Using $^{224}Ra/^{228}Th$ disequilibrium to quantify benthic fluxes of dissolved inorganic carbon and nutrients into the Pearl River estuary

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We elaborate a newly developped $^{224}Ra/^{228}Th$ disequilibrium approach to quantify benthic fluxes of dissolved inorganic carbon (DIC) and nutrients into the Pearl River Estuary (PRE), China. Depth profiles of ^{224}Ra and ^{228}Th in bulk sediments were collected along a transect in the PRE. Together with bulk sediment measurements, dissolved ^{224}Ra, DIC, and nutrients ($NO_2^-+NO_3^-$, NH_4^+) in porewater and in the overlying waters were also determined. Benthic fluxes of ^{224}Ra were estimated from the observed deficit of ^{224}Ra in the sediments using a one-dimensional (1D) mass balance exchange model. We demonstrated that irrigation was the predominant process that controls solute transfer across the sediment-water interface, whereas molecular diffusion and sediment mixing together contributed <5% of the total ^{224}Ra fluxes from bottom sediments. Based on the mass balance of water column ^{224}Ra, an independent approach was proposed to estimate site-specific residence times of water mass. The results show that water residence times ranged from 0.7±0.1 to 4.9±1.1 d in the PRE.

In the upper several centimeters of sediments, dissolved ^{224}Ra activities were generally well correlated with DIC and NH_4^+ concentrations, indicating that ^{224}Ra is an excellent proxy of these species. We were then allowed to utilize the $^{224}Ra/^{228}Th$ disequilibrium approach to derive reliable estimates of the benthic fluxes of DIC and NH_4^+. We demonstrated that sediment interstitial waters delivered approximately $36\pm2\times10^9$ mol of DIC and $\sim14\pm1\times10^9$ mol of NH_4^+ into the PRE in the dry season. This benthic flux of DIC is equivalent to ~15% of the riverine input in this season. In terms of NH_4^+, our results indicate that bottom sediments are a predominant source of water column NH_4^+ in the PRE. Overall, our results suggest that porewater injection is an important process and must be considered in the mass balance of DIC and nutrients in estuaries