GROUND-WATER AGE AND ATMOSPHERIC TRACERS: SIMULATION STUDIES AND ANALYSIS OF FIELD DATA FROM THE MIRROR LAKE SITE, NEW HAMPSHIRE

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Abstract

The use of environmental tracers in characterization of ground-water systems is investigated through mathematical modeling of ground-water age and atmospheric tracer transport, and by a field study at the Mirror Lake site, New Hampshire. Theory is presented for modeling ground-water age using the advective-dispersive transport equation. The transport equation includes a zero-order source of unit strength, corresponding to the rate of aging, and can accommodate matrix diffusion and other exchange processes. The effect of temperature fluctuations and layered soils on transport of atmospheric gases to the water table is investigated using a one-dimensional numerical model of chlorofluorocarbon (CFC-11) transport. The nonlinear relation between temperature and Henry's Law coefficient (reflecting air/water phase partitioning) can cause the apparent recharge temperature to be elevated above the annual mean temperature where the water table is shallow. In addition, fine-grained soils can isolate the air phase in the unsaturated zone from the atmosphere. At the USGS' Mirror Lake, New Hampshire fractured-rock research site CFC concentrations near the water table are depleted where dissolved oxygen is low. CFC-11 and CFC-113 are completely absent under anaerobic conditions, while CFC-12 is as low as one-third of modern concentrations. Anaerobic biodegradation apparently consumes CFC's near the water table at this site. One area of active degradation appears to be associated with streamflow loss to ground water. Soil gas concentrations are generally close to atmospheric levels, although some spatial correlation is observed between depleted concentrations of CFC-11 and CFC-113 in soil gas and water-table samples. Results of unsaturated-zone monitoring indicate that recharge occurs throughout the year in the watershed, even during summer evapotranspiration periods, and that seasonal temperature fluctuations occur as much as 5 meters below land surface. Application of ground-water age and CFC-11 transport models to the large-scale ground-water system at Mirror Lake

illustrates the similarities between age and chemical transport. Generally, bedrock porosities required to match observed apparent ages from CFC concentrations are high relative to porosities measured on cores. Although matrix diffusion has no effect on steady-state age, it can significantly reduce CFC concentrations in fractured rock in which the effective porosity is low.

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Chapter 1 Introduction

Estimation of flow and transport properties of large-scale ground-water systems is difficult because small-scale measurements cannot be directly up-scaled, and because large-scale field experiments cannot be easily conducted. The presence of environmental tracers, such as atmospheric gases, can serve as ongoing experiments on the large-scale system (e.g. Plummer et al., 1993). Interpretation of tracer transport via quantitative simulation can yield estimates of large-scale properties. In this approach, the historic source function is used as a boundary condition for the transport model, and simulated concentrations are compared directly to measurements. If tracer concentrations are affected by processes other than advection and dispersion, then those additional processes must be included in the transport model.

A simple method of interpreting environmental tracer data is by age dating; the measured concentration is used to estimate ground-water age. For example, Chlorofluorocarbon (CFC) concentrations in ground water can be converted to a recharge date when the water was isolated from the atmosphere, based on the record of increasing atmospheric levels. The difference between the recharge date and the sampling date is the ground-water age. The ground-water age can be compared to advective travel times, and hydraulic properties and effective porosity can be estimated (e.g. Reilly et al., 1994). This method ignores dispersion.

This thesis explores two main topics in the use of ground-water age-dating tracers, and CFC's in particular, in estimation of large-scale flow and transport properties. The first topic is the relation between solute concentration and ground-water age in systems affected by dispersion, mixing, and matrix diffusion. In Chapter Two, a method is presented that bridges the gap between modeling ground-water age using advection alone, and simulating tracer concentrations using advection, dispersion and

exchange processes. Simulations of ground-water age and CFC concentration are compared and contrasted for a fractured-rock field site in Chapter Five.

The second topic is the effect of additional processes, primarily temperature fluctuations and degradation reactions, on transport of CFC's from the atmosphere to ground water. The effects of fluctuating temperature and nonuniform soil properties on CFC concentrations at the water table are simulated in Chapter Three. A previously observed problem with CFC's as tracers is that under certain low-oxygen conditions degradation can significantly reduce concentrations (Plummer et al., 1993). In Chapter Four, a field study of CFC concentrations at the water table focuses on degradation reactions that may completely remove CFC's from recharge waters. Based on this field study, the input source function of CFC-11 to ground water is modified in Chapter Five for the large-scale transport model to account for degradation in some areas of the watershed.

Chapter Two presents a theory of direct simulation of ground-water age by transport modeling. The theory bridges the two current approaches for interpretation of age-dating environmental tracers: comparison of ground-water age dates to advective (piston flow) travel times, and simulation of environmental tracer concentrations using the advective-dispersive transport equation. The impact of matrix diffusion, an important process in fractured rocks, on ground-water age is theoretically examined. Several examples illustrate the application of the theory to characterize age in different ground-water systems. Chapter Two is an extension of Goode (1996).

The effects of temperature fluctuations and material heterogeneities on dissolved gas transport from the land surface to the water table are examined in Chapter Three. A one-dimensional transport model is developed and applied to unsaturated-zone conditions representative of humid eastern climates. Simulations examine CFC-11 transport under nonisothermal conditions in which partitioning into the air and water phases changes as a

function of temperature. The impact of a fine-grained soil above the water table on air-phase diffusion is also examined.

Chapter Four is a field study of the unsaturated zone at the Mirror Lake site (Hsieh et al, 1993). Use of CFC's to age date saturated-zone ground water is based on an assumption of chemical equilibrium between the water table and the atmosphere. However, CFC concentrations at the water table are significantly degraded in some locations in the Mirror Lake watershed. The relation between CFC's, dissolved oxygen, redox indicators, and stream/aquifer interaction is examined based on field data collected over a three-year period at the site. Preliminary summaries of the findings reported here have been presented at scientific meetings (see abstracts: Goode, 1997; Goode et al., 1997).

Large-scale ground-water age and CFC-11 transport is simulated in Chapter Five. These simulations use the theory of Chapter Two, and modifications to a USGS transport model (Konikow et al., 1996) to approximate the effects of matrix diffusion on transport. The flow model used is derived from that of Tiedeman and others (1997). Results of the transport and age simulation are compared and contrasted. CFC-11 results are qualitatively compared to results from field sampling (Busenberg and Plummer, 1996).

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Chapter 6 Summary and Conclusions

This thesis addresses several issues associated with environmental tracers in ground water. Topics include mathematical and numerical modeling of age in complex ground-water systems, effects of temperature on atmospheric tracer transport to the water table, and a field study of CFC's at the water table. Specific examples and applications are drawn from the USGS fractured-rock research site at Mirror Lake, New Hampshire.

Chapter Two presents a theoretical model of ground-water age transport that can be used to characterize systems influenced by advection as well as matrix diffusion and dispersion. This approach bridges the gap between current approaches of treating transport as piston flow, or advection alone, focusing on ground-water age, and of simulating advective-dispersive transport, focusing on tracer concentrations. The theory presented is general and accounts directly for the effects of dispersion, matrix diffusion, and other processes on ground-water age. Simulation results using this method can be compared to apparent ages from tracer concentrations, and can be used to illustrate ground-water transport conditions in an intuitive age framework. However, this method does not supplant simulation of tracer transport as the best approach to estimating transport properties from observed concentrations because all processes that affect measured concentrations of a particular tracer, such as decay and sorption, can be explicitly included in the simulation. Errors in apparent age from tracer data, for example due to mixing, cannot be rectified by the proposed method.

In Chapter Three, the effects of temperature fluctuations on CFC-11 transport from the land surface to the water table in humid areas are examined by simulation. Generally, air-phase diffusion is sufficient to maintain water-table concentrations close to those in equilibrium with the atmosphere. A determining factor is the extent of temperature fluctuations at the highest location above the water table where moisture

contents are nearly saturated. Air-phase diffusion below this point will be unable to rapidly transport CFC's from the atmosphere to the underlying water table and a lag will occur due to water-phase transport in the unsaturated zone. If temperature fluctuations are large at this point, then concentration of CFC's in the water column will be elevated compared to the equilibrium partitioning at the mean temperature. This is caused by the nonlinear relation between temperature and Henry's Law coefficient, and will affect all dissolved gases, depending on the curvature of their temperature relation. Fine-grained porous media generally hold more moisture than coarse-grained materials and can restrict vertical CFC transport by limiting air-phase diffusion.

A three-year field study of the unsaturated zone and water table at the Mirror Lake site, New Hampshire, is presented in Chapter Four. Field data collected included water levels and unsaturated-zone pressure head, moisture content by TDR, and soil temperature. Water samples were collected from shallow piezometers and analyzed at USGS labs for general chemistry as well as dissolved gases, including CFC's, tritium, and other constituents. Results indicate that in some areas of the watershed CFC concentrations at the water table are significantly degraded by anaerobic biodegradation. CFC-11 and CFC-113 are completely absent at several locations, while CFC-12 is degraded to about one-third of modern levels. Independent evidence of anaerobic degradation includes methane concentrations and hydrogen gas concentrations. The latter suggest that methanogenesis and sulfate reduction are active terminal electron-accepting processes. Oxygen and CFC gas transport to the water table is presumed to be limited by normally high moisture content in the fine-grained glacial drift at the site. An area of observed streamflow loss corresponds to an area of active degradation, suggesting a link between the supply of organic carbon from the stream bottom and degradation in the aquifer. Where dissolved oxygen concentrations are above 4-5 mg/L, CFC concentrations are in equilibrium with the modern atmosphere, assuming equilibration temperatures ranging between 4 and 8 °C.

Chapter Five extends some of the general results of Chapter Two to a particular case of ground-water flow in glacial drift and bedrock at the Mirror Lake site, New Hampshire. Results from the age transport model indicate that ground-water ages in the bedrock are not markedly different than those of the glacial drift. As expected for a relatively homogeneous parameterization of hydraulic and transport properties, oldest ground-water ages exist beneath discharge locations where older water from deep in the aquifer rises to the land surface. CFC-11 transport simulation results can account for degradation of CFC-11 in streamflow entering the aquifer, a process that cannot be included in the general age model. This leads to low CFC-11 concentration beneath a losing stream reach, while the ground-water age is very young. Low CFC-11 concentrations are also observed where old water rises from deep in the aquifer to discharge at lower parts of the Mirror Lake watershed. CFC-11 concentrations are not related to age for waters older than about 50 years, because the atmospheric concentration before that time was essentially zero. The impact of matrix diffusion depends on the rate coefficient for exchange between the flowing water and the immobile water within the rock. If this exchange rate is small, then matrix diffusion has a minor retardation effect on ages and CFC-11 concentrations. However, in the case of age, the steady-state age distribution (after many, many years) is independent of the rate coefficient. CFC-11 concentrations in the bedrock can be significantly decreased by matrix diffusion, given the small porosity of the active flow fractures.

Future Work

Theoretical work on the effect of mixing on ground-water ages estimated from tracer data, and methods to account for this during interpretation of field data, are much needed. The theory presented here for ground-water age is developed only for the mass-weighted average age. Because the input functions of environmental tracers are not purely linear, the age associated with the concentration of a mixture is not equivalent to the average age of the mixture. Ground-water samples, especially from large pumping wells and springs, represent mixtures of water having different sources, pathways, and travel times. The ground-water age modeling framework presented here may provide a basis for methods to simulate the distribution of ages within a given volume, and the age distribution could then be directly related to corrsponding concentrations through convolution.

One of the aspects of seasonal temperature that is not considered here is the interaction between changing temperature and variable recharge. Here only steady-flow conditions are considered. There may be important effects of changing temperature that will be manifest only when a variable recharge function, such as that due to snowmelt in the early spring and evapotranspiration during summer, is coupled with the temperature fluctuation. Such studies would probably require more sophisticated coupled flow and heat transport models, in contrast to the methods here in which the temperature is independent of flow. However, preliminary simulations using isothermal flow hydraulic properties could be made using the numerical tools developed here.

A remaining question about the field results from the Mirror Lake site is the extent to which the observed CFC degradation at the water table affects CFC concentration in the bedrock. Additional spatial coverage of the watershed would help clarify this issue, although drilling is difficult in much of the area due to the steepness of the watershed, and boulders in the glacial drift. Loss of CFC's from bedrock samples

would yield apparent ages older than actual ages, but comparison of CFC-12 age dates and tritium concentrations suggests the opposite result, that the CFC-12 age dates are too young. More detailed study of transport processes between the glacial drift and bedrock, and within the bedrock, particularly the role of matrix diffusion and spatial variability, would be required to interpret CFC concentrations in bedrock at this site.

The large-scale transport model used here for illustration of age and CFC-11 transport does not incorporate smaller-scale spatial variability which exists, but can not be accurately quantified for the entire watershed. Some of the features evident in these simulations are not apparent in the measured CFC concentrations in bedrock at the site. This is similar to the lack of match between simulated vertical head gradients and observed vertical head gradients in the large-scale flow model. The large-scale model does not include these small-scale features, and these small-scale features may control CFC concentration. Given this inconsistency, it may be necessary to use stochastic modeling, perhaps in a conditional simulation framework, to generate plausible realizations of hydraulic and transport properties in the basin that yield simulation results consistent with observed field data.