Relationship between total dissolved solids and electrical conductivity in Marcellus hydraulic fracturing fluids

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ABSTRACT

The production of hydraulic fracturing fluids (HFFs) in natural gas extraction and their subsequent management results in waste streams highly variable in total dissolved solids (TDS). Because TDS measurement is time-consuming, it is often estimated from electrical conductivity (EC) assuming dissolved solids are predominantly ionic species of low enough concentration to yield a linear TDS-EC relationship: \( \text{TDS (mg/L)} = K_e \times \text{EC (μS/cm)} \) where \( K_e \) is a constant of proportionality. HFFs can have TDS levels from 20,000 to over 300,000 mg/L wherein ion-pair formation and non-ionized solutes invalidate a simple TDS-EC relationship. Therefore, the composition and TDS-EC relationship of several fluids from Marcellus gas wells in Pennsylvania were assessed. Below EC of 75,000 μS/cm, TDS (mg/L) can be estimated with little error assuming \( K_e = 0.7 \). For more concentrated HFFs, a curvilinear relationship (\( R^2 = 0.99 \)) is needed: \( \text{TDS} = 27,078e^{1.05 \times 10^{-5} \times \text{EC}} \). For hypersaline HFFs, the use of an EC/TDS meter underestimates TDS by as much as 50%. A single linear relationship is unreliable as a predictor of brine strength and, in turn, potential water quality and soil impacts from accidental releases or the suitability of HFFs for industrial wastewater treatment.

Key words | electrical conductivity, hydraulic fracturing, Marcellus shale, produced water, total dissolved solids

INTRODUCTION

Natural gas extraction from the Marcellus Formation by injecting fluid at high pressure to release entrapped gas generates significant amounts of brine. Flowback water produced during initial well stimulation and produced water generated during active gas extraction are collectively called hydraulic fracturing fluids (HFFs). These HFFs brines are characterized by high total dissolved solids (TDS), typically being 150,000 mg/L (Gregory et al. 2011). Although predominantly Na and Ca chlorides, the composition of brines produced as by-products of oil and gas exploration is highly variable because they originate from a variety of geological environments (Dresel & Rose 2010). Moreover, the concentrations of dissolved constituents tend to increase with time after the initial well stimulation (Haluszczak et al. 2013).

Besides the inherent variability of HFFs as they emerge from the well head, the produced waters can be commingled with available freshwater sources (surface waters, municipal water supplies, acid mine drainage (AMD) waters) for recycling and reuse in the hydraulic fracturing process (Kondash et al. 2014). If stored in impoundments, dilution by precipitation and evaporation alters the TDS of the brines. Both the generation and post-generation admixture with other water sources results in fluids with widely varying compositions and salinities. Haluszczak et al. (2015) reported TDS in flowback brines from Marcellus gas wells to range from 7,520 to 197,000 mg/L. Values above 300,000 mg/L have been reported (Barbot et al. 2013).

The highly variable strength and composition of these fluids present significant logistical challenges in terms of reuse, treatment, transportation, and disposal. In HFFs, the concentration of toxic (Ba, Sr) and radioactive (Ra) elements are positively correlated with salinity (Vengosh et al. 2014). Thus, rapid assessment of the potential impact of spills on surface waters, groundwater, and landscapes depends on accurate characterization of fluid salinity. The suitability for wastewater treatment (Ferrar et al. 2013), potential for reuse, and selection of disposal options all depend on proper characterization of the overall strength of these fluids.

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As the principal characterization parameter of brine salinity, the constituents comprising TDS can be evaluated collectively or individually. Commonly, a known volume of sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness at 180 °C and the mass of residual solids is quantified gravimetrically (APHA 2005). There are several potential errors and interferences associated with TDS measurement (Walton 1989; APHA 2005). Alternatively, TDS can be determined by summation of all the ionic constituent concentrations from a comprehensive sample analysis.

Because these methods are tedious and do not provide real-time quantification of fluid strength, electrical conductivity (EC) is frequently used as a surrogate for TDS (APHA 2005). The use of EC is based on the observed linear relationship between specific conductance and ionic strength for fluids with conductance ranging from 10–10,000 μS/cm (Lind 1970). A common expression is:

\[
\text{TDS (mg/L)} = k_e \times \text{EC(μS/cm)}
\]

where \(k_e\) is a constant of proportionality. The TDS-EC relationship is affected by the ionic composition of the water and the concentration of dissolved species. For most natural waters, the \(k_e\) value varies from 0.55 to 0.85 (Walton 1989; Atekwana et al. 2004), and the average of these two extremes (0.7) is widely used (Walton 1989).

This study was conducted as part of a larger research project investigating vegetation, soil, and groundwater impacts from accidental releases of fluids from Marcellus gas well production activities. In preparing HFF samples with a wide range of targeted salinities, we found that a simple relationship like Equation (1) produced significant errors. Since EC is frequently used as a surrogate for TDS in HFF characterization (Godsey 2003), assessment of drinking water supplies (Boyer et al. 2011; Soeder 2015), streams affected by hydraulic fracturing activities (NESC 2012) and quantifying the impact on natural aquatic systems (Zinabu et al. 2002; Atekwana et al. 2004), it is important to evaluate the relationship between TDS and EC. Thus, the primary objective was to quantify the relationship between TDS and EC over the wide range of salinities encountered in Marcellus HFFs. Implications of results for HFF management and impact assessment are explored.

## METHODS

Samples of HFFs were collected from active production wells in the Marcellus Shale region of Pennsylvania. Eight individual samples were collected from on-site tanks and impoundments where they were being held prior to recycling or disposal. Samples of HFF used in this study include both flowback and produced water. Flowback is defined as the fracturing fluid that quickly returns to the surface, and produced water is the fracturing fluid that returns to the surface throughout the life of the well and is enriched with materials from the shale formation (USEPA 2010).

Samples were filtered to 0.45 μm and acidified with 5% reagent-grade nitric acid. Elemental analysis was completed by the Penn State Agricultural Analytical Services Laboratory. Cations were analyzed by ICP-AES (inductively coupled plasma atomic emission spectroscopy) in accordance with EPA method 200.7 (USEPA 1994). Anions were analyzed by ion chromatography in accordance with Standard Method 4110.B (APHA 2005). TDS was measured by SM 2540C (APHA 2005). Reported results are the average of three replicates. EC was measured on the filtered samples using an Orion Versastar Advanced EC meter (ThermoFisher Scientific, Waltham, MA, USA). Measurements were repeated until three consecutive results agreed within 5%. Four of the eight samples (A–D) were randomly selected and used to characterize the TDS-EC relationship across a range of solution strengths. Serial dilutions of HFF samples were prepared by mixing 0.45 μm filtered HFF samples with deionized water. The remaining four HFF samples (E–H) were then used to validate the observed TDS-EC relationship.

Statistical analysis was completed using MS Excel and Minitab version 17.3. Least squares regression was completed at a 95% significance level (α = 0.05) to obtain a best-fit exponential curve of the data. Discrete \(k_e\) values were derived using segmented linear regression analysis (\(α = 0.05\)). Breakpoints were determined using the application software SegReg to maximize R² values for individual linear segments. Using SegReg, the breakpoint is determined numerically by selecting a series of tentative breakpoints and performing a linear regression on both sides of them. The breakpoint that provides the largest coefficient of determination (indicating the fit of the regression lines to the observed data values) was selected as the true breakpoint.

## RESULTS AND DISCUSSION

### Composition of brines

Analysis of the brines is presented in Table 1. The highly variable strength of these fluids as reflected by the range
of TDS (∼43,000 to 230,000 mg/L) is consistent with previous studies (Dresel & Rose 2010; Haluszczak et al. 2013).

The cationic composition of HFFs is dominated by Na and Ca (Dresel & Rose 2010) with Ba and Sr considered as ‘fingerprint’ elements in Marcellus-derived HFFs (Brantley et al. 2014). The reason for the high Mg in fluid F is not immediately apparent; however, Dresel & Rose (2010) note that the variable Mg concentration in such fluids is related to exchange of Ca and Mg during dolomitization in deep reservoir rocks.

Chloride is the dominant anion in all the fluids. Bromide, which is highly correlated with Cl⁻ (Harkness et al. 2015), can be present at significant levels because brines from wells penetrating the Marcellus Formation originate from evaporation of seawater (Haluszczak et al. 2013). Sulfate tends to be low in these brines, because it is depleted due to precipitative formation of CaSO₄(s) and pyrite in the subsurface concentrated brines (Dresel & Rose 2010; Barbot et al. 2013). The pH of most of the HFFs fall within the pH 5.8–6.6 reported previously (Haluszczak et al. 2013), but two (C, D) are more acidic, likely reflecting the use of AMD as a substitute for the freshwater component of HFFs (Kondash et al. 2014). This would be consistent with the relatively low sulfate in these samples since blending of AMD and HFFs induces precipitation of barite (Kondash et al. 2014).

### Table 1 TDS, EC and major cation and anion concentrations in the HFF samples

<table>
<thead>
<tr>
<th>Fluid ID</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS (mg/L)</td>
<td>224,575</td>
<td>65,108</td>
<td>191,621</td>
<td>230,209</td>
<td>104,140</td>
<td>126,450</td>
<td>105,500</td>
<td>43,370</td>
</tr>
<tr>
<td>EC (μS/cm)</td>
<td>208,250</td>
<td>89,235</td>
<td>186,667</td>
<td>205,533</td>
<td>121,100</td>
<td>142,800</td>
<td>121,600</td>
<td>60,300</td>
</tr>
<tr>
<td>TDS/EC ratio</td>
<td>1.08</td>
<td>0.73</td>
<td>1.03</td>
<td>1.12</td>
<td>0.86</td>
<td>0.89</td>
<td>0.87</td>
<td>0.72</td>
</tr>
<tr>
<td>Alk. (mg/L CaCO₃)</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
<td>198</td>
<td>183</td>
<td>153</td>
<td>198</td>
</tr>
<tr>
<td>pH</td>
<td>5.8</td>
<td>6.7</td>
<td>4.6</td>
<td>2.7</td>
<td>6.2</td>
<td>6.2</td>
<td>6.1</td>
<td>6.3</td>
</tr>
</tbody>
</table>

| Anions (mg/L) | | | | | | | | |
| Cl⁻ | 131,400 | 41,300 | 121,700 | 134,700 | 66,600 | 103,500 | 61,600 | 27,000 |
| Br⁻ | 1,881 | 549 | 1,612 | 1,834 | 590 | 1,510 | 541 | 251 |
| SO₄²⁻ | 14 | 14 | 38 | 8 | 280 | 841 | 208 | 205 |

| Cations (mg/L) | | | | | | | | |
| Na⁺ | 40,820 | 12,160 | 35,450 | 39,420 | 19,490 | 4,250 | 18,450 | 7,920 |
| Mg²⁺ | 2,080 | 680 | 2,100 | 2,360 | 2,144 | 27,570 | 2,133 | 1,306 |
| Ca²⁺ | 20,730 | 7,210 | 20,830 | 24,480 | 11,340 | 2,320 | 10,660 | 4,390 |
| Ba²⁺ | 1,300 | 70 | 190 | 310 | 159 | 6 | 72 | 35 |
| Sr²⁺ | 3,530 | 990 | 3,240 | 3,960 | 1,350 | 280 | 1,780 | 720 |

Alk., alkalinity; n/d, not determined.

### TDS-EC relationship

Serial dilution of four fluids (A–D) was used to characterize the TDS-EC relationship (Figure 1). For lower salinities, TDS and EC are linearly related. Deviation from linearity begins to occur when EC reaches ∼75,000–85,000 μS/cm. This non-linearity of the TDS-EC relationship can arise from a number of factors. While conductivity is entirely dependent on ionic charge, TDS is not. There can be non-ionized substances in solution which contribute to TDS but not EC. Neutral dissolved species like silicic acid (Day & Nightingale 1974) and non-ionic organic constituents preclude use of a simplified TDS-EC relationship (Atekwana et al. 2004).

The composition of ions also has an influence on the relationship of EC to TDS. In addition to non-ionized solutes, the measurement of TDS takes into account sodium, potassium, calcium, and magnesium as major cations and bicarbonate, sulfate, chloride, and nitrate as major anions. Other cations and anions (Sr²⁺, F⁻, Br⁻, I⁻, and Fe³⁺) are often excluded from TDS summation calculations (Walton 1989) because in most cases they contribute relatively little compared to the major ions. An exception for HFFs is bromide (Table 1), which is elevated in gas well brines (Dresel & Rose 2010; Brantley et al. 2014). The relative contributions to EC for the major ions are unequal since the molar conductance of individual ions varies. Bicarbonate
has the lowest molar conductance followed by sodium, potassium, chloride, hydroxide, and hydrogen with the greatest conductance. Not only does each ion have its own current-carrying ability, but interactions due to size, charge, and ion-pairing increase the complexity (Walton 1989) of predicting the EC-TDS relationship. But as the solution salinity increases, ions are crowded together and those of opposite charge begin to associate as ion-pairs, and in the context of conducting electricity, behave more like neutral species. Thus, with progressively increasing salinity (e.g. TDS), the change in EC becomes smaller. This is reflected in the progressive increase in $k_c$ value (slope) in Figure 1.

Other studies have documented the variability of $k_c$ for similar fluids of variable composition. Walton (1989) found that one simple $k_c$ value could not be used for the range of fluids encountered in the desalination industry and thus recommended variable $k_c$ values for estimating TDS from direct EC measurement. Ali et al. (2012) found that the ratio of TDS to EC ranged from 0.58 to 0.67 for industrial wastewaters. A curvilinear TDS-EC relationship was reported previously for oil and gas well brines in Pennsylvania (Dresel & Rose 2010), although in that study most of the reported TDS values were determined by summation of the analyzed constituent concentrations. A second-order polynomial regression was used to describe the relationship between TDS and EC of soil saturation extracts (Simon & Garcia 1999).

Despite the considerable differences in the chemical composition of brines A-D (Table 1), the TDS-EC relationship follows a similar pattern. For EC values from 10,000-75,000 μS/cm, a linear relationship ($\alpha = 0.05$) between EC and TDS is observed ($R^2 = 0.995$) and is defined by the equation $TDS = 0.7*EC$. For EC values >75,000 μS/cm, the relationship with TDS is no longer linear, and using such a relationship results in a TDS that is as much as 50% below the actual value.

To better predict TDS as a function of EC for fluids with EC >75,000 μS/cm, least squares regression was conducted using data from fluids A-D (Figure 2). The resulting exponential equation ($TDS = 27.078e^{1.05*10^{-0.09*EC}}$) provides a very good fit of the data ($R^2 = 0.99$). Using this equation, the percent error (measured TDS – predicted TDS/ measured TDS) averaged 4.4% with a maximum error of 7.7%, clearly superior to the linear approximation.

**Use of commercial EC meters**

Whereas the exponential equation provides improved prediction of TDS and can be useful in laboratory or
In experimental settings, it is inappropriate for field applications. In practice, EC/TDS meters measure specific conductance and report TDS using Equation (1) and a fixed or programmable $k_e$ factor. Most meters contain an operating mode that reports a TDS directly without displaying the $k_e$ factor.

A review of eight EC/TDS meters produced by leading manufacturers of scientific equipment was conducted to evaluate how $k_e$ is utilized in reporting TDS. The default value for $k_e$ is different depending on the meter, and pre-programmed default values range from 0.5 to 0.65. Specific reasons as to why one default value is used over another are not provided, nor is an explanation provided as to when this default value may need to be adjusted. All meters reviewed use a linear relationship (e.g. Equation (1)) to convert EC to TDS. For the range of HFFs encountered in practice, this results in significant error.

Six of eight meters reviewed do offer a user-adjustable $k_e$ factor. The range over which the $k_e$ factor can be adjusted also varies and can be as wide as 0.3–1.0. One meter rated to measure EC up to 20,000 $\mu$S/cm allows for a TDS factor as high as 1.0. This wide range of available $k_e$ values is potentially misleading given that TDS/EC ratios approaching 1.0 are generally not observed until EC values exceed 100,000 $\mu$S/cm (Walton 1989; Dresel & Rose 2010; Haluszczak et al. 2015).

Notably, none of the accompanying manuals provide an explanation regarding adjustment of $k_e$, nor do they provide suitable EC ranges for specific $k_e$ values. One manual does suggest that the TDS factor can be calculated by measuring the actual TDS by gravimetric analysis (SM 2450C) and dividing this value by the sample EC. This too, however, may be somewhat misleading in that the directions do not instruct that this exercise should be carried out over the full range of EC values anticipated.

In summary, the findings of this review suggest that users must be knowledgeable of the capabilities and limitations of EC/TDS meters prior to use on hypersaline fluids. In addition to measurement range, adjustable $k_e$ capabilities must be confirmed. Note that multiple $k_e$ values will be required when sampling HFFs with variable TDS concentrations. Further, diluting an HFF sample prior to measurement and multiplying the resulting TDS reading by the dilution factor will result in a high degree of error for reasons explained in this research. If accurate reporting of TDS in HFF is to be accomplished using field-measured EC, it is recommended that a plot similar to that in Figures 1 and 2 be generated for the HFF of interest.

Therefore, to establish discrete $k_e$ values across the range of EC concentrations observed in HFFs, segmented linear regression analysis was completed. Breakpoints were defined at EC values that resulted in maximum $R^2$.
values for each segment. The $k_e$ value for each segment is then defined as the average TDS/EC ratio within the given range. Results of the analysis are provided in Table 2. The $R^2$ values for the individual segments range from 0.968 to 0.995, indicating strong correlations.

To compare the measured data points to the TDS predicted by the segmented $k_e$ values, the percent error was calculated (Table 2). The average error across the individual segments were in the range 3.3–4.6% with a maximum error of 8.8%. These results suggest that the error associated with using discrete $k_e$ values is comparable to the error associated with use of the exponential equation.

To validate the best-fit equation and discrete $k_e$ values as approximations of TDS, four additional HFFs (E, F, G and H) were evaluated (Table 1). TDS and EC were measured for each of these HFFs at two concentrations (Table 3). The TDS values predicted by the discrete $k_e$ values and the best-fit equation were calculated to determine the error associated with each method. Similar to the initial evaluation, the error observed in validation averaged between 3.9% and 4.7% with a maximum error of 8.0%. Interestingly, the average and maximum error were actually lower for the discrete $k_e$ values suggesting that the range of $k_e$ values listed in Table 2 provide an acceptable approximation of TDS.

While the developed approach provides a good framework for describing the TDS-EC relationship for fluids collected in this study, it is of interest to know its usefulness for describing other brines. Studies providing detailed methodology on the determination of TDS and EC and which also acknowledge the accompanying analytical challenges for hypersaline fluids are scarce. The extensive report of Dresel & Rose (2003), however, does provide measured TDS and EC and analysis details for numerous conventional oil and gas wells in western Pennsylvania. Their data have been included in Figure 2 and show reasonably good agreement with our data. While this comparison suggests the relationships developed herein may be applicable to a broader range of HFFs, the spatial and temporal salinity variations in such brines (Barbot et al. 2016) dictate empirical validation of the TDS-EC relationship for greater prediction certainty using other fluids.

### CONCLUSIONS

Experiments documented the relationship between TDS and EC for multiple HFFs diluted to reflect the typical practice of blending HFFs with alternate water sources that occur in their handling, storage, and recycling. Assumption of a linear relationship between TDS and EC produced significant error

#### Table 2

<table>
<thead>
<tr>
<th>EC range (μS/cm)</th>
<th>$k_e$</th>
<th>Segment $R^2$</th>
<th>% Error (avg/max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000–75,000</td>
<td>0.7</td>
<td>0.995</td>
<td>3.3/7.7</td>
</tr>
<tr>
<td>75,000–120,000</td>
<td>0.8</td>
<td>0.973</td>
<td>4.6/8.0</td>
</tr>
<tr>
<td>120,000–160,000</td>
<td>0.9</td>
<td>0.975</td>
<td>3.4/8.8</td>
</tr>
<tr>
<td>160,000–210,000</td>
<td>1.0</td>
<td>0.968</td>
<td>3.6/8.4</td>
</tr>
</tbody>
</table>

$^a$Linear regression ($\alpha = 0.05$) coefficient of determination for given segment.

$^b$Average/maximum % error ((Measured TDS – $k_e$)/Measured TDS) $\times$ 100 for given segment.

#### Table 3

<table>
<thead>
<tr>
<th>Fluid</th>
<th>EC (μS/cm)</th>
<th>Measured TDS (mg/L)</th>
<th>Predicted TDS by $k_e$</th>
<th>Predicted TDS by equation$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>60,300</td>
<td>43,370</td>
<td>0.7 42,210 2.7%</td>
<td>42,210 2.7%</td>
</tr>
<tr>
<td>H2</td>
<td>89,367</td>
<td>67,133</td>
<td>0.8 71,494 6.5%</td>
<td>71,494 6.5%</td>
</tr>
<tr>
<td>E1</td>
<td>121,067</td>
<td>104,143</td>
<td>0.9 108,960 4.6%</td>
<td>108,960 4.6%</td>
</tr>
<tr>
<td>G1</td>
<td>121,567</td>
<td>105,497</td>
<td>0.9 109,410 3.7%</td>
<td>109,410 3.7%</td>
</tr>
<tr>
<td>F1</td>
<td>142,800</td>
<td>126,450</td>
<td>0.9 128,520 1.6%</td>
<td>128,520 1.6%</td>
</tr>
<tr>
<td>E2</td>
<td>178,267</td>
<td>172,933</td>
<td>1.0 178,267 3.1%</td>
<td>178,267 3.1%</td>
</tr>
<tr>
<td>F2</td>
<td>162,767</td>
<td>158,071</td>
<td>1.0 162,767 3.0%</td>
<td>162,767 3.0%</td>
</tr>
<tr>
<td>G2</td>
<td>199,300</td>
<td>212,167</td>
<td>1.0 199,300 6.1%</td>
<td>199,300 6.1%</td>
</tr>
</tbody>
</table>

$^a$TDS (mg/L) = 27,078$e^{1.05 \times 10^{-4}EC(\mu S/cm)}$.  
$^b$Average/maximum % error ((Measured TDS – $k_e$)/Measured TDS) $\times$ 100 for given segment.
when using an EC/TDS meter to report TDS, especially when used on solutions with EC values exceeding 100,000 μS/cm. The mathematical relationship for transforming EC readings to TDS for hypersaline HFFs (Figure 2) is not convenient for field use. Reasonably accurate TDS results can be obtained by selecting the appropriate \( k \) value (Table 2) based on the measured EC. While a curvilinear relationship is plausible for all brines, the variable conditions under which shale gas wastewaters are generated suggest the relationship developed is unlikely to be precisely accurate for all fluids. Its use, however, should allow for improved prediction of water quality and soil impacts from accidental releases of HFFs.

REFERENCES


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