

CHAPTER 2

THEORY

2.1 STABLE ISOTOPE RELATIONSHIPS

2.1.1 GENERAL

The standard delta notation for reporting stable isotopes in water was introduced in the section 1.3. Isotope relationships of importance to the current work will be briefly considered.

Fractionation refers to the change in isotope composition during a physical or chemical process or exchange. For many fractionating phenomena, the change may be predicted by factors that can be calculated or measured by experiment. Fractionation factors are discussed by all isotope texts, two easily readable reviews are those by O'Neil (1986a,b). The isotopic fractionation factor α between two substances A and B is defined as

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad (2.1)$$

where R is the ratio of heavy to light isotope. In terms of δ values,

$$\alpha_{A-B} = \frac{1000 + \delta_A}{1000 + \delta_B} \quad (2.2)$$

Fractionations are also reported as Δ values, the difference between the

delta values, which is approximately related to α as follows,

$$\Delta_{A-B} = \delta_A - \delta_B \cong 1000 \ln \alpha_{A-B} \quad (2.3)$$

Also in use is the ϵ fractionation factor, practically equal to Δ in the case of hydrogen and oxygen, where

$$\epsilon = 1000 (\alpha - 1) \quad (2.4)$$

Fractionation factors have been established for a great number of pairs of substances and states, and collected in such publications as Friedman and O'Neil (1977). Of particular interest in the context of this study are those between liquid water and its vapour between 0 and 100°C (Majoube, 1971). The presence of high concentrations of solutes affects these fractionation factors, as shown by the graphs of Friedman and O'Neil (1977). Sodium chloride has no apparent effect on the Δ_{O-18} of 9.3‰, at 25 °C, but reduces Δ_D from 81‰ of pure water to 70‰ at a molality of 5 (175 g l⁻¹ Cl) at 20°C, with a linear interpolation between the two (Stewart & Friedman, 1975).

The sign as well as magnitude of Δ may change over a large range of temperature (a "crossover"); deuterium is enriched in vapour relative to liquid water if high pressure enables the two phases to co-exist above 220°C (O'Neil, 1986b), but this effect is not met in most near-surface hydrologic scenarios.

2.1.2 RELATIONSHIP BETWEEN DEUTERIUM AND OXYGEN-18

Examination of the relationship between δD and $\delta^{18}O$ in natural water bodies is of importance in many stable isotope investigations, as was introduced in section 1.3. Craig (1961a) showed that rainwaters from

around the world, except those from closed basins and/or which have undergone excessive evaporation, fall on a line on a $\delta D - \delta^{18}O$ plot with the relation

$$\delta D = 8 \delta^{18}O + 10 \quad (2.5)$$

which is known as the meteoric line. Much work has been done since, but Craig's original observation still holds well in most situations (one exception being in the Mediterranean and Arabian areas, "closed basins"). Isotopically lighter rainfall occurs near the poles and at high altitudes, and heavier in the warm tropics. At an individual location the range of values in a large number of rainfall events is large, but usually fall on a line similar to that defined by Craig (e.g. Hughes & Allison, 1984); local data should be used if available and reliable (several years' data is required for reliable averages and meteoric lines). Many ground and surface waters, where not greatly affected by evaporation, have isotopic compositions that fall on or very near the meteoric line, demonstrating their origin as precipitation; the waters of the main aquifers of the Great Artesian Basin fall into this category, for example (Airey *et al.*, 1979).

More generally the expression may be written

$$\delta D = S \delta^{18}O + d, \quad (2.6)$$

where S is the slope of the relationship on a $\delta D - \delta^{18}O$ plot, and d is the intercept or deuterium excess. With respect to a mineral phase and water, the term hydration line is used.

The relationship between δD and $\delta^{18}O$ in an open, evaporating water body and its derived vapour does not yield a line of slope 8, but rather

of a slope of about 5, depending on the relative humidity h (or h_a) of the air. This is explained as due to additional "kinetic" fractionation, due to slightly different diffusion rates that occur in the film of air above the water surface, the effect for oxygen being similar to that for hydrogen (Craig & Gordon, 1965). At high humidity, there is rapid, two-way molecular exchange between liquid and vapour phases of water, so that the kinetic fractionation is small and the slope S closer to 8, while at low humidity many more molecules leave the liquid than enter it (evaporation is high), kinetic fractionation is more important, and the slope S lower. Where unsaturated soil intervenes between the evaporating liquid water and the atmosphere, vapour diffusion occurs over a longer interval, and the effect of kinetic fractionation is greater. This was demonstrated in the laboratory for constant-feed pans covered with different thicknesses of mulch by Allison *et al.* (1983), and slopes from 5 to as low as 2 have been observed from very dry evaporating soils (Barnes & Allison, 1988). Assuming the diffusivities of the two heavy isotopes of water to be approximately equal, and ignoring osmotic effects, the relationship is predicted by (Barnes & Allison, 1983)

$$S = \frac{\alpha_{18} \left[\frac{[(1-h_a)\eta_2 + \epsilon_2](1 + \delta D_{18}^{res}) - h_a(\delta D_{18}^{res} - \delta D_{18}^a)}{[(1-h_a)\eta_{18} + \epsilon_{18}](1 + \delta O_{18}^{res}) - h_a(\delta O_{18}^{res} - \delta O_{18}^a)} \right]}{\alpha_2} \quad (2.7)$$

and

$$d = \delta D_{18}^{res} - S \delta O_{18}^{res} \quad (2.8)$$

in the zone where only liquid transport occurs. Note that h_a , atmospheric relative humidity, ϵ and δ need to be in absolute ratios, not percent or permil, e.g. 0.4, 0.0093 and 0.989, not 40%, 9.3% and -11%. Subscripts 2 and 18 refer to deuterium and oxygen-18 respectively, and the subscript *res* to reservoir (water source, e.g.

water table) values. The symbol η_i represents the diffusion ratio excess of species i ,

$$\eta_i = (r_i/r) - 1 \approx n [(D^v/D_i^v) - 1], \quad (2.9)$$

where r is the notional resistance to diffusion of the species or of "normal" (or light) water, D^v is the vapour diffusivity in air, and n a proportionality constant, equal to 1 for static, purely diffusional transport, 0.5 for fully turbulent conditions, and 0.67 for flow over a smooth surface, such as a water body. The appropriate value for evaporation beneath a soil varies from about 0.5 when the water table is at the surface, increasing to 1.0 as the depth to water table increases; this has the effect of decreasing S (Allison *et al.*, 1982; Barnes & Allison, 1983).

The equilibrium fractionation factors between the water of crystallisation of gypsum and its parent precipitating solution were determined by Sofer (1978) following work by Gonfiantini and Fontes (1963) and Fontes and Gonfiantini (1967) as being almost temperature independent, with the values of

$$\alpha_{18} = 1.0040 \quad \text{and} \quad \alpha_2 = 0.980, \quad (2.10)$$

i.e. the hydration water is enriched in oxygen-18 and depleted in deuterium relative to the precipitating solution, when in equilibrium.

These relations can be used to calculate the theoretical brine isotopic composition from the isotopic composition of gypsum water. The slope of the hydration line is negative,

$$\Delta_2 / \Delta_{18} = -5$$

in contrast to that of water liquid-vapour which is +8. The equilibration fractionation factors for many other hydrated, hydroxylated and oxygen bearing minerals are available; it is not uncommon for the slope of the hydration line to be negative.

2.2 DIFFUSION THEORY

2.2.1 GENERAL

2.2.1.1 Fick's Law

Diffusion results from the random thermal (Brownian) motion of atoms, ions or molecules. If two parts of a region are at a different concentration C of a substance at a distance x apart, and able to move, more atoms (ions, molecules) will tend to move from the part of the region of higher concentration to the part of lower concentration than the reverse. In one dimension the steady state flux, or nett amount crossing unit cross-section in unit time, is given by the relation known as Fick's first law (Fick, 1855)

$$F = -D \frac{dC}{dx} \quad (2.11)$$

where F is the flux and dC/dx the concentration gradient over the area of interest. The negative sign is present as movement occurs from areas of high to low concentration. This equation *defines* D , the diffusion coefficient or diffusivity, as the constant of proportionality between F and dC/dx , a quantity that may be determined experimentally. The dimensions of D are L^2T^{-1} , properly m^2s^{-1} although a lot of early data are in cm^2s^{-1} and other units are sometimes employed. An analogous equation can be written in two or three dimensions.

In simple systems like dilute solutions of uncharged solutes or mixtures of gases D may be nearly constant over a range of concentrations, but in complex solutions such as soil and ground waters involving ions, D will usually depend on the concentration of the ion considered, and on that of other ions present as well.

Fick's first law may be derived from thermodynamic principles in ideal systems, but in a complex medium as presented by naturally occurring porous media the equation defines an operational or effective diffusivity (Nye, 1979). Where the flux F is the required unknown in a system being studied, an estimate of $D_{\text{effective}}$ must generally be made by modifying the diffusion coefficient obtained from the literature or experiments in simpler systems. The matter of determining a suitable D will be the main concern of this section.

2.2.1.2 Effect of Companion Ions

The diffusion coefficients so far discussed have largely concerned a single ion or gas. In a solution, such rates strictly apply only to an isotope concentration gradient of that species in a constant concentration of that ion. This same D also applies where the ion is only a very minor component of a mixture, so that variations in its concentration have no effect on the total cation-anion balance and concentration.

Two other cases need to be considered. Where there is a concentration gradient of a dissolved salt, to maintain electroneutrality the balancing cations and anions must diffuse at the same rate. Similarly, in counter diffusion, where different anions or cations are moving in opposite directions, the rates must be the same. The modification to the flux F_A of an ion A due to other ions is given by (Nye, 1966). For a simple completely dissociating binary salt with cation and anion of equal charge, the bulk (salt) diffusion coefficient is given by

$$D_{12} = 2D_1 D_2 / (D_1 + D_2) \quad (2.12)$$

where subscripts 1 and 2 represent the two components. For Na Cl diffusing in water, the limiting (as concentration approaches zero) self diffusion coefficients of Cl^- and Na^+ at 25°C are 2.045 and $1.333 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ respectively at 25°C (Robinson & Stokes, 1959, p317), and the calculated diffusivity of Na Cl $1.61 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, the same as the measured value. It is the bulk diffusivity of sodium chloride that must be used in examining the chloride profiles presented in this work, not the self diffusivity of the chloride ion alone.

2.2.1.3 Effect of Concentration and Temperature

For low gradients of concentration the effective diffusivity D can usually be considered fairly constant, but for large concentration differences D can vary by a few percent. The variation of D for sodium chloride in aqueous solution at 25°C are shown in figure 2.2.1 of Harned and Owen (1958), and some values of various alkaline chlorides tabulated in table 2.2.1 (ibid).

The effect of temperature on diffusivity is more significant, as the Brownian motion of the particles is greater at higher temperatures, and viscosity less. The approximate thermodynamic relation is

$$\frac{D_{T_1}}{D_{T_2}} = \frac{T_1 \eta_2}{T_2 \eta_1} \quad (2.13)$$

where T_1 and T_2 are absolute temperatures (Kelvin), and η_1 and η_2 are the viscosity of water (not solution) at those temperatures (Jost, 1960).

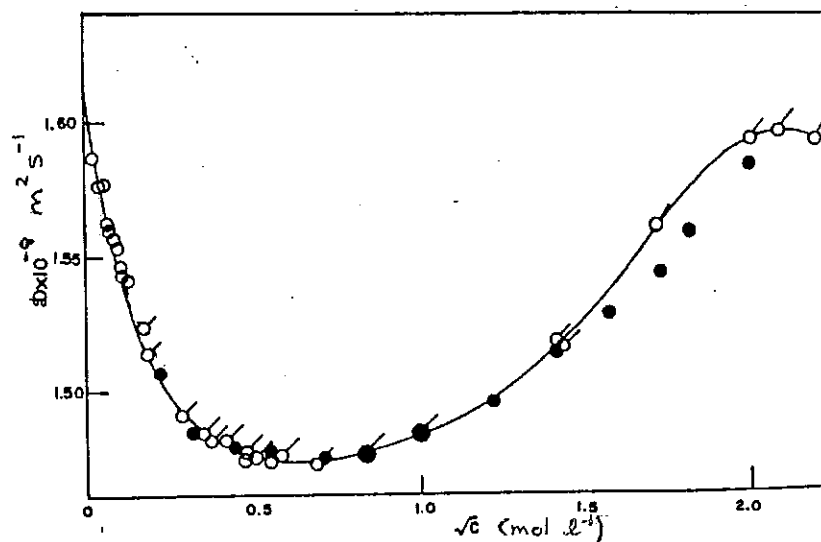


Fig. 2-2-1. The diffusion coefficient of sodium chloride in aqueous solutions at 25° by the conductometric method (circles), Gouy interference method (circles with dash) and diaphragm cell method (dots).

TABLE 2-2-1 DIFFUSION COEFFICIENTS OF ALKALI AND ALKALINE EARTH METAL CHLORIDES OVER ENTIRE CONCENTRATION RANGES AT 25°.

c (mol l ⁻¹)	D × 10 ⁻⁹ m ² s ⁻¹				
	NaCl ⁽¹⁾	KCl ⁽²⁾	CsCl ⁽³⁾	CaCl ⁽³⁾	BaCl ⁽³⁾
0.0	(1.611)	(1.994)	(2.044)	(1.335)	(1.386)
.001	1.535	1.962	2.009	1.258	1.317
.002	1.574	1.951	1.996	1.239	1.298
.005	1.559	1.933	1.975	1.210	1.263
.01	1.545	1.915	1.954	1.188	1.238
.02	1.530	1.892	1.930	1.161	1.212
.05	1.507	1.862	1.892	1.137	1.176
.1	1.482	1.842	1.870	1.122	1.160
.2	1.473	1.835	1.850	1.122	1.150
.5	1.473	1.850	1.860	1.150	1.160
1.	1.485	1.893	1.902	1.220	1.177
2.	1.518	2.001	2.029	1.308	—
3.	1.565	2.111	2.173	1.278	—
4.	1.594	2.207	2.111	1.078	—
5.	1.590	—	2.363	0.725	—
6.	—	—	2.335	0.402	—

(1) V. Vitagliano and P. A. Lyons, *J. Am. Chem. Soc.*, 78, 1849 (1956).
 (2) L. J. Gosting, *Ibid.*, 72, 4418 (1950).
 (3) P. A. Lyons and J. F. Riley, *ibid.*, 76, 5216 (1954).

from Harned & Owen, 1958.

2.2.1.4 Measurement of Diffusivity and Literature Values of Relevance

A variety of methods are available for measuring the diffusivity of gases, liquids, and solutes, such as described in Jost (1960). The diffusivity of sodium chloride at different concentrations from Harned and Owen are given in section 2.2.1.2. Values at different temperatures may be calculated by equation 2.13 using data for the variation of the viscosity of water (Weast, 1979). Harris *et al.* (1978) give values of D for Na and Cl at 10°C and various concentrations, given in table 2.2.2, with an added column of D_{NaCl} calculated by equation 2.12. The measured 10°C data do not show the same pattern as at 25°C, but rather decrease monotonically with increasing concentration. The following columns give values calculated using equation 2.13, and the errors, which are very large at high concentrations. Great caution should therefore be used in applying equation 2.13 at high concentrations, more than a few degrees away from the temperature of known measurements.

The diffusivity of the isotopes of water as vapour in air (N_2) was measured by Merlivat (1978) at 21°C and atmospheric pressure. Her value for natural water vapour in nitrogen was $2.44 \pm 0.04 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The following ratios were calculated

$$D_{\text{HD}^{16}\text{O}}^{\text{v}} / D_{\text{H}_2^{16}\text{O}}^{\text{v}} = 0.9755 \pm 0.0009$$

and

$$D_{\text{H}_2^{18}\text{O}}^{\text{v}} / D_{\text{H}_2^{16}\text{O}}^{\text{v}} = 0.9723 \pm 0.0007$$

so that only about 2.5% error is induced if diffusion coefficients for natural water vapour in air are used. She found that these differences could not be accounted for solely by the mass differences between water molecules, but that the displacement of the centre of gravity by the

TABLE 2.2.2

Ionic Self and Salt Diffusion Coefficients of Sodium Chloride, at 10°C,
Measured and Calculated.

C mol/l	Measured at 10°C		calculated from 25°C data		
	D _{Na+} ¹	D _{Cl-} ¹	D _{NaCl} ²	D _{NaCl} ³	error (%)
0.0	(0.878)	(1.372)	1.071	1.044	-2.4
0.5	0.849	1.286	1.023	0.958	-6.4
1.0	0.823	1.229	0.986	0.962	-2.4
3.0	0.705	0.967	0.815	1.014	+24
5.0	0.543	0.694	0.609	1.031	+69

Units of diffusion $\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

1 Mills et al., 1978

2 Calculated by equation 2.12

3 Calculated by equation 2.13

heavy isotopes was also important. The diffusivity of water vapour in air at 8°C is $2.39 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (Weast, 1979), showing the small dependence of this parameter on temperature. The viscosity of air varies only from 170.8 to 190.4 micropoise between 0°C and 40°C (Weast, 1979), so that the use of Merlivat's diffusivity value appears quite justified within 10°C or so of the temperature of measurement, 21°C .

Values for the diffusivity of water in the liquid phase are obtained from Mills (1973) for deuterium and tritium, the latter not presented, and Harris and Woolf (1980) for oxygen-18. The former were measured by the diaphragm-cell technique ($\pm 0.2\%$) and the latter by n.m.r. (nuclear magnetic resonance) spin-echo technique ($\pm 1\%$). These are presented in the temperature range covered in table 2.2.3, with the ratios to normal water. Values are for diffusion in normal water at one atmosphere pressure. The relative difference is greater for oxygen-18 water than deuterated water, to a much greater extent than for water vapour.

2.2.2 DIFFUSION IN POROUS MEDIA

To consider the meaning of an effective diffusivity D in a porous medium, it is helpful to begin with a simplified system and work towards a better approximation of the complex situation found in nature.

2.2.2.1 Geometric Effects

Consider first a still volume of solution, or a still volume of a gas mixture, at steady state, across which exists a concentration gradient of an isotope of the species in question, with a constant total concentration to avoid any effect of C on D (Fig. 2.2.2a). Here Fick's law may be simply applied and the D determined is the self diffusivity of

TABLE 2.2.3

Self Diffusion Coefficients of Water

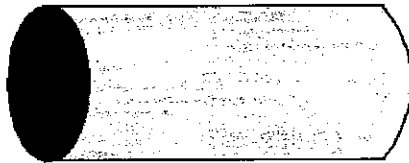
Temperature °C	H ₂ ¹⁶ O Mills	H ₂ ¹⁶ O H&W	HD ¹⁶ O Mills	D [*] /D	H ₂ ¹⁸ O H&W	D [*] /D
1	1.149		1.128	0.982		
4	1.276	1.27			1.20	0.945
5	1.313		1.295	0.986		
10		1.56			1.45	0.929
15	1.777					
25	2.299	2.30	2.272	0.988	2.19	0.952
35	2.919					
45	3.575	3.55	3.532	0.988	3.38	0.952
60		4.70			4.49	0.955

Units of diffusion $\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

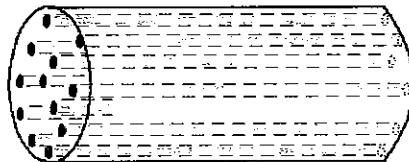
Mills refers to his 1973 paper

H&W refers to Harris & Woolf, 1980

a: Solution alone



b: Parallel, solution filled tubes in a solid matrix



c: Irregular pore spaces in a solid matrix

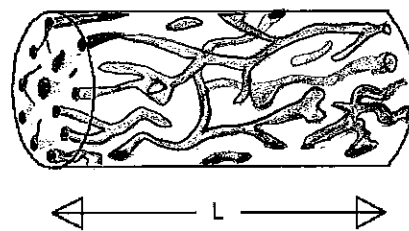


FIGURE 2.2.2 Illustration of geometric effects on diffusion in a porous medium.

the species at that total concentration, D_{self} or D_0 , i.e. $D = D_0$. This parameter may be measured by various experimental techniques and is available in physical chemistry literature for most substances.

Next consider the same volume where the species may move only in a series of pipes of unreactive material parallel to the direction of movement (Fig. 2.2.2b). Within each pipe the previous equation will apply, per unit area of open pipe. Considering the cross-section as a whole, flux will be reduced compared to the first case by the proportion of open to total area $a_{\text{open}}/a_{\text{total}}$. It is seen that this is the same as the ratio of the open to total volume, i.e. the porosity of the material p . Hence

$$D = D_0 p \quad \text{and} \quad F = -D_0 p \frac{dC}{dx}. \quad (2.14, 2.15)$$

In solute movement, volumetric water content should be used rather than porosity, and for movement of gases the air filled porosity.

In a natural porous aggregate the joined fluid filled (water or air as the case may be) may not be well considered as parallel pipes, but of variably sized pores with irregular connections. The path that a diffusing species must travel at the microscopic scale is around intervening particles and sections of pores filled with another blocking phase (e.g. air for water solutes) is longer than the macroscopic length L (Fig. 2.2.2c). The ratio of macroscopic to microscopic travel path is sometimes denoted L/L_e (Porter *et al.*, 1960) and the overall effect (actually $(L/L_e)^2$) is known as the tortuosity τ , referring to the tortuous path individual particles must take. Allowing for tortuosity in addition to appropriate porosity,

$$D = D_0 p \tau \quad \text{and} \quad F = -D_0 p \tau \frac{dC}{dx}. \quad (2.14, 2.15)$$

If on average particles moved at 45° to the direction of the maximum pressure gradient, as can be envisaged for a simple granular medium of spherical particles, τ should be $1/\sqrt{2}$ or 0.71: tortuosities of 0.65 to 0.7 in glass beads have been measured for the diffusion of tritiated water (Nakayama & Jackson, 1963). This figure would seem to be an upper bound as nearly all natural systems of irregular grains and pore geometries have lower estimates for τ .

Tortuosity can be directionally dependant (anisotropic) if the matrix and pores of a porous medium are plate or rod shaped and aligned, as in many shales and some clays (Fig. 2.2.3). Note that more tortuous paths result in lower τ values by the way it is defined.

2.2.2.2 Anion Exclusion

This effect is usually only important in the movement of aqueous anions in porous media that contain clay minerals or organic matter. Under commonly occurring pH conditions (other than quite acid) the surfaces of individual clay particles are negatively charged by the nature of their crystalline structure. This negative charge is made up by an excess of cations in the bathing solution immediately adjacent to the clay surface (those immediately adjacent are referred to as the Stern layer), and conversely a deficit of anions in the same zone. This "anion exclusion" effect has been well studied and described by double layer theory (e.g. Bolt & de Haan 1979). The distribution of monovalent anions and cations near the surface of a montmorillonite particle is shown in figure 2.2.4. The more concentrated the aqueous solution bathing the clay particle, the less the distance affected by anion exclusion. The thickness of the affected layer is not only controlled by the total electrolyte concentration, but also by the mineralogical composition of

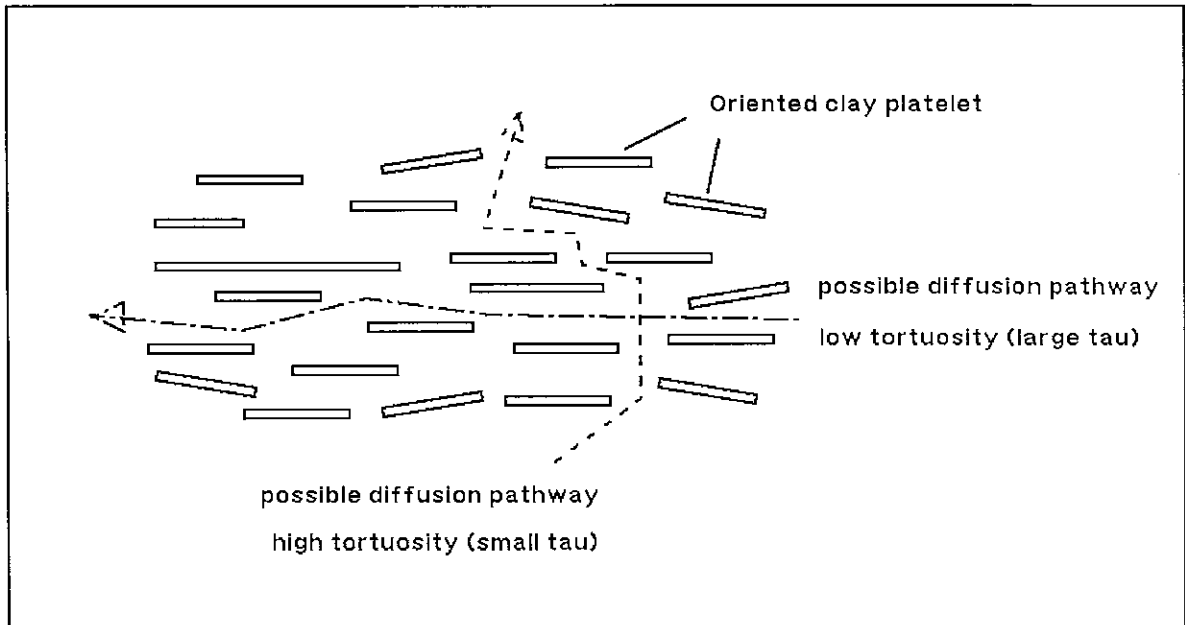


FIGURE 2.2.3 Illustration of anisotropy of tortuosity
in an oriented clay

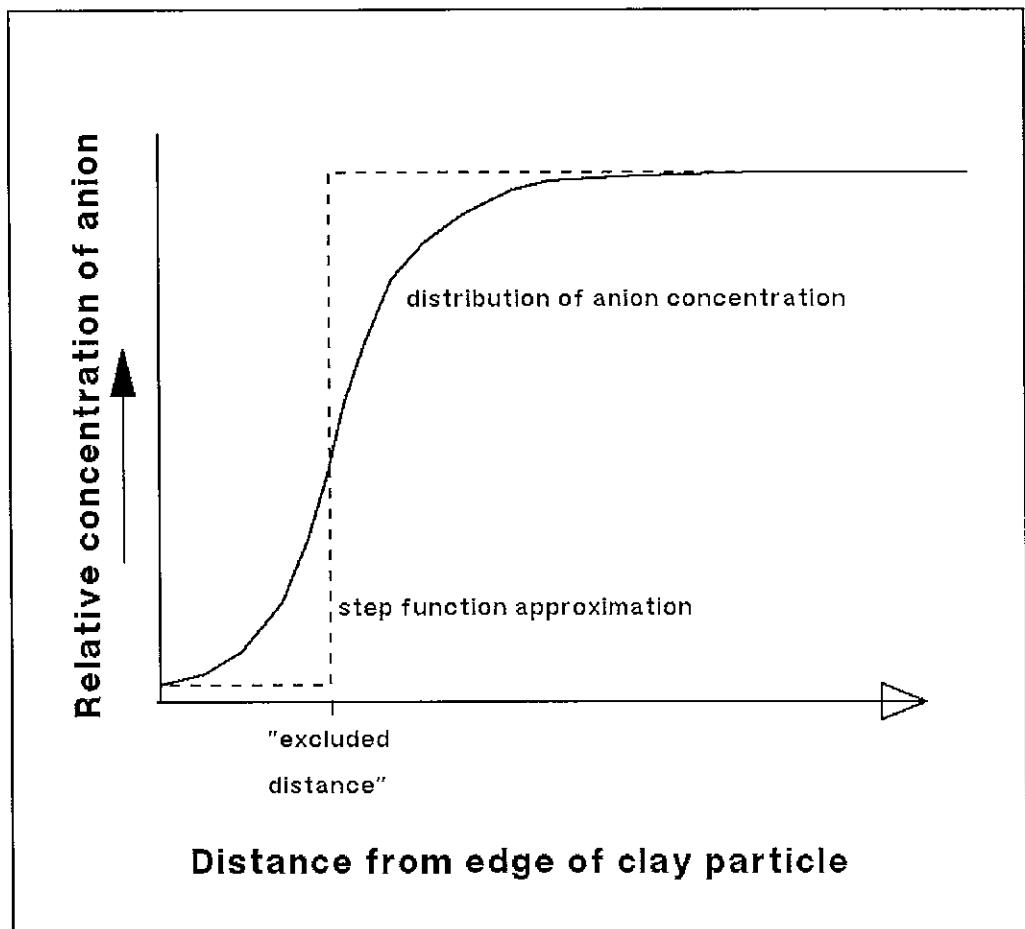


FIGURE 2.2.4 Distribution of anions near a clay particle surface after Bolt and de Haan (1979)

the medium and the valency and hydration of the ions in the solution (Nielsen *et al.*, 1986). For example, the distance tends to be less for divalent ions.

Although the distribution of ions away from such a surface is gradual, it is usually convenient, and for many purposes sufficient, to consider an excluded volume within the pore space to contain no anions at all (Fig. 2.2.4). The distance involved depends on the parameters mentioned above, but typically is of the order of $5 - 100 \times 10^{-10}$ m (Bolt & de Haan, 1979). As clays may have surface areas of $500 \text{ m}^2 \text{ g}^{-1}$ (*ibid*), soils or rocks with high clay mineral contents may exclude anions from up to $0.20 \text{ cm}^3 \text{ g}^{-1}$ (Bresler, 1973), though usually less. Exclusion of only $0.001 \text{ cm}^3 \text{ g}^{-1}$ may be important at low water contents. Expressed as a proportion of total water volume in soil, excluded volumes of about 0.3 are not uncommon, and 0.1 may occur even in sandy material (James & Rubin, 1986). Gvirtzman *et al.* (1986) calculated that excluded volume was about 50% of the total volumetric water content in a clay loam, but virtually negligible in a sandy unit.

The first effect of anion exclusion as concerns diffusion is that it changes the actual pore water concentration of an anion by reducing the volume of water in which it is contained, compared to the concentration calculated by many standard analytical methods. If anion exclusion is the same throughout the medium, the gradient dC/dx is not affected. In mass flow (convection) ion will move faster than bulk water by being confined to larger pores where water velocities are above average, an effect that has been documented in many laboratory studies (e.g. Bond *et al.*, 1982). For diffusion, the flux of an anion is reduced due to a lesser available cross-sectional area, i.e. the porosity to be used is

$p_{\text{effective}} = \theta_{\text{tot}} - \theta_{\text{ex}}$, where θ_{tot} and θ_{ex} are the total and excluded water volumes respectively. At low water contents anions may be excluded

from neck connecting pores that cations are not, so that tortuosity may increase (lower τ) for the anions compared to cations in the same material.

2.2.2.3 Other Matrix Effects

The simple assumption of a matrix unreactive with the species moving in the intervening fluid is sufficient for some solutes or gases in some situations. Often interactions with the matrix have a very marked effect on fluxes. Anion exclusion has already been discussed, and the most important of these are considered below.

Adsorption on Matrix Components

Many ions and some gases are adsorbed onto the surface of matrix particles. Where the surface area per mass or volume of matrix is great, as with clays, this may have great effects on the diffusive flux, particularly in the non-steady state. The effects of adsorption/desorption are most strongly felt in the case of aqueous cations in clayey materials, or anions at low pH. It has the effect of retarding the progress of diffusion of ions, by up to several orders of magnitude compared to non-adsorbing species (e.g. Bradbury & Green, 1985).

One way to handle the effect of adsorption is to consider the fraction of their time that a diffusible ion spends in the solution phase (Nye, 1979). It can be included as a multiplicative factor in the calculation of D_{eff} called $1/\mathcal{R}$, where \mathcal{R} is the retardation factor, related to the adsorption isotherm or partition coefficient, depending on the approach. For the purposes of this work chloride is assumed to exist only as a dissolved ion, except where halite (solid NaCl) is present in

the soil matrix, and retardation is assumed to be negligible.

Flux through Solid Matrix Components

Diffusion can and does occur in the solid phase as well as the liquid and gaseous, though at much slower rates as the atoms are much more strongly bound. The values of diffusivity for H^+ in water and K^+ in an illitic clay are $10^{-8} \text{ m}^2 \text{ s}^{-1}$ and $10^{-27} \text{ m}^2 \text{ s}^{-1}$ respectively, for instance (Nye, 1979). The movement of ions through the solid phase is sometimes significant however, and is usually referred to as an excess flux F_E , so that

$$F = -D \frac{dC(\text{aq})}{dx} + F_E \quad (2.18)$$

if needed (ibid). This excess flux can be important at very low water contents (Rowell *et al.*, 1967, for Na^+), but for most situations is negligible.

Electrostatic and Viscosity Effects

Close to a negatively charged clay surface, cations are not as highly hydrated as those in the pore solution further away. This changes their effective size and energy status, as they require more energy to move, being attracted to the clay particle surface, especially in the first or Stern layer. This effect can be handled conceptually by considering only a fraction of these exchangeable adsorbed cations to have the same mobility as fully hydrated, freely dissolved ions. This proportion will vary with cation type, clay mineralogy and pore solution composition, but tentative values vary from 0.05 to 0.6 (Nye, 1979). The

proportion of fully mobile ions can be also included as a multiplicative term in the calculation of D (Kemper, 1986).

There is evidence of increased viscosity of water in the immediate vicinity of clay surfaces (ibid), which would increase the energy needed for movement and hence reduce D . Both these effects, which are very hard to distinguish, are only likely to be significant at low water contents. Porter *et al.* (1960) gave the symbol γ to a multiplicative factor to be incorporated into the calculation of D from D_0 and L/L_e ,

$$D = D_0 \gamma (L/L_e)^2 . \quad (2.19)$$

Tortuosity τ , and γ are usually difficult to distinguish, although this has been attempted. Van Shaik and Kemper (1966), attempted the separation by measuring both DHO and ^{36}Cl diffusion on oriented clay. The overall effect may be combined into the impedance factor f that will be discussed shortly.

2.2.2.4 Vapour Diffusion

The diffusion of water vapour follows the same laws as liquid diffusion so long as the appropriate coefficients are used. It may be necessary to take into account the presence of the interaction of vapour with liquid water remaining in the soil even where only vapour movement is occurring.

The correct unit for measurement of water vapour content, N , in soil is mass or volume per volume of soil air. It is usually convenient to express this as the product of the saturated concentration in air at the appropriate temperature and the relative humidity, that can be measured by psychometry or calculated from soil water suction (allowing for

osmotic effects of dissolved or hygroscopic solids present). Thus

$$\text{flux} = \rho F = D_{\text{eff}} \frac{dN}{dx} \quad (2.20)$$

where ρ is the density of liquid water, F the flux in m s^{-1} ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$), and $N = N_{\text{sat}} h$, h being the relative humidity. The variation of N_{sat} with temperature is given in standard texts such as Weast (1979).

2.2.2.5 Liquid-Vapour Diffusion of Water

Considerations so far have applied to gas diffusion in air filled pores, and solute movement in water filled pores. Where both liquid and gaseous phases coexist, as in the vadose or unsaturated zone, the same considerations apply, with some further allowances. As gases are generally soluble in water, an adsorption - desorption term may be required to successfully model the diffusion of a gas. The presence of water in smaller, and gases in larger pores can cause the geometric factor, tortuosity, to vary with water content, generally lowering τ by increasing path lengths.

In the case of water itself and its isotopes, movement can occur in both the liquid and vapour phases (Philip & de Vries, 1957). Generally the nature of water content profiles is that at over discrete intervals movement is dominated by one phase, but two phase movement is considered to be important at some water contents. It is suspected that the total diffusive flux of water in such a situation is greater than the sum of parallel liquid and vapour flow, due to series flow or short-circuiting (Philip & de Vries, 1957); this is discussed and demonstrated in sections 2.2.4.3 and .4.

2.2.2.6 Non Steady State

In the real world the assumption of steady state is frequently unrealistic, although an understanding of processes at this conceptual level is necessary before progress can be made on time-dependent phenomena. Fick's second law is found by combining the first law with that of conservation of mass. In the one dimensional case, conservation of mass may be written

$$\frac{-dq}{dx} = \frac{dC}{dt} \quad (2.21)$$

and substituting $q = -D \frac{dC}{dx}$ gives

$$\frac{-d}{dx} \left(-D \frac{dC}{dx} \right) = \frac{dC}{dt} \quad (2.22)$$

Where D does not vary with x , this simplifies to

$$D \frac{d^2 C}{dx^2} = \frac{dC}{dt}, \text{ or } \frac{\partial C}{\partial t} = \text{div} (D \text{ grad } C) \quad (2.23, 2.24)$$

in three-dimensional form, which are commonly quoted forms of Fick's second law.

Where a solute is also adsorbed, the form may be written

$$\frac{\partial C}{\partial t} = D \frac{\theta}{\theta + b_1} \frac{\partial^2 C}{\partial x^2} \quad (2.25)$$

(Kemper, 1986), where b_1 is the constant from the linear model of the adsorption isotherm

$$S_a = b_1 C + b_0 \quad (2.26)$$

S_a being the adsorbed amount per unit volume of medium at the solution concentration C . Knowledge of the adsorption isotherm is vital in interpreting and predicting diffusion coefficients for strongly adsorbed species, such as phosphate (e.g. Hira & Singh, 1977) and organic solvents (e.g. Johnson *et al.*, 1989).

Analytical solutions to Fick's laws for many geometrical and other boundary conditions are given in such texts as Crank (1975), or by analogy to heat conduction in Carslaw and Jaeger (1959). Walker *et al.* (1988) and Richardson *et al.* (1988) have developed the theory of non-steady-state movement of water and isotopes during evaporation from bare soils, but the work is yet to be applied in the field.

2.2.3 THEORY FOR DIFFUSION OF CHLORIDE AND WATER ISOTOPES IN SOILS

The theory of diffusion in porous media has been discussed in a fairly general way. The discussion will now concentrate on developing the most appropriate form of the equations for application to the species investigated in this work, namely chloride, deuterium and oxygen-18, and the use of convection-diffusion theory to estimate water fluxes (particularly discharge driven by evaporation) from profiles of those species in the unsaturated (and top of the saturated) zone.

2.2.4 THE IMPEDANCE FACTOR

Of all the components of Fick's first law adopted for porous media, it is the geometric/surface effect that is the most difficult to obtain realistic estimates of, particularly its dependence on water content. The effects of tortuosity, interconnectedness of pores, and surface phenomena (electrostatic, viscous) are difficult to distinguish, and are

often combined into an impedance or formation factor f . This convention is adopted for this work, so the steady state equation is written

$$F = f p D_0 \frac{dC}{dx} \quad (2.27)$$

where p is again the appropriate volumetric air or water filled porosity. Various empirical, semi-empirical, or theoretical attempts have been made to give a function for the variation of f with p . The subscripts l and g will be used with f to distinguish liquid and gaseous impedance factors, the two not necessarily the same at the same point. It should be noted that some workers use tortuosity τ in the same sense as f here, presumably as the geometric effect is thought to dominate surface effects. Van Schaik and Kemper (1966) did separate geometric and surface effects and found f_l in their system of oriented clay to be about half of geometric tortuosity ($\tau = 0.5$ at $\theta_v = 0.7$), so the distinction is not just academic at least in some materials.

In order to obtain the most appropriate value(s) of f to allow useful interpretation of field data, the literature was extensively searched, and will be reviewed below with that aim.

2.2.4.1 Impedance Factor for Gaseous Diffusion in Soil

Early work by Penman (1940) measuring the diffusion of gases through soil suggested f_g could be assigned a constant value of 0.66, even though still earlier work (Buckingham 1904) had suggested $f_g = p_a$ itself. Penman used carbon disulphide and acetone vapours in dry soil and glass beads, and his constant $f_g = 0.66$ held for air-filled porosities (p_a) from 0.15 to 0.7. Using a similar technique and ethanol vapour, van Bavel (1952) found $f_g = 0.5$ to 0.6 in sandy soil and glass beads, with p_a

between 0.25 and 0.415. Ball *et al.* (1981) measured the diffusivity of the inert gas krypton in cores by its radioactive isotope ^{85}Kr and found f_g in dry silt loam to vary from 0.45 to 0.33 for p_a of 0.53 to 0.43. Many authors have argued that it is too gross a simplification to assign f_g a constant value over such a range of p_a , and many formulations have been proposed regarding the relationship between the two. A partial list of published expressions relating f_g to p_a is given in table 2.2.4, adapted from Weeks *et al.* (1982). Most of these are empirical relations except for Marshall (1959) and Millington (1959) which are based on theoretical pore distribution models.

One of the common difficulties experienced in soil physics generally is the often encountered difference between laboratory and field measurements of parameters. Various means of measuring gaseous diffusivities in the field have been documented, some of which are briefly described in Rolston and Brown (1977); field and laboratory measurements for this parameter are sometimes quite different. The field studies of Weeks *et al.* (1982) and Kreamer *et al.* (1988) are of particular interest as they were carried out to depths of 45 and 12m respectively in unsaturated profiles, the former using the "natural" distribution of two anthropogenic fluorocarbons, and the latter injected tracer gas. Using trial-and-error fitting of a numerical model with six layers, Weeks *et al.* deduced a mean f_g of 0.11 for p_a in the range 0.15 - 0.24. Five of the various formulations (table 2.2.4) predicted f_g ranging from 0.10 to 0.26. The injected tracer work of Kreamer *et al.* is perhaps less certain, but measured $f_g = 0.4$ in aeolian sand with $p_a = 0.22$, compared to calculations varying from 0.13 to 0.47 by five methods. Interestingly the second best estimate of 0.47 came from the simple Marshall (1959) model $f_g = p_a^{0.5}$. Marshall's model was unsuccessful, however, in sandy clay ($p_a = 0.06$), predicting 0.22 when the measured

TABLE 2.2.4

Partial List of Published Expressions Relating Gaseous Impedance Factor
to Air-Filled and Total Porosity of Media

(Compiled by Weeks *et al.*, 1982).

Investigator	Gaseous Impedance Factor	
	dry soil	wet soil
Buckingham (1904)	p_t	p_a
Penman (1940)	0.66	0.66
van Bavel (1951)	0.6	0.6
Marshall (1959)	$p_a^{1/2}$	
Millington (1959)	$p_a^{1/3}$	$p_a^{1/3} (p_a/p_t)^2$
Wesseling (1962)		$0.9p_a - 0.1$
Grable & Siemer (1968)	0.66	$5.25 p_a^{2.36}$
Currie (1970)		$p_t^{1/2} (p_a/p_t)^4$
de Jong & Schappert (1972)		$0.31 - 0.59(p_t - p_a)$
Lai <i>et al.</i> (1976)		$p_a^{4/3}$
Albertson (1979)		$0.777(p_a/p_t) - 0.274$

p_a = air-filled porosity

p_t = total porosity

value was about 0.1 or less. Kreamer *et al.* (1988) had difficulty in establishing p_a and allowing for sorption, so could not decide which formulation gave the best result. They concluded however that the large variations in predicted f_g "suggest that the empirical equations tend to be applicable only to the materials for which they were developed and that they be used with care. In fact, their large variance indicates the need to experimentally determine ... tortuosity in situations where the accurate prediction of gaseous diffusion rates is important."

In an attempt to allow for the distribution of pores and series/parallel paths existing in soil, and so make a more generally applicable formulation, Nielson *et al.* (1984, 1988) proposed a "spherical-particle tortuosity equation"

$$\tau = [1 + 0.61(1-p_a)^{2/3}]^{-(1 + \text{GSD}/22)} \quad (2.28)$$

(correct form from the 1988 reference), where GSD is the geometric standard deviation of the pore size distribution. This formula attempts to allow for the lower diffusion coefficients encountered in poorly sorted materials where fine particles tend to clog the pores between large particles (large GSD), as compared to clean materials (low GSD; recalling that for glass beads $f \cong 0.6$). Collin and Rasmuson (1988a,b) comment on this calculation, preferring that of Millington and Shearer (1971). The latter uses a dual porosity model to allow for aggregated media.

Much of the information required to make an estimate of f_g for the tops of the field profiles investigated by this work is not available, not even a good value for p_a , due to the generally "fluffy" nature of the fine grained to sandy material (largely of aeolian origin) that blankets most of the field area, and which occurs where vapour diffusion of water

is important. It seems appropriate then to adopt a constant value of $f_g = 0.6$ as the material is generally quite dry and of high porosity.

2.2.4.2 Impedance Factor for Chloride Diffusion in Soil

Chloride, by nature of its common occurrence, high solubility, and low reactivity, has made it a widely studied and used tracer of water and solute movement in soil science and hydrology. The diffusion of chloride has been extensively studied, and reviewed recently in the M.Sc. thesis of C.D. Johnston (1987). A collation of f_1 values for water contents between 0.0 and 0.6 from selected published works is shown in figure 2.2.5 (taken from Johnston, 1987). Although for individual soils a curvilinear relationship is apparent, as a general rule f_1 takes on the form

$$f_1 = a\theta_v + b, \quad (2.29)$$

where a and b are empirically derived constants characteristic of a soil type, and θ_v is the volumetric water content. Various laboratory methods were employed to obtain the impedance factors plotted, those working with "undisturbed" soil cores being more likely to reflect field values. The individual techniques will not be elaborated on, but many employed artificial radioactive ^{36}Cl as a tracer, while others employed regular chloride and nitrate, ions of similar diffusive properties if biological transformations are eliminated. From Johnston's graph, a general f_1 line for heavy clay (most similar to the weathered shale of this projects field profiles) might be

$$f_1 = 0.8 \theta_v - 0.05 \quad (2.30)$$

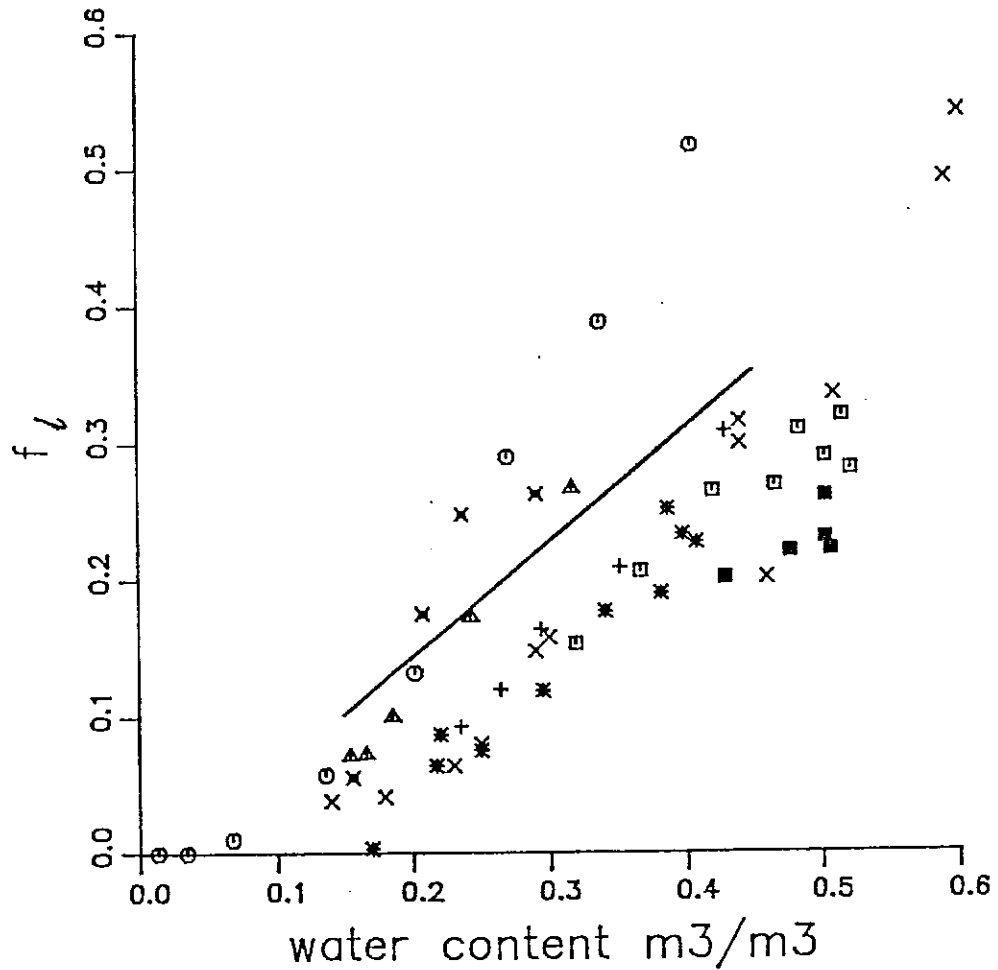


FIGURE 2.2.5 The impedance factor for the diffusion of chloride in heavy soils as a function of water content.

Comparison of the relationship between f_l and θ for the E2 samples (—) with other published values. Porter *et al.* (1960), Apishapa silty clay loam (\blacktriangle), Pierre clay (+); Rowell *et al.* (1967) Upper Greensand sandy clay loam (\odot); Barraclough and Nye (1979) Begbroke sandy loam (\times); Barraclough and Tinker (1981) Stockyard sandy loam (\times); Barraclough and Tinker (1982) Highfield silty clay loam, repacked (\square), undisturbed (\blacksquare); Pinner and Nye (1982) undisturbed Evesham clay loam (\ast).

(Johnston, 1987)

for $0.05 < \theta_v < 0.55$, which in the absence of measured values, is adopted for this work.

The other soil physical variable affecting diffusivity of chloride that has been investigated is bulk density (Hira & Singh, 1977; Sen & Deb, 1979; Barraclough & Tinker, 1981; Bhadoria & Datta, 1984; Melsheri & Deb, 1986). Generally, for a given soil and water content (or suction) τ increases with bulk density to some optimum then falls a little, perhaps due to denser packing of particles under compression. Such studies are useful in agricultural and waste disposal contexts where bulk density may be manipulated, but will not be considered further in this study.

2.2.4.3 Impedance Factor and Two Phase Flow for Water Isotopes in Soil

The diffusion of water in liquid and vapour may well be compared to solutes and gases in many ways, but is both simpler and more complex, particularly where the two pathways occur in parallel and/or series. The use of *soil water* or *capillary* diffusivity needs to be distinguished from *water self* diffusivity, or isotope diffusivity (Kunze and Kirkham, 1964). The former relates the movement of water in response to water content gradients, and the soil water diffusivity is related to hydraulic conductivity and the water content-potential relation by

$$D_{\text{soil water}} = K(\theta) / \left(\frac{d\theta}{d\psi} \right) \quad (2.31)$$

where $K(\theta)$ is the hydraulic conductivity at some water content θ , and $d\theta/d\psi$ the water capacity of the soil (Marshall & Holmes, 1979, p95).

The self diffusivity of water in porous media has been measured by a few workers using deuterated and tritiated water. The first published work appears to be that of Kunze and Kirkham (1961), who used DHO at high concentration. They used cylindrical half-cells filled with either Colo clay loam soil or 28 μm glass beads, one half doped with deuterated

water. The half cells were brought together and then sectioned after a suitable time. This is a common laboratory method and will be referred to as the half-cell method. Water was extracted by vacuum distillation and reduced to hydrogen gas over metallic calcium, for measurement in a general purpose mass spectrometer with an accuracy of 5ppm. Effective diffusivities were half that of water for the glass beads, and a quarter for the clay loam (f_1 of about 0.5 and 0.25).

Nakayama and Jackson (1963) had a more detailed look at the diffusion of water in agar, loam soils and glass beads at different water contents. They used columns to which a pulse of tritiated water was applied, and the column later sliced up and water recovered by vacuum distillation for scintillation counting. D_o was measured by extrapolating results from agar gel at three concentrations. Results at one or two water contents are show below (Tab. 2.2.5).

Table 2.2.5

Impedance Factors of THO in Some Materials
(after Nakayama and Jackson 1963)

Sample	$\theta_v \text{ m}^3 \text{ m}^{-3}$	$p_{tot} \text{ m}^3 \text{ m}^{-3}$	f_1
28 μm beads	0.359	0.381	0.65
28 μm beads	0.178	0.381	0.70
203 μm beads	0.349	0.376	0.70
Adelanto loam	0.385	0.443	0.42
Colo clay loam	0.440	0.560	0.36
Ft Collins lm	0.368	0.476	0.45
Pachappa loam	0.365	0.459	0.48

These impedance factors are similar to those that would be expected for chloride in glass beads and loams. Nakayama and Jackson did further detailed experiments with Pachappa loam however that showed a dramatic peak in diffusion coefficient at about $\theta_v = 0.04$ (fig. 2.2.6). They assigned the increase to the contribution of water vapour, the diffusivity of tritiated water being about 1000 times greater in air than in liquid water. At very low water contents they thought the drop in D to be due to absorption of the remaining water on the soil particles (the layer calculated to be only two molecules thick at $\theta_v = 0.04$). The reducing effect of adsorption on diffusivity was discussed in section 2.2.2.3.

Deuterated water was used by Van Shaik and Kemper (1966) together with ^{36}Cl to examine diffusion in an oriented clay (Na-bentonite). Parallel to the long axes of the clay plates, with water content between 0.61 and 0.75 $\text{m}^3 \text{m}^{-3}$, they measured $f_1 = 0.20$ to 0.34 (f_1 being the product of geometric tortuosity 0.49 to 0.62, and fluidity (surface effects factor) 0.40 to 0.55). The experiments were on a very small scale, using clay blocks of 1.5 cm square and a few millimetres high.

More recently Scott and Paetzold (1978) published a paper on the effects of soil moisture on the diffusion coefficients and activation energies of tritiated water, chloride and metribuzin (a herbicide) by the half cell method. They used two horizons of a silt loam (Captina). Graphs of their diffusion coefficient and transmission (impedance) factor data as functions of water content are given in figures 2.2.7 and .9, discussed in the following section. They found maximum D and f_1 for THO at 0.05 g g^{-1} (about 0.045 $\text{m}^3 \text{m}^{-3}$) water content, but did not extend the experiments to lower water contents to define the peak found by Nakayama and Jackson at 0.04 $\text{m}^3 \text{m}^{-3}$. They found that with decreasing water content D and f_1 of THO fell at first, as was the case with chloride and

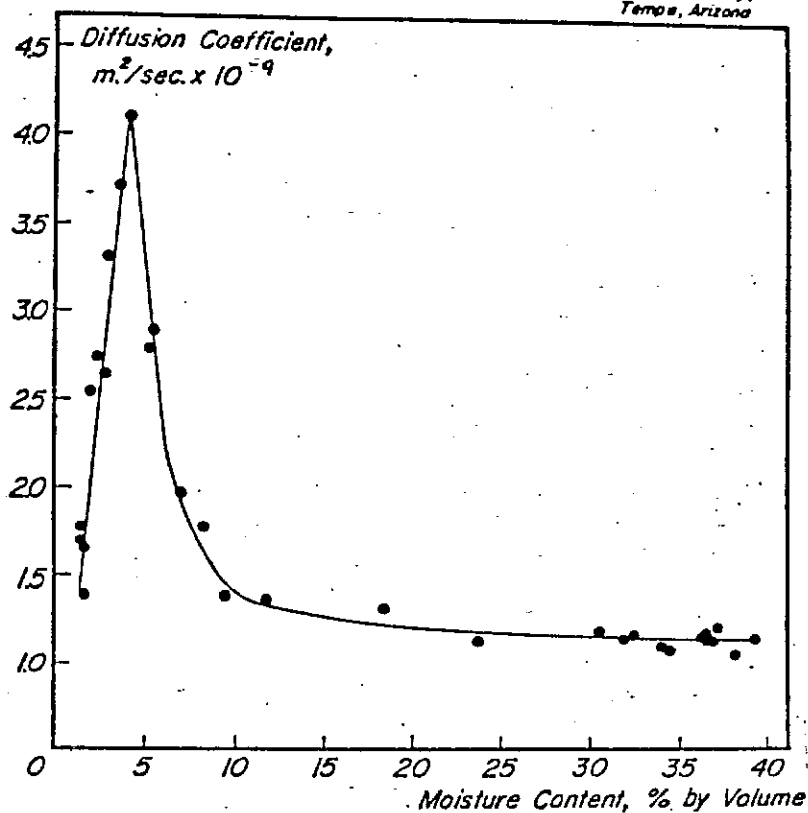


FIGURE 2.2.6 The effective diffusion coefficient of tritiated water in Pachappa loam at different water contents. From Nakayama & Jackson, 1963,

the herbicide, as expected from other works mentioned earlier. As the air-filled porosity became greater and interconnection better, vapour diffusion became important and D and f of THO rose while the others continued to diminish. The same authors investigated the effect of temperature on D at different θ_g (Tab. 2.2.6). Water (and the slightly volatile metribuzin, not listed) showed greater increases with temperature than chloride, especially at low water content where vapour movement is important.

Measurements such as those of Nakayama and Jackson, and Scott and Paetzold, are scarce in the literature, and as noted by Barnes and Allison (1988), "...direct measurements ... on a range of materials seem warranted"; the lack of the same limits the accuracy of works such as that presented here.

Table 2.2.6

Self-Diffusion Coefficients of Tritiated Water and Chloride as a Function of Soil Temperature in The Captina Silt Loam Ap Horizon
(Data of Scott & Paetzold, 1978)

Solute	Water content $g\ g^{-1}$	Temperature, $^{\circ}C$		
		35	23	5
		$D \times 10^{10}\ m^2\ s^{-1}$		
THO	0.05	33.5 \pm 4.0	21.5 \pm 1.1	3.4 \pm 0.6
	0.10	18.2 \pm 1.0	16.1 \pm 0.6	4.9 \pm 0.2
	0.20	12.0 \pm 1.2	9.8 \pm 0.2	6.7 \pm 0.4
Cl	0.05	0.66 \pm 0.10	0.57 \pm 0.12	0.31 \pm 0.13
	0.10	3.94 \pm 0.61	2.56 \pm 0.58	1.21 \pm 0.11
	0.20	6.67 \pm 0.81	4.20 \pm 0.59	-

2.2.4.4 Modelling f_1 vs θ for Water Isotopes

An attempt can be made to explain the curves of f_1 vs θ obtained by the two pairs of authors just discussed, shown together in figure 2.2.7. The contribution of vapour diffusion can be calculated and incorporated into the factor f_1 . Note that this may take values in excess of 1.0, as with Nakayama and Jackson, while tortuosity τ may not.

The effective vapour diffusivity in a non-reactive porous medium, expressed in units compatible with liquid diffusion, is

$$D^v = D_0^v \tau (p - \theta_v) \frac{N_{sat}}{\rho} \quad (2.32)$$

At 25°C, $N_{sat} = 0.022 \text{ kg m}^{-3}$, $\rho \cong 1000 \text{ kg m}^{-3}$, and $D_0^v = 2.44 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, so that

$$D^v = \tau (p - \theta_v) \times 5.4 \times 10^{-10} \quad (2.33)$$

This is equivalent to an f_1 relative to water content and liquid water diffusivity ($2.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) of

$$f_1 = \frac{D^v}{\theta_v D_0^l} = \frac{0.54}{2.2} \frac{\tau (p - \theta_v)}{\theta_v} = 0.245 \tau \frac{p - \theta_v}{\theta_v} \quad (2.34)$$

Assuming $\tau = 0.66$ for argument's sake, this relationship is shown in figures 2.2.8 and .9 for the detailed experimental data available, marked Fl(vap), and alone gives a good estimate at low water contents (above $0.04 \text{ m}^3 \text{ m}^{-3}$ for Nakayama and Jackson).

The f_1 due to liquid movement alone is considered as two cases. The first, marked Fl(liq,l), follows the form $(\theta_v - \theta_0)/\theta_v$, using experimental data at water saturation and estimates of non-participating water, θ_0 ,

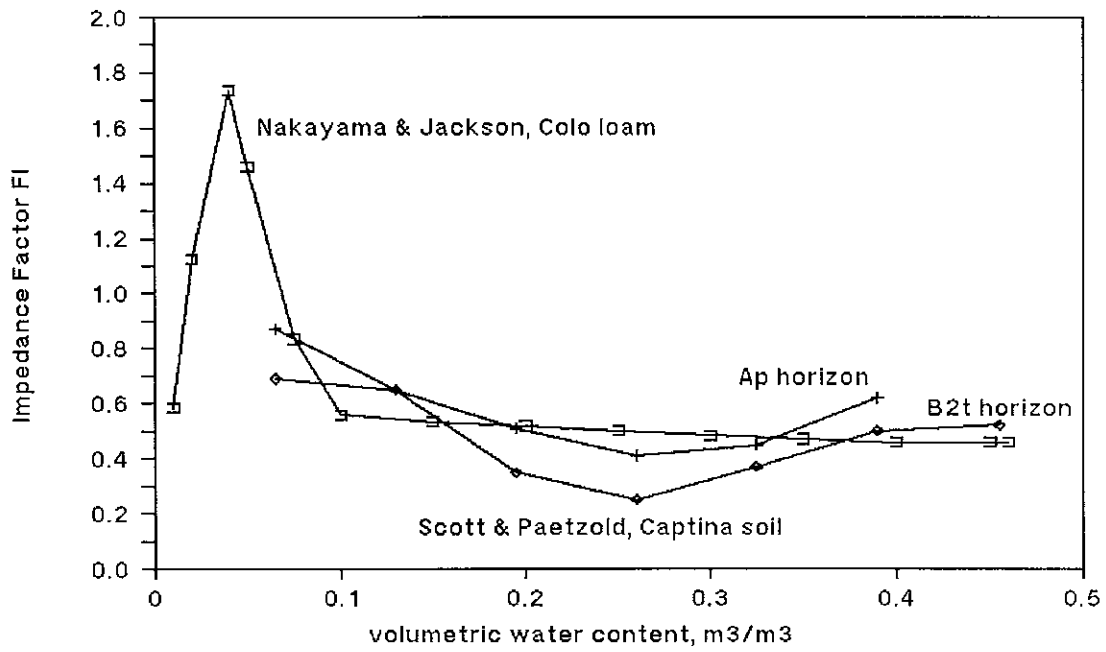


figure 2.2.8 Impedance factor for water isotopes as a function of water content
Summary of Laboratory Data

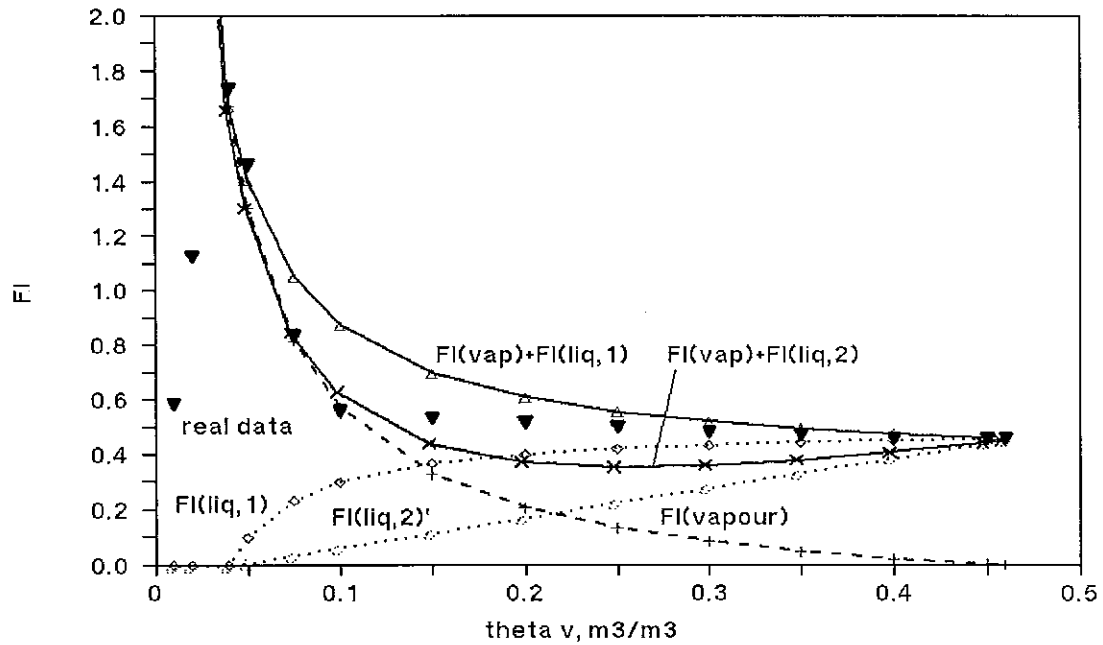
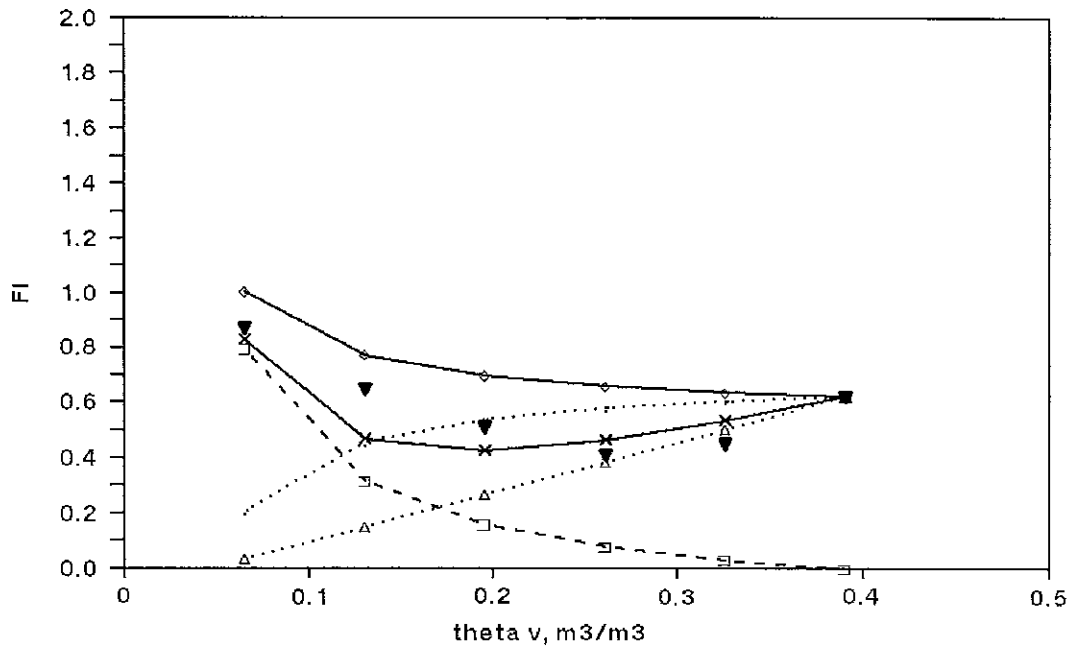


FIGURE 2.2.7 Impedance Factor as a Function of Water Content, THO
to match Nakayama & Jackson, 1963

a to match Scott & Paetzold, 1978, Ap horizon



b to match Scott & Paetzold, 1978, B2t horizon

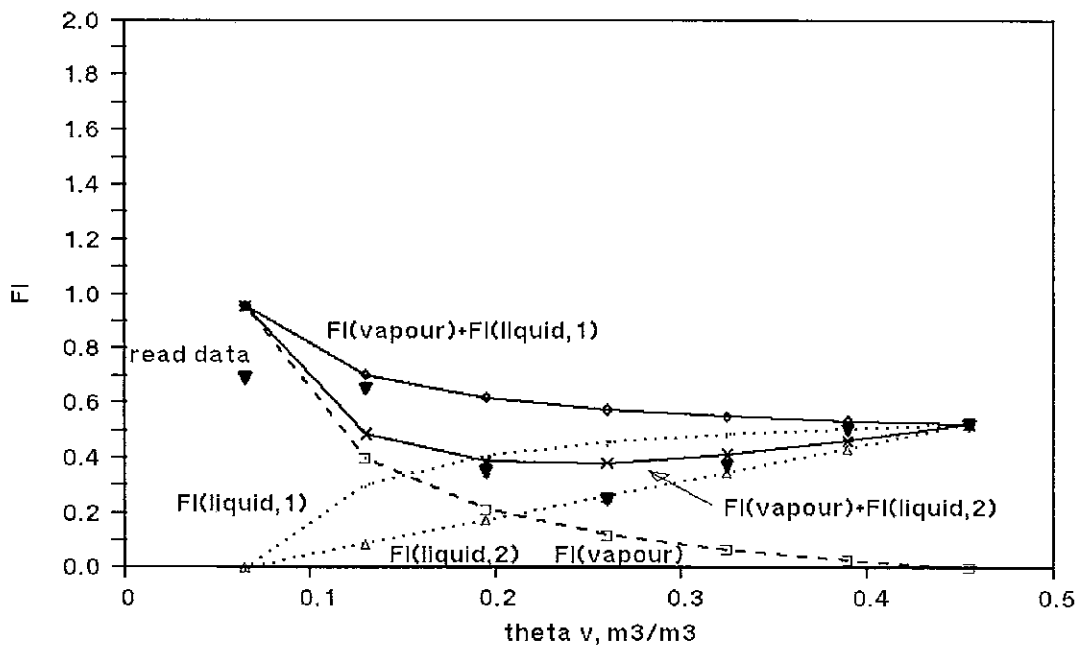


FIGURE 2.2.9 Impedance factor as a function of water content modelled to match published data

given by the authors. The second case Fl(liq,2) uses a simple linear interpolation as proposed for the chloride ion.

In a model of strictly parallel flow, the two f_1 's may simply be summed to be used for total water flux, as marked on the plots. Parallel model 2 models the minima of Scott and Paetzold's data better, while model 1 is better, especially at intermediate water contents, for Nakayama and Jackson's where no minimum is apparent.

Series flow of isotopes is also quite likely to be occurring along flow-lines with alternating stretches of liquid and vapour. In a simple tube of unit length, containing a (single) portion θ_v of liquid and $1-\theta_v$ of vapour, at steady-state the flux through each phase is equal, and the effective diffusivity given by

$$\frac{1}{D} = \frac{1-\theta_v}{D_0^v} + \frac{\theta_v}{D_0^l} \quad (2.35)$$

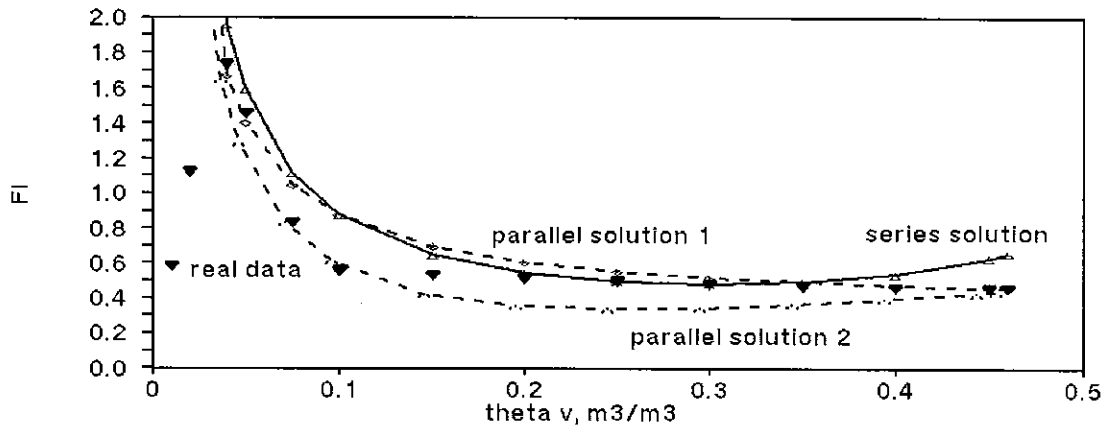
In a porous medium of porosity p , ignoring any non-participating water and assuming equal tortuosities,

$$\frac{\tau p}{D} = \frac{p-\theta_v}{p} \frac{1}{D_0^v} + \frac{\theta_v}{p} \frac{1}{D_0^l} \quad (2.36)$$

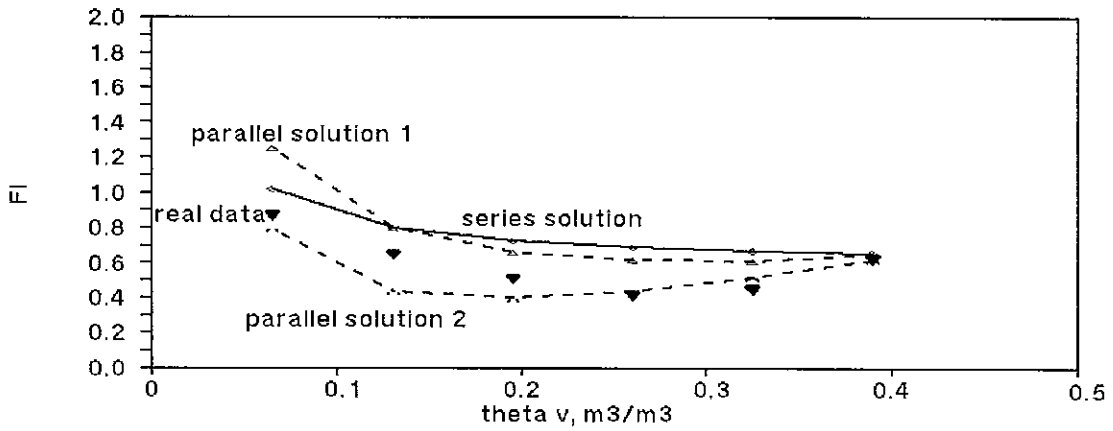
The equivalent f_1 is again $D/\theta_v D_0^l$. Using $\tau = 0.66$ again, the series solution is shown with the two parallel solutions and measured data in figure 2.2.10.

In a natural medium some combination of series and parallel flow is likely to occur, and it is not useful to try and take the models any further on existing information. The shapes of the f_1 versus θ curves can be explained by application of existing theory, though the match is far from perfect. Over the range of water contents encountered in those parts of field profiles of this project, in a clayey material with no

a to match Nakayama & Jackson, 1963



b to match Scott & Paetzold, 1978, Ap horizon



c to match Scott & Paetzold, 1978, B2t horizon

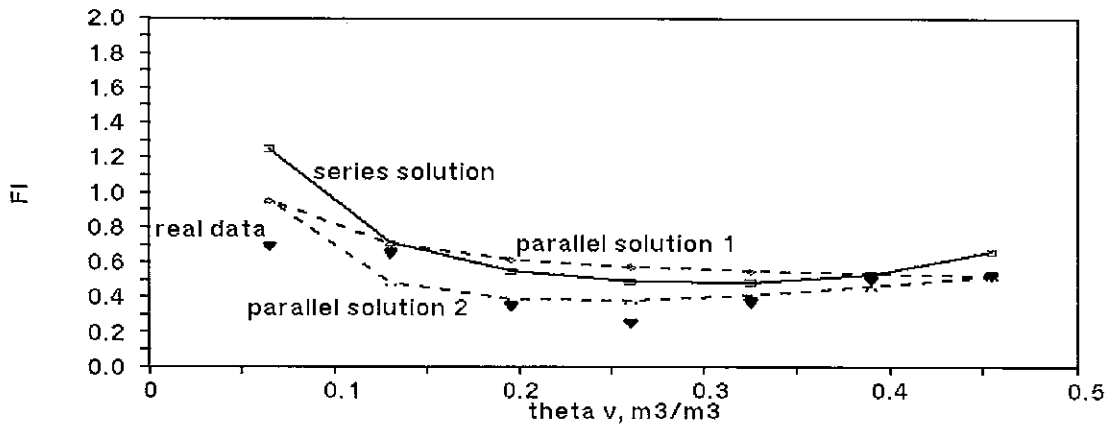


FIGURE 2.2.10 Impedance factor as a function of water content to match published data

laboratory measurements having been made, it is most sensible to use a "constant" value for f_1 . Using figure 2.2.7, $f_1 \cong 0.5$ is chosen, realising it could be between perhaps 0.3 and 0.7, $\pm 40\%$.

2.3 CONVECTION-DIFFUSION THEORY

Barnes and Allison (1988) have recently reviewed the use of stable isotopes of water in tracing water movement in the unsaturated zone, particularly with regard to the convection-diffusion theory used to estimate evaporation from shallow water-tables. Much of the following theoretical development follows their work, with emphasis on the theory as it may be applied in the particular field area of this study.

Acknowledgement is given to one of my supervisors, Dr Glen Walker, for assistance in the mathematical derivation of the theory.

An explanation of the enrichment of heavy isotopes of water during evaporation from a free water body into the atmosphere was provided by Craig and Gordon (1965). This work was extended to evaporation of water from saturated, then unsaturated soils. Zimmermann *et al.* (1967) demonstrated in the laboratory that the enrichment of deuterium in the pore water of a saturated soil experiencing steady evaporation decreased exponentially with depth from a surface maximum, with a characteristic decay length approximately proportional to the evaporation rate. The work was extended to unsaturated soils by Münnich *et al.* (1980) and Barnes and Allison (1983),

The exponential profile is explained as due to the competition between upward convective flux of the isotope (or more generally, any solute) $E c$, where E is the evaporatively driven flux of water, and c the

concentration of the solute, and the downwards movement by diffusion due to the concentration gradient set up by enrichment at the evaporating surface, which by Fick's law is $D \partial c / \partial z$. The flux F is therefore given at any depth z , given one-dimensional vertical flow, by

$$F = Ec + D \frac{\partial c}{\partial z} . \quad (2.37)$$

At steady state, both E and the flux of solute F is constant with depth z , ($\partial F / \partial z = 0$), so taking the derivative of the equation, and assuming D is constant with depth

$$0 = E \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} , \text{ or} \quad (2.38)$$

$$\frac{\partial^2 c}{\partial z^2} = \frac{-E}{D} \frac{\partial c}{\partial z} , \quad (2.39)$$

which has the solution

$$c(z) = A \exp \left(\frac{-E}{D} z \right) + B , \quad (2.40)$$

where A and B are constants determined by the boundary conditions.

Taking natural logarithms of the modulus of each side,

$$\ln | c(z) - B | = \ln | A | + \frac{-E}{D} z \quad (2.41)$$

and so the slope of a plot of $\ln | c(z) - B |$ versus z plot is $-E/D$.

Since D can be estimated as described in the previous sections, an estimate for E is obtained.

For evaporation from a soil, the boundary conditions are, for the

upper boundary, $z = d_0$, $c = c_0$ (this is the "evaporating front" with maximum c); and for the lower boundary, $z = d_1$, $c = c_1$, so that

$$A = \frac{c_1 - c_0}{\exp\left(\frac{-E}{D} d_1\right) - \exp\left(\frac{-E}{D} d_0\right)} \quad \text{and} \quad (2.42)$$

$$B = c_0 - \frac{(c_1 - c_0) \exp\left(\frac{-E}{D} d_0\right)}{\exp\left(\frac{-E}{D} d_1\right) - \exp\left(\frac{-E}{D} d_0\right)}. \quad (2.43)$$

In many instances we may set $d_0 = 0$, and $d_1 = \infty$ (effectively, so deep as that c is not changing with depth and so c_1 is the "reservoir value"), so

$$A = c_0 - c_1, \quad \text{and} \quad B = c_1, \quad (2.44)$$

(Zimmermann *et al.*, 1967; Barnes & Allison, 1983). The ratio $-E/D$ is therefore obtained by the slope of a $\ln|c - c_1|$ vs z plot. Where the bottom boundary is quite shallow, this solution does not hold, particularly for $E/D < 1$. In this case, the solutions to A and B are

$$A = (c_0 - c_1) / \left(1 - \exp\left(\frac{-E}{D} d_1\right)\right) \quad \text{and} \quad (2.45)$$

$$B = \frac{c_0 - c_1 \exp\left(\frac{-E}{D} d_1\right)}{1 - \exp\left(\frac{-E}{D} d_1\right)}. \quad (2.46)$$

Using these relations in equation (2.40), and subtracting c_1 from both sides, one finds

$$c - c_1 = \frac{(c_0 - c_1) \left(\exp\left(\frac{-E}{D} z\right) - \exp\left(\frac{-E}{D} d_1\right) \right)}{1 - \exp\left(\frac{-E}{D} d_1\right)} \quad (2.46)$$

$$\Rightarrow \frac{c - c_1}{c_0 - c_1} = \frac{\exp\left(\frac{-E}{D} z\right) - \exp\left(\frac{-E}{D} d_1\right)}{1 - \exp\left(\frac{-E}{D} d_1\right)} \quad (2.47)$$

$$\Rightarrow \ln |c - c_1| = \ln |c_0 - c_1| + \ln \left| \frac{\exp\left(\frac{-E}{D} z\right) - \exp\left(\frac{-E}{D} d_1\right)}{1 - \exp\left(\frac{-E}{D} d_1\right)} \right| \quad (2.48)$$

$$\Rightarrow \frac{\partial}{\partial z} \ln |c - c_1| = \frac{\partial}{\partial z} \ln \left| \frac{\exp\left(\frac{-E}{D} z\right) - \exp\left(\frac{-E}{D} d_1\right)}{1 - \exp\left(\frac{-E}{D} d_1\right)} \right| \quad (2.49)$$

The right hand side of equation 2.47 was calculated as a function of depth for a range of E/D and d_1 , the depth from the evaporating front to water table (where this can be considered to set the bottom boundary condition). Examples of the logarithmic curves against depth are shown in figure 2.3.1. The slopes of the curves, calculated by linear regression with the bottom four points excluded, are plotted as a family of curves representing different E/D ratios against $\partial \ln |c - c_1| / \partial z$ in figure 2.3.2. This nomogram is used to infer E/D for holes where a shallow bottom boundary condition is suspected.

The assumption of constant D with depth is only reasonable where both lithology and water content are constant. In unsaturated profiles at least the latter will vary. As the main determinant of effective diffusivity is water content, Barnes and Allison (1983) introduced a modified depth function,

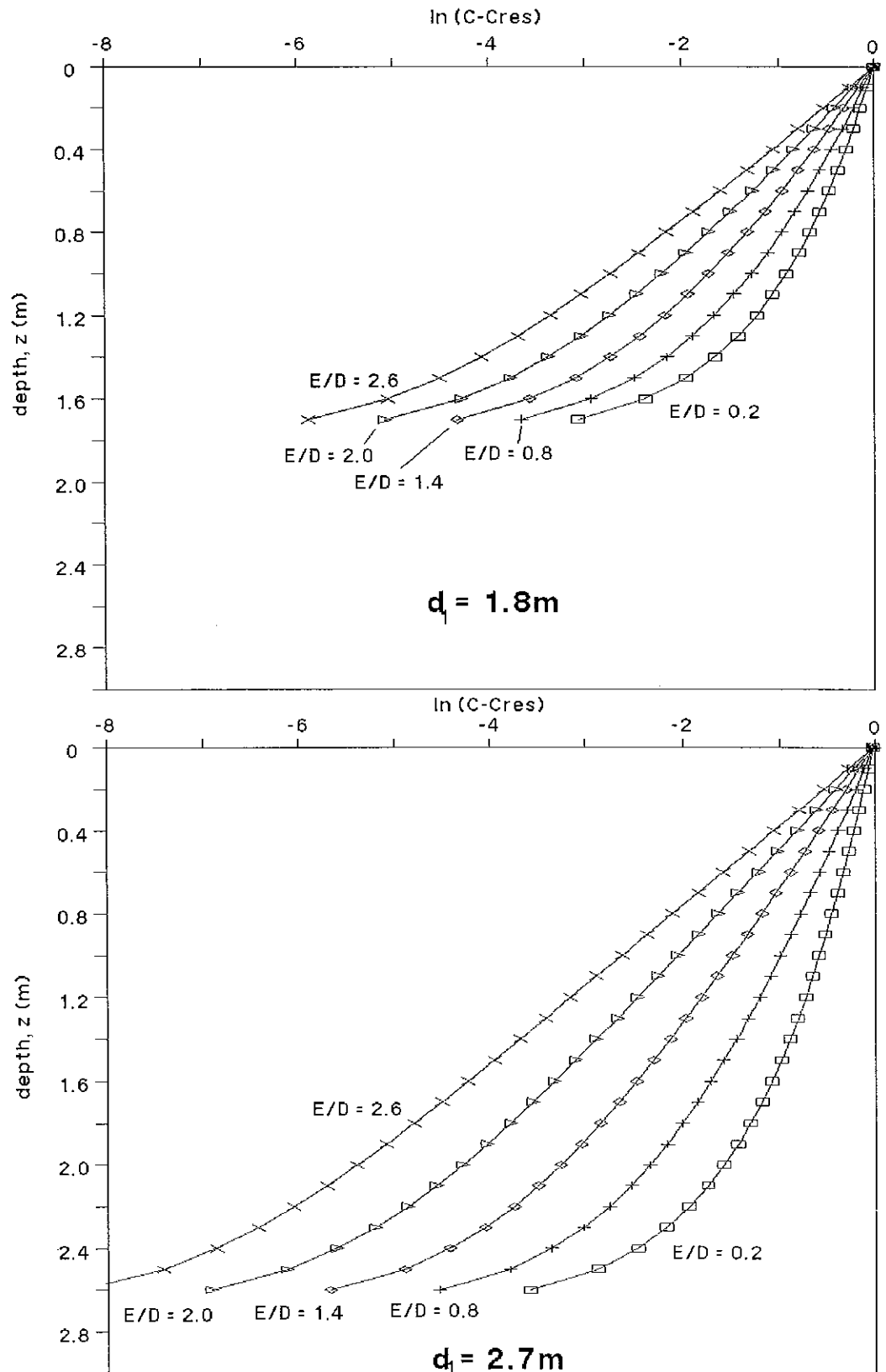


FIGURE 2.3.1 Calculated curves of $\ln(C-Cres)$ for different E/D ratios and two different bottom boundary conditions d_1

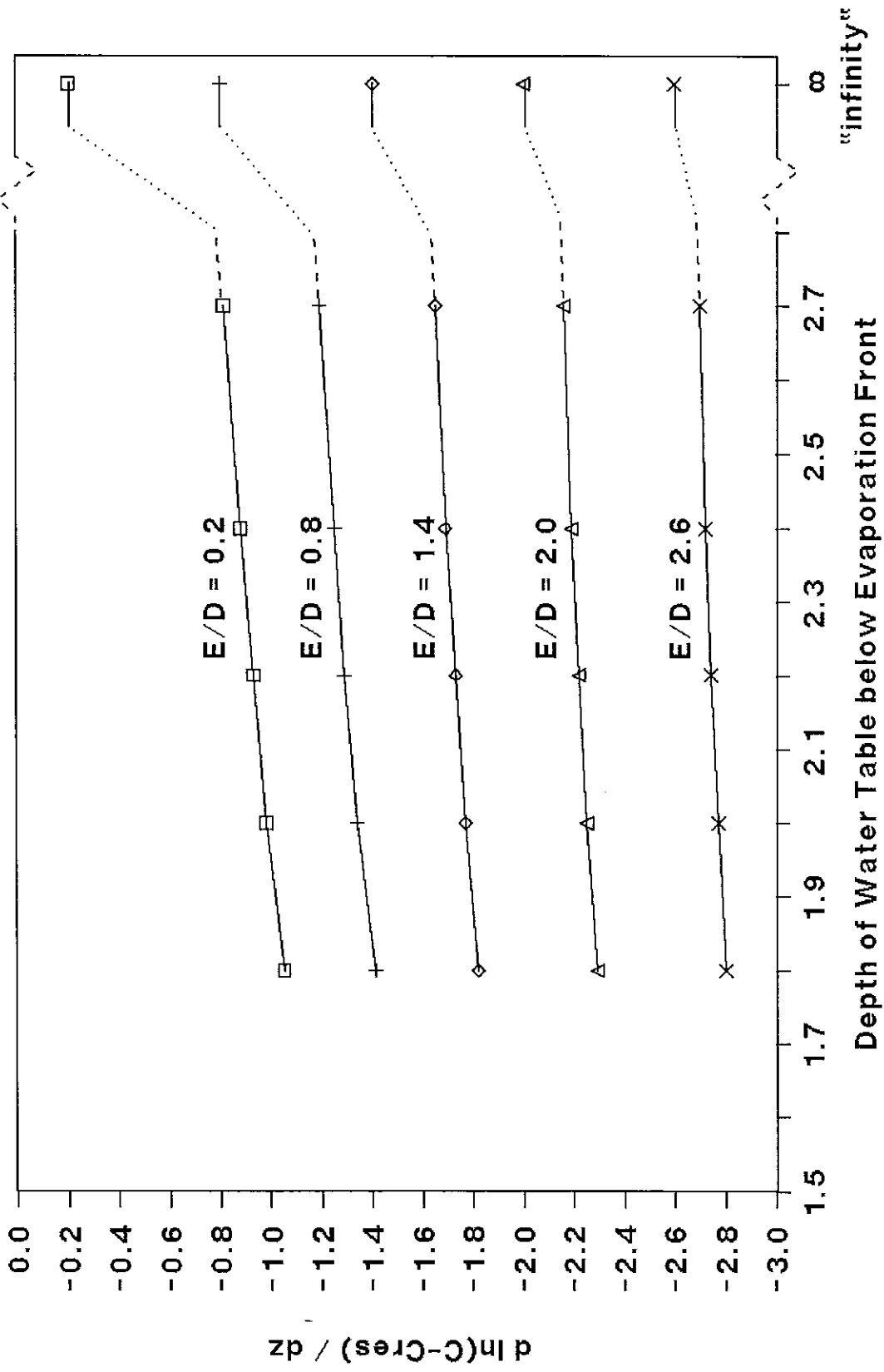


FIGURE 2.3.2 Nomogram for the estimation of E/D from $d \ln(C-C_{res}) / dz$ for shallow water tables (Steady-State)

$$f_z = \bar{\theta}_v \int_{z_{ef}}^z dz / \theta_v, \quad (2.50)$$

where θ_v is the volumetric water content, $\bar{\theta}_v$ its mean, and z_{ef} the depth of the evaporating front, where the concentration of heavy isotope is at a maximum. For chloride ion, z_{ef} is the lowest depth of the presence of solid NaCl (halite), to fulfill the boundary condition. This modification assumes that the formation factor (tortuosity) remains constant over the interval involved. The depth function was further modified to account for the contribution of vapour transmission (Barnes & Allison, 1984).

Barnes and Allison (1983) were also able to account for the region of vapour transport between the evaporation front and the soil surface. Further data required are the average humidity and water-vapour isotope values of the atmosphere, and an estimate of evaporation rate made. The sampling interval used in this project did not permit the use of the vapour transport zone to be well defined, and so this additional evaporation estimate could not be made, and the theory is not pursued further here. The actual position of the evaporation front, z_{ef} , can also be used to gain an estimate of evaporation rate, providing the air-filled porosity can be estimated, from

$$E = \frac{N_{sat} D^v (h_{ef} - h_a)}{\rho z_{ef}} \quad (2.51)$$

where N_{sat} is the saturated water vapour concentration at the given temperature, D^v is the effective vapour diffusivity, h_a the relative humidity of the atmosphere at the surface of the soil, h_{ef} that at the evaporation front, and ρ the density of liquid water. An estimate made by this means is expected to have a greater scatter than one made from a

profile of many points, particularly as z_{ef} may be known relatively inaccurately.

A comparison of theoretical, laboratory and field isotope profiles is given in figure 2.3.3 (Barnes & Allison, 1983, 1988).

An alternative to using the modified depth function is to consider the case where diffusivity is allowed to vary with depth, $D(z)$. The assumption of steady state (constant E and $\partial F/\partial z = 0$) is retained.

Equation 2.21 is then better written

$$F = Ec + D(z) \frac{\partial c}{\partial z} \quad (2.53)$$

Using the boundary conditions $z_{ef} = 0$, $c = c_0$, and noting that the flux q is equal to Ec_1 , where c_1 is the reservoir value at $z = \infty$, the solution is

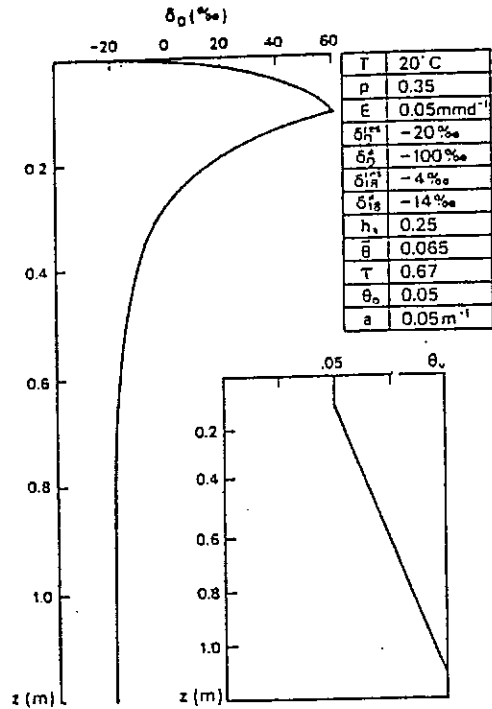
$$c(z) = c_1 + (c_0 - c_1) \exp\left(-\int_0^z \frac{E}{D(\zeta)} d\zeta\right) \quad (2.53)$$

Taking natural logarithms and rearranging,

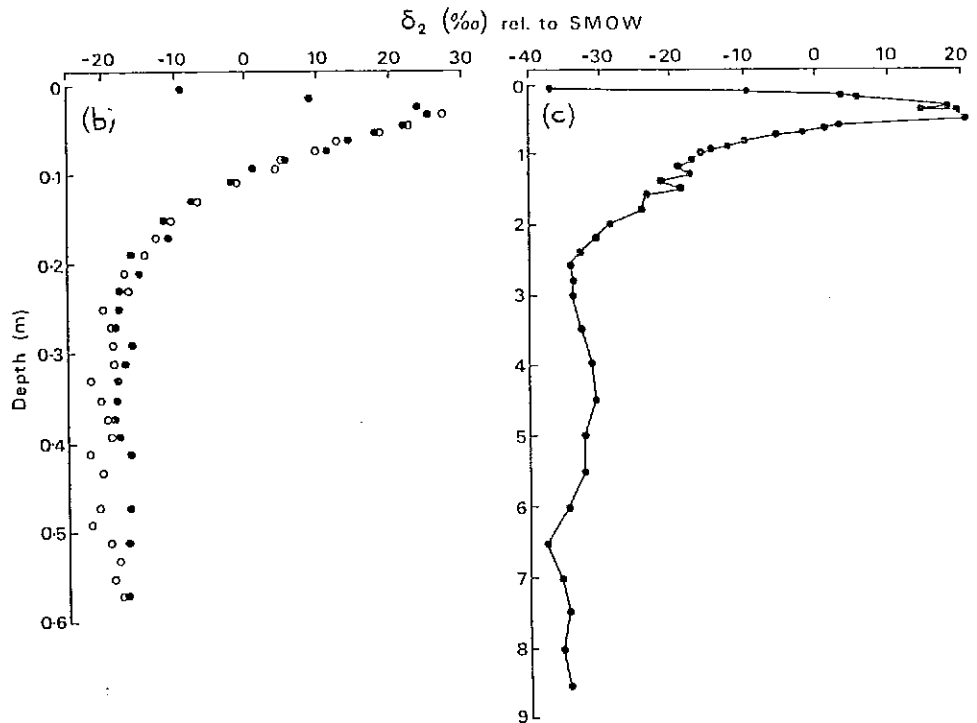
$$\ln\left|\frac{c - c_1}{c_0 - c_1}\right| = -\int_0^z \frac{E}{D(\zeta)} d\zeta \quad (2.49)$$

thus a plot of the left-hand-side of the above against depth produces a curve, the slope of which at any one depth is $-E/D(z)$; and since E is constant, the relative variation of D with depth is easily obtained.

Although the convection-diffusion theory was developed initially with isotopes of water, it can be applied to other conservative, non-absorbing solutes with little modification, if the boundary conditions are met. With the solute chloride, the upper boundary condition is met when the concentration at or near the evaporation front is maintained at



Q. Theoretical curve of isotope (D) variation with depth. The table shows the parameters used, and the inset shows the water content/depth relationship assumed.



Isotope profiles in unsaturated soils. (b) Experimental, steady-state profile (c) field profile from an unvegetated arid zone sand dune.

FIGURE 2.3.3 Theoretical, laboratory and field isotope profiles under steady-state evaporation. From Barnes & Allison 1983, 1988.

saturation by the presence of a solid chloride phase, typically halite (NaCl). Thus Allison and Barnes (1985) and Ullman (1985) obtained evaporation estimates from Lakes Frome and Eyre respectively, where a salt crust was evident at the surface. Appropriate sodium chloride diffusivities must be used. The presence of concentrated solutions of salt affects the total suction of the soil solution, and induces a water vapour gradient between areas of higher and lower concentration. The relative humidity above a saturated NaCl solution is about 77%, depending on temperature, and this considerably reduces the evaporation rate compared to pure water. Indeed, when the relative humidity of the atmosphere rises above that, condensation will occur on a salt crust (Kinsman, 1976).

The presence of high salt concentrations appears to reduce evaporation considerably, although the full mechanism of this effect is yet to be well understood. By reducing the chemical potential of the soil water the high salt concentrations affect vapour movement in the soil. There is also a secondary effect in that a salt crust on the ground surface also tends to increase albedo so that less solar energy is adsorbed. This helps explain why measured evaporation rates beneath salt crusts are low compared to those without a crust with the same water table depth, and why evaporation even from a visibly damp salt pan is so much less than that from a free-water surface under the same climatic circumstances (c.f. Allison & Barnes, 1985).

2.4 ESTIMATION OF VAPOUR FLUX FROM SUCTION AND CHLORIDE DATA

The two most important parameters that control the relative humidity and therefore vapour gradient in the soil profile are the osmotic and

matric suctions. If both are known, it is possible then to calculate an estimate of the vapour gradient and flux in the upper part of a soil profile, where vapour flux dominates. This gives an "instantaneous" estimate of evaporation at the surface, realising that there can be "negative" evaporation, a downward flux, which may be associated with condensation within the soil profile.

The activity of water (which is also the equilibrium relative humidity, N/N_0) due to the suctions is calculated from

$$\ln (N/N_0) = \frac{-\pi V_m}{R T} \quad (2.54)$$

where R is the universal gas constant, $8.314 \text{ J K}^{-1}\text{mol}^{-1}$, T the absolute temperature (taken as 25°C or 298K), V_m the molar volume of water, $1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ (Marshall & Holmes, 1988). Osmotic suction π may be approximated in the first order from van't Hoff's equation (Marshall & Holmes, 1988),

$$\pi V = nRT \quad (2.55)$$

where n is the number of moles of solute and V the volume involved. Treating the chloride to be associated with and completely dissociated from sodium ions, sodium chloride causes an osmotic suction of approximately $4540 \text{ kPa mol}^{-1}$, one mole of chloride being 35.45 g l^{-1} . Where halite saturation is reached the relative humidity due to salt is taken to be 77%. The effect of matric suction ψ on N/N_{sat} may also be calculated from equation 2.50, replacing π by ψ . The two suctions are additive in their effect on $\ln(N/N_0)$, so that individually calculated relative humidities are multiplicative. Flux is calculated from a relative humidity gradient by

$$F = D_0^v p f_g \frac{N_{\text{sat}}}{\rho} \frac{dh}{dz}. \quad (2.56)$$

Values appropriate to the field area are $D_0^v = 2.44 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$,
 $p = 0.40 \text{ m}^3 \text{ m}^{-3}$, $f_g = 0.6$, $N_{\text{sat}} = 0.022 \text{ kg m}^{-3}$, and $\rho = 1000 \text{ kg m}^{-3}$.

Because of the difficulty in measuring suction, the approximate nature of van't Hoff's law especially at high solute concentrations, and "best guess" values for p and f_g , such estimates must be considered very approximate, but provide an independent check on at least the order-of-magnitude of convection-diffusion evaporation estimates.