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METHODS AND MODELS FOR ESTIMATING ADVECTIVE PORE WATER EXCHANGE IN TIDAL FLATS

Timothy J. Shaw

Introduction

The tidal flat sediments of the Wadden Sea system are both conduit and bioreactor for dissolved and particulate material from terrestrial and marine sources. In this function the system is a model for the unique biogeochemical regime of tidal flat and marsh sediment systems throughout the world. As in similar systems, the sediments are a diffuse source for a variety of chemical reaction products and may well be a sink for authigenic mineral phases. The permeability of the Wadden Sea sediments, coupled with cyclic physical forcing by tides, storms, and sea level rise, result in the advective exchange of water between sediments and the tidal prism. The dissolved and particulate constituents of the water are subject to a range of reaction environments as they exchange between pelagic environment and microbially rich benthic environment. This process is reflected in a large variation of the concentrations of reactive species such as Mn^{2+} and alkalinity in the water column as a function of tidal height (SCHNETGER *et al.*, 2001). The well-constrained surface water runoff (from the Siels) does not support the variation in chemical inputs indicated by the variations in water column load. The goal of this study is to investigate methods for quantifying the exchange of chemical constituents and water between the Wadden Sea system and the open ocean.

The magnitude of non-point source chemical inputs to the coastal ocean requires new methods for quantifying chemical exchange between the coastal environment and the open ocean (MOORE, 1996; SHAW *et al.*, 1998; KREST *et al.*, 2000). Processes such as submarine groundwater discharge (SGD) and advective mixing through permeable sediments contribute to the net terrestrial/ocean exchange. A large fraction of the exchange can be attributed to reactions occurring in submarine systems associated with the unique chemical environment and the large microbial populations. The relatively high rates of exchange in these systems (due to permeability) and the high rates of reactions (due to the microbial community) often preclude making estimates of exchange based on solid chemical reservoirs or pore water profiles. In short, the processing and exchange of materials is too fast to use methods appropriate for sediment diagenesis models. Likewise, lack of a discernable end member of a source water mass prevents the use of typical estuarine mixing models based on salinity gradients. Alternative models of exchange utilize the soluble daughters of solid-bound radionuclides as tracers of exchange in permeable sediments and aquifers (RAMA & MOORE, 1996; CABLE *et al.*, 1996; KREST, 2000; HANCOCK *et al.*, 2000). 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). In this study we examine the utility of the two short-lived Ra isotopes (^{224}Ra and ^{223}Ra) as tracers of exchange of the tidal prism in the Wadden Sea system with the open North Sea.

Our proposed application of ^{223}Ra and ^{224}Ra as tracers of exchange is founded on their utility in mass balance estimates and mixing tracers (HANCOCK *et al.*, 2000; MOORE, 2000). Both ^{223}Ra and ^{224}Ra are supplied to coastal waters primarily via interaction with sands, sediments, groundwaters, and rivers. Similarly, most critical nutrients and micronutrients share similar source functions in coastal ocean systems. Coastal ocean waters are enriched in ^{223}Ra and ^{224}Ra compared to

open ocean waters because of the relatively short half lives of both isotopes with respect to open ocean mixing times. The ratios of the parent isotopes of ^{223}Ra and ^{224}Ra (^{227}Th and ^{228}Th) in the shallow sediment sources should be relatively constant; implying the daughters should be released into coastal waters at a relatively constant ratio. These isotopes can provide an exchange tracer (as an end member pair) between Wadden Sea waters and offshore waters of the North Sea as ^{223}Ra and ^{224}Ra inventory. These inventories are increased as a function of the magnitude of exchange between tidal flat sediments and the tidal prism. The inventories are depleted as a function of decay and lateral mixing of the tidal prism with coastal waters. In more general terms, we expect to be able to quantify the physical forcing (as exchange and lateral mixing) in the Wadden Sea system through the ^{223}Ra and ^{224}Ra inventory.

Methods

Water column samples (60 L) were filtered through a 5 micron filter and passed through a Mn-fiber cartridge (~1 L/min.) to concentrate the Ra isotopes. Each Mn-fiber sample containing ^{223}Ra and ^{224}Ra was partially dried and placed in a gas circulation system described by MOORE & ARNOLD (1996). Helium was circulated over the Mn-fiber to sweep the ^{219}Rn and ^{220}Rn generated by ^{223}Ra and ^{224}Ra decay through a 1.1-L scintillation cell where alpha particles from the decay of Rn and daughters were recorded by a photomultiplier tube (PMT) attached to the scintillation cell. Signals from the PMT were routed to a delayed coincidence system adapted for Ra measurements by MOORE & ARNOLD (1996). The delayed coincidence system utilizes the difference in decay constants of the short-lived Po daughters of ^{219}Rn and ^{220}Rn to identify alpha particles derived from ^{219}Rn or ^{220}Rn decay and hence to determine activities of ^{223}Ra and ^{224}Ra on the Mn fiber.

Results and discussion

The activities of ^{223}Ra and ^{224}Ra in the waters of the Wadden Sea strongly varied as a function of tidal cycle. In general there was an inverse relationship between tidal height and concentration. Fig. 1 shows a time series of ^{223}Ra and ^{224}Ra measurements for four complete tidal cycles in the water column of the Wadden Sea during a spring tide in January 2000. The first two cycles were measured at the Otzumer Balje and the second two were collected in the backbarrier region between Spiekeroog and Neuharlingersiel. The large variation between high and low tides are consistent with relatively high inputs of both Ra isotopes on the falling tide and later dilution at high tide as the tidal prism exchanges with the North Sea.

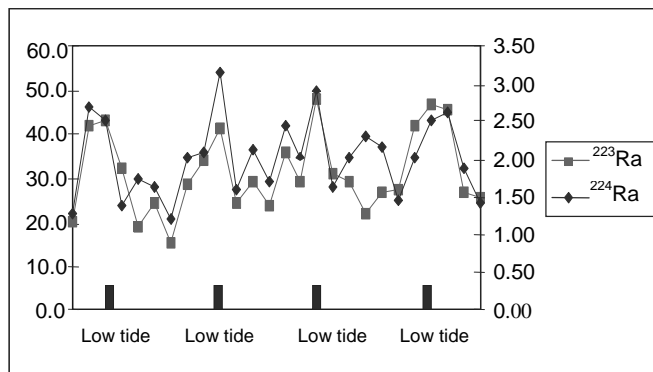


Fig. 1. Activities of ^{223}Ra and ^{224}Ra (dpm/100 L) in the water column of the Wadden Sea at Otzumer Balje and in the backbarrier system.

The observed variations in the activities of ^{223}Ra and ^{224}Ra cannot be explained by a cycle of input and decay due to the

short time scale of the variations, thus exchange with a low-activity North Sea must be significant to the cycle. Further, the contribution of the Siel waters to Ra input is small with respect to the input. These observations suggest the significance of the input of reaction products into the Wadden Sea from tidal flat pore waters. The net export of material from the Wadden Sea will be a function of the rate with which the tidal prism exchanges with North Sea waters. We use the variations in the activities of ^{223}Ra and ^{224}Ra to quantify that export through a simple mass balance model of the stationary oscillation of their inventories.

Model approach

We have generated a mass balance for the inventories of the short-lived Ra isotopes (^{223}Ra and ^{224}Ra) based on time series measurements over several tidal cycles and seasons. This is an adaptation of the method used by HANCOCK *et al.*, (2000). We assume that the system is in a stationary state with respect to the variation in the activities of ^{223}Ra and ^{224}Ra during the tidal cycle. Thus, the variation is a stable function of the tidal cycle, and the input is balanced by decay and exchange through the course of the cycle. The assumption takes the form

$$dN/dT = F - \lambda N + C_{\text{sys}} V_{\text{mix}} - C_{\text{ocean}} V_{\text{mix}},$$

where N is the inventory of either ^{223}Ra or ^{224}Ra , F is the input flux of either ^{223}Ra or ^{224}Ra , λN is the decay component of the loss of the isotope, C_{sys} is the concentration (activity) of the isotope in the prism, C_{ocean} is the concentration (activity) of the isotope in the open ocean water, and V_{mix} is the volume of the prism that is mixed during the tidal cycle.

The input is estimated as the increase of inventory on a falling tide. The decay is known as a function of time and the exchange rate is determined by matching the mass balance model results to observations.

Volume and inventory are scaled to tidal height at time i as: We assume that flux is proportional to the area of tidal flat that is exposed rather than total area. We scale F to the difference

$$V_i = \frac{h_i}{h_{\text{max}}} V_{\text{max}} \quad N_i = C_i \frac{h_i}{h_{\text{max}}} V_{\text{max}} = C_i V_i$$

in the surface of the tidal flat and the water level as:

$$F_i = \frac{h_c}{h_i} F_{\text{min}}$$

where F_i is Flux at time i , F_{min} is a minimum flux (based on observation), h_c is the approximate height at exposure and h_i is the height at point i in the tidal cycle.

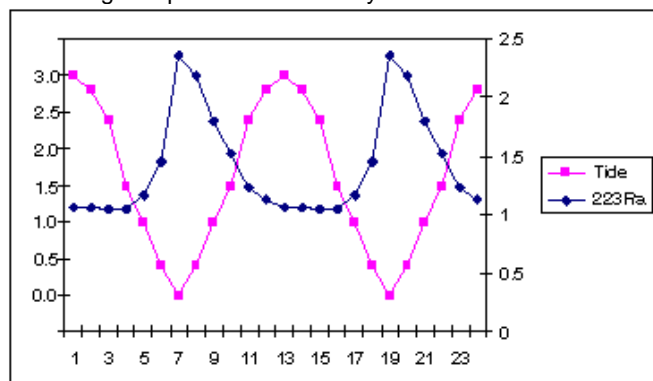


Fig. 2. Model simulation of the oscillation of the activity of ^{223}Ra as a function of tidal height.

The model was time stepped through a symmetric tidal cycle to find a stable stationary state with respect to the cycle of Ra activity. Fig. 2 presents a stable oscillation based on the data

from the January 2000 data set. The model is constrained by the input and the maximum range in concentration, resulting in a narrow output range (as a mixing rate). In the case of the January 2000 data, mass balance was stable for a mixing rate of approximately one third of the tidal prism per tidal cycle. This yields a residence time for the water of the Wadden Sea of slightly more than three tidal cycles (when the residual volume is added to the tidal prism). This result shows remarkable agreement with the estimates of STANEV *et al.* (2003) based on physical mixing models.

Conclusions

The close agreement between the mixing rates generated by ^{223}Ra and ^{224}Ra inventories and those generated by physical mixing models indicates the utility of these isotopes as short time-scale mixing tracers. These results suggest that Ra isotopes can be used as mixing tracers, in the same manner that salinity is used in more traditional estuary systems. This is particularly important where small variations in salinity preclude salt balance estimates of exchange. More importantly, the source and input mechanism for these isotopes is closely linked to the advective exchange of waters with permeable sediments. Thus ^{223}Ra and ^{224}Ra are ideal tracers for the input and exchange for diagenetic reaction products associated with permeable tidal flat sediments.

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