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RESEARCH ARTICLE

Salinity or sum of constituents—Methods comparison for computing dissolved solids concentrations in streams of the Upper Colorado River Basin

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Abstract

The Colorado River is an important water source in the southwestern United States and northern Mexico. High concentrations of dissolved solids in the river, sourced mainly from the Upper Colorado River Basin (UCOL), cause hundreds of millions of dollars in damages annually to crops and infrastructure. Determinations of total dissolved solids (TDS) in river and tributary samples often rely on summed concentrations of constituents in solution reported as the sum of constituents (SOC), which includes the bicarbonate concentration converted to the equivalent carbonate mass that would be present as a residue after drying. Alternatively, salinity, similar to SOC but including the entire concentration of bicarbonate in solution, may be used as a measure of dissolved solids. Use of SOC results may under-represent actual dissolved-solids concentrations and loads in streams where bicarbonate is a substantial component of the dissolved solids in solution. The objective of this manuscript is to evaluate the differences between the SOC and salinity determinations of dissolved solids in UCOL streams and rivers. Water-quality data from the U.S. Geological Survey were used to compute salinity concentrations at UCOL stream sites for comparison with SOC determinations. Results from 8,001 samples at 418 UCOL sites indicate a median increase in dissolved solids of 20% (13% and 30%, 25th and 75th percentiles, respectively) using the salinity method compared with SOC results. Differences in dissolved solids attributable to the computational approach for handling bicarbonate at UCOL sites were significantly greater than laboratory variability based on results from 890 replicate analyses. Salinity may be a more useful indicator of water quality than SOC in systems with substantial proportions of bicarbonate in the composition of dissolved solids, including the Colorado River and UCOL sites.

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Abbreviations: ROE, residue on evaporation; SOC, sum of constituents; TDS, total dissolved solids; UCOL, Upper Colorado River Basin.

Introduction

The Colorado River (Fig 1) in the southwestern United States (U.S.) is one of the most important water resources in the region, meeting the water needs of 40 million people in the U.S. and Mexico and supplying irrigation for 2.2 million hectares of agricultural land [1]. Elevated concentrations of dissolved solids in streams and rivers of the Upper Colorado River Basin (UCOL), defined as the drainage area upstream of Lees Ferry, Arizona, are an important water-quality issue in the basin and the UCOL is the source of most of the $> 8{\times}10^6$ metric tons of dissolved solids that annually are discharged from Lake Mead into the lower River [2]. High dissolved solids in the Colorado River annually cause hundreds of millions of dollars in damages, mostly in corrosion of pipes and machinery and in the reduction of agricultural output related to water quality [3], and present challenges for the Bureau of Reclamation's obligations for delivery of Colorado River water to Mexico [4]. Understanding dissolved-solids concentrations in UCOL rivers and streams is important for scientists studying trends in concentrations and loads in the basin and evaluating the effectiveness of salinity control measures.



Fig 1. The Colorado River and Upper Colorado River Basin study area (UCOL) within the southwestern United States. Basemap and boundaries from the U.S. Geological Survey [5].

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Dissolved solids in UCOL streams and rivers are naturally sourced from sedimentary rocks [6, 7], including the Eocene Green River Formation [8], the Paradox Member of the Pennsylvanian Hermosa Formation, and the Upper Cretaceous Mancos Shale. If carbonate, gypsum, anhydrite, halite, and silicate rocks in these units contact groundwater, they will dissolve and be transported to rivers and streams as baseflow or flow from springs [9]. Runoff from precipitation and snowmelt may contact these rocks at land surface in some locations, also increasing dissolved solids in receiving streams and rivers. Irrigation, particularly flood irrigation, applied to agricultural lands composed of these sedimentary units also contribute dissolved solids to UCOL streams [7].

Historically, concentrations of total dissolved solids (TDS) in water samples have been determined by analytical laboratories using two methods: (1) TDS has been determined based on the weight of the residue of a filtered water sample after drying at elevated temperatures (residue on evaporation, or ROE) [10–12], and (2) a second method developed as a quality-control check for ROE involving summation of the concentrations of the individual constituents measured in solution, or SOC [10, 11, 13, 14]. During the heating and drying required by the ROE method, some bicarbonate in solution is volatilized as carbon dioxide and water, with carbonate residue remaining [10, 11, 13, 14]:

$$2HCO_3^-(aq) \rightarrow CO_3^{2-}(s) + CO_2(g) + H_2O(g) \quad (1)$$

To facilitate the comparison of SOC results with ROE results as a quality-control check, the traditional calculation of SOC replicates the effects of CO_2 volatilization illustrated in Eq 1 by converting bicarbonate concentration to a dried-equivalent carbonate concentration, using the stoichiometry of Eq 1, before summing the carbonate with other dissolved constituents in the water sample. The use of this conversion (Eq 2) results in a lower contribution to the dissolved solids determination than if the unconverted bicarbonate concentration were used:

$$HCO_3^-(mg/L) \times \frac{1\ mmole\ HCO_3^-}{61.0158\ mg\ HCO_3^-} \times \frac{1\ mmole\ CO_3^{2-}}{2\ mmole\ HCO_3^-} \times \frac{60.008\ mg\ CO_3^{2-}}{1\ mmole\ CO_3^{2-}} = CO_3^{2-}(mg/L) \quad (2)$$

[molar masses given in millimoles (mmol) to reduce the number of conversions for concentrations in mg/L]

As a simplification of Eq 2, the dried-equivalent carbonate concentration can be calculated by multiplying the bicarbonate concentration in the water sample by 0.4917. When bicarbonate and carbonate concentrations are not available, alkalinity can be used as a surrogate [11, 13–16]. The dried-equivalent carbonate concentration can be calculated from alkalinity by using the molecular weights ($CaCO_3$ = 100.09 g/mol, CO_3^{2-} = 60.008 g/mol) in a manner similar to Eq 2, which simplifies to multiplying the alkalinity (as mg/L of $CaCO_3$) by 0.5995.

Over time, the SOC method of determining TDS became not only a quality-control check on ROE results, but often the primary method of TDS determination in water. For example, since passage of the Clean Water Act in 1972 [17], of the more than 61,000 UCOL TDS results in the U.S. Geological Survey (USGS) National Water Information System (NWIS) database (https://waterdata.usgs.gov/nwis), 71% were from SOC determinations, a ratio of 2.4-to-1 to ROE analyses (S1 Table) [18].

Salinity also is a measure of the mass of dissolved salts in a given mass of solution [19]. While the term salinity is often used interchangeably with TDS (e.g., [13, 20]), salinity determinations differ from TDS in use of the full concentration of dissolved constituents, importantly, the full bicarbonate concentrations [21]. The greater the proportion of bicarbonate in the dissolved solids of a water sample, the greater the difference in computed dissolved-solids concentration using TDS compared with salinity. Water-quality computational models, including

WATEQ [22] and PHREEQC [23], compute dissolved solids by using salinity determinations that include bicarbonate concentration without conversion to dried-equivalent carbonate (e.g., [24]).

Bicarbonate itself is not a human health concern in drinking water [25] and does not appear on the U.S. Environmental Protection Agency's (USEPA) primary [26] or secondary [27] drinking water standards, except as part of the 500 mg/L TDS secondary standard for aesthetic and corrosive effects. Notably, by specifying a standard for TDS, the USEPA secondary standard is based on the dried-equivalent dissolved-solids concentration and not the full concentration of dissolved constituents in water. Bicarbonate in water may have negative effects on aquatic organisms [28–36], some crops [37–41], and soil permeability [42, 43]. Both pitting [44] and corrosion-protective effects [44–46] are seen in iron pipes in contact with bicarbonate solutions.

Others have discussed differences between methods of dissolved-solids determination [10, 11, 13, 47]. The effects of fully accounting for bicarbonate in salinity determinations of dissolved solids compared to using TDS metrics that are influenced by volatilization of a portion of the bicarbonate are evaluated in this study for UCOL rivers and streams. Specifically, the TDS method of SOC is evaluated in this manuscript because of its widespread use and, unlike ROE, it allows for comparison to salinity determinations from the same analytical results.

Data and methods

The USGS method for determining SOC (NWIS parameter code 70301) includes major ions (calcium, magnesium, sodium, chloride, sulfate, potassium), additional minor ions when available (e.g., ammonia, bromide, iodide, and phosphate), and prioritizes the use of bicarbonate and carbonate concentrations over alkalinity [11, 13]:

$$\text{SOC} = (0.4917 \times \text{bicarbonate}) + \text{carbonate} + \text{additional ions} \quad (3)$$

SOC values in this manuscript are parameter code 70301 results from the USGS NWIS database (https://waterdata.usgs.gov/nwis) [18] and are not computed from individual ion concentrations. Results for bicarbonate concentrations and SOC were obtained for 418 surface-water sites in the UCOL (hydrologic unit code number 14) [5] from October 15, 1986 through December 8, 2022. Samples that lacked either bicarbonate ion or SOC concentrations were excluded from the dataset (S2 Table) [18]. Bicarbonate concentrations during this period ranged from 0.9 mg/L from the Animas River below Silverton, CO (USGS site number 09359020) on November 6, 2020, to a maximum of 2,530 mg/L from the Piceance Creek at White River, CO (USGS site number 09306222) on July 23, 2018, and the median was 146 mg/L. Concentrations of SOC ranged from 19 mg/L at Cross Creek near Minturn, CO (USGS site number 09065100) on July 31, 1998, and 19 mg/L at Vallecito Creek near Bayfield, CO (USGS site number 09352900) on June 4, 1966, to a maximum of 167,000 mg/L from the Animas River at Farmington, NM (USGS site number 09364500) on February 25, 2021, with a median of 399 mg/L. Although the maximum was very high relative to the median, other similarly high concentrations were observed around the same time (e.g., 114,000 mg/L from San Juan River near Fruitland, NM on February 25, 2021, and 111,000 mg/L from San Juan River at Nenahnezad, NM on February 24, 2021).

To evaluate differences between dissolved-solids determinations using SOC and salinity methods, salinity was computed at these same UCOL sites from SOC results by adding back in the full bicarbonate concentration:

$$\text{salinity} = (\text{SOC} - 0.4917 \times \text{bicarbonate}) + \text{bicarbonate} \quad (4)$$

or

$$\text{salinity} = \text{SOC} + 0.5083 \times \text{bicarbonate} \quad (5)$$

Salinity results (S2 Table) [18] ranged from 24.1 to 167,136 mg/L, with a median of 478 mg/L.

Results and discussion

Paired SOC and bicarbonate concentrations were available for 8,001 samples (including 712 provisional results) from UCOL surface-water sites. Salinity was computed for these samples using Eq 5 and compared to SOC results from NWIS (S2 Table). The magnitude of difference between salinity and SOC at UCOL sites ranged from <1 mg/L to 1,286 mg/L, with 25th percentile, median, and 75th percentile increases of 53, 74, and 101 mg/L, respectively (Fig 2A). Differences between salinity and SOC were greater with increasing SOC concentrations (Fig 2A). Dissolved-solids concentrations determined using the salinity calculation were greater than concentrations using the SOC calculation by a median of 20% relative to SOC, with an interquartile range of 13–30% (S2 Table, Fig 2B).

To determine if the magnitude of differences between SOC and salinity determinations of dissolved solids were within typical sample variability (including sample collection, processing, and analytical variability) at UCOL sites, replicate sample data (water samples collected sequentially or concurrently, processed and analyzed separately) for quality-control (QC) SOC analyses were obtained from NWIS. QC replicate results were available for 890 pairs of environmental and replicate samples in UCOL streams (S3 Table). The median percent difference between replicate results (calculated as the difference between replicates divided by the average of the replicates) was 0.67% (Fig 2C). The percent difference between salinity and SOC relative to SOC was significantly greater than replicate variability (Wilcoxon rank sum test, $p < 2.2\times10^{-16}$, one-tailed).

The relation between SOC and salinity is not a constant scaling of SOC results over time, and the difference can vary substantially at a site throughout the year. For example, data from Eagle River at Gypsum, CO (USGS site number 09069000) indicate higher percent difference in salinity relative to SOC during the months of May and June than for the rest of the year (Fig 3A). This increase is likely related to elevated streamflow during this time period (Fig 3B), which dilutes overall dissolved-solids concentrations but increases the proportion of bicarbonate relative to other constituents. Tillman and others [4] found substantially higher dissolved-solids concentrations in UCOL streams during lower-flow baseflow conditions in August through March and lower concentrations during high-flow snowmelt conditions of May and June, also implying a runoff dilution of dissolved-solids concentrations. The inconsistent proportion of bicarbonate in dissolved solids through time at sites may make salinity a better method for understanding temporal trends in dissolved solids at a site, or spatial trends between sites. Specific conductance (SC) can also be used as a proxy for salinity measurements for use in real-time dissolved-solids monitoring, as the SC instrument measures the ionic composition of the water (and not the dried-equivalent composition).

To demonstrate the variability in the magnitude of difference between SOC and salinity determinations of dissolved-solids concentrations over time at an important UCOL streamgage site, time-series results for data from the Colorado River at Lees Ferry, AZ (USGS site number 0938000) monitoring location are presented (Fig 4). The Lees Ferry streamgage, located 24 km downstream from the United States' second largest reservoir (Lake Powell), is used to monitor the quality and quantity of water that passes from the upper to the lower Colorado River basins [48]. The difference in salinity relative to SOC ranged from 14% to 21% at the site, with 25th, 50th, and 75th percentiles of 16%, 17%, and 18%, respectively–a relatively

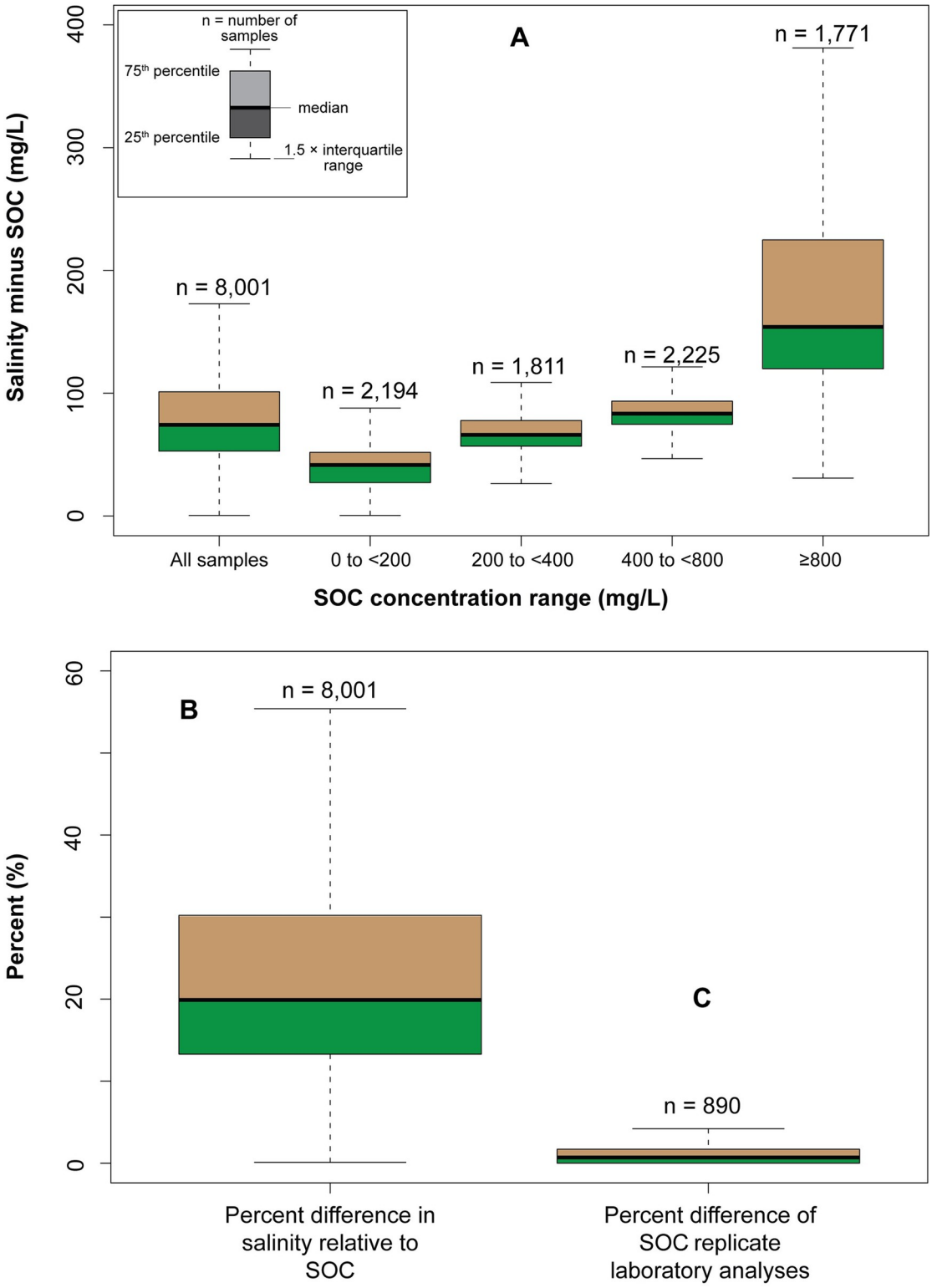


Fig 2. Boxplots showing distributions of magnitude of difference between salinity and SOC determinations of dissolved solids (A), percent difference in salinity relative to SOC (B), and percent difference (difference/average) of replicate SOC analyses (C).

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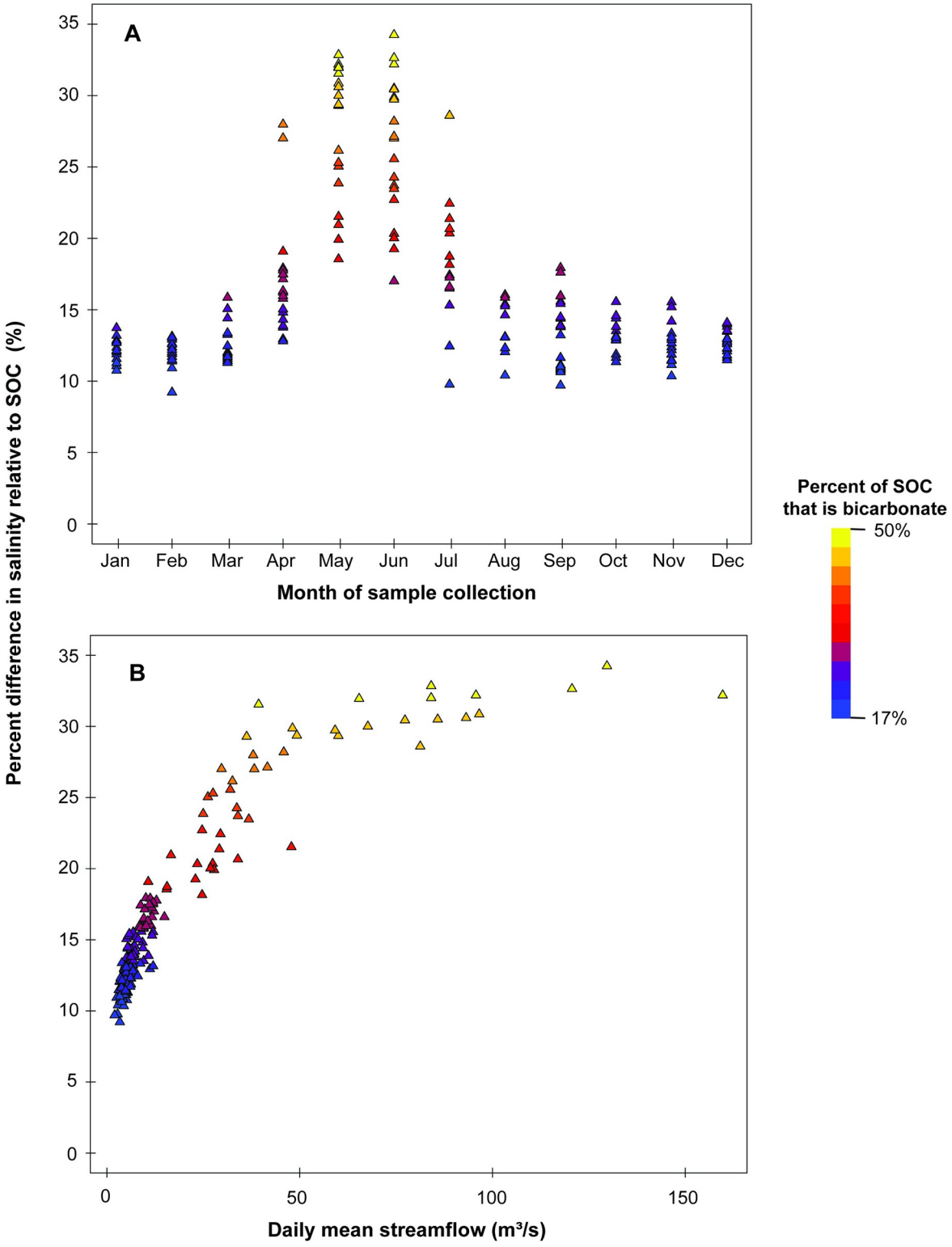


Fig 3. Percent difference in salinity relative to SOC at Eagle River at Gypsum, CO (USGS site number 0906900) plotted against the month of observation (A) and plotted against daily mean streamflow (B) from nearby (<200 m) Eagle River below Gypsum, CO (USGS site number 09070000) [18].

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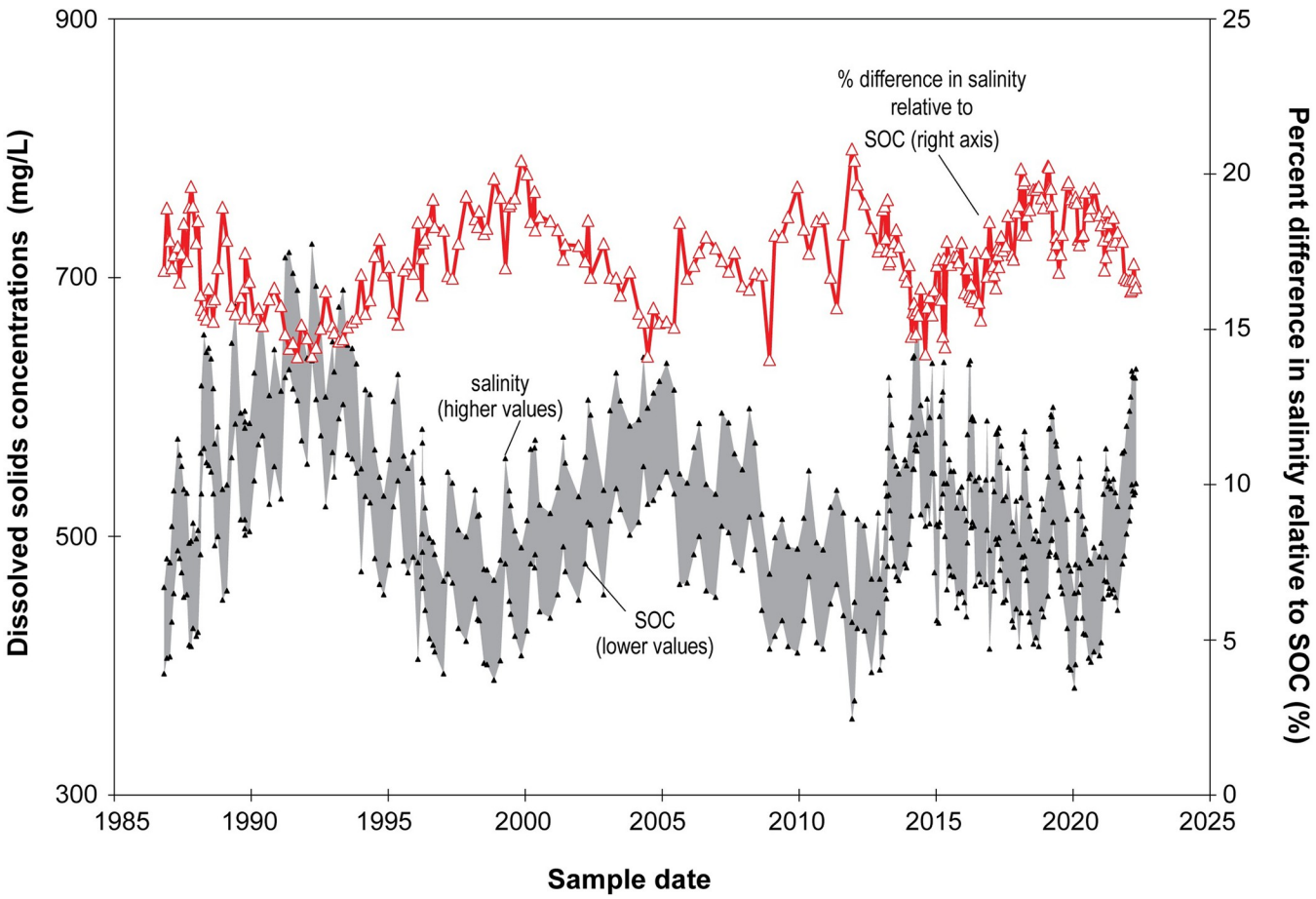


Fig 4. Time-series plots of SOC, salinity, and the percent difference in salinity relative to SOC for the monitoring site Colorado River at Lees Ferry, AZ (USGS site number 09380000).

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narrow distribution reflecting the integrating effect of the upstream reservoir. Differences between SOC (lower values) and salinity (higher values) in Fig 4 are attributable to an assumption of partial volatilization of the bicarbonate in the calculation of SOC when used as a quality check for TDS as ROE versus accounting for the entire bicarbonate concentration in salinity, respectively. Higher dissolved-solids concentrations computed using the salinity method compared with the current SOC method may have implications for understanding dissolved-solids loads entering the lower Colorado River basin.

To provide perspective on UCOL results relative to other river basins, dissolved-solids determinations using salinity and SOC were compared for streams in each of the regional hydrologic units (HUC-2s; [5]) in the U.S. Sample results for SOC and alkalinity from rivers and streams were obtained from the USGS NWIS database [18] and salinity was computed using Eq 5 as before. Results (Fig 5) indicate that the median increase in salinity relative to SOC for UCOL streams of 20% is among the lowest quarter of the 20 hydrologic regions in the U.S. The Great Lakes, Alaska, Pacific Northwest, and Upper Mississippi regions all indicate median increase of >35% in salinity determinations relative to SOC, with the highest median percent difference in the Tennessee region of 41%. Bicarbonate is a substantial portion of dissolved solids in other U.S. river basins besides the UCOL and salinity may also be an appropriate measure of dissolved solids in these regions as well.

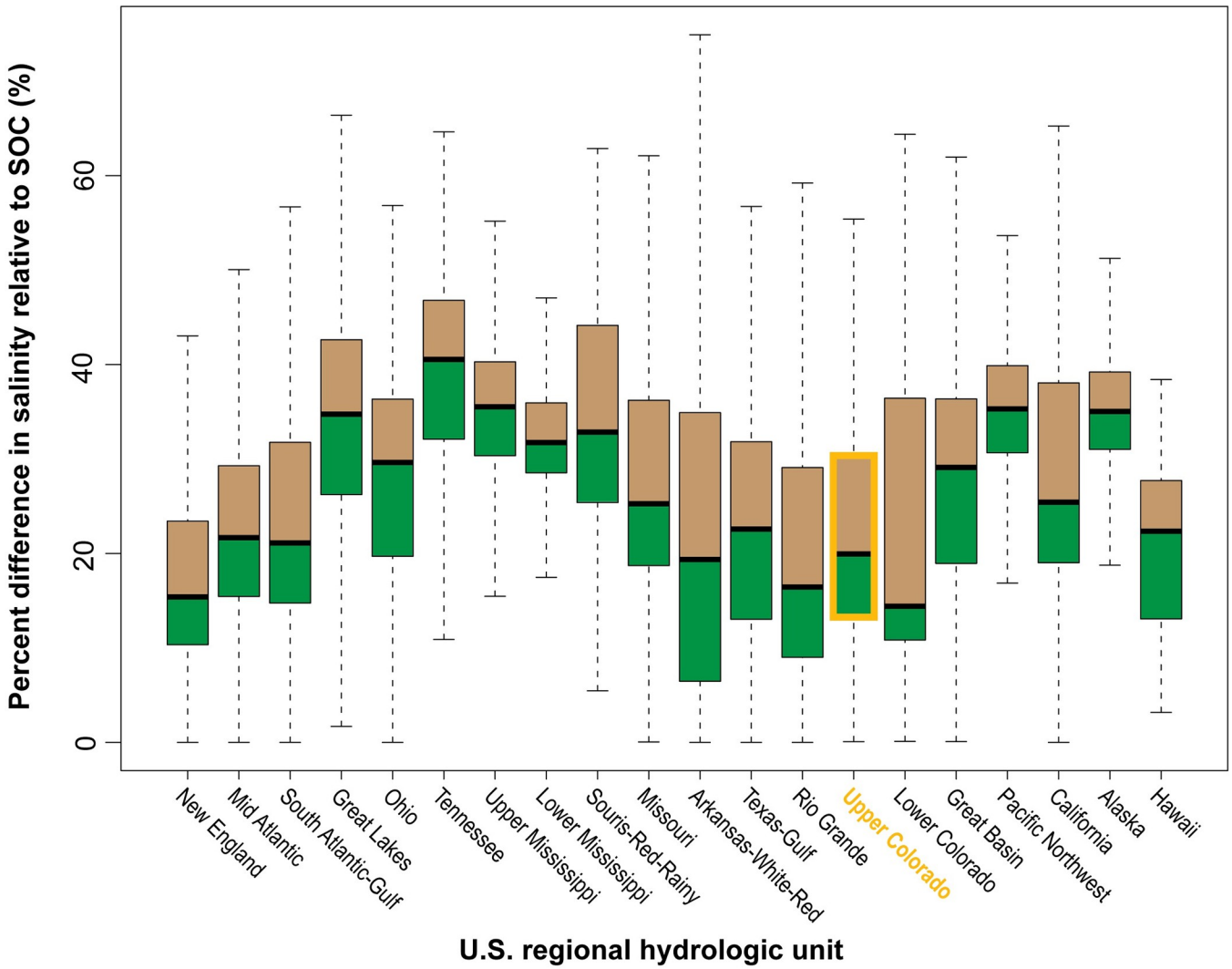


Fig 5. Percent difference in salinity relative to SOC determinations of dissolved-solids concentrations for available sample results in regional hydrologic units in the U.S. UCOL results are highlighted in gold.

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Summary and conclusions

The Colorado River is an important water resource in the southwestern United States and northern Mexico, but high concentrations of dissolved solids in the river cause hundreds of millions of dollars in damages annually to crops and infrastructure, mostly from corrosion and reduced agricultural yields [3]. TDS concentrations in river and tributary samples are often computed by first converting bicarbonate concentration to a dried-equivalent carbonate concentration that would be present as a residue after sample drying, and then summing the concentrations of the individual constituents measured in solution. The practical effect of using SOC calculated with dried-equivalent carbonate concentrations as a measure of dissolved solids is an under-representation of dissolved solids in water samples where bicarbonate is present. Although bicarbonate itself is not a human health concern and is only an issue for aquatic ecosystems at high concentrations, an accurate understanding of dissolved-solids concentrations in UCOL rivers and streams is important for scientists studying salinity issues in the basin.

Results from 8,001 samples at 418 UCOL sites indicate a median increase in TDS of 20% (13% and 30%, 25th and 75th percentiles, respectively) when the bicarbonate concentration is fully accounted for (salinity), relative to SOC results using the conversion to dried-equivalent carbonate concentration. Increases in salinity relative to SOC are not constant over time at all UCOL sites and may vary substantially at sites where the bicarbonate portion of dissolved solids changes during the year. This may pose challenges for investigations of dissolved-solids trends at, or between, sites with changing proportions of bicarbonate concentrations in dissolved solids. At the Colorado River at Lees Ferry monitoring site located at the outlet between the upper and lower basins, dissolved-solids concentrations determined using the salinity method were 16–18% higher than concentrations using the SOC method. Including a full accounting of bicarbonate in dissolved-solids determinations would change the characterization of dissolved solids in the UCOL and provide additional information to be considered as part of water-quality investigations in the basin.

There is currently no guidance on a standard method for determining dissolved-solids concentrations in water. The purpose of this manuscript is to raise awareness of the difference between SOC and salinity measures of dissolved solids and how these terms are often, inappropriately, used interchangeably. If measurements of sample alkalinity are available, then salinity determinations of dissolved-solids concentrations can easily be computed from SOC results.

Supporting information

S1 Table. Number of residue on evaporation (ROE) and sum of constituents (SOC) analyses for surface-water sites in the Upper Colorado River Basin in the U.S. Geological Survey National Water Information System (NWIS) database, by year.
(XLSX)

S2 Table. Sum of constituents (SOC) and bicarbonate sample results for surface-water sites in the Upper Colorado River Basin from the U.S. Geological Survey National Water Information System (NWIS) database from October 15, 1986 through December 8, 2022.
(XLSX)

S3 Table. Replicate quality control sample results for sum of constituent (SOC) analyses for surface-water sites in the Upper Colorado River Basin in the U.S. Geological Survey National Water Information System (NWIS) database.
(XLSX)

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