

## CHLORIDE MASS BALANCE TO DETERMINE WATER FLUXES BENEATH KCl FERTILIZED CROPS

J. S. Tyner, G. O. Brown, J. R. Vogel, J. Garbrecht

**Abstract.** *The utilization of Chloride Mass Balance (CMB) to determine water fluxes has generally been restricted to applications in arid to semi-arid environments, because only in such environments does the chloride deposited by precipitation and dry fallout concentrate sufficiently by evapotranspiration for accurate measurement. This study successfully applied CMB to dryland winter wheat plots with 860 mm of precipitation per year. Soil cores were collected from long-term dryland winter wheat test plots located near Stillwater, OK, which had known, constant applications of the fertilizer KCl for the past 29 years. This additional chloride was sufficient to allow for accurate chloride concentration measurement. Groundwater recharge rates of 12.2 to 38.9 mm/yr were calculated with recharge increasing with fertilizer N. These fluxes may be overestimated by up to 20% based on anion exclusion measurements from adjacent soil cores. Numerical modeling of the chloride distributions beneath the plots supported the assumptions of CMB.*

**Keywords.** *chloride mass balance, wheat, groundwater recharge*

In 1997, Oklahoma winter wheat production covered 5.4 million acres or 58% of the total harvested acreage and 12% of the total state area (Oklahoma Agricultural Statistics Service, 1998). As elsewhere, the threat of nitrate groundwater contamination from fertilizer has been a concern for many years. As part of an effort to estimate the nitrate flux from winter wheat production, Chloride Mass Balance (CMB) was employed to estimate the water flux beneath the root zone. It is assumed all downward water and solute flux beyond the reach of plant roots will ultimately reach the groundwater table. Thus, the mass flux of any conservative solute such as nitrate, may be computed as the product of its soil water concentration and the downward water flux. Nitrate concentrations are relatively easy to measure, however the water flux is difficult to accurately quantify using traditional methods.

A commonly applied method to estimate recharge is a hydrologic water balance, but the evapotranspiration component is difficult to estimate. Also, when recharge is small compared to precipitation a poor evapotranspiration estimate can lead to relatively large errors in computed recharge. Another method to estimate recharge relies on using suction lysimeters to measure soil suction vertically within the unsaturated soil column. Soil suction along with estimates of the unsaturated hydraulic conductivity allows the application of the Buckingham flux law (Buckingham, 1907). Again estimation errors arise in the presence of low recharge rates since the difference in head between lysimeters at varying depths may be relatively small and because

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hydraulic conductivity is so strongly dependent on the soil suction. Under such conditions a tracer method such as CMB is more promising.

The objectives of this study are to estimate the water flux beneath the root zone beneath experimental winter wheat plots using CMB, and to verify assumptions of CMB by numerical modeling of the measured field conditions. The estimation of the water flux allows for the subsequent assessment of the potential for groundwater contamination by nitrates under fertilized winter wheat plots. To this end, 2.5 m deep soil cores were collected from long-term dryland winter wheat (*Triticum aestivum* L.) test plots located near Stillwater, OK. The soil cores were evaluated for water content, bulk density, and chloride concentration at various depths. By equating the chloride mass flux at the surface to the chloride mass flux at depth, CMB provides estimates of the vertical downward water flux beneath the experimental winter wheat plots. Each test plots had identical management for the previous 29 years with the exception of four different nitrogen fertilizer application rates (0, 45, 90, 135 kg/ha/yr of N). The results of different N application are visibly apparent with the zero N application wheat plots being small and yellowish, while the 90 and 135 N application wheat plots are lush and dark green. Utilization of CMB on the four different groups of fertilizer application rate plots allows a comparison of groundwater recharge between healthy and N limited winter wheat crops. The water flux was also numerically modeled for the conditions of the experimental winter wheat plots to help validate assumptions of CMB.

### **The Long Term Plots**

Long-term winter wheat fertility tests were established at the Oklahoma State University (OSU) Agricultural Research Station in 1969. Since then, continuous dryland winter wheat has been cultivated on 6.1 m by 18.3 m plots in Kirkland clay loam (fine, mixed, thermic Udertic Paleutoll). The plots are located in a topographically high location, which prevents runoff. To minimize cross plot contamination, the plots were disked parallel to the plot length and approximately perpendicular to the slope. The area receives an average of 860 mm of precipitation per year and the groundwater table is at a depth of approximately 5 m. Figure 1 shows typical values for percent sand, percent clay, and bulk density versus depth from soil cores collected in this study. While variations of the particle size distributions with depth are present, no discrete textural layers were discernable by visual inspection. Similarly, textural variations were not constant between cores.

Plots are grouped by fertilizer application rate (A, B, C, and D), with each group having four replications. Treatments and replicate test plots were placed in a random pattern throughout a single field. The test plot groups and corresponding fertilizer application rates are given in Table 1. The N, P, and K sources for the sixteen plots are  $\text{NH}_4\text{NO}_3$  (34-0-0), triple superphosphate (0-20-0), and KCl (0-0-56), respectively (Raun and Johnson, 1995).

Prior to the establishment of the winter wheat fertility tests in 1969, the fields were used from 1957 to 1968 for winter wheat production and fertilized as shown at the bottom of Table 1. Prior to 1957 the use of the land is unknown, but it is likely that wheat or legumes were grown without fertilization or irrigation after its first cultivation in approximately 1890. Also listed in Table 1 are the average grain yields from 1993, which represent typical current yields for the test plots. The reason winter wheat yield can be sustained with zero N application (Group A plots) has previously been studied on adjacent test plots. In those plots there has been no N fertilization for 100 years and the plant N source is primarily supplied by mineralization of soil organic matter, which has declined from 3.7 to 1.0% by dry weight (Bowman, et. al., 1996).

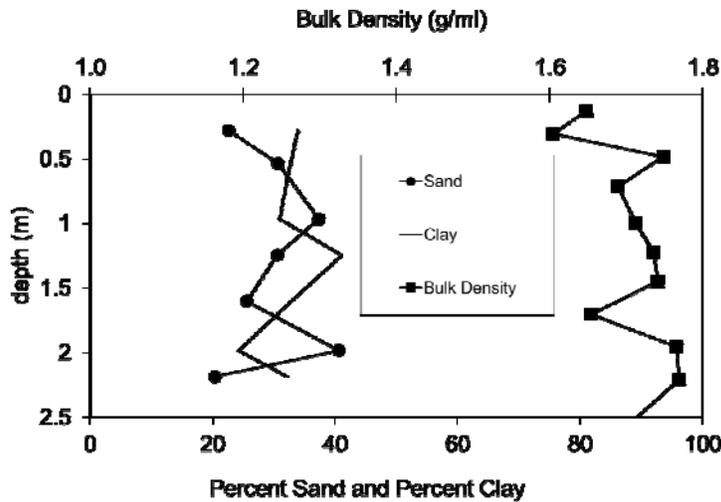


Figure 1 – Typical soil texture and bulk density.

Table 1. Test Plot Fertilizer Treatments.

Plot Groups	Fertilizer Applied 1969 to Present (kg/ha/yr)			Grain Yield (kg/ha/yr)
	N	P	K / Cl	
A	0	29	38 / 34.4	1480
B	45	29	38 / 34.4	1870
C	90	29	38 / 34.4	1930
D	134	29	38 / 34.4	1970
A,B,C,D	Fertilizer Applied 1957 to 1968 (kg/ha/yr)			Grain Yield
	54	22	0 / 0	Unknown

### Soil Sampling

After the 1997 and 1998 wheat harvests, 67 mm diameter continuous soil cores were collected to a depth of approximately 2.5 m using a hydraulic soil sampler in direct push mode. Brown et al. (1994) have previously shown that this sample size and collection method is adequate to describe the density variation of the soil matrix. The cores were cut into 50 mm long samples and then further split longitudinally into two sub-samples. The first sub-sample was used to measure gravimetric moisture content (ASTM, 1993). Soluble pore water extracts were obtained from the second sub-sample using a 1:1 soil-deionized water extract (Mulvaney, 1996). The chloride concentration of the extract was measured by ion chromatography using a Dionex 2000i. Attempts to extract pore water by high-speed centrifugation were generally unsuccessful due to the relatively low water content and high clay content of the samples. Sections of the core not used for other analyses were used to determine bulk density using the Clod Method (Blake and Hartage, 1986).

### CMB Theory

CMB has been applied extensively to estimate groundwater recharge in arid regions (Bresler, 1973; Allison et al., 1985; Johnston, 1987; Phillips, 1994; Tyner, 1998). It equates the mass flux of chloride at the ground surface to the mass flux of chloride beneath the depth of evapotranspiration. Chloride is applied naturally at the soil surface from precipitation and dry

fallout. Under steady state, 1-D flow, the chloride mass flux at any depth will equal the chloride mass flux at the surface. Scanlon (1991) defines the chloride mass flux under steady state conditions by

$$\dot{m} = -D \frac{dC}{dz} + Cq \quad (1)$$

Solving for  $q$  yields the volumetric water flux

$$q = \frac{1}{C} \left[ \dot{m} + D \frac{dC}{dz} \right] \quad (2)$$

where  $q$  is the volumetric water flux,  $C$  is the pore water chloride concentration,  $\dot{m}$  is the chloride mass flux,  $D$  is the hydrodynamic dispersion coefficient, and  $z$  is the vertical space coordinate. As water moves downward through the soil profile, some of it is removed by evapotranspiration, reducing the water flux and causing the remaining pore water chloride to become increasingly concentrated. Thus, equation (2) is normally applied beneath the root zone where no additional water is removed by evapotranspiration. In arid regions, it is often assumed that  $D$  is negligible (Allison et al., 1985, Phillips, 1994) and equation (2) simplifies to

$$q = \dot{m}/C \quad (3)$$

The pore water age at a given depth can be calculated by dividing the mass of chloride in the profile above that depth by the surface chloride mass flux

$$t_z = \frac{\int_0^z \theta C dz}{\dot{m}} \quad (4)$$

where  $t_z$  is the pore water age at a depth of  $z$  and  $\theta$  is the volumetric moisture content (Phillips, 1994).

In this study the sum of chloride from fertilizer and precipitation minus the chloride removed by harvesting was used to determine the net amount of chloride applied to the plots annually. The primary source of chloride for the test plots was an annual application of KCl that added 34.4 kg/ha/yr of chloride. Precipitation added approximately 1.65 kg/ha/yr of chloride (NADP/NTN, 1983). Precipitation input was estimated by multiplying the average precipitation chloride concentration with the annual precipitation rate. Crop harvesting resulted in losses of 0.8 to 1.1 kg/ha/yr of chloride. These losses were calculated by multiplying the chloride concentration in the wheat grain (Engel et al., 1998) by the annual wheat grain harvest. Normally CMB is only applied in arid and semi-arid regions that exhibit very low groundwater recharge (i.e. high chloride concentrations). In areas with higher recharge rates, the chloride concentration is generally too low to be measured accurately. We were able to apply CMB in this sub-humid area with 860 mm of precipitation per year (Myers, 1982) because of the relatively large amount of chloride that was artificially added by fertilization.

### CMB Assumptions

Assumptions of CMB include: 1) vertical downward piston displacement adequately represents the chloride transport (i.e. little to no preferential flow), 2) chloride is not retarded by adsorption nor accelerated by anion exclusion, 3) chloride is conservative, 4) chloride application rate is constant and known, 5) there is no appreciable runoff or runoff from the sampling sites, and 6) steady state conditions prevail in the soil column (Johnston, 1987; Dettinger, 1989; Scanlon 1992; USGS, 1994; Ginn and Murphy, 1997).

### Assumption 1

Violation of assumption 1 can occur at two scales, a small scale (smaller than the sample size), and a large scale (larger than the sample size). If preferential flow occurs at a small scale, CMB will yield a result equal to the volumetrically weighted harmonic mean of the individual water fluxes within the sample measured. This can be shown with the knowledge that pore water extracted from a soil sample by dilution results in a chloride concentration of

$$C = \frac{\sum_{i=1}^n \theta_i F_i C_i}{\sum_{i=1}^n \theta_i F_i} \quad (5)$$

where  $\theta_i$  and  $C_i$  are the volumetric water content and pore water chloride concentration of the  $i^{th}$  flowpath within the sample respectively, and  $F_i$  is the volume of the  $i^{th}$  flowpath within the sample divided by the total volume of the sample. Substituting equation (5) into equation (3) results in

$$q_{CMB} = \frac{\dot{m} \sum_{i=1}^n \theta_i F_i}{\sum_{i=1}^n \theta_i F_i C_i} \quad (6)$$

where  $q_{CMB}$  is the water flux calculated using CMB. Assuming that  $\dot{m}$  is constant across an area and no mixing between flow paths occurs, then equation (3) can be inverted and generalized to show

$$C_i = \dot{m} / q_i \quad (7)$$

where  $q_i$  is the water flux of the  $i^{th}$  flowpath.

Substituting equation (7) into equation (6) results in

$$q_{CMB} = \frac{\sum_{i=1}^n \theta_i F_i}{\sum_{i=1}^n \frac{\theta_i F_i}{q_i}} \quad (8)$$

which is equivalent to the volumetrically weighted harmonic mean of the fluxes within the sample. The actual water flux of the sample,  $q_A$ , is of course equal to the total of the flowpaths

$$q_A = \sum_{i=1}^n F_i q_i = \dot{m} \sum_{i=1}^n \frac{F_i}{C_i} \quad (9)$$

where the right hand side of equation (9) results from the substitution of equation (7).

As an example of the error associated with small-scale preferential flow, if a soil sample has two flowpaths, the first with  $\theta_1 = 0.15$ ,  $F_1 = 0.2$ , and  $C_1 = 100$  mg/l, and the other with  $\theta_2 = 0.45$ ,  $F_2 = 0.8$  and  $C_2 = 200$  mg/l, applying equation (6), CMB will calculate  $q_{CMB} = 192$  mg/l. The true flux through the sample is calculated using equation (9) and results in  $q_A = \dot{m} / 167$  mg/l. Thus,  $q_{CMB}$  is 13% smaller than  $q_A$  in this example.  $q_{CMB}$  will always be less than  $q_A$  unless all of the  $q_i$  are equal in which case  $q_{CMB}$  will be equivalent to  $q_A$ . However, if

the intent is to calculate the water flux,  $q_{CMB}$  is a useful estimate and the error associated with using  $q_{CMB}$  versus  $q_A$  may be small relative to other experimental errors. Difficulties can arise if the preferential flow takes place through large macropores which may not contain water and chloride during the time of sampling (Wood, 1999). Given the clay loam soil, the moisture contents of the test plots (approximately 0.28), and a visual inspection of the cores, macropores and thus macropore flow does not seem likely beneath an appreciable depth.

If preferential flow occurs on a scale larger than the sample size, the fluxes calculated are accurate, but they can not be extrapolated without consideration of the large-scale variability. Indication of large-scale preferential flow is evidenced by a large coefficient of variation for the measured water fluxes between cores.

Lastly, although it is often stated that an assumption of CMB is vertical flow, this is not strictly required. A more precise statement is that CMB measures the vertical component of flow within a porous media. As long as the flow has some vertical downward component, CMB results will be an estimate of that vertical component of flow.

#### Assumption 2

Chloride ions often experience anion exclusion because most soils have a negative charge. Applying CMB to a soil that exhibits anion exclusion results in a measured water flux that is greater than the true water flux. Chloride in clay rich soils has been measured traveling at velocities up to twice as much as the corresponding water velocities (Gvirtzman et al., 1986). In a similar nearby soil, Brown and Allred (1993) found that anions traveled up to 20% faster than corresponding water velocities which would result in a potential overestimate of groundwater recharge using CMB by the same amount. Since both chloride and nitrate have a similar charge they generally behave similarly in regards to anion exclusion. Thus, the estimate of water flux based on chloride is appropriate for the ultimate goal of estimating nitrate flux even if minor anion exclusion is occurring.

#### Assumption 3

Chloride is assumed to be conservative based a history of use as a tracer and Hem's (1985) statement:

“Chloride ions do not significantly enter into oxidation or reduction reactions, form no important solute complexes with other ions unless the chloride concentration is extremely high, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles. The circulation of chloride ions in the hydrologic cycle is largely through physical processes.”

Since the measured chloride concentrations are not high, the assumption of conservative behavior appears valid.

#### Assumption 4

Assumption 4 has historically been the most problematic because data describing the amount of chloride present in precipitation and dry fallout is difficult to obtain. Another problem is that if a soil column represents a long time period of infiltration, it is difficult to determine if the environmental conditions at the site have been temporally consistent with the measured chloride input data (Edmunds and Gaye, 1994; Murphy et al., 1996; Love et al., 2000). Since the artificially applied chloride, in the form of KCl, makes up approximately 95% of the chloride added to the plots over the last 29 years, the difficulty of estimating atmospherically deposited chloride becomes relatively insignificant.

### Assumption 5

The single annual fertilizer application, which represents a relatively large percentage of total chloride added to the plots, strengthens the assumption that significant amounts of chloride will not be added or lost from the plots by runoff or runoff. Since KCl is highly soluble and applied only once a year, it would take a very strong precipitation event just after fertilization to wash away the KCl before it could be dissolved and infiltrate into the upper soil column, which is a very unlikely scenario. Runoff or runoff of water thus will only be at rainfall chloride concentrations, which is relatively insignificant to the total chloride mass balance.

### Assumption 6

At a time scale of weeks or months water flux rates are mostly in an unsteady state because weather and agricultural practices changes throughout the year. However, over a time scale of years, the test plots are believed to be in a pseudo steady state condition.

## **Numerical Modeling**

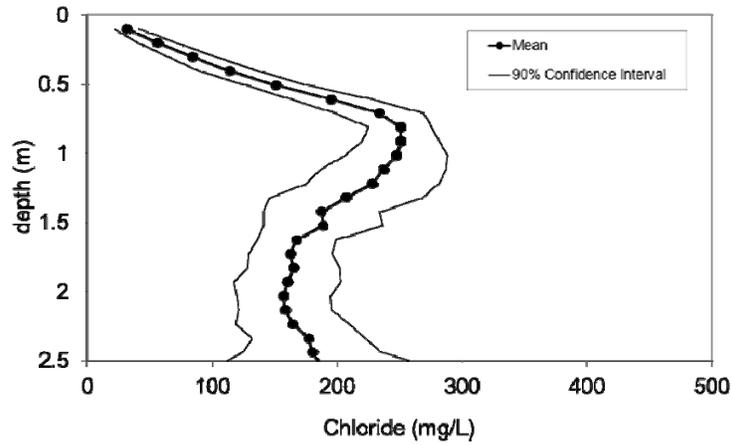
Numerical modeling was carried out using Hydrus 1-D version 7.0 (1998) to determine if the application of uniform 1-D transport and reasonable values for the transport parameters could accurately reproduce the water and chloride transport through the soil profile. The numerical model solves the Richards equation for one-dimensional transport of water, heat, and multiple solutes in variably saturated media while including a sink term to account for water uptake by plant roots. An initial model time step of 0.1 days with a maximum of 1 day was used for a duration of 29 years. The upper boundary was modeled with a constant flux rate equal to the average precipitation rate of 860 mm/yr and a chloride concentration equaling the net annual chloride applied to the plots divided by the annual precipitation. This is an acceptable simplification due to the low transport rates of water and solutes within the fine textured soil. The lower boundary was modeled with a zero hydraulic gradient and constant chloride concentration flux at a depth adequate to preclude an influence on the simulation.

Initial modeling was conducted using Hydrus's default hydrologic parameter values for a typical clay loam soil. These hydrologic values included Van Genuchten's soil water retention parameter ( $\alpha$ ), soil water retention exponent ( $n$ ), and saturated hydraulic conductivity ( $K_s$ ). Root water uptake versus depth was calibrated to achieve the measured chloride concentrations within the root zone. Next  $\alpha$ ,  $n$ , and  $K_s$  were calibrated to provide the measured volumetric water content throughout the soil column. Finally, the dispersivity was estimated by optimizing the fit of the modeled chloride dispersion ahead of the chloride bulge to measured values. Although dispersion was included in the model, the results section will explain why  $D$  is assumed to be negligible in regards to the water flux calculations of equation (2).

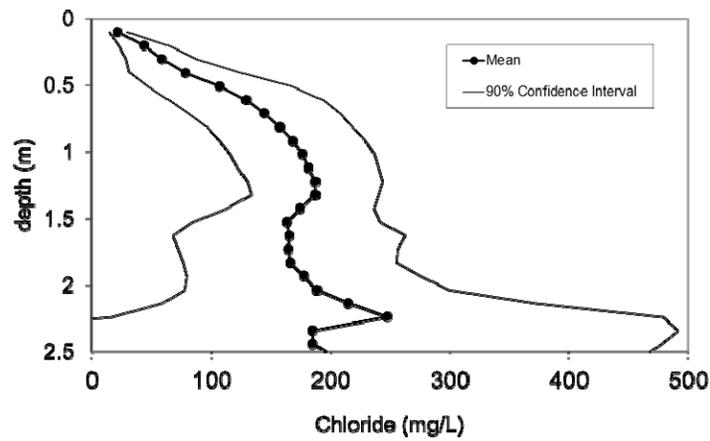
## **Results**

### Measured Chloride Profiles

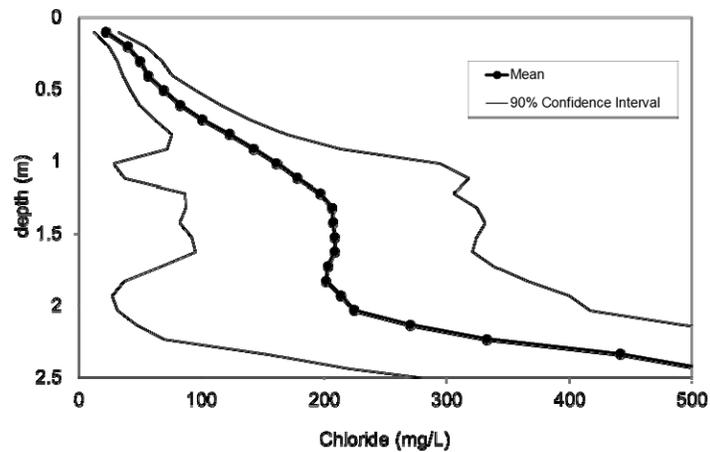
Measured chloride concentrations varied from plot to plot making the true signal sometimes difficult to recognize. For this reason, the mean and 90% confidence intervals of the chloride concentrations were plotted versus depth for plot groups A, B, C, and D in Figures 2, 3, 4, and 5, respectively. The confidence intervals were plotted assuming a normal distribution. Every depth of every group was considered its own population so there were a maximum of eight points per population. As a result of the small number of points per depth, the true distribution could not be found directly and the normal confidence intervals that are shown may contain error resulting from the choice of the distribution.



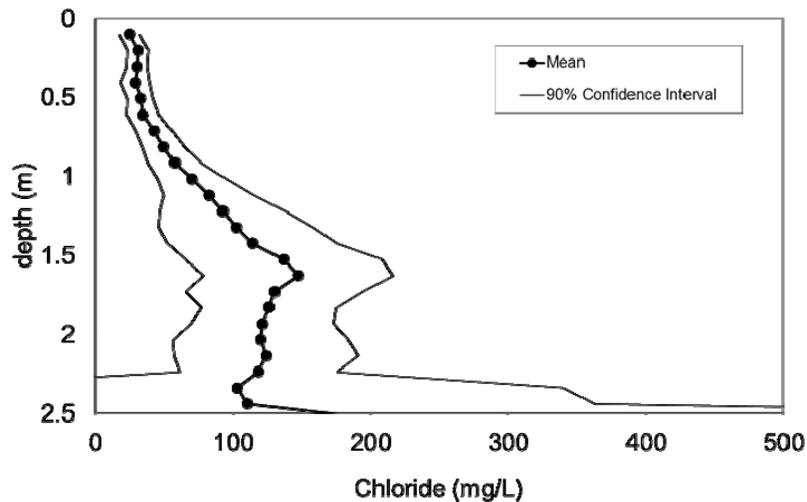
**Figure 2-Sample mean and 90% confidence intervals of population mean for chloride concentrations of Group A Cores.**



**Figure 3-Sample mean and 90% confidence intervals of population mean for chloride concentrations of Group B Cores.**



**Figure 4-Sample mean and 90% confidence intervals of population mean for chloride concentrations of Group C Cores.**



**Figure 5-Sample mean and 90% confidence intervals of population mean for chloride concentrations of Group D Cores.**

The group A data (Figure 2) show a well-defined chloride bulge. This bulge is only present because the bottom of the system has not reached steady state in regards to the additional chloride flux since 1969. A pseudo steady state condition has been achieved throughout the root depth as will be shown in the modeling section. Given sufficient time, the chloride concentration would be expected to reach a relatively constant value beneath the root depth at approximately 0.8 m. Chloride profiles for Group B and C test data (Figure 3 and 4) are similar to a depth of about 2 m. Beneath this depth the chloride content of the Group C test data seems to increase dramatically. This apparent increase must be tempered with the knowledge that the higher mean chloride concentrations beneath a depth of 2 m are described by fewer samples due to the difficulty in collecting intact cores to such depths. A possible mechanism to obtain such high chloride concentrations beneath 2 m may be associated with the prairie conditions present prior to initial cultivation as discussed in the next section. The chloride profiles for group B and C test data also show a deeper root depth, approximately 1.25 m, than the Group A test data. Since the Group A plots have received zero N as  $\text{NH}_4\text{NO}_3$  over the past 29 years, it is plausible that being nitrogen limited has restricted the root growth below 0.8 m in the Group A plots.

Shallow chloride concentrations for group D test data (Figure 5) are lower than the concentrations in the other plots, which correlates to a higher water flux. The chloride gradient is especially small in the upper 0.6 m. It is possible that the strong vegetative growth due to larger  $\text{NH}_4\text{NO}_3$  applications may provide an improved surface soil structure and increased surface infiltration.

#### Water Fluxes

Table 2 presents the mean and standard deviation (SD) of the chloride concentration at the root depth and its associated water flux from equation (3). The mean water fluxes were calculated from chloride data of individual cores, not the averaged chloride data (Figures 4 – 7). These fluxes may be overestimated by up to 20% based on anion exclusion measurements from adjacent soil cores. The estimates of water flux are the only regional long-term dryland winter wheat recharge estimates available in the literature with the exception of Berg et al. (1991). Berg measured 3 to 25 mm/yr of recharge, which is consistent with the present water flux estimates, beneath winter wheat fields in northwestern Oklahoma that average 690 mm/yr of precipitation. In his study Berg also found that replacing the native mixed grasslands with terraced winter

wheat increased the recharge enough to cause salt seeps in adjacent low lying areas. Lower recharge rates present before initial cultivation in the area currently occupied by the Stillwater test plots may explain the high chloride concentrations seen beneath a depth of 2 m within the Group C test data.

**Table 2. Chloride Concentrations and Fluxes Calculated Using CMB**

Group	Number of Cores		Cl Bulge (mg/l)	Water flux (mm/yr)
A	8	Mean	295	12.2
		SD	62.6	2.6
B	8	Mean	219	17.0
		SD	63.4	5.2
C	7	Mean	173	25.4
		SD	93.9	13.6
D	8	Mean	137	38.9
		SD	101	25.1

It is interesting that as the  $\text{NH}_4\text{NO}_3$  application rate increases from the Group A plots to the Group D plots, apparently so does the sample mean water flux. The hypothesis that water fluxes from each plot group have identical population distribution functions was tested using the Kruskal-Wallis test (Conover, 1980). At the 90% level of confidence the hypothesis is accepted, but at a more rigorous 75% level of confidence the hypothesis is rejected. It is therefore likely that the water fluxes between different plot groups are from different populations. We are uncertain of the cause of the differences in water fluxes between plot groups. Again, higher N application produces noticeably more vigorous plants, that in turn, may provide an improved surface soil structure with greater infiltration and less runoff. However, the denser plant stands should also produce greater transpiration, thus reducing net groundwater recharge.

#### Modeling

Hydrologic parameters used to model the water fluxes and chloride concentrations are given in Table 3. The measured chloride concentrations, modeled chloride concentration at 28 or 29 years (1997 and 1998 samples, respectively), 200 years, and pore water age calculated from equation (4), were plotted for two of the cores (Figure 6 and 7). Two hundred years was arbitrarily chosen as a time period to represent steady state conditions throughout the soil columns. For simplicity, all 28 and 29 years modeling results will be referred to as 29 years for the remainder of the paper.

**Table 3. Model Simulation Input Parameters.**

Core	$\alpha$ (1/mm)	$n$	$K_s$ (mm/d)	Dispersivity (mm)	Porosity	Residual Saturation	Bulk density (gm/ml)
A-1-98	0.0019	1.25	62.4	110	0.41	0.095	1.7
A-4-97	0.0019	1.20	62.4	30	0.41	0.095	1.7

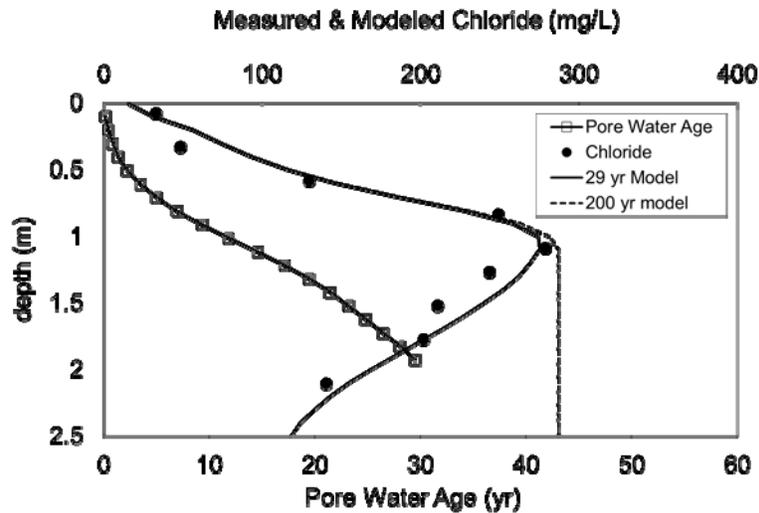


Figure 6-Modeling and pore water age of Core A-1-98.

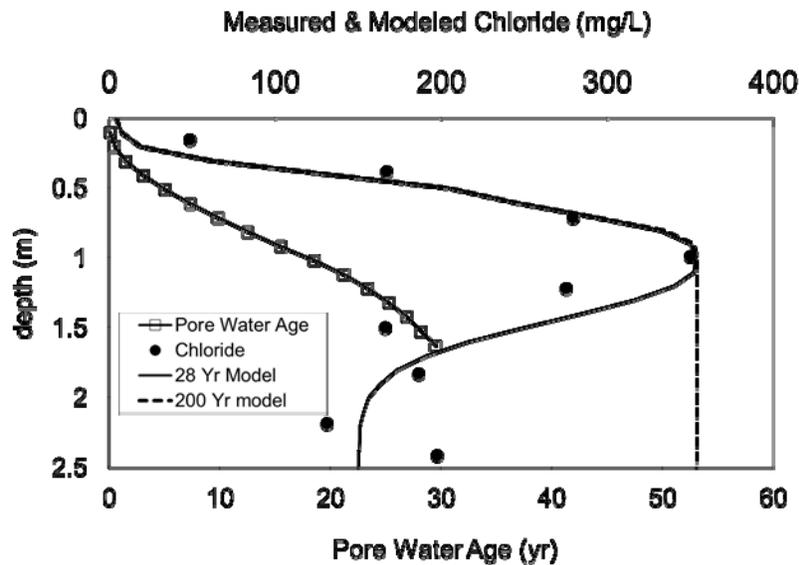


Figure 7-Modeling and pore water age of Core A-4-97.

The modeled chloride bulges at 29 years match the measured chloride data quite well. This is significant since measured and modeled water contents were also maintained. Therefore the known mass of chloride applied over the past 29 years has been measured in the field and modeled using CMB assumptions with reasonable values for soil hydraulic parameters. Notice also that the pore water ages at the base of the chloride bulges are reasonably close to 29 years, the period of KCl application. This agreement again shows conservation of chloride mass using CMB assumptions. Calibrating hydraulic parameters to fit the modeled data with the measured data does not ensure that the model parameters are accurate, but it does strengthen the argument that at least two of CMB assumptions, no preferential flow and no significant loss of chloride in runoff. More importantly, it verifies the general shape of the chloride concentration curve created by the addition of KCl for 29 years.

The simplification of equation (2) to equation (3) by excluding  $D$  was supported by comparing the maximum concentrations of the modeled chloride concentrations at 29 years and 200 years. At 29 years the modeled chloride pulse has not reached equilibrium beneath the root depth and displays a large chloride concentration gradient. At 200 years the modeled chloride pulse is at equilibrium and no chloride concentration gradient exists below the root depth. Since the root depth chloride concentration at 29 years matches the root depth chloride concentration at 200 years, both the 29 and 200 year simulations will yield similar water fluxes at the root depth using equation (3). In other words, even when a chloride gradient beneath the root zone exists (29 years), the calculated water flux is similar to when a gradient does not exist (200 years). Therefore, at a 29 year time scale  $D$  is negligible and the simplification from equation (2) to equation (3) is justified. The similarities in maximum modeled chloride concentrations between 29 and 200 years also strongly implies that the plots have reached a pseudo steady state condition to the base of the root depth during the 29 years of the KCl application.

### **Conclusions**

Net annual groundwater recharge under dryland winter wheat in Oklahoma was estimated using CMB and duplicated with numerical modeling using CMB assumptions. Both CMB and modeling provided a consistent interpretation of the measured data. The success of the CMB application was due in large part to accurate knowledge of the chloride applied as KCl fertilizer over the last 29 years. Confidence in the results is also a consequence of the site, where the low recharge rates and the large water-holding capacity of the fine textured soil kept all applied chloride within the measured soil profile. Application of fertilizer chloride allowed the chloride input, arguably the most difficult parameter to estimate in a typical CMB application, to be calculated with more certainty. The ability to achieve chloride mass balance while numerically modeling the measured chloride concentration profiles is consistent with the hypothesis that assumptions required for application of the CMB were met. Recharge rates under dryland winter wheat ranged from 12.2 to 38.9 mm per year and increased with increasing N fertilizer application. These fluxes may be overestimated by up to 20% based on anion exclusion measurements from adjacent soil cores. A possible cause for the correlation between water flux and N applied is that the more vigorous plants produced by the higher N rates created a soil structure with greater infiltration and less runoff.

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