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et al.

Publication Date

DOI

Peer reviewed
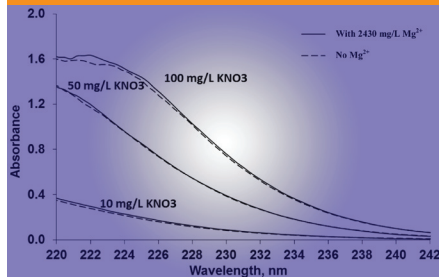
A new sensor, based on ultraviolet absorption spectroscopy, was proposed in previous work for in situ measurement of nitrate in the vadose zone. This work investigated the interference of different ions and dissolved organic carbon (DOC) in the soil solution on the absorption by nitrate. High concentrations of DOC highly interfere with nitrate absorption. A methodology for sensor placement in the soil and value correction was developed and demonstrated to allow for an accurate estimation of nitrate concentration.

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Analysis of Ion and Dissolved Organic Carbon Interference on Soil Solution Nitrate Concentration Measurements Using Ultraviolet Absorption Spectroscopy

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Nitrate is often present in surface water, soil solution, and groundwater at undesirable or toxic levels. This study follows development of an in situ nitrate monitoring probe and examines its performance in the presence of potentially interfering ionic species and dissolved organic carbon (DOC). Ultraviolet (UV) absorption spectroscopy measurements of aqueous NO_3^- were obtained under conditions where prevalent ionic species (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Zn^{2+}, Cu^{2+} Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Cl^- $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-}, and HCO_3^-) and DOC were present at maximum characteristic concentrations for a range of pH levels, allowing UV interference on NO_3^- concentrations from individual ions to be investigated. While most solutions did not show interference, Fe^{2+} ions and DOC absorbed ultraviolet light strongly in regions of the spectrum where NO_3^- also exhibited significant absorption. Natural water samples showed very low concentrations of Fe^{2+}, which do not cause interference with nitrate measurements. A two-wavelength measurement scheme was adopted to correct for the potential interference of DOC in measurements of aqueous NO_3^-. A multivariate calibration is presented to account for possible interference from both DOC and other ions in solution. The application of the UV spectroscopy probe is especially useful for deep vadose zone measurements of nitrate, as typically DOC concentrations will exponentially decrease with depth, and ion interference will be low.

Abbreviations: DOC, dissolved organic carbon; MCL, maximum contaminant level; NPS, nonpoint source; UV, ultraviolet; VIS, visible.

Nonpoint source (NPS) pollution from various sources continues to adversely impact groundwater quality. In all, it is estimated that about 30 to 50% of the Earth's land surface is affected by NPS pollutants (Corwin et al., 1997), with a large fraction caused by agrochemicals and nutrients (e.g., N, P). Nitrate is the dominant N species of interest because nitrate-containing fertilizers are commonly used in agriculture as well as for fertilization of golf courses, lawns, and gardens. Nitrate contamination of groundwater is of particular concern due to the adverse health effects of ingesting water with unsafe nitrate levels.

Regulatory limits of NO_3^- concentrations in drinking water were set by the USEPA to 10 mg/L NO_3–N (USEPA, 1977), corresponding to about 50 mg/L NO_3^- equivalent. The presence of NO_3^- in the bloodstream reduces the ability of red blood cells to carry oxygen, thereby causing serious health effects, in particular for infants by the condition of methemoglobinemia or "blue baby syndrome." Moreover, studies have shown elevated NO_3^- levels to cause cancer, birth defects, and other health concerns (Fewtrell, 2004). Various studies report extensive large populations exposed to elevated nitrate concentrations (Spalding and Exner, 1993). For example, more than 4 million people in the United States are exposed to drinking water that exceeds the maximum contaminant level (MCL) of 10 mg/L for nitrate, and the spatial extent of groundwater with nitrate levels exceeding

the MCL is expected to continue increasing. It is estimated that nitrate contamination affects about 10% of California's public drinking water supply wells, at a minimum (Anton et al., 1988).

Because of this, significant efforts have been directed toward development of sensors for NO_3^- monitoring (Moorcroft et al., 2001). For NO_3^- aqueous solutes to reach groundwater, following land surface application, they must pass through the unsaturated soil or vadose zone. There is strong interest in detailed sampling of nitrate in soil water for ecological purposes to increase understanding of nutrient limitations in natural ecosystems (Simunek and Hopmans, 2009). Adequate monitoring of soil solution is required to assess leaching potential of NO_3^- to deeper vadose zones and groundwater. Ideally, one would measure the NO_3^- concentration in situ, but few methodologies are available, and most require extraction of soil samples or soil solution extraction using porous solution samplers, and are therefore time-consuming and expensive. Moreover, interpretation of these measurements can only be as meaningful as the manner in which the basic field data or samples are collected (Weihermuller et al., 2007).

In the present research we focus on in situ absorption spectroscopy in the UV portion of the spectrum. This method has been shown to be useful for long-duration monitoring of natural waters (Beaton et al., 2012; Johnson and Coletti, 2002; Rieger et al., 2004), and this method was also used for soil solution sampling (Shaw et al., 2010; Tuli et al., 2013, 2009). In the latter case, a prototype soil solution monitoring technique was developed to measure long-term in situ nitrate concentration, with real-time concentration measurements using a UV fiber-optic sensor deployed into a stainless-steel porous cup. The measurement technique does not require soil solution extraction but is based on in situ soil solution equilibration by diffusion between the porous cup and the surrounding soil medium.

In our previous work (Shaw et al., 2010; Tuli et al., 2013, 2009), we focused on developing UV absorption spectroscopy methodologies to measure $NO_3^-{}_{(aq)}$ concentrations under conditions where nitrate ions were the only significant absorbing species present. In practice, however, it is likely that many other ionic species occur in combination in both soil solution and groundwater. It is expected that some of these species might interfere with the nitrate absorption signal. The objective of the present research is to extend our previous research on UV absorption measurements of NO_3^- by evaluating the potential for measurement interference from ionic species (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Zn^{2+}, Cu^{2+} Mn^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+}, H^+/OH^- (pH 4–10), Cl^-, $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-}, and HCO_3^-) present at maximum characteristic levels in soil solution (Barber, 1995; Wolt, 1994) (Table 1), as well as interference by DOC.

Because of the large number of species considered, we evaluated NO_3^- absorption spectra for only limited combinations of the species in Table 1. In particular, we dissolved KNO_3 in deionized

Table 1. Species considered for interference with their tested concentration.

Species	Concentration
	mg/L
Na^+	2299
K^+	391
Ca^{2+}	4008
Mg^{2+}	2430
NH_4^+	1801
Zn^{2+}	0.0654
Cu^{2+}	0.0636
Mn^{2+}	5494
Fe^{2+}	698, 1396
Fe^{3+}	5.59×10^{-4}
Al^{3+}	2.698
Cl^-	3545
SO_4^{2-}	9607
$H_2PO_4^-$	0.670
HPO_4^{2-}	0.660
HCO_3^-	6101
DOC	0–100

water to produce K^+ and NO_3^-. Therefore, K^+ was always present in the experiments; however, it is noted that K^+ does not appreciably absorb UV radiation in the region of interest for sensing NO_3^-. We then introduced DOC or other compounds that yielded specific ions of interest. For example, $CaCl_2$ was used to produce Ca^{2+} and Cl^- ions in solution. In general, KNO_3 was evaluated only in combination with a single additional ion-producing species in these experiments.

Experimental Methods
Principles of Ultraviolet Spectroscopy for Nitrate Analysis

Ultraviolet spectroscopy has been employed for analysis of aqueous NO_3^- levels for several decades (Shaw et al., 2010). The UV absorption peaks for aqueous NO_3^- occur at wavelengths of about 201 and 302 nm. However, it is difficult to measure the 201- and 302-nm absorbance bands simultaneously because the 201-nm band absorbs much more strongly than the 302-nm band (Meyerstein and Treinin, 1961). Both peaks are relatively broad, thus enabling useful absorption data to be obtained at wavelengths away from the peaks, which is what was done here. The absorbance measurements of our study were obtained with a fiber optic T300-RT-UV-VIS transmission (where VIS denotes visible) dip probe from Ocean Optics, Inc. A Heraeus FiberLight UV source (Heraeus Noblelight LLC) was used to provide light for the measurements and a two-channel Ocean Optics SD-2000 UV-VIS spectrometer was used for spectrum analysis. The UV dip probe contained two optical fibers and a plano-convex lens contained within a stainless-steel holder. Ultraviolet light from the Heraeus

light source was directed into the illumination fiber of the dip probe. This fiber terminated near a plano-convex lens that was located at the end of the stainless-steel tube. This lens directed the light along a path through the liquid and onto a mirror that was placed a fixed distance (typically ~5 mm) away from the lens. The reflected light was focused by the lens onto the read fiber, which transferred the attenuated light back to the spectrometer. The total path length through the liquid was about 10 mm. The dip probe included a reference fiber to correct for light intensity fluctuations of the light source. A schematic with details of the sensing element of the UV probe is shown in Fig. 1. For additional details of the construction and testing of UV spectroscopy probe, we refer the reader to Tuli et al. (2009) and Shaw et al. (2010). The probe was made from stainless steel for deep soil installation and to minimize corrosion of the porous cup.

The optical system used in these experiments could measure UV–VIS absorption spectra from about 200 to 600 nm. We typically used absorbance spectra with wavelengths near to or longer than 220 nm, which provided accurate results while still allowing strong signals with minimum detectable nitrate levels of about 1 mg/L. For example, NO_3^- absorbance data over the range 220 to 300 nm, as obtained with the UV probe described, are shown in Fig. 2a, where absorbance is defined as the negative logarithm of the ratio of transmitted over incident light intensity.

Ultraviolet Interference Measurements

The experiments were performed such that KNO_3 was present in combination with either one set of competing ions (e.g., Ca^{2+}, Cl^-) or DOC (Table 1), allowing UV interference on nitrate levels from individual ions and DOC to be investigated. In the interference experiments, we measured UV absorption spectra of aqueous KNO_3 solutions (producing NO_3^- ions) at various KNO_3 loadings. We also measured the UV absorption spectra of each individual ion in Table 1 (without KNO_3 being present) as well as the absorption spectra of NO_3^- in the presence of each individual ion in Table 1. This was also done for DOC. The specific ions and their concentrations that were considered for interference were chosen to represent the wide range of ions present in soil and to represent maximum expected concentrations (Adams, 1971; Barber, 1995; Dahlgren, 1993; Wolt and Graveel, 1986; Wolt, 1994). The DOC levels were also selected to represent characteristic levels for a wide range of mineral soils (Inamdar et al., 2012; Jones and Willett, 2006).

The DOC solutions were obtained by reacting 250 g of compost in 1 L of water for 12 h on a laboratory shaker and centrifuging (15,344 RCF, 20 min). Remaining particulate matter was removed via filtration using a 0.8-μm nylon filter. Since the analysis of ions in solution is central to this research, dialysis of the DOC solution was performed (3500 MWCO; Fisherbrand Regenerated Cellulose, Fischer Scientific) at pH 4.0 to minimize interference from associated inorganic ions. Dialysis was complete when the
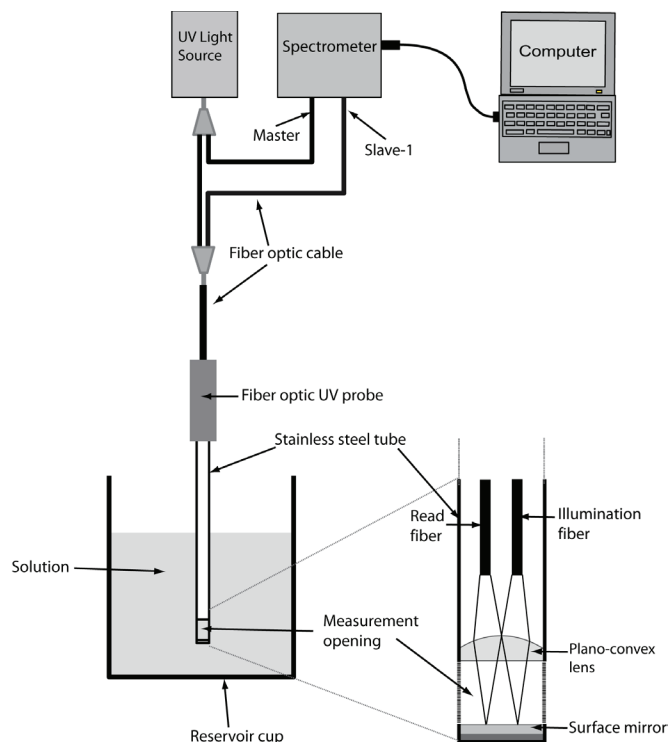

Fig. 1. Schematic of the fiber optic system with its tip detail and experimental set up in aqueous solution.

pH of the external solution remained unchanged for a 12-h period. The resulting stock DOC solution was diluted to examine potential interference for nitrate measurements for DOC concentrations ranging from 0 to 100 mg C/L.

The tested solutions were prepared by dissolving KNO_3 and each of the following compounds into deionized water: NaCl, $CaCl_2$, $MgSO_4$, $NaHCO_3$, NH_4Cl, $MnCl_2$, $FeCl_2$, KCl, $AlCl_3$, NaH_2PO_4, Na_2HPO_4, $ZnCl_2$, $CuCl_2$, $FeCl_3$, HCl, NaOH, and DOC. As noted previously, each solution contained KNO_3 and only one of the compounds listed above. It was generally necessary to allow equilibration times of up to 1 d or more so that stable and repeatable measurements were obtained. The concentration of each of the ions was typically fixed at the prescribed values of Table 1, although in some cases different concentrations were investigated as well. The KNO_3 concentration levels were varied from 0 to 200 mg/L by mass.

In addition to these soil water solutions, natural water samples from 27 experimental sites in California's Sacramento Valley (Table 2) were tested to study interfering Fe^{2+} and DOC presence, as well as to test the validity of the presented correction schemes (Table 2).

Results and Discussion

We first consider the spectral data for all of the ions. Figure 2 shows measured UV absorbance spectra for the ions considered. Figure
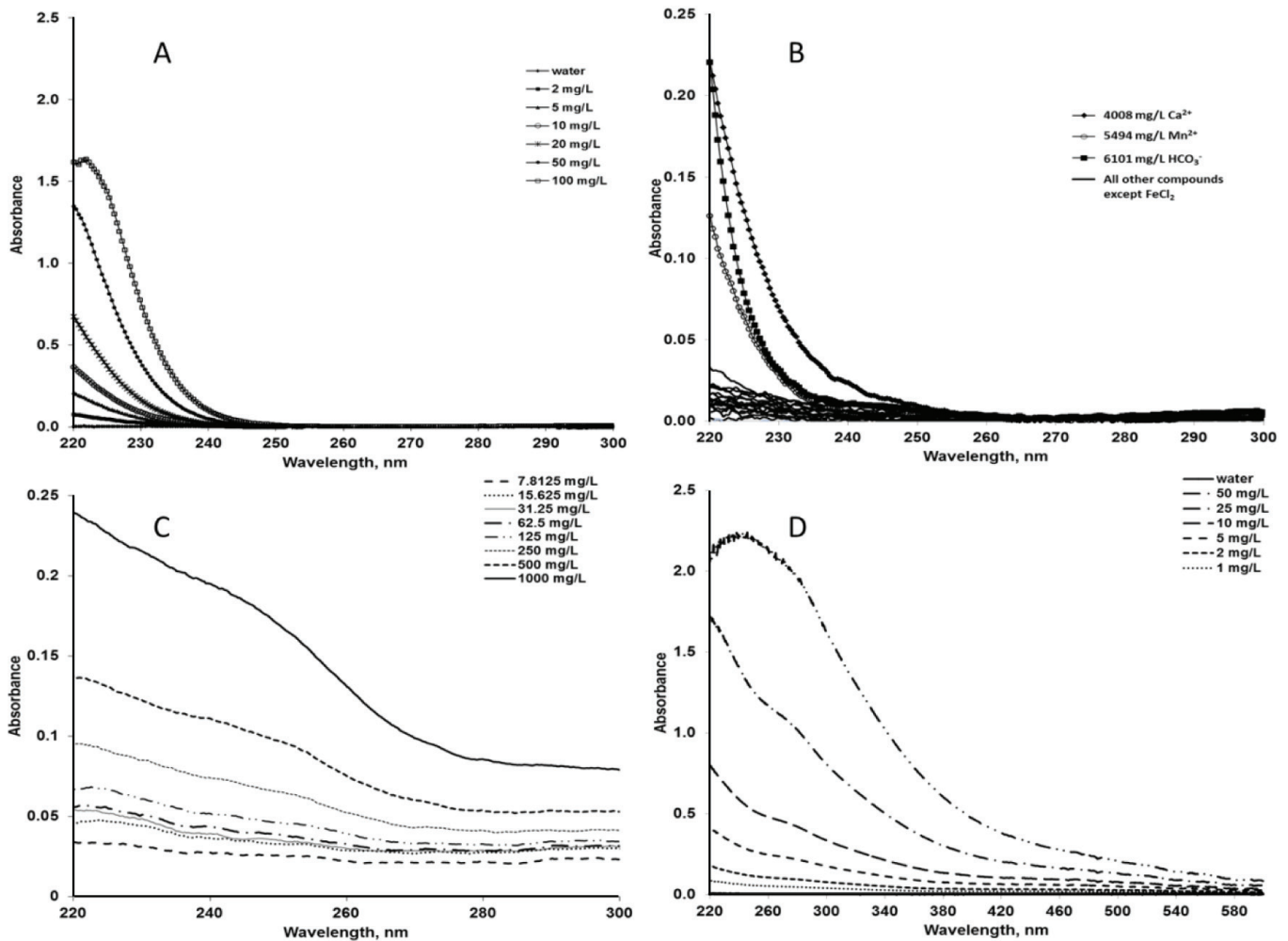
Fig. 2. Absorbance spectra of (A) NO_3^-, (B) other ions except NO_3^- and Fe^{2+}, (C) Fe^{2+}, and (D) dissolved organic carbon (DOC).

2A shows UV absorption spectra over the wavelength range of 220 to 300 nm for aqueous NO_3^-, clearly showing that the UV method is sensitive to nitrate concentration (Tuli et al., 2009). The reference spectrum in each case, and in all cases discussed later, was deionized water. By using these spectral data, calibration data were obtained to relate the absorbance at a given wavelength to the amount of NO_3^- present in aqueous samples.

Figure 2B shows the measured absorption data for all other ions except Fe^{2+}, which is shown in Fig. 2C. The data in Fig. 2B are shown separately from those of nitrate absorption because of their differences in absorption magnitudes. Specifically, the absorbance levels for the ions in Fig. 2B were small, relative to the absorbance levels in Fig. 2A, for the higher NO_3^- loadings of interest. The relatively high absorbance of Ca^{2+} and HCO_3^- is not of significant importance because usually in soils they are present together, and precipitation will happen at much lower concentrations (Back, 1963). The Mn^{2+} also shows higher absorbance relative to the other ions, but the probability of measuring in a location with such high

concentration of Mn^{2+} is very low (Chen et al., 1999). The absorbance levels of Fe^{2+} (Fig. 2C) were appreciable and show that for the highest loading (1000 mg/L Fe^{2+} ions) detector noise becomes a significant issue at wavelengths around 220 nm. In addition, Fe^{2+} absorbs strongly at the wavelengths for which NO_3^- is significantly absorbed, indicating ion interference.

Figure 2D shows the absorption spectrum for DOC. Similar to Fe^{2+}, DOC absorption levels are large, and detector noise becomes significant at wavelengths smaller than about 300 nm for DOC concentrations of 25 mg C/L DOC and higher. In addition, our results showed that DOC absorption is strong at the same wavelength range for which NO_3^- is absorbed, indicating ion signal interference. For DOC concentrations larger than 50 mg C/L, the UV absorption signal is completely quenched, thus preventing conducting useful NO_3^- measurements. However, diffusion tests showed that the stainless porous cup acts like a filter, effectively preventing most of the high molecular weight DOC constituents to diffuse inside the cup of the probe, thereby largely avoiding

Table 2. Measured Fe^{2+} (Viollier et al., 2000), dissolved organic carbon (DOC) (Qian and Mopper, 1996), spectrophotometric NO_3^- (Doane and Horwath, 2003), and nitrate probe NO_3^- in samples from the Sacramento delta. Absorption ratio column shows the ratio of twice the absorption at 275 nm to the absorption at 220 nm times 100 nm.

Sample name (sample locations in central California)	Fe^{2+}	DOC	NO_3^-	NO_3^- probe	Abs. ratio
		ppm???			
Rice field soil, Biggs Research Station, Biggs	0.26	108.30	0.18	0.86	24.72
Rice field soil, Sacramento Valley	0	68.69	16.49	13.39	28.14
Bale soil, Napa	0	60.36	1.31	1.93	44.05
Redding soil, Lodi	0	32.43	0.72	1.62	17.31
San Joaquin soil, Lodi	0	29.87	1.41	2.53	−14.74
Clay pan soil, Browns Valley†	0	33.42	10.47	11.05	4.14
Top soil, Browns Valley	0	38.95	0.36	1.06	−71.43
Restored site soil 1, Galt	0	117.30	2.46	5.18	40.94
Restored site soil 2, Galt	0	60.05	1.46	1.69	26.67
Restored site soil 3, Galt	0	62.70	1.39	1.14	−37.04
Putah Creek, Davis	0	11.73	0.21	1.18	86.63
Calusa Drain, Woodland	0	2.23	0.03	−1.16	72.41
Calusa Drain 2, Woodland	0	3.83	1.47	10.74	28.51
Yolo Bypass, Sacramento	0	19.13	0.00	−0.01	93.47
American River, Sacramento	0	3.37	0.00	−1.48	84.62
Sacramento River, Sacramento	0	3.43	0.00	−1.52	82.93
Delta Drainage, Lodi	0	5.83	1.00	6.18	38.53
Mossdale 1, San Joaquin River, Manteca	0	4.14	0.32	1.97	54.98
Mossdale 2, Trancy Rd., Stockton	0	6.15	1.74	13.24	36.09
S. Mulkome River, Hwy. 12 Fairfield	0	2.56	0.19	−0.05	63.93
S. Molkumne River, Fairfield	0	2.31	0.22	0.15	55.05
Jackson Slough, Lodi	0.26	5.08	0.00	−0.57	90.22
Drainage 2, Hwy. 12, Fairfield	0.29	6.91	0.27	−2.27	102.44
Sacramento River-Rio Vista	0	2.33	0.61	0.35	65.38
Rice field water, Twitchell Island, Rio Vista	0	10.74	0.00	−1.16	97.22
Well water 1 dairy CAFO, Modesto†	0	8.26	35.81	37.61	9.25
Well water 2 dairy CAFO, Modesto†	0	2.70	59.67	59.96	5.46

† Locations where twice the absorption value at 275 nm was lower than 10% the absorption value at 220 nm.

interference by high DOC concentrations. Specifically, diffusion experiments using a DOC concentration of 50 mg C/L showed that the DOC concentration in the sampling cup was only 5.5 mg C/L (with dialysis) or 16 mg C/L (without dialysis) after 96 h. Separate diffusion experiments using inorganic ions showed that pseudo-equilibrium was reached after 96 h (for additional details about the properties of the stainless-steel cup, see Tuli et al., 2009).

The data in Fig. 2C and 2D show the broadband nature of the Fe^{2+} and DOC absorption spectrums; that is, these species can exhibit appreciable absorption in the nitrate-sensitive wavelength range and at about 460 nm for Fe^{2+} and 600 nm for DOC. It was found, however, that for all ions other than Fe^{2+}, interference with the nitrate UV absorption signal was small. As an example, Fig. 3 shows representative data for a small interference case with Mg^{2+} ions. This figure includes data from Fig. 2A (i.e., no $MgSO_4$) and also data including 2430 mg/L Mg, for NO_3^- concentrations between 10 and 100 mg/L. The data in Fig. 3 show that the presence of $MgSO_4$ does not interfere with the nitrate measurements.
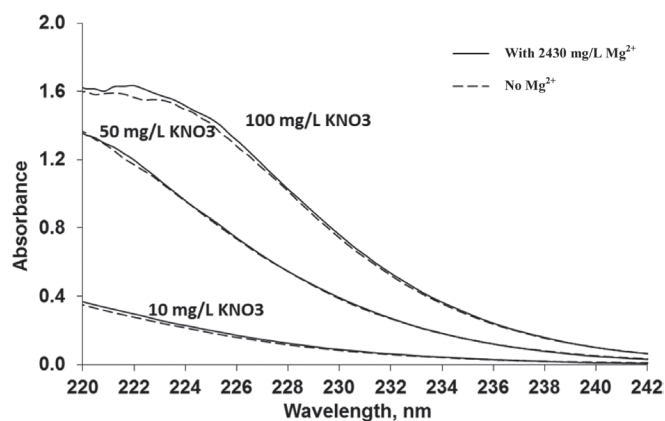

Fig. 3. Absorption data for aqueous KNO_3 in the presence of 2430 mg/L Mg^{2+} (0.1 M $MgSO_4$) (dashed lines), as well as aqueous KNO_3 without $MgSO_4$.

As noted earlier, the Fe^{2+} ion exhibited broadband absorption over a spectral region that included the nitrate absorption spectrum (Fig. 2). Because of the strong Fe^{2+} absorption spectrum, we were unable to provide accurate measurements of nitrate ions if Fe^{2+}

was present at levels higher than about 1400 mg/L Fe^{2+}. For this high concentration, the specific interference is demonstrated in Fig. 4 for nitrate absorption between 2 and 200 mg/L. The Fe^{2+} measurement data also clearly show the significant noise levels for the higher NO_3^- concentrations in the 220-and 230-nm range, as caused by light absorption, reducing light intensity to levels comparable to the noise level of the spectrometer. However, previous studies have shown that only a small fraction of the total Fe in soil is soluble and are unlikely to reach such high concentrations in natural soil systems (Rattan et al., 2005). Furthermore, none of the water samples collected for this study (Table 2) had high levels of Fe^{2+} present. In fact, Fe^{2+} concentrations in all of the water samples were lower than 1 mg/L and therefore did not interfere with NO_3^- measurements. Significant Fe^{2+} interference might be experienced in flooded soils or groundwater where the redox potential causes Fe^{3+} in soil minerals to be converted to Fe^{2+} (Van Breemen, 1988).

Figure 5A through 5C present UV absorption spectra for NO_3^- with different levels of DOC (10, 25, and 50 mg C/L). It is noted that as the DOC level increases, the UV signal by the NO_3^- is increasingly modulated and completely quenched at 50 mg C/L (Fig. 5C). The basis of this behavior is not clear at present, but it is likely that DOC is reacting with NO_3^- to quench the NO_3^- absorption signal.

Despite the issue of DOC affecting nitrate measurements, nitrate concentrations have previously been determined in the presence of DOC using a dual wavelength correction scheme (Armstrong, 1963). Using this method, UV absorption is measured at 220 nm and calibrated to nitrate concentration. A second absorbance measurement is made at 275 nm. This value is then multiplied by 2 and subtracted from the 220-nm absorbance value. The new, adjusted, 220-nm absorption value is used with the calibration curve to estimate nitrate concentration. The multiplied absorption value measured at 275 nm cannot be higher than 10% of the reading at 220 nm for this method to be accurate. Analyzing the water samples in Table 2, we see that only three locations satisfy the low DOC concentrations (marked by †). For these locations, nitrate estimation using the probe was within 5% of the nitrate estimation using a spectrophotometric method (Doane and Horwath, 2003). We believe that for installations in deep vadose zones and in soils below the rooting zone, where DOC concentrations are commonly near or below 10 mg/L (Cronan and Aiken, 1985; Easthouse et al., 1992; Pabich et al., 2001), the nitrate probe has excellent potential for in situ determination of nitrate concentrations.

Even for fields that use compost or manure slurry as fertilizers, DOC concentrations typically rapidly decrease with depth due to soil adsorption (Jardine et al., 1989) and biodegradation (Kalbitz et al., 2000). For example, Liang et al. (2012) found DOC concentrations lower than 50 mg/L at a depth of 30 cm under a field that was fertilized with manure for 15 yr. Liu et al. (2013) found that
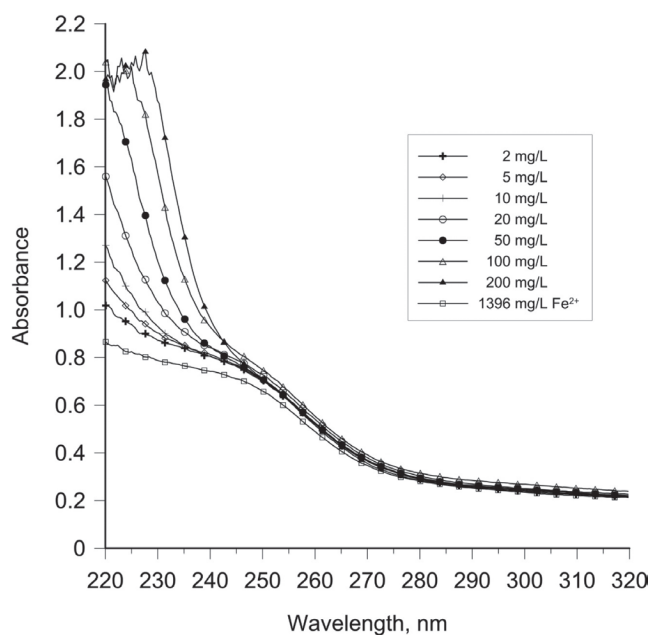

Fig. 4. Absorption data for KNO_3 in the presence of 1396 mg/L Fe^{2+} (0.025 M $FeCl_2$). The mg/L ppm??? levels refer to the mass of KNO_3 divided by the mass of solution times 10^6.

after almost 30 yr of manure application, DOC concentrations exponentially declined with depth and reached around 50 mg/L at a depth of 90 cm. Furthermore, del Castilho et al. (1993) found the DOC concentration to be usually low (50 mg/L) at depths of 50 to 80 cm for a field with applied cattle manure slurry. Based on these papers it can be assumed that installing the probe at a depth of 1 m will help to avoid interference by DOC absorption.

For situations where DOC and other interfering ion concentrations are consistently high (Pabich et al., 2001), we propose to conduct a multivariate calibration (Johnson and Coletti, 2002; Rieger et al., 2004), as presented in the Appendix.

Conclusions

The nitrate probe was developed for in situ measurement of nitrate concentration in the vadose zone, as described in Shaw et al. (2010) and Tuli et al. (2009). We investigated the interference of different ions and dissolved organic carbon that are usually present in soil solution on the absorption of nitrate ions. Results show that specific ions (Ca^{2+}, HCO_3^-, Fe^{2+}) may cause interference in the nitrate absorption range. However, these ions are usually present in sufficiently low concentrations in soil solutions that they do not interfere. We found that DOC interferes with the nitrate measurement in the 200- to 300-nm range. However, the microporosity of the metal cup greatly reduces DOC migration into the porous cup of the nitrate sensor. For conditions where DOC concentrations inside the cup quench the UV signal, we adopted a two wavelength correction scheme to estimate NO_3^- concentration. This approach allowed for determination of NO_3^- in samples for which twice

the absorbance value measured at 275 nm was less than 10% of the value measured at 220 nm. Under conditions of both high DOC and other interfering ions, we present a multivariate calibration of the nitrate probe. However, this calibration is site specific and depends on the quality of DOC and specific interfering ions. We believe that the application of the UV spectroscopy probe is especially suitable for deep vadose zone applications where interfering ion and DOC concentrations are typically low.

Additional field testing of the UV probe is required to evaluate the level of DOC filtration for high DOC conditions and corrosion level of the stainless-steel probe. However, the UV in situ nitrate probe shows high potential for nitrate monitoring in deep vadose zones, enabling developing nitrate management guidelines that minimize groundwater contamination by nitrate leaching.

Acknowledgments

◦ Appendix

Multivariate Calibration of Nitrate Probe in the Presence of Dissolved Organic Carbon and Interfering Ions

The results of Fig. 2 suggest the following three-wavelength correction procedure for determining the concentration of KNO_3 in the presence of DOC and $FeCl_2$. First, we note that an absorbance measurement at $\lambda_3 = 600$ nm can be used to determine the amount of DOC present as it is the only species that is sensitive at this wavelength. A measurement at $\lambda_2 = 260$ nm can be used to infer the Fe^{2+} concentration, as NO_3 does not significantly absorb at this wavelength. Finally, an absorbance measurement at about $\lambda_1 = 235$ nm will provide information on the amount of nitrate in combination with DOC and Fe^{2+}.

The use of three wavelengths implies that the KNO_3 levels are a function of the absorbances: $A(\lambda_1) = A_1, A(\lambda_2) = A_2,$ and $A(\lambda_3) = A_3$.
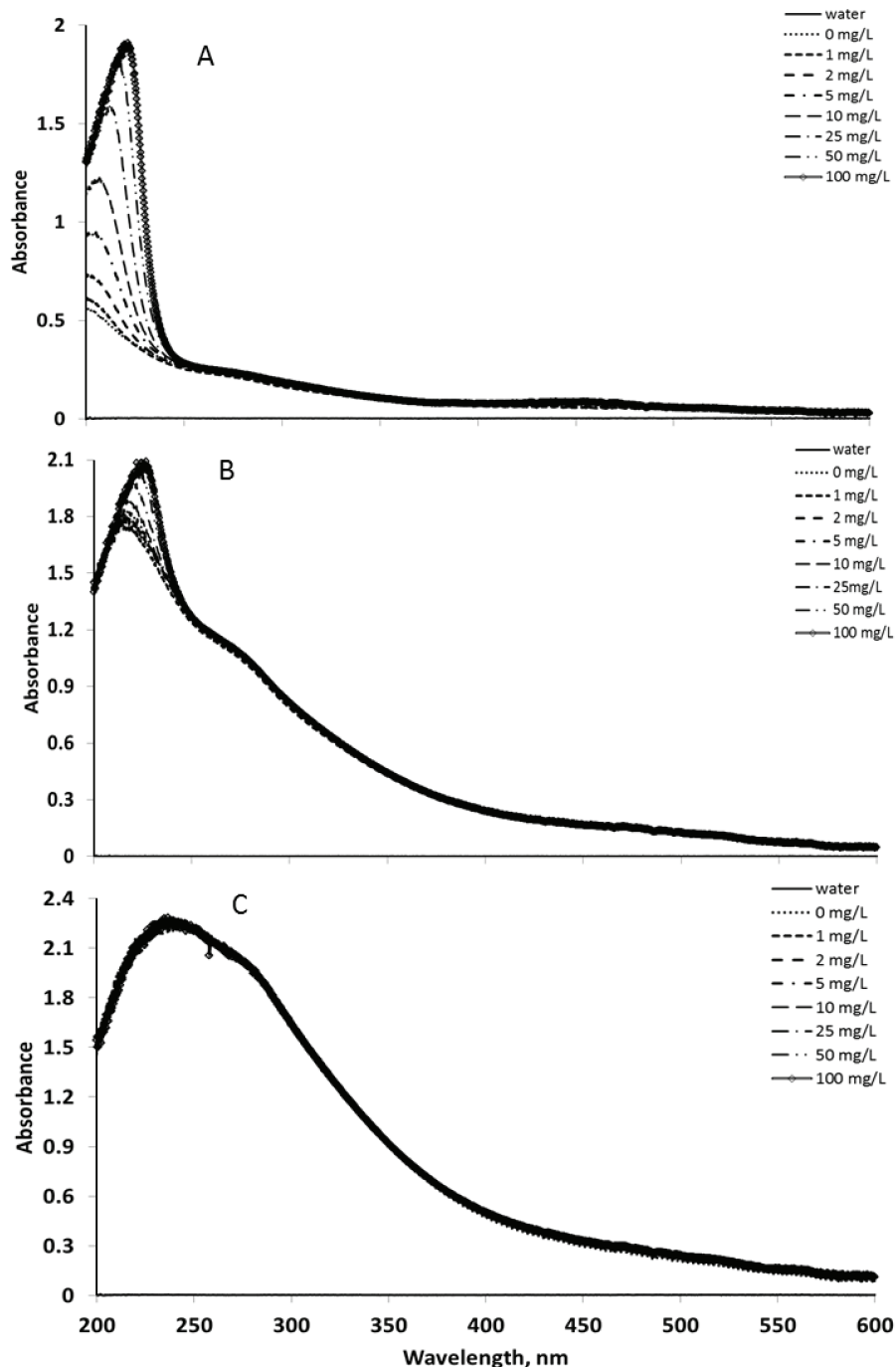

Fig. 5. Absorption data for KNO_3 in the presence of (a) 10, (b) 25, and (c) 50 mg C/L DOC. The mg/L ~~ppm???~~ levels refer to the mass of KNO_3 divided by the mass of solution.

We assumed that the absorbance data could be best expressed by a nonlinear multivariate polynomial of order 2, with the regression parameters evaluated by minimizing differences between the measured and true nitrate levels for all species in Table 1 with $\lambda_1 = 235.9$ nm, $\lambda_2 = 260.3$ nm, and $\lambda_3 = 600.3$ nm. This led to the following equation:

$$KNO_3 \text{ (mg/L)} = a_0 + a_1 A_1 + a_2 A_2 + a_3 A_3 + a_{11} A_1^2 + a_{12} A_1 A_2 + a_{13} A_1 A_3 + a_{22} A_2^2 + a_{23} A_2 A_3 + a_{33} A_3^2 \quad [A1]$$

where $a_0 = -2.45$, $a_1 = 404.1$, $a_2 = -545.64$, $a_3 = 138.00$, $a_{11} = 58.41$, $a_{12} = -222.06$, $a_{22} = 277.84$, $a_{13} = -309.91$, $a_{23} = -1193.05$, and $a_{33} = 1568.93$.

Figure 6 presents the KNO_3 mg/L levels predicted, for the laboratory solutions, using Eq. [A1] and the true KNO_3 levels in the presence of the other ions and DOC. The solid line in this figure represents perfect agreement between the regression model and experiment with the symbols corresponding to the various mixtures. We conclude that the multivariate calibration is accurate to within about 25 mg/L or better. The largest errors occur when either DOC or Fe^{2+} are present. If neither of these species is present in significant amounts, the accuracy of the detection scheme will improve significantly to within 5% of the true concentration.

Fig. 6. Comparison between calculated and actual KNO_3 loadings. The solid line is the 1:1 line, representing perfect agreement between experimental and calculated KNO_3 values.

References

Adams, F. 1971. Ionic concentrations and activities in soil solutions. Soil Sci. Soc. Am. Proc. 35:420–426. doi:10.2136/sssaj1971.03615995003500030028x

Anton, E.C., J.L. Barnickol, and D.R. Schnaible. 1988. Nitrate in drinking water: Report to the legislature. Division of Water Quality Rep. 88-11WQ. California State Water Resources Control Board, Sacramento, CA.

Armstrong, F.A.J. 1963. Determination of nitrate in water by ultraviolet spectrophotometry. Anal. Chem. 35:1292–1294. doi:10.1021/ac60202a036

Back, W. 1963. Preliminary results of a study of calcium carbonate saturation of ground water in central Florida. Hydrol. Sci. J. 8:43–51.

Barber, S.A. 1995. Soil nutrient bioavailability: A mechanistic approach. 2nd ed. John Wiley & Sons, New York.

Beaton, A.D., C.L. Cardwell, R.S. Thomas, V.J. Sieben, F.E. Legiret, E.M. Waugh, P.J. Statham, M.C. Mowlem, and H. Morgan. 2012. Lab-on-chip measurement of nitrate and nitrite for in situ analysis of natural waters. Environ. Sci. Technol. 46:9548–9556. doi:10.1021/es300419u

Chen, M., L.Q. Ma, and W.G. Harris. 1999. Baseline concentrations of 15 trace elements in Florida surface soils. J. Environ. Qual. 28:1173–1181. doi:10.2134/jeq1999.00472425002800040018x

Corwin, D.L., P.J. Vaughan, and K. Loague. 1997. Modeling nonpoint source pollutants in the vadose zone with GIS. Environ. Sci. Technol. 31:2157–2175. doi:10.1021/es960796v

Cronan, C.S., and G.R. Aiken. 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. Geochim. Cosmochim. Acta 49:1697–1705. doi:10.1016/0016-7037(85)90140-1

Dahlgren, R.A. 1993. Comparison of soil solution extraction procedures-effect on solute chemistry. Commun. Soil Sci. Plant Anal. 24:1783–1794. doi:10.1080/00103629309368917

del Castilho, P., W.J. Chardon, and W. Salomons. 1993. Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manured acidic, loamy-sand soil. J. Environ. Qual. 22:689–697. doi:10.2134/jeq1993.00472425002200040009x

Doane, T.A., and W.R. Horwath. 2003. Spectrophotometric determination of nitrate with a single reagent. Anal. Lett. 36:2713–2722. doi:10.1081/AL-120024647

Easthouse, K.B., J. Mulder, N. Christophersen, and H.M. Seip. 1992. Dissolved organic-carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, southern Norway. Water Resour. Res. 28:1585–1596. doi:10.1029/92WR00056

Fewtrell, L. 2004. Drinking-water nitrate, methemoglobinemia, and global burden of disease: A discussion. Environ. Health Perspect. 112:1371–1374. doi:10.1289/ehp.7216

Inamdar, S., N. Finger, S. Singh, M. Mitchell, D. Levia, H. Bais, D. Scott, and P. McHale. 2012. Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. Biogeochemistry 108:55–76. doi:10.1007/s10533-011-9572-4

Jardine, P.M., N.L. Weber, and J.F. Mccarthy. 1989. Mechanisms of dissolved organic-carbon adsorption on soil. Soil Sci. Soc. Am. J. 53:1378–1385. doi:10.2136/sssaj1989.03615995005300050013x
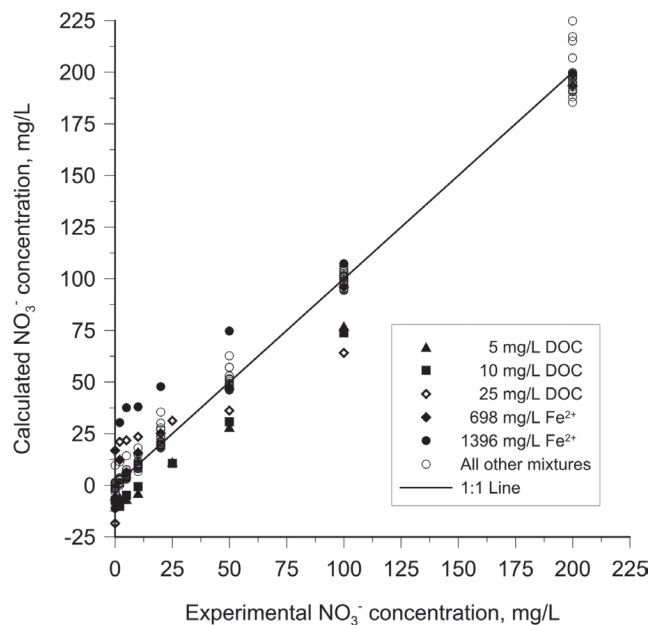
Johnson, K.S., and L.J. Coletti. 2002. In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. Deep Sea Res. Part I Oceanogr. Res. Pap. 49:1291–1305. doi:10.1016/S0967-0637(02)00020-1

Jones, D.L., and V.B. Willett. 2006. Experimental evaluation of methods to quantify dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in soil. Soil Biol. Biochem. 38:991–999. doi:10.1016/j.soilbio.2005.08.012

Kalbitz, K., S. Solinger, J.H. Park, B. Michalzik, and E. Matzner. 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Sci. 165:277–304. doi:10.1097/00010694-200004000-00001

Liang, Q., H.Q. Chen, Y.S. Gong, M.S. Fan, H.F. Yang, R. Lal, and Y. Kuzyakov. 2012. Effects of 15 years of manure and inorganic fertilizers on soil organic carbon fractions in a wheat-maize system in the North China Plain. Nutr. Cycl. Agroecosyst. 92:21–33. doi:10.1007/s10705-011-9469-6

Liu, E.K., C.R. Yan, X.R. Mei, Y.Q. Zhang and T.L. Fan. 2013. Long-term effect of manure and fertilizer on soil organic carbon pools in dryland farming in northwest China. Plos One 8 doi:10.1371/journal.pone.0056536.

Meyerstein, D., and A. Treinin. 1961. Absorption spectrum of NO_3^- in solution. Trans. Faraday Soc. 57:2104–2112. doi:10.1039/tf9615702104

Moorcroft, M.J., J. Davis, and R.G. Compton. 2001. Detection and determination of nitrate and nitrite: A review. Talanta 54:785–803. doi:10.1016/S0039-9140(01)00323-X

Pabich, W.J., I. Valiela, and H.F. Hemond. 2001. Relationship between DOC concentration and vadose zone thickness and depth below water table in groundwater of Cape Cod, USA. Biogeochemistry 55:247–268. doi:10.1023/A:1011842918260

Qian, J.G., and K. Mopper. 1996. Automated high performance, high-temperature combustion total organic carbon analyzer. Anal. Chem. 68:3090–3097. doi:10.1021/ac960370z

Rattan, R.K., S.P. Datta, P.K. Chhonkar, K. Suribabu, and A.K. Singh. 2005. Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—A case study. Agric. Ecosyst. Environ. 109:310–322. doi:10.1016/j.agee.2005.02.025

Rieger, L., G. Langergraber, M. Thomann, N. Fleischmann, and H. Siegrist. 2004. Spectral in-situ analysis of NO_2, NO_3, COD, DOC and TSS in the effluent of a WWTP. Water Sci. Technol. 50:143–152.

Shaw, B.D., A. Tuli, J.-B. Wei, and J.W. Hopmans. 2010. Analytical modeling of soil solution monitoring by diffusion in porous cups. Transp. Porous Media 81:341–360. doi:10.1007/s11242-009-9404-3

Simunek, J., and J.W. Hopmans. 2009. Modeling compensated root water and nutrient uptake. Ecol. Modell. 220:505–521. doi:10.1016/j.ecolmodel.2008.11.004

Spalding, R.F., and M.E. Exner. 1993. Occurrence of nitrate in groundwater—A review. J. Environ. Qual. 22:392–402. doi:10.2134/jeq1993.00472425002200030002x

Tuli, A., J.W. Hopmans, T. Kamai and B.D. Shaw. 2013. In-situ soil nitrate ion concentration sensor. U.S. Patent 8,444,937 B2. Date issued: 21 May 2013.

Tuli, A., J.-B. Wei, B.D. Shaw, and J.W. Hopmans. 2009. In situ monitoring of soil solution nitrate: Proof of concept. Soil Sci. Soc. Am. J. 73:501–509. doi:10.2136/sssaj2008.0160

USEPA. 1977. National interim primary drinking water regulations. USEPA, Washington, DC.

USEPA. 1992. National survey of pesticides in drinking water wells. Phase II results. Office of Water, Office of Pesticides and Toxic Substances, USEPA, Washington, DC. ????NOT CITED???

Van Breemen, N. 1988. Effects of seasonal redox processes involving iron on the chemistry of periodically reduced soils. In: J.W. Stucki et al., editors, Iron in soils and clay minerals. Springer, New York. p. 797–809.

Viollier, E., P.W. Inglett, K. Hunter, A.N. Roychoudhury, and P. Van Cappellen. 2000. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. Appl. Geochem. 15:785–790. doi:10.1016/S0883-2927(99)00097-9

Weihermuller, L., J. Siemens, M. Deurer, S. Knoblauch, H. Rupp, A. Gottlein, and T. Pütz. 2007. In situ soil water extraction: A review. J. Environ. Qual. 36:1735–1748. doi:10.2134/jeq2007.0218

Wolt, J., and J.G. Graveel. 1986. A rapid routine method for obtaining soil solution using vacuum displacement. Soil Sci. Soc. Am. J. 50:602–605. doi:10.2136/sssaj1986.03615995005000030012x

Wolt, J.D. 1994. Soil solution chemistry. John Wiley & Sons, New York.