**Generalized Chloride Mass Balance: Forward and
Inverse Solutions for One-Dimensional Tracer
Convection Under Transient Flux**

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Summary

Forward and inverse solutions are provided for analysis of inert tracer profiles resulting from one-dimensional convective transport under fluxes which vary with time and space separately. The developments are displayed as (but not restricted to) an extension of conventional chloride mass balance (CMB) techniques (used to analyze vertical unsaturated aqueous-phase transport over large time scales in arid environments) to account for transient as well as space-dependent water fluxes. The solutions presented allow incorporation of transient fluxes and boundary conditions in CMB analysis, and allow analysis of tracer profile data which is not constant with depth below extraction zone in terms of a rational water transport model. A closed-form inverse solution is derived which shows uniqueness of model parameter and boundary condition (including paleoprecipitation) estimation, for the specified flow model. Recent expressions of the conventional chloride mass balance technique are derived from the general model presented here; the conventional CMB is shown to be fully compatible with this transient flow model and it requires the steady-state assumption on chloride mass deposition only (and not on water fluxes or boundary conditions). The solutions and results are demonstrated on chloride profile data from west central New Mexico.

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1.0 Introduction

The conventional chloride mass balance (CMB) has been used over two decades to estimate recharge over large time scales in arid environments (Eriksson and Khunak Sen 1969; Allison and Hughes 1978; Stone 1984; Sharma and Hughes 1985; Matthias et al. 1986; Sukhija et al. 1988; Edmunds et al. 1988; Cook et al. 1989, 1992; Scanlon 1991, 1992; Phillips 1994). In this mass balance approach, the chloride concentration in the pore water, originating from atmospheric fallout, is inversely proportional to the flux of water through the sediments. The CMB method is especially applicable to arid and semi-arid regions where evapotranspirative enrichment of the pore water produces a distinct chloride profile in the unsaturated zone.

As the conventional CMB method has been applied and refined over the last few decades, the implicit assumptions in this method have been repeatedly evaluated. These assumptions are 1) the precipitation and the accumulation rate of atmospheric chloride can be averaged over the relevant period; 2) chloride is an inert tracer; 3) flow is one-dimensional, vertical downward, piston-type; and 4) water and tracer mass influxes are steady. As pointed out in Scanlon (1991) these assumptions are usually taken to imply a constant chloride profile below the root zone. However, a constant profile concentration in fact requires the additional assumption of a steady-state water flux, which has been explicitly adopted by some authors (e.g., Gardner 1967; Tyler and Walker 1994; and Cook et al. 1994). Nevertheless, as shown in many recent articles, field profiles can vary strongly with depth (cf. Scanlon 1991; Phillips 1994). These observations have led to critical examinations of the CMB assumptions.

In initial studies, current-day measurements of the precipitation and chloride accumulation rate were used as the long-term average rates. More recently, paleoclimatic information has been used to derive long-term estimates of precipitation, which represent similar time scales as the recharge estimates from CMB (e.g., pollen records, Murphy et al. 1995). Likewise, a long-term average rate of chloride accumulation has been determined by dividing the calculated natural ^{36}Cl fallout at a given latitude by measured $^{36}\text{Cl}/\text{Cl}$ ratios of rainwater and deep pore water (Phillips et al. 1988; Scanlon et al. 1990). Measuring multiple $^{36}\text{Cl}/\text{Cl}$ ratios in the pore-water profile gives an average chloride accumulation rate corresponding to a wide range of pore-water ages (e.g., over Holocene, Murphy et al. 1996).

The assumption that chloride is an inert tracer is justified in most arid and semi-arid geologic settings, especially where sand dominates the sediment profile. In clay-rich sediments, anion exclusion or ion sieving may occur, resulting in anion velocities greater than the velocity of the pore water (Gvirtzman and Margaritz 1986; James and Rubin 1986; McCord et al. 1994). Gvirtzman and Margaritz (1986) reported anion velocities that were double the velocity of water at a clay loam field site, while at a sandy soil site the water and anions had almost the same velocity. At the other extreme of transport, immobilization of a tracer, plants are sometimes suggested as an irreversible sink for chloride. Although a portion of chloride is cycled in desert plants, the yearly time scale of this process is insignificant compared to the scale of the CMB measurements (hundreds to thousands of years); hence, chloride mass cannot be removed by plants on a scale that would affect the recharge estimate.

One-dimensional, vertically downward, piston-type flow is also a reasonable assumption in sandy sediments where the soil moisture content is low. Violation of this assumption can occur when water and chloride are redistributed laterally, as may result from strong lateral gradients in water content, as incurred by preferential flow. Preferential flow is more likely under saturated or near-saturated flow conditions (e.g., Nkedi-Kizza et al. 1983; De Smedt and Wierenga 1984), and has not been observed under low soil moisture conditions, except in the active root zone (Tyler and Walker 1994). In arid regions, infrequent but intense rainfall events can result in preferential flow in the active root zone, but only under specific conditions will preferential flow occur below this zone (e.g., drainages where large volumes of runoff accumulate and saturate sediments well below the root zone). Since recharge is the net downward residual flux below the root zone, preferential flow in the root zone is ignored when calculating recharge rates with long-term tracers such as CMB. This has little impact on the long-term recharge rate because the time-scale of transport through the root extraction zone is short relative to the long time-scale represented by CMB. As shown by Tyler and Walker (1994), however, variable solute velocities through the root zone must be accounted for when modeling convective transport regardless of the tracer.

Chloride concentration variations with depth can derive from both surface water input variations over time and surface chloride mass deposition variations over time (Edmunds and Walton 1980). Analysis of depth-variable profile concentrations has primarily involved the conventional CMB with the profile depths discretized into corresponding periods of "effectively constant environmental conditions." The assumptions of constant tracer mass and water influx are sometimes associated with constant recharge although this is not integral to the method. On the contrary, forward models incorporating transient fluxes and boundary conditions are rare. This report shows that closed-form transient solutions can be obtained under relatively general assumptions about the transport. A transport model that is a generalization of the steady-state water flux model to transient conditions is presented with its analytical solution. A closed-form inverse of this model is formally and algorithmically developed, thus illustrating that under the assumed transport processes a unique paleorecharge (e.g., inverse) exists corresponding to a given tracer profile.

2.0 Model Formulation

2.1 Development of a Transient Flux Model

The conventional CMB model (Phillips 1994; Scanlon 1991) is extended to account for transient conditions under the following assumptions:

- chloride behaves as an inert tracer in the aqueous phase
- water flux occurs vertically downward
- extraction of water from the soil column via evapotranspiration is represented via a specified extraction-zone sink term (Raats 1974; Tyler and Walker 1994), which is linear in average annual precipitation (and otherwise time-invariant)
- water content is time-invariant.

All quantities represent local time (e.g., annual) averages, but are admitted as transient on larger time scales. The balance equations for solute and water in the 1-D porous media column (of unit square meter cross-sectional area) are

$$\frac{\partial c\theta}{\partial t} + \frac{\partial qc}{\partial x} = 0 \quad (1a)$$

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial x} = -q_{ex} \quad (1b)$$

where depth below ground surface

x = depth

t = time

$c = c(x,t)$ (chloride concentration in soil water [M/L])

$\theta = \theta(x,t)$ (volumetric water content [L^3/L^3])

$q = q(x,t)$ (convective water flux [L/T])

$q_{ex} = q_{ex}(x,t)$ (evapotranspirative removal of water in the root zone [$1/T$]).

The fully steady-state model is obtained from Equation 1a and 1b by zeroing both time derivatives, which yields the ordinary differential equations

$$\frac{dc}{dx} = 0 \quad (2a)$$

$$\frac{dq}{dx} = -q_{ex} \quad (2b)$$

The fully steady-state model has been used in CMB determination of recharge below the root zone (e.g., Tyler and Walker 1994); in this case recharge itself appears as a parameter of the root-zone water extraction model. Alternatively, the steady-state assumption has been applied to the tracer mass deposition alone (although this exclusivity has not always been explicit in the literature) and the water flux model is unspecified other than the piston-flow requirement; recharge is estimated by cumulating the tracer mass in the profile (e.g., Stone 1984; Scanlon 1991; Phillips 1994). The procedure used in this latter case to calculate recharge by the CMB approach is described in detail in Appendix A.

Because the water extraction function is zero below the root zone (e.g., for $x > x_r$) the fully steady-state model implies a constant $c(x) = c'$ (and a constant recharge) for $x > x_r$. However recent studies have discovered significant variations in tracer concentrations at depths well below the root-zone, which in turn has prompted speculation as to the potential causes of these variations. The catalogue includes lateral flows, periodic preferential flow, widely fluctuating groundwater levels, and transient paleoclimatology (cf. Scanlon 1991; Phillips 1994). While it is apparent that no single factor is controlling tracer variations globally, transient climatology has been highlighted as a likely cause in undisturbed arid sites (e.g., Edmunds and Walton 1980; Scanlon 1991; Cook et al. 1992). This phenomenon is associated with transient annual precipitation and therefore transient root-zone extractions and transient vertical water fluxes. These

transients violate the assumptions in deriving Equation 2 and so a steady-state flux model cannot be used to analyze profile data.

To overcome these limitations, a more general transient flux model is constructed as follows. Without further simplification we may recast the basic balance Equations 1a and 1b in terms of derivatives of $c(x,t)$. Expanding derivatives in Equation 1a and grouping terms in $c(x,t)$, and then using Equation 1b, gives

$$\theta \frac{\partial c}{\partial t} + q \frac{\partial c}{\partial x} = c q_{ex} \quad (3a)$$

while adopting the assumption of steady water content (cf. Tyler and Walker 1994 and Phillips 1994 for discussion of the validity of this assumption in arid environments) reduces Equation 1b to

$$\frac{\partial q}{\partial x} = -q_{ex} \quad (3b)$$

All quantities are as defined previously, but water content is dependent on space only [$\theta = \theta(x)$]. With static θ , Equation 3a and 3b represent dynamic quantities and their derivatives that are averaged over natural infiltration and redistribution events. Thus interdependencies between θ , q , and q_{ex} as usually specified by constitutive theories are not relied upon. Note that this also means that the quantities are effective and, if they exist, are not necessarily equal to present day measured values.

Initial and boundary information is specified as follows. We take the initial condition to be $c(x,0) = c_i(x) = 0$ for simplicity and without loss of generality. Boundary water influx is assumed equal to the average annual precipitation $p(t)$. Boundary tracer concentration is represented (on an average annual basis) by dividing the annual natural tracer deposition (wet and dry combined) by the average annual precipitation, under the assumption that the tracer mass is uniformly diluted in the annual average precipitation. Thus tracer concentration in the influx $p(t)$ is specified as $c_o(t) = M_o(t)/p(t)$ where $M_o(t)$ is the mass deposited annually. Chloride from mineral sources varies with lithology (e.g., see Murphy et al. 1996), and is usually insignificant in silica sand systems. Therefore, the absence of mineral sources of tracer is assumed in this development (given information on rock chloride concentrations and leaching rates, non-atmospheric sources of chloride could be accounted for in the model).

2.2 Forward Solution

The forward solution is the relation expressing concentration profile as a function of boundary input concentration, precipitation history, and extraction function. The assumption which is basic to the subsequent analysis is that the extraction function $q_{ex}(x,t)$ is factorable into terms $p(t)$ (precipitation influx at $x = 0$, exclusively time-dependent) and $q_{exo}(x)$ (water extraction function corresponding to unit precipitation, exclusively space-dependent). Thus

$$q_{ex}(x,t) = p(t)q_{exo}(x). \quad (4)$$

This reduction, although unverified, intuitively represents at first order the notion that water extraction by plants increases with annual precipitation as vegetation density increases with precipitation. An important ramification is that recharge flux $q(x,t)$ then also separates into factors $p(t)q_o(x)$, as can be shown by separation of variables applied to Equations 3b with 4. Here $q_o(x)$ is the dimensionless flux of water through the column according to the specified extraction model under unit precipitation (e.g., for $p(t) = 1$). This form is a generalization of the steady-state water extraction function introduced by Raats (1974) and used in Tyler and Walker (1994), and results in the solution to Equation 3b:

$$q(x,t) = p(t) q_o(x) = p(t) \left[1 - \int_0^x q_{exo}(x') dx' \right] \quad (5)$$

For the extraction model $q_{exo}(x)$ [1/L] we adopt the uniform function in parameters α (fraction of precipitation that is not extracted) and x_r (depth of root zone). This model is taken for simplicity. The steps in the derivation may be repeated for exponential (e.g., Raats 1974) extraction functions as well.

$$q_{exo}(x) = \begin{cases} (1-\alpha) / x_r & x < x_r \\ 0 & x_r < x \end{cases} \quad (6)$$

The consequences of Equations 5 and 6 are that recharge below the root zone is solely time-dependent and linearly proportional to precipitation; $q(x > x_r, t) = p(t) q_o(x > x_r) = \alpha p(t)$, where α is the fraction of precipitation that passes the extraction zone. This derives from integration of Equation 3b using Equation 5 and the fact that $q(0,t) = p(t)$. Use of Equations 4 and 5 and the time-invariance assumption on θ allow Equation 3a to be recast as

$$\theta(x) \frac{\partial c}{\partial t} + p(t) q_o(x) \frac{\partial c}{\partial x} = c p(t) q_{exo}(x) \quad (7)$$

Equation 7 is a boundary-value problem solved by the method of characteristics (Appendix B) yielding

$$P(t) - P(t_o) = \tau_o(x) \quad (8a)$$

$$c(x,t) = \frac{c_o(P^{-1}[P(t) - \tau_o(x)])}{q_o(x)} \quad (8b)$$

where

$$P(t) = \text{cumulative precipitation, that is, } P(t) = \int_0^t p(t') dt'$$

$$\tau_o(x) = \text{travel-time to depth } x \text{ of solute for } p(t) = 1; \tau_o(x) = \int_0^x \theta(x') dx' / q_o(x')$$

$$P^{-1}(\Pi) = \text{the inverse function of } P(t)$$

$q_o(x)$ = flux at depth x for $p(t) = 1$ (defined as the bracketed term in Equation 5).

The transient solution found in Equations 8a and 8b preserves the deformation (stretching/compression) of the boundary influx history within the profile under the assumptions that water content is time-invariant and that the water extraction function is factorable into exclusively space- and time-dependent terms. Emphasis is given to the fact that this transient model is supposed to represent time-averaged processes. Further, the transient solution has the form of a simple generalization of the conventional CMB equation (Equation A1 in Appendix A), as can be shown by combining the Equations 8a and 8b to make $c(x,t) q_o(x) = q_o(0) c(0,t_o(x,t))$ (where $t_o(x,t)$ is defined by Equation 8a).

2.3 Inverse Solution

The inverse solution is an expression for the model parameters and/or input properties (e.g., recharge) in terms of the current concentration profile and other available data. Various inversion schemes may be devised depending on available data. In our case we seek the historical recharge function $q(x,t) = p(t) q_o(x)$, where the spatial factor $q_o(x)$ has parameters x_r (depth of extraction zone) and α (fraction of precipitation not extracted). Extraction zone depth is estimated from the tracer profile or from plant rooting depth information and so the remaining unknowns are α and $p(t)$, the determination of which is done by inversion of Equations 8a and 8b, in two respective stages. In the first stage Equation 8a is used to track solute position at some depth L below the root zone and at present time t_{now}

$$P(t_{now}) - P(t_o) = \tau_o(L; \alpha) \quad (9)$$

where entry time t_o is given by the basic mass balance relation

$$\int_{t_o}^{t_{now}} M_o(t) dt = \int_0^L c(x, t_{now}) \theta(x) dx \quad (10a)$$

and where the parameterization of travel-time on α is now explicit:

$$\tau_o(L; \alpha) = \int_0^L \frac{\theta(x')}{q_o(x; \alpha)} dx' \quad (10b)$$

and $q_o(x; \alpha)$ is defined in Equation 5. The left-hand side of Equation 9 may be expressed in known (or approximated) quantities, written in a quasi-analytical solution for the right-hand side, and the solution inverted to determine α . The average precipitation for the period from t_o to t_{now} is by definition $\bar{p} \equiv [P(t_{now}) - P(t_o)] / [t_{now} - t_o]$; we assume an estimate of $\bar{p}$ is available from paleoclimatic information. Thus the left-hand side of Equation 9 is written as $\bar{p} (t_{now} - t_o)$. The travel time τ_o can be expressed in the approximate analytical form via Equations 5 and 6 (see Appendix C; the travel time for the exponential extraction [Raats 1974] is also given):

$$\tau_o(L, \alpha) = \frac{\bar{\theta}_r x_r}{1 - \alpha} \ln(\alpha) + \frac{1}{\alpha} \Theta(L; x_r) \quad (11)$$

where $\Theta(L; x_r)$ is the cumulative water content below the extraction zone (from x_r to L), and where we have replaced $\theta(x)$ in the extraction zone with its effective average over root zone depth, $\bar{\theta}_r$. Thus, Equation 9 can be written as

$$\bar{p} \cdot (t_{now} - t_o) = \frac{\bar{\theta}_r x_r}{1 - \alpha} \ln(\alpha) + \frac{1}{\alpha} \Theta(L; x_r) \quad (12)$$

Equation 12 balances the water entering the column since t_o . The two terms on the right-hand side are the travel-times in the extraction zone and below, respectively. The right-hand side of Equation 12 is positive and monotonic decreasing in α with range covering the positive real axis. Thus a unique solution to Equation 12 for α exists and can be easily found by iterative techniques (e.g., Newton-Raphson). Note that $\Theta(L; x_r) = \bar{\theta}_L (L - x_r)$ where $\bar{\theta}_L$ is the average water content below the extraction zone, thus average water content can be used at depths below the root zone as well. Recall however that both in and below the extraction zone the time-invariance assumption on water content (dynamics are ignored) renders the water contents in Equation 12 (and in Equation 8) effective properties, different from measured values. This error is expected to be small at the low water contents at depth encountered in arid sites (Phillips 1994). Magnitude of errors in the extraction zone (intuitively larger because water contents vary more strongly there) are also controlled for small α as inspection of Equation 12 shows. Thus it is presumed here that fluctuations in flux are associated with fluctuations in velocity rather than fluctuations in water content (cf. Tyler and Walker 1994). The only information used in the inverse solution is the chloride mass deposition rate, the specification of the extraction function, and the total profile chloride mass. The inversion results in an overall average estimate of α , the recharge expressed as a percentage of the average annual precipitation. This corresponds to a simple block model of the tracer profile. Finally, note also that when a solute front with *known* entry time t_o is observed below the root zone, the inversion gives the averaged recharge associated with the fully steady CMB technique, but without using concentration information. In this case the inversion of Equation 8a provides an essentially independent estimate of fully averaged recharge, which can be compared to CMB estimates.

In the second stage of the inversion, Equation 8b is used to estimate $p(t)$ given x_r and α , completing the definition of the time and space dependent recharge function. Specifically, the chloride concentration data within the profile are now used to distribute the full-term average recharge over the time horizon of the tracer transport. For simplicity we take $t_o = 0$. Equation 8b can be recast (Appendix D) as

$$\frac{dP^{-1}(s)}{ds} = \frac{1}{M_o(P^{-1}(s))} c^*(X_o(P^* - s)) q_o(X_o(P^* - s)) \quad (13)$$

where

$$P^* = \overline{p} \cdot t_{now} \text{ (cm)}$$

$$c^*(x) = c(x, t_{now}), \text{ current tracer profile (ppm)}$$

$$X_o(t) = \text{displacement function for } p(t) = 1 \text{ (inverse function of } \tau_o(x)), \text{ (cm)}$$

s = variable on $[0, P^*]$ representing $P(t_o)$ where t_o is entry time for solute

currently appearing at $x = X_o(P^* - s)$ (cm). Formally $s = s(x) = P^* - \tau_o(x)$.

Equation 13 is an ordinary differential equation in the function $P^{-1}(s)$, and may in principle be solved by numerical integration depending on the complexity in the specification of M_o . A direct solution is obtained here for the case where M_o is constant (this corresponds to the steady-state mass deposition assumption in the CMB). The integral of Equation 13 provides the inverse of the cumulative precipitation:

$$P^{-1}(s) = \frac{1}{m_o} \int_0^s c^*(X_o(P^* - s')) q_o(X_o(P^* - s')) ds' \equiv I(s) \quad (14)$$

Equation 14 is a relation between known quantities (on the right-hand side) and the inverse of the integral of the precipitation function (on the left-hand side) in terms of the variable s . The relation can be readily transformed to provide the desired precipitation function, $p(t)$. In simple terms, the right-hand side of Equation 14, $I(s_i)$ for various values of $s_i = s(x_i)$, the ordering of s_i and $I(s_i)$ are inverted, and is differenced s_i over $I(s_i)$ to obtain points $(I(s_i), \delta s_i)$ which are points in $(t, p(t))$. Formal and numerical procedures for taking the inverse are given in Appendix E. These procedures demonstrate that a closed-form inverse exists when chloride mass deposition is steady, and thus show the separate identifiability of both the fraction of precipitation which is recharged and the precipitation history itself.

On the contrary, this route is probably not the most efficient for computations. The conventional (and more efficient) CMB with "consistent" averaging is fully compatible with the inverse solution to the transport as depicted in this report and can be used to obtain the same paleorecharge estimates. The meaning of "consistent" is detailed as follows. The conventional CMB usually involves averaging data within depth intervals which are dictated by the occurrence of generally constant tracer mass with water content (see Appendix A). Specification of the intervals, however, does not take into account sample scale in relation to the frequency of the tracer concentration variations. That is, sample size and spacing are assumed sufficient to reflect the scale of fluctuations resulting from paleoclimatic variations, and fluctuations at frequencies above the sampling scale are treated as unimportant. This averaging amounts to a prefiltering of the data. An assessment of this prefiltering is beyond the present scope, but it is highlighted here as a difference in the ways the present inverse and the conventional CMB inverses are presented. Thus in comparison one may apply the CMB procedure and the present procedure to either the original data (at "high resolution") or to the prefiltered data, as long as it is done consistently. Under a consistent comparison, it can be shown that the conventional CMB and the present inverse are identical depictions of the transport according to Equation 8. Specifically, the CMB is in fact not necessarily a steady-state model with respect to either water

fluxes or boundary concentrations, but is steady only with respect to the deposition of tracer mass at the surface. This has not been entirely clear in the literature. This result is shown formally in Appendix F, where the conventional CMB as expressed by Equation A14 in Appendix A is derived from Equation 8. (It should be noted that the same form of the CMB arises from Equation 10a when tracer mass deposition M_o is constant - this relation is used in the generalized CMB to get the profile bottom pore water age). The equivalence is also demonstrated in the following application where both the formal inverse described above and the conventional CMB inverse (at "high resolution") are used to construct paleoprecipitation functions.

3.0 Application

To demonstrate the forward and inverse solutions, the foregoing developments are applied to chloride profile data from a borehole in western central New Mexico (termed 'SLCF05' in Stone 1984). The data represent 54 samples covering 16.5 m of alluvium and 1.5 m of (coal bearing) bedrock at the bottom of the hole. The water table was encountered at 16.5 m. Average annual precipitation $\bar{p}$ is estimated at 25.1 cm/yr and chloride mass deposition M_o was assumed constant at 94 mg/m²/yr. Bulk density of material was assumed constant at 1.4 g/cm and volumetric water contents were calculated by multiplying gravimetric water contents by this value. All core data is assumed representative of conditions within a square vertical column of square meter cross-sectional area.

Both the two-stage inverse method (termed the generalized chloride mass balance [GCMB]) and the conventional CMB at high resolution were applied to the profile data to determine the recharge history at the site. The pore water age at the maximum depth was calculated via Equation A14. The total chloride mass in the meter-square column profile (calculated in the right-hand side of Equation A14 is 1415 grams. Dividing this by M_o gives the estimate of pore water age at $x = L$ of 15,057 years [this is $t_{now} - t_o(x)$]. The fraction of precipitation which becomes recharge, α , was found by the GCMB by solving Equation 12 for α via Newton-Raphson iteration; the resulting value is 0.0012. The paleoprecipitation function was then found by solving Equation 14 via the algorithm outlined in Appendix E. In turn, the paleorecharge history according to the high-resolution CMB was determined. First Equation A11 was used to determine recharges corresponding to each depth interval between chloride samples; then Equation A14 was used to calculate pore water ages at the endpoints of each interval. Finally the value of α according to the high-resolution CMB was estimated by dividing the cumulative recharge since t_{now} (years ago) by the estimate of cumulative precipitation $\bar{p} \cdot t_{now}$; this value is 0.0010. To examine the effects of profile interval-averaging as part of the conventional CMB, the graphical procedure of Appendix A as exercised in Stone (1984) was taken as a representation of paleorecharge. The method underlying the calculation of this averaged recharge function is akin to the procedure for the high-resolution CMB method, but using Equation A10) instead of Equation A11. A value for α was also calculated for the conventional CMB by dividing the cumulative recharge by the estimate of cumulative precipitation $\bar{p} \cdot t_{now}$, yielding $\alpha = 0.0009$ for the conventional CMB. The paleorecharge functions obtained by both the generalized CMB and the high-resolution CMB are in good agreement as depicted in Figure 1. The estimates of current recharge are 0.06 mm/yr (GCMB), 0.08 mm/yr

(high-resolution CMB), and 0.08 mm/yr (conventional CMB).^a The recharge history according to the conventional CMB shows the effect of profile interval averaging in its departure from the high resolution CMB results. These values of α are likely biased in all three cases by the reliance on $\bar{p} \cdot t_{now}$ as an estimate of cumulative precipitation. This estimate is based on *recent* precipitation and on the contrary we have an indication - assuming the model conditions - of higher levels of paleoprecipitation. This does not affect the forward or inverse models as applied here, however, because α and $\bar{p}$ trade-off without affecting the recharge estimates or profile simulations.

To see the corresponding forward simulation of the existing chloride profile, the paleorecharge function determined by the GCMB inverse was converted to a paleoprecipitation function (by dividing the recharge function by α). This precipitation function was used to specify the boundary flux and boundary concentration in the forward model Equation 8a and 8b. To see the analogous forward simulation of the profile associated with either the high-resolution or conventional CMB, one must adopt a transient flux model (such as ours found in Equations 8a and 8b) because no particular forward model is associated with either the high-resolution or conventional CMB. This is because these methods were developed as piecewise steady-state flux extensions of the original, simple steady-state (flux and mass deposition) piston-flow model see Equations 2a and 2b with Equation A1] *in the inverse sense only*, in that no corresponding forward

Figure 1. Paleorecharge histories in years before present (yBP) by conventional (averaged) CMB, high-resolution CMB, and GCMB for data from Well SLCF05 of Stone (1984).

- (a) These values of α are likely biased in all three cases by the reliance on $\bar{p} \cdot t_{now}$ as an estimate of cumulative precipitation. This estimate is based on *recent* precipitation and on the contrary we have an indication - assuming the model conditions - of higher levels of paleoprecipitation. This does not affect the forward or inverse models as applied here, however, because α and $\bar{p}$ trade-off without affecting the recharge estimates or profile simulations.

model is jointly specified.^b The approach taken here for both the conventional and high-resolution CMB, was to simply apply the same assumptions underlying the forward model developed in this paper (e.g., assign all recharge transience to the linear relationship between paleoprecipitation and water extraction [and recharge]); this allows specification of the respective paleoprecipitation functions by dividing the recharge function by the respective α , as done in the case of the GCMB above. The precipitation functions are then used as above in the forward model Equations 8a and 8b to estimate the existing chloride profile. The resulting profile simulations by the generalized and high-resolution CMB methods are shown in Figure 2a together with the measured chloride profile, with good agreement, highlighting the formal result of Appendix F that the high-resolution CMB is consistent with the transient flux model posed here. The profile simulation by the conventional CMB is shown with the data in Figure 2b, and reflects the effects of averaging, now in terms of the measurable quantity (the current profile). Thus to the degree that the forward model is a

Figure 2. Forward modeling validation of inversion by GCMB and by high-resolution CMB. Shaded area represents the measured chloride profile (a). Forward modeling of inversion by conventional CMB (b).

- (b) This development history explains how a constant precipitation has been associated freely with a transient subsurface recharge, without specification of a transient extraction function, in many recent works on the conventional CMB.

reasonable depiction of the time-averaged infiltration process, the effect of interval averaging as practiced in the conventional CMB is to introduce the observed error between measured concentration and modeled concentrations shown in Figure 2b.

4.0 Conclusions

A rational, physically-based, but time-averaged model for one-dimensional vertical transient piston-flow infiltration of water and inert tracer has been developed and explored as a tool for estimating paleorecharge and paleoprecipitation via analysis of tracer concentration profiles in arid environments. This model is based on the assumption that a linear relationship exists between average annual precipitation and average annual water flux. Under this assumption, a convenient analytical forward solution to the model is derived. Under the additional assumption of constant chloride mass deposition at the surface, a closed-form inverse solution is derived, and this solution is shown consistent with the purely tracer mass-based CMB when the latter is applied at the same resolution as the transient flow model. The conventional CMB approach (e.g., Phillips 1994) provides estimates of recharge history which are consistent with (but averages of) those of the transient water flux models examined here. This highlights the fact that the conventional CMB approach to pore water dating requires the steady-state assumption on chloride mass deposition but not on water flux itself.^c

The important contributions of this work are as follows. Recent applications of the conventional CMB technique involve specification of the water flux environment as a chain of steady-states (this approach is often termed "quasi-steady state"), without any corresponding physical basis for the transport process (e.g., in the absence of a forward model incorporating transient water fluxes). This has led to applications involving apparently conflicting assumptions (such as constant boundary flux [precipitation] but transient flux at depth, and no particular transience in water extraction). The forward model presented here is one way of providing a complete physical description of the transport process, one which is self-consistent (in that forward and inverse operators are inverse functions of each other, and so uniqueness and identifiability is ensured), as well as consistent with the balancing of chloride tracer mass which is the basis for the conventional CMB. The closed-form inverse derived illustrates that under the transport processes assumed, the model has a unique inverse (e.g., recharge history). As more parameters are treated as unknowns, relative non-uniquenesses arise, for instance between α and $\bar{p}$, and between M_o and t_{now} . That is, as long as Equation 9 is satisfied, multiple values of α and $\bar{p}$ will fit a particular profile and recharge function.

We have illustrated in a mathematical framework that the conventional CMB is steady state only with respect to the tracer mass deposition (and not with respect to the water flux). The conventional CMB is shown to differ in recharge estimation from the technique presented here only in the prefiltering (interval-averaging) of the tracer profile data. When the conventional CMB is applied at the same resolution as that used for the GCMB, results identical to those obtained by the transient inverse method presented are

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obtained. This is not surprising because the conventional CMB honors the basic mass balance of tracer, although it does so without a fully specified transport model.

These results are not to be construed as a proposal for the use of higher resolution (less averaging) CMB methods in application. This judgement requires case-specific information on the other potential causes of profile concentration variation (e.g., transient mass deposition). Rather, it is pointed out that interval averaging can significantly change the representation of the profile, and infers certain assumptions about the scales of variability of the profile concentrations as viewed through the sample support, which are not usually critically assessed in application. Here a forward model is provided which can be used to examine the magnitude of this change in terms of measurable quantities (e.g., differences between the simulated profile and the measured concentrations).

The forward and inverse models presented may be useful for examining more complex processes. While the mathematical developments are not indicated as computationally advantageous over the CMB, the general tools that appear in the Appendices may be useful for dealing with more general water fluxes. The same mathematical approach can in principle be used to address transport involving exogenous variation in the root zone extraction function (e.g., arising from ecological plant successions), the presence of rock sources of chloride, and different transients in wet vs. dry chloride mass deposition (e.g., constant dry mass deposition and constant wet chloride concentration in precipitation), to name a few variations.

Finally, it is important to note that when the entry time of a tracer currently at a depth below the root zone is known, the formal inverse method provides a valuable alternative to the CMB. When such information is available, such as the location of an anthropogenic tracer (e.g., "bomb-pulse" tracer) front with known deposition time, the determination of the fraction of precipitation that becomes recharge, α , can be done via inverting Equation 9 as before but *without* using any tracer information. This can be done because it is no longer necessary to use the profile mass to determine the residence time, $t_{now} - t_o(x)$. This provides an essentially independent estimate of α , and with current precipitation, and independent estimate of recharge, which can be compared to results using the actual pore water tracer concentration values.

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Appendix A

The formalism underlying the calculation of recharge by the conventional CMB using the graphical technique suggested in most recent applications (e.g., Allison et al. 1985; Scanlon 1991; Phillips 1994) is presented. The graphical procedure is intended to identify a representative interval-averaged chloride concentration, where the intervals represent periods of generally constant water and chloride fluxes. For instance, "The value of C_{Cl} is best determined by plotting cumulative Cl content (mass Cl per unit volume of soil) with depth against cumulative water content (volume water per unit volume soil) at the same depths. Such a plot usually shows straight-line segments whose slope corresponds to C_{Cl} for that depth interval" (Phillips 1994, pg 17).

The starting point for the mathematical framework is the solution of the conventional CMB model in Equation 2a under steady-state conditions:

$$q(x) c(x) = q(0) c(0) \quad (A1)$$

The product $q(0) c(0)$ is simply the chloride mass deposited at the surface, M_o . For any root-zone extraction function of finite support (e.g., $q_{ex}(x) = 0$ for $x > x_r$, where x_r is the bottom of the root zone), the corresponding solution of the coupled water flux model Equation 2b requires $q(x)$ to be a constant below the root zone. Therefore the recharge $q(x)$ satisfies

$$q(x) c(x) = M_o \quad (A2)$$

Thus the forward and inverse solutions are simply

$$c(x) = M_o/q(x) \quad (A3)$$

for the profile simulation and

$$q(x) = M_o/c(x) \quad (A4)$$

for the recharge estimation, respectively. The fully steady-state CMB perspective of both tracer concentrations and water fluxes with depth is depicted in Figure A1. Figure A1 illustrates that all quantities are represented as constant below the root zone and that tracer concentration is magnified by the elimination of water by extraction, to the constant concentration occurring below the root zone.

The graphical approach noted above is an extension of this basic method to profiles resulting from a train of steady states, where cumulative water content is used to rescale the depth axis in order to factor out variations in water content. In other words, the chloride mass curve is "sampled" at equal increments of cumulative water content instead of at equal increments of cumulative distance (depth). Then linear segments of the plot correspond to chloride masses which are constant with increasing water content and are assumed to represent uniform environmental conditions for the corresponding period. Mathematically the procedure can be expressed as follows. First, note that the specification of piecewise linear transience in recharge (determined by depth x) requires us to reformulate the basic relation in Equation A2 in terms of a flux that depends on solute entry time (parameterized on x), $t_o(x)$:

Figure A1. Variation of tracer concentration in soil water and water flux with depth according to fully steady state CMB model.

$$q(x; t_o(x)) c(x) = M_o \quad (\text{A5})$$

The cumulative chloride mass is

$$M(x) = \int_0^x c(x') \theta(x') dx' \quad (\text{A6})$$

and the cumulative water content is

$$\Theta(x) = \int_0^x \theta(x') dx' \quad (\text{A7})$$

Because water content is positive, its space integral as shown in Equation A7 is monotonically increasing and so has an inverse function X

$$X(\Theta) = \Theta^{-1}(\Theta) \quad (\text{A8})$$

which, given the value of cumulative water content $\Theta = \Theta(x)$, returns the corresponding depth $x = X(\Theta)$. This new scaling of depth in terms of increments of cumulative water content, $X(\Theta)$, can be used as an independent variable (an axis) for defining cumulative chloride mass

$$M(x) = M(X(\Theta)) = M'(\Theta) \quad (\text{A9})$$

In the conventional graphical procedure, $M'(\Theta)$ is the function plotted, with Θ as the independent variable, and the required concentration (the derivative of M' with respect to Θ) is averaged by the difference $\Delta M' / \Delta \Theta$, taken over a linear portion of the plot. This difference provides the averaged concentration needed for the inversion of Equation A5 to determine the historical recharge corresponding to an interval Δx :

$$q(\Delta x; t_o(\Delta x)) = \frac{M_o}{\Delta M' / \Delta \Theta} = M_o / \overline{c_\Theta}(\Delta x) \quad (\text{A10})$$

where $\overline{c_\Theta}(\Delta x)$ is the normalized and θ -weighted average of the soil water concentration c over the increment of depth Δx (Δx is $x_2 - x_1$ where $x_2 = X(\Theta_2)$ and $x_1 = X(\Theta_1)$). For comparison, the analogous form using unscaled depth is

$$q(\Delta x; t_o(\Delta x)) = \frac{M_o}{\Delta C / \Delta x} = M_o / \overline{c_x}(\Delta x) \quad (\text{A11})$$

where $\overline{c_x}(\Delta x)$ is simply the average chloride concentration over the depth increment Δx . Two particular aspects of these relations are noted here. First, in the absence of averaging (that is, in the "high resolution" limit as $\Delta x \rightarrow 0$), Equations A10 and A11 are equivalent because the limit of $\overline{c_\Theta}(\Delta x)$ as $\Delta x \rightarrow 0$ is $c(x)$ (as can be shown by applying the chain rule to $dM'/d\Theta$). Also note that if the water content is taken as uniform with depth (as is often done formally), the representations yield equivalent estimates because

$$\frac{\Delta M'}{\Delta \Theta} = \frac{\theta \Delta C}{\theta \Delta x} = \frac{\Delta C}{\Delta x} \quad (\text{A12})$$

While Equation A10 yields average recharges for periods of roughly constant climatic conditions, it tells us nothing about the timing of these periods. The residence time of the solute at a particular depth, under the assumptions of piston flow and constant chloride mass deposition, is directly calculable from the fundamental mass balance relation

$$t - t_o = \frac{1}{M_o} \int_0^x c(x') \theta(x') dx' \quad (\text{A13})$$

where the quantity $t - t_o$ is by definition the porewater age. This relation has been used to date the solution occurring at the depths identified for Equation A10. Thus for the depth $x_I = X(\Theta_I)$, we have

$$(t - t_o)_{x_1} = \frac{1}{Mo} \int_0^{x_1} c(x') \theta(x') dx' \quad (A14)$$

Equations A10 and A14 can be used jointly to reconstruct the history of recharge below the root zone, under the assumptions of constant chloride deposition and exclusive piston flow. Note that this is accomplished without a steady-state assumption on water flux itself.

Appendix B

Equation 7 is solved under specified boundary water flux $q(0,t) = p(t)$ and boundary concentration $c(0,t) = c_o(t) = M_o(t)/p(t)$, by the method of characteristics.

$$\theta(x) \frac{\partial c}{\partial t} + p(t) q_o(x) \frac{\partial c}{\partial x} = c p(t) q_{exo}(x) \quad (B1)$$

The ordinary differential equations arising from Equation B1 are (Zachmanoglu and Thoe 1986)

$$\frac{p(t) dt}{1} = \frac{\theta dx}{q_o} = \frac{\theta dc}{c q_{exo}} \quad (B2)$$

where the left-hand side equality defines the trajectory in (x,t) of a solute front entering the system at (x_o, t_o) (the first characteristic), and the right-hand side equality determines the change in solute concentration along that trajectory due to water extraction in the root zone (the second characteristic). The first characteristic may be explicitly integrated to solve for the trajectory function (the ease with which this is done results from the separation of variables in Equation 4):

$$\int_{t_o}^t p(t) dt = \int_{x_o}^x \frac{\theta(x')}{q_o(x)} dx' \quad (B3)$$

or formally (with $x_o = 0$ as all solute enters at ground surface)

$$P(t; t_o) = \tau_o(x) \quad (B4)$$

where terms are as defined for Equation 8. Because both θ and q_o are finite positive functions, $\tau_o(x)$ is monotone increasing and has an inverse, written formally as

$$X_o(t; t_o) = \tau_o^{-1}(P(t) - P(t_o)) \quad (B5)$$

Using now the trajectory condition specified in Equation B4 as the path of integration, the second characteristic (the right-hand side of Equation B2) can be rewritten as

$$\frac{p(t) q_{exo}(x) dt}{\theta(x)} = \frac{dc}{c} \quad (B6)$$

We specify integration along the path of Equation B4 by parameterizing the position coordinate (in the left-hand side of Equation B6) on time via use of the inverse Equation B5:

$$\frac{-p(t') q_{exo}(X_o(P(t'; t_o)))}{\theta(X_o(P(t'; t_o)))} dt' = \frac{dc}{c} \quad (B7)$$

We now do some manipulations to facilitate integration of Equation B7. From the separation of variables in Equation 5 it is clear that under unit precipitation the total change in water flux at a point x is equal to the water extracted at x (this follows directly from the right-hand side of Equation 5). That is,

$$\frac{dq_o(x)}{dx} = -q_{exo}(x) \quad (B8)$$

Writing the total derivative on the left-hand side of Equation B8 for the moving front coordinate $x = X_o(P(t; t_o))$ and expanding via the chain rule renders Equation B8 as

$$\frac{dq_o(X_o)}{dX_o} = \frac{dq_o(X_o(P(t; t_o)))}{dt} \cdot \frac{1}{v_o(X_o(P(t; t_o)))} \cdot \frac{1}{p(t)} = -q_{exo}(X_o(P(t; t_o))) \quad (B9)$$

where we have defined a unit-precipitation velocity $v_o(x) = q_o(x)/\theta(x)$. Substituting this expression for $q_{exo}(X_o)$ into the numerator of Equation B7 gives

$$\frac{-dq_o(X_o(P(t; t_o)))}{dt} \cdot \frac{dt}{q_o(X_o(P(t; t_o)))} = \frac{dc}{c} \quad (B10)$$

or

$$\frac{-d \ln q_o(X_o(P(t; t_o)))}{dt} dt = \frac{dc}{c} \quad (B11)$$

Integrating,

$$\int_{t_o}^t \frac{-d \ln q_o(X_o(P(t; t_o)))}{dt} dt = \int_{Co(t_o)}^{C(t; t_o, Co(t_o))} \frac{dc}{c} \quad (B12)$$

we obtain the solution to Equation B7:

$$-\ln q_o(X_o(P(t;t_o))) + \ln q_o(X_o(P(t_o;t_o))) = \ln C(t;t_o, C_o(t_o)) - \ln C_o(t_o) \quad (\text{B13})$$

or, expressed as the characteristic solution C (the solute concentration along the solute front trajectory),

$$C(t;t_o, C_o(t_o)) = \frac{C_o(t_o) q_o(X_o(P(t_o;t_o)))}{q_o(X_o(P(t;t_o)))} \quad (\text{B14})$$

Finally the complete solution to the original model Equation 7 is obtained by parameterizing the starting point t_o of the solute front in Equation B14 on space and time by tracking the front along the first characteristic. From Equation B4 we have (with positive $p(t)$ and thus invertible $P(t)$),

$$t_o = P^{-1}[P(t) - \tau_o(x)] \quad (\text{B15})$$

which with Equation B14 yields the desired solution,

$$c(x,t) = \frac{c_o(P^{-1}[P(t) - \tau_o(x)])}{q_o(x)} \quad (\text{B16})$$

where we have used the fact that $q_o(0) = 1$.

Appendix C

Here we derive an approximate analytical expression for unit-precipitation travel time under uniform and exponential water extraction models (Raats 1974; Tyler and Walker 1994). Travel time is defined in Equation 10. The relation between the water flux and the extraction model appearing in Equation A1 is given by the solution to Equation 3b which appears in Equation 5. We show the derivation for the exponential water extraction model and present final solutions for both uniform and exponential extractions. Both models are linear in (conventionally constant) precipitation " P " in their original forms (cf. Tyler and Walker 1994) and so can be cast in terms of unit precipitation by simply taking $P' = 1$. Both models are also in parameters α (fraction of precipitation that is not extracted) and x_r (depth of root zone). The unit-precipitation extraction model of the exponential type is

$$q_{exo}(x) = \begin{cases} \frac{\lambda(1-\alpha)}{x_r(1-e^{-\lambda})} e^{[-\lambda x/x_r]} & x < x_r \\ 0 & x_r < x \end{cases} \quad (C1)$$

and its integral (appearing in Equation 5) is

$$\int_0^x q_{exo}(x) dx = \begin{cases} \frac{(1-\alpha)}{(1-e^{-\lambda})} [1 - e^{[-\lambda x/x_r]}] & x < x_r \\ 1-\alpha & x_r < x \end{cases} \quad (C2)$$

Writing this integral in Equation 5 and using Equation 5 in Equation 10 gives

$$\tau_o(L;\alpha) = \int_0^{x_r} \frac{\theta(x)}{1-(1-\alpha) \left[\frac{1-\exp(-\lambda x/x_r)}{1-\exp(-\lambda)} \right]} dx + \int_{x_r}^L \frac{\theta(x)}{\alpha} dx \quad (C3)$$

Note, however, that the first integral is the time spent in the root zone and, for $L \gg x_r$, in arid systems, is relatively small. The second term can be easily expressed in terms of the cumulative water content, the first term cannot. Equation C5 can be solved numerically. An alternative is to replace the water

content in the root zone (e.g., in the first term) with an average ($\theta(x) = \bar{\theta}_r$) to allow reduction of the integral to yield what becomes an approximate analytical solution. Measured values of water content may or may not be indicative of the average in the root zone, because the model value of water content is already an effective one, supposedly representing time-averaged processes on the order of one year. Intuitively the method of specifying the effective water content (whether it be as an average or as some depth-dependent function) should have ramifications for the form of the water extraction function which itself is effective. Use of an average value for water content allows direct solution of Equation C3, yielding

$$\tau_o(L;\alpha) = \frac{\bar{\theta}_r}{\theta_r} \frac{x_r(\ln(\alpha) + \lambda - e^{-\lambda}(\ln(\alpha) + \lambda))}{\lambda(\alpha - e^{-\lambda})} + \frac{1}{\alpha} \Theta(L;x_r) \quad (C4)$$

where $\Theta(L;x_r)$ is the cumulative water from the bottom of the root zone to the depth L .

The analogous solution for unit-precipitation travel-time under uniform extraction (defined in Equation 6) is

$$\tau_o(L;\alpha) = \frac{\bar{\theta}_r}{\theta_r} \frac{-x_r \ln(\alpha)}{(1-\alpha)} + \frac{1}{\alpha} \Theta(L;x_r) \quad (C5)$$

Finally, note that because the second term is linear in cumulative water content, the second term can be calculated using the average water content below the root zone, $\bar{\theta}_L$. That is, $\bar{\theta}_L \cdot (L - x_r)$ may be substituted for $\Theta(L;x_r)$ into either Equation C6 or C7 without further approximation.

Appendix D

This appendix presents the derivation of Equation 13, the formal inverse procedure, from Equation 8b. We begin with Equation 8b.

$$c(x,t) = \frac{c_o(P^{-1}[P(t) - \tau_o(x)])}{q_o(x)} \quad (D1)$$

written for the current profile data $c^*(x)$ at time t_{now} (with $P(t_{now}) = P^*$),

$$c^*(x) = \frac{c_o(P^{-1}[P^* - \tau_o(x)])}{q_o(x)} \quad (D2)$$

Now rearranging per $q_o(x)$ and using the definition of the boundary concentration as annual chloride mass dissolved in annual precipitation, $c_o(t) = M_o(t)/p(t)$ [units: if M_o is in $\text{cg}/\text{m}^2/\text{yr}$ and p is in $\text{cm}/\text{m}^2/\text{yr}$, then c is in ppm];

$$c^*(x) q_o(x) = \frac{M_o(P^{-1}[P^* - \tau_o(x)])}{p(P^{-1}[P^* - \tau_o(x)])} \quad (D3)$$

Again rearranging to isolate p ,

$$p(P^{-1}[P^* - \tau_o(x)]) = \frac{M_o(P^{-1}[P^* - \tau_o(x)])}{c^*(x) q_o(x)} \quad (D4)$$

On the left-hand side we have $p(P^{-1})$, a function of the inverse of its own integral, which here turns out to be the reciprocal of the derivative of the argument P^{-1} , as follows. As a basic change of variables we set $s(x) = P^* - \tau_o(x)$ and for notational convenience we make $R(s) = P^{-1}(s)$. Then the left-hand side of Equation D4 can be written as $p(R(s))$. By definition the precipitation is the derivative of its integral, and the left-hand side becomes

$$p(R) = \frac{dP(R)}{dR} = \frac{dP(P^{-1}(s))}{dP^{-1}(s)} = \frac{ds}{dP^{-1}(s)} = \left[\frac{dP^{-1}(s)}{ds} \right]^{-1} \quad (D5)$$

because $P(P^{-1}(s)) = s$. This same result can also be found through a chain rule expansion as in

$$\frac{dP(R(s(x)))}{dx} = \frac{dP}{dR} \cdot \frac{dR}{ds} \cdot \frac{ds}{dx} \quad (D6)$$

Using the result in Equation D5 we can write Equation D4 as

$$\frac{dP^{-1}(s)}{ds} = \frac{c^*(x) q_o(x)}{M_o(P^{-1}(s))} \quad (D7)$$

where

$$s(x) = P^* - \tau_o(x) \quad (D8)$$

Equation D7 can be expressed in exclusive terms of s through inversion of Equation D8, e.g, by replacing x via

$$x = X_o(P^* - s) \quad (D9)$$

With this change of variables Equation D7 becomes the result appearing in Equation 13:

$$\frac{dP^{-1}(s)}{ds} = \frac{c^*(X_o(P^* - s)) q_o((P^* - s))}{M_o(P^{-1}(s))} \quad (D10)$$

Appendix E

Here the inverse using Equation 14 is discussed formally and in terms of a numerical procedure. Formally, Equation 14 maps s through the operator $I(s)$ into values of $P^{-1}(s)$:

$$I(s): s \Rightarrow P^{-1}(s) \quad (E1)$$

But by definition $s = P(t_o)$, and $P^{-1}(P(t_o)) = t_o$, so the mapping is equivalently

$$I(P(t_o)): P(t_o) \Rightarrow t_o \quad (E2)$$

The mapping I is invertible for positive and bounded integrand in Equation 14 (this requires positive bounded chloride concentration profile and positive bounded chloride mass deposition). Under these conditions inversion of I gives the cumulative precipitation function:

$$I^{-1}(t_o): t_o \Rightarrow P(t_o) \quad (E3)$$

Thus an algorithm to find the precipitation function is as follows:

- Discretize the depth coordinate x on $[0, L]$ to make the set of points $\{x_i\}$. Note that L and t_{now} must together satisfy Equation 9.
- Compute the set of points $\{s_i\}$ using the defining relation between x and s , Equation D8; $s_i = P^* - \tau_o(x_i)$.
- Compute $I_i = I(s_i)$ using Equation 14, to generate the ordered pairs (s_i, I_i) .
- Reverse the ordering of the pairs to read (I_i, s_i) . This reversal is inversion of I , and the new ordered pairs are points in $(t_o, P(t_o))$ respectively.
- Difference the data I_i to create $(I_i, \Delta s_i)$. These are points on $(t, p(t))$.

The key to the algorithm is the transformation of points $\{s_i\}$ in the s -domain to points $\{t_i\}$ in the t_o -domain through the change of variables $s = P(t_o)$. Because s is on $[0, P^*]$, t_o is on $[0, t_{now}]$ and the domain of $p(t)$ is represented (although the points t_i are nonuniformly distributed).

Appendix F

The conventional CMB method, consisting of Equations A11 and A14 of Appendix A, are derived from the general forward solution in Equation 8 at "high resolution" (e.g., in the absence of averaging of the data). As pointed out in Appendix A, at high resolution Equations A10 and A11 are equivalent. To begin we restate Equation 8 written in terms of present day measurements [$P(t) = P^*$; $c(x, t) = c^*(x)$]:

$$P^* - P(t_o) = \tau_o(x) \quad (\text{F1a})$$

$$c^*(x) = \frac{c_o(P^{-1}[P^* - \tau_o(x)])}{q_o(x)} \quad (\text{F1b})$$

First we derive Equation A11, written here in terms of pointwise concentrations:

$$q(x; t_o(x)) = M_o / c^*(x) \quad (\text{F2})$$

by first rearranging Equation F1a to express t_o as a function of independent x

$$P(t_o(x)) = P^* - \tau_o(x) \quad (\text{F3})$$

and inserting this into Equation F1b to obtain

$$c^*(x) q_o(x) = c_o(t_o(x)) \quad (\text{F4})$$

But $c_o(t_o)$ is by definition $M_o/p(t_o)$, so Equation F4 can be rearranged as

$$q_o(x) p(t_o(x)) = M_o / c^*(x) \quad (\text{F5})$$

The left-hand side of Equation F5 is (by Equation 5) $q(x, t_o(x))$ and so Equation F2 is obtained. Secondly we derive Equation A14; we start from Equation F1b by replacing $c_o(t_o)$ with $M_o/p(t_o)$, multiplying by $\theta(x)$ and integrating over depth:

$$\int_0^x \theta(x') c^*(x') dx' = M_o \int_0^x \frac{\theta(x')}{q_o(x')} \frac{dx'}{P^{-1}[P^* - \tau_o(x')]} \quad (\text{F6})$$

Making the change of variables $s(x) = P^* - \tau_o(x)$ on the right-hand side and recalling from Appendix D, Equation D5 that the function of its own inverse integral, $p(P^{-1})$ is the reciprocal of the derivative of the argument,

$$p[P^{-1}(s)] = \frac{dP(P^{-1}(s))}{dP^{-1}(s)} = \left[\frac{dP^{-1}(s)}{ds} \right]^{-1} \quad (F7)$$

allows Equation F6 to be written as

$$\int_0^x \theta(x') c^*(x') dx' = M_o \int_0^x \frac{\theta(x')}{q_o(x')} \frac{dP^{-1}(s(x'))}{ds(x')} dx' \quad (F8)$$

The chain rule can be used to simplify the right-hand side (and we use the definition of the travel-time, $d\tau(x) = q_o(x) dx / \theta(x)$):

$$\frac{dP^{-1}(s(x))}{ds(x)} = \frac{dP^{-1}(P^* - t(x))}{dx} A \left[\frac{ds(x)}{dx} \right]^{-1} = - \frac{dP^{-1}(P^* - t(x))}{dx} \frac{q_o(x)}{\theta(x)} \quad (F9)$$

so that Equation F8 becomes

$$\int_0^x \theta(x') c^*(x') dx' = - M_o \int_0^x \frac{dP^{-1}[s(x')]}{dx'} dx' \quad (F10)$$

or simply

$$\int_0^x c^*(x') \theta(x') dx' = - M_o P^{-1}[s(x')]_0^x \quad (F11)$$

which on expanding $s(x)$ becomes

$$\int_0^x c^*(x') \theta(x') dx' = - M_o [P^{-1}[P^* - \tau_o(x)] - P^{-1}[P^*]] \quad (F12)$$

or, using Equation F3,

$$\int_0^x c^*(x') \theta(x') dx' = M_o(t - t_o(x)) \quad (F13)$$

which is Equation A14 , the desired result.