



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

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Abstract

We extended the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium approach to examine benthic fluxes of a variety of metals, ranging from alkaline earth (Ba) to redox sensitive elements (U, Mn, and Fe), into the Pearl River Estuary (PRE), China. Depth profiles of ^{224}Ra and ^{228}Th in bulk sediment, as well as dissolved ^{224}Ra and trace metals in porewater were measured along a transect within the estuary in July 2015. Significant deficit of ^{224}Ra relative to ^{228}Th was commonly observed in the upper 0–15 cm sediment. We took advantage of the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium in the bottom sediments to construct a full mass balance of ^{224}Ra in the overlying water column. We demonstrated that porewater exchange (PEX) processes with scale lengths of several centimeters are the predominant mechanism for solute transport between sediments and overlying waters in the PRE. In contrast, deep porewater flow or submarine groundwater discharge (SGD) with scale lengths of “meters to kilometers” are a negligible component in the water column budget of ^{224}Ra .

Strong correlations between dissolved ^{224}Ra and trace metals (Ba, U, Mn, and Fe) in porewater were frequently observed in the study region. This likely reflects a fact that geochemical cycling of alkaline earth elements (e.g., Ra and Ba) and redox sensitive elements (like U) in sediments was closely linked to diagenetic reactions of manganese and iron oxides. This linkage makes it possible to quantify benthic fluxes of alkaline earth and redox sensitive metals using $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium in sediments. Benthic Ba fluxes based on $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium were found to vary from virtually nil to $320 \mu\text{mol m}^{-2} \text{d}^{-1}$ within the PRE. The highest flux was identified at salinity = 3.0–7.8 and could lead to an elevation of $54 \text{ nmol Ba l}^{-1}$ in the water column, which well reproduced the Ba excess frequently observed in the low salinity domain of the estuary. Benthic fluxes of redox sensitive U ranged from -0.42 (“–” denotes flux into sediment) to $1.3 \mu\text{mol m}^{-2} \text{d}^{-1}$. This could only cause a change of -0.1 to $0.3 \text{ nmol U l}^{-1}$ in the water column, which is very small when compared to the U concentration of $13\text{--}14 \text{ nmol l}^{-1}$ in the northern South China Sea. We therefore predicted that water column U in the PRE must behave conservatively during mixing. This prediction is consistent with historical measurements of water column U concentration within the PRE. Large benthic fluxes of Mn and Fe were generally acquired with the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium method. They varied from virtually nil up to $97 \text{ mmol m}^{-2} \text{d}^{-1}$, and from zero to $27 \text{ mmol m}^{-2} \text{d}^{-1}$, respectively. These estimates are 1–2 orders of magnitude higher than historical measurements based on the traditional incubation method in other coastal settings.

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Nonetheless, they are in 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.

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1. INTRODUCTION

Trace metals play a pivotal role in ocean biogeochemistry. Transition elements Fe and Mn are essential micronutrients for marine phytoplankton (e.g., [Martin et al., 1990](#); [Middag et al., 2011](#)), and fluctuations in their supply rates to the open ocean were presumably responsible for the glacial/interglacial cycles in atmospheric carbon dioxide concentration in the geological past (e.g., [Martin, 1990](#)). Alkaline earth element Ba generally bears a strong linear relationship with silicate in the oceans (e.g., [Chow and Goldberg, 1960](#)). Hence it is considered to be a nutrient-like element and has been extensively used as a proxy of paleoproductivity (e.g., [Dymond et al., 1992](#)). In oxygenated seawater, uranium exists as stable uranyl-carbonate complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ (e.g., [Langmuir, 1978](#)). However, when the redox potential is sufficiently low, U(VI) can be reduced into insoluble U(IV) and be removed from the water column. As such, it has been widely used as a paleoredox proxy (e.g., [Scholz et al., 2014](#)). Quantitative knowledge of addition and removal processes of these trace metals is critically important for a better understanding of ocean biogeochemistry and for their full utilization as geochemical proxies.

Rivers are a major pathway by which trace metals sourced from continental weathering are transported into the open ocean. However, estuaries connecting rivers and the ocean greatly modify the river-transported signals through a variety of addition and removal processes. For instance, when plotted with respect to salinity, dissolved Ba concentrations fall above the theoretical dilution line in the estuarine mixing zone. These Ba excesses were ascribed either to its desorption from river-borne particles (e.g., [Li and Chan, 1979](#)), or to submarine discharge of groundwater with high concentration of Ba (e.g., [Moore, 1997](#)). In most estuaries, there is a linear correlation between dissolved U concentration and salinity, indicative of conservative behavior of U during estuarine mixing. However, removal and addition of U from and to the water column have also been documented in some estuaries. Removal of U during estuarine mixing was ascribed to the uptake of this element into bottom sediments under suboxic conditions (e.g., [Carroll and Moore, 1993](#)). Likewise, addition of U was interpreted as a result of the input of sediment porewater with elevated U concentration ([McKee et al., 1987](#)). Mn and Fe play an extremely important role in estuarine geochemistry because their oxide and hydroxide compounds are effective scavengers for a wide range of trace metals. Under certain estuarine conditions, Mn may behave in a conservative manner (e.g., [Holliday and Liss, 1976](#)). However, as a redox-sensitive element, Mn readily undergoes redox transformation between Mn

(II) and Mn(IV). During estuarine mixing, a large portion of soluble Mn(II) delivered by rivers can be oxidized into insoluble Mn(IV) oxides and subsequently be removed from the water column. Conversely, the reduction of Mn(IV) oxides in anoxic estuarine sediments during early diagenesis releases Mn(II) into the ambient porewater, which may subsequently migrate upward into the overlying water column. As a consequence, Mn exhibits various behaviors in different estuaries (e.g., [Knox et al., 1981](#); [Joung and Shiller, 2016](#)). In contrast to Mn, removal of dissolved Fe has been commonly observed during estuarine mixing, and was ascribed to the salt-induced flocculation and precipitation of Fe-humic colloids (e.g., [Boyle et al., 1977](#)). Nonetheless, due to the diagenetic reduction of Fe(III) oxides, porewaters in anoxic estuarine sediments are typically enriched in dissolved Fe(II), the concentration of which can be several orders of magnitude higher than that of the overlying water. As such, if some fraction of Fe(II) in porewater escapes into the overlying water column, it could exert an impact on the estuarine geochemistry of Fe.

Overall, evidence for the important role of bottom sediments in estuarine geochemistry of trace metals is not in dispute. However, it is a major challenge in marine chemistry to accurately quantify benthic fluxes of trace metals, particularly in very dynamic estuarine settings. Historical measurements of benthic trace metal fluxes might be biased due to the inherent limitations associated with the traditional core incubation method (e.g., [Shi et al., 2018](#)). In this aspect, the recently developed $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium approach circumvents the difficulty of imposing interference on the natural system with the incubation method, and has been proven to be a robust tool for quantifying benthic fluxes of dissolved inorganic carbon (DIC) and nutrients from coastal sediments (e.g., [Cai et al., 2014, 2015](#); [Hong et al., 2017](#)). Here, we extend this approach to examine benthic fluxes of trace metals (i.e., Ba, U, Mn, and Fe) into the Pearl River Estuary (PRE), China. Our results will provide a new perspective on estuarine geochemistry of trace metals.

2. SAMPLING AND ANALYTICAL METHODS

2.1. Study area

The PRE, a north-south bell-shaped estuary with an area of $\sim 1180 \text{ km}^2$, is located in the southern China ([Fig. 1](#)). It receives $\sim 55\%$ of the freshwater and $\sim 46\%$ of the particles discharged by the Pearl River ([Zhao, 1990](#)). As a result, the estuary is characterized by high sedimentation rates of $>1.0\text{--}7.0 \text{ cm yr}^{-1}$ ([Chen, 1991](#); [Zhou et al., 2004](#)). Fine-grained sediments cover $>90\%$ of the seabed within the estuary. In summer, the benthos is dominated

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