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Application of the practical salinity scale to the waters of San Francisco estuary

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A B S T R A C T

The Practical Salinity Scale 1978 (PSS-78)—developed using samples of standard seawater—is widely used as a conductivity-based measure of salinity in oceans and estuaries. Here we evaluate the application of the scale across San Francisco Estuary where salinity reflects a mixture of seawater, riverine inflows, and agricultural return flows from islands within the estuary. We employ an extensive salinity data set that includes measurements of specific electrical conductance (EC) and major ion concentrations to demonstrate the scale's applicability in this estuary. We find the scale to be valid in waters dominated by seawater intrusion as well as in waters dominated by the largest riverine input to the estuary, i.e. the Sacramento River. In these waters, we further find that the scale to be valid well below its recommended lower-bound value of 2.0. However, the scale under-estimates salinity in waters dominated by the San Joaquin River, the second largest riverine input to the estuary. Similarly, the scale under-estimates salinity in agricultural return flows to the estuary. This work shows that a singular PSS-78 relationship cannot be used to accurately compute salinity across the entire estuary from EC measurements—a finding of considerable importance for salinity monitoring and modeling applications. Using data from the estuary, we propose appropriate corrections to the scale for these drainage-influenced waters. We recommend further research into how these modified PSS-78 formulations can be used to more accurately estimate salinity and ionic constituent concentrations in this and other estuaries.

1. Introduction

Practical salinity is a common metric used to simulate salt transport in estuaries (e.g. Selberg et al., 2001; Dagg and Breed, 2003; Gay and O'Donnell, 2009). The Practical Salinity Scale 1978 (PSS-78) (Lewis, 1980), a conductivity-based measure of salinity, was designed for use with oceanic waters. However, according to UNESCO (1981), "… these equations should be used with caution in waters that have a chemical composition different from standard seawater."

The San Francisco Estuary (Fig. 1), the water body of interest in this work, encompasses waters in its upper reaches (including the Sacramento-San Joaquin River Delta or Delta) that reflect non-oceanic chemical compositions. Specifically, waters in these upper reaches have chemical signatures associated with freshwater inflows as well as agricultural return flows. Here we employ an extensive salinity data set that includes measurements of specific conductance (EC) and major ion concentrations to evaluate the scale's applicability and limitations within the estuary and propose appropriate corrections to the scale for these non-oceanic waters.

2. Background

2.1. Study area

The San Francisco Estuary is the largest estuary on the west coast of the Americas and drains an area of nearly 195,000 km^2. The estuary includes San Francisco Bay, other smaller bays and the delta formed by the Sacramento, San Joaquin, and other smaller rivers (Delta) (Fig. 1). The estuary margin and its contributing watershed are highly developed, including large agricultural and urbanized areas across its lower elevations. The watershed is bounded by the Sierra Nevada and Coastal Mountain ranges, precipitation on which is a major source of freshwater flow to the estuary. The salinity and major ion composition of waters across the estuary thus reflect the mixing of seawater with these freshwater sources. Each of these sources has a unique ionic signature, corresponding to both natural and anthropogenic factors (Fig. 2). Compared to the sodium and chloride-dominated seawater boundary, the ionic composition of the Sacramento River is a mix of major cations and anions that is dominated by bicarbonate. The ionic composition of the San Joaquin River, which falls between these two boundaries, is influenced by snow-melt driven Sierra runoff and agricultural return flows from the western portion of the watershed. The salt loads associated with these chemically distinct inflows, characterized by high

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seasonal and interannual variability, affects the ionic composition of water across the salinity gradient in the estuary. Within the Delta are a network of leveed islands that have been developed for agriculture; drainage from these islands is also a source of water to the Delta channels. The chemistry of these return flows is not well-characterized, adding yet another source of variability to the ionic composition of the estuary's waters.

2.2. Practical salinity scale

The Practical Salinity Scale 1978 or PSS-78 (Lewis, 1980), developed from standard seawater samples, is widely used as a conductivity-based measure of salinity in oceans and estuaries. The scale produces a dimensionless quantity that is defined as a function of a conductivity ratio (sample conductivity divided by seawater conductivity), temperature and pressure. The scale, by definition, returns a value of 35 for seawater with a conductivity ratio of unity. Lewis (1980) reports that the scale is valid over the range of 2–42. Hill et al. (1986) presents a standard correction to the scale to extend the applicability of PSS-78 below a value of 2. This correction is based on dilutions of standard seawater with deionized water and thus is strictly applicable to waters that have the same proportional ionic makeup as seawater.

Noting that salinity in the study area is generally reported as specific electrical conductance (conductivity normalized to a standard temperature of 25 °C and atmospheric pressure—here abbreviated as EC), Schemel (2001) presents the following simplified version of PSS-78 assuming a standard temperature and atmospheric pressure:

$$S = K_o + K_1 * R^{0.5} + K_2 * R + K_3 * R^{1.5} + K_4 * R^2 + K_5 * R^{2.5} \quad (1)$$

where $K_o = 0.0120$, $K_1 = -0.2174$, $K_2 = 25.3283$, $K_3 = 13.7714$, $K_4 = -6.4788$, $K_5 = 2.5842$, $\sum K = 35$, and R is the conductivity ratio (sample conductivity divided by seawater conductivity).

PSS-78 continues to be widely used for estimation of estuarine salinity—i.e. in waters with potentially varying ionic composition due to freshwater influences—although it is recognized that different ions contribute differently to the conductivity of a water sample, based on their ionic radius and charge. The evaluation of PSS-78 presented in this work was motivated by the knowledge of the strong variation in ionic chemistry across the salinity gradient in the study area as described above.

Furthermore, contemporary research has recognized that there is a small numerical difference between practical salinity and the "absolute" salinity of seawater, which is defined as the mass of solids dissolved in solution per unit mass of seawater (Millero et al., 2008; Pawlowicz, 2010; Wright et al., 2011). Accounting for this small difference, a practical salinity of 35 has a reference-composition salinity of 35.16504 g/kg (Millero et al., 2008).

3. Methods

3.1. Data: units of measurement, sources, screening & filling

Grab sample data collected from the primary source waters in the study area were used to evaluate the sources' fidelity to PSS-78. In addition to EC, these data included concentrations of total dissolved solids (TDS) and major ions. Major ions include the anions bromide (Br^-), chloride (Cl^-), sulfate (SO_4^{2-}) and alkalinity and the cations sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+). EC values are reported in SI units of microsiemens per cm (μS/cm) and TDS and ion concentrations are generally reported in concentration units of mg/L. Alkalinity data are reported as mg/L of calcium carbonate.

These data were collected and continue to be collected by the California Department of Water Resources (CDWR) in support of its Municipal Water Quality Investigations program (Hutton et al., 2022a). A subset of these grab sample data was compiled from CDWR's Water Data Library http://www.water.ca.gov/waterdatalibrary/to represent distinct regions of the study area, including the western Delta and downstream bays, Delta inflow from the Sacramento River, Delta inflow from the San Joaquin River, and return flows from in-Delta agriculture (i.e. Delta agricultural drainage).

Denton (2015) notes that the quality of salinity grab sample data in the study area is generally very good and the robustness of correlations

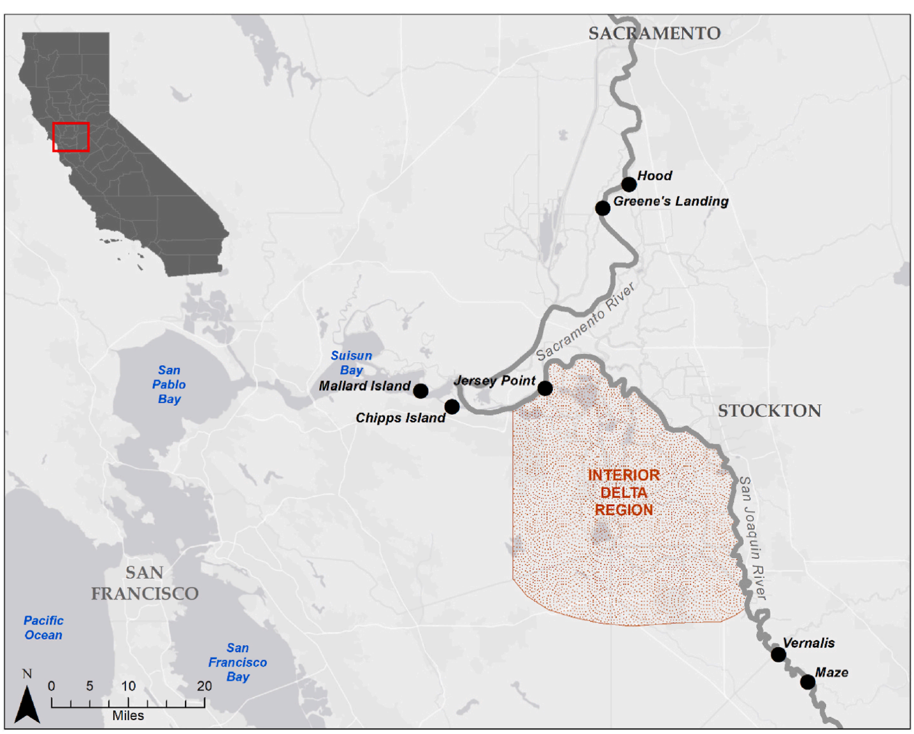

Fig. 1. San Francisco Estuary location map, showing the interior Delta region, major riverine inflows, and selected monitoring locations.

between various ionic constituents and EC at many locations within the study area allows for easy identification of data outliers and errors. In this work, we adhered to the following protocol to screen outliers.

- Grab sample data were checked for “testability”. A testable data sample was defined as one that had a measured value for EC, TDS, Cl^-, SO_4^{2-}, Na^+, and Mg^{2+}. Testability was enforced to ensure that samples were generally mass- and charge-balanced.
- Following the check for “testability”, two additional screening criteria were imposed:
  - o A data point associated with a single constituent was removed if, when plotted against EC or TDS, fell outside the 99% prediction band (three standard errors) for the testable set of observations for that constituent.
  - o An entire sample, including all data points associated with it, was removed if three or more constituents in that sample fell outside the 95% prediction band (two standard errors) for the testable set of observations for the constituents.

The above protocol is based on the assumptions that, while total salinity can exhibit unusual behavior under extreme hydrologic conditions, i) relationships between individual constituents and total salinity exhibit consistent behavior and ii) major departures from these relationships are indicative of outlier behavior. Table 1 summarizes the number of screened data points by monitoring location; this table also indicates the periods in which these data were collected.

Missing ion concentration data were filled using previously developed regression relationships with EC (Hutton et al., 2022b) to allow for calculation of mass-based salinity concentrations for comparison with conductivity-based practical salinity values. The filling exercise resulted in the following number of samples by region: 405 samples for the western Delta and downstream bays, 601 samples for the Sacramento River (at Hood and Greene’s Landing), and 543 samples for the San Joaquin River (at Vernalis and Maze). The agricultural drainage data set included 781 samples (at multiple locations), none of which were filled. As Table 1 reveals, filling contributes a small proportion of ion data to the samples, with Br^- being the exception. We note that, given that Br^- concentration is low relative to total salinity concentration, errors introduced through the filling process are considered negligible.

3.2. Calculation of mass-based salinity

Salinity concentrations were calculated as the sum of the eight major ions described above. This calculated salinity concentration was used as the basis for comparison with conductivity-based practical salinity values to evaluate the fidelity of PSS-78 to measured data in the study area. As part of the salinity calculation, alkalinity data were converted to equivalent concentrations of bicarbonate (HCO_3^-) in mg/L by multiplying the former by 1.22 (Hem, 1985). Further, these equivalent HCO_3^- concentrations were decreased by a gravimetric factor (mg/L HCO_3^- x 0.4917 = mg/L CO_3^{2-}) assuming that roughly half the bicarbonate is volatilized as carbon dioxide and water and the computed CO_3^{2-} value is used in the salinity calculation. As noted by Hem (1985), the resulting salinity calculation corresponds to the conditions that would exist in the dry residue of a TDS measurement. Finally, this ion sum (i.e. calculated salinity) was converted from mg/L to parts per thousand (ppt) by accounting for sample density, where seawater density at 25 °C was assumed to be 1.024 and pure water was assumed to be 1.000 (Riley and Skirrow, 1965). Salinity associated with the screened and filled samples from the western Delta and downstream bays range from 0.06 to 10.89 ppt. Similarly, screened and filled salinity samples associated with the Sacramento River, San Joaquin River, and Delta agricultural drainage range from 0.04 to 0.13 ppt, 0.06–0.99 ppt, and 0.07–1.78 ppt, respectively.

4. Results

Here we summarize our findings on the applicability of PSS-78 to the major source waters of the San Francisco Estuary. We compare measured ion sums with conductivity-based salinity estimates for the western Delta and downstream bays, Sacramento River, San Joaquin River, Delta agricultural drainage, and the interior Delta. Based on these

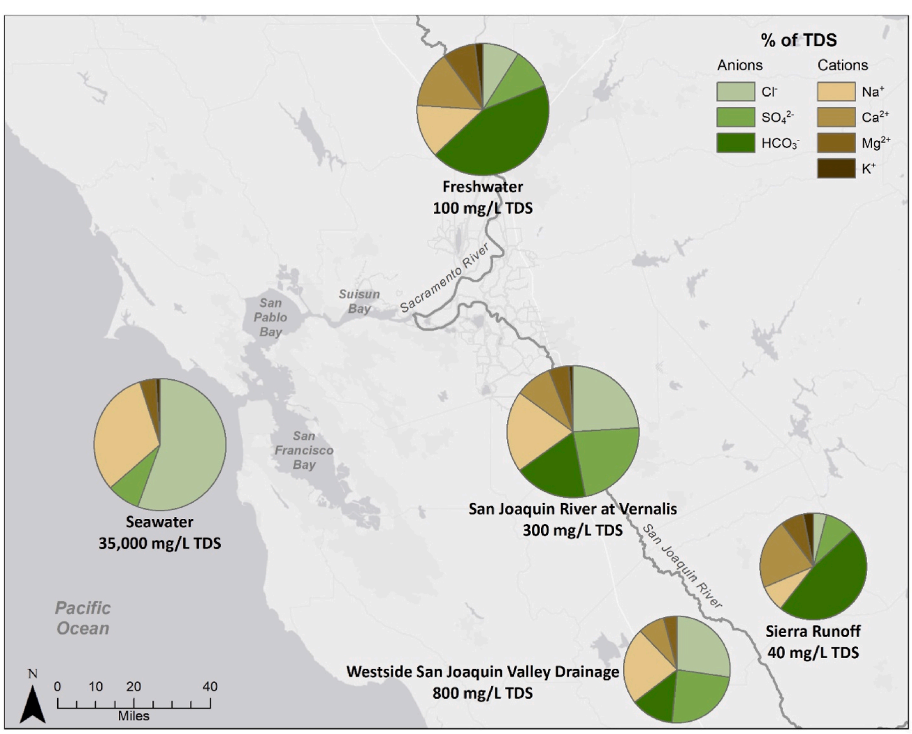

Fig. 2. Mineralogy of primary water sources in study area.

Table 1
Number of specific conductance and ion data points by monitoring location.

EC/Ion	Western Delta & Downstream Bays				Sacramento River			San Joaquin River (SJR)				Agricultural Drainage
	Sac. R. @ Mallard	Sac. R. @ Chipps	SJR @ Jersey	∑	Sac. R. @ Hood	Sac. R. @ Greene's	∑	SJR near Vernalis	SJR @ Maze	SJR near Vernalis	∑	Various Locations
	1986–2019	2019–2019	1990–1995		1982–2020	1983–1998		1982–2005	1988–1994	2005–2020		1990–2001
EC	382	3	20	405	445	156	601	341	62	140	543	781
Br^-	335	3	20	358	297	80	377	280	38	140	458	781
Cl^-	381	3	20	404	444	154	598	339	62	140	541	781
SO_4^{2-}	377	3	20	400	444	151	595	340	62	140	542	781
Alkalinity	376	3	20	399	438	153	591	340	61	140	541	781
Na^+	378	3	20	401	442	152	594	338	59	140	537	781
Ca^{2+}	379	3	20	402	441	155	596	338	56	140	534	781
Mg^{2+}	374	3	20	397	442	154	596	338	60	140	538	781
K^+	377	3	20	400	436	155	591	330	61	139	530	781

comparisons, modified PSS-78 relationships are presented for the San Joaquin River and Delta agricultural drainage. We also present an inverse formulation for the standard PSS-78 relationship that allows for estimating EC as a function of practical salinity.

4.1. Regional fidelity of mass-based salinity measurements to PSS-78

4.1.1. Assumed value for seawater EC

Computing practical salinity from EC measurements using Eq. (1) requires calculation of the conductivity ratio R. Computing this ratio requires specification of seawater EC. Riley and Skirrow (1965) reports an EC value of 53,025 μS/cm at a salinity of 35 ppt and T = 25 °C. Schemel (2001) suggests a similar value of 53,087 μS/cm based on Poisson (1980). We found that a seawater EC of 52,300 μS/cm provides an optimal fit (sum-of-squares minimization) between the ion sum and practical salinity for the screened and filled data associated with the western Delta and downstream bays. We use this optimized value for all work reported here.

4.1.2. Western Delta & downstream bays

Salinity data collected in the western Delta and downstream bays align very closely with the PSS-78 estimates. Panel (a) of Fig. 3 presents a scatter plot comparing practical salinity estimates from Eq. (1) and ion sums reported in ppt. The data align closely along the 1:1 line. We note that the fit below 2 psu is not noticeably different from the higher salinity data. Panel (b) of Fig. 3 presents a frequency analysis of differences between practical salinity and ion sum. 72% of the ion sum data fall within ±3% of the practical salinity estimate; 90% of the ion sum data fall within ±5% of the practical salinity estimate.

4.1.3. Sacramento River

Salinity data collected from the Sacramento River (at Hood and Greene's Landing) also align very closely with the PSS-78 estimates, even though the mineralogy of the water in this region is calcium carbonate (Van Winkel and Eaton, 1910) and thus significantly different from seawater. Panel (a) of Fig. 4 presents a scatter plot comparing practical salinity estimates from Eq. (1) and ion sums. The data align closely along the 1:1 line. Note that these salinity data are much lower than the lower limit of 2 suggested by Lewis (1980). Panel (b) of Fig. 4 presents a frequency analysis of differences between practical salinity and ion sum. 62% of the data fall within a ±3% residual; 85% of the data fall within a ±5% residual.

4.1.4. San Joaquin River & Delta Agricultural Drainage

As shown in Panel (a) of Fig. 5, PSS-78 underestimates the relationship between measured ion sum and EC in the San Joaquin River (at Vernalis and Maze) by approximately 10% when EC exceeds 800 μS/cm. To remedy this bias, a more representative PSS-78 relationship was developed (i.e. corrected) through least-squares regression analysis of

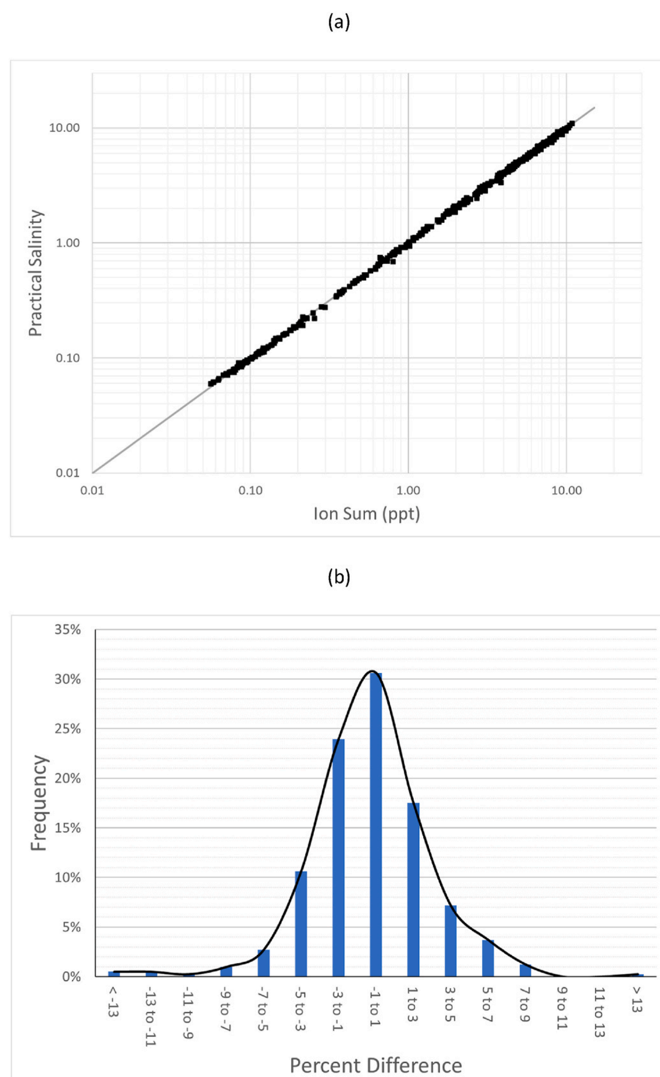

Fig. 3. Fidelity of Ion Concentration Sum to PSS-78: Western Delta & Downstream Bay Data. Panel (a) compares practical salinity and ion sum (in ppt) along a 1:1 line. Panel (b) shows the frequency of differences between practical salinity and ion sum.

the available San Joaquin River data. We found the following quadratic relationship (with zero intercept) to provide a good fit to the data in the applicable range of 120–1690 μS/cm EC:

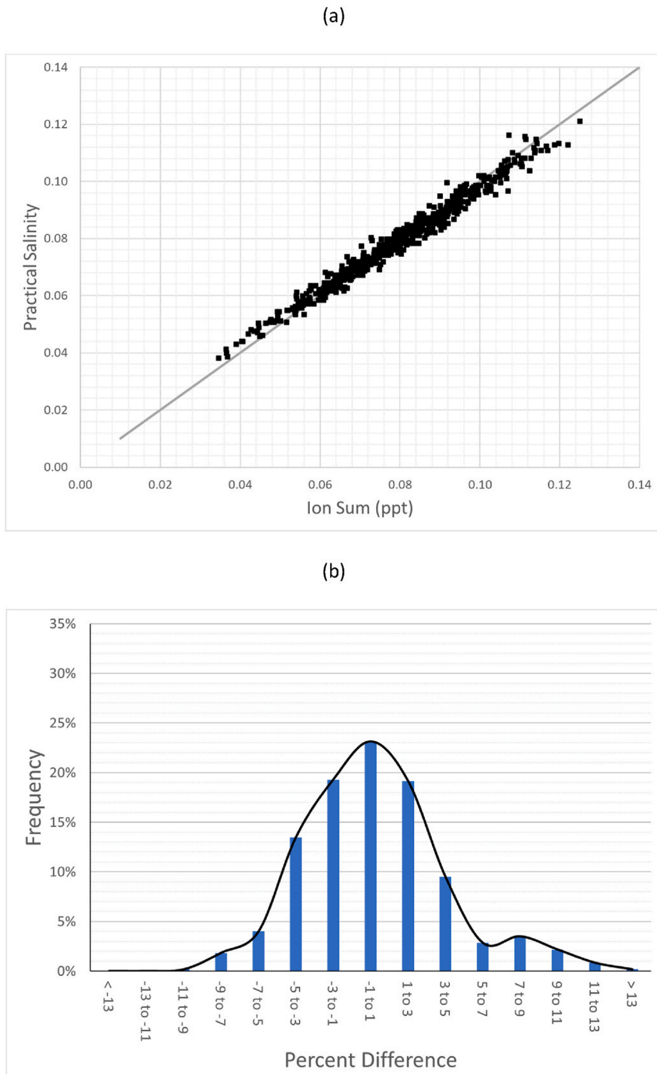

Fig. 4. Fidelity of Ion Concentration Sum to PSS-78: Sacramento River Data. Panel (a) compares practical salinity and ion sum (in ppt) along a 1:1 line. Panel (b) shows the frequency of differences between practical salinity and ion sum.

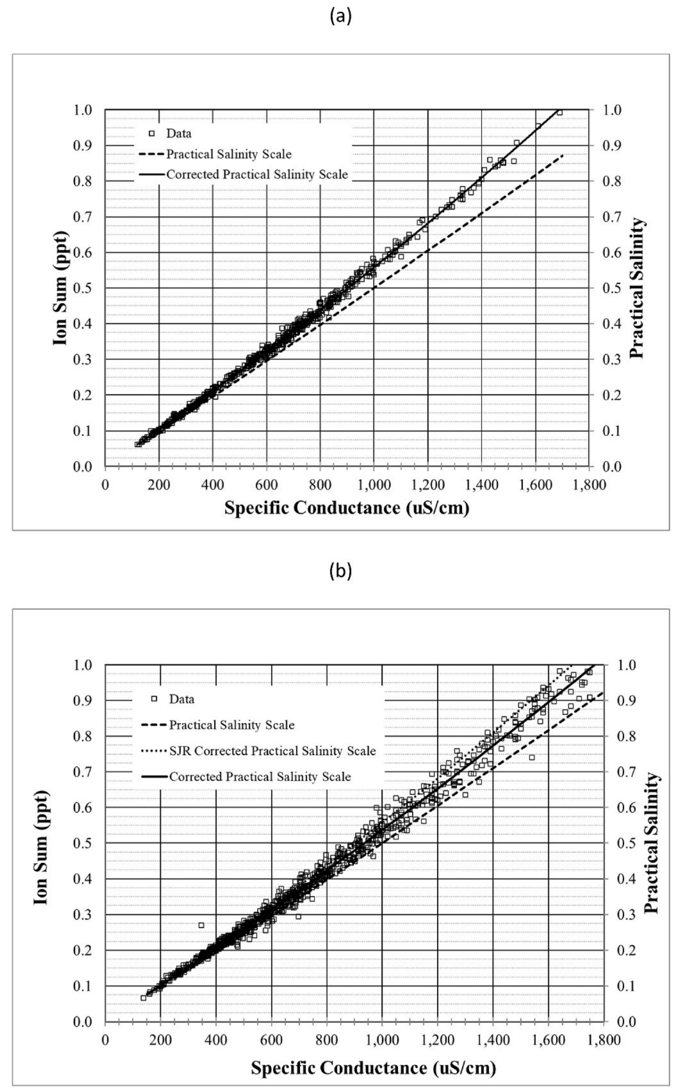

Fig. 5. Ion Sum vs. Specific Conductance. Panel (a) overlays uncorrected and corrected PSS-78 on San Joaquin River data. Panel (b) overlays uncorrected and corrected PSS-78 on agricultural drainage data. Panel (b) also overlays the San Joaquin River correction.

$$S = \omega_1 * EC + \omega_2 * EC^2 \tag{2}$$

where S is in units of ppt, EC is in units of μS/cm, ω_1 = 5.08E-4 ± 1.72E-6 (mean ± 1 SE), ω_2 = 5.07E-8 ± 1.77E-9, coefficient of determination R^2 = 0.999 and standard error of estimate SEE = 0.009 ppt. Panel (a) of Fig. 5 shows that the corrected relationship fits well with the observed data. Panel (a) of Fig. 6 presents a scatter plot comparing modified practical salinity estimates and ion sum. The data align closely along the 1:1 line. Panel (b) of Fig. 6 presents a frequency analysis of differences between modified practical salinity and ion sum. 75% of the data fall within a ±3% residual; 94% of the data fall within a ±5% residual.

As shown in Panel (b) of Fig. 5, the relationship between measured ion sum and EC in Delta agricultural drainage is approximately bounded by the uncorrected PSS-78 relationship (lower bound) and the San Joaquin River corrected PSS-78 relationship (upper bound). Following the methodology described above for the San Joaquin River, a more representative PSS-78 relationship was developed (i.e. corrected) through least-squares regression analysis of a subset (n = 745) of the available agricultural drainage data. Since standard modeling practice assumes an average static time series of monthly in-Delta drainage quality (CDWR, 1995), we excluded data exceeding 1800 μS/cm from the regression analysis. We again found a zero-intercept quadratic relationship (see Eq. (2)) to provide a good fit to the data in the applicable range of 137–1790 μS/cm EC, with ω_1 = 4.99E-4 ± 2.65E-6, ω_2 = 3.81E-8 ± 2.27E-9, coefficient of determination R^2 = 0.998 and standard error of estimate SEE = 0.020 ppt. Panel (b) of Fig. 5 shows that the corrected relationship fits well with the observed data. Panel (a) of Fig. 7 presents a scatter plot comparing modified practical salinity estimates and ion sum. The data align closely along the 1:1 line; however, scatter along the line is clearly greater than for the other source waters evaluated. Panel (b) of Fig. 7 presents a frequency analysis of differences between modified practical salinity and ion sum. 51% of the data fall within a ±3% residual, 76% of the data fall within a ±5% residual and 98% of the data fall within a ±11% residual.

To assess whether separate revised model fits were justified for the San Joaquin River and Delta agricultural drainage data, we performed k-fold cross-validation on two different models: i) a fit where the parameters were forced to be the same for both data sets (labelled as "same fit") and i) separate fits allowing parameters to vary between data sets (labelled as "different fits"). We used 30 random grouped folds, where data points were in the same group until they were separated from the next observation by at least three weeks. In each fold, all members of a group were either used as training data or held out as test data, and the

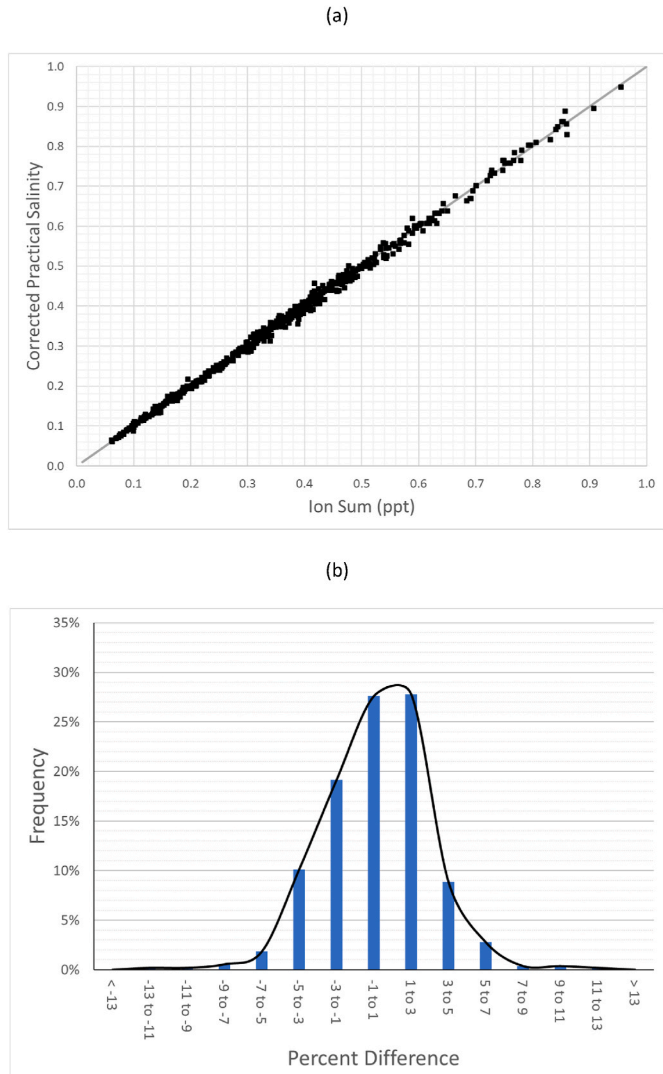

Fig. 6. Fidelity of Ion Concentration Sum to Corrected PSS-78: San Joaquin River Data. Panel (a) compares corrected practical salinity and ion sum (in ppt) along a 1:1 line. Panel (b) shows the frequency of differences between corrected practical salinity and ion sum.

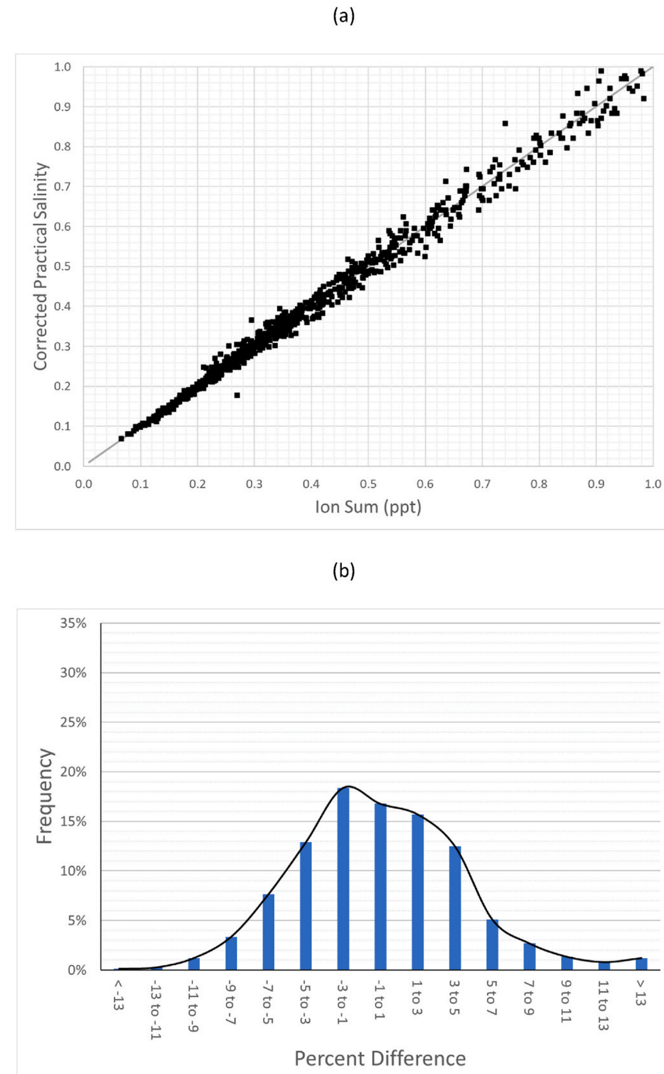

Fig. 7. Fidelity of Ion Concentration Sum to Corrected PSS-78: Agricultural Drainage Data. Panel (a) compares corrected practical salinity and ion sum (in ppt) along a 1:1 line. Panel (b) shows the frequency of differences between corrected practical salinity and ion sum.

same data points were used to train both models in each case. Fig. 8 shows the posterior distribution of the overall RMSE on the held-out data. The average of the "different fits" distribution is 0.085 less than that of the "same fit". We consider the difference in this predictive accuracy measure to be significant enough to justify having separate fits for the different datasets.

4.1.5. *Interior delta*

We utilized additional measurements of EC and major ion concentrations (not reported in Table 1) to assess the fidelity of mass-based salinity measurements to PSS-78 within the interior Delta region. The ionic makeup of waters in this region fluctuates temporally as well as spatially, reflecting complex hydrodynamic conditions that result in varying degrees of seawater intrusion and freshwater inflow contribution. We found that relationships between measured ion sum and EC in this region are bounded by the PSS-78 relationship and the corrected San Joaquin River relationship. The authors evaluate the complex ionic relationships of the interior Delta elsewhere ("Hutton et al., in review").

4.2. *Inverse formulation of standard PSS-78 equation*

Salinity is typically measured at high spatial and temporal resolution throughout the study area as specific conductance. Therefore, when model simulations are conducted for the transport of practical salinity, a need exists to estimate EC from the simulated practical salinity values for validation of simulation results. We generated model constants for an inverse formulation of Eq. (1) as a function of a salinity ratio:

$$R = K_0' + K_1' * I^{0.5} + K_2' * I + K_3' * I^{1.5} + K_4' * I^2 + K_5' * I^{2.5} \tag{3}$$

where values of model constants K_o' through K_5' and associated standard errors are presented in Table 2, $\sum K' = 1.0$, I is the practical salinity ratio (sample salinity divided by seawater salinity = 35), and R is previously defined. Model constants were determined through least-squares regression analysis; data for the regression analysis were generated assuming a range of EC values and computing practical salinity values from Eq. (1). We tested the goodness-of-fit of Eq. (3) using ion sum and EC data representing the western Delta and downstream bays. This test demonstrated a good fit, with 73% of the data falling within a ±3% residual, 92% of the data falling within a ±5% residual, and 99% of the

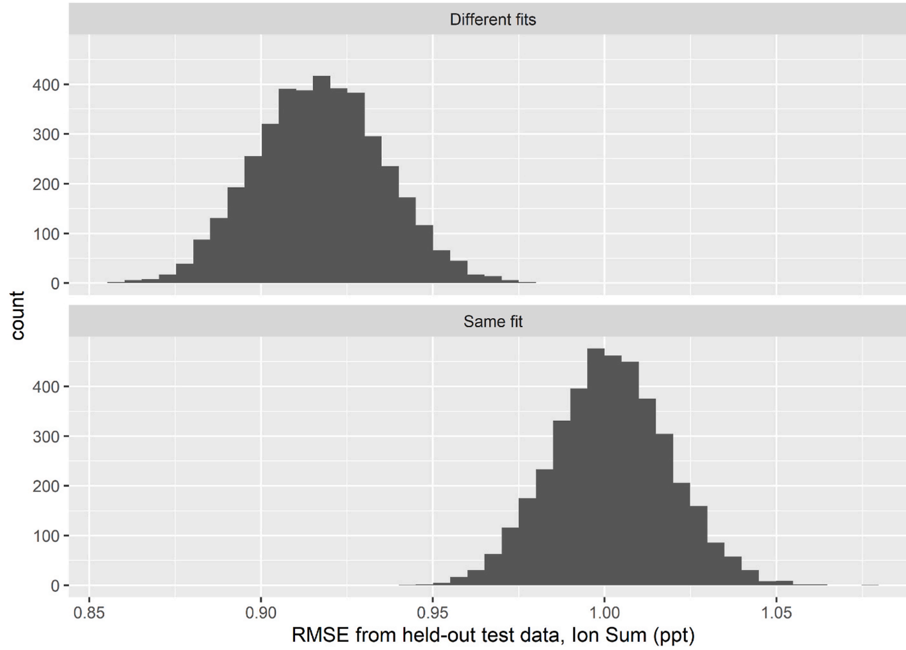

Fig. 8. A K-fold cross-validation was performed to justify separate PSS-78 corrections for the San Joaquin River and Delta Agricultural Drainage data sets.

Table 2
Eq. (3) Inverse PSS-78 model constants.

	Inverse PSS-78 Constants	Standard Errors
K_0'	−0.0008	1.81E-5
K_1'	0.0190	3.29E-4
K_2'	1.2893	1.79E-3
K_3'	−0.4932	4.15E-3
K_4'	0.2706	4.27E-3
K_5'	−0.0850	1.62E-3

data falling within a ±11% residual. Inverse relationships between salinity and EC could easily be developed for the San Joaquin River and in-Delta agricultural drainage through least-squares regression analysis; however, such an analysis was not undertaken as part of this work.

5. Summary & discussion

The key findings from this work are summarized in the following bullets.

- PSS-78 is well-aligned with mass-based measurements of salinity (i.e. ion sum) in the western Delta and downstream bays as well as the Sacramento River.
- PSS-78 underestimates ion sum measurements in the San Joaquin River as well as in Delta agricultural return flows. We propose modified (corrected) PSS-78 model constants to address these deviations; these constants were developed using least-squares regression analysis. Because these flows are characterized by a more narrow range of salinity than seen in the western Delta and downstream bays, the corrected relationships could be represented by quadratic models and did not require the structural complexity of the standard PSS-78 equation.
- Relationships between measured ion sum and EC in the interior Delta are bounded by the PSS-78 and corrected San Joaquin River relationships.
- An inverse formulation of the standard PSS-78 equation was developed to estimate EC as a function of practical salinity.
- Lewis (1980) cautions against the use of PSS-78 below practical salinity values of 2. However, we found the PSS-78 relationships (both uncorrected and corrected) to be valid over the full range of salinity throughout the study area.

Our findings highlight an issue of considerable importance when using practical salinity as a constituent for salt transport simulations in the San Francisco estuary. As noted previously, given the prevalence of EC measurements in the study area, a need exists to convert back and forth between EC and the selected salt transport constituent for validation of simulation results with observed data. However, our work demonstrates that the relationship between PSS-78 and EC is not universal within the study area and assuming a singular relationship may introduce considerable error in monitoring and modeling applications. This observation, which relates to fundamental variations in how ions uniquely affect conductivity, is likely to be an important consideration in other estuaries when significant differences in source water ionic composition exists. Similar to San Francisco Estuary, these differences may have a bearing on an accurate understanding of salt transport, which is often needed for evaluating ecological and human beneficial uses. We recommend additional research to address this issue, in San Francisco and in other estuaries, including consideration of alternate salt simulation constituents and developing informed guidance on converting between EC and salinity constituents.

CRediT authorship contribution statement

Paul H. Hutton: Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Sujoy B. Roy:** Writing – review & editing, Writing – original draft, Validation, Project administration.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Paul Hutton reports financial support was provided by State Water Contractors. Sujoy Roy reports financial support was provided by State Water Contractors. Paul Hutton reports a relationship with State Water Contractors that includes: consulting or advisory.

Data availability

Data will be made available on request.

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