[
\bar{r} = \frac{\dot{n}_{\text{H}_2\text{O},p}}{\dot{n}_{\text{H}_2\text{O},f}}
\]

and total molality \( b \) is defined as the sum of ion molalities in mol/kg, for all ion species \( i \) in solution:\n
\footnote{LWS calculations account for speciation effects, derived from unspeciated ion concentrations measured in a laboratory. LWS molality calculations include the following anions: Br, Cl, CO_3, HCO_3, SO_4, and HSO_4. LWS molality calculations include the following cations: Ba,
\[ b = \sum_{i} b_i \quad (7) \]

LWS is a function of feed and product composition, recovery ratio, and ambient temperature and pressure (Mistry et al., 2011; Mistry, A.Hunter and Lienhard, 2013). Figure 5 shows how LWS increases with recovery ratio and TDS. A characteristic seawater solution curve is included for comparison to BGW. A 35,000 mg/L mixture has a minimum least work of separation (MLWS) of approximately 0.74 kWh/m$^3$, over 3 times the amount of a 10,000 mg/L brackish solution. Table 1 includes LWS evaluated at 0%, 50%, 70%, and 90% recovery for various brackish and seawater solutions, including those in Fig. 5.

![Figure 5: LWS as a function of recovery ratio ranging from 0%-90% and TDS for one seawater solution and three BGW solutions containing different TDS concentrations and different solute ratios. LWS values are listed in Table 1.](image)

Ca, Fe(II), K, Mg, Mn, Na, Sr, BaOH, Fe(II)OH, Fe(II)HCO$_3$, MgOH, MnOH, and MnHCO$_3$. In contrast, total measured molality calculations are done with only unspeciated ion concentrations that can be measured in a laboratory. Total measured molality calculations include the following anions: Br, Cl, CO$_3$, HCO$_3$, and SO$_4$. Total measured molality calculations include the following cations: Ba, Ca, Fe, K, Mg, Mn, Na, and Sr. Total measured molality calculations are used to determine correlations between LWS and measurable parameters.
Table 1: LWS in kWh/m³ at 0%, 50%, 70%, and 90% recovery r for brackish and seawater solutions containing different TDS concentrations and different solute ratios.

<table>
<thead>
<tr>
<th>TDS (mg/L)</th>
<th>r = 0%</th>
<th>r = 50%</th>
<th>r = 70%</th>
<th>r = 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 mg/L</td>
<td>0.0084</td>
<td>0.012</td>
<td>0.014</td>
<td>0.021</td>
</tr>
<tr>
<td>2,500 mg/L</td>
<td>0.050</td>
<td>0.069</td>
<td>0.086</td>
<td>0.13</td>
</tr>
<tr>
<td>5,000 mg/L</td>
<td>0.11</td>
<td>0.15</td>
<td>0.19</td>
<td>0.28</td>
</tr>
<tr>
<td>7,500 mg/L</td>
<td>0.15</td>
<td>0.20</td>
<td>0.25</td>
<td>0.38</td>
</tr>
<tr>
<td>10,000 mg/L</td>
<td>0.20</td>
<td>0.28</td>
<td>0.35</td>
<td>0.54</td>
</tr>
<tr>
<td>35,000 mg/L</td>
<td>0.74</td>
<td>1.0</td>
<td>1.4</td>
<td>2.5</td>
</tr>
</tbody>
</table>

3.2 Calculations

To determine LWS, we use the code developed by Thiel (Thiel and Lienhard, 2014) for the Pitzer mixed electrolyte model (Pitzer, 1987; Harvie, Møller and Weare, 1984; Harvie and Weare, 1980). In this paper, LWS is given for a pure product stream ($a_{H_2O,p} = 1, b_{s,p} = 0$ in Eq. (5)) at atmospheric pressure and is evaluated at 80% recovery, because functioning BGW desalination systems typically operate at 75% - 90% recoveries (Greenlee et al., 2009).

4 Trends in LWS

We explore trends in LWS as a function of TDS, specific conductance, total molality, and ionic strength, as well as effects of various solute ratios related to BGW origin and geochemical processes. First, we develop simplified equations for LWS as a function of recovery ratio and TDS, specific conductance, total measured molality, and ionic strength, all of which have correlation coefficients greater than 0.8. These equations allow LWS to be estimated based on various types of proxy data (TDS, specific conductance, molality, ionic strength) with varying levels of precision, thus offering simplified alternatives to numerical modeling. We then examine how groundwater ion composition influences LWS. We investigate differences in LWS at a fixed TDS and SC by comparing separation requirements of major ion constituents.
4.1 Simplified correlation equations for LWS based on USGS dataset

Correlation coefficients are determined between LWS (as determined from the thermodynamic model) and various other measurements of solution properties (see Table 2). Hardness and alkalinity are weakly correlated to LWS, while TDS, specific conductance, total measured molality and ionic strength are more strongly correlated to LWS.

Table 2: Correlation coefficient $R$ of various chemical water properties $P$ with LWS.

<table>
<thead>
<tr>
<th>Parameter $P$</th>
<th>Correlation Coefficient $R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molality (mol/kg)</td>
<td>0.99</td>
</tr>
<tr>
<td>Specific Conductance ($\mu$S/cm)</td>
<td>0.95</td>
</tr>
<tr>
<td>Total dissolved solids (mg/L)</td>
<td>0.93</td>
</tr>
<tr>
<td>Ionic strength (mol/kg)</td>
<td>0.81</td>
</tr>
<tr>
<td>Hardness (mg/L)</td>
<td>0.31</td>
</tr>
<tr>
<td>Alkalinity (mg/L)</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Therefore, linearized equations for LWS per unit of product as a function of recovery ratio and chosen parameter $P$ are developed for TDS, SC, total measured molality, and ionic strength. These equations can be written as:

$$\frac{\dot{W}_{\text{least}}}{m_p} = Y \times f(r) \times P$$  \hspace{1cm} (8)

where $Y$ is a dimensional constant of magnitude 1 (see Table 3). The function $f(r)$ is a unitless sixth-order polynomial fit for each parameter with LWS computed at recoveries ranging from 0%-90%:

$$f(r) = \sum_{n=0}^{6} a_n r^n$$  \hspace{1cm} (9)

The polynomial accounts for the increase in LWS as a function of recovery ratio. As a result, LWS can be evaluated at a recovery of up to 90%. Table 4 contains the constants necessary for evaluating Eq. (9).
Table 3: Dimensions and symbols of $Y$ for TDS, SC, molality, and ionic strength.

<table>
<thead>
<tr>
<th>Parameter $P$</th>
<th>TDS</th>
<th>SC</th>
<th>Molality</th>
<th>Ionic strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol for $Y$</td>
<td>$A$</td>
<td>$D$</td>
<td>$B$</td>
<td>$C$</td>
</tr>
<tr>
<td>Units of $Y$</td>
<td>kWh/m$^3$</td>
<td>kWh/m$^3$</td>
<td>kWh/m$^3$</td>
<td>kWh/m$^3$</td>
</tr>
<tr>
<td></td>
<td>mg/L</td>
<td>µS/cm</td>
<td>mol/kg</td>
<td>mol/kg</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Constants needed to evaluate $f(r)$ for TDS, SC, molality, and ionic strength.

<table>
<thead>
<tr>
<th>Parameter $P$</th>
<th>TDS</th>
<th>SC</th>
<th>Molality</th>
<th>Ionic strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>$a_i \times 10^5$</td>
<td>$a_i \times 10^6$</td>
<td>$a_i \times 10$</td>
<td>$a_i \times 10$</td>
</tr>
<tr>
<td>0</td>
<td>1.380</td>
<td>10.26</td>
<td>5.911</td>
<td>3.047</td>
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<td>4.141</td>
<td>2.386</td>
<td>1.258</td>
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<tr>
<td>2</td>
<td>3.196</td>
<td>24.08</td>
<td>13.93</td>
<td>6.727</td>
</tr>
<tr>
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<td>−129.9</td>
<td>−75.31</td>
<td>−36.63</td>
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<tr>
<td>4</td>
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<td>361.3</td>
<td>209.8</td>
<td>102.8</td>
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<tr>
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<td>−442.3</td>
<td>−257.2</td>
<td>−126.5</td>
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<tr>
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<td>27.75</td>
<td>209.0</td>
<td>121.6</td>
<td>60.0</td>
</tr>
</tbody>
</table>

It is important to note that the simplified LWS equations are based on BGW data. Therefore, any water containing a TDS outside of 500 - 10,000 mg/L may increase the departure of Eq. (8) from actual LWS values. Table 5 includes the corresponding BGW ranges for specific conductance, molality, and ionic strength, as well as the average relative percent error and standard deviation between LWS approximations [Eq. (8)] and actual LWS [Eq. (3)] for the four parameters.

Table 5: Average relative percent error and standard deviation between LWS approximation [Eq. (8)] and actual LWS [Eq. (3)].

<table>
<thead>
<tr>
<th>Parameter $P$</th>
<th>TDS</th>
<th>SC</th>
<th>Molality</th>
<th>Ionic strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>500 - 10,000</td>
<td>17 - 23,400</td>
<td>0.0024 - 0.34</td>
<td>0.0021 - 0.31</td>
</tr>
<tr>
<td>Range units</td>
<td>mg/L</td>
<td>µS/cm</td>
<td>mol/kg</td>
<td>mol/kg</td>
</tr>
<tr>
<td>Percent error</td>
<td>20.2</td>
<td>16.5</td>
<td>6.31</td>
<td>30.8</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>15.8</td>
<td>18.2</td>
<td>5.66</td>
<td>23.5</td>
</tr>
</tbody>
</table>
4.1.1 Total dissolved solids

Feedwater to desalination systems is typically described in terms of TDS. Therefore, establishing a simple equation for the baseline energy requirement of a specified feedwater TDS may prove quite useful for those in the desalination industry. The correlation coefficient between TDS and LWS, 0.93, indicates that these two parameters have a fairly linear relationship, as illustrated in Fig. 6; however, the scatter in this relation is considerable, and further knowledge of the water composition can be used to reduce the uncertainty (see Section 4.2). The best-fit line in this figure captures the linearity between TDS and LWS, revealing, as expected, that LWS increases with increasing TDS.

![Graph showing the relationship between Total dissolved solids (mg/L) and Least work (kWh/m³)](image)

\[
\frac{\dot{W}_{\text{least}}^{\text{min}}}{\dot{m}_p} = A \times f(0.8) \times TDS
\]

\[R^2 = 0.85\]

Figure 6: LWS as a function of TDS for 28,000 BGW samples with complete composition data. Each dot represents a BGW sample. The best-fit line and its equation, as well as the coefficient of determination, are included in red on the plot. This representation has two separate trends occurring above and below the best fit line (see discussion in Sect. 4.3.2).

4.1.2 Specific conductance

Specific conductance (SC) measures a saline water solution’s ability to conduct electricity. Instrumentation for SC data acquisition is readily available and inexpensive, and
has an accuracy of over 95%. Therefore, this parameter can easily be measured in the field. The correlation coefficient between specific conductance and LWS, 0.95, reflects the approximately linear relationship between these two parameters. LWS generally increases with specific conductance, as shown in Fig. 7. Some highly anomalous points in Fig. 7 represent database errors, possibly in SC units. Within the SC range specified in Table 5, LWS can be determined with reasonable accuracy with one simple field measurement.

![Graph](image)

Figure 7: LWS as a function of specific conductance for 27,000 BGW samples with complete composition and SC data. Each dot represents a BGW sample. The best-fit line and its equation, as well as the coefficient of determination, are included in red on the plot.

4.1.3 Molality

The correlation coefficient between total measured molality [Eq. (7)] and LWS, 0.99, signifies that these two parameters have an almost perfectly linear relationship, corresponding to expected behavior based on the physics (see Section 4.2) (Pitzer, 1973). Figure 8 demonstrates that LWS grows with increasing molality with less apparent relative uncertainty than the TDS or SC relations (Figs. 6 and 7). Therefore, the average error and standard deviation for the molality-based correlation are less than those for the
TDS-based and SC-based correlations, respectively. Because the correlation coefficient of molality with LWS is almost one and the average error is quite low, Eq. 8 can be used to calculate LWS with high accuracy, when compared to the Pitzer-Kim thermodynamic model, for samples containing 500-10,000 mg/L of TDS.

\[
\frac{\dot{W}_{\text{least}}}{\dot{m}_p} = B \times f(0.8) \times b \\
R^2 = 0.98
\]

Figure 8: LWS as a function of total measured molality for 28,000 BGW samples with complete composition data. Each dot represents a BGW sample. The best-fit line and its equation, as well as the coefficient of determination, are included in red on the plot.

### 4.1.4 Ionic strength

Molal ionic strength is defined in terms of the charge \( z \) and molality of each ion species (Robinson and Stokes, 2002):

\[
I = \frac{1}{2} \sum_i b_i z_i^2 
\]

The summation includes all solute ion species \( i \) in solution that are used in total measured molality calculations. The correlation coefficient between ionic strength and LWS, 0.81, implies that these two variables have a relatively strong linear dependence on one another, as shown in Fig. 9. Although Fig. 9 shares a triangular-like shape with Fig. 6, ionic strength fans outward from the origin far more than TDS. Figure 9 includes a best-fit line, showing that LWS increases with ionic strength.
4.2 Comparison of different proxies

Various measurement proxies for LWS are compared in decreasing order of correlation coefficient with LWS:

1. Total measured molality and LWS have a near-perfect linear correlation for BGW solutions, due to the separation physics of dilute solutions. LWS is directly related to the feed solution’s osmotic pressure, which is a colligative property of mixtures. Colligative properties depend only on the number of moles of solute per unit solution for ideal (dilute) solutions, which are approximated by the low solute concentrations found in BGW (Atkins and Jones, 2010). Therefore, LWS is directly related to molality in dilute solutions. The minor discrepancy between the molality-based correlation and the Pitzer mixed electrolyte model are attributed to deviations from electroneutrality of the original data (< 5%) and effects of nonideality and speciation in these dilute solutions: the molality-based correlation effectively sets the solvent activity coefficient to one, when in reality the activity
minimally deviates from one.

2. SC is a measure of how easily current flows through a solution; current is simply the flow of free-moving charge, which, in BGW solutions, are the ions. Thus, the greater the molality, the more free-to-move charges, and the greater the conductivity. The relationship between concentration [e.g., molality] and conductivity is linear at very low concentrations and non-linear at high concentrations (Robinson and Stokes, 2002). Because molality is directly related to LWS in BGW, SC is also related to LWS, but the variations in valence of ions influence SC separately from molality.

3. TDS, the sum of solute mass fractions, is related to molality, but with a weighting by solutes. Because molality and TDS are thereby correlated, LWS is also strongly correlated with TDS. However, TDS’s mass dependence results in a weaker correlation between TDS and LWS than molality or SC.

4. Ionic strength is a function of molality and ionic charge. Increasing ion molality results in higher LWS, while increasing ionic charge results in lower LWS. Therefore, ionic strength alone cannot generally be used to estimate LWS.

Correlations 1-3 can be used to estimate desalination energy requirements of BGW depending on availability of field measurements. SC requires one simple field measurement, whereas molality requires multiple measurements to establish ion concentrations. When ion concentration data are available, thermodynamic modeling or a molality-based approximation for LWS should be used. If ion concentration data are incomplete, the TDS-based correlation provides a quick and simple way to approximate LWS for a solution containing a specified TDS. Ionic strength should not be used to estimate LWS; this parameter requires molality measurements, and if those are available, using the molality-based correlation will provide a much better LWS approximation.

4.3 Effects of major ions on LWS

4.3.1 Major ions

The dominant cations $C$ in the USGS dataset’s groundwater samples are calcium and sodium, whereas the dominant anions $A$ are bicarbonate, sulfate and chloride. Here
we consider the distribution of five major electrolytes in BGW samples: calcium bicarbonate, calcium sulfate, sodium bicarbonate, sodium sulfate and sodium chloride. We denote an anion or cation major on a mass basis when it accounts for over 50% of the total mass concentration of the anion or cation, respectively:

\[
\text{major ion} = \frac{m_i}{\sum_{i \in \{C \text{ or } A\}} m_i} > 0.5
\]  

(11)

Sodium and calcium constitute the major cation in 51% and 25% of BGW samples, respectively. Almost all of the remaining BGW samples contain a combination of sodium and calcium as major cations (i.e., \( m_{Na} + m_{Ca} > 0.5 \sum_{i \in \{C\}} m_i \)). Bicarbonate, sulfate, and chloride are major anions in 48%, 26% and 9.0% of BGW samples, respectively. The remaining samples contain a combination of the three as dominant anions (i.e., \( m_{Cl} + m_{SO_4} + m_{HCO_3} > 0.5 \sum_{i \in \{A\}} m_i \)).

4.3.2 Compositional effects at fixed TDS and SC

Figure 6 shows that the TDS-based fit, Eq. (8), does not capture the full dependence of Eq. (3) on the specific ions in groundwater: two distinct trends appear above and below the best-fit line. This separation shows that BGW samples with equal TDS can have different separation requirements. The presence of different sets of constituent ions accounts for this phenomenon. Figure 10 is a plot of LWS for six single electrolyte solutions containing a TDS of 1,000 mg/L. The five salts shown are the major electrolytes found in BGW samples in the dataset. Regarding cations, water with sodium tends to require more work to achieve separation than water with calcium at fixed TDS. The general trend among anions is that separation energy decreases in going from chloride to bicarbonate to sulfate. Consequently, heavier electrolytes tend to require a lower LWS, partly because of lower molality, increased ion pairing and higher ionic charge (monovalence vs. divalence) (Mistry, A.Hunter and Lienhard, 2013).
To further investigate compositional effects on the correlations in Figs. 6 and 7, we replotted the data using colors to indicate the different major cations and anions in the samples (Fig. 11). Figures 11(a) and 11(c) show that samples in which sodium is the major cation tend to have higher separation requirements than those for which calcium is the major cation at any given TDS or SC. Figures 11(b) and 11(d) illustrate that separation requirements tend to increase from sulfate to bicarbonate to chloride at any given TDS or SC. Figure 11(b) also shows that the dominant anions in BGW solutions result in two distinct trends in LWS as a function of TDS: BGW samples with chloride as the major anion form the upper trend, while BGW samples with sulfate as the dominant anion form the lower trend. Consequently, anions appear to be the predominant factor in LWS differences at fixed TDS.

Figure 10: LWS for five single electrolyte solutions containing a TDS of 1000 mg/L as a function of recovery ratio ranging from 0%-90%.
Figure 11: LWS evaluated at 80% recovery as a function of (a,b) TDS and (c,d) SC for BGW samples with complete composition data. Each dot corresponds to a BGW sample and is colored based on its major cation and its major anion [Eq. (11)].

5 Geographic distribution of LWS and chemical composition across the U.S.

LWS is computed and mapped for 28,000 BGW samples with complete constituent ion data across the U.S. We also map BGW samples, requiring a low LWS and located in high water stress regions, to highlight areas that hold higher potential for desalination. Because LWS and water stress vary considerably across the U.S., location must be considered in decision-making regarding desalination system selection and design. Because LWS depends on major ion concentration and TDS of a solution, we also study the geographic distribution of these parameters across the U.S. TDS is mapped for 46,000
BGW samples, while major ions concentration is mapped for 28,000 BGW samples that have complete constituent ion data.

5.1 LWS

Figure 12 illustrates that LWS for BGW samples in the USGS dataset varies considerably across the United States. Figure 13 shows the water stress level of the BGW samples for which LWS is calculated. Water stress is equal to the ratio of total withdrawals for freshwater uses to total available renewable supply in a given area annually, as defined by Gassert et al. (Gassert et al., 2013). A higher percentage indicates that more water users are competing for a limited water supply. For example, in extremely high stress areas, more than 80% of water available to domestic, agricultural and industrial users is withdrawn annually. Many samples are located in areas experiencing high or extremely high levels of water stress, i.e., a large disparity between freshwater supply and freshwater demand.
Figure 12: (a) Map of LWS (evaluated at 80% recovery) for 28,000 BGW samples with complete composition data. Each dot represents a groundwater sample, and each dot color corresponds to one of five LWS brackets, specified in (b). (b) Histogram showing the number of samples that fall into each LWS bracket.
Figure 13: Map of water stress levels (Gassert et al., 2013) at the locations of 28,000 BGW samples across the continental United States. Water stress is defined as:

\[
\text{water stress} = \frac{\text{total annual water withdrawals}}{\text{total annual renewable supply}} \times 100
\]

Water stress values are given in percentage; higher values indicate more competition among users for water. Areas with available renewable supply and withdrawals less than 0.03 m/m² and 0.012 m/m², respectively, are labeled as ‘arid and low water use’ (Gassert et al., 2013).

Groundwater samples that fall in the two highest water stress brackets from Fig. 13 and the two lowest LWS brackets from Fig. 12 are mapped in Fig. 14. MLWS represents a baseline of energy costs required for desalination, independent of technology used, while high water stress indicates that more water users are competing for a limited water supply. Therefore, Fig. 14 highlights regions with higher potential for desalination to play a role in reducing the gap between high water demand and low water supply locally, though other costs and limitations will be important factors in addition to LWS.
Figure 14: Map of BGW samples that fall into two lowest LWS brackets from Fig. 12 and the two highest water stress brackets from Fig. 13. Each dot represents a BGW sample, and each color represents a pair of LWS and water stress brackets. Clusters of dots suggest areas with high potential for desalination based on LWS and stress.

5.2 Chemical composition

The distribution of BGW chemical composition, both TDS and ion constituents, is central to evaluating the resource. Variations in BGW chemical composition can be used to understand the origin of BGW and possibly interpolate or extrapolate its occurrence where data are limited, based on hydrogeologic setting. Overall chemical composition may impact BGW treatment and use options, and specific ion constituents may interfere with specific BGW uses (McMahon et al., 2016; Stanton et al., 2017). Furthermore, BGW samples with similar TDS can have different energy requirements if their chemical compositions differ (see Sec. 4.3.2). Therefore, TDS, major cations, and major anions are mapped across the U.S. Regions in states and/or principal aquifers containing clusters of TDS or major ions highlight composition characteristics that are typically dominant.
in a given area. As a result, we identify clusters, which will likely prove useful in: 1) determining the most important water parameters to measure when collecting data in the field; 2) selecting desalination technology; 3) estimating desalination energy costs; 4) minimizing membrane scaling in membrane-based desalination systems; and 5) selecting sites for groundwater wells. It is emphasized that the existing data are not uniformly distributed and tend to be biased in favor of freshwater and shallow resources.

5.2.1 Total dissolved solids

Figure 15 illustrates the variability in TDS of 46,000 BGW samples across the continental U.S. Approximately 91% of the samples contain 500 - 3,000 mg/L TDS, and these samples are present in all parts of the U.S. for which data are available. Particularly high densities of groundwater samples occur in the Dakotas, Texas, Central Valley in California and southeastern Kansas.

\footnote{Waters with calcium, magnesium, sulfate, and carbonate have a higher scaling propensity (Roy, Sharqawy and Lienhard, 2015).}
Figure 15: (a) Map of TDS ranging from 500-10,000 mg/L of 46,000 BGW samples across the U.S. Each dot corresponds to a groundwater sample, and each dot color corresponds to one of four TDS brackets, specified in (b). (b) Histogram showing the number of samples that fall into each of these brackets.
5.2.2 Major cations

Figure 16 maps the two major cations, calcium and sodium, across the continental U.S. for 28,000 BGW samples. North Dakota, Texas and California have the largest number of groundwater samples, accounting for the larger number of ion clusters found in these states. Calcium is the major cation in Connecticut, Illinois, Indiana, Iowa, Kansas, Kentucky, Minnesota, Missouri, Nebraska, Ohio, Oklahoma, Pennsylvania, and Wisconsin, while sodium dominates in the remaining states (Fig. 18(a)). Despite sodium’s prevalence, calcium maintains a considerable presence in almost all states. Clusters of calcium and sodium can be found in both landlocked and coastal regions, though sodium tends to have a larger presence in coastal areas presumably due to seawater intrusion in some areas.
Figure 16: Maps of groundwater samples with (a) calcium and (b) sodium concentrations of greater than 50% of total cation concentration for 28,000 BGW samples with complete composition data. Each dot represents a groundwater sample.
5.2.3 Major anions

Figure 17 maps the three major anions, chloride, bicarbonate, and sulfate, across the continental U.S. North Dakota, Texas, and California have the largest number of groundwater samples, accounting for the larger number of ion clusters found in these states. Chloride is the dominant anion in Alabama, Arizona, Florida, Massachusetts, New Hampshire, New Jersey and Oregon (Fig. 18(b)); chloride can be found in both landlocked and coastal areas, though it typically occurs nearer to saline bodies of water. Sulfate is the dominant anion in Colorado, Connecticut, Delaware, Georgia, Montana, South Dakota, Tennessee and Wyoming (Fig. 18(b)); compared to chloride and bicarbonate, sulfate has a larger presence inland relative to coastal areas. Bicarbonate is the dominant anion in the remaining states (Fig. 18(b)); it has an extensive reach across the nation in almost all coastal and landlocked areas with available BGW data. The USGS data show that bicarbonate is likely to be the dominant anion in relatively low TDS samples. Therefore, a bias towards freshwater also denotes a bias towards bicarbonate samples. Despite bicarbonate’s prevalence, both chloride and sulfate have considerable presences in California, Texas, Michigan, North Dakota and Utah, and sulfate has sizable occurrences in Arizona, Florida, Iowa, Kansas, New Mexico, Ohio and Oklahoma. Unlike dominant cations, major anions data display a more uneven distribution across states, in part due to the consideration of three rather than two ions in the anions case.
Figure 17: Maps of groundwater samples with (a) chloride, (b) bicarbonate, and (c) sulfate concentrations of greater than 50% of total anion concentration for 28,000 BGW samples with complete composition data. Each dot represents a groundwater sample.
Figure 18: Stacked chart of (a) major cations, calcium and sodium, and (b) major anions, chloride, sulfate and bicarbonate, in each state. Each bar corresponds to a state in the continental U.S. Each color represents a major cation or anion.
6 Extension of USGS LWS correlations and trends to international datasets

This section demonstrates that the USGS LWS composition trends at fixed TDS and LWS simplified equations for TDS and molality should apply to groundwater samples from other areas of the world. SC and ionic strength correlations are not considered due to lack of data and correlation weakness with LWS, respectively. In order to compare USGS results to international data, a least work analysis is conducted on 5,650 BGW samples in Asia, Australia, Europe, North America, and South America.

6.1 Effects of major ions on LWS at fixed TDS

Figure 19 shows LWS as a function of TDS and ion composition for the international samples, with the USGS samples faded in the background. The major ions in the international samples are the same as those in the U.S. Calcium and sodium are the major cations, with sodium as the most commonly dominant like in the U.S. The major anions are chloride (65%), followed by bicarbonate (33%) and sulfate (2%). This anion distribution differs from that in the U.S. data, which contains bicarbonate (48%) as the most commonly dominant anion. This disparity reflects some limitations in data. The majority of international data comes from the South Australian CSHSA, in which sodium chloride is the most commonly dominant electrolyte partly due to seawater intrusion in this region. Data constraints prevented us from achieving more extensive inland coverage, where sulfate as the major anion might be more common.

For BGW samples with chloride or bicarbonate as the dominant anion, the international data follow the same trajectory as the USGS data (Fig. 19(a)): the Cl-dominated international samples form the same ‘upper trend’ above the U.S. best fit line as the Cl-dominated U.S. data (Fig. 11(b)), and high concentrations of bicarbonate also occur in lower TDS samples. Relatively few of the international samples contain sulfate as the major anion and conform to the ‘lower trend’ in Fig. 11(b). As for the U.S. samples, separation energy decreases in going from chloride to bicarbonate to sulfate for anions and from sodium to calcium for cations.
6.2 Simplified correlation equations for LWS

Because of differences in major ion frequency in the USGS and international samples, their TDS linear regressions do not match precisely (Fig. 20(a)). However, if we apply the USGS TDS correlation for LWS to the international samples,

\[
\frac{W_{\text{least}}}{m_p} = A \times f(r) \times TDS_{\text{international}}
\]  

where \(f(r)\) can be found in Table 4, the average relative percent error between the LWS correlation [Eq. (12)] and actual LWS [Eq. (8)] matches that of the USGS data (20.2%). The standard deviation of the error in the international data is 6.38% compared to the USGS value of 15.8%. The international data set has a more linear trajectory and thus smaller standard deviation from its average percent error, compared to its U.S. counterpart which contains a wider range of compositions (Fig. 19(b)). These results suggest that the TDS-based USGS equation for LWS [Eq. (8)] derived from diverse water types can be extended approximately to groundwater samples elsewhere; however, because groundwater composition varies significantly from location to location, local and regional correlations may provide better fits in areas with more limited geochemical variation.
Because most of the international samples contain high concentrations of chloride, we also consider linear regressions for the USGS and international data samples in which only chloride is the dominant anion. Figure 20(b) illustrates that the two linear regressions almost perfectly match one another, reaffirming the fact that the Cl-dominated international samples overlap with the Cl-dominated U.S. samples. From these samples, we develop a new linearized equation for LWS per unit of product as a function of recovery ratio and TDS, with the same format as Eq. (8). The accuracy of this new result is shown by the high value of $R^2 = 0.99$. Table 6 contains the constants necessary for evaluating this equation, which can be used generally where chloride is known to be the dominant anion. For cases in which TDS is known but ionic content is unknown, the more general USGS TDS correlation established for groundwater of more diverse composition can be used.

![Figure 20: USGS and international data linear regressions for LWS as a function of TDS when (a) all samples regardless of composition are considered and (b) samples with chloride as the dominant anion are considered.](image-url)
Table 6: Constants needed to evaluate $f(r)$ [Eq. (9)] for the Cl-specific TDS version of Eq. (8). Constants are based on U.S. and international data.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_i \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-94.33</td>
</tr>
<tr>
<td>6</td>
<td>44.34</td>
</tr>
</tbody>
</table>

When complete ion composition is known and chloride is not the dominant anion, the molality-based USGS correlation ($R^2 = 0.98$) should be used to estimate LWS. If we apply the USGS correlation for LWS as a function of molality to the international samples (Fig. 21), the average relative percent error between the LWS correlation and actual LWS in the international data (6.32%) almost perfectly matches that in the USGS data (6.31%); the standard deviation in the international data is 1.74% compared to the USGS value of 5.66%, due to wider ranges of compositions in the USGS data. These results suggest that the molality-based USGS equation for LWS [Eq. (8)] can be extended to any groundwater sample regardless of ionic content.

Figure 21: LWS as a function of molality for the international data with molality-based USGS correlation for comparison.
7 Implications of USGS composition and LWS results on water resource planning

Previous sections show that BGW composition (TDS, major ions) and LWS required for BGW desalination vary considerably across the U.S. and in other countries. Consequently, location is crucial in desalination decision-making, as a specific location for a BGW desalination plant may correspond to a particular BGW feedwater. Identifying clusters of ions on maps in Section 5 can aid in the location and thus the source water selection process. Once the brackish feedwater is selected, it will undergo desalination before use in high quality applications. The most widely used desalination system for BGW is brackish water reverse osmosis (BWRO); Figure 22 illustrates the multiple processes that typically comprise a BWRO plant. For a given source water composition to a plant, the scaling propensity, correlating to pretreatment, and LWS, correlating to desalination stage performance, can be used to improve the overall plant performance.

Figure 22: A process diagram for a typical BWRO plant. Groundwater pumped from wells undergoes pretreatment, depending on its composition, before being fed into the desalination stage. The desalinated water leaving the RO system then undergoes post-treatment. The final product water is distributed using service pumps to storage tanks or the end consumer.

7.1 LWS: a benchmark for the performance of various desalination technologies

Figure 23 shows the energy consumption of RO, Electrodialysis Reversal (EDR) and Closed Circuit Reverse Osmosis (CCRO), technologies used for BGW desalination, at a fixed feed salinity. The technologies produce different specific energy consumption (SEC) depending on recovery ratio, but they are all bounded by the LWS. Differences in performance become more pronounced at the higher recoveries that are characteristic of BGW systems. Therefore, LWS serves as a robust benchmark for characterizing the performance of the desalination stage of any plant (e.g., the RO stage in Fig. 22), regardless of what desalination technology is used. LWS effectively represents the work that must be done to overcome the varying osmotic pressure through a system at a
given recovery ratio, impacting factors such as driving force (operating pressures in RO or voltage in EDR) and membrane area that determine the energy consumption of a given system. While all real systems will use more energy than LWS, systems that are more energy efficient will operate closer to LWS.

Figure 23: Energy consumption of RO, CCRO, and EDR at a fixed salinity compared to LWS at various recoveries (modified from Nayar et al., 2015).

LWS benchmarks the specific energy consumption (SEC) of the desalination stage of a plant, but Fig. 24 shows that it does not represent the SEC of the entire plant, i.e., of all stages in Fig. 22. The breakdown of plant SEC varies on a case-by-case basis depending on plant parameters such as design, size and fouling propensity of the feedwater. Figure 25 reflects the differences in the SEC breakdowns of two BWRO plants in California; it also shows that pretreatment, RO, and post-treatment energy requirements are typically lumped together in available datasets. Isolating the individual SEC of these three stages would be very useful in allowing for a direct comparison of LWS to RO SEC. This represents a gap in the publicly available data that might usefully be filled in future reporting on real plants.
Figure 24: LWS compared to SEC of 10 BWRO plants with complete feedwater composition data (Veerapaneni et al., 2011; Batista-Garcia et al., 2015). The lighter region represents the difference in plant SEC and LWS.

Figure 25: SEC breakdown of the Richard A. Reynolds and Chino I BWRO plants in California (data from Veerapaneni et al., 2011).
7.2 Scaling propensity of major electrolytes and silica

The saturation index is a commonly used metric for quantifying the potential for salt crystallization in aqueous solutions:

\[
SI = \log \left( \frac{Q}{K_{sp}} \right) = \log \left( \frac{d_A \cdot d_C \cdot d_{\text{aq}}}{K_{sp}} \right)
\]

where \( Q \) is the activity product and \( K_{sp} \) is the solubility product. When \( SI < 0 \) for a particular salt, the solid phase salt tends to dissolve in solution. When \( SI > 0 \) for a particular salt, the solid phase salt tends to precipitate out of solution. Consequently, the saturation indices of the salts in a solution can be used to measure the potential of scale formation on membranes in desalination systems when the solution is used as feedwater. When \( SI < -0.7 \) for a particular salt, the solution can be used as feedwater in desalination systems operating at up to approximately 80% recovery without causing salt crystallization\(^4\), i.e., no pretreatment of feedwater for that salt is required. When \(-0.7 \leq SI < 0\), some pretreatment of feedwater may be required before desalination, and when \( SI \geq 0 \), pretreatment of feedwater is required before desalination.

Figures 26 - 28 illustrate saturation indexes of the USGS samples for which least work of separation is calculated. We consider the scaling propensity of: calcium carbonate (as aragonite or calcite, and through the Langelier Saturation Index); calcium sulfate (as anhydrite or gypsum); and silica (as chalcedony or quartz) at 80% recovery. We focus on these because divalent ions (\( \text{Ca}^{2+}, \text{CO}_3^{2-}, \text{SO}_4^{2-} \)) tend to be less soluble. The plots also include SI limits for 70% and 90% recovery to cover the range of typical operating recoveries for BGW systems. Identifying clusters of samples that may require pretreatment \((-0.7 \leq SI < 0\)) or definitely require pretreatment \((SI \geq 0)\) on the SI maps may assist in selecting locations for desalination where membrane scaling is at a minimum.

\(^{4}\text{SI} < -0.7 \) limit is approximate. At \( SI = \log \frac{d_{\text{aq}}}{K_{sp}} = -0.7 \), the activity of the solute is 5 times less than its activity at its solubility limit. If the activity coefficient does not significantly change, then the concentration would also be 5 times less than at its solubility limit. At a recovery of 80%, the concentration factor \( CF = \frac{1}{1 - r} = 5 \). Therefore, when the activity coefficient does not change as the solute concentration increases, \( SI = -0.7 \) at the beginning of the process corresponds to \( SI = 0 \) at the end of the (80% recovery) process. The same methodology is applied for determining the approximate SI limits at 70% recovery \((SI = -0.4)\) and 90% recovery \((SI = -1)\). In reality, the activity does increase with concentration, though by a minimal amount in dilute solutions such as BGW.
Figure 26: Calcium carbonate saturation indexes (SI) of USGS BGW samples for (a,b) aragonite; (c,d) calcite; and (e,f) the Langelier Saturation Index.
Figure 27: Calcium sulfate saturation indexes (SI) of USGS BGW samples for (a,b) anhydrite and (c,d) gypsum.
In the majority of the USGS groundwater samples, calcium sulfate likely would not pose scaling problems, while calcium carbonate and silica would be more likely to do so (Fig. 29). Pretreatment processes can be used to reduce the concentration of these scalants in feedwater to below their solubility limits before entering the desalination system in a plant. The degree of pretreatment required, based on the scaling propensity of salts in solution, will impact plant capital and operating expenditures, as well as total SEC. Typical pretreatment processes include the addition of antiscalants to promote super-saturation, such as lime-soda ash or caustic soda for silica removal and hydrochloric or sulfuric acid for calcium carbonate removal.

Figure 28: Silica saturation indexes (SI) of USGS BGW samples for (a,b) chalcedony and (c,d) quartz.
8 Conclusions

The USGS major-ions dataset and three international datasets for groundwater were used to assess the minimum work required for BGW desalination. The impact of various groundwater ions has been studied, and simplified curve fits for estimating LWS from various measured quantities were considered. Scaling propensity has also been assessed. The following conclusions have been reached:

1. BGW composition (TDS, major ions, SI) and LWS required for BGW desalination vary considerably across the United States and around the world. Therefore, knowledge of the local water composition is needed in decision-making regarding
2. In the USGS data and the international data, the major cations in BGW are calcium and sodium, while the major anions are bicarbonate, sulfate, and chloride. In the U.S., sodium is the most commonly dominant cation, while bicarbonate is the most commonly dominant anion. In the available non-U.S. data, sodium is the most commonly dominant cation, while chloride is the most commonly dominant anion. Cluster identification of these ions can be used to assist in determining the key water parameters in a given area, in estimating desalination energy costs, and in minimizing membrane scaling in membrane-based desalination systems. More investment in chemical analyses of BGW would be helpful for this type of assessment.

3. At any given value of TDS or SC, water in which calcium is the dominant cation tends to require less work to achieve separation than water in which sodium dominates. The general trend among anions is that LWS increases from sulfate to bicarbonate to chloride at fixed TDS.

4. Regions that hold the potential for desalination to reduce the disparity between high water demand and low water supply can be found throughout the U.S. Similar desalination potential analysis can be extended to other parts of the world with groundwater samples that require a low LWS and lie in water-stressed regions.

5. Simplified equations were tested using samples from the USGS database for estimating LWS as a function of TDS \( (R = 0.93) \), SC \( (R = 0.95) \), molality \( (R = 0.99) \), and ionic strength \( (R = 0.81) \). The SC-based correlation enables estimation of LWS with a single commonly reported field measurement (SC). The molality-based correlation, based on measured total concentrations of major solutes, can be used to determine LWS with very high accuracy. Solute activity-based calculations using the Pitzer-Kim model are theoretically more correct; however, when solute concentrations are low as in BGW, LWS primarily depends on the number of moles of solute species per unit of solution.

6. The USGS simplified equations for LWS as a function of TDS and molality were applied to the international data, showing that they can represent much of the diversity of groundwater samples from around the world. When groundwater ionic content is unknown, the USGS TDS correlation \( (R^2 = 0.85) \) can be used to estimate LWS. When chloride is known to be the dominant anion, the Cl-specific TDS
equation, based on USGS and international chloride dominant solutions \( R^2 = 0.99 \), can be used to determine LWS. When complete ionic content is known and chloride is not the dominant anion, the USGS molality correlation \( R^2 = 0.98 \) can be used to approximate LWS.

7. LWS represents a metric independent of technology to which desalination system energy consumption can be compared in order to evaluate performance. LWS and total plant SEC are not necessarily correlated. More data on the energy consumption of individual desalination stages of plants would be useful.

8. The majority of the USGS groundwater samples at 80% recovery without pre-treatment are likely to experience scaling of calcium carbonate and silica, but not of calcium sulfate. Different forms of pretreatment can be used to reduce these scalant concentrations in solution before the feed enters the desalination system.

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