

Using $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium to quantify benthic fluxes of trace metals into the Pearl River Estuary: From alkaline earth elements (Ba) to redox sensitive metals (U, Mn, and Fe)

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The $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium method was extended to examine benthic fluxes of a variety of trace metals, ranging from alkaline earth elements (Ba) to redox sensitive metals (U, Mn, and Fe), into the Pearl River Estuary, China. By taking advantage of the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium in bottom sediments to construct a mass balance of water column ^{224}Ra , we showed that pore water exchange processes with scale lengths of centimeters are the predominant mechanism for solute transport between sediments and overlying waters in the PRE. In contrast, submarine groundwater discharge with scale lengths of "meters to kilometers" are negligible in the water column budget of ^{224}Ra .

Strong correlations between dissolved ^{224}Ra and trace metals in pore waters likely reflects a fact that geochemical cycling of Ra, Ba and U in sediments was closely linked to diagenetic reactions of manganese and iron oxides. Hence, it is possible to quantify benthic fluxes of these trace metals using $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium. The highest flux of Ba was identified at $S=3.0-7.8$ and could reproduce the Ba excess frequently observed in the low salinity domain of the estuary; Benthic input could only cause a very small change of U concentration in the water, which would not influence the conservative mixing of water column U in the PRE. This is consistent with historical measurements of water column U concentration in the PRE; Large benthic fluxes of Mn and Fe were generally acquired with the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium method. They are 1–2 orders of magnitude higher than historical measurements based on the traditional incubation method in other coastal settings. Nonetheless, they are in excellent agreement with a simple consideration of Mn and Fe mass balances in the sediment. An important implication of this study is that the role of coastal sediments in estuarine geochemistry of trace metals may need to be re-evaluated.