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Comparison of electrical conductivity calculation methods for natural waters

R. Blaine McCleskey[1]*, *D. Kirk Nordstrom*[1], *and Joseph N. Ryan*[2]
[1]U.S. Geological Survey, 3215 Marine St., Suite E 127, Boulder, CO 80303, USA
[2]University of Colorado Boulder, 428 UCB, Boulder, CO 80309-0428, USA

Abstract

The capability of eleven methods to calculate the electrical conductivity of a wide range of natural waters from their chemical composition was investigated. A brief summary of each method is presented including equations to calculate the conductivities of individual ions, the ions incorporated, and the method's limitations. The ability of each method to reliably predict the conductivity depends on the ions included, effective accounting of ion pairing, and the accuracy of the equation used to estimate the ionic conductivities. The performances of the methods were evaluated by calculating the conductivity of 33 environmentally important electrolyte solutions, 41 U.S. Geological Survey standard reference water samples, and 1593 natural water samples. The natural waters tested include acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water impacted by municipal waste water. The three most recent conductivity methods predict the conductivity of natural waters better than other methods. Two of the recent methods can be used to reliably calculate the conductivity for samples with pH values greater than about 3 and temperatures between 0 and 40°C. One method is applicable to a variety of natural water types with a range of pH from 1 to 10, temperature from 0 to 95°C, and ionic strength up to 1 m.

Electrical conductivity is one of the most frequently measured water-quality parameters. It has been used to assess the salinity (Lewis 1980; Wilson 1981; Visconti et al. 2010), ionic strength (Ponnamperuma et al. 1966; Lind 1970; Polemio et al. 1980; Pintro and Inoue 1999), major solute concentrations (Pollak 1954; McNeil and Cox 2000), and total dissolved solids (Gustafson and Behrman 1939; Singh and Kalra 1975; Lystrom et al. 1978; Day and Nightingale 1984) of natural waters and soil solutions. Several methods have been published that can be used to calculate the conductivity of natural waters and soil extracts from their chemical composition (Rossum 1949; McNeal et al. 1970; Tanji and Biggar 1972; Rossum 1975; Marion and Babcock 1976; Laxen 1977; Talbot et al. 1990; Wüest et al. 1996; Pawlowicz 2008; Appelo 2010; Visconti et al. 2010; McCleskey et al. 2012). In addition to providing a better understanding of the chemical behavior of dissolved solutes, the calculated conductivity can be used to check the accuracy of chemical analyses (Rossum 1975; Laxen 1977; Miller et al. 1988; McCleskey et al. 2012) and to estimate the transference (or transport) number of ions that substantially contribute to the conductivity. Each method uses a different approach to calculate the conductivity, and as a result, the success of each method differs for natural waters. Many of the existing conductivity methods are limited by the lack of conductivity data that were available in the literature for relevant electrolytes including carbonate species and transition metals (Pawlowicz 2008). Consequently, some environmentally important ions are not incorporated into the existing methods. Besides the ions included, the methods differ in their estimation of ionic molar conductivities, temperature compensation, and treatment of ion pairs. We present a summary and critical comparison of eleven conductivity methods by calculating the conductivity of electrolyte solutions that are commonly found in natural waters, U.S. Geological Survey standard reference water samples prepared from river samples, and a wide range of natural waters including acid mine water, geothermal water, seawater, dilute mountain water, and river water impacted by municipal waste water.

Several methods were not included in the comparison because the calculated conductivity was not based on the

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*Corresponding author: E-mail: rbmccles@usgs.gov; (303) 541-3079

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chemical composition but instead on laboratory conductivity measurements (Miller et al. 1988) or the method was incorporated into a computer program, which we were unable to obtain (Talbot et al. 1990). As far as we know, the Talbot et al. (1990) method was the first conductivity method to use the speciated ions calculated using a geochemical model. There are also theoretical methods intended primarily for industrial applications (Anderko and Lencka 1997; Wang et al. 2004) that are not included in this comparison. These theoretical methods have been successfully extended to concentrated aqueous solutions and may be well-suited for determining the conductivity of brines. However, empirical equations are typically used to determine the conductivity in multi-component systems having low-to-medium concentrations typically studied in environmental research (Visconti et al., 2010).

Electrical conductivity conventions

The electrical conductivity (κ) of a solution can be measured precisely and accurately with a conductivity meter and probe using the following equation:

$$\kappa = K_{cell} G \tag{1}$$

where K_{cell} is the conductivity cell constant and G is the conductance. The K_{cell} is the ratio of the distance between conductivity cell plates to the area of the plates. The conductivity of a solution depends on the ions that are present, their concentrations, and the solution temperature. The conductivity is typically referenced to 25°C (κ_{25}) because the conductivity increases 1% to 3% per °C (Robinson and Stokes 1965). The κ_{25} is typically calculated using the following equation:

$$\kappa_{25} = \frac{\kappa}{1 + \alpha\left(t - 25°\mathrm{C}\right)} \tag{2}$$

where κ is the conductivity at the solution temperature, t, in °C, and α is the temperature compensation factor. Most conductivity meters designed for field use automatically report κ_{25}. Some manufacturers use a linear α (0.019-0.020$°\mathrm{C}^{-1}$), some use a non-linear α, and some allow the user to choose the α.

Electrical conductivity is a collective measure of dissolved ions (Hem 1982), and having the capability to determine the contribution of individual ions to the conductivity increases the usefulness of the measurement. The conductivity of an aqueous solution is related to the concentration and mobility of ions in solution (Harned and Owen 1958). The following equation, or one slightly modified, is used by several methods (e.g., Laxen 1977; Pawlowicz 2008; Appelo 2010; McCleskey et al. 2012) for calculating conductivity of a mixed electrolyte solution from its chemical composition:

$$\kappa = \sum \lambda_i m_i \tag{3}$$

where λ is the ionic molar conductivity and m is the speciated molality of the i^{th} ion. To determine a solution's conductivity using Eq. 3, the λ_i and m_i must be known for the major ions in solution. The m is often determined using a geochemical speciation code, which calculates the theoretical concentration of free ions and ion-pairs. As an alternative to using m, some methods use the analytical concentration (C) of major ions (e.g., Rossum 1949; McNeal et al. 1970; Tanji and Biggar 1972; Rossum 1975; Laxen 1977; Wüest et al. 1996). In addition to Eq. 3, there are other equations used to calculate κ (e.g., McNeal et al. 1970; Rossum 1975). With the exception of the method of McNeal et al. (1970), the success of a conductivity method depends on the accuracy of the λ_i, the major ion concentrations, and the chemical speciation (Visconti et al. 2010; McCleskey et al. 2012).

Materials and procedures

Electrical conductivity methods

Electrical conductivity calculations that are applicable to a wide range of water samples must include the ions that contribute substantially to the conductivity. To identify these ions, the transport numbers (t) were determined for 1593 water samples (McCleskey et al. 2012). The transport number is the relative contribution of a given ion to the overall conductivity and depends on its concentration and ionic molar conductivity. The transport number of the following ions (listed from highest to lowest) were found to contribute substantially ($t > 0.02$) to the conductivity of at least 1 of 1593 water samples: H^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, F^-, NO_3^-, Al^{3+}, Fe^{2+}, HSO_4^-, Li^+, OH^-, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, $NaSO_4^-$, and $NaSO_3^-$. Methods that do not incorporate these ions may underestimate the conductivity of some natural waters. The ions included in each method are tabulated in Table 1. Of the eleven conductivity methods, the methods presented by Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012) are the most comprehensive. Apart from the methods presented by McCleskey et al. (2012) and Appelo (2010), none of the methods incorporate Fe and Al. Acid mine drainage waters, which are generated from the oxidation of pyrite, are of great environmental concern and frequently contain high concentrations of Fe, Al, and other transition metals.

A brief summary of the κ and λ equations used by each of the methods is listed in Table 2. Two approaches have been used to calculate κ_{25}. One approach is to directly calculate the conductivity at 25°C, κ_{25}. This approach, used by Rossum (1949), McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Marion and Babcock (1976), Laxen (1977), and Visconti et al. (2010), uses only the ionic conductivity (λ) at 25°C. The determination of λ is simplified because it is only a function of concentration and not temperature. However, λ depends on both temperature and ionic strength (Robinson and Stokes 1965). Furthermore, the speciated ion concentration may be different at 25°C than at the sample temperature because dissociation constants are a function of temperature (Nordstrom and Munoz 1994). In addition, the calculated κ_{25} may not be comparable to the measured κ_{25}, which depends on α (Eq. 2). Therefore, meaningful comparisons between the

Table 1. Summary of the ions included in electrical conductivity methods. The ions are grouped by those which have been determined to contribute a major ($t > 0.1$), moderate ($0.1 > t > 0.02$), minor ($t < 0.02$), or an unknown amount to the conductivity of natural waters.

Ion	Rossum (1949)	McNeal et al. (1970)	Tanji and Biggar (1972)	Rossum (1975)	Marion and Babcock (1976)	Laxen (1977)	Wüest et al. (1996)	Pawlowicz (2008)	Appelo (2010)	Visconti et al. (2010)	McCleskey et al. (2012)
Major											
H^+				x				x	x	x	x
Na^+	x	x	x	x	x	x	x	x	x	x	x
Ca^{2+}	x	x	x	x	x	x	x	x	x	x	x
Mg^{2+}	x	x	x	x	x	x	x	x	x	x	x
NH_4^+							x	x			x
K^+		x	x	x		x	x	x	x	x	x
Cl^-	x	x	x	x	x	x	x	x	x	x	x
SO_4^{2-}	x	x	x	x	x	x	x	x	x	x	x
HCO_3^-	x	x	x	x	x	x	x	x	x	x	x
CO_3^{2-}	x	x	x	x	x		x	x	x	x	x
F^-								x	x		x
NO_3^-	x	x	x	x	x	x	x	x	x	x	x
Al^{3+}									x		x
Fe^{2+}									x		x
HSO_4^-									x		x
Moderate											
Li^+								x	x		x
OH^-				x				x	x	x	x
Fe^{3+}									x		x
Cu^{2+}								x	x		x
Mn^{2+}									x		x
Zn^{2+}								x	x		x
$NaSO_4^-$					x				x		x
$NaCO_3^-$									x		x
Minor											
Ba^{2+}								x	x		x
Br^-								x	x		x
Cs^+											x
Sr^{2+}								x	x		x
KSO_4^-									x		x
Unknown											
Ag^+								x			
I^-								x			
ClO_4^-								x			
La^{3+}								x			
$MgHCO_3^+$					x				x		
$H_2PO_4^-$					x				x		
HPO_4^{2-}					x				x		

Table 2. The electrical conductivity (κ) and ionic conductivity (λ) equations used by each method. [κ, electrical conductivity; κ_{25}, electrical conductivity at 25°C; λ, ionic conductivity; λ_0, limiting ionic conductivity; *i*, i^{th} ion; *C*, molar concentration; *N*, normality; *m*, molality; *z*, ionic charge; *I*, ionic strength; *Dw*, water diffusion coefficient; *F*, Faraday's constant; *R*, gas constant, *T*, temperature; γ_{sc}, activity coefficient; *p*, pressure; and variables defined by method (*a, A, b, B, c, d, f, k, r, Z*, θ, Γ, and μ)].

Method	κ equation*	λ equation	Ion Conc.	Reference
A	$\kappa_{25} = \sum \lambda_i C_i$	$\lambda_i = \lambda_{\sim 0.001N}$	Analytical	Rossum (1949)
B	$\kappa_{25} = \sum k_i C_i^b$		Analytical	McNeal et al. (1970)
C	$\kappa_{25} = \sum k_1 + k_2 C_i + k_3 C_i^2 + k_4 C_i^3$		Analytical	McNeal et al. (1970)
D	$\kappa_{25} = \sum \lambda_i C_i$	$\lambda_i = \lambda_{0,i} - aC_i^{1/2}$	Analytical	Tanji and Biggar (1972)
E	$\kappa_{25} = \lambda_{0,i} C - \left(k_1 \lambda_{0,i} + k_2\right) C_i^{1.5}$		Analytical	Rossum (1975)
F	$\kappa_{25} = \sum \lambda_i m_i z_i$	$\lambda_i = \mu_j^0 - \left[k_1\left(\lambda^0\right)\left(z_j\right)\sum c_n r_j^n + k_2 \lvert z_j \rvert\right] \frac{I^{1/2}}{1 + k_3 a I^{1/2}}$	Analytical	Marion and Babcock (1976)
G	$\kappa_{25} = \sum \lambda_i N_i$	$\lambda_i = \lambda_{0,i} - A \frac{I^{1/2}}{1 + I^{1/2}}$	Analytical	Laxen (1977)
H	$\kappa = \sum \lambda_{0,i} f_i z_i C_i$	$\lambda_{0,i} = a_i + b_i T + c_i T^2 + d_i T^3$	Analytical	Wüest et al. (1996)
I	$\kappa = \sum C_i z_i \lambda_i (I) \theta_i \Gamma(p)$	$\lambda_i = \frac{\lambda_{0,i}}{1 + a_i z_i I^{1/2}}$	Analytical†	Pawlowicz (2008)
J	$\kappa = \sum \left(\lambda_{0,i} \gamma_{SC} m_i\right)$	$\lambda_{0,i} = \frac{z^2 F^2}{RT} D_w$	Speciated	Appelo (2010)
K	$\kappa_{25} = b_0 + b_1 \left(\sum \lvert z_i \rvert \lambda_i C_i\right)$	$\lambda_i = \lambda_{0,i} - aC_i^{1/2}$	Analytical or Speciated	Visconti et al. (2010)
L	$\kappa = \sum \lambda_i m_i$	$\lambda_i = \lambda_{0,i}(T) - A(T) \frac{I^{1/2}}{1 + BI^{1/2}}$	Speciated	McCleskey et al. (2012)

*The κ_{25} is calculated directly using the κ equation presented in this table for methods A–G and K. For methods H, I, J, and L, the κ_{25} is calculated using Eq. 2.
†Speciation is accounted for using θ_i.

calculated and measured κ_{25} may not be feasible when the sample temperature is not close to 25°C. The other approach, used by Wüest et al. (1996), Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012), is to calculate the conductivity (κ) and then calculate the κ_{25} using Eq. 2. This approach is more complex because λ is a function of both concentration and temperature. In addition, this approach allows for improved interpretation of conductivity measurements, including determination of transport numbers of important ions (McCleskey et al. 2012). Also, meaningful comparisons between the calculated and measured κ_{25} can be achieved if the same α is used.

Summary of methods

Method A—Rossum (1949)

This method includes eight ions (Table 1) and calculates κ_{25} directly. The method was developed to check the accuracy of water analyses and at one time was recommended as a quality assessment procedure (APHA 1971). It consists of a table of factors, which gives the conductivity contributed by an ion when multiplied by the concentration of the ion. The factors are essentially the ionic equivalent conductivity at 0.001 N (Table 2) because the method requires that the conductivity of the sample be diluted to between 90 and 120 µS cm^{-1}. Dilution minimizes the effects of ion interactions and the major ion concentrations are expected to be approximately 0.001 N or less. However, dilution causes the conductivity to differ from the actual water sample because ion pairs may occur in the original sample, decreasing the conductivity from the calculated conductivity. It is also subject to dilution errors and to errors caused by hydrolysis and precipitation reactions when the sample is diluted. Hydrolysis and precipitation reactions are likely for samples of low pH containing high concentrations of Al or Fe. Because of these complications and changes to the conductivity on dilution, this method was excluded from further comparisons.

Method B and C—McNeal et al. (1970)

This method includes nine ions (Table 1) and calculates κ_{25} directly. McNeal et al. (1970) tested three different techniques for calculating the individual ion conductivities. These techniques also assume that the conductivity of a solution is the sum of the conductivity of the major ions. Two of these techniques use an exponential (Table 2, method B) or a third-order polynomial (Table 2, method C) equation rather than the simple product of λC. For methods B and C, the constants k_i and b are given in McNeal et al. (1970). A third technique, a graphical one, was also developed in which individual ion conductivities were extrapolated from a series of linear equations plotted on a graph. Whereas this third technique is convenient, its precision is low and produces less accurate conductivity calculations.

McNeal et al. (1970) claimed that the polynomial method (method C) proved to be the most accurate. However, we tested the accuracy of both the exponential (B) and polynomial (C) methods using the electrolytes in McCleskey et al. (2012) and found that the polynomial equation greatly overestimated the conductivity for solutions below 200 µS cm^{-1} (Fig. 1). The polynomial method (C) does not work for dilute solutions because the calculated conductivity approaches k_1. The conductivity of many natural waters is less than 200 µS cm^{-1}; thus, the polynomial method (C) is not reliable for many potable or dilute surface waters. Only the exponential equation (B) was compared with the other conductivity methods in this manuscript.

Method D— Tanji and Biggar (1972)

This method includes nine ions (Table 1), calculates κ_{25} directly (Table 2), and uses analytical ion concentrations. The ionic conductivity (λ) is in the form of the square root law (Robinson and Stokes 1965), which is known to work well at low concentrations, but which has been shown to fail at ionic strengths above 0.01 m (Jones and Dole 1930). Furthermore, λ_0 is the limiting ionic conductivity for the i^{th} ion at 25°C, and a is an empirical coefficient ranging from 2 to 9 depending on the salt concentration and ion association effects. The a parameter is adjusted to best fit the measured κ_{25} of the waters tested. For this comparison, the adjustable empirical coefficient (a) was set to 4.6 because it produced the smallest average residual when compared with the measured conductivities of the natural waters tested.

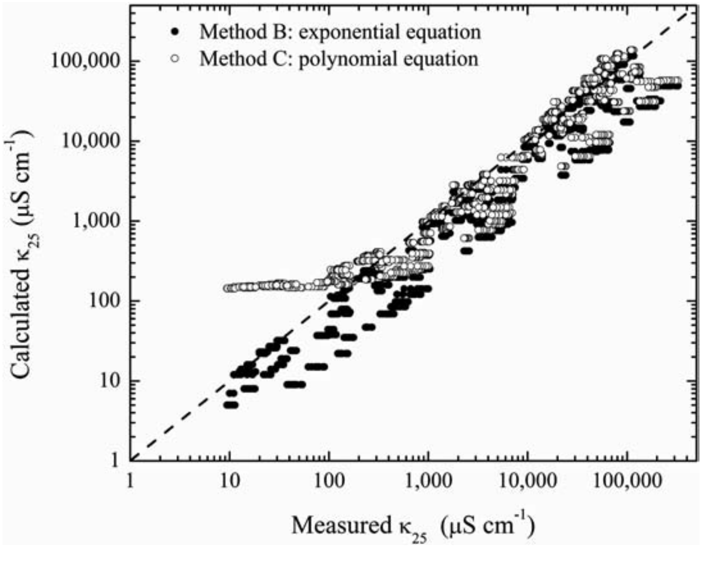

Fig. 1. Comparison of the calculated and measured using the McNeal et al. (1970) exponential (B) and polynomial (C) methods for the electrolytes in McCleskey (2011).

Method E—Rossum (1975)

This method includes eleven ions applicable to natural waters (Table 1), calculates κ_{25} directly, and has been recommended as a standard method to check the accuracy of water analyses (APHA 1999). It does not directly account for ion pairing and uses a modification of the Onsager limiting law to determine the conductivity of a solution. The constants k_1 and k_2 are associated with the relaxation and the electrophoretic effects (Robinson and Stokes 1965). The method requires a series of computations incorporating the limiting ionic equivalent conductivities (λ_0) and the mobility function (q) from the theory of relaxation (Robinson and Stokes 1965) to compute λ_0, k_1, and k_2.

Method F—Marion and Babcock (1976)

This method includes nine ions and four ion pairs (Table 1) and calculates κ_{25} directly. The modified Onsager-Fuoss equation (Onsager and Fuoss 1932; Harned and Owen 1958) was used to calculate the ionic equivalent conductivity. For method F, λ_0 is the limiting conductivity at 25°C, z is the ionic charge, a is the mean distance of closest approach of ions in solution, I is the speciated ionic strength, and μ_j^0 and r_j^n are variables that are used to account for the relaxation effect and are calculated using five additional equations. The λ equation is complex and must be solved by successive approximations. The method is not conducive to calculating the conductivity of a large number of natural samples without incorporation into a computer program. Consequently, it is excluded from further comparisons.

Method G—Laxen (1977)

This method includes eight ions (Table 1) and calculates κ_{25} directly. It uses total ion concentrations and does not account for ion pairing. The ionic conductivity is not a function of temperature since λ_0 is the limiting conductivity at 25°C. The variable A is the Onsager's limiting slope and I is the total ionic strength. The A term can be solved for mono- and divalent ions using straightforward equations presented by Laxen (1977). The speciation code WATEQ4F, version 2.31, incorporated the Laxen method (USGS 2012a); however, speciated concentrations, rather than analytical concentrations, were used. For this comparison, the method was not modified by using WATEQ4F.

Method H—Wüest et al. (1996)

This method includes ten ions and calculates κ. Method H was specifically designed to calculate the conductivity of Lake Malawi at various depths. Consequently, many important ions are not included and the approach for determining κ_{20} (rather than κ_{25}) is nonconventional. The κ_{20} is calculated using a temperature correction factor (f_T) for the water of the epilimnion, metalimnion, and hypolimnion separately and the f_T are not pertinent to determining κ_{25}. Eq. 2 was used to determine κ_{25} for this comparison. Temperature-dependent pressure corrections are also included in the Wüest method but are not applicable to this comparison. The λ_0 is only a function of temperature and concentration is accounted for using a reduction coefficient (f_i) for each ion based on its concentration. The parameters used to determine f_i are included in Wüest et al. (1996).

Method I—Pawlowicz (2008)

This method includes twenty-three ions, calculates κ, and κ_{25} is then calculated using Eq. 2. Pawlowicz's estimation of λ, which was originally proposed by Walden (1924), is superior to earlier methods because $\lambda_{0,i}$ and a_i are functions of temperature. Whereas the method utilizes analytical concentrations, speciation is accounted for using an ionic strength-dependent reduction factor (θ_i) for pairing and speciation effects in a binary electrolyte. The θ_i is less than 1 and is based on a Gaussian curve using the following equation:

$$\theta = 1 - A_{jk} e^{-w_{jk}\left(\log\left(I^{1/2}\right) - \log\left(\left(I_{jk}^{0}\right)^{1/2}\right)\right)^2} \qquad (4)$$

where A_{jk}, I_{jk}^0, and w_{jk} are parameters representing the amplitude, center, and width, respectively, of a Gaussian curve used to estimate the pairing reduction. Numeric values needed to calculate the conductivity are listed in Pawlowicz (2008). Pressure-related changes are also included in the Pawlowicz method (p), but are relatively small (on the order 0.1% per 100 m water depth) and are not included in this comparison. The method was incorporated into a spreadsheet that was used to calculate κ_{25} for all test samples.

Method J—Appelo (2010)

This method includes a total of 50 ions and ion pairs [see the data file "phreeqd.dat" in PHREEQCI version 2.18 (USGS 2012b)], calculates κ using the speciated chemical composition, and κ_{25} is determined using Eq. 2. The limiting ionic conductivity (λ_0) of a solute species is determined using its diffusion coefficient (D_w), ionic charge (z), Faraday's constant (F), gas constant (R), and absolute temperature (T). Multiplying the limiting ionic conductivity ($\lambda_{0,i}$) with the speciated concentration (m) and the activity coefficient (γ_{sc}) and summing up for all the solutes, gives an estimate of the κ. Appelo's method is unique in that it relates the ionic conductivity to diffusion coefficients. The approach allows for the inclusion of the most ions because diffusion coefficients are reported for many ions (e.g., Lobo 1975; Lobo and Quaresma 1981; Lobo and Quaresma 1989). The U.S. Geological Survey geochemical model PHREEQCI 2.18 (USGS 2012b) incorporates Appelo's method and was used to calculate κ for all test samples.

Method K—Visconti et al. (2010)

This method includes eleven ions (Table 1) and calculates κ_{25} directly. It uses either total or speciated ion concentrations. Visconti et al. (2010) assessed several different empirical equations to calculate soil solution conductivity and found that an equation in the form of method K (Table 2) gave the best predictions. The constants b_0 and b_1 differ depending on whether the speciated ion concentrations are available. Method K is in the form of a linear equation and the intercept, b_0, is 210 or 270 µS cm^{-1} for speciated and analytical ion concentrations, respectively. Whereas the method appears to work well for soil solutions with conductivities greater than 20,000 µS cm^{-1}, the conductivities of many natural waters are less than 210–270 µS cm^{-1}. Thus, similar to method C, method J is not reliable for many dilute waters, and consequently, was excluded from further comparisons.

Method L—McCleskey et al. (2012)

This method includes a total of 28 ions and ion pairs, calculates κ using the speciated chemical composition, and κ_{25} is determined using Eq. 2. The ionic conductivity (λ equation) is calculated using an equation of the form proposed by Lattey (1927), where λ_0 and A are functions of temperature, B is an empirical constant, and I is the speciated ionic strength. McCleskey et al. (2012) present a set of equations used to compute the ionic molal conductivity. The λ equation is a linear equation when plotted against $(I^{1/2})(1 + BI^{1/2})^{-1}$, and for dilute solutions, it approaches the behavior of the square root law, which is known to work well at low concentrations (Jones and Dole 1930; Harned and Owen 1958). The U.S. Geological Survey geochemical model WATEQ4F (Ball and Nordstrom 1991; USGS 2012a) was used to calculate the chemical speciation, λ, and κ_{25}.

The reliability of geochemical model simulations was discussed in detail by Nordstrom (2004) and largely depends on the thermodynamic database used. In a comparison of 14 different geochemical codes, WATEQ was found to perform favorably for seawater and river water analyses (Nordstrom et al. 1979). In addition to the McCleskey et al. (2012) method, the WATEQ4F database was also used to determine the speciated ion concentrations for the Appelo (2010) method, which is incorporated into PHREEQCI.

Water quality data sources

The capability of the methods to accurately calculate the conductivity of natural waters was investigated by calculating the conductivity of (1) 33 binary electrolyte solutions that are commonly found natural waters (McCleskey 2011), (2) 41 U.S. Geological Survey standard reference water samples (SRWS) prepared from river samples, and (3) 1593 natural waters. Although the 33 binary electrolyte solutions found in natural waters reported by McCleskey (2011) are excellent samples to identify the limitations of most methods, only rarely are the conductivities of natural waters dominated by only two ions. Forty-one USGS SRWS prepared from river waters were also tested because the reported ion concentrations and conductivities are very accurate. The SRWS is a natural surface water sample in which the major ion concentrations and conductivities have been determined by multiple laboratories and the most probable values (MPV) has been reported. The average charge balance for the SRWSs was 0.9 ± 1%. Additional information about the USGS SRWS program, including how the MPV values are determined, can be obtained from the USGS Standard Reference Sample Project (USGS 2012c). However, the chemical compositions of the SRWSs do not encompass a wide range of natural water types. Therefore, the conductivities were calculated for 1593 additional natural samples including acid mine water, geothermal water, seawater, dilute mountain water, and river water impacted by municipal waste water. All 1593 samples had a charge imbalance of less than 10%. The ranges of conductivity (κ_{25}), pH, temperature, and major ion and trace metal concentrations for all samples in the database as well as the complete chemical analyses of the 1593 natural water samples are reported by McCleskey et al. (2012). Depending on the model, unit conversions were performed using density data reported by Söhnel and Novotnŷ (1985).

Assessment

We compared the performance of the methods presented by McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), Wüest et al. (1996), Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012) by calculating the conductivity for the waters listed above. The accuracy of each method was compared by calculating the conductivity imbalance ($\delta\kappa_{25}$) for each sample using the following equation:

$$\delta\kappa_{25}(\%) = \frac{\kappa_{25}\ calculated - \kappa_{25}\ measured}{\kappa_{25}\ measured} \times 100 \qquad (5)$$

Laboratory solutions

The conductivity was first calculated for 33 electrolyte solutions relevant to natural waters. Because the electrolyte concentrations and corresponding conductivities reported in McCleskey (2011) are accurate and in agreement with the data in the literature, comparisons using these data can be used to rigorously determine the limitations of the methods by their ability to predict the conductivities of the electrolytes most important to natural waters. The electrolytes tested include KCl, NaCl, HCl, LiCl, NH_4Cl, CsCl (Fig. 2), $CaCl_2$, $MgCl_2$, $BaCl_2$, $SrCl_2$, $FeCl_2$, $CaSO_4$ (Fig. 3), Na_2SO_4, K_2SO_4, H_2SO_4, $Fe_2(SO_4)_3$, Cs_2SO_4, $FeSO_4$ (Fig. 4), $Al(NO_3)_3$, $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, and $Mn(NO_3)_2$ (Fig. 5), Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, NaOH (Fig. 6), KNO_3, KBr, NaF, and KF (Fig. 7). The ionic strengths of the electrolytes ranged from 10^{-4} to 1 m, the κ_{25} ranged from 9 to 200,000 µS cm^{-1}, and the temperature ranged from 5 to 90°C. The same temperature compensation factor (α = 0.019, Eq. 2) was used to calculate the κ_{25} for the measured conductivities in McCleskey (2011) and for the calculated conductivities for the methods requiring temperature compensation [Wüest et al. (1996), Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012)]. The other methods calculate κ_{25} and do not require temperature compensation.

For each electrolyte, the $\delta\kappa_{25}$ was determined using methods B, D, E, G, H, I, J, and L and plotted against κ_{25} and either ionic strength or pH (Figs. 2-7). Dashed lines are shown at ± 10% for reference. The McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), and Wüest et al. (1996) methods do not include the ions necessary to accurately predict the κ_{25} of LiCl, CsCl, $BaCl_2$, $SrCl_2$, $FeCl_2$, Cs_2SO_4, $Fe_2(SO_4)_3$, $FeSO_4$, $Al(NO_3)_3$, $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Mn(NO_3)_2$, NaOH, KBr, NaF, or KF solutions. The McNeal et al. (1970), Tanji and Biggar (1972), Laxen (1977), Wüest et al. (1996) methods do not include the H^+ ion and cannot accurately predict the conductivity of HCl or H_2SO_4 solutions.

For the ions that are included in the McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), and Wüest et al. (1996) methods, the conductivity of fully dissociated uni-univalent electrolytes can be predicted up to ionic strengths of 0.1 m and for solutions containing divalent ions the conductivity can be predicted up to 0.03 m. At the higher ionic strengths, the Rossum (1975) method generally overestimates the conductivity, and the McNeal et al. (1970), Tanji and Biggar (1972), and Laxen (1977) methods often underestimate the conductivity. However, for electrolytes that readily form ion pairs, the McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), and Laxen (1977) methods overestimate the conductivity, as is the case for $CaSO_4$ solutions (Fig. 3, ionic strengths greater 0.004) because these methods do not account for ion pairing. For the ions that are included in the Wüest et al. (1996) method, the conductivity can be used to calculate the conductivity up to about 0.01 m, but the f_i does not accurately correct for concentration effects at higher ionic strengths.

The Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012) methods are significant improvements over earlier methods. For most electrolytes, these three methods can correctly predict the κ_{25} up to 0.1 m. For some electrolytes, the κ_{25} predicted with the Pawlowicz (2008) method is only accurately calculated for temperatures below 35°C (e.g., LiCl, NH_4Cl, Na_2CO_3, K_2CO_3, and NaOH). Furthermore, the Pawlowicz (2008) method does not have the capability to calculate the conductivity of several transition-metal electrolytes, including Al^{3+}, Fe^{3+}, Fe^{2+}, and Mn^{2+}. The ionic strength-dependent reduction factor used by Pawlowicz (2008) appears to overcorrect for ion pairing in Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3, NaF, and KF solutions, which results in an under-estimation of conductivity. In addition, the reduction factor parameters for HSO_4^- are not included, and as a result, the conductivity is overestimated for some H_2SO_4 solutions near pH 2 (Fig. 4). Even though Fe^{+3} is not included in the method, the conductivity is overestimated for $Fe_2(SO_4)_3$ solutions likely because the ion pair $FeSO_4^+$ is not accounted for and the pH of the solutions was near 2.

The Appelo (2010) method does not accurately predict the conductivity of HCl and H_2SO_4 or the conductivity of electrolytes prepared in acid solutions [e.g., $FeCl_2$, $Fe_2(SO_4)_3$, $FeSO_4$, $Al(NO_3)_3$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, and $Mn(NO_3)_2$]. Because the mode of transport for the H^+ is different than most other ions

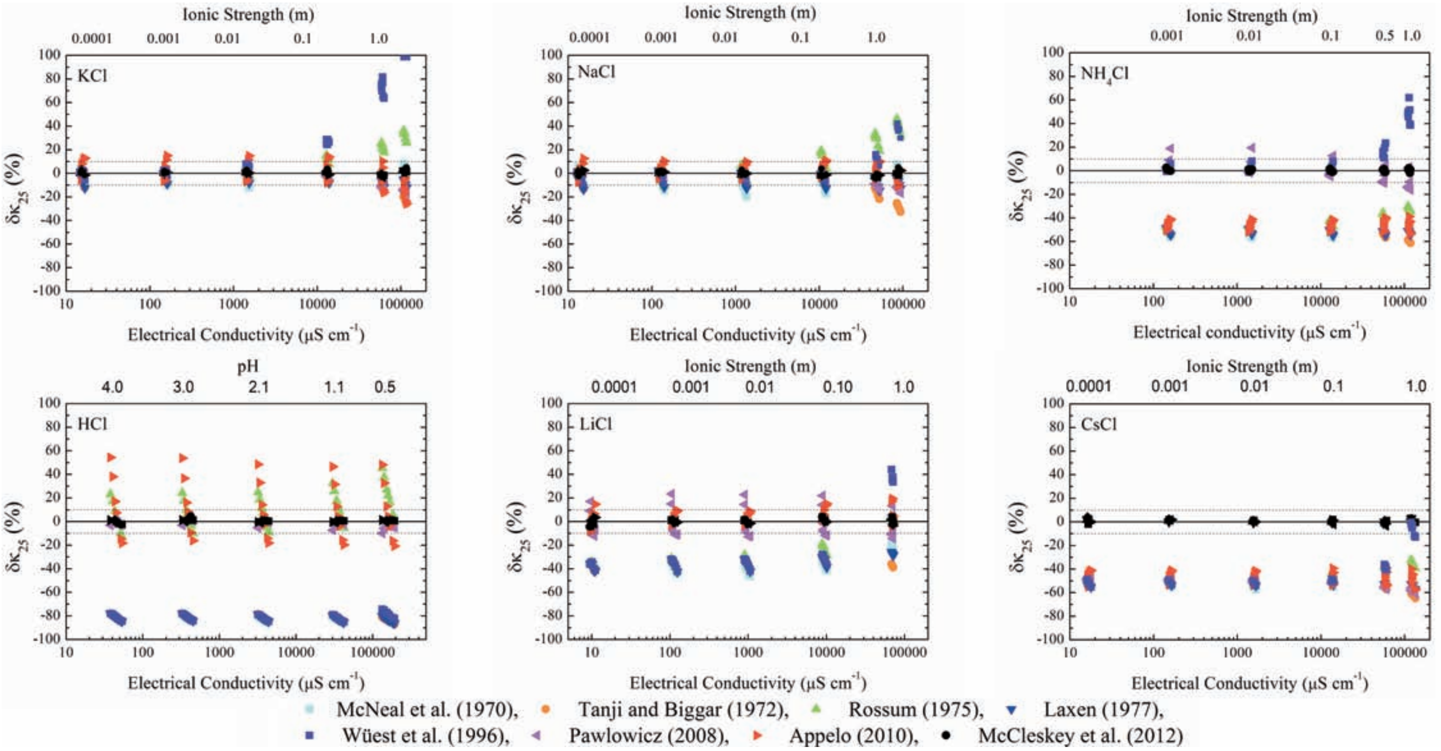

Fig. 2. Electrical conductivity imbalance (δκ*25*) determined from seven methods plotted against electrical conductivity and either ionic strength or pH for KCl, NaCl, NH$_4$Cl, HCl, LiCl, and CsCl.

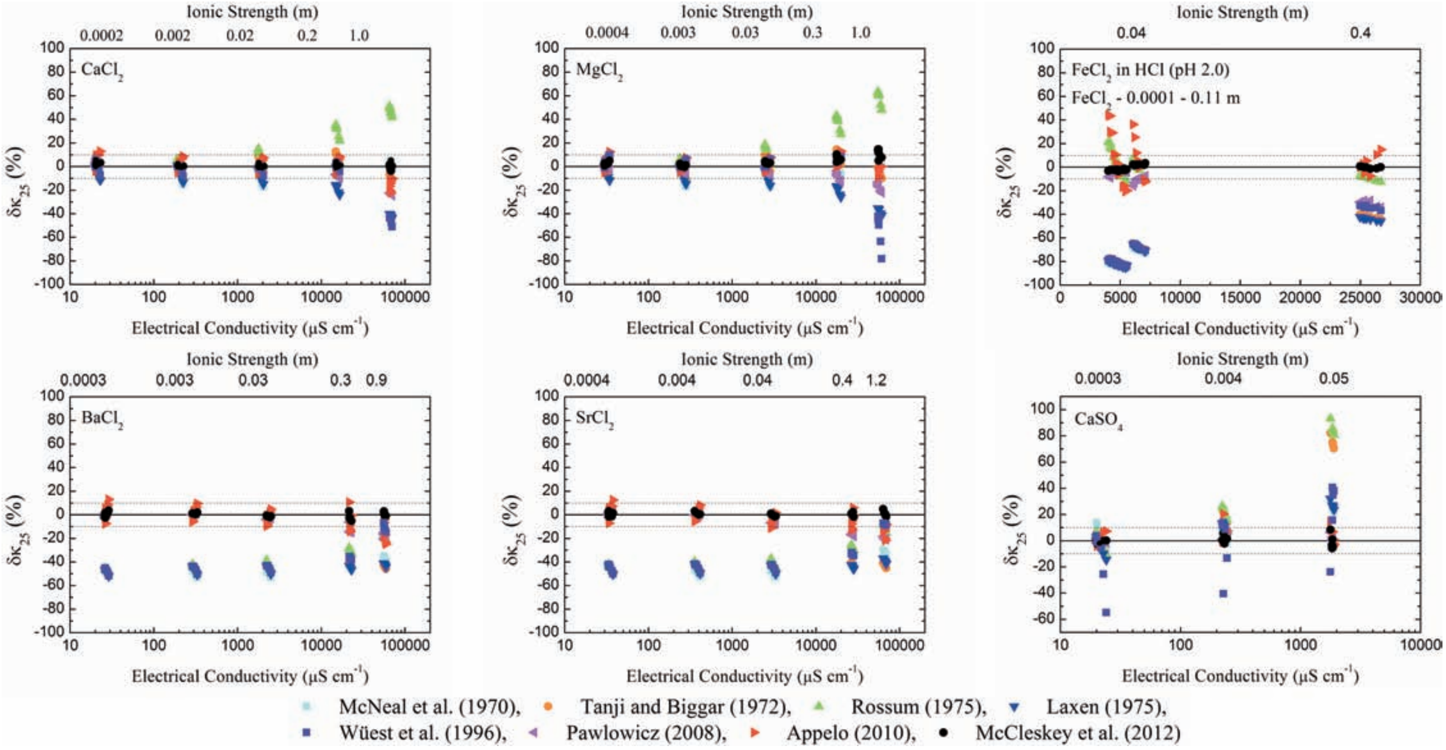

Fig. 3. Electrical conductivity imbalance (δκ*25*) determined from seven methods plotted against electrical conductivity and ionic strength for CaCl$_2$, MgCl$_2$, FeCl$_2$, BaCl$_2$, SrCl$_2$, and CaSO$_4$.

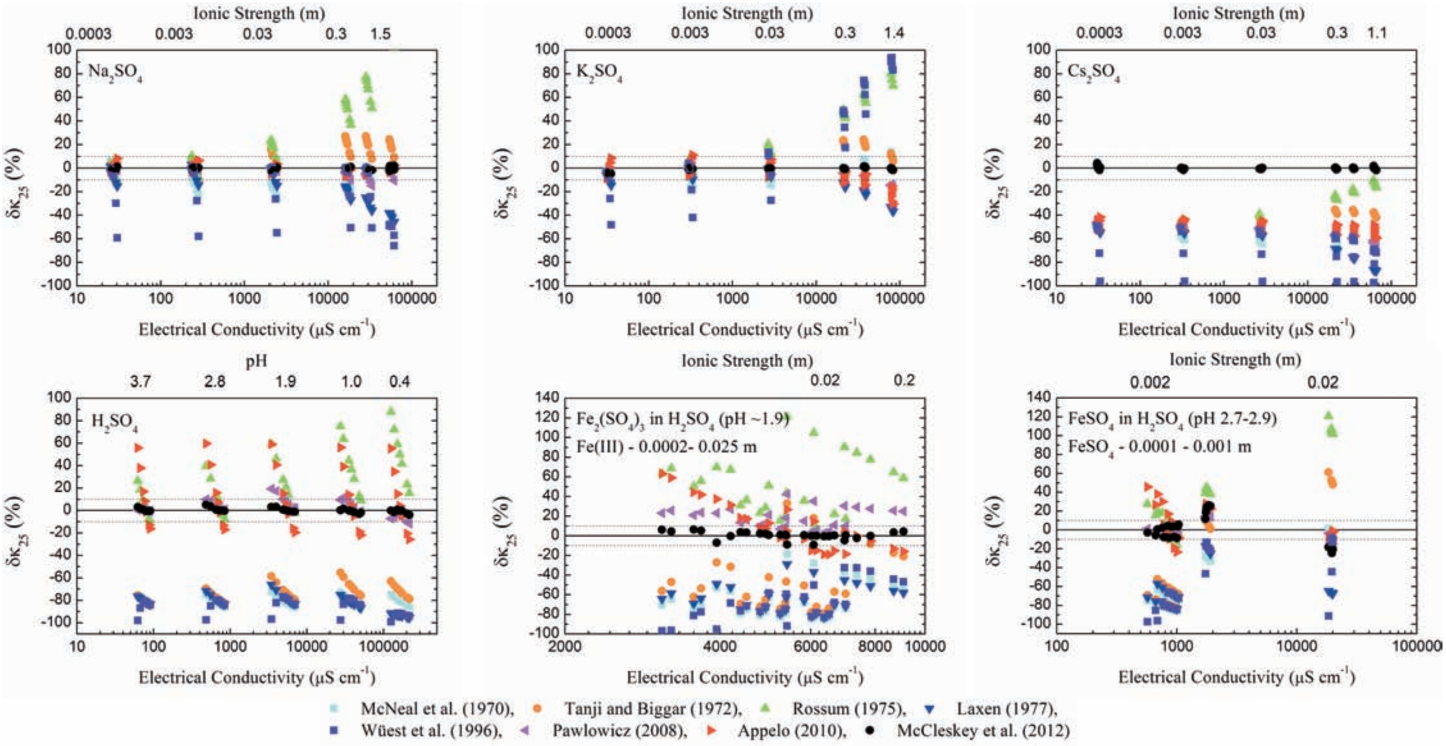

Fig. 4. Electrical conductivity imbalance (δκ*25*) determined from seven methods plotted against electrical conductivity and either ionic strength or pH for Na$_2$SO$_4$, K$_2$SO$_4$, Cs$_2$SO$_4$, H$_2$SO$_4$, Fe$_2$(SO$_4$)$_3$, and FeSO$_4$.

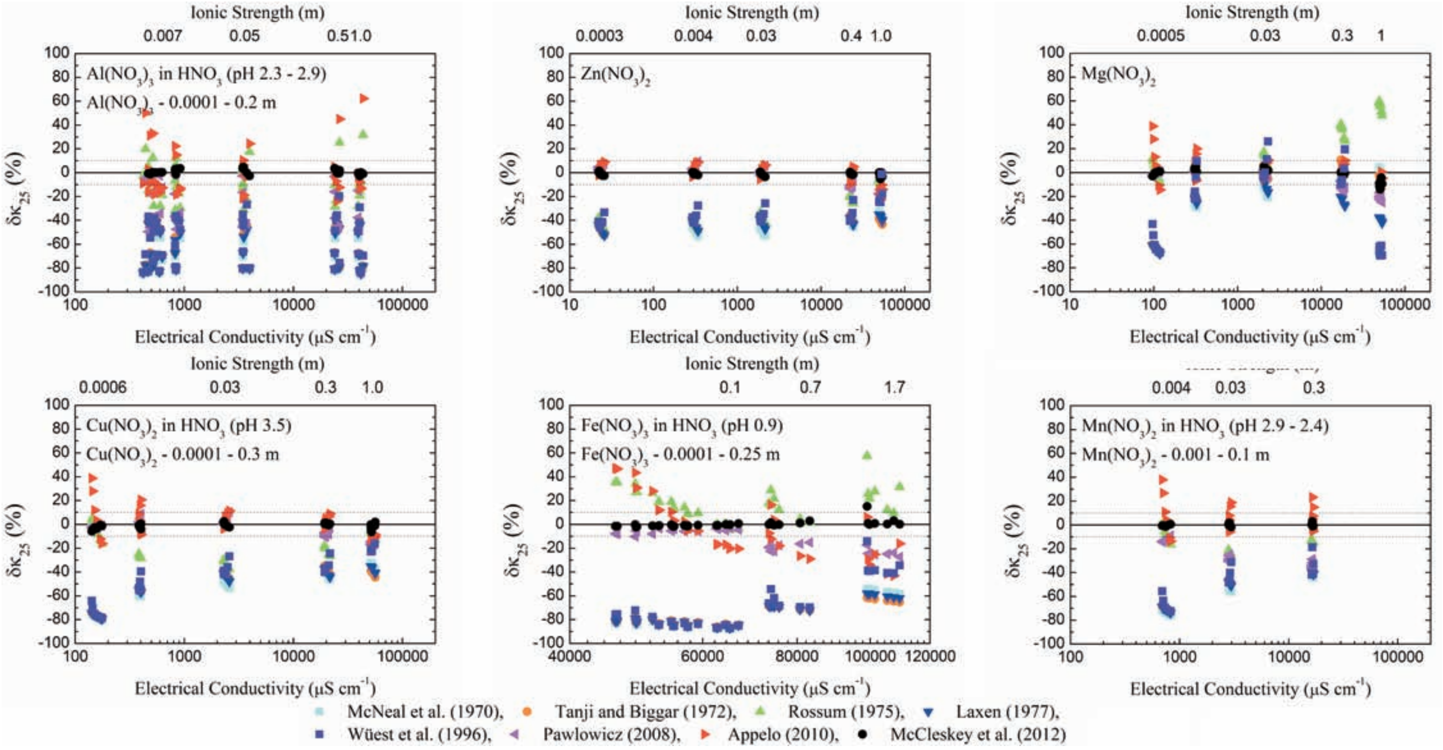

Fig. 5. Electrical conductivity imbalance (δκ*25*) determined from seven methods plotted against electrical conductivity and ionic strength for Al(NO$_3$)$_3$, Zn(NO$_3$)$_2$, Mg(NO$_3$)$_2$,Cu(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and Mn(NO$_3$)$_2$.

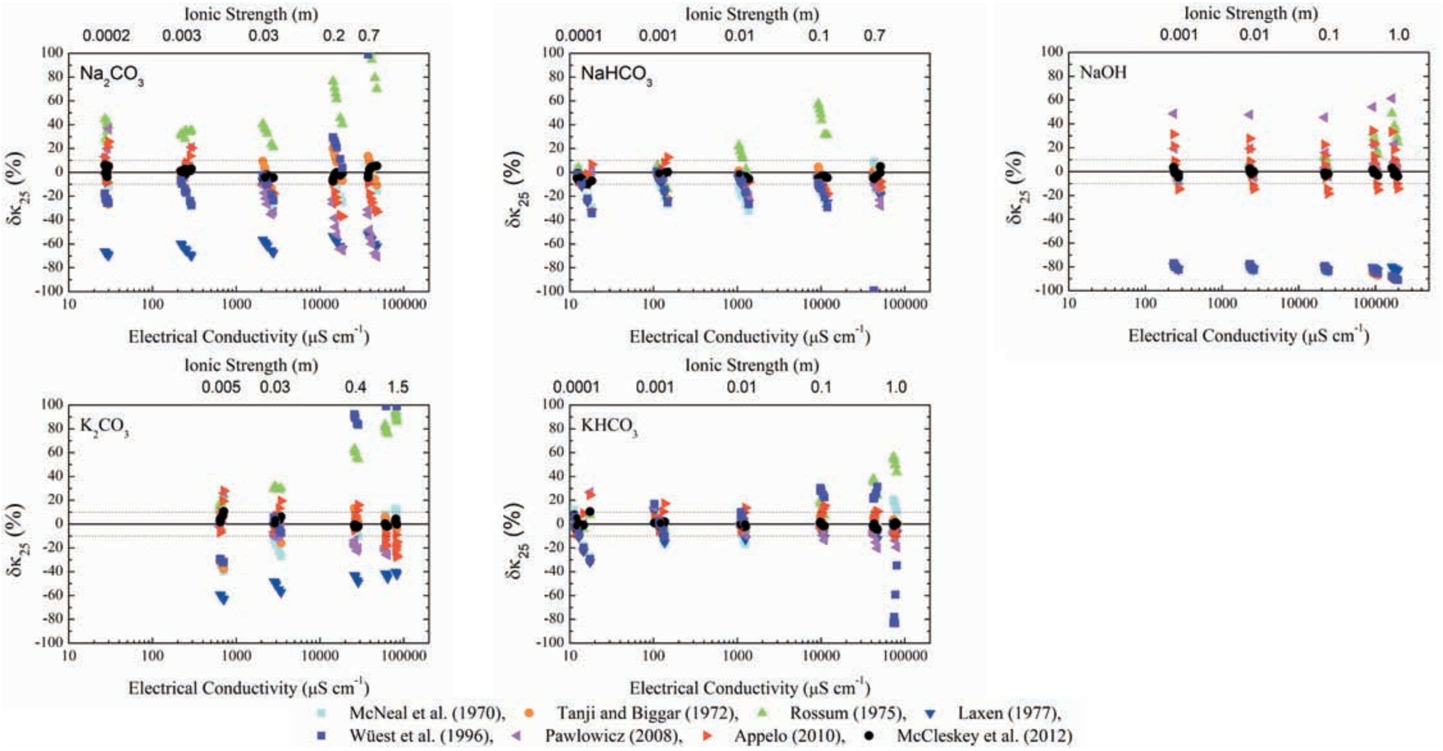

Fig. 6. Electrical conductivity imbalance (δκ*25*) determined from seven methods plotted against electrical conductivity and ionic strength for Na_2CO_3, $NaHCO_3$, NaOH, K_2CO_3, and $KHCO_3$.

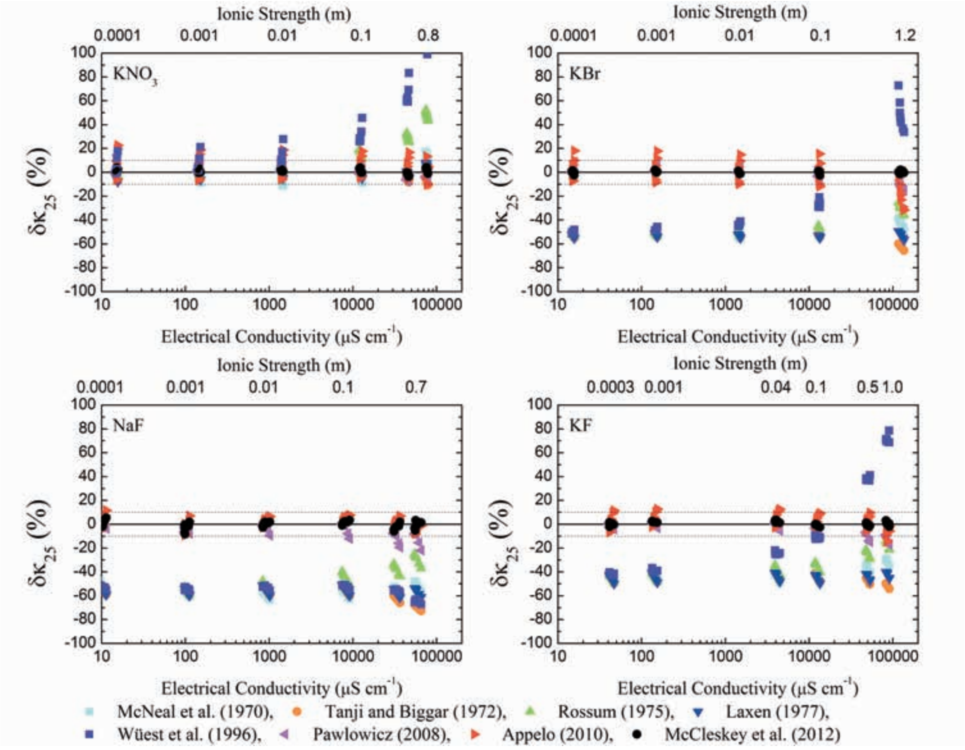

Fig. 7. Electrical conductivity imbalance (δκ*25*) determined from seven methods plotted against electrical conductivity and ionic strength for KNO_3, KBr, NaF, and KF.

in solution (Robinson and Stokes 1965), the relationship between the ionic conductivity and the diffusion coefficient (method I, λ equation) may not be valid for H^+ from 5 to 90°C.

A statistical summary of the capability of each method to determine the conductivity of the electrolytes applicable to natural waters is shown as a series of box plots in Fig. 8. The ability of the McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), and Wüest et al. (1996) methods to calculate the conductivity of the electrolytes applicable to natural waters is hindered by the exclusion of many important ions and by the lack of accounting for ion pairing. The Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012) conductivity methods clearly outperform the other methods. The variability in the method presented by Pawlowicz (2008) is primarily caused by the exclusion of many transition metals (Al^{3+}, Fe^{3+}, Fe^{2+}, and Mn^{2+}). Apart from a few high-temperature (>35°C) and low pH measurements, conductivity can often be reliably predicted using the Pawlowicz (2008) method up to 0.1 m for the ions included in the method. The method of Appelo (2010) can be used to reliably calculate the conductivity for waters with pH values above 4 and temperatures below 35°C.

For every electrolyte tested, the method presented by McCleskey et al. (2012) outperforms the other methods and reliably predicts the conductivity of the electrolytes applicable to natural waters (Fig. 2–8). For 1250 comparisons (Fig. 8), the mean and median $\delta\kappa_{25}$ were 0.1. Based on this evaluation, 99% of the calculated κ_{25} were within 7.5% of the measured values (Fig. 8). The worst predictions were for high concentrations of $MgCl_2$ (Fig. 3), for which an ion pair not accounted for by the geochemical models may be responsible. The McCleskey et al. (2012) method outperformed the other methods using these laboratory test solutions, however, it was designed using these data. The performance of these methods should be tested on other natural water samples.

Natural water samples

The calculated conductivities of known electrolyte solutions are useful for determining the applicable composition and temperature range for each method, but the definitive test is how accurately the methods can calculate the conductivity of natural waters. For each method tested, the conductivity of 41 U.S. Geological SRWSs were determined using the reported MPVs. The MPVs reported for the major ions are expected to be very accurate; therefore, SRWSs are ideal test samples for determining the capability of conductivity methods for natural waters. The SRWSs had a range of pH (2.74–10.2), ionic strength (0.0012–0.026), and conductivity (102 $\mu S \cdot cm^{-1}$–2079 $\mu S \cdot cm^{-1}$). The $\delta\kappa_{25}$ and a statistical summary of the results for each method is shown as a series of box plots in Fig. 9. The

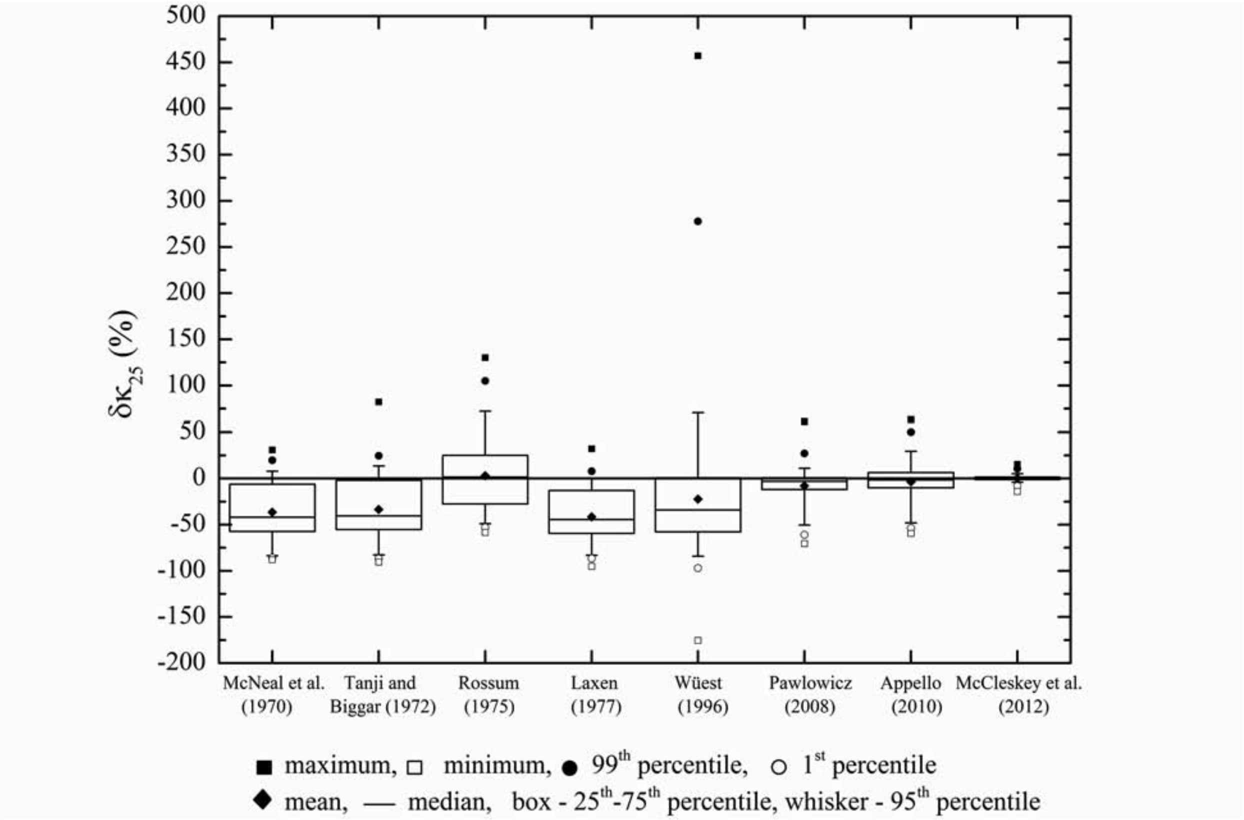

Fig. 8. Box plots showing the electrical conductivity imbalance ($\delta\kappa 25$) for 1250 comparisons of electrolytes pertinent to natural waters for the electrical conductivity method presented in McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), Wüest et al. (1996), Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012).

method presented by McCleskey et al. (2012) was the most effective at calculating κ_{25} for the SRWSs. The mean $\delta\kappa_{25}$ calculated using the method of McCleskey et al. (2012) for the U.S. Geological Survey SRWS was –0.5% with a standard deviation of 1.3%. The methods presented by Appelo (2010) and Pawlowicz (2008) also performed well for all samples. The mean $\delta\kappa_{25}$ calculated using the method of Appelo (2010) was –3.5% with a standard deviation of 1.3 % and the mean $\delta\kappa_{25}$ calculated using the method of Pawlowicz (2008) was 1.0% with a standard deviation of 2.0%.

The chemical compositions of the SRWSs do not encompass all natural water types; therefore, the conductivity of 1593 natural water samples, including acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water impacted by municipal waste, water were calculated. Some of the water samples were selected specifically to identify the limits of the conductivity methods—those with low pH, high temperature, or high ionic strength. The speciated charge imbalances, determined using WATEQ4F (Ball and Nordstrom 1991), for all the samples in this data set is ≤ ± 10%. Fig. 10 contains box plots of the $\delta\kappa_{25}$ of the 1593 natural water samples determined using the conductivity methods compared here. For natural waters, the Pawlowicz (2008) method, the Appelo (2010) method, and the McCleskey et al. (2012) method better predict conductivities than do the methods of McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), Wüest et al. (1996). For this set of natural water samples, the mean $\delta\kappa_{25}$ calculated using the method presented in McCleskey et al. (2012) was –0.7% with a standard deviation of 5.2%. The mean $\delta\kappa_{25}$ calculated using the Pawlowicz (2008) method was 0.7% with a standard deviation of 6.0%. The mean $\delta\kappa_{25}$ calculated using the Appelo (2010) method was –0.9% with a standard deviation of 9.9%. Also, the $\delta\kappa_{25}$ range determined with the method presented in McCleskey et al. (2012) (–19% to 20%) was smaller than the $\delta\kappa_{25}$ range determined by the methods of Pawlowicz (2008) (–21% to 28%) or Appelo (2010) (–83% to 36%).

For the three best performing methods, the Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012) methods, the $\delta\kappa_{25}$ for the 1593 natural water samples including the 41 SRWSs were plotted against temperature, pH, and conductivity (Fig. 11). For many samples below pH 3.5, the Pawlowicz (2008) method overestimates the conductivity (Fig. 11B). The likely reason for overestimating the conductivity for waters of low pH is the exclusion of HSO_4^- from the ionic-strength reduction factor. There is not a clear trend with temperature, but the largest errors are for temperatures above 70°C. For samples with conductivity less than 900 µS cm^{-1}, the Pawlow-

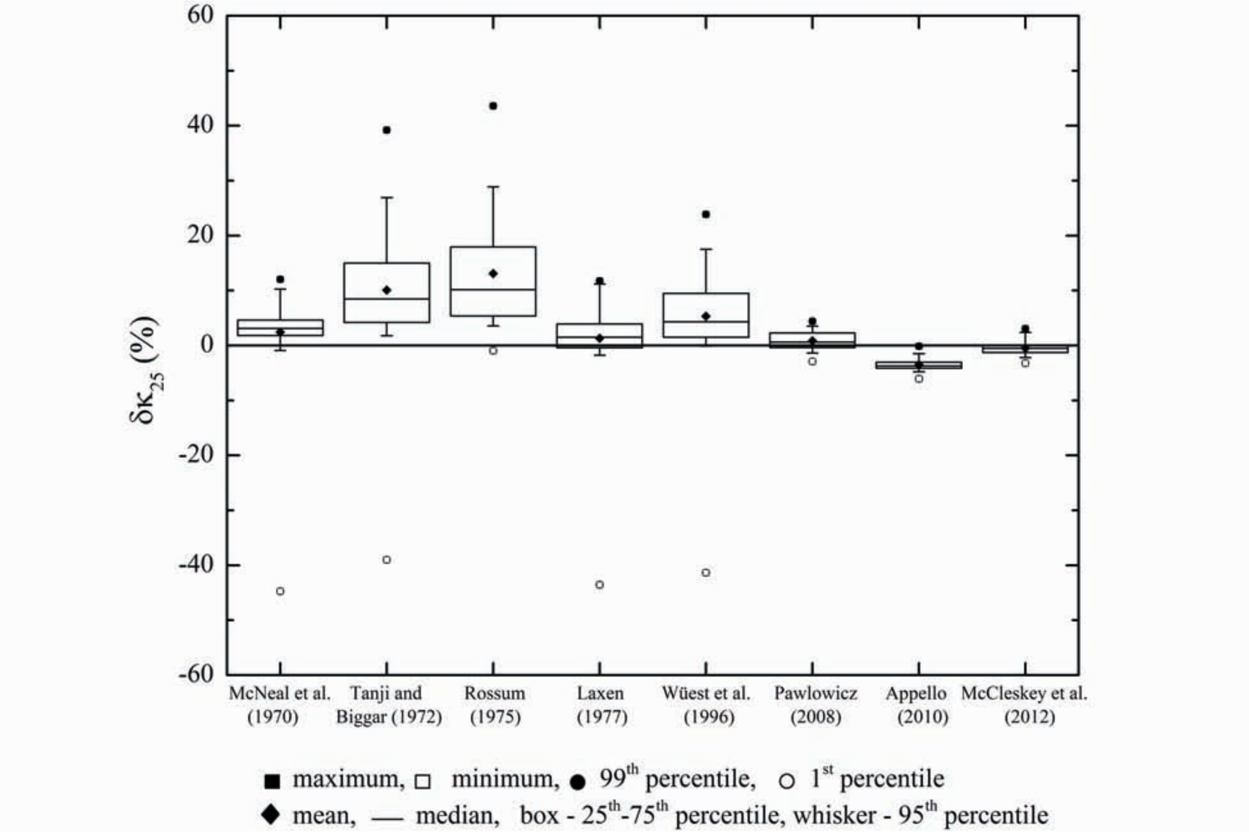

Fig. 9. Box plots showing the electrical conductivity imbalance (δκ*25*) for 41 USGS SRWSs for the electrical conductivity method presented in McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), Wüest et al. (1996), Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012).

icz (2008) method reliably calculated the conductivity (Fig. 11C). For samples having a conductivity less than 900 µS cm^{-1}, for which the Pawlowicz (2008) method is reliable (–10% < $\delta\kappa_{25}$ < 10%), the pH ranged from 2.8 to 9.8, and the temperature ranged from 0 to 92°C. For many samples above 40°C (Fig. 11 D) and below pH 3.5 (Fig. 11 E), the Appelo (2010) method significantly overestimates the conductivity. The likely reason for overestimating the conductivity for water of low pH is that the relationship between the ionic conductivity and the diffusion coefficient (Table 2, Method J) may not be valid for H^+ from 5 to 90°C. The method presented in McCleskey et al. (2012) can be used to calculate the conductivity of natural waters over a wider range of temperature (0 to 95°C), pH (1 to 10), conductivity (30 to 77,000 µS cm^{-1}), and ionic strength (< 1) (Fig. 11G-I).

Discussion

We investigated the potential of several methods to reliably calculate the electrical conductivities of natural waters from their chemical compositions. The methods presented in Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012) clearly outperform all other methods. They are the most rigorous, incorporate the most ions applicable to natural waters, and better predict the conductivity over a wide range of temperatures and concentrations. Apart from a few high-temperature (>35°C) or low pH (<3.5) samples, conductivity can often be reliably predicted using the Pawlowicz (2008) and Appelo (2010) methods up to 0.1 m for the ions included in the method. The method presented in McCleskey et al. (2012) does as well as or better than the Pawlowicz (2008) and Appelo (2010) methods of predicting the conductivity of many natural waters (pH 4 to 9, <35°C, and <1000 µS cm^{-1}). However, the conductivity method presented in McCleskey et al. (2012) is more reliable than the Pawlowicz (2008) and Appelo (2010) methods for the more extreme samples with pH < 3.5, high temperatures (>35°C), and high ionic strength (<1 m). In addition, for some samples containing high concentrations of transition metals, for example some acid mine waters, the method presented in McCleskey et al. (2012) is more reliable than the Pawlowicz (2008) method because the parameters for Al^{3+}, Fe^{3+}, Fe^{2+}, and Mn^{2+} are not included in the Pawlowicz (2008) method.

Comments and recommendations

Each of the three best performing methods—Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012)—are capable of accurately calculating the conductivity of many natural water samples. However, there are modifications that may improve the performance of each of these methods. The Pawlowicz (2008) method may be improved by incorporating

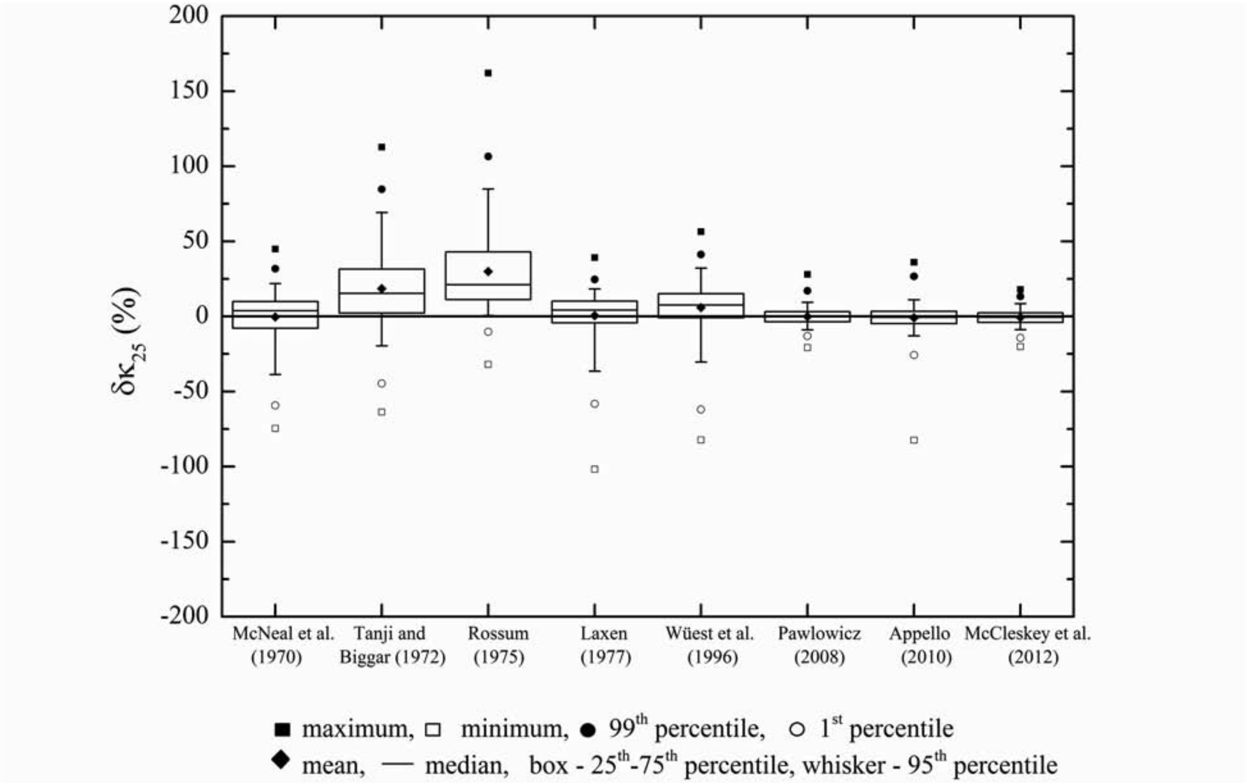

Fig. 10. Box plots showing the electrical conductivity imbalance for 1593 natural waters for the electrical conductivity method presented in McNeal et al. (1970), Tanji and Biggar (1972), Rossum (1975), Laxen (1977), Wüest et al. (1996), Pawlowicz (2008), Appelo (2010), and McCleskey et al. (2012).

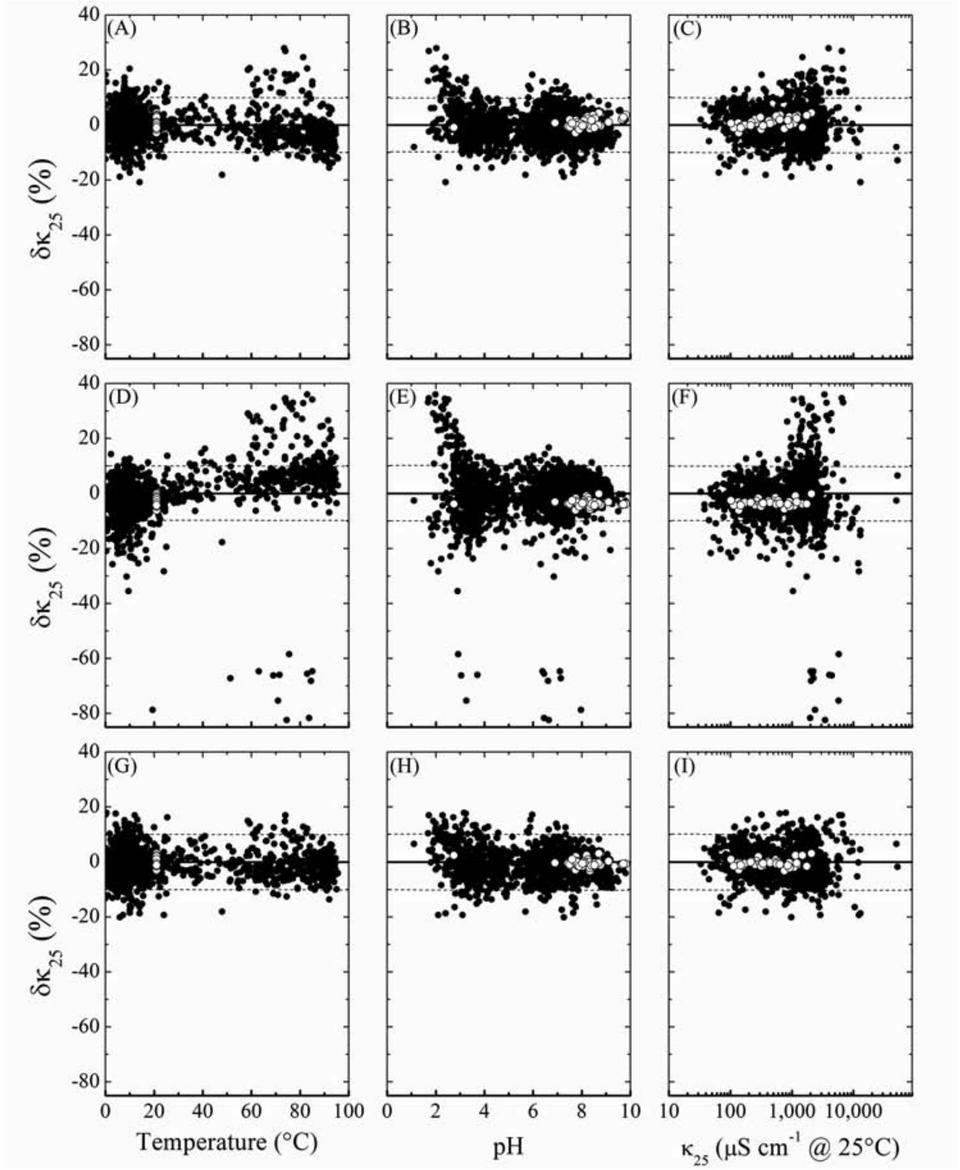

Fig. 11. Plots of electrical conductivity imbalance ($\delta\kappa 25$) against temperature, pH, and conductivity for 1593 natural waters (solid symbols) and 41 SRWS (open symbols) determined with the Pawlowicz (2008) method (A–C), the Appelo (2010) method (D–F), and the McCleskey et al. (2012) method (G–I).

the speciated ion concentrations rather than an ion reduction factor to account for ion pairing and by incorporating some important transition metals including Fe, Al, and Mn. The Appelo (2010) method could be improved by using a different approach to calculate λ for H^+ and OH^-. The Appelo method accurately estimates the λ for most ions because they move as individual entities through solution, and there are well-known relationships between temperature, viscosity, and diffusion coefficients. However, the mode of transport of the H^+ and OH^- ions is different than that of other ions. The H^+ and OH^- ions migrate by what has been termed a "jump or transfer" of a proton from one water molecule to the next as H_3O^+ and $H_3O_2^-$ (Robinson and Stokes 1965), therefore the temperature/diffusion coefficient approach used to calculate λ is not valid for H^+ and OH^-. Even though the McCleskey et al. (2012) method includes 28 environmentally important ions, the method could be improved by incorporating additional ions. The most straightforward approach may be to adapt the diffusion coefficient approach to calculate λ for additional ions.

Additionally, none of the methods are suited for brines. Either the calculated speciation using WATEQ4F or PHREEQCI (using the ion-association model, Ball and Nordstrom 1991) or λ (McCleskey 2011) are not accurate at high ionic strengths. One possibility is to use theoretical methods intended primarily for industrial applications (Anderko and Lencka 1997; Wang et al. 2004). These theoretical methods have been successfully extended to concentrated aqueous solutions and may be well-suited for determining the conductivity of brines.

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