

International Meeting on Soil Fertility Land Management and Agroclimatology. Turkey, 2008. p:195-207

In situ Monitoring of Soil Solution Nitrate in Saturated and Unsaturated Sandy Soil

Atac Tuli^{1*}, Jing-Bin Wei², Ben Shaw², and Jan Hopmans¹

¹University of California, Dept. of Land, Air and Water Resources, Davis, CA 95616, U.S.A.

²University of California, Dept. of Mechanical and Aeronautical Engineering, Davis, CA 9561, U.S.A.

*atuli@ucdavis.edu; Fax: +1 530 752 5262; Phone: +1 530 752 1210

ABSTRACT

A lack of in-situ instrumentation limits continuous monitoring of soil solution concentration to evaluate environmental (contaminants) and agricultural management (plant nutrients) practices. We developed a prototype soil solution monitoring technique, to measure long-term in-situ nitrate concentration, consisting of an in-situ stainless-steel porous cup, with real time concentration measurements using a UV fiber-optic sensor and Ion Selective Electrode (ISE). 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 medium. The technique is presented for nitrate solution with sandy soil using new designed of solution samplers. Analytical solutions are presented to evaluate solute diffusion coefficients, as controlled by a variety of soil water contents. The principles of operation are demonstrated for diffusion a saturated and unsaturated Oso Flaco Sand, illustrating the potential application solution samplers in a soil environment.

INTRODUCTION

In-situ solution samplers are essential tools for water quality assessment in surface water, groundwater, as well as for vadose zone monitoring of agricultural and industrial chemicals, and for ecological monitoring of soil nutrients. There is increasing interest in detailed sampling of soil water solutions for soil ecological purposes, so as to better understand nutrient limitations in natural ecosystems (Simunek and Hopmans, 2008).

Several methodologies have been developed to measure concentrations of inorganic solutes in soils. The soil solution extraction is still the preferred method when a time series of solute concentration is required. However, the soil solution extraction can affect the concentration measurement directly by way of the suction applied (Grossmann and Udluft, 1991). Also, as pointed out by Essert and Hopmans (1998) and Poss et al. (1995), the magnitude of the applied suction will determine the soil pore sizes from which solution will be extracted, thereby affecting the measured soil solution concentration. Although ceramic solution cups are generally accepted as the material of choice for soil solution extraction (Weihermuller et al., 2007), these do have limitations. On the other hand, stainless steel porous cups are strong and durable comparison to ceramic cup with fragile nature, and porous steel materials are available with a wide range of air entry pressures, thus providing for an excellent alternative to ceramic cups.

An alternative approach to monitor soil solution concentration is by applying the passive diffusion technique introduced by Moutonnet et al. (1993), allowing for ionic equilibrium between the

solution inside the porous cup and the surrounding soil solution by ionic diffusion. Riga and Charpentier (1998) developed a mathematical method to estimate equilibrium time, and they showed that equilibration times for nitrate diffusion can be weeks, especially for unsaturated soils. After a field evaluation of both the diffusion and vacuum extraction method, Poss et al. (1995) concluded that both sampling devices are suitable for nitrate leaching monitoring, considering that the diffusion method provides for a much more time-integrated measurement.

Rather than by using soil solution extraction (Moutonnet et al., 1993) we present two alternative in-situ methodologies. The fiber optic measurements involved measuring ion levels in the water contained within the sampling cups with ultraviolet (UV) absorption spectroscopy techniques (Jaffe and Orchin, 1962; Knowles and Burgess, 1984). Ultraviolet spectroscopy has been employed for analysis of aqueous nitrate levels for several decades. Ultraviolet absorption spectroscopy has also been used to measure other ionic and nonionic species in water such as bromides and sucrose (Johnson and Coletti, 2002; Roig and Thomas, 2003), but has not been applied to date for in situ soil solution concentration measurements.

The other alternative in-situ methodology is to use ion-selective electrodes by inserting into solution sampler. Despite disadvantages such as electrode fouling, electrode drift, ion interference and frequent calibration requirement, and the need for temperature compensation, the ISE technology provides for a rapid and convenient method for soil nitrate concentrations after extraction of the soil solution (Dahnke, 1971).

The main objective of the study was to test the ionic diffusion method using both the ISE specific electrode and UV fiber optics technology for in-situ measurement of nitrate (NO_3^- -N) concentration. We used two types of stainless steel cups with different porosity and permeability values. Moreover, we compared the measured NO_3^- -N diffusion concentration inside the SS porous cups with two analytical models. We believe that in concept, the presented technology is an important step towards continuous, long-term deployment and real-time monitoring of NO_3^- -N soil solution concentration in situ.

MATERIAL and METHODS

The principal objective of this study was to experimentally test the diffusion equilibration method for nitrate, and to compare results with analytical solutions of diffusion in liquid, saturated and unsaturated sand. For this purpose, we monitored diffusion of nitrate across the porous wall of a stainless steel (SS) cup by way of either an ion-selective electrode (ISE) or by a UV adsorption method using fiber-optic technology in liquid and sandy soil conditions. We tested simple analytical solutions that were fit to the diffusion data, providing for solute diffusion coefficients from solution into the porous SS cup. The experiments were conducted for liquid diffusion across a range of outside reservoir volumes, for two

types of stainless steel porous cups of different grade and size, and for a saturated and unsaturated sandy soil.

The simple experimental set up consists of an inside reservoir with radius r_i (L) (excluding the porous wall) consisting of a stainless steel (SS) porous cup containing a known volume of deionized water where $C_i(r, 0) = 0$, and an outside reservoir of inside radius r_o (L), containing a known volume of NO_3^- -N solution at predetermined concentration (Fig. 1). We denote the outside radius of the SS cup as r_{iw} (L), to include the thickness of the SS cup wall. At $t = 0$, the stainless steel cup filled with de-ionized water was immersed into the reservoir filled with the NO_3^- -N solution. Diffusion experiments were terminated after the cup concentration was about 90 % of the final NO_3^- -N equilibration concentration (Riga and Charpentier, 1998).

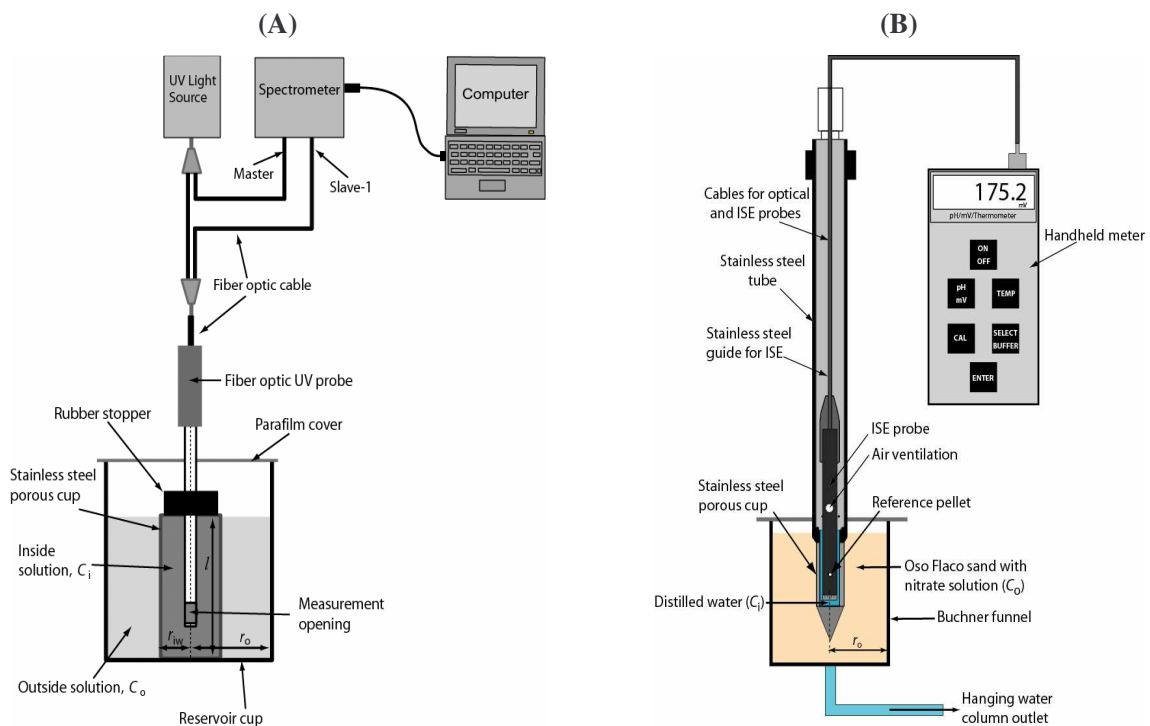


Figure 1. Schematic of the (A) fiber optic system and experimental set up in liquid and (B) ISE system with Oso Flaco Sand.

Electrical Circuit Analog (ECA) Model

A simplified model to predict the time-varying NO_3^- -N concentrations can be developed by way of using a simple electric circuit analog (Tuli et al., 2008). We denote the average NO_3^- -N concentrations inside and outside the porous cup as C_i (M L^{-3}) and C_o (M L^{-3}), respectively, with corresponding reservoir

volumes of V_i (L^3) and V_o (L^3), respectively. For simplicity, the volume of solution within the porous wall material can reasonably be assumed to be negligible.

The NO_3^- -N diffusion rate, J ($M T^{-1}$), is given by

$$J = \frac{C_o - C_i}{R_c}, \quad (1)$$

where R_c ($T L^{-3}$) is the overall resistance to diffusion through the liquids and across the porous cup. In addition, J can be identified as the time-rate-of-change of the average concentrations in the inner and outer reservoirs, or:

$$J = V_i \frac{dC_i}{dt} = -V_o \frac{dC_o}{dt}. \quad (2)$$

We require that mass is conserved, or

$$C_i V_i + C_o V_o = C_{ave} V_t, \quad (3)$$

where $V_t = V_i + V_o$ (L^3) and C_{ave} ($M L^{-3}$) is the average NO_3^- -N concentration after full equilibration, so that NO_3^- -N levels are the same everywhere. By combining Eqs. (1) - (3), an ordinary differential equation can be developed with subjecting to the initial condition $C_i(0) = 0$, leading to $C_{ave} = C_o(0)/(1 + V_i/V_o)$, where $C_i(0)$ and $C_o(0)$ are the NO_3^- -N concentrations at the time $t = 0$. The solution of ordinary differential equation can then be written as:

$$\ln\left(1 - \frac{C_i}{C_{ave}}\right) = -at, \quad (4)$$

so that a plot of $\ln(1 - C_i/C_{ave})$ as a function of time, t , yields a straight line with slope $-a$. By measuring the slope of the data, which determines the variable a , the overall resistance to NO_3^- -N diffusion can be computed. This overall wall resistance can be related to the effective diffusion coefficient of the porous cup to NO_3^- -N by assuming that NO_3^- -N diffusion through the wall is quasi-steady, and by solving Laplace's equation in cylindrical coordinates (Incropera et al., 2007).

$$R_c = \frac{\ln(r_{iw} / r_i)}{2\pi l D_E}, \quad (4)$$

where l is inside height of the SS cup. Substituting Eq. (4) into $a = (V_i / R_c V_i V_o)$, we can compute the effective diffusion coefficient, D_E , using that incorporates both liquid diffusion and diffusion through the porous cup ($L^2 T^{-1}$). We note that r_{iw} and r_i are the outside and inside radius of the stainless steel porous cup, respectively.

Riga and Charpentier (RC) Model

The analytical solution introduced by Riga and Charpentier (1998) was used assuming a constant spatial diffusion coefficient across the inside and outside reservoir, neglecting the reduced diffusion

across the porous cup wall. This analytical solution also assumes radial symmetry across the inside cup and outside reservoir. The initial uniform concentration inside the porous cup ($t = 0$), C_i , is brought into instantaneous contact with an infinite and homogeneous cylindrical source with concentration C_o ($C_o > C_i$). The general solution is given as Eq. (3.10) in section 3.2 of Crank (1975). With $C_i = 0$, the concentration change in the center of the cup can be written as (Riga and Charpentier, 1998)

$$\frac{C(0,t)}{C_o} = \exp(-r_{iw}^2/4D_E t) \quad (10)$$

where D_E is effective diffusion coefficient ($L^2 T^{-1}$), r_{iw} is the outside radius of the stainless steel cup (L), and $C(0,t)$ denotes the NO_3^- -N concentration ($M L^{-3}$) as a function of time in the center of the cup, with $0 \leq t \leq \infty$. The effective diffusion coefficient of the experimental system with the porous cup was treated as a fitting parameter, to be estimated using the MS Excel solver (Wraith and Or, 1998), minimizing the objective function consisting of the sum of the squared error between independently-measured concentrations and model output.

Nitrate Measurements

Ultraviolet (UV) Absorption Spectroscopy

Ion concentration levels in solution were analyzed using ultraviolet (UV) absorption spectroscopy techniques (Jaffe and Orchin, 1962; Knowles and Burgess, 1984). When light passes through a sample, the light interacts with atoms and molecules in its path by scattering and absorption, with absorption occurring at specific wavelengths corresponding to transitions between different energy levels.

The optical system used in these experiments could measure UV-VIS absorption spectra from about 200 nm to 700 nm. For the NO_3^- -N concentration range between 0 and 100 $mg L^{-1}$, we used absorbance spectra in the wavelength range 235 nm to 240 nm, which provided accurate results while still allowing strong (but not saturated) signals with minimum detectable values of about 1 $mg L^{-1}$. Figure 2 shows absorbance spectra over this range. By using these spectral data, calibration data were obtained to relate the absorbance at a given wavelength to the amount of NO_3^- -N present in the sample. The absorbance measurements of our study were done with a fiber optic T300-RT-UV-VIS transmission (where VIS denotes visible) dip probe that was obtained from Ocean Optics. A Heraeus FiberLight UV source was used to provide light for the measurements and a two-channel Ocean Optics SD-2000 UV-VIS spectrometer was used for spectrum analysis (Figure 1A). The dip probe included a reference fiber to correct for light intensity fluctuations of the light source.

Ion Selective Electrode (ISE) Method

The Ion Selective Electrode (ISE) method is a relatively simple and inexpensive analytical tool for measuring specific ion concentrations in the presence of other ions. An ISE converts the activity of a specific ion dissolved in a solution into an electrical potential to be measured by a handheld millivolt (mV) meter (Figure 1B). The electrical voltage is theoretically dependent on the logarithm of the ionic activity based on the Nernst equation (Durst 1969). For practical use, an ISE should be calibrated using KNO_3 solutions with concentrations between 1 and 100 mg L^{-1} NO_3^- -N as standard solutions. The ISE must be calibrated using standard solutions before each measurement.

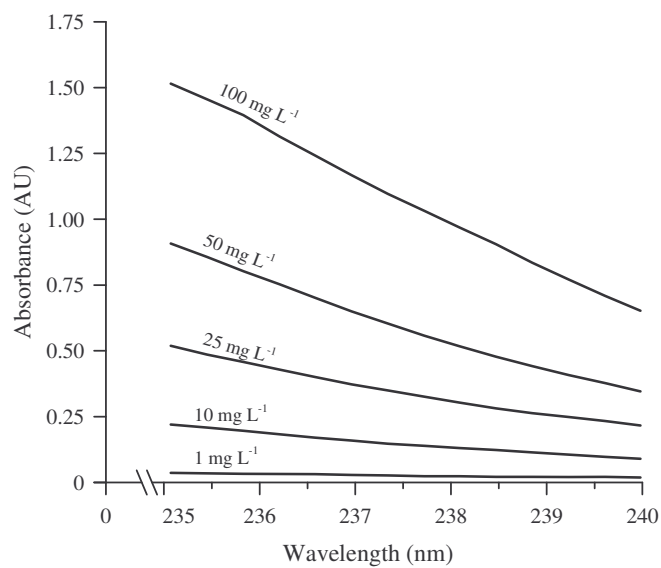


Figure 2. Plot of NO_3^- -N absorbance spectra between 235 and 240 nm.

Ion Diffusion in Liquid Phase (experiments 1 through 6)

To investigate the size effect of the reservoir cup to the diffusion of NO_3^- -N solution, experiments 1 through 4 (Table 1) were conducted for a range of ratio values, as defined by outside radius (r_{iw}) of a SS cup divided by radius of outside reservoir (r_o), or $r_{iwo} = r_{iw}/r_o$. This set of experiments was chosen to establish a range of diffusion equilibration times for the same SS Cup I (OD. 0.0191 m, ID. 0.0157m, inside height 0.0376 m) with a porosity of $0.15 \text{ m}^3 \text{ m}^{-3}$. Values for r_{iwo} were 0.82, 0.50, 0.31, and 0.16. This range in r_{iwo} values was obtained by changing the outside reservoir cup (Fig. 1A) with the desired diameter cup. For each of the 4 experiments, we filled the outside reservoir with a predetermined volume (V_o) of 50 mg L^{-1} NO_3^- -N solution (using KNO_3). Subsequently, the SS cup was filled with distilled water and placed in the center of the outside reservoir at $t = 0$. For $t > 0$, the concentration changes inside the SS cup as caused by diffusion were monitored continuously using the UV dip probe (Figure 1A). The

reservoir was covered with parafilm to prevent evaporation during the diffusion experiments. In experiments 5 and 6, we tested the ISE probe for SS Cup I with r_{iwo} values of 0.58 and 0.77 and using a 25 mg L⁻¹ NO₃-N solution as the outside reservoir concentration.

Ion Diffusion in Saturated and Unsaturated Sand (Experiments 7, 8, and 9)

To compare nitrate (NO₃-N) concentration measurements in soil between UV and ISE probes, a diffusion experiment was conducted for a saturated sand (experiments 7 and 8 with volumetric water content of 0.434 m³ m⁻³) with 100 mg L⁻¹ NO₃-N solution. Oso Flaco fine sand was wet-packed with nitrate (NO₃-N)

solution in a Buchner funnel to a final bulk density of 1,500 kg m⁻³, resulting in an outside solution reservoir volume of 756 ml (Table 1). The Buchner funnel was covered to prevent evaporation. For the unsaturated case (experiment 9), 0.37 m suction was applied to the sample through a ceramic barrier at the bottom of the Buchner funnel, resulting in a volumetric water content of 0.347 m³ m⁻³. At $t=0$, Cup II (OD. 0.0193 m, ID. 0.0154 m, inside height 0.0476 m) with a porosity of 0.19 m³ m⁻³ was filled with 12 ml distilled water and the change in concentration with time was monitored at different time intervals by lowering the ISE into the porous cup at predetermined time intervals (Figure 1B).

Table 1. Parameters for all presented diffusion experiments.

Experiment	Probe	Medium	SS Cup Type	r_{iwo}	r_o	V_i	V_o	V_t	C_o	C_{ave}	R_c	$t_{1/2}^\ddagger$	t_{95}^\ddagger
					cm	ml	ml	mg L ⁻¹	s ml ⁻¹	h	h		
1	UV	Liquid	Cup I	0.16	6.03	5.5	363.5	369.0	50	49.3	28984.2	30.2	131.1
2	UV	Liquid	Cup I	0.31	3.03	5.9	100.5	106.4	50	47.2	21513.7	23.1	100.4
3	UV	Liquid	Cup I	0.49	1.93	5.1	29.7	34.8	50	42.7	21095.3	17.7	76.2
4	UV	Liquid	Cup I	0.82	1.17	5.2	5.2	10.4	50	24.9	23324.5	11.7	50.1
5	ISE	Liquid	Cup I	0.58	1.64	4.5	21.6	26.1	25	20.7	11399.8	8.2	35.6
6	ISE	Liquid	Cup I	0.77	1.24	7.3	7.7	15.0	25	12.8	10452.3	7.5	32.6
7	ISE†	Sand	Cup II	0.12	7.80	11.9	755.6	767.5	100	98.4	11535.8	26.0	112.6
8	UV†	Sand	Cup II	0.12	7.80	11.9	755.6	767.5	100	98.4	11923.8	26.9	116.4
9	ISE	Sand	Cup II	0.12	7.80	11.9	604.1	616.0	100	98.1	36666.0	82.4	356.1

† Both probes were used in the same experiment; ‡ Time for concentration at 50 and 95 % level of the final concentration

RESULTS and DISCUSSION

Diffusion in Liquid Phase by ISE and UV Spectroscopy

In a set of experiments 1 through 4, we tested the diffusion equilibration method using both the RC (Riga and Charpentier, 1998) and ECA (Electrical Circuit Analog) model, and estimated the effective diffusion coefficient for nitrate (NO₃-N) in water solution using 4 sizes of outside reservoirs with radii, r_o , varying from 6.03 to 1.17 cm, with the same SS cup with inside (r_i) radius of 0.79 cm and wall thickness of 0.17 cm. Thus, as r_o is smaller, the r_{iwo} ratio increases from 0.16 to 0.82 (fifth column of Table 1). The diffusion coefficients were estimated for each r_{iwo} value for both analytical solutions, using

the parameters listed in Table 1. The results for the time-change in concentration in the SS cup are presented in Fig. 3 for each of the 4 ratios. As r_{iwo} decreases, both the average equilibration concentration, C_{ave} , and the equilibration time will increase, because of the corresponding increase in the outside reservoir size.

To confirm such conclusions, we calculated the half-life ($t_{1/2}$), and time to 95 % of the final equilibration concentration (t_{95}) for all diffusion experiments in Table 1. The half-life is independent of the concentration gradient and provides for an objective time constant of the diffusion process. As is intuitively clear, the presented $t_{1/2}$ -values increase with decreasing r_{iwo} values, or as the outside reservoir is larger in diameter. The RC model provides for a point solution ($r = 0$) in the center of the SS cup, whereas the ECA solution focuses on average liquid concentration. However, we should realize that the sensor tip of both the ISE and UV probe are of finite sizes (O.D. 1.23 cm for ISE and O.D. 0.635 cm for UV probe), so that the measurements are likely a better approximation to the ECA model, as the measurement volumes of both probes are relatively large, thereby violating the point solution of the RC model.

Table 2. Estimated D_E values and their goodness of model fit.

Experiment	Probe	Medium	r_{iwo}	ECA Model			RC Model		
				$D_E, \text{cm}^2/\text{s}$	R^2	SE, mg L^{-1}	$D_E, \text{cm}^2/\text{s}$	R^2	SE, mg L^{-1}
1	UV	Liquid	0.16	0.026×10^{-5}	0.99	1.49	0.286×10^{-5}	0.99	2.15
2	UV	Liquid	0.31	0.034×10^{-5}	0.99	0.97	0.370×10^{-5}	0.98	2.19
3	UV	Liquid	0.49	0.039×10^{-5}	1.00	0.49	0.462×10^{-5}	0.95	2.61
4	UV	Liquid	0.82	0.031×10^{-5}	0.99	0.89	0.281×10^{-5}	0.90	2.58
5	ISE	Liquid	0.58	0.070×10^{-5}	0.98	0.79	0.860×10^{-5}	0.97	0.97
6	ISE	Liquid	0.77	0.076×10^{-5}	0.96	0.77	0.469×10^{-5}	0.67	2.50
7	ISE [†]	Sand	0.12	0.063×10^{-5}	1.00	1.80	0.421×10^{-5}	0.97	5.87
8	UV [†]	Sand	0.12	0.061×10^{-5}	1.00	3.22	0.371×10^{-5}	0.96	5.64
9	ISE	Sand	0.12	0.020×10^{-5}	0.99	1.12	0.150×10^{-5}	0.87	4.01

[†] Both probes were used in the same experiment

Overall, by visual inspection, the ECA model fits the measured concentrations better than the RC model, especially at later times. As expected, the ECA solutions and the experimental data should approach C_{ave} at long times, simply from the principle of mass balance, whereas the RC solution will approach to C_o . Therefore, one would expect that the D_E values for the ECA model are more representative than those estimated using the RC model. However, both models incorporate the increasing cup resistance to diffusion, thereby reducing D_E , relative to that of the diffusion coefficient of nitrate (NO_3^- -N) in water, D_o , only. We note that D_o for nitrate is $1.902 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Vanysek, 2008), whereas D_E values vary from 0.026 - $0.039 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (ECA model) and 0.28 - $0.46 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (RC model),

respectively. The effective diffusion coefficients values, estimated from the ECA and RC model are presented in the fifth and eighth columns of Table 2. The values of diffusion coefficients from both models are about one order-of-magnitude different. Also, the standard error of the predictions (SE) were consistently lower for the ECA model predictions than for the RC model, indicating that the ECA model produces better fitting results. Both diffusion models are affected by the size of the outside reservoir, as quantified by r_{iwo} (Table 2). Regarding the ECA-model, we expect that the resistance to diffusion (R_c) will increase with lower r_{iwo} values (higher r_o), leading to lower values of D_E . In a subsequent set of experiments 5 and 6, we evaluated diffusion using the ISE electrode (Tables 1 and 2). Estimated D_E values were about 2 to 3 times larger as compared to the UV measurements. We concluded that various factors can explain this difference. First, diffusion by the fiber optics method is expected to be smaller, because of the partial shielding of the sensor tip, which can account for about 30 % of the difference. This partial shielding will inhibit diffusion of nitrate ions to the sensor element, thereby decreasing the estimated diffusion coefficient. Moreover, as the sensor diameter of the ISE is about twice as large as that of the UV, one would expect higher and more accurate diffusion coefficient values, as measured with the ISE sensor, because it provides better measurement of the average concentration of the SS cup.

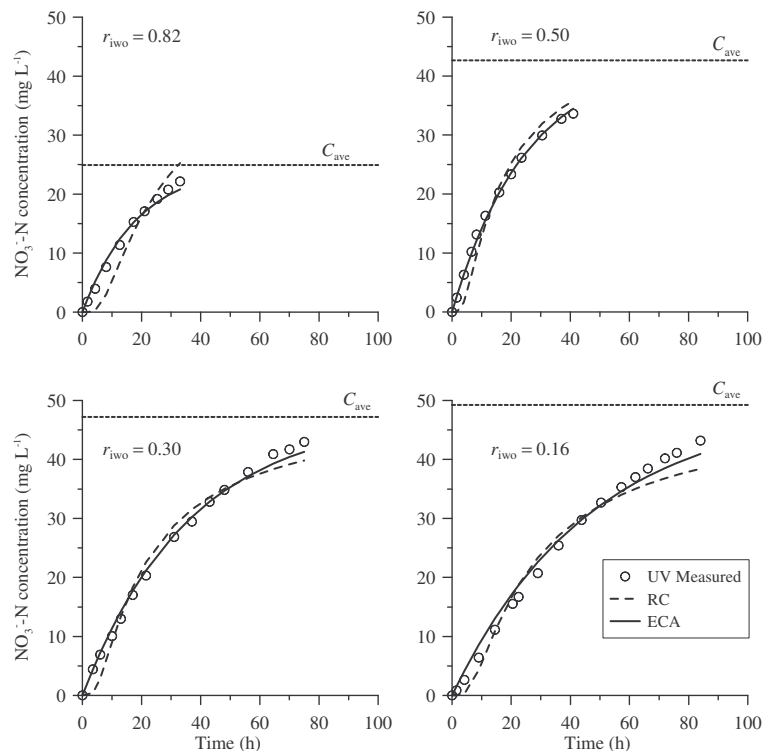


Figure 3. Model fitting of RC and ECA models to nitrate concentration data for different r_{iwo} values (Experiments 1 through 4).

Diffusion in Saturated and Unsaturated Soil by ISE and UV Spectroscopy

Using SS Cup type II and a soil solution concentration of $100 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ solution, both the UV and ISE probe were compared in experiments 7 and 8, to determine nitrate ($\text{NO}_3\text{-N}$) diffusion for the saturated Oso Flaco sand (Fig. 6). At approximately equal times, both probes were inserted sequentially into the SS cup one after the other for solution nitrate ($\text{NO}_3\text{-N}$) measurements. Both the RC and ECA model were fitted to the experimental data for ISE (Fig. 4A) and UV method (Fig. 4B). Both probes produced similar results of concentration changes as a function of time. This can be expected since both probes were mixing the cup contents when they were inserted and removed. At unsaturated conditions (experiment 9), the ECA model was produced better fitting results than the RC model (Fig 4C).

Fitting results (Table 2) of the ECA model were excellent for saturated sand ($R^2 = 1.0$ and $SE = 1.80$ and 3.22) for both probes and unsaturated sand ($R^2 = 0.99$ and $SE = 1.12$), whereas the RC model underestimated the measured data at early times and overestimated at later times (Fig 4). The half-life time, $t_{1/2}$, and calculated time required for t_{95} were quite similar for both probes (Table 2). The half-life time at unsaturated condition is much longer than saturated sand indicating proportional increase in equilibration time for unsaturated soils, as ion diffusions in partially-saturated soils are controlled by the degree of saturation and the pore water tortuosity (Tuli et al., 2004). The estimated diffusion coefficient values as determined by ISE and UV measurements were nearly identical, with slightly lower values using the RC model. Intuitively, one would expect the diffusion coefficient of nitrate in the saturated sand to be lower than for the liquid solution. However, the fitting results produced equal or larger D_E values for the sand diffusion experiments. We provide two reasons. First, it is very likely that the porous steel only is controlling nitrate diffusion into the SS cup, as its porosity is much smaller than for the sandy soil (Table 1). Second, the porosity of SS cup II is higher than of cup I (0.15 versus $0.19 \text{ cm}^3 \text{ cm}^{-3}$). As the diffusion expressions (Jury et al., 1991) predict, diffusion is proportional to porosity, thus partly explaining the higher diffusion coefficient and lower diffusion resistance (Table 1) values for SS Cup II. As before, the slightly lower D_E values as determined with the UV method are likely caused by the partial blocking of the sensor tip. The estimated diffusion coefficient of unsaturated sand was much lower than saturated sand due to the increasing diffusion resistance (Table 1) and tortuosity of for the diffusion (Tuli et al., 2004).

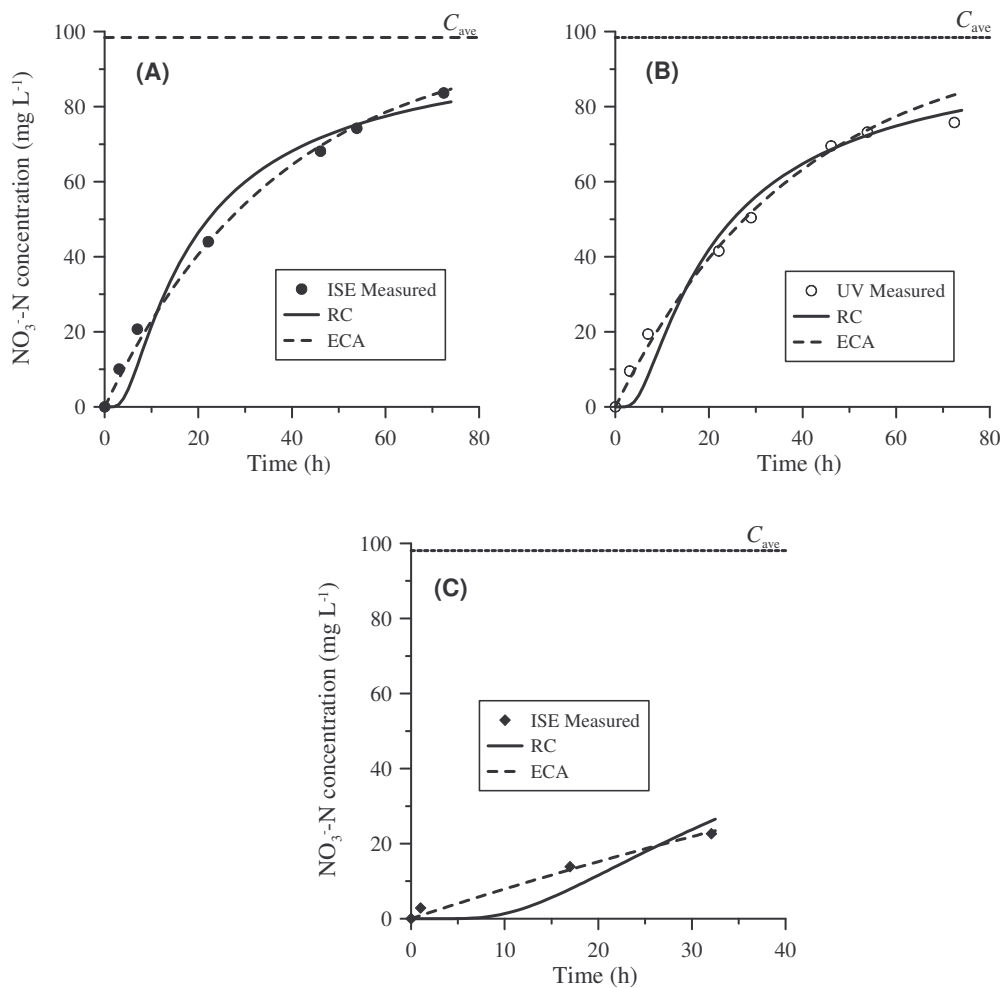


Figure 4. Fitting of RC and ECA models to nitrate diffusion as measured (A) ISE, (B) UV probes (Experiments 7 and 8 at saturation) and (C) ISE (Experiment 9 at unsaturated conditions).

CONCLUSIONS

We propose that continuous long-term deployment and real-time monitoring of the soil solution can be accomplished with both UV fiber optic technology and ion specific electrode measurements. The results for solution nitrate showed that the UV and ISE probes produced similar successful results for Oso Flaco sand. To evaluate the concept of the diffusion equilibration method, the effective diffusion coefficient of nitrate was determined by fitting experimental diffusion data to two analytical model solutions. Both the Electrical Circuit Analog (ECA) and the Riga and Charpentier (1998) (RC) model generally fitted the experimental data, but resulted in nitrate diffusion coefficients that were about one order of magnitude different between the two theoretical diffusion models. We concluded, however, that the performance of the ECA model was significantly better than the RC model. The calculations showed

that increasing the outside cup radius significantly increased the half-life time and overall resistance to molecular diffusion, thereby lowering the values of the fitted nitrate diffusion coefficient. In concept, we showed that the application of UV technology can be used for real-time monitoring of nitrate ($\text{NO}_3\text{-N}$) concentration in soil solution.

REFERENCES

- Crank, J. 1975. The mathematics of diffusion. 2d ed. Clarendon Press, Oxford, Eng.
- Dahnke, W.C. 1971. Use of the nitrate specific ion electrode in soil testing. *Soil Sci. and Plant Anal.*, 2:73-84.
- Durst, R.A. 1969. Ion-selective electrodes. Proceedings of the Nat. Bureau of Standards Symposium. January 30-31, 1969, Gaithersburg, MA. 452 pages.
- Essert, S, and J.W. Hopmans. 1998. Combined tensimeter-solution sampling probe. *Soil and Tillage Res.* 45(3):299-309.
- Grossmann, J., and P. Udluft. 1991. The Extraction of Soil-Water by the Suction-Cup Method - a Review. *Journal of Soil Science* 42:83-93.
- Incropera, F.P., D.P. DeWitt, T.L. Bergman, and A.S. Lavine. 2007. Fundamentals of heat and mass transfer. John Wiley and Sons, Inc., Hoboken.
- Jaffe, H.H., and M. Orchin. 1962. Theory and applications of ultraviolet spectroscopy. John Wiley and Sons, Inc., New York.
- Johnson, K.J., 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 Research Part I – Oceanographic Res. Let.* 49: 1291-1305.
- Jury, W.A., W.R. Gardner, and W.H. Gardner. 1991. *Soil Physics*, John Wiley & Sons, Inc., New York.
- Knowles, A. and C. Burgess. 1984. *Practical absorption spectrometry*. Chapman and Hall, London.
- Kim, H.J., J.W. Hummel, K.A. Sudduth and P.P. Motavalli. 2007. Simultaneous analysis of soil macronutrients using ion-selective electrodes. *Soil Sci. Soc. Am. J.* 71:1867-1877.
- Moutonnet, P., J.F. Pagenel, and J.C. Fardeau. 1993. Simultaneous field measurement of Nitrate-Nitrogen and matric pressure head. *Soil Sci. Soc. Am. J.* 57:1458-1462.
- Poss, R., A.D. Noble, F.X. Dunin and W. Reyenga. 1995. Evaluation of ceramic cup samplers to measure nitrate leaching in the field. *Eur. J. Soil Sci.* 46:667-674.
- Riga, P. and S. Charpentier. 1998. Ionic-equilibrium time inside ceramic cups in unsaturated porous media. *Soil Sci. Soc. Am. J.* 62:574-579.
- Roig, B. and O. Thomas. 2003. UV monitoring of sugars during wine making. *Carbohydrate Research* 338:79-83.

- Simunek, J., and J.W. Hopmans. 2008. Compensated root water and nutrient uptake. *Ecological Modeling*. (Submitted).
- Tuli, A. and J.W. Hopmans. 2004. Effect of degree of fluid saturation on transport coefficients in disturbed soils. *European Journal of Soil Science*, 55: 147-164, doi: 10.1046/j.1365-2389.2003.00551.x .
- Tuli, A., J.B. Wei, B.D. Shaw and J.W. Hopmans. 2008. In situ monitoring of soil solution nitrate: Proof of concept. *Soil Sci. Soc. Am. J.* (Submitted).
- Vanysek, P. 2008. Ionic conductivity and diffusion at infinite dilution., In *CRC Handbook of Chemistry and Physics*, 88th Edition (Internet Version 2008), David R. Lide, ed., CRC Press/Taylor and Francis, Boca Raton, FL.
- Weihermuller, L., J. Siemens, M. Deurer, S. Knoblauch, H. Rupp, A. Gottlein, and I. Putz. 2007. In situ soil water extraction: A review. *J. Env. Qual.* 36:1735-1748.
- Wraith, J.M., and D. Or. 1998. Nonlinear parameter estimation using spreadsheet software. *J. Nat. Resour. Life Sci. Educ.* 27:13-19.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation Biocomplexity program by the funded proposal 0410055 - Development of Multi-Functional Heat Pulse Probe for Ecological and Soil Hydrological Monitoring of Plant Root Zones.