EVALUATION OF MOISTURE FLUX FROM CHLORIDE DATA IN DESERT SOILS*

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ABSTRACT

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Chloride-concentration data from 10 soil profiles in a 40 km^2 area of the Chihuahuan Desert of Texas were used to assess chloride mass balance methods of evaluating moisture flux. The relative importance of advective and diffusive transport mechanisms was determined. Moisture fluxes were calculated from measured chloride concentrations on the basis of a steady-state flow model. To evaluate controls on unsaturated flow, moisture fluxes from this study were compared with those from other regions.

The chloride profiles displayed large variations in concentrations and had (a) low chloride concentrations ($\leq$ 100 g m^{-3}) near land surface, (b) maximum chloride concentrations (1,900 to 9,300 g m^{-3}) at depths of 1.3 to 4.6 m, and (c) gradually decreasing chloride concentrations with depth below the peak. Steep concentration gradients (up to 12,000 g m^{-3} m^{-1}), characteristic of chloride profiles in these desert soils, indicate a potential for molecular diffusion; however, low moisture contents ($\leq$ 0.1) in the zone of steep concentration gradients resulted in diffusive fluxes that were 2 to 3 orders of magnitude lower than the advective fluxes; therefore, diffusive fluxes were neglected in flux calculations. Because the chloride accession rate was assumed to be constant throughout the study area, calculated moisture fluxes are inversely proportional to chloride concentrations in the soil water. Highest moisture fluxes (up to 6 mm yr^{-1}) were calculated near land surface and are related to chloride leaching as a result of precipitation. Within the upper meter of the unsaturated zone, soil moisture fluxes decreased sharply to 0.1 mm yr^{-1} as most of the water evapotranspired in this zone. Soil moisture fluxes decreased to a minimum at the chloride peak and then increased gradually as chloride concentrations decreased with depth below the peak. Reductions in chloride concentrations below the peak are attributed to differences in moisture fluxes as a result of paleoclimatic variations. Comparisons of chloride profiles from different regions indicate that geomorphic setting plays a major role in controlling moisture flux in the unsaturated zone.

INTRODUCTION

Chloride profiles have been used in a variety of settings to evaluate moisture fluxes in the unsaturated zone (Allison et al., 1985; Phillips et al., 1988). In arid

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systems, downward water flux is very difficult to quantify because it represents a small percentage of the total water balance. The chloride mass balance approach, which provides estimates of moisture flux during long time periods, has many advantages over conventional physical approaches in partly vegetated, arid systems because meteorologic data from these systems indicate large interannual variations in precipitation that would necessitate monitoring physical parameters over a long time to obtain reliable estimates of moisture flux. The water balance approach, in which downward water flux is computed from the difference between precipitation, evapotranspiration, and runoff, is generally inaccurate in arid systems because evapotranspiration constitutes most of the total water budget and estimates of evapotranspiration from micrometeorologic techniques are not sufficiently accurate in partly vegetated desert regions. The use of Darcy's Law to estimate moisture fluxes is also problematic because of the complexity of flow in desert soils where liquid and vapor transport may occur in response to water potential and temperature gradients. Highly nonlinear relationships between moisture content, water potential, and hydraulic conductivity result in large uncertainties in these flux calculations.

In contrast to physical methods that provide moisture flux data for the duration of the monitoring period, profiles of chloride concentrations yield information on moisture fluxes over long periods (up to 50,000 yr; Allison et al., 1985). In addition, unlike many of the physical methods in which the accuracy of moisture flux calculations decreases as the flux decreases, the accuracy of flux estimates from the chloride mass balance approach does not necessarily decrease because chloride concentrations increase as the moisture flux decreases. This increase in chloride concentrations results from evapotranspiration because chloride is nonvolatile and because plant uptake is minimal. Chloride data also provide information on spatial variability in downward water movement because each profile represents a point estimate of moisture flux. Good agreement has been found between estimates of moisture flux based on the chloride approach and those based on tritium data in a humid region (Allison et al., 1985). Results from chloride profiles have also been corroborated with data from stable isotope profiles (Sharma and Hughes, 1985; Fontes et al., 1986).

Thick unsaturated zones in arid regions are being considered as potential sites for radioactive waste disposal facilities because low precipitation and high evapotranspiration rates result in low recharge potentials and because the low permeability of a thick unsaturated zone may provide a natural barrier to radionuclide migration to the water table. The unsaturated zone in a 40 km^2 area of the Chihuahuan Desert in Texas (Fig. 1) is being considered as a potential repository of low-level radioactive waste. The objective of this study was to

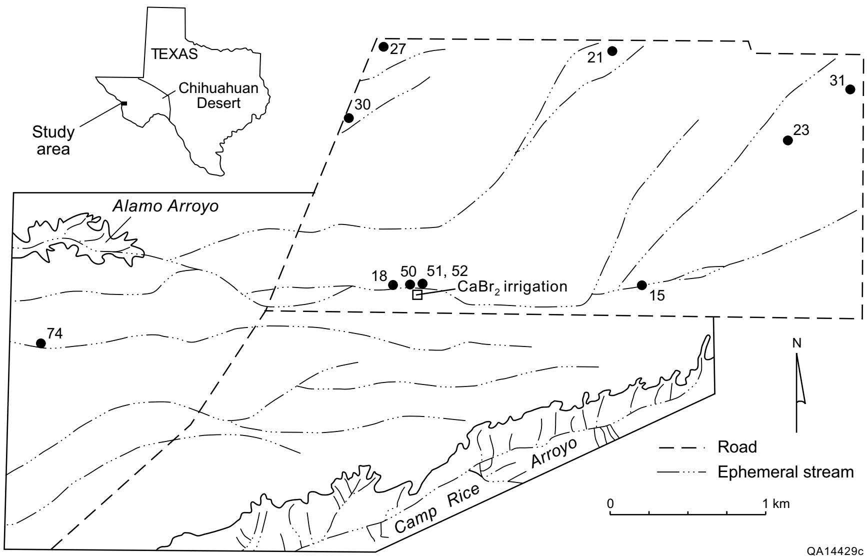

Figure 1. Location of sampled boreholes. Inset shows location of study area within the Chihuahuan Desert of Texas.

evaluate the moisture flux and its spatial variability in the upper 15 m of the unsaturated zone of this system. This paper focuses on chemical methods of analyzing water movement based on the distribution of environmental chloride. Key components of the research include evaluation of (1) the chloride mass balance method for determination of moisture fluxes, (2) the relative importance of advective and diffusive fluxes, (3) the spatial variability in moisture fluxes, and (4) controls on chloride profiles and moisture fluxes based on comparisons with other regions.

Chloride Mass Balance

Chloride concentrations in soil water have been used to evaluate moisture fluxes in semiarid systems (Bresler, 1973; Peck et al., 1981; Sharma and Hughes, 1985; Johnston, 1987). Chloride is an ideal tracer because it is chemically conservative. According to the theory of chloride transport (Bresler, 1973; Peck et al., 1981), the solute flux (J_S), under steady-state conditions, can be described by:

$$J_s = -D_h(\theta, v)\frac{\partial c}{\partial z} + cq_w \qquad (1)$$

where D_h is the hydrodynamic dispersion coefficient, a function of θ (the volumetric moisture content) and v (the average soil moisture velocity); z is the vertical space coordinate; c is the concentration; and q_w is the volumetric soil-moisture flux. J_s was approximated by the mean annual precipitation rate (P: 280 mm yr^{-1} [J. Griffiths, pers. comm., 1990]), times the chloride concentration in precipitation and in dry fallout (Cl_p) for this study area (Sharma and Hughes, 1985; Mattick et al., 1987). The mean chloride concentration (Cl_p: 0.29 g m^{-3}) was calculated from the prebomb $^{36}Cl/Cl$ ratio (0.46×10^{-12}) measured in soil water from borehole 51, and the natural ^{36}Cl fallout at the site estimated as 20 atoms ^{36}Cl m^{-2} s^{-1} (Bentley et al., 1986; Scanlon et al., 1990). The resultant J_s value was 0.08 g m^{-2} yr^{-1}.

Rearranging equation (1) yields the soil-moisture flux:

$$q_w = \frac{1}{c}\left(J_s + D_h(\theta,v)\,\frac{\partial c}{\partial z}\right) \qquad (2)$$

The first term in the outer parentheses represents the flux that results from advection and the second term represents the flux from dispersion. The mechanical dispersion coefficient (D_m) and the effective molecular diffusion coefficient (D_e) comprise the hydrodynamic dispersion coefficient. D_m is assumed to be negligible because flow velocities are less than 7 m yr^{-1}, which Olsen and Kemper (1968) specify as the water velocity below which mechanical dispersion can be ignored. D_e includes the effects of tortuosity and water content. Recent studies of D_e values of silts, sands, and gravels indicate that D_e is primarily a function of moisture content and only secondarily dependent on soil type (Conca, in press; Conca and Wright, 1990). At low-moisture fluxes, the diffusive flux may be dominant. The diffusive flux was estimated from the first derivative of c(z) times D_e. Cubic splines were fitted to the observed chloride profiles to smooth the data and to calculate the first derivative in equation (2). Moisture content data from the profiles were used to calculate D_e based on the relationship between moisture content and D_e from Conca (pers. comm., 1990). The moisture flux is divided by the volumetric moisture content to obtain the moisture velocity (q_w/θ), which represents the actual rate of solute transport.

In many arid systems the hydrodynamic dispersion coefficient was assumed to be negligible (Allison et al., 1985; Stone, 1990) and equation (2) was simplified to:

$$q_w = J_s / c \qquad (3)$$

The travel time (t) represented by chloride at depth z can be evaluated by dividing the total mass of chloride from the surface to that depth by the chloride flux:

$$t = \frac{\Sigma Cl_{sw} \times z}{J_s} \tag{4}$$

where c is approximated by Cl_{SW} (chloride concentration in soil water).

Chloride profiles provide a qualitative estimate of moisture flux because there are many assumptions associated with the chloride mass balance approach. These assumptions are:

(1) one-dimensional, vertical, downward, piston-type flow; (2) precipitation as the only source of chloride; (3) mean annual precipitation and chloride concentration of precipitation constant through time; and (4) steady-state chloride flux equal to the chloride accession rate in rainfall. The accuracy of the flux estimates from chloride data depends on the reliability of the physical flow model used to interpret the data. Although this model of chloride movement predicts that chloride concentrations should increase through the root zone and remain constant below the root zone, many previously published chloride profiles show that chloride concentration decreases below the peak; therefore, some of the assumptions associated with the model may not be valid for different systems. The reduction in chloride concentration below the peak was attributed to groundwater dilution (Phillips et al., 1988), nonpiston-type flow (Sharma and Hughes, 1985), or failure of the steady-state flow assumption as a result of paleoclimatic variations (Allison et al., 1985; Phillips and Stone, 1985). An alternative method was used to analyze some chloride profiles in Western Australia that did not assume a downward moisture flux (Peck et al., 1981). This analysis showed that steep concentration gradients below the chloride peak resulted in the flux being dominated by diffusion rather than advection and that the calculated moisture flux was upward, in contrast to the downward flux assumed by the chloride mass balance theory. These studies underline the importance of evaluating the conceptual flow model that is used to analyze the chloride data and the applicability of the assumptions to each study area.

Anion exclusion may also affect the accuracy of flux estimates based on chloride data. Most studies of anion exclusion are restricted to laboratory column experiments in which ionic Cl or ^{36}Cl migrated faster than ^{3}H (Biggar and Nielsen, 1962; Krupp et al., 1972; Wierenga and van Genuchten, 1989). Faster migration of Cl relative to that of ^{3}H was also recorded in field tracer experiments (Gvirtzman et al., 1986; van de Pol et al., 1977). Calculated anion velocities were as much as twice the estimated water velocities in clay-rich soils (Gvirtzman et al., 1986; James and Rubin, 1986). In desert soils, such as in New Mexico and the present study area, deeper penetration of ^{3}H relative to that of ^{36}Cl was attributed to downward movement of ^3H in the vapor phase (Phillips et al., 1988; Scanlon, in press). These data suggest that although Cl may be excluded from the liquid phase, flux estimates based on Cl data should not overestimate the water (liquid + vapor) flux in desert soils.

Study Area Description

This study area (31° 25' N, 105° 40' E) is located in the Hueco Bolson, which is a 200-m- thick sediment-filled basin within the Chihuahuan Desert of Texas (Fig. 1). The Hueco Bolson is part of the Rio Grande Rift and formed as a result of Basin and Range deformation during the Tertiary (Henry and Price, 1986). The unsaturated zone consists of 0 to 15 m of silty to gravelly loam of the Tertiary and Quaternary Camp Rice Formation, underlain by approximately 140 m of clay with interbedded silt and sand of the upper Tertiary Fort Hancock Formation. Shallow coarse-grained material was deposited in alluvial and eolian environments, whereas the deeper clay sediments were deposited in a predominantly lacustrine environment. A discontinuous layer of caliche occurs at a depth of 1 to 2 m.

Regional climate is subtropical arid (Larkin and Bomar, 1983); mean annual precipitation is 280 mm and has large interannual variations that range from 110 to 440 mm in El Paso, located 65 km northwest of the study area. Approximately 60% of the precipitation falls between June 1 and September 30 as convective storms. Mean annual potential evapotranspiration (Class A pan) is approximately seven times mean annual precipitation.

The present surface of the Hueco Bolson is an alluvial plain that slopes 1 to 1.5% toward the Rio Grande. Modern ephemeral streams that drain the alluvial plain lack well-defined channels (maximum relief 0.6 m). The upper reaches of the ephemeral streams drain into incised channels (arroyos) southwest of the study area (Fig. 1). Streams are generally dry except after precipitation events. Shrubs, such as creosote (*Larrea tridentata*) and mesquite (*Prosopis glandulosa*), are common and root to depths of 1 to 5 m. The topography is relatively flat with slopes of less than 1%. Because of the low topography, precipitation events predominantly result in sheet flow across the area (S. Akhter, pers. comm., 1989).

METHODS

To determine ambient moisture and chloride contents, approximately 230 soil samples were collected from 10 boreholes drilled during 1988 and 1989 (Fig. 1). These boreholes were rotary drilled with hollow-stem augers without drilling fluids. Samples were collected in Shelby tubes, and the sampling interval varied from approximately 0.3 to 1 m. Many of the boreholes were drilled to the top of the clay-rich Fort Hancock Formation at a depth of 10 to 15 m, which the auger could not penetrate.

Gravimetric-moisture content was determined by drying at least 80 g of soil at 105°C for 48 hr. Although volumetric-moisture content could not be directly determined in 90% of the samples because the material was not sufficiently cohesive, volumetric-moisture content of these samples was calculated from gravimetric-moisture content using a bulk density of 1.4 (average bulk density measured in 27 samples). To determine chloride content, double-deionized water was added to the oven-dried soil sample in a 1:1 or 2:1 ratio. Samples were agitated on a reciprocal shaker table for 8 hr, then centrifuged for 10 min at 5,000 rpm. The supernatant was filtered through 0.45 μm filters. Chloride was then analyzed by ion chromatography or by potentiometric titration. To test if oven drying had any effect on chloride concentration, four samples at field moisture were split and one half of each was oven dried. Soil texture of these samples was not determined. Comparison of the chloride concentrations of the splits showed that oven drying had no effect on chloride concentrations.

Textures of approximately 100 soil samples were measured. The samples were ground to disaggregate calichified materials. The greater-than-2-mm fraction was determined by dry sieving, and the percent of sand, silt, and clay was evaluated by hydrometer analysis following Bouyoucos (1962). Sediment samples that contained gravel were classified according to Folk (1974) and those that did not contain gravel were classified according to the U.S. Department of Agriculture (1975).

RESULTS AND DISCUSSION

In the following sections, 6 of the 10 measured chloride profiles are described in detail; descriptions of the other profiles can be found in Scanlon (in press). The chloride profiles are plotted at different scales in figure 2. All measured chloride profiles are bulge shaped and consist of low chloride concentrations near the surface, at depths of generally less than 0.3 m, and maximum chloride concentrations at depths of 1.3 to 4.6 m that decrease to low concentrations with depth (Fig. 2). Chloride profiles display a wide variability in their maximum chloride concentrations, which range from 1,900 g m^{-3} (Figs. 2c and 2h) to 9,300 g m^{-3} (Fig. 2aa).

The chloride profile from borehole 15 is characterized by low concentrations (< 100 g m^3) in the upper meter of the unsaturated zone (Fig. 2c). This zone of low concentration corresponds to high moisture content (0.11 to 0.19 m^3 m^{-3}) that reflects infiltration of a recent precipitation event. Below this surficial leached zone, chloride concentrations increase sharply to 1,900 g m^{-3} as a result of

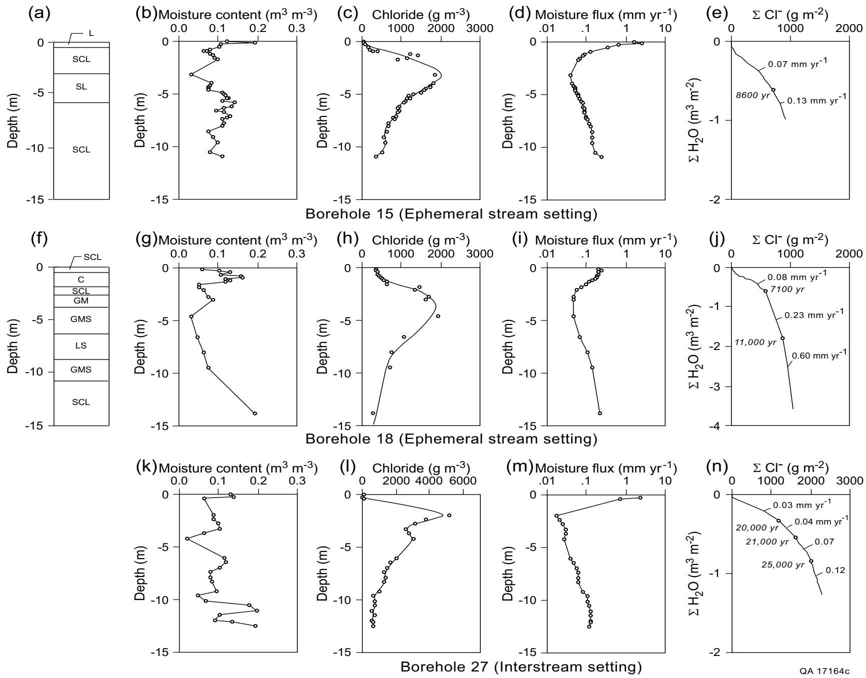

Figure 2(a-ac). Data from six boreholes on soil texture, moisture content, chloride concentration, and fitted cubic spline, and calculated moisture flux based on equation (3) plotted against depth, and cumulative chloride plotted against cumulative water content. Note the different scales used for various profiles. Soil textures: g, gravel; s, sand; l, loam; c, clay; msg, muddy sandy gravel; gms, gravelly muddy sand; ls, loamy sand; sl, sandy loam; scl, sandy clay loam; cl, clay loam; gm, gravelly mud; and sc, sandy clay.

evapotranspirative enrichment. Chloride concentration gradients increased with depth at rates of up to –900 g m^{-3} m^{-1}. The peak chloride concentration was recorded at a depth of 3.2 m. Chloride concentrations decrease gradually to 340 g m^{-3} below the peak, and chloride concentration gradients range from 500 g m^{-3} m^{-1} to 10 g m^{-3} m^{-1} in this zone. Chloride concentrations in samples from the shallow zone of borehole 18 are much higher (350 to 400 g m^{-3}) (Fig. 2h) and the moisture contents much lower (0.06 to 0.13 m^3 m^{-3}) (Fig. 2g) than those from borehole 15 because borehole 18 was sampled after a long dry period. The chloride concentration gradients, peak concentrations, and depth of the chloride peak are similar in the profiles from boreholes 15 and 18. Both profiles sample the ephemeral stream setting.

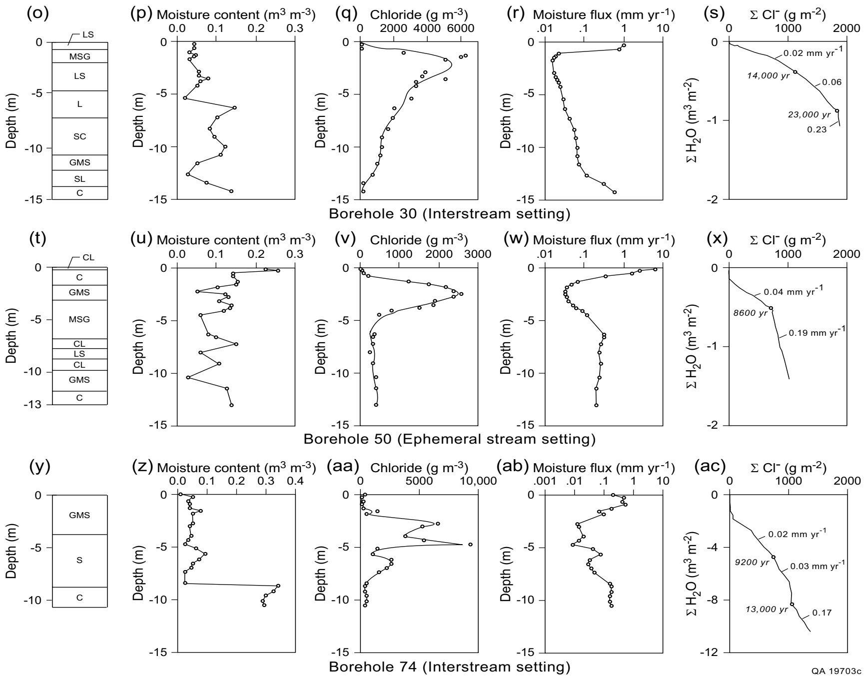

Figure 2. (continued)

Boreholes 27 and 30 were located in interstream settings (Fig. 1) and their chloride profiles are similar (Figs. 2l and 2q). Both profiles have a leached section of approximately 0.5 m. Chloride concentration gradients are very steep above the peak (≥ –6,000 g m^{-3} m^{-1}), whereas these gradients are much lower (2,000 to 10 g m^{-3} m^{-1}) below the peak.

Borehole 50 was sampled in an ephemeral stream after a rainfall event. The shallow zone is characterized by low chloride concentrations (2 to 7 g m^{-3}) and high moisture contents (0.14 to 0.26 m^3 m^{-3}) (Figs. 2u and 2v). Below the surficial leached zone, moisture content shows no systematic relationship with depth. Chloride concentration gradients above the chloride peak are ≥ –2,000 g m^{-3} m^{-1}, whereas those below the peak range from 1,200 to 5 g m^{-3} m^{-1}. Comparisons of chloride concentrations in samples from nearby (10 m away) borehole 51 (Fig. 1) give an indication of local variability. Peak chloride concentrations (2,000 g m^{-3}) are similar in the two profiles; however, the depth of the peak is approximately 1 m deeper in the profile from borehole 50.

Chloride concentrations in samples from borehole 74 (Fig. 2aa), also located in an ephemeral stream setting (Fig. 1), are higher than those recorded in all other profiles. The chloride profile is multipeaked and not as smooth as other measured profiles. Chloride concentration gradients are steepest in this profile (up to 12,000 g m^{-3} m^{-1}) and vary markedly with depth. The soil texture above 8 m depth (gravelly muddy sand to sand; Fig. 2y) is much coarser grained than that in the other profiles (predominantly sandy clay loam). The transition from shallow coarse material to deeper clay corresponds to a marked increase in moisture content of 0.3 m^3 m^{-3} (Fig. 2z). The clay-rich Fort Hancock Formation is found at a shallower depth (8 m) in this borehole than in the other boreholes to the northeast (13 to 15 m in boreholes 23, 30, and 50).

Chloride concentrations in the surficial sediments vary depending on the relationship between the sampling time and precipitation events. At depths greater than approximately 0.5 m, chloride concentrations represent longer time periods and are not affected by individual precipitation events. No systematic relationship was found between the chloride profiles and the present geomorphic setting. The lack of a relationship may result from these two geomorphic systems being hydrologically similar because most of the runoff occurs as sheet flow (S. Akhter, pers. comm., 1989), and the topographic difference between the two settings is small (0.6 m). Alternative hypotheses are that the geomorphic systems are not stable over the long time periods reflected in these chloride profiles, or that soil textural variations are more important in controlling moisture flux, as shown by the profile from borehole 74.

Transport Mechanisms

The general advection-dispersion equation (equation 2) was fitted to the chloride concentration data to evaluate the relative importance of advection and diffusion. Smooth chloride profiles are generally thought to reflect redistribution of chloride as a result of diffusion. Chloride concentration gradients were up to 12,000 g m^{-3} (borehole 74). These large concentration gradients should yield high diffusive fluxes. Effective diffusion coefficients (D_e) estimated from the moisture content data in the profiles and the relationship between moisture content and D_e developed by Conca (pers. comm., 1990) was approximately 10^{-11} m^2 s^{-1} in most profiles. The range in D_e (10^{-10} to 10^{-12}) was higher in samples from borehole 74 because the range of moisture content was greater with lower moisture contents in the coarser grained material and higher moisture contents in the clay section (Fig. 2z).

Above the chloride peak, increasing chloride concentrations with depth gave rise to upward diffusive fluxes that ranged from 10^{-3} to 10^{-4} mm yr^{-1}. Below the chloride peak, downward diffusive fluxes ranged from 10^{-3} to 10^{-5} mm yr^{-1}. Although the multipeaked chloride profile from borehole 74 could be expected to reflect lower diffusive fluxes in this profile relative to those in other profiles, the diffusive fluxes are actually similar because the effect of steeper concentration gradients cancels the lower D_e values in samples from borehole 74. The low calculated diffusive fluxes for all profiles (10^{-3} to 10^{-5} mm yr^{-1}) are attributed in part to low moisture contents (≤ 0.1 m^3 m^{-3}) in the zone of high concentration gradients. D_e gradually decreases with moisture content, from a value of 10^{-9} m^2 s^{-1} at a moisture content of 0.5 m^3 m^{-3} to a value of 10^{-10} m^2 s^{-1} at a moisture content of 0.1 m^3 m^{-3} (Conca, in press). Below a moisture content of 0.1 m^3 m^{-3}, D_e decreases sharply to 10^{-13} m^2 s^{-1} at a moisture content of 0.01 to 0.005 m^3 m^{-3}. Another factor that contributes to the low diffusive fluxes is that the effects of absolute concentrations and steep concentration gradients on the diffusive flux cancel each other (equation 2) as the zones of high chloride concentrations and steep concentration gradients coincide.

In contrast to the diffusive flux, which varies in direction according to the chloride concentration gradients, the calculated advective flux must always be downward because the chloride approach assumes a constant downward chloride flux. The calculated advective flux ranges from 10^{-2} to 10^{-1} mm yr^{-1} in most profiles and is approximately 2 to 3 orders of magnitude higher than the diffusive flux. These data suggest that the diffusive flux can be neglected and soil moisture flux can be approximated by the advective flux, as seen in equation (3).

Because the chloride flux is assumed to be constant throughout the study area, variations in the soil moisture chloride concentrations reflect differences in moisture flux. Therefore, the chloride concentration in soil water increases to the peak value as the moisture flux decreases, and chloride concentrations decrease below the peak as moisture flux increases (Fig. 2). The highest moisture fluxes were recorded in samples from the shallow zone of borehole 50 (Fig. 2w) where chloride had been leached (≤ 10 g m^{-3}) by a recent precipitation event. The advective fluxes in all profiles decrease sharply to 0.1 mm yr^{-1} within the top meter of the unsaturated zone because almost 100% of the soil water is evapotranspired in this zone. Calculated moisture fluxes are at a minimum where soil moisture chloride concentrations peak, and they increase gradually with depth below the peak as chloride concentrations decrease. Soil moisture velocities (q_w/θ) generally parallel soil moisture flux profiles and are approximately 2 orders of magnitude greater than soil moisture fluxes.

In addition to diffusion, chloride concentration gradients also give rise to osmotic potential gradients that cause advective flux in the direction of higher chloride concentrations. Osmotic potentials (ψ_π; units mega Pascals, MPa) were calculated from soil water chloride concentrations according to the Vant Hoff equation (Campbell, 1985):

$$\psi_\pi = (\nu C \chi \text{ R T})/1000$$

where ν is the number of osmotically active particles (2 for NaCl), C is the concentration (moles kg^{-1}), χ is the osmotic coefficient (Robinson and Stokes, 1959), R is the gas constant

(8.3142 J $mole^{-1}$ $°K^{-1}$), and T is temperature (°K). Osmotic coefficients decrease with increasing chloride concentration. Maximum osmotic potential gradients of 2 MPa m^{-1} were calculated for the chloride profile from borehole 74 (Scanlon et al., in press). The remaining profiles were characterized by osmotic potential gradients generally less than 0.4 MPa m^{-1}. These osmotic potential gradients are negligible compared with the measured water potential gradients (≤ 15 MPa m^{-1} in borehole 74 [Scanlon et al., in press]), and fluxes resulting from the osmotic potential gradients should have a minimal effect on flow.

Validity of Assumptions of Chloride Approach

As outlined in the introduction, many assumptions are used to estimate moisture fluxes from chloride data, and the validity of these assumptions in this study area needs to be examined. The one-dimensional vertical flow assumption is considered valid because, except at borehole 74 where topographic slopes are up to 2%, all chloride profiles are from topographically flat areas having slopes of less than 1%. In sloping topography, the chloride method underestimates moisture fluxes because lateral flow is neglected (Mattick et al., 1987). The direction of moisture flux is assumed to be downward. If the moisture flux were in fact upward, the highest chloride concen-trations would occur at the land surface, as seen in chloride profiles from the Sahara (Fontes et al., 1986). Maximum chloride concentrations observed at depths of 1.3 to 4.6 m in the Hueco Bolson indicate that the net moisture flux is downward in this depth interval of the unsaturated zone. Precipitation is assumed to be the only source of chloride; there are no chloride sources or sinks below the root zone. The sediments in this study area are terrestrial and do not contain any chloride of marine origin. The low observed chloride concentrations in soil water indicate that chloride is not in equilibrium with chloride minerals. The bases of some of the profiles are characterized by chloride

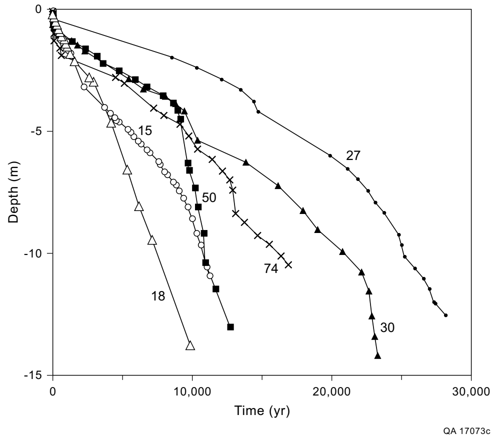

Figure 3. Chloride mass balance age calculated according to equation (4). Borehole numbers shown adjacent to each line.

concentrations as low as 100 g m^{-3}, which further indicates that any in situ chloride source is negligible.

The piston-flow assumption is more difficult to assess. The applicability of piston flow depends on the temporal and spatial scales being considered. Near the soil surface where desiccation cracks develop, nonpiston flow may be dominant. Higher moisture fluxes based on groundwater chloride relative to those based on chloride concentration in the unsaturated zone in many areas have been attributed to nonpiston flow or bypass of the matrix with low-chloride water (Peck et al., 1981; Sharma and Hughes, 1985; Johnston, 1987). Chloride profiles in these areas are generally smooth, which indicates that the smoothness of the profiles does not help discriminate between piston and nonpiston flow. Flow along preferential pathways that bypasses the matrix is used to explain the reduction in chloride concentrations below the peak in some profiles (Sharma and Hughes, 1985). Many profiles characterized by a large amount of preferential flow are from wetter regions (precipitation 800 to 1,200 mm yr^{-1} [Sharma and Hughes, 1985; Johnston, 1987]) than the Hueco Bolson (precipitation 280 mm yr^{-1}). The water potentials (matric and osmotic potentials) in the Hueco Bolson are very low (–2 to –16 MPa [Scanlon et al., in press]); therefore, most of the water is adsorbed onto grain surfaces and is unlikely to move along larger openings or root channels.

The long time period represented by chloride profiles in this study (10,000 to 30,000 yr; Fig. 3) spans paleoclimatic variations and may invalidate the steady-state subsurface flow assumption. The decrease in soil water chloride concentrations below the peak may represent temporally varying precipitation, chloride input, moisture flux, or other environmental conditions (Allison et al., 1985). To examine the possibility of changing environmental conditions, cumulative chloride concentration was plotted against cumulative water content for each borehole. Cumulative water content was used instead of depth to factor out variations in water content (Allison et al., 1985). Moisture fluxes were calculated from the straight-line portions of these plots, which signify uniform environmental conditions. In these flux calculations, Cl_{sw} is the weighted mean soil water chloride concentration in a depth interval that has a constant ratio of cumulative chloride to water content; the constant ratio indicates uniform environmental conditions during a period of recharge. Profiles have either multiple line segments or curved lines, both of which suggest varying environmental conditions (Figs. 2e, 2j, 2n, 2s, 2x, and 2ac). An increase in slope of the cumulative-chloride-versus-water-content profiles with depth reflects past conditions with greater water and/or chloride flux than present rates of flux. If a constant chloride flux is assumed, calculated moisture fluxes range from 0.03 to 0.7 mm yr^{-1}. Many of the profiles indicate a change in the moisture flux from 9,000 to 6,000 yr, higher moisture fluxes having occurred before this period and lower moisture fluxes from this period to the present. This is consistent with paleoclimatic data that suggest that the climate during the late Wisconsinan and early Holocene (22,000 to 8,000 yr) was much wetter than middle to late Holocene (8,000 yr to present) (Van Devender and Spaulding, 1979). In addition to higher precipitation rates in the past, the seasonality of the precipitation is also thought to differ, winter frontal storms being dominant before 8,000 yr, summer convective storms being more typical of the climate since then (Van Devender and Spaulding, 1979), which would further reduce the moisture flux from 8,000 yr to the present.

Controls on Chloride Profiles and Moisture Fluxes

Chloride profiles and moisture fluxes from the Hueco Bolson were compared with those from other regions to evaluate controls on unsaturated flow and solute transport processes. Possible controls on these processes include climate and paleoclimate, geomorphic and hydrologic settings, and soil texture.

Moisture fluxes from chloride profiles in sand dunes in a humid region in Western Australia ranged from 50 to 115 mm yr^{-1}, which is much higher than those estimated for sand dunes in an arid region (flux 0.06 mm yr^{-1}) in South Australia (Table 1). The wetter region was characterized by up to 50% flow along preferential pathways that bypassed the matrix (Sharma and Hughes, 1985). Moisture flux differences between these two regions are much greater than flux

TABLE 1

Comparison of physical and chemical data from Texas, New Mexico, and Australia

	Precipitation (mm/yr^{-1})	Water table depth (m)	Geomorphic setting	Soil texture	Maximum chloride (g/m^{-3})	Moisture flux (mm/yr^{-1})
Texas[a]						
(Hueco Bolson)	280 (arid)	150	Ephemeral stream	Clay to muddy-sandy-gravel	9300	0.01 to 0.7
			interstream	Clay to muddy-sandy-gravel	6300	0.03 to 0.27
New Mexico[b,c]	444 or 385	30	Playa		≤ 100	2.8-12.4[c]
(Eastern)	(semiarid)		Sand hills		≤ 300	1.3-4.3[a]
(Central) 24 km N of Socorro[d,e]	220 (arid)	5	Pleistocene alluvium	Sandy loam to loamy sand	60 to 2720	1-3
(3*) (3**)		100	Holocene terrace	sand		1-3
40 km NE of Las Cruces[d]	220 (arid)	100		Sandy loam to Sandy clay loam	680	0.1
South Australia 100 km NE of Adelaide[f]	300 (arid)	28-40	Undisturbed calcrete		7500	0.1-0.17
			1° sinkhole		22500	0.07-0.09
			2° sinkhole		30	≥ 60
			Vegetated dunes		20000	0.06
			Cleared dunes			13
Western Australia 40 km N of Perth[g]	800 (humid)	90	Dunes	sand	250 -500	50-115

This paper; [b]Phillips and Stone, 1985; [c]Stone (1990); [d]Mattick et al., 1987; Phillips et al., 1988; [e]Phillips et al., 1984; [f]Allison et al., 1985; [g]Sharma and Hughes, 1985.

differences attributed to paleoclimatic variations in the Hueco Bolson (0.01 to 0.26 mm yr^{-1}) and in South Australia (0.01 to 0.17 mm yr^{-1}) (Allison et al., 1985). Calculated moisture fluxes are directly affected by uncertainty in the estimated chloride accession rate. Estimated moisture fluxes for chloride profiles in eastern New Mexico ranged from 1 to 12 mm yr^{-1} (Stone, 1990) based on measured chloride concentrations in precipitation of 2.4 g m^{-3}; however, moisture fluxes for the same chloride profiles were four times less when a value of chloride concentration of precipitation from a nearby area of 0.6 g m^{-3} was used (Phillips and Stone, 1985).

Chloride profiles were measured in a variety of geomorphic settings in New Mexico and South Australia. Geomorphic settings that varied from sand hills to playas (depressions that are frequently ponded) were sampled in eastern New Mexico, and moisture fluxes ranged from 1 to 4 mm yr^{-1} in the sandy areas to 12 mm yr^{-1} in the playas (Stone, 1990). The moisture-flux estimate for the playas represents the lower limit of the actual moisture flux because runoff into the playa was not included in the calculations. Undisturbed calcrete, primary and secondary sinkholes, and vegetated and unvegetated sand dunes were sampled for chloride in South Australia (Allison et al., 1985). Calculated moisture fluxes in the undisturbed calcrete and primary sinkhole ranged from 0.07 to 0.17 mm yr^{-1}, and an increase in moisture flux in the past was attributed to paleoclimatic variations. Because runoff was not included in the chloride calculations for secondary sinkholes, the recharge estimate of 60 mm yr^{-1} represents the lower limit of moisture flux in this geomorphic setting. Higher moisture fluxes in the unvegetated dunes relative to the vegetated dunes signify the importance of transpiration in reducing the moisture flux in these systems (Table 1). These variations in moisture flux with geomorphic setting are much greater than those recorded between ephemeral stream and interstream settings in the Hueco Bolson, probably because differences in topography between these two geomorphic systems in the Hueco Bolson are small (0.6 m).

The subsurface hydrologic system may also affect the shape of the chloride profile and calculated moisture fluxes. The unsaturated zone in the northern Sahara is characterized by maximum chloride concentrations at the soil surface and an exponential decrease in concentration to the water table that is at a depth of 20 m (Fontes et al., 1986). The profiles are attributed to groundwater discharge, which is corroborated by stable isotope data. The lack of sensitivity of the chloride profiles to subsurface hydrology is demonstrated by two closely spaced (2 km apart) chloride profiles in New Mexico. The water table in the Pleistocene alluvium site near Socorro is 5 m deep, and measured water potentials are high (≥ -0.8 MPa) (Stephens and Knowlton, 1986). The water table is much deeper in the Holocene terrace (Table 1), and under steady-state flow equilibrium water potentials should be approximately 1 order of magnitude lower than those in the Pleistocene alluvium. Soil texture in both systems ranges from sandy loam to sand. Moisture fluxes based on chloride profiles are similar (1 to 3 mm yr^{-1}) and suggest that long-term moisture fluxes are insensitive to variations in water potential in the unsaturated zone or in water-table depth.

The effect of soil texture on calculated moisture fluxes was examined by comparing chloride profiles and moisture fluxes in Holocene terrace environments near Socorro and in another site near Las Cruces (Phillips et al., 1988). Water-table depth and geomorphic setting are similar in both areas (Table 1). Lower moisture fluxes calculated from chloride profiles near Las Cruces relative to those recorded in the Holocene terrace area were attributed to finer grained sediments near Las Cruces compared with those measured in the Holocene terrace (Table 1). Large porosities associated with finer grained sediments retain water for longer periods of time in the shallow zone where it is more readily evapotranspired.

The combined effects of grain size and climatic factors also affect transport mechanisms in the unsaturated zone. Soil texture in profiles from an area in Western Australia ranges from gravel in the shallow zone (1 to 5 m) to clay at a depth of 5 to 30 m (Peck et al., 1981; Johnston, 1987). Precipitation rates are high in this area (600 to 1,300 mm yr^{-1}) and result in high moisture contents of 0.4 m^3 m^{-3} in the clay section. The chloride profiles are bulge shaped and are characterized by steep concentration gradients. The combination of high moisture contents in the clay and steep chloride concentration gradients results in downward diffusive fluxes being dominant below the chloride peak and net upward advective fluxes of 0.05 to 0.5 mm yr^{-1} below the chloride peak in some profiles.

Implications for Waste Disposal

Data from chloride profiles have direct implications for evaluation of waste-disposal sites. One of the primary uncertainties associated with waste disposal is the prediction of long-term climatic variations and their effect on moisture flux. Chloride profiles in the Hueco Bolson represent up to 30,000 yr of moisture flux and probably span paleoclimatic variations. The range in moisture fluxes, represented by the chloride profiles, can be used to evaluate sensitivity of contaminant migration from proposed sites to variations in flux. Moisture fluxes in wetter regions may approximate the flux beneath leaking waste-disposal facilities in more arid systems. Flow along preferential pathways appears to be more prevalent in wetter climates (Sharma and Hughes, 1985; Johnston, 1987). If unsaturated flow bypasses the matrix, contaminant transport rates would be much greater than those estimated on the basis of piston flow.

Comparison of chloride profiles in several regions showed that calculated recharge rates are much more sensitive to geomorphic settings than to paleoclimatic variations. Because of the strong dependence of moisture flux on geomorphic setting it is important to characterize geomorphic variations within an area and to measure chloride profiles in each setting to adequately quantify recharge at a site. The variability in moisture fluxes gives some indication of the number of chloride profiles required to obtain an estimate of the areal moisture flux.

CONCLUSIONS

Chloride profiles were quite variable in the study area, and maximum concentrations ranged from 1,900 to 9,300 g m^{-3} m^{-1}. Although chloride-concentration gradients were steep (up to 12,000 g m^{-3} m^{-1}), diffusive moisture fluxes were negligible (10^{-3} to 10^{-5} mm yr^{-1}) because of the low observed moisture contents ($\leq$ 0.1 m^3 m^{-3}) in the zone of steep concentration gradients. Advective moisture fluxes ranged from 10^{-1} to 10^{-2} mm yr^{-1} in most profiles and approximated the total moisture flux. Because the chloride flux (0.08 g m^{-2} yr^{-1}) was assumed to be constant throughout the area, the moisture flux was inversely related to the chloride concentration in the soil water. Reductions in chloride concentration with depth below the peak were attributed to higher moisture fluxes in the past, an inference that was generally consistent with paleoclimatic reconstructions of the area.

Comparisons among chloride profiles in different regions indicated that variations in geomorphic setting, climate, and soil texture are among the primary controls of moisture fluxes in the unsaturated zone. Information on the relative importance of different controls on unsaturated moisture flux can be used to evaluate various parameters in site characterization studies related to waste disposal. In addition, data on soil moisture flux variations provided by chloride profiles can be used in sensitivity analyses related to performance assessment of different sites.

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