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Electrical Conductivity of Agricultural Drainage Water in Iowa

Brett A. Zimmerman
Iowa State University

Amy L. Kaleita
Iowa State University, kaleita@iastate.edu

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Abstract

Assessing the effectiveness of management strategies to reduce agricultural nutrient efflux is hampered by the lack of affordable, continuous monitoring systems. Generalized water quality monitoring is possible using electrical conductivity. However environmental conditions can influence the ionic ratios, resulting in misinterpretations of established electrical conductivity and ionic composition relationships. Here we characterize specific electrical conductivity (k_{25}) of agricultural drainage waters to define these environmental conditions and dissolved constituents that contribute to k_{25}. A field investigation revealed that the magnitude of measured k_{25} varied from 370 to 760 ÂµS cm^{-1}. Statistical analysis indicated that variability in k_{25} was not correlated with drainage water pH, temperature, nor flow rate. While k_{25} was not significantly different among drainage waters from growing and post-growing season, significant results were observed for different cropping systems. Soybean plots in rotation with corn had significantly lower conductivities than those of corn plots in rotation with soybeans, continuous corn plots, and prairie plots. In addition to evaluating k_{25} variability, regression analysis was used to estimate the concentration of major ions in solution from measured k_{25}. Regression results indicated that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, SO_4^{2-} were the major drainage constituents contributing to the bulk electrical conductivity. Calculated ionic molal conductivities of these analytes suggests that HCO_3^-, Ca^{2+}, NO_3^-, and Mg^{2+} account for approximately 97% of the bulk electrical conductivity.

ELECTRICAL CONDUCTIVITY OF AGRICULTURAL DRAINAGE WATER IN IOWA

B. A. Zimmerman, A. L. Kaleita

ABSTRACT. *Assessing the effectiveness of management strategies to reduce agricultural nutrient efflux is hampered by the lack of affordable, continuous* in-situ *monitoring systems. Generalized water quality monitoring is possible using electrical conductivity. However environmental conditions can influence the ionic ratios, resulting in misinterpretations of established electrical conductivity and ionic composition relationships. Here we characterize specific electrical conductivity (k_{25}) of agricultural drainage waters to define these environmental conditions and dissolved constituents that contribute to k_{25}. A field investigation revealed that the magnitude of measured k_{25} varied from 370 to 760 µS cm^{-1}. Statistical analysis indicated that variability in k_{25} was not correlated with drainage water pH, temperature, nor flow rate. While k_{25} was not significantly different among drainage waters from growing and post-growing season, significant results were observed for different cropping systems. Soybean plots in rotation with corn had significantly lower conductivities than those of corn plots in rotation with soybeans, continuous corn plots, and prairie plots. In addition to evaluating k_{25} variability, regression analysis was used to estimate the concentration of major ions in solution from measured k_{25}. Regression results indicated that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, SO_4^{2-} were the major drainage constituents contributing to the bulk electrical conductivity. Calculated ionic molal conductivities of these analytes suggests that HCO_3^-, Ca^{2+}, NO_3^-, and Mg^{2+} account for approximately 97% of the bulk electrical conductivity.*

Keywords. Electrical conductivity, Salinity, Subsurface drainage, Total dissolved solids.

Agricultural subsurface drainage efflux of nutrients stresses ecosystems in receiving surface waters, represents economic losses to farmers, and degrades soil fertility. Continuous, low cost, and reliable *in-situ* monitoring is essential for the development of effective nutrient mitigation strategies, which are aimed at reducing these environmental and economic impacts. However, limitations in current available sensor technology have hindered the affordability of these sensors. Gali et al. (2012) proposed the use of electrical conductivity as a low-cost alternative means for indirectly monitoring nutrient loadings in agricultural drainage waters. The viability of this is supported by Patni et al. (1998), who found that groundwater electrical conductivities at depths of 1.2 m were significantly correlated to the concentration of NO_3^- in no-till and conventionally tilled plots near Ottawa, Canada. To better understand these results and evaluate electrical conductivity's applicability to agricultural subsurface drainage water quality monitoring, we must first consider what is being measured with electrical conductivity and how it has been successfully used in the past and present.

Electrolytic solutions like agricultural drainage waters contain dissociated electrolytes consisting of positively and negatively charged ions (cations and anions, respectively). Under an applied external electrical current, cations will react to the electric potential gradient by migrating to the cathode and anions will respond by migrating to the anode (Miller et al., 1988). If the applied electrical field is generated by an alternating current source, the electrolytic solution obeys Ohm's Law (eq. 1):

$$V = iR \qquad (1)$$

Ohm's Law defines electric potential (V) as the product of electrical current (i) and resistance (R). Resistance is directly proportional to the length (L), area (A), and resistivity (ε) of the material in which the current is conveyed (eq. 2). Electrical conductivity (k) (eq. 3) is the reciprocal of resistance and is expressed in units of µS cm^{-1}.

$$R = \frac{\varepsilon\,A}{L} \qquad (2)$$

$$k = \frac{1}{\varepsilon} = \frac{i\,L}{V\,A} \qquad (3)$$

The conductivity of an electrolytic solution is dependent on the mobility (μ) of ions that carry the electrical current (Miller et al., 1988). Ion mobility (eq. 4) is proportional to the charge (q) divided by the sum of hydrodynamic friction (ζ_H) and dielectric friction (ζ_D) (Wolynes, 1980; Koneshan et al., 1998a).

$$\mu = \frac{q}{\zeta_H + \zeta_D} \qquad (4)$$

Dielectric friction ζ_D is a function of Debye relaxation time, dielectric constants of the solvent, charge of the ion, and ion radius. Hydrodynamic friction ζ_H is directly proportional to the ion radius and bulk viscosity of the conductor (or solvent) (Koneshan et al., 1998b). As the solvent's temperature increases, bulk viscosity decreases, which in turn allows for greater ion mobility (Miller et al., 1988). Consequently, ε is inversely proportional to temperature, while k is directly proportional to temperature. Therefore, k is typically standardized to a reference temperature (25°C is used throughout this study) with the following equation:

$$k_{25} = \frac{k}{1 + \alpha(T - 25)} \qquad (5)$$

where measured electrical conductivity (k) is expressed in units of µS cm^{-1}, temperature (T) is in °C, the temperature compensation factor (α) is a constant that typically ranges from 0.019 to 0.020 (Miller et al., 1988; Hayashi, 2004; McCleskey et al., 2012), and specific electrical conductivity (k_{25}) is the k standardized to the reference temperature of 25°C (µS cm^{-1}) (McCleskey et al., 2012). Upon performing this conversion, measured electrical conductivity becomes primarily dependent on the cumulative concentration of total dissolved solids (TDS) in solution. The relationship between k_{25} (µS cm^{-1}) and TDS (ppm) is most simply represented by a factor of proportionality (K) (eq. 6) (Walton 1989; Marandi et al., 2013).

$$K = \frac{TDS}{k_{25}} \qquad (6)$$

The relationship given in equation 6 is commonly used by commercially available TDS meters, which automatically calculate TDS from measured k_{25} and a standard K of 0.70 (Walton, 1989). However, the proportionality constant, K, is an ambiguous variable that can range of 0.50 to 1.00 depending on the solution's ionic composition (Walton, 1989; McNeil and Cox, 2000; Marandi et al., 2013). The magnitude of K is dependent on the concentration, size, and valence of ions present in the solution (McNeil and Cox, 2000).

For well-defined waters with relatively consistent ionic compositions, K can be used in conjunction with k_{25} to reliably estimate TDS at accuracies of 95% or greater (Miller et al., 1988). Given this attribute, along with the availability of low-cost and easily operated commercially available meters, k_{25} monitoring has proven to be a popular and reliable alternative for monitoring TDS in a wide variety applications. These applications include: industrial effluent (Binkley et al., 2000), wastewater (Voichick, 2008; USGS 2012), natural waters (McNeil and Cox, 2000; Goodrich et al., 2009; McCleskey et al., 2012), and landfill leachate in groundwater (Abu-Rukah and Al-Kofahi, 2001). Additionally, k_{25} is also used as quality control check for chemical analysis of solutions (Marandi et al., 2013). In agriculture, electrical conductivity monitoring of irrigation waters helps to reduce the risk of soil salinization (Wilcox, 1955).

Few studies have evaluated k in agricultural drainage waters and even fewer have done so with waters characteristic to Iowa. A review of the literature revealed that studies of similar scope are directed toward understanding soil salinization caused by drainage water reuse in semi-arid regions (Rhoades et al., 1989; Oster and Grattan, 2002). However, environmental conditions in the humid regions of the Midwest produce drainage waters with significantly different compositions than those of the semi-arid regions; arid soils typically have much greater total dissolved solids concentrations (Bower, 1974). The most relevant studies include Patni et al. (1998) and Gali et al. (2012), who used k_{25} to evaluate nutrient concentrations in waters leached from agricultural landscapes. It is important to note that these studies evaluated k_{25} correlations with NH_4^+, NO_3^-, and total P without consideration of other major dissolved constituents. Primary drainage water constituents consist of the following cations: calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{2+}); and anions: bicarbonate (HCO_3^-), nitrate (NO_3^-), chloride (Cl^-), and sulfate (SO_4^{2-}) (Zimmerman, 2016). As previously stated, k_{25} is dependent on all constituents, therefore estimating the concentration of a single constituent based on k_{25} is subject to great inaccuracy. Gali et al. (2012) suggested that these inaccuracies can be reduced by understanding how environmental conditions influence relationships between k_{25} and individual constituents.

A seasonal analysis of dissolved constituents in agricultural drainage waters by Zimmerman (2016) quantifies how the ionic composition can vary between two time periods representing distinctly different environmental conditions. The study concluded that concentrations of HCO_3^-, Ca^{2+}, and Mg^{2+} were significantly greater in drainage samples collected after the growing season (September through December) than early growing season drainage samples (May and June); Cl^- and NO_3^- were greater in growing season drainage; Na^+ and SO_4^{2-} remained relatively constant throughout both seasons. Furthermore, the study determined that the drainage composition was significantly different among cropping systems. Corn cropping systems had greater losses of Mg^{2+} and Cl^-; soybean cropping systems had greater losses of Ca^{2+}; SO_4^{2-} was different among all soybean and corn cropping systems; HCO_3^- and NO_3^- were consistent among all cropping systems. These results illustrate the high degree of variability among most major ions as result of seasonal changes in climate, crop uptake, relative abundance of ions, microbial activity, etc. Given that k_{25} is a function of all ion concentrations, sizes, and charges it can be expected that seasonal and cropping system variability in the ionic composition will also be reflected by the magnitude of k_{25}.

However, even if the relationships proposed by Gali et al. (2012) were established for different environmental conditions, k_{25} could not be used to confidently make accurate and reliable estimates for individual ion concentrations without frequent sampling. Primary ions which contribute most to electrical conductivity will have the most relationship to k_{25}, but even these estimated concentrations would be subject to error caused by the presence of other ions. These limitations again come down to the fact that k_{25} is a generalized parameter representing the ionic composition as a whole. Regardless, the composition as a whole can still be informative, and

it is therefore important to understand how environmental conditions and land management practices influence k_{25}. Other environmental conditions of interest include drainage water flow, temperature, and pH.

Terman (1977), Steele et al. (1984), and Heng et al. (1991) found strong linear correlations between major cations and anions in agricultural drainage waters. In each of these studies, increasing the concentration of NO_3^- resulted in a nearly equal increase in Ca^{2+}. Zimmerman (2016) observed similar characteristics among HCO_3^- and Ca^{2+}. The production of both NO_3^- and HCO_3^- is largely influenced by percolation rate, soil temperature, and pH (Sabey, 1958; Raymond and Cole, 2003; Seitzinger et al., 2006). Therefore, it is reasonable to assess whether or not these changes in the ionic composition are correlated with changes in drainage rate, drainage water pH, and drainage water temperature.

In this study we perform a field investigation to characterize the electrical conductivity of agricultural drainage waters using a low cost portable electrical conductivity meter. Specifically we will: 1) compare field k_{25} measurements from a handheld EC meter with controlled laboratory measurements to ensure that field measurements can be performed reliably; 2) verify that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, SO_4^{2-} represent all major constituents contributing to the bulk electrical conductivity; 3) quantify each major ion's contribution toward the bulk electrical conductivity using ionic molal conductivity methods described by McCleskey et al. (2012); 4) evaluate the effect of different cropping systems and seasons on the magnitude of measured electrical conductivity; and 5) determine if drainage water flow, pH, and temperature significantly influence k_{25} measurements as a result of changes in the ionic composition. In so doing we hope to complement the work performed by Gali et al. (2012) by gaining further insight to k_{25} viability and versatility as a low-cost alternative for agricultural subsurface drainage water quality monitoring.

MATERIALS AND METHODS

SITE DESCRIPTION

Drainage water samples and field measurements for specific electrical conductivity, pH, and temperature were collected at the Iowa State University's Comparison of Biofuel Cropping System (COBS) research site located in Boone County, Iowa (Liebman, et al., 2007; Daigh et al., 2015). The COBS research site was established in 2008 and consists of 24 plots, each measuring 61 m long by 27 m wide, in a randomized complete block design with four replicates each of six cropping system treatments. Soils at COBS consist of Webster clay loam and Nicollet loams (NRCS, 2016). Nicollet and Webster soils are classified as hydrologic soil group B and C. Drainage water sampling was performed on 16 different plots. Sampled plots represent four of the six cropping systems at COBS: (1) C2 – corn year in corn/soybean rotation; (2) S2 – soybean year in corn/soybean rotation; (3) CC – continuous corn with stover removal; and (4) P – continuous prairie. No-till practices were uniform across all cropping systems. Nitrogen fertilizer was applied as UAN-32 in two applications. The first application was performed in the spring, prior to seed planting, at a rate of 87 kg N ha^{-1} on C2 and CC cropping systems. After plant emergence, an additional 134 kg N ha^{-1} was applied to C2 plots and 112 kg N ha^{-1} on CC plots. Drainage is provided by corrugated tiles placed at a depth of 1.1 m along the center line – length wise. Plots are hydraulically separated by additional drainage tiles placed between plots. Drained water is conveyed to a sump pit where flow is monitored by an *in-situ* flow meter and flow proportionate samples are collected in a 5 L polypropylene container. Cumulative flow volumes were recorded at the time of sample collection. Average daily drainage flow rate was calculated as the cumulative flow between sampling events divided by the number of days between sampling events.

MEASURED FIELD PARAMETERS AND LABORATORY ANALYSES

The Hach Pocket Pro + Multi 2 meter (Hach, Loveland, Colo.) was used in this study to measure drainage water specific electrical conductivity ($k_{25,Field}$), pH, and temperature in degrees Celsius at the time of drainage water sampling directly from collected samples. The meter has three auto-setting operating ranges for each measurable parameter. Specifications for meter performance in the ranges applicable to measured quantities include a k_{25} range of 200 to 1999 µS cm^{-1}, resolution of 1 µS cm^{-1}, and accuracy of ±1%. Calibrations were performed the day of sample collection with a single point (1413 µS cm^{-1}) standard KCl solution. The meter automatically standardizes electrical conductivity measurements to 25°C using a temperature compensation factor of 0.02 in equation 5. A total of 65 water samples were field-measured in this way, as shown in table 1, during June, September, and December 2015. Water was tested roughly weekly during June but adjusted in response to rainfall to collect data during periods of tile flow, and in response to rainfall events during September and December, when the tiles are not normally continuously flowing.

A total 23 flow proportionate drainage water samples, collected in the months of June, September, and December, 2015 were subject to chemical analysis by the Iowa State Hygienic Laboratory (ISHL) in Ankeny, Iowa, in addition to having the field measurements described above. Table 1 shows the number of samples collected and analyzed for each cropping system and time period. Analytes consisted of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+. Methods employed by ISHL include: EPA 300 for SO_4^{2-}, Cl^-, NO_3^-; EPA 200.7 for Ca^{2+}, Mg^{2+}, and Na^+; LAC 10-107-06-IJ for $NH3$; SM 2320B for Alkalinity as $CaCO_3$ (reports HCO_3^- and CO_3^{2-}). Selection of analytes was based on the literature review performed by Zimmerman (2016), who identified major dissolved constituents in drainage water samples at the COBS research site; Zimmerman (2016) was a parallel study and collected drainage samples overlap.

We also measured specific electrical conductivity ($k_{25,Lab}$) in 18 of the 23 collected samples. Laboratory methods for electrical conductivity were conducted in accordance to Standard Methods 2510B. According to APHA (2012), laboratory analyses for specific electrical conductivity have a resolution of 1 µS cm^{-1} and accuracy of ± 1%. Reported lab

Table 1. Summary of water samples collected and measured.[a]

		No. of Complete Samples		No. of Samples with Field Msmts Only	
Cropping System	2015 Crop	Growing Season	Post-Growing Season	Growing Season	Post-Growing Season
C2: Corn/Soybean	Corn	3	5	11	0
S2: Soybean Corn	Soybean	4	4	10	0
CC: Continuous Corn	Corn	3	2	9	0
P: Continuous Prairie	Prairie	2	0	12	0

[a] Complete samples are those with both field measurements and laboratory measurements. Other samples had field measurements only.

results, however were given at resolution of 10 μS cm⁻¹. Calibrations were performed with a (1412 μS cm⁻¹) standard KCl solution. Specific electrical conductivity was standardized to 25°C using a temperature compensation factor of 0.0191 in equation 5. Results from the laboratory were used to ensure quality and consistency of field measurements by performing simple linear regression to estimate the laboratory observations with field observations. Pearson correlation coefficient was used to describe the quality of the relationship between field and laboratory conductivities.

VERIFICATION OF PRIMARY IONS

To characterize drainage water electrical conductivity we first need to define the constituents that contribute its bulk electrical conductivity. A comprehensive literature review and field investigation by Zimmerman (2016) indicated that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-} represented the major ions in COBS drainage waters; these results were not validated by any particular water quality analysis. As is the case for many water quality parameters, direct measurement of total dissolved solids (TDS) is costly, time consuming, and prone to user error. Validation was therefore performed in the present study by using the relationship given in equation 6 where measured electrical conductivity is proportionate to the cumulative TDS concentration.

First, the constant of proportionality (K) was calculated (eq. 5) for complete samples (those with both lab and field measurements) collected from C2, S2, and CC drainage waters at the COBS research site. Calculated K values were then evaluated to identify statistically different K factors representing sampling groups having significantly different ionic compositions, thereby ensuring a high level of accuracy in $\sum$ions:$k_{25,Field}$ regression (described below). It is important to note that the sample size of collected growing season drainage water samples were insufficient to perform a strong statistical analysis among cropping systems, therefore the following analysis was conducted on growing and post-growing season samples irrespective of the cropping system in which the samples were acquired. Samples from prairie cropping systems were excluded since no samples were collected in the post-growing season. The Shapiro Wilk test for normality and Levene test for equality of variance performed on the calculated K values of growing and post-growing season sampling groups showed that K is normally distributed in the growing season and post-growing season, and variances are homogeneous (table 1). On this basis we used an independent-samples t-test to determine that K was greater among post-growing season samples than growing season samples, *p-valu*e (1-sided) < 0.001 (table 1). Therefore, regression of $\sum$ions:$k_{25,Field}$ was done separately for the growing season and post-growing season.

Total dissolved solids was calculated as the cumulative concentration (ppm) of major ions ($\sum$ions) reported by the ISHL analysis of complete samples. Because theory (eq. 6) defines $k_{25,Field}$ as being proportionate to TDS ($\sum$ions), regression through the origin (RTO) was calculated to predict $\sum$ions using measured $k_{25,Field}$. The corresponding residual error between the observed $\sum$ions and predicted $\sum$ions was then used to determine the extent to which $k_{25,Field}$ was caused by the primary ions (i.e., verification of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+ as primary ions that contribute the $k_{25,Field}$).

IONIC MOLAL CONDUCTIVITY

Patni et al. (1998) and Gali et al. (2012) used k_{25} to estimate the concentration of individual ions in agricultural drainage waters. While k_{25} captured general ion concentration trends, estimated values had low accuracy and precision. To better understand the causes for error in these estimated concentrations, we need to consider the magnitude of change in k_{25} caused by the concentration of all ions in solution. In the preceding section we used the relationship described by equation 6 to validate that major ions contributing to the electrical conductivity of agricultural drainage waters consisted of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+ based on their cumulative concentration in ppm. This simplified relationship is possible because the specific electrical conductivity of an electrolytic solution is dependent on the concentration, valence, and size of ions present in the solution. Note that accurate estimation of TDS using k_{25} from equation 6 requires a well-defined constant of proportionality which is specific to the solution's overall ionic composition, and because equation 6 does not account for ion valence we cannot use this method to calculate each major ion's individual contribution toward the drainage water's bulk specific electrical conductivity. To calculate these individual conductivities we directly employed ionic molal conductivity methods developed by McCleskey et al. (2012). Ion speciation methods discussed in McClesky et al. (2012) were performed on a variety of natural waters with great accuracy; calculated conductivities were within -0.7 ± 5% of measured conductivities in 1593 water samples. The following methods and equations are the summarized procedures used to calculate ion conductivities for drainage water samples collected in this study. For additional information regarding empirical constants, detailed procedures, applicability, and discussion refer to McCleskey et al. (2012).

The calculated bulk electrical conductivity (k_{calc}) (S cm⁻¹) of an electrolytic solution is the cumulative sum of each ion's electrical conductivity (k_i), which is defined as the ion's ionic molal conductivity (λ_i) (mS kg cm⁻¹ mol⁻¹) multiplied by the speciated molality (m_i) (mol kg⁻¹).

$$k_{calc} = \sum k_i = \sum 1000 \lambda_i \, m_i \qquad (7)$$

In equation 8, ion molality (m_i) was determined from concentrations reported by the chemical analysis and ionic molal conductivity (λ_i) was calculated as:

$$\lambda_i = \lambda^\circ - \frac{A \, I^{0.5}}{1 + B \, I^{0.5}} \qquad (8)$$

where λ° and A are temperature dependent equations, B is an empirically derived constant (λ°, A, and B are unique to each ion; refer to McCleskey et al. (2012) for exact equations and constants), and the solution's ionic strength (I) is a function of the speciated molality and the charge (z_i) of the ith ion.

$$I = 0.5 \sum m_i \, z_i^2 \qquad (9)$$

EFFECT OF CROPPING SYSTEM AND SEASON ON ELECTRICAL CONDUCTIVITY

While k_{25} is dependent on the ionic concentration, it is also dependent on the valence and size of ions that make up the electrolytic solution. Accordingly, two solutions having different ionic concentrations could have the same measured k_{25} (Walton, 1989; Marandi et al., 2013). To effectively use k_{25} as a tool for agricultural drainage water quality monitoring, it is essential that k_{25} consistently correlates to the concentration of ions in solution. This can be achieved if the ionic composition remains relatively constant with respect to the component ion ratios (Marandi et al., 2013). However, as Zimmerman (2016) illustrates, the component ion ratios can be variable among different cropping systems and seasons. Here we perform analyses on $k_{25,Field}$ measured in samples collected during the growing and post-growing seasons, and among cropping systems to determine if $k_{25,Field}$ can effectively represent significant changes in the ionic composition observed by Zimmerman (2016).

Hypothesis testing was performed to determine if $k_{25,Field}$ was statistically different among cropping systems during the growing season. Post-growing season observations were not included in this testing because the influence of cropping system on ionic composition is most pronounced during the growing season, which is a result of soil fertilizer amendments prior to planting and crop uptake of nutrients. Sample $k_{25,Field}$ populations of cropping systems C2, S2, CC, and P were subject to a test for normality and equality of variance prior to conducting inferential analyses regarding differences among sampling distributions. A Shapiro-Wilk test indicated the S2 and P $k_{25,Field}$ data were not normally distributed (table 2). Homogeneity of variance among cropping systems was supported by the non-parametric Conover test for equal variance, p-$value$ = 0.135. A Kruskal-Wallis test was performed to determine if the median $k_{25,Field}$ values were equal among sampling groups C2, S2, CC, and P. Test results suggest that at least one group median was different p-$value$ < 0.001. Given these results, independent two-sample comparisons were then carried out on the ranks using the Mann-Whitney test for equal medians. Results for were evaluated at alpha level 0.05.

Hypothesis testing was also conducted to determine if $k_{25,Field}$ was statistically different for the growing season compared to the post-growing season. The growing season pairie observations were excluded because there were no corresponding observations of prairie in the post-growing season. A Shapiro-Wilk test indicated the data could be considered normally distributed, but a Levene's test for equality of variances indicated the variances could not be considered equal (p-$value$ = 0.024). An independent samples Welch's t-test was therefore employed to evaluate the effect of season on measured $k_{25,Field}$ in agricultural drainage water.

CORRELATIONS WITH FLOW, pH, AND TEMPERATURE

A total of 54 observations with the Hach Pocket Pro + Multi 2 meter were recorded for each of the following parameters during the growing season in cropping systems C2, S2, CC, and P: electrical conductivity ($k_{25,Field}$), pH, and temperature. A correlation analysis was performed on drainage rate, drainage water pH, and drainage water temperature with respect to $k_{25,Field}$ to quantify the influence of readily observable parameters on electrical conductivity. Significant correlations are of interest since these parameters represent low-cost measurements of different environmental conditions that could potentially influence k_{25}. Assumptions for normality were tested using the Shapiro-Wilk test, evaluated at alpha level 0.05. Test results indicated that our assumption for normality was rejected for drainage water $k_{25,Field}$ and drainage flow rate (tables 2 and 4). Therefore, the Kendall-Tau ranked correlation test was calculated to evaluate k_{25} dependency on temperature, pH, and flow.

RESULTS

COMPARISON OF FIELD AND LAB ELECTRICAL CONDUCTIVITY MEASUREMENTS

Field and laboratory observations of electrical conductivity showed a strong linear relationship, which is illustrated by figure 1 and a Pearson correlation coefficient of 0.96. However, figure 1 also shows that laboratory conductivities were consistently greater than field observations. Simple linear regression was calculated to predict laboratory conductivities (M = 661, SD = 32) $\mu S \, cm^{-1}$ using the observed field conductivities (M = 638, SD = 28) $\mu S \, cm^{-1}$. Results from regression indicated that $k_{25,Field}$ was a good estimator for $k_{25,Lab}$ F (1, 16) = 197, p < 0.001, R^2 = 0.925. Standard error of estimated values (9 $\mu S \, cm^{-1}$) was minimal relative to the mean and standard deviation of observed values. While these datasets disagree slightly in terms of magnitude, overall the laboratory and field measurements responded proportionately to sample compositions (regression slope of 1.08 is close to 1). McCleskey et al. (2012) noted that accurate comparisons between calculated and measured conductivities requires the use of a uniform temperature compensation factor. With calibration, resolution, and accuracy being approximately equal among both k_{25} methods, and each method uses the same linear equation (eq. 5) to calculate k_{25}, it is likely that differences in observed magnitude are due to different temperature compensation factors. Laboratory methods utilized a temperature compensation factor of 0.0191 while field methods used 0.02. Specific electrical conductivity and the temperature compensation factor are inversely related in
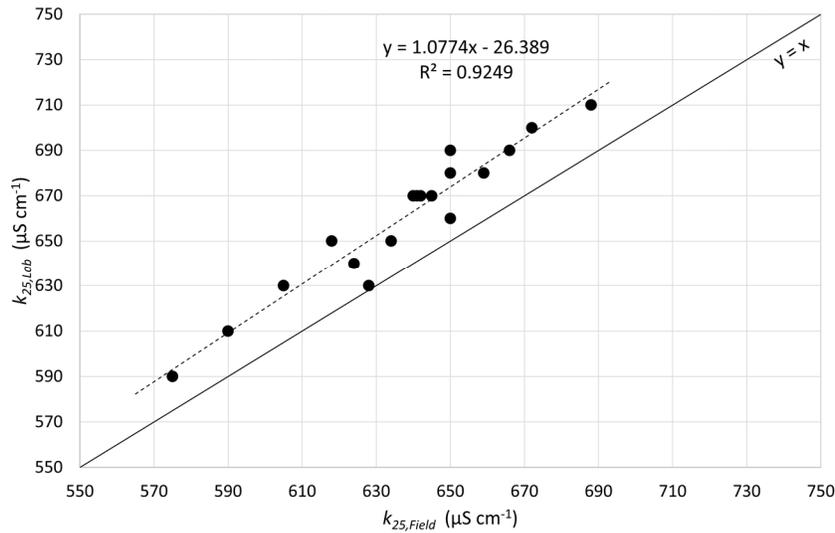
Figure 1. Comparison of field and laboratory specific electrical conductivity measurements on sampled drainage water at the COBS research site. The two agree closely but the laboratory measurements are consistently slightly higher.

equation 5. Therefore, the higher temperature compensation factor used in field measurements would have resulted in greater specific electrical conductivities than those observed in laboratory conductivities which used a lower temperature compensation factor.

VERIFICATION OF PRIMARY IONS

Regression through the origin (RTO; Eisenhauer, 2013) was used to predict $\sum$ions from measured electrical conductivity ($k_{25,Field}$) for complete growing season samples and post-growing season samples (fig. 2). Residuals from the estimated $\sum$ions concentration by measured $k_{25,Field}$ and seasonal proportionality factors (K) resulted in a root mean square error (RMSE) of 9 ppm and 7 ppm for the growing and post-growing seasons respectively. The magnitude of these values represents a mean error of ±1.7% in the growing season with respect to observed cumulative ion concentrations ppm (table 1), and ±1.2% mean error in post-growing season samples. This is in agreement with the expected error (1.2%) caused by minor TDS constituents (Zimmerman, 2016). Therefore, we can conclude major ions contributing

to the electrical conductivity in COBS drainage water samples are HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-}.

IONIC MOLAL CONDUCTIVITY

One of the primary components of this study was to evaluate each ion's individual contribution to the bulk electrical conductivity in sampled drainage waters. To quantifying these speciated contributions, we employed the ionic molal conductivity method described in McCleskey et al. (2012) due to its wide applicability to a variety of waters having similar ionic constituents, pH ranges, and temperatures.

Ion concentrations obtained from chemical analysis of 23 complete drainage samples from cropping systems C2, S2, CC, and P collected at the COBS research site were used to calculate sample ionic strength (M = 0.0108, SD = 0.0008 mol kg^{-1}) according to equation 9. Results for mean calculated conductivities, along with mean observed ion concentrations, are shown in figure 3.

As illustrated by figure 3, HCO_3^- and Ca^{2+} are the largest contributors to conductivity ($\mu S\ cm^{-1}$) and mass concentration (ppm). Cumulatively, these two ions represent 75% of
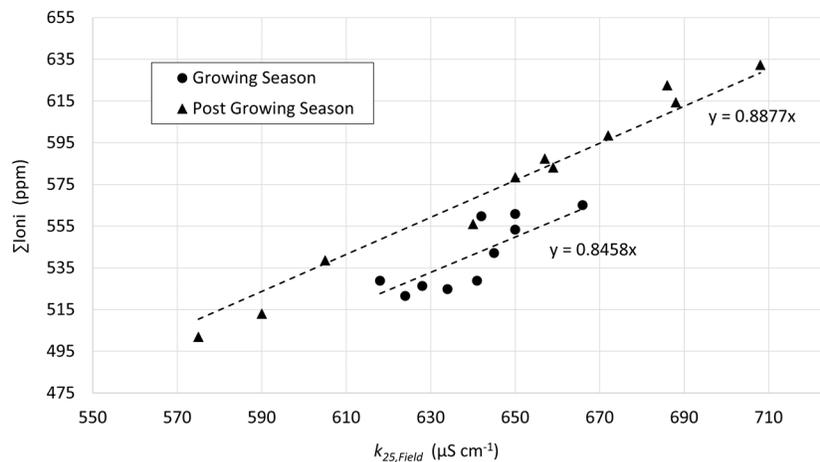

Figure 2. Measured specific electrical conductivity ($k_{25,Field}$) plotted against the cumulative concentration of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+ in drainage water samples collected during the growing and post-growing season at the COBS research site.
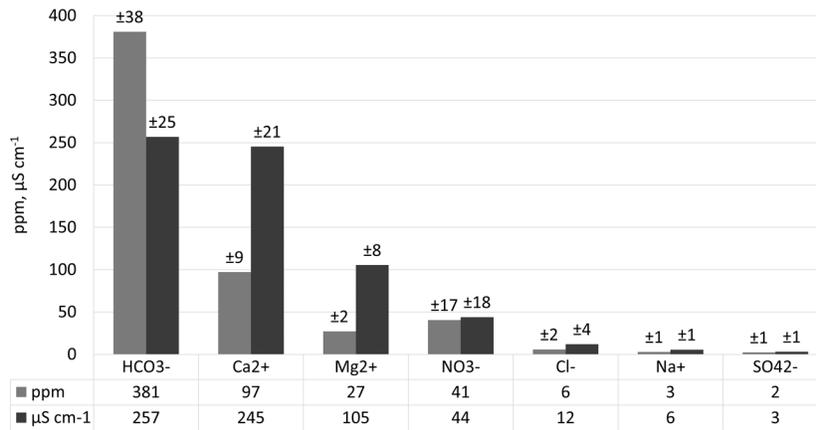
Figure 3. Mean calculated conductivities (µS cm⁻¹) and mean observed concentrations (ppm) of major ions observed in 23 complete drainage water samples from the COBS research site located in Boone County, Iowa. Standard deviations are listed above each parameter.

the calculated bulk electrical conductivity ($M = 673$, $SD = 44$) µS cm⁻¹ and 86% of the total concentration of major ions ($M = 557$, $SD = 41$) ppm. Magnesium and NO_3^- combined, account for a moderate proportion of the electrical conductivity (22% combined) and cumulative ion concentration (12%). Chloride, Na^{2+}, and SO_4^{2-} are minor contributors to electrical conductivity (3%) and cumulative concentration of major ions (2%). Variability among ion conductivities and concentrations was greatest in HCO_3^-, Ca^{2+}, and NO_3^-.

To ensure this molal ionic conductivity method accurately portrays the true conductivities, we evaluated the cumulative calculated electrical conductivity ($k_{25,Calc}$) (eq. 7) with respect to field and laboratory measured electrical conductivities ($k_{25,Field}$) and ($k_{25,Lab}$). The Pearson product moment correlation coefficient of r = 0.93, indicates there is an overall significant linear agreement between the $k_{25,Calc}$ and $k_{25,Field}$ datasets (fig. 4). A strong linear relationship with r = 0.87 was also observed between $k_{25,Calc}$ and $k_{25,Lab}$ (fig. 5). While the level of precision between $k_{25,Calc}$ and $k_{25,Field}$ was slightly higher than $k_{25,Calc}$ with $k_{25,Lab}$, $k_{25,Calc}$ yielded values that were more accurate to $k_{25,Lab}$ ($RMSE = 19$ µS cm⁻¹) than to $k_{25,Field}$ ($RMSE = 35$ µS cm⁻¹).

Figures 1 and 4 show that all $k_{25,Calc}$ and $k_{25,Lab}$ values were greater in magnitude than the corresponding values of $k_{25,Field}$. As stated above, low accuracy between $k_{25,Lab}$ and

$k_{25,Field}$ was thought to have been caused by different temperature compensation factors used in equation 5. This could at also partially explain the low accuracy observed between $k_{25,Calc}$ and $k_{25,Field}$ values. It is also important to note that post-growing season residuals were greater than growing season residuals in both plots of $k_{25,Field}$ and $k_{25,Lab}$ with $k_{25,Calc}$ (figs. 4 and 5). Again, this is likely due to the temperature compensation factor not being calibrated to the ionic composition of growing and post-growing season drainage water samples.

EFFECT OF CROPPING SYSTEM AND SEASON ON ELECTRICAL CONDUCTIVITY

Field measurements for drainage water electrical conductivity ($k_{25,Field}$) ranged from 387 to 760 µS cm⁻¹ (table 2). Both extremes were observed within 3 days following the largest rainfall event (7.94 cm) in June. The lowest recorded $k_{25,Field}$ occurred in drainage from a continuous unfertilized prairie plot during the initial drainage period; the pH for this water sample was 6.92, which was the lowest observed pH during the study period. The highest observed conductivity was recorded in drainage from a corn plot in annual rotation with soybeans (cropping system-C2) three days following the initiation of this drainage event; measured pH (7.32) fell in the 35th cumulative percentile of all observations. Soybean plots in annual rotation with corn (S2 cropping systems) had
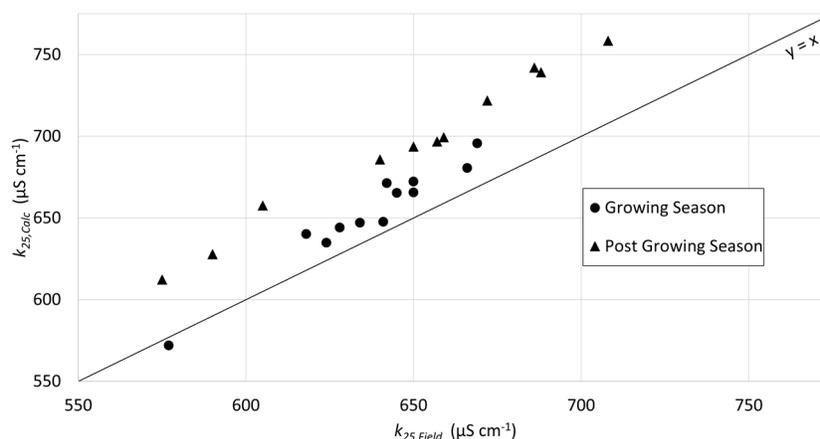

Figure 4. Calculated electrical conductivity at 25°C ($k_{25,Calc}$) against measured specific electrical conductivity ($k_{25,Field}$).
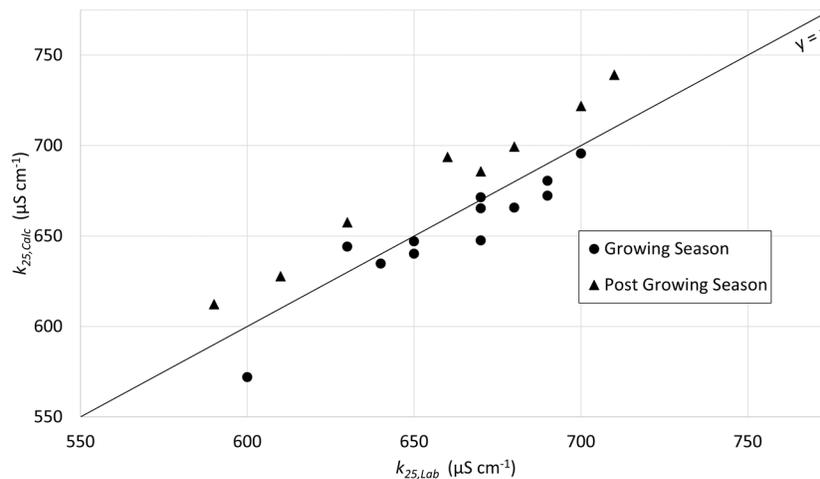
Figure 5. Calculated electrical conductivity at 25°C ($k_{25,Calc}$) against laboratory measured specific electrical conductivity ($k_{25,Lab}$).

Table 2. Summary statistics for measured electrical conductivity, $k_{25,Field}$ (μS cm⁻¹) of drainage waters at the COBS research site including mean, standard deviation, range, and results of the Shapiro-Wilk test of normality (p<0.05 indicates data are not normally distributed).

Sampling Group	n	Mean ± SD	Range	Shapiro-Wilk p
C2	14	685 ± 42	628-760	0.433
S2	14	595 ± 76	430-650	< 0.001
CC	12	663 ± 26	618-698	0.423
P	14	624 ± 127	387-734	0.001
GS[a]	54	641 ± 85	387-760	< 0.001
GS[b]	10	640 ± 14	618-666	0.226
PGS	11	648 ± 42	575-708	0.573

[a] All growing season $k_{25,Field}$ measurements.

[b] Growing season $k_{25,Field}$ measurements of complete samples only.

the lowest mean conductivity, while drainage from C2 plots had the largest mean conductivities (table 2). Variability in $k_{25,Field}$ was lowest among continuous corn plots (cropping system-CC), and greatest among continuous prairie plots (cropping system-P) (table 2). Mean $k_{25,Field}$ across all drainage samples was 642 μS cm⁻¹ with a standard deviation of 79 μS cm⁻¹.

Cropping System Analysis

As previously stated, the ionic composition of drainage water is influenced by cropping system. Because k_{25} is dependent on the ionic composition, it was of interest to evaluate $k_{25,Field}$ variability among different cropping systems. Results from the two sample Mann-Whitney tests (table 3) suggest that the median $k_{25,Field}$ measured in cropping system, S2, is significantly different than the median $k_{25,Field}$ of C2,

Table 3. Mann-Whitney test results for a null hypothesis of equal median $k_{25,Field}$ (μS cm⁻¹) values among sampling groups in comparison.

Comparators	C2[a]	S2	CC
S2	**U = 182**	-	-
	(p < 0.001)		
CC	U = 106	**U = 20**	-
	(p = 0.269)	**(p < 0.001)**	
P	U = 111	**U = 5**	U = 70.5
	(p = 0.566)	**(p = 0.036)**	(p = 0.504)

[a] Bolded p-values less than 0.05 indicate the medians are significantly different.

CC, and P cropping systems. The $k_{25,Field}$ of C2 was not significantly different from CC or P cropping systems. Similarly, the median $k_{25,Field}$ of CC was not significantly different from the P cropping system. These results coincide with those of Zimmerman (2016) who observed significantly higher concentrations of Mg^{2+} and Cl^- in COBS drainage samples from C2 and CC cropping systems in comparison to that of S2 systems. These specific differences in the ionic composition could explain why $k_{25,Field}$ was similar among C2 and CC cropping systems but different than S2 systems.

Seasonal Analysis

Results from the 2-sided Welch's t-test were not significant at alpha level 0.05 (p=0.908), indicating that $k_{25,Field}$ was not different among growing season and post-growing season drainage waters. These results are contrary to what was expected, given that Zimmerman (2016) observed significant differences in the ionic composition among GS and PGS samples at the COBS research site. It may be that while the relative proportions of ions varied, their total strength was similar.

CORRELATION WITH DRAINAGE FLOW RATE, pH, AND TEMPERATURE

Results from the correlation test showed that measured electrical conductivity, k_{25}, is independent of drainage water temperature, pH, and flow (table 4). It is important to remember that temperature in this analysis represents an indicator for different ionic compositions, which can influence the magnitude of measured electrical conductivity. This is different than temperature's influence on the solvent's viscosity, which is automatically accounted for using equation 5.

Table 4. Summary statistic for field measured drainage water pH, temperature (°C), and flow rate (cm d⁻¹), including mean, standard deviation, range, result of the Shapiro-Wilk test of normality (p<0.05 indicates the data are not normally distributed), and Kendall's Tau rank correlation against $k_{25,Field}$.

Parameter	Mean ± SD	Range	Shapiro-Wilk p	Kendall's Tau (τ)
pH	7.4 ± 0.2	6.9-7.9	0.113	-0.178
Temp	22.3 ± 1.7	19.5-25.7	0.075	0.115
Flow	0.231 ± 0.181	0.011-0.590	< 0.001	0.118

CONCLUSION

Hand-held multi-parameter meters, like the one used in this study, are a cost-effective, reliable, and accurate tool for generalized water quality monitoring of TDS. In this study, EC data from a Hach Pro + Multi 2 meter was compared to specific electrical conductivity as measured in accordance with SM 2510B. Laboratory conductivities exhibited the same trend as the field measurements ($r = 0.970$), but were 23 µS cm^{-1} greater on average; this may be due to inconsistent temperature compensation factors among the two methods. We therefore concluded that field electrical conductivity measurements had high precision, but were inaccurate in comparison to laboratory measurements. Further investigation with calculated electrical conductivities provided additional evidence that field measurements tended to underestimate the drainage water electrical conductivity.

Based on a comprehensive literature review and field investigation, Zimmerman (2016) determined that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^+, and SO_4^{2-} were the sole primary ions in agricultural drainage waters at COBS. This was verified in the present study which showed that measured electrical conductivity was a good estimator for the cumulative concentration of major ions. Thus HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, Na^+ are the major ions responsible for the bulk electrical conductivity of these drainage water samples.

The majority of the bulk electrical conductivity was produced by HCO_3^-, Ca^{2+}, and Mg^{2+}, which cumulatively accounted for 90% of the total calculated electrical conductivity. Calculated conductivities for the NO_3^- and Cl^- averaged approximately 7% and 2% of the bulk electrical conductivity, while SO_4^2 and Na^+ were less than 1% each. Furthermore, calculated conductivities indicated that variability was least among Mg^{2+}, SO_4^{2-}, Cl^-, and Na^+.

Several published results have shown that the composition of agricultural drainage water is dependent on cropping system, season, pH, temperature, and drainage flow rate. In contrast, in our study, k_{25} was not significantly different among growing and post-growing season drainage, nor was k_{25} dependent on pH, temperature, or drainage flow rate. Cropping system effects were seen, however, with statistically significant differences seen in k_{25} from observed drainage in cropping systems C2, CC, and P compared to S2 systems. These results coincide with results in Zimmerman (2016), which suggested that ionic composition (indicated by the concentrations of Ca^{2+}, Mg^{2+}, and Cl^-) of S2 cropping systems were significantly different than C2 and CC systems.

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