



Biogeochemical Processes in Coastal Aquifers and Permeable Sediments

Preface

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Recent changes in our understanding of the mechanisms of chemical exchange and benthic flux in coastal systems has led to a paradigm shift in our assessment of chemical inputs to the ocean (Moore, 1999; Boudreau et al., 2001). Studies have demonstrated that discharge from coastal aquifers, and flow through permeable sediments, constitute major mechanisms for chemical exchange in coastal systems (Moore, 1996; Huettel et al., 1996; Shaw et al., 1998; Moore, 1999; Huettel and Rusch, 2000; Jahnke et al., 2000; Krest et al., 2000; Boudreau et al., 2001). The articles presented in this volume reflect discussions that were part of a conference titled “Subterranean Coastal Environments: Biogeochemical Processes, Fluxes and Impacts” held at the Hanse Institute for Advanced Study in Delmenhorst, Germany, in May of 2001. Within this special volume, methods for evaluating the physiochemical conditions and processes that lead to flow in permeable systems are discussed as well as some of the consequences to chemical exchange in coastal ocean environments. A brief overview of each of these articles and their significance to understanding permeable systems is presented below.

A number of studies have documented significant chemical fluxes associated with discharge/exchange of seawater that flows through shallow permeable sediments and sands. The advective flow in these systems is driven by pressure gradients associated with current flow over uneven bed forms (Harrison et al., 1983; Huettel et al., 1996) as well as oscillatory pressure gradients induced by waves and tides (Falter and Sansone, 2000). Chemical exchange in such systems is due in part to penetration of particulate phases into the permeable medium and subsequent degradation of those phases. (Huettel et al., 1996; Huettel and Rusch 2000). Rapid diagenesis and high exchange rates result in benthic fluxes of degradation products of biogenic material that eclipse fluxes associated with low permeability sediments (traditional diffusive systems). However, in order to evaluate the importance of these processes, the spatial distribution of permeable sediments needs to be evaluated. Forster et al., (this volume) have undertaken a study to test the utility of sediment grain size distribution and porosity in the prediction of permeability. Forster et al., (this volume) have measured the spatial distribution of permeability in

shallow sediments of the southern Baltic Sea to verify the criteria for the prediction of permeability. The results of this study give some insight into the expanse of permeable sediments (40%–60% of the study area) and provide one of the tools necessary to evaluate the importance of permeable sediments to early diagenesis.

Recent investigations of chemical exchange at the groundwater seawater/ interface have sparked considerable excitement based on the magnitude of these fluxes with respect to river inputs (Moore, 1996; Moore 1997; Shaw et al., 1998; Krest et al., 2000). However, these investigations have also sparked considerable controversy based (in part) on the misconception that the observed chemical fluxes are accompanied by a proportional fresh water flux. This controversial assumption arose from Moore's (1996) calculation of an endmember source of the chemical flux, but the controversy was exacerbated by differing usage of the term submarine groundwater discharge (SGD) by the scientific community. For the purpose of this discussion, we define SGD as a range of advective processes that encompass freshwater/seawater mixing as well as recycling of seawater through permeable sediments on the continental shelf. Assessing the magnitude of this non-point source exchange with the coastal ocean waters requires new process tracers. The relatively high rates of exchange in these systems (due to permeability) and the high rates of reactions (due to the solid bound microbial community) preclude making estimates of exchange based on solid chemical reservoirs or pore water profiles. In short, the processing and mixing of materials is too fast to use methods appropriate for sediment diagenesis models. Likewise, lack of a discernable end member water source prevents the use of typical estuarine mixing models based on salinity gradients. Alternative mixing models utilize the soluble daughters of solid-bound radionuclides as tracers of exchange in permeable sediments and aquifers (Rama and Moore 1995; Cable et al., 1996; Krest et al., 2000; Charette et al., 2001). In these approaches the end member water mass is identified by chemical alteration due to reactions with the solid phase during flow/exchange with the permeable solid phase. The Ra daughters of the U/Th decay series have proved to be useful tracers due to their solubility and range of half-lives (3.6 days to 1600 years). Crotwell and Moore (this volume) demonstrate the challenges involved in differentiating multiple non-point source chemical inputs to coastal systems and the utility of the long lived Ra isotopes (^{228}Ra and ^{226}Ra) as exchange tracers. The nutrient mass balance in the system described (Port Royal Sound) includes a recent diagenetic source as well as inputs from an ancient aquifer (the upper Floridian). The approach used in Port Royal Sound by Moore and Crotwell (this volume) provide a model for evaluating the impact of non-point source nutrient flux to global mass balance.

A major challenge we face as we try to incorporate fluxes in permeable systems into chemical mass balances for the coastal ocean is differentiating degradation products from terrestrial and marine particulate sources. Differentiating terrestrial from marine sources is particularly difficult (and significant) in the permeable sediments underlying coastal marsh systems. Tidal inundation of this land/ocean transition zone results in penetration of the waters of the tidal prism into the per-

meable shallow aquifer on a daily basis (Hancock et al., 2000; Gardner and Reeves 2002). The volume of water filling and draining the aquifer with diurnal tidal forcing constitutes a major exchange of groundwater, yet there may be little net flow of fresh water from land to sea associated with this process. Some assume that a large terrestrially derived chemical flux must be accompanied by a significant fresh water flux. However, the assumption of a terrestrial source does not require a large freshwater component to the discharge if the source is a sufficiently reactive solid phase. Such is clearly the case for the desorption of Ra and Ba from solids within the groundwater/seawater mixing zone (Moore 1996; Shaw et al., 1998). A significant component of the chemical exchange (flux) results from the degradation of the particulate component of the mobile phase. In shelf sands, much of the reactive particulate component of the mobile phase is marine biogenic material. In contrast, the mobile phase in shallow aquifers at the terrestrial/ocean boundary contains a range of terrestrial and marine particulate and colloidal phases. The reactivity of these phases may change dramatically as the physiochemical environment varies in coastal aquifers. The importance of these processes is indicated by the net export of dissolved inorganic carbon (DIC) from these systems (Cai et al., 2003). Goni and Gardner (this volume) and Duncan and Shaw (this volume) examine the reactivity and net exchange of components of the mobile phase in the shallow coastal aquifer underlying a salt marsh system in North Inlet, South Carolina (USA). Goni and Gardner (this volume) characterize the fate of dissolved organic carbon (DOC) as a function of physiochemical regime in the forest/marsh transition of a transect of the aquifer. Duncan and Shaw (this volume) examine the behavior of rare earth elements (REE) and redox sensitive elements (RSE) along a longer transect of the same aquifer. Both of these studies indicate the importance of diagenetic reactions in these systems to the mass balance of organic carbon and trace elements in the coastal and global ocean.

The fate and reactivity of organic carbon in coastal marsh systems may control a significant fraction of the terrestrial to marine carbon flux. Much of the terrestrial carbon reaching the coastal zone is thought to be refractory, yet in the marine system, this material can become labile (Hedges et al., 1997). The role of the coastal marsh system in this process is indicated by the degradation of terrestrial DOC (Goni and Gardner, this volume) and magnitude of the export of DIC (Cai et al., 2003). One important factor in this process may be a local source for labile organic carbon that supports DIC export and possibly, the co-metabolism of refractory terrestrial organic carbon. Sundby et al., (this volume) examine the role of marsh plants in controlling diagenesis in salt marsh systems on a seasonal basis. This study uses pore water redox constituents to verify the dominant control of diagenetic reaction pathways by marsh plant root systems. Of equal importance is the dramatic seasonal change in plant root mass in these systems and the potential of this material as a labile DOC source. This article, and well as others of this volume, demonstrates the need to expand our investigations

of processes controlling chemical exchange in the sediments and aquifers of the terrestrial/ocean boundary.

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