Quantitative Chemical Mass Transfer in Coastal Sediments During Early Diagenesis: Effects of Biological Transport, Mineralogy, and Fabric

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LONG-TERM GOALS

Multicomponent reaction transport models used to study early diagenesis in marine systems are typically limited by rudimentary descriptions of bioirrigation (enhanced solute transport) and generally cannot be used to simulate lateral and temporal variations in bioirrigation. It is the goal of this project to develop better representations of bioirrigation, through both stochastic and inverse modeling approaches, and to incorporate these improvements into the existing 1-D steady state multicomponent reaction-transport model, STEADYSED (Van Cappellen and Wang, 1996). In addition, the bioirrigation model will be further developed in order to represent sediments in 2D (or 3D) and at nonsteady state conditions, so that spatial and temporal heterogeneities may be incorporated directly into an early diagenesis model.

OBJECTIVES

The overall objective of the study is to develop better representations of the spatial and temporal variation of bioirrigation in early diagenesis models. Specific tasks for FY00 included, (1)fully developing a stochastic model that uses ecological data to model bioirrigation in natural and laboratory environments, (2) fully developing a 1D inverse model, including a quality function to assess the meaningfulness of model results, (3) using the 1D inverse model to extract bioirrigation coefficients for a variety of marine environments, (4) exploring correlations between organic matter oxidation rates and bioirrigation intensities, (5) developing a quantitative link between inverse and stochastic bioirrigation modeling approaches, and (6) beginning to develop a 2D (or 3D), nonsteady state bioirrigation model.

APPROACH

A collaborative effort between researchers at Western Michigan University (C.Koretsky) and at Utrecht University (C. Meile and P. Van Cappellen) resulted in the development of an inverse, steady-state, 1D reaction-transport model. This model includes terms accounting for diffusion, advection, reaction and bioirrigation (e.g., Emerson et al., 1984; Boudreau, 1996),

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right) - R - v\frac{\partial C}{\partial z} + \alpha\left(C_0 - C\right) = 0$$

where C is concentration of a given chemical species of interest, t is time, z is depth with respect to the sediment-water interface, D is the diffusion coefficient of the chemical species of interest, R is the depth-dependent rate of production or consumption of that species, v is the advective velocity, α is the depth-dependent bioirrigation coefficient and C_0 is the concentration of the species at the sediment-water interface. The inverse model uses a downhill simplex algorithm to optimize modeled irrigation coefficient profiles, and uses Monte Carlo simulations to reduce the effects of spatial correlation and to eliminate local minima encountered by the downhill simplex algorithm (Meile et al., 2000). Analytical uncertainty associated with measured data used in the model may result in non-unique solutions. To distinguish ‘good’ solutions from ‘poor’ solutions, a quantitative quality function was developed using synthetic bioirrigation coefficient profiles (i.e., known solutions). The quality function is based on the sensitivity of the calculated concentration profile to the parameter profile, as well as on the goodness of fit between measured and calculated concentration profiles, and was developed using synthetic model runs where model results could be compared to the true underlying solution.

The inverse model was used with published chemical data to extract depth-dependent bioirrigation coefficients for a variety of marine environments. For each bioirrigation coefficient profile, the quality function was calculated, in order to assess the quality of the derived profiles. Bioirrigation coefficients were used to calculate irrigation fluxes of O_2 in these environments, and organic carbon degradation rates for these environments were compiled. Future work will address correlations between rates of organic carbon oxidation and biorrigation intensity in marine environments.

A stochastic model of bioirrigation has been developed (Koretsky et al., 1999) to function as a link between the inverse bioirrigation model and ecological data. The model allows the spatial and temporal heterogeneity of bioirrigation to be assessed, by combining macrofaunal burrow shapes and sizes (e.g., Basan and Frey, 1977; Teal, 1958) measured in the field or in laboratory tanks (e.g. Furukawa et al., 2000) with probability distributions to derive mean depth-dependent burrow surface areas. The burrow surface areas represent the available surface area for solute exchange, and will be linked to depth-dependent bioirrigation coefficients from the inverse model. The model will be calibrated using laboratory data collected by Y. Furukawa (Office of Naval Research), D. Lavoie (Office of Naval Research) and S. Bentley (Louisiana State University).

WORK COMPLETED

A 1D steady-state inverse model that can be used to derive unbiased depth-dependent bioirrigation coefficients has been developed. This model includes a quantitative quality function that can be used to assess the meaningfulness of non-unique model results. The 1D inverse model has been applied to four marine environments (Buzzards Bay, MA; Washington Shelf, WA; Sapelo Island, GA; Svalbard, Norway). Depth-dependent bioirrigation coefficient profiles from these sites have been used to calculate O_2 irrigation fluxes. For profiles with high associated quality functions, these results have been found to compare well with measured O_2 fluxes. The stochastic model has been completed and used to simulate depth-dependent burrow surface areas in a natural environment (Sapelo Island, GA).

RESULTS

The inverse model was used to derive unbiased, depth-dependent bioirrigation coefficients at four marine environments. Bioirrigation coefficients in two of these environments, Buzzard's Bay, MA and Washington Shelf, WA exhibit distinct subsurface maxima. These results, which are associated with high values of the quality function, suggest that bioirrigation coefficient profiles may be quite complex. Previous bioirrigation models, which typically impose an *a priori* depth-dependence to the bioirrigation coefficient profiles, are unable to identify this complex depth-dependence. Features such as subsurface maxima are probably not model artefacts, but likely represent the presence of U-shaped macrofaunal burrows that tend to occur at specific depths. In fact, a core from Washington Shelf, WA shows evidence of a burrow at the very same depth that inverse model results suggest a subsurface maximum in bioirrigation (Smethie et al., 1981; Meile et al., 2000).

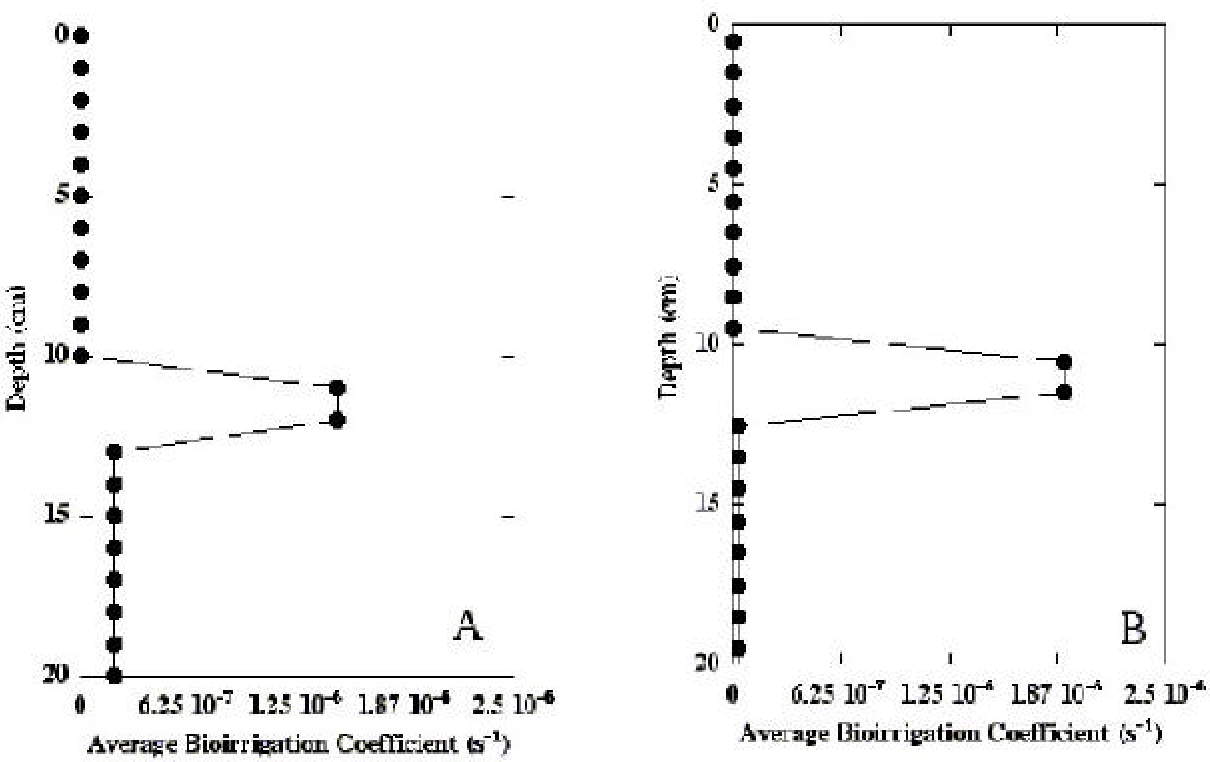

Figure 1. Bioirrigation coefficient profiles for (A) Buzzard's Bay, MA and (B) Washington Shelf, WA. A core described for the Washington Shelf site by Smethie et al (1981) contains a burrow at a depth of ~10 cm.

A quantitative quality function was developed that may be used to assess inverse model results. The quality function was used to assess calculated bioirrigation coefficient profiles for four marine environments. For one of these environments, Sapelo Island, GA, the quality function suggests that bioirrigation coefficient profiles that give an excellent match to measured data are, nonetheless, of relatively poor quality.

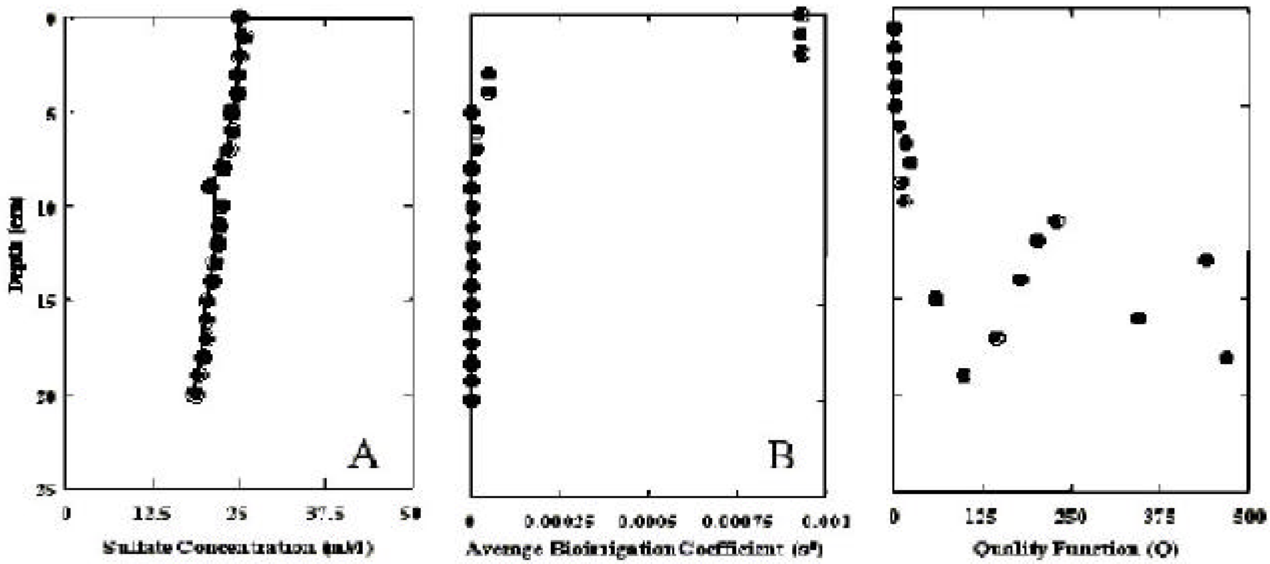

Figure 2. (A) Calculated (line) and measured (circles) concentration profiles for a vegetated saltmarsh site at Sapelo Island, GA. (B) Depth-dependent bioirrigation coefficient profile calculated using sulfate concentration profiles shown in (A) and reduction rates (not shown). (C) Quality function (Q) as a function of depth (circles). Minimum acceptable value of Q is 0.4, based on synthetic model results.Values of Q associated with very high bioirrigation coefficients in the upper few cm (B) are less than 0.4.

The bioirrigation coeffient profiles derived for the four marine sites using the inverse model were used to calculate O_2 irrigation fluxes. At three of these sites (Washington Shelf, WA; Svalbard, Norway; Buzzard's Bay, MA), calculated fluxes were in good agreement with measured O_2 fluxes. However, at the only site where bioirrigation coefficient profiles were associated with very low values of the quality function (Sapelo Island, GA), calculated fluxes were considerably higher than measured fluxes. This highlights the utility of the quality function in assessing model results.

IMPACT/APPLICATIONS

The 1D steady-state inverse model that has been developed allows an unbiased derivation of depth-dependent bioirrigation coefficients using measured solute concentration and rate profiles. In addition, the quality function allows non-unique model results to be assessed quantitatively. Thus, model results which give a good fit to measured data, but which are not of high quality can be easily identified. The 2D model, which is still being developed, will give us a valuable tool for assessing lateral and temporal heterogeneity in bioirrigation and the effects of such heterogeneities of sediment biogeochemistry. The stochastic model allows ecological data to be directly incorporated into the bioirrigation model, and will also function as a tool for futhering our understanding of spatial and temporal heterogeneities in bioirrigation. Linking the inverse and stochastic models will allow the effects of changing macrofaunal activity (due to storms, pollution or other environmental changes) to be used to predict the resultant effect on chemical fluxes in the sediments.

TRANSITIONS

The 1D steady-state inverse model is currently available to the public (Meile et al., 2000). This model can be used to constrain bioirrigation within sediments, and may also be used to constrain reaction rate profiles in sediments or within the water column.

RELATED PROJECTS

Seasonal pore water profiles of dissolved species (e.g., Fe(II)/Fe(III), SO_4(-II), H_2S, PO_4^{-3}, NH_3 and Mn) have been measured along a transect in a saltmarsh at Sapelo Island, GA (Koretsky et al., 2000). The seasonal oscillation of microbial community structure at these same sites was studied in collaboration with T. DiChristina and C. Moore (Georgia Institute of Technology). Intrepretation of spatial and temporal oscillations in the saltmarsh biogeochemistry has been greatly aided by results of inverse and stochastic models developed in this study. The relative compression of redox zones in these sediments has been shown to strongly depend on the depth and intensity of bioirrigation. In addition, preliminary studies of the influence of vegetation on redox zonation suggest that plants may trap particles that are subsequently redistributed by bioturbation. This may lead to an enhancement of microbial activity in newly colonized sediments, and to more compressed redox zonation. Models developed in this study may also be of use in understanding the influence of bioturbation on sediment biogeochemistry. A global relationship between bioirrigation intensities and rates of organic carbon degradation may be usedful in constraining irrigation intensities or rates of organic carbon degradation in modern and ancient ocean sediments. Yoko Furukawa (Office of Naval Research), Sam Bentley (Louisiana State University) and Dawn Lavoie (Office of Naval Research) have characterized burrow sizes and shapes, burrow flushing frequencies and velocities and average burrow 'lifetimes', both in tank experiments and in the field. The stochastic and inverse models will be calibrated using their controlled tank experiments, and will be used to interpret field data.

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